DRAFT FINAL

LONG-TERM MONITORING AND MAINTENANCE PLAN UPDATE

SHEPLEY'S HILL LANDFILL

FORMER FORT DEVENS ARMY INSTALLATION, DEVENS, MA

APRIL 2015

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SOVEREIGN CONSULTING INC.

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CERTIFICATION:

I hereby certify that the enclosed Report, shown and marked in this submittal, is that proposed to be incorporated with Contract Number W912WJ-10-D-0003 DO#0013. This Document has been prepared in accordance with USACE Scope of Work and is hereby submitted for Government Approval.

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ABBREVIATIONS, ACRONYMS, AND SYMBOLS

ADR	Automated Data Review
AOC	Area of Contamination
As	Arsenic
ATP	Arsenic Treatment Plant
BOH	Board of Health
BCT	Base Closure Team
bgs	Below Ground Surface
BRAC	Base Realignment and Closure
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CH_4	Methane
CIP	Clean in Place
ClO_2	Chlorine Dioxide
CO	Carbon Monoxide
CO_2	Carbon Dioxide
COC	Contaminant of Concern
CQC	Contractor Quality Control
CSM	Conceptual Site Model
cy	Cubic Yard
Devens	Former Fort Devens
DOD	Department of Defense
DPT	Direct Push Technology
DO	Dissolved Oxygen
DQO(s)	Data Quality Objectives
DTW	Depth to Water
ELAP	Environmental Laboratory Accreditation Program
EW	Extraction Well
FBRO	Filter Bed Roll-off
FM	Flux Maintenance
ESD	Explanation of Significant Differences
FS	Feasibility Study
gpm	Gallon per Minute
H_2S	Hydrogen Sulfide
IDW	Investigation-Derived Wastes
LEL	Lower Explosive Limit
LTM	Long Term Monitoring
LTMMP	Long Term Monitoring and Maintenance Plan
LUC	Land Use Control
LUCIP	Land Use Control Implementation Plan
MA	Massachusetts
MassDEP	Massachusetts Department of Environmental Protection
MCL	Maximum Contaminant Level
MCP	Massachusetts Contingency Plan
MF	Microfiltration
MS/MSD	Matrix Spike/Matrix Spike Duplicate
NAE	New England District

NAVD	North American Vertical Datum
NELAC	National Environmental Lab Accreditation Conference
NIA	North Impact Area
NTCRA	Non-Time Critical Removal Action
O_2	Oxygen
ORP	Oxidation-Reduction Potential
PID	Photoionization Detector
POTW	Publically Owned Treatment Works
PVC	Polyvinyl Chloride
QA/QC	Quality Assurance/Quality Control
QAPP	Quality Assurance Project Plan
QSM	Quality Systems Manual
RAO	Removal Action Objective
RI	Remedial Investigation
ROD	Record of Decision
RQS	Rock Quality Designation
SAR	Supplemental Assessment Report
SDG	Sample Delivery Group
SHL	Shepley's Hill Landfill
SOP	Standard Operating Procedure
Sovereign	Sovereign Consulting Inc.
PPE	Personal Protective Equipment
USACE	United States Army Corp of Engineers
USEPA	United States Environmental Protection Agency
VOC	Volatile Organic Compound

1.0 INTRODUCTION

Pursuant to the Contract Modification for #W912WJ-10-D-0003 Task Order 0013, Sovereign Consulting Inc. (Sovereign), on behalf of the US Army Corps of Engineers New England District (USACE-NAE) and the Army Base Realignment and Closure (BRAC) Environmental Office at Devens, Massachusetts has updated the 2007 Shepley's Hill Landfill (SHL) Revised Long Term Monitoring and Maintenance Plan (LTMMP) (CH2M Hill, 2007) and the 2009 SHL Revised LTMMP Addendum (ECC, 2009). The updated LTMMP includes revisions, as deemed appropriate, to the groundwater monitoring program, treatment plant monitoring, landfill gas monitoring, and landfill cap inspection/maintenance. Further, this update documents long-term monitoring associated with the installation of a hydraulic barrier wall on the eastern side of SHL which is designed to restrict arsenic flux from SHL towards Plow Shop Pond and the implementation of land use controls (LUCs) in the north impact area (NIA) north of SHL. Lastly, the updated LTMMP provides information such that the long-term effectiveness of the cap and Contingency Remedy may be evaluated per the remedial action objectives of the 1995 Record of Decision (ROD), the 2005 and 2013 Explanations of Significant Differences (ESDs).

1.1 Objectives and Report Organization

The objectives of this updated LTMMP are as follows:

- Summarize the site description and historical background;
- Summarize the current Removal Action Objectives (RAOs) and the remedy components applied to address these RAOs;
- Summarize the Conceptual Site Model (CSM);
- Define and evaluate the existing LTMMP program by assessing the fate and transport of Contaminants of Concern (COCs), the CSM, and the groundwater model;
- Specify all Data Quality Objectives (DQOs) to be utilized in remedy performance assessments within the established groundwater decision framework;
- Incorporate the barrier wall remedy for the SHL and the Long Term Monitoring (LTM) for the NIA; and
- Incorporate necessary monitoring for the LUCs in the NIA.

Section 2.0 of this report summarizes the existing LTMMP technical approach as it relates to the CSM, remedy performance objectives, and new data collection. **Section 3.0** of this report presents the DQOs for the revised monitoring and maintenance for the landfill, barrier wall, arsenic treatment plant, and other monitoring locations. **Section 4.0** summarizes all the updated LTMMP monitoring procedures, analyses, frequencies, and quality assurance/quality control and data validation. **Section 5.0** summarizes the Institutional Control Monitoring Plan. Finally, **Section 6.0** outlines all necessary reports to be completed following each monitoring event within the LTMMP.

1.2 Background and Site Description

Devens, Massachusetts (MA) is located approximately 35 miles northwest of the city of Boston, within the towns of Ayer, Shirley (Middlesex County), Harvard and Lancaster (Worcester

County). The former Fort Devens was established in 1917 for military training and logistical support during World War I. Fort Devens became a permanent base in 1931, and continued service until its Base Realignment and Closure Committee closure in 1996. **Figure 1** depicts the area and topography of the former base and surrounding area.

SHL encompasses approximately 84 acres in the northeast corner of the main post of the former Fort Devens (**Figure 2**). The landfill is bordered to the northeast by Plow Shop Pond, to the west by Shepley's Hill, to the south by recent commercial development, and to the east by land formerly containing a railroad roundhouse. Nonacoicus Brook, which drains Plow Shop Pond, is located north of the landfill.

SHL was reportedly operating by the early 1940s, and evidence from test pits within the landfill suggests earlier usage, possibly as early as the mid-nineteenth century. The landfill contains a variety of waste materials, including incinerator ash, demolition debris, asbestos, sanitary wastes, glass, and other wastes. The maximum depth of the refuse occurs in the central portion of the landfill and is estimated to be about 40 feet below ground surface (bgs). The volume of waste in the landfill has been estimated at over 1.3 million cubic yards (cy), of which approximately 160,000 cy (11%) is below the water table. The saturated wastes appear to be emplaced in a wetland; at least two areas previously mapped as wetlands were filled (Harding ESE, 2002) and have been found to be underlain by peat deposits (Sovereign, 2011).

The landfill was closed in five phases between 1987 and 1992-93 in accordance with Massachusetts Regulations at 310 CMR 19.000. The Massachusetts Department of Environmental Protection (MassDEP) approved the closure plan in 1985. Closure consisted of installing a 30 to 40-mil polyvinyl chloride (PVC) membrane cap, covered with soil and vegetation and incorporating gas vents. Closure also included installation of wells to monitor groundwater quality around the landfill, and construction of drainage swales to control surface water runoff. MassDEP issued a Landfill Capping Compliance Letter approving the closure in February 1996.

Subsequent to closure of the landfill, remedial investigations (RIs) completed under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) evaluated soil, sediment, surface water, and groundwater conditions at and in the immediate vicinity of the landfill. The results confirmed the presence of various contaminants, particularly certain inorganics including arsenic and volatile organic compounds (VOCs), in groundwater, sediment, and surface water at or adjacent to SHL. A Feasibility Study (FS) and ROD resulted in a remedy that required long term monitoring and maintenance of the existing landfill cap and groundwater monitoring.

The ROD (USAEC, 1995) required the Army to perform groundwater monitoring and five-year reviews to evaluate the effectiveness of the selected remedial action, which relied heavily on the previously installed landfill cap to attain groundwater cleanup goals by 2008 and to reduce potential exposure risks. If groundwater contaminant concentrations, primarily arsenic, met risk-based performance standards (cleanup goals) over time, the ROD did not require further action; however, if cleanup goals were not met, the ROD required implementation of a groundwater extraction contingency remedy. Due to continued elevated contaminant

concentrations, the Army installed and operated a groundwater extraction and treatment system in March 2006 as a contingency remedy to address groundwater contamination emanating from the northern portion of the landfill (CH2M Hill, 2005a).

In 2011, the AOC 72 RI (AMEC, 2011) concluded that components of the current remedy – landfill capping and groundwater extraction – did not eliminate groundwater flow and arsenic migration from SHL into Red Cove / Plow Shop Pond, identified as Area of Contamination (AOC) 72. The AOC 72 RI results suggested that groundwater discharge contributed arsenic to sediment that could accumulate to levels resulting in conditions that posed unacceptable risks, and therefore a remedy that minimized such arsenic-in-groundwater flux to Red Cove would be most protective. Consequently, a low-permeability groundwater barrier wall was installed between the SHL and AOC 72 as part of a Non-Time Critical Removal Action (NTCRA) from August to September 2012 to mitigate arsenic flux to Red Cove/Plow Shop Pond by groundwater flow from the SHL. Documentation of the barrier wall installation was provided in the Removal Action Completion Report (Sovereign, 2013d).

1.3 Remedial Action Objectives

The following Remedial Action Objectives (RAOs) were stipulated in the ROD (USAEC, 1995):

- Protect potential residential receptors from exposure to contaminated groundwater migrating from the landfill having chemicals in excess of maximum contaminant levels (MCLs).

- Prevent contaminated groundwater from contributing to the contamination of Plow Shop Pond sediments in excess of human health and ecological risk-based concentrations.

1.4 Summary of Remedy Components to Address RAOs

The current components of the SHL remedy selected to address the RAOs are as follows:

Landfill Capping Remedy Component: The landfill was closed in five phases between 1987 and 1992-93 in accordance with Massachusetts regulations at 310 CMR 19.000. The MassDEP approved the closure plan in 1985. Closure consisted of installing a 30 to 40-mil PVC membrane cap, covered with soil and vegetation and incorporating gas vents. Closure also included installation of wells to monitor groundwater quality around the landfill, and construction of drainage swales to control surface water runoff. MassDEP issued a Landfill Capping Compliance Letter approving the closure in February 1996. Inspections of the landfill cap are conducted yearly and include vegetative maintenance, landfill gas monitoring, and visual inspections of the capped area. Results and/or corrective actions are detailed in annual reports.

Groundwater Extraction Contingency Remedy Component: In the years following the capping of the landfill, data gathered at SHL indicated that the capping of the landfill was not resulting in a reduction of arsenic concentration in groundwater north of the landfill as originally expected. This triggered the installation of a contingency supplemental remedy for

SHL, a groundwater extraction system/Arsenic Treatment Plant (ATP). The ATP was designed to remove arsenic from extracted groundwater through co-precipitation with iron followed by microfiltration (MF). The extraction system consists of two extraction wells (EWs) located at the northwestern portion of the landfill cap. These extraction wells, EW-1 and EW-4 are capable of achieving the required combined target extraction rate of 50 gallons per minute (gpm) by either operating simultaneously or independently of one another to maximize plant influent flow. Subsequently, groundwater enters the ATP influent stream, and then is dosed with chlorine dioxide which oxidizes and precipitates the inorganic metals, arsenic, iron, and manganese. These precipitates are then filtered by a microfiltration system, and the effluent or treated water is discharged to the Devens publically owned treatment works (POTW) collection system. Every 15 minutes, the MF control unit conducts flux maintenance (FM), which backwashes the filtered precipitates from the membranes. These solids are fed to the inclined plate clarifier (IPC) and allowed to settle out of suspension and form a residual sludge. The backwash effluent supernatant is fed through two bag filters configured in parallel and discharged to the plant effluent sump. The sludge is then pumped out of the IPC, dosed with polymer to increase flocculation, and carried over to the filter bed roll-off (FBRO). The accumulated sludge is removed from the plant at least once a month for disposal. This remedy has been in place since September 2005.

Barrier Wall Remedy Component: Following several years of operation of the ATP and monitoring of the landfill cap, it was determined that neither remedy was preventing the flow of impacted groundwater to the Red Cove area of Plow Shop Pond. To mitigate the arsenic-in-groundwater flux from SHL to Red Cove/Plow Shop Pond and reduce risk to environmental receptors consistent with local conditions in Plow Shop Pond, a low permeable barrier wall was installed along the eastern limit of the landfill and to the west of Red Cove in 2012 as part of a NTCRA. The barrier wall extended from the ground surface, through the landfill cap and a thin mantling of waste, through native sandy glacial deposits and glacial till, and to the bedrock surface. The boundaries and length of the barrier wall were based on the identified areas of impacted sediment in Red Cove, groundwater concentrations along the eastern edge of the SHL, and particle track analysis as predicted by the SHL groundwater model. The barrier wall was designed to intercept and divert groundwater flowing in the overburden soils away from Red Cove. It consists of an 850-foot long minimum barrier that extends through the overburden soils to the top of competent rock, with an effective hydraulic conductivity of 1×10^{-7} cm/sec.

1.5 Background of Existing LTMMP

The ROD and the original LTMMP established incremental reduction of risk rather than incremental reduction in concentration of individual contaminants as a measure of progress toward attainment of cleanup levels to focus on the cleanup of arsenic, which was the primary contributor to risk.

The existing LTMMP provides the basis for monitoring groundwater within and adjacent to the SHL, landfill gas sampling, and landfill inspections that have been conducted since the mid-1990s and includes monitoring of the arsenic groundwater extraction, treatment, and POTW discharge system. Therefore, as outlined above, the existing LTMMP is germane to only the landfill cap and the ATP remedy components. The LTMMP provides a framework of operation,

monitoring, and sampling to meet the objectives of the ROD (USAEC, 1995). During the five-year review in 2007, the revised LTMMP made use of methods utilized historically and optimized the location and frequency of monitoring based upon historical analytical data collected under the LTMMP and the implemented goals of the ATP Contingency Remedy Component. This LTMMP Update is designed to outline a revised monitoring and maintenance plan for all of the planned and implemented remedy components at SHL, inclusive of the landfill cap, the ATP, the barrier wall, and the impacts in the NIA.

2.0 EXISTING LTMMP PROGRAM AND CONCEPTUAL SITE MODEL

The following is a description of the existing LTMMP Program, overall conceptual site model and status of the continued evaluation of selected remedy components in achieving the necessary RAOs at SHL.

2.1 Summary of the Current LTMMP

The current LTMMP program consists of the collection of data to monitor the performance of the landfill cap and the ATP system conducted through the long-term monitoring of groundwater and landfill gas. The objective of the current program was to provide a comprehensive, revised LTMMP, thereby merging previous LTM and remedy performance monitoring activities into a single program. It was/is intended to be a dynamic monitoring program that will be further optimized through the process of annual evaluations of collected data and the issuance of annual reports with recommendations.

The objective and technical approach of the current program consists of a series of quantitative monitoring programs designed to meet the goals of the ROD (USACE, 1995) such as hydraulic monitoring including quarterly and semiannual sampling and gauging events at select wells and treatment system operation and maintenance including monthly and/or quarterly monitoring of system influent and effluent. The *Revised Long Term Monitoring and Maintenance Plan for Shepley's Hill Landfill Devens, Massachusetts,* (CH2M Hill, 2007) and *Revised Long Term Monitoring and Maintenance Plan Addendum –Shepley's Hill Landfill and Treatment Plant, Long-Term Monitoring and O&M Services* (ECC, 2009) present in great detail the existing LTMMP. The current LTMMP network of wells was selected based on remediation effectiveness from the evaluation of historical data in conjunction with annual landfill cover and treatment plant monitoring.

Annual performance assessments of the current program have been focused on system hydraulics and capture/control of groundwater at the north end of SHL. Consistent with EPA guidance including *A Systematic Approach for Evaluation of Capture Zones at Pump and Treat Systems* (USEPA, 2008), a multiple lines of evidence approach has been taken with respect to the performance assessment. The individual assessment components, their data requirements, and a brief summary of the results are provided in the various Shepley's Hill Landfill Annual Reports and within the 2010 Five Year Review Report.

The data quality objectives for the collection of future data outlined in this LTMMP are to gather the data necessary to document and evaluate the performance of all of the remedy components, including the landfill cap/cover, the arsenic treatment plant, the barrier wall and the associated long-term monitoring of environmental media designed to document the performance of the selected remedy. The data are also used to further expand upon the overall CSM as it relates to the long term performance of the remedy. The CSM is detailed in **Section 2.2**., below.

2.2 Conceptual Site Model

2.2.1 Background / Summary

The CSM for SHL is updated through the collection of new data which include but are not limited to supplemental investigations conducted between 2009 and 2014 as documented in the 2009 *Supplemental Groundwater and Landfill Cap Assessment for Long-Term Monitoring and Maintenance Report* (AMEC, 2009), the 2011 *Shepley's Hill Landfill Supplemental Groundwater and Landfill Cap Assessment for Long-term Monitoring and Maintenance - Addendum Report* (Sovereign, 2011), and the *Shepley's Hill Landfill 2012 and 2013 Annual Reports* (Sovereign, 2013c and 2014a) and long term monitoring and operation of the ATP. Potential sources of arsenic in groundwater include bedrock, till, landfill waste, peat, and aquifer sand overlying bedrock and underlying waste or peat. Due to the placement of the cap on the landfill, any potential leachate from the landfill waste is now limited to the ~10% of the waste that is present within the saturated zone. Recent studies (Harding ESE, 2002; Sovereign, 2011) indicate that the predominant source of the dissolved arsenic beneath the landfill is naturally occurring arsenic entrained in iron oxyhydroxides in the aquifer sand that is released into groundwater from the aquifer sands by naturally occurring and landfill-induced reducing conditions caused by carbon degradation and oxygen depletion leading to anaerobic conditions. Evidence for this conclusion is several-fold and includes results of vertical profiling in the landfill that does not exhibit an arsenic vertical concentration profile suggestive of the landfill waste as the primary source of arsenic in the system, results of scanning electron microscopy of aquifer sands detailing the prevalence and volume of arsenic entrained in iron oxyhydroxides, and column studies associated with the flushing of oxygen-depleted water through aquifer sands resulting in the release of dissolved arsenic in the test cells. In addition, concurrent research on arsenic occurrence in groundwater in other parts of the world noted the importance of buried peat layers in mobilizing arsenic through the very same reductive dissolution mechanism (Appelo, 2006).

There is further evidence that indicates the landfill is not the primary source of arsenic and that conditions favoring a natural origin for the elevated arsenic in groundwater are known to be present [e.g., regional occurrence of high arsenic in both bedrock minerals and in overburden iron oxyhydroxide coatings, presence of peat deposits, low oxidation-reduction potential (ORP), etc.] (Gannett Fleming, 2011). If significant amounts of arsenic leached from the landfill waste, then the underlying sands would be enriched with arsenic (Keimowitz et al., 2005). This has not been observed (Sovereign, 2011). The arsenic concentrations in the soil profiles increase with depth to the top of the till and bedrock, and arsenic contents found in the aquifer sands are similar in concentration as those found locally and regionally in the vicinity of Fort Devens (USACE, 2004). Arsenic in all materials (aquifer sand, waste, bedrock, etc.) is mobilized by

reducing conditions at the site, and this process will persist for as long as reducing conditions remain.

There are two sources of carbon and reducing conditions at the SHL. Historically, the peat and wetlands underlying the landfill and in the NIA likely provided reducing conditions that mobilized arsenic through reductive dissolution of iron oxyhydroxides on which arsenic was entrained. This would have occurred prior to the development of the landfill extending back over 10,000 years, as this process is well documented in published scientific literature. The landfill was placed on top of the existing wetlands and underlying peat, and degradation of the waste rapidly created additional reducing conditions.

These processes are similar to those noted at the Winthrop Landfill in southern Maine (Keimowitz, 2005). For example, (1) the aquifer at both sites has an arsenic source not derived from landfill waste but from geologically naturally occurring arsenic that was and is mobilized by reducing conditions imposed by landfill waste and by peat deposits and wetlands (bogs); (2) studies at SHL (Harding ESE, 2002; Sovereign, 2011) and Winthrop (MACTEC, 2006) have shown that the source is arsenic entrained in iron oxyhydroxides in the aquifer sand underlying and surrounding the landfill; and (3) evidence indicates the landfills were unlikely significant sources of arsenic. Arsenic leached from the landfill waste would have enriched the sands, especially immediately below the waste, with arsenic (Keimowitz et. al., 2005). This has not occurred at either site, and the arsenic concentrations in the soil profiles at SHL generally increase with depth to the top of the till and bedrock. Further, (4) both landfills are impacted by pre-existing wetlands and underlying peat deposits whereby degradation of the landfill waste created additional reducing conditions that added to the mobilization of the arsenic in the underlying aquifer sands and increased the aerial extent of the reducing conditions beyond the boundaries of the wetlands and peat. The main exception is that peat bogs and wetlands lie adjacent to the Winthrop landfill and not beneath it such as exists at SHL. The ability of peat and reduced wetlands to behave like landfill waste as a source of reducing conditions is well documented (Bozkurt et al., 2001).

Further, the mechanisms responsible for the elevated arsenic at the SHL appear to be the same as those at the Winthrop Landfill where arsenic contamination occurs (Keimowitz et. al., 2005). The difference between the concentrations of arsenic in groundwater at SHL and at the Winthrop Landfill is attributed to the difference in concentrations of naturally occurring arsenic located in the aquifer material beneath each landfill. The aquifer material at SHL contains an average of 14,000 µg/kg in the upper aquifer sands in contrast to the average of 4,900 µg/kg arsenic reported for aquifer material at Winthrop. More importantly, the bottom 10-20 feet of each boring at the SHL consisted of sand, glacial till or bedrock containing an average 38,000 µg/kg of arsenic. Thus a higher potentially soluble source of arsenic exists at SHL compared to Winthrop, and the SHL inventory of arsenic can be expected to be an order of magnitude greater than that found at the Winthrop Landfill. In addition, it is important to note that the pump and treat system at the Winthrop Landfill was ultimately terminated, as it was determined to be not effective in remediating arsenic to achieve restoration of the aquifer and that land use and institutional controls were sufficient to meet the RAO for receptor protection (MACTEC, 2006).

Estimates of the time it would take to flush aqueous phase arsenic in the system to background conditions through the landfill and up to Nonacoicus Brook and wetlands approach 300 years under best case conditions (clean, oxic water replaces groundwater with no arsenic remobilization). The residual or background level of arsenic that is achievable by flushing is not known but could approach 1,500 ug/L based on the solubility of expected residual arsenic solid phases (Appelo, 2006; Smedley and Kinniburgh, 2002; USGS, 2011). Thus even with no new additions of arsenic from any non-native source, significant time to achieve local background is required and the new ambient arsenic level will almost certainly be several orders of magnitude above current MCLs for groundwater. Estimates of flushing residual carbon in the landfill footprint to lessen reducing conditions is estimated to be at least two times (2x) the time it takes to flush arsenic from the system or over 500 years (Keimowitz, 2005; Bozkurt et al., 2001).

Restoration of the aquifer to MCLs or even to less than 100 ppb throughout the area downgradient of the landfill in the NIA in a reasonable time frame appears unlikely given (1) the volume of naturally occurring arsenic in aquifer sands beneath SHL and longevity of reducing conditions exacerbated by the presence of the landfill, and (2) the continuing enrichment of the aquifer sands and groundwater with arsenic via the upwelling of arsenic rich groundwater from Shepley's Hill as documented by recent EPA studies.

The existing data set from groundwater investigations along Nonacoicus Brook does not suggest that arsenic is discharging to the Brook at appreciable concentrations and continues to suggest that an oxygenated zone is present which naturally precipitates arsenic into iron solids near or beneath Nonacoicus Brook as the low-dissolved oxygen groundwater mixes with oxidized water from the north and beneath the Brook (Sovereign, 2014a). Investigations completed in 2013 and 2014 continues to document that arsenic remains at depth, more than 40 feet below the Brook elevation and, taken with the 2010 data collected north of the Brook, indicates that the arsenic concentrations appear to decline rapidly at depth in proximity of Nonacoicus Brook, which appears to represent a groundwater discharge divide.

Historically, elevated arsenic concentrations in groundwater at SHL have impacted Red Cove/Plow Shop Pond which is located down-gradient and in close proximity to the northern portion of the landfill. To mitigate arsenic-in-groundwater flux from SHL to Red Cove/Plow Shop Pond and reduce risk to environmental receptors consistent with local conditions in Plow Shop Pond, a low permeable barrier wall was installed in 2012 along the eastern edge of SHL. The barrier wall has subsequently intercepted and diverted groundwater flowing in the overburden soils away from Red Cove and toward the northern end of the landfill. With the installation of the barrier wall between the landfill and Red Cove, the arsenic flux to Red Cove is expected to be significantly reduced (Sovereign, 2013d). The effects of the barrier wall are being monitored and the CSM will be updated as necessary to account for the effects of the barrier wall with respect to flow and flux to the east and north.

2.2.2 Contaminant Fate and Transport

As outlined above, arsenic is released into groundwater from the aquifer sands and bedrock by both naturally-occurring and landfill-induced reducing conditions caused by carbon degradation and oxygen depletion that lead to anaerobic conditions. Portions of the landfill overlay pre-existing, buried peat deposits that induced reducing conditions prior to

emplacement of the landfill over the buried peat and associated wetlands. Therefore, it can be concluded that the buried peat deposits within the landfill footprint also likely caused arsenic mobilization to the north end of the site toward Nonacoicus Brook as well as east toward Plow Shop Pond prior to the placement of waste.

2.2.2.1 North Impact Area

In order to refine the understanding of the extent of chemically-reducing conditions in the NIA and update the CSM, a supplemental investigation was conducted in the spring of 2013 and the winter of 2014 in the NIA. The scope of this investigation was detailed in the May 2013 *Work Plan for Long-Term Monitoring and Maintenance Update* (Sovereign, 2013b). As part of this investigation dissolved arsenic concentrations, ORP, dissolved oxygen, and other geochemical parameters were measured at select locations in the NIA. Components of this evaluation included the completion of vertical arsenic profiling, permanent monitoring well installation, and monitoring well sampling and analysis. Data tables summarizing the data collected in the spring 2013 and winter 2014 supplemental investigation are presented in **Appendix A**, and a full discussion and interpretation of all of the data will be provided in the 2013 and 2014 Annual Reports (Sovereign, 2014a).

Well sampling north of the landfill and in the NIA since 2001 indicates that both in-situ carbon degradation and the presence of the landfill has resulted in reducing conditions in the aquifer. This has been confirmed by the low dissolved oxygen, elevated dissolved methane concentrations, elevated dissolved carbon, elevated ammonia concentrations, and elevated arsenic and iron concentrations. Thus, both the geochemistry of the landfill has induced reducing conditions and the naturally occurring conditions continue to mobilize arsenic in that area.

Nonacoicus Brook appears to represent a groundwater discharge divide. Recent (2013) sampling continues to document no elevated arsenic in the monitoring wells directly north of the brook. The bedrock delineation and general elevation of the northern-most wells indicates that the bedrock surface is much higher in elevation on the north side of the wetlands and brook than the southern side. Hydraulic data gathered from wells on the north side of the brook suggest a westerly/southwesterly groundwater flow component. This flow of groundwater from the north contains higher concentrations of dissolved oxygen that would create a redox boundary which should precipitate arsenic into iron solids near or beneath Nonacoicus Brook as oxygen-depleted groundwater emanating from the landfill area migrates north and mixes with oxidized water from the north and beneath the Brook.

Recent work (2013) included advancement of vertical profiles and groundwater monitoring wells immediately near the southern edge of Nonacoicus Brook to address concerns that arsenic may discharge to the Brook in localized areas. As presented in the *2013 Shepley's Hill Landfill Annual Report* (Sovereign, 2014a), arsenic-impacted groundwater was encountered at 50 to 60 feet below grade immediately south of the Brook and has not been encountered from 10 to 40 feet below grade at each location based on the results of groundwater profiling activities conducted in 2013 at SHM-13-03 and in 2014 at SHM-13-14S/D and SHM-13-15. Consequently, the existing data set does not suggest that arsenic is discharging to the Brook at appreciable

concentrations and continues to suggest that an oxygenated zone is present which naturally precipitates arsenic into iron solids near or beneath Nonacoicus Brook as the low-dissolved oxygen groundwater mixes with oxidized water from the north and beneath the Brook. Work completed in 2013 and 2014 continues to document that arsenic remains at depth, more than 40 feet below the Brook elevation and, taken with the 2010 data collected north of the Brook, indicates that the arsenic concentrations appear to decline rapidly at depth in proximity of the Brook.

Previous modeling work suggested that groundwater flow direction curves westward as groundwater approaches the brook and previous assessments assumed that as groundwater flow curved westward, elevated concentrations of arsenic would be found in a similar pattern. However, the amalgam of data collected between 2001 and 2014 at this time do not show any elevated arsenic in groundwater in monitoring wells installed in line with the groundwater flow bend to the west at the Brook. Arsenic appears to remain in the aquifer in a relatively narrow band trending north, between profile point SHM-10-21 and SHM-10-25.

As the existing LTMMP does not include the monitoring of any of the new investigation points in the NIA, **Section 3**, below, provides updates to the monitoring plan that will provide long term monitoring of locations in the core of the impact area, along the edge of the Brook and in downgradient locations to the west.

2.2.2.2 Red Cove

Elevated arsenic concentrations in groundwater at SHL have subsequently impacted Red Cove/Plow Shop Pond which is located down-gradient and in close proximity to the northern portion of the landfill. Red Cove is a shallow cove with a water depth of less than one meter. As detailed by AMEC within the 2011 *Remedial Investigation Report for AOC 72*, arsenic flux to Red Cove was estimated at approximately 14.6 to 20 g/day with the landfill cap in place before the groundwater extraction and ATP were installed (AMEC, 2011).

The Army evaluated whether a significant risk to human health or the environment exists at Plow Shop Pond/Red Cove (AMEC, 2011) and determined the evaluation of a removal action was warranted to reduce current and potential risks to human health and the environment posed by contaminants that originate from SHL. As a result, a low-permeability groundwater barrier wall between the SHL and AOC 72 was determined to be an acceptable SHL remedy component to help mitigate impacts associated with AOC 72. The installation of the barrier wall in 2012 along the eastern edge of SHL, in combination with the landfill cap and ATP remedy components, was intended to meet the RAO objective (i.e., *prevent contaminated groundwater from contributing to the contamination of Plow Shop Pond sediments in excess of human health and ecological risk-based concentrations)*.

Prior to the installation of the barrier wall, supplemental pre-construction data collection activities were performed from 2011 to 2012 in the area of the proposed wall as detailed in the 2012 *Removal Action Work Plan for the Shepley's Hill Barrier Wall* (Sovereign, 2012) to refine and update the CSM in the area of the proposed wall and address several of the field data needs identified during the conceptual design of the barrier wall. As part of this investigation,

geotechnical composition of the submerged aquifer sands, bedrock depth and competency along the proposed wall, hydraulic conductivity of the shallow bedrock aquifer, and arsenic concentrations in groundwater along the proposed wall were evaluated.

The geotechnical samples collected from the overburden documented a generally homogeneous overburden consisting of loose sand material generally from the surface to bedrock, with locally-absent layers of dense till material immediately above bedrock. No significant geological variation was observed over the length of the wall. The maximum depth to bedrock was 64 feet below grade, and the shallowest depth to rock was 20 feet below grade. Bedrock hydraulic conductivity and transmissivity were determined to be low, and groundwater arsenic concentrations within the bedrock ranged from 71 µg/L in shallower fractures to 3 µg/L in deeper fractures. Conversely, dissolved arsenic profiling in the overburden documented arsenic concentrations ranging from 269 µg/L to 512 µg/L. The difference in concentration from the overburden to the shallow rock fractures suggested that the primary source of the arsenic flux into Red Cove was through the overburden (Sovereign, 2012).

Following the installation of the wall, hydraulic monitoring events were conducted periodically along both the up- and down-gradient sides of the wall to provide hydraulic monitoring data for the barrier wall. Results of the monitoring events demonstrated a positive difference in hydraulic head between the up- and down-gradient monitoring locations along the barrier wall and indicated that the barrier wall was effective in mitigating flow to Red Cove/Plow Shop Pond. With the barrier wall in place, flow patterns in the Red Cove area have changed permanently, with reduced gradient toward the pond east of the wall and greater gradient to the north on the west side of the wall (Sovereign, 2014a). Consequently, with the installation of the barrier wall between the landfill and Red Cove in 2012, the arsenic flux is expected to be significantly reduced (see **Section 3.5.2**).

The investigation data collected prior to and following the installation of the barrier wall has been utilized in the LTMMP to refine the understanding of the CSM and to evaluate remedy performance. However, the existing LTMMP does not incorporate sufficient monitoring for the long-term evaluation of the effectiveness of the barrier wall in achieving the RAO and, therefore, will be updated to achieve that DQO **(Section 3).**

2.3 Groundwater Model Update

An update to the Shepley's Hill Landfill groundwater flow model version SHL104 was completed in 2013(Sovereign, 2013f). The update included a series of significant revisions, as well as a thorough review and modification of various model parameters based upon available data where possible. To address the 2014 BCT comments on the model, ongoing model revisions will be documented in a separate report to be finalized and submitted in 2015.

During the annual reporting process, the model will incorporate LTMMP generated site-wide hydraulic data to continually evaluate model calibration and sensitivity and will be utilized to conduct advective travel time analysis and reverse (backward in time) and forward (forward in time) particle tracking simulations to evaluate remedy performance. The results of the model analysis will be documented in each subsequent Annual Report for SHL.

2.4 Evaluation of New Data to Existing LTMMP

The USEPA installed a series of piezometers in the area of the ATP extraction wells in 2012 to delineate the ATP capture zone and to provide a baseline of data from this area following the construction of the barrier wall. Two piezometers, the first screened across the water table and the second screened within the deep overburden aquifer, were installed at each location (Lockheed Martin, 2012). These wells will be incorporated into the LTMMP monitoring program (see **Section 3.1.2**), and hydraulic and geochemical data from these piezometers will be used with data collected from other nearfield and downgradient monitoring wells to evaluate remedy performance in the area of the ATP through gradient vector analysis, capture zone width calculation, drawdown assessment, and model simulations.

The results of the data collected to-date define the down-gradient extent of the arsenic impacted groundwater at Nonacoicus Brook in a band measuring approximately 300-350 ft wide bound generally between SHM-10-10 to the west and SHM-10-27 to the east, at a depth of 25 to 50 ft below grade. This observation along with the geochemistry data suggests that either Nonacoicus Brook is protected from arsenic impacts by naturally occurring redox conditions near the Brook and/or the groundwater flow divide north of the Brook and/or the extent of arsenic-impacted groundwater at this area has reached its downgradient extent of migration.

This redox zone appears to be located in the vicinity of SHM-10-10. The boundary appears to consist of three features: (1) a bedrock surface that controls the flow of landfill impacted water to the Brook but also brings groundwater from the north and northeast of the Brook that counters the landfill flow, (2) intrusion of more oxidized groundwater from the north side of the landfill, and (3) mixing of clean water resulting in precipitation of arsenic that does not impact the water quality in the Brook or wetlands.

Further, the data collected during the 2010 through 2014 field investigations are consistent with data collected historically throughout the NIA. This indicates the arsenic plume in the NIA is stable and limited to an area along West Main and Shirley Streets. In addition, data collected from the western area of the NIA does not indicate that the core of the arsenic impacted groundwater extends westward, but rather trends roughly north.

The northern most wells currently monitored as part of the LTMMP are located along Sculley Road. Based on recent data from the NIA, select wells between the current LTM wells and Nonacoicus Brook will be added to the LTM well network to monitor the fate and transport of arsenic as reducing groundwater approaches the Brook and to monitor the overall stability of arsenic concentrations in the core of the impacted area beneath West Main Street.

Furthermore, the existing LTMMP does not incorporate sufficient monitoring for the long-term evaluation of the effectiveness of the barrier wall. Results of the initial monitoring events conducted upon the completion of the barrier wall indicate a positive difference in hydraulic head between the up- and down-gradient monitoring locations along the barrier wall and that the barrier wall is effective in mitigating flow to Red Cove/Plow Shop Pond. Consequently, a long-term monitoring program in the area of the barrier wall will be implemented, and select

wells located on both the up- and down-gradient side of the barrier wall will be added to the LTM well network to monitor the long-term effectiveness of the wall.

3.0 UPDATED LTMMP PROGRAM

This LTMMP Update modifies the current monitoring well network at SHL to enhance the ability to evaluate the effectiveness of the individual remedial components underway at SHL that together encompass the remedy. To this end, this LTMMP update addresses five remedial program elements with the overall goal and strategy of providing sufficient data to proceed forward along the groundwater decision framework and monitor the remedy performance for SHL. These five elements include:

1. Continued maintenance of the landfill cap;
2. On-going monitoring and performance evaluation of the ATP remedy;
3. Hydraulic and geochemical performance monitoring of the barrier wall remedy;
4. Performance monitoring of the LUCs for the NIA; and
5. An update to the groundwater monitoring well network at SHL encompassing select monitoring locations installed between 2010 and 2014 and on-going maintenance of institutional controls institutional controls in the NIA.

Concerning the fourth and fifth elements and the completion of additional assessment activities between 2010 and 2014 in the area of impacted groundwater north of Sculley Road and the railroad right of way (referred to as the NIA), it is anticipated that long term monitoring will become a component of the remedy that will address groundwater in the NIA and will be formalized into the ROD through a future ESD. Whereas natural subsurface processes such as dispersion, volatilization, biodegradation, adsorption, and chemical reactions with subsurface materials can reduce COC concentrations, the extent and rate of attenuation depends on a variety of parameters such as COC types and concentration, temperature, moisture, and redox state. For an inorganic COC such as arsenic, fate and transport of the COC is the primary factor monitored as well as the nature and extent of reducing waters (aquifer geochemistry) present in the areas of attainment. The implementation of LUCs in the NIA in 2014 (see **Figure 3** for the area of LUCs) supplemented the LTM in the NIA by eliminating future potential for direct exposure to groundwater in the NIA through prohibiting the use or installation of drinking water or irrigation wells in the impacted area. The data collected in the completion of these elements will provide the basis for evaluating progress toward achieving the RAOs at SHL.

3.1 Data Quality Objectives for the Updated LTMMP Program

The data quality objectives (DQOs) of the updated LTMMP in the most general sense are to collect data of sufficient quality and quantity to enable monitoring of groundwater, landfill gas, and performance of the SHL remedy components such that the Army, regulatory agencies, and other stakeholders may regularly evaluate the protectiveness of the groundwater remedy and its ability to meet the RAOs outlined in the ROD. Furthermore and as stated in the May 2014 USEPA guidance document *Groundwater Remedy Completion Strategy* (OSWER 9200.2-144), "the

DQO process is designed to refine project information needs and focus monitoring efforts on collecting the appropriate type and amount of data so that data support key decisions. This strategy is intended to provide a technical and scientific process for evaluating when sufficient data have been obtained to assess the likelihood that a groundwater remedy has or will achieve the RAOs and associated cleanup levels in a reasonable timeframe."

Per the *Data Quality Objective Process for Hazardous Waste Site Investigations* (EPA QA/G-4HW)(USEPA, 2000), a seven-step process is used to specify DQOs for the collection of environmental data. These steps include:

- State the Problem;
- Identify the Decision;
- Identify Inputs to the Decision;
- Define the Study Boundaries;
- Develop a Decision Rule;
- Specify Limits of Decision Errors; and,
- Optimize the Design for Obtaining Data.

By using the DQO Process, stakeholders can assure that the type, quantity, and quality of environmental data used in decision making will be appropriate for the intended application. For SHL, DQOs vary in terms of study boundaries, decision rules, and optimization. However, in general terms as applied to SHL, the goals in defining the DQOs for the various remedy components at SHL include:

- Routine evaluation to determine if each remedy component is working effectively toward meeting the RAOs in the ROD in a reasonable timeframe;
- Determination if existing data are sufficient to determine if each remedy component is working toward meeting the RAOs;
- If there are insufficient data to determine if a remedy component is successful, determining both the quantity, quality, and necessary duration of data gathering needs to make an evaluation of each component;
- If the data indicate the remedy component will not meet the RAOs in the ROD, then alternatives need to be evaluated.

Many of the DQOs detailed below involve the collection of groundwater samples over an extended period of time in various sub-areas of SHL to be used to evaluate the long term effectiveness of the combined remedy components. The approximate remedy life cycle time frames detailed below are used to measure progress towards meeting the goals in the ROD to determine if the remedy is performing as expected.

The LTMMP groundwater monitoring wells have been selected for assessment of remediation effectiveness from existing wells based on historical analytical results and both hydrologic and geochemical monitoring and modeling to provide representative samples in key sub-areas of the SHL remedy, including:

- Upgradient Areas – these are groundwater bearing zones discharging into the saturated overburden beneath the SHL footprint that encompass groundwater migrating in overburden toward SHL from the south and west and groundwater discharging from bedrock into the overburden beneath the SHL footprint or into the NIA. Monitoring of these upgradient groundwater zones is useful in understanding the levels of dissolved arsenic and dissolved oxygen entering the aquifer at the SHL and ultimately migrating to the north. These areas will be monitored to meet the DQO's requirement for overall remedy component evaluations.

- Landfill Area – these are wells located in the SHL landfill footprint and historically contain some of the highest dissolved arsenic concentrations. Monitoring of the landfill area wells is critical in determining the rate of reduction in arsenic and changes in geochemical parameters at the landfill area which provides insight into the overall performance of remedy components.

- Barrier Wall Area – these are wells located on the eastern and western side of the barrier wall and can be used to monitor the hydraulic effect of the barrier wall in diverting groundwater flow to the north and thereby mitigating arsenic input to Red Cove.

- Nearfield Area – these are wells located in the vicinity of the ATP extraction wells near the northern toe of the landfill. Monitoring of these locations is key to evaluating the 3-dimensional nature of the hydraulic capture of the ATP remedy as well as tracking changes in both arsenic concentrations and changes in redox conditions north of the extraction system.

- North Impact Area – these wells are located beyond the downgradient capture zone of the ATP and will be used 1) for the LTM program in the NIA and 2) to monitor the performance of the ATP remedy in achieving the RAOs in the area of attainment. Data from the NIA wells will also be used to assess redox changes as well as arsenic concentrations in groundwater over time.

Annual reviews and periodic 5 year reviews built into the LTM process are the vehicles used to optimize the data collection moving forward. DQOs related to the specific remedy components in place are detailed in the subsections below. The first five steps of the DQO process are addressed in the rest of this subsection. The last two steps of the DQO process are addressed in **Section 3.2**.

3.1.1 DQOs for the Landfill Cap/Containment Remedy Monitoring, Maintenance and Performance Evaluation

DQO Step 1: The specific DQO framework for the evaluation of the effectiveness of the long term monitoring of the landfill cap is designed to answer the following question:

Does the landfill cap continue to meet all landfill closure requirements in accordance with the SHL ROD?

DQO Step 2: The decision statements that will require continued data collection are as follows:

- Determine that the existing cap remedy is performing as designed to preserve the integrity of the final cover system; and
- Determine that long term trends in landfill gas production are consistent with the established life cycle of the landfill.

DQO Step 3: Information needed to support the decision statements is as follows:

- Visual inspection of the landfill cap on an annual basis to identify potential problems including settling, erosion, problematic vegetative growth, etc.; and
- Annual collection of landfill gas monitoring data.

DQO Step 4: Define the Study Boundaries:

The study boundary for this remedy assessment is the area within and adjacent to the landfill footprint. The timeframe for the collection of data in monitoring the effectiveness of a landfill cap is generally 30 years, consistent with the 30-year monitoring required under landfill management procedures.

The landfill cap was installed in 1993 and has been in place for 22 years. Therefore it can be expected that landfill cap inspections and landfill gas monitoring will continue for the next 8 years (through 2023) after which continued monitoring/inspection may become unnecessary.

DQO Step 5: Combining the Outputs from the Previous DQO Steps, a Decision Rule is developed as follows:

- If the integrity of the final cover system is maintained and long term trends in landfill gas production are consistent with the established life cycle of the landfill, then the landfill cap is operating as designed.

This LTMMP Update does not change or modify the remedy performance objectives and/or monitoring requirements of the landfill cap from the previous LTMMP. Annual landfill inspections will continue per the existing plan. Components of the landfill cap monitoring such as landfill gas screening at wellheads that have exhibited no landfill gas production consistently for several years will be evaluated for future exclusion and/or decommissioning as part of the annual reporting process and/or 5-year review process.

Should the annual inspections reveal evidence of unacceptable gas building beneath the landfill or failure of the cap integrity, significant modification to the cap remedy in terms of repair, re-engineering, or re-design may need to be evaluated.

3.1.2 DQOs for the Groundwater Remedy

DQO Step 1: The specific DQO framework for the evaluation of the effectiveness of the Groundwater Remedy is designed to answer the following questions:

Will the ATP remedy component meet the overall SHL remedy objectives including the protection of potential residential receptors from exposure to arsenic-impacted groundwater through the effective control and management of arsenic-impacted groundwater beneath the landfill and sufficiently change downgradient groundwater redox chemistry such that the NIA can achieve groundwater restoration goals within a reasonable timeframe?

Is arsenic-impacted groundwater discharging to Nonacoicus Brook surface water or sediment at concentrations that could pose a risk to human or environmental receptors.

Are the specified NIA Land Use Controls that prevent access to groundwater effective?

DQO Step 2: The decision statements that will require continued data collection are as follows:

- Determine if the ATP is having a beneficial impact sufficient to meet MCLs throughout the NIA area of attainment within a reasonable timeframe, protect residential receptors from exposure to arsenic-impacted groundwater, ***and*** reduce levels of arsenic-impacted groundwater concentrations within the ATP capture zone (i.e., the landfill area) such that groundwater concentrations would not further degrade or impact the downgradient aquifer, as demonstrated through some or all of the following lines of evidence:

    - Statistically significant decreases, as calculated using the latest version of ProUCL software, in dissolved arsenic-impacted groundwater concentrations down-gradient of the ATP capture zone (i.e., NIA and the northern portion of the nearfield areas);
    - Statistically significant changes, as calculated using the latest version of ProUCL software, in geochemical parameters down-gradient of the ATP capture zone (i.e., nearfield and NIA) that indicate a shift in overall redox conditions necessary to decrease arsenic-impacted groundwater concentrations;
    - Statistically significant decreases, as calculated using the latest version of ProUCL software, in arsenic-impacted groundwater concentrations within the ATP capture zone (i.e., the landfill and the southern portion of the nearfield areas);
    - Statistically significant changes, as calculated using the latest version of ProUCL software, in the geochemical parameters within the capture zone (i.e., the landfill area) that indicate a shift in overall redox conditions necessary to decrease arsenic concentrations; and,
    - Statistically significant decreases, as calculated using the latest version of ProUCL software, in dissolved arsenic influent concentrations to the ATP.

- Determine that ATP operation continues to capture groundwater migrating from beneath the landfill to off-site areas;

- Determine that the ATP operation continues to meet all established O&M requirements including the discharge permit criteria.

- Determine if shallow arsenic-impacted groundwater within 10 to 20 feet of the surface water elevation of Nonacoicus Brook has the potential to discharge to surface water or sediments within the Brook at concentrations which may pose a risk to human or ecological receptors.

- Determine that remedy LUCs are being effectively implemented as per the LUCIP.

DQO Step 3: Information needed to support the decision statements is as follows:

- Collection of arsenic-impacted groundwater from monitoring wells within the capture zone (landfill and nearfield wells located at the northern end of the landfill), within the area immediately downgradient of the capture zone (the remaining nearfield wells), and within the NIA followed by statistical data reduction for the evaluation of arsenic and geochemical parameter trends;

- Continued collection of hydraulic data to allow for periodic hydraulic capture assessments including updates to the overall SHL groundwater flow model using hydraulic data collected during future monitoring to verify groundwater particle flow paths showing capture of groundwater particles originating at the landfill;

- Collection of influent and effluent data from the ATP to meet system discharge permits and to document decreases in dissolved arsenic influent concentrations over time; and

- Collection of LUCIP specified monitoring and survey data.

DQO Step 4: Define the Study Boundaries:

The study boundary for this set of DQOs is defined by monitoring wells located upgradient of the ATP (landfill area), in the area surrounding the ATP (Nearfield Area), and the impacted aquifer area downgradient of the ATP in the NIA (the area of arsenic impacts that trends roughly north from the ATP towards Nonacoicus Brook).

Long term monitoring should continue to allow the collection of data sufficient to prepare a statistical analysis to document both the stability of arsenic concentrations and confirm that arsenic-impacted groundwater is not impacting the Nonacoicus Brook. It is anticipated that 10 to 20 years of data will be necessary to evaluate trends sufficiently. Monitoring in the NIA has been performed since 1999; therefore, a sufficient data set for statistical analysis should be available within the next 5 years. During and after statistical analysis of the data, monitoring may continue to confirm that arsenic-impacted groundwater is not impacting the Nonacoicus Brook.

DQO Step 5: Combining the Outputs from the Previous DQO Steps, the Decision Rule is developed as follows:

- If it is determined that the ATP remedy component is not having a statistically significant effect on the aquifer or the system has reached a point of diminished returns

as determined through the performance metrics specified below, then the effectiveness of the ATP remedy component should be re-evaluated.

- The long-term monitoring of the NIA is determined to be adequate, if groundwater quality data indicate that:
    - the NIA arsenic-impacted groundwater concentrations are decreasing and not appearing in other areas of the NIA which have not been impacted to date;
    - the groundwater within 10 to 20 feet of the surface water of Nonacoicus Brook does not pose a potential risk to human or environmental receptors; and,
    - the LUCs to prevent access to groundwater are effective.

Long term groundwater monitoring within the landfill, nearfield and NIA areas is necessary to measure dissolved arsenic and other geochemical parameter trends in the aquifer both beneath the landfill and in groundwater migrating north from the northern toe of the landfill, to ensure that the impacted area remains limited to its present locale, and to continue to demonstrate that arsenic-impacted groundwater is not discharging to Nonacoicus Brook at concentrations posing either a human or ecological risk. Based on the site conditions and high uncertainty that aquifer restoration goals can be achieved, the remedial duration or "reasonable timeframe" is estimated to be 100 years and is the basis for determining the performance metrics. The remedy performance metric is the statistically significant reduction in arsenic concentrations in groundwater, potentially coupled with a shift in geochemical parameters (e.g. increases in dissolved oxygen and oxidation-reduction potential in the aquifer), as determined by sampling data from the landfill, nearfield and NIA area monitoring wells. The goal of this monitoring is to estimate the length of time required for ATP remedy operation by evaluating both when the groundwater conditions beneath the landfill will no longer have a detrimental impact on downgradient aquifer conditions and when the groundwater restoration goals will be achieved such that the ATP can cease operation.

Based on the ATP being operational since 2006, and accounting for an additional five year period of operation under this LTMMP Update (i.e., ATP operation through 2020), the performance metrics for the groundwater remedy are statistically significant decreases or changes, as calculated using the latest version of ProUCL software, in dissolved arsenic and geochemical concentrations in groundwater within and downgradient of the ATP capture zone as detailed in DQO Step 2. If landfill, nearfield or NIA area wells do not show statistically significant decreases or changes in arsenic and geochemical concentrations over that time period, then the effectiveness of the ATP remedy should be re-evaluated. However, if arsenic concentrations decrease and/or beneficial changes in geochemistry are documented in a majority of key wells in the landfill, nearfield area and NIA, and data trends and modeling indicate that the system has not reached a point of diminished returns, then the ATP should continue to operate until that point of diminished returns is met at which time the effectiveness of the ATP remedy should be re-evaluated.

Monitoring wells proposed for statistical evaluation of dissolved arsenic trends include the following:

Landfill Area Wells	
Annual Sampling	
N5-P1	SHP-99-29X
SHM-10-07	SHM-10-11
SHM-10-13	SHM-10-12
SHM-10-15	SHM-10-14
Nearfield Area Wells	
Semi-Annual Sampling	**5 Year Sample Cycle**
SHM-93-22B	SHL-23
SHL-96-5B	
SHM-05-41B	
SHM-05-41C	
Annual Sampling	
SHL-5	SHM-96-5C
SHL-8S	SHM-05-41A
SHL-8D	SHM-05-42A
SHL-9	SHM-05-42B
SHL-22	SHM-10-06
SHM-93-22C	SHM-10-06A
EPA-PZ-2012-1A/B	SHM-10-16
EPA-PZ-2012-3A/B	EPA-PZ-2012-2A/B
EPA-PZ-2012-5A/B	EPA-PZ-2012-4A/B
EPA-PZ-2012-7A/B	EPA-PZ-2012-6A/B
NIA Wells	
Semi-Annual Sampling	**Annual Sampling**
SHM-13-03	SHM-05-40X
SHM-13-04	SHM-99-31C
SHM-13-06	SHM-99-32X
SHM-13-07	SHM-10-10
SHM-13-08	SHM-13-02
	SHM-13-05
	SHM-13-14S/D
	SHM-13-15
5 Year Sample Cycle	
SHM-13-01	SHM-07-03
SHM-10-02	SHM-10-05A
SHM-10-03	SHM-10-08
SHM-10-04	

Monitoring of upgradient groundwater is also necessary to determine the overall quality of groundwater entering the SHL aquifer from the south and west. Data to date suggests that groundwater entering SHL from the south generally has little dissolved arsenic. The decision

rule for the monitoring of upgradient groundwater is the on-going long term statistical stability of dissolved arsenic and key geochemical parameters in upgradient monitoring wells. If long term monitoring of upgradient locations continues to show stability, then the remaining data can be adequately assessed toward remedy evaluation. If the data show instability, then a re-evaluation of the CSM may be necessary. Key wells that are proposed for statistical evaluation are as follows:

- SHL-12, SHL-15, and SHL-24

Based on the historical stability of these data points, the proposed frequency of sampling for these upgradient locations is a 5-year cycle (to be sampled as part of the fall sampling event of the designated year), considering the long term potential monitoring timeframe in this area (100 years).

3.1.3 DQOs for Barrier Wall Monitoring

DQO Step 1: The specific DQO framework for the evaluation of the effective performance of the Barrier Wall is designed to answer the following question:

Will the SHL Barrier Wall meet the SHL remedy objective to prevent contaminated groundwater from contributing to the contamination of Plow Shop Pond sediments in excess of human health and ecological risk-based concentrations?

DQO Step 2: The decision statements that will require continued data collection are as follows:

- Determine that the barrier wall is preventing arsenic-impacted groundwater from the landfill area to the west from migrating east and discharging to surface water in Plow Shop Pond; and,

- Determine that over time arsenic flux to Red Cove is mitigated.

DQO Step 3: Information needed to support the decision statements is as follows:

- Collection of hydraulic head data on either side of the barrier wall on a periodic basis to confirm a hydraulic head differential across the wall as the primary indicator of barrier wall effectiveness; and,

- Collection of dissolved arsenic data from groundwater monitoring wells on the up-gradient and down-gradient sides of the barrier wall to document a reduction in arsenic concentration across the wall and ultimately a decrease in arsenic concentrations entering Red Cove.

DQO Step 4: Define the Study Boundaries:

The study boundary for this set of DQOs is the area immediately up-gradient and down-gradient (west and east, respectively) of the barrier wall. The barrier wall was installed in 2012

with an approximate life cycle of 100 years. Based on the recent implementation date of the remedy, long term hydraulic monitoring will be required for the foreseeable future.

DQO Step 5: Combining the Outputs from the Previous DQO Steps, the Decision Rule is developed as follows:

- If there is a hydraulic head differential and a statistically significant decrease in arsenic concentration across the barrier wall from west (upgradient) to east (downgradient), then the barrier wall is having a beneficial impact.

Long term monitoring of the barrier wall area is designed to collect hydraulic head data on either side of the barrier wall to verify the effectiveness of the barrier wall in diverting groundwater flow from Red Cove supplemented with periodic groundwater sampling of key indicator wells to verify a reduction in arsenic flux to Red Cove. Periodic updates to the SHL groundwater flow model can provide estimates of groundwater flow reductions across the barrier wall to supplement these data.

Previous modeling suggests that existing arsenic-impacted groundwater on the eastern side of the wall may require several years to flush from the aquifer; therefore, the statistically significant decrease in arsenic concentration on the eastern side of the wall is not expected to occur until after 5 years of operational life. Future data collection optimization including the collection of additional sediment and surface water samples from Red Cove may be recommended in this area considering the long term life cycle of the barrier wall.

Key piezometers for monitoring hydraulic head differential are the barrier wall piezometers PZ-12-01 through PZ-12-10. Hydraulic heads will be monitored on a semi-annual basis at these locations to monitor the head differential. Monitoring wells in the barrier wall area proposed for the hydraulic head monitoring and groundwater sampling to evaluate arsenic concentration and other geochemical parameter trends include the following:

Semi-Annual Sampling	Annual Sampling
SHL-11	SHL-4
SHL-20	SHL-10
SHM-11-02	SHL-19
	SHM-11-06
	SHP-01-36X
	SHP-01-37X
	SHP-01-38A

The results of the hydraulic monitoring will be evaluated and compared to the design model predictions to demonstrate that the flow of groundwater beneath SHL is being diverted to the north, as expected. Should groundwater head differentials across the wall become negligible and/or arsenic flux to Red Cove is calculated, as detailed in **Section 3.5.2**, to increase in future years, engineered corrective measures will be considered to evaluate the potential cause and implement repairs, modifications and/or alternate remedy components considered to meet this RAO.

3.2 Sampling Design

3.2.1 Limits of Decision Errors

DQO Step 6: Specify the limits of decision errors:

The tolerable limits on decision errors, which will be used to establish performance goals for limiting uncertainty in the data, will be minimized through the evaluation and validation of all data prior to decision-making. For each remedy, data or information collection efforts will be designed such that, when implemented, they will generate newly-collected data that are of sufficient quality and quantity to address the project's goals (determined from Step 2). The adequacy of one or more existing sources of information or data may then be evaluated using a Type 1/ Type 2 error analysis if needed to determine the acceptability of the data to support the project's intended use.

At minimum, data validation will be performed for each sample delivery group after each sampling event using the ADR.net (Automated Data Review) software along with a chemist review of the ADR results. The ADR output will be adjusted by the chemist based on professional judgment to complete the validation process. The laboratory's analytical data packages will be reviewed to assess adherence to acceptable laboratory practices and the data validation requirements specified in Massachusetts Department of Environmental Protection Massachusetts Contingency Plan (MCP) Compendium of Analytical Methods, EM-200-1-10, and the Department of Defense Quality Systems Manual (QSM) for Environmental Laboratories, and applicable analytical methods. The level of data validation will be performed with reference to the project QAPP (Sovereign, 2013a) and EPA Region I Tier II Guidance. For Tier II data review, data quality objectives will be assessed by review of the Contract Laboratory Program-like summary forms, with no review of the associated raw data.

3.2.2 Data Acquisition

DQO Step 7: Optimize the design for obtaining data:

Table 1 and **Table 2** list the wells selected for long-term monitoring and whether they are shallow, mid-depth, deep overburden/till, or bedrock wells. **Figure 4** depicts the location of these long-term monitoring locations. This list includes wells to monitor groundwater as it travels near the eastern edge of the landfill and as it moves away from the landfill at its northern extreme. **Appendix B** presents baseline data for each existing monitoring well.

Since 2010, additional wells have been installed within the landfill, throughout the NIA, and along the barrier wall to further enhance the monitoring network. Data from these newly installed wells were evaluated with the purpose of updating the LTM network. Based on data collected from SHL and the NIA since 2010, wells were added or removed from the list of LTM wells with the goal to monitor and assess conditions throughout the study area as the SHL remedy affects aquifer conditions at SHL and the NIA.

The network will be continuously assessed and optimized in future years through annual reports. Recommendations made in the annual reports to increase or reduce the numbers of wells or to change analytes will be formally incorporated into revisions of the LTMMP during the next five-year review.

Groundwater sampling will be conducted in accordance with the *Site Specific Quality Assurance Project Plan* (QAPP) *for Shepley's Hill Landfill Supplemental Investigations, Long-Term Monitoring and Treatment System O&M Services* (Sovereign, 2013a). This document is included as **Appendix C** and will be amended, as needed, annually. Groundwater sampling and hydraulic monitoring frequencies, provided in **Tables 1** and **2**, may be summarized as follows:

- Groundwater Sampling Semiannual Events: The spring event will be focused on the arsenic-impacted area, where key wells are located for assessing the performance of the various remedy components as detailed above. The semiannual events will be conducted for a minimum of three years (through 2018) to document seasonal fluctuations. Thereafter, the semiannual events will be discontinued, and the former semiannual wells will be sampled annually during the fall sampling event.

- Groundwater Sampling Annual Events: During the fall, a synoptic groundwater chemistry event will be conducted involving the landfill area, barrier wall area, extraction well areas, and NIA monitoring areas. During the next five year review process, the current LTM wells that are monitored annually will be evaluated, and select wells will be designated for 5-year sampling events.

- Groundwater Sampling 5-Year Monitoring Events: Selected wells, considered less critical to performance evaluation but still of interest, will be included in the fall chemistry event every 5 years. This 5-year event will be designed to provide a larger scale snapshot of groundwater chemistry in all study areas including upgradient areas, landfill areas, barrier wall areas, extraction well area, and the NIA.

- Hydraulic Monitoring Annual Events: A comprehensive synoptic water-level data-set of the entire network of Upgradient, Landfill, Barrier Wall Performance, nearfield, and NIA wells will be completed in conjunction with the fall annual sampling event. These hydraulic monitoring events will include those wells scheduled for semi-annual and annual sampling as well as those wells scheduled for hydraulic monitoring only.

Spring events will be conducted in April/May and fall events in October/November timeframes. All groundwater samples will be collected in accordance with the USEPA Low Stress Purging and Sampling Procedures, Revision 3 (USEPA, 2010), and all samples to be analyzed for dissolved metals, including arsenic, iron, and manganese, and dissolved organic carbon will be field filtered using a 0.45-µm filter. Sampling will include the use of field instruments for measuring ORP, DO, pH, conductivity, temperature, and turbidity, and groundwater samples will be submitted for laboratory analysis of dissolved (field filtered) arsenic, sulfate, total alkalinity, dissolved manganese, dissolved iron, dissolved organic carbon, and chloride as detailed with laboratory methods on **Table 3**. Analyses will be performed by labs accredited in accordance with the National Environmental Laboratory Accreditation

Conference (NELAC) and certified in Massachusetts. The laboratory will be certified by the Environmental Laboratory Accreditation Program (ELAP) and will follow the DOD QSM latest version.

Previously, groundwater samples were analyzed for several additional water quality analytes, nitrate/nitrite, sulfide, ammonia, calcium, magnesium, sodium and potassium. However, due to the rationale presented below, the testing for these analytes will be discontinued.

- Nitrate/nitrite: This redox couple was originally analyzed in order to estimate redox potential in the groundwater using the Nernst equation. Unfortunately, most samples yielded non-detectable concentrations for either nitrate or nitrite rendering the calculation useless. There is no reason to further analyze for this redox couple.
- Sulfide: This part of the sulfate/sulfide redox couple was originally analyzed in order to estimate redox potential in the groundwater using the Nernst equation similar to the nitrate/nitrite couple. Unfortunately, most samples yielded non-detectable sulfide concentrations due to rapid precipitation of metal sulfides rendering the calculation useless. There is no reason to further analyze for this part of the sulfate/sulfide redox couple.
- Ammonia: While ammonia is a good indicator of reducing conditions, it is difficult to determine reliably and does not provide any more information than bicarbonate or manganese do for identifying the extent of reducing conditions in the landfill. It therefore can be eliminated without sacrificing reliable redox information.
- Calcium, Magnesium, Sodium and Potassium: These elements have primarily been determined in water samples to provide a complete major cation and anion balance profile for the samples. The data were used to determine charge imbalance to ensure that no major chemical parameters had been neglected as part of the analytical program. It has been established over the years that charge balance occurs regularly in the samples indicating that both the sampling protocol and laboratory protocol have produced an accurate depiction of water quality in the samples. Any significant deviation in sulfate or chloride in future samples would suggest that these analytes again be checked.

The location and frequency of monitoring presented here will be optimized as data are collected and evaluated through the annual reporting process. Any modifications will be made through Annual Report recommendations and future revisions to the LTMMP. Any changes to this sampling protocol must be agreed upon mutually by the Army and the appropriate regulatory agencies.

The remaining SHL and NIA groundwater wells and piezometers not designated for long-term sampling or hydraulic monitoring were evaluated for future use, and those wells and piezometers which were determined to be of no future value were selected for abandonment. The proposed list of wells and piezometers to be abandoned and the rationale for abandonment are included as **Table 4**.

3.3 Landfill Monitoring and Maintenance

Long term monitoring and maintenance of the landfill final cover system is required for a period of 30 years from landfill closure to preserve the integrity of the cover system and identify potential problems for timely repair. The basis for this section of the plan is found in the Feasibility Study and Proposed Plan (ABB, 1995).

3.3.1 Annual Inspections

Annual inspections shall be conducted by individuals knowledgeable in landfills, as well as plant growth concerns, in order to detect and identify problems such as erosion, settlement or movement of soil on the cap, etc. Annual inspections will include the following:

Monitoring wells: Inspect the landfill monitoring wells for damage to the protective casing and cap, if present. Ensure locks are in working condition.

Piezometers: Inspect the piezometers for damage to the protective casing and cap, if present. Ensure locks are in working condition.

Cover surface: Inspect for bare spots greater than 100 ft., and note locations for future monitoring. Inspect the surface for evidence of disruption due to frost heaves.

Vegetative Growth: Inspect the overall condition (healthy or distressed), the need for water and the need to mow. Also look for unwanted vegetation such as purple loosestrife and overgrown vegetation in drainage swales.

Landfill Gas vents: Inspect for damage, observe if gas is being vented.

Drainage Swales: Inspect for any repairs needed for run-off drainage control structures and for erosion of the banks or adjacent areas.

Culverts: Inspect for silting, debris build up, and need for repair or clean out.

Catch basins: Inspect for silting of the basins, the need for clean out, loose rims, and proper grading around the rims.

Settlement: Inspect for slopes flatter than 2 %, development of depressions or ponding of water. Inspect existing depression at northern end of landfill for additional settlement.

Erosion and Sedimentation: Inspect the landfill surface for cracks or erosion gullies. Check swales, embankments, hillsides for erosion and sedimentation of surrounding areas.

Access Roads: Inspect the access roads around and to the landfill for needed repairs.

Security Fencing: Inspect for damage to, or breeches in, the fencing.

Wetlands Encroachment: Inspect the entire landfill perimeter for encroachment of wetlands species.

3.3.1.1 Landfill Inspection Checklist

The Landfill Inspection Checklist is presented in **Appendix D**. Annual inspections will be performed visually using the checklist, and the completed checklists shall be retained until monitoring is no longer required.

3.3.1.2 Corrective Action

The completed checklist will be reviewed for an overall condition assessment. If the integrity of the landfill cap and associated systems are deemed to be compromised in any way, it shall be documented on the checklist and reported to the Army who will determine the required corrective actions.

3.3.2 Vegetative Maintenance

To preserve the integrity of the final cover system, the maintenance of the vegetative layer is critical, as erosion can be minimized through the promotion of good vegetative growth. The vegetative layer shall be inspected and maintained annually, which will induce the propagation of acceptable vegetation, prohibit growth of small trees, brush, unwanted vegetation and associated root structure, and allow easy access for inspection of the landfill cover. The inspection and maintenance shall be undertaken by individuals who have a thorough knowledge of types of vegetation that are to be encouraged to propagate and the types that are to be eliminated. The vegetative layer shall be cut in early fall to a manageable height, but not less than eight inches. This vegetative maintenance will also help when performing the visual surveys for the other items to be inspected.

3.3.3 Settlement Monitoring

Any existing depressions will be monitored for additional settlement and if detected will be corrected, as required. Surveying of the landfill cap may be performed if visual inspection of the cap indicates slopes of less than 2% or if the development of additional depressions or ponding of water is observed. If the slopes of the landfill decrease to less than a 2% due to settlement, the impacted area may be analyzed by the Army to determine the proper course of action. Actions could involve placing additional cover material on the landfill to re-establish the required slope, regrading, or providing additional drainage swale area.

3.3.4 Landfill Gas Monitoring

A passive gas vent system has been installed consisting of 18 gas vents. Drawing 833-90-01 Sheets 1 - 5, on file with the New England Division of the Army Corp of Engineers, shows the grid plan with the vent locations and identifications. Gas sampling of these vents will be used to establish long-term trends with regards to gas production and venting. The combustible gas survey will determine whether methane, hydrogen sulfide or VOCs have accumulated in the subsurface of the landfill site. Additionally, 25 perimeter soil gas probes have been installed along the northwest and southern edges of the landfill.

3.3.4.1 Frequency and Parameters

Landfill gas field sampling from the gas vents and perimeter soil gas probes shall be performed annually. Gas samples will be field analyzed for the following parameters: Total VOC concentration, percent Oxygen (O_2), Hydrogen Sulfide (H_2S) concentration, Percent Lower Explosive Limit (LEL), Carbon Monoxide (CO) concentration, percent Carbon Dioxide (CO_2), and percent Methane (CH_4). If no gas has been detected at a vent for five consecutive years, then the vent shall be pressure tested to determine if it is working properly. If the vent is found to be clogged it shall be repaired as required.

3.3.4.2 Monitoring Equipment and Sample Analysis

The soil gas samples obtained from the permanent gas vents and perimeter soil gas probes shall be analyzed with field analytical equipment including a portable landfill gas analyzer, combustible gas indicator, and a photoionization detector (PID). The monitoring is conducted by first capping off vents and connecting an adjustable flow rate sampling pump to sample port (barbs) on the cap. Prior to sampling, two vent volumes will be purged from the soil gas vent using the adjustable flow rate sampling pump. The analytical devices are in turn connected to the sampling port following purging of the vents. All analytical devices are equipped with internal pumps. The perimeter soil gas probes are constructed with ports for sampling and are also purged prior to sampling.

A portable landfill gas analyzer shall be used to measure percent LEL, percent CO_2, and percent CH_4. A combustible gas indicator shall be used to measure percent O_2, H_2S concentration, and CO concentration. A PID will be used to screen for total VOCs concentration.

All instruments shall be calibrated according to manufacture instructions prior the start of the sampling. The portable landfill gas analyzer and combustible gas indicator shall be calibrated using mixed gases supplied by the instrument manufacture. The PID shall be calibrated to 100 ppm isobutylene and a zero gas. Calibration of all instruments will be checked at the end of the day. Results will be recorded on a form similar to the Landfill Gas Monitoring form in **Appendix E**.

3.4 ATP Operation and Monitoring

3.4.1 System Description, Operations, and Maintenance

The arsenic treatment system is designed to remove arsenic from extracted groundwater through co-precipitation with iron followed by microfiltration. The treatment system is housed in a 40-foot by 40-foot steel building and consists of the following components:

- Extraction system (two extraction wells);
- Chlorine dioxide (ClO_2) generation and addition;
- Coagulation via a contact tank with a direct drive batch tank mixer;
- MF of oxidized solids;
- Solids removal via an IPC;

- Bag filtration and discharge of the IPC decant water;
- Polymer aided flocculation of sludge using a FBRO; and,
- Discharge to the Devens POTW.

The extraction system consists of two extraction wells (EW) located at the northwestern portion of the landfill cap. These extraction wells, EW-1 and EW-4, are capable of achieving the required combined extraction rate of 50 gpm by either operating simultaneously or independently of one another to maximize plant influent flow. Subsequently, groundwater enters the ATP influent stream, and then is dosed with chlorine dioxide which oxidizes and precipitates the inorganic metals, arsenic, iron, and manganese. These precipitates are then filtered by a microfiltration system and the effluent or treated water is discharged to the Devens POTW collection system. Every 15 minutes, the MF control unit backwashes the filtered precipitates from the membranes. These solids are fed to the IPC and allowed to settle out of suspension and form a residual sludge. The backwash effluent supernatant is fed through two bag filters configured in parallel and discharged to the plant effluent sump. The sludge is then pumped out of the IPC, dosed with polymer to increase flocculation, and carried over to the FBRO. The accumulated sludge is removed from the plant approximately once every two weeks for disposal.

A licensed plant operator will be on site at least two times a week, to monitor and maintain the system's efficiency of removing arsenic from the groundwater to meet the effluent discharge arsenic concentration standard of 75 µg/L as well as the other requirements stated in the discharge permit (**Appendix F).** During these visits, the operator will perform all necessary system repairs and routine maintenance tasks, and if specific repairs are beyond the operator's capability, the operator will supervise over a qualified subcontractor. These procedures are designed to ensure proper system operation and to meet discharge requirements.

3.4.2 Influent/Effluent Monitoring

To verify that the system is meeting discharge requirements, system sampling will be performed at the sample locations/frequencies for selected analytes in accordance with the discharge permit requirements established with the MassDevelopment Wastewater Treatment Facility. This permit was initially established with MassDevelopment on July 14, 2003 and was subsequently amended prior to system start-up in August 2005. The current discharge permit became effective on June 28, 2013 and expires on June 28, 2016. Current permit effluent limitations and monitoring (type and frequency) and reporting requirements are outlined within the permit and summarized below:

LOCAL EFFLUENT LIMITATIONS REQURIED SAMPLING

Parameter	Sampling Frequency	Limitation
Arsenic	Monthly	0.20 mg/l
Chromium (total)	Annually	0.40 mg/l
Cadmium	Annually	0.045 mg/l
Copper	Annually	0.75 mg/l
Lead	Annually	0.20 mg/l

Parameter	Sampling Frequency	Limitation
Silver	Annually	0.30 mg/l
Selenium	Annually	0.03 mg/l
Mercury	Annually	0.001 mg/l
Total Toxic Organics (TTO)	Annually	5.0 mg/l
Total Petroleum Hydrocarbons (TPH)	Annually	100 mg/l
pH (units)	Continuous	5.5-9.5

As noted in the table above, arsenic is sampled monthly, and other parameters are sampled quarterly or annually. The permit requires that the daily load for arsenic not exceed 0.10 pounds per day. In addition, the permit includes a "Special Condition" requiring weekly sampling of the effluent arsenic concentration in the event that the arsenic concentration exceeds 75 µg/L in a permit required monthly sampling. The Contingency Remedy was modified to include treatment to the process to ensure that neither the concentration nor the mass-related limitations are exceeded.

In addition, a continuous pH meter with chart recorder has been installed on the effluent discharge line of the system. The permit requires that:

…a pH meter shall be used continuously to measure the pH of the discharge. The pH meter shall be a continuous monitoring instrument with a chart recorder. All charts shall be maintained on file onsite for a minimum of 3 years. At a minimum, the pH meter shall be calibrated weekly and a calibration log maintained on file onsite for a minimum of 3 years.

In addition to those parameters with effluent limitations noted on the table above, the following additional parameters are currently monitored quarterly: Flow (MGD), barium, manganese, magnesium, chloride, nitrate, and sulfate. Based on discussions with the MassDevelopment Utilities Supervisor, further monitoring of these parameters in the effluent are no longer necessary for compliance with the permit. Consequently, they will be removed under a permit revision.

In accordance with the permit, monthly and quarterly monitoring reports are to be submitted to the MassDevelopment Utilities Supervisor and the United Water Industrial Pretreatment Coordinator. Copy of the current discharge permit is included as **Appendix F**.

VOC analysis (EPA Method 8260) will be conducted on the system influent annually, concurrently with the discharge permit required annual effluent sampling. Annual dissolved methane and ethane sampling of the system influent will also be conducted at this time.

During the ATP start-up testing operations, the process influent and effluent was sampled extensively for arsenic, iron, and manganese, to evaluate influent and effluent concentrations of these constituents. This was conducted such that chemical additions needed to coagulate these species could be evaluated, and the dosage could be optimized. Influent inorganic loading characteristics shall be assessed quarterly throughout the year to gauge system loading and to

ensure that a sufficient iron concentration is maintained to promote iron and arsenic precipitant coagulation.

3.5 Barrier Wall Monitoring

The installation of the SHL/Red Cove barrier wall in the summer 2012 has altered the hydrogeology of the aquifer in this area. Prior to installation, a portion of the groundwater flowing beneath SHL discharged to Red Cove in Plow Shop Pond. Monitoring of these conditions documented that a remedy was required to achieve the RAO of preventing contaminated groundwater from impacting Red Cove. The barrier wall was therefore designed to limit the flux of arsenic in groundwater to Red Cove by limiting the amount of groundwater which would flow and discharge from SHL to Red Cove.

3.5.1 Hydraulic Head Monitoring

During the construction of the barrier wall during summer and fall 2012 at the SHL, a series of overburden groundwater piezometers were installed along the barrier wall alignment to provide hydraulic performance monitoring of the barrier wall. Well screens for each of the piezometers were set at similar depths across the length of the wall to the extent possible considering the saturated overburden thickness. The piezometers consist of five (5) sets of wells (two wells per set), with one point per set located up-gradient of the barrier wall (westerly side) and the other down-gradient (easterly side) of the barrier wall. **Figure 2** displays the locations of the piezometers. The spatial orientation of the piezometers was determined based on both a review of the depth to rock observations documented during the barrier wall construction and based on lateral spacing considerations to allow for a pair at the barrier wall hinge point closest to Red Cove. The piezometers were off-set approximately eight to ten feet from each side (or the edge) of the barrier wall.

Weekly hydraulic monitoring events were conducted in November 2012 followed by monthly hydraulic monitoring events from December 2012 through April 2013. During each monitoring event, an electronic water level meter was used to measure depth to water (DTW) with an accuracy of ± 0.01 feet from the top of casing of each piezometer. Results of the monitoring events demonstrated a positive difference in hydraulic head at each piezometer couplet location along the barrier wall. The maximum hydraulic head differential observed in paired piezometers during the six month period was 1.83 ft. (PZ-12-09 and PZ-12-10), towards the southern end of the wall. The minimum head differential observed in paired piezometers was during the six month period was 0.27 ft. (PZ-12-01 and PZ-10-02) at the northern end of the wall. It is presumed that the greater head differential to the south is due to a combination of a less saturated thickness in the southern portion of the barrier wall as compared to the northern portion and the expected increase in velocity (and corresponding lowering of hydraulic head) of the groundwater as it flows north.

A summary of historic barrier wall piezometer hydraulic monitoring data collected from November 2012 to April 2013 is detailed in **Table 5**, which provides detailed water table elevations measured at each piezometer pair during each monitoring event. Additionally, **Table 5** tallies the current head differential between each pair along with the change in head differential from one monitoring event to the next.

As presented on **Table 2,** continued hydraulic monitoring of the piezometers located along the barrier wall will be conducted as part of the semiannual LTM gauging events. In addition, the existing well network associated with the SHL monitoring program will be used, as necessary, to compliment the hydraulic information obtained from the piezometers to adequately assess the hydraulic gradient in the area of the wall.

3.5.2 Arsenic Flux to Red Cove

Arsenic flux calculations will utilize hydraulic head differential data across the barrier wall and will provide a range of potential flux based on the input of a range of arsenic concentrations to the formula. Specifically, flux will be calculated by multiplying the yield (gallons per minute) using Darcy's Law of aquifer flowing around the southern end of the wall and across the wall by the concentration (ug/L) of arsenic in the water from wells located adjacent to Red Cove, and multiplying by conversion factors to obtain the flux estimate in grams per day. Those wells designated for barrier wall performance monitoring and from which the data for flux calculations will be obtained are presented on **Tables 1** and **2**.

Previous modeling suggests that existing arsenic-impacted groundwater on the eastern side of the wall may require several years to flush from the aquifer; therefore, the statistically significant decrease in arsenic concentration on the eastern side of the wall is not expected to occur until after 5 years of operational life. Consequently, calculation of arsenic flux will be conducted at the end of the next 5-year review period.

4.0 SAMPLING PROCEDURES

The following sections detail all the appropriate methods, Standard Operating Procedures (SOPs), activities, and equipment necessary for a LTM sampling event. All the information presented references the Standard Army Procedures and most recent EPA low flow sampling SOP (EQASOP-GW001 – **Appendix G**).

4.1 Environmental Media Monitoring

The long term monitoring program for groundwater will include the following sample location points listed in **Tables 1** and **2**. Refer to **Section 3.1** for descriptions of the sampling point selection, frequency, and analysis.

4.2 Pre-sampling Activities

Prior to conducting the sampling event, the appropriate equipment and supplies shall be obtained, and the laboratory shall be contacted (approximately two weeks prior to commencement of event) to communicate and coordinate the sampling event. Arrangements will be made with the laboratory to prepare and deliver sampling kits to a specified location.

4.2.1 Equipment and Supplies

Equipment required for sampling the monitoring wells includes but is not limited to: laboratory sampling kits (sample containers, caps, labels, coolers, custody seals, etc.); peristaltic or submersible pumps; Teflon lined polyethylene, PVC, Tygon or stainless steel tubing; safety glasses and gloves; water level indicator; pH/DO/ORP/Conductivity/Temp meters; turbidity meters; flow through cells; PID; deionized water decontamination supplies; graduated purge water container (minimum 5 gallons); keys to well locks; ice or blue ice packs; field analysis forms; and chain-of-custody forms. All purging, sampling and decontamination equipment and procedures will be in accordance with Standard Army Procedures and up to date EPA low-flow purging and sampling procedures (EQASOP-GW001 – **Appendix G**). Samples will be collected directly from tubing connected to the pump discharge. Tubing will be preferably well dedicated. If tubing is not well-dedicated, fresh (unused) tubing will be used at each sampling location.

4.2.2 Equipment Calibration

All field equipment shall be calibrated at the beginning of each day of use. Standard equipment will include pH/DO/ORP/Conductivity/Temperature/Turbidity meter and a PID. Calibration samples will be collected exclusively for field analysis and not submitted for laboratory analysis. Probes used to measure field parameters shall be rinsed with distilled water between each sample points.

4.2.3 Site Location, Security and Access

Monitoring well locations are shown on the site map found in **Figure 2**. Most wells are located within a secured area and arrangements must be made for access. A key must be obtained from the Army for entry to the site.

4.2.4 Initial Well Opening and Inspection

Upon removing the locking cap and the well casing protective cap, any odors noted will be recorded in the Monitoring Well Sampling Log Form (**Appendix H)**. The headspace of the well casings shall be checked for total VOCs immediately upon removing the well cover using a PID. Any damage or evidence of tampering will be recorded in the logbook.

4.2.5 Water Level Measurements

Prior to well purging or sampling, groundwater measurements will be made using an electronic water level indicator. Water levels will be recorded from the top of the well plastic casing and will be recorded to the nearest 0.01 foot. The probe will be rinsed following the appropriate decontamination procedures detailed in **Section 4.5.3** between sample points. The depth to water will be measured in each well using the decontaminated water level indicator, taking care not to lower the probe below the water surface any further than necessary. Depth to water will be determined with as little physical disturbance of the water in the wells as possible. Note that dedicated tubing may be suspended in the well during water-level measurements. All water level measurements shall be taken on the same day as sample collection. Water level measurements shall be recorded on the Monitoring Well Sampling Log Form located in **Appendix H**.

4.3 Sampling Activities

All activities to be completed prior to sample collection are presenting in the following sections.

4.3.1 Well Purging

Prior to sampling or performing field analyses, each well will be purged in accordance with EPA's most up to date low-flow purging and sampling procedures (EQASOP-GW001 – **Appendix G**). This will be done to ensure that representative samples may be obtained. Water drawdown during purging shall be less than 0.3 feet.

Wells will be purged using an adjustable rate, low-flow submersible or peristaltic pump. This will be accomplished by lowering a section of plastic tubing into the well so that the lower (intake) end of the tubing is approximately midpoint of the well screen. Purging shall continue until field parameter measurements meet stabilization criteria; yet, if after two hours of purging the field parameters have not stabilized, sample collection may commence. Tubing which comes into contact with well water must be constructed of a material which will not contaminate samples. If sampling for VOCs only tubing of Teflon® construction may be reused and must be decontaminated between sample points. If PVC tubing is used, it must be dedicated to the well. The field measured parameters are: pH, temperature, DO, ORP, conductivity and turbidity. Purging data shall be recorded on the Monitoring Well Sampling Log Form in **Appendix H**.

4.3.2 Sample Containers and Preservatives

Containers: Sample containers will be obtained from the laboratory and shall not be reused. Ground water samples will only be collected in laboratory indicated containers depending on the specific analyte and method of analysis.

Preservatives: If preservatives are necessary, the laboratory will provide sample containers with preservatives added. The appropriate personal protective equipment (PPE) and safe handling measures should be taken when handling sample containers with preservatives, as some preservatives may cause harm if not handled correctly. All samples will be kept in an ice chest until delivery to the laboratory. The laboratory will recheck the pH prior to analysis to insure that the lab-prepared preservatives were not compromised.

Holding Times: The time between sample collection and initiation of laboratory analyses will be determined by the specific test analysis and applicable EPA reference. Any analysis of samples after the prescribed holding time will be flagged during data validation and evaluated for data usability.

4.4 Sample Collection

After purging and stabilization, water samples will be field filtered using a 0.45-µm filter and collected by allowing the pump discharge to flow gently down the inside of the sample container with minimal turbulence to prevent aeration and agitation.

4.4.1 Sample Identification

The system for identifying and tracking the samples, associated field data, and the method of relating the data to the proper samples will be recorded in permanently bound and weatherproof logbook and/or field data sheets maintained by the field team. Team members will record all information related to sampling procedures, time, field and weather conditions, unusual events, sample descriptions (including sample depth), instrument readings, and Chain-of-Custody data. Field documentation will be written in indelible ink. Additional sample types, areas of origin, and sub sample types will be allocated as necessary.

Site-specific sample identification numbers will be assigned prior to sample collection. Each sample will be identified in the field notebook and field sampling form by an alpha-numeric code following the identification scheme outline below. The site-specific sample number will consist of the following:

Groundwater Samples

Notation: SHM-XX-XX-MMDDYY

Where: SHM indicates Groundwater Sample,
-XX-XX indicates year and well location identifier, and
-MMDDYY is the 6-digit date on which the sample was collected.

Ex: SHM-10-01-102212; Groundwater sample from well location SHM-10-01 collected on October 22, 2012.

Duplicate Samples

Notation: DUP- MMDDYY

Where: DUP indicates blind duplicate sample, and
-MMDDYY is the 6-digit date on which sample was collected.

Ex: DUP-102212; Duplicate sample collected on October 22, 2012.

Field Rinsate Blank Samples

Notation: RB- MMDDYY

Where: RB indicates field Rinsate Blank sample, and
-MMDDYY is the 6-digit date on which sample was collected.

Ex: RB-102212; Field Rinsate Blank sample collected on October 22, 2012.

4.4.2 Quality Assurance/Quality Control Samples

During each sampling event field QA/QC samples shall be collected in accordance with the project QAPP. All field QA/QC samples shall be preserved, shipped and analyzed with the other samples from the sampling event. A summary of required field QA/QC samples is presented below:

Field Duplicate	Matrix Spike (MS)	Matrix Spike Duplicate (MSD)	Equipment Rinsate Blank
1 per 10 field samples	1 per 20 field samples	1 per 20 field samples	1 per each day decontamination of sampling equipment is completed

4.4.2.1 Field Duplicate Sample

Field duplicate samples shall be taken immediately following the preparation of the field sample collected from the sampling location. Field duplicate samples shall be prepared in the same way as the field samples and shall be identified as a duplicate on the sample container label. The specific sampling location of field duplicate samples shall be selected using random method. Field duplicate samples will be collected at a frequency of one per ten field samples.

4.4.2.2 Rinsate Blank

A rinsate blank is collected during each day of sampling that sampling equipment decontamination is conducted to check for potential contamination due to sample equipment construction or improper decontamination procedures. The rinsate blank shall be prepared as follows:

a) The sampling equipment sample will be decontaminated following standard applicable decontamination SOPs;
b) De-ionized shall be rinsed over the decontaminated sampling equipment and collected in the appropriate sample container; and
c) The sample container shall be labeled as a rinsate blank.

4.4.2.3 Matrix Spike/Matrix Spike Duplicates

Matrix spike (MS) and matrix spike duplicate (MSD) samples shall be taken immediately following the preparation of the regular sample collected from the sampling location. The MS/MSD samples shall be prepared and identified on the sample container label in the same manner as the regular sample and noted on the Chain of Custody. A MS/MSD sample set is to be collected for every 20 regular field samples collected. The specific sampling location of MS/MSD samples shall be selected using random method.

4.5 Post-Sampling Activities

All post-sampling activities are presented in the sections below.

4.5.1 Chain-of-custody

Chain-of-Custody records provide documentation of the handling of each sample from the time of its collection to its destruction. Sovereign will initiate sample custody upon collection of samples. The Chain-of-Custody forms will be placed in weatherproof plastic bags and taped to the inside lid of the cooler. The cooler will be sealed with a minimum of two custody seals, one on either side of the cooler lid. The Chain-of-Custody forms will be used for recording pertinent information about the types and numbers of samples collected and shipped for analysis. Sample identification numbers will be included on the Chain-of-Custody form to ensure that no error in identification is made during shipment. The Chain-of-Custody procedures shall be performed in accordance with Appendix F of EM-200-1-3 (USACE, 2001).

A sample is considered "in custody" if it:

- Is in a person's actual possession.
- Is in view after being in physical possession.
- Is locked so that no one can tamper with it after having been in physical custody.
- Is in a secured area, restricted to authorized site personnel only.

Per this definition, samples that are secured within sample refrigerators and/or freezers in locked, secured location awaiting laboratory pickup are considered "in custody".

4.5.2 Sample Delivery/Shipment to Laboratory

If samples are to be transported to by way of Federal Express or a similar shipping method, each sealed container will need to comply with the following shipping requirements. Sample jars will be packed in bubble wrap and then placed in leak-proof plastic bags and placed in containers compatible with the intended analysis and properly preserved prior to relinquishment/shipment to the laboratory. Thermal ice chests/coolers will be packed with foam padding to cushion the sample containers. Ice will be placed inside sealed plastic bags and packed in the cooler surrounding and atop the packed samples. A Chain-of-Custody form will be placed in a waterproof plastic bag and taped to the inside lid of the cooler. Ice chests will be taped shut with strapping tape, and wrapped around the cooler in at least two places. Tape will also be put over the drain plug (if present) to prevent leaking. Ice chests will be sealed with numbered and signed custody seals that are signed and dated. Custody seal numbers should be included on the Chain-of-Custody and logged in the field team sample logbook. This packaging and shipment is in accordance with Region 1 EPA protocol. Prior to shipment, a QC check will be performed to ensure samples have been properly identified and packaged, and that appropriate documentation (Chain-of-Custody) will accompany them.

Samples that are delivered to the off-site laboratory or relinquished to a laboratory courier shall be placed in appropriate transportation containers and preserved as required. Samples should be packed in such a manner as to minimize the possibility of sample container breakage.

Samples provided to an off-site laboratory courier must be sealed inside a cooler secured with a minimum of two numbered and signed custody seals. Custody seal numbers should be included on the Chain-of-Custody and logged in the field team sample logbook. The Chain-of-Custodies should be transferred to the laboratory using the appropriate relinquishment procedures, but do not need to be placed in the transportation container. Prior to shipment, a QC check will be performed to ensure samples have been properly identified and packaged, and that appropriate documentation (Chain-of-Custody) will accompany them.

4.5.3 Equipment Decontamination

All sampling equipment must be properly decontaminated prior to sample collection, between sampling locations, and following a sampling event. Decontamination of equipment is necessary to prevent cross-contamination between samples. In addition, rust should be removed from any part of the sampling equipment that may contact the sample. All equipment such as pumps, water level meters, water quality meters, and miscellaneous tools and equipment which contact the sample will be decontaminated. Decontamination will occur between individual sampling locations. USEPA Region 1 Decontamination SOP No. 2000 is used as a guideline for this procedure. Decontamination chemicals (i.e. nitric acid or methanol) will be collected and containerized for off-site disposal.

4.5.4 Investigation-Derived Waste

Decontamination fluids containing methanol or nitric acid will be containerized, labeled, sealed with a custody seal, and removed for disposal per applicable hazardous and/or non-hazardous waste generation procedures. All other potential wastes generated during sampling activities will be returned to the ground at the point of collection, consistent with USEPA and MassDEP requirements.

4.5.5 Data Validation

Data validation will be performed for each SDG from each sampling event using the ADR.net (Automated Data Review) software along with a chemist review of the ADR results. The ADR output will be adjusted by the project chemist based on professional judgment to complete the validation process. The laboratory's analytical data packages will be reviewed to assess adherence to acceptable laboratory practices and the data validation requirements specified in MCP Compendium of Analytical Methods, EM-200-1-10, and the Department of Defense QSM for Environmental Laboratories, and applicable analytical methods. The level of data validation will be performed with reference to the project QAPP and EPA Region I Tier II Guidance. For Tier II data review, data quality objectives will be assessed by review of the Contract Laboratory Program-like summary forms, with no review of the associated raw data.

4.6 Field Documentation

This section documents Chain-of-Custody, sample, and field observation documentation procedures.

4.6.1 Field Log Books

The field logbook along with supplemental field data sheets will enable the sampling activity to be reconstructed without relying on the collector's memory. Logbooks will be kept in the possession of the field member responsible for sampling activities or in a secure place during fieldwork. The following information will be recorded in the field logbook:

- Name and title of author, and date and time of entry.
- Name and address of field contact.
- Names and responsibilities of field crewmembers.
- Names and titles of any site visitors.
- Sample collection method (s).
- Number and volume of sample(s) taken.
- Information concerning sampling changes, scheduling modifications, and change orders.
- Details/Sketch of sampling location(s), including depth.
- Date and time of sample collection.
- Weather conditions.
- Field observations.
- Any field measurements made.
- Sample identification number(s).
- Information from containers, labels of reagents used, water type (e.g.., deionized) used for blanks, etc.
- Sampling methodology.
- Sample preservation.
- Analytical method(s) to be performed.
- Sample distribution and transportation.
- Sample documentation (i.e.., Chain-of-Custody record numbers).
- Decontamination procedures.
- Documentation for investigation-derived wastes (IDW) (i.e., contents and approximate volume of waste, disposal method).
- Documentation of any scope of work changes required by field conditions.
- Signature and date (entered by personnel responsible for observations).

4.6.2 Field Sample Collection Sheets

Field sample collection sheets enable the sampling activity to be reconstructed without relying on the collector's memory. These sheets will include:

- Names and responsibilities of field crewmembers.
- Sampling point location identification; including construction and integrity descriptions.
- Sampling point hydraulic data if applicable.
- All field measurements (e.g. water quality data, weather conditions, etc).
- Decontamination procedures.
- Any in-situ filtering processes.
- Sampling equipment and field parameter monitoring equipment descriptions, such as type, model, and serial number.

- Documentation of any changes in field conditions or observations during the sampling process.
- Signature and date (entered by personnel responsible for observations).

Copies of applicable field sample collection sheets can be found in **Appendix H**.

4.6.3 Photographic Documentation

Photographs of field activities will be logged as part of all field efforts and will be maintained within the project file.

4.6.4 Project File

Completed project file records shall be maintained by the Army and shall be updated regularly by project administrators as needed. Project records shall be maintained during the regulatory lifespan of the site.

5.0 INSTITUTIONAL CONTROL MONITORING PLAN

One of the SHL project RAOs is to protect potential residents from exposure to contaminated groundwater migrating from the landfill at levels that pose a risk to human health and the environment. The current ROD does not specifically address implementation of LUCs for any non-Army property located north of the landfill (i.e., the groundwater impacted off-site or the "north impacted area" or NIA), because the extent of the impact was not defined at the time. Post-ROD investigations have established that the SHL has impacted groundwater north and downgradient of SHL within the NIA.

The NIA LUCs were documented in the December 2013 *ESD for Land Use Controls to Restrict Groundwater Use* (Sovereign, 2013g), and the area of LUCs are presented on **Figure 3**. Upon submittal of the ESD, a LUCIP for the LUCs in the NIA was submitted in August 2014 to describe the procedures for implementing the LUCs in the NIA (Sovereign, 2014b).

5.1 Land Use Control Objectives

Groundwater in the NIA would pose an unacceptable risk to human health if used for drinking water and may cause unacceptable risk to human health if used for irrigation purposes. Therefore, administrative and/or legal LUCs are being incorporated as a component of the selected groundwater remedy for the site as part of an ESD. The performance objectives of the LUCs shall be to:

- Restrict access to groundwater so the potential exposure pathway to the contaminants would remain incomplete;

- Prohibit the withdrawal and/or future use of water, except for monitoring, from the aquifer within the identified groundwater LUC boundary; and

- Maintain the integrity of any current or future monitoring system.

5.2 Institutional Controls

To meet the LUC performance objectives, the following institutional controls in the form of governmental permitting, zoning, public advisories, prohibitive directives (e.g., no drilling of drinking water wells) and other legal restrictions are utilized within the NIA.

- The Ayer Board of Health (BOH) Well Regulations (Adopted January 10, 2001) – Town of Ayer permitting requirements for the installation and use of new drinking water wells.

- Moratorium on Groundwater Use within the Area of Land Use Controls - The Ayer BOH has issued a Moratorium on Groundwater Use, as adopted and amended by the Town of Ayer on May 6, 2013 and May 20, 2013, respectively.

- The Zoning By-Laws of the Town of Ayer (Adopted March 3, 1973 and Updated May 2001; Subdivision Control Regulations Updated 1987); Town of Ayer Building Department Permitting Requirements. Specifically, any new homes located in areas serviced by public utilities are required to obtain connection permits from the town's Department of Public Works.

- The Massachusetts Drinking Water Regulation 310 CMR 22.00 – the state regulatory permitting and approval process for any new drinking water supply wells in Massachusetts that propose to service more than 25 customers or exceed a withdrawal rate of 100,000 gallons per day.

5.3 Land Use Control Maintenance and Inspection

The Army intends to implement the following affirmative measures to further ensure that the LUC performance objectives are being met.

- Public education and outreach via ongoing periodic distribution of educational materials and groundwater use surveys to be distributed to all property owners and residents with the stated goal of confirming that no groundwater wells are in use within the entire Area of LUCs.

- Meet with the Ayer BOH on an annual basis, or more frequently if needed, to discuss the implementation of LUCs and provide an updated Area of Land Use Control map(s) that document the current and projected location of groundwater contamination within the Town of Ayer.

All LUCs will be maintained until either (1) the concentrations of COCs in the groundwater are at such levels as to allow unrestricted use and exposure, or (2) the Army, with the prior concurrence of the EPA and MassDEP, modifies or terminates the LUC in question. Specific details regarding the LUCs including timing of public education and outreach and on-going

public involvement are detailed in the ESD and LUCIP for the LUCs (Sovereign, 2013g and 2014b).

6.0 REPORTING REQUIREMENTS

A summary of site activities and frequencies and associated reporting requirements is provided in the table below:

Activity	Frequency	Reporting Requirement
Groundwater Monitoring	Semi-annual	Included within Annual Report
Groundwater Analytical Data Validation	Within 60 days of sampling	Electronic Data Deliverable
Landfill Gas Monitoring	Annual	Included within Annual Report
Landfill Maintenance and Inspection	Annual	Included within Annual Report
LUC Performance	Annual	Included within Annual Report

Groundwater monitoring raw analytical data will be submitted to the USEPA and the MassDEP within 60 days of completion of the monitoring events. A summary of the completed groundwater monitoring activities and data analysis will be included with the Annual report.

Annual reports shall include a description of sites activities and a summary of the environmental monitoring programs conducted during the past year associated with the SHL, including landfill maintenance and inspection, landfill gas monitoring, ATP operation, maintenance and monitoring, groundwater monitoring, and LUC maintenance. As part of annual reporting, performance of all the remedy components shall be evaluated to ascertain if the selected remedy is anticipated to meet the RAOs. Annual reports shall be submitted to the Army, USEPA and the MassDEP.

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FIGURES

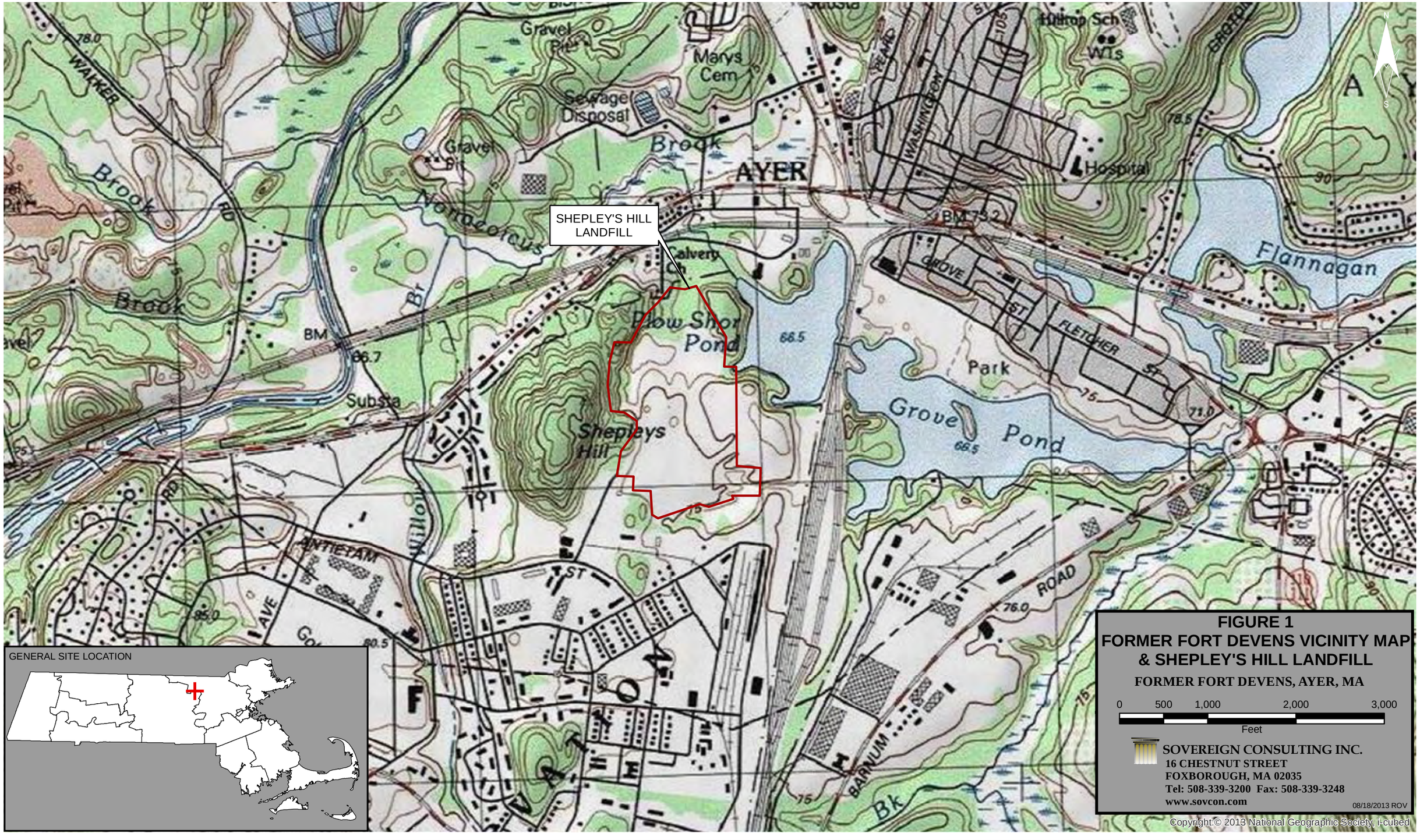

FIGURE 1
FORMER FORT DEVENS VICINITY MAP & SHEPLEY'S HILL LANDFILL

FORMER FORT DEVENS, AYER, MA

0 500 1,000 2,000 3,000
Feet

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SHM-10-04
SHM-10-17
DEP-08-03
SHM-10-24
SHM-10-18
SHM-13-03
SHM-10-23
SHSG-13-02G
DEP-08-07
SHP-07-01A
SHM-10-20
SHM-10-21
SHM-10-25
SHX-01-06X
SHX-01-07X
SHM-10-03
SHX-01-08X
SHM-13-10
SHM-10-10
DEP-08-08
SHX-01-14X
SHM-10-05A
SHM-10-22
SHM-10-27
SHM-13-09
SHM-10-05
SHX-01-12BX
SHM-10-26
SHP-07-01BD
SHX-01-12AX
SHM-13-05
SHP-07-01CD/CS
SHM-13-08
SHM-05-39A
SHX-01-09X
SHM-05-39B
SHM-13-02
SHM-13-07
SHM-99-38A/B
SHM-10-02
SHM-13-06
SHX-01-10X
SHM-99-33C
SHP-05-49A/B
SHP-07-01DD/DS
SHP-07-01D
SHX-01-13X
SHM-10-01
SHM-13-12
SHM-13-04
SHM-99-32X
SHP-07-03A
SHX-01-11X
SHM-10-19
SHM-13-13
SHP-05-48A/B
SHP-99-34B
SHP-99-34A
SHM-10-08
SHM-05-40X
SHP-07-03B
SHM-07-05X
SHP-07-01BS
SHP-99-31C
SB-3
SHP-07-03E
SHP-99-31B
SHM-10-09
SHM-13-11
SHP-99-31A
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SHM-07-03/
SB-07-03
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SB-07-02
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SHM-10-16
SHL-22
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SHP-07-03D
SHM-05-41B
SHM-93-22B
SHM-13-01
SHM-05-41A
SHL-5
SB-07-01
SHM-05-41C
SHM-93-22C
SHP-05-47A/B
SHL-9
PSP-01
SHL-8D/8S
EPA-PZ-2012-7A/B
SHL-13
EPA-PZ-2012-2A/B
EPA-PZ-2012-1A/B
SHM-96-5C
EPA-PZ-2012-6A/B
EW-04
SHP-05-45A/B
EPA-PZ-2012-3A/B
EW-01
SHP-05-46A/B
SHM-10-06A
SHL-23
SHM-10-06
SHL-21
N1-P1
N1-P2
N1-P3
EPA-PZ-2012-4A/B
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SHP-01-36X
SHM-11-06
SHP-05-44
RSK-30
RSK-35
SHP-01-37X
N2-P1, N2-P2
RSK-34
SHM-11-01
RSK-33
PZ-12-03
PZ-12-02
PZ-12-01
SHM-10-14
RSK-1-7
SHL-20
SHL-11
RSK-16-21
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SHP-01-38A/B
RSK-32
RSK-49
PZ-12-04
RSK-8-12,48
N5-P1/N5-P2
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SHP-99-29X
SHM-10-13
SHM-11-07
N3-P1, N3-P2
RSK-28
RSK-36-43, 47
SHM-10-15
SHM-11-02
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SHL-4
RSK-27
PZ-12-05
SHM-11-05
RSK-25
RSK-26
SHL-19
SHM-10-07
PZ-12-07
SHL-10
SHM-11-03
SHM-93-10C
SHM-11-08
SHM-93-10D
RSK-24
PZ-12-09
SHM-93-10E
PZ-12-08
PZ-12-10
SHL-14
UNKNOWN WELL
SHM-93-01A
SHM-10-12
SHL-3
N4-P1
N4-P2
N4-P3
SHP-99-01C
SHL-1
SHP-99-35X
SHP-99-01B
SHL-18
SHM-93-18B
N6-P1
SHL-7
SHM-95-27X
SHM-10-11
SHL-15
32M-92-01X
32Z-01-07X
AOC 32
32M-01-13X
N7-P1
N7-P2
SHL-16
SHM-93-24A
SHL-24
32M-01-15X
32Z-01-06X
32Z-01-08X
32M-99-11X
32Z-01-11X
AOC 32
32M-01-14XBR
32M-01-14XOB
SHL-17
32M-92-04X
B204-01
SHL-12
32M-92-06X
32-4
SHL-25
32M-99-09X
32M-01-17X
32M-01-18X
32M-99-08X
32-3
32M-99-10X
POL-1
32Z-01-16X
32M-92-05X
32M-92-07X
B204-02
32Z-01-10X
32Z-99-02X
Legend
OVERBURDEN MONITORING WELL/PIEZOMETER
MONITORING WELL - DESTROYED
GROUNDWATER PROFILING LOCATION/MONITORING WELL
GROUNDWATER PROFILING LOCATION
BEDROCK MONITORING WELL
EXTRACTION WELL
SOIL BORING
STREAM GAUGE
BARRIER WALL
FIGURE 2 - NORTHERN IMAPCT AREA AND SHEPLEY'S HILL LANDFILL SITE PLAN
FORMER FORT DEVENS, AYER, MA
0 150 300 600 900
Feet
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TOWN OF AYER
AREA OF LAND USE CONTROLS
PLOW SHOP POND
SHEPLEY'S HILL LANDFILL
Legend
Area of Land Use Controls
Property Bounary (Approx)
FIGURE 3 - AREA OF LAND USE CONTROLS
FORMER FORT DEVENS, AYER, MA
0 150 300 600 900
Feet
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NORTH IMPACT AREA WELLS

NEARFIELD AREA WELLS

BARRIER WALL AREA WELLS

LANDFILL AREA WELLS

UPGRADIENT AREA WELLS

AOC 32

SHSG-13-03G
SHM-10-04
SHM-13-15
DEP-08-03
SHP-07-01BD
SHM-10-17
SHM-10-18
SHM-13-03
SHM-10-24
SHM-10-23
SHSG-13-02G
DEP-08-07
SHM-10-20
SHP-07-01A
SHM-10-21
SHM-13-14S/D
SHM-13-10
SHX-01-08X
SHM-10-25
SHX-01-06X
SHX-01-07X
SHM-10-03
DEP-08-08
SHM-10-10
SHM-10-27
SHX-01-14X
SHM-10-22
SHM-13-09
SHX-01-12BX
SHM-10-26
SHX-01-12AX
SHP-07-01CD/CS
SHM-13-08
SHX-01-09X
SHM-13-07
SHM-13-02
SHM-10-02
SHM-13-06
SHX-01-10X
SHP-07-01DD/DS
SHP-07-01D
SHM-10-01
SHX-01-13X
SHM-13-12
SHM-13-04
SHP-07-03A
SHM-10-19
SHX-01-11X
SHM-10-08
SHM-13-13
SHP-07-03B
SHP-07-01BS
SHP-07-03E
SHM-10-09
SHM-13-11
SHSG-13-01G
SHP-07-03C
SB-07-02
DEP-08-05
SHP-07-03D
SHM-13-01
SB-07-01
SHM-05-40X
SHM-07-05X
SB-3
SHM-07-03/
SB-07-03
SHM-10-16
SHM-05-41A
SHM-05-41B
SHM-05-41C
SHM-05-05A
SHM-10-05
SHM-13-05
SHM-05-39A
SHM-05-39B
SHM-99-33A/B
SHM-99-33C
SHP-05-49A/B
SHM-99-32X
SHP-05-48A/B
SHP-99-34B
SHP-99-34A
SHP-99-31C
SHP-99-31B
SHP-99-31A
SHM-05-42A/B
SHL-22
SHM-93-22B
EPA-PZ-2012-5A/B
SHM-96-5B
SHL-5
SHP-05-47A/B
SHSG-14-01G
PSP-01
SHL-8D/8S
SHL-13
EPA-PZ-2012-2A/B
SHM-96-5C
EPA-PZ-2012-1A/B
EPA-PZ-2012-3A/B
SHM-93-22C
SHL-9
EPA-PZ-2012-7A/B
EPA-PZ-2012-6A/B
EW-04
EW-01
SHP-05-46A/B
SHP-05-45A/B
SHL-23
SHM-10-06A
SHL-21
SHM-10-06
N1-P1
N1-P2
N1-P3
EPA-PZ-2012-4A/B
SHP-05-43
SHP-01-36X
SHM-11-06
SHP-05-44
RSK-30
RSK-35
SHP-01-37X
N2-P1, N2-P2
SHM-11-01
RSK-34
RSK-33
PZ-12-03
PZ-12-02
PZ-12-01
SHM-10-14
RSK-1-7
SHL-20
SHL-11
RSK-16-21
SHP-01-38A
SHM-11-04
SHP-01-38B
RSK-32
RSK-49
PZ-12-04
RSK-8-12,48
N5-P1/N5-P2
RSK-29
N3-P1, N3-P2
SHP-99-29X
SHM-10-13
SHM-11-07
RSK-36-43, 47
RSK-28
SHM-10-15
RSK-23
SHM-11-02
RSK-13-15
PZ-12-06
SHL-4
RSK-27
PZ-12-05
SHM-11-05
RSK-25
RSK-26
SHL-19
PZ-12-07
SHM-10-07
SHL-10
SHM-11-03
SHM-93-10C
SHM-11-08
SHM-93-10D
RSK-24
PZ-12-09
SHP-93-10E
PZ-12-08
PZ-12-10
UNKNOWN WELL
SHM-93-01A
SHL-3
SHL-14
SHM-10-12
N4-P1
N4-P2
N4-P3
SHP-99-01B/C
SHL-1
SHP-99-35X
SHL-18
SHM-93-18B
N6-P1
SHL-7
SHM-95-27X
SHM-10-11
SHL-15
32M-92-01X
32Z-01-07X
SHL-16
32M-01-13X
N7-P1
N7-P2
SHM-93-24A
SHL-24
32Z-01-06X
32M-01-15X
32M-99-11X
32Z-01-11X
32M-92-04X
32M-01-14XBR
32M-01-14XOB
SHL-17
B204-01
32-4
SHL-12
32M-92-06X
SHL-25
32M-99-09X
32M-01-17X
32M-99-08X
32M-01-18X
32-3
32M-99-10X
POL-1
32Z-01-16X
32M-92-05X
32M-92-07X
B204-02
32Z-01-10X
32Z-99-02X

Legend

- OVERBURDEN MONITORING WELL/PIEZOMETER
- MONITORING WELL - DESTROYED
- GROUNDWATER PROFILING LOCATION/MONITORING WELL
- GROUNDWATER PROFILING LOCATION
- BEDROCK MONITORING WELL
- EXTRACTION WELL
- SOIL BORING
- STREAM GAUGE
- BARRIER WALL
- SHM-10-11 LTM WELL/ PIEZOMETER ANNUAL SAMPLING (FALL)
- PZ-12-08 LTM WELL/ PIEZOMETER SEMI-ANNUAL SAMPLING (SPRING/FALL)
- SHM-93-10C LTM WELL/ PIEZOMETER 5 YEAR SAMPLING (FALL)
- SHP-99-01B LTM WELL/ PIEZOMETER HYDRAULIC MONITORING ONLY

FIGURE 4
LONG-TERM MONITORING WELL NETWORK

FORMER FORT DEVENS, AYER, MA

0 150 300 600 900

Feet

SOVEREIGN CONSULTING INC.
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01/28/2013 ROV
Updated 03/05/2015 ROV

TABLES

TABLE 1
LTMMP SAMPLING AND HYDRAULIC MONITORING PROGRAM
Shepley's Hill Landfill, Devens, Massachusetts

Monitoring Interval	Well ID	TOC Elevation (ft msl)	Screen Interval (ft bgs)	Screen Elevation (ft msl)	Interval Description	DQO for Inclusion within the LTMMP
UPGRADIENT AREA						
Every 5 Years	SHL-12	248.67	--	--	Shallow Overburden/WT	Wells upgradient of source are necessary for determining groundwater parameters of what is entering the source zone
	SHL-15	259.93	--	--	Shallow Overburden/WT	Wells upgradient of source are necessary for determining groundwater parameters of what is entering the source zone
	SHL-24	239.6	110.0 - 120.0*	126.7 - 116.7	Deep Overburden	Wells upgradient of source are necessary for determining groundwater parameters of what is entering the source zone
LANDFILL AREA						
Annual	N5-P1	242.62	144.0 - 149.0*	96.39 - 91.39	Bedrock	Well provides the bedrock monitoring within the landfill source area. Sampled historically, use to chart trends in source zone chemistry.
	SHP-99-29X	243.32	19.0 - 29.0	222.38 - 212.38	Shallow Overburden/WT	Similar screen interval and close proximity to N5-P2, however much higher As concentrations. Sampled historically, use to chart trends in source zone chemistry.
	SHM-10-07	246.87	40.0 - 50.0	206.87 - 196.87	Mid-Depth Overburden	Provides an additional sampling point within the Landfill Area, east of historically sampled wells.
	SHM-10-11	263.2	50.0 - 60.0	210.86 - 200.86	Deep Overburden	Wells upgradient of source are necessary for determining groundwater parameters of what is entering the source zone
	SHM-10-12	254.6	45.0 - 55.0	207.02 - 197.02	Mid-Depth Overburden	Provides an additional sampling point within the Landfill Area, south of historically sampled wells.
	SHM-10-13	244.75	60.0 - 70.0	184.75 - 174.75	Deep Overburden	Provides an additional deep sampling point within the Landfill Area, east of historically sampled wells.
	SHM-10-14	237.61	60.0 - 80.0	177.61 - 157.61	Deep Overburden	Provides an additional deep sampling point within the Landfill Area, north of historically sampled wells.
	SHM-10-15	243.76	45.0 - 55.0	198.76 - 188.76	Mid-Depth Overburden	Provides an additional sampling point within the Landfill Area, south and east of historically sampled wells.
BARRIER WALL AREA						
Semi-Annual	SHL-11	235.48	12.0 - 27.0	221.97 - 206.97	Shallow Overburden/WT	Evaluates barrier wall contaminant removal performance. Sampled historically, use to chart trends in source zone chemistry.
	SHL-20	235.96	39.0 - 49.0	195.69 - 185.69	Deep Overburden/Till	Evaluates barrier wall contaminant removal performance. Sampled historically, use to chart trends in source zone chemistry.
	SHM-11-02	240.77	52.0 - 66.0	186.63 - 172.63	Bedrock	Monitors/evaluates possiblility of As migration through bedrock beneath the barrier wall.
Annual	SHL-4	227.54	3.0 - 13.0	222.50 - 212.50	Shallow Overburden/WT	Historically sampled annually, continued annual sampling to monitor As concentrations on downgradient side of barrier wall.
	SHL-10	247.95	24.0 - 39.0	222.58 - 212.58	Shallow Overburden/WT	Historically sampled bi-annually; remains part of LTM plan to monitor As concentrations on the downgradient/southern side of the barrier wall
	SHL-19	240.52	20.0 - 30.0	218.43 - 208.43	Shallow Overburden/WT	Historically sampled annually, continued annual sampling to monitor As concentrations on downgradient side of barrier wall.
	SHM-11-06	236.2	25.0 - 35.0	208.27 - 198-27	Shallow Overburden	Added to annual sampling to monitor As concentrations as groundwater migrates north along the barrier wall
	SHP-01-36X	224.84	3.0 - 8.0	217.10 - 212.10	Shallow Overburden/WT	Historically sampled annually, continued annual sampling to monitor As concentrations along Plow Shop Pond edge.
	SHP-01-37X	222.84	1.0 - 6.0	217.64 - 212.64	Shallow Overburden/WT	Historically sampled annually, continued annual sampling to monitor As concentrations along Plow Shop Pond edge.
	SHP-01-38A	220.9	1.5 - 6.5	217.27 - 212.27	Shallow Overburden/WT	Historically sampled annually, continued annual sampling to monitor As concentrations along Plow Shop Pond edge and downgradient of the barrier wall
NEARFIELD AREA						
Semi-Annual	SHM-93-22B	219.42	82.3 - 92.3	136.62 - 126.63	Mid-Depth Overburden	Sampled historically, to evaluate ATP effectiveness and trends.
	SHM-96-5B	218.95	80.0 - 90.0	137.43 - 127.43	Base of Sand/Till	Sampled historically, to evaluate ATP effectiveness and trends.
	SHM-05-41B	222.3	62.0 - 64.0	160.6 - 158.6	Mid-Depth Overburden	Sampled historically, to evaluate ATP effectiveness and trends.
	SHM-05-41C	222.56	88.0 - 93.0	134.94 - 129.94	Deep Overburden/Till	Sampled historically, to evaluate ATP effectiveness and trends.
Annual	SHL-5	217.62	3.0 - 13.0	213.81 - 203.81	Shallow Overburden/WT	Historically sampled historically to evaluate ATP effectiveness and trends; relatively low detections (<50 ug/L since March 1993) so reduced sampling to annually.
	SHL-8S	220.99	52.0 - 54.0	166.95 - 164.95	Mid-Depth Overburden	Historically sampled semi-annually; no detections since October 2007, so reduced sampling to annually
	SHL-8D*	220.79	68.0 - 70.0	150.95 - 148.95	Deep Overburden	Historically sampled semi-annually; no detections since October 2007, so reduced sampling to annually
	SHL-9	221.99	15.0 - 25.0	205.88 - 195.88	Shallow Overburden/WT	Historically sampled historically to evaluate ATP effectiveness and trends; relatively low detections (<50 ug/L since October 2002) so reduced sampling to annually.
	SHL-22	219.59	105.0 - 115.0	114.06 - 104.06	Deep Overburden	Historically sampled historically to evaluate ATP effectiveness and trends; relatively low detections (<100 ug/L since October 2008) so reduced sampling to annually.
	SHM-93-22C	220.7	124.3 - 134.3	94.72 - 84.72	Bedrock	Historically sampled historically to evaluate ATP effectiveness and trends; relatively low detections (<100 ug/L since installation in 1993) so reduced sampling to annually.
	SHM-96-5C	218.4	50.0 - 60.0	167.41 - 157.41	Mid-Depth Overburden	Historically sampled historically to evaluate ATP effectiveness and trends; relatively low detections (<70 ug/L since October 2001) so reduced sampling to annually.
	SHM-05-41A	222.45	42.0 - 44.0	180.78 - 178.78	Shallow Overburden	Historically sampled historically to evaluate ATP effectiveness and trends; relatively low detections (<50 ug/L since September 2006) so reduced sampling to annually.
	SHM-05-42A	216.84	40.0 - 42.0	173.66 - 171.66	Shallow Overburden	Historically sampled historically to evaluate ATP effectiveness and trends; relatively low detections (<5 ug/L since installation in 2005) so reduced sampling to annually.
	SHM-05-42B	216.82	70.0 - 72.0	143.66 - 141.66	Deep Overburden	Historically sampled historically to evaluate ATP effectiveness and trends; relatively low detections (<300 ug/L since April 2008) so reduced sampling to annually.
	SHM-10-06	232.91	69.5 - 79.5	160.49 - 150.49	Deep Overburden	Added to annual sampling to provide an additional monitoring point along the eastern edge of the landfill.
	SHM-10-06A	248.55	77.0 - 87.0	169.0 - 159.0	Deep Overburden	Added to annual sampling to replace SHL-21. SHM-10-06A has a deeper screen interval and higher As concentrations as compared to SHL-21.
	SHM-10-16	219.24	75.0 - 85.0	144.24 - 134.24	Deep Overburden	Added to annual sampling to provide an additional monitoring point northwest of the treatment plant.
	EPA-PZ-2012-1A/B	222.75 / 222.50	20.0 - 25.0 / 70.0 - 75.0	202.75 - 197.75 / 152.50 - 147.50	Shallow/Deep Overburden	Provides an additional shallow/deep sampling point in the nearfield area, east of the treatment plant.
	EPA-PZ-2012-2A/B	222.34 / 222.32	20.0 - 25.0 / 75.0 - 80.0	202.34 - 197.34 / 147.32 - 142.32	Shallow/Deep Overburden	Provides an additional shallow/deep sampling point in the nearfield area, northeast of the treatment plant.
	EPA-PZ-2012-3A/B	222.60 / 222.51	20.0 - 25.0 / 70.0 - 75.0	202.60 - 197.60 / 152.51 - 147.51	Shallow/Deep Overburden	Provides an additional shallow/deep sampling point in the nearfield area, north of the treatment plant.
	EPA-PZ-2012-4A/B	226.54 / 226.34	20.0 - 25.0 / 70.0 - 75.0	206.54 - 201.54 / 156.34 - 151.34	Shallow/Deep Overburden	Provides an additional shallow/deep sampling point in the nearfield area, north of the treatment plant.
	EPA-PZ-2012-5A/B	218.91 / 218.31	20.0 - 25.0 / 80.0 - 85.0	198.91 - 193.91 / 138.31 - 133.31	Shallow/Deep Overburden	Provides an additional shallow/deep sampling point in the nearfield area, west of the treatment plant.
	EPA-PZ-2012-6A/B	234.21 / 234.03	25.0 - 30.0 / 75.0 - 80.0	209.21 - 204.21 / 159.03 - 154.03	Shallow/Deep Overburden	Provides an additional shallow/deep sampling point in the nearfield area, west of the treatment plant.
	EPA-PZ-2012-7A/B	234.08 / 233.92	25.0 - 30.0 / 60.0 - 65.0	209.08 - 204.08 / 173.92 - 168.92	Shallow/Mid-Depth Overburden	Provides an additional shallow/deep sampling point in the nearfield area, west of the treatment plant.
Every 5 Years	SHL-23	241.26	23.0 - 33.0	216.36 - 206.36	Shallow Overburden/WT	Historically sampled bi-annually to monitor/evaluate possible western migration route downgradient of source area
NORTH IMPACT AREA						
Semi-Annual	SHM-13-03	211.7	42.0 - 52.0	167.83 - 157.83	Deep Overburden	Monitors the leading/northern edge of the As impacted groundwater
	SHM-13-04	227.01	20.0 - 30.0	207.01 - 197.01	Shallow Overburden	Monitors As concentrations within the core of the As impacted groundwater
	SHM-13-06	223.89	36.0 - 46.0	188.23 - 178.23	Deep Overburden/Till	Monitors As concentrations within the core of the As impacted groundwater
	SHM-13-07	225.61	27.0 - 37.0	198.61 - 188.61	Mid-Depth Overburden	Monitors As concentrations within the core of the As impacted groundwater
	SHM-13-08	227.9	55.0 - 65.0	173.17 - 163.17	Mid-Depth Overburden/Till	Monitors As concentrations within the core of the As impacted groundwater
Annual	SHM-05-40X	223.34	32.0 - 34.0	191.55 - 189.99	Mid-Depth Overburden/Till	Sampled historically annually. Monitors As concentrations within the core of arsenic impacted groundwater.
	SHP-99-31C	214.72	68.0 - 78.0	141.97 - 131.97	Deep Overburden	Sampled historically annually. Monitors As concentrations within the core of As impacted groundwater at depth.
	SHM-13-05	225.11	75.0 - 85.0	150.57 - 140.57	Deep Overburden	Monitors eastern boundary of As impacted groundwater
	SHM-99-32X	221.37	72.0 - 82.0	147.07 - 137.07	Deep Overburden	Sampled historically annually. Monitors As concentrations within the core of As impacted groundwater.
	SHM-10-10	217.12	56.0 - 66.0	159.43 - 149.43	Deep Overburden/Till	Monitors the northern edge of the As impacted groundwater.
	SHM-13-02	218.7	60.0 - 70.0	156.88 - 146.88	Deep Overburden	Monitors the northern edge of the As impacted groundwater.
Every 5 Years	SHM-07-03	227.86	25.0 - 35.0	203.01 - 193.01	Shallow Overburden	Added sample location to monitor/evaluate possible western migration route.
	SHM-10-05A	235.07	50.0 - 60.0	185.24 - 175.24	Mid-Depth Overburden	Added sample location to monitor/evaluate the eastern extent of the NIA.
	SHM-13-01	208.07	39.0 - 49.0	166.79 - 156.79	Deep Overburden	Added sample location to monitor/evaluate the western extent of the NIA.
	SHM-10-02	223.07	53.0 - 63.0	167.12 - 157.12	Mid-Depth Overburden	Added sample location to monitor/evaluate the western extent of the NIA.
	SHM-10-03	232.06	58.5 - 68.5	171.2 - 161.2	Mid-Depth Overburden	Added sample location to monitor/evaluate the northern extent of the NIA.
	SHM-10-04	212.63	55.0 - 65.0	154.73 - 144.73	Mid-Depth Overburden	Added sample location to monitor/evaluate the northern extent of the NIA.
	SHM-10-08	214.41	46.0 - 56.0	165.68 - 155.68	Deep Overburden/Till	Added sample location to monitor/evaluate the western extent of the NIA.

Semi-Annual Samping (Spring and Fall)
Annual Sampling (Fall)
Sampling Every 5 Years (Fall)

Notes:
ft bgs = feet below ground surface
ft msl = feet mean sea level
* Includes estimated values derived from Supplemental Groundwater Investigation (Harding ESE, 2003).
Adapted from Final Revised Long Term Monitoring and Maintenance Plan (CH2MHill, 2007).

TABLE 2
LTMMP HYDRAULIC MONITORING ONLY
Shepley's Hill Landfill, Devens, Massachusetts

Monitoring Interval	Well ID	TOC Elevation	Screen Interval	Screen Elevation	Interval Description	DQO for Inclusion within the LTMMP
Upgradient Area						
Annual	SHL-17	233.83	--	--	Shallow Overburden/WT	Provides an additional hydraulic monitoring point upgradient of the landfill
LANDFILL AREA						
Annual	N5-P2	242.67	20.0 - 25.0*	220.39 - 215.39	Shallow Overburden/WT	Historically sampled annually, reduced to hydraulic monitoring only due to close proximity to N5-P1, SHM-10-13, SHM-10-14, and SHM-10-15.
	N7-P1	255.6	65.0 - 69.0*	188.51 - 183.51	Bedrock	Historically used for hydraulic monitoring purposes.
	N7-P2	256.07	29.0 - 35.0*	224.51 - 218.51	Shallow Overburden/WT	Historically used for hydraulic monitoring purposes.
	SHP-95-27X	237.46	--	--	Shallow Overburden/WT	Historically used for hydraulic monitoring purposes.
	SHL-18	237.56	--	--	Shallow Overburden/WT	Historically used for hydraulic monitoring purposes.
	N6-P1	258.46	84.0 - 88.0*	171.78 - 167.78	Bedrock	Historically used for hydraulic monitoring purposes.
	SHP-99-01B	272.55	4.0 - 8.0	267.13 - 263.13	Shallow Overburden	Provides an additional hydraulic monitoring point on the western side of the landfill
	SHP-99-01C	273.56	19.7 - 29.7	254.66 - 244.66	Bedrock	Provides an additional hydraulic monitoring point on the western side of the landfill
	SHP-99-35X	257.5	30.2 - 40.2	225.99 - 215.99	Shallow Overburden/WT	Historically used for hydraulic monitoring purposes.
BARRIER WALL AREA						
Semi-Annual	PZ-12-01	237.55	24.0 - 34.0	209.78 - 199.78	Shallow Overburden/WT	Hydraulic monitoring of groundwater east of the barrier wall
	PZ-12-02	237.81	24.0 - 34.0	209.68 - 199.68	Shallow Overburden/WT	Hydraulic monitoring of groundwater west of the barrier wall
	PZ-12-03	236.42	22.0 - 32.0	210.76 - 200.76	Shallow Overburden/WT	Hydraulic monitoring of groundwater east of the barrier wall
	PZ-12-04	238.22	22.0 - 32.0	212.97 - 202.97	Shallow Overburden/WT	Hydraulic monitoring of groundwater west of the barrier wall
	PZ-12-05	238.81	26.0 - 36.0	210.05 - 200.05	Mid-Depth Overburden	Hydraulic monitoring of groundwater east of the barrier wall
	PZ-12-06	242.24	26.0 - 36.0	212.35 - 202.35	Mid-Depth Overburden	Hydraulic monitoring of groundwater west of the barrier wall
	PZ-12-07	244.63	18.0 - 28.0	222.79 - 212.79	Mid-Depth Overburden	Hydraulic monitoring of groundwater east of the barrier wall
	PZ-12-08	244.88	18.0 - 28.0	223.70 - 213.70	Mid-Depth Overburden	Hydraulic monitoring of groundwater west of the barrier wall
	PZ-12-09	241.94	22.0 - 32.0	216.26 - 206.26	Shallow Overburden/WT	Hydraulic monitoring of groundwater east of the barrier wall
	PZ-12-10	242.29	22.0 - 32.0	216.83 - 206.84	Shallow Overburden/WT	Hydraulic monitoring of groundwater west of the barrier wall
Annual	N1-P1	230.01	--	--	Deep Overburden	Historically used for hydraulic monitoring purposes.
	N1-P2	230.03	--	--	Mid-Depth Overburden	Historically used for hydraulic monitoring purposes.
	N1-P3	230.18	--	--	Shallow Overburden/WT	Historically used for hydraulic monitoring purposes.
	N2-P1	222.16	--	--	Deep Overburden	Historically used for hydraulic monitoring purposes.
	N2-P2	222.0	--	--	Mid-Depth Overburden	Historically used for hydraulic monitoring purposes.
	N3-P1	220.86	33.0 - 35.0*	185.73 - 183.73	Bedrock	Historically used for hydraulic monitoring purposes.
	N3-P2	242.67	4.0 - 9.0*	214.73 - 209.73	Water Table	Historically used for hydraulic monitoring purposes.
	SHL-3	246.89	24 - 34	222.89 - 212.89	Mid-Depth Overburden	Historically used for hydraulic monitoring purposes.
	SHP-01-38B	221.06	18.0 - 23.0	200.87 - 195.87	Deep Overburden	Historically used for hydraulic monitoring purposes.
	SHP-05-43	260.66	50.5 - 60.5	207.83 - 197.83	Shallow Overburden	Historically used for hydraulic monitoring purposes.
	SHP-05-44	258.08	51.0 - 61.0	207.79 - 197.49	Mid-Depth Overburden	Historically used for hydraulic monitoring purposes.
	SHM-11-07	240.86	41.0 - 46.0	197.19	Mid-Depth Overburden/Till	Hydraulic monitoring of groundwater upgradient and slightly removed from the barrier wall
NEARFIELD AREA						
Annual	SHL-13	220.71	5.0 - 20.0	213.47 - 198.47	Shallow Overburden/WT	Historically sampled annually, reduced to hydraulic monitoring only due to As concentrations less than 5 ppb since sampling initiated in 2006. Also close proximity to SHL-8S/D, which is sampled annually and exhibited As concentrations below detection limits since October 2007
	SHP-05-45A	228.47	20.0 - 25.0	206.33 - 201.33	Shallow Overburden	Historically used for hydraulic monitoring purposes.
	SHP-05-45B	229.1	65.0 - 75.0	161.73 - 151.73	Mid-Depth Overburden	Historically used for hydraulic monitoring purposes.
	SHP-05-46A	227.63	20.0 - 25.0	206.1 - 201.1	Shallow Overburden	Historically used for hydraulic monitoring purposes.
	SHP-05-46B	228.22	65.0 - 75.0	161.35 - 151.35	Mid-Depth Overburden	Historically used for hydraulic monitoring purposes.
	SHP-05-47A	217.53	1.0 - 2.0	212.5 - 211.5	Water Table	Historically used for hydraulic monitoring purposes.
	SHP-05-47B	215.4	3.0 - 4.0	210.47 - 209.47	Water Table	Historically used for hydraulic monitoring purposes.
NORTH IMPACT AREA						
Annual	SHP-05-48A	217.3	1.0 - 2.0	212.09 - 211.09	Water Table	Historically used for hydraulic monitoring purposes.
	SHP-05-48B	215.93	2.0 - 3.0	211.03 - 210.03	Water Table	Historically used for hydraulic monitoring purposes.
	SHP-05-49A	216.67	1.0 - 2.0	211.26 - 210.26	Water Table	Historically used for hydraulic monitoring purposes.
	SHP-05-49B	215.15	2.5 - 3.5	210.66 - 209.66	Water Table	Historically used for hydraulic monitoring purposes.
	SHM-05-39A	221.54	37.0 - 39.0	184.79 - 182.79	Mid-Depth Overburden	Historically sampled annually, reduced to hydraulic monitoring only due to close proximity to SHM-05-40X and SHM-99-31C. Newly installed wells SHM-13-.05 are located downgradient of this sampling location have been added to the sampling plan
	SHM-05-39B	221.52	66.0 - 68.0	155.78 - 153.78	Deep Overburden	Historically sampled annually, reduced to hydraulic monitoring only due to close proximity to SHM-05-40X and SHM-99-31C. Newly installed wells SHM-13-05 are located downgradient of this sampling location have been added to the sampling plan
	SHP-99-31A	214.35	4.0 - 14.0	208.76 - 198.76	Shallow Overburden/WT	Historically sampled annually, reduced to hydraulic monitoring only due to shallow well construction. Higher As concentrations have been historically detected within the deepest well of the triplet (SHP-99-31C)
	SHP-99-31B	214.4	50.0 - 60.0	162.44 - 152.44	Mid-Depth Overburden	Historically sampled annually, reduced to hydraulic monitoring only due to mid-depth well construction. Higher As concentrations have been historically detected within the deepest well of the triplet (SHP-99-31C)
	SHP-99-34 B	224.58	74.5 - 79.5	148.0 - 143.0	Deep Overburden	Historically used for hydraulic monitoring purposes.
	SHM-10-01	209.52	60.5 - 70.5	146.14 - 136.14	Deep Overburden/Till	Added to provide an additional hydraulic monitoring point along the western portion of the NIA
SURFACE WATER						
Annual	PSP-01	218.16	--	--	Staff Gauge	Historically used for monitoring surface water elevations within Plow Shop Pond.
	SHSG-13-01G	208.29	--	--	Staff Gauge	Added to monitor surface water elevations within Nonacoicus Brook and to aid in hydraulic modeling
	SHSG-13-02G	211.67	--	--	Staff Gauge	Added to monitor surface water elevations within Nonacoicus Brook and to aid in hydraulic modeling
	SHSG-13-03G	211.07	--	--	Staff Gauge	Added to monitor surface water elevations within Nonacoicus Brook and to aid in hydraulic modeling

Semi-Annual Hydraulics Only
Annual Hydraulics Only

Notes:
ft bgl = feet below ground level
ft msl = feet mean sea level
All wells included in the SHL LTM sampling program are to be gauged at minimum annually in addition to those wells listed above.
* Includes estimated values derived from Supplemental Groundwater Investigation (Harding ESE, 2003).
Adapted from Final Revised Long Term Monitoring and Maintenance Plan (CH2MHill, 2007).
During five-year review periods, hydraulic monitoring will be preformed semi-annually for all wells.

TABLE 3
GROUNDWATER SAMPLE ANALYTICAL PROGRAM
Shepley's Hill Landfill, Devens, Massachusetts

Analytical Parameters	Analytical Method
Dissolved Arsenic	**EPA 6020A**
Dissolved Metals Iron Manganese	**EPA 6010C**
Alkalinity	**SM2320B**
Chloride	**SM4500CL C**
Sulfate	**EPA 300**
Dissolved Organic Carbon	**SM5310B**
Field Parameters pH Temperature Specific Conductance Dissolved Oxygen Oxygen Reduction Potential VOCs (headspace)	**Field Instruments**

TABLE 4
WELL AND PIEZOMETER ABANDONMENT LIST
Shepley's Hill Landfill, Devens, Massachusetts

Well ID	Screen Depth	General Location	Rationale for Abandonment
SHP-99-01B	4 - 8	West side of landfill on ridge	Western shallow monitoring point between the landfill and Shepley's Hill is unneeded
SHL-1	Unknown	West side of landfill on ridge	Well obstructed
SHM-93-24A	14 - 24	South of landfill across railroad tracks	Very close to SHL-24, which is an upgradient 5-yr monitoring point
SHM-93-18B	78.5 - 88.5	East of landfill	Very close to SHL-18, which is a hydraulic monitoring point
SHM-93-10D	Unknown	Between barrier wall and pond	This well was thought to be abandoned but still has water in it
SHL-21	42 - 52	On hill east of ATP	Located near SHM-10-06A which is monitored annually
SHM-07-05X	Unknown	South portion of NIA, in road	Located near SHM-05-40X and has no historical data
SHM-99-33A/B	Unknown	South portion of NIA, in road	Located near SHM-05-39A/B, which are used for hydraulic monitoring, and SHM-99-31C, which is monitored annually
SHM-99-34A	Unknown	Southeast portion of NIA, along edge of road	The steel casing of this piezometer was observed to have been damaged to the extent that gauging is no longer possible. It is also located adjacent to SHP-99-34B which is monitored annually.
SHP-07-01BS	Unknown	Central portion of the NIA	This piezometer has not been observed in the field. If located, it will be abandoned due to its location between SHM-13-03 and SHM-13-07.
SHP-07-01BD	Unknown	Central portion of the NIA	This piezometer has not been observed in the field. If located, it will be abandoned due to its location between SHM-13-03 and SHM-13-07.
Unknown Well	Unknown	Southwest of the barrier wall	The identification and construction of this well is unknown. Also, this well is located near PZ-12-10.

Table 5
Historic Barrier Wall Hydraulic Monitoring Data
Shepley's Hill Landfill, Devens, Massachusetts

Date: 11-5-12 - Day 53 after Barrier Construction Completion

Well ID	Top of Casing Elev.	DTW (ft)	WT Elev.	Current Δ
PZ-12-01	237.54	20.51	217.03	
PZ-12-02	237.77	20.47	217.3	0.27
PZ-12-03	236.4	19.37	217.03	
PZ-12-04	238.2	20.42	217.78	0.75
PZ-12-05	238.7	21.49	217.21	
PZ-12-06	242.22	24.24	217.98	0.77
PZ-12-07	244.63	26.89	217.74	
PZ-12-08	244.88	26.26	218.62	0.88
PZ-12-09	241.93	23.03	218.9	
PZ-12-10	242.28	22.35	219.93	1.03

Date: 11-16-12 - Day 64 after Barrier Construction Completion

Well ID	Top of Casing Elev.	DTW (ft)	WT Elev.	Current Δ	Δ from 11/5/12
PZ-12-01	237.54	20.63	216.91		
PZ-12-02	237.77	20.52	217.25	0.34	0.07
PZ-12-03	236.4	19.52	216.88		
PZ-12-04	238.2	20.42	217.78	0.90	0.15
PZ-12-05	238.7	21.66	217.04		
PZ-12-06	242.22	24.26	217.96	0.92	0.15
PZ-12-07	244.63	27.34	217.29		
PZ-12-08	244.88	26.31	218.57	1.28	0.4
PZ-12-09	241.93	23.76	218.17		
PZ-12-10	242.28	22.62	219.66	1.49	0.46

Date: 11-21-12 - Day 69 after Barrier Construction Completion

Well ID	Top of Casing Elev.	DTW (ft)	WT Elev.	Current Δ	Δ from 11/5/12	Δ from 11/16/12
PZ-12-01	237.54	20.59	216.95			
PZ-12-02	237.77	20.49	217.28	0.33	0.06	-0.01
PZ-12-03	236.4	19.45	216.95			
PZ-12-04	238.2	20.37	217.83	0.88	0.13	-0.02
PZ-12-05	238.7	21.59	217.11			
PZ-12-06	242.22	24.20	218.02	0.91	0.14	-0.01
PZ-12-07	244.63	27.32	217.31			
PZ-12-08	244.88	26.29	218.59	1.28	0.4	0
PZ-12-09	241.93	23.89	218.04			
PZ-12-10	242.28	22.69	219.59	1.55	0.52	0.06

Table 5
Historic Barrier Wall Hydraulic Monitoring Data
Shepley's Hill Landfill, Devens, Massachusetts

Date: 11-28-12 - Day 76 after Barrier Construction Completion

Well ID	Top of Casing Elev.	DTW (ft)	WT Elev.	Current Δ	Δ from 11/5/12	Δ from 11/16/12	Δ from 11/21/12
PZ-12-01	237.54	20.72	216.82				
PZ-12-02	237.77	20.56	217.21	0.39	0.12	0.05	0.06
PZ-12-03	236.4	19.64	216.76				
PZ-12-04	238.2	20.42	217.78	1.02	0.27	0.12	0.14
PZ-12-05	238.7	21.77	216.93				
PZ-12-06	242.22	24.24	217.98	1.05	0.28	0.13	0.14
PZ-12-07	244.63	27.42	217.21				
PZ-12-08	244.88	26.35	218.53	1.32	0.44	0.04	0.04
PZ-12-09	241.93	24.01	217.92				
PZ-12-10	242.28	22.77	219.51	1.59	0.56	0.1	0.04

Date: 12-13-12 - Day 91

Well ID	Top of Casing Elev.	DTW (ft)	WT Elev.	Current Δ	Δ from 11/5/12	Δ from 11/16/12	Δ from 11/21/12	Δ from 11/28/12
PZ-12-01	237.54	21.00	216.54					
PZ-12-02	237.77	20.83	216.94	0.4	0.13	0.06	0.07	0.01
PZ-12-03	236.4	19.91	216.49					
PZ-12-04	238.2	20.68	217.52	1.03	0.28	0.13	0.15	0.01
PZ-12-05	238.7	22.05	216.65					
PZ-12-06	242.22	24.51	217.71	1.06	0.29	0.14	0.15	0.01
PZ-12-07	244.63	27.77	216.86					
PZ-12-08	244.88	26.63	218.25	1.39	0.51	0.11	0.11	0.07
PZ-12-09	241.93	24.37	217.56					
PZ-12-10	242.28	23.06	219.22	1.66	0.63	0.17	0.11	0.07

Date: 1-16-13 - Day 125

Well ID	Top of Casing Elev.	DTW (ft)	WT Elev.	Current Δ	Δ from 11/5/12	Δ from 11/16/12	Δ from 11/21/12	Δ from 11/28/12	Δ from 12/13/12
PZ-12-01	237.54	20.65	216.89						
PZ-12-02	237.77	20.61	217.16	0.27	0	-0.07	-0.06	-0.12	-0.13
PZ-12-03	236.4	19.42	216.98						
PZ-12-04	238.2	20.50	217.70	0.72	-0.03	-0.18	-0.16	-0.3	-0.31
PZ-12-05	238.7	21.57	217.13						
PZ-12-06	242.22	24.33	217.89	0.76	-0.01	-0.16	-0.15	-0.29	-0.3
PZ-12-07	244.63	27.30	217.33						
PZ-12-08	244.88	26.44	218.44	1.11	0.23	-0.17	-0.17	-0.21	-0.28
PZ-12-09	241.93	23.11	218.82						
PZ-12-10	242.28	22.58	219.70	0.88	-0.15	-0.61	-0.67	-0.71	-0.78

Table 5
Historic Barrier Wall Hydraulic Monitoring Data
Shepley's Hill Landfill, Devens, Massachusetts

Date: 2-14-13 - Day 154

Well ID	Top of Casing Elev.	DTW (ft)	WT Elev.	Current Δ	Δ from 11/5/12	Δ from 11/16/12	Δ from 11/21/12	Δ from 11/28/12	Δ from 12/13/12	Δ from 1/16/13
PZ-12-01	237.54	20.89	216.65							
PZ-12-02	237.77	20.72	217.05	0.4	0.13	0.06	0.07	0.01	0	0.13
PZ-12-03	236.4	19.79	216.61							
PZ-12-04	238.2	20.57	217.63	1.02	0.27	0.12	0.14	0	-0.01	0.3
PZ-12-05	238.7	21.92	216.78							
PZ-12-06	242.22	24.42	217.80	1.02	0.25	0.1	0.11	-0.03	-0.04	0.26
PZ-12-07	244.63	27.68	216.95							
PZ-12-08	244.88	26.55	218.33	1.38	0.5	0.1	0.1	0.06	-0.01	0.27
PZ-12-09	241.93	24.19	217.74							
PZ-12-10	242.28	22.83	219.45	1.71	0.68	0.22	0.16	0.12	0.05	0.83

Date: 3-12-13 - Day 180

Well ID	Top of Casing Elev.	DTW (ft)	WT Elev.	Current Δ	Δ from 11/5/12	Δ from 11/16/12	Δ from 11/21/12	Δ from 11/28/12	Δ from 12/13/12	Δ from 1/16/13	Δ from 2/14/13
PZ-12-01	237.54	20.57	216.97								
PZ-12-02	237.77	20.46	217.31	0.34	0.07	0	0.01	-0.05	-0.06	0.07	-0.06
PZ-12-03	236.4	19.43	216.97								
PZ-12-04	238.2	20.36	217.84	0.87	0.12	-0.03	-0.01	-0.15	-0.16	0.15	-0.15
PZ-12-05	238.7	21.58	217.12								
PZ-12-06	242.22	24.21	218.01	0.89	0.12	-0.03	-0.02	-0.16	-0.17	0.13	-0.49
PZ-12-07	244.63	27.27	217.36								
PZ-12-08	244.88	26.27	218.61	1.25	0.37	-0.03	-0.03	-0.07	-0.14	0.14	-0.13
PZ-12-09	241.93	23.67	218.26								
PZ-12-10	242.28	22.19	220.09	1.83	0.8	0.34	0.28	0.24	0.17	0.95	0.12

Date: 4-22-13 - Day 221

Well ID	Top of Casing Elev.	DTW (ft)	WT Elev.	Current Δ	Δ from 11/5/12	Δ from 11/16/12	Δ from 11/21/12	Δ from 11/28/12	Δ from 12/13/12	Δ from 1/16/13	Δ from 2/14/13	Δ from 3/12/13
PZ-12-01	237.54	20.80	216.74									
PZ-12-02	237.77	20.41	217.36	0.62	-0.66	0.28	0.29	0.23	0.22	0.35	0.22	0.28
PZ-12-03	236.4	19.81	216.59									
PZ-12-04	238.2	20.14	218.06	1.47	0.72	0.57	0.59	0.45	0.44	0.75	0.45	0.6
PZ-12-05	238.7	21.91	216.79									
PZ-12-06	242.22	23.99	218.23	1.44	0.67	0.52	0.53	0.39	0.38	0.68	0.42	0.19
PZ-12-07	244.63	27.62	217.01									
PZ-12-08	244.88	26.05	218.83	1.82	0.94	0.54	0.54	0.5	0.43	0.71	0.44	0.57
PZ-12-09	241.93	24.11	217.82									
PZ-12-10	242.28	22.69	219.59	1.77	0.74	0.28	0.22	0.18	0.11	0.89	0.06	-0.06

Even Numbered Piezometers - East of the Barrier Wall
Odd Numbered Piezometers - West of the Barrier Wall
Station Locations are approximate for spacial orientation only.
Barrier Wall Construction Completion Date - 9/13/12

APPENDIX A

TABLE 1
GROUNDWATER PROFILE SAMPLE RESULTS
Spring 2013
Shepley's Hill Landfill, Devens, MA

Location	Sample ID	Date	Time	Depth (ft)	Dissolved Arsenic ug/L	Turbidity NTU	DO mg/L	pH	Temp Celcius	Spec Cond uS/cm	ORP mV	Notes
SHM-13-01	GP-13-01-015	5/7/2013	11:00	15	<1.0	0.98	8.95	5.98	12.07	696	93.9	Geoprobe Profiling Refusal Depth = 51 feet
	GP-13-01-025	5/7/2013	12:05	25	<1.0	10.3	5.84	5.96	11.74	729	88.7	Rotosonic Bedrock Confirmation Depth = 51 feet
	DUP-050713-F	5/7/2013	12:05	25	<1.0	10.3	5.84	5.96	11.74	729	88.7	
	GP-13-01-035	5/7/2013	13:05	35	<1.0	4.23	8.69	6.48	14.62	428	53.4	
	GP-13-01-045	5/7/2013	14:05	45	<1.1	Max	2.61	6.24	11.45	350	12.0	
	GP-13-01-051	5/7/2013	15:05	51	<1.3	Max	0.83	7.50	15.82	438	-206.7	
SHM-13-02	GP-13-02-015	4/15/2013	10:20	15	0.93 J	19.7	4.06	4.93	9.46	124	108.2	Geoprobe Profiling Refusal Depth = 71 feet
	GP-13-02-025	4/15/2013	11:20	25	0.82 J	37.0	3.24	5.58	11.72	250	84.7	Rotosonic Bedrock Confirmation Depth = 71 feet
	GP-13-02-035	4/15/2013	12:50	35	0.93 J	76.3	1.74	5.76	12.17	338	60.1	
	DUP-041513-F	4/15/2013	12:30	35	0.99 J	76.3	1.74	5.76	12.17	338	60.1	
	GP-13-02-045	4/15/2013	13:45	45	0.95 J	14.2	0.23	5.96	12.78	465	-4.5	
	GP-13-02-055	4/15/2013	14:45	55	0.89 J	3.88	0.23	6.09	12.53	280	-10.1	
	GP-13-02-065	4/15/2013	16:16	65	0.95 J	12.0	0.45	6.55	12.59	251	-85.9	
	GP-13-02-071	4/16/2017	10:05	71	1.2	40.1	0.41	6.65	12.09	223	-69.1	
SHM-13-03	GP-13-03-010	4/16/2013	12:45	10	0.6 J	0.15	9.44	6.10	11.86	761	59.3	Geoprobe Profiling Refusal Depth = 55 feet
	GP-13-03-020	4/16/2013	13:50	20	1.7	760	0.35	6.09	11.21	639	-25.4	Rotosonic Bedrock Confirmation Depth = 53 feet
	GP-13-03-030	4/16/2013	15:55	30	17.6	0.82	0.46	5.79	11.69	343	-35.0	
	GP-13-03-040	4/17/2013	09:30	40	22.6	35.3	2.08	6.07	12.03	492	-15.0	
	GP-13-03-050	4/17/2013	10:55	50	357	42.8	2.68	6.52	12.33	622	-70.3	
SHM-13-04	GP-13-04-025	4/8/2013	14:00	25	3,510	5.10	0.45	6.25	12.27	322	-56.7	Geoprobe Profiling Refusal Depth = 45 feet
	GP-13-04-035	4/8/2013	15:00	35	21.1	39.7	0.46	5.93	12.60	83	60.0	Rotosonic Bedrock Confirmation Depth = 45feet
	DUP-040813-F	4/8/2013	15:00	35	21.6	39.7	0.46	5.93	12.60	83	60.0	
	GP-13-04-045	4/9/2013	11:30	45	3	1,431	5.39	5.95	13.46	106	-7.2	
	DUP-040913-F	4/9/2013	11:30	45	--	1,431	5.39	5.95	13.46	106	-7.2	
SHM-13-05	GP-13-05-020	4/9/2013	15:25	20	0.6 J	1.35	0.70	5.01	10.91	165	55.9	Geoprobe Profiling Refusal Depth = 84 feet
	GP-13-05-030	4/10/2013	15:55	30	0.55 J	28.1	0.25	6.28	11.48	328	-428.6	Rotosonic Bedrock Confirmation Depth = 85 feet
	GP-13-05-040	4/10/2013	15:00	40	0.67 J	4.89	0.30	5.83	10.93	230	-338.7	
	GP-13-05-050	4/10/2013	14:10	50	33.5	11.5	0.32	6.33	11.01	327	-176.6	
	GP-13-05-060	4/10/2013	13:25	60	69.4	50.8	0.32	6.71	10.93	639	-168.3	
	GP-13-05-070	4/10/2013	12:25	70	2.4	70.4	0.36	6.23	10.72	716	-317.3	
	GP-13-05-080	4/10/2013	11:25	80	56.8	74.4	0.31	6.63	10.85	1,169	-154.4	
	DUP-041013-F	4/10/2013	11:25	80	57.9	74.4	0.31	6.63	10.85	1,169	-154.4	
	GP-13-05-084	4/10/2013	10:40	84	96.5	83.0	0.35	6.85	11.13	1,152	-126.2	
SHM-13-06	GP-13-06-020	4/17/2013	14:25	20	<1.0	1.37	4.02	5.38	12.96	1,442	75.2	Geoprobe Profiling Refusal Depth = 58 feet
	GP-13-06-030	4/17/2013	15:35	30	236	39.7	0.51	5.74	13.14	560	-3.7	Rotosonic Bedrock Confirmation Depth = 57 feet
	DUP-041713-F	4/17/2013	15:35	30	244	39.7	0.51	5.74	13.14	560	-3.7	
	GP-13-06-040	4/18/2013	10:55	40	3,380	2,471	0.11	6.87	12.79	388	-123.4	
	DUP-041813-F	4/18/2013	10:55	40	--	2,471	0.11	6.87	12.79	388	-123.4	
	GP-13-06-050	4/18/2013	11:55	50	1,650	3,652	0.23	6.5	12.55	179	-60.7	
	GP-13-06-058	4/18/2013	13:15	58	85	2,531	0.26	6.69	13.48	187	-51.5	
SHM-13-07	GP-13-07-021	4/18/2017	15:25	21	<1.8	2.65	4.41	6.21	11.83	2,069	119.5	Geoprobe Profiling Refusal Depth = 48 feet
	GP-13-07-031	4/19/2013	09:30	31	3,170	3.06	1.23	6.64	13.09	310	-87.1	
	GP-13-07-041	4/19/2013	10:35	41	1,650	742	0.26	7.09	14.64	635	-156.8	
	GP-13-07-048	4/19/2013	11:35	48	135	Max	0.13	6.62	14.46	477	-84.2	
SHM-13-08	GP-13-08-025	4/22/2013	10:25	25	1.7	1.38	0.73	6.04	11.69	1898	1.3	Geoprobe Profiling Refusal Depth = 71 feet
	DUP-042213-F	4/22/2013	10:25	25	1.7	1.38	0.73	6.04	11.69	1898	1.3	Rotosonic Bedrock Confirmation Depth = 71 feet
	GP-13-08-035	4/22/2013	11:25	35	1.5	2,015	0.7	6.41	12.93	732	-217.1	
	GP-13-08-045	4/22/2013	12:30	45	2	946	0.08	5.98	12.39	563	-233.8	
	GP-13-08-055	4/22/2013	13:45	55	288	Max	0.05	6.87	12.75	301	-203.8	
	GP-13-08-065	4/22/2013	14:45	65	1,080	Max	0.05	6.71	12.74	534	-124.6	
	DUP-042213-F (EPA dup)	4/22/2013	14:45	65	--	Max	0.05	6.71	12.74	534	-124.6	
	GP-13-08-071	4/22/2013	15:55	71	20.6	1,287	0.11	6.98	11.74	687	-175.2	

TABLE 1
GROUNDWATER PROFILE SAMPLE RESULTS
Spring 2013
Shepley's Hill Landfill, Devens, MA

Location	Sample ID	Date	Time	Depth (ft)	Dissolved Arsenic ug/L	Turbidity NTU	DO mg/L	pH	Temp Celcius	Spec Cond uS/cm	ORP mV	Notes
SHM-13-09	GP-13-09-025	4/23/2013	10:10	25	<1.3	19.8	0.23	6.32	9.89	637	-16.4	Geoprobe Profiling Refusal Depth = 100 feet
	GP-13-09-035	4/23/2013	11:05	35	152	2,310	0.07	6.63	10.12	611	-122.7	
	GP-13-09-045	4/23/2013	12:05	45	77.2 J	Max	0.10	6.98	9.84	515	-168.5	
	DUP-042313-F	4/23/2013	12:05	45	165 J	Max	0.10	6.98	9.84	515	-168.5	
	GP-13-09-055	4/23/2013	13:25	55	4.2	Max	0.15	6.91	9.74	301	-124.5	
	GP-13-09-065	4/23/2013	14:40	65	59.5	Max	0.13	6.72	10.1	250	-143.4	
	GP-13-09-075	4/23/2013	15:50	75	12.2	Max	0.08	6.77	10.62	399	-164.1	
	GP-13-09-085	4/24/2013	10:15	85	9.6	Max	0.06	6.76	14.51	564	-450.1	
	GP-13-09-095	4/24/2013	11:50	95	12.1	Max	0.07	6.94	19.02	980	-527.5	
SHM-13-10	GP-13-10-25	4/24/2013	14:45	25	0.78 J	6.61	0.64	5.03	12.9	261	-4.6	Geoprobe Profiling Refusal Depth = 83 feet
	GP-13-10-35	4/24/2013	15:40	35	1.6	Max	0.07	5.91	14.35	399	-331.2	
	GP-13-10-45	4/25/2013	09:00	45	12.5	Max	0.10	6.57	12.46	646	-139.5	
	DUP-042413-F	4/25/2013	09:00	45	14.7	Max	0.10	6.57	12.46	646	-139.5	
	GP-13-10-55	4/25/2013	10:40	55	17.5	Max	1.74	6.62	13.99	953	-93.0	
	GP-13-10-65	4/25/2013	11:50	65	3.9	726	0.63	6.42	15.87	782	-65.4	
	GP-13-10-75	4/25/2013	13:00	75	3	2,538	1.45	6.08	13.41	1,036	-24.3	
	DUP-042413A-F	4/25/2013	13:00	75	2.9	2,538	1.45	6.08	13.41	1,036	-24.3	
	GP-13-10-83	4/25/2013	14:25	83	5.8	Max	0.36	6.99	13.23	1,123	-166.6	
SHM-13-11	GP-13-11-025	5/8/2013	10:27	25	<1.0	1.68	7.40	6.31	11.98	349	69.0	Geoprobe Profiling Refusal Depth = 58 feet
	GP-13-11-035	5/8/2013	12:26	35	<1.0	181	7.69	6.75	11.94	313	66.1	
	DUP-050813-F	5/8/2013	12:26	35	<1.0	181	7.69	6.75	11.94	313	66.1	
	GP-13-11-045	5/8/2013	13:52	45	<1.0	157	6.42	6.54	11.81	304	58.4	
	GP-13-11-055	5/8/2013	15:10	55	<1.6	Max	0.29	6.55	12.12	130	-62.0	
SHM-13-12	GP-13-12-008	4/12/2013	12:00	8	0.89 J	6.30	4.47	5.82	5.76	117	-54	Geoprobe Profiling Refusal Depth = 87 feet
	GP-13-12-17	4/12/2013	10:40	17	0.82 J	5.67	0.30	6.22	8.07	366	-214	
	GP-13-12-27	4/12/2013	09:40	27	0.76 J	1.69	4.35	6.25	9.9	249	-693	
	DUP-041213-F	4/12/2013	09:40	27	0.86 J	1.69	4.35	6.25	9.9	249	-693	
	GP-13-12-37	4/11/2013	15:25	37	0.61 J	51	6.59	6.00	10.71	937	55.4	
	GP-13-12-47	4/11/2013	14:25	47	0.95 J	1,775	6.26	5.75	10.67	864	76.6	
	GP-13-12-57	4/11/2013	13:25	57	1.6	3,568	4.56	5.86	10.27	467	36.6	
	GP-13-12-67	4/11/2013	12:25	67	0.71 J	103	6.65	5.54	10.79	515	90.7	
	GP-13-12-77	4/11/2013	11:22	77	0.84 J	24.50	4.29	5.87	10.69	464	NM	
	GP-13-12-87	4/11/2013	10:15	87	24.1	4.48	0.30	7.39	10.86	443	-164.8	
SHM-13-13	GP-13-13-025	5/9/2013	10:05	25	0.81 J	79.80	6.56	6.18	11.03	662	49.3	Geoprobe Profiling Refusal Depth = 41 feet
	DUP-050913-F	5/9/2013	10:05	25	--	79.80	6.56	6.18	11.03	662	49.3	
	GP-13-13-035	5/9/2013	11:05	35	0.61 J	Max	6.69	6.01	11.48	315	65.0	
	GP-13-13-041	5/9/2013	12:32	41	0.83 J	109.80	3.20	6.57	12.89	276	-33.4	

Notes

The data has been validated.
NA - Not Applicable
NM - Not Measured
ug/L is micrograms per liter
mg/l - miligrams per liter
J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
All samples were field filtered prior to laboratory submittal.

TABLE 2
GROUNDWATER RESULTS
January to February 2014
Shepley's Hill Landfill, Devens, MA

Groundwater Profiling Results

Location	Sample ID	Date	Time	Depth (ft)	Arsenic Test Kit ppb	Dissolved Arsenic ug/L	Turbidity NTU	DO mg/L	pH	Temp Celcius	Spec Cond uS/cm	ORP mV	Notes
SHM-13-14S/D	GP-13-14-010	1/31/2018	1030	10	0	<2.0	0.98	0.27	5.96	7.46	390	51.5	Geoprobe Profiling Refusal Depth = 68 feet
	GP-13-14-020	1/31/2018	1135	20	0	<2.0	87.9	1.38	5.82	9.97	341	-60.6	Deep Well Screen = 45-55 feet
	DUP-013014-F	1/31/2018	0000	20	NA	<2.0	NA	NA	NA	NA	NA	NA	Shallow Well Screen = 5-15 feet
	GP-13-14-030	1/31/2018	1235	30	0	<2.0	75	1.00	6.06	10.21	415	-325.4	MS/MSD collected from 10 feet
	GP-13-14-040	1/31/2018	1335	40	0	<2.0	43.6	0.36	6.22	10.87	711	-335.6	
	GP-13-14-050	1/31/2018	1440	50	50-60	48.9	898	0.22	6.87	10.39	352	-275.3	
	GP-13-14-060	1/31/2018	1540	60	0-5	2.4 J	47.2	1.44	6.37	10.16	461	-367.1	
	GP-13-14-068	1/31/2018	1630	68	0	3.6 J	3965	0.61	7.15	9.96	637	-424.7	
SHM-13-15	GP-13-15-010	2/4/2018	1320	10	0	<2.0	2.30	0.90	6.11	9.57	510	17.6	Geoprobe Profiling Refusal Depth = 60 feet
	DUP-020314-F	2/4/2018	0000	10	NA	<2.0	NA	NA	NA	NA	NA	NA	Well Screen = 50-60 feet
	GP-13-15-020	2/4/2018	1425	20	0	<2.0	850	0.78	6.21	10.38	398	-77.8	Bedrock was confirmed with rollerbit at 60 feet below
	GP-13-15-030	2/4/2018	1530	30	0	<2.0	87	0.92	6.22	10.39	340	-69.8	grade. Due to broken rods, profiling samples
	GP-13-15-040	2/5/2018	1015	40	0	<2.0	64.8	0.94	6.64	10.74	463	-154.0	GP-13-15-060 and GP-13-15-070 were both collected
	GP-13-15-050	2/5/2018	1113	50	0	<2.0	103	3.93	6.72	10.49	385	-62.1	from the 60-foot interval. See note below.
	GP-13-15-060	2/5/2018	1220	60	10-20	35.5	OVR	1.34	6.85	10.45	899	-139.6	
	GP-13-15-070	2/5/2018	1355	60	50-60	34.0	2643	1.03	6.92	10.65	914	-157.4	

Notes

NA - Not Applicable
NM - Not Measured
ug/L is micrograms per liter
mg/l - miligrams per liter
ppb - parts per billion
OVR - out of range
J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
All samples were field filtered prior to laboratory submittal.

*During profiling activities at SHM-13-15, Geoprobe rods were advanced to what was initially believed to be refusal at 70 feet below grade. However, upon rod retrieval, the first 10-foot section of rods was missing, and only 60 feet of rods were recovered. During well installation, a rollerbit was used to confirm bedrock at 60 feet. Consequently, it was determined that the first 10 feet of rods were broken against bedrock at 60 feet while attempting to advance deeper, and the 60-foot profiling interval was sampled twice (GP-13-15-060 and GP-13-15-070).

Groundwater Sampling Results

Location	Sample ID	Date	Arsenic (ug/L)	Calcium (ug/L)	Iron (ug/L)	Magnesium (ug/L)	Manganese (ug/L)	Potassium (ug/L)	Sodium (ug/L)	Turbidity NTU	DO mg/L	pH	Temp Celcius	Spec Cond uS/cm	ORP mV	Alkalinity mg CaCO3/L	Ammonia mg/l	Nitrogen (Nitrite +Nitrate) mg/l	Sulfide mg/l	Chloride mg/l	Sulfate mg/l	DOC mg/l
SHM-13-14S	SHM-13-14S	2/19/2014	2.0 U	22200	241	2720 J	55.5	3600 J	63900	1.97	0.59	5.88	6.53	440	96.3	58.0	0.60	1.5	1.3 U	91.0	9.6 J	1.2
SHM-13-14D	SHM-13-14D	2/19/2014	7.9	10100	11800	1170 J	1190	4340 J	55200	26.0	0.09	6.85	9.18	349	-82	81.0	1.8	0.22	1.3 U	48.0	12.3	1.9
SHM-13-15	SHM-13-15	2/19/2014	3.8 J	86900	623	12700	4860	5450	29200	42.3	0.44	6.59	9.16	642	-172.7	273	0.68	0.050 U	1.3 U	46.0	7.7 J	2.9
	DUP	2/19/2014	3.9 J	86900	633	12700	4870	5390	29200	NA	NA	NA	NA	NA	NA	278	0.65	0.050 U	1.3 U	46.5	5.2 J	2.9

Notes

ug/L is micrograms per liter
mg/l - miligrams per liter
DOC - Dissolved Organic Carbon
U - The analyte was not detected above laboratory detection limits
J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
All samples were field filtered prior to laboratory submittal.

TABLE 3
GROUNDWATER MONITORING WELL RESULTS
Shepley's Hill Landfill, Devens Massachusetts

Well ID	Sample ID	Date	Arsenic		Calcium		Iron		Magnesium		Manganese		Potassium		Sodium		Turbidity	DO	pH	Temp	Spec Cond	ORP	Alkalinity	Ammonia	Nitrite	Nitrate	Nitrogen (Nitrite +Nitrate)	Sulfide	COD	TOC	Chloride	Sulfate	DOC	DIC	Notes
			Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	NTU	mg/L		Celcius	uS/cm	mV	mg CaCO3/L	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	
SHL-4	SHL-4-101607	10/16/2007	7.5	NA	35000	NA	1800	NA	7000	NA	631	NA	4900	NA	13000	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHL-4-101410	10/14/2010	3.1	NA	36000	NA	180	NA	4600	NA	255	NA	7500	NA	14000	NA	0.03	0.46	6.01	12.20	334	47	110	NA	NA	<0.10	NA	NA	NA	NA	25	7.2	NA	NA	
	SHL-4-101111	10/7/2011	1.4	NA	8100	NA	30 J	NA	2000	NA	31	NA	1800 J	NA	2100	NA	0	1.44	5.65	12.55	82	274	32	NA	NA	0.33	NA	NA	NA	NA	1.6	2.3	NA	NA	
	SHL-4-101612	10/16/2012	3.8	NA	18000	NA	880	NA	2900	NA	125	NA	4000.0	NA	2800	NA	0.84 B	0.34	5.69	13.55	162	47	55	NA	NA	0.02 J	NA	NA	NA	NA	13	0.65 J	NA	NA	
	SHL-4-052413	5/24/2013	NA	2.6	NA	30500	NA	57.8 J	NA	4300 J	NA	481	NA	4460 J	NA	18200	0.36	0.27	6.1	10.39	278	107.1	123	1.4	0.004 U	0.079 U	NA	1.4 U	NA	NA	12.8	14.6	2.4	NA	
	DUP-02-052413	5/24/2013	NA	2.7	NA	30900	NA	59.6 J	NA	4300 J	NA	478	NA	4440 J	NA	18600	NA	NA	NA	NA	NA	NA	129	8.9	0.004 U	0.079 U	NA	1.4 U	NA	NA	13.3	15.1	2.5	NA	
	SHL-4-111913	11/19/2013	NA	6.2	NA	28300	NA	637	NA	3860 J	NA	1830	NA	5910	NA	45700	0.06	0.33	6.13	11.52	427	35.2	112	1.3	0.0051 U	0.24	NA	1.5 U	NA	NA	18	69.3	3.3	NA	
	SHL-4-100814	10/8/2014	NA	37	NA	25800	NA	8030 J	NA	3410 J	NA	2480 J	NA	4620 J	NA	15300	11.7	0.3	6.2	17.71	239	4.2	114	0.065 U	NA	NA	0.075 J	1.3 U	NA	NA	6	14.8	2.7	NA	
SHL-5	SHL-5-101807	10/18/2007	16.2	NA	9400	NA	6300	NA	1700	NA	362	NA	1900 J	NA	1400 J	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHL-5-042210	4/22/2010	3.4	NA	7400	NA	1200	NA	1200	NA	237	NA	1400 J	NA	2200	NA	0.56	0.09	5.86	7.21	90	-254	25	NA	NA	0.053 J	NA	NA	NA	NA	3.6	<1.0	NA	NA	
	SHL-5-101110	10/11/2010	4.8	NA	15000	NA	610	NA	2100	NA	425	NA	2400 J	NA	3300	NA	0.44	0.34	5.39	13.90	123	108	20	NA	NA	<0.10	NA	NA	NA	NA	2.9	2.1	NA	NA	
	SHL-5-040511	4/5/2011	1	NA	6400	NA	170	NA	1000	NA	157	NA	<2500	NA	1600 J	NA	0.2	0.34	5.78	4.28	60	85.2	12	NA	NA	0.14	NA	NA	NA	NA	3.7	2.2	NA	NA	
	SHL-5-101111	10/11/2011	5.5	NA	9100	NA	700	NA	1200	NA	193	NA	1500 J	NA	2800	NA	1	0.14	5.28	15.15	78	130	33	NA	NA	<0.10	NA	NA	NA	NA	0.6	1.1	NA	NA	
	SHL-5041012	4/10/2012	3.7	NA	7700	NA	1500	NA	1100	NA	233 J	NA	1200 J	NA	2100	NA	2100	0.54	5.54	7.73	84	111.8	24	NA	NA	0.040 J	NA	NA	NA	NA	3.3	<1.7	NA	NA	
	SHL-5-101512	10/15/2012	4.5	NA	11000	NA	1000	NA	1600	NA	310	NA	1700 J	NA	2600	NA	4.1	0.49	5.42	13.98	99	82.4	37	NA	NA	0.07 J	NA	NA	NA	NA	2.9	4.7	NA	NA	
	SHL-5-052113	5/21/2013	NA	3.7	NA	10900	NA	999	NA	1500 J	NA	286	NA	1390 J	NA	2140	3.36	0.36	5.59	10.81	100	82.9	23.2	0.18	0.004 U	0.079 U	NA	1.4 U	NA	NA	16.2	4.5 U	4.1	NA	
	SHL-5-102213	10/22/2013	NA	15.1	NA	11500	NA	2380	NA	1650 J	NA	429	NA	1780 J	NA	3590 J	0.90	0.86	5.73	13.75	88	-89.4	43.8	NA	0.0051 U	0.059 U	NA	NA	NA	NA	4.3	0.87 J	NA	NA	
	SHL-5-042214	4/22/2014	NA	2.0 U	NA	7390	NA	282	NA	849 J	NA	159	NA	1500	NA	36200	1.63	0.43	5.87	6.33	235	141.4	27.4	0.11	NA	NA	0.050 U	1.3 U	NA	NA	62.7	4.5 J	5.1	NA	
	SHL-5-101314	10/13/2014	NA	13.3	NA	9530	NA	8390	NA	2500 U	NA	320	NA	2500 U	NA	28800	1.27	0.18	5.98	13.05	205	4.7	41.4	0.065 U	NA	NA	0.050 U	1.3 U	NA	NA	35	5.6 J	10.3	NA	
SHL-8S	SHL-8S-101807	10/18/2007	22.6	NA	3600	NA	80	NA	660	NA	56	NA	1300 J	NA	5900	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHL-8S-0422210	4/22/2010	0.6	NA	5600	NA	<50	NA	960	NA	<10	NA	1300 J	NA	6200	NA	0.01	2.39	6.28	9.85	101	-91	20	NA	NA	0.17	NA	NA	NA	NA	6.7	6.6	NA	NA	
	SHL-8S-101110	10/11/2010	<0.5	NA	6000	NA	<50	NA	1000	NA	3.8 J	NA	1300 J	NA	6300	NA	0.47	1.72	6.15	10.20	78	145	20	NA	NA	<0.10	NA	NA	NA	NA	7.5	5.0	NA	NA	
	SHL-8S-040511	4/5/2011	<0.5	NA	6200	NA	50	NA	1100	NA	16	NA	1300 J	NA	6100	NA	0	4.37	6.15	10.24	77	138	21	NA	NA	0.22	NA	NA	NA	NA	6.4	6.1	NA	NA	
	SHL-8S-100611	10/6/2011	<0.5	NA	6700	NA	60	NA	1200	NA	14	NA	1400 J	NA	6200	NA	0	2.24	6.06	10.38	82	175	21	NA	NA	<0.10	NA	NA	NA	NA	7.1	5.4	NA	NA	
	SHL-8S-041012	4/10/2012	0.6	NA	6000	NA	30 J	NA	970	NA	32 J	NA	1300 J	NA	6100	NA	<580	6.9	6.21	9.98	97	139.8	20	NA	NA	0.16	NA	NA	NA	NA	5200	<4.0	NA	NA	
	SHL-8S-101512	10/15/2012	<0.5	NA	5200	NA	30 J	NA	960	NA	35	NA	1100 J	NA	4900	NA	1.1 B	4.56	6.37	12.55	51	110.1	19	NA	NA	0.15	NA	NA	NA	NA	7.4	4.3	NA	NA	
	SHL-8S-052813	5/28/2013	NA	0.93 J	NA	6800	NA	<100	NA	<5000	NA	<15	NA	<5000	NA	5970	1.33	5.94	6.4	10.32	74	146.2	22.1	0.081 J	0.004 U	0.24	NA	1.4 U	NA	NA	6.0	6.2	16.2	NA	
	SHL-8S-102213	10/22/2013	NA	2.0 U	NA	6730	NA	30 U	NA	1180 J	NA	2.5 U	NA	1330 J	NA	6060	0.7	2.49	6.2	10.77	75	230	17.5	NA	0.0051 U	0.18	NA	NA	NA	NA	6.8	6.4 J	NA	NA	
	SHL-8S-042214	4/22/2014	NA	2.0 U	NA	6880	NA	79.4 J	NA	1200 J	NA	6.1 J	NA	1410 J	NA	6050	0.62	5.53	6.54	10.07	77	160.8	26.3	0.066 U	NA	NA	0.26	1.3 U	NA	NA	6.3	6.0 J	0.55 J	NA	
	SHL-8S-100914	10/9/2014	NA	2.0 U	NA	7040	NA	50 U	NA	2500 U	NA	83.1	NA	2500 U	NA	6020	1.5	0.53	6.06	10.82	84	127.8	25.1	0.065 U	NA	NA	0.17	1.3 U	NA	NA	5.0	7.8 J	0.59 J	NA	
SHL-8D	SHL-8D-101807	10/18/2007	11.8	NA	18000	NA	22 J	NA	2600	NA	80	NA	970 J	NA	9100	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHL-8D-042210	4/22/2010	0.6	NA	12000	NA	17 J	NA	1800	NA	<10	NA	<2500	NA	7400	NA	0.03	1.50	6.28	10.25	167	-121	36	NA	NA	0.16	NA	NA	NA	NA	12	7.5	NA	NA	
	SHL-8D-101110	10/11/2010	<0.5	NA	8800	NA	<50	NA	1200	NA	13	NA	970 J	NA	7300	NA	0.98	3.65	6.02	11.31	102	14.3	23	NA	NA	<0.10	NA	NA	NA	NA	9.6	8.0	NA	NA	
	SHL-8D-040511	4/5/2011	<0.5	NA	11000	NA	<50	NA	1400	NA	<10	NA	950 J	NA	9200	NA	0	3.47	6.13	10.18	0.124	88	20	NA	NA	0.08 J	NA	NA	NA	NA	19	7.0	NA	NA	
	DUP-040511	4/5/2011	<0.5	NA	6300	NA	40 J	NA	1100	NA	14	NA	1400 J	NA	6200	NA	0	3.47	6.13	10.18	0.124	88	21	NA	NA	0.22	NA	NA	NA	NA	6.3	5.7	NA	NA	
	SHL-8D-100611	10/6/2011	<0.5	NA	8100	NA	60	NA	1100	NA	<10	NA	<2500	NA	7400	NA	0	5.39	6.13	10.55	91	43	22	NA	NA	<0.10	NA	NA	NA	NA	7.9	7.6	NA	NA	
	SHL-8D-041112	4/11/2012	<0.5	NA	14000	NA	<50	NA	1700	NA	<10	NA	<2500	NA	8000	NA	<130	0.83	5.89	9.45	164	89.6	5	NA	NA	0.09 J	NA	NA	NA	NA	12	<5.8	NA	NA	
	SHL-8D-101512	10/15/2012	<0.5	NA	10000	NA	<50	NA	1600	NA	4 J	NA	810 J	NA	7500	NA	1.2 B	2.19	6.17	12.99	92	60.5	18	NA	NA	0.05 J	NA	NA	NA	NA	24	6.4	NA	NA	
	SHL-8D-052113	5/21/2013	NA	0.72 J	NA	9730	NA	30 U	NA	1490 J	NA	2.5 U	NA	1070 J	NA	14800	0.32	1.67	6.12	13.65	138	48.7	27.6	0.081 U	0.004 U	0.089 J	NA	1.4 U	NA	NA	30.2	6.2	0.64 U	NA	
	SHL-8D-102213	10/22/2013	NA	2.0 U	NA	8190	NA	30 U	NA	1260 J	NA	2.5 U	NA	759 J	NA	7350	0.00	3.25	6.21	11.08	90	83.9	13.1	NA	0.0051 U	0.087 J	NA	NA	NA	NA	11.8	7.5 J	NA	NA	
	SHL-8D-042214	4/22/2014	NA	2.0 U	NA	9790	NA	30 U	NA	1590 J	NA	2.5 U	NA	1010 J	NA	13700	0.15	2.08	5.92	10.88	147	146.6	11.0	0.066 U	NA	NA	0.057 U	1.3 U	NA	NA	28.2	6.3 J	0.73 J	NA	
	SHL-8D-100914	10/9/2014	NA	2.0 U	NA	11900	NA	50 U	NA	2500 U	NA	7.5 U	NA	2500 U	NA	17300	0.6	0.77	5.88	10.89	204	101.8	16.4	0.065 U	NA	NA	0.050 U	1.3 U	NA	NA	42.5	7.2 J	0.41 J	NA	
SHL-9	DUP02-101607	10/16/2007	33.5	NA	27000	NA	11000	NA	1700	NA	518	NA	2500	NA	4100	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHL-9-042110	4/21/2010	25.2	NA	20000	NA	6300	NA	1600	NA	447	NA	2000 J	NA	3900	NA	4.1	0.12	6.58	8.38	204	-74	580	NA	NA	0.066 J	NA	NA	NA	NA	6.3	6.6	NA	NA	
	SHL-9-101210	10/12/2010	38.4	NA	23000	NA	11000	NA	1900	NA	442	NA	2400 J	NA	6700	NA	0.89	0.21	6.35	10.20	204	-70	770	NA	NA	<0.10	NA	NA	NA	NA	7.3	4.3	NA	NA	
	SHL-9-040611	4/6/2011	25.7	NA	21000	NA	7500	NA	1600	NA	467	NA	2000 J	NA	4600	NA	24	0.27	6.48	7.65	0.16	-38.7	580	NA	NA	<0.10	NA	NA	NA	NA	3.4	<6.8	NA	NA	
	SHL-9-100711	10/7/2011	39.8	NA	23000	NA	9500	NA	1900	NA	409	NA	2600	NA	5900	NA	-55	0.27	6.26	11.78	223	-55.1	670	NA	NA	<0.10	NA	NA	NA	NA	14	7.8	NA	NA	
	SHL-9-041012	4/10/2012	29.5	NA	23000	NA	9500	NA	1900	NA	354 J	NA	2400 J	NA	7000	NA	4600	0.34	6.2	8.47	268	-19.3	860	NA	NA	0.040 J	NA	NA	NA	NA	5.0	4.4	NA	NA	
	SHL-9-101712	10/17/2012	36.4	NA	24000	NA	8300	NA	2100	NA	357	NA	2500	NA	6500	NA	0.72 B	0.36	6.94	9.12	210	-80.3	85	NA	NA	0.17	NA	NA	NA	NA	4.4	6.8	NA	NA	
	SHL-9-052813	5/28/2013	NA	30.0	NA	25400	NA	9590 J	NA	1440 J	NA	497	NA	2470 J	NA	6560	1.71	0.27	6.51	9.04	199	-54.1	88.4	0.61	0.15	0.15	NA	1.4 U	NA	NA	5.5	4.5 U	4.6	NA	
	SHL-9-102313	10/23/2013	NA	33.1	NA	26300	NA	8890	NA	2520 J	NA	439	NA	2550 J	NA	6280	0.58	0.22	6.52	10.87	160	-76.4	63.5	NA	0.0051 U	0.25	NA	NA	NA	NA	22.7	2.1 J	NA	NA	
	SHL-9-042314	4/23/2014	NA	22.2	NA	26200	NA	9530	NA	2360 J	NA	533	NA	2560 J	NA	7330	20.0	0.71	6.28	7.41	211	5.3	62.4	0.066 U	NA	NA	0.050 U	1.3 U	NA	NA	24.2	6.7 J	4.8	NA	
	SHL-9-100914	10/9/2014	NA	28.5	NA	26900	NA	9820	NA	2790 J	NA	469	NA	2660 J	NA	8320	7.51	0.11	6.45	9.67	183	-42.1	55.6	0.43	NA	NA	0.10	1.3 U	NA	NA	36.5	8.5 J	4.5	NA	
SHL-10	SHL-10-101607	10/16/2007	0.59 J	NA	5800	NA	45 J	NA	790	NA	14	NA	830 J	NA	1200 J	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHL-10-101410	10/14/2010	0.9	NA	11000	NA	<50	NA	1500	NA	<10	NA	1700 J	NA	1200 J	NA	1	9.16	6.51	12.8	89	136.9	31	NA	NA	0.35	NA	NA	NA	NA	1.3	6.0	NA	NA	
	SHL-10-101612	10/16/2012	0.7	NA	86000	NA	<50	NA	1100	NA	<10	NA	1300 J	NA	1200 J	NA	0.36 B	0.87	6.89	9.75	73	59.1	26	NA	NA	0.35	NA	NA	NA	NA	1.1	4.2	NA	NA	
	SHL-10-052213	5/22/2013	NA	1.2	NA	8260	NA	30.0 J	NA	877 J	NA	2.5 U	NA	1320 J	NA	1220 J	1.22	10.05	6.62	11.46	55	149.8	24.3	0.081 U	0.004 U	0.18	NA	1.4 U	NA	NA	5.8	4.6 J	1.6	NA	
	SHL-10-100814	10/8/2014	NA	2.0 U	NA	12500	NA	50 U	NA	2500 U	NA	7.5 U	NA	2500 U	NA	2500 U	8.11	8.68	6.54	10.9	76	173.6	33.8	0.065 U	NA	NA	0.31	1.3 U	NA	NA	2.8	9.8 J	0.57 J	NA	
SHL-11	SHL-11-101607	10/16/2007	686.5	NA	34000	NA	48000	NA	5200	NA	2320	NA	9500	NA	23000	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHL-11-101310	10/13/2010	694	NA	39000	NA	60000	NA	5300	NA	2620	NA	9100	NA	21000	NA	0.72	0.24	6.38	12.66	580	-70	230	NA	NA	<0.10	NA	NA	NA	NA	19	6.1	NA	NA	
	SHL-11-100611	10/6/2011	654.9	NA	42000	NA	50000	NA	5600	NA	2250	NA	9200	NA	15000	NA	4	0.3	6.2	13.13	597	-41.2	240	NA	NA	<0.16	NA	NA	NA	NA	15	1.6	NA	NA	
	SHL-11-101512	10/15/2012	647.0	NA	35000	NA	34000	NA	5500	NA	1540	NA	6800	NA	16000	NA	79	0.35	6.71	14.82	365	-108.2	200	NA	NA	0.15	NA	NA	NA	NA	20	19	NA	NA	
	SHL-11-052313	5/23/2013	NA	496	NA	47800	NA	19800	NA	6490	NA	2430	NA	6480	NA	24400	8.5	0.18	6.75	12.24	462	-96.0	160	2.5	0.004 U	0.30	NA	1.4 U	NA	NA	41.2	19.5	2.1	NA	
	SHL-11-102213	10/22/2013	NA	752	NA	45000	NA	27600	NA	5900	NA	3610	NA	8470	NA	27300	0.43	0.42	6.54	12.75	530	-97.6	164	NA	0.0051 U	0.34	NA	NA	NA	NA	42.7	20.2	NA	NA	
	SHL-11-042314	4/23/2014	NA	587	NA	47600	NA	25100	NA	6810	NA	3950	NA	7700	NA	24300	4.94	0.26	6.45	10.27	390	-54.9	157	2.3	NA	NA	0.35	1.3 U	NA	NA	47.7	20.0	1.9	NA	
	SHL-11-100814	10/8/2014	NA	793	NA	64100	NA	44700	NA	8720	NA	4320	NA	10100	NA	44900	5.51	0.44	6.61	12.39	623	-90.3	242	0.065 U	NA	NA	0.089 J	1.3 U	NA	NA	42.5	69.5	2.8	NA	
SHL-13	SHL-13-101807	10/18/2007	1.6	NA	6900	NA	110	NA	1500	NA	503	NA	980 J	NA	24000	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHL-13-101110	10/11/2010	<0.5	NA	11000	NA	<50	NA	2000	NA	11	NA	1300 J	NA	45000	NA	3.08	2.54	5.62	15.52	317	169	19	NA	NA	<0.10	NA	NA	NA	NA	82	6.5	NA	NA	
	SHL-13-100611	10/6/2011	2.8	NA	8700	NA	520	NA	1900	NA	179	NA	920 J	NA	36000	NA	0	0.25	5.72	14.61	0.273	42	18	NA	NA	0.05 U	NA	NA	NA	NA	66	4.7	NA	NA	
	SHL-13-101512	10/15/2012	1.0	NA	10000	NA	400	NA	1800	NA	484	NA	1300 J	NA	30000	NA	0.23 B	0.67	5.91	16.26	254	61.5	23	NA	NA	0.28	NA	NA	NA	NA	61	5.5	NA	NA	
	SHL-13-102213	10/22/2013	NA	2.0 U	NA	11300	NA	43.3 J	NA	2290 J	NA	29.6	NA	1360 J	NA	40100	0.2	0.35	6.08	13.87	269	127	23	NA	0.0051 U	0.059 U	NA	NA	NA	NA	61	8.0 J	NA	NA	
SHL-15	SHL-15-101607	10/16/2007	42	NA	21000	NA	3400	NA	2800	NA	570	NA	4900	NA	7600	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHL-15-101410	10/14/2010	25	NA	26000	NA	2800	NA	3400	NA	342	NA	5300	NA	8400	NA	1	0.21	5.73	11.49	241	-0.3	70	NA	NA	0.68	NA	NA	NA	NA	11	20	NA	NA	
	SHL-15-100611	10/6/2011	70.4	NA	25000	NA	8200	NA	2300	NA	512	NA	4600	NA	2100	NA	0.9	0.27	6.17	12.36	403	66.1	140	NA	NA	1.8	NA	NA	NA	NA	22	14	NA	NA	
	SHL-15-101612	10/16/2012	24.2	NA	29000	NA	3200	NA	3800	NA	271	NA	7100	NA	1200	NA	1.3	3.27	5.98	13.11	348	-18.7	84	NA	NA	0.58	NA	NA	NA	NA	26	14	NA	NA	
	SHL-15-102213	10/22/2013	NA	34.9	NA	27000	NA	6610	NA	3340 J	NA	437	NA	6480	NA	12100	2.08	0.31	5.91	13.48	266	-23.6	90.9	NA	0.0051 U	0.56	NA	NA	NA	NA	16.7	10.1	NA	NA	
SHL-19	SHL-19-101607	10/16/2007	8.851	NA	24000	NA	50000	NA	3800	NA	2700	NA	3600	NA	4200	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHL-19-101410	10/14/2010	234.8	NA	25000	NA	23000	NA	3500	NA	3260	NA	3700	NA	2800	NA	40	0.57	5.86	11.03	240	22	80	NA	NA	<0.10	NA	NA	NA	NA	2.2	22	NA	NA	
	SHL-19-100711	10/7/2011	62.9	NA	11000	NA	7700	NA	1900	NA	1460	NA	2800	NA	2100	NA	13	3.66	4.97	13.12	107	128	38	NA	NA	0.22	NA	NA	NA	NA	1.2	13	NA	NA	
	SHL-19-101612	10/16/2012	138.3	NA	21000	NA	10000	NA	3800	NA	1060	NA	3400	NA	3200	NA	79	0.27	5.67	10.52	194	22	66	NA	NA	0.18	NA	NA	NA	NA	2.3	22	NA	NA	
	DUP-101612	10/16/2012	133.0	NA	21000	NA	10000	NA	3800	NA	1070	NA	3500	NA	3300	NA	59	NA	NA	NA	NA	NA	66	NA	NA	0.17	NA	NA	NA	NA	2.3	22	NA	NA	
	SHL-19-052413	5/24/2013	NA	3.8	NA	18300	NA	1460	NA	3150 J	NA	580	NA	2710 J	NA	2930 J	17.0	1.01	5.86	10.83	137	98.9	55.3	0.094 J	0.004 U	0.32	NA	1.4 U	NA	NA	1.0	12.6	1.8	NA	
	SHL-19-102413	10/24/2013	NA	33.6	NA	22200	NA	8380	NA	3670 J	NA	1630	NA	3260 J	NA	2970 J	123	0.5	6.76	11.54	110	-85.9	64.6	NA	0.0051 U	0.4	NA	NA	NA	NA	2.8	16.6	NA	NA	
	SHL-19-100814	10/8/2014	NA	3.1 J	NA	17500	NA	5640	NA	2770 J	NA	2210 J	NA	2790 J	NA	3380 J	30.7	0.52	6.09	12.78	180	29.6	62.1	0.065 U	NA	NA	0.33	1.3 U	NA	NA	2.5	18.4	2.4	NA	
SHL-20	SHL-20-101607	10/16/2007	3.362	NA	66000	NA	7200	NA	9300	NA	6540	NA	6100	NA	28000	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHL-20-101310	10/13/2010	4.4	NA	43000	NA	250	NA	5900	NA	544	NA	7300	NA	21000	NA	1.71	0.20	6.43	12.04	395	88	140	NA	NA	1.2	NA	NA	NA	NA	20	8.8	NA	NA	
	SHL-20-100611	10/6/2011	7.3	NA	40000	NA	350	NA	5700	NA	820	NA	6400	NA	18000	NA	1.6	0.27	6.17	12.36	403	66.1	140	NA	NA	1.8	NA	NA	NA	NA	22	14	NA	NA	
	SHL-20-101512	10/15/2012	139.2	NA	36000	NA	1800	NA	4900	NA	3000	NA	7000.0	NA	15000	NA	16	2.43	6.36	12.74	277	50.1	120	NA	NA	0.34	NA	NA	NA	NA	22	22	NA	NA	
	SHL-20-052213	5/22/2013	NA	621	NA	32700	NA	17700	NA	3890 J	NA	2150	NA	7240	NA	24900	0.54	0.19	6.75	12.18	414	-85.6	111	5.3	0.004 U	0.37	NA	1.4 U	NA	NA	35.7	30.5	1.4	NA	
	SHL-20-102213	10/22/2013	NA	632	NA	22200	NA	38500	NA	2530 J	NA	1590	NA	8310	NA	22100	4.10	1.87	6.51	12.80	443	-93.6	81	NA	0.006 J	0.39	NA	NA	NA	NA	49.7	23.0	NA	NA	
	DUP-102213	10/22/2013	NA	641	NA	22200	NA	38900	NA	2510 J	NA	1590	NA	8310	NA	22200	NA	NA	NA	NA	NA	NA	81	NA	0.0051 U	0.37	NA	NA	NA	NA	49.7	23.1	NA	NA	
	SHL-20-042314	4/23/2014	NA	701	NA	27400	NA	40700 J	NA	4540 J	NA	1760	NA	7770	NA	24300	6.31	0.85	6.21	10.96	499	-58.7	120	1.8	NA	NA	0.26	1.3 U	NA	NA	50.2	26.0	1.6	NA	
	SHL-20-100814	10/8/2014	NA	763	NA	38200	NA	52500	NA	7160	NA	1700	NA	8160	NA	27400	2.43	0.43	6.4	12.94	620	-87.8	153	0.065 U	NA	NA	0.078 J	1.3 U	NA	NA	61	4.0 J	2.0	NA	
	Duplicate-100814	10/8/2014	NA	750	NA	37600	NA	52200	NA	7020	NA	1690	NA	7650	NA	27200	2.43	0.43	6.4	12.94	620	-87.8	153	0.065 U	NA	NA	0.091 J	1.3 U	NA	NA	60	4.0 J	2.5	NA	

TABLE 3
GROUNDWATER MONITORING WELL RESULTS
Shepley's Hill Landfill, Devens Massachusetts

Well ID	Sample ID	Date	Arsenic		Calcium		Iron		Magnesium		Manganese		Potassium		Sodium		Turbidity	DO	pH	Temp	Spec Cond	ORP	Alkalinity	Ammonia	Nitrite	Nitrate	Nitrogen (Nitrite +Nitrate)	Sulfide	COD	TOC	Chloride	Sulfate	DOC	DIC	Notes
			Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	NTU	mg/L		Celcius	uS/cm	mV	mg CaCO3/L	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	
SHL-21	SHL-21-101607	10/16/2007	0.81 J	NA	5100	NA	40 J	NA	580	NA	4.6 J	NA	1000 J	NA	2600	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHL-21-101310	10/13/2012	0.9	NA	4700 J	NA	<50	NA	500	NA	<10	NA	890 J	NA	2500	NA	1	9.01	5.59	11.85	46	178.3	12	NA	NA	<0.10	NA	NA	NA	NA	1.4	6.0	NA	NA	
	SHL-21-101512	10/15/2012	1.1	NA	5300	NA	<50	NA	700	NA	6 J	NA	970 J	NA	2200	NA	1.8	4.97	6.26	11.32	39	185.9	18	NA	NA	0.09 J	NA	NA	NA	NA	5.1	NA	NA	NA	
SHL-22	SHL-22-101607	10/16/2007	55.1	NA	100000	NA	370	NA	13000	NA	4320	NA	5400	NA	34000	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHL-22-042110	4/21/2010	69.6	NA	100000	NA	580	NA	12000	NA	6670	NA	4800	NA	30000	NA	0.05	0.10	6.77	9.19	933	-40	340	NA	NA	0.066 J	NA	NA	NA	NA	21	5.9	NA	NA	
	SHL-22-101210	10/12/2010	46.5	NA	110000	NA	430	NA	13000	NA	7510	NA	4600	NA	31000	NA	0.03	0.31	6.47	9.75	783	-14.1	380	NA	NA	<0.10	NA	NA	NA	NA	23	5.9	NA	NA	
	DUP-01-101210	10/12/2010	49.0	NA	111000	NA	480	NA	13000	NA	12000	NA	4600	NA	31000	NA	0.03	0.31	6.47	9.75	783	-14.1	370	NA	NA	0.12	NA	NA	NA	NA	22	5.8	NA	NA	
	SHL-22-040611	4/6/2011	57.9	NA	110000	NA	650	NA	13000	NA	8020	NA	4900	NA	31000	NA	0	0.22	6.67	8.16	0.75	-43.6	370	NA	NA	<210	NA	NA	NA	NA	22	<5.3	NA	NA	
	SHL-22-100711	10/7/2011	45.7	NA	110000	NA	580	NA	13000	NA	8280	NA	4700	NA	28000	NA	0	0.27	6.54	11.06	776	15.3	380	NA	NA	<0.10	NA	NA	NA	NA	22	5.3	NA	NA	
	SHL-22-041012	4/10/2012	41.9	NA	100000	NA	610	NA	12000	NA	8180 J	NA	5000	NA	29000	NA	2000 J	2.13	6.42	8.8	981	-20.6	380	NA	NA	0.066 J	NA	NA	NA	NA	22	<2.2	NA	NA	
	DUP-01012	4/10/2012	43.6	NA	110000	NA	600	NA	12000	NA	8340 J	NA	5000	NA	29000	NA	1300 J	2.13	6.42	8.8	981	-20.6	380	NA	NA	0.40 J	NA	NA	NA	NA	20	<1.4	NA	NA	
	SHL-22-101712	10/17/2012	16.5	NA	100000	NA	340	NA	12000	NA	8570	NA	4500	NA	2600	NA	0.85 B	0.45	6.72	9.76	705	-20.2	360	NA	NA	<0.10	NA	NA	NA	NA	21	6.0	NA	NA	
	SHL-22-052813	5/28/2013	NA	34.1	NA	114000	NA	453	NA	14400	NA	9200	NA	5070	NA	27800	0.91	1.28	6.68	9.22	492	18.7	400	0.27	0.004 U	0.079 U	NA	1.4 U	NA	NA	19.5	5.8	2.2	NA	
	DUP-052813	5/28/2013	NA	33.3	NA	114000	NA	440	NA	14100	NA	8580	NA	<5000	NA	27300	NA	NA	NA	NA	NA	NA	396	0.28	0.004 U	0.079 U	NA	1.4 U	NA	NA	20.5	5.5	2.2	NA	
	SHL-22-102313	10/23/2013	NA	53.1	NA	114000	NA	615	NA	13700	NA	9700	NA	4790 J	NA	27400	0.00	0.39	6.7	10.6	511	-6.9	388	NA	0.0051 U	0.059 U	NA	NA	NA	NA	20.2	6.6 J	NA	NA	
	DUP02-102313	10/23/2013	NA	54.3	NA	112000	NA	610	NA	13500	NA	10300	NA	4830 J	NA	26700	NA	NA	NA	NA	NA	NA	389	NA	0.0051 U	0.059 U	NA	NA	NA	NA	19.7	6.6 J	NA	NA	
	SHL-22-042414	4/24/2014	NA	49.2	NA	106000	NA	564	NA	13200	NA	9430	NA	4510 J	NA	27300	0.18	0.16	6.71	8.19	757	7.1	393	0.11	NA	NA	0.050 U	1.3 U	NA	NA	19.7	5.9 J	2.2	NA	
	SHL-22-100914	10/9/2014	NA	44.5	NA	97100	NA	436	NA	12300	NA	8820	NA	4230 J	NA	25700	1.99	0.31	6.67	10.21	526	5.8	378	0.065 U	NA	NA	0.050 U	1.3 U	NA	NA	19.5	7.2 J	1.8	NA	
	DUP-100914	10/9/2014	NA	39.6	NA	97300	NA	405	NA	12400	NA	8740	NA	4190 J	NA	25700	1.99	0.31	6.67	10.21	526	5.8	377	0.065 U	NA	NA	0.050 U	1.3 U	NA	NA	19	7.1 J	2	NA	
SHL-23	SHL-22-101707	10/17/2007	0.73 J	NA	2800	NA	210	NA	250	NA	14	NA	990 J	NA	1000 J	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHL-23	8/12/2010	NA	0.14 J	NA	2230	NA	16.9 J	NA	163	NA	6.87	NA	990	NA	1400	NA	10.06	6.45	10.42	25	209.8	4.3	0.0496 J	<0.002	0.07	NA	<0.10	<7.0	NA	1.3	4.9	<1.0	< 8	Test Kit (Filtered) < 5
	SHL-23-101310	10/13/2010	<0.5	NA	2500	NA	28 J	NA	180	NA	8.5 J	NA	1000 J	NA	1500 J	NA	1	10.43	4.98	11.53	31	264.1	4.3	NA	NA	<0.10	NA	NA	NA	NA	1.9	5.5	NA	NA	
	SHL-23-101512	10/15/2012	<0.5	NA	2300	NA	20 J	NA	190	NA	0.011	NA	980 J	NA	1600 J	NA	1.1 B	11.55	5.32	11.31	24	290.1	4.8	NA	NA	0.08 J	NA	NA	NA	NA	2.1	4.8	NA	NA	
	DUP-101512	10/15/2012	<0.5	NA	2300	NA	20 J	NA	190	NA	9.0 J	NA	980 J	NA	1600 J	NA	1.2 B	NA	NA	NA	NA	NA	4.7	NA	NA	0.07 J	NA	NA	NA	NA	2.1	4.8	NA	NA	
N5-P1	N-5,P-1-101210	10/12/2010	3488	NA	81000	NA	20000	NA	10000	NA	7010	NA	4400	NA	19000	NA	1	0.31	6.06	12.27	1353	-61.8	300	NA	NA	<0.10	NA	NA	NA	NA	20	<11	NA	NA	
	N-5,P-1-101011	10/10/2011	4942	NA	62000	NA	40000	NA	8100	NA	6440	NA	5200	NA	14000	NA	2	0.18	6.6	12.71	548	-60	280	NA	NA	0.10	NA	NA	NA	NA	16	9.5	NA	NA	
	N-5,P-1-101812	10/18/2012	2286	NA	83000	NA	6500	NA	11000	NA	671	NA	3900	NA	17000	NA	18	0.55	6.79	11.67	386	-100	270	NA	NA	0.10	NA	NA	NA	NA	20	11	NA	NA	
	N-5,P-1-101812	10/22/2013	NA	2500	NA	89500	NA	7520	NA	11600	NA	8570	NA	4330 J	NA	17300	0.46	0.57	6.73	13.56	620	-69.5	313	NA	0.0051 U	0.059 U	NA	NA	NA	NA	17.7	11	NA	NA	
	N5-P1-100814	10/8/2014	NA	327	NA	56900	NA	563	NA	7580	NA	2010	NA	2500 U	NA	9430	0.61	0.25	7.2	13.75	303	-108.3	230	0.076 U	NA	NA	0.050U	1.3 U	NA	NA	19.5	16.8	2.4	NA	
N5-P2	N-5,P-2-101210	10/12/2010	24.5	NA	150000	NA	70000	NA	13000	NA	422	NA	16000	NA	18000	NA	1	0.35	6.43	12.08	519	-60.7	700	NA	NA	<0.10	NA	NA	NA	NA	14	1.0	NA	NA	
	N-5,P-2-101011	10/10/2011	27.4	NA	150000	NA	72000	NA	13000	NA	476	NA	16000	NA	15000	NA	2	0.17	6.2	12.83	1080	-32	690	NA	NA	0.14	NA	NA	NA	NA	14	1.0	NA	NA	
	N-5,P-2-101712	10/17/2012	26.1	NA	140000	NA	66000	NA	12000	NA	421	NA	1500	NA	15000	NA	82	1.21	6.25	14.87	850	-132.4	640	NA	NA	0.09 J	NA	NA	NA	NA	13	<2.0	NA	NA	
	N-5,P-2-102213	10/22/2013	NA	21.2	NA	162000	NA	75400	NA	14400	NA	459	NA	15400	NA	15200	3.36	0.72	6.34	14.15	1271	-71.6	652	NA	0.0051 U	0.46	NA	NA	NA	NA	15.3	0.67 J	NA	NA	
SHM-93-10C	SHM-93-10C-101607	10/16/2007	9.8	NA	72000	NA	140	NA	4000	NA	67	NA	5200	NA	9200	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-93-10C-101410	10/14/2010	8.7	NA	70000	NA	26 J	NA	3600	NA	38	NA	4700	NA	8300	NA	1	0.3	7.31	12.1	469	-30.7	170	NA	NA	<0.10	NA	NA	NA	NA	23	1.9	NA	NA	
	SHL-93-10C-101612	10/16/2012	8.1	NA	66000	NA	30 J	NA	3600	NA	6 J	NA	4800	NA	8400	NA	1.0 B	1.23	7.28	9.45	434	16.3	180	NA	NA	<0.10	NA	NA	NA	NA	23	18	NA	NA	
SHM-93-22B	SHM-93-22B-042110	4/21/2010	947.5	NA	73000	NA	48000	NA	11000	NA	6210	NA	9200	NA	27000	NA	5.2	0.11	6.71	8.10	953	-125	380	NA	NA	0.13	NA	NA	NA	NA	22	4.4	NA	NA	
	DUP-042110	4/21/2010	980.3	NA	73000	NA	48000	NA	10000	NA	6220	NA	9100	NA	27000	NA	140	0.11	6.71	8.10	953	-125	350	NA	NA	0.13	NA	NA	NA	NA	21	3.9	NA	NA	
	SHM-93-22B-101110	10/11/2010	827.6	NA	80000	NA	37000	NA	11000	NA	8280	NA	8000	NA	28000	NA	1.18	0.29	6.52	9.52	745	-83.2	350	NA	NA	<0.10	NA	NA	NA	NA	24	3.7	NA	NA	
	SHM-93-22B-040611	4/6/2011	1039	NA	80000	NA	45000	NA	11000	NA	8620	NA	8500	NA	29000	NA	8.6	0.23	6.57	6.96	749	-78.8	330	NA	NA	<0.17	NA	NA	NA	NA	26	<3.5	NA	NA	
	SHM-93-22B-101111	10/11/2011	1072	NA	79000	NA	38000	NA	11000	NA	8540	NA	9000	NA	26000	NA	5	0.16	6.36	11.13	704	-63	330	NA	NA	0.12	NA	NA	NA	NA	23	3.6	NA	NA	
	SHM-93-22B-041012	4/10/2012	1271	NA	74000	NA	35000	NA	10000	NA	8100 J	NA	9500	NA	26000	NA	95000	0.37	6.25	8.73	908	-59.8	340 J	NA	NA	0.090 J	NA	NA	NA	NA	19	<1.9	NA	NA	
	SHM-93-22B-101712	10/17/2012	879	NA	74000	NA	23000	NA	10000	NA	9020	NA	8100	NA	2800	NA	39	0.55	6.54	10.83	415	-141.4	340	NA	NA	0.14	NA	NA	NA	NA	22	4.4	NA	NA	
	SHM-93-22B-052813	5/28/2013	NA	1150	NA	77800	NA	30000	NA	12200	NA	9680	NA	8480	NA	28300	71.0	0.22	6.57	8.92	471	80.4	337	1.3	0.004 U	0.36	NA	1.4 U	NA	NA	21.5	45 U	2.9	NA	
	SHM-93-22B-102313	10/23/2013	NA	1150	NA	78200	NA	31300	NA	11300	NA	9450	NA	8040	NA	28000	1.2	0.39	6.59	10.17	485	1.8	334	NA	0.0051 U	3.26	NA	NA	NA	NA	20.7	4.4 J	NA	NA	
	SHM-93-22B-042414	4/24/2014	NA	997	NA	73400	NA	28300 J	NA	10800	NA	10600 J	NA	7360	NA	29900	0.5	0.14	6.48	7.63	734	-66.3	329	0.54	NA	NA	0.050 U	1.3 U	NA	NA	22.2	2.9 J	2.8	NA	
	SHM-93-22B-100814	10/8/2014	NA	690	NA	73200	NA	19300	NA	10700	NA	11700	NA	7320	NA	30100	3.4	0.29	6.51	10.27	503	-43.8	338	0.12	NA	NA	0.055 J	1.3 U	NA	NA	20.5	4.9 J	2.7	NA	
SHM-93-22C	SHM-93-22C-101607	10/16/2007	72.5	NA	89000	NA	1700	NA	15000	NA	494	NA	4800	NA	25000	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	DUP01-101607	10/16/2007	72	NA	87000	NA	1600	NA	14000	NA	478	NA	4600	NA	24000	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-93-22C-042110	4/21/2010	14.6	NA	34000	NA	280	NA	3400	NA	105	NA	4700	NA	9300	NA	2.2	1.10	8.23	11.33	321	-38	110	NA	NA	0.29	NA	NA	NA	NA	10	6.1	NA	NA	
	SHM-93-22C-101210	10/12/2010	15.8	NA	39000	NA	290	NA	3600	NA	58	NA	4500	NA	10000	NA	1.05	0.58	7.82	10.86	286	-103.1	110	NA	NA	<0.10	NA	NA	NA	NA	12	5.8	NA	NA	
	SHM-93-22C-040611	4/6/2011	13.9	NA	45000	NA	350	NA	3500	NA	36	NA	4200	NA	9000	NA	0	0.78	8.84	9.93	284	-1	120	NA	NA	<0.23	NA	NA	NA	NA	10	<6.0	NA	NA	
	SHM-99-22C-100511	10/5/2011	13.9	NA	40000	NA	380	NA	3100	NA	84	NA	3700	NA	7900	NA	1	0.14	7.5	12.07	282	-42	120	NA	NA	0.21	NA	NA	NA	NA	8.4	6.1	NA	NA	
	SHM-93-22C-041112	4/11/2012	25.4	NA	41000	NA	980	NA	3500	NA	136	NA	4200	NA	9400	NA	1600	1.26	7.46	8.17	361	-105.3	120	NA	NA	<0.10	NA	NA	NA	NA	9.9	<6.6	NA	NA	
	SHM-93-22C-101712	10/17/2012	21.7	NA	39000	NA	590	NA	3400	NA	140	NA	4000	NA	9000	NA	0.30 B	0.41	8.04	8.4	140	-163.1	120	NA	NA	0.07 J	NA	NA	NA	NA	10	6.9	NA	NA	
	SHM-99-22C-052813	5/28/2013	NA	19.7	NA	40000	NA	568	NA	<5000	NA	140	NA	<5000	NA	9550	3.37	0.45	7.83	10.73	196	-145.7	133	0.081 U	0.004 U	0.079 U	NA	1.4 U	NA	NA	10.0	7.5	3.6	NA	
	SHM-99-22C-102313	10/23/2013	NA	25.1	NA	41900	NA	555	NA	3920 J	NA	154	NA	4170 J	NA	9830	0.31	0.40	7.79	10.87	198	-164.8	137	NA	0.0051 U	0.059 U	NA	NA	NA	NA	11.3	7.0 J	NA	NA	
	SHM-99-22C-042414	4/24/2014	NA	31.9	NA	40500	NA	397	NA	4020 J	NA	145	NA	3820 J	NA	10000	0.82	0.17	7.77	8.94	294	-89.5	140	0.066 U	NA	NA	0.050 U	1.3 U	NA	NA	11.3	6.3 J	3.5	NA	
	SHM-03-22C-100814	10/8/2014	NA	45.6	NA	97100	NA	519	NA	12300	NA	8800	NA	4230 J	NA	25300	0.73	0.25	6.65	10.92	743	18.2	375	19.5	NA	NA	0.050 U	1.3 U	NA	NA	19.5	7.9 J	2.4	NA	
SHM-96-5B	SHM-96-5B-101707	10/17/2007	750	NA	81000	NA	5000	NA	12000	NA	11400	NA	9200	NA	28000	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-96-5B-010808	1/8/2008	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-96-5B-042210	4/22/2010	1504 J	NA	70000 J	NA	21000 J	NA	11000	NA	9840 J	NA	8600	NA	24000	NA	0.18	0.16	6.51	10.22	883	-278	330 J	NA	NA	0.073 J	NA	NA	NA	NA	19	4.4	NA	NA	
	SHM-96-5B-101110	10/11/2010	846.2	NA	81000	NA	9300	NA	11000	NA	11500	NA	7900	NA	27000	NA	0.24	0.13	6.34	11.16	685	-35	320	NA	NA	<0.10	NA	NA	NA	NA	21	4.5	NA	NA	
	SHM-96-5B-040511	4/5/2011	2030	NA	71000	NA	30000	NA	11000	NA	9510	NA	<8500	NA	23000	NA	1	0.19	6.54	10.15	681	-60	340	NA	NA	0.23	NA	NA	NA	NA	17	3.8	NA	NA	
	SHM-96-5B-100611	10/6/2011	1895	NA	80000	NA	17000	NA	12000	NA	11000	NA	8600	NA	26000	NA	4.4	0.38	6.15	12.86	702	-19.8	310	NA	NA	<0.10	NA	NA	NA	NA	20	4.1	NA	NA	
	SHM-96-5B-041012	4/10/2012	1681	NA	76000	NA	19000	NA	10000	NA	10300 J	NA	9000	NA	28000	NA	42000	0.25	6.35	9.83	869	-43	330	NA	NA	0.060 J	NA	NA	NA	NA	18	<1.6	NA	NA	
	SHM-96-5B-101512	10/15/2012	1376	NA	66000	NA	13000	NA	10000	NA	9160	NA	7100	NA	22000	NA	52	0.69	6.56	14.74	475	-71.6	320	NA	NA	0.11	NA	NA	NA	NA	18	5.4	NA	NA	
	SHM-96-5B-052113	5/21/2013	NA	1400	NA	75300	NA	20000	NA	12700	NA	9670	NA	7970	NA	23700	9.01	0.36	6.42	10.75	652	-43.7	315	2.3	0.004 U	0.079 U	NA	1.4 U	NA	NA	18.7	5.4	2.7	NA	
	SHM-96-5B-102213	10/22/2013	NA	1660	NA	76500	NA	24700	NA	11600	NA	9980	NA	8000	NA	24000	0.58	1.31	6.55	11.55	560	-69.0	315	NA	0.0051 U	0.31	NA	NA	NA	NA	17.7	5.0 J	NA	NA	
	SHM-96-5B-042214	4/22/2014	NA	1340	NA	73300	NA	17100	NA	11500	NA	9810	NA	7760	NA	24000	4.61	0.73	6.21	10.14	642	-29.4	345	0.066 U	NA	NA	0.27	1.3 U	NA	NA	18.2	4.5 J	2.4	NA	
	DUP-042214	4/22/2014	NA	1390	NA	75000	NA	17600	NA	11900	NA	10400	NA	7810	NA	24600	NA	NA	NA	NA	NA	NA	333	0.066 U	NA	NA	0.28	1.3 U	NA	NA	18.2	4.5 J	2.2	NA	
	SHM-96-5B-100914	10/9/2014	NA	991	NA	72600	NA	13100	NA	11100	NA	10500	NA	6630	NA	24800	0.41	0.12	6.53	12.11	484	-54.8	318	1.3	NA	NA	0.097 J	1.3 U	NA	NA	17	5.7 J	2.7	NA	
SHM-96-5C	SHM-96-5C-101707	10/17/2007	61.1	NA	69000	NA	60000	NA	11000	NA	3980	NA	13000	NA	30000	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-96-5C-042210	4/22/2010	31.2	NA	75000	NA	15000	NA	9300	NA	6860	NA	13000	NA	36000	NA	0.19	0.14	6.31	9.84	1008	-267	30	NA	NA	0.1	NA	NA	NA	NA	34	<1.0	NA	NA	
	SHM-96-5C-101110	10/11/2010	26.4	NA	71000	NA	15000	NA	8600	NA	7160	NA	13000	NA	34000	NA	0.49	0.12	6.19	10.55	712	-51	310	NA	NA	<0.10	NA	NA	NA	NA	31	2.0	NA	NA	
	SHM-96-5C-040511	4/5/2011	35	NA	70000	NA	22000	NA	9500	NA	8890	NA	14000	NA	32000	NA	15	0.20	6.33	9.38	744	-32.2	340	NA	NA	0.22	NA	NA	NA	NA	28	1.6	NA	NA	
	SHM-96-5C-100611	10/6/2011	24.5	NA	70000	NA	13000	NA	9700	NA	8140	NA	14000	NA	31000	NA	4.6	0.22	6.16	12.15	721	-3.1	310	NA	NA	<0.60	NA	NA	NA	NA	28	1.7	NA	NA	
	SHM-96-5C-041012	4/10/2012	8.7	NA	67000	NA	4400	NA	9300	NA	13600 J	NA	18000	NA	33000	NA	6600	0.11	6	9.48	885	32.7	310	NA	NA	<0.100	NA	NA	NA	NA	27	<2.0	NA	NA	
	SHM-96-5C-101712	10/17/2012	7.7	NA	66000	NA	1100	NA	9800	NA	15000	NA	15000	NA	29000	NA	0.62 B	0.84	6.3	11.96	396	-71.0	300	NA	NA	<0.10	NA	NA	NA	NA	27	2.6	NA	NA	
	SHM-96-5C-052813	5/28/2013	NA	10.4	NA	68800	NA	2200	NA	11800	NA	12600	NA	14100	NA	29700	4.82	0.18	6.29	9.98	482	-64.9	318	3.8	0.004 U	0.079 U	NA	1.4 U	NA	NA	24.0	4.5 U	3.8	NA	
	SHM-96-5C-102213	10/22/2013	NA	5.5	NA	67300	NA	609	NA	9910	NA	12900	NA	17400	NA	32300	0.10	1.41	6.21	11.63	529	-20.1	315	NA	0.0051 U	0.059 U	NA	NA	NA	NA	19.2	3.4 J	NA	NA	
	SHM-96-5C-042214	4/22/2014	NA	10.9	NA	63000	NA	3980	NA	10200	MA	10400	NA	16400	NA	29200	3.66	0.16	6.18	9.79	618	7.8	326	0.20	NA	NA	0.067 J	1.3 U	NA	NA	20.2	2.6 J	3.8	NA	
	SHM-96-5C-100914	10/9/2014	NA	17.7	NA	63800	NA	7300	NA	10200	NA	8310	NA	12700	NA	28100	0.35	0.07	6.39	11.75	466	-28.1	302	4.50	NA	NA	0.11	1.3 U	NA	NA	18.0	3.5 J	2.8	NA	
SHP-99-29X	SHP-99-29X-101807	10/18/2007	2953	NA	11000	NA	44000	NA	990	NA	10400	NA	530 J	NA	2600	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHP-99-29X-102907	10/29/2007	2800	NA	12000	11000	42000	41000	980	960	10000	10000	700	NA	2800	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHP-99-29X-101210	10/12/2010	3156	NA	12000	NA	44000	NA	1100	NA	9310	NA	<2500	NA	3200	NA	1	0.13	5.67	11.90	270	-8.8	130	NA	NA	<0.10	NA	NA	NA	NA	2.5	4.9	NA	NA	
	SHP-99-29X-101112	10/11/2012	1457	NA	11000	NA	50000	NA	1300	NA	4210	NA	2100 J	NA	2900	NA	6	0.27	5.54	12.07	287	-1	110	NA	NA	0.17	NA	NA	NA	NA	4.1	3.0 J	NA	NA	
	SHP-99-29X-101712	10/17/2012	2739	NA	8400	NA	32000	NA	760	NA	5510	NA	<2500	NA	2200	NA	3.6	0.29	5.82	11.32	191	-75.7	92	NA	NA	0.13	NA	NA	NA	NA	1.6	4.8	NA	NA	
	SHP-99-29X-102213	10/22/2013	NA	2760	NA	9970	NA	43300	NA	889 J	NA	6430	NA	638 J	NA	2500 J	4.29	0.90	6.02	13.10	230	-48.3	101	NA	0.0051 U	0.16	NA	NA	NA	NA	2.3	5.6 J	NA	NA	
	SHP-99-29X-100714	10/7/2014	NA	3000	NA	12500	NA	49100	NA	2500 U	NA	8510	NA	2500 U	NA	2630 J	13.2	0.13	5.92	11.60	180	-17.8	120	0.50	NA	NA	1.50	1.3 U	NA	NA	3.0	7.8 J	1.5	NA	

TABLE 3
GROUNDWATER MONITORING WELL RESULTS
Shepley's Hill Landfill, Devens Massachusetts

Well ID	Sample ID	Date	Arsenic		Calcium		Iron		Magnesium		Manganese		Potassium		Sodium		Turbidity	DO	pH	Temp	Spec Cond	ORP	Alkalinity	Ammonia	Nitrite	Nitrate	Nitrogen (Nitrite +Nitrate)	Sulfide	COD	TOC	Chloride	Sulfate	DOC	DIC	Notes
			Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	NTU	mg/L		Celcius	uS/cm	mV	mg CaCO3/L	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	
SHP-99-31A	SHP-99-31A-101707	10/17/2007	22.7	NA	12000	NA	12000	NA	800	NA	798	NA	680 J	NA	13000	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHP-99-31A-011008	1/10/2008	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHP-99-31A-101310	10/13/2010	17.4	NA	15000	NA	13000	NA	1200	NA	675	NA	1000 J	NA	16000	NA	0.24	0.11	5.83	13.63	241	6.4	32	NA	NA	<0.10	NA	NA	NA	NA	46	5.6	NA	NA	
	SHP-99-31A-100511	10/5/2011	18.4	NA	11000	NA	8100	NA	790	NA	427	NA	<2500	NA	9700	NA	1.8	0.28	5.55	15.55	151	3.2	38	NA	NA	<0.10	NA	NA	NA	NA	3	6.6	NA	NA	
	SHP-99-31A-101812	10/18/2012	17.7	NA	16000	NA	11000	NA	1500	NA	519	NA	840 J	NA	15000	NA	2.2	0.42	5.78	13.71	169	-6.0	22	NA	NA	0.07 J	NA	NA	NA	NA	46	15	NA	NA	
	SHP-99-31A-102313	10/23/2013	NA	14.2	NA	10600	NA	4210	NA	971 J	NA	311	NA	500 U	NA	11900	3.79	1.02	5.83	12.48	145	41.9	15.3	NA	0.0051 U	0.059 U	NA	NA	NA	NA	25.7	9.7 J	NA	NA	
	DUP01-102313	10/23/2013	NA	14.6	NA	10600	NA	4250	NA	960 J	NA	308	NA	500 U	NA	11900	NA	NA	NA	NA	NA	NA	15.3	NA	0.0051 U	0.059 U	NA	NA	NA	NA	25.7	9.7 J	NA	NA	
SHP-99-31B	SHP-99-31B-101707	10/17/2007	85.5	NA	44000	NA	28000	NA	5100	NA	1210	NA	6800	NA	16000	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHP-99-31B-011008	1/10/2008	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-99-31B	8/12/2010	NA	28.8	NA	16500	NA	14600	NA	1930	NA	478	NA	3860	NA	8460	NA	0.19	6.03	10.74	186	33.9	86	4.1	<0.002	<0.01	NA	<0.10	11 J	NA	4	3	6.5	28	Test Kit (Filtered) 5
	SHP-99-31B-101310	10/13/2010	39.2	NA	18000	NA	11000	NA	1800	NA	481		3400	NA	5800	NA	0.19	0.15	6.27	10.58	211	-71	86	NA	NA	<0.10	NA	NA	NA	NA	3.4	3.8	NA	NA	
	SHP-99-31B-100511	10/5/2011	59.3	NA	17000	NA	10000	NA	1700	NA	460	NA	3000	NA	4600	NA	0.19	0.22	6.22	11.8	201	-46	83	NA	NA	<0.10	NA	NA	NA	NA	3.3	4.1	NA	NA	
	SHP-99-31B-101812	10/18/2012	60.1	NA	17000	NA	9400	NA	1800	NA	405	NA	3000	NA	3700	NA	1.3	0.31	6.31	10.42	175	-85.0	73	NA	NA	0.09 J	NA	NA	NA	NA	2.3	5.3	NA	NA	
	SHP-99-31B-102313	10/23/2013	NA	61.6	NA	16900	NA	9460	NA	1880 J	NA	448	NA	3030 J	NA	3510 J	1.02	2.42	6.56	11.15	176	-57.7	63.5	NA	0.0051 U	0.20	NA	NA	NA	NA	4.3	7.6 J	NA	NA	
SHP-99-31C	SHP-99-31C-101707	10/17/2007	292.1	NA	86000	NA	44000	NA	13000	NA	4050	NA	16000	NA	38000	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHP-99-31C-011008	1/10/2008	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-99-31C-101310	10/13/2010	239.4	NA	87000	NA	22000	NA	11000	NA	5250	NA	8500	NA	32000	NA	0.25	0.16	6.46	10.61	811	-80	350	NA	NA	<0.10	NA	NA	NA	NA	30	3.5	NA	NA	
	SHM-99-31C-100511	10/5/2011	244	NA	90000	NA	22000	NA	12000	NA	6040	NA	7900	NA	31000	NA	1.9	0.27	6.5	11.61	809	-59.2	340	NA	NA	<.300	NA	NA	NA	NA	27	3.9	NA	NA	
	SHP-99-31C-101812	10/18/2012	206.4	NA	83000	NA	17000	NA	11000	NA	5450	NA	7200	NA	30000	NA	19	0.64	6.75	13.81	641	-117.1	310	NA	NA	0.12	NA	NA	NA	NA	28	5.2	NA	NA	
	SHP-99-31C-102313	10/23/2013	NA	205	NA	90900	NA	16400	NA	12800	NA	6160	NA	7220	NA	30600	3.71	0.23	6.7	11.13	737	-95.7	348	NA	0.0051 U	0.22	NA	NA	NA	NA	32.2	5.7 J	NA	NA	
	SHM-99-31C-101314	10/13/2014	NA	180	NA	77800	NA	15800	NA	11200	NA	5060	NA	7200	NA	28800	4.22	0.17	6.71	10.85	634	-78.4	315	0.065 U	NA	NA	0.050 U	1.3 U	NA	NA	24.5	6.0 J	4.2	NA	
SHM-99-32X	SHP-99-32X-101707	10/17/2007	206.2	NA	78000	NA	60000	NA	11000	NA	3480	NA	12000	NA	34000	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHP-99-32X-011008	1/10/2008	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-99-32X-101310	10/13/2010	173.4	NA	100000	NA	25000	NA	14000	NA	8600	NA	6600	NA	38000	NA	0.42	0.16	6.51	10.49	879	-77	390	NA	NA	<0.10	NA	NA	NA	NA	39	3.9	NA	NA	
	SHM-99-32X-100411	10/4/2011	172.8	NA	98000	NA	24000	NA	13000	NA	10100	NA	6200	NA	38000	NA	5	0.33	6.42	11.54	825	-36	380	NA	NA	.040 J	NA	NA	NA	NA	32	2.4	NA	NA	
	DUP01-100411	10/4/2011	174.6	NA	100000	NA	25000	NA	13000	NA	10400	NA	6400	NA	39000	NA	5	0.33	6.42	11.54	825	-36	380	NA	NA	<0.10	NA	NA	NA	NA	32	2.5	NA	NA	
	SHM-99-32X-101712	10/17/2012	130.6	NA	87000	NA	23000	NA	12000	NA	10700	NA	5800	NA	34000	NA	28	0.63	6.54	10.52	469	-136.4	370	NA	NA	0.14	NA	NA	NA	NA	36	2.8	NA	NA	
	DUP-101712	10/17/2012	134.4	NA	86000	NA	23000	NA	12000	NA	10700	NA	5800	NA	35000	NA	24	NA	NA	NA	NA	NA	360	NA	NA	0.31	NA	NA	NA	NA	36	2.5	NA	NA	
	SHM-99-32X-102313	10/23/2013	NA	107	NA	83700	NA	18400	NA	11500	NA	10900	NA	5250	NA	33400	0.37	0.17	6.45	11.17	704	-77.9	342	NA	0.0051 U	0.27	NA	NA	NA	NA	32.2	2.9 J	NA	NA	
	SHM-99-32X-101314	10/13/2014	NA	93.5	NA	73400	NA	16800	NA	10000	NA	9670	NA	4590 J	NA	32300	17.39	1.89	6.64	11.19	462	-83	280	0.41	NA	NA	0.059 J	1.3 U	NA	NA	32.5	4.9 J	2.1	NA	
	Dup-101314	10/13/2014	NA	94.9	NA	73100	NA	17000	NA	10200	NA	9620	NA	4630 J	NA	32400	17.39	1.89	6.64	11.19	462	-83	287	0.42	NA	NA	0.055 J	1.3 U	NA	NA	32.5	4.8 J	2.1	NA	
SHP-01-36X	SHP-01-36X-101607	10/16/2007	16.7	NA	8900	NA	6900	NA	1700	NA	309	NA	1500 J	NA	25000	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHP-01-36X-101410	10/14/2010	14.2	NA	9700	NA	2300	NA	1600	NA	168	NA	1000 J	NA	25000	NA	1	0.12	6.5	15.80	218	-78	24	NA	NA	<0.10	NA	NA	NA	NA	40	9.2	NA	NA	
	SHP-01-36X-101011	10/10/2011	30.8	NA	10000	NA	2700	NA	2000	NA	53	NA	<2500	NA	24000	NA	1	0.18	5.82	19.76	208	-43	28	NA	NA	<0.10	NA	NA	NA	NA	46	4.3	NA	NA	
	SHP-01-36X-101612	10/16/2012	17.8	NA	15000	NA	2600	NA	2600	NA	83	NA	1800 J	NA	33000	NA	23	0.36	6.52	15	379	-73.4	40	NA	NA	0.07 J	NA	NA	NA	NA	63	5.1	NA	NA	
	SHP-01-36X-111913	11/19/2013	NA	4.8	NA	17400	NA	75.2 J	NA	2540 J	NA	23.4	NA	2230 J	NA	42000	0.63	7.07	6.42	6.79	351	118.8	24.2	0.093 J	0.0051 U	0.064 J	NA	1.5 U	NA	NA	75.5	23.7	NA	2.8	
	SHP-01-36X-100914	10/9/2014	NA	10.8	NA	14700	NA	535	NA	2800 J	NA	67.8	NA	2500 U	NA	47700	2.99	0.32	6.27	17.35	329	39.2	26.2	0.065 U	NA	NA	0.050 U	1.3 U	NA	NA	110	8.1 J	3.1	NA	
SHP-01-37X	SHP-01-37X-101607	10/16/2007	26.6	NA	10000	NA	8200	NA	1600	NA	588	NA	2200 J	NA	28000	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHP-01-37X-101410	10/14/2010	22.5	NA	12000	NA	6700	NA	1700	NA	761	NA	1500 J	NA	32000	NA	0.29	0.42	6.21	16.68	300	-43	44	NA	NA	<0.10	NA	NA	NA	NA	60	<1.0	NA	NA	
	SHP-01-37X-101612	10/16/2012	10.2	NA	11000	NA	3900	NA	2200	NA	321	NA	1600 J	NA	29000	NA	1.6	0.38	6.4	14.67	287	-105.8	37	NA	NA	0.42	NA	NA	NA	NA	62	3.0	NA	NA	
	SHP-01-37X-111913	11/19/2013	NA	4.7	NA	28700	NA	1430	NA	2840 J	NA	569	NA	3970 J	NA	42500	0.43	3.12	5.64	6.85	433	123.3	4.4 J	0.087 J	0.0051 U	0.059 U	NA	1.5 U	NA	NA	75.5	78.1	2.0 U	NA	
	SHP-01-37X-100914	10/9/2014	NA	8.5	NA	9970	NA	3410	NA	2500 U	NA	158	NA	2500 U	NA	45200	0.1	1.8	6.22	17.13	350	28	12	0.065 U	NA	NA	0.050 U	1.3 U	NA	NA	80	8.0 J	3.1	NA	
SHP-01-38A	SHP-01-38A-101607	10/16/2007	781.4	NA	32000	NA	37000	NA	5400	NA	848	NA	12000	NA	24000	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHP-01-38A-101410	10/14/2010	651.8	NA	28000	NA	28000	NA	3500	NA	716	NA	8300	NA	20000	NA	1	0.91	6.37	12.81	433	-70	140	NA	NA	<0.10	NA	NA	NA	NA	28	18	NA	NA	
	SHP-01-38A-101211	10/12/2011	557.9	NA	38000	NA	31000	NA	4500	NA	892	NA	11000	NA	19000	NA	3	0.21	5.95	13.44	500	-39	200	NA	NA	<0.08	NA	NA	NA	NA	24	11	NA	NA	
	SHP-01-38A-101512	10/15/2012	660.6	NA	33000	NA	3000	NA	4200	NA	710	NA	8700	NA	22000	NA	30	0.36	6.19	12.84	499	-73.1	180	NA	NA	0.15	NA	NA	NA	NA	44	18	NA	NA	
	SHP-01-38A-052313	5/23/2013	NA	412	NA	11800	NA	10200	NA	1260 J	NA	254	NA	4390 J	NA	8320	4.3	0.12	6.66	10.79	156	-70.1	64.1	2.9	0.004 U	0.35	NA	1.4 U	NA	NA	5.3	6.3	2.1	NA	
	SHP-01-38A-111913	11/19/2013	NA	247	NA	39800	NA	17900	NA	2450 J	NA	2200	NA	8410	NA	23000	0.31	1.25	6.14	12.33	435	-20.7	79.2	1.2	0.0051 U	1.1	NA	1.5 U	NA	NA	7	115	2.2	NA	
	SHP-01-38A-100914	10/9/2014	NA	263	NA	17100	NA	23500	NA	2500 U	NA	2490	NA	6140	NA	20600	0.37	0.16	6.23	14.12	256	-47	93.7	0.065 U	NA	NA	0.14	1.3 U	NA	NA	10.5	49.2	19.8	NA	
SHP-01-38B	SHP-01-38B-052313	5/23/2013	NA	900	NA	53400	NA	47100	NA	8140	NA	2240	NA	9270	NA	23500	0.0	0.30	6.62	10.78	583	-109.1	190	5.2	0.004 U	0.26	NA	1.4 U	NA	NA	51.7	4.5 U	3.6	NA	
SHM-05-39A	SHM-05-39A-101707	10/17/2007	2.415	NA	29000	NA	52000	NA	38000	NA	1250	NA	8200	NA	10000	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-05-39A-010908	1/9/2008	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-05-39A	8/12/2010	NA	236	NA	16600	NA	24500	NA	1860	NA	680	NA	6530	NA	12300	NA	0.35	6.45	11.37	263	-52.9	100	4.01	<0.002	0.009 J	NA	<0.10	11 J	NA	7.1	6	2.9	27	Test Kit (Filtered) 100
	SHM-05-39A-101310	10/13/2012	246.3	NA	18000	NA	26000	NA	1900	NA	744	NA	6000	NA	10000	NA	0.17	0.2	6.63	11.29	297	-92	110	NA	NA	<0.10	NA	NA	NA	NA	13	4.3	NA	NA	
	SHM-05-39A-100411	10/4/2011	227.1	NA	16000	NA	17000	NA	1600	NA	541	NA	5500	NA	6600	NA	2	0.16	6.62	12.05	213	-66	87	NA	NA	<0.10	NA	NA	NA	NA	3.6	3.8	NA	NA	
	SHL-05-39A-101612	10/16/2012	76.3	NA	14000	NA	3900	NA	1400	NA	52	NA	4900	NA	13000	NA	40	0.37	6.28	14.29	149	69.6	50	NA	NA	2.1	NA	NA	NA	NA	17	4.8	NA	NA	
	SHL-05-39A-102413	10/24/2013	NA	146	NA	15800	NA	14700	NA	1770 J	NA	575	NA	5290	NA	5080	0.35	0.23	6.7	11.9	133	-94.3	51.5	NA	0.0051 U	0.3	NA	NA	NA	NA	19.2	4.0 J	NA	NA	
SHM-05-39B	SHM-05-39B-101707	10/17/2007	3.094	NA	99000	NA	10000	NA	14000	NA	5920	NA	9300	NA	47000	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-05-39B-010908	1/9/2008	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-05-39B-101310	10/13/2010	162	NA	92000	NA	3200	NA	12000	NA	5510	NA	7000	NA	130000	NA	3.54	0.19	6.75	12.93	896	-68.1	300	NA	NA	<0.10	NA	NA	NA	NA	130 J	4.0 J	NA	NA	
	DUP-02-101310	10/13/2010	174.7	NA	91000	NA	3300	NA	11000	NA	5450	NA	6600	NA	120000	NA	3.54	0.19	6.75	12.93	896	-68.1	300	NA	NA	0.36	NA	NA	NA	NA	190	6.2	NA	NA	
	SHM-05-39B-100511	10/5/2011	308.1	NA	100000	NA	5000	NA	13000	NA	6130	NA	6500	NA	60000	NA	3	0.11	6.85	13.12	919	-66	420	NA	NA	<0.10	NA	NA	NA	NA	93 J	3.2	NA	NA	
	DUP02-100511	10/5/2011	311.4	NA	100000	NA	5100	NA	13000	NA	6250	NA	6600	NA	60000	NA	3	0.11	6.85	13.12	919	-66	350	NA	NA	<0.10	NA	NA	NA	NA	39	1.8	NA	NA	
	SHM-05-39B-101612	10/16/2012	364.4	NA	100000	NA	6100	NA	14000	NA	6320	NA	6400	NA	40000	NA	55	1.67	6.91	15.3	1365	-126.7	420	NA	NA	0.08 J	NA	NA	NA	NA	37	1.97 J	NA	NA	
	SHM-05-39B-102413	10/24/2013	NA	113	NA	16500	NA	9580	NA	1660 J	NA	1230	NA	3040 J	NA	61900	0.97	0.40	6.93	10.76	278	-95.3	71.2	NA	0.0051 U	0.16	NA	NA	NA	NA	88.7	3.8 J	NA	NA	
SHM-05-40X	SHM-05-40X-101807	10/18/2007	4445	NA	50000	NA	58000	NA	7500	NA	1330	NA	7300	NA	19000	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-05-40X-103107	10/31/2007	4058	2620	51000	48000	57900	43500	7800	7300	1427	1244	7600	7560	20000	19900	7.89	1.62	6.71	11.02	565	-134.1	220	NA	NA	N	NA	0.1 U	NA	0.5 U	13	1.7	NA	NA	
	SHM-05-40X-100710	10/7/2010	3637	NA	34000	NA	35000	NA	4900	NA	828	NA	5600	NA	14000	NA	0.34	0.22	6.47	10.68	409	-106.1	160	NA	NA	0.14	NA	NA	NA	NA	12	5.8	NA	NA	
	SHM-05-40X100511	10/5/2011	3703	NA	29000	NA	30000	NA	3800	NA	804	NA	5500	NA	13000	NA	4.1	0.24	6.48	10.52	3.95	-77.3	159	NA	NA	<0.10	NA	NA	NA	NA	11	4.2	NA	NA	
	SHM-05-40X-101712	10/17/2012	2974	NA	32000	NA	3000	NA	4800	NA	0.829	NA	5400	NA	13000	NA	40	0.19	6.71	10.62	374	-133.2	150	NA	NA	0.15	NA	NA	NA	NA	9.7	5.9	NA	NA	
	SHM-05-40X-102413	10/24/2013	NA	3100	NA	37500	NA	28800	5610	NA	911	NA	NA	6590	NA	15100	2.21	0.32	6.87	10.62	253	-136.3	165	NA	0.0053 J	0.28	NA	NA	NA	NA	13.3	4.8 J	NA	NA	
	SHM-05-40X-101314	10/13/2014	NA	3070	NA	39200	NA	40800	NA	6420	NA	1080	NA	7720	NA	13800	8.65	0.39	6.85	10.5	334	-130.2	178	0.065 U	NA	NA	0.053 U	1.3 U	NA	NA	12	5.4 J	5.8	NA	
SHM-05-41A	SHM-05-41A-101707	10/17/2007	24.9	NA	8200	NA	3400	NA	1700	NA	356	NA	1800 J	NA	3400	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-05-41A-010908	1/9/2008	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-05-41A-042110	4/21/2010	26.9	NA	9200	NA	2900	NA	1400	NA	388	NA	2100 J	NA	2100	NA	0.15	0.09	6.6	9.53	121	-34	37	NA	NA	0.075 J	NA	NA	NA	NA	1.4	7.9	NA	NA	
	SHM-05-41A-100710	10/7/2010	66.7	NA	10000	NA	4900	NA	1600	NA	395	NA	2000 J	NA	1800 J	NA	0.67	0.26	6.09	10.18	95	1.3	31	NA	NA	0.053 J	NA	NA	NA	NA	3.0	7.3	NA	NA	
	SHM-05-41A-040411	4/4/2011	20.9	NA	10000	NA	2800	NA	1600	NA	539	NA	<2500	NA	1900 J	NA	2.7	0.32	6.46	8.44	100	1.8	37	NA	NA	0.13	NA	NA	NA	NA	2.5	6.7	NA	NA	
	SHM-05-41A-100411	10/4/2011	18.4	NA	12000	NA	3200	NA	1900	NA	636	NA	2000 J	NA	2100	NA	3.9	0.48	5.76	10.99	107	44.9	41	NA	NA	<0.10	NA	NA	NA	NA	2.2	5.2	NA	NA	
	SHM-05-41A-04112	4/11/2012	15.5	NA	8500	NA	2400	NA	1300	NA	424	NA	1600 J	NA	2200	NA	1200	0.52	6.2	9.56	111	18.4	30	NA	NA	0.020 J	NA	NA	NA	NA	3.0	<6.2	NA	NA	
	SHM-05-41A-101712	10/17/2012	10.3	NA	97000	NA	2300	NA	1500	NA	592	NA	1600 J	NA	2000	NA	1.4	0.35	6.25	12.98	90	-33.5	34	NA	NA	0.08 J	NA	NA	NA	NA	2.0	6.1	NA	NA	
	SHM-05-41A-052213	5/22/2013	NA	12.3	NA	9930	NA	5530	NA	1440 J	NA	569	NA	1630 J	NA	2610 J	3.79	0.76	6.27	10.43	101	17.6	33.2	0.081 U	0.004 U	0.079 U	NA	1.4 U	NA	NA	3.3	7.9	1.2	NA	
	SHM-05-41A-102313	10/23/2013	NA	12.5	NA	9230	NA	4560	NA	1390 J	NA	534	NA	1660 J	NA	2680 J	0.66	0.35	6.42	10.17	69	-18.0	40.5	NA	0.0051 U	0.059 U	NA	NA	NA	NA	2.8	5.8 J	NA	NA	
	SHM-05-41A-042314	4/23/2014	NA	9.7	NA	9430	NA	6240	NA	1410 J	NA	576	NA	1710 J	NA	12400	6.28	0.72	6.22	9.27	172	45.3	35.0	0.066 U	NA	NA	0.069 J	1.3 U	NA	NA	21.2	4.9 J	1.9	NA	
	SHM-05-41A-100914	10/9/2014	NA	14.2	NA	9350	NA	8040	NA	2500 U	NA	552	NA	2500 U	NA	2930 J	0.42	0.08	6.39	10.94	81	-20.0	38.2	0.065 U	NA	NA	0.050 U	1.3 U	NA	NA	3.5	6.8 J	1.5	NA	

TABLE 3
GROUNDWATER MONITORING WELL RESULTS
Shepley's Hill Landfill, Devens Massachusetts

Well ID	Sample ID	Date	Arsenic		Calcium		Iron		Magnesium		Manganese		Potassium		Sodium		Turbidity	DO	pH	Temp	Spec Cond	ORP	Alkalinity	Ammonia	Nitrite	Nitrate	Nitrogen (Nitrite +Nitrate)	Sulfide	COD	TOC	Chloride	Sulfate	DOC	DIC	Notes
			Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	NTU	mg/L		Celcius	uS/cm	mV	mg CaCO3/L	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	
SHM-05-41B	SHM-05-41B-101707	10/17/2007	2591	NA	48000	NA	100000	NA	6000	NA	1770	NA	12000	NA	14000	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-05-41A-010908	1/9/2008	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	DUP-010908	1/9/2008	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-05-041B	8/9/2010	1440	1130	16000	14500 J	35200	28000	2400	2080	736	656 J	10000	8770 J	14900	12800 J	NA	0.32	6.43	11.75	310	42.6	NA	NA	NA	NA	NA	NA	NA	NA	NA	2.6	32	Test Kit (Filtered) 500	
	SHM-05-41B-042110	4/21/2010	1372	NA	14000	NA	32000	NA	2000	NA	662	NA	8600	NA	11000	NA	9.6	0.08	6.74	9.6	392	-124	120	NA	NA	0.12	NA	NA	NA	NA	7.0	5	NA	NA	
	SHM-05-41B-100710	10/7/2010	1036	NA	12000	NA	27000	NA	1700	NA	605	NA	8400	NA	7500	NA	1.64	0.35	6.65	10.29	259	-86.8	100	NA	NA	0.10	NA	NA	NA	NA	2.9	5.3	NA	NA	
	SHM-05-41B-040411	4/4/2011	1045	NA	12000	NA	27000	NA	1800	NA	605	NA	9000	NA	5900	NA	0.5	0.16	6.73	8.44	266	-80.4	120	NA	NA	0.23	NA	NA	NA	NA	1.5	5.7	NA	NA	
	SHM-05-41B-100411	10/4/2011	1369	NA	9900	NA	26000	NA	1400	NA	494	NA	8700	NA	5600	NA	5.8	0.35	6.29	10.92	209	-61.2	83	NA	NA	<0.10	NA	NA	NA	NA	1.5	3.5	NA	NA	
	SHM-05-41B-04112	4/11/2012	770.8	NA	6800	NA	13000	NA	1000	NA	304	NA	6700	NA	5000	NA	8400	0.14	6.44	10.02	199	-57.2	66	NA	NA	NA	0.14	NA	NA	NA	3.0	<3.3	NA	NA	
	SHM-05-41B-101712	10/17/2012	859.5	NA	13000	NA	26000	NA	2100	NA	629	NA	8500	NA	3500	NA	41	0.22	6.58	12.23	259	-150.1	100	NA	NA	0.16	NA	NA	NA	NA	3.1	4.1	NA	NA	
	SHM-05-41B-52213	5/22/2013	NA	812	NA	18400	NA	32300	NA	3450 J	NA	780	NA	9330	NA	5150	3.03	0.26	6.55	9.98	302	-94.0	97.2	0.16	0.004 U	0.40	NA	1.4 U	NA	NA	5.8	8.7	2.8	NA	
	SHM-05-41B-102313	10/23/2013	NA	716	NA	12700	NA	21400	NA	2430 J	NA	583	NA	7500	NA	3780 J	4.49	0.46	6.88	10.05	155	-120.4	81	NA	0.0051 U	0.26	NA	NA	NA	NA	4.3	4.7 J	NA	NA	
	SHM-05-41B-042314	4/23/2014	NA	678	NA	17000	NA	25900	NA	3200 J	NA	766	NA	7690	NA	3350	15.0	0.47	6.6	9.33	245	-37.7	87.6	0.066 U	NA	NA	0.31	1.3 U	NA	NA	3.8	5.2 J	2.3	NA	
	DUP-042314	4/23/2014	NA	704	NA	17700	NA	27100	NA	3330 J	NA	800	NA	7980	NA	3310 J	15.0	0.47	6.6	9.33	245	-37.7	86.5	0.066 U	NA	NA	0.35	1.3 U	NA	NA	4.3	5.2 J	2.2	NA	
	SHM-05-41B-100914	10/9/2014	NA	638	NA	17400	NA	24300	NA	2780 J	NA	752	NA	6690	NA	3140 J	10.7	0.41	6.76	10.49	195	-93.0	97	4.6	NA	NA	0.050 U	1.3 U	NA	NA	2.5	5.3 J	1.7	NA	
SHM-05-41C	SHM-05-41C-101707	10/17/2007	684.5	NA	97000	NA	18000	NA	13000	NA	3260	NA	4200	NA	36000	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-05-41C-010908	1/9/2008	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-05-41C-042110	4/21/2010	896	NA	92000	NA	18000	NA	11000	NA	2860	NA	3500	NA	34000	NA	0.8	0.11	7.17	10.06	963	-167	350	NA	NA	0.079 J	NA	NA	NA	NA	30	<1.0	NA	NA	
	SHM-05-41C-100710	10/7/2010	787	NA	97000	NA	19000	NA	12000	NA	3100	NA	3500	NA	33000	NA	0.43	0.29	7.01	10.71	753	-132	350	NA	NA	0.11	NA	NA	NA	NA	29	<1.0	NA	NA	
	SHM-05-41C-040411	4/4/2011	749.8	NA	98000	NA	16000	NA	12000	NA	3170	NA	<3700	NA	100000	NA	19	0.28	7.03	8.67	1132	-99	250	NA	NA	0.18	NA	NA	NA	NA	130	2.9	NA	NA	
	SHM-05-41C-100411	10/4/2011	917	NA	98000	NA	19000	NA	11000	NA	3240	NA	3600	NA	33000	NA	4.8	0.36	6.28	11.14	775	-88.7	340	NA	NA	<0.10	NA	NA	NA	NA	28	.30 J	NA	NA	
	SHM-05-41C-041112	4/11/2012	764.8	NA	94000	NA	18000	NA	11000	NA	3160	NA	3700	NA	35000	NA	150000	0.19	7	9.2	929	-116.8	330	NA	NA	<0.10	NA	NA	NA	NA	30	<2.1	NA	NA	
	SHM-05-41C-101812	10/18/2012	782.2	NA	95000	NA	17000	NA	12000	NA	3190	NA	3500	NA	33000	NA	170	0.7	6.93	9.02	714	-164.5	350	NA	NA	0.08 J	NA	NA	NA	NA	28	0.81 J	NA	NA	
	SHM-05-41C-052113	5/21/2013	NA	709	NA	102000	NA	14700	NA	13400	NA	2530	NA	3490 J	NA	118000	2.7	0.26	6.98	11.50	1081	-98.5	375	0.081 U	0.004 U	0.45	NA	1.4 U	NA	NA	153	4.5 U	3.9	NA	
	SHM-05-41C-102313	10/23/2013	NA	890	NA	106000	NA	16200	NA	13000	NA	2940	NA	3580 J	NA	33700	0.44	0.93	7.16	10.08	511	-165.9	364	NA	0.0051 U	0.28	NA	NA	NA	NA	28.7	1.4 J	NA	NA	
	SHM-05-41C-042314	4/23/2014	NA	1490	NA	82900	NA	17600	NA	11300	NA	1660	NA	3130 J	NA	305000	4.91	0.57	7.14	9.46	1905	-121.7	378	0.066 U	NA	NA	0.23	1.3 U	NA	NA	437	4.2 J	4.5	NA	
	SHM-05-41C-100914	10/9/2014	NA	946	NA	93700	NA	16000	NA	12600	NA	2540	NA	3030 J	NA	77300	0.42	0.14	7.13	10.97	6.99	-152.2	368	4.5	NA	NA	0.28	0.080 J	NA	NA	2.6 J	4.1	NA	NA	
SHM-05-42A	SHM-05-42A-101707	10/17/2007	1.01 J	NA	5600	NA	180	NA	1200	NA	8.1 J	NA	1900 J	NA	1000 J	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-05-42A	8/12/2010	NA	1.25	NA	6700	NA	388	NA	1160	NA	140	NA	1470	NA	2040	NA	1.20	6.50	10.39	61	89.5	18	0.0189 J	<0.002	<0.01	NA	<0.10	<7.0	NA	1.6	5.6	<1.0	9.4	Test Kit (Filtered) < 5
	SHM-05-42A-042210	4/22/2010	2.5	NA	5200	NA	1200	NA	980	NA	153	NA	1200 J	NA	1900 J	NA	3.5	5.11	6.08	9.63	0.071	-95	160	NA	NA	0.12	NA	NA	NA	NA	2.0	5.8	NA	NA	
	SHM-05-42A-101310	10/13/2010	1.2	NA	7600	NA	250	NA	1300	NA	138	NA	1600 J	NA	2000	NA	1	0.31	5.75	9.82	70	102.7	230	NA	NA	<0.10	NA	NA	NA	NA	2.2	5.9	NA	NA	
	SHM-05-42A-040511	4/5/2011	1.1	NA	7100	NA	200	NA	1100	NA	105	NA	<2500	NA	<2500	NA	0	0.16	6.05	8.76	70	95.2	210	NA	NA	0.12	NA	NA	NA	NA	2.3	6.4	NA	NA	
	SHM-05-42A-100711	10/7/2011	0.8	NA	6200	NA	100	NA	1000	NA	15	NA	1600 J	NA	1600 J	NA	0.08	1.95	5.23	10.27	61	156.3	190	NA	NA	0.24	NA	NA	NA	NA	1.8	4.5	NA	NA	
	SHM-05-42A-041112	4/11/2012	2.3	NA	5400	NA	500	NA	880	NA	29	NA	1600 J	NA	1600 J	NA	2700	6.09	5.6	9	63	186.2	170	NA	NA	0.11	NA	NA	NA	NA	2.7	<3.8	NA	NA	
	SHM-05-42A-101812	10/18/2012	0.7	NA	8100	NA	45 J	NA	1400	NA	42 J	NA	2200 J	NA	2100	NA	0.73 B	0.54	6.04	9.87	66	125.5	23	NA	NA	<0.10	NA	NA	NA	NA	3.3	4.3	NA	NA	
	SHM-05-42A-052213	5/22/2013	NA	0.89 J	NA	6420	NA	224	NA	981 J	NA	103	NA	2060 J	NA	2350 J	0.00	0.38	6.06	9.61	62	86.2	23.2	0.081 U	0.004 U	0.079 U	NA	1.4 U	NA	NA	2.8	5.6	0.65 J	NA	
	SHM-05-42A-102313	10/23/2013	NA	2.0 U	NA	6520	NA	111	NA	976 J	NA	66	NA	1880 J	NA	2420 J	0.28	2.53	6.09	7.97	61	73.2	23	NA	0.0051 U	0.11	NA	NA	NA	NA	2.8	6.3 J	NA	NA	
	SHM-05-42A-042314	4/23/2014	NA	2.0 U	NA	8100	NA	961	NA	1160 J	NA	193	NA	2020 J	NA	2860 J	0.88	0.23	5.86	9.16	62	101.2	23.0	0.066 U	NA	NA	0.053 J	1.3 U	NA	NA	4.3	7.5 J	3.1	NA	
	SHM-05-42A-100914	10/9/2014	NA	2.0 U	NA	11000	NA	130	NA	2500 U	NA	130	NA	2500 U	NA	3160 J	2.20	0.09	5.81	10.57	73	123.7	34.9	0.065 U	NA	NA	0.050 U	1.3 U	NA	NA	5.5	7.6 J	0.87 J	NA	
SHM-05-42B	SHM-05-42B-101707	10/17/2007	304.4	NA	77000	NA	94000	NA	12000	NA	1700	NA	20000	NA	39000	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-05-42B-010908	1/9/2008	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-05-42B-042210	4/22/2010	72.2	NA	56000	NA	37000	NA	7800	NA	2540	NA	11000	NA	26000	NA	6	0.19	6.52	9.77	863	-272	290	NA	NA	0.13	NA	NA	NA	NA	23	5.2	NA	NA	
	SHM-05-42B-101310	10/13/2010	197.2	NA	56000	NA	47000	NA	7300	NA	2710	NA	11000	NA	24000	NA	1	0.53	6.52	9.89	691	-64.6	300	NA	NA	<0.10	NA	NA	NA	NA	25	3.9	NA	NA	
	SHM-05-42B	4/1/2011	188.9	NA	59000	NA	61000	NA	8500	NA	3070	NA	12000	NA	29000	NA	0	0.25	6.44	8.79	759	-63	340	NA	NA	0.29	NA	NA	NA	NA	32	3.3	NA	NA	
	SHM-05-42B-100711	10/7/2011	230	NA	59000	NA	61000	NA	9000	NA	2790	NA	11000	NA	32000	NA	0.3	0.26	6.36	10.42	755	-44.1	330	NA	NA	0.12	NA	NA	NA	NA	31	3.4	NA	NA	
	SHM-05-42B-041112	4/11/2012	238.7	NA	51000	NA	58000	NA	7200	NA	2520	NA	10000	NA	30000	NA	37000	0.54	6.45	9.55	895	-59	320	NA	NA	0.60 J	NA	NA	NA	NA	26	<2.4	NA	NA	
	SHM-05-42B-101812	10/18/2012	240.6	NA	57000	NA	52000	NA	9000.0	NA	2600	NA	9900 J	NA	31000	NA	48	0.69	6.53	10.17	643	-116.8	300	NA	NA	0.21	NA	NA	NA	NA	25	3.2	NA	NA	
	SHM-05-42B-052213	5/22/2013	NA	238	NA	66000	NA	51100	NA	11300	NA	2900	NA	9310	NA	28000	1.2	0.37	6.58	9.92	655	-49.9	318	9.5	0.004 U	0.28	NA	1.4 U	NA	NA	27.7	4.5 U	3.4	NA	
	SHM-05-42B-102313	10/23/2013	NA	232	NA	60900	NA	43200	NA	9300	NA	3280	NA	8820	NA	27500	0.96	0.16	6.48	10.79	654	-105.7	313	NA	0.0051 U	0.18	NA	NA	NA	NA	20.7	3.3 J	NA	NA	
	SHM-05-42B-042314	4/23/2014	NA	229	NA	65900	NA	38000	NA	10100	NA	6110	NA	8550	NA	28900	3.08	0.14	6.43	9.36	643	-36.9	308	0.066 U	NA	NA	0.40	1.3 U	NA	NA	17.7	2.0 J	3.9	NA	
	SHM-05-42B-100914	10/9/2014	NA	215	NA	63500	NA	34300	NA	9150	NA	6450	NA	7650	NA	25100	3.4	0.1	6.6	10.69	498	-78.6	293	3.8	NA	NA	0.055 J	1.3 U	NA	NA	17	1.5 J	2.9	NA	
	Duplicate-100914	10/9/2014	NA	213	NA	62400	NA	34200	NA	9120	NA	6460	NA	7630	NA	25100	3.4	0.1	6.6	10.69	498	-78.6	293	3.8	NA	NA	0.058 J	1.3 U	NA	NA	17.5	2.8 J	2.5	NA	
SHP-05-045A	SHP-05-045A	8/9/2010	36.4	33.7	NA	NA	21600	22100	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.30	6.20	13.97	294	-32.2	NA	NA	NA	NA	NA	NA	NA	NA	NA	3.6	48	Test Kit (Filtered) 10	
SHP-05-046B	SHP-05-046B	8/9/2010	50.6	81.4	NA	NA	26800	34800	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.81	5.71	12.93	662	3	NA	NA	NA	NA	NA	NA	NA	NA	NA	14	150	Test Kit (Filtered) 80	
SHM-07-03	SHM-07-03	10/31/2007	44.4 J	<0.5	9300	8300	10700	73 J	2900	830	494.4	210.9	2200 J	1060 J	4100	3210	NA	NA	NA	NA	NA	NA	21.2	<0.075	0.006 J	<0.05	NA	<0.1	<20	NA	6.4	24	NA	NA	
	SHM-07-03	8/12/2010	NA	0.29 J	NA	6580	NA	53.8	NA	550	NA	9.68	NA	841	NA	11600	NA	6.61	5.81	12.25	81	133.9	18	0.0239 J	<0.002	0.59	NA	<0.10	<7.0	NA	8.2	10	<1.0	12	Test Kit (Filtered) < 5
	DUP2-081210	8/12/2010	NA	0.77	NA	6860	NA	58	NA	568	NA	9.66	NA	893	NA	12100	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-07-03-052813	5/28/2013	NA	1.0	NA	5930	NA	<100	NA	<5000	NA	<15	NA	<5000	NA	23800	12.02	4.82	5.81	12.84	147	139.2	16.6	0.081 U	0.004 U	0.87	NA	1.4 U	NA	NA	28.5	6.4	1.3	NA	
SHM-07-05X	SHM-07-05	10/31/2007	14.7	NA	21000	NA	391	NA	2900	NA	81.1	NA	15000	NA	32000	NA	5.01	1.85	7.61	11.1	429	19	46	0.278	0.01 J	<0.05	NA	<0.1	<20	NA	60	12	NA	NA	
	SHM-07-05	8/12/2010	NA	3180	NA	21500	NA	22500	NA	2990	NA	544	NA	4530	NA	11500	NA	0.40	6.45	11.43	256	-21.5	94	2.42	0.01 J	0.06	NA	<0.10	<7.0	NA	8.9	8.1	2	24	Test Kit (Filtered) > 500
	DUP-081210	8/12/2010	NA	3220	NA	21700	NA	22700	NA	2960	NA	545	NA	4540	NA	11500	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
SHM-10-01	SHM-10-01-071310	7/13/2010	1.16 J	0.68 J	42400	42700	508	373	3700	3680	10500 J	10600	2300	2290	9340	9160	3.34	0.18	6.19	12.38	297	63.5	130	0.264	< 0.002	< 0.01	NA	< 0.1	11 J	1.3	12	6.8	NA	NA	
	SHM-10-01	8/12/2010	NA	3.51 J	NA	41600	NA	886	NA	3530	NA	10700	NA	2230	NA	11100	NA	0.49	6.61	11.86	291	42.2	130	0.241	<0.002	<0.01	NA	<0.10	<7.0	NA	14	7.0	1.5	31	Test Kit (Filtered) < 5
	SHM-10-01-090810	9/8/2010	8.15	7.87	43100	43500	1740	1680	3680	3780	10200	10300	2220	2280	8880	8770	0.15	0.12	6.31	12.68	299	11.3	140	0.344	< 0.002	< 0.01	NA	< 0.1	12 J	1.6	11	8.7	1.6	37	
	SHM-10-01-102412	10/24/2012	NA	1.4	NA	21500	NA	210	NA	1900 J	NA	NA	NA	1800 J	NA	7200	0.95	0.40	6.39	11.51	143	48.3	88.6	0.10 U	<0.010	0.1 U	NA	2.0 U	NA	NA	8.5	6.2 U	NA	NA	
	SHM-10-01-052913	5/29/2013	NA	1.3	NA	18900	NA	124	NA	1690 J	NA	5970 J	NA	1770 J	NA	6900	0.00	0.16	6.53	10.58	160	51.2	72.9	0.26	0.004 U	0.079 U	NA	1.4 U	NA	NA	4.0	6.5	5.3	NA	
SHM-10-02	SHM-10-02-071510	7/15/2010	0.74	0.43 J	113000	117000	1190	881	15700	16100	2110	2180	3880	4010	49500	53300	3.47	0.45	6.42	12.24	836	80.8	250	0.248	< 0.002	< 0.01	NA	< 0.1	< 7	2.4	160	20	NA	NA	
	Dup-071510	7/15/2010	0.59	0.45 J	114000	117000	1170	890	15600	16100	2130	2170	3980	4000	51400	53100	NA	NA	NA	NA	NA	NA	250	0.231	< 0.002	< 0.01	NA	< 0.1	< 7	2.5	160	21	NA	NA	
	SHM010-02-090710	9/7/2010	1.11	1.07	115000 J	114000 J	973	843	16000	16000	2190	2190	4020	4040	48100	50700	0.64	0.87	5.94	12.45	881	-258.3	260	0.238	< 0.002	< 0.01	NA	< 0.1	< 7	2.6	120	19	2.5	62	
	SHM-10-02-102212	10/22/2012	NA	1.1	NA	133000	NA	100 UJ	NA	18200	NA	NA	NA	4100 J	NA	37400	1.78	0.48	6.52	12.18	726	40.2	448	0.13 J	<0.010	0.10 U	NA	2.0 U	NA	NA	61.5	7.4 U	NA	NA	
	Duplicate-102212	10/22/2012	NA	<1.0	NA	135000 b	NA	60.7 J	NA	18500	NA	NA	NA	4100 J	NA	37600 Q	1.78	0.48	6.52	12.18	726	40.2	448	0.65	<0.010	<0.11	NA	<2.0	NA	NA	60.0	7.2	NA	NA	
	SHM-10-02-052913	5/29/2013	NA	1.5	NA	137000	NA	33.7 J	NA	20100	NA	2450	NA	4300 J	NA	41200	1.04	0.2	6.53	11.37	537	73.2	444	0.35	0.004 U	0.079 U	NA	1.4 U	NA	NA	61.5	8.8	3.8	NA	
SHM-10-03	SHM-10-03-071410	7/14/2010	2.36	0.78 J	112000	109000	1630	866	12900	12600	122	153	6490	6000	474000	473000	31.7	1.47	6.60	16.09	3331	75.7	96	0.035 J	0.02	0.52	NA	< 0.1	25	0.64	1000	38	NA	NA	
	DUP-071410	7/14/2010	4.59	0.5 J	112000	111000	2440	843	13000	127000	151	134	6580	6060	483000	474000	NA	NA	NA	NA	NA	NA	95	0.0269 J	0.02	0.51	NA	< 0.1	47	0.73	1000	36	NA	NA	
	SHM-10-03-090710	9/7/2010	1.47 J	0.51 J	153000	157000	1420	1030	18200	18500	72.8	44	6920	6880	536000	536000	13.4	1.72	6.31	11.93	3341	148.1	78	0.0392 J	< 0.002	0.55	NA	< 0.1	43	0.66	1100	39	< 1	26	
	DUP-090710	9/7/2010	1.51 J	0.71 J	149000	154000	1480	1040	17700	18000	70.2	51.7	6670	6840	510000	526000	NA	NA	NA	NA	NA	NA	75	0.0204 J	< 0.002	0.6	NA	< 0.1	31	0.66	1100	39	NA	NA	
	SHM-10-03-102312	10/23/2012	NA	1.0 U	NA	129000	NA	79 J	NA	15200	NA	NA	NA	6000	NA	359000	21.9	1.45	6.51	13.75	2230	-3.6	57.2	0.10 U	<0.010	0.47	NA	2.0 U	NA	NA	900	38.2	NA	NA	
	SHM-10-03-052413	5/24/2013	NA	1.5	NA	145000	NA	50.6 J	NA	17200	NA	37	NA	6270	NA	432000	3.68	0.61	6.54	11.49	1981	61.5	71.8	0.081 U	0.004 J	0.47	NA	1.4 U	NA	NA	870	35.4	0.72 J	NA	
	DUP-01-052413	5/24/2013	NA	1.5	NA	136000	NA	131	NA	16100	NA	194	NA	6190	NA	405000	NA	NA	NA	NA	NA	NA	66.3	0.081 U	0.004 U	0.47	NA	1.4 U	NA	NA	870	39.7	0.64 U	NA	
SHM-10-04	SHM-10-04-071410	7/14/2010	1.62	0.64	60300 J	57800	3800 J	5190	12300 J	11800	2190	2500	4230	5220	33400 J	35400	17.7	0.23	6.37	10.82	630	9.9	99	0.0666 J	0.11	3.8	NA	< 0.1	13 J	2.7	74	84	NA	NA	
	SHM-10-04-090710	9/7/2010	1.0 J	0.79 J	72100	72800	1880	1650	14500	14600	3210	3100	4050	3990	35800	35200	4.28	0.23	5.99	12.1	656	43.7	100	0.0585 J	0.5	3.7	NA	< 0.1	< 7	2.6	92	87	2.7	43	
	SHM-10-04-102212	10/22/2012	NA	1.0 U	NA	57100	NA	100 U	NA	12600	NA	NA	NA	3200 J	NA	37500	4.15	0.27	5.89	11.64	460	65	81.4	0.10 U	0.023	6.6	NA	2.0 U	NA	NA	82.5	70.9	NA	NA	
	SHM-10-04-052913	5/29/2013	NA	1.0	NA	61500	NA	<100	NA	13700	NA	622	NA	<5000	NA	39300	1.67	0.16	6.01	10.18	382	180.1	99.5	0.13	0.012	6.5	NA	1.4 U	NA	NA	83.0	81.7	1.9	NA	
	DUP-052913	5/29/2013	NA	0.95 J	NA	61200	NA	<100	NA	14000	NA	660	NA	<5000	NA	39000	NA	NA	NA	NA	NA	NA	93.9	0.13	0.013	6.9	NA	1.4 U	NA	NA	82.0	82.3	1.7	NA	
SHM-10-05A	SHM-10-05A-071510	7/15/2010	4.7	4.6	14200	14500	1970	1880	1660	1670	590	620	1990	1990	22800	23900	5.12	1.42	6.29	19.06	186	31.7	43	0.0184 J	0.01 J	0.38	NA	< 0.1	< 7	0.93	34	10	NA	NA	
	SHM-10-05A-090810	9/8/2010	5.68	5.21	14100	14200	790	677	1600	1600	105	122	1770	1830	19600	19700	8.92	3.2	5.27	20.2	200	-29	36	0.0335 J	< 0.002	0.46	NA	< 0.1	55	0.96	29	11	< 1	20	
	SHM-10-05A-102312	10/23/2012	NA	3.0	NA	15300	NA	68 J	NA	1800 J	NA	NA	NA	1700 J	NA	16100	4.3	4.84	6.04	14.43	208	164.8	42.1	0.10 U	<0.010	1.2	NA	2.0 U	NA	NA	30.5	8	NA	NA	
	SHM-10-05 (EPA)	10/24/2012	<20	NA	16000	NA	5700	NA	2100	NA	21	NA	1400	NA	20000	NA	NA	NA	NA	NA	NA	NA	48	NA	NA	NA	NA	NA	NA	NA	4.0	3.3	NA	NA	
	SHM-10-05A-052213	5/22/2013	NA	3.1	NA	13800	NA	30 U	NA	1720 J	NA	16.1	NA	1610 J	NA	18900	2.47	1.31	6.26	13.51	145	158.1	38.7	0.081 U	0.004 U	0.62	NA	1.4 U	NA	NA	30.7	7.2	0.79 J	NA	
	DUP-052213	5/22/2013	NA	3.1	NA	14100	NA	30 U	NA	1720 J	NA	15.4	NA	1580 J	NA	19400	NA	NA	NA	NA	NA	NA	38.7	0.081 U	0.004 U	0.64	NA	1.4 U	NA	NA	30.7	7.3	0.69 J	NA	

TABLE 3
GROUNDWATER MONITORING WELL RESULTS
Shepley's Hill Landfill, Devens Massachusetts

Well ID	Sample ID	Date	Arsenic		Calcium		Iron		Magnesium		Manganese		Potassium		Sodium		Turbidity	DO	pH	Temp	Spec Cond	ORP	Alkalinity	Ammonia	Nitrite	Nitrate	Nitrogen (Nitrite +Nitrate)	Sulfide	COD	TOC	Chloride	Sulfate	DOC	DIC	Notes
			Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	NTU	mg/L		Celcius	uS/cm	mV	mg CaCO3/L	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	
SHM-10-06	SHM-10-06-070810	7/8/2010	2210 J	1680 J	40900	41000 J	130000 J	117000	7360	7140	724	699	11700	11800	18200	17900	21.4	0.55	6.62	21.74	754	-93.8	360	5.5	< 0.002	0.03	NA	< 0.1	29	4.8	17	0.89	NA	NA	
	DUP-070810	7/8/2010	2520	1520	46500	41100	149000	117000	8400	7200	829	712	13100	12300	20700	19000	NA	NA	NA	NA	NA	NA	370	5.58	< 0.002	0.033	NA	< 0.1	25	4.7	17	0.84	NA	NA	
	SHM-10-06-090810	9/8/2010	2580	2710	48200	50300	144000	145000	8270	8800	9.54	9.63	13500	13800	22800	23700	3.72	2.83	6.16	11.59	783	-64.3	300	5.13	< 0.002	0.13	NA	< 0.1	33	4.2	15	0.49 J	5	93	
	SHM-10-06-102312	10/23/2012	NA	2300	NA	36100	NA	111000	NA	6300	NA	NA	NA	11300	NA	17200	3.38	1.18	6.57	15.78	587	-122.1	184	6.1	<0.010	0.13	NA	2.0 U	NA	NA	16.5	5.0 U	NA	NA	
	SHM-10-06 (EPA)	10/23/2012	1900	NA	37000	NA	110000	NA	6600	NA	1900	NA	11000	NA	22000	NA	NA	NA	NA	NA	NA	NA	117	NA	NA	NA	NA	NA	NA	NA	14	0.99	NA	NA	
	SHM-10-06-052313	5/23/2013	NA	1980	NA	36100	NA	107000	NA	6500	NA	1890	NA	11500	NA	17000	4.66	0.86	6.60	13.22	473	-120.7	227	8.5	0.004 U	0.29	NA	1.4 U	NA	NA	16.2	4.5 U	3.7	NA	
	SHM-10-06-100814	10/8/2014	NA	1900	NA	37900	NA	92000	NA	7270	NA	2080	NA	9960	NA	16500	3.49	0.41	6.73	11.45	515	-119.3	238	0.065 U	NA	NA	0.079 J	1.3 U	NA	NA	18	4.8 J	2.9	NA	
SHM-10-06A	SHM-10-06A-070710	7/7/2010	64.8	61	15700	15300 J	20900 J	19900 J	2090	2030	1650 J	1620	4700	4520	7490	7260	5.38	1.49	6.51	19.74	209	-22.6	100	2.69	< 0.002	0.03 J	NA	< 0.1	16 J	3.4	3.4	2.5 B	NA	NA	
	DUP-070710	7/7/2010	65.1	60.1	15800	15500	21200	20200	2080	2070	1660	1650	4740	4680	7640	7560	NA	NA	NA	NA	NA	NA	97	2.59	< 0.002	0.032 J	NA	< 0.1	20	3.3	3.4	2.9 B	NA	NA	
	SHM-1--06A-090910	9/9/2010	102	94.2	33000	33300	44600	42900	4940	4640	3940	4080	8130	7640	13200	13200	40.6	0.39	5.94	10.65	431	-157.3	190	3.9	< 0.002	< 0.01	NA	< 0.1	17 J	4	11	3.2	3.3	58	
	DUP-090910	9/9/2010	102	83	31800	25300	42700	32300	4810	3280	3820	3130	7970	5990	12900	9240	NA	NA	NA	NA	NA	NA	150	5.05	< 0.002	< 0.01	NA	< 0.1	19 J	4.4	11	3.2	NA	NA	
	SHM-10-06A-102412	10/24/2012	NA	72	NA	13200	NA	19900	NA	2600 J	NA	NA	NA	3600 J	NA	5800	13.91	0.63	5.9	10.98	190	-203	67	0.10 U	<0.010	0.24	NA	2.0 U	NA	NA	4.5	5.9 U	NA	NA	
	SHM-10-06A (EPA)	10/24/2012	80	NA	14000	NA	20000	NA	2700	NA	2100	NA	3100	NA	9400	NA	NA	NA	NA	NA	NA	NA	46	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-10-06A-052213	5/22/2013	NA	72.8	NA	9380	NA	11400	NA	1700 J	NA	1430	NA	3060 J	NA	3860 J	3.67	0.55	6.57	12.60	90	-12.3	48.6	1.5	0.004 U	0.52	NA	1.4 U	NA	NA	1.8	4.5 U	1.9	NA	
	SHM-10-06A-112013	11/20/2013	NA	22.9	NA	8330	NA	3410	NA	933 J	NA	1960	NA	3430 J	NA	2940 J	0.44	0.22	6.49	9.34	107	-61.6	53.9	1.1	0.0051 U	0.14	NA	1.5 U	NA	NA	1.5	2.1 J	1.8	NA	
	SHM-10-06A-100714	10/7/2014	NA	95.6	NA	18900	NA	27800	NA	3030 J	NA	3480	NA	3800 J	NA	5850	4.63	0.41	6.19	11.77	199	-25.1	119	1.1	NA	NA	0.38	1.3 U	NA	NA	10.0	2.7 J	5.4	NA	
SHM-10-07	SHM-10-07-052710	5/27/2010	816 J	818 J	62200 J	60600 J	75800 J	70600 J	12200	9590	3230 J	3110 J	17900	16000	36400	35100 J	237	0.15	6.97	13.43	751	-195	300	6.02	< 0.002	0.008 J	NA	< 0.1	45	3.6	48	8.6	NA	NA	
	DUP-052710	5/27/2010	827	825	62600	61100	75800	71800	12100	9660	3280	3130	18100	16100	36900	35700	NA	NA	NA	NA	NA	NA	280	5.78	< 0.002	0.013 J	NA	< 0.1	58	3.5	48	9.3	NA	NA	
	SHM-10-07-090910	9/9/2010	979	918	47400	43200	62300	56800	6360	5610	2050	1940	13200	11400	26400	24400	15.4	0.43	6.54	12.39	635	-105.6	240	5.6	< 0.002	< 0.01	NA	< 0.1	29	3.8	41	2.3	3.5	52	
	SHM-10-07-102212	10/22/2012	NA	1100	NA	43700	NA	69000	NA	5300	NA	NA	NA	11400	NA	23900	21.3	0.13	6.45	12.10	516	-86	191	6.2	<0.010	0.16	NA	2.0 U	NA	NA	46.5	5.0 U	NA	NA	
	SHM-10-07 (EPA)	10/22/2012	990	NA	48000	NA	66000	NA	5700	NA	2200	NA	11000	NA	29000	NA	NA	NA	NA	NA	NA	NA	143	NA	NA	NA	NA	NA	NA	NA	58	0.14	NA	NA	
	SHM-10-07-052313	5/23/2013	NA	1210	NA	56000	NA	94900	NA	6700	NA	2670	NA	13300	NA	28500	4.60	1.23	6.5	12.03	561	-109.6	243	7.6	0.004 U	0.26	NA	1.4 U	NA	NA	61.7	5.6	3.5	NA	
	SHM-10-07-100714	10/7/2014	NA	861	NA	39700	NA	53330	NA	4820 J	NA	2150	NA	10100	NA	26300	44.00	0.27	6.8	12.23	634	-92.8	162	6.1	NA	NA	0.082 J	1.3 U	NA	NA	55	1.9 J	2.8	NA	
SHM-10-08	SHM-10-08-071510	7/15/2010	2.72	0.73 J	160000	152000	2610	1310 J	21100	19900 J	910	885 J	5370	4590	44300 J	44500	7.15	0.21	6.73	10.95	917	33.7	480	< 0.017	< 0.002	< 0.01	NA	< 0.1	< 7	4	71	15	NA	NA	
	SHM-10-08-090710	9/7/2010	1.4	1.55	182000	195000	1270	1260	23600	25000	359	376	5240	5470	46400	NA	1.37	3.61	6.19	12.1	1079	-233	500	0.084	< 0.002	< 0.01	NA	< 0.1	17 J	4.1	79	15	3.8	110	
	SHM-10-08-102212	10/22/2012	NA	1.9	NA	137000	NA	37 J	NA	16800	NA	NA	NA	4500 J	NA	35900	0.0	0.40	6.63	11.59	713	45.1	459	0.10 U	<0.010	0.10 U	NA	2.0 U	NA	NA	53.5	7.8 U	NA	NA	
	SHM-10-08-052113	5/21/2013	NA	1.9	NA	152000	NA	42.8 J	NA	19500	NA	242	NA	4800 J	NA	40200	1.7	0.49	6.73	11.86	721	7.8	499	0.18	0.004 U	0.079 U	NA	1.4 U	NA	NA	55.7	10.4	3.2	NA	
SHM-10-10	SHM-10-10-071310	7/13/2010	2.0 J	1.25 J	95100	92800	1020	799	12100	11900	24600	24200	3580	3600	26500	26100	4.52	0.85	6.61	12.10	658	28.7	350	0.155	< 0.002	< 0.01	NA	< 0.1	29	3.6	19	0.56 J	NA	NA	
	DUP-071310	7/13/2010	1.34 J	1.13 J	92400	94600	925	804	11800	12100	24100	24800	3490	3610	26500	27500	NA	NA	NA	NA	NA	NA	350	0.145	< 0.002	< 0.01	NA	< 0.1	40	3.6	18	0.38 J	NA	NA	
	SHM-10-10	8/12/2010	NA	3.62 J	NA	83800	NA	1180	NA	10700	NA	22000	NA	3590	NA	28500	NA	0.76	6.57	11.27	622	-9.1	320	0.201	<0.002	<0.01	NA	<0.10	25	NA	23	0.79 J	3.9	70	
	SHM-10-10-090810	9/8/2010	2.57 J	2.4 J	107000	96800	833	700	13200	12000	27400	25200	3750	3410	29600	27100	0.71	0.16	6.55	13.13	617	63.3	320	0.148	< 0.002	< 0.01	NA	< 0.1	55	3.7	17	0.34 J	3.8	76	
	DUP-090810	9/8/2010	2.58 J	6.66	96300	101000	825	929	11900	12600	27400	25800	3380	3560	26600	28500	NA	NA	NA	NA	NA	NA	330	0.168	< 0.02	0.019 J	NA	< 0.1	45	3.9	17	0.26 J	NA	NA	
	SHM-10-10-102412	10/24/2012	NA	1.0	NA	74500	NA	180	NA	8100	NA	NA	NA	2700 J	NA	21300	3.25	0.28	6.55	12.06	464	37.6	295	0.10 U	<0.010	0.10 U	NA	2.0 U	NA	NA	21	5.0 U	NA	NA	
	Duplicate	10/24/2012	NA	1.1	NA	75200	NA	179	NA	8260	NA	NA	NA	2830 J	NA	21400 Q	NA	NA	NA	NA	NA	NA	305	<0.10	<0.010	<0.11	NA	<2.0	NA	NA	21	<5.0	NA	NA	
	SHM-10-10-052913	5/29/2013	NA	1.7	NA	83000	NA	82.5 J	NA	9460	NA	26400	NA	3040 J	NA	32100	0.46	3.07	6.62	11.22	579	48.8	343	0.25	0.004 U	0.079 U	NA	1.4 U	NA	NA	18.5	4.5 U	2.9	NA	
	SHM-10-10-112013	11/20/2013	NA	2.0 J	NA	77900	NA	48.7 J	NA	8500	NA	23300	NA	3050 J	NA	22900	0.39	0.36	6.53	11.98	557	75.2	256	0.55	0.0051 U	0.060 J	NA	1.5 U	NA	NA	61	2.9 J	15.8	NA	
	SHM-10-10-101014	10/10/2014	NA	2.6 J	NA	85800	NA	50 U	NA	10800	NA	25800	NA	4100 J	NA	31000	0.98	0.26	6.57	12.08	484	78.8	327	0.066 J	NA	NA	0.050 U	1.3 U	NA	NA	44	4.0 J	3.5	NA	
SHM-10-11	SHM-10-11	8/30/2010	356	342 J	23900	21200 J	60600	55700	2770	2530	2490	2320	5410	5150	12400	11800	4.05	1.68	6.12	13.19	419	-32	160	2.79	<0.002	0.019 J	NA	<0.10	22	NA	24	19	3.3	62	
	SHM-10-11-101910	10/19/2010	470	463	21900	22200	60500	61000	2840	2900	2160	2260	5310	5390	12700	13000	4.28	0.41	6.28	11.57	4.14	-42.1	140	3.13	0.01 J	< 0.01	NA	< 0.10	19	NA	23	19 J	3.4	71	
	SHM-10-11-102312	10/23/2012	NA	440	NA	20900	NA	56100	NA	2700 J	NA	NA	NA	4700 J	NA	12600	1.1	1.78	6.27	11.18	304	-34	76.7	3.4	<0.010	0.19	NA	2.0 U	NA	NA	26	29.3	NA	NA	
	SHM-10-11(EPA)	10/23/2012	460	NA	22000	NA	56000	NA	3000	NA	2200	NA	4400	NA	17000	NA	NA	NA	NA	NA	NA	NA	67	NA	NA	NA	NA	NA	NA	NA	25	28	NA	NA	
	SHM-10-11-052313	5/23/2013	NA	460	NA	22500	NA	65100	NA	3160 J	NA	2510	NA	4820 J	NA	14300	2.01	0.80	6.15	11.25	287	-46.1	102	3.9	0.004 U	0.31	NA	1.4 U	NA	NA	21.2	30.3	2.9	NA	
	DUP-052313	5/23/2013	NA	464	NA	22500	NA	64400	NA	2990 J	NA	2480	NA	4730 J	NA	13700	NA	NA	NA	NA	NA	NA	126	3.8	0.004 U	0.24	NA	1.4 U	NA	NA	21.2	31.6	2.8	NA	
	SHM-10-11-111913	11/19/2013	NA	432	NA	23400	NA	60400	NA	2630 J	NA	2400	NA	4880 J	NA	13900	0.45	0.33	6.41	10.63	421	-43.5	121	3.9	0.0051 U	0.088 J	NA	1.5 U	NA	NA	30	34.7	2.7	NA	
	DUPLICATE-111913	11/19/2013	NA	444	NA	24100	NA	60500	NA	2690 J	NA	2450	NA	4990 J	NA	14200	NA	NA	NA	NA	NA	NA	130	3.9	0.0051 U	0.11	NA	1.5 U	NA	NA	29.5	35	2.7	NA	
SHM-10-12	SHM-10-12	8/30/2010	2880	3560	25000	33000	78600	104000	1940	2500	5400	7000	5480	7040	7090	8780	8.43	3.55	6.04	14.41	460	-34.9	240	3.7	<0.002	0.035 J	NA	<0.10	31	NA	3.7	1.7	4.1	110	
	DUP-083010	8/30/2010	3210	3410	27900	30600	89700	96000	2190	2360	6120	6520	6190	6480	7880	8610	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-10-12-102010	10/20/2010	2980	3120	29000	29000	88700	90000	2180	2200	6070	6200	482-	4900	5220	5060	1.6	0.32	5.93	10.92	432	-14.5	240	3.8	< 0.02	< 0.01	NA	< 0.10	33	NA	4.4	1.4	4.3	130	
	DUP-102010	10/20/2010	3160	3000	29200	28300	90900	87400	2240	2120	6320	6030	4940	4670	5210	4870	NA	NA	NA	NA	NA	NA	230	3.61	< 0.002	< 0.01	NA	< 0.10	41	NA	4.4	1.3	4.5	140	
	SHM-10-12-102312	10/23/2012	NA	4100	NA	21900	NA	78600	NA	1800 J	NA	NA	NA	4300 J	NA	3500 J	0.2	0.29	5.74	11.49	322	8.4	131	4.3	<0.010	0.14	NA	2.0 U	NA	NA	2.5	<5.0	NA	NA	
	SHM-10-12 (EPA)	10/23/2012	3100	NA	23000	NA	76000	NA	1900	NA	5700	NA	4100	NA	7200	NA	NA	NA	NA	NA	NA	NA	65	NA	NA	NA	NA	NA	NA	NA	3.5	1.8	NA	NA	
	SHM-10-12 D (EPA)	10/23/2012	3100	NA	23000	NA	77000	NA	1900	NA	5800	NA	4100	NA	7300	NA	NA	NA	NA	NA	NA	NA	65	NA	NA	NA	NA	NA	NA	NA	3.5	1.8	NA	NA	
	SHM-10-12-052313	5/23/2013	NA	3580	NA	29700	NA	56300	NA	2720 J	NA	6450	NA	3630 J	NA	5440	4.36	0.26	6.09	11.84	302	-44.9	171	3.2	0.004 U	0.41	NA	1.4 U	NA	NA	7.3	7.9	23.9	NA	
	SHM-10-12-111913	11/19/2013	NA	3570	NA	25300	NA	89600	NA	2090 J	NA	6270	NA	4390 J	NA	4090 J	0.16	0.72	6.35	10.49	428	-19.3	210	3.5	0.0051 U	0.41	NA	1.5 U	NA	NA	4	3.8 J	3.5	NA	
	SHM-10-12-100714	10/7/2014	NA	3510	NA	24500	NA	84100	NA	2500 U	NA	6970	NA	4140 J	NA	3830 J	0.43	0.31	6.02	13.99	368	-29.1	191	3.9	NA	NA	0.078 J	1.3 U	NA	NA	3.5	4.0 J	3.9	NA	
SHM-10-13	GP-10-13-090110	9/1/2010	619 J	575	68000	61400	88600	84100	10500	9900	1900	1850 J	12500	12200	15300	14500	18.8	2.76	6.32	13.57	782	-68.6	380	9.7	< 0.002	0.01 J	NA	< 0.1	33	NA	18	< 0.12	5.6	140	
	SHM-10-13-101910	10/19/2010	700	672	67200	65000	95500	94600	9840	10100	2100	2060	12300	12500	15600	15900	12	0.12	6.27	12.48	743	-52.5	360	9.36	0.01 J	< 0.01	NA	< 0.10	36	NA	21	< 0.12	8.7	140	
	DUP-101910	10/19/2010	648	674	60300	64200	87500	94700	8720	9920	1960	2090	11000	12200	13900	16100	NA	NA	NA	NA	NA	NA	360	9.13	< 0.002	< 0.01	NA	< 0.10	36	NA	20	0.25 J	6.8	150	
	SHM-10-13-102312	10/23/2012	NA	670	NA	76300	NA	68800	NA	9500	NA	NA	NA	10500	NA	14900	14.2	0.11	6.42	12.49	597	-44.5	296	9.1	<0.010	0.19	NA	2.0 U	NA	NA	17	5.3 U	NA	NA	
	SHM-10-13 (EPA)	10/23/2012	630	NA	80000	NA	66000	NA	9800	NA	2200	NA	10000	NA	18000	NA	NA	NA	NA	NA	NA	NA	240	NA	NA	NA	NA	NA	NA	NA	18.0	0.11 J	NA	NA	
	SHM-10-13-052313	5/23/2013	NA	565	NA	65500	NA	83400 J	NA	8960	NA	1130	NA	11600	NA	14600	14.4	0.22	6.35	12.59	571	-91.7	292	9.0	0.004 U	0.14	NA	1.4 U	NA	NA	19.7	4.5 U	5.1	NA	
	SHM-10-13-100714	10/7/2014	NA	532	NA	72600	NA	55700	NA	9530	NA	1670	NA	11400	NA	19200	3.05	0.20	6.56	11.83	527	-112.2	266	6.9	NA	NA	0.13	1.3 U	NA	NA	24.5	22	4.7	NA	
SHM-10-14	SHM-10-14-090210	9/2/2010	4280	4100	69300	55300	75200	73000	4310	4150	4700	4720	18800	17600 J	15500	15200	34.7	0.18	6.35	14.48	645	-87.4	360	3.96	< 0.002	< 0.01	NA	< 0.10	43	NA	6.3	3.7	8.7	120	
	SHM-10-14-101910	10./19/10	5990 J	5860	70800	57900	98300	92700	3980	3720	4350 J	4180	11400	101000	8500	8080	34.5	0.36	6.35	11.99	693	-38.6	320	5.28	0.01 J	0.08	NA	< 0.10	62	NA	4.8	0.67 J	62	140	
	SHM-10-14-102312	10/23/2012	NA	6200 J	NA	43100	NA	94400	NA	3300 J	NA	NA	NA	6700	NA	5100	4.88	0.13	6.26	12.4	445	-41	194	3.0	<0.010	0.15	NA	2.0 U	NA	NA	5.0	5.0 U	NA	NA	
	SHM-10-14 (EPA)	10/23/2012	5900	NA	44000	NA	87000	NA	3300	NA	3900	NA	6200	NA	9000	NA	NA	NA	NA	NA	NA	NA	124	NA	NA	NA	NA	NA	NA	NA	4.5	1.1	NA	NA	
	SHM-10-14-052313	5/23/2013	NA	5540	NA	44300	NA	83100	NA	3420 J	NA	2800	NA	7020	NA	5610	10.08	0.20	6.24	11.43	467	-67.0	241	7.4	0.004 U	0.19	NA	1.4 U	NA	NA	5.8	6.4	21.3	NA	
	SHM-10-14-100814	10/8/2014	NA	5380	NA	47300	NA	92100	NA	3620 J	NA	2810	NA	7130	NA	5590	4.56	0.19	6.30	13.73	482	-76.1	283	0.065 U	NA	NA	0.074 J	1.3 U	NA	NA	5.5	1.8 J	23.2	NA	
SHM-10-15	GP-10-15-090110	9/1/2010	7930	8110	61300	61500	62500	63300	7700	7880	10400	10700	6910	6880	13700	13900	16.3	0.25	6.21	16.02	503	-52.7	210	2.67	0.01	<0.01	NA	<0.10	33	NA	5.7	3.8	4.2	82	
	SHM-10-15-090110	9/1/2010	7930	8110	61300	61500	62500	63300	7700	7880	10400	10700	6910	6880	13700	13900	16.3	0.25	6.21	16.02	503	-52.7	240	2.26	< 0.002	< 0.01	NA	< 0.10	22	NA	11.0	8.4	3.2	NA	
	DUP-090110	9/1/2010	7610	6460	58500	46800	58700	48900	7470	6050	9900	8240	6390	5200	13100	11200	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-10-15-102010	10/20/2010	6090	6230	51200	51800	50400	52000	6440	6530	8440	8680	5350	5500	11600	12400	59.5	0.36	5.94	11.95	510	-10.9	230	2.15	0.01 J	< 0.01	NA	< 0.10	64	NA	12.0	10	4	95	
	SHM-10-15-102312	10/23/2012	NA	7000	NA	46800	NA	46600	NA	5800	NA	NA	NA	5100	NA	10400	5.1	0.2	6.43	11.98	376	-49	172	2.2	<0.010	0.12	NA	2.0 U	NA	NA	10.0	9.5 U	NA	NA	
	Duplicate-102312	10/23/2012	NA	7810	NA	45400 b	NA	44900	NA	5690	NA	NA	NA	4920 J	NA	10300 Q	NA	NA	NA	NA	NA	NA	213	2.5	<0.010	0.19	NA	<2.0	NA	NA	11.0	9.7	NA	NA	
	SHM-10-15 (EPA)	10/23/2012	5800	NA	49000	NA	45000	NA	6100	NA	8000	NA	4700	NA	14	NA	NA	NA	NA	NA	NA	NA	147	NA	NA	NA	NA	NA	NA	NA	9.5	10	NA	NA	
	SHM-10-15-052413	5/24/2013	NA	1090	NA	77200	NA	8290	NA	<5000	NA	1960	NA	6450	NA	6720	11.97	0.49	6.37	15.1	440	-73.9	196	1.4	0.004 U	0.079 U	NA	1.4 U	NA	NA	7.5	7.4	3.4	NA	
	SHM-10-15-112013	11/20/2013	NA	5740	NA	48800	NA	47400	NA	6030	NA	8210	NA	5070	NA	10700	10.31	0.38	6.51	10.41	48	-65.9	210	2.8	0.0051 U	0.28	NA	1.5 U	NA	NA	9.5	10.9	2.8	NA	
	SHM-10-15-100714	10/7/2014	NA	5870 J	NA	50100	NA	46500 J	NA	6190	NA	8530 J	NA	4860 J	NA	10600	29.7	0.08	6.45	12.26	351	-90.8	207	2.0	NA	NA	0.078 J	1.3 U	NA	NA	9.0	11.6	2.6	NA	
SHM-10-16	SHM-10-16-090210	9/2/2010	487	495	69700	73900	50200	53100	13800	14100	1710	1790	14600	15500	30800	31400	78.5	0.17	6.98	11.4	784	-233.8	330	3.31	< 0.002	< 0.01	NA	< 0.1	36	NA	31	2.9	5.3	91	
	DUP-090210	9/2/2010	542	489	76800	70700	55100	51100	15000	13500	1860	1680	15800	14700	33400	0.05	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	SHM-10-16-102010	10/20/2010	1180	1090	73200	68100	51800	46900	13100	12000	1250	1150	12500	11800	31500	30700	34.6	0.34	6.77	10.63	793	-129.2	320	3.34	< 0.002	< 0.01	NA	< 0.10	57	NA	28	3.2	10	100	
	SHM-10-16-102312	10/23/2012	NA	1600	NA	71200	NA	41700	NA	11100	NA	NA	NA	9800	NA	25300	0.65	0.26	6.64	10.15	533	-86.2	281	4.3	<0.010	0.14	NA	2.0 U	NA	NA	24.5	6.8 U	NA	NA	
	SHM-10-16 (EPA)	10/24/2012	1500	NA	74000	NA	<40	NA	12000	NA	<20	NA	9500	NA	31000	NA	NA	NA	NA	NA	NA	NA	247	NA	NA	NA	NA	NA	NA	NA	24	3	NA	NA	
	SHM-10-16-052813	5/28/2013	NA	1350	NA	72900	NA	42700	NA	11600	NA	1280	NA	10600	NA	26500	0.08	0.15	6.71	9.39	632	-128.0	309	5.4	0.004 U	0.18	NA	1.4 U	NA	NA	21	4.7 J	3.8	NA	
	SHM-10-16-112013	11/20/2013	NA	1530	NA	78800	NA	44500	NA	11800	NA	1480	NA	10300	NA	29400	0.84	0.19	6.75	9.39	677	-115.6	312	3.2	0.0051 U	0.25	NA	1.5 U	NA	NA	24	2.9 J	3.7	NA	
SHM-11-02	SHM-11-02-102212	10/22/2012	NA	7.1	NA	82700	NA	2000	NA	5900	NA	NA	NA	4700 J	NA	18000	19.6	0.21	7.32	14.43	468	-135	228	0.10 U	<0.010	0.15	NA	2.0 U	NA	NA	42	15.9	NA	NA	
	SHM-11-02-112013	11/20/2013	NA	3.2 J	NA	32900	NA	2470	NA	2960 J	NA	146	NA	7470	NA	21300	21.3	0.3	8.38	10.82	241	-279.2	92.4	0.087 U	0.0051 U	0.34	NA	1.5 U	NA	NA	35	9.9 J	37.9	NA	
	SHM-11-02-042414	4/24/2014	NA	2.0 U	NA	12400	NA	1270	NA	1810 J	NA	268	NA	7630	NA	18800	22.7	0.79	7.23	10.77	196	-118.3	51.5	0.066 U	NA	NA	0.050 U	1.3 U	NA	NA	34.7	5.3 J	42.0	NA	
	SHM-11-02-100714	10/8/2014	NA	2.0 U	NA	34000	NA	5030	NA	6030	NA	224	NA	5630	NA	20400	19	0.06	7.91	15.44	351	-289	109	0.075 J	NA	NA	0.084 J	1.3 U	NA	NA	40.5	1.2 J	20.8	NA	
SHM-11-06	SHM-11-06-102212	10/22/2012	NA	920	NA	51500	NA	84100	NA	7200	NA	NA	NA	12300	NA	15500	4.24	1.8	6.41	13.11	561	-83	287	0.19	<0.010	0.19	NA	2.0 U	NA	NA	20.5	5.0 U	NA	NA	
	SHM-11-06-052813	5/28/2013	NA	1020	NA	45900	NA	73200	NA	7250	NA	990	NA	11100	NA	17000	3.19	0.34	6.54	12.08	495	-105.7	262	8.3	0.004 U	0.40	NA	1.4 U	NA	NA	20.0	6.8	3.1	NA	
	SHM-11-06-112013	11/20/2013	NA	1000	NA	45500	NA	74600	NA	6460	NA	938	NA	10800	NA	18200	2.23	0.36	6.45	9.29	578	-104.4	220	2.2	0.0051 U	0.22	NA	1.5 U	NA	NA	23.0	6.8 J	3.2	NA	
	SHM-11-06-100814	10/8/2014	NA	825	NA	39900	NA	63600	NA	6220	NA	818	NA	8250	NA	18500	2.18	0.2	6.53	12.69	633	-88.3	173	0.065 U	NA	NA	0.11	1.3 U	NA	NA	35.5	5.2 J	2.7	NA	

TABLE 3
GROUNDWATER MONITORING WELL RESULTS
Shepley's Hill Landfill, Devens Massachusetts

Well ID	Sample ID	Date	Arsenic		Calcium		Iron		Magnesium		Manganese		Potassium		Sodium		Turbidity	DO	pH	Temp	Spec Cond	ORP	Alkalinity	Ammonia	Nitrite	Nitrate	Nitrogen	Sulfide	COD	TOC	Chloride	Sulfate	DOC	DIC	Notes
			Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	Total (ug/L)	Dissolved (ug/L)	NTU	mg/L		Celcius	uS/cm	mV	mg CaCO3/L	mg/l	mg/l	mg/l	(Nitrite +Nitrate) mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	
PZ-12-01	PZ-12-01-052813	5/28/2013	NA	441	NA	54500	NA	27100	NA	7200	NA	3930	NA	<5000	NA	27400	4.19	0.23	6.50	12.41	421	-86.3	201	1.4	0.004 U	0.32	NA	1.4 U	NA	NA	38.0	13.6	2.4	NA	
PZ-12-02	PZ-12-02-052113	5/21/2013	NA	627	NA	50900	NA	58600	NA	5760	NA	1330	NA	11100	NA	20500	4.58	0.15	6.37	12.33	665	-87.0	213	12.1	0.004 U	0.46	NA	1.4 U	NA	NA	42.2	4.5 U	2.8	NA	
PZ-12-03	PZ-12-03-052413	5/24/2013	NA	659	NA	59500	NA	40100	NA	8110	NA	2950	NA	8340	NA	45500	1.94	0.23	6.6	12.21	563	-105.4	227	2.9	0.004 U	0.51	NA	1.4 U	NA	NA	52.7	20.8	3.3	NA	
PZ-12-04	PZ-12-04-052413	5/24/2013	NA	610	NA	40900	NA	56300	NA	5160	NA	1310	NA	10500	NA	24900	4.29	0.29	6.53	13.29	447	-86.9	171	6.4	0.004 U	0.38	NA	1.4 U	NA	NA	50.7	5.0	3.5	NA	
PZ-12-05	PZ-13-05-052213	5/22/2013	NA	741	NA	47000	NA	67700	NA	5140	NA	1710	NA	9110	NA	16500	0.87	0.31	6.46	12.24	571	-99.6	188	0.081 U	0.004 U	0.34	NA	1.4 U	NA	NA	31.2	4.5 U	2.4	NA	
PZ-12-06	PZ-12-06-052413	5/24/2013	NA	244	NA	67300	NA	54600	NA	8140	NA	1350	NA	17100	NA	21800	2.9	1.57	6.23	13.02	700	-71.6	293	14.9	0.004 U	0.32	NA	1.4 U	NA	NA	51.0	10.4	29.5	NA	
PZ-12-07	PZ-12-07-052413	5/24/2013	NA	484	NA	24600	NA	29000	NA	2980 J	NA	1620	NA	3300 J	NA	9640	18	0.29	6.41	11.54	276	-390	105	1.1	0.004 U	0.5	NA	1.4 U	NA	NA	6.3	12.7	2.2	NA	
PZ-12-08	PZ-12-08-052413	5/24/2013	NA	1.9	NA	14000	NA	174	NA	2570 J	NA	361	NA	2810 J	NA	6580	9.2	2.68	5.90	10.63	125	131.7	46.4	0.087 J	0.004 U	0.95	NA	1.4 U	NA	NA	5.8	7.4	6.9	NA	
PZ-12-09	PZ-12-09-052113	5/21/2013	NA	1.1	NA	20000	NA	30 U	NA	2550 J	NA	176	NA	2460	NA	11200	3.46	3.83	6.34	13.24	187	112.6	55.3	0.081 U	0.004 U	0.34	NA	1.4 U	NA	NA	4.3	27.0	1.1	NA	
PZ-12-10	PZ-12-10-052213	5/22/2013	NA	0.69 J	NA	5370	NA	30 U	NA	845 J	NA	2.5 U	NA	1490 J	NA	1060 J	1.1	10.37	5.88	10.19	43	191.3	15.5	0.081 U	0.004 U	0.19	NA	1.4 U	NA	NA	1.8	4.5 U	2.0	NA	
SHM-13-01	SHM-13-01-112113	11/21/2013	NA	2.2 J	NA	3750 J	NA	30 U	NA	415 J	NA	7.4 J	NA	801 J	NA	31100	0.31	6.48	6.46	10.15	163	165.1	25.3	0.087 U	0.0051 U	0.46	NA	1.5 U	NA	NA	32	11.9	0.82 J	NA	
	DUPLICATE-112113	11/21/2013	NA	2.2 J	NA	3810 J	NA	30 U	NA	402 J	NA	7.6 J	NA	818 J	NA	31700	NA	NA	NA	NA	NA	NA	26.4	0.087 U	0.0051 U	0.45	NA	1.5 U	NA	NA	33	11.7	0.75 J	NA	
SHM-13-02	SHM-13-02-052913	5/29/2013	NA	2.5	NA	44200	NA	30 U	NA	3970 J	NA	7960	NA	3690 J	NA	10600	0.22	0.16	7.23	11.5	311	-107.7	160	0.13	0.004 U	0.079 U	NA	1.4 U	NA	NA	9.5	6.5	33.6	NA	
	SHM-13-02-112113	11/21/2013	NA	2.7 J	NA	40600	NA	250	NA	3740 J	NA	9490	NA	2390 J	NA	12300	1.84	0.1	6.99	10.89	24	-17	161	0.14	0.0051 U	0.059 U	NA	1.5 U	NA	NA	8	5.7 J	1.9	NA	
	SHM-13-02-101014	10/10/2014	NA	2.6 J	NA	64700	NA	261	NA	6340	NA	15800	NA	2600 J	NA	17200	0.26	0.22	6.72	12.04	430	-8.6	220	0.065 U	NA	NA	0.050 U	1.3 U	NA	NA	31	5.0 J	1.6	NA	
SHM-13-03	SHM-13-03-052913	5/29/2013	NA	318	NA	97700	NA	13600	NA	15000	NA	6740	NA	9460	NA	35400	1.20	0.14	6..56	11.72	730	-99.2	372	0.71	0.004 U	0.35	NA	1.4 U	NA	NA	39	5.6	4.4	NA	
	SHM-13-03-112013	11/20/2013	NA	137	NA	112000	NA	11200	NA	15300	NA	9640	NA	6970	NA	34700	0.54	0.4	6.5	10.26	563	-41.8	391	0.2	0.0051 U	0.059 U	NA	1.5 U	NA	NA	38	5.0 J	4.3	NA	
	SHM-13-03-042314	4/23/2014	NA	120	NA	71000	NA	6770	NA	9690	NA	7990	NA	5190	NA	27100	0.22	0.16	6.1	9.27	433	-12.5	287	0.066 U	NA	NA	0.050 U	1.3 U	NA	NA	24.2	4.7 J	7.3	NA	
	SHM-13-03-101014	10/10/2014	NA	80.8	NA	98400	NA	7590	NA	13600	NA	12100	NA	5710	NA	33400	0.69	0.13	6.53	12.63	557	-57.7	390	0.81	NA	NA	0.050 U	1.3 U	NA	NA	37.5	4.7 J	3.7	NA	
	Dup-101014	10/10/2014	NA	82.1	NA	98300	NA	7760	NA	13800	NA	11900	NA	5780	NA	33800	0.69	0.13	6.53	12.63	557	-57.7	393	0.81	NA	NA	0.050 U	1.3 U	NA	NA	37.0	4.8 J	3.8	NA	
SHM-13-04	SHM-13-04-052813	5/28/2013	NA	2060	NA	33100	NA	40900	NA	<5000	NA	2130	NA	<5000	NA	80200	3.63	0.71	6.46	11.7	717	-73.6	39.8	1.2	0.020	0.57	NA	1.4 U	NA	NA	200	10	1.8	NA	
	SHM-13-04-042414	4/24/2014	NA	61.1	NA	16000	NA	334	NA	1670 J	NA	238	NA	2800 J	NA	106000	2.18	3.21	6.35	10.57	866	92.4	29.6	0.54	NA	NA	0.60	1.3 U	NA	NA	167	10.0	0.92 J	NA	
	SHM-13-04-101314	10/13/2014	NA	693	NA	11100	NA	6410	NA	2500 U	NA	392	NA	2690 J	NA	68700	2.31	2.04	6.48	11.94	464	-13.2	41.4	0.065 U	NA	NA	0.31	1.3 U	NA	NA	110	12.5	1.6	NA	
SHM-13-05	SHM-13-05-052813	5/28/2013	NA	8.9	NA	111000	NA	597	NA	22800	NA	4680	NA	11000	NA	42400	2.05	0.27	6.88	11.14	629	-136.0	423	0.70	0.004 U	0.079 U	NA	1.4 U	NA	NA	37	12.3	4.7	NA	
	SHM-13-05-112113	11/21/2013	NA	6.8	NA	116000	NA	1860	NA	19800	NA	5720	NA	8910	NA	40000	2.11	0.44	7.94	10.27	44	-154.6	425	0.095 J	0.0051 U	0.059 U	NA	1.5 U	NA	NA	41.5	11.4	4.5	NA	
	SHM-13-05-101314	10/13/2014	NA	11	NA	118000	NA	4580	NA	19800	NA	5940	NA	8050	NA	38600	1.11	0.44	6.88	11.04	686	-159.0	455	0.59	NA	NA	0.050 U	1.3 U	NA	NA	36.0	8.4 J	3.6	NA	
SHM-13-06	SHM-13-06-061313	6/13/2013	NA	3180 J	NA	21400	NA	19700 J	NA	1440 J	NA	1830	NA	3210 J	NA	16300	4.07	0.14	7.16	12.43	287	-154.4	84	2.1	0.004 U	0.22	NA	1.4 U	NA	NA	19	6.4	1.0	NA	
	SHM-13-06-112113	11/21/2013	NA	2540	NA	18600	NA	39900 J	NA	1911 J	NA	2490	NA	3920 J	NA	59400	1.24	0.25	6.84	11.33	587	-119.4	33	2.8	0.0051 U	0.24	NA	1.5 U	NA	NA	145	11.4	1.5	NA	
	SHM-13-06-042414	4/24/2014	NA	2850	NA	12500	NA	25000	NA	1260 J	NA	1820	NA	3030 J	NA	49600	2.51	0.28	6.94	11.71	446	-104.3	61.3	0.066 U	NA	NA	0.25	1.3 U	NA	NA	69.7	8.9 J	1.5	NA	
	SHM-13-06-101314	10/13/2014	NA	2360	NA	14400	NA	25400	NA	2500 U	NA	1570	NA	3410 J	NA	78700	1.23	0.1	7.04	11.99	569	-145.6	45.8	0.065 U	NA	NA	0.050 U	1.3 U	NA	NA	130.0	9.9 J	1.1	NA	
SHM-13-07	SHM-13-07-112113	11/21/2013	NA	1340	NA	20900	NA	30000	NA	2720 J	NA	2710	NA	5310	NA	126000	4.7	0.14	6.8	12.5	773	-97.4	45	2.4	0.0052 J	0.26	NA	1.5 U	NA	NA	225	12.1	1.6	NA	
	SHM-13-07-042414	4/24/2014	NA	1280	NA	34300	NA	39200	NA	4220 J	NA	3660	NA	4580 J	NA	82500	26.8	0.29	6.84	10.97	734	-106.1	30.7	3.0	NA	NA	0.41	1.3 U	NA	NA	212	7.7 J	1.2	NA	
	SHM-13-07-101014	10/10/2014	NA	962	NA	16600	NA	25200	NA	2500 U	NA	2160	NA	4970 J	NA	106000	4.9	0.15	6.9	12.82	787	-126.3	62.1	2.8	NA	NA	0.050 U	1.3 U	NA	NA	165	16	8.8	NA	
SHM-13-08	SHM-13-08-061313	6/13/2013	NA	928	NA	23200	NA	35900	NA	3540 J	NA	941	NA	8360	NA	14200	2.92	0.74	6.84	12.75	378	-122.4	141	6.1	0.004 U	0.32	NA	1.4 U	NA	NA	8.5	7.3	2.8	NA	
	DUPLICATE-061313	6/13/2013	NA	972	NA	23200	NA	36600	NA	3580 J	NA	958	NA	8530	NA	14400	NA	NA	NA	NA	NA	NA	140	6.2	0.004 U	0.40	NA	1.4 U	NA	NA	8.5	7.4	2.8	NA	
	SHM-13-08-112113	11/21/2013	NA	994	NA	23200	NA	35400	NA	4080 J	NA	826	NA	8600	NA	11600	0.98	0.24	6.84	11.32	323	-131.1	116	5.1	0.0051 U	0.15	NA	1.5 U	NA	NA	8	3.7 J	3.2	NA	
	SHM-13-08-042414	4/24/2014	NA	1040	NA	30400	NA	50600	NA	4940 J	NA	1170	NA	9510	NA	15000	1.14	0.38	6.89	11.26	439	-123.8	173	2.9	NA	NA	0.32	1.3 U	NA	NA	14.8	4.9 J	3.8	NA	
	DUP-042414	4/24/2014	NA	1030	NA	31700	NA	51300	NA	4950 J	NA	1180	NA	9490	NA	15200	NA	NA	NA	NA	NA	NA	174	2.9	NA	NA	0.34	1.3 U	NA	NA	14.3	4.8 J	3.5	NA	
	SHM-13-08-101314	10/13/2014	NA	978	NA	26100	NA	52200 J	NA	3780 U	NA	1160	NA	12300	NA	85700	0.39	0.16	6.9	11.81	733	-146.1	140	8.9	NA	NA	0.071 J	1.3 U	NA	NA	130	6.5 J	3.6	NA	
SHM-13-14S	SHM-13-14S	2/19/2014	NA	2.0 U	NA	22200	NA	241	NA	2720 J	NA	55.5	NA	3600 J	NA	63900	1.97	0.59	5.88	6.53	440	96.3	58.0	0.60	NA	NA	1.5	1.3 U	NA	NA	91.0	9.6 J	1.2	NA	
	SHM-13-14S-101014	10/10/2014	NA	2.0 U	NA	21100	NA	94. 1 J	NA	2900 J	NA	86.9	NA	3570 J	NA	62700	0.88	0.45	5.87	12.82	320	139.4	75.2	0.065 U	NA	NA	0.5	1.3 U	NA	NA	100.0	8.1 J	1.9	NA	
SHM-13-14D	SHM-13-14D	2/19/2014	NA	7.9	NA	10100	NA	11800	NA	1170 J	NA	1190	NA	4340 J	NA	55200	26.0	0.09	6.85	9.18	349	-82	81.0	1.8	NA	NA	0.22	1.3 U	NA	NA	48.0	12.3	1.9	NA	
	SHM-13-14D-101014	10/10/2014	NA	9.6	NA	24900	NA	20900	NA	2960 J	NA	2910	NA	7520	NA	178000	1.2	0.19	6.75	12.4	1233	-79.6	43.6	3.3	NA	NA	0.071 J	1.3 U	NA	NA	320.0	7.2 J	1.3	NA	
SHM-13-15	SHM-13-15	2/19/2014	NA	3.8 J	NA	86900	NA	623	NA	12700	NA	4860	NA	5450	NA	29200	42.3	0.44	6.59	9.16	642	-172.7	273	0.68	NA	NA	0.050 U	1.3 U	NA	NA	46.0	7.7 J	2.9	NA	
	DUP	2/19/2014	NA	3.9 J	NA	86900	NA	633	NA	12700	NA	4870	NA	5390	NA	29200	NA	NA	NA	NA	NA	NA	278	0.65	NA	NA	0.050 U	1.3 U	NA	NA	46.5	5.2 J	2.9	NA	
	SHM-13-15-101014	10/10/2014	NA	8.1	NA	80400	NA	1050	NA	11700	NA	4480	NA	5080	NA	30700	0.23	0.15	6.56	13.35	704	20.4	315	0.94	NA	NA	0.050 U	1.3 U	NA	NA	37.5	5.5 J	2.8	NA	
SHP-13-03	SHP-13-03-042314	4/23/2014	NA	7.9	NA	19200	NA	115	NA	2690 J	NA	1400	NA	2520 J	NA	59900	NA	5.6	8.79	13.13	434	-106.0	51.5	0.066 U	NA	NA	0.050 U	1.3 U	NA	NA	113	6.4 J	4.0	NA	
EPA-PZ-2012-1A	EPA-PZ2012-1A-101314	10/13/2014	NA	2.0 U	NA	19700	NA	121	NA	2500 U	NA	937	NA	2500 U	NA	4450	0.36	0.38	5.93	10.09	145	109	40.3	0.065 U	NA	NA	0.050 U	1.3 U	NA	NA	21.5	5.1 J	2.2	NA	
	Duplicate-101314	10/13/2014	NA	2.0 U	NA	19900	NA	119	NA	2500 U	NA	941	NA	2500 U	NA	4380 J	0.36	0.38	5.93	10.09	145	109	40.3	0.065 U	NA	NA	0.050 U	1.3 U	NA	NA	21.5	4.8 J	1.4	NA	
EPA-PZ-2012-1B	EPA-PZ2012-1B-101314	10/13/2014	NA	160	NA	73800	NA	21500	NA	10400	NA	6900	NA	8320	NA	29300	28.2	0.14	6.54	10.92	587	-58.8	304	0.074 J	NA	NA	0.050 U	1.3 U	NA	NA	16.5	3.8 J	2.4	NA	
EPA-PZ-2012-2A	EPA-PZ2012-2A-101414	10/14/2014	NA	2.0 U	NA	4090 J	NA	50 U	NA	2500 U	NA	7.5 U	NA	2500 U	NA	2500 U	0.69	5.63	5.89	10.64	40	223.4	7.6	0.065 U	NA	NA	0.086 J	1.3 U	NA	NA	1.5	7.7 J	1.2	NA	
EPA-PZ-2012-2B	EPA-PZ2012-2B-101414	10/14/2014	NA	2.0 U	NA	29900	NA	51.7 J	NA	4750 J	NA	5910	NA	7060	NA	14300	0.55	0.56	6.37	11.5	298	112.9	152	0.065 U	NA	NA	0.050 U	1.3 U	NA	NA	11.5	3.5 J	2.2	NA	
EPA-PZ-2012-3A	EPA-PZ2012-3A-100814	10/8/2014	NA	21.2	NA	20700	NA	19200	NA	3350 J	NA	730	NA	4760 J	NA	10200	0	0.5	5.86	11.68	299	0.4	108	0.065 U	NA	NA	0.071 J	1.3 U	NA	NA	15.0	1.2 J	8.4	NA	
EPA-PZ-2012-3B	EPA-PZ20123B-100914	10/9/2014	NA	3830	NA	52700	NA	62100	NA	9120	NA	5930	NA	8300	NA	18200	12.1	0.21	6.7	11.18	658	-113.9	265	0.065U	NA	NA	0.11	1.3 U	NA	NA	15.5	48.6	2.5	NA	
EPA-PZ-2012-4A	EPA-PZ2012-4A-100814	10/8/2014	NA	4.8	NA	55400	NA	16500	NA	8300	NA	2740	NA	5050	NA	23700	0.47	0.03	6.03	13.04	690	-26.8	45.8	0.065 U	NA	NA	0.085 J	1.3 U	NA	NA	145.0	10.4	6.3	NA	
EPA-PZ-2012-4B	EPA-PZ-2012-4B-100614	10/6/2014	NA	2680	NA	39700	NA	76800	NA	7020	NA	784	NA	9200	NA	12800	3.33	0.35	6.6	12.92	578	-118.5	208	4.9	NA	NA	0.12	1.3 U	NA	NA	15.5	4.9 J	2.6	NA	
	SHL-Duplicate-100614	10/6/2014	NA	2970	NA	41000	NA	79300	NA	7510	NA	876	NA	9430	NA	13300	3.33	0.35	6.6	12.92	578	-118.5	203	4.9	NA	NA	0.33	1.3 U	NA	NA	15.5	2.2 J	3.6	NA	
EPA-PZ-2012-5A	EPA-PZ2012-5A-101414	10/14/2014	NA	2.0 U	NA	4600 J	NA	6450	NA	2500 U	NA	85.6	NA	2500 U	NA	5360	2.68	0.07	5.57	11.27	93	71.1	24	0.065 U	NA	NA	0.050 U	1.3 U	NA	NA	16.5	7.2 J	6	NA	
EPA-PZ-2012-5B	EPA-PZ2012-5B-101414	10/14/2014	NA	3.2 J	NA	73400	NA	471	NA	10000	NA	11900	NA	7070	NA	30400	0.01	0.16	6.44	11.01	598	34.3	311	0.071 J	NA	NA	0.050 U	1.3 U	NA	NA	6.5	3.6 J	1.9	NA	
EPA-PZ-2012-6A	EPA-PZ2012-6A-100914	10/9/2014	NA	2.0 U	NA	22000	NA	50 U	NA	2500 U	NA	7.5 U	NA	2850 J	NA	31400	0.97	7.4	6.28	9.37	323	177.3	31.6	0.32	NA	NA	0.68	1.3 U	NA	NA	41.0	21.9	0.87 J	NA	
EPA-PZ-2012-6B	EPA-PZ2012-6B-100914	10/9/2014	NA	515	NA	13300	NA	18000	NA	2500 U	NA	1020	NA	2500 U	NA	2500 U	0.73	0.54	6.94	9.84	158	-123.2	49.1	0.14	NA	NA	0.050 U	1.3 U	NA	NA	1.5	3.7 J	9.5	NA	
EPA-PZ-2012-7A	EPA-PZ2012-7A-101414	10/14/2014	NA	2.0 U	NA	17800	NA	50 U	NA	2500 U	NA	121	NA	3800 J	NA	105000	1.04	1.8	6.6	13.19	604	97	60	0.065 U	NA	NA	0.22	1.3 U	NA	NA	150.0	9.3 J		NA	
EPA-PZ-2012-7B	EPA-PZ2012-7B-101414	10/14/2014	NA	1250	NA	15600	NA	34800	NA	2500 U	NA	1460	NA	3030 J	NA	3140 J	3.18	0.2	6.67	12.9	229	-92.9	77.4	0.065 U	NA	NA	0.050 U	1.3 U	NA	NA	0.77 U	4.9 J	2.4	NA	
RB	RB-112013	9/6/2010	NA	2 U	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	RB-112113	11/21/2013	NA	2 U	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	Rinse Blank	2/19/2014	NA	2.0 U	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	RB-042214	4/22/2014	NA	2.0 U	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	RB-042314	4/23/2014	NA	2.0 U	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	RB-042414	4/24/2014	NA	2.0 U	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	RB-100614	10/6/2014	NA	2.0 U	NA	2500 U	NA	50 U	NA	2500 U	NA	7.5 U	NA	2500 U	NA	2500 U	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	RB-100714	10/7/2014	NA	2.0 U	NA	2500 U	NA	50 U	NA	2500 U	NA	7.5 U	NA	2500 U	NA	2500 U	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	RB-100814	10/8/2014	NA	2.0 U	NA	2500 U	NA	50 U	NA	2500 U	NA	7.5 U	NA	2500 U	NA	2500 U	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	RB-100914	10/9/2014	NA	2.0 U	NA	2500 U	NA	50 U	NA	2500 U	NA	7.5 U	NA	2500 U	NA	2500 U	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	RB-101014	10/10/2014	NA	2.0 U	NA	2500 U	NA	50 U	NA	2500 U	NA	7.5 U	NA	2500 U	NA	2500 U	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	RB-101314	10/13/2014	NA	2.0 U	NA	2500 U	NA	50 U	NA	2500 U	NA	7.5 U	NA	2500 U	NA	2500 U	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	
	RB-101414	10/14/2014	NA	2.0 U	NA	2500 U	NA	50 U	NA	2500 U	NA	7.5 U	NA	2500 U	NA	2500 U	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	

Notes:

NA: Not Applicable
ug/L: micrograms per liter
mg/l: miligrams per liter
J: Estimated Results
B: Analyte was detected in the associated me
Q: Absoulte value of concentration is greater
b: Absoulte value of concentration is greater

TABLE 4
SITE-WIDE SURVEY DATA
June 2013 and February 2014
Shepley's Hill Landfill, Devens, Massachusetts

June 2013 Base Survey

Location ID	Latitude	Longitude	Ground Elevation	Roadbox or Standpipe Elevation	Top of Casing or Staff Elevation
DEP-08-05	3,028,333.87	628,608.01	207.96	N/A	208.78
EW-01	3,027,960.18	629,942.49	226.95	226.8	226.77
EW-04	3,027,990.84	629,895.19	227.4	227.05	227.06
N-1 P-1	3,027,867.76	630,723.38	227.78	230.44	230.01
N-1 P-2	3,027,867.76	630,723.38	227.78	230.44	230.03
N-1 P-3	3,027,867.76	630,723.38	227.78	230.44	230.18
N-2 P-1	3,027,311.16	630,658.52	220.53	222.82	222.16
N-2 P-2	3,027,311.16	630,658.52	220.53	222.82	222
N-3 P-1	3,027,130.24	630,777.88	218.73	221.57	220.86
N-3 P-2	3,027,130.24	630,777.88	218.73	221.57	220.86
N-5 P-1	3,027,173.21	629,805.75	240.39	243.65	242.62
N-5 P-2	3,027,173.21	629,805.75	240.39	243.65	242.67
N-6 P-1	3,026,338.61	630,017.06	255.78	258.52	258.46
N-7 P-1	3,025,618.25	629,990.92	253.51	256.53	255.6
N-7 P-2	3,025,618.25	629,990.92	253.51	256.53	256.07
PZ-12-01	3,027,384.39	630,488.32	233.78	237.73	237.55
PZ-12-02	3,027,384.00	630,467.48	233.68	237.93	237.81
PZ-12-03	3,027,193.61	630,474.29	232.76	236.53	236.42
PZ-12-04	3,027,194.22	630,452.75	234.97	238.4	238.22
PZ-12-05	3,027,087.35	630,479.09	236.05	238.91	238.81
PZ-12-06	3,027,082.18	630,454.66	238.35	242.38	242.24
PZ-12-07	3,026,971.76	630,568.41	240.79	244.82	244.63
PZ-12-08	3,026,962.26	630,546.01	241.7	245.29	244.88
PZ-12-09	3,026,801.33	630,740.71	238.26	242.16	241.94
PZ-12-10	3,026,778.24	630,723.91	238.83	242.45	242.29
SHL-09	3,028,146.90	630,009.59	220.88	222.53	221.99
SHL-1	3,026,531.80	629,259.23	270.13	272.28	271.66
SHL-10	3,026,867.43	630,877.10	246.58	248.67	247.95
SHL-11	3,027,316.46	630,495.93	233.97	235.93	235.48
SHL-13	3,028,105.48	630,540.06	218.48	221.2	220.71
SHL-15	3,025,829.38	629,326.44	258.83	260.24	259.93
SHL-18	3,026,475.16	631,186.42	235.71	237.81	237.56
SHL-19	3,026,945.67	630,664.79	238.43	240.79	240.52
SHL-20	3,027,329.51	630,463.22	234.69	236.02	235.96
SHL-21	3,027,884.35	630,363.98	258.11	260.14	259.94
SHL-22	3,028,162.75	630,056.48	219.06	219.38	219.59
SHL-23	3,027,916.82	629,712.69	239.36	241.48	241.26
SHL-24	3,025,638.53	631,302.97	236.7	239.77	239.6
SHL-3	3,026,705.40	630,911.03	246.36	247.66	246.89
SHL-4	3,027,057.36	630,575.73	225.5	227.78	227.51
SHL-5	3,028,125.05	630,192.11	216.81	217.86	217.62
SHL-8 D	3,028,127.50	630,407.22	218.95	221.24	220.79
SHL-8 S	3,028,127.50	630,407.22	218.95	221.24	220.99
SHM-05-39A	3,028,544.28	629,761.38	221.79	221.78	221.54
SHM-05-39B	3,028,543.68	629,765.33	221.78	221.78	221.52
SHM-05-40X	3,028,514.20	629,636.82	223.55	223.53	223.34
SHM-05-41A	3,028,290.82	629,796.11	222.78	222.74	222.45
SHM-05-41B	3,028,299.22	629,796.25	222.6	222.56	222.3
SHM-05-41C	3,028,285.47	629,795.79	222.94	222.9	222.56
SHM-05-42A	3,028,376.14	630,017.63	213.66	216.93	216.84
SHM-05-42B	3,028,376.14	630,017.63	213.66	216.93	216.82
SHM-07-03	3,028,444.64	629,410.99	228.01	228	227.86
SHM-07-05X	3,028,513.39	629,631.98	223.62	N/A	223.41
SHM-10-01	3,028,617.32	628,868.44	206.64	209.74	209.52
SHM-10-02	3,028,700.13	628,381.41	220.12	223.23	223.07
SHM-10-03	3,029,000.27	628,436.33	229.7	232.26	232.06
SHM-10-04	3,029,485.34	628,959.21	209.73	212.81	212.63
SHM-10-05A	3,028,943.39	630,441.84	235.24	235.39	235.07
SHM-10-06	3,027,882.86	630,215.55	229.99	233.08	232.91
SHM-10-06A	3,027,895.73	630,300.71	246	248.74	248.55
SHM-10-07	3,026,889.84	630,301.76	244.76	N/A	N/A
SHM-10-08	3,028,526.47	628,351.74	211.68	214.54	214.41
SHM-10-10	3,028,873.64	629,105.25	215.43	217.25	217.12
SHM-10-11	3,025,971.51	629,990.62	260.86	263.46	263.2
SHM-10-12	3,026,718.54	629,717.49	252.02	254.77	254.6
SHM-10-13	3,027,156.89	629,906.12	241.41	244.87	244.75
SHM-10-14	3,027,372.85	629,784.78	234.81	237.75	237.61
SHM-10-15	3,027,489.15	630,744.35	241.91	243.76	243.76
SHM-10-16	3,028,355.25	629,834.23	216.72	219.45	219.24
SHM-11-02	3,027,075.57	630,457.57	238.63	240.77	N/A
SHM-11-06	3,027,590.18	630,411.28	233.27	236.39	236.2
SHM-11-07	3,027,132.35	630,414.39	238.19	241.01	240.86
SHM-13-01	3,028,294.76	628,556.66	205.79	208.32	208.07
SHM-13-02	3,028,713.88	628,980.64	216.88	219.01	218.7
SHM-13-03	3,028,990.91	629,173.39	209.83	212.17	211.7
SHM-13-04	3,028,606.18	629,479.56	228.25	227.28	227.01
SHM-13-05	3,028,776.73	629,829.47	225.57	225.37	225.11
SHM-13-06	3,028,694.87	629,245.10	224.23	224.23	223.89
SHM-13-07	3,028,760.82	629,331.42	225.69	N/A	N/A
SHM-13-08	3,028,837.54	629,515.32	228.17	228.18	227.9
SHM-13-09	3,028,911.60	629,631.24	227.36	N/A	N/A

TABLE 4
SITE-WIDE SURVEY DATA
June 2013 and February 2014
Shepley's Hill Landfill, Devens, Massachusetts

Location ID	Latitude	Longitude	Ground Elevation	Roadbox or Standpipe Elevation	Top of Casing or Staff Elevation
SHM-13-10	3,028,954.59	629,718.31	227.57	N/A	N/A
SHM-13-11	3,028,459.48	629,058.34	223.1	N/A	N/A
SHM-13-12	3,028,587.71	628,952.96	208.3	N/A	N/A
SHM-13-13	3,028,537.40	629,134.58	224.44	N/A	N/A
SHM-93-10C	3,026,845.85	630,886.07	245.8	248.1	247.61
SHM-93-10D	3,026,828.78	630,894.48	245.36	248.16	247.94
SHM-93-18B	3,026,453.24	631,180.16	235.29	237.66	237.32
SHM-93-22B	3,028,169.62	630,071.79	218.92	220.62	219.42
SHM-93-22C	3,028,158.24	630,045.82	219.02	221.02	220.7
SHM-93-24A	3,025,647.36	631,308.05	236.08	239.53	239.28
SHM-96-5B	3,028,112.90	630,158.12	217.43	219.12	218.95
SHM-96-5C	3,028,105.43	630,172.69	217.41	218.62	218.4
SHM-99-32X	3,028,574.64	630,168.76	219.07	221.46	221.27
SHP-01-36X	3,027,688.84	630,737.88	220.1	224.02	N/A
SHP-01-37X	3,027,498.37	630,696.92	218.64	222.84	N/A
SHP-01-38A	3,027,171.48	630,545.54	218.77	220.9	N/A
SHP-01-38B	3,027,178.16	630,544.01	218.87	221.06	N/A
SHP-05-43	3,027,747.03	630,532.51	258.33	261.3	260.66
SHP-05-44	3,027,588.88	630,586.00	255.49	258.5	258.08
SHP-05-45A	3,027,961.96	629,995.28	226.33	228.68	228.47
SHP-05-45B	3,027,956.95	629,995.37	226.73	229.27	229.1
SHP-05-46A	3,027,946.44	630,041.53	226.1	227.79	227.63
SHP-05-46B	3,027,941.11	630,041.25	226.35	228.37	228.22
SHP-05-47A	3,028,226.53	630,523.15	213.5	N/A	217.53
SHP-05-47B	3,028,226.47	630,523.79	213.47	N/A	215.4
SHP-05-48A	3,028,569.63	630,046.35	213.09	N/A	217.3
SHP-05-48B	3,028,569.69	630,045.57	213.03	N/A	215.93
SHP-05-49A	3,028,663.85	630,250.05	212.26	N/A	216.67
SHP-05-49B	3,028,663.65	630,250.63	212.16	N/A	215.15
SHP-95-27X	3,026,164.53	630,752.70	235.44	237.71	237.46
SHP-99-01B	3,026,537.28	629,226.62	271.13	272.74	272.55
SHP-99-01C	3,026,540.97	629,215.98	271.36	273.84	273.56
SHP-99-29X	3,027,143.23	629,539.01	241.38	243.52	243.32
SHP-99-31A	3,028,559.08	629,895.03	212.76	214.75	214.35
SHP-99-31B	3,028,559.47	629,901.16	212.44	214.38	214.4
SHP-99-31C	3,028,561.83	629,908.75	209.97	214.9	214.72
SHP-99-34A	3,028,552.44	630,294.37	222.5	BROKEN	BROKEN
SHP-99-34B	3,028,552.43	630,291.14	222.55	224.58	N/A
SHP-99-35X	3,026,547.20	629,722.70	256.19	257.91	257.92
SHP-07-03A	3,028,553.08	628,346.17	N/A	N/A	217.85
PSP-01	3,028,156.83	630,618.86	N/A	N/A	218.16
SHMSG-13-01G	3,028,450.26	628,521.28	N/A	N/A	208.29
SHMSG-13-03G	3,029,540.87	629,804.73	N/A	N/A	211.07
SHMSG-13-02G	3,029,055.69	629,127.28	N/A	N/A	211.67

February 2014 Supplemental Survey

Location ID	Latitude	Longitude	Ground Elevation	Roadbox or Standpipe Elevation	Top of Casing or Staff Elevation
MW SHL-12	3,025,341.62	630,003.02	247.4	249.08	248.67
MW SHL-17	3,025,390.83	630,287.49	232.07	234.19	233.83
MW SHL-25	3,025,251.89	629,698.61	256.28	258.31	258.05
SHM-10-07	3,026,889.84	630,301.76	244.76	247.29	246.87
MW SHM13-07	3,028,758.20	629,333.65	226.12	226.12	225.61
MW SHM13-14 S	3,029,020.58	629,392.28	208.01	211.15	211.02
MW SHM13-14 D	3,029,016.63	629,391.87	207.94	210.81	210.7
MW SHM13-15	3,029,072.16	629,273.49	N/A	210.78	210.55
MW EPA-PZ-1A	3,028,055.09	630,191.08	219.4	222.87	222.75
MW EPA-PZ-1B	3,028,057.07	630,192.81	219.35	222.73	222.5
MW EPA-PZ-2A	3,028,124.80	630,287.48	218.84	222.44	222.34
MW EPA-PZ-2B	3,028,124.81	630,290.55	218.96	222.47	222.32
MW EPA-PZ-3A	3,028,088.27	630,062.62	219.19	222.7	222.6
MW EPA-PZ-3B	3,028,086.20	630,064.85	219.3	222.65	222.51
MW EPA-PZ-4A	3,028,045.58	629,992.14	223.36	226.68	226.54
MW EPA-PZ-4B	3,028,044.09	629,989.95	223.5	226.4	226.34
MW EPA-PZ-5A	3,028,185.36	630,152.88	215.35	219.06	218.91
MW EPA-PZ-5B	3,028,185.95	630,155.29	215.16	218.44	218.31
MW EPA-PZ-6A	3,028,066.40	629,894.69	230.69	234.4	234.21
MW EPA-PZ-6B	3,028,069.37	629,894.19	230.83	234.17	234.03
MW EPA-PZ-7A	3,028,106.70	629,801.11	234.37	234.37	234.08
MW EPA-PZ-7B	3,028,109.20	629,800.14	234.22	234.22	233.92
SHSG 14-01G	3,028,212.91	630,568.48	N/A	N/A	217.41

Notes:
Reference elevations based on the survey preformed in June 2013 and February 2014.
The survey was conducted on the Massachusetts State Plane Coordinate System and vertically on North American Vertical Datum (NAVD) 1988 datum
N/A - not applicable, indicating the element was not included in the survey

TABLE 5
HYDRAULIC MONITORING RESULTS
Shepley's Hill Landfill, Devens, Massachusetts

Location ID (Well/Peizometer/Staff description) (Reference Elevation)	Gauge Date Date	Depth to Water (ft)	Groundwater / Surface Water Elevation (ft)
N-1, P-1	11/5/2012	14.24	215.77
3/4 inch, stickup	5/15/2013	14.39	215.62
230.01	6/11/2013	13.31	216.70
	10/21/2013	17.44	212.57
	4/22/2014	13.89	216.12
	10/6/2014	14.05	215.96
N-1, P-2	11/5/2012	13.89	216.14
3/4 inch, stickup	5/15/2013	14.34	215.69
230.03	6/11/2013	13.26	216.77
	10/21/2013	17.44	212.59
	4/22/2014	13.85	216.18
	10/6/2014	13.95	216.08
N-1, P-3	11/5/2012	13.48	216.70
3/4 inch, stickup	5/15/2013	13.81	216.37
230.18	6/11/2013	13.80	216.38
	10/21/2013	17.48	212.70
	4/22/2014	13.55	216.63
	10/6/2014	13.21	216.97
N-2, P-1	11/5/2012	5.30	216.86
3/4 inch, stickup	5/15/2013	5.59	216.57
222.16	6/11/2013	4.49	217.67
	10/21/2013	9.08	213.08
	4/22/2014	5.40	216.76
	10/6/2014	4.99	217.17
N-2, P-2	11/5/2012	5.15	216.85
3/4 inch, stickup	5/15/2013	5.35	216.65
222.0	6/11/2013	4.31	217.69
	10/21/2013	8.09	213.91
	4/22/2014	5.20	216.80
	10/6/2014	4.86	217.14
N-3, P-1	11/5/2012	3.93	216.93
3/4 inch, stickup	5/15/2013	4.20	216.66
220.86	6/11/2013	3.18	217.68
	10/21/2013	7.70	213.16
	4/22/2014	4.05	216.81
	10/6/2014	3.60	217.26
N-3, P-2	11/5/2012	3.96	216.90
3/4 inch, stickup	5/15/2013	4.22	216.64
220.86	6/11/2013	3.12	217.74
	10/21/2013	8.70	212.16
	4/22/2014	4.05	216.81
	10/6/2014	3.64	217.22
N-5, P-1	11/5/2012	24.36	218.26
3/4 inch, stickup	5/15/2013	23.54	219.08
242.62	6/11/2013	23.27	219.35
	10/21/2013	24.70	217.92
	4/22/2014	23.87	218.75
	10/6/2014	24.22	218.40
N-5, P-2	11/5/2012	24.88	217.79
3/4 inch, stickup	5/15/2013	23.70	218.97
242.67	6/11/2013	23.47	219.20
	10/21/2013	24.40	218.27
	4/22/2014	24.58	218.09
	10/6/2014	24.74	217.93
N-6, P-1	11/5/2012	37.95	220.51
3/4 inch, stickup	5/15/2013	37.04	221.42
258.46	6/11/2013	36.94	221.52
	10/21/2013	37.88	220.58
	4/22/2014	37.75	220.71
	10/6/2014	38.10	220.36

TABLE 5
HYDRAULIC MONITORING RESULTS
Shepley's Hill Landfill, Devens, Massachusetts

Location ID (Well/Peizometer/Staff description) (Reference Elevation)	Gauge Date Date	Depth to Water (ft)	Groundwater / Surface Water Elevation (ft)
N-7, P-1	11/5/2012	31.70	223.90
3/4 inch, stickup	5/15/2013	31.29	224.31
255.6	6/11/2013	30.83	224.77
	10/21/2013	31.81	223.79
	4/22/2014	31.45	224.15
	10/6/2014	32.21	223.39
N-7, P-2	11/5/2012	31.85	224.22
3/4 inch, stickup	5/15/2013	31.49	224.58
256.07	6/11/2013	31.09	224.98
	10/21/2013	32.00	224.07
	4/22/2014	31.61	224.46
	10/6/2014	32.41	223.66
SHL-1	6/11/2013	Obstruction at 7.53'	--
2 inch, stickup	10/21/2013	Dry at 7.85'	--
271.66	4/22/2014	2.27	269.39
	10/6/2014	dry at 7.93'	--
SHL-3	11/5/2012	29.05	217.84
2 inch, stickup	5/15/2013	29.70	217.19
246.89	6/11/2013	28.71	218.18
	10/21/2013	32.00	214.89
	4/22/2014	29.20	217.69
	10/6/2014	29.56	217.33
SHL-4	11/5/2012	10.29	217.22
2 inch, stickup	5/15/2013	10.62	216.89
227.51	6/11/2013	9.89	217.62
	10/21/2013	13.75	213.76
	4/22/2014	10.49	217.02
	10/6/2014	10.40	217.11
SHL-5	11/5/2012	2.86	214.76
2 inch, stickup	5/15/2013	4.79	212.83
217.62	6/11/2013	1.50	216.12
	10/21/2013	6.60	211.02
	4/22/2014	2.55	215.07
	10/6/2014	6.45	211.17
SHL-8S	11/5/2012	7.54	213.45
2 inch, stickup	5/15/2013	8.21	212.78
220.99	6/11/2013	6.81	214.18
	10/21/2013	9.70	211.29
	4/22/2014	6.90	214.09
	10/6/2014	8.57	212.42
SHL-8D	11/5/2012	7.46	213.33
2 inch, stickup	5/15/2013	8.11	212.68
220.79	6/11/2013	6.80	213.99
	10/21/2013	9.55	211.24
	4/22/2014	6.80	213.99
	10/6/2014	8.56	212.23
SHL-9	11/5/2012	9.68	212.31
2 inch, stickup	5/15/2013	10.31	211.68
221.99	6/11/2013	16.09	205.90
	10/21/2013	11.10	210.89
	4/22/2014	8.67	213.32
	10/6/2014	11.36	210.63
SHL-10	11/5/2012	30.28	217.67
2 inch, stickup	5/15/2013	31.04	216.91
247.95	6/11/2013	30.01	217.94
	10/21/2013	33.70	214.25
	4/22/2014	30.56	217.39
	10/6/2014	31.09	216.86
SHL-11	11/5/2012	18.55	216.93
2 inch, stickup	5/15/2013	18.70	216.78
235.48	6/11/2013	17.81	217.67
	10/21/2013	21.70	213.78
	4/22/2014	18.50	216.98
	10/6/2014	18.49	216.99

TABLE 5
HYDRAULIC MONITORING RESULTS
Shepley's Hill Landfill, Devens, Massachusetts

Location ID (Well/Peizometer/Staff description) (Reference Elevation)	Gauge Date Date	Depth to Water (ft)	Groundwater / Surface Water Elevation (ft)
SHL-12	4/22/2014	22.65	226.02
4 inch, stickup	10/6/2014	23.70	224.97
248.67			
SHL-13	11/5/2012	6.61	214.10
2 inch, stickup	5/15/2013	7.30	213.41
220.71	6/11/2013	5.58	215.13
	10/21/2013	9.23	211.48
	4/22/2014	6.02	214.69
	10/6/2014	6.95	213.76
SHL-15	11/5/2012	18.87	241.06
4 inch, stickup	5/15/2013	17.58	242.35
259.93	6/11/2013	17.44	242.49
	10/21/2013	20.32	239.61
	4/22/2014	16.11	243.82
	10/6/2014	20.23	239.70
SHL-17	4/22/2014	7.75	226.08
4 inch, stickup	10/6/2014	accessible due to deep ponding/floodir	--
233.83			
SHL-18	11/5/2012	18.61	218.95
4 inch, stickup	5/15/2013	19.39	218.17
237.56	6/11/2013	18.30	219.26
	10/21/2013	21.55	216.01
	4/22/2014	18.71	218.85
	10/6/2014	19.60	217.96
SHL-19	11/5/2012	22.61	217.91
4 inch, stickup	5/15/2013	23.39	217.13
240.52	6/11/2013	22.14	218.38
	10/21/2013	26.25	214.27
	4/22/2014	22.98	217.54
	10/6/2014	23.55	216.97
SHL-20	11/5/2012	18.48	217.48
4 inch, stickup	5/15/2013	18.30	217.66
235.96	6/11/2013	17.84	218.12
	10/21/2013	20.30	215.66
	4/22/2014	18.40	217.56
	10/6/2014	18.79	217.17
SHL-21	11/5/2012	45.24	214.70
4 inch, stickup	5/15/2013	45.89	214.05
259.94	6/11/2013	44.94	215.00
	10/21/2013	47.85	212.09
	4/22/2014	44.70	215.24
	10/6/2014	46.71	213.23
SHL-22	11/5/2012	7.32	212.27
4 inch, stickup	5/15/2013	8.09	211.50
219.59	6/11/2013	6.67	212.92
	10/21/2013	8.70	210.89
	4/22/2014	6.46	213.13
	10/6/2014	8.86	210.73
SHL-23	11/5/2012	28.35	212.91
4 inch, stickup	5/15/2013	28.69	212.57
241.26	6/11/2013	27.70	213.56
	10/21/2013	29.70	211.56
	4/22/2014	26.30	214.96
	10/6/2014	30.35	210.91
SHL-24	11/5/2012	15.74	223.86
4 inch, stickup	5/15/2013	16.27	223.33
239.6	6/11/2013	14.93	224.67
	10/21/2013	16.98	222.62
	4/22/2014	15.75	223.85
SHL-25	4/22/2014	26.08	231.97
4 inch, stickup	10/6/2014	28.64	229.41
258.05			

TABLE 5
HYDRAULIC MONITORING RESULTS
Shepley's Hill Landfill, Devens, Massachusetts

Location ID (Well/Peizometer/Staff description) (Reference Elevation)	Gauge Date Date	Depth to Water (ft)	Groundwater / Surface Water Elevation (ft)
SHM-05-39A	11/5/2012	11.41	210.13
2 inch w/roadbox	5/15/2013	11.92	209.62
221.54	6/11/2013	10.93	210.61
	10/21/2013	12.49	209.05
	4/22/2014	10.54	211.00
	10/6/2014	12.35	209.19
SHM-05-39B	11/5/2012	12.32	209.20
2 inch w/roadbox	5/15/2013	12.71	208.81
221.52	6/11/2013	11.77	209.75
	10/21/2013	13.08	208.44
	4/22/2014	11.29	210.23
	10/6/2014	13.00	208.52
SHM-05-40X	11/5/2012	14.21	209.13
2 inch w/roadbox	5/15/2013	14.65	208.69
223.34	6/11/2013	13.86	209.48
	10/21/2013	15.10	208.24
	4/22/2014	13.11	210.23
	10/6/2014	15.05	208.29
SHM-05-41A	11/5/2012	10.60	211.85
2 inch w/roadbox	5/15/2013	11.29	211.16
222.45	6/11/2013	9.95	212.50
	10/21/2013	11.90	210.55
	4/22/2014	9.66	212.79
	10/6/2014	12.11	210.34
SHM-05-41B	11/5/2012	10.40	211.90
2 inch w/roadbox	5/15/2013	11.09	211.21
222.3	6/11/2013	9.79	212.51
	10/21/2013	11.70	210.60
	4/22/2014	9.48	212.82
	10/6/2014	11.96	210.34
SHM-05-41C	11/5/2012	10.67	211.89
2 inch w/roadbox	5/15/2013	11.42	211.14
222.56	6/11/2013	10.09	212.47
	10/21/2013	11.95	210.61
	4/22/2014	9.78	212.78
	10/6/2014	12.41	210.15
SHM-05-42A	11/5/2012	4.71	212.13
3/4 inch, stickup	5/15/2013	5.45	211.39
216.84	6/11/2013	4.00	212.84
	10/21/2013	6.16	210.68
	4/22/2014	3.90	212.94
	10/6/2014	6.13	210.71
SHM-05-42B	11/5/2012	4.73	212.09
3/4 inch, stickup	5/15/2013	5.45	211.37
216.82	6/11/2013	4.04	212.78
	10/21/2013	6.14	210.68
	4/22/2014	3.90	212.92
	10/6/2014	6.20	210.62
SHM-93-10C	11/5/2012	28.93	218.68
4 inch, stickup	5/15/2013	29.45	218.16
247.61	6/11/2013	28.47	219.14
	10/21/2013	31.50	216.11
	4/22/2014	29.03	218.58
	10/6/2014	29.75	217.86
SHM-93-10D	11/5/2012	29.90	218.04
4 inch, stickup	5/15/2013	30.55	217.39
247.94	6/11/2013	29.84	218.10
	10/21/2013	32.80	215.14
	4/22/2014	30.11	217.83
	10/6/2014	30.75	217.19
SHM-93-18B	11/5/2012	18.35	218.97
4 inch, stickup	5/15/2013	19.12	218.20
237.32	6/11/2013	17.96	219.36
	10/21/2013	21.20	216.12
	4/22/2014	18.39	218.93
	10/6/2014	19.30	218.02

TABLE 5
HYDRAULIC MONITORING RESULTS
Shepley's Hill Landfill, Devens, Massachusetts

Location ID (Well/Peizometer/Staff description) (Reference Elevation)	Gauge Date Date	Depth to Water (ft)	Groundwater / Surface Water Elevation (ft)
SHM-93-22B	11/5/2012	7.15	212.27
4 inch, stickup	5/15/2013	8.92	210.50
219.42	6/11/2013	6.53	212.89
	10/21/2013	8.50	210.92
	4/22/2014	9.30	210.12
	10/6/2014	8.74	210.68
SHM-93-22C	11/5/2012	8.33	212.37
4 inch, stickup	5/15/2013	9.10	210.32
220.7	6/11/2013	7.81	211.61
	10/21/2013	9.96	209.46
	4/22/2014	7.42	212.00
	10/6/2014	9.95	209.47
SHM-96-5B	11/5/2012	6.26	212.69
4 inch, stickup	5/15/2013	7.01	211.94
218.95	6/11/2013	6.56	212.39
	10/21/2013	7.80	211.15
	4/22/2014	5.50	213.45
	10/6/2014	7.77	211.18
SHM-96-5C	11/5/2012	5.69	212.71
4 inch, stickup	5/15/2013	6.46	211.94
218.4	6/11/2013	5.04	213.36
	10/21/2013	7.30	211.10
	4/22/2014	5.00	213.40
	10/6/2014	7.22	211.18
SHP-99-31A	11/5/2012	2.10	212.25
2 inch, stickup	5/15/2013	3.81	210.54
214.35	6/11/2013	3.90	210.45
	10/21/2013	4.42	209.93
	4/22/2014	3.30	211.05
	10/6/2014	4.42	209.93
SHP-99-31B	11/5/2012	3.86	210.54
2 inch, stickup	5/15/2013	4.43	209.97
214.4	6/11/2013	3.29	211.11
	10/21/2013	4.98	209.42
	4/22/2014	3.03	211.37
	10/6/2014	4.85	209.55
SHP-99-31C	11/5/2012	4.13	210.59
2 inch, stickup	5/15/2013	4.71	210.01
214.72	6/11/2013	3.58	211.14
	10/21/2013	5.31	209.41
	4/22/2014	1.90	212.82
	10/6/2014	5.10	209.62
SHM-99-32X	11/5/2012	9.70	211.67
2 inch, stickup	5/15/2013	10.32	211.05
221.37	6/11/2013	9.09	212.28
	10/21/2013	11.15	210.22
	4/22/2014	8.98	212.39
	10/6/2014	10.75	210.62
SHP-01-36X	11/5/2012	7.27	216.75
3/4 inch, stickup	5/15/2013	7.55	216.47
224.02	6/11/2013	6.43	217.59
	10/21/2013	11.15	212.87
	4/22/2014	7.39	216.63
	10/6/2014	6.89	217.13
SHP-01-37X	11/5/2012	5.98	216.86
3/4 inch, stickup	5/15/2013	6.21	216.63
222.84	6/11/2013	5.15	217.69
	10/21/2013	9.95	212.89
	4/22/2014	6.12	216.72
	10/6/2014	5.61	217.23
SHP-01-38A	11/5/2012	3.85	217.05
3/4 inch, stickup	5/15/2013	4.11	216.79
220.9	6/11/2013	3.06	217.84
	10/21/2013	7.30	213.60
	4/22/2014	3.97	216.93
	10/6/2014	3.69	217.21

TABLE 5
HYDRAULIC MONITORING RESULTS
Shepley's Hill Landfill, Devens, Massachusetts

Location ID (Well/Peizometer/Staff description) (Reference Elevation)	Gauge Date Date	Depth to Water (ft)	Groundwater / Surface Water Elevation (ft)
SHP-01-38B	11/5/2012	4.00	217.06
3/4 inch, stickup	5/15/2013	4.23	216.83
221.06	6/11/2013	3.19	217.87
	10/21/2013	7.45	213.61
	4/22/2014	4.10	216.96
	10/6/2014	3.87	217.19
SHP-05-43	11/5/2012	44.68	215.98
3/4 inch, stickup	5/15/2013	45.15	215.51
260.66	6/11/2013	44.39	216.27
	10/21/2013	47.65	213.01
	4/22/2014	44.52	216.14
	10/6/2014	45.45	215.21
SHP-05-44	11/5/2012	41.68	216.40
3/4 inch, stickup	5/15/2013	42.04	216.04
258.08	6/11/2013	41.20	216.88
	10/21/2013	44.90	213.18
	4/22/2014	41.65	216.43
	10/6/2014	41.99	216.09
SHP-05-45A	11/5/2012	16.12	212.35
2 inch, stickup	5/15/2013	16.82	211.65
228.47	6/11/2013	15.57	212.90
	10/21/2013	17.07	211.40
	4/22/2014	15.24	213.23
	10/6/2014	17.89	210.58
SHP-05-45B	11/5/2012	16.85	212.25
2 inch, stickup	5/15/2013	17.53	211.57
229.1	6/11/2013	16.25	212.85
	10/21/2013	17.65	211.45
	4/22/2014	15.90	213.20
	10/6/2014	18.31	210.79
SHP-05-46A	11/5/2012	14.79	212.84
2 inch, stickup	5/15/2013	15.56	212.07
227.63	6/11/2013	14.26	213.37
	10/21/2013	16.00	211.63
	4/22/2014	14.05	213.58
	10/6/2014	17.43	210.20
SHP-05-46B	11/5/2012	15.48	212.74
2 inch, stickup	5/15/2013	16.23	211.99
228.22	6/11/2013	14.91	213.31
	10/21/2013	16.68	211.54
	4/22/2014	14.70	213.52
	10/6/2014	17.15	211.07
SHP-05-47A	11/5/2012	4.79	212.74
1 inch, no standpipe	5/15/2013	5.39	212.14
217.53	6/11/2013	Inaccessible (High Water Level)	--
	10/21/2013	Dry @ 5.75'	--
	4/22/2014	4.69	212.84
SHP-05-47B	11/5/2012	2.63	212.77
1 inch, no standpipe	5/15/2013	2.82	212.58
215.4	6/11/2013	Inaccessible (High Water Level)	
	10/21/2013	3.95	211.45
	4/22/2014	1.92	213.48
SHP-05-48A	11/5/2012	5.94	211.36
1 inch, no standpipe	5/15/2013	Dry	--
217.3	6/11/2013	Inaccessible (Under Water)	--
	10/21/2013	Dry @ 5.25'	--
	4/22/2014	4.71	212.59
	10/6/2014	Dry @ 5.5'	--
SHP-05-48B	11/5/2012	3.53	212.40
1 inch, no standpipe	5/15/2013	4.03	211.90
215.93	6/11/2013	Inaccessible (Under Water)	--
	10/21/2013	Dry @ 5.00'	--
	4/22/2014	3.47	212.46
	10/6/2014	dry @ 5.25'	--

TABLE 5
HYDRAULIC MONITORING RESULTS
Shepley's Hill Landfill, Devens, Massachusetts

Location ID (Well/Peizometer/Staff description) (Reference Elevation)	Gauge Date Date	Depth to Water (ft)	Groundwater / Surface Water Elevation (ft)
SHP-05-49A	11/5/2012	5.63	211.04
1 inch, no standpipe	5/15/2013	Dry	--
216.67	6/11/2013	Inaccessible (Under Water)	--
	10/21/2013	Dry @ 5.76'	--
	4/22/2014	5.63	211.04
	10/6/2014	dry @ 6.0'	--
SHP-05-49B	11/5/2012	3.95	211.20
1 inch, no standpipe	5/15/2013	4.42	210.73
215.15	6/11/2013	Inaccessible (Under Water)	--
	10/21/2013	4.33	210.82
	4/22/2014	3.85	211.30
	10/6/2014	4.45	210.70
SHP-95-27X	11/5/2012	14.23	223.23
3/4 inch, stickup	5/15/2013	16.45	221.01
237.46	6/11/2013	13.88	223.58
	10/21/2013	17.88	219.58
	4/22/2014	14.83	222.63
	10/6/2014	17.23	220.23
SHP-99-29X	11/5/2012	24.58	218.74
2 inch, stickup	5/15/2013	22.79	220.53
243.32	6/11/2013	22.73	220.59
	10/21/2013	24.50	218.82
	4/22/2014	23.34	219.98
	10/6/2014	24.85	218.47
SHP-99-34A	11/5/2012	Damaged	--
	5/15/2013	Damaged	--
NSVD	6/11/2013	Damaged	--
	4/22/2014	Damaged	--
	10/6/2014	Damaged	--
SHP-99-34B	11/5/2012	13.26	211.32
1 inch, stickup	5/15/2013	13.29	211.29
224.58	6/11/2013	12.66	211.92
	10/21/2013	14.20	210.38
	10/6/2014	13.83	210.75
SHP-99-35X	11/5/2012	37.50	220.42
2 inch, stickup	5/15/2013	36.85	221.07
257.92	6/11/2013	36.87	221.05
	10/21/2013	36.90	221.02
	4/22/2014	37.05	220.87
	10/6/2014	34.90	223.02
EW-01	5/15/2013	27.86	198.94
8 inch extraction, vault	6/11/2013	14.17	212.63
226.80	10/21/2013	15.51	211.29
	4/22/2014	13.85	212.95
	10/6/2014	16.57	210.23
EW-04	5/15/2013	37.53	189.52
8 inch extraction, vault	6/11/2013	14.19	212.86
227.05	10/21/2013	15.85	211.20
	4/22/2014	13.88	213.17
	10/6/2014	16.61	210.44
PZ-12-01	11/5/2012	20.51	217.04
2 inch, stickup	5/15/2013	20.67	216.88
237.55	6/11/2013	19.90	217.65
	10/21/2013	23.50	214.05
	11/19/2013	21.55	216.00
	4/22/2014	20.55	217.00
	10/6/2014	20.61	216.94
PZ-12-02	11/5/2012	20.47	217.34
2 inch, stickup	5/15/2013	20.37	217.44
237.81	6/11/2013	19.88	217.93
	10/21/2013	22.50	215.31
	11/19/2013	21.51	216.30
	4/22/2014	20.40	217.41
	10/6/2014	20.80	217.01

TABLE 5
HYDRAULIC MONITORING RESULTS
Shepley's Hill Landfill, Devens, Massachusetts

Location ID (Well/Peizometer/Staff description) (Reference Elevation)	Gauge Date Date	Depth to Water (ft)	Groundwater / Surface Water Elevation (ft)
PZ-12-03	11/5/2012	19.37	217.05
2 inch, stickup	5/15/2013	19.63	216.79
236.42	6/11/2013	19.55	216.87
	10/21/2013	22.80	213.62
	11/19/2013	20.34	216.08
	4/22/2014	19.48	216.94
	10/6/2014	19.29	217.13
PZ-12-04	11/5/2012	20.42	217.80
2 inch, stickup	5/15/2013	20.10	218.12
238.22	6/11/2013	19.73	218.49
	10/21/2013	21.85	216.37
	11/19/2013	22.31	215.91
	4/22/2014	20.33	217.89
	10/6/2014	20.73	217.49
PZ-12-05	11/5/2012	21.49	217.32
2 inch, stickup	5/15/2013	21.73	217.08
238.81	6/11/2013	20.70	218.11
	10/21/2013	24.77	214.04
	11/19/2013	22.45	216.36
	4/22/2014	21.64	217.17
	10/6/2014	20.47	218.34
PZ-12-06	11/5/2012	24.24	218.00
2 inch, stickup	5/15/2013	23.91	218.33
242.24	6/11/2013	23.54	218.70
	10/21/2013	25.70	216.54
	11/19/2013	25.53	216.71
	4/22/2014	24.19	218.05
	10/6/2014	24.52	217.72
PZ-12-07	11/5/2012	26.89	217.74
2 inch, stickup	5/15/2013	27.49	217.14
244.63	6/11/2013	26.95	217.68
	10/21/2013	30.43	214.20
	11/19/2013	28.49	216.14
	4/22/2014	27.23	217.40
	10/6/2014	27.57	217.06
PZ-12-08	11/5/2012	26.26	218.62
2 inch, stickup	5/15/2013	26.02	218.86
244.88	6/11/2013	25.59	219.29
	10/21/2013	27.50	217.38
	11/19/2013	27.22	217.66
	4/22/2014	26.14	218.74
	10/6/2014	26.58	218.30
PZ-12-09	11/5/2012	23.03	218.91
2 inch, stickup	5/15/2013	24.32	217.62
241.94	6/11/2013	22.80	219.14
	10/21/2013	25.20	216.74
	11/19/2013	24.70	217.24
	4/22/2014	23.49	218.45
	10/6/2014	24.60	217.34
PZ-12-10	11/5/2012	22.35	219.94
2 inch, stickup	5/15/2013	22.89	219.40
242.29	6/11/2013	23.16	219.13
	10/21/2013	23.55	218.74
	11/19/2013	23.76	218.53
	4/22/2014	22.42	219.87
	10/6/2014	23.58	218.71
SHM-10-01	11/5/2012	4.15	205.37
1.5 inch, stickup	5/15/2013	3.52	206.00
209.52	6/11/2013	2.45	207.07
	10/21/2013	4.02	205.50
	4/22/2014	2.96	206.56
	10/6/2014	4.09	205.43
SHM-10-02	11/5/2012	17.25	205.82
1.5 inch, stickup	5/15/2013	18.64	204.43
223.07	6/11/2013	16.50	206.57
	10/21/2013	18.35	204.72
	4/22/2014	17.21	205.86
	10/6/2014	18.46	204.61

TABLE 5
HYDRAULIC MONITORING RESULTS
Shepley's Hill Landfill, Devens, Massachusetts

Location ID (Well/Peizometer/Staff description) (Reference Elevation)	Gauge Date Date	Depth to Water (ft)	Groundwater / Surface Water Elevation (ft)
SHM-10-03	11/5/2012	26.16	205.90
1.5 inch, stickup	5/15/2013	26.38	205.68
232.06	6/11/2013	25.47	206.59
	10/21/2013	26.97	205.09
	4/22/2014	25.68	206.38
	10/6/2014	27.10	204.96
SHM-10-04	11/5/2012	6.25	206.38
1.5 inch, stickup	5/15/2013	6.11	206.52
212.63	6/11/2013	5.26	207.37
	10/21/2013	6.18	206.45
	4/22/2014	5.11	207.52
	10/6/2014	6.24	206.39
SHM-10-05A	11/5/2012	25.18	209.89
1.5 inch w/ roadbox	5/15/2013	25.56	209.51
235.07	6/11/2013	24.67	210.40
	10/21/2013	26.14	208.93
	4/22/2014	24.23	210.84
	10/6/2014	25.41	209.66
SHM-10-06	11/5/2012	18.84	214.07
1.5 inch, stickup	5/15/2013	19.46	213.45
232.91	6/11/2013	19.18	213.73
	10/21/2013	20.80	212.11
	4/22/2014	18.23	214.68
	10/6/2014	20.32	212.59
SHM-10-06A	11/5/2012	34.29	214.26
1.5 inch, stickup	5/15/2013	34.93	213.62
248.55	6/11/2013	33.64	214.91
	10/21/2013	36.50	212.05
	4/22/2014	33.77	214.78
	10/6/2014	35.67	212.88
SHM-10-07	11/5/2012	28.76	218.11
2 inch, stickup	5/15/2013	27.07	219.80
246.87	6/11/2013	26.95	219.92
	10/21/2013	28.20	218.67
	4/22/2014	27.74	219.13
	10/6/2014	28.02	218.85
SHM-10-08	11/5/2012	8.59	205.82
1.5 inch, stickup	5/15/2013	9.01	205.40
214.41	6/11/2013	7.78	206.63
	10/21/2013	9.81	204.60
	4/22/2014	8.75	205.66
	10/6/2014	9.90	204.51
SHM-10-10	11/5/2012	10.51	206.61
1.5 inch, stickup	5/15/2013	10.63	206.49
217.12	6/11/2013	9.74	207.38
	10/21/2013	10.76	206.36
	4/22/2014	9.90	207.22
	10/6/2014	10.82	206.30
SHM-10-11	11/5/2012	41.14	222.06
2 inch, stickup	5/15/2013	40.36	222.84
263.2	6/11/2013	33.62	229.58
	10/21/2013	41.00	222.20
	4/22/2014	40.99	222.21
	10/6/2014	41.46	221.74
SHM-10-12	11/5/2012	34.80	219.80
2 inch, stickup	5/15/2013	33.09	221.51
254.6	6/11/2013	40.22	214.38
	10/21/2013	34.61	219.99
	4/22/2014	34.55	220.05
	10/6/2014	34.93	219.67
SHM-10-13	11/5/2012	26.51	218.24
2 inch, stickup	5/15/2013	25.73	219.02
244.75	6/11/2013	25.47	219.28
	10/21/2013	26.86	217.89
	4/22/2014	26.09	218.66
	10/6/2014	26.92	217.83

TABLE 5
HYDRAULIC MONITORING RESULTS
Shepley's Hill Landfill, Devens, Massachusetts

Location ID (Well/Peizometer/Staff description) (Reference Elevation)	Gauge Date Date	Depth to Water (ft)	Groundwater / Surface Water Elevation (ft)
SHM-10-14	11/5/2012	20.49	217.12
2 inch, stickup	5/15/2013	19.93	217.68
237.61	6/11/2013	19.46	218.15
	10/21/2013	21.20	216.41
	4/22/2014	19.68	217.93
	10/6/2014	21.22	216.39
SHM-10-15	11/5/2012	25.09	218.67
2 inch, stickup	5/15/2013	23.86	219.90
243.76	6/11/2013	24.74	219.02
	10/21/2013	25.15	218.61
	4/22/2014	24.43	219.33
	10/6/2014	25.41	218.35
SHM-10-16	11/5/2012	7.31	211.93
2 inch, stickup	5/15/2013	8.03	211.21
219.24	6/11/2013	7.70	211.54
	10/21/2013	8.64	210.60
	4/22/2014	6.40	212.84
	10/6/2014	8.80	210.44
SHM-11-02	11/5/2012	22.81	217.96
Bedrock, standpipe	5/15/2013	22.74	218.03
240.77	6/11/2013	22.10	218.67
	10/21/2013	24.79	215.98
	4/22/2014	22.83	217.94
	10/6/2014	23.11	217.66
SHM-11-06	11/5/2012	19.82	216.38
2 inch, stickup	5/15/2013	20.11	216.09
236.2	6/11/2013	19.39	216.81
	10/21/2013	22.30	213.90
	4/22/2014	19.60	216.60
	10/6/2014	20.71	215.49
SHM-11-07	11/5/2012	22.95	217.91
3/4 inch, stickup	5/15/2013	22.61	218.25
240.86	6/11/2013	22.19	218.67
	10/21/2013	24.28	216.58
	4/22/2014	22.89	217.97
	10/6/2014	23.26	217.60
SHM-13-01	6/11/2013	Inaccessible (High Water Level)	--
2 inch, stickup	10/21/2013	3.22	204.85
208.07	4/22/2014	2.06	206.01
	10/6/2014	3.36	204.71
SHM-13-02	5/15/2013	12.50	206.20
2 inch, stickup	6/11/2013	11.50	207.20
218.7	10/21/2013	12.91	205.79
	4/22/2014	11.92	206.78
	10/6/2014	12.97	205.73
SHM-13-03	5/15/2013	5.10	206.60
2 inch, stickup	6/11/2013	4.23	207.47
211.7	10/21/2013	5.08	206.62
	4/22/2014	4.33	207.37
	10/6/2014	5.12	206.58
SHM-13-04	5/15/2013	19.15	207.86
2 inch, stickup	6/11/2013	18.49	208.52
227.01	10/21/2013	19.45	207.56
	4/22/2014	17.79	209.22
	10/6/2014	19.55	207.46
SHM-13-05	5/15/2013	16.78	208.33
2 inch, stickup	6/11/2013	15.99	209.12
225.11	10/21/2013	17.06	208.05
	4/22/2014	15.50	209.61
	10/6/2014	17.95	207.16
SHM-13-06	6/11/2013	16.39	207.50
2 inch w/ roadbox	10/21/2013	17.50	206.39
223.89	4/22/2014	16.32	207.57
	10/6/2014	17.55	206.34

TABLE 5
HYDRAULIC MONITORING RESULTS
Shepley's Hill Landfill, Devens, Massachusetts

Location ID (Well/Peizometer/Staff description) (Reference Elevation)	Gauge Date Date	Depth to Water (ft)	Groundwater / Surface Water Elevation (ft)
SHM-13-07	4/22/2014	17.79	207.82
2 inch w/ roadbox	10/6/2014	18.97	206.64
225.61			
SHM-13-08	6/11/2013	19.71	208.19
2 inch w/ roadbox	10/21/2013	20.05	207.85
227.9	4/22/2014	19.33	208.57
	10/6/2014	19.69	208.21
SHM-13-14S	4/23/2014	3.36	207.66
2 inch, stickup	10/6/2014	3.80	207.22
211.02			
SHM-13-14D	4/23/2014	2.91	207.79
2 inch, stickup	10/6/2014	3.60	207.10
210.7			
SHM-13-15	4/23/2014	3.11	207.44
2 inch, stickup	10/6/2014	3.81	206.74
210.55			
SHM-07-03	5/15/2013	19.85	208.01
2 inch w/ roadbox	6/11/2013	19.24	208.62
227.86	10/21/2013	20.50	207.36
	4/22/2014	18.23	209.63
	10/6/2014	20.52	207.34
SHP-07-03A	6/11/2013	11.13	206.72
1 inch steel piezometer	10/21/2013	13.21	204.64
217.85	4/22/2014	Dry @ 11.45	--
	10/6/2014	13.32	204.53
SHM-07-05X	5/15/2013	14.57	208.84
2 inch w/ roadbox	6/11/2013	14.39	209.02
223.41	10/21/2013	14.85	208.56
	4/22/2014	15.22	208.19
	10/6/2014	14.85	208.56
SHP-99-01C	5/15/2013	11.00	262.56
2 inch, stickup	6/11/2013	9.25	264.31
273.56	10/21/2013	24.33	249.23
	4/22/2014	8.03	265.53
	10/6/2014	24.19	249.37
SHP-99-01B	5/15/2013	5.91	266.64
2 inch, stickup	6/11/2013	4.84	267.71
272.55	10/21/2013	Dry @ 9.80'	--
	4/22/2014	4.01	268.54
	10/6/2014	dry @ 9.81'	--
SHM-93-24A	5/15/2013	16.64	222.64
4 inch, stickup	6/11/2013	15.00	224.28
239.28	10/21/2013	17.41	221.87
	4/22/2014	16.07	223.21
PSP-01	11/5/2012	2.00	216.83
staff gauge	5/15/2013	1.75	216.58
214.83	6/11/2013	3.85	218.68
	7/20/2013	1.50	216.33
	10/21/2013	Dry due to pond construction	--
	4/22/2014	1.82	216.65
SHSG-13-01G	7/20/2013	3.50	205.13
staff gauge	10/21/2013	Unable to read - muddy staff	NA
201.63	4/23/2014	3.05	204.68
	10/7/2014	2.90	204.53
SHSG-13-02G	7/20/2013	2.12	207.13
staff gauge	10/21/2013	Unable to read - muddy staff	--
205.01	4/23/2014	2.55	207.56
	10/7/2014	2.90	207.91
SHSG-13-03G	7/20/2013	2.86	207.27
staff gauge	10/21/2013	Unable to read - muddy staff	--
204.41	4/23/2014	3.45	207.86
	10/7/2014	3.79	208.20

TABLE 5
HYDRAULIC MONITORING RESULTS
Shepley's Hill Landfill, Devens, Massachusetts

Location ID (Well/Peizometer/Staff description) (Reference Elevation)	Gauge Date Date	Depth to Water (ft)	Groundwater / Surface Water Elevation (ft)
SHP-13-03	4/22/2014	2.55	--
NSVD	10/7/2014	2.90	--
SHSG-14-01G	4/23/2014	2.00	212.75
staff gauge			
210.75			
EPA-PZ-2012-1A	5/15/2013	11.59	211.16
EPA pizometer	4/22/2014	10.10	212.65
222.75	10/6/2014	12.39	210.36
EPA-PZ-2012-1B	5/15/2013	11.34	211.16
EPA pizometer	4/22/2014	9.85	212.65
222.5	10/6/2014	12.09	210.41
EPA-PZ-2012-2A	5/15/2013	11.11	211.23
EPA pizometer	4/22/2014	9.60	212.74
222.34	10/6/2014	11.77	210.57
EPA-PZ-2012-2B	5/15/2013	11.10	211.22
EPA pizometer	4/22/2014	9.70	212.62
222.32	10/6/2014	11.71	210.61
EPA-PZ-2012-3A	5/15/2013	11.03	211.57
EPA pizometer	4/22/2014	9.40	213.20
222.6	10/6/2014	11.84	210.76
EPA-PZ-2012-3B	5/15/2013	10.95	211.56
EPA pizometer	4/22/2014	9.45	213.06
222.51	10/6/2014	11.15	211.36
EPA-PZ-2012-4A	5/15/2013	15.18	211.36
EPA pizometer	4/22/2014	13.56	212.98
226.54	10/6/2014	16.06	210.48
EPA-PZ-2012-4B	5/15/2013	15.09	211.25
EPA pizometer	4/22/2014	13.34	213.00
226.34	10/6/2014	16.15	210.19
EPA-PZ-2012-5A	4/22/2014	6.69	212.22
EPA pizometer	10/6/2014	9.07	209.84
218.91			
EPA-PZ-2012-5B	5/15/2013	7.68	210.63
EPA pizometer	4/22/2014	6.12	212.19
218.31	10/6/2014	8.38	209.93
EPA-PZ-2012-6A	5/15/2013	22.82	211.39
EPA pizometer	4/22/2014	21.28	212.93
234.21	10/6/2014	23.83	210.38
EPA-PZ-2012-6B	5/15/2013	22.78	211.25
EPA pizometer	4/22/2014	21.27	212.76
234.03	10/6/2014	23.67	210.36
EPA-PZ-2012-7A	4/22/2014	20.95	213.13
EPA pizometer	10/6/2014	23.71	210.37
234.08			
EPA-PZ-2012-7B	5/15/2013	22.72	211.20
EPA pizometer	4/22/2014	21.00	212.92
233.92	10/6/2014	23.59	210.33

Notes:
Reference elevations based on the survey preformed in June 2013 and/or February 2014
EPA Piezometer water level data was based off of the transducer reading at 12:00 PM on the day noted
Dry - Well dry at time of gauging event
NSVD - No survey data available for location
TOC - Top of casing

APPENDIX B

Summary of Historical Arsenic Concentrations
Shepley's Hill Landfill
Devens, Massachusetts

Well ID	Total or Dissolved	IPC (T)	IPCFIL (D)	N-5, P-1 (T)	N-5, P-1 (D)	N-5, P-2 (T)	N-5, P-2 (D)	PSP-01 (T)	SHL-3 (T)	SHL-4 (T)	SHL-4 (D)	SHL-5 (T)	SHL-5 (D)	SHL-8S (T)	SHL-8S (D)	SHL-8D (T)	SHL-8D (D)	SHL-9 (T)	SHL-9 (D)	SHL-10 (T)	SHL-10 (D)	SHL-11 (T)	SHL-11 (D)	SHL-13 (T)	SHL-13 (D)	SHL-15 (T)	SHL-15 (D)	SHL-19 (T)	SHL-19 (D)	SHL-20 (T)	SHL-20 (D)	SHL-21 (T)	SHL-22 (T)	SHL-22 (D)	SHL-23 (T)	SHM-93-10C (T)	SHM-93-10D (T)	SHM-93-22B (T)
Sample Month-Year	**Units**																																				
August-91	ug/l								**35**	**260**		**23**						**37**		**67**		**320**						**340**		**98**			**27**					
Dec-91	ug/l								**120**	**140**		**38**						**67**		**120**		**320**						**710**		**89**			**25**					
Mar-93	ug/l								6.5	2.54		**11.4**						**42.4**		**280**		**340**						**390**		**330**			**32.9**			**21.3**		
Jun-93	ug/l																																			**18.1**		
Nov-96	ug/l								NS	**48.8**		**12**						**46.9**		3.4 B		**332**						**138**		**244**			**24.8**			**12.4**		**324**
May-97	ug/l								**10 U**	**73.6 J**		**10 U**						**16.1 J**		**10 U**		**252 J**						**10 U**		**10 U**			**10 U**			**10 U**		**318 J**
Oct-97	ug/l								**10 U**	**180**		**10 U**						**25.2**		**209**		**366**						**298**		**227**			**34.8**			**10.5**		**352**
May-98	ug/l								5 U	**37.4**		5 U						**15**		5 U		**346**						**77.5**		**238**			**10.6**			7.5		**365**
Nov-98	ug/l								5.4 U	**89.1**		**11.5**						**27.2**		5.4 U		**376**						**145**		**218**			5.4 U			**10.2**		**406**
May-99	ug/l								2.7 B	**78.2**		5.0 B						**71.3**		2.7 B		**431**						**156**		**216**			**12.2 B**			**10.8 B**		**707**
Nov-99	ug/l								1.9 U	**61.3**		6.5						**28.5**		1.9 U		**492**						**176**		**215**			7.3			8.7		**1440**
May-00	ug/l								2.5 U	**116**		2.5 U						**15**		2.5 U		**404**						**41.4**		**216**			**14.6**			5.9 J		**1360**
Nov-00	ug/l								**17.4**	**91.5**		**13.8**						**31.4**		4.2 U		**523**						**154**		**172**			**45**			8.8		**1180**
May-01	ug/l								4.1 U	**50.8**		**13.8**						**15.1**		4.1 U		**487**						**129**		**186**			**47.6**			6.9		**1540**
Oct-01	ug/l								1.5 U	**66**		**14.8**						**28.1**		1.5 U		**573**						**183**		**165**			**44.2**			**10.1**		**1670**
May-02	ug/l								2.8 B	**47.8 B**		**11.9 B**						**144**		4.0 B		**469**						**66.9**		**154**			**55.9 B**			**11.0 B**		**2040**
Oct-02	ug/l								3.2 U	**66.1**		3.2 U						**29**		3.2 U		**648**						**164**		**175**			**77.1**			7.1		**159**
May-03	ug/l								4.7 U	**26.6**		7.3						**13.4**		4.7 U		**498**						**36.1**		**197**			**101**			9.8		**2070**
Nov-03	ug/l								4.1 U	**13.4**		4.7 B						**30.6**		4.1 U		**639**						**83.6**		**194**			**76.4**			5.2 U		**2500**
May-04	ug/l								2.6 U	**27.2**		7.4 B						**19.8**		2.6 U		**502**						**75**		**136**			**88.1**			7.2 B		**1690**
Nov-04	ug/l								5.8 U	**19.5**		6.8 B						**32.2**		5.8 U		**617**						**121**		**156**			**65.4**			**10.6 B**		**2360**
Jun-05	ug/l								4.5 U	**10.1**		7.0 B								4.5 U		**524**						**26.3**		**159**						8.1 B		
Jan-06	ug/l									5 U		5 U						**18**		5 U		**567**						**156**		**189**			**154**			**11**		**3320**
Apr-06	ug/l			**4940**		**22**		5 U						5 U		5 U		**21**						5 U		**18**						5 U	**171**		5 U		**14**	**3690**
Jun-06	ug/l			**5970**		**46**		6	5 U	5 U		6		5 U		5 U		**21**		5 U		**700**		5 U		**16**		**1790**		**346**			**167**		5 U	**12**		**3440**
Sep-06	ug/l			**4560**		**22**		**10**						5 U		5 U		**46**						5 U		**44**						5 U	**109**		5 U		**14**	**3110**
Dec-06	ug/l			**1930**		**30**		5 U	5 U	5 U		8		5 U		5 U		**51**		5 U		**668**		5 U		**93**		**142**		**361**		5 U	**115**		5 U	**10**	**12**	**3100**
Apr-07	ug/l													3 U		3 U		**26**														3 U	**98**		3 U			**2800**
May-07	ug/l											6.2																										
Oct-07	ug/l			**4856**		**28.1**				7.5		**16.2**		**22.6**		**11.8**		**34.1**		0.59 J		**686.5**		1.6		**42**		**885.1**		**336.2**		0.81 J	**55.1**		0.73 J	9.8	**10.3**	**1978**
Apr-08	ug/l											4.1		0.5 U		0.5 U		**14.6**														1.1	**106.2**		0.19 J			**1721**
Oct-08	ug/l			**1748**		**26.8**				2.3		4.9		1 UJ		1 UJ		**40.7**		1 UJ		**663.5**		3.3		**75**		**173.6**	**28**	7.9		1 U	**81**		1 UJ	**10.1**	**23.4**	**1374**
Jan-09	ug/l	**188.9**	1.4																																			
Apr-09	ug/l											3.6		0.5 U		0.5 U		**18.1**														1.2	**98.7**		0.5 U			**1128**
Oct-09	ug/l			**4429**		**30.5**				**15.1**		**12.3**		0.5 U		0.5 U		**37.6**				**709.1**		0.5 U		**26.7**		**136.9**	**38.8**	**23.8**			**48.3**					**832.3**
Apr-10	ug/l											3.4		0.6		0.6		**25.2**															**69.6**					**947.5**
Jul-10	ug/l																																					
Aug-10	ug/l																																					
Sep-10	ug/l																																					
Oct-10	ug/l			**3488**		**24.5**				3.1		4.8		0.5 U		0.5 U		**38.4**		0.9		**694**		0.5 U		**25**		**234.8**	**56.1**	4.4		0.9	**46.5**		0.5 U	8.7		**827.6**
Apr-11	ug/l											1		0.5 U		0.5 U		**25.7**															**57.9**					**1039**
Oct-11	ug/l			**4942**		**27.4**				1.4		5.5		0.5 U		0.5 U		**39.8**				**654.9**		2.8		**70.4**		**62.9**		7.3			**45.7**					**1072**
Apr-12	ug/l											3.7		0.6		0.5 U		**29.5**															**41.9**					**1271**
Oct-12	ug/l			**2286**		**26.1**				3.8		4.5		0.5 U		0.5 U		**36.4**		0.7		**647**		1.0		**24.2**		**138.3**		**139.3**		1.1	**43.6**		0.5 U	8.1		**879**
May-13	ug/l										2.6		3.7		0.93 U		0.72 U		**30.0**		1.2		**496**						3.8		**621**			**33.3**					
Oct-13	ug/l				**2,500**		**21.2**						**15.1**		2.0 U		2.0 U		**33.1**		1.2		**752**		2.0 U		**34.9**		**33.6**		**641**			**54.3**					
Nov-13	ug/l										6.2																											
Feb-14	ug/l																																					
Apr-14	ug/l												2.0 U		2.0 U		2.0 U		**22.2**				**587**								**701**			**49.2**					
Oct-14	ug/l				**327**						**37**		**13.3**		2.0 U		2.0 U		**28.5**		2.0 U		**793**						3.1		**763**			**44.5**					

Notes:
Shaded and bolded values exceeds the MCL Standard
ug/l = micrograms per liter
J - The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
U - The analytes was non-detect at the reporting limit shown.

Summary of Historical Arsenic Concentrations
Shepley's Hill Landfill
Devens, Massachusetts

Well ID	Total or Dissolved	SHM-93-22B (D)	SHM-93-22C (T)	SHM-93-22C (D)	SHM-96-5B (T)	SHM-96-5B (D)	SHM-96-5C (T)	SHM-96-5C (D)	SHP-99-29X (T)	SHP-99-29X (D)	SHM-99-31A (T)	SHM-99-31A (D)	SHM-99-31B (T)	SHM-99-31B (D)	SHM-99-31C (T)	SHM-99-31C (D)	SHM-99-32X (T)	SHM-99-32X (D)	SHP-01-36X (T)	SHP-01-36X (D)	SHP-01-37X (T)	SHP-01-37X (D)	SHP-01-38A (T)	SHP-01-38A (D)	SHP-01-38B (D)	SHM-05-39A (T)
Sample Month-Year	**Units**																									
August-91	ug/l																									
Dec-91	ug/l																									
Mar-93	ug/l		**68.9**																							
Jun-93	ug/l		**49.8**																							
Nov-96	ug/l		**44.6**		**1440**		**71**																			
May-97	ug/l		**40.4**		**3,300 J**		**43.2**																			
Oct-97	ug/l		**10 U**		**2040**		**43.1**																			
May-98	ug/l		**31.6**		**4300**		**49.5**																			
Nov-98	ug/l		**51.1**		**3080**		**46.8**																			
May-99	ug/l		**42.8**		**3490**		**57**																			
Nov-99	ug/l		**33.2**		**2700**		**44.8**																			
May-00	ug/l		**34.4**		**5110**		**52.2**																			
Nov-00	ug/l		**47.8**		**2500**		**40.3**																			
May-01	ug/l		**19.7**		**3800**		**80.5**																			
Oct-01	ug/l		**31.6**		**1850**		**41.1**																			
May-02	ug/l		**30.5 B**		**3800**		**50.4 B**																			
Oct-02	ug/l		**30.1**		**1970**		**41.3**																			
May-03	ug/l		**21**		**3920**		**55.1**																			
Nov-03	ug/l		**29.8**		**3380**		**48.3**																			
May-04	ug/l		**27.8**		**3950**		**47.1**																			
Nov-04	ug/l		**34.9**		**2110**		**49.5**																			
Jun-05	ug/l		**15.8**																							
Jan-06	ug/l		**23**		**4130**		**43**																			
Apr-06	ug/l				**2110**		**47**				9		**56**		**270**		**168**		**24**		**41**		**550**			**289**
Jun-06	ug/l		**17**		**2760**		**51**				**12**		**53**		**273**		**186**		**22**		**49**		**496**			**288**
Sep-06	ug/l				**1570**		**37**				**23**		**74**		**305**		**202**		**30**		**46**		**681**			**270**
Dec-06	ug/l		**73**		**2980**		**24**				**16**		**72**		**301**		**176**		**19**		**46**		**623**			**248**
Apr-07	ug/l		**76**		**2030**		**47**																			
May-07	ug/l																									
Oct-07	ug/l		**72.5**		**750**		**61.1**		**2953**		**22.7**		**85.5**		**292.1**		**206.2**		**16.7**		**26.6**		**781.4**			**241.5**
Apr-08	ug/l		**29.4**		**1597**		**54.7**																			
Oct-08	ug/l		**17.7**		**747.8**		**51.8**		**2106**		**16.2**		**79.5**		**260.3**		**203.9**		**27.9**		**38.1**		**602.4**			**275.6**
Jan-09	ug/l																									
Apr-09	ug/l		**21.7**		**1401**		**44.2**																			
Oct-09	ug/l		**74.7**		**776.3**		**27.5**		**1686**		**20.4**		**56.7**		**223.5**		**196.8**		**18.7**		**35.1**		**663.7**			**259.5**
Apr-10	ug/l		**14.6**		**1504 J**		**31.2**																			
Jul-10	ug/l																									
Aug-10	ug/l																									
Sep-10	ug/l																									
Oct-10	ug/l		**15.8**		**846.2**		**26.4**		**3156**		**17.4**		**39.2**		**239.4**		**173.4**		**14.2**		**22.5**		**651.8**			**246.3**
Apr-11	ug/l		**13.9**		**2030**		**35**																			
Oct-11	ug/l		**13.9**		**1895**		**24.5**		**1457**		**18.4**		**59.3**		**244**		**172.8**		**30.8**		**20.2**		**557.9**			**227.1**
Apr-12	ug/l		**25.4**		**1681**		8.7																			
Oct-12	ug/l		**21.7**		**1376**		7.7		**2739**		**17.7**		**60.1**		**206.4**		**130.6**		**17.8**		**10.2**		**660.5**			**76.3**
May-13	ug/l	**1150**		**19.7**		**1400**		**10.4**																	**900**	
Oct-13	ug/l	**1150**		**25.1**		**1660**		5.5		**2760**		**14.6**		**61.6**		**205**		**107**								
Nov-13	ug/l																			4.8		4.7		**247**		
Feb-14	ug/l																									
Apr-14	ug/l	**997**		**31.9**		**1340**		**10.9**																		
Oct-14	ug/l	**690**		**45.6**		**991**		**17.7**		**3000**						**180**		**93.5**		**10.8**		8.5		**263**		

Notes:
Shaded and bolded values exceeds the MCL Standard
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U - The analytes was non-detect at the reporting limit shown.

Summary of Historical Arsenic Concentrations
Shepley's Hill Landfill
Devens, Massachusetts

Well ID	Total or Dissolved	SHM-05-39A (D)	SHM-05-39B (T)	SHM-05-39B (D)	SHM-05-40X (T)	SHM-05-40X (D)	SHM-05-41A (T)	SHM-05-41A (D)	SHM-05-41B (T)	SHM-05-41B (D)	SHM-05-41C (T)	SHM-05-41C (D)	SHM-05-42A (T)	SHM-05-42A (D)	SHM-05-42B (T)	SHM-05-42B (D)	SHM-07-03 (D)	SHM-07-05X (T)	SHM-07-05X (D)	SHM-10-01 (T)	SHM-10-01 (D)	SHM-10-02 (T)	SHM-10-02 (D)	SHM-10-03 (T)	SHM-10-03 (D)	SHM-10-04 (T)
Sample Month-Year	**Units**																									
August-91	ug/l																									
Dec-91	ug/l																									
Mar-93	ug/l																									
Jun-93	ug/l																									
Nov-96	ug/l																									
May-97	ug/l																									
Oct-97	ug/l																									
May-98	ug/l																									
Nov-98	ug/l																									
May-99	ug/l																									
Nov-99	ug/l																									
May-00	ug/l																									
Nov-00	ug/l																									
May-01	ug/l																									
Oct-01	ug/l																									
May-02	ug/l																									
Oct-02	ug/l																									
May-03	ug/l																									
Nov-03	ug/l																									
May-04	ug/l																									
Nov-04	ug/l																									
Jun-05	ug/l																									
Jan-06	ug/l																									
Apr-06	ug/l		**590**		**3610**		**54**		**2420**		**626**		5 U		**266**											
Jun-06	ug/l		**634**		**3420**		**52**		**2720**		**614**		5 U		**241**											
Sep-06	ug/l		**415**		**3510**		**41**		**2730**		**640**		5 U		**276**											
Dec-06	ug/l		**412**		**4070**		**36**		**2280**		**666**		5 U		**296**											
Apr-07	ug/l						**30**		**1990**		**627**		3 U		**249**											
May-07	ug/l																									
Oct-07	ug/l		**309.4**		**4445**		**24.9**		**2591**		**684.5**		1.01 J		**304.4**		<0.5	**14.7**								
Apr-08	ug/l						**26.9**		**2349**		**662.2**		2.5		**266.2**											
Oct-08	ug/l		**241.2**		**4920**		**18.7**		**1910**		**789.3**		1 U		**256**											
Jan-09	ug/l																									
Apr-09	ug/l						**22.1**		**1497**		**895.3**		2		**255.7**											
Oct-09	ug/l		**338.8**		**3833**		**16.3**		**1464**		**828.7**		1 U		**211.4**											
Apr-10	ug/l						**26.9**		**1372**		**896**		2.5		**72.2**											
Jul-10	ug/l																			1.16 J	0.68 J	0.74	0.43 J	2.36	0.78 J	1.62
Aug-10	ug/l																0.29 J		**3180**		3.51 J					
Sep-10	ug/l																			8.15	*7.87*	1.11	1.07	1.47 J	0.51 J	1.0 J
Oct-10	ug/l		**162**		**3637**		**66.7**		**1036**		**787**		1.2		**197.2**											
Apr-11	ug/l						**20.9**		**1045**		**749.8**		1.1		**188.9**											
Oct-11	ug/l		**308.1**		**3703**		**18.4**		**1369**		**917**		0.8		**230**											
Apr-12	ug/l						**15.5**		**770.8**		**764.8**		2.3		**238.7**											
Oct-12	ug/l		**364.4**		**2974**		**10.3**		**859.5**		**782.2**		0.7		**240.6**						1.4		1.1		1.0 U	
May-13	ug/l							**12.3**		**812**		**709**		0.89 U		**238**	1.0				1.3		1.5		1.5	
Oct-13	ug/l	**146**		**113**		**3100**		**12.5**		**716**		**890**		2.0 U		**232**										
Nov-13	ug/l																									
Feb-14	ug/l																									
Apr-14	ug/l							9.7		**678**		**1490**		2.0 U		**229**										
Oct-14	ug/l					**3070**		**14.2**		**638**		**946**		2.0 U		**215**										

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Summary of Historical Arsenic Concentrations
Shepley's Hill Landfill
Devens, Massachusetts

Well ID	Total or Dissolved	SHM-10-04 (D)	SHM-10-05A (T)	SHM-10-05A (D)	SHM-10-06 (T)	SHM-10-06 (D)	SHM-10-06A (T)	SHM-10-06A (D)	SHM-10-07 (T)	SHM-10-07 (D)	SHM-10-08 (T)	SHM-10-08 (D)	SHM-10-10 (T)	SHM-10-10 (D)	SHM-10-11 (T)	SHM-10-11 (D)	SHM-10-12 (T)	SHM-10-12 (D)	SHM-10-13 (T)	SHM-10-13 (D)	SHM-10-14 (T)	SHM-10-14 (D)	SHM-10-15 (T)	SHM-10-15 (D)	SHM-10-16 (T)	SHM-10-16 (D)
Sample Month-Year	**Units**																									
August-91	ug/l																									
Dec-91	ug/l																									
Mar-93	ug/l																									
Jun-93	ug/l																									
Nov-96	ug/l																									
May-97	ug/l																									
Oct-97	ug/l																									
May-98	ug/l																									
Nov-98	ug/l																									
May-99	ug/l																									
Nov-99	ug/l																									
May-00	ug/l																									
Nov-00	ug/l																									
May-01	ug/l																									
Oct-01	ug/l																									
May-02	ug/l																									
Oct-02	ug/l																									
May-03	ug/l																									
Nov-03	ug/l																									
May-04	ug/l																									
Nov-04	ug/l																									
Jun-05	ug/l																									
Jan-06	ug/l																									
Apr-06	ug/l																									
Jun-06	ug/l																									
Sep-06	ug/l																									
Dec-06	ug/l																									
Apr-07	ug/l																									
May-07	ug/l																									
Oct-07	ug/l																									
Apr-08	ug/l																									
Oct-08	ug/l																									
Jan-09	ug/l																									
Apr-09	ug/l																									
Oct-09	ug/l																									
Apr-10	ug/l																									
Jul-10	ug/l	0.64	4.7	4.6	**2210 J**	**1680 J**	**64.8**	**61**	**816 J**	**818 J**	2.72	0.73 J	2.0 J	1.25 J												
Aug-10	ug/l													3.62 J	**356**	**342 J**	**2880**	**3560**								
Sep-10	ug/l	0.79 J	5.68	5.21	**2580**	**2710**	**102**	**94.2**	**979**	**918**	1.4	1.55	2.57 J	2.4 J					**619 J**	**575**	**4280**	**4100**	**7930**	**8110**	**487**	**495**
Oct-10	ug/l														**470**	**463**	**2980**	**3120**	**700**	**672**	**5990 J**	**5860**	**6090**	**6230**	**1180**	**1090**
Apr-11	ug/l																									
Oct-11	ug/l																									
Apr-12	ug/l																									
Oct-12	ug/l	1.0 U		3.0		**2300**		**72**		**1100**		1.9		1.0		**440**		**4100**		**670**		**6200 J**		**7000**		**1600**
May-13	ug/l	1.0		3.1		**1980**		**72.8**		**1210**		1.9		1.7		**460**		**3580**		**565**		**5540**		**1090**		**1350**
Oct-13	ug/l																									
Nov-13	ug/l							**22.9**						2.0 J		**432**		**3570**						**5740**		**1530**
Feb-14	ug/l																									
Apr-14	ug/l																									
Oct-14	ug/l					**1900**		**95.6**		**861**				2.6 J				**3510**		**532**		**5380**		**5870 J**		

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Summary of Historical Arsenic Concentrations
Shepley's Hill Landfill
Devens, Massachusetts

Well ID	Total or Dissolved	SHM-11-02 (D)	SHM-11-06 (D)	PZ-12-01 (D)	PZ-12-02 (D)	PZ-12-03 (D)	PZ-12-04 (D)	PZ-12-05 (D)	PZ-12-06 (D)	PZ-12-07 (D)	PZ-12-08 (D)	PZ-12-09 (D)	PZ-12-10 (D)	SHM-13-01 (D)	SHM-13-02 (D)	SHM-13-03 (D)	SHM-13-04 (D)	SHM-13-05 (D)	SHM-13-06 (D)	SHM-13-07 (D)	SHM-13-08 (D)	SHM-13-14S (D)	SHM-13-14D (D)	SHM-13-15 (D)	EPA-PZ-2012-1A (D)	EPA-PZ-2012-1B (D)	EPA-PZ-2012-2A (D)	EPA-PZ-2012-2B (D)	EPA-PZ-2012-3A (D)	EPA-PZ-2012-3B (D)
Sample Month-Year	**Units**																													
August-91	ug/l																													
Dec-91	ug/l																													
Mar-93	ug/l																													
Jun-93	ug/l																													
Nov-96	ug/l																													
May-97	ug/l																													
Oct-97	ug/l																													
May-98	ug/l																													
Nov-98	ug/l																													
May-99	ug/l																													
Nov-99	ug/l																													
May-00	ug/l																													
Nov-00	ug/l																													
May-01	ug/l																													
Oct-01	ug/l																													
May-02	ug/l																													
Oct-02	ug/l																													
May-03	ug/l																													
Nov-03	ug/l																													
May-04	ug/l																													
Nov-04	ug/l																													
Jun-05	ug/l																													
Jan-06	ug/l																													
Apr-06	ug/l																													
Jun-06	ug/l																													
Sep-06	ug/l																													
Dec-06	ug/l																													
Apr-07	ug/l																													
May-07	ug/l																													
Oct-07	ug/l																													
Apr-08	ug/l																													
Oct-08	ug/l																													
Jan-09	ug/l																													
Apr-09	ug/l																													
Oct-09	ug/l																													
Apr-10	ug/l																													
Jul-10	ug/l																													
Aug-10	ug/l																													
Sep-10	ug/l																													
Oct-10	ug/l																													
Apr-11	ug/l																													
Oct-11	ug/l																													
Apr-12	ug/l																													
Oct-12	ug/l	7.1	**920**																											
May-13	ug/l		**1020**	**441**	**627**	**659**	**610**	**741**	**224**	**484**	1.9	1.1	0.69 J		2.5	**318**	**2060**	8.9	**3180 J**		**928**									
Oct-13	ug/l																													
Nov-13	ug/l	3.2 J	**1000**											2.2 J	2.7 J	**137**		6.8	**2540**	**1340**	**994**									
Feb-14	ug/l																					2.0 U	7.9	3.8 J						
Apr-14	ug/l	2.0 U														**120**	**61.1**		**2850**	**1280**	**1040**									
Oct-14	ug/l	2.0 U	**825**												2.6 J	**80.8**	**693**	**11**	**2360**	**962**	**978**	2.0 U	9.6	8.1	2.0 U	**160**	2.0 U	2.0 U	**21.2**	**3830**

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Summary of Historical Arsenic Concentrations
Shepley's Hill Landfill
Devens, Massachusetts

Well ID	Total or Dissolved	EPA-PZ-2012-4A (D)	EPA-PZ-2012-4B (D)	EPA-PZ-2012-5A (D)	EPA-PZ-2012-5B (D)	EPA-PZ-2012-6A (D)	EPA-PZ-2012-6B (D)	EPA-PZ-2012-7A (D)	EPA-PZ-2012-7B (D)
Sample Month-Year	**Units**								
August-91	ug/l								
Dec-91	ug/l								
Mar-93	ug/l								
Jun-93	ug/l								
Nov-96	ug/l								
May-97	ug/l								
Oct-97	ug/l								
May-98	ug/l								
Nov-98	ug/l								
May-99	ug/l								
Nov-99	ug/l								
May-00	ug/l								
Nov-00	ug/l								
May-01	ug/l								
Oct-01	ug/l								
May-02	ug/l								
Oct-02	ug/l								
May-03	ug/l								
Nov-03	ug/l								
May-04	ug/l								
Nov-04	ug/l								
Jun-05	ug/l								
Jan-06	ug/l								
Apr-06	ug/l								
Jun-06	ug/l								
Sep-06	ug/l								
Dec-06	ug/l								
Apr-07	ug/l								
May-07	ug/l								
Oct-07	ug/l								
Apr-08	ug/l								
Oct-08	ug/l								
Jan-09	ug/l								
Apr-09	ug/l								
Oct-09	ug/l								
Apr-10	ug/l								
Jul-10	ug/l								
Aug-10	ug/l								
Sep-10	ug/l								
Oct-10	ug/l								
Apr-11	ug/l								
Oct-11	ug/l								
Apr-12	ug/l								
Oct-12	ug/l								
May-13	ug/l								
Oct-13	ug/l								
Nov-13	ug/l								
Feb-14	ug/l								
Apr-14	ug/l								
Oct-14	ug/l	4.8	**2680**	2.0 U	3.2 J	2.0 U	**515**	2.0 U	**1250**

Notes:
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U - The analytes was non-detect at the reporting limit shown.

APPENDIX C
(CD)

FINAL

SITE SPECIFIC QUALITY ASSURANCE PROJECT PLAN FOR SHEPLEY'S HILL LANDFILL SUPPLEMENTAL INVESTIGATIONS, LONG-TERM MONITORING AND TREATMENT SYSTEM O&M SERVICES

FORMER FORT DEVENS ARMY INSTALLATION

DEVENS, MASSACHUSETTS

MAY 2010
UPDATED NOVEMBER 2012
UPDATED APRIL 2013

Prepared for:
U.S. Army Corp of Engineers
New England District
Concord, Massachusetts

Prepared by:
Sovereign Consulting Inc.
Contract No.: W912WJ-10-D-0003
Task Order: 0002

SOVEREIGN CONSULTING INC.

NOTICE

The United States Department of Defense, Department of the Army, funded wholly or in part the preparation of this document and work described herein under Contract No. W912WJ-10-D-0003 and Task Order 0002. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

SITE SPECIFIC QUALITY ASSURANCE PROJECT PLAN FOR SHEPLEY'S HILL LANDFILL SUPPLEMENTAL INVESTIGATIONS, LONG-TERM MONITORING AND TREATMENT SYSTEM O&M SERVICES

FORMER FORT DEVENS ARMY INSTALLATION DEVENS, MASSACHUSETTS

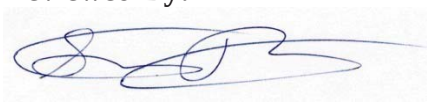
FINAL VERSION

May 2010 / Updated November 2012 and April 2013

CERTIFICATION:

I hereby certify that the enclosed report, shown and marked in this submittal, is that proposed to be incorporated with Contract Number W912WJ-10-D-0003 TO#0002. This Document was prepared in accordance with U.S. Army Corps of Engineers Scope of Work and is hereby submitted for Government Approval.

Reviewed By:



10/29/13

Sovereign Project Manager **Date**

10/29/13

Sovereign Quality Control Manager **Date**

Received By:

IORIO.MARYELLEN.1228893800

Digitally signed by IORIO.MARYELLEN.1228893800
DN: c=US, o=U.S. Government, ou=DoD, ou=PKI, ou=USA, cn=IORIO.MARYELLEN.1228893800
Date: 2013.10.29 09:11:12 -04'00'

USACE Project Manager **Date**

TABLE OF CONTENTS

ATTACHMENT

Attachment A	Accutest Laboratories and Alpha Analytical Sample Preparation and Analytical SOPs (on CD-ROM)
Attachment B	Landfill Discharge Permit

QAPP Worksheet #1
Title and Approval Page

Site Name/Project Name: Shepley's Hill Landfill Supplemental Investigations, Long-Term Monitoring and Treatment System O&M Services
Site Location: Devens, Massachusetts

Title: SHL-QAPP
Revision Number: 2

Revision Date: 04/12/13

Site Specific Quality Assurance Project Plan for Shepley's Hill Landfill Supplemental Investigations, Long-Term Monitoring, and Treatment System O&M Services
Document Title

United States Army / United States Army Corps of Engineers -NAE
Lead Organizations

Jonathan Chaffee / Sovereign Consulting Inc.
Preparer's Name and Organizational Affiliation

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Preparer's Address, Telephone Number, and E-mail Address

05/19/2010 Updated 11/07/12 and 4/12/13
Preparation Date (Day/Month/Year)

Investigative Organization's Project Manager:_____
Signature

Steven Passafaro / Sovereign Consulting
Printed Name/Organization/Date

Investigative Organization's Project QA Officer:_____
Signature

Eric Simpson / Sovereign Consulting
Printed Name/Organization/Date

Lead Organization's Project Manager:_____
Signature

Robert Simeone / United States Army
Printed Name/Organization/Date

Approval Signatures:_____
Signature

Printed Name/Title/Date

Approval Authority

Other Approval Signatures:_____
Signature

Printed Name/Title/Date

Document Control Number: SHLSOV-01

QAPP Worksheet #2
QAPP Identifying Information

Site Name/Project Name: Shepley's Hill Landfill Supplemental Investigations and Long-Term Monitoring and Treatment System O&M Services
Site Location:Devens, Massachusetts
Site Number/Code: N/A
Operable Unit: N/A
Contractor Name: Sovereign Consulting Inc.
Contractor Number: W912WJ-10-D-003
Contract Title: Shepley's Hill Landfill Supplemental Investigation
Work Assignment Number: Task 02

Title: SHL-QAPP
Revision Number: 2
Revision Date: 04/12/13
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1. Identify guidance used to prepare QAPP:

   Uniform Federal Policy for Quality Assurance Project Plans (IDQTF 2005a and 2005b)

2. Identify regulatory program: _EPA CERLA

3. Identify approval entity: United States Army

4. Indicate whether the QAPP is a generic or a **project-specific UFP-QAPP**. (underline one)

5. List dates of scoping sessions that were held: _N/A

6. List dates and titles of QAPP documents written for previous site work, if applicable:

   Title: N/A Approval Date: _N/A

7. List organizational partners (stakeholders) and connection with lead organization:_____

   USACE-NAE – Supervising Contractor; BEC – Principal field representative for responses at Devens

8. List data users: EPA, MassDEP, US Army, USACE-NAE, Sovereign Consulting Inc.

___

9. If any required QAPP elements and required information are not applicable to the project, then circle the omitted QAPP elements and required information on the attached table. Provide an explanation for their exclusion below:

   Worksheet 16 (Project Schedule / Timeline Table) – The project schedule is provided to USACE and BRAC under separate cover. Worksheet 16 is not included.

   Worksheet 22 (Field Calibration, Maintenance, Testing, and Inspection Table) – The information from Worksheet 22 is included in the Long-Term Maintenance and Monitoring Plans and Field Sampling Plans.

   Worksheet 27 (Sample Custody Requirements) -The information from Worksheets 27 is included in the Field Sampling Plan.

_____

Worksheets and/or Required Information that are not applicable to the project are highlighted and shown in ***bold italic*** print. An explanation for their omission is contained in Worksheet #2, Item 9.

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	QAPP Worksheet # or Crosswalk to Related Documents
Project Management and Objectives		
2.1 Title and Approval Page	- Title and Approval Page	1
2.2 Document Format and Table of Contents 2.2.1 Document Control Format 2.2.2 Document Control Numbering System 2.2.3 Table of Contents 2.2.4 UFP-QAPP Identifying Information	- Table of Contents - UFP-QAPP Identifying Information	2
2.3 Distribution List and Project Personnel Sign-Off Sheet 2.3.1 Distribution List 2.3.2 Project Personnel Sign-Off Sheet	- Distribution List - Project Personnel Sign-Off Sheet	3 4
2.4 Project Organization 2.4.1 Project Organizational Chart 2.4.2 Communication Pathways 2.4.3 Personnel Responsibilities and Qualifications 2.4.4 Special Training Requirements and Certification	- Project Organizational Chart - Communication Pathways - Personnel Responsibilities and Qualifications Table - Special Personnel Training Requirements Table	5 6 7 ***8***
2.5 Project Planning/Problem Definition 2.5.1 Project Planning (Scoping) 2.5.2 Problem Definition, Site History, and Background	- Project Planning Session Documentation (including Data Needs tables) - Project Scoping Session Participants Sheet - Problem Definition, Site History, and Background - Site Maps (historical and present)	 9 10
2.6 Project Quality Objectives and Measurement Performance Criteria 2.6.1 Development of Project Quality Objectives Using the Systematic Planning Process 2.6.2 Measurement Performance Criteria	- Site-Specific PQOs - Measurement Performance Criteria Table	11 12

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	QAPP Worksheet # or Crosswalk to Related Documents
2.7 Secondary Data Evaluation	- Sources of Secondary Data and Information - Secondary Data Criteria and Limitations Table	13
2.8 Project Overview and Schedule 2.8.1 Project Overview 2.8.2 Project Schedule	- Summary of Project Tasks - Reference Limits and Evaluation Table ***- Project Schedule/Timeline Table***	14 15 ***16***
Measurement/Data Acquisition		
3.1 Sampling Tasks 3.1.1 Sampling Process Design and Rationale 3.1.2 Sampling Procedures and Requirements 3.1.2.1 Sampling Collection Procedures 3.1.2.2 Sample Containers, Volume, and Preservation 3.1.2.3 Equipment/Sample Containers Cleaning and Decontamination Procedures 3.1.2.4 Field Equipment Calibration, Maintenance, Testing, and Inspection Procedures 3.1.2.5 Supply Inspection and Acceptance Procedures 3.1.2.6 Field Documentation Procedures	- Sampling Design and Rationale - Sample Location Map - Sampling Locations and Methods/ SOP Requirements Table - Analytical Methods/SOP Requirements Table - Field Quality Control Sample Summary Table - Sampling SOPs - Project Sampling SOP References Table ***- Field Equipment Calibration, Maintenance, Testing, and Inspection Table***	17 18 19 20 21 ***22***
3.2 Analytical Tasks 3.2.1 Analytical SOPs 3.2.2 Analytical Instrument Calibration Procedures 3.2.3 Analytical Instrument and Equipment Maintenance, Testing, and Inspection Procedures 3.2.4 Analytical Supply Inspection and Acceptance Procedures	- Analytical SOPs - Analytical SOP References Table - Analytical Instrument Calibration Table - Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table	 23 24 25

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	QAPP Worksheet # or Crosswalk to Related Documents
3.4 Quality Control Samples 3.4.1 Sampling Quality Control Samples 3.4.2 Analytical Quality Control Samples	- QC Samples Table - Screening/Confirmatory Analysis Decision Tree	28
3.5 Data Management Tasks 3.5.1 Project Documentation and Records 3.5.2 Data Package Deliverables 3.5.3 Data Reporting Formats 3.5.4 Data Handling and Management 3.5.5 Data Tracking and Control	- Project Documents and Records Table - Analytical Services Table - Data Management SOPs	29 30
Assessment/Oversight		
4.1 Assessments and Response Actions 4.1.1 Planned Assessments 4.1.2 Assessment Findings and Corrective Action Responses	- Assessments and Response Actions - Planned Project Assessments Table - Audit Checklists - Assessment Findings and Corrective Action Responses Table	31 32
4.2 QA Management Reports	- QA Management Reports Table	33
4.3 Final Project Report		
Data Review		
5.1 Overview		
5.2 Data Review Steps 5.2.1 Step I: Verification 5.2.2 Step II: Validation 5.2.2.1 Step IIa Validation Activities 5.2.2.2 Step IIb Validation Activities 5.2.3 Step III: Usability Assessment 5.2.3.1 Data Limitations and Actions from Usability Assessment 5.2.3.2 Activities	- Verification (Step I) Process Table - Validation (Steps IIa and IIb) Process Table - Validation (Steps IIa and IIb) Summary Table - Usability Assessment	34 35 36 37
5.3 Streamlining Data Review 5.3.1 Data Review Steps To Be Streamlined 5.3.2 Criteria for Streamlining Data Review 5.3.3 Amounts and Types of Data Appropriate for Streamlining		

Distribution List

UFP-QAPP Recipients	Title	Organization	Telephone Number	Fax Number	E-mail Address	Document Control Number
Ginny Lombardo	Project Manager	USEPA	617-918-1754	N/A	Lombardo.Ginny@epamail.epa.gov	SHL-SOV1
David Chaffin	Project Manager	MassDEP	508-792-4007	N/A	David.Chaffin@state.ma.us	SHL-SOV1
Robert Simeone	BRAC Environmental Coordinator	Devens Reserve Forces Training Area	978-796-2205	N/A	robert.j.simeone.civ@mail.mil	SHL-SOV1
Maryellen Iorio	Program Manager	USACE-NAE	978-318-8433	978-318-8614	Maryellen.Iorio@usace.army.mil	SHL-SOV1
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Eric Simpson	QA/QC Officer	Sovereign	508-339-3200	508-339-3248	esimpson@sovcon.com	SHL-SOV1
Phillip Villeneuve / Jonathan Chaffee	Field Team Leader	Sovereign	508-339-3200 413-540-0650	508-339-3248 413-540-0656	pvilleneuve@sovcon.com jchaffee@sovcon.com	SHL-SOV1
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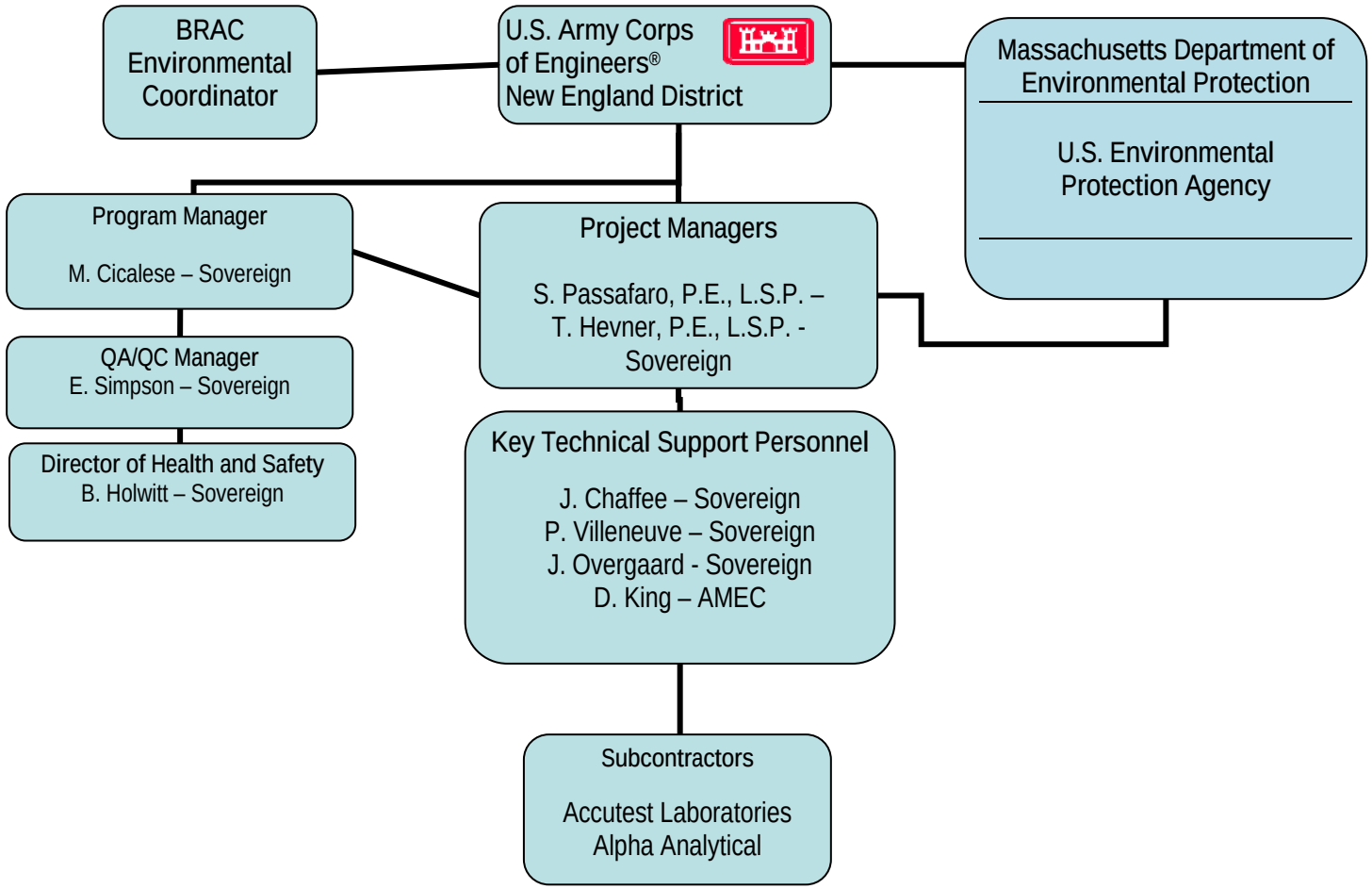
Denise King	Project Chemist	AMEC	978-692-9090	978-692-6633	denise.king@amec.com	SHL-SOV1
Frank D'Agostino	Laboratory Project Manager	Accutest Laboratories	508-481-6200	508-481-7753	frankd@accutest.com	SHL-SOV1
Katie O'Brien	Laboratory Project Manager	Alpha Analytical	508-898-9220	N/A	kobrien@alphalab.com	SHL-SOV1

Project Personnel Sign-Off Sheet

Organization: Sovereign Consulting Inc.

Project Personnel	Title	Telephone Number	Signature	Date UFP-QAPP Read
Marc Cicalese	Program Manager	973-439-5757		
Steven Passafaro	Project Manager	508-339-3200		
Eric Simpson	QA/QC Officer	508-339-3200		
Thomas Hevner	Project Manager	508-339-3200		
Phillip Villeneuve	Field Team Leader	413-540-0650		
Jonathan Chaffee	Field Team Leader	508-339-3200		
Denise King	Project Chemist	978-692-9090		
Jason Overgaard	Treatment Plant Operator	413-540-0650		

Project Organizational Chart



Communication Pathways

Communication Drivers	Responsible Entity	Name	Phone Number	Procedure (Timing, Pathways, etc.)
Manage all Project Phases	Contractor Project Manager	Steven Passafaro/Thomas Hevner	508-339-3200	Steven Passafaro / Thomas Hevner is Sovereign Consulting's liaison to Robert Simone and Maryellen Iorio
UFP-QAPP changes in the field	Field Team Leader	Jonathan Chaffee	508-339-3200	The Field Team Leader will contact Steven Passafaro with changes to UFP-QAPP in the field.
UFP-QAPP Amendments	Contractor Project Manager	Steven Passafaro	508-339-3200	Steven Passafaro will contact Robert Simone and Maryellen Iorio with any major changes the UFP-QAPP.
Daily QA/QC Reports	Field Team Leader	Phil Villeneuve Jonathan Chaffee	508-339-3200	The Field Team Leader will complete daily QA/QC Reports.
Field and Analytical Corrective Action	Contractor QA/QC Officer	Eric Simpson	508-339-3200	The need for field and analytical issue corrective actions will be determined by Eric Simpson.

Personnel Responsibilities and Qualifications Table

Name	Title	Organizational Affiliation	Responsibilities
Marc Cicalese	Program Manager	Sovereign Consulting Inc.	Program Manager
Steven Passafaro	Project Manager	Sovereign Consulting Inc.	Project Manager
Thomas Hevner	Project Manager	Sovereign Consulting Inc.	Project Manager
Eric Simpson	QA/QC Officer	Sovereign Consulting Inc.	QA/QC Officer
Phillip Villeneuve	Field Team Leader	Sovereign Consulting Inc.	Field Team Leader
Jonathan Chaffee	Field Team Leader	Sovereign Consulting Inc.	Field Team Leader
Jason Overgaard	Treatment Plant Operator	Sovereign Consulting Inc.	Treatment Plant Operator
Denise King	Project Chemist	AMEC	Project Chemist

Special Personal Training Table

Project Function	Specialized Training	Personnel Group Receiving Training	Organizational Affiliation	Location of Training Records/Certificates
Treatment Plant Operator	Grade 2 Industrial MA Wastewater Operators License	Treatment Plant Operator	Sovereign	Sovereign Human Resources departments.
Field sampling	OSHA 40 Hour HAZWOPER with annual 8 hour refreshers	All field sampling personnel	Sovereign	Sovereign Human Resources departments.
Site Supervision	OSHA 8 Hour Site Supervisor	Site Supervisor	Sovereign	Sovereign Human Resources departments.

Project Scoping Session Participants Sheet

Site Name/Project Name: Devens – Shepley's Hill Landfill/ SHL Supplemental Investigations
Site Location: Devens MA and Ayer MA
Projected Date(s) of Sampling: 6/1/10 to 10/14/10
Project Manager: Phil McBain

Date of Session: 3/18/10
Scoping Session Purpose: Discuss Investigation Scope for Pending Workplan

(a) Name	(b) Title	(c) Affiliation	(d) Phone #	(e) E-mail Address	(f) Project Role
Robert Simeone	BRAC Environmental Coordinator	USACE	978-796-2205	Robert.j.simeone.civ@mail..mil	Army BEC
Ellen Iorio	Project Manager	USACE	978-318-8433	Maryellen.Iorio@usace.army.mil	Army ETL
Ginny Lombardo Bill Brandon	Project Manger	USEPA	617-918-1754	Lombardo.ginny@epa.gov Brandon.bill@epa.gov	Regulatory Oversight
Dave Chaffin Hui Liang	Project Manager	MassDEP	508-792-4007	David.Chaffin@state.ma.us Hui.liang@state.ma.us	Regulatory Oversight
Marc Grant	Program Manager	AMEC	978-692-9090	Marc.grant@amec.com	Army Contractor
Phil McBain	Project Manager	Sovereign	508-339-3200	PMcbain@sovcon.com	Army Contractor

Comments/Decisions: Phase I investigation methods and logistics were discussed, including direct push profiling, field screening, analytical testing, and decision-making based on preliminary results

Action Items: Army will submit an addendum to the January 2010 Plan. - Completed

Consensus Decisions: There is basic agreement on the investigation approach; additional details on methods and proposed locations will be provided in the workplan addendum.

Site Name/Project Name: Devens – Shepley's Hill Landfill / North Impact Area Investigations
Site Location: Concord, MA
Projected Date(s) of Sampling: 10/12 to 06/13
Project Manager: Steven Passafaro

Date of Session: 10/11/12
Scoping Session Purpose: Discuss Investigation Scope for Pending Work Plan

(a) Name	(b) Title	(c) Affiliation	(d) Phone #	(e) E-mail Address	(f) Project Role
Robert Simeone	BRAC Environmental Coordinator	USACE	978-796-2205	Robert.j.simeone.civ@mail..mil	Army BEC
Ellen Iorio	Project Manager	USACE	978-318-8433	Maryellen.Iorio@usace.army.mil	Army ETL
Daniel Groher	Project Engineer	USACE	978-318-8059	Daniel.M.Groher@usace.army.mil	Army ETL
Mark Koenig	Project Chemist	USACE	978-318-8059	Mark.R.Koenig@usace.army.mil	Army ETL
Michael Kulbersh	Physical Scientist	USACE	978-318-8059	Michael.R.Kulbersh@usace.army.mil	Army ETL
Darrell Moore	Contract Officer	USACE	978-318-8059	Darrell.A.Moore@usace.army.mil	Army ETL
Marc Cicalese	Program Manager	Sovereign	973-439-5757	MCicalese@sovcon.com	Army Contractor
Eric Simpson	QA Supervisor	Sovereign	508-339-3200	ESimpson@sovcon.com	Army Contractor
Steven Passafaro	Project Manager	Sovereign	508-339-3200	SPassafaro@sovcon.com	Army Contractor
Phil McBain	Project Manager	Sovereign	508-339-3200	PMcbain@sovcon.com	Army Contractor

Comments/Decisions:	Investigation objectives, rationale, and methods for the North Impact Area were discussed, including direct push profiling, permanent well installation, isotope sampling, and model refinement.
Action Items:	Sovereign will submit a final outline of the proposed scope of work prior to completion of the work plan.
Consensus Decisions:	There is basic agreement on the investigation approach; additional details on methods and proposed locations will be provided in the workplan addendum.

Problem Definition

Shepley's Hill Landfill encompasses approximately 84 acres in the northeast corner of the main post of the former Fort Devens (see FSP (AMEC 2010) for site maps). The landfill is bordered to the northeast by Plow Shop Pond, to the north by Nonacoicus Brook (which drains the pond), to the west by Shepley's Hill, to the south by recent commercial development, and to the east by land formerly containing a railroad roundhouse.

The landfill was reportedly operating by the early 1900s, and evidence from test pits within the landfill suggests earlier usage, possibly as early as the mid-nineteenth century. The landfill contains a variety of waste materials, potentially including incinerator ash, demolition debris, asbestos, sanitary wastes, spent shell casings, glass, and other wastes.

The landfill was closed in five phases between 1987 and 1992-93 in accordance with Massachusetts regulations 310 CMR 19.000. The Massachusetts Department of Environmental Protection (MassDEP) approved the closure plan in 1985. Closure consisted of installing a 30-mil and 40-mil polyvinyl chloride (PVC) membrane cap, covered with soil and vegetation and incorporating gas vents. Closure also included installation of wells to monitor groundwater quality around the landfill, and construction of drainage swales to control surface water runoff. MassDEP issued a Landfill Capping Compliance Letter approving the closure in February 1996.

Subsequent to closure, remedial investigations (RIs) under CERCLA evaluated soil, sediment, surface water, and groundwater conditions at and in the immediate vicinity of the landfill. The results confirmed the presence of various contaminants, particularly certain inorganic and volatile organic compounds (VOCs), in groundwater, sediments and surface water at or adjacent to Shepley's Hill Landfill. A Feasibility Study (FS) and Record of Decision (ROD) resulted in a remedy that required long term monitoring and maintenance of the existing landfill cap and groundwater monitoring. The ROD included a contingency provision, which required that a pump and treat system be installed if groundwater contaminant concentrations (primarily arsenic) did not meet risk-based performance standards over time. Due to continued elevated contaminant concentrations, the Army installed and operates a groundwater extraction and treatment system to address groundwater contamination emanating from the northern portion of the landfill.

Project Quality Objectives/Systematic Planning Process Statements

Who will use the data? The primary data users will be USACE and the U.S. Army BRAC; the secondary users will include USEPA Region I, MADEP, MassDev, and Sovereign.
What will the data be used for? The data will be used by Sovereign to prepare Monthly Status and Quarterly Treatment System Reports, Groundwater Monitoring Reports, Annual Reports and updates to the LTMMP. USACE will use the data and the conclusions of the reports to answer environmental questions and support the project decision conditions.
What types of data are needed? (target analytes, analytical groups, field screening, on-site analytical or off-site laboratory techniques, sampling techniques) AOC-specific analytical data requirements are presented in the RLTMMP Addendum (ECC, December 2009), Work Plan for Long-Term Monitoring and Maintenance Plan (Sovereign, March 2013), and the most recent Landfill Discharge Permit (Attachment B).
How "good" do the data need to be in order to support the environmental decision? The data must be of comparable quality to the LTM Program data collected in past sampling events. The data must be of sufficient quality to support evaluation of results against the requirements of the AOC ROD and to allow for accurate evaluation of the LTM optimization options.
How much data are needed? (number of samples for each analytical group, matrix, and concentration) The groundwater monitoring well network list and frequency is included in the RLTMMP Addendum (ECC, December 2009). Other select wells to be sampled are included in the Work Plan for Long-Term Monitoring and Maintenance Plan (Sovereign, March 2013). Analyses are listed on QAPP Worksheet #19. Treatment System sampling requirements and frequencies are included in the most recent Landfill Discharge Permit (Attachment B). Analyses are listed on QAPP Worksheet #19.
Where, when, and how should the data be collected/generated? Groundwater sampling will be performed semi-annually during the Fall and Spring. General groundwater sampling procedures are presented in the RLTMMP (CH2M Hill, May 2007) and the Work Plan for Long-Term Monitoring and Maintenance Plan (Sovereign, March 2013). Treatment system effluent sampling will be conducted monthly for arsenic and quarterly and annually for other parameters as defined by the most recent Landfill Discharge Permit (Attachment B).
Who will collect and generate the data? A Sovereign field team under the supervision of the field team leader will be responsible for all groundwater sampling. A Treatment Plant Operator will be responsible for conducting all required treatment system effluent sampling. Analytical data will be generated by Alpha Analytical and Accutest Laboratories. Both laboratories are certified under the Environmental Laboratory Accreditation Program (ELAP) and compliant with the DoD QSM version 4.2.
How will the data be reported? Laboratory data will be reported in analytical packages (produced in .PDF format) that will, at a minimum, contain all necessary information to allow for validation in accordance with the EPA Region Tier II protocols. The laboratory will J qualify results down to the MDL, where applicable. The laboratory will produce SEDD Stage 2a deliverables or higher, consistent with DOD QSM valid values that have been screened against the ADR.Net project eQAPP provided by AMEC. The laboratory will provide AMEC with SEDD Stage 2a deliverables (.xml file with warning log files) that are error-free.
How will the data be archived? Complete project file records will be maintained in Sovereign's Foxboro, Massachusetts, office and AMEC's, Portland, Oregon and Westford, MA offices, and will be updated by the project administrators under the PMs' direction. Project records will be maintained during the regulatory lifespan of the contract.

Measurement Performance Criteria Table

Matrix	Treatment System Influent and Effluent
Analytical Group[1]	Metals
Laboratory	Alpha Analytical
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2&3]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	SW-846 6020A, 6010C and 7470A/L-22, L-23 and L-24	Accuracy	80%-120% Recovery	Matrix Spike/Matrix Spike Duplicates and Laboratory Control Samples	A
		Accuracy/Bias-Contamination	No target compounds ≥ ½ LOQ	Method Blanks	A
		Accuracy/Bias	Initial and continuing calibration standards within standards specified by the laboratory SOP	Initial and continuing calibration standards	A
		Precision- Overall	RPD<30% when detects for both duplicates are ≥ LOQ	Field Duplicates	S&A
		Precision- Lab	RPD < 20%	Matrix Spike/Matrix Spike Duplicate	A
		Sensitivity	Initial calibration acceptance limits specified by the DoD QSM.	LOQ set at low level calibration standard	A

Measurement Performance Criteria Table (continued)

Matrix	Treatment System Influent and Effluent
Analytical Group[1]	Metals
Laboratory	Alpha Analytical
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2&3]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	SW-846 6020A, 6010C and 7470A/L-22, L-23 and L-24	Sensitivity	Limit of Detection (LOD) must produce a response at least 3 times greater than instrument noise level	LOD studies	A
		Sensitivity	Instrument detection limit (IDL) must be ≤ LOD	IDL studies	A
		Precision- Lab	RPD < 20%	Laboratory Duplicate	A

[1]If information varies within an analytical group, separate by individual analyte.
[2]Reference number from QAPP Worksheet #23.
[3] Digestion method 3005A

Measurement Performance Criteria Table

Matrix	Groundwater
Analytical Group[1]	Metals
Laboratory	Accutest Laboratories
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2&3]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	SW-846 6020A & 6010C/ L-1 & L-13	Accuracy	80%-120% Recovery	Matrix Spike/Matrix Spike Duplicates and Laboratory Control Samples	A
		Accuracy/Bias-Contamination	No target compounds ≥ ½ LOQ	Method Blanks	A
		Accuracy/Bias	Initial and continuing calibration standards within standards specified by the laboratory SOP	Initial and continuing calibration standards	A
		Precision- Overall	RPD<30% when detects for both duplicates are ≥ LOQ	Field Duplicates	S&A
		Precision- Lab	RPD < 20%	Matrix Spike/Matrix Spike Duplicate	A
		Sensitivity	Initial calibration acceptance limits specified by the DoD QSM	LOQ set at low level calibration standard	A

Measurement Performance Criteria Table (continued)

Matrix	Groundwater
Analytical Group[1]	Metals
Laboratory	Accutest Laboratories
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2&3]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	SW-846 6020A & 6010C/ L-1 and L-13	Sensitivity	Limit of Detection (LOD) must produce a response at least 3 times greater than instrument noise level	LOD studies	A
		Sensitivity	Instrument detection limit (IDL) must be ≤ LOD	IDL studies	A
		Precision- Lab	RPD < 20%	Laboratory Duplicate	A

[1]If information varies within an analytical group, separate by individual analyte.
[2]Reference number from QAPP Worksheet #23.
[3] Digestion method 3010A

Measurement Performance Criteria Table

Matrix	Treatment System Effluent
Analytical Group[1]	Chloride
Laboratory	Alpha Analytical
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	SM4500CL E/ L-20	Accuracy	90%-110% Recovery	Laboratory Control Sample	A
		Accuracy	58%-140% Recovery	Matrix Spike/Matrix Spike Duplicates	A
		Accuracy/Bias-Contamination	No target compounds ≥ ½ LOQ	Method Blanks	A
		Accuracy/Bias	Initial and continuing calibration standards within standards specified by the laboratory SOP	Initial and continuing calibration standards	A
		Precision- Lab	RPD < 7%	Matrix Spike/Matrix Spike Duplicates	A
		Precision- Overall	RPD<30% when detects for both duplicates are ≥ LOQ for water.	Field Duplicates	S&A
		Sensitivity	Initial calibration acceptance limits specified by the laboratory SOP	LOQ set at low level calibration standard	A

Measurement Performance Criteria Table (continued)

Matrix	Treatment System Effluent
Analytical Group[1]	Chloride
Laboratory	Alpha Analytical
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	SM4500CL E/ L-20	Sensitivity	Limit of Detection (LOD) must produce a response at least 3 times greater than instrument noise level	LOD studies	A
		Precision- Lab	RPD < 7%	Laboratory Duplicate	A

[1]If information varies within an analytical group, separate by individual analyte.
[2]Reference number from QAPP Worksheet #23.

Measurement Performance Criteria Table

Matrix	Treatment System Effluent
Analytical Group[1]	Sulfate
Laboratory	Alpha Analytical
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	EPA 300.0/L-26	Accuracy	90%-110% Recovery	Laboratory Control Sample	A
		Accuracy	60%-140% Recovery	Matrix Spike/Matrix Spike Duplicates	A
		Accuracy/Bias-Contamination	No target compounds ≥ ½ LOQ	Method Blanks	A
		Accuracy/Bias	Initial and continuing calibration standards within standards specified by the laboratory SOP	Initial and continuing calibration standards	A
		Precision- Lab	RPD < 20%	Matrix Spike/Matrix Spike Duplicates	A
		Precision- Overall	RPD<30% when detects for both duplicates are ≥ LOQ for water.	Field Duplicates	S&A
		Sensitivity	Initial calibration acceptance limits specified by the laboratory SOP	LOQ set at low level calibration standard	A

Measurement Performance Criteria Table (continued)

Matrix	Treatment System Effluent
Analytical Group[1]	Sulfate
Laboratory	Alpha Analytical
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	EPA 300.0/L-26	Sensitivity	Limit of Detection (LOD) must produce a response at least 3 times greater than instrument noise level	LOD studies	A
		Precision- Lab	RPD < 20%	Laboratory Duplicate	A

[1]If information varies within an analytical group, separate by individual analyte.
[2]Reference number from QAPP Worksheet #23.

Measurement Performance Criteria Table

Matrix	Groundwater
Analytical Group[1]	Chloride
Laboratory	Accutest Laboratories
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	SM4500CL C/L-3	Accuracy	80%-120% Recovery	Laboratory Control Sample	A
		Accuracy	75%-125% Recovery	Matrix Spike/Matrix Spike Duplicates	A
		Accuracy/Bias-Contamination	No target compounds ≥ ½ LOQ	Method Blanks	A
		Accuracy/Bias	Initial and continuing calibration standards within standards specified by the laboratory SOP	Initial and continuing calibration standards	A
		Precision- Lab	RPD < 20%	Matrix Spike/Matrix Spike Duplicates	A
		Precision- Overall	RPD<30% when detects for both duplicates are ≥ LOQ for water.	Field Duplicates	S&A
		Sensitivity	Initial calibration acceptance limits specified by the laboratory SOP	LOQ set at low level calibration standard	A

Measurement Performance Criteria Table (continued)

Matrix	Groundwater
Analytical Group[1]	Chloride
Laboratory	Accutest Laboratories
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	SM4500CL C/L-3	Sensitivity	Limit of Detection (LOD) must produce a response at least 3 times greater than instrument noise level	LOD studies	A
		Precision- Lab	RPD < 20%	Laboratory Duplicate	A

[1]If information varies within an analytical group, separate by individual analyte.
[2]Reference number from QAPP Worksheet #23.

Measurement Performance Criteria Table

Matrix	Groundwater
Analytical Group[1]	Sulfate
Laboratory	Accutest Laboratories
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	EPA 300.0/L-4	Accuracy	90%-110% Recovery	Laboratory Control Sample	A
		Accuracy	80%-120% Recovery	Matrix Spike/Matrix Spike Duplicates	A
		Accuracy/Bias-Contamination	No target compounds ≥ ½ LOQ	Method Blanks	A
		Accuracy/Bias	Initial and continuing calibration standards within standards specified by the laboratory SOP	Initial and continuing calibration standards	A
		Precision- Lab	RPD < 20%	Matrix Spike/Matrix Spike Duplicates	A
		Precision- Overall	RPD<30% when detects for both duplicates are ≥ LOQ for water.	Field Duplicates	S&A
		Sensitivity	Initial calibration acceptance limits specified by the laboratory SOP	LOQ set at low level calibration standard	A

Measurement Performance Criteria Table (continued)

Matrix	Groundwater
Analytical Group[1]	Sulfate
Laboratory	Accutest Laboratories
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	EPA 300.0/L-4	Sensitivity	Limit of Detection (LOD) must produce a response at least 3 times greater than instrument noise level	LOD studies	A
		Precision- Lab	RPD < 20%	Laboratory Duplicate	A

[1]If information varies within an analytical group, separate by individual analyte.
[2]Reference number from QAPP Worksheet #23.

Measurement Performance Criteria Table

Matrix	Treatment System Effluent
Analytical Group[1]	Nitrate
Laboratory	Alpha Analytical
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	EPA 353.2/ L-25	Accuracy	90%-110% Recovery	Laboratory Control Sample	A
		Accuracy	83%-113% Recovery	Matrix Spike/Matrix Spike Duplicate	A
		Accuracy/Bias-Contamination	No target compounds ≥ ½ LOQ	Method Blanks	A
		Accuracy/Bias	Initial and continuing calibration standards within standards specified by the laboratory SOP	Initial and continuing calibration standards	A
		Precision- Overall	RPD<30% when detects for both duplicates are ≥ LOQ for water.	Field Duplicates	S&A
		Precision- Lab	RPD < 6%	Matrix Spike/Matrix Spike Duplicate	A
		Sensitivity	Initial calibration acceptance limits specified by the laboratory SOP	LOQ set at low level calibration standard	A

Measurement Performance Criteria Table (continued)

Matrix	Treatment System Effluent
Analytical Group[1]	Nitrate
Laboratory	Alpha Analytical
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	EPA 353.2/ L-25	Sensitivity	Limit of Detection (LOD) must produce a response at least 3 times greater than instrument noise level	LOD studies	A
		Precision- Lab	RPD < 6%	Laboratory Duplicate	A

[1]If information varies within an analytical group, separate by individual analyte.
[2]Reference number from QAPP Worksheet #23.

Measurement Performance Criteria Table

Matrix	Groundwater
Analytical Group[1]	Ammonia
Laboratory	Accutest Laboratories
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	SM4500NH3 BC/ L-5	Accuracy	80%-120% Recovery	Laboratory Control Sample	A
		Accuracy	75%-125% Recovery	Matrix Spike/Matrix Spike Duplicate	A
		Accuracy/Bias-Contamination	No target compounds ≥ ½ LOQ	Method Blanks	A
		Accuracy/Bias	Initial and continuing calibration standards within standards specified by the laboratory SOP	Initial and continuing calibration standards	A
		Precision- Overall	RPD<30% when detects for both duplicates are ≥ LOQ	Field Duplicates	S&A
		Precision- Lab	RPD < 20%	Matrix Spike/Matrix Spike Duplicate	A
		Sensitivity	Initial calibration acceptance limits specified by the laboratory SOP	LOQ set at low level calibration standard	A

Measurement Performance Criteria Table (continued)

Matrix	Groundwater
Analytical Group[1]	Ammonia
Laboratory	Accutest Laboratories
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	SM4500NH3 BC / L-5	Sensitivity	Limit of Detection (LOD) must produce a response at least 3 times greater than instrument noise level	LOD studies	A
		Precision- Lab	RPD < 20%	Laboratory Duplicate	A

[1]If information varies within an analytical group, separate by individual analyte.
[2]Reference number from QAPP Worksheet #23.

Measurement Performance Criteria Table

Matrix	Groundwater
Analytical Group[1]	Nitrate/Nitrite
Laboratory	Accutest Laboratories
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	EPA 353.2/ L-6	Accuracy	90%-110% Recovery	Laboratory Control Sample	A
		Accuracy	90%-110% Recovery	Matrix Spike/Matrix Spike Duplicate	A
		Accuracy/Bias-Contamination	No target compounds ≥ ½ LOQ	Method Blanks	A
		Accuracy/Bias	Initial and continuing calibration standards within standards specified by the laboratory SOP	Initial and continuing calibration standards	A
		Precision- Overall	RPD<30% when detects for both duplicates are ≥ LOQ for water.	Field Duplicates	S&A
		Precision- Lab	RPD < 10%	Matrix Spike/Matrix Spike Duplicate	A
		Sensitivity	Initial calibration acceptance limits specified by the laboratory SOP	LOQ set at low level calibration standard	A

Measurement Performance Criteria Table (continued)

Matrix	Groundwater
Analytical Group[1]	Nitrate/Nitrite
Laboratory	Accutest Laboratories
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	EPA 353.2/ L-6	Sensitivity	Limit of Detection (LOD) must produce a response at least 3 times greater than instrument noise level	LOD studies	A
		Precision- Lab	RPD < 20%	Laboratory Duplicate	A

[1]If information varies within an analytical group, separate by individual analyte.
[2]Reference number from QAPP Worksheet #23.

Measurement Performance Criteria Table

Matrix	Groundwater
Analytical Group[1]	Sulfide
Laboratory	Accutest Laboratories
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	SM4500-S^{-2} F/ L-7	Accuracy	80%-120% Recovery	Laboratory Control Sample	A
		Accuracy	75%-125% Recovery	Matrix Spike/Matrix Spike Duplicate	A
		Accuracy/Bias-Contamination	No target compounds ≥ ½ LOQ	Method Blanks	A
		Accuracy/Bias	Initial and continuing calibration standards within standards specified by the laboratory SOP	Initial and continuing calibration standards	A
		Precision- Overall	RPD<30% when detects for both duplicates are ≥ LOQ for water.	Field Duplicates	S&A
		Precision- Lab	RPD < 20%	Matrix Spike/Matrix Spike Duplicate	A
		Sensitivity	Initial calibration acceptance limits specified by the laboratory SOP	LOQ set at low level calibration standard	A

Measurement Performance Criteria Table (continued)

Matrix	Groundwater
Analytical Group[1]	Sulfide
Laboratory	Accutest Laboratories
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	SM4500-S^{-2} F/ L-7	Sensitivity	Limit of Detection (LOD) must produce a response at least 3 times greater than instrument noise level	LOD studies	A
		Precision- Lab	RPD < 20%	Laboratory Duplicate	A

[1]If information varies within an analytical group, separate by individual analyte.
[2]Reference number from QAPP Worksheet #23.

Measurement Performance Criteria Table

Matrix	Groundwater
Analytical Group[1]	Alkalinity
Laboratory	Accutest Laboratories
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	SM2320B / L-8	Accuracy	80%-120% Recovery	Laboratory Control Sample	A
		Accuracy	80%-120% Recovery	Matrix Spike/Matrix Spike	A
		Accuracy/Bias-Contamination	No target compounds ≥ ½ LOQ	Method Blanks	A
		Accuracy/Bias	Initial and continuing calibration standards within standards specified by the laboratory SOP	Initial and continuing calibration standards	A
		Precision- Overall	RPD<30% when detects for both duplicates are ≥ LOQ for water.	Field Duplicates	S&A
		Precision- Lab	RPD < 20%	Matrix Spike/Matrix Spike Duplicate	A
		Sensitivity	Initial calibration acceptance limits specified by the laboratory SOP	LOQ set at low level calibration standard	A

Measurement Performance Criteria Table (continued)

Matrix	Groundwater
Analytical Group[1]	Alkalinity
Laboratory	Accutest Laboratories
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	SM2320B / L-8	Sensitivity	Limit of detection (LOD) must produce a response at least 3 times greater than instrument noise level	LOD studies	A
		Precision- Lab	RPD < 20%	Laboratory Duplicate	A

[1]If information varies within an analytical group, separate by individual analyte.
[2]Reference number from QAPP Worksheet #23.

Measurement Performance Criteria Table

Matrix	Groundwater
Analytical Group[1]	Total Dissolved Solids
Laboratory	Accutest Laboratories
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	SM2540C / L-9	Accuracy	N/A	Laboratory Control Samples	A
		Accuracy/Bias-Contamination	No target compounds ≥ ½ LOQ	Method Blanks	A
		Accuracy/Bias	Initial and continuing calibration standards within standards specified by the laboratory SOP	Initial and continuing calibration standards	A
		Precision- Lab	N/A	Matrix Spike/Matrix Spike Duplicate	A
		Precision- Overall	RPD<30% when detects for both duplicates are ≥ LOQ for water.	Field Duplicates	S&A
		Sensitivity	Initial calibration acceptance limits specified by the laboratory SOP	LOQ set at low level calibration standard	A

Measurement Performance Criteria Table (continued)

Matrix	Groundwater
Analytical Group[1]	Total Dissolved Solids
Laboratory	Accutest Laboratories
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	SM2540C / L-9	Sensitivity	Limit of detection (LOD) must produce a response at least 3 times greater than instrument noise level	LOD studies	A
		Precision- Lab	RPD < 5%	Laboratory Duplicate	A

[1]If information varies within an analytical group, separate by individual analyte.
[2]Reference number from QAPP Worksheet #23.

Measurement Performance Criteria Table

Matrix	Groundwater
Analytical Group[1]	Total Suspended Solids
Laboratory	Accutest Laboratories
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	SM2540D / L-10	Accuracy	N/A	Matrix Spike/Matrix Spike Duplicates and Laboratory Control Samples	A
		Accuracy/Bias-Contamination	No target compounds ≥ ½ LOQ	Method Blanks	A
		Accuracy/Bias	Initial and continuing calibration standards within standards specified by the laboratory SOP	Initial and continuing calibration standards	A
		Precision- Overall	RPD<30% when detects for both duplicates are ≥ LOQ for water.	Field Duplicates	S&A
		Precision- Lab	RPD < 5%	Laboratory Duplicate	A
		Sensitivity	Initial calibration acceptance limits specified by the laboratory SOP	LOQ set at low level calibration standard	A

Measurement Performance Criteria Table (continued)

Matrix	Groundwater
Analytical Group[1]	Total Suspended Solids
Laboratory	Accutest Laboratories
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	SM2540D / L-10	Sensitivity	Limit of detection (LOD) must produce a response at least 3 times greater than instrument noise level	LOD studies	A

[1]If information varies within an analytical group, separate by individual analyte.
[2]Reference number from QAPP Worksheet #23.

Measurement Performance Criteria Table

Matrix	Groundwater
Analytical Group[1]	Total/Dissolved Organic Carbon
Laboratory	Accutest Laboratories
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	SM5310B / L-11	Accuracy	80%-120% Recovery	Laboratory Control Samples	A
		Accuracy	75%-125% Recovery	Matrix Spike/Matrix Spike Duplicates	A
		Accuracy/Bias-Contamination	No target compounds ≥ ½ LOQ	Method Blanks	A
		Accuracy/Bias	Initial and continuing calibration standards within standards specified by the laboratory SOP	Initial and continuing calibration standards	A
		Precision- Overall	RPD<30% when detects for both duplicates are ≥ LOQ for water.	Field Duplicates	S&A
		Precision- Lab	RPD < 20%	Matrix Spike/Matrix Spike Duplicate	A
		Sensitivity	Initial calibration acceptance limits specified by the laboratory SOP	LOQ set at low level calibration standard	A

Measurement Performance Criteria Table (continued)

Matrix	Groundwater
Analytical Group[1]	Total/Dissolved Organic Carbon
Laboratory	Accutest Laboratories
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	SM5310B / L-11	Sensitivity	Limit of Detection (LOD) must produce a response at least 3 times greater than instrument noise level	LOD studies	A
		Precision- Lab	RPD < 20%	Laboratory Duplicate	A

[1]If information varies within an analytical group, separate by individual analyte.
[2]Reference number from QAPP Worksheet #23.

Measurement Performance Criteria Table

Matrix	Groundwater
Analytical Group[1]	Chemical Oxygen Demand
Laboratory	Accutest Laboratories
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	SM5220C / L-12	Accuracy	80%-120% Recovery	Laboratory Control Sample	A
		Accuracy	75%-125% Recovery	Matrix Spike/Matrix Spike Duplicates	A
		Accuracy/Bias-Contamination	No target compounds ≥ ½ LOQ	Method Blanks	A
		Accuracy/Bias	Initial and continuing calibration standards within standards specified by the laboratory SOP	Initial and continuing calibration standards	A
		Precision- Overall	RPD<30% when detects for both duplicates are ≥ LOQ for water.	Field Duplicates	S&A
		Precision- Lab	RPD < 20%	Matrix Spike/Matrix Spike Duplicate	A
		Sensitivity	Initial calibration acceptance limits specified by the laboratory SOP	LOQ set at low level calibration standard	A

Measurement Performance Criteria Table (continued)

Matrix	Groundwater
Analytical Group[1]	Chemical Oxygen Demand
Laboratory	Accutest Laboratories
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	SM5220C / L-12	Sensitivity	Limit of detection (LOD) must produce a response at least 3 times greater than instrument noise level	LOD studies	A
		Precision- Lab	RPD < 20%	Laboratory Duplicate	A

[1]If information varies within an analytical group, separate by individual analyte.
[2]Reference number from QAPP Worksheet #23.

Measurement Performance Criteria Table

Matrix	Groundwater
Analytical Group[1]	Hardness
Laboratory	Accutest Laboratories
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP or FSP	SM2340C/ L-14	Accuracy	80%-120% Recovery	Matrix Spike/Matrix Spike Duplicates and Laboratory Control Samples	A
		Accuracy/Bias-Contamination	No target compounds ≥ ½ LOQ	Method Blanks	A
		Accuracy/Bias	Initial and continuing calibration standards within standards specified by the laboratory SOP	Initial and continuing calibration standards	A
		Precision- Overall	RPD<30% when detects for both duplicates are ≥ LOQ.	Field Duplicates	S&A
		Precision- Lab	RPD < 20%	Matrix Spike/Matrix Spike Duplicate and Lab Duplicate	A
		Sensitivity	Initial calibration acceptance limits specified by the laboratory SOP	LOQ set at low level calibration standard	A

[1]If information varies within an analytical group, separate by individual analyte.
[2]Reference number from QAPP Worksheet #23.

Measurement Performance Criteria Table

Matrix	Treatment System Effluent
Analytical Group[1]	Total Toxic Organics - VOCs
Laboratory	Alpha Analytical
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP	EPA 624 / L-16	Accuracy	Lab established control limits-see project EQAPP for analyte specific limits	Laboratory Control Sample	A
		Accuracy	Lab established control limits-see project EQAPP for analyte specific limits	Matrix Spike/Matrix Spike Duplicates	A
		Accuracy/Bias-Contamination	No target compounds ≥ ½ LOQ	Method Blanks	A
		Accuracy/Bias	Initial and continuing calibration standards within standards specified by the laboratory SOP	Initial and continuing calibration standards	A
		Precision- Overall	RPD<30% when detects for both duplicates are ≥ LOQ for water.	Field Duplicates	S&A
		Precision- Lab	RPD < 30%	Matrix Spike/Matrix Spike Duplicate	A
		Sensitivity	Initial calibration acceptance limits specified by the laboratory SOP	LOQ set at low level calibration standard	A

Measurement Performance Criteria Table (continued)

Matrix	Treatment System Effluent
Analytical Group[1]	Total Toxic Organics - VOCs
Laboratory	Alpha Analytical
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP	EPA 624 / L-16	Sensitivity	Limit of detection (LOD) must produce a response at least 3 times greater than instrument noise level	LOD studies	A
		Accuracy	Area counts of the internal standard peaks must be between 50-200% of the areas of the internal standards in the calibration verification standard.	Internal Standards	A
		Accuracy	80%-120% Recovery	Surrogates	A
		Precision- Lab	RPD < 30%	Laboratory Duplicate	A

[1]If information varies within an analytical group, separate by individual analyte.
[2]Reference number from QAPP Worksheet #23.

Measurement Performance Criteria Table

Matrix	Treatment System Effluent
Analytical Group[1]	Total Toxic Organics - SVOCs
Laboratory	Alpha Analytical
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP	EPA 625 / L-18	Accuracy	Lab established control limits-see project EQAPP for analyte specific limits	Laboratory Control Sample	A
		Accuracy	Lab established control limits-see project EQAPP for analyte specific limits	Matrix Spike/Matrix Spike Duplicates	A
		Accuracy/Bias-Contamination	No target compounds ≥ ½ LOQ	Method Blanks	A
		Accuracy/Bias	Initial and continuing calibration standards within standards specified by the laboratory SOP	Initial and continuing calibration standards	A
		Precision- Overall	RPD<30% when detects for both duplicates are ≥ LOQ for water.	Field Duplicates	S&A
		Precision- Lab	RPD < 30%	Matrix Spike/Matrix Spike Duplicate	A
		Sensitivity	Initial calibration acceptance limits specified by the laboratory SOP	LOQ set at low level calibration standard	A

Measurement Performance Criteria Table (continued)

Matrix	Treatment System Effluent
Analytical Group[1]	Total Toxic Organics - SVOCs
Laboratory	Alpha Analytical
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP	EPA 625 / L-18	Sensitivity	Limit of detection (LOD) must produce a response at least 3 times greater than instrument noise level	LOD studies	A
		Accuracy	Area counts of the internal standard peaks must be between 50-200% of the areas of the internal standards in the calibration verification standard.	Internal Standards	A
		Accuracy	Lab established control limits-see project EQAPP for surrogate specific limits	Surrogates	A
		Precision- Lab	RPD < 30%	Laboratory Duplicate	A

[1]If information varies within an analytical group, separate by individual analyte.
[2]Reference number from QAPP Worksheet #23.

Measurement Performance Criteria Table

Matrix	Treatment System Effluent
Analytical Group[1]	Total Toxic Organics – PCBs
Laboratory	Alpha Analytical
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP	EPA 608 / L-19	Accuracy	40%-140% Recovery	Laboratory Control Sample	A
		Accuracy	40%-140% Recovery	Matrix Spike/Matrix Spike Duplicates	A
		Accuracy/Bias-Contamination	No target compounds ≥ ½ LOQ	Method Blanks	A
		Accuracy/Bias	Initial and continuing calibration standards within standards specified by the laboratory SOP	Initial and continuing calibration standards	A
		Precision- Overall	RPD<30% when detects for both duplicates are ≥ LOQ for water.	Field Duplicates	S&A
		Precision- Lab	RPD < 50%	Matrix Spike/Matrix Spike Duplicate	A
		Sensitivity	Initial calibration acceptance limits specified by the laboratory SOP	LOQ set at low level calibration standard	A

Measurement Performance Criteria Table (continued)

Matrix	Treatment System Effluent
Analytical Group[1]	Total Toxic Organics – PCBs
Laboratory	Alpha Analytical
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP	EPA 608 / L-19	Sensitivity	Limit of detection (LOD) must produce a response at least 3 times greater than instrument noise level	LOD studies	A
		Accuracy	30%-150% Recovery	Surrogates	A
		Precision- Lab	RPD < 50%	Laboratory Duplicate	A

[1]If information varies within an analytical group, separate by individual analyte.
[2]Reference number from QAPP Worksheet #23.

Measurement Performance Criteria Table

Matrix	Treatment System Effluent
Analytical Group[1]	Total Toxic Organics – Pesticides
Laboratory	Alpha Analytical
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP	EPA 608 / L-19	Accuracy	30%-150% Recovery (no chlordane or toxaphene)	Laboratory Control Sample	A
		Accuracy	Lab established control limits-see project EQAPP for analyte specific limits	Matrix Spike/Matrix Spike Duplicates	A
		Accuracy/Bias-Contamination	No target compounds ≥ ½ LOQ	Method Blanks	A
		Accuracy/Bias	Initial and continuing calibration standards within standards specified by the laboratory SOP	Initial and continuing calibration standards	A
		Precision- Overall	RPD<30% when detects for both duplicates are ≥ LOQ for water.	Field Duplicates	S&A
		Precision- Lab	RPD < 30%	Matrix Spike/Matrix Spike Duplicate	A
		Sensitivity	Initial calibration acceptance limits specified by the laboratory SOP	LOQ set at low level calibration standard	A

Measurement Performance Criteria Table (continued)

Matrix	Treatment System Effluent
Analytical Group[1]	Total Toxic Organics – Pesticides
Laboratory	Alpha Analytical
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP	EPA 608 / L-19	Sensitivity	Limit of detection (LOD) must produce a response at least 3 times greater than instrument noise level	LOD studies	A
		Accuracy	30%-150% Recovery	Surrogates	A
		Precision- Lab	RPD < 30%	Laboratory Duplicate	A

[1]If information varies within an analytical group, separate by individual analyte.
[2]Reference number from QAPP Worksheet #23.

Measurement Performance Criteria Table

Matrix	Treatment System Effluent
Analytical Group[1]	Total Petroleum Hydrocarbons
Laboratory	Alpha Analytical
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP	EPA 1664 / L-27	Accuracy	64%-132% Recovery	Laboratory Control Sample	A
		Accuracy	64%-132% Recovery	Matrix Spike/Matrix Spike Duplicates	A
		Accuracy/Bias-Contamination	No target compounds ≥ ½ LOQ	Method Blanks	A
		Accuracy/Bias	Initial and continuing calibration standards within standards specified by the laboratory SOP	Initial and continuing calibration standards	A
		Precision- Overall	RPD<30% when detects for both duplicates are ≥ LOQ for water.	Field Duplicates	S&A
		Precision- Lab	RPD < 34%	Matrix Spike/Matrix Spike Duplicate	A
		Sensitivity	Initial calibration acceptance limits specified by the laboratory SOP	LOQ set at low level calibration standard	A

Measurement Performance Criteria Table (continued)

Matrix	Treatment System Effluent
Analytical Group[1]	Total Petroleum Hydrocarbons
Laboratory	Alpha Analytical
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP	EPA 1664 / L-27	Sensitivity	Limit of detection (LOD) must produce a response at least 3 times greater than instrument noise level	LOD studies	A
		Precision- Lab	RPD < 34%	Laboratory Duplicate	A

[1]If information varies within an analytical group, separate by individual analyte.
[2]Reference number from QAPP Worksheet #23.

Measurement Performance Criteria Table

Matrix	Treatment System Influent
Analytical Group[1]	VOCs – 8260C
Laboratory	Alpha Analytical
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP	SW-846 8260C / L-15	Accuracy	DoD QSM Limits and MCP CAM limits for Non-DoD analytes	Laboratory Control Sample	A
		Accuracy	DoD QSM Limits and MCP CAM limits for Non-DoD analytes	Matrix Spike/Matrix Spike Duplicates	A
		Accuracy/Bias-Contamination	No target compounds ≥ ½ LOQ	Method Blanks	A
		Accuracy/Bias	Initial and continuing calibration standards within standards specified by the DoD QSM	Initial and continuing calibration standards	A
		Precision- Overall	RPD<30% when detects for both duplicates are ≥ LOQ for water.	Field Duplicates	S&A
		Precision- Lab	RPD < 30%	Matrix Spike/Matrix Spike Duplicate	A
		Sensitivity	Initial calibration acceptance limits specified by the DoD QSM	LOQ set at low level calibration standard	A

Measurement Performance Criteria Table (continued)

Matrix	Treatment System Influent
Analytical Group[1]	VOCs – 8260C
Laboratory	Alpha Analytical
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP	SW-846 8260C / L-15	Accuracy	DoD QSM Limits	Surrogates	A
		Sensitivity	Limit of detection (LOD) must produce a response at least 3 times greater than instrument noise level	LOD studies	A

[1]If information varies within an analytical group, separate by individual analyte.
[2]Reference number from QAPP Worksheet #23.

Measurement Performance Criteria Table

Matrix	Treatment System Influent
Analytical Group[1]	Dissolved Gases
Laboratory	Alpha Analytical
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP	RSK-175 / L-28	Accuracy	80%-120% Recovery	Laboratory Control Sample	A
		Accuracy	80%-120% Recovery	Matrix Spike/Matrix Spike Duplicates	A
		Accuracy/Bias-Contamination	No target compounds ≥ ½ LOQ	Method Blanks	A
		Accuracy/Bias	Initial and continuing calibration standards within standards specified by the laboratory SOP	Initial and continuing calibration standards	A
		Precision- Overall	RPD<30% when detects for both duplicates are ≥ LOQ for water.	Field Duplicates	S&A
		Precision- Lab	RPD < 25%	Matrix Spike/Matrix Spike Duplicate	A
		Sensitivity	Initial calibration acceptance limits specified by the laboratory SOP	LOQ set at low level calibration standard	A

Measurement Performance Criteria Table (continued)

Matrix	Treatment System Influent
Analytical Group[1]	Dissolved Gases
Laboratory	Alpha Analytical
Concentration Level	Low

Sampling Procedure	Analytical Method/SOP[2]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
See LTMMP	RSK-175 / L-28	Sensitivity	Limit of detection (LOD) must produce a response at least 3 times greater than instrument noise level	LOD studies	A
		Precision- Lab	RPD < 25%	Laboratory Duplicate	A

[1]If information varies within an analytical group, separate by individual analyte.
[2]Reference number from QAPP Worksheet #23.

Secondary Data Criteria and Limitations Table

Secondary Data	Data Source (Originating Organization, Report Title, and Date)	Data Generator(s) (Originating Org., Data Types, Data Generation/Collection Dates)	How Data Will Be Used	Limitations on Data Use
Scope of Work Planning	AMEC Earth & Environmental Inc., Shepley's Hill Landfill Supplemental Investigation Workplan, January 2010.	N/A	Included original version of the site specific QAPP	SOPs and Laboratory standards not provided
Specifications of groundwater monitoring, landfill gas monitoring and landfill cap maintenance.	Revised Long Term Monitoring and Maintenance Plan for Shepley's Hill Landfill, Devens, Massachusetts	CH2M Hill, May 2007	To ensure project activities are in compliance with the SHLF LTM Program.	No known limitations.
Specifications of groundwater monitoring, landfill gas monitoring and landfill cap maintenance.	Revised Long Term Monitoring and Maintenance Plan Addendum for Shepley's Hill Landfill, Devens, Massachusetts	ECC, December 2009	To ensure project activities are in compliance with the SHLF LTM Program.	No known limitations.

Summary of Project Tasks

Sampling Tasks: Sampling of groundwater from network of SHLF monitoring wells and collection of groundwater profiling samples during drilling. Sampling Groundwater Treatment System influent and effluent.

Analysis Tasks: Laboratory analysis includes metals in groundwater and water quality along with other selected analysis as defined by Landfill Discharge Permit (Attachment B).

Quality Control Tasks: A set of routine quality control samples accompanies each set of samples sent to the laboratory. The type and frequency of QC is summarized in Worksheet #20.

Secondary Data: See Worksheet #13

Data Management Tasks: Electronic data deliverables (EDD) will be in the in the SEDD Stage 2a or higher format.

Documentation and Records: Data packages are tracked at the laboratory by assignment of sample delivery group (SDG) numbers. The laboratory sends PDF formats of all data packages to Sovereign. Data packages are recorded, tracked, and stored at secure on-site and off-site electronic storage locations.

Assessment/Audit Tasks: Sovereign personnel perform assessments and internal audits of sampling and analysis processes. These audits consist of systems (e.g., field sampling and laboratory inspections) and performance (e.g., analysis of QA split samples) audits. External audits of sampling procedures and laboratory processes by USACE, USEPA, or MassDEP may also be conducted.

Data Review Tasks: The Laboratory Data Consultant, Inc. (LDC) Automated Data Review software (ADR.Net) will be used to review the analytical data. The AMEC project chemist will review the ADR.Net report for all data generated for the project. The laboratory will produce SEDD Stage 2a or higher deliverables, consistent with DOD QSM valid values that have been screened against the ADR.Net project eQAPP provided by AMEC. The laboratory will provide AMEC with SEDD Stage 2a deliverables (.xml file with warning log files) that are error-free.

Reference Limits and Evaluation Table

Matrix: Treatment System Influent and Effluent
Analytical Group: Metals – SW-846 6020A (Arsenic only), 6010C, 7470A (Hg)
Laboratory: Alpha Analytical
Concentration Level: Low

Analyte	CAS Number	Discharge Limitations[3] (mg/L)	Analytical Method[1] (mg/L)		Laboratory Limits[2] (mg/L)		
			LODs	LOQs	MDLs	LODs	LOQs
Arsenic	7440-38-2	0.2	N/A	N/A	0.000161	0.0004	0.0005
Barium	7440-39-3	N/A	N/A	N/A	0.003	0.002	0.010
Cadmium	7440-43-9	0.045	N/A	N/A	0.001	0.003	0.004
Chromium	7440-47-3	0.40	N/A	N/A	0.002	0.005	0.01
Copper	7440-50-8	0.75	N/A	N/A	0.005	0.0063	0.010
Iron	7439-89-6	N/A	N/A	N/A	0.02	0.025	0.05
Lead	7439-92-1	0.20	N/A	N/A	0.003	0.010	0.010
Magnesium	7439-95-4	N/A	N/A	N/A	0.04	0.1	0.10
Manganese	7439-96-5	N/A	N/A	N/A	0.002	0.0025	0.010
Mercury	7439-97-6	0.001	N/A	0.0002	0.0000631	0.0002	0.0002
Selenium	7782-49-2	0.03	N/A	N/A	0.003	0.01	0.010
Silver	7440-22-4	0.30	N/A	N/A	0.002	0.005	0.007

N/A = Not available
[1]Analytical LODs and LOQs are those documented in validated methods.
[2]Laboratory MDLs, LODs and LOQs are the limits that the laboratory determined for the specific analytical method.
[3] Discharge Limitations are from Landfill Discharge Permit included in Attachment B.

Reference Limits and Evaluation Table

Matrix: Groundwater
Analytical Group: Metals – SW-846 6020A (arsenic only) and 6010C
Laboratory: Accutest Laboratories
Concentration Level: Low

Analyte	CAS Number	EPA MCLs[3] (ug/L)	Analytical Method[1] (ug/L)		Laboratory Limits[2] (ug/L)		
			LODs	LOQs	MDLs	LODs	LOQs
Aluminum	7429-90-5	50 (NSDWR)	N/A	N/A	40	150	200
Arsenic	7440-38-2	10	N/A	N/A	0.407	0.50	1
Calcium	7440-70-2	N/A	N/A	N/A	38	150	5,000
Chromium (total)	7440-47-3	100	N/A	N/A	1.4	5.0	10
Iron	7439-89-6	300 (NSDWR)	N/A	N/A	20	30	100
Lead	7439-92-1	15	N/A	N/A	1.7	2.5	5.0
Magnesium	7439-95-4	N/A	N/A	N/A	59	200	5,000
Manganese	7439-96-5	50 (NSDWR)	N/A	N/A	0.123	2.5	15
Nickel	7440-02-0	N/A	N/A	N/A	0.57	1.5	40
Potassium	7440-09-7	N/A	N/A	N/A	160	500	5,000
Sodium	7440-23-5	N/A	N/A	N/A	60	200	5,000

N/A = Not available
[1]Analytical LODs and LOQs are those documented in validated methods.
[2]Laboratory MDLs, LODs and LOQs are the limits that the laboratory determined for the specific analytical method.
[3]Represents the USEPA Maximum Contaminant Level (MCL) and the National Secondary Drinking Water Regulations (NSDWR).

Reference Limits and Evaluation Table

Matrix: Treatment System Effluent
Analytical Group: General Chemistry Methods
Laboratory: Alpha Analytical
Concentration Level: Low

Analyte	Reference Method	Discharge Limitations[3] (mg/L)	Analytical Method[1] (mg/L)		Laboratory Limits[2] (mg/L)		
			MDLs	LOQs	MDLs	LODs	LOQs
Chloride	SM4500Cl E	N/A	N/A	N/A	0.21	0.8	1.0
Nitrate	EPA 353.2	N/A	N/A	N/A	0.02	0.05	0.1
Sulfate	EPA 300.0	N/A	0.02	N/A	0.229	0.5	1.00
Total Petroleum Hydrocarbons	EPA 1664A	100	1.4	5.0	0.860	3	4.00

N/A = Not available
[1]Analytical LODs and LOQs are those documented in validated methods.
[2]Laboratory MDLs, LODs and LOQs are the limits that the laboratory determined for the specific analytical method.
[3] Discharge Limitations are from Landfill Discharge Permit included in Attachment B.

Reference Limits and Evaluation Table

Matrix: Groundwater
Analytical Group: Water Quality Methods
Laboratory: Accutest Laboratories
Concentration Level: Low

Analyte	Reference Method	EPA MCLs[3] (mg/L)	Analytical Method[1] (mg/L)		Laboratory Limits[2] (mg/L)		
			MDLs	LOQs	MDLs	LODs	LOQs
Chloride	SM4500Cl C	250 (NSDWR)	N/A	N/A	0.3	0.75	1.0
Nitrate/Nitrite[4]	EPA 353.2	1	N/A	N/A	0.0287	0.0794	0.11
Sulfate	EPA 300.0	250 (NSDWR)	0.02	N/A	0.034	0.50	10.0
Ammonia, Nitrogen	SM4500NH3-BC	N/A	N/A	N/A	0.029	0.083	0.1
Sulfide	SM4500S^{-2}F	N/A	N/A	N/A	0.47	1.5	2.0
Alkalinity	SM2320B	N/A	N/A	N/A	1.0	2.7	5.0
Total Dissolved Solids	SM2540C	50 (NSDWR)	N/A	N/A	3.5	8.0	10
Total Suspended Solids	SM2540D	N/A	N/A	N/A	1.7	3.0	4.0
Total/Dissolved Organic Carbon	SM5310B	N/A	N/A	1	0.23	0.78	1.0
Chemical Oxygen Demand	SM5220C	N/A	N/A	N/A	5.1	16.0	20
Hardness	SM2340C	N/A	N/A	N/A	1.2	3.0	4.0

N/A = Not available
[1]Analytical LODs and LOQs are those documented in validated methods.
[2]Laboratory MDLs, LODs and LOQs are the limits that the laboratory determined for the specific analytical method.
[3]Represents the USEPA Maximum Contaminant Level (MCL) and the National Secondary Drinking Water Regulations (NSDWR).
[4]Represents the lower of the Nitrate and Nitrite USEPA MCL.

Reference Limits and Evaluation Table

Matrix: Treatment System Effluent
Analytical Group: Total Toxic Organics - VOCs
Laboratory: Alpha Analytical
Concentration Level: Low

Analyte	CAS Number	Reference Method	Discharge Limitations[3] (ug/L)	Analytical Method[1] (ug/L)		Achievable Laboratory Limits[2] (ug/L)		
				MDLs	LOQs	MDLs	LODs	LOQs
Ethylbenzene	100-41-4	EPA 624	5,000	7.2	N/A	0.33	1	1.0
Styrene	100-42-5	EPA 624	5,000	N/A	N/A	0.30	1	1.0
cis-1,3-Dichloropropene	10061-01-5	EPA 624	5,000	5.0	N/A	0.32	1	1.5
trans-1,3-Dichloropropene	10061-02-6	EPA 624	5,000	N/A	N/A	0.30	1	1.5
1,4-Dichlorobenzene	106-46-7	EPA 624	5,000	N/A	N/A	0.85	2	5.0
Acrolein	107-02-8	EPA 624	5,000	N/A	N/A	1.9	4	8.0
1,2-Dichloroethane	107-06-2	EPA 624	5,000	2.8	N/A	0.36	1	1.5
Acrylonitrile	107-13-1	EPA 624	5,000	N/A	N/A	1.9	4	10
Vinyl Acetate	108-05-4	EPA 624	5,000	N/A	N/A	2.9	4	10
4-Methyl-2-pentanone	108-10-1	EPA 624	5,000	N/A	N/A	2.4	4	10
Toluene	108-88-3	EPA 624	5,000	6.0	N/A	0.35	1	1.0
Chlorobenzene	108-90-7	EPA 624	5,000	6.0	N/A	0.32	1	3.5
2-Chloroethyl vinyl ether	110-75-8	EPA 624	5,000	N/A	N/A	0.62	2	10
Dibromochloromethane	124-48-1	EPA 624	5,000	3.1	N/A	0.33	1	1.0
Tetrachloroethene	127-18-4	EPA 624	5,000	4.1	N/A	0.38	1	1.5
p/m-Xylene	1330-20-7P/M	EPA 624	5,000	N/A	N/A	0.66	2	2.0
Xylenes (Total)	1330-20-7TOTAL	EPA 624	5,000	N/A	N/A	0.66	2	2.0
cis-1,2-Dichloroethene	156-59-2	EPA 624	5,000	N/A	N/A	0.33	1	1.0
trans-1,2-Dichloroethene	156-60-5	EPA 624	5,000	1.6	N/A	0.34	1	1.5
1,3-Dichlorobenzene	541-73-1	EPA 624	5,000	N/A	N/A	0.93	2	5.0

Reference Limits and Evaluation Table

Matrix: Treatment System Effluent
Analytical Group: Total Toxic Organics - VOCs
Laboratory: Alpha Analytical
Concentration Level: Low

Analyte	CAS Number	Reference Method	Discharge Limitations[3] (ug/L)	Analytical Method[1] (ug/L)		Laboratory Limits[2] (ug/L)		
				MDLs	LOQs	MDLs	LODs	LOQs
Carbon Tetrachloride	56-23-5	EPA 624	5,000	2.8	N/A	0.33	1	1.0
2-Hexanone	591-78-6	EPA 624	5,000	N/A	N/A	2.5	4	10
Acetone	67-64-1	EPA 624	5,000	N/A	N/A	1.8	4	10
Chloroform	67-66-3	EPA 624	5,000	1.6	N/A	0.29	1	1.5
Benzene	71-43-2	EPA 624	5,000	4.4	N/A	0.31	1	1.0
1,1,1-Trichloroethane	71-55-6	EPA 624	5,000	3.8	N/A	0.30	1	2.0
Bromomethane	74-83-9	EPA 624	5,000	N/A	N/A	1.3	2	5.0
Chloromethane	74-87-3	EPA 624	5,000	N/A	N/A	0.89	2	10
Dibromomethane	74-95-3	EPA 624	5,000	N/A	N/A	0.175	1	1.0
Chloroethane	75-00-3	EPA 624	5,000	N/A	N/A	0.31	1	2.0
Vinyl chloride	75-01-4	EPA 624	5,000	N/A	N/A	0.30	1	2.0
Methylene Chloride	75-09-2	EPA 624	5,000	2.8	N/A	0.65	2	5.0
Carbon Disulfide	75-15-0	EPA 624	5,000	N/A	N/A	0.90	2	5.0
Bromoform	75-25-2	EPA 624	5,000	4.7	N/A	0.32	1	1.0
Bromodichloromethane	75-27-4	EPA 624	5,000	2.2	N/A	0.30	1	1.0
1,1-Dichloroethane	75-34-3	EPA 624	5,000	4.7	N/A	0.31	1	1.5
1,1-Dichloroethene	75-35-4	EPA 624	5,000	2.8	N/A	0.28	1	1.0
Trichlorofluoromethane	75-69-4	EPA 624	5,000	N/A	N/A	0.33	1	5.0
1,2-Dichloropropane	78-87-5	EPA 624	5,000	6.0	N/A	0.28	1	3.5
2-Butanone	78-93-3	EPA 624	5,000	N/A	N/A	2.2	4	10

Reference Limits and Evaluation Table

Matrix: Treatment System Effluent
Analytical Group: Total Toxic Organics - VOCs
Laboratory: Alpha Analytical
Concentration Level: Low

Analyte	CAS Number	Reference Method	Discharge Limitations[3] (ug/L)	Analytical Method[1] (ug/L)		Laboratory Limits[2] (ug/L)		
				MDLs	LOQs	MDLs	LODs	LOQs
1,1,2-Trichloroethane	79-00-5	EPA 624	5,000	5.0	N/A	0.34	1	1.5
Trichloroethene	79-01-6	EPA 624	5,000	1.9	N/A	0.33	1	1.0
1,1,2,2-Tetrachloroethane	79-34-5	EPA 624	5,000	6.9	N/A	0.35	1	1.0
o-Xylene	95-47-6	EPA 624	5,000	N/A	N/A	0.30	1	1.0
1,2-Dichlorobenzene	95-50-1	EPA 624	5,000	N/A	N/A	0.75	2	5.0

N/A = Not available
[1]Analytical LODs and LOQs are those documented in validated methods.
[2]Laboratory MDLs, LODs and LOQs are the limits that the laboratory determined for the specific analytical method.
[3] Discharge Limitations are from Landfill Discharge Permit included in Attachment B. Total toxic organics not to exceed 5,000 ug/L.

Reference Limits and Evaluation Table

Matrix: Treatment System Effluent
Analytical Group: Total Toxic Organics - PCBs
Laboratory: Alpha Analytical
Concentration Level: Low

Analyte	CAS Number	Reference Method	Discharge Limitations[3] (ug/L)	Analytical Method[1] (ug/L)		Laboratory Limits[2] (ug/L)		
				MDLs	LOQs	MDLs	LODs	LOQs
Aroclor 1016	12674-11-2	EPA 608	5,000	N/A	N/A	0.066	0.2	0.250
Aroclor 1221	11104-28-2	EPA 608	5,000	N/A	N/A	0.064	0.2	0.250
Aroclor 1232	11141-16-5	EPA 608	5,000	N/A	N/A	0.037	0.2	0.250
Aroclor 1242	53469-21-9	EPA 608	5,000	0.065	N/A	0.072	0.2	0.250
Aroclor 1248	12672-29-6	EPA 608	5,000	N/A	N/A	0.061	0.2	0.250
Aroclor 1254	11097-69-1	EPA 608	5,000	N/A	N/A	0.041	0.2	0.250
Aroclor 1260	11096-82-5	EPA 608	5,000	N/A	N/A	0.038	0.1	0.250

N/A = Not available
[1]Analytical LODs and LOQs are those documented in validated methods.
[2]Laboratory MDLs, LODs and LOQs are the limits that the laboratory determined for the specific analytical method.
[3] Discharge Limitations are from Landfill Discharge Permit included in Attachment B. Total toxic organics not to exceed 5,000 ug/L.

Reference Limits and Evaluation Table

Matrix: Treatment System Effluent
Analytical Group: Total Toxic Organics - Pesticides
Laboratory: Alpha Analytical
Concentration Level: Low

Analyte	CAS Number	Reference Method	Discharge Limitations[3] (ug/L)	Analytical Method[1] (ug/L)		Laboratory Limits[2] (ug/L)		
				MDLs	LOQs	MDLs	LODs	LOQs
Heptachlor Epoxide	1024-57-3	EPA 608	5,000	0.083	N/A	0.006	0.0195	0.020
Endosulfan Sulfate	1031-07-8	EPA 608	5,000	0.066	N/A	0.005	0.0195	0.040
Aldrin	309-00-2	EPA 608	5,000	0.004	N/A	0.003	0.0195	0.020
Alpha-BHC	319-84-6	EPA 608	5,000	0.003	N/A	0.004	0.009375	0.020
Beta-BHC	319-85-7	EPA 608	5,000	0.006	N/A	0.006	0.0195	0.020
Delta-BHC	319-86-8	EPA 608	5,000	0.004	N/A	0.003	0.009375	0.020
Endosulfan II	33213-65-9	EPA 608	5,000	0.004	N/A	0.004	0.009375	0.040
4,4-DDT	50-29-3	EPA 608	5,000	0.012	N/A	0.005	0.0195	0.040
cis-Chlordane	5103-71-9	EPA 608	5,000	N/A	N/A	0.004	0.009375	0.020
trans-Chlordane	5103-74-2	EPA 608	5,000	N/A	N/A	0.008	0.0195	0.020
Endrin Ketone	53494-70-5	EPA 608	5,000	N/A	N/A	0.005	0.0195	0.040
Chlordane	57-74-9	EPA 608	5,000	0.014	N/A	0.042	0.125	0.200
gamma-BHC (Lindane)	58-89-9	EPA 608	5,000	0.009	N/A	0.003	0.009375	0.020
Dieldrin	60-57-1	EPA 608	5,000	0.002	N/A	0.003	0.009375	0.040
Endrin	72-20-8	EPA 608	5,000	0.006	N/A	0.004	0.009375	0.040
Methoxychlor	72-43-5	EPA 608	5,000	N/A	N/A	0.006	0.0195	0.100
4,4-DDD	72-54-8	EPA 608	5,000	0.011	N/A	0.005	0.0195	0.040
4,4-DDE	72-55-9	EPA 608	5,000	0.004	N/A	0.004	0.009375	0.040
Endrin Aldehyde	7421-93-4	EPA 608	5,000	0.023	N/A	0.003	0.009375	0.040
Heptachlor	76-44-8	EPA 608	5,000	0.003	N/A	0.004	0.009375	0.020

Reference Limits and Evaluation Table

Matrix: Treatment System Effluent
Analytical Group: Total Toxic Organics - Pesticides
Laboratory: Alpha Analytical
Concentration Level: Low

Analyte	CAS Number	Reference Method	Discharge Limitations[3] (ug/L)	Analytical Method[1] (ug/L)		Laboratory Limits[2] (ug/L)		
				MDLs	LOQs	MDLs	LODs	LOQs
Toxaphene	8001-35-2	EPA 608	5,000	0.240	N/A	0.126	0.375	0.400
Endosulfan I	959-98-8	EPA 608	5,000	0.014	N/A	0.006	0.0195	0.020

N/A = Not available
[1]Analytical LODs and LOQs are those documented in validated methods.
[2]Laboratory MDLs, LODs and LOQs are the limits that the laboratory determined for the specific analytical method.
[3] Discharge Limitations are from Landfill Discharge Permit included in Attachment B. Total toxic organics not to exceed 5,000 ug/L.

Reference Limits and Evaluation Table

Matrix: Treatment System Effluent
Analytical Group: Total Toxic Organics - SVOCs
Laboratory: Alpha Analytical
Concentration Level: Low

Analyte	CAS Number	Reference Method	Discharge Limitations[3] (ug/L)	Analytical Method[1] (ug/L)		Laboratory Limits[2] (ug/L)		
				MDLs	LOQs	MDLs	LODs	LOQs
p-Nitroaniline	100-01-6	EPA 625	5,000	N/A	N/A	0.55	2	5.0
4-Nitrophenol	100-02-7	EPA 625	5,000	2.4	N/A	1.2	2	10
Benzyl alcohol	100-51-6	EPA 625	5,000	N/A	N/A	0.47	1	2.0
4-Bromophenyl phenyl ether	101-55-3	EPA 625	5,000	1.9	N/A	0.67	1	2.0
Azobenzene	103-33-3	EPA 625	5,000	N/A	N/A	0.58	1	2.0
2,4-Dimethylphenol	105-67-9	EPA 625	5,000	2.7	N/A	1.2	2	5.0
4-Chloroaniline	106-47-8	EPA 625	5,000	N/A	N/A	0.83	1	5.0
3-Methylphenol/4-methylphenol	108-39-4	EPA 625	5,000	N/A	N/A	0.47	1	5.0
Bis(2-chloroisopropyl)ether	108-60-1	EPA 625	5,000	5.7	N/A	0.50	1	2.0
Phenol	108-95-2	EPA 625	5,000	1.5	N/A	0.26	1	5.0
Bis(2-chloroethyl)ether	111-44-4	EPA 625	5,000	5.7	N/A	0.39	1	2.0
Bis(2-chloroethoxy)methane	111-91-1	EPA 625	5,000	5.3	N/A	0.40	1	5.0
Bis(2-ethylhexyl)phthalate	117-123-7	EPA 625	5,000	2.5	N/A	1.4	2	3.0
Di-n-octylphthalate	117-84-0	EPA 625	5,000	2.5	N/A	0.53	1	5.0
Hexachlorobenzene	118-74-1	EPA 625	5,000	1.9	N/A	0.65	1	2.0
Anthracene	120-12-7	EPA 625	5,000	1.9	N/A	0.47	1	2.0
1,2,4-Trichlorobenzene	120-82-1	EPA 625	5,000	1.9	N/A	0.67	1	5.0
2,4-Dichlorophenol	120-83-2	EPA 625	5,000	2.7	N/A	0.43	1	5.0
2,4-Dinitrotoluene	121-14-2	EPA 625	5,000	5.7	N/A	0.45	1	5.0
Pyrene	129-00-0	EPA 625	5,000	1.9	N/A	0.44	1	2.0

Reference Limits and Evaluation Table

Matrix: Treatment System Effluent
Analytical Group: Total Toxic Organics - SVOCs
Laboratory: Alpha Analytical
Concentration Level: Low

Analyte	CAS Number	Reference Method	Discharge Limitations[3] (ug/L)	Analytical Method[1] (ug/L)		Laboratory Limits[2] (ug/L)		
				MDLs	LOQs	MDLs	LODs	LOQs
Dimethyl phthalate	131-11-3	EPA 625	5,000	1.6	N/A	0.45	1	5.0
Dibenzofuran	132-64-9	EPA 625	5,000	N/A	N/A	0.47	1	2.0
Benzo(g,h,i)perylene	191-24-2	EPA 625	5,000	4.1	N/A	0.53	1	2.0
Indeno(1,2,3-cd)pyrene	193-39-5	EPA 625	5,000	3.7	N/A	0.48	1	2.0
Benzo(b)fluoranthene	205-99-2	EPA 625	5,000	4.8	N/A	0.48	1	2.0
Fluoranthene	206-44-0	EPA 625	5,000	2.2	N/A	0.51	1	2.0
Benzo(k)fluoranthene	207-08-9	EPA 625	5,000	2.5	N/A	0.48	1	2.0
Acenaphthylene	208-96-8	EPA 625	5,000	3.5	N/A	0.50	1	2.0
Chrysene	218-01-9	EPA 625	5,000	2.5	N/A	0.56	1	2.0
Benzo(a)pyrene	50-32-8	EPA 625	5,000	2.5	N/A	0.48	1	2.0
2,4-Dinitrophenol	51-28-5	EPA 625	5,000	42	N/A	1.4	2	20
4,6-Dinitro-2-methylphenol	534-52-1	EPA 625	5,000	24	N/A	0.59	2	10
Dibenzo(a,h)anthracene	53-70-3	EPA 625	5,000	2.5	N/A	0.48	1	2.0
Benzo(a)anthracene	56-55-3	EPA 625	5,000	7.8	N/A	0.82	1	2.0
4-Chloro-3-methylphenol	59-50-7	EPA 625	5,000	3.0	N/A	0.50	1	2.0
2,6-Dinitrotoluene	606-20-2	EPA 625	5,000	1.9	N/A	0.46	1	5.0
n-Nitrosodi-n-propylamine	621-64-7	EPA 625	5,000	N/A	N/A	0.39	1	5.0
Aniline	62-53-3	EPA 625	5,000	N/A	N/A	0.46	1	2.0
N-Nitrosodimethylamine	62-75-9	EPA 625	5,000	N/A	N/A	0.55	1	2.0
Benzoic Acid	65-85-0	EPA 625	5,000	N/A	N/A	1.0	5	50

Reference Limits and Evaluation Table

Matrix: Treatment System Effluent
Analytical Group: Total Toxic Organics - SVOCs
Laboratory: Alpha Analytical
Concentration Level: Low

Analyte	CAS Number	Reference Method	Discharge Limitations[3] (ug/L)	Analytical Method[1] (ug/L)		Laboratory Limits[2] (ug/L)		
				MDLs	LOQs	MDLs	LODs	LOQs
Hexachloroethane	67-72-1	EPA 625	5,000	1.6	N/A	0.66	1	2.0
4-Chlorophenyl phenyl ether	7005-72-3	EPA 625	5,000	4.2	N/A	0.61	1	2.0
Hexachlorocyclopentadiene	77-47-4	EPA 625	5,000	N/A	N/A	2.1	5	20
Isophorone	78-59-1	EPA 625	5,000	2.2	N/A	0.35	1	5.0
Acenaphthene	83-32-9	EPA 625	5,000	1.9	N/A	0.55	1	2.0
Diethyl phthalate	84-66-2	EPA 625	5,000	1.9	N/A	0.45	1	5.0
Di-n-butyl phthalate	84-74-2	EPA 625	5,000	2.5	N/A	0.54	1	5.0
Phenanthrene	85-01-8	EPA 625	5,000	5.4	N/A	0.49	1	2.0
Benzyl butyl phthalate	85-68-7	EPA 625	5,000	2.5	N/A	0.46	1	5.0
n-Nitrosodiphenylamine	86-30-6	EPA 625	5,000	1.9	N/A	0.70	1	2.0
Fluorene	86-73-7	EPA 625	5,000	1.9	N/A	0.49	1	2.0
Carbazole	86-74-8	EPA 625	5,000	N/A	N/A	0.53	1	2.0
Hexachlorobutadiene	87-68-3	EPA 625	5,000	0.9	N/A	0.81	1	2.0
Pentachlorophenol	87-86-5	EPA 625	5,000	3.6	N/A	1.2	2	5.0
2,4,6-Trichlorophenol	88-06-2	EPA 625	5,000	2.7	N/A	0.45	1	5.0
2-Nitroaniline	88-74-4	EPA 625	5,000	N/A	N/A	0.40	1	5.0
2-Nitrophenol	88-75-5	EPA 625	5,000	3.6	N/A	0.48	1	10
1-Methylnaphthalene	90-12-0	EPA 625	5,000	N/A	N/A	0.64	1	2.0
Naphthalene	91-20-3	EPA 625	5,000	1.6	N/A	0.72	1	2.0
2-Methylnaphthalene	91-57-6	EPA 625	5,000	N/A	N/A	0.55	1	2.0

Reference Limits and Evaluation Table

Matrix: Treatment System Effluent
Analytical Group: Total Toxic Organics - SVOCs
Laboratory: Alpha Analytical
Concentration Level: Low

Analyte	CAS Number	Reference Method	Discharge Limitations[3] (ug/L)	Analytical Method[1] (ug/L)		Laboratory Limits[2] (ug/L)		
				MDLs	LOQs	MDLs	LODs	LOQs
2-Chloronaphthalene	91-58-7	EPA 625	5,000	1.9	N/A	0.47	1	2.0
3,3'-Dichlorobenzidine	91-94-1	EPA 625	5,000	16.5	N/A	0.85	1	5.0
Benzidine	92-87-5	EPA 625	5,000	44	N/A	0.26	5	20
2-Methylphenol	95-48-7	EPA 625	5,000	N/A	N/A	0.53	1	5.0
2-Chlorophenol	95-57-8	EPA 625	5,000	3.3	N/A	0.34	1	2.0
2,4,5-Trichlorophenol	95-95-4	EPA 625	5,000	N/A	N/A	0.45	1	5.0
Nitrobenzene	98-95-3	EPA 625	5,000	1.9	N/A	0.50	1	2.0
3-Nitroaniline	99-09-2	EPA 625	5,000	N/A	N/A	0.59	1	5.0

N/A = Not available
[1]Analytical LODs and LOQs are those documented in validated methods.
[2]Laboratory MDLs, LODs and LOQs are the limits that the laboratory determined for the specific analytical method.
[3] Discharge Limitations are from Landfill Discharge Permit included in Attachment B. Total toxic organics not to exceed 5,000 ug/L.

Reference Limits and Evaluation Table

Matrix: Treatment System Influent
Analytical Group: Dissolved Gases
Laboratory: Alpha Analytical
Concentration Level: Low

Analyte	CAS Number	Reference Method	EPA MCLs[3] (ug/L)	Analytical Method[1] (ug/L)		Laboratory Limits[2] (ug/L)		
				MDLs	LOQs	MDLs	LODs	LOQs
Methane	74-82-8	RSK-175	N/A	<50	500	N/A	1	5.00
Ethane	74-84-0	RSK-175	N/A	<5	100	N/A	0.27	0.50

N/A = Not available
[1]Analytical LODs and LOQs are those documented in validated methods.
[2]Laboratory MDLs, LODs and LOQs are the limits that the laboratory determined for the specific analytical method.
[3]Represents the USEPA Maximum Contaminant Level (MCL) and the National Secondary Drinking Water Regulations (NSDWR).

Reference Limits and Evaluation Table

Matrix: Treatment System Influent
Analytical Group: VOCs
Laboratory: Alpha Analytical
Concentration Level: Low

Analyte	CAS Number	Reference Method	EPA MCLs[3] (ug/L)	Analytical Method[1] (ug/L)		Laboratory Limits[2] (ug/L)		
				MDLs	LOQs[4]	MDLs	LODs	LOQs
Ethylbenzene	100-41-4	SW846 8260C	700	N/A	0.03	0.17	0.25	1.0
Styrene	100-42-5	SW846 8260C	100	N/A	0.27	0.36	0.50	1.0
cis-1,3-Dichloropropene	10061-01-5	SW846 8260C	N/A	N/A	N/A	0.14	0.25	0.50
trans-1,3-Dichloropropene	10061-02-6	SW846 8260C	N/A	N/A	N/A	0.16	0.50	0.50
n-Propylbenzene	103-65-1	SW846 8260C	N/A	N/A	0.10	0.17	0.25	2.0
n-Butylbenzene	104-51-8	SW846 8260C	N/A	N/A	0.10	0.19	0.25	2.0
p-Chlorotoluene	106-43-4	SW846 8260C	N/A	N/A	0.06	0.18	0.25	2.0
1,4-Dichlorobenzene	106-46-7	SW846 8260C	75	N/A	0.04	0.19	0.25	1.0
1,2-Dibromoethane	106-93-4	SW846 8260C	0.05	N/A	0.10	0.19	0.50	2.0
1,2-Dichloroethane	107-06-2	SW846 8260C	5	N/A	0.02	0.13	0.25	1.0
4-Methyl-2-pentanone	108-10-1	SW846 8260C	N/A	N/A	N/A	0.42	2.00	5.0
Isopropyl ether	108-20-3	SW846 8260C	N/A	N/A	N/A	0.42	0.25	2.0
1,3,5-Trimethylbenzene	108-67-8	SW846 8260C	N/A	N/A	0.06	0.17	0.25	2.0
Bromobenzene	108-86-1	SW846 8260C	N/A	N/A	0.11	0.15	0.25	2.0
Toluene	108-88-3	SW846 8260C	1,000	N/A	0.08	0.16	0.25	1.0
Chlorobenzene	108-90-7	SW846 8260C	100	N/A	0.03	0.18	0.25	1.0
Tetrahydrofuran	109-99-9	SW846 8260C	N/A	N/A	N/A	0.83	2.00	5.0
1,2,4-Trichlorobenzene	120-82-1	SW846 8260C	70	N/A	0.20	0.22	0.25	2.0
Dibromochloromethane	124-48-1	SW846 8260C	N/A	N/A	0.07	0.15	0.50	1.0
Tetrachloroethene	127-18-4	SW846 8260C	5	N/A	0.05	0.18	0.25	1.0

Reference Limits and Evaluation Table

Matrix: Treatment System Influent
Analytical Group: VOCs
Laboratory: Alpha Analytical
Concentration Level: Low

Analyte	CAS Number	Reference Method	EPA MCLs[3] (ug/L)	Analytical Method[1] (ug/L)		Laboratory Limits[2] (ug/L)		
				MDLs	LOQs[4]	MDLs	LODs	LOQs
p/m-Xylene	1330-20-7P/M	SW846 8260C	10[5]	N/A	N/A	0.33	0.50	2.0
sec-Butylbenzene	135-98-8	SW846 8260C	N/A	N/A	0.12	0.18	0.25	2.0
1,3-Dichloropropane	142-28-9	SW846 8260C	N/A	N/A	0.08	0.21	0.25	2.0
cis-1,2-Dichloroethene	156-59-2	SW846 8260C	70	N/A	0.06	0.19	0.25	1.0
trans-1,2-Dichloroethene	156-60-5	SW846 8260C	100	N/A	N/A	0.16	0.25	1.0
Methyl tert butyl ether	1634-04-4	SW846 8260C	N/A	N/A	N/A	0.16	2.00	2.0
1,3-Dichlorobenzene	541-73-1	SW846 8260C	N/A	N/A	0.05	0.19	0.25	1.0
Carbon tetrachloride	56-23-5	SW846 8260C	5	N/A	0.02	0.13	0.50	1.0
1,1-Dichloropropene	563-58-6	SW846 8260C	N/A	N/A	0.12	0.17	0.50	2.0
2-Hexanone	591-78-6	SW846 8260C	N/A	N/A	N/A	0.51	2.00	5.0
2,2-Dichloropropane	594-20-7	SW846 8260C	N/A	N/A	0.08	0.20	2.00	2.0
Ethyl ether	60-29-7	SW846 8260C	N/A	N/A	N/A	0.13	0.50	2.0
1,1,1,2-Tetrachloroethane	630-20-6	SW846 8260C	N/A	N/A	0.07	0.16	0.50	1.0
Ethyl-tert-butyl ether	637-92-3	SW846 8260C	N/A	N/A	N/A	0.18	0.50	2.0
Acetone	67-64-1	SW846 8260C	N/A	N/A	N/A	1.4	2.00	5.0
Chloroform	67-66-3	SW846 8260C	N/A	N/A	0.04	0.16	0.25	1.0
Benzene	71-43-2	SW846 8260C	5	N/A	0.03	0.16	0.25	0.50
1,1,1-Trichloroethane	71-55-6	SW846 8260C	200	N/A	0.04	0.16	0.25	1.0
Bromomethane	74-83-9	SW846 8260C	N/A	N/A	0.03	0.26	0.50	2.0
Chloromethane	74-87-3	SW846 8260C	N/A	N/A	0.05	0.18	0.50	2.0

Reference Limits and Evaluation Table

Matrix: Treatment System Influent
Analytical Group: VOCs
Laboratory: Alpha Analytical
Concentration Level: Low

Analyte	CAS Number	Reference Method	EPA MCLs[3] (ug/L)	Analytical Method[1] (ug/L)		Laboratory Limits[2] (ug/L)		
				MDLs	LOQs[4]	MDLs	LODs	LOQs
Dibromomethane	74-95-3	SW846 8260C	N/A	N/A	0.01	0.36	0.50	2.0
Bromochloromethane	74-97-5	SW846 8260C	N/A	N/A	0.09	0.14	0.50	2.0
Chloroethane	75-00-3	SW846 8260C	N/A	N/A	N/A	0.13	0.50	2.0
Vinyl chloride	75-01-4	SW846 8260C	2	N/A	0.04	0.14	0.50	1.0
Methylene chloride	75-09-2	SW846 8260C	5	N/A	N/A	0.29	0.50	2.0
Carbon disulfide	75-15-0	SW846 8260C	N/A	N/A	N/A	0.30	0.50	2.0
Bromoform	75-25-2	SW846 8260C	N/A	N/A	0.20	0.25	0.50	2.0
Bromodichloromethane	75-27-4	SW846 8260C	N/A	N/A	0.03	0.19	0.25	1.0
1,1-Dichloroethane	75-34-3	SW846 8260C	N/A	N/A	0.03	0.15	0.25	1.0
1,1-Dichloroethene	75-35-4	SW846 8260C	7	N/A	N/A	0.14	0.50	1.0
Trichlorofluoromethane	75-69-4	SW846 8260C	N/A	N/A	N/A	0.16	0.50	2.0
Dichlorodifluoromethane	75-71-8	SW846 8260C	N/A	N/A	0.11	0.24	0.50	2.0
1,2-Dichloropropane	78-87-5	SW846 8260C	5	N/A	0.02	0.13	0.50	1.0
2-Butanone	78-93-3	SW846 8260C	N/A	N/A	N/A	1.9	2.00	5.0
1,1,2-Trichloroethane	79-00-5	SW846 8260C	5	N/A	0.08	0.14	0.50	1.0
Trichloroethene	79-01-6	SW846 8260C	5	N/A	0.02	0.17	0.25	1.0
1,1,2,2-Tetrachloroethane	79-34-5	SW846 8260C	N/A	N/A	0.20	0.14	0.25	1.0
1,2,3-Trichlorobenzene	87-61-6	SW846 8260C	N/A	N/A	0.14	0.23	0.25	2.0
Hexachlorobutadiene	87-68-3	SW846 8260C	N/A	N/A	0.10	0.22	0.50	0.60
Naphthalene	91-20-3	SW846 8260C	N/A	N/A	0.10	0.22	0.25	2.0

Reference Limits and Evaluation Table

Matrix: Treatment System Influent
Analytical Group: VOCs
Laboratory: Alpha Analytical
Concentration Level: Low

Analyte	CAS Number	Reference Method	EPA MCLs[3] (ug/L)	Analytical Method[1] (ug/L)		Laboratory Limits[2] (ug/L)		
				MDLs	LOQs[4]	MDLs	LODs	LOQs
o-Xylene	95-47-6	SW846 8260C	10[5]	N/A	0.06	0.33	0.50	1.0
o-Chlorotoluene	95-49-8	SW846 8260C	N/A	N/A	0.08	0.17	0.25	2.0
1,2-Dichlorobenzene	95-50-1	SW846 8260C	600	N/A	0.05	0.18	0.25	1.0
1,2,4-Trimethylbenzene	95-63-6	SW846 8260C	N/A	N/A	0.09	0.19	0.25	2.0
1,2-Dibromo-3-chloropropane	96-12-8	SW846 8260C	0.2	N/A	0.50	0.33	2.00	2.0
1,2,3-Trichloropropane	96-18-4	SW846 8260C	N/A	N/A	0.09	0.18	0.50	2.0
tert-Butylbenzene	98-06-6	SW846 8260C	N/A	N/A	0.33	0.18	0.25	2.0
Isopropylbenzene	98-82-8	SW846 8260C	N/A	N/A	0.10	0.19	0.25	2.0
Tertiary-amyl methyl ether	994-05-8	SW846 8260C	N/A	N/A	N/A	0.28	0.50	2.0
p-Isopropyltoluene	99-87-6	SW846 8260C	N/A	N/A	0.26	0.19	0.25	2.0
1,4-Dioxane	123-91-1	SW846 8260C	N/A	N/A	N/A	41	200	250

N/A = Not available
[1]Analytical LODs and LOQs are those documented in validated methods.
[2]Laboratory MDLs, LODs and LOQs are the limits that the laboratory determined for the specific analytical method.
[3]Represents the USEPA Maximum Contaminant Level (MCL) the National Secondary Drinking Water Regulations (NSDWR).
[4] Analytical LOQs are based on narrow-bore capillary column with 25-ml sample volume.
[5] Represents the EPA MCL for total xylenes.

Sampling Design and Rationale

Describe and provide a rationale for choosing the sampling approach (e.g., grid system, biased statistical approach): The sampling approach for Supplemental Investigations, LTM and O&M of the SHLF is based on historical data and the hydrologic monitoring and modeling to provide representative samples for assessment of remedial effectiveness. Recommendations relating to improvements of optimization of monitoring or treatment plant/well field operations will be made in annual reports and updates to the LTMMP. Five year reviews will continue to be conducted to evaluate the remedies in a comprehensive manner. In addition, to format reviews, the well field/treatment system contractor will be providing the BRAC and USACE with regular updates concerning the operations of the system.
Describe the sampling design and rationale in terms of what matrices will be sampled, what analytical groups will be analyzed and at what concentration levels, the sampling locations (including QC, critical, and background samples), the number of samples to be taken, and the sampling frequency (including seasonal considerations): The groundwater monitoring well network, well descriptions and sampling frequencies are included in the RLTMMP (CH2M Hill, May 2007), the RLTMMP Addendum (ECC, December 2009), and the Work Plan for Long-Term Monitoring and Maintenance Plan (Sovereign, March 2013). Treatment system sampling will be performed at sample location and at frequencies established in the most recent Landfill Discharge Permit (Attachment B).

Sampling Locations and Methods/SOPs Requirements

The current groundwater sample monitoring network is provided included in the RLTMMP Addendum (ECC, December 2009). Groundwater sampling procedures are discussed in Section 3.6 of the RLTMMP (CH2M HILL; May 2007). In addition, other select monitoring wells to be sampled along with profiling sample locations are detailed in the Work Plan for Long-Term Monitoring and Maintenance Plan (Sovereign, March 2013). All groundwater samples from monitoring wells will be collected following the EPA Region 1 guidance, "*Low Stress (low flow) Purging and Sampling Procedure for the Collection of Groundwater Samples from Monitoring Wells*" (EPA, July 30,1996 Revised January 19, 2010). Treatment System Monitoring requirements and procedures are included in the Landfill Discharge Permit (Attachment B).

UFP-QAPP Worksheet #19
Analytical SOP Requirements Table

Matrix	Analytical Group	Analytical and Preparation Method / SOP Reference	Container Type[1]	Sample Container Size[2]	Preservation Requirements	Maximum Holding Time
Groundwater	Metals	EPA 3010A - 6020A & 6010C / L-1, L-2 & L-13	P	500 mL	Nitric acid to pH <2	180 days from sampling to analysis
Groundwater	Chloride	SM4500Cl C / L-3	P	250 mL	Cool ≤6°C	28 days from sampling to analysis
Groundwater	Sulfate	EPA 300.0 / L-4	P	250 mL	Cool ≤6°C	28 days from sampling to analysis
Groundwater	Ammonia	SM4500NH3 BC / L-5	P	500 mL	Sulfuric acid to pH <2; Cool ≤6°C	28 days from sampling to analysis
Groundwater	Nitrate/Nitrite	EPA 353.2 / L-6	P	250 mL	Sulfuric acid to pH <2; Cool ≤6°C	28 days from sampling to analysis
Groundwater	Sulfide	SM4500-S-2 F / L-7	P	250 mL	Zinc acetate and NaOH, no headspace; Cool ≤6°C	7 days from sampling to analysis
Groundwater	Alkalinity	SM2320B / L-8	P	250 mL	Cool ≤6°C, no headspace	14 days from sampling to analysis
Groundwater	Total Dissolved Solids (TDS)	SM2540C / L-9	P	1 liter	Cool ≤6°C	7 days from sampling to analysis
Groundwater	Total Suspended Solids (TSS)	SM2540D / L10	P	1 liter	Cool ≤6°C	7 days from sampling to analysis
Groundwater	Total/Dissolved Organic Carbon (TOC/DOC)	SM5310B / L-11	G	2 - 40 mL vials	Sulfuric acid to pH <2; Cool ≤6°C	28 days from sampling to analysis
Groundwater	Chemical Oxygen Demand (COD)	SM5220C / L-12	P	250 mL	Sulfuric acid to pH <2, Cool ≤6°C	28 days from sampling to analysis

UFP-QAPP Worksheet #19
Analytical SOP Requirements Table

Matrix	Analytical Group	Analytical and Preparation Method / SOP Reference	Container Type[1]	Sample Container Size[2]	Preservation Requirements	Maximum Holding Time
Groundwater	Hardness	SM2340C / L-14	P	Combined with metals analysis	Nitric acid to pH <2	180 days from sampling to analysis
System Influent	VOCs	SW-846 8260 / L-15	G	2 - 40 mL vials	Hydrochloric acid to pH <2, Cool ≤6°C	14 days from sampling to analysis
System Influent	Dissolved Gases	RSK-175 / L-28	G	2 - 40 mL vials	Hydrochloric acid to pH <2, Cool ≤6°C	14 days from sampling to analysis
System Effluent	Metals	EPA 3005A - 6020A, 6010C & 7470A / L-21, L-22, L-23 & L-24	P	500 mL	Nitric acid to pH <2	28 days from sampling to analysis for mercury and 180 days from sampling to analysis for all other metals
System Effluent	VOCs	EPA 624 / L-16	G	2 - 40 mL vials	Na2S2O3, Cool ≤6°C	3 days from sampling to analysis
System Effluent	SVOCs	SW-846 3510C - EPA 625 / L-17 & L-18	G	2 - 1000 mL vials	Na2S2O3, Cool ≤6°C	7 days from extraction
System Effluent	Pest/PCBs	SW-846 3510C - EPA 608 / L-17 & L-19	G	2 - 1000 mL vials	Na2S2O3, Cool ≤6°C	7 days from extraction
System Effluent	TPH	EPA 1664 / L-27	G	2 - 1000 mL vials	Hydrochloric acid to pH <2, Cool ≤6°C	28 days from sampling to analysis
System Effluent	Nitrate	EPA 353.2 / L-25	P	250 mL	Cool ≤6°C	48 hours from sampling to analysis
System Effluent	Chloride	SM4500Cl E / L-20	P	250 mL	Cool ≤6°C	28 days from sampling to analysis
System Effluent	Sulfate	EPA 300.0 / L-26	P	250 mL	Cool ≤6°C	28 days from sampling to analysis

[1]G = Glass, amber; P = Polyethylene.
[2] In some cases, multiple sample analyses can be combined into one sample container.

Field Quality Control Sample Summary Table

Medium/ Matrix	Analytical Parameter	Conc. Level	Analytical Method	No. of Sampling Locations	No. of Field Duplicates	Inorganic		No. of Field Blanks	No. of Equip. Blanks	No. of QA Split Samples[1]	Total No. of Samples to Lab [2]
						No. of MSD	No. of MS				
CHEMICAL ANALYSES											
Groundwater - Monitoring Wells											
Groundwater	Dissolved Metals [3]	Low	6020A / 6010C	TBD	1/10	1/20	1/20	None Proposed	1/Day	None Proposed	TBD
Groundwater	Water Quality	Low	WQ Suite [4]	TBD	1/10	1/20	1/20[5]	None Proposed	1/Day	None Proposed	TBD
Groundwater Profiles											
Groundwater	Dissolved Arsenic Profile	Low	6020A	TBD	1/10	1/20	1/20	None Proposed	1/Day	None Proposed	TBD

Notes:
MS = Matrix spike
MSD = Matrix spike duplicate

[1] Quality Assurance (QA) split samples (samples sent to a government designated independent testing laboratory) will be collected if directed by USACE-NAE, USEPA, or MassDEP.

[2] Total number of samples to lab consists of: number of sampling locations + number of field duplicate pairs + number of MS/MSD + number of equipment blanks.

[3] Metals lists include: arsenic, calcium, iron, magnesium , manganese, sodium , and potassium .

[4] Water Quality (WQ) suite includes: Chloride by Method 4500Cl C; sulfate by EPA 300.0; ammonia by Method SM4500NH3-BC; nitrate/nitrite by EPA 353.2; sulfide by SM4500S^2F; alkalinity by SM2320B; total dissolved solids by SM2540C; total suspended solids by SM2540D; total/dissolved organic carbon by SM5310B; chemical oxygen demand by SM5220C; and hardness by SM2340C.

[5] Matrix spike samples are applicable to all analyses except TDS and TSS.

Project Sampling SOP References Table

Reference Number	Title, Revision Date, and/or Number	Originating Organization	Equipment Type	Modified for Project Work? (Y/N)	Comments
SOP #2044	Monitor Well Development 23 October 2001	EPA	See SOP	N	None
SOP #2043	Manual Water Level Measurements 11 February 2000	EPA	See SOP	N	None
SOP #2016	Sediment Sampling 17 November 1994	EPA	See SOP	N	None
SOP #2013	Surface Water Sampling 17 November 1994	EPA	See SOP	N	None
SOP #2006	Sampling Equipment Decontamination	EPA	See SOP	N	None
SOP #2048	Monitor Well Installation 18 March 1996	EPA	See SOP	N	None
EQASOP-GW 001	Low Stress (Low Flow) Purging and Sampling Procedures for the Collection of Groundwater Samples from Monitoring Wells (Revision 3) 19 January 2010	EPA	See SOP	N	None

Analytical SOP References Table

Reference Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
L-1	Metals by Inductively Coupled Plasma – Mass Spectrometry – ref. method SW846 6020A, Revision 1, February 2007, Revision date March 21, 2013	Definitive	Metals	ICP-MS	Accutest	N
L-2	Digestion of Non-Potable Waters for Flame and ICP Analysis Including Antimony (Sb) – ref. method SW846 3010A Rev. 1 July 1992, Revision date March 21, 2013	Digestion	Metals	Hot Plate or Digestion Block	Accutest	N

Reference Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
L-3	Chloride, ref. method 4500Cl C, Revision date December 21, 2010	Definitive	Chloride	Titration	Accutest	N
L-4	Determination of Inorganic Anions by Ion Chromatography Using the IC2000, ref. method: EPA 300.0, SW846 9056A, Revision date July 18, 2011	Definitive	Sulfate	Ion Chromatograph	Accutest	N
L-5	Total Nitrogen, Ammonia,– ref. method SM 4500NH3B&C, Revision date October 28, 2011	Definitive	Ammonia	Spectrophotometer	Accutest	N

Reference Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
L-6	Nitrate/Nitrite and Nitrate only by Cadmium Reduction Analysis (Lachat Autoanalyzer)– ref. method 353.2 Rev. 2.0, Revision date April 4, 2013	Definitive	Nitrate/Nitrite	Lachat Auto Analyzer	Accutest	N
L-7	Sulfide- ref. 4500-S F, Revision date April 4, 2013	Definitive	Sulfide	Titration	Accutest	N
L-8	Alkalinity, Total (pH 4.5) – ref. method SM2320B, Revision date April 4, 2013	Definitive	Alkalinity	Titration	Accutest	N
L-9	Total Dissolved Solids (Total Filterable Residue) – ref. method SM2540C, Revision date October 28, 2011	Definitive	Total Dissolved Solids	Gravimetric	Accutest	N

Reference Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
L-10	Total Suspended Solids (Non-Filterable Residue), - ref. method SM2540D, Revision date October 27, 2011	Definitive	Total Suspended Solids	Gravimetric	Accutest	N
L-11	Total Organic Carbon in Aqueous Samples – ref method SW846 9060A Modified and SM5310B, Revision date October 25, 2012	Definitive	Total/Dissolved Organic Carbon	Infrared	Accutest	N
L-12	Chemical Oxygen Demand – ref. method SM5220C, Revision date April 4, 2013	Definitive	Chemical Oxygen Demand	Titration	Accutest	N

Reference Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
L-13	Metals by Inductively Coupled Plasma Atomic Emission Spectrometry – ref. method SW846 6010C, Revision date February 21, 2013	Definitive	Metals	ICP-AES	Accutest	N
L-14	Hardness as CaCO3 – ref method SM2340C, Revision date April 43, 2013	Definitive	Hardness	Titration	Accutest	N
L-15	Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS); Method SW-8260C; ID No.: 2108, Revision 6, 11/07/2012	Definitive	VOCs	GC/MS	Alpha	N
L-16	Volatile Organic Compounds – Non Potable Water; Method EPA 624; ID No.: 2022, Revision 5, 03/15/2013	Definitive	VOCs	GC/MS	Alpha	N

Reference Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
L-17	Separatory Funnel Liquid – Liquid Extraction; EPA Method 3510C; ID No.: 1948, Revision 5, 1/15/2013	NA	SVOCs, Pesticides & PCBs	NA	Alpha	N
L-18	Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS); Method EPA 625; ID No.: 2110, Revision 3, 11/30/2012	Definitive	SVOCs	GC/MS	Alpha	N
L-19	Organochlorine Pesticides and PCBs by Capillary Column Gas Chromatography; Method 608; ID No.: 2122, Revision 4, 11/28/2012	Definitive	Pesticides & PCBs	GC/electron capture detector (ECD)	Alpha	N
L-20	Chloride; Method SM 4500Cl-E; ID No: 2216, Revision 4, 1/8/2013	NA	Chloride	Lachat Auto Analyzer	Alpha	N

Reference Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
L-21	Hot Block Digestion for Aqueous Samples; Method 3005A, ID No.: 2134, Revision 2, 3/26/2012	NA	Metals	Hot Block	Alpha	N
L-22	Inductively Coupled Plasma – Atomic Emission Spectrometry; Method 6010C; ID No.: 2144, Revision 2, 4/18/2012	Definitive	Metals	ICP-AES	Alpha	N
L-23	Inductively Coupled Plasma – Mass Spectrometry; Method 6020A; ID No.: 2156, Revision 3, 8/2/2012	Definitive	Metals	ICP-MS	Alpha	N
L-24	Mercury in Liquid Waste (Automated Cold-Vapor Technique); Method EPA 7470A; ID No.: 2145, Revision 2, 4/18/2012	Definitive	Metals	Cold vapor-atomic absorption (CVAA)	Alpha	N

Reference Number	Title, Revision Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
L-25	Nitrate, Nitrite and Nitrate/Nitrite Nitrogen; Method 353.2; ID No.: 2217, Revision 4, 1/16/13	Definitive	General Chemistry	Lachat Auto Analyzer	Alpha	N
L-26	Determination of Inorganic Anions by Ion Chromatography; Method 300.0; ID No.: 2214, Revision 3, 10/4/12	Definitive	General Chemistry	IC	Alpha	N
L-27	Oil and Grease; Total Petroleum Hydrocarbons by n-Hexane Extraction and Gravimetric Method; Method 1664A; ID No.: 2209, Revision 5, 2/7/13	Definitive	General Chemistry	Solid Phase Extraction (SPE) System	Alpha	N
L-28	Dissolved Gases; EPA SOP RSK-175; ID No.: 2189, Revision 3, 8/2/12	Definitive	Organics	GC/flame ionization detector (FID) – thermal conductivity detector (TCD)	Alpha	N

Analytical Instrument Calibration Table

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
ICP-AES	Metals	Initial: daily;	Initial: r ≥ 0.995;	Perform maintenance, Recalibrate, Prepare new standards; Reanalyze impacted samples	Analyst	L-13 & L-22
		Second Source Calibration Verification (ICV): after each ICAL	ICV: %D ± 10%			
		Continuing Calibration Verification (CCV): After every 10 samples	CCV: %D ± 10%			
		Low level: daily, after initial	Low level: %D ± 20%			
ICP-MS	Metals	Initial: daily;	Initial: r ≥ 0.995	Perform maintenance, Recalibrate, Prepare new standards; Reanalyze impacted samples	Analyst	L-1 & L-23
		ICV: After each ICAL	ICV: %D ± 10%			
		CCV: After every 10 samples	CCV: %D ± 10%			
		Low level: daily, after initial	Low level: %D ± 20%			
CVAA	Mercury	Initial: daily;	Initial: r ≥ 0.995;	Perform maintenance, Recalibrate, Prepare new standards; Reanalyze impacted samples	Analyst	L-24
		ICV: daily, after initial	ICV: %D ± 10%			
		CCV: After every 10 samples	CCV: %D ± 20%			

Analytical Instrument Calibration Table

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
GC/MS	VOCs	Initial: Prior to sample analysis, min. 5-point ICAL;	Initial: $r \geq 0.995$ or other options identified in DoD QSM	Perform maintenance, Recalibrate, Prepare new standards;	Analyst	L-15 & L-16
		ICV: After each ICAL	ICV: %D ± 20%			
		CCV: Daily before sample analysis and every 12 hours	CCV: %D ± 20%	Reanalyze impacted samples		
GC/MS	SVOCs	Initial: Prior to sample analysis, min. 5-point ICAL;	Initial: $r \geq 0.995$;	Perform maintenance, Recalibrate, Prepare new standards;	Analyst	L-18
		ICV: After each ICAL	ICV: %D ± 20%			
		CCV: Daily before sample analysis and every 12 hours	CCV: %D ± 20%	Reanalyze impacted samples		

Analytical Instrument Calibration Table

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
GC/ECD	Pesticides & PCBs	Initial: Prior to sample analysis, min. 3-point ICAL;	Initial: r ≥ 0.995	Perform maintenance, Recalibrate, Prepare new standards; Reanalyze impacted samples	Analyst	L-19
		ICV: After each ICAL	ICV: %D ± 15%			
		CCV: Daily before sample analysis and every 12 hours	CCV: %D ± 15%			
GC/FID/TCD	Dissolved Gases	Initial: Prior to sample analysis, min. 5-point ICAL;	Initial: r ≥ 0.995;	Perform maintenance, Recalibrate, Prepare new standards; Reanalyze impacted samples	Analyst	L-28
		ICV: After each ICAL	ICV: %D ± 20%			
		CCV: Daily before and after sample analysis and after every 10 samples	CCV: %D ± 20%			
IC	Sulfate	Initial: Prior to sample analysis, min. 3-point ICAL;	Initial: r ≥ 0.995;	Perform maintenance, Recalibrate, Prepare new standards; Reanalyze impacted samples	Analyst	L-4 & L-26
		ICV: After each ICAL	ICV: %D ± 10%			
		CCV: Daily before and after sample analysis and after every 10 samples	CCV: %D ± 10%			

[1]See Analytical SOP References table (Worksheet #23).

Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table

Instrument/ Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
ICP-AES	Check pump tubing	NA		Daily	No defects	Record all actions, inspect system, clean and/or correct problem	Analyst	L-13 & L-22
	Check the filter and power supply vents	NA		Weekly	Filters and vents not clogged			
	Check the nebulizer, torch, and injector tube	NA		Weekly	No issues			
	Clean the pump	NA		Monthly	No issues			
	Change the sampler tip	NA		Monthly or as needed	No defects			
	Check the re-circulating pump lines.	NA		As needed	No defects			
ICP-MS	Check pump tubing	NA		Daily	No defects	Record all actions, inspect system, clean and/or correct problem	Analyst	L-1 & L-23
	Check the nebulizer, torch, and injector tube	NA		Weekly	No issues			
	Change the sampler tip	NA		Monthly or as needed	No defects			
	Check the re-circulating pump lines.	NA		As needed	No defects			
	Clean the slides on the autosampler	NA		Daily	No defects			

Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table

Instrument/ Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
CVAA	Check lines	NA		Daily	No defects	Record all actions, inspect system, clean and/or correct problem	Analyst	L-24
	Clean absorption cell	NA		Daily	No issues			
	Clean the pump	NA		Monthly or as needed	No issues			
GC/MS	Check Instrument tune (BFB for VOCs and DFTPP for SVOCs)	NA		Daily	No defects	Record all actions, inspect system, clean and/or correct problem	Analyst	L-15, L-16 & L-18
	Check gas pressure and supply	NA		Daily	No issues			
	Bake out trap and column, manual tune if not in criteria, change septa as needed, cut column (watch for jagged column edge), change trap as necessary.	NA		Monthly or as needed	No defects			

[1]See Analytical SOP References table (Worksheet #23).

Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table

Instrument/ Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
GC/ECD	Check pressure and gas supply	NA		Daily	No defects	Record all actions, inspect system, clean and/or correct problem	Analyst	L-19
	Clean and / or replace the detector	NA		As needed	No issues			
	Change septa and/or liner as needed, replace or cut column	NA		As needed	No issues			
GC/FID/TCD	Check pressure and gas supply	NA		Daily	No defects	Record all actions, inspect system, clean and/or correct problem	Analyst	L-28
	Check Liner, seal, septum, and column	NA		Daily	No issues			
	Change septa and/or liner as needed, replace or cut column as needed.	NA		As needed	No defects			
IC	Check gas supply	NA		Daily	No issues	Record all actions, inspect system, clean and/or correct problem	Analyst	L-4 & L-26
	Check pistons	NA		Daily	No issues			
	Replace column	NA		As needed	No defects			

[1]See Analytical SOP References table (Worksheet #23).

Sample Handling System

SAMPLE COLLECTION, PACKAGING, AND SHIPMENT
Sample Collection (Personnel/Organization): Sovereign field personnel
Sample Packaging (Personnel/Organization): Sovereign field personnel
Coordination of Shipment (Personnel/Organization): Sovereign field personnel
Type of Shipment/Carrier: Federal Express or courier
SAMPLE RECEIPT AND ANALYSIS
Sample Receipt (Personnel/Organization): Sample custodian/Accutest Laboratories or Alpha Analytical
Sample Custody and Storage (Personnel/Organization): Sample custodian/Accutest Laboratories or Alpha Analytical
Sample Preparation (Personnel/Organization): Sample preparation technician/Accutest Laboratories or Alpha Analytical
Sample Determinative Analysis (Personnel/Organization): Analyst/Accutest Laboratories or Alpha Analytical
SAMPLE ARCHIVING
Field Sample Storage (No. of days from sample collection): Sixty days from data reporting, approximately 90 days from sample collection.
Sample Extract/Digestate Storage (No. of days from extraction/digestion): Six months from data reporting, approximately 7 months from sample collection.
Biological Sample Storage (No. of days from sample collection): NA
SAMPLE DISPOSAL
Personnel/Organization: Contract laboratories or other arrangements, as necessary (i.e., return to Sovereign for disposal)
Number of Days from Analysis: Sixty days

Field QC Samples Table

Matrix	GW
Analytical Group	All
Concentration Level	Low
Sampling SOP	See FSPs
Analytical Method/ SOP Reference	See Worksheet 23
Sampler's Name	Field Personnel
Field Sampling Organization	Sovereign
Analytical Organization	Accutest Laboratories
No. of Sample Locations	TBD

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Equipment Blanks/ Rinsate Blanks	Each day that decontamination is performed per equipment type	No target compounds ≥ LOQ	Resample and/or qualify data	Field Sampler and Data Validator	Accuracy/bias-Contamination	No target compounds ≥ LOQ
Cooler Temperature Blanks	Cooler temperature blanks are not used. However, cooler temperatures are measured using an infrared temperature gun, or equivalent	4^0C, ± 2^0C, or as stated in Worksheet #19	Resample and/or qualify data	Field Sampler and Data Validator	Accuracy/bias-Preservation	4^0C, ± 2^0C, or as stated in Worksheet #19

Field QC Samples Table (continued)

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field Duplicates	1/10	30% difference	Resample and/or qualify data	Field Sampler and Data Validator	Precision	30% difference
Matrix Spike Duplicate	1/20	See Worksheet 12	Reanalyze or qualify data	Analyst	Precision	See Worksheet 12
Matrix Spike	1/20	See Worksheet 12	Reanalyze or qualify data	Analyst	Bias	See Worksheet 12
Field Splits	As requested by USACE-NAE, USEPA, and/or MassDEP (may be up to 10%)	In accordance with regulatory agency guidelines	Investigate cause of discrepancy between split sample results. Adjust sampling or analysis SOP to attain comparable sample results	Field Sampler or Analyst	Accuracy/bias and Precision	In accordance with regulatory agency guidelines
PT sent to Laboratory	As needed, based on Sovereign or regulatory request.	In accordance with PT acceptance limits	Investigate cause of non attainment of acceptable results. Adjust analysis SOP to attain accurate results	Analyst	Accuracy/bias	In accordance with PT acceptance limits

Laboratory Analytical QC Samples Table

Matrix	GW
Analytical Group	All
Concentration Level	Low
Sampling SOP	See FSPs
Analytical Method/ SOP Reference	See Worksheet 23
Sampler's Name	Field Personnel
Field Sampling Organization	Sovereign
Analytical Organization	Accutest Laboratories
No. of Sample Locations	TBD

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1/extraction batch	< ½ LOQ	Locate source of contamination, correct problem, re-extract and analyze associated samples	Analyst	Accuracy/bias (contamination)	< ½ LOQ
Calibration Blank	Before beginning a sample run, after every 10 samples, and at the end of the sequence	< ½ LOQ	Locate source of contamination, correct problem, re-analyze calibration blank and previous ten samples	Analyst	Accuracy/bias (contamination)	< ½ LOQ

Laboratory Analytical QC Samples Table (continued)

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory Duplicate	1/20 for inorganics	See worksheet 12	Reanalyze or qualify data	Analyst	Precision	See worksheet 12
Matrix Spike	1/20	See worksheet 12	Evaluate sample concentration to verify that spiked amount is greater than 4x sample concentration. Reanalyze if analytical problem. Qualify data.	Analyst	Bias/Accuracy	See worksheet 12
Matrix Spike Duplicates	1/20	See Worksheet 12	Evaluate sample concentration to verify that spiked amount is greater than 4x sample concentration. Reanalyze if analytical problem. Qualify data.	Analyst	Precision and Bias	See Worksheet 12
Laboratory Control Sample (LCS)	1/extraction batch	See Worksheet 12	Evaluate exceedance and impact on sample data. Re-extract batch if necessary	Analyst	Accuracy	See Worksheet 12

Laboratory Analytical QC Samples Table (continued)

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Limit of Detection (LOD)	Quarterly	LODs must produce a response greater than 3 times the instrument noise level; using standard concentration within 2-3 times the detection limit.	Check for errors. Repeat LOD study, if necessary	Analyst	Sensitivity	LOD must produce a response greater than 3 times the instrument noise level
Instrument Detection Limit (IDL)	Quarterly	IDL must be ≤LOD	Check for errors. Repeat IDL, if necessary	Analyst	Sensitivity	IDL must be ≤ LOD
Proficiency Testing (PT) Samples	As needed or requested	Within acceptance limits of USEPA or commercial vendor criteria	Qualify associated sample data	Data validator	Bias	Within acceptance limits of USEPA or commercial vendor criteria
Initial Calibration (ICAL)	Prior to analyzing samples	See Worksheet 12	Perform maintenance; Re-calibrate; Prepare new standards	Analyst	Accuracy	See Worksheet 12

Laboratory Analytical QC Samples Table (continued)

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Continuing Calibration verification (CCV)	After every 10 samples and at the end of an analytical sequence	See Worksheet 12	Correct problem; re-run CCV. Repeat ICAL, if necessary. Re-analyze all samples since last successful ICAL or CCV.	Analyst	Accuracy	See Worksheet 12
Independent Calibration Check (ICV) standard	Once after each initial calibration; prior to sample analysis	Within ± 10%	Correct problem and verify ICV. If that fails, repeat ICAL.	Analyst	Accuracy	Within ± 10%

[1] See Fixed Laboratory Method/SOP Reference Table (Worksheet #23).

Field QC Samples Table

Matrix	Treatment System
Analytical Group	All
Concentration Level	Low
Sampling SOP	See FSPs
Analytical Method/ SOP Reference	See Worksheet 23
Sampler's Name	Field Personnel
Field Sampling Organization	Sovereign
Analytical Organization	Alpha Analytical
No. of Sample Locations	TBD

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Cooler Temperature Blanks	Cooler temperature blanks are not used. However, cooler temperatures are measured using an infrared temperature gun, or equivalent	4^0C, ± 2^0C, or as stated in Worksheet #19	Resample and/or qualify data	Field Sampler and Data Validator	Accuracy/bias-Preservation	4^0C, ± 2^0C, or as stated in Worksheet #19

Laboratory Analytical QC Samples Table

Matrix	Treatment System
Analytical Group	All
Concentration Level	Low
Sampling SOP	See FSPs
Analytical Method/ SOP Reference	See Worksheet 23
Sampler's Name	Field Personnel
Field Sampling Organization	Sovereign
Analytical Organization	Alpha Analytical
No. of Sample Locations	TBD

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method Blank	1/extraction batch	< ½ LOQ	Locate source of contamination, correct problem, re-extract and analyze associated samples	Analyst	Accuracy/bias (contamination)	< ½ LOQ
Calibration Blank	Before beginning a sample run, after every 10 samples, and at the end of the sequence	< ½ LOQ	Locate source of contamination, correct problem, re-analyze calibration blank and previous ten samples	Analyst	Accuracy/bias (contamination)	< ½ LOQ
Laboratory Duplicate	1/20 for inorganics	See worksheet 12	Reanalyze or qualify data	Analyst	Precision	See worksheet 12

Laboratory Analytical QC Samples Table (continued)

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory Control Sample (LCS)	1/extraction batch	See Worksheet 12	Evaluate exceedance and impact on sample data. Re-extract batch if necessary	Analyst	Accuracy	See Worksheet 12
Limit of Detection (LOD)	Quarterly	LODs must produce a response greater than 3 times the instrument noise level; using standard concentration within 2-3 times the detection limit.	Check for errors. Repeat LOD study, if necessary	Analyst	Sensitivity	LOD must produce a response greater than 3 times the instrument noise level
Instrument Detection Limit (IDL)	Quarterly	IDL must be ≤LOD	Check for errors. Repeat IDL, if necessary	Analyst	Sensitivity	IDL must be ≤LOD
Initial Calibration (ICAL)	Prior to analyzing samples	See Worksheet 12	Perform maintenance; Re-calibrate; Prepare new standards	Analyst	Accuracy	See Worksheet 12
Continuing Calibration verification (CCV)	After every 10 samples and at the end of an analytical sequence	See Worksheet 12	Correct problem; re-run CCV. Repeat ICAL, if necessary. Re-analyze all samples since last successful ICAL or CCV.	Analyst	Accuracy	See Worksheet 12
Independent Calibration Check (ICV) standard	Once after each initial calibration; prior to sample analysis	Within ± 10%	Correct problem and verify ICV. If that fails, repeat ICAL.	Analyst	Accuracy	Within ± 10%

[1] See Fixed Laboratory Method/SOP Reference Table (Worksheet #23).

Project Documents and Records Table

Sample Collection Documents and Records	Field Analysis Documents and Records	Laboratory Analysis Documents and Records	Data Assessment Documents and Records	Other
Field Notes	Equipment Calibration Logs	Sample Receipt, Custody, and Tracking Records	Field Sampling Audit Checklists	Project planning documents
COC Records	Equipment Maintenance, Testing, and Inspection Logs	Standard Traceability Logs	Fixed Laboratory Audit Checklists	Telephone logs, e-mails, faxes, and correspondence
Air Bills	Corrective Action Forms	Instrument Calibration Logs	Data Validation Reports	Project deliverables
Boring Logs		Sample Preparation Logs	PT Results (if applicable)	Permits
Sample Labels		Run Logs	QA Results (if applicable)	Site maps
Custody Seals		Equipment Maintenance, Testing, and Inspection Logs	Corrective Action Reports	
Corrective Action Forms		Non-Conformance Forms or Corrective Action Forms		
Photographs		Field Sample Results		
		Results for Standards, QC Checks, and QC Samples		
		Instrument Printouts (raw data) for Field Samples, Standards, QC Checks, and QC Samples		
		Data Package Completeness Checklists		

Project Documents and Records Table

Sample Collection Documents and Records	Field Analysis Documents and Records	Laboratory Analysis Documents and Records	Data Assessment Documents and Records	Other
		Sample Disposal Records Electronic and/or hard copies of data reports LOD and/or LOQ study results IDL study results Initial demonstration of capability records Training records PT sample results (if applicable)		

Analytical Services Table

Matrix	Analytical Group	Concentration Level	Sample Locations/ID Numbers	Analytical SOP	Data Package Turnaround Time	Laboratory/Organization (Name and Address, Contact Person and Telephone Number)	Backup Laboratory/Organization (Name and Address, Contact Person and Telephone Number)
GW	Metals and General Chemistry	Low	GW	L-1 through L-14	21 Calendar Days	Accutest Laboratories 495 Technology Center Marlborough, MA 01752 Frank D'Agostino 508-481-6200	Alpha Analytical 8 Walkup Drive Westborough, MA 01581 Katie O'Brien 508-898-9220
Treatment System	Metals, VOCs, SVOCs, Pesticides, PCBS, Dissolved Gases, and General Chemistry	Low	Treatment System	L-15 through L-28	21 Calendar Days	Alpha Analytical 8 Walkup Drive Westborough, MA 01581 Katie O'Brien 508-898-9220	Accutest Laboratories 495 Technology Center Marlborough, MA 01752 Frank D'Agostino 508-481-6200

Planned Project Assessments Table

Assessment Type	Frequency	Internal or External	Organization Performing Assessment	Person(s) Responsible for Performing Assessment (Title and Organizational Affiliation)	Person(s) Responsible for Responding to Assessment Findings (Title and Organizational Affiliation)	Person(s) Responsible for Identifying and Implementing Corrective Actions (CA) (Title and Organizational Affiliation)	Person(s) Responsible for Monitoring Effectiveness of CA (Title and Organizational Affiliation)
Field Sampling Technical Systems Audit	At start of sampling and regularly thereafter	Internal	Sovereign	Sovereign Field Team Leader	Sovereign Field Personnel	Sovereign Field Team Leader	Sovereign Field Team Leader
ELAP Laboratory Validation Program	PT samples analyzed twice per year; inspection Every 2 years	External	ELAP	Accrediting Authority	Contract laboratory QA Coordinator or Technical Operations Manager	Contract laboratory QA Coordinator or Technical Operations Manager	Contract laboratory QA Coordinator or Technical Operations Manager
Proficiency Testing Samples	Periodically	Internal or External	Sovereign or government agencies	Sovereign or government agencies	Contract laboratory QA Coordinator or Technical Operations Manager	Contract laboratory QA Coordinator or Technical Operations Manager	AMEC Project Chemist

Assessment Findings and Corrective Action Responses

Assessment Type	Nature of Deficiencies Documentation	Individual(s) Notified of Findings (Name, Title, Organization)	Timeframe of Notification	Nature of Corrective Action Response Documentation	Individual(s) Receiving Corrective Action Response (Name, Title, Org.)	Timeframe for Response
Field Assessments	Memo or email	Steven Passafaro, Project Manager, Sovereign	Verbal notification next business day; written within 1 week	Corrective action report	Steven Passafaro, Project Manager, Sovereign	As soon as possible depending on nature of deficiency
Data Review and Validation	Validation Report	Denise King, Project Chemist, AMEC	Within 28 days of receipt of laboratory report	Written notifications of findings to the laboratory	Frank D'Agostino, Laboratory Project Manager, Accutest and Katie O'Brien, Laboratory Project Manager, Alpha	As soon as possible

QA Management Reports Table

Type of Report	Frequency (daily, weekly monthly, quarterly, annually, etc.)	Projected Delivery Date(s)	Person(s) Responsible for Report Preparation (Title and Organizational Affiliation)	Report Recipient(s) (Title and Organizational Affiliation)
Data Validation Reports	As data is generated and reported	See Work Plan Addendum for project schedule	AMEC Data Validator	Sovereign Project Manager or key technical resource lead for study area
Final Project Reports	As data is compiled and interpreted	See Work Plan Addendum for project schedule	Sovereign Project Manager	USACE-NAE, USEPA, MassDEP

Verification (Step I) Process Table

Verification Input	Description	Internal/ External	Responsible for Verification (Name, Organization)
Sample collection	The field sampler will verify that chain of custody forms are filled out accurately and completely. Sample identifications will be verified. The designed laboratory and method of analysis will be verified against the task work plan specifications.	Internal	Field Samplers
Sample receipt	Upon receipt at the laboratory, the sample custodian verifies that sample preservation and volume is satisfactory for the designated analysis. The sample custodian notifies the laboratory project manager if any inconsistencies or deficiencies are noted in the samples upon receipt.	External	Laboratory Sample Custodians
Sample preparation	The sample preparation technician verifies that the sample is in satisfactory condition for extraction/digestion procedures. Notes are taken on unusual color or condition of samples. The laboratory project manager is notified of any significant issues with the sample.	Internal	Laboratory Sample Preparation Technicians
Sample analysis	The analyst verifies that sample results and QC are satisfactory and consistent. Analysis anomalies are noted in the data package. The section supervisor and/or laboratory project manager are notified of any QC deficiencies.	Internal	Laboratory Analyst
Data review	Chemistry data review is performed in a three stage process by 1) analyst 2) peer review (analyst or section supervisor) and 3) laboratory project manager (completeness, report narrative review).	External	Laboratory Analyst, Peer, Laboratory Project Manager

Validation (Steps IIa and IIb) Process Table

Step IIa/IIb	Validation Input	Description	Responsible for Validation (Name, Organization)
IIa	Field SOPs	Review field personnel adherence to sample collection procedures detailed in the sampling SOPs.	Sovereign
IIa	Field Analytical Activities	Review of field analytical data against UFP-QAPP requirements.	Sovereign
IIa	Analytical SOPs	Review laboratories adherence to analytical SOPs.	AMEC
IIa/IIb	UFP-QAPP QC Limits	Verify all UFP-QAPP required QC samples were analyzed at the required frequency.	Sovereign/AMEC
IIa	Laboratory Data	Run all laboratory data through ADR software and have chemist review report	AMEC

Validation (Steps IIa and IIb) Summary Table

Step IIa/IIb	Matrix	Analytical Group	Concentration Level	Validation Criteria	Data Validator (title and organizational affiliation)
IIa/IIb	GW and Treatment System	Metals 6020A/6010C/7470A	Low	National Functional Guidelines for Inorganic Superfund Data Review EPA-540-R-10-011 January 2010	Denise King, AMEC
IIa/IIb	GW and Treatment System	Water Quality Criteria	Low	Methods, SOP and UFP-QAPP requirements	Denise King, AMEC
IIa/IIb	Treatment System	PCBs, Pesticides, VOCs (624), SVOCs, and Dissolved Gases	Low	Methods, SOP and UFP-QAPP requirements	Denise King, AMEC
IIa/IIb	Treatment System	VOCs-8260	Low	National Functional Guidelines for Superfund Organic Methods Data Review EPA-540-R-08-01 June 2008	Denise King, AMEC

Usability Assessment

Data usability is typically performed by the project manager, with recommendations or input by the project chemist, data validator, or other team member when data are compiled and viewed from an overall project perspective. Typical data usability assessment details follow:

Precision: If poor overall precision of data is observed, it may be an indication of poor sampling technique, field sample non-homogeneity, sample transport problems, or analytical methodology variations. For sample non-homogeneity issues, data must be interpreted accordingly (i.e., more representative concentrations may be obtained from averaging sample concentrations over an appropriately sized area of concern). If poor precision is related to sampling techniques, transport, or methodology phenomena (such as poor sample extraction efficiencies) causes and corrective actions will be taken.

Accuracy/bias: If poor overall accuracy of data is observed, the cause may be related to sampling techniques, sample transport problems, sample matrix, or analytical methodology limitations. Positive or negative biases can be caused by poor sampling techniques such as ineffective decontamination procedures or use of inappropriate sample containers or preservation procedures. Improvements in sampling techniques must be taken to correct these deficiencies. Poor accuracy can also be attributed to matrix effects (evidenced by poor recovery of spiked analytes) or by methodology limitations (e.g., poor extraction efficiency). If this phenomenon is observed, investigations into modifications to improve the accuracy of analytical SOPs will be made.

Representativeness: Lack of representativeness among samples is observed by poor precision of sample duplicates, from samples in close proximity, or from samples collected at various time intervals (e.g., long term groundwater monitoring programs). If field duplicate precision indicates that spatial variability is an issue, additional scoping meetings or subsequent re-sampling may be warranted.

Comparability: Lack of comparability among samples may be attributed to differences in sampling techniques, analytical protocols, or reporting procedures. If different field personnel collect samples, an evaluation of the consistency in protocols will be performed. If samples are analyzed by different analytical methodologies, an evaluation of possible sources of discrepancies will be undertaken. If split samples are collected and analyzed at independent laboratories, an investigation into possible inconsistencies between procedures will be investigated. Reporting procedures will be reviewed to verify that results are reported on the same unit basis (e.g., dry weight basis for soil).

Usability Assessment

Completeness: Data completeness is determined based on the number of usable data points compared to the number of samples collected for a specific matrix and method. Lack of completeness for samples may be attributed to sample transport issues (i.e., breakage of samples) or laboratory issues (i.e., poor quality control resulting in rejection of data). If data completeness goals (100% wells; 100% Treatment samples; and 95% for profile samples) are not met, causes of failure will be determined and corrective action measures will be taken.

Sensitivity (Limit of Quantitation (LOQ), Limit of Detection (LOD): Laboratory sensitivity (quantitation limits) must be adequate to achieve project objectives (comparison to applicable regulatory standards). Laboratory limits of quantitation are set at the lowest calibration standard and are verified annually. Limits of detections are performed quarterly to statistically determine the lowest limit of detection achievable for a specific matrix and methodology. Methods are chosen based on their ability to achieve project sensitivity objections. Laboratory sensitivity may be adversely impacted if sample interferences are present, resulting in sample dilutions which raise the LOQ. Investigations into the source of interferences and their removal from sample extracts will be undertaken if this situation occurs.

Overall Evaluation: An overall evaluation of the laboratory data will be made to interpret the data from a general perspective. Lack of consistency between data points in an overall evaluation may be attributed to sample collection issues (such as improper preservation, cross contamination, ineffective decontamination) or analytical methodology limitations (ineffective extraction efficiency, cross contamination, presence of interferences, etc.). If outlier data points are apparent from a general overall evaluation, further investigations into causes will be made. Project report narratives will highlight possible anomalous data points, including discussing possible causes and corrective actions.

Attachment A

Lab Manager: Brad Madadian
QA Manager: Robert Treggiari

TEST NAME: METALS BY INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETRY (ICP-MS)

METHOD REFERENCE: SW846 6020A, Revision 1, February 2007.

Revised Sections: Spike Blank – definition; added manager signatures

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for the determination of total and dissolved metals in water samples and in waste extracts or in solid or aqueous digests.

2.0 SUMMARY

2.1 Samples are prepared for analysis by digestion. The prepared samples are introduced into radio frequency plasma by pneumatic nebulization. There the energy transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass to charge ratio by a quadrupole mass spectrometer. The ions transmitted through the quadrupole are detected by an electron multiplier and the ion information is processed by a data handling system.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. Current reporting limits for this method have been established at the levels listed in Table 1. The reporting limits are dependent upon the metal being analyzed and are in all cases greater than the IDL and the MDL for each element. Note: Many clients require special reporting limits. Refer to the scheduling sheets and check with the metals supervisor for additional information.

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.3 Experimental MDLs are determined initially (prior to analysis), on an annual basis, and after major maintenance to equipment. MDL data is archived with Quality Assurance. Refer to the most recent study for current MDLs. Refer to the SOP for MDLs (MQA245) for additional detail regarding MDL study procedures. Electronic MDL data is found in the annual “MDL” folder on the QA server (LINUXMA1).

4.0 DEFINITIONS

BATCH. A group of 20 samples or less that behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit within a 24 hour period. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. It is recommended that the calibration check standard be run at a frequency of 10 percent or every 2 hours during an analysis run, whichever is more frequent, and at the end of the analysis sequence. For this method, the mid-level calibration check standard criteria is ± 10 percent of the true value and the relative standard deviation for the replicates that are greater than 5 times the reporting limit is less than 5 percent. The exception to this rule is if the recovery on the calibration check standard is high and the samples to be reported are less than the reporting limit.

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. It must be run after each calibration. The external check standard criteria is ± 10% of the true value and the replicates that are greater than 5 times the reporting limit should have a relative standard deviation of less than 5 percent. If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 sample batch. A sample batch is defined as a maximum of 20 field samples in a preparation batch over a time period of 24 hours. Assess laboratory performance against the control limits of 80 to 120 percent. In house limits should also be generated once sufficient data is available to support the default limits. If the lab control or spike blank is outside of the control limits for a parameter, all samples must be redigested and reanalyzed for that parameter. The exception is if the lab control or spike blank recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with a sample case narrative.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against default limits of 75 to 125 % recovery. In house limits should be generated once sufficient data is available. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result}) \times 100}{(\text{Amount Spiked})} = \text{Matrix Spike Recovery}$$

MATRIX SPIKE DUPLICATES: Intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix. A matrix spike duplicate is digested at a minimum of 1

in 10 samples. The relative percent difference (RPD) between the matrix spike duplicate and the matrix spike should be assessed. The matrix spike duplicate RPD is calculated as shown below.

$$\frac{(|\text{Spiked Sample Result} - \text{Spiked Duplicate Result}|) \times 100}{(\text{Spiked Sample Result} + \text{Spiked Duplicate Result})/2} = \text{Spike Duplicate RPD}$$

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 sample batch. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be redigested and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. MDLs should be determined approximately once per year for frequently analyzed parameters.

REAGENT BLANK. The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE. Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER. Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water.

STANDARD ADDITION. The practice of adding a known amount of an analyte to a sample immediately prior to analysis. It is typically used to evaluate interferences.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will

result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Health and Safety Plan and Personal Protection Policy, which include the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents must be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

6.0 PRESERVATION & HOLDING TIME

6.1 All water samples should be preserved with nitric acid to a pH of 2 or less. All solid samples should be stored in a refrigerator at 4 degrees C until digestion.

6.2 All samples should be analyzed within 6 months of the date of collection.

7.0 INTERFERENCES

7.1 Several types of interferences can cause inaccuracies in trace metals determinations by ICP-MS. These interferences are discussed below.

7.2 Isobaric elemental interferences are caused by isotopes of different elements which form singly or doubly charged ions of the same nominal mass-to-charge ratio and which cannot be resolved by the mass spectrometer in use. If isobaric interferences are present in the ion being analyzed, then the data must be corrected by measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the element of interest.

7.3 Abundance sensitivity is a property that defines the degree to which the wings of a mass peak contribute to adjacent masses and is affected by ion energy and quadrupole operating pressure. Wing overlap interferences may result when a small ion peak is being measured next to a large one. Spectrometer resolution should be adjusted to minimize these interferences.

7.4 Isobaric polyatomic ion interferences are caused by ions consisting of more than one atom which have the same nominal mass-to-charge ratio as the isotope of interest, and which cannot be resolved by the mass spectrometer in use. Refer to method 200.8 and 6020 for lists of common interferences and correction equations to be applied. If these interferences

cannot be avoided by the use of different isotopes, then correction equations should be applied to the data. Alternatively, collision/reaction cell technology can be applied to physically and chemically remove interferences.

7.5 Physical interferences can occur during the transfer of the solution to the nebulizer (viscosity effects).

7.6 Memory interferences can be caused by build up on the sampler and skimmer cones, and from buildup of sample material in the torch and spray chamber. Some elements, such as mercury, can suffer from severe memory effects. In that case, gold is added to the rise solution to decrease the Hg rinse out time.

8.0 APPARATUS

8.1 Currently there is one ICP-MS instrument available for use in the lab. The Aglilent 7500CX ICP-MS with collision/reaction cell capacity and the associated autosampler.

8.2 Class A volumetric glassware as needed and instrument autosampler tubes.

8.2.1 All glassware must be washed with soap and tap water and then soaked in a 10% nitric acid bath for several hours. It must then be rinsed at least 3 times with distilled, deionized water.

8.3 Polypropylene bottles for standard storage. These bottles must also be cleaned as outlined above.

9.0 REAGENTS

9.1 All chemicals listed below are reagent grade unless otherwise specified. Deionized water must be used whenever water is required. Note: All reagents can be scaled up or down proportionately if different final volumes are required.

9.2 Hydrochloric acid, trace metals grade.

9.3 Nitric acid, trace metals grade. Note – ultra trace grade may be required if lower detection limits than normal are needed.

9.4 Standard stock solutions available from Inorganic Ventures, Ultra Scientific, Agilent or equivalent. Note: All standards must be ICP-MS quality standards or must be demonstrated to be free of interferences at the levels of use. Standards should come labeled with an expiration date and certificate of concentrations from the manufacturer. If both of these items are not received, then the manufacturer should be contacted before use of the standard.

9.5 Calibration Standards: These can be made up by diluting the stock solutions to the appropriate concentrations. Fresh calibration standards should be prepared a minimum of every two weeks.

9.5.1 Standards should be made in a low acid matrix. Concentrations of 1 to 2 percent nitric acid and 0 to 0.6 percent hydrochloric acid are suggested, although any acid concentration that provides good analytical results may be used. High chloride concentrations may cause interferences so chloride concentrations should be limited. HCl may be omitted if silver and antimony are not elements of interest.

9.5.2 Refer to the Reagent Application for the make-up and concentrations of standards and stock solutions being used to calibrate the ICP-MS. Suggested standard levels are shown in Table 2. Calibrations must consist of a minimum of a blank and a high standard. The calibration must be verified with a low check at the reporting limit at the time of analysis

9.5.3 All standards should be stored in acid washed FEP fluorocarbon bottles.

9.6 Pulse/Analog (P/A) Factor and Tuning/Performance Check Solution. Mix 1.0 ml of PA Tuning 1 solution and 1.0 ml of PA Tuning 2 solution (available from Aglient, part number 5188-6524) and bring to 100 ml final volume with a solution of 1% nitric acid and 0.6% HCl. This final solution contains 200 ppb of As, Be, Cd, Zn; 100 ppb of Mg, Ni, and Pb; 50 ppb of Al, Ba, Bi, Co, Cr, Cu, In, Li^6, Lu, Mn, Na, Sc, Sr, Th, Tl, U, and V; and 25 ppb of Y and Yb; 100 ppb of Ge, Mo, Pd, Ru, Sb, Sn ; and 50 ppb of Ir and Ti.

9.7 Tuning Standard. This solution is used to verify mass calibration and thermal stability and must contain a mix of elements representing all of the mass regions of interest. Elements include 1 ppb Ce, Co, Li, Mg, Tl, and Y.

9.8 Internal Standards. Internal standards are added to all calibration standards, quality control, and samples during analysis, normally using a second channel of the peristalic pump and a mixing manifold. For full mass range scans, a minimum of three internal standards must be used. It is recommended that all elements have an internal within a mass range of 50.

9.8.1 A stock solution containing 100 ppm of Li, Sc, Ge, Y, In, Tb, and Bi. 1 ml stock solution to 100 ml final volume with a solution of 1% nitric acid and 0.6% HCl. The concentration of this final solution is 1 ppm, with a 0.25 mm IS pump tubing equates to approximately 50 ppb in the plasma. Refer to Table 3 for internal standard masses and associated Tune.

9.9 Calibration /Rinse Blank. The calibration and rinse blanks are prepared by diluting acids to the same concentrations found in the standards. The calibration blank is used to establish the analytical calibration curve and the rinse blank is used to flush the instrument between samples in order to reduce memory interferences.

9.10 Continuing Calibration Verification Check (CCV). This solution is prepared by adding either mixed or single element metals solutions to a solution containing the same acid matrix as the calibration standards. The metals should be at concentrations near the middle of the calibration curve. (Note: This check is run after the calibration, after every 10 samples or

every 2 hours during an analysis run, whichever is more frequent, and at the end of the sample run.) Refer to Table 2 for suggested concentrations for the CCV.

9.10.1 Method 6020 does not specify the source of the CCV check. However, it is recommended that these be prepared from the same source as the calibration as it required in method 200.8

9.11 Matrix Spike and Spike Blank Solution. Suggested levels for the final concentrations of the spike are shown in Table 4. This solution is prepared by adding either mixed or single element metals solutions to a solution containing 1 % nitric acid and 0 to 0.6 % HCl and diluting to a fixed final volume with this acid mixture. 0.5 ml of this stock solution should be added to spike blank and the matrix spike before they are digested and brought to a final volume of 50 ml. For this particular method, a lab control (Section 9.12) is used more frequently than a spike blank. In situations where any odd elements, such as B, Sr, and Sn, is of interest for a specific project, besides a lab control, a spike blank spiked with these elements is also digested.

9.12 Lab Control Solution. This solution is prepared by adding either mixed or single element metal solutions to a solution containing 1 % nitric acid and 0 to 0.6 % HCl and diluting to a fixed final volume with this acid mixture. 50 ml of this solution is digested and brought to a final volume of 50 ml.

9.13 Interference Element Check Solutions. The purpose of the ICSA and ICSAB solutions is to demonstrate the magnitude of interferences and provide an adequate test of any corrections. It is recommended that the following solutions be purchased commercially.

9.13.1 ICSA Solution. The ICSA solution contains only the interfering elements. The recommended concentrations are shown below. The ICSA solution must be made fresh weekly.

Al	100 mg/L
Ca	100 mg/L
Fe	100 mg/L
Mg	100 mg/L
Na	100 mg/L
P	100 mg/L
K	100 mg/L
S	100 mg/L
C	200 mg/L
Cl	1000 mg/L
Mo	2.00 mg/L
Ti	2.00mg/L

9.13.2 ICSAB Solution. The ICSAB solution contains both the interferents and the analytes of interest. The recommended concentrations are shown below. The ICSAB solution must be made fresh weekly.

Al	100 mg/L
Ca	100 mg/L
Fe	100 mg/L
Mg	100 mg/L
Na	100 mg/L
P	100 mg/L
K	100 mg/L
S	100 mg/L
C	200 mg/L
Cl	1000 mg/L
Mo	2.00 mg/L
Ti	2.00mg/L
As	0.020 mg/l
Cd	0.020 mg/l
Cr	0.020 mg/l
Co	0.020 mg/l
Cu	0.020 mg/l
Mn	0.020 mg/l
Ni	0.020 mg/l
Ag	0.020 mg/l
Zn	0.020 mg/l

9.14 Initial Calibration Verification (ICV) or Quality Control Sample (QCS). The metals in this solution should be at final concentrations that are at the mid-point of the calibration curve. This solution is prepared by adding either mixed or single element metals solutions to a solution containing 1 % nitric acid and 0 to 0.6 % hydrochloric acid and diluting to a fixed final volume with this acid mixture. The ICV sample must be from a separate source from the calibration standards. This solution should be stored in a FEP fluorocarbon or previously unused polyethylene bottle. Refer to Table 2 for suggested concentrations for the ICV.

9.15 CRI Standards (also referred to as LLCCV). The CRI standard must contain the elements of interest at (or below) the reporting limit for each element. The CRI level is at the reporting limit as shown in Table 1. This should be prepared by diluting calibration standard(s) to the reporting limit level for each element. They should be made in the same matrix as the calibration standards. Note: The CRI must be verified at the RL before any dilutions are applied. For example, Be is verified at 0.5 ug/l and the water reporting limit is 1.0 ug/l with a 1:2 dilution.

9.16 Liquid Argon or Argon Gas. Argon, high purity grade (99.995%), is supplied by Air Products, Inc in the large outdoor tank. No lab monitoring of the tank is normally necessary.

9.17 Helium Gas. Helium, high purity grade (99.995%), is supplied by Air Products, in a small cylinder tank. The lab monitoring of the tank is necessary. This is required for running the reaction cell.

10.0 INITIAL INSTRUMENT SET-UP PROCEDURE FOR THE AGILENT 7500CX ICP-MS

10.1 A general procedure on how to operate the Agilent 7500CX ICP-MS is given below. Refer to the operation manual for further details.

10.2 Before bringing up the instrument, make sure that the lines, the torch, the nebulizer, and the spray chamber are clean, and that there are no leaks in the torch area.

10.3 Turn the vacuum pump and the heat exchanger on and verify that the liquid argon is turned on and the helium gas is turned on.

10.4 Connect the pump tubing and engage the peristaltic pump.

10.5 Put a new solution of acid rinse into the rinse reservoir. (Note: the composition of the rinse solution may be periodically changed to minimize sample introduction problems and sample carryover.) Make sure that sufficient internal standard solution is present.

10.6 Open the ICP-MS Chem Station Top software. Click on the instrument and open the instrument control panel. Click the plasma on. The instrument will automatically go through the start-up cycle. Then let the instrument warm up for at least 30 minutes.

10.7 Every one to two days or as needed, tune the instrument. Tuning must always be done after moving the position of the torch or the cones. Tuning can be done either manually or by following autotune procedures. It is recommended that autotune procedures be followed initially and then manual tuning be done as a second step. The purpose of tuning is to optimize the instrument for the highest sensitivity while obtaining low levels of oxides and doubly charged species. After the tune is complete, make sure to save the optimized parameters.

10.7.1 Open the ICP-MS top software, click on the instrument, and open the ICP-MS tuning page

10.7.2 Click file and open the NOGAS.U file. Keep the internal standard line in a solution of 1% nitric acid and 0.6% hydrochloric acid. Using the ALS (autosampler) send the probe to the 1 ppb Agilent tuning solution (see 9.7). On the tuning page, click start under the RTD window to see the counts and RSD values. Do not start the tune process until the count and mean have similar readings and the RSD is < 5%. Click stop under RTD window.

10.7.3 On the tuning page, go to file, select Generate Multi_Mode Report, type the date on the pop-up window, and click OK. This will perform the tuning of the instrument using both the NOGAS and the Helium mode. Print the tune and save it as MAXXXXX_Tune.pdf.

10.7.4 Also tune the instrument for NOGAS and the Helium mode separately if necessary, then generate Multi_Mode report.

10.7.4.1 On the tuning page, open the NOGAS.U file, go to file, select Generate Report, type the date on the pop-up window, and click OK. This will perform the tuning of the instrument using NOGAS mode.

10.7.4.2 On the tuning page, open the He.U file, go to file, select Generate Report, type the date on the pop-up window, and click OK. This will perform the tuning of the instrument using Helium mode.

10.8 On a daily basis, perform a cross calibration to align the pulse and analog signals.

10.8.1 Go to the ICP-MS Top portion of the software and be sure that the NOGAS.U file is open. Using ALS, send the probe to the P/A factor solution. This solution is diluted from a concentrated mixture of PA Tuning 1 and PA Tuning 2 solution which can be purchased from Agilent Technologies.

10.8.2 In the ICP-MS Tuning page, under the Tune, click P/A factor. Click run in the popup window. Some elements may have too low or too high sensitivity. In this case, rerun the P/A factor process one or more times.

10.8.3 Print and save the P/A factor report as MAXXXX_PA.pdf.

10.9 Before calibrating, run and print out a performance test. This must include the following items.

10.9.1 Demonstrate instrument stability by running the tuning solution a minimum of five times. Relative standard deviations of the absolute signals must be less than 5 percent for all elements in the tuning solution. If this criteria is not met, correct the problem and then repeat the stability test. Print the results of this test and store with the raw data for the run.

10.9.2 Verify acceptable mass calibration by running the tuning solution and monitoring the peak width measured at 5% of peak maximum for 7Li, 59Co, 115In and 205Tl. If the peak widths are outside of the range of 0.65 to 0.85 and the masses are off more than 0.1 amu, then redo the mass calibration as outlined in 10.8 before proceeding.

10.9.3 To run this performance test, be sure that the NOGAS.U file is open. Set up the daily run sequence. Select TN_6020.M method and run. This method is set up to run 5 replicates. After the performance test is finished, click print (in case of TN200_8.M is also ran as part of performance test, combine the portions of the performance test together in a PDF converter window) and then save this as MAXXXX_perf.pdf.

10.10 Before starting sample analysis, set up the internal standards. Internal standards are added to all calibration standards, quality control, and samples during analysis, normally using a second channel of the peristaltic pump and a mixing manifold. Refer to Table 3 and Section 9.8 for additional information.

10.11 To start running samples, open the ICP-MS Top window, and then click method followed by load. Selection the method from the list. The normal method used for 6020 analyses is EPA6020V.M

10.11.1 Click sequence and then click load. Select the latest sequence or template from the list.

10.11.2 Click Edit the sample log table and type in the standards and samples. Save the sequence as MMDDYY.s (i.e: 063012.s). Be sure to load the saved sequence again. Click Position and Run to start the run.

10.11.2.1 At the pop-up window, the data Bach directory line will show file name as C:\ICPMH\1\DATA\12F30XXX.B\. (i.e: 12F30XXX.B, 12 is the year; F is the month, in this case is 6; 30 is the date) Click on run sequence. This will open the data analysis page.

10.12 Calibrate the instrument using a minimum of a calibration blank and three non-zero standards that bracket the desired sample concentration range. (Note: The calibration standards may be included in the autosampler program or they may be run separately.) A correlation coefficient of 0.998 or better must be obtained using a first order (linear) curve fit. A minimum of three replicate integrations are required for all data acquisitions.

10.12.1 In between each analysis of a separate standard or sample, a rinse blank must be run through the lines of the sample introduction system. Each sample or standard should be aspirated for a minimum of 30 seconds prior to the acquisition of data to allow equilibrium to be established.

10.12.2 Alternatively, a calibration may be done with a blank and a high standard. This calibration must then be confirmed with low level and mid-level calibration standards that are run immediately after the calibration is complete. The low level check must have recoveries within 70 to 130 % to be acceptable and the mid-level check must have recoveries within 90 to 110 %to be acceptable.

10.13 After the instrument is properly calibrated, begin by analyzing the ICV solution. The ICV must be run after each calibration. For the ICV, all elements to be reported must be within 10 % of the true value and the replicates that are greater than 5 times the reporting limit should have a relative standard deviation of less than 5 %. If the ICV is outside of criteria, then the problem must be identified and corrected before samples can be run and reported for the element(s) that are outside of criteria. Correction of the problem can be verified by rerunning the check standard(s) and showing that they meet QC criteria.

10.13.1 An ICB may be run after the ICV, but is not required for this method. If it is run, then all elements must be less than reporting limit (lower limit of quantitation) for each element.

10.13.2 Run the CRI (LLCCV) solution right after the ICV and ICB, (or any other place at the beginning of the run after the ICV, ICB and before any real samples are analyzed). For the CRI, all elements of interest must be within 30% of the true value or within client specified limits.

10.14 Then analyze the CCV and CCB check standards. For the CCV, all elements to be reported must be within 10 % of the true value and the replicates that are greater than 5 times the reporting limit should have a relative standard deviation of less than 5 %. For the CCB, all elements to be reported must normally be less than the reporting limit (lower limit of quantitation). If either the CCV or CCB do not meet criteria, then elements failing this criteria must not reported in the area bracketed by this QC.

10.14.1 The internal standard levels in the CCV and CCB must also be within 30% of the internal standard level for the initial calibration. If they are outside of these levels, then no samples can be reported in the area bracketed by this QC.

10.15 After the initial QC is completed and before any samples are analyzed, the ICSA and ICSAB solutions must be analyzed. The method does not list specific criteria for the ICSA and ICSAB, but in house criteria will be applied. For all the spiked elements, the analyzed results must be within 20 % of the true value. For unspiked elements, the interfering element solution should contain less than the absolute value of 3 times the reporting limit for each element. If these criteria are not met, then samples with significant interferences can not be reported until the instrument is optimized and the ICSA and ICSAB are within specifications.

10.15.1 If the run is longer than 12 hours, a second ICSA, ICSAB pair must be analyzed before the next 12 hours is started.

10.15.2 If mass changes are made for the analysis of an element, all QC criteria must be met for the new mass and it must be verified that appropriate correction factors are in place.

10.15.3 The Agilent 7500CX includes collision/reaction cell technology. The instrument is tuned both in regular (non-cell) mode and in helium (collision/reaction) cell mode. This technology is used to minimize interferences during analysis. If this technology is not applied, then correction factors for interferences must be added into the method. Table 1 includes which elements are run using collision/reaction cell technology.

10.16 After the initial analytical quality control has been analyzed, the samples and the preparation batch quality control should be analyzed. Depending on the type of digestion and the sample matrix, samples and the associated QC should normally be diluted by a factor of from 2 to 5 before analysis. This dilution factor should be indicated in the sample ID file on the instrument.

10.16.1 Each sample analysis must be a minimum of 3 integrations. For samples containing levels of elements greater than approximately 5 times the reporting limits, the relative standard deviations for the replicates should be less than 10%. If not, reanalyze the sample. If, upon reanalysis, the RSDs are acceptable, then report the data from the reanalysis. If RSD's are not acceptable on reanalysis, then the results for that element may, on the reviewer's discretion, be footnoted that there are possible analytical problems indicated by a high RSD between replicates. In some cases, an additional dilution analysis may be needed. Check with the area supervisor or manager for additional information.

10.16.2 The internal standard levels must be monitored for all samples and quality control. If the internal standard is not within 30% of the internal standard level for the initial calibration blank, then the sample must be diluted by a factor of 5 to bring the internal standard to within the correct range. If the internal standard is still outside of the range after the initial 1:5 dilution, then additional dilutions must be done until the internal standard is within the appropriate range.

10.16.2.1 If an internal standard is present in a sample, then do not use that internal standard. For example, Y is sometimes seen in real samples. If the Y recoveries are high relative to the other internal standards, then do not use the Y internal standard.

10.16.3 For any readings that exceed the linear range for a given element, a dilution is required. After a high reading, the sample following the high one must be examined for possible carryover. A verification may be necessary by rinsing the lines with an acid solution and then rereading the sample.

10.16.4 Indicate dilution factors for samples using df followed by the dilution factor after the sample ID. There should be a space between the sample number and the df.

10.17 Between each sample, flush the nebulizer and solution uptake system with a blank rinse solution for a minimum of 30 seconds or for the required period of time to ensure that analyte memory effects are not occurring. (60 seconds is recommended for normal methods excluding Hg and B. Longer times may be needed when Hg and B are being analyzed.)

10.18 Analyze the continuing calibration verification solution and the continuing calibration blank after every ten samples and at the end of the sample run.

10.18.1 For the CCV, all elements to be reported must be within 10 % of the true value and the replicates that are greater than 5 times the reporting limit should have a relative standard deviation of less than 5 %. If the CCV solution is not within 10 % of the true value, no samples can be reported in the area bracketed by the failing CCV for the failing element.

10.18.2 For the CCB, all elements to be reported must be less than the reporting limit (lower limit of quantitation).

10.18.3 The internal standard levels in the CCV and CCB must also be within 30% of the internal standard level for the initial calibration. If they are outside of these levels, then no samples can be reported in the area bracketed by this QC.

10.19 The CRI (LLCV) must be analyzed at the end of each calibration (analysis) batch. The acceptance criterion for the CRI check is 70 to 130% recovery. If an element does not meet this criterion, then all samples for that element in the concentration range between the CRI and the CCV must be reanalyzed. Samples containing concentrations higher than the CCV may be reported as long as CCV criteria are met.

10.19.1 More frequent CRI (LCCV) checks may be analyzed during the course of the run if system stability at the low end of the calibration is questionable or if the lab wants to ensure that fewer samples will have to be submitted for reanalysis if there is a failed CRI at the end of a run.

10.19.2 It is recommended that the CRI check be run bracketing every 4 to 8 hour period of analysis. It may be run as frequently as every 10 samples if the supervisor or manager deems that this is necessary.

10.20 After the run is completed, convert the data file to a CSV format using the option on the results screen. First save the file on the local drive using the file naming system described below. Update the run in the LIMS and enter the run name into the workgroup using lower case characters. Then copy the data from the local drive to the LIMS drive.

10.20.1 The file should be named as followed- initial instrument indicator (XA), date (MMDD), year, run type (soil, water, or mixed), and sequential run number for that day. For example, the first water run from 06/30/12 would be designated xa063012w1.csv.

10.21 Calculations are done in the LIMS using the calculations shown below.

10.21.1 Calculation for aqueous samples.

$$\text{Original sample concentration of metal } (\mu g/l) = \frac{(\text{conc. in the digestate } (\mu g/l)) \times (\text{final digestate volume (ml)})}{(\text{Initial sample volume (ml)})}$$

10.21.2 Calculation for solid samples.

$$\text{Original sample concentration of metal (mg/kg)} = \frac{(\text{conc. in the digestate } (\mu g/l)) \times (\text{final digestate volume (ml)})}{(\text{Initial sample weight (g)}) \times (\%\text{sol}/100)}$$

10.22 At the end of the analysis day the ICP-MS must be brought down using the following sequence.

- Rinse the tip in a solution of 1 % nitric acid and 0.6 % hydrochloric acid for 10 minutes and in DI water for 20 minutes. (Note: a stronger acid solution may be needed depending on the matrix of the samples that were analyzed.)
- Turn off the plasma using off button.
- Release the tension on the pump tubing.
- Turn off the heat exchanger.
-

11.0 QC REQUIREMENTS

11.1 This section outlines the QA/QC requirements necessary to meet the method 6020.

11.2 Instrument Detection Limits (IDLs). IDLs must be established for all analytes a minimum of once per quarter. They are calculated by taking the average of the standard deviations of three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day.

11.3 LLQC (Lower Limit of Quantitation Check Sample) or LOQ Verification sample. A sample must be digested and analyzed initially and on an as needed basis to verify the quantitation limits for the method. Recoveries of this check must be within 70 to 130% of the true value. If recoveries are outside of this level, then the reporting limit must be increased to a level that can be verified.

11.3.1 For DOD work, the LOQ verification must be analyzed quarterly.

11.4 Method Detection Limits (MDLs). MDLs should be established for all analytes, using a solution spiked at approximately 2 to 5 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate analyses by 3.14, which is the student's t value for a 99% confidence level. MDLs should be determined approximately once per year or whenever there is a significant change in the background or instrument response. In general, if the amount spiked for the MDL is greater than 10 times the actual MDL, then the MDL should be redone with a lower spike level.

11.5 Linear Calibration ranges. The upper limit of the linear dynamic range needs to be established for each wavelength used by determining the signal responses from a minimum of three, preferably five, different concentration standards across the linear range. The linear calibration range which may be used for the analysis of samples should be judged by the analyst from the resulting data. The data, calculations and rationale for the choice of range made must be documented and kept on file. A standard at the upper limit must be prepared, analyzed and quantitated against the normal calibration curve. The calculated value should be within 10% (±10%) of the true value. Linear calibration ranges should be determined whenever there is a significant change in instrument response. They must be done at least every six months. For any readings that exceed the linear range for a

given element, a dilution is required. In addition, if there significant interferences generated from elements above the linear range, than these elements must also be diluted so that accurate interfering element corrections can be applied. Normal linear range values by element are shown in Table 2.

11.6 Initial Calibration Verification (ICV) or Quality Control Sample (QCS) and Initial Calibration Blank (ICB). After every new calibration, an ICV must be analyzed. The analysis of the ICV may be followed by the analysis of the ICB, although this is not required by the method.

11.6.1 For the ICV, all elements to be reported must be within 10 % of the true value and the replicates that exceed 5 times the reporting limit should have a relative standard deviation of less than 5 %. The ICV must be from a different source than the calibration standards and must be near the mid-point of the calibration curve. If the ICV does not meet criteria, then the problem must be identified and corrected before samples can be run and reported for the element(s) that are outside of criteria. Correction of the problem can be verified by rerunning the check standard and showing that it meets QC criteria.

11.6.2 If an ICB is analyzed, than all elements to be reported must be less than the RL (LLOQ). If the ICB is outside of criteria, then the problem must be identified and corrected before samples can be run and reported for the element(s) that are outside of criteria. Correction of the problem can be verified by rerunning the check standard and showing that it meets QC criteria. Analysis of a CCB before running any reportable samples can be used to verify that the system meets calibration blank requirements.

11.7 Continuing Calibration Verification (CCV) and Continuing Calibration Blank (CCB). Analyze the continuing calibration verification solution and the continuing calibration blank after every 10 sample and at the end of the sample run.

11.7.1 For the CCV, all elements to be reported must be within 10 % of the true value and the replicates that are greater than 5 times the reporting limit should have a relative standard deviation of less than 5 %. The CCV should be made from the same source as the calibration standards at a concentration near the mid-level of the calibration curve. If an element does not meet the recovery criteria of the CCV, than no samples can be reported for that element in the area bracketed by the CCV.

11.7.2 For the CCB, all elements to be reported must be less than the reporting limit (LLOQ). If an element does not meet this criterion, then no samples can be reported for that element in the area bracketed by the CCB.

11.7.3 The internal standard levels in the CCV and CCB must also be within 30% of the internal standard level for the initial calibration. If they are outside of these levels, then no samples can be reported in the area bracketed by this QC.

11.8 Interference Check Standards. After the initial QC is completed and before any samples are analyzed, the ICSA and ICSAB solutions must be analyzed. The method does not give

specific criteria for the ICSA and ICSAB, but in house criteria should be applied. For all the spiked elements, the analyzed results must be within 20 % of the true results. For unspiked elements, the interfering element solution should contain less than the absolute value of 3 times the reporting limit for each element. If these criteria are not met, then samples with significant interferences can not be reported until the correction factors are optimized and the ICSA and ICSAB are within specifications.

11.8.1 If the run is longer than 12 hours, a second ICSA, ICSAB pair must be analyzed before the next 12 hours is started.

11.8.2 If mass changes are made for the analysis of an element, all QC criteria must be met for the new mass and it must be verified that appropriate correction factors are in place.

11.9 Low Level Calibration Verification (CRI or LLCCV). The CRI standard containing the elements of interest at (or below) the reporting level for each element. The CRI (LLCV) must be analyzed at the beginning and end of each calibration (analysis) batch. The acceptance criterion for the CRI check is 70 to 130% recovery. If an element does not meet this criterion, then all bracketed samples for that element in the concentration range between the CRI and the CCV must be reanalyzed. Samples containing concentrations higher than the CCV may be reported as long as CCV criteria are met.

11.9.1 More frequent CRI (LCCV) checks may be analyzed during the course of the run if system stability at the low end of the calibration is questionable or if the lab wants to ensure that fewer samples will have to be submitted for reanalysis if there is a failed CRI at the end of a run.

11.9.2 It is recommended that the CRI check be run bracketing every 4 to 8 hour period of analysis. It may be run as frequently as every 10 samples if the supervisory staff deems that this is necessary.

11.10 Method Blank. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 sample batch. If the method blank does not contain target analytes at a level that interferes with the project-specific DQOs, then the method blank is considered acceptable.

11.10.1 The default SOP limit for the method blank is that is must be less than one half of the reporting limit.

11.10.2 In addition, the blank is considered acceptable if it is less than 10% of the regulatory limit, or less than 10% of the lowest sample concentration for each analyte in a given preparation batch, whichever is greater.

11.10.3 If the method blank does not meet criteria, then it can be reanalyzed along with any associated samples. If it is still unacceptable, then all associated samples must be redigested and reanalyzed along with the other appropriate batch QC samples.

11.11 Lab Control Sample or Spike Blank. The laboratory must digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 sample batch. The laboratory should assess laboratory performance of the lab control and spike blank against recovery limits of 80 to 120 %. In house lab control and spike blank limits may also be generated to support these default limits. If the lab control or spike blank is outside of the control limits for a given element, all samples must be redigested and reanalyzed for that element.

11.11.1 If solid lab controls are used, then the manufacturer's limits should be applied.

11.12 Matrix Spike. The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Recoveries should be assessed against default limits of 75 to 125 %. In house limits may be generated for this method for informational purposes only. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote and it is recommended that a post-digest spike be analyzed for the out of control element(s). If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect. Note: Both the matrix spike amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

$$\frac{\text{(Spiked Sample Result - Sample Result)}}{\text{Amount Spiked}} \times 100 = \text{matrix spike recovery}$$

11.12.1 If a post-digest spike is required, the sample should be spiked with approximately 2 times the sample level or two times the reporting limits, whichever is greater. Limits of 80 to 120 % are normally applied. The serial dilution is used to confirm any matrix effects. The post-digest spike recovery must be footnoted on the matrix spike recovery or otherwise noted in the quality control summary report.

11.13 Matrix Spike Duplicate (MSD) or Matrix duplicate (DUP). The laboratory must digest a matrix spike duplicate or matrix duplicate sample for a minimum of 1 in 20 samples. The relative percent difference (rpd) between the MSD and the MS or between the DUP and the sample should be assessed. The rpd is calculated as shown below. The control limit for the duplicate rpd is method defined as 20%. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control. Note: Both the duplicate amount and the sample amount are calculated to the IDL for any given element. Any value less than the IDL is treated as zero.

11.13.1 If a MSD or duplicate is out of control, then the data should be checked carefully to confirm that the high rpd for a given element is not a result of an analytical problem. If an analytical problem is suspected, the MSD or duplicate must be reanalyzed for confirmation. If the initial and reanalysis are in agreement (within 20%), then the high rpd is a result of preparation or sample issues and further analysis of the initial preparation is not required. If the initial and reanalysis are not in agreement due to an analytical problem, then any affected samples in the associated batch should also be reanalyzed for that element.

11.13.2 If more than 50% of the elements in a sample (that have levels of at least 5 times the reporting limit) have a high RPD, then the MSD or duplicate should be redigested for confirmation, unless the sample matrix is such that the non-homogeneity of the sample is visually apparent. If the results confirm, the results from the original MSD or duplicate should be flagged as indicative of possible sample non-homogeneity. If the results do not confirm, then the whole batch should be digested and reanalyzed.

11.13.3 If 50% or less of the elements in a sample (that have levels of at least 5 times the reporting limit) have a high rpd, then the high rpd(s) should be footnoted as indicating possible sample non-homogeneity unless other problems are suspected. If problems are suspected, the reviewer will initiate redigestion and reanalysis of the batch.

11.13.4 The calculations used to calculate RPD are shown below.

$$\frac{(|\text{MS Result} - \text{MSD Result}|) \times 100}{(\text{MS Result} + \text{MSD Result})/2} = \text{MSD RPD}$$

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

11.14 Serial Dilution. A serial dilution is required on a frequency of one in 20 samples. It is normally done on the same sample as is used for the matrix spike. If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally a factor of at least 100 times greater than the concentration in the reagent blank), then an analysis of a fivefold (1+4) dilution must agree to within ±10% of the original determination. If not, an interference effect must be suspected and the serial dilution result for the element with the suspected interference must be footnoted. The serial dilution is calculated as shown below.

$$\frac{(\text{Sample result} - \text{Serial dilution result}) \times 100}{\text{Sample result}} = \text{Serial dilution percent difference}$$

11.14.1 Results of less than the IDL are treated as 0. The concentration in the reagent blank is normally < 3 times the IDL, so the factor of 100 times the concentration in the reagent blank (listed above) so the limits should be applied to sample concentrations of greater than 300 times the IDL.

11.15 Lower Limit of Quantitation check sample (LLQC). The LLQC is a sample at the reporting limit that is taken through the entire preparation and analytical process. This standard must be analyzed when reporting limits are initial established and on an as needed basis after that. The LLQC is equivalent to the LOQ (Limit of quantitation) standard which must be analyzed quarterly for the DOD QSM program. The limits of quantitation are verified when all analytes in the LLQC sample are detected within 30% of their true value. If the limits cannot

be verified at the spiked level, then the quantitation limit must be adjusted to a level where verification is successful.

13.0 DOCUMENTATION REQUIREMENTS

13.1 If samples or QC checks require reanalysis, a brief explanation of the reason must be documented on the run log. All instrument data should be exported to the LIMS system.

13.2 All standard preparations must be entered and completed in the Reagent Application. All information requested must be completed. All standards must have a lot number that is generated by Reagent Application on the bottle before being used.

13.3 The Instrument Maintenance Logbook must be completed when any type of maintenance is performed on the instrument daily.

13.4 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

13.5 Supervisory (or peer) personnel must routinely review (approximately once per month) all laboratory logbooks to ensure that information is being recorded properly. Additionally, the maintenance of the logbooks and the accuracy of the recorded information should also be verified during this review.

14.0 INSTRUMENT MAINTENANCE

14.1 Recommended periodic maintenance includes the items outlined below.

14.1.1 Change the pump tubing weekly or as needed.

14.1.2 Clean the nebulizer, torch, and injector tube every two to four weeks or more often as needed.

14.1.3 Change the sampler tip as needed (every one to two months).

14.1.4 Clean the recirculating pump lines as needed.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 15.2

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

15.2.1 Non hazardous aqueous wastes.

15.2.2 Hazardous aqueous wastes

15.2.3 Chlorinated organic solvents

15.2.4 Non-chlorinated organic solvents

15.2.5 Hazardous solid wastes

15.2.6 Non-hazardous solid wastes

16.0 ADDITIONAL REFERENCES

Refer to other SOP's for ICP-MS analysis (EPA 200.8).

TABLE 1: ELEMENTS, MASSES, AND REPORTING LIMIT

Mass and Element	Associated Tune (1 = no gas, 2= helium)	CRI (LOQLL) CRI Check	Normal Digested Aqueous Sample Reporting Limit (Dilution Factor of 2) in ug/l.	Normal Digested Solid Sample Reporting Limit (Dilution Factor of 5) in mg/kg.	Comments
9Be	1	0.5	1	0.25	
11B	1	5	10	2.5	
23Na	1	250	500	125	
24Mg	1	250	500	125	
27Al	1	25	50	12.5	
39K	1	250	500	125	
44Ca	1	250	500	125	
47Ti	1	1	2	0.5	
51V	2	1	2	0.5	
52Cr	2	1	2	0.5	
55Mn	2	0.5	1	0.25	
56Fe	2	25	50	12.5	
59Co	2	0.5	1	0.25	
60Ni	2	1	2	0.5	
63Cu	2	1	2	0.5	
66Zn	2	2	4	1	

75As	2	0.5	1	0.25	
78Se	2	0.5	1	0.25	
88Sr	1	5	10	2.5	
98Mo	1	1	2	0.5	.
107Ag	1	0.5	1	0.25	
111Cd	2	0.5	1	0.25	
120Sn	1	5	10	2.5	
121Sb	1	0.5	1	0.25	123Sb is the method recommended line, but 121Sb is used instead. Xe is a possible interference for 123Sb and is sometimes found as a contaminant in argon.
137Ba	1	1	2	0.5	
182W	1				
205Tl	1				
208Pb	1	0.5	1	0.25	206Pb,207Pb, and 208Pb summed and reported under 208Pb

TABLE 2: RECOMMENDED STANDARDS AND ICV AND CCV LEVELS AND NORMAL LINEAR RANGES

Mass and Element	STDA	STDB	STDC	STDD	STDE	STDF	STDG	STDH	LINEAR RANGE	ICV	CCV
9Be	0	0.5	5	25	50	100	0	0	1000	60	50
11B	0	0.5	5	25	50	100	0	0	1000	60	50
23Na	0	0.5	5	25	50	100	1000	10000	100000	5500	5000
24Mg	0	0.5	5	25	50	100	1000	10000	100000	5500	5000
27Al	0	0.5	5	25	50	100	1000	10000	100000	5500	5000
39K	0	0.5	5	25	50	100	1000	10000	100000	5500	5000
44Ca	0	0.5	5	25	50	100	1000	10000	100000	5500	5000
47Ti	0	0.5	5	25	50	100	0	0	1000	60	50
51V	0	0.5	5	25	50	100	0	0	1000	60	50
52Cr	0	0.5	5	25	50	100	0	0	1000	60	50
55Mn	0	0.5	5	25	50	100	0	0	1000	60	50
56Fe	0	0.5	5	25	50	100	1000	10000	100000	5500	5000
59Co	0	0.5	5	25	50	100	0	0	1000	60	50
60Ni	0	0.5	5	25	50	100	0	0	1000	60	50
63Cu	0	0.5	5	25	50	100	0	0	1000	60	50
66Zn	0	0.5	5	25	50	100	0	0	1000	60	50
75As	0	0.5	5	25	50	100	0	0	1000	60	50
78Se	0	0.5	5	25	50	100	0	0	1000	60	50
88Sr	0	0.5	5	25	50	100	0	0	1000	60	50
95Mo	0	0.5	5	25	50	100	0	0	1000	60	50
107Ag	0	0.5	5	25	50	100	0	0	200	60	50
111Cd	0	0.5	5	25	50	100	0	0	1000	60	50
120Sn	0	0.5	5	25	50	100	0	0	1000	60	50
121Sb	0	0.5	5	25	50	100	0	0	1000	60	50
137Ba	0	0.5	5	25	50	100	0	0	1000	60	50
182W	0	0.5	5	25	50	100	0	0	1000	60	50
205Tl	0	0.5	5	25	50	100	0	0	1000	60	50
208Pb	0	0.5	5	25	50	100	0	0	1000	60	50

TABLE 3: INTERNAL STANDARD MASSES AND ELEMENTS

Mass and Element	Associated Tune for ISTD (1 = no gas, 2= helium)	Comments
6Li	1	
45Sc	1, 2	
72Ge	1,2	
89Y	1, 2	Sometimes found in soil matrices. Monitor recoveries with other internal standards. Optional
103Rh	1	
115In	1, 2	
159Tb	1	
175Lu	1	Optional
209Bi	1	

TABLE 4: MS AND BLANK SPIKE CONCENTRATIONS

Element	Soils Final Concentration in mg/kg	Aqueous Final Concentration in µg/l
Ag	20	200
Al	200	2000
As	50	500
B	100	1000
Ba	200	2000
Be	50	500
Ca	2500	25000
Cd	50	500
Co	50	500
Cr	50	500
Cu	50	500
Fe	200	2000
K	2500	25000
Mg	2500	25000
Mn	50	500
Mo	100	1000
Na	2500	25000
Ni	100	500
Pb	50	1000
Sb	50	500
Se	50	500
Tl	50	500
V	50	500
Zn	50	500
Sn	100	1000
Sr	50	500
Ti	50	500

Lab Manager: Brad Madadian

QA Officer: Robert Treggiari

TITLE: DIGESTION OF NON-POTABLE WATERS FOR FLAME AND ICP ANALYSIS INCLUDING ANTIMONY (Sb).

TEST METHODS REFERENCE: SW846 3010A Rev. 1 July 1992

REVISED SECTIONS: 11.3

1.0 SCOPE & APPLICATION

1.1 This method is applicable for the digestion of aqueous, TCLP extracts, and wastes that contain small amount of suspended solids. After digestion, the samples can be analyzed by ICP. This digestion method is based upon SW846 method.

Note: this method must not be used for drinking water samples. Please refer to the drinking water SOP

1.2 Test Code: METDIG

2.0 SUMMARY

2.1 A representative aliquot of sample (50 ml) is digested with nitric acid and dilute hydrochloric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to low volume, it is cooled and diluted to final volume of 50 ml with DI water. Sample is then mixed and filtered if it contains suspended solids.

3.0 METHOD REPORTING AND DETECTION LIMITS

3.1 See the determinative method for detection limits.

4.0 DEFINITIONS

4.1 ALIQUOT - a measured portion of a sample, or solution, taken for sample preparation and/or analysis.

4.2 BATCH – A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20 then each group of 20 samples or less will all be handled as a separate batch.

4.3 CONTAMINATION - a component of a sample or an extract that is not representative of the environmental source of the sample. Contamination may stem from other samples, sampling

equipment, while in transit, from laboratory reagents, laboratory environment, or analytical instruments.

4.4 DEIONIZED WATER (DI water) - water that has passed through Accutest's deionization system. Used as reagent water (water that an interferant is not observed at or above the minimum quantitation limit of the parameters of interest). Also called reagent water.

4.5 FIELD SAMPLE - a portion of material to be analyzed that is contained in single or multiple containers and identified by a unique sample number.

4.6 INSUFFICIENT QUANTITY - when there is not enough volume to perform any of the required operations: sample digestion or analysis, MS/MSD, etc.

4.7 MATRIX - the predominant material of which the sample to be analyzed is composed. For the purpose of this SOP, a sample matrix is water. Matrix is not synonymous with phase (liquid or solid).

4.8 MATRIX EFFECT - in general, the effect of a particular matrix (water or soil/sediment) on the constituents with which it contacts. This is particularly pronounced for clay particles which may adsorb chemicals and catalyze reactions. Matrix effects may prevent extraction of target analytes. In addition, non-target analytes may be extracted from the matrix causing interferences.

4.9 MATRIX SPIKE - aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific analytes and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery. The matrix spike recovery is calculated as shown below.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{(\text{Amount Spiked})} \times 100 = \text{Matrix Spike Recovery}$$

4.10 MATRIX SPIKE DUPLICATE - a second aliquot of the original sample that is spiked in order to determine the precision of the method. The matrix spike duplicate RPD is calculated as shown below.

$$\frac{(|\text{MS Result} - \text{MSD Result}|) \times 100}{(\text{MS Result} + \text{MSD Result})/2} = \text{MSD RPD}$$

4.11 METHOD BLANK - an analytical control consisting of all reagents that is carried throughout the entire digestion and analytical procedure. The method blank is used to define the level of laboratory, background, and reagent contamination.

4.12 RELATIVE PERCENT DIFFERENCE (RPD) - as used in this SOP to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero.

4.13 SPIKE BLANK – DI water fortified (spiked) with known quantities of specific analytes and subjected to the entire analytical procedure in order to indicate the accuracy of the analysis.

5.0 HEALTH & SAFETY

5.1 All safety practices must be followed as outlined in the Accutest Laboratories Employee Safety Handbook and Chemical Hygiene Plan. Safety glasses, gloves, and lab coats must be worn. All samples, solutions, and extracts must be treated as unknown and potentially hazardous.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level.

5.3 All acid digestion procedures will take place under a working hood. Verify the hood is working before use. Tape a strip of kim-wipe or plastic to the hood sash for visual verification of hood function.

6.0 PRESERVATION & HOLDING TIME

6.1 Preservation: Samples must be preserved to < 2.0 pH with nitric acid at the time of collection or upon receipt by the laboratory. Sample must be cooled to 4°C ±2°C upon collection.

6.2 Holding Time: Samples must be digested and analyzed within 6 months of the time of collection.

6.3 Samples should be collected in 250-ml plastic bottles.

7.0 APPARATUS & MATERIALS

The apparatus needed for this digestion procedure are listed below. It should be noted that hot plates and beakers with watch glasses may be used in place of the digestion block and digestion tubes.

7.1 Equipment

7.1.1 Digestion block. Designed to hold sample digestion tubes and capable of temperature control. Environmental Express HOT BLOCK or equivalent.

7.2 Materials

7.2.1 Sample digestion tubes. 60 ml polypropylene tubes.
7.2.2 Ribbed watch glass. Polypropylene.
7.2.3 Automatic pipetter bottles.
7.2.4 Polypropylene filter funnels.
7.2.5 Whatman #41 filter paper or equivalent
7.2.6 Filtermate 2u Teflon

8.0 STANDARDS & REAGENTS

All chemicals listed below are trace metal grade unless otherwise specified. Distilled, deionized water should be used whenever water is required.

8.1 Nitric Acid. Baker instra-analyzed or equivalent.

8.2 Hydrochloric Acid. Baker instra-analyzed or equivalent.

8.3 Hydrochloric acid (1 +1). Add 500 ml of concentrated HCl to 400 ml of DI water. Cool and dilute to 1 liter.

8.4 Metals Spiking Solutions. All metals spiking solutions should be made up in a solution of 2 % nitric acid following the procedures outlined in the table 1.

Spiking Solution	Element	Stock Conc. in mg/l	Vol. of Stock in ml	Final Vol. of Spiking Solution in ml	Spiking Solution Conc. in mg/l
Ag Spike Solution	Ag	1000.00	2.00	100.00	20.00
ICP Spike Solution 1	As	1000.00	5.00	100.00	50.00
	Be	1000.00	5.00		50.00
	Cd	1000.00	5.00		50.00
	Co	1000.00	5.00		50.00
	Cr	1000.00	5.00		50.00
	Cu	1000.00	5.00		50.00
	Mn	1000.00	5.00		50.00
	Ni	1000.00	5.00		50.00
	Sb	1000.00	5.00		50.00
	Se	1000.00	5.00		50.00
	Sr	1000.00	5.00		50.00
	Ti	1000.00	5.00		50.00
	Tl	1000.00	5.00		50.00
	V	1000.00	5.00		50.00
	Zn	1000.00	5.00		50.00
ICP Spike Solution 2	Al	10000.00	2.00	100.00	200.00
	Ba	1000.00	20.00		200.00
	Fe	10000.00	2.00		200.00
	Pb	1000.00	10.00		100.00
ICP Mineral Spike	Ca	10000.00	25.00	100.00	2500.00
	Mg	10000.00	25.00		2500.00
	K	10000.00	25.00		2500.00
	Na	10000.00	25.00		2500.00
ICP B Spike	Au	1000.00	10.00	100.00	100.00
ICP Au Spike	B	1000.00	10.00	100.00	100.00
ICP Mo Spike	Mo	1000.00	5.00	100.00	50.00
ICP Pd Spike	Pd	1000.00	10.00	100.00	100.00
ICP Pt Spike	Pt	1000.00	10.00	100.00	100.00
ICP Si Spike	Si	1000.00	10.00	100.00	100.00

ICP Sn Spike	Sn	1000.00	10.00	100.00	100.00
ICP W Spike	W	1000.00	10.00	100.00	100.00
ICP Zr Spike	Zr	1000.00	5.00	100.00	50.00
ICP Li Spike	Li	10000.00	10000.00	100.00	2500.00

Table 1

9.0 INTERFERENCES

9.1 Aqueous samples can contain diverse matrix types which may contain a variety of interferences. Spiked samples can be used to determine if these interferences are adequately treated in the digestion process. For a discussion of other interferences, refer to specific analytical methods.

10.0 PROCEDURE

10.1 Measure out 50 ml of each sample into a labeled digestion tube. Make sure that the sample has been thoroughly mixed. Make sure that the sample identification is accurately recorded with the digestion tube numbers on the sample digestion log. In addition to the samples, a Matrix Spike, a Matrix Spike Duplicate, a Spike Blank and a Method Blank should be set up with each batch of 20 samples. Add 0.50 ml of the spiking solutions to the Matrix Spike, Matrix Spike Duplicate and Spike Blank. Check with the metals supervisor for the spiking solutions (refer to Table 1) to use for each batch.

10.2 Add 1.5 ml of concentrated nitric acid to all quality control and samples.

10.3 Place the numbered tubes into a digestion block. Heat the block until the samples are at a gentle reflux (90-95°C). Record the temperature.

10.4 Reduce the volume of each sample to approximately 5 to 10 mls.

10.5 Add an additional 1.5 ml of concentrated nitric acid to all quality control and samples. Cover with watch glasses. Heat the samples at a gentle reflux until the volume is again at approximately 5 to 10 mls.

Note: This step may be omitted if the sample appears completely digested at the end of step 10.4. Signs of a complete digestion are if the digestate is light in color and/or the appearance does not change with continued refluxing.

10.6 Add 5 ml of 1+1 HCl to each sample and reflux for additional 15 minutes. Cool.

10.7 Filter the samples through Whatman #41 filter paper or by using Filtermate 2u Teflon (if needed), dilute to final volume of 50 ml with distilled, deionized water and mix. The sample is now ready for analysis by ICP or FLAME AAS.

10.8 Glassware cleaning

10.8.1 All glassware should be washed with soap and tap water and then soaked in 5 % nitric acid. It should then be rinsed at least 3 times with distilled, deionized water. Store upside down or in sealed bins to prevent accumulation of dust.

11.0 QUALITY ASSURANCE

11.1 Below is a summary of the quality control requirements, performance criteria and general corrective action guidelines for this method .Make sure to check with the laboratory supervisor for any additional client specific quality control requirements.

11.2 **Method Blank.** The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different day. The method blank must contain the analyte at a level less than the reporting limit(less than ½ the reporting limit for certain clients). If the method blank contains over that limit, the samples must be reanalyzed.

11.3 **Spike Blank.** The laboratory must analyze a spike blank with each set of samples. A minimum of one spike blank is required for every 20 samples. For a running batch, a new spike blank is required for each different analysis day. Until sufficient lab control data becomes available (usually a minimum of 20-30 analyses) the laboratory should assess the laboratory performance of the spike blank against recovery limits of 80-120 %. If the lab control recovery is high and the results of the samples to be reported are less than the reporting limit, then the sample results can be reported with a sample case narrative. If the samples are above the reporting limit or if the lab control recovery is low, report to the laboratory supervisor. In most cases the lab control and the samples must be re-prepped and reanalyzed.

11.4 **Matrix Spike.** The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The spike recovery should be assessed using in house limits. Until these limits can be generated, default limits of 75-125 % recovery should be applied. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample can not be assessed against the control limits and should be footnoted to that effect.

11.5 **Matrix Spike Duplicate.** The laboratory must analyze a Matrix Spike Duplicate for a minimum of 1 in 20 samples. This second aliquot of the original sample that is spiked in order to determine the precision of the method. The relative percent difference (RPD) between the Matrix Spike duplicate and the Matrix Spike should be assessed using in house limits. Until these limits can be generated, then default limits of $\pm$20% RPD should be applied.

12.0 DOCUMENTATION

12.1 Record all digestion information in Metal Digestion automated logbook. The information required includes the digestion tube number, the sample identification, the initial sample volume, the final sample volume, the acids used, the spikes used, and the temperature. The analyst should write additional information such as unusual sample characteristics in the comments section. All spiking solution information should be entered in the metals reagents and standards logbook.

12.2 The standard preparation logbook must be completed for all standard preparations. All information requested must be completed; the page must be signed and dated by the respective person.

12.3 The Accutest lot number must be cross-referenced on the standard vial/container. The expiration date must be noted on the standard vial/container

12.4 All laboratory logbooks must be routinely reviewed and initialed or signed by the lab manager.

12.5 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

13.0 DATA REVIEW & REPORTING

13.1 See the determinative method SOP for data review and reporting. The Laboratory Manager and Quality Assurance Officer should review the digestion logbook and reagents and standards logbook on a periodic basis.

14.0 POLLUTION PREVENTION & WASTE MANAGEMENT

14.1 Pollution Prevention. Users of this method must perform all procedural steps that control the creation and/or escape of wastes of hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids, or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 14.2

14.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the Sample and Waste Disposal SOP. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

14.2.1 Non-hazardous aqueous wastes
14.2.2 Hazardous aqueous wastes
14.2.3 Chlorinated organic solvents
14.2.4 Non-chlorinated organic solvents
14.2.5 Hazardous solid wastes
14.2.6 Non-hazardous solid wastes

15.0 ADDITIONAL REFERENCES

15.1 No additional references are required for this method.

ACCUTEST LABS
STANDARD OPERATING PROCEDURE

Lab Manager: Brad Madadian

QA Officer: Robert Treggiari

TITLE: CHLORIDE

TEST METHOD REFERENCE: 4500 Cl C. Standard Methods for the Examination of Water and Wastewater 21th Edition, 2005

TEST CODES: CHL

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Revised Sections: ***Test Method Ref., 10.1; 10.2***

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the determination of chloride in surface waters, saline waters, and domestic and industrial wastes. A modification of this method can be used to determine soluble chloride in soil samples.
Note: This method should not be used for drinking waters.

2.0 SUMMARY OF METHOD

2.1 Sample is titrated with mercuric nitrate in the presence of mixed diphenylcarbazone-xylene cyanol FF indicator with sample pH adjusted to 2.5+/-0.1 by HNO3. The end point of the titration is the formation of the blue-violet mercury diphenylcarbazone complex.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The Reporting Limit (RL) is based on the lowest calibration standard. RL'S may vary depending on matrix difficulties and sample volumes or weight and percent moisture.

3.2 The reporting limit for this method has been established at 1.0 mg/l for waters and 10 mg/l for soils.

3.3 Method Detection Limits

3.3.1 Detection limits are experimentally determined using the procedures described in 40 CFR, Part 136, Appendix B. Actual reported MDLs incorporate the sample weight or volume analyzed and sample dilutions if needed, which may cause MDL variations from sample to sample.

3.3.2 In general, MDLs are determined through the analysis of at least 7 replicate blank spikes (using the same procedures for sample analysis). The MDL is calculated by multiplying the standard deviation of the replicate concentrations by the appropriate Student's t value (3.143 for 7 replicates). If more than 7 replicates are analyzed refer to 40 CFR, Part 136, Appendix B for the appropriate student's t value . MDL studies are performed on an annual basis or after any major changes to the

instrumentation. For additional detail regarding MDL studies, refer to the MDL SOP MQA245.

3.3.3 The MDL represents the lowest reportable concentration of an individual analyte that meets the method qualitative identification criteria.

3.3.4 Current MDL studies are filed with Quality Assurance. Obsolete MDL studies are archived with the QA files. Electronic MDL data is found in the annual "MDL" folder on the QA server (LINUXMA1).

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source to verify the accuracy of the analysis. An external check must be run a minimum of once per quarter for all analyses where a check is commercially available. The laboratory should assess laboratory performance of a external check standard using the control limits generated by the external check supplier. If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK OR LAB CONTROL SAMPLE. Prepare and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. For a running batch, a new spike blank is required for each different analysis day. In house limits should also be generated once sufficient data is available to generate limits (usually a minimum of 20 to 30 analyses). If the lab control is outside of the control limits for a parameter, all samples must be reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag. Note: If control limits are not available, then default limits of 80 to 120 percent should be used.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX SPIKE: Aliquot of matrix (water or solid) fortified (spiked) with known quantities of specific compounds, and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring the recovery. A matrix spike sample is analyzed at a minimum of 1 in 20 samples. The percent recovery of matrix spike should be assessed. In house limits are generated once sufficient data is available to generate limits (usually a minimum of 20 to 30 analysis).

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than

5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not available, use default limits of ± 20% RPD.

$$\frac{(\,|\,\text{Sample Result} - \text{Duplicate Result}\,|\,) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

METHOD BLANK. The laboratory must prepare and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different analysis day. If no digestion/extraction step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be re-prepped and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). MDLs should be established for all appropriate methods, using a solution spiked at approximately 2-5 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of three replicate analyses by 3.14, which is the student's t value for a 99% confidence level. MDLs should be determined approximately once per year for frequently analyzed parameters.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. - water in which an interferant is not observed at or above the minimum quantitation limit of the parameters of interest. Accutest uses deionized water (municipal water which passes through Accutest's DI treatment system).

REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

5.0 HEALTH & SAFETY

5.1 The analyst should follow normal safety procedures as outlined in the Accutest Laboratory Employee Safety Manual and Chemical Hygiene Plan which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and should be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is

responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets should be made available to all personnel involved in these analyses.

6.0 PRESERVATION & HOLDING TIME

6.1 The samples should be stored at 4^0 C $\pm$ 2°C.

6.2 The samples should be analyzed within 28 days of the date of collection.

7.0 INTERFERENCES

7.1 Anions and cations at concentrations normally found in surface waters do not interfere, although bromide and iodide are titrated with mercuric nitrate in the same manner as chloride. Chromate, ferric, and sulfite ions interfere when present in concentrations greater than 10 mg/l. The sulfite interference can be eliminated by oxidizing 50 ml of the sample solution with hydrogen peroxide

8.0 APPARATUS

8.1 Micro-burette
8.2 Erlenmeyer flasks or beakers.
8.3 Stirring plate.
8.4 Stir bars.
8.5 pH Paper

9.0 REAGENTS

9.1 Standard Sodium chloride, 0.0141 N: Dissolve 824.0 mg of sodium chloride that has been dried at 140^0 C for 1 hour in DI water in a 1 liter volumetric flask and dilute to a final volume of 1 liter with DI water. **Note:** this solution can also be purchased.

9.2 0.1 N, Nitric acid solution. Add 6.4 ml of concentrated nitric acid to DI water in a 1000 ml volumetric flask and dilute to the final volume with DI water.

9.3 0.1 N, Sodium hydroxide solution. Dissolve 4.0 g of sodium hydroxide in approximately 800 ml of DI water and dilute to a final volume of 1000 ml with DI water.

9.4 Mercuric nitrate titrant (0.0141 N): Dissolve 2.42 g of mercuric nitrate ($Hg(NO_3)2.H_2O$) in 25 ml of DI water acidified with 0.25 ml of concentrated nitric acid. Dilute to a final volume of 1 liter with DI water. Filter if necessary. Standardize against standard sodium chloride solution (9.1) using the same procedure outlined below to determine chloride concentrations. Adjust the titrant to 0.0141 N. This should be stored in a dark bottle. **Note;** This solution can be purchased. Make sure if purchased, to receive and file the certificate of tracability since this standard has been standardized against a primary standard. Use the normality provided with this certificate for calculation.

9.5 Acidic mixed Indicator reagent: Dissolve, in the order named, 0.250 g of s-diphenylcarbazone, 4 ml conc HNO3, and 30 mg xylene cyanol FF in 100 ml of 95% ethyl alcohol or isopropyl alcohol. Store in a dark bottle in the refrigerator for a maximum of 1 months.

Note: Deterioration causes a slow end point and high results.

9.6 Non-acidic mixed Indicator reagent: Dissolve, in the order named, 0.250 g of s-diphenylcarbazone, and 30 mg xylene cyanol FF in 100 ml of 95% ethyl alcohol or isopropyl alcohol. Store in a dark bottle in the refrigerator for a maximum of 1 months.

9.7 Sodium Chloride Spiking Solution A (2000 mg/L): Dissolve 3.296 g of sodium chloride that has been dried at 600^0 C for 1 hour in DI water in a 1 liter volumetric flask and dilute to a final volume of 1 liter with DI water.

9.8 Sodium Chloride spiking solution B (250 mg/L): Dilute 25 ml of solution 9.7 in 200 ml of DI water.

9.9 All applicable standard/reagent preparation information, including vendor, lot number, date of preparation, calculations, and initials must be entered in the appropriate standard/reagent preparation logbook. Vendors typically used by Accutest include Fisher Scientific, VWR, Accustandard, Supelco, Chemservices, Ultra, and ERA. Additional vendors may be utilized as necessary.

10.0 PROCEDURE

Below is a step by step procedure for the analysis of samples for CHL. Use the automated spreadsheet for documentation, calculations of Standardization, and the analysis. This application can be found on server.

Note: Make sure that the mercuric nitrate titration solution has been standardized before starting this procedure. If the certificate of analysis is not provided, standardize in replicates containing 5 ml of of standard NaCl (9.1) and 10 mg sodium bicarbonate(NaHCO3) diluted to 100 ml with DI water. Titrate following the procedures outlined in steps 10.2 through 10.5 below using the 100 ml of standard.

10.1 For soil samples, homogenize sample and do not include any large rocks or debris in sample aliquot. Proceed to weigh out 15.0 g of sample and add 150 ml of DI water. Stir or tumble samples for 1 hour. Filter the sample through GFF filter paper and continue with steps 10.2 through 10.5 below.

10.2 Measure 50 ml aliquots of sample or sample filtrate for soils, and two more aliquots for sample duplicate and matrix spike. For the method blank and spike blank 50 ml of DI water. Spike the matrix spike sample and the blank spike with 2.00 ml of 250 mg/L chloride spiking solution. For soil samples; spike the matrix spike sample and the blank spike with 6.00ml of 250mg/L chloride solution (B).

Note: **Samples containing greater than 100 mg/l of chloride should be analyzed with dilutions.**

10.3 Add 1 ml of acidic mixed indicator reagent (9.5) and a stirring bar to the sample and mix well. The color of the solution must turn to green-blue at this point. For most potable waters, the pH will be 2.5 +/- 0.1 upon addition of this indicator.

10.3.1 A light green indicates pH less than 2.0,

10.3.2 A pure blue indicates pH more than 3.8

10.4 Because the pH control is critical, adjust the pH of highly alkaline or acid samples to 2.5+/- 0.1 with 0.1 N HNO3, or 0.1 N NaOH. Determine the amount of acid or alkali required to obtain the above pH and discard this sample portion. Treat a separate sample portion with the determined amount of acid or alkali and continue analysis using the non acidic mixed indicator (9.6).

10.5 Titrate the sample with 0.0141N mercuric nitrate while stirring. The end point is reached when a blue-violet color persists throughout the solution.

10.6 If the sample is above 100 mg/l of chloride, dilute the sample and analyze the dilution as described in 10.2 through 10.5 above.

11.0 CALCULATION

11.1 Water samples should be calculated using the equation shown below.

$$\text{chloride in mg/l} = \frac{(B - A) \times N \times 35450}{\text{ml of sample}}$$

11.2 Soil samples should be calculated using the equation shown below.

$$\text{chloride in mg/kg} = \frac{(B - A) \times N \times 35450 \times \text{final volume}}{(\text{g of sample})(\%\text{sol}/100)}$$

12.0QC REQUIREMENTS

12.1 Below is a summary of the quality control requirements for this method. Make sure to check with the laboratory supervisor or manager for any additional client specific quality control requirements.

12.2 Method Detection Limits (MDLs). MDLs should be established using a solution spiked at approximately 3-5 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of the replicate

analyses by 3.14, which is the student's t value for a 99% confidence level . MDLs should be determined approximately once per year.

12.3 Method Blank. The laboratory must analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different analysis day. The method blank must contain the analyte at less that the reporting limit. If the method blank contains an analyte level over that limit, the samples must be reanalyzed.

12.4 Spike Blank. The laboratory must analyze a spike blank with each set of samples. A minimum of one spike blank is required for every 20 samples. The net recovery should be within 20 percent of the true value.

12.5 External Check Sample. The laboratory must analyze an external check standard at least once per month. It is recommended that this be analyzed with each batch or when available. The recovery should be assessed, the limits supplied by the external check manufacturer should be applied.

12.6 Matrix Duplicate. The laboratory must prepare a duplicate sample for a minimum of 1 in 20 samples. The relative percent difference (rpd) between the duplicate and the sample should be assessed. The duplicate rpd is calculated as shown below.

12.6.1 The duplicate RPD should be assessed using in house limits. Until these limits can be generated, then default limits of 20 percent RPD should be applied. If a duplicate is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control.

12.6.2 The duplicate RPD should be calculated as shown below.

$$\frac{(\text{Sample Result} - \text{Duplicate Result}) \times 100}{(\text{Sample Result} + \text{Duplicate Result}) \times 0.5} = \% \text{ RPD}$$

12.7 Matrix Spike. The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The spike recovery should be assessed using in house limits. Until these limits can be generated, default limits of 75-125% recovery should be applied. If a matrix spike recovery is out of control, then the recovery should be flagged with the appropriate footnotes. If the matrix spike amount is less than one fourth of the sample amount, then the sample can be assessed against the control limits and should be footnoted to that effect.

$$\frac{(\text{Matrix Spike Result} - \text{Original Sample Result}) \times 100}{\text{Amount of Spike}}$$

12.8 Prior to running samples, the laboratory must demonstrate initial proficiency by generating data of acceptable accuracy and precision (P&A study) for target analyte in a clean matrix. This procedure must be repeated on an annual basis, whenever new staff are trained, or when significant changes in instrumentation are made.

12.8.1 Four blank spikes are prepared and analyzed using the same procedures and conditions as samples. Calculate the average recovery and standard deviation of the recoveries of the analytes in each of the four QC samples. Until in-house limits are established for initial and annual demonstration of capabilities, use the recoveries of 80-120% as guidance for evaluating the results.

12.9 Quality control data are generated at least on an annual basis by QA using an in-house program. Blank spike and MS/Dup data are pooled for the previous year (or other specified time frame) and the data is processed and evaluated by QA. The annual QC data is filed with QA.

13.0 DOCUMENTATION

13.1 The Standard preparation log application must be completed for all standard preparations. All information requested must be completed.

13.2 The Accutest lot number must be cross-referenced on the standard vial/container.

13.3 Any comments or observations concerning the sample that may influence the analytical procedure.

13.4 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of corrections must appear next to the correction.

13.5 All laboratory logs must be reviewed and initialed or signed by the lab manager.

14.0 DATA REVIEW

14.1 The analyst conducts the primary review of all data. This review begins with a check of all Instrument and method quality control and progresses through sample quality control concluding with a check to assure that the client's requirements have been executed. The analyst has the authority and responsibility to perform corrective action for any out-of-control parameter of non-conformance.

14.1 A secondary review is performed by department managers, and it includes review of the data produced by their department. All manual calculations, QC criteria, and a department manager may reject data, initiate reanalysis, take additional corrective action, or reprocess data.

14.2 The laboratory director performs a full tertiary review of the data package following its assembly. This review includes an evaluation of QC data against acceptance criteria and a check of the data package contents to assure that all analytical requirements and specifications were executed.

14.3 Spot-check reviews are performed by the Quality Assurance Officer focusing on all elements of the deliverable including the client's specifications and requirements, analytical quality control, sample custody documentation and sample identification.

15.0REPORTING

15.1 A results page including positive results and/or RLs, units, methodology, analysis dates, and data qualifiers are reported. Additional quality control data including matrix duplicate RPDs, matrix spike recovery, blank spike and method blank results may be reported upon request of the client.

15.2 Data may be submitted to the client in a specified electronic format (EDD).

15.3 Once the data is approved by the laboratory manager, it may be accessed by clients via LabLink™.

15.4 Procedures for handling non-conforming data.

15.4.1 If quality control data does not meet criteria the non-conformance must be discussed in a case narrative and footnoted on the applicable quality control report summary.

15.4.2 If preservation or holding time criteria is not met and the samples are analyzed the result page must be footnoted with this information, and the non-conformance must be discussed in a case narrative or other suitable communication (telephone conversation log or email). Client notification documentation should be included with the data (telephone conversation log, fax, or email).

16.0 POLLUTION PREVENTION & WASTE MANAGEMENT

16.1 Pollution Prevention. Users of this method must perform all procedural steps that controls the creation and/or escape of wastes of hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids, or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 17.2

16.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the Sample and Waste Disposal SOP. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

16.2.1 Non-hazardous aqueous wastes
16.2.2 Hazardous aqueous wastes
16.2.3 Chlorinated organic solvents
16.2.4 Non-chlorinated organic solvents
16.2.5 Hazardous solid wastes
16.2.6 Non-hazardous solid wastes
16.2.7 Microbiological wastes

17.0 ADDITIONAL REFERENCES

17.1 No additional references are required for this method.

ACCUTEST LABORATORIES
STANDARD OPERATING PROCEDURE

Lab Manager: Nancy Cobb

QA Manager: [signature]

Effective Date: July 27, 2011

Title: Determination of Inorganic Anions by Ion Chromatography Using the IC2000

METHOD REFERENCES: EPA 300.0, SW846 9056A

Revised Sections: ***Method, 1.1.1, 11.9.5, 13.2.1.1, 13.2.1.2, 13.2.2.1, 13.2.4, 13.2.5, 13.5***

1.0 SCOPE AND APPLICATION

1.1 This method is for the measurement of anions such as bromide, chloride, fluoride, nitrate, nitrite, ortho-phosphate, and sulfate by ion chromatography. The method is applicable to potable and non-potable water, solids after extractions, and neutral leachates.

1.1.1 Accutest does not hold NELAC certification for these methods for nitrate, nitrite and orthophosphate; therefore, these parameters cannot be reported from methods EPA 300.0 or SW846 9056A. They are, however, included in the standards for these analyses to provide information on column and chromatographic conditions.

2.0 SUMMARY OF METHOD

2.1 A small volume of sample is introduced into an ion chromatograph. The anions of interest are separated and measured, using a system comprised of a guard column, and analytical column, a suppressor column, and a conductivity detector.

2.2 Detection limits vary with the instrument conditions and calibration levels used.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 Reporting Limit. The normal reporting limit for this method is normally established at or above the lowest non-zero concentration standard in the calibration curve. Detected concentrations below this concentration are not reported unless MDL reporting is being done.

3.1.1 Standard reporting limits for this method are shown below. Other reporting limits may be used as long as all quality control requirements are met.

Compound	Reporting Limit
Fluoride	0.2 mg/l
Chloride	2.0 mg/l
Bromide	0.50 mg/l
Sulfate	10.0 mg/l

3.2 Method Detection Limit. Experimentally determine MDLs using the procedure specified in 40 CFR, Part 136, Appendix B. This value represents the lowest reportable concentration of an individual compound that meets the method qualitative identification criteria.

3.2.1 For this method, MDLs must be determined every six months, when a new operator begins work or whenever there is a significant change in the background or instrument response.

3.2.1.1 A significant change in instrument response is monitored using Limit of Detection (LOD) standards. New LOD standards must be analyzed whenever a column is changed or whenever else an analyst suspects that instrument sensitivity has changed substantially. If the LOD standards indicate a significant change, than a full new MDL study must be analyzed.

3.2.1.2 Limit of Detection (LOD). The limit of detection (LOD) for each method and target analyte of concern is established after the completion of the MDL by running a sample at a level less than the RL and approximately 1 to 4 times the calculated MDL. If the LOD verification fails, then the laboratory must repeat the detection limit determination and LOD verification at a higher concentration or perform and pass two consecutive LOD verifications at a higher concentration and set the LOD at the higher concentration. Once the LOD is set, than that LOD level should be used to verify ongoing instrument sensitivity.

3.2.1.2.1 The normal acceptance criteria for the LOD for this method is defined by this SOP as being in the range from 10 to 200% recovery.

3.2.1.2.2 Typical LOD levels for IC following the conditions outlined in this SOP are 0.050 mg/l for bromide, 0.25 mg/l for chloride, 0.025 mg/l for fluoride and 0.5 mg/l for sulfate.

3.2.2 Process all raw data for the replicate analysis in each MDL study.

4.0 DEFINITIONS

BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

CALIBRATION CHECK STANDARD. The calibration check standard is a mid-range calibration standard. It is recommended that the calibration check standard be run at a frequency of approximately 10 percent. (For some methods this is mandatory and for some it is a recommendation only. Refer to individual method SOP's) For most methods, the mid-level calibration check standard criteria is ± 10 percent of the true value. The exception to this rule is if the recovery on the calibration check standard is high and the samples to be reported are less than the detection limit.

EXTERNAL CHECK STANDARD. The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run a minimum of once per quarter for all analyses where a check is commercially available. The laboratory should initially assess laboratory performance of a check standard using the control limits generated by the external check supplier. In house limits should

also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 20 samples. Assess laboratory performance against the control limits specified in the SOP. In house limits should also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the lab control is outside of the control limits for a parameter, all samples must be redigested or redistilled and reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag. Note: If control limits are not specified in the SOP, then default limits of 80 to 120 percent should be used.

MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

MATRIX DUPLICATE: A duplicate sample is digested at a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified in the SOP, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient matrix spike data is available to generate limits (usually a minimum of 20 to 30 analyses). If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect. Note: If control limits are not specified in the SOP, then default limits of 75 to 125 percent should be used.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{(\text{Amount Spiked})} \times 100 = \text{Matrix Spike Recovery}$$

MATRIX SPIKE DUPLICATES: Intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. For a running batch, a new method blank is required for each different digestion day. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains

levels over the reporting limits, the samples must be redigested or redistilled and reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

METHOD DETECTION LIMITS (MDLS). The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards that cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

LIMIT OF DETECTION (LOD): An estimate of the minimum amount of a substance that an analytical process can reliably detect. An LOD is analyte- and matrix-specific and may be laboratory-dependent.

5.0 HEALTH & SAFETY

5.1 The analyst must follow normal safety procedures as outlined in the Accutest Laboratory Safety Manual which includes the use of safety glasses and lab coats. In addition, all acids are corrosive and must be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical must be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets must be made available to all personnel involved in these analyses.

6.0 COLLECTION, PRESERVATION, AND HOLDING TIME

6.1 For bromide, chloride, and fluoride, no special preservations are required. For nitrite, orthophosphate, and sulfate, the sample must be cooled to 4 °C. For nitrate, the sample must be preserved to a pH of less than 2 with sulfuric acid unless it is analyzed within 48 hours.

6.2 Bromide, chloride, fluoride, and sulfate must all be analyzed within 28 days. If nitrate is preserved with sulfuric acid, it must also be analyzed within 28 days. Nitrite, orthophosphate, and unpreserved nitrate must be analyzed within 48 hours.

6.2.1 It is recommended that separate samples be collected and preserved for nitrate so that the longer holding time may always be applied.

7.0 APPARATUS AND MATERIALS

7.1 Ion Chromatograph with a guard column, an analytical column, a suppressor column, and a conductivity conductor. This SOP is written for the use with the Dionex ICS-2000 instrument. The ICS-2000 is run using the external water mode with the suppressor and using internally generated eluent. No manual eluent preparation is required for the ICS-2000 instruments. The columns used are listed below. Alternate columns may be used if all method requirements can be met.

7.1.1 Suppressor column, ASRS Ultra 4 mm. Dionex part number 061561

7.1.2 Guard Column, IONPAC AG18 4 mm. Dionex part number 060551.

7.1.3 Analytical Column, IONPAC AS18 4 mm. Dionex part number 060549,

7.2 Analytical balance, capable of weighing to 4 places.

7.3 Volumetric flasks, class A.

7.4 Volumetric pipets, class A or autopipeters. Note: If autopipeters are used, make sure that the calibration is checked before use as specified in the autopipeter SOP.

7.5 Helium tank and regulator. On the IC-2000 instruments, helium is used only for head pressure on the water reservoirs. The pressure should be set at approximately 6 psi.

7.6 Magnetic stirrers and stirring bars (for solid samples)

7.7 Nylon 0.20 um membrane filters or equivalent, that can be attached to the end of the syringe.

8.0 REAGENTS

All chemicals listed below are reagent grade unless otherwise specified. Deionized water must be used whenever water is required.

8.1 Stock Standard Solutions, 4000 mg/L and 16000 mg/l: The stock standard solution must be prepared for chloride and sulfate as listed below.

8.1.1 For the potassium sulfate, dry the salt at 104 deg. C for a minimum of 2 hours or to constant weight and store in a desiccator before use. Dry the sodium chloride for 1 hour at approximately 600 deg. C and cool and store in a desiccator before use.

8.1.2 Chloride and Sulfate 4000 mg/l stock: Dissolve 6.594g of sodium chloride (NaCl) and 7.256g of potassium sulfate (K_2SO_4) in 500 mL of DI water and dilute to 1 liter. This stock standard may be stored for 1 month.

8.1.3 Chloride and Sulfate 16000 mg/l stock. : Dissolve 6.594g of sodium chloride (NaCl) and 7.256g of potassium sulfate (K_2SO_4) in 200 mL of DI water and dilute to 250 ml. This stock standard may be stored for 1 month.

8.2 Stock standard solutions, 1000 mg/l: Stock standard solutions must be prepared for each anion as listed below. If no other instructions are noted, then dry the salt at 104 deg. C for a minimum of 2 hours or to constant weight and store in a desiccator before use.

8.2.1 Bromide stock: Dissolve 1.2876 g of sodium bromide (NaBr) in reagent water and dilute to 1 liter. This stock standard may be stored for 1 month.

8.2.1.1 Dry the sodium bromide at 150 deg. C for a minimum of 6 hours. Cool and store in a desiccator before use.

8.2.2 Fluoride stock: Dissolve 2.2100 g of sodium fluoride (NaF) in reagent water and dilute to 1 liter. This stock standard may be stored for 1 month.

8.2.3 Nitrate stock: Dissolve 6.0679 g of sodium nitrate ($NaNO_3$) in reagent water and dilute to 1 liter. This stock standard may be stored for 1 month.

8.2.4 Nitrite stock: Dissolve 4.9257 g of sodium nitrite ($NaNO_2$) in reagent water and dilute to 1 liter. This stock standard may be stored for 1 month.

8.2.5 Orthophosphate stock: Dissolve 4.3937 g of potassium phosphate (KH_2PO_4) in reagent water and dilute to 1 liter. This stock standard may be stored for 1 month.

8.2.6 Mixed spiking solution stock: Dissolve the following compounds in approximately 200 ml of DI water in a 250 ml volumetric flask: 0.3219 g of sodium bromide (NaBr), 0.221 g of sodium fluoride (NaF), 0.607 g of sodium nitrate, 0.4926 g of sodium nitrite, and 0.4394 g of potassium phosphate. Dilute to a final volume of 250 ml with DI water and mix well. This stock standard may be stored for 1 month.

8.3 Working standard and spiking solutions: Solutions containing bromide, chloride, fluoride, nitrate, and sulfate must be made fresh weekly. Solutions containing nitrite and orthophosphate should be made fresh daily but can be made weekly as long as they are not

reported and used for retention time recognition only. Note: Levels shown below are suggested levels and may be changed to meet different reporting limit requirements.

8.3.1 Standard Intermediate "A" (100 mg/l chloride and sulfate). Using a volumetric autopipet, transfer 2.50 mL of 4000 mg/l stock into 75 ml DI and dilute to 100 ml.

8.3.2 Standard B Intermediate.

8.3.2.1 Pipette the following amounts of the stocks shown into a 100 ml volumetric flask. Dilute to final volume of 100 ml and mix well.
10.0 ml of 1000 mg/l Fluoride = 100 mg/l
10.0 ml of 1000 mg/l Nitrite = 100mg/l
25.0 ml of 1000 mg/l Bromide = 250 mg/l
10.0 ml of 1000 mg/l Nitrate = 100 mg/l
10.0 ml of 1000 mg/l Orthophosphate = 100 mg/l

8.3.2.2 Then take 20.0 ml of the solution from 8.3.2.1 and dilute to a final volue of 100 ml with DI water. Mix well.

8.3.3 Spiking Solution Soup. Using a class A pipette or cylinder, transfer 50 ml of 16000 mg/L chloride and sulfate stock (8.1.3) and 50 ml of the mixed spiking solution stock (8.2.6) together in a 100ml volumetric flask. Final concentrations in the spiking solution are shown below. This solution is stable for one week for fluoride, chloride, bromide, nitrate, and sulfate. It should be made fresh daily for nitrite and orthophosphate if is being used for quantiation purposes.

Analyte	Conc. In spiking solution	Conc in spike blank
Fluoride	200 mg/l	2.00 mg/l
Nitrite	200 mg/l	2.00 mg/l
Bromide	500 mg/l	5.00 mg/l
Nitrate	200 mg/l	2.00 mg/l
Orthophosphate	200 mg/l	2.00 mg/l
Chloride	2000 mg/l	80.0 mg/l
Sulfate	2000 mg/l	80.0 mg/l

8.3.3.1 Use 0.5 ml of this solution to 50 ml DI for spike blank or 0.5 ml to 50 ml of sample for matrix spikes for aqueous samples. Use 1.0 ml of this solution to 10 g of sample (to be brought to 100 ml final volume) for soil matrices.

8.4 Calibration standard solutions: Solutions containing bromide, chloride, fluoride, nitrate, and sulfate must be made fresh monthly. Solutions containing nitrite and orthophosphate should be made fresh daily, but can be made weekly as long as they are not reported and used for retention time recognition only. Note: Levels shown below are suggested levels and may be changed to meet different reporting limit requirements.

8.4.1 Standard A. This is the blank and contains DI water only.

8.4.2 Standard B. Pipette the following amounts of stocks shown into a 100 ml volumetric flask: 0.50 ml of intermediate "A" and 0.25 ml of intermediate "B"

8.4.3 Standard C. Pipette the following amounts of stocks shown into a 100 ml volumetric flask: 2.00 ml of intermediate "A" and 0.50 ml of intermediate "B"

8.4.4 Standard D. Pipette the following amounts of stocks shown into a 100 ml volumetric flask: 10.0 ml of intermediate "A" and 2.00 ml of intermediate "B"

8.4.5 Standard E. This standard level is normally also used as the CCV standard. Pipette the following amounts of stocks shown into a 100 ml volumetric flask: 50.0 ml of intermediate "A" and 10.0 ml of intermediate "B"

8.4.6 Standard F and CCV. Pipette the following amounts of stocks shown into a 200 ml volumetric flask: 10.0 ml of 4000 mg/l chloride and sulfate stock and 30.0 ml of intermediate "B" and 1.5 ml of 1000 mg/l bromide stock.

8.4.7 Standard G. Pipette the following amounts of stocks shown into a 100 ml volumetric flask: 10.0 ml of 4000 mg/l chloride and sulfate stock and 30.0 ml of intermediate "B" and 1.0 ml of 1000 mg/l of bromide stock.

8.4.8 The final concentrations in the suggested standards outlined above are shown in the table below. All units are in mg/l.

Anion	STDA	STDB	STDC	STDD	STDE	STDF	STDG
F	0.0	0.05	0.1	0.4	2	3	6.0
CHL	0	0.5	2	10	50	200	400
NO2	0.0	0.05	0.1	0.4	2	3	6.0
BRO	0.0	0.125	0.25	1	5	15	25
NO32	0.0	0.05	0.1	0.4	2	3	6.0
OPO4	0.0	0.05	0.1	0.4	2	3	6.0
SO4	0	0.5	2	10	50	200	400

8.5 ICV (External Check Solution.) The ICV can be made in the same manner as the standard curve from a separate source than the standards. It must be within the range of the curve. Alternatively, it can be purchased from a outside supplier.

8.6 0.2N H_2SO_4 for suppressor regeneration: Pipet 1.0 ml of concentrated H_2SO_4 into 100 ml DI and dilute to final volume of 200ml with DI.

8.7 0.1M Oxalic Acid for metals column clean-up: Dissolve 6.3 g of oxalic acid into approx. 300 mL of DI water. Bring to final volume of 500 mL with DI water.

8.8 10X eluent concentrate (300mM KOH) for hydrophilic ionic contamination clean-up.

8.9 Acetonitrile, reagent grade

8.10 1M HCl: Add 8.3 ml of concentrated hydrochloric acid to approximately 70 ml of deionized water. Dilute to a final volume of 100 ml and mix well.

9.0 INTERFERENCES

9.1 Interferences can be caused by substances with retention times that are similar to and

overlap those of the anion of interest. This interference is especially important at low concentrations.

9.2 The acetate anion elutes early during the chromatographic run and can cause elution times of other anions to vary when large amounts of acetate are present. High levels of acetate also can cause interference with the fluoride peak. Therefore, this method is not recommended for leachates containing acetic acid.

9.3 Large amounts of an anion can interfere with the peak resolution of an adjacent anion. High concentrations of an anion can also cause the peak to be misidentified on the chromatograph due to the large width of the peak.

10.0 SAMPLE PREPARATION PROCEDURE

10.1 For soil samples, follow the preparation outlined below.

10.1.1 Mix the sample well and remove any artifacts. Remove a 10.0 g aliquot of sample and add 100 ml of DI water. Mix the resulting slurry for 1 hour using a magnetic stirring device. Then let settle for a minimum of 1 hour. Filter the resulting slurry through a 0.45 um membrane filter before analysis.

10.1.1.1 The longer mixing time is used because performance evaluation and known soil sample analysis indicate lower recoveries when a 10 minute mixing time is used.

10.1.2 For matrix spikes, make sure to spike the aliquot of the sample directly and then add the 100 ml of water and stir.

10.1.3 Check with the lab supervisor if there is insufficient sample to use a 10.0 g aliquot. Smaller aliquots may be used if a homogeneous portion of the sample can be obtained. The sample must always be extracted with 10 times the sample weight of DI water.

10.2 For water samples, filter all samples through 0.45 um filters before analysis. Matrix spikes must be spiked before filtration.

11.0 ION CHROMATOGRAPHY ANALYSIS PROCEDURE FOR THE ICS-2000 INSTRUMENTS

11.1 Check to make sure that the helium tank pressure is > 100 PSI and the pressure gauge by the eluent bottles is set at 6 PSI.

11.2 Fill the eluent generation bottle(s) that are to be used with deionized water (resistance of 18.2 megaohms or greater), making sure that they are pressurized with helium. On the instrument panel (or in the software) set the water volume at the level in the bottles and adjust the flow rate up to 1.0 ml/min. Check the KOH is set at the proper molarity. Normally it should be set at 30 mM. Also fill the external water bottle(s) for the supressor with deionized water.

11.3 Check the lines coming out of the supressor for air bubbles. Bubbles should be present. If not, then check to make sure the current is on and the suppressor is working properly.

11.4 Check the pump waste line and see if bubbles are present. If they are present, then prime

the pump using the procedure described below.

11.4.1 Hit the prime button on the front panel.

11.4.2 Open up the pressure transducer on the pump by turning it 3 turns to the left. Then enter OK on the front panel.

11.4.3 Put the syringe in the syringe prime knob and turn it 3 times to the left and begin to slowly pull back on the syringe to 10 ml. Check for air bubbles on the pump waste line. If not air bubbles are present, then close the syringe priming knob and shut the pump off. Then close the pressure transducer knob.

11.4.4 Allow the instrument conditions to settle and then check the pressure and check for air bubbles. If there is still a problem, the priming procedure may be repeated.

11.5 In the software, go to the browser and go to the correct instrument panel (1 or 2). Then connect the instrument. Monitor the baseline until it is stable.

11.6 Go to the template sequences and edit a sequence for the samples in the run. If a calibration is being using from an earlier run, make sure to copy the calibration into the front of the sequence. After the sequence is generated, then save it using the file name (instrument, date, run). Refer to the instrument manuals or help screens in the program for help in using the software. A summary of the instrument conditions required for the analysis of perchlorate is shown below. Note: the retention time window for each anion must not exceed ± 10% of that anions retention time from the calibration. Refer to section 13.7 for more discussion of the proper application of retention time.

Column: IonPac AG18, AS18
Eluent: 30 mM KOH
Surpressor setting: approximately 100 mAmps. This setting will be autogenerated.
Flow Rate: 1.0 ml/min
Inj. Volume: 12.5 µl
Pump pressure – should be around 2000 psi
Detection: Suppressed conductivity, SRS Ultra II, external water mode

11.7 Load the autosampler and turn it on. The autosampler should then move to the first sample. A print-out of the autosampler table should be generated showing the order that the samples are loaded into the autosampler.

11.8 Start the run. Monitor the results as the run is going to make sure that problems are identified quickly. Note: the initial demonstration of capability, including instrument MDL's and linear calibration ranges, must be completed before samples can be run.

11.8.1 Data files should be saved using the naming scheme of instrument, year (last 2 digits), month, day, run number followed by the extension of .ic. For example, the first IC run on instrument 2 on May 20, 2005 would be named 205052001. This name should always be used in the workgroup description in the LIMS system.

11.8.2 It is recommended that a new calibration be run a minimum of once per month. (It is required that a calibration be run once per quarter.) Calibrations standards may be

varied from the one stated in this SOP depending on the levels of each anion that are to be reported. A minimum of 5 standards and a blank are required and a low standard must be at or below the reporting limit for each anion. A correlation coefficient of 0.995 is required. If this correlation coefficient is not met, than the instrument must be recalibrated.

11.8.3 After the calibration, a low check at the reporting limit must be run. This low check must have the levels in standard B or at the reporting limit for the calibration outlined in this SOP and recoveries must be in the range of 75 to 125. On a daily basis, it is recommended that an external check is analyzed and recoveries must be within a range of 90 to 110 percent. (This check must be analyzed at a minimum with each new calibration.) Continuing calibration checks and continuing calibration blanks must be run every 10 samples. The continuing calibration checks must have recoveries in the range of 90 to110 percent. Refer to the quality control section of this SOP for more detail on these quality control samples.

11.9 After the run is completed, review all of the chromatograms and check for overlapping peaks, dilutions, etc.

11.9.1 If the retention time of any anion in the ICV or CCV check standards has shifted more than 10% from the original calibration curve retention time, then no results can be reported for that anion. The column should be reconditioned, if necessary, and the instrument recalibrated before any more samples are reported for that anion. Affected samples are reanalyzed after the problem has been corrected.

11.9.2 If a sample peak has shifted significantly from the original retention time (and the ICV and CCV check standards are within the 10% retention time window), then verify the reported result using post-digest spike on that sample. Do not report results from peaks where the retention time has shifted more than 10 percent unless the peak can be verified using a post-digest spike.

11.9.3 For large or overlapping peaks, make dilutions. If at all possible, make dilutions and reruns on the same run as the original sample.

11.9.4 Refer to section 13.7 for information on how to determine the appropriate retention time window.

11.9.5 Certain soil samples for bromide have been seen to have positive interferences. For bromide soil samples of a similar matrix, if the sample results are greater than the RL, dilute at least one sample per batch to confirm reported results. If the sample shows possible matrix interference, then the associated samples in the batch should also be run on dilution.

11.10 Review all data and update the appropriate tests in the LIMS system. A write-up including a run log, a calibration summary, batch quality control summary, and copies of all chromatograms should be turned into the area supervisor for each batch.

11.10.1 If edits are needed in the calibration after the data has been calculated, the run can be reprocessed using the batch function in the software. Refer to the instrument manuals or on-screen help for addition information.

12.0 INSTRUMENT MAINTENANCE

12.1 Whenever a new suppressor is put in place or when the baseline is unstable or very high, the suppressor should be regenerated. The procedure below is for the Ultra 4 mm suppressor.

12.1.1 Using a disposable plastic syringe, push approximately 3 mL of 0.2(200mN) H_2SO_4 through the ELUENT OUT port and 5 mL of 0.2N H_2SO_4 through the REGIN IN port respectively.

12.1.2 Allow the suppressor to sit for approximately 20 minutes to fully hydrate the suppressor screens and membranes.

12.1.3 Re-connect the suppressor to the system in the recycle mode.

12.2 Periodically, due to the matrix of samples, both guard and analytical columns become degraded and cleaning them becomes necessary. This is evidenced in changing retention times, round-shaped peaks, tailing peaks and overall poor integration. The metals cleanup should be done a minimum of once per month, while the others should be done a minimum of once per quarter.

12.2.1 There are 3 recommended cleanup solutions for the AS18A and AG18 columns.

12.2.2 Metal contamination column clean-up: Use 500 ml of 0.1M oxalic acid solution.

12.2.3 Low valency hydrophilic ionic contamination column clean-up. Use 500 ml of 10X eluent concentrate (300 mM KOH).

12.2.4 High valency hydrophobic ion 200mM HCl in 80% acetonitrile: The acetonitrile solution is stored in a separate eluent bottle because acetonitrile slowly breaks down in acidic aqueous solutions. Prepare 2 bottles (E1 and E2) with the following 500-mL solutions: E1: 100% Acetonitrile and E2: 1M HCl using DI water.

12.3 Column Clean-up Procedure.

12.3.1 Prepare 500 mL solution of the appropriate cleanup solution from 12.2.1

12.3.2 Disconnect the ASRS-ULTRA from the IonPac AS18A Analytical column. **Make sure to reverse the order of the guard and analytical column in the eluent flow path.** Contaminants that have accumulated on the guard column can be eluted onto the analytical column and irreversibly damage it. If in doubt, clean each column separately. Double check that the eluent flows in the direction designated on each of the column labels.

12.3.3 Set the pump flow rate to 1.0 mL/min for an AS18A 4-mm analytical or guard column.

12.3.4 Rinse the column for 15 minutes with DI water before pumping the chosen cleanup solution over the columns.

12.3.5 Pump the cleanup solution through the column for at least 60 minutes.

12.3.6 Rinse the column for 15 minutes with DI water before pumping eluent over the column.

12.3.7 Equilibrate the columns with eluent before resuming normal operation for at least 30 minutes.

12.3.8 Reconnect the ASRS-ULTRA and place the guard column in line between the injection valve and the analytical column.

13.0 QC REQUIREMENTS

13.1 For this method, MDLs must be determined every six months, when a new operator begins work or whenever there is a significant change in the background or instrument response. The MDL study is done following the procedure outlined in the Accutest laboratory MDL SOP. A minimum of seven replicates spiked at 3 to 5 times the MDL must be taken through the procedure for each anion. If instrument conditions (columns, etc.) are modified, then a new MDL must be done. Refer to section 3.2 for additional information

13.1.1.1 A significant change in instrument response is monitored using Limit of Detection (LOD) standards. New LOD standards must be analyzed whenever a column is changed or whenever else an analyst suspects that instrument sensitivity has changed substantially. If the LOD standards indicate a significant change, than a full new MDL study must be analyzed.

13.1.1.2 Limit of Detection (LOD). The limit of detection (LOD) for each method and target analyte of concern is established after the completion of the MDL by running a sample at a level less than the RL and approximately 1 to 4 times the calculated MDL. If the LOD verification fails, then the laboratory must repeat the detection limit determination and LOD verification at a higher concentration or perform and pass two consecutive LOD verifications at a higher concentration and set the LOD at the higher concentration. Once the LOD is set, than that LOD level should be used to verify ongoing instrument sensitivity. The normal acceptance criteria for the LOD for this method is defined by this SOP as being in the range from 10 to 200% recovery.

13.2 A batch is defined as a maximum of 20 samples in one day. A method blank and a spike blank are required to be run with every batch. Additionally two matrix spikes and a duplicate are required for every 20 samples. In some cases a matrix spike duplicate may be required in place of a duplicate.

13.2.1 The default SOP limit for the method blank is that it must contain less than one half of the reporting limit of each anion that is reported and this sample must be run with each set of samples in a batch. If the blank contains more than ½ of the reporting level, then all samples must be reanalyzed. If no sample volume remains to be reanalyzed, then the data must be flagged. (The exception is if the sample results are less than the reporting limit.)

13.2.1.1 Method 300.0 states that values greater than the MDL should be suspect, this is not appropriate for the concentration levels being applied for

this analysis. MDL's are generally at least 10 times lower than reporting limits for all analytes and values over the MDL do not impact data usability.

13.2.1.2 Method 9056A also allows that the method blank can be < 10% of the regulatory limit, or <10% of the lowest sample concentration.

13.2.2 For method 300.0, the recovery of the spike blank must be within the limits of 90 to 110% recovery for each anion that is reported and this sample must be run with each set of samples in a batch. If the recoveries are outside of this range, then all associated samples must be reanalyzed. If no sample volume remains to be reanalyzed, then the data must be flagged.

13.2.2.1 Limits of 80 to 120% are acceptable if only method 9056A is being cited.

13.2.3 The matrix spike is spiked with all anions of interest. Method limits of 80 to 120 % recovery must be applied. Control limits must be generated from laboratory data to support method limits. If the recoveries are outside of this range, and all other method quality control is within limits, then matrix interference should be suspected.

13.2.4 For method 300.0 either duplicates or matrix spike duplicates, control limits of 20% RPD must be applied for all sample values within the calibration range (up to 10 times the reporting limit). If the RPD values are outside of this range, and all other method quality control is within limits, then sample non-homogeneity should be suspected and a footnote should be added to the QC report. RPD are also considered acceptable if the two values are within plus or minus the reporting limit of each other for samples that are less than 4 times the reporting limit.

13.2.5 For method 9056A, control limits of 15% are applied for sample values that are approximately mid-curve and higher. Samples higher than 4 times the reporting limit, but less than the mid range of the curve should be judged using a control limit of 50%. Samples that are less than 4 times the reporting limit are considered acceptable if the two values are within plus or minus the reporting limit of each other). If the RPD values are outside of this range, and all other method quality control is within limits, then sample non-homogeneity should be suspected and a footnote should be added to the QC report.

13.3 An external source must be analyzed at least once per quarter and/or after every new calibration. This external must be within the range of 90 to 110 % recovery. If this criteria is not met, the problem must be corrected and the external source reanalyzed. It is recommended that the external source be analyzed with each batch to verify the standard values obtained.

13.4 It is recommended that a new calibration be run a minimum of once per month. (It is required that a calibration be run once per quarter.) Calibrations standards may be varied from the one stated in this SOP depending on the levels of each anion that are to be reported. A minimum of 5 standards and a blank are required and a low standard must be at or below the reporting limit for each anion. A correlation coefficient of 0.995 is required.

$$r = \frac{\Sigma(x - \bar{x})(y - \bar{y})}{\sqrt{\Sigma(x - \bar{x})^2 \Sigma(y - \bar{y})^2}}$$

Where r = correlation coefficient
x = amount of analyte
y = response of instrument

$\bar{x}$ = average of x values

$\bar{y}$ = average of y values

13.4.1 A new calibration is required when standard retention times shift by more than 10% from the original calibration.

13.5 A low check at the reporting limit for each anion must be run after each calibration. Recoveries for this low check must be in the range of 75 to 125 for all reported anions. If the recoveries are not in this range, the problem must be identified and the instrument recalibrated. If only samples for method 9056A are being reported, then the limits can be extended to 50 to 150%, but normally the tighter limits should be applied.

13.6 Continuing Calibration Verification (CCV) Checks at or near the mid-level of the curve must be run at the beginning and the end of the run and after every 10 samples throughout the run. Every CCV must be followed by a continuing calibration blank (CCB). The CCV must have results within 90 to 110 % of the true value. If the results are outside of that range for a CCV, then all bracketed samples must be reanalyzed. The results for the CCB must be less than the reporting limit for an analyte. If they are not, then all bracketed samples for that analyte must be reanalyzed.

13.7 Retention Time Windows. The width of the retention time window used to make identification should be based upon measurements of the actual retention time variations of standards over the course of an analysis. A suggested window would be three times the standard deviation of the retention time windows for an analysis day or period of time covered by a calibration. However, sample concentration and matrix can greatly affect retention time and the experience of the analyst and reviewer should weigh heavily in the interpretation of a chromatogram. Therefore, 10 % is defined as the widest window that can be used. If an analyte is outside of that window, it cannot be reported unless that peak is confirmed with a post-digest spike.

13.7.1 For given analytes, tighter windows should be applied to make sure that the peaks are being accurately identified. For both fluoride and bromide, tighter windows are normally applied in the instrument software. These windows must be supported by the criteria outlined above.

13.7.1.1 For fluoride, a 2% window is typically applied.

13.7.1.2 For chloride and sulfate, a 10% window is typically applied.

13.7.1.3 For bromide, a 5% window is typically applied.

13.7.2 Analyst judgment must play an important role in this judgment. For example, organic acid peaks may be difficult to differentiate from fluoride based on a fixed percentage retention time window, but may require peak overlays and/or post-digest spikes to clearly identify the fluoride peaks. Large anion peaks may also push out retention times so that one peak may be mis-identified as a different peak. The analyst must recognize these potential problem areas and run samples on dilution as appropriate so that the normal retention time windows are accurate.

14.0 DOCUMENTATION REQUIREMENTS

14.1 All reagents must be recorded in a reagent logbook with manufacturers, lot numbers, and expiration dates. All reagent information must be cross referenced on the sample worksheet.

14.2 All instrument data must be exported to the LIMS system and a copy of the run log must be included in the logbook by the instrument.

14.3 A data package consisting of a manual run log, a LIMS run log, a calibration summary, batch quality control summary, and copies of all chromatograms must be turned into the area reviewer for each batch. The analyst should also complete the preliminary review in the LIMS system.

14.4 Refer to EQA044 for procedures and documentation that must be followed when peaks are manually integrated.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 15.2.

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the waste management SOP, EHS004. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

15.2.1 Non hazardous aqueous wastes.

15.2.2 Hazardous aqueous wastes

15.2.3 Chlorinated organic solvents

15.2.4 Non-chlorinated organic solvents

15.2.5 Hazardous solid wastes

15.2.6 Non-hazardous solid wastes

16.0 ADDITIONAL REFERENCES

16.1 Dionex Instrument and column manuals

16.2 EQA044 Manual Integration SOP.

TITLE: **TOTAL NITROGEN, AMMONIA**

TEST METHOD REFERENCE: 4500-NH3 C. Standard Methods for the Examination of Water and Wastewater 21 Edition, 1992

REVISED SECTIONS: 8.3

1.0 SCOPE AND APPLICATION

1.1 This method is used as a measure of the ammonia in distilled samples and is applicable to all drinking waters, surface and saline waters, domestic and industrial wastes, soils, and sludges. This method is based on method 4500-NH3 C,18th Edition, following distillation based on method 4500-NH3 B, 18th Edition of Standard Methods.

NOTE: **This SOP describes only the manual analysis of the distilled samples for ammonia. Refer to the current distillation SOP (MGN106) for details on how to perform the distillation.**

1.2 Test code: AMN

2.0 SUMMARY

2.1 The ammonia in the distillate is determined colorimetrically by nesslerization. The graduated yellow to brown colors produced by nesslerization is measured at wavelength of 425 nm.

3.0 METHOD REPORTING LIMIT AND DETECTION LIMIT

3.1 The reporting limit (RL) is based on the lowest calibration standard. RL's may vary depending on matrix difficulties, sample volumes or weights, and percent moisture. Detected concentrations below this concentration cannot be reported without qualification.

3.2 The Method Detection Limit (MDL) represents the lowest reportable concentration of an individual analyte that meets the method qualitative identification criteria.

3.3 Method Detection limits (MDLs) are experimentally determined using the procedures described in 40 CFR, Part 136, Appendix B. Actual reported MDLs incorporate the sample volume analyzed and sample dilutions if needed, which may cause MDL variations from sample to sample.

3.4 In general, MDLs are determined through the analysis of at least 7 replicate blank spikes (using the same procedures for sample analysis). The MDL is calculated by multiplying the standard deviation of the replicate concentrations by the appropriate Student's t value (3.143 for 7 replicates). If more than 7 replicates are analyzed refer to 40 CFR, Part 136, Appendix B for the appropriate student's t value. MDLs are determined initially (prior to analysis), on an annual basis, and after major maintenance to equipment. MDL data is archived with Quality Assurance. Refer to the most recent study for current MDLs. Refer to the SOP for MDLs (MQA245) for additional detail regarding MDL study procedures.

3.5 Current MDLs may be entered into the LIMS, and may be viewed by printing out the compound list from the LIMS. Additionally, MDLs are reported on the result page upon client request. Current MDL studies are

filed with Quality Assurance. Obsolete MDL studies are archived with the QA files. Electronic MDL data is found in the annual "MDL" folder on the QA server (LINUXMA1).

4.0 DEFINITIONS

4.1 ALIQUOT - a measured portion of a sample, or solution, taken for sample preparation and/or analysis.

4.2 BATCH – A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20 (or 10 for certain methods), then each group of 20 samples (or 10 samples for certain methods) or less will all be handled as a separate batch.

4.3 CALIBRATION BLANK - a volume of acidified deionized/distilled water.

4.4 CALIBRATION STANDARDS – a series of known solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve).

4.5 CONTINUING CALIBRATION VERIFICATION – analytical standard run every 10 samples or 2 hours, whichever is more frequent, to verify the calibration of the analytical system.

4.6 CONTAMINATION - a component of a sample or an extract that is not representative of the environmental source of the sample. Contamination may stem from other samples, sampling equipment, while in transit, from laboratory reagents, laboratory environment, or analytical instruments.

4.7 CORRELATION COEFFICIENT – A NUMBER (r) which indicates the degree of dependence between two variables (concentration – absorbance). The more dependent they are the closer the value to one.

4.8 FIELD SAMPLE - a portion of material to be analyzed that is contained in single or multiple containers and identified by a unique sample number.

4.9 FIELD BLANK – this is any sample that is submitted from the field and is identified as a blank. This includes rinsates and equipment blanks, etc.

4.10 HOLDING TIME – the elapsed time expressed in days from the date of sampling until the date of its analysis.

4.11 MATRIX - the predominant material of which the sample to be analyzed is composed. For the purpose of this SOP, a sample matrix is either water or soil/sediment. Matrix is <u>not</u> synonymous with phase (liquid or solid).

4.12 MATRIX DUPLICATE - a second aliquot of the original sample prepared and analyzed in order to determine the precision of the method.

4.13 MATRIX SPIKE- aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds (for this SOP-AMN) and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

4.14 METHOD BLANK - an analytical control consisting of all reagents that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background, and reagent contamination.

4.15 REAGENT WATER - water in which an interferant is not observed at or above the minimum quantitation limit of the parameters of interest. Accutest uses deionized water (municipal water which passes through Accutest's DI treatment system).

4.16 RELATIVE PERCENT DIFFERENCE (RPD) - As used in this SOP to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero.

5.0 HEALTH AND SAFETY

5.1 All safety practices must be followed as outlined in the Accutest Laboratories Employee Safety Handbook and Chemical Hygiene Plan. Safety glasses, gloves, and lab coats must be worn. All samples, solutions, and extracts must be treated as unknown and potentially hazardous.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level.

6.0 COLLECTION, PRESERVATION & HOLDING TIMES

6.1 Collection and Preservation

6.1.1 Containers: Samples should be collected in 500 ml plastic containers. Additional sample may be necessary if used for QC.

6.1.2 Preservation: Water samples should be preserved with sulfuric acid to a pH of less than 2 and kept under refrigeration at 4°C ±2°C until they are distilled. Soil samples should also be refrigerated at 4°C ±2°C until distillation.

6.1.3 Samples with residual chlorine should be treated with sodium thiosulfate prior to distillation (refer to distillation SOP MGN106.

6.2 Holding Time: Samples should be analyzed within 28 days of time of collection.

7.0 APPARATUS

7.1 Spectrophotometer with an attached PC

7.2 Volumetric flasks

7.3 Volumetric pipettes

7.4 Spectrophotometer cuvettes

7.5 Graduated plastic beakers.

8.0 REAGENTS

Note: All chemicals listed below are reagent grade unless otherwise specified. Distilled, deionized water should be used whenever water is required. Make sure to properly label all reagents and record the reagent preparation in the reagent log book. All applicable reagent preparation information, including vendor, lot number, date of preparation, calculations, and initials must be entered in the reagent preparation logbook. Vendors typically used by Accutest include Fisher Scientific, VWR, Chemservices, Ultra, and ERA. Additional vendors may be utilized as necessary.

8.1 Ammonium chloride, stock solution, 1000 mg/l: Dissolve 3.819 g of ammonium chloride in distilled water and bring to a final volume of 1 liter in a volumetric flask.

8.2 Ammonium standard solution, 10 mg/l: Dilute 1.0 ml of 1000 mg/l ammonium chloride solution to 100 ml with DI water.

8.3 Ammonia Calibration Curve: The calibration curve can be made from the above 10 mg/l standard solution as shown below. All standards shown below should be diluted to 100 ml with DI water. These standards must be distilled along with the samples.

Amt. of 10 mg/l std.	Final Conc. in mg/l
1.00 ml	0.100 mg/l
3.0 ml	0.300 mg/l
5.00 ml	0.500 mg/l
8.0 ml	0.800 mg/l
10.0 ml	1.00 mg/l
20.0 ml	2.00 mg/l

8.4 Nessler reagent: Dissolve 100 g of mercuric iodide and 70 g potassium iodide in a small volume of distilled water. Add this mixture slowly, while stirring, to a cooled solution of 160 g NaOH in 500 ml of DI water. Dilute the mixture to 1 Liter. This solution is stable for at least one year if stored in a pyrex bottle out of direct sunlight. This can be purchased commercially.

9.0 INTERFERENCES

9.1 Cyanate will hydrolyze to some extent even at the pH of 9.5 at which the distillation is carried out. Volatile alkaline compounds, such as certain ketones, aldehydes, and alcohols, may cause an off-color upon nesslerization in the distillation method. Residual chlorine must be removed by treating the sample with sodium thiosulfate prior to distillation. Removal of residual chlorine should occur immediately on sampling or upon laboratory receipt of the sample.

10.0 PROCEDURE

10.1 Turn on the spectrophotometer so that it can warm up for at least 30 minutes before starting an analysis. From the PC attached to the spectrophotometer, go to "**windows explorer"**, and click on **MAFILE1\apps\WC_DATA** server. Click on Ammonia directory. Click to open ammonia excel spreadsheet. Type your sequence and the related information such as date, name, workgroup number, etc.

10.2 Pour out 50 ml of each standard and of an external reference solution into labeled graduated plastic beakers. Add 2.0 ml of Nessler solution to each standard and mix. Do not proceed with sample distillates at this time.

10.3 Let the color develop for 20 minutes.

10.4 Adjust the wavelength on the spectrophotometer to 425 nm, and zero the instrument according to the procedure described in the manual.

10.5 Record the absorbance of each standard solution by clicking on **" print "** key on the spectrophotometer's key pad. Data will be directly placed on the spreadsheet. Rinse the spectrophotometer cell with deionized water and a few milliliters of the standard/sample solution prior to filling the sample cell.

10.6 Calculated linear regression values for the standards will appear on the excel spreadsheet. Verify the values are within acceptable limits (Corr. coef. >0.995, absolute value of intercept <0.5 MDL, slope=comparable to previous values). If the values are not within acceptable limits, verify spectrophotometer settings, rezero the instrument, and reanalyze the standards. If the curve is still not within specifications, prepare new standards and repeat procedure.

10.7 Analyze the external reference solution (section 11.4), and verify the calculated value is within the solution specifications. If it is not, notify the supervisor immediately.

10.8 If there are no problems with the curve or external, proceed with the samples following the procedure outlined in steps 10.2 and 10.3 above. Make sure to prepare check standards to read with the samples.

10.9 Once all standards and samples were analyzed, Click on the **"print"** button on excel spreadsheet, to have a hard copy of the analysis.

10.10 Click on **"Export to LIMS"** button on the spreadsheet. This will transfer the data to the "**export"** folder of the Ammonia directory.

10.11 Go to **"Export"** folder and drag the created file (Workgroup number with extension of the test code, ie, GN1234.AMN) to the **WC (S)** drive. This is the processing branch of the LIMS for Wet chemistry tests.

10.12 Once the run is processed in the LIMS, go to GNAPP, and review the run. Package all raw data, and logbook copies in a folder, and turn the package to the area manager for data review and quality control check.

11.0 QUALITY ASSURANCE

11.1 Below is a summary of the quality control requirements for this method. Make sure to check with laboratory supervisor or manager for any additional client specific quality control requirements.

11.2 **Method Blank**. The laboratory must analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. The method blank must not contain the analyte at greater than the reporting limit. If the method blank contains an analyte level over that limit, the samples must be re-prepped (if the samples are non-detected they may be reported without qualification).

11.3 **Spike Blank.** The laboratory must analyze a spike blank with each set of samples. A Minimum of one spike blank is required for every 20 samples. The spike blank recovery should be assessed using in house limits. Until these limits can be generated, then the default limit of ±20 percent of the true value The net recovery should be within 20 percent of the true value. If the spike blank is outside of this range, the samples must

be reanalyzed. Alternatively, If the blank spike recovery is high and the results of the samples to be reported are less than the reporting limit, then the sample results can be reported with no flag. If the lab recovery is low or the samples have positive results for the target analyte the samples must be reanalyzed.

11.4 **External Check Sample (also referred to as an initial calibration verification – ICV).** The laboratory must distill and analyze an external check standard with every initial calibration. The limits supplied by the manufacturer should be applied. If the results for the external QC check are outside of the range, do not continue analysis. Consult the laboratory supervisor. Do not analyze samples until the problem is resolved.

11.5 **Matrix Duplicate.** The laboratory must prepare a duplicate sample for a minimum of 1 in 20 samples.The relative percent difference (RPD) between the duplicate sample and the original should be assessed. The Duplicate RPD should be calculated as shown below

$$\frac{\text{(Original Sample Result – Duplicate Result) x 100}}{\text{(Original Sample Result + Duplicate Result) x 0.5}} = \%\ \text{RPD}$$

The Duplicate RPD should be assessed using in house limits. Until these limits can be generated, then the default limit of 20 percent RPD should be applied. If a duplicate RPD is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control.

11.6 **Matrix Spike.** The laboratory must add a known amount of each analyte to a minimum of of 1 in 20 samples. The spike recovery should be assessed using in house limits. Until these limits can be generated, default limits of 75-125 % recovery should be applied. If a matrix spike recovery is out of control, then the recovery should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample can be assessed against the control limits and should be footnoted to that effect.

$$\frac{\text{(Matrix Spike Result – Original Result) x 100}}{\text{Amount of spike}}$$

11.7 **CCV.** Continuing Calibration Verification, Analytical standard run every 10 samples to verify the calibration of the analytical system. The acceptance criteria for CCV is $\pm$ 10 % of the true value. If CCV fails, all samples bracketed with this QC must be re-analyzed.

11.8 **CCB.** Continuing Calibration Blank, A blank that does not contain the analyte of interest (ammonia) and is analyzed to verify the calibration of the analytical system. CCB must be less than the reporting detection limit and must be analyzed after the CCV. If CCB is greater than the reporting detection limit, all samples bracketed with this QC must be re-analyzed.

11.9 A Precision and accuracy (P&A) study is performed as an initial determination of capability, on an annual basis (continued demonstration of capability – a successful PT result may be used in place of a P&A for continued DOC), and if any significant changes have been made to the instrument. In general, 4 replicates or blank spikes are analyzed using the same procedures and conditions for sample analysis. The percent recoveries and relative percent differences are compared to either default or in-house control limits. If percent recovery criteria are not met, corrective action must be taken to bring the system back into control, and a satisfactory P&A study must be run. The P&A study must be performed using a source independent from the calibration standards (second source).

11.10 Quality Control data is generated (control charts) and reviewed on an annual basis by Quality Assurance (blank spike/ matrix spike recoveries and matrix duplicate RPDs).

12.0 DOCUMENTATION

12.1 Which method was used.

12.2 The instrument Maintenance logbook must be completed when any type of maintenance is performed on the instrument. Each instrument will have a separate log

12.3 The initial volume aliquoted for distillation.

12.4 The final volume of the distillate.

12.5 Any comments or observations concerning the sample that may influence the analytical procedure.

12.6 All QC spikes must have documented the lot number of the spike solution used, the volume added and the concentration of the spiking solution.

12.7 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of corrections must appear next to the correction.

12.8 All logbook pages must be reviewed and signed by the lab manager.

13.0 DATA REVIEW

13.1 The analyst conducts the primary review of all data. This review begins with a check of all Instrument and method quality control and progresses through sample quality control concluding with a check to assure that the client's requirements have been executed. The analyst has the authority and responsibility to perform corrective action for any out-of-control parameter of non-conformance.

13.2 A secondary review is performed by department managers, and it includes review of the data produced by their department. All manual calculations, QC criteria, and a comparison of the data package to client specified requirements are checked. The department manager may reject data, initiate reanalysis, take additional corrective action, or reprocess data.

13.3 The laboratory director performs a full tertiary review of the data package following its assembly. This review includes an evaluation of QC data against acceptance criteria and a check of the data package contents to assure that all analytical requirements and specifications were executed.

13.4 Spot-check reviews are performed by the Quality Assurance Officer focusing on all elements of the deliverable including the client's specifications and requirements, analytical quality control, sample custody documentation and sample identification.

14.0 DATA REPORTING

14.1 A results page including positive results and/or RLs, units, methodology, analysis dates, and data qualifiers are reported. Additional quality control data including calibration summaries, MS/duplicate percent recoveries and RPDs, spike blank recoveries, method blank results, and raw data may be reported upon request of the client.

14.2 Data may be submitted to the client in a specified electronic format (EDD).

14.3 Data may be submitted to the client as an electronic hardcopy (e-hardcopy).

14.4 Once the data is approved by the laboratory manager, it may be accessed by clients via LabLink™.

14.5 Procedures for handling non-conforming data.

14.5.1 If quality control data does not meet criteria the non-conformance must be discussed in a case narrative and footnoted on the applicable quality control report summary.

14.5.2 If preservation or holding time criteria is not met and the samples are analyzed the result page must be footnoted with this information, and the non-conformance must be discussed in a case narrative or other suitable communication (telephone conversation log or email). Client notification documentation should be included with the data (telephone conversation log, fax, or email).

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Pollution Prevention. Users of this method must perform all procedural steps that controls the creation and/or escape of wastes of hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids, or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 15.2.

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the Sample and Waste Disposal SOP. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

15.1.1 Non-Hazardous aqueous wastes
15.1.2 Hazardous aqueous wastes
15.1.3 Chlorinated organic solvents
15.1.4 Non-chlorinated organic solvents
15.1.5 Hazardous solid wastes
15.1.6 Non-hazardous solid wastes
15.1.7 Microbiological wastes

16.0 METHOD PERFORMANCE

16.1 Method performance is evaluated by the annual QC limits (control charts) generated by QA, and the annual MDL study results. Refer to section 3.5 for MDLs, and section 11.10 for QC limits.

17.0 ADDITIONAL REFERENCES

17.1 No additional references are required for this method.

Lab Manager: Brad Madadian

QA Officer: Robert Treggiari

TITLE: NITRATE/NITRITE AND NITRATE ONLY BY CADMIUM REDUCTION ANALYSIS (LACHAT AUTOANALYZER)

TEST METHOD Reference: EPA 353.2 (water) Rev.2.0 1993; EPA 353.2 Mod. (soil)

REVISED SECTIONS*:* Section 8.0 notation

1.0 SCOPE & APPLICATION

1.1 This method is based on EPA method 353.2 and used as a measure of the nitrate/nitrite or nitrate only in drinkingwater and wastewater samples. A modification of the method can be used as a measure of the nitrate/nitrite in soil samples.

2.0 SUMMARY

2.1 The nitrate is reduced to nitrite by a cadmium reduction column. The nitrite is then determined by diazotizing with sulfanilamide and coupling with N-(1-napthyl)-ethylenediamine dihydrochloride to form a high colored azo dye which is measured colorimetrically.

3.0 METHOD REPORTING LIMIT AND DETECTION LIMIT

3.1 The reporting limit (RL) is based on the lowest calibration standard. RL's may vary depending on matrix difficulties, sample volumes or weights, and percent moisture. Detected concentrations below this concentration cannot be reported without qualification.

3.2 The Method Detection Limit (MDL) represents the lowest reportable concentration of an individual analyte that meets the method qualitative identification criteria.

3.3 Method Detection limits (MDLs) are experimentally determined using the procedures described in 40 CFR, Part 136, Appendix B. Actual reported MDLs incorporate the sample volume analyzed and sample dilutions if needed, which may cause MDL variations from sample to sample.

3.4 In general, MDLs are determined through the analysis of at least 7 replicate blank spikes (using the same procedures for sample analysis). The MDL is calculated by multiplying the standard deviation of the replicate concentrations by the appropriate Student's t value (3.143 for 7 replicates). If more than 7 replicates are analyzed refer to 40 CFR, Part 136, Appendix B for the appropriate student's t value. MDLs are determined initially (prior to analysis), on an annual basis, and after major maintenance to equipment. MDL data is archived with Quality Assurance. Refer to the most recent study for current MDLs. Refer to the SOP for MDLs (MQA245) for additional detail regarding MDL study procedures.

3.5 Current MDLs may be entered into the LIMS, and may be viewed by printing out the compound list from the LIMS. Additionally, MDLs are reported on the result page upon client request. Current MDL studies are filed with Quality Assurance. Obsolete MDL studies are archived with the QA files. Electronic MDL data is found in the annual "MDL" folder on the QA server (LINUXMA1).

4.0 DEFINITIONS

4.1 ALIQUOT - a measured portion of a sample, or solution, taken for sample preparation and/or analysis.

4.2 BATCH – A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20 (or 10 for certain methods), then each group of 20 samples (or 10 samples for certain methods) or less will all be handled as a separate batch.

4.3 CALIBRATION CHECK STANDARD/CONTINUING CALIBRATION VERIFICATION (CCV). The calibration check standard is a mid-range calibration standard. It is recommended that the calibration check standard or CCV must be run at a frequency of approximately 10 percent. For most methods, the mid-level calibration check standard criteria is $\pm$ 10 percent of the true value. Refer to the specific quality control section for each SOP. The exception to this rule is if the recovery on the calibration check standard is high and the samples to be reported are less than the detection limit.

4.4 CALIBRATION – the establishment of an analytical curve based on the absorbance, emission intensity, or other measured characteristic of known standards. The calibration standards must be prepared using the same type of acid or concentration of acids as used in the sample preparation.

4.5 CALIBRATION STANDARDS – a series of known solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve).

4.6 DRY WEIGHT – the weight of a sample based on percent solids. The weight after drying. See Percent Moisture.

4.7 CONTAMINATION - a component of a sample or an extract that is not representative of the environmental source of the sample. Contamination may stem from other samples, sampling equipment, while in transit, from laboratory reagents, laboratory environment, or analytical instruments.

4.8 EXTERNAL CHECK STANDARD/INITIAL CALIBRATION VERIFICATION(ICV). The external check standard or ICV is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run a minimum of once per quarter for most analyses where a check is commercially available. The laboratory should initially assess laboratory performance of a check standard using the control limits generated by the external check supplier. Refer to the quality control section for each SOP. If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

4.9 FIELD SAMPLE - a portion of material to be analyzed that is contained in single or multiple containers and identified by a unique sample number.

4.10 FIELD BLANK – this is any sample that is submitted from the field and is identified as a blank. This includes trip blanks, rinsates, equipment blanks, etc.

4.11 HOLDING TIME – the elapsed time expressed most commonly in days from the date of sampling until the date of its analysis.

4.12 INTERFERENTS – substances which affect the analysis for the analyte of interest.

4.13 INITIAL CALIBRATION - analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the mass spectrometer or electron capture detector to the target compounds.

4.14 INSUFFICIENT QUANTITY - when there is not enough volume (water sample) or weight (soil/sediment) to perform any of the required operations: sample analysis or extraction, percent moisture, MS/MSD, etc.

4.15 MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

4.16 MATRIX DUPLICATE: A duplicate sample is digested/distilled/analyzed at a minimum of 1 in 10 samples (or 10 samples for certain methods). The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

4.17 MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 10 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits of 90-110%. In house limits are generated once sufficient matrix spike data is available to generate limits (usually a minimum of 20 to 30 analyses). If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect. Note:

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{(\text{Amount Spiked})} \times 100 = \text{Matrix Spike Recovery}$$

4.18 METHOD BLANK. The laboratory must digest or distill (as appropriate to the method) and/or analyze a method blank with each set of samples. A minimum of one method blank is required for

every 10 samples. If no digestion step is required, then the method blank is equivalent to the reagent blank. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

4.19 PERCENT MOISTURE - an approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at 105 °C. The percent moisture determined in this manner also includes contributions from all compounds that may volatilize at or below 105 °C, including water. Percent moisture may be determined from decanted samples and from samples that are not decanted.

4.20 RELATIVE PERCENT DIFFERENCE (RPD) - To compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero. In contrast, see percent difference.

4.21 REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. (Note: for methods requiring no preparation step, the reagent blank is equivalent to the method blank.) Either a reagent blank or a method blank must be analyzed with each batch of 20 samples or less. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

4.22 REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents that conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

4.23 REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. Water in which an interferant is not observed at or above the minimum quantitation limit of the parameters of interest. Accutest uses deionized water (municipal water which passes through Accutest's DI treatment system).

4.24 REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

4.25 SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 10 samples. Assess laboratory performance against the control limits of 90-110%. In house limits should also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). In house limits must equal or better than the required limits. If the lab control is outside of the control limits for a parameter, all

samples must be redigested or redistilled and reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag.

4.26 STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards that cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation.

5.0 HEALTH & SAFETY

5.1 All safety practices must be followed as outlined in the Accutest Laboratories Employee Safety Handbook and Chemical Hygiene Plan. Safety glasses, gloves, and lab coats must be worn. All samples, solutions, and extracts must be treated as unknown and potentially hazardous.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level.

6.0 COLLECTION, PRESERVATION, AND HOLDING TIMES

6.1 Collection and Preservation

6.1.1 Containers 250 ml plastic container (water); 300 ml glass container (soil)

6.2 Preservation Both soils and water samples should be kept under refrigeration at 4°C until analysis. Water samples should be preserved with sulfuric acid to a pH of less than 2 if they are to be analyzed for nitrate + nitrite. If nitrate only is requested, then the sample can be separated into 2 aliquots. The nitrate + nitrite aliquot should be preserved with sulfuric acid and the nitrite aliquot should be unpreserved.

6.3 Holding Time: All preserved samples should be analyzed within 28 days of the date of collection. Unpreserved samples must be analyzed within 48 hours of the time of collection. Nitrite must be analyzed within 48 hours.

7.0 APPARATUS & MATERIALS

7.1 Automated continuous flow analyzer designed to deliver and react sample and reagents in the required order and ratios. Currently, the Lachat 8000 Automated Ion Analyzer is being used.

7.2 Autosampler XYZ

7.3 Multichannel pump

7.4 Reaction manifold, including cadmium-copper reduction column.

7.5 Colorimetric detector

7.6 Real time data acquisition device (either electronic or hard copies).

7.7 Balance. Analytical balance capable of accurately weighing to the nearest 0.0001 g.

7.8 Volumetric glassware. Class A volumetric pipettes and flasks as required.

8.0 STANDARDS & REAGENTS

NOTE: All chemicals listed below are reagent grade unless otherwise specified. Distilled, deionized water should be used whenever water is required. All applicable standard/reagent preparation information, including vendor, lot number, date of preparation, calculations, and initials must be entered in the appropriate standard/reagent preparation logbook. Vendors typically used by Accutest include Fisher Scientific, VWR, Accustandard, Absolute Standards, Supelco, Chemservices, Ultra, and ERA. Additional vendors may be utilized as necessary.

8.1 15 N Sodium Hydroxide. In a 1 liter beaker, slowly add 150 g of NaOH to 250 ml of DI water. Swirl until dissolved. **Caution - the solution will get very hot!!**

8.2 Ammonium Chloride Buffer Solution. In a 1000 ml beaker, dissolve 85.0 g ammonium chloride (NH_4Cl) and 1.0 g disodium ethylenediamine tetraacetic acid dihydrate (Na_2 EDTA $2H_2O$) in about 800 ml of DI water. Adjust the pH up to 8.5 with 15 M sodium hydroxide. Dilute to 1000ml with DI water in a 1000 ml volumetric flask and mix. Degas this solution with He at 20 psi for 2 min.

NOTE: Ammonium chloride has been found occasionally to contain significant nitrate contamination. If the zero cannot be set, this may be the problem. An alternative way for making ammonium chloride buffer is:
In the hood, to a 1000 ml volumetric flask add 500 ml of DI water, 105 ml concentrated Hcl, 95 ml ammonium hydroxide (NH_4OH), and 1.0 g disodium EDTA. Dissolve and dilute to the mark with DI water. Adjust the pH to 8.5 with concentrated ammonium hydroxide. Degas this solution with He at 20 psi for 2 min.

8.3 Sulfanilamide color reagent. Add 100 ml of concentrated phosphoric acid (H_3PO_4), 40.0 g of sulfanilamide, and 1.0 g of N-(1-napthyl)ethylenediamine dihydrochloride (NED) to a 1 liter volumetric containing approximately 600 ml of DI water. Stir to dissolve and dilute to a final volume of 1 liter with DI water. Store in a dark bottle. This solution is stable for approximately 1 month. Degas this solution with He at 20 psi for 2 min.

8.4 Hydrochloric Acid, 1 N. Add 8 ml of concentrated HCl to approximately 85 ml of DI water. Dilute to a final volume of 100 ml with DI water.

8.5 Carrier solution. Degassed DI water. Degas DI water with He. Use He at 20 psi for 2 min.

8.6 Two percent copper sulfate solution. Dissolve 20 g of copper sulfate (CuSO4.5H2O) in approximately 800 ml of DI water in a 1 liter volumetric flask. Dilute to a final volume of 1 liter and mix well.

8.7 Cadmium reduction column. The cadmium reduction column should be prepared as described below.

Note 1: It is recommended that extra cadmium be prepared through step 6.8.3 so that new columns may be packed as needed.

Note 2: Cadmium is toxic. Make sure to wear gloves for all procedures and collect any cadmium waste in a marked solid waste container.

8.7.1 Place 10 to 20 g of coarse cadmium granules in a beaker. Cadmium granules ranging from 0.3 to 1.5 mm in diameter are recommended. Wash the Cd first with acetone and then with DI water. Then wash the Cd with two 50 ml portions of 1 N HCl. Rinse the Cd granules well with DI water.

8.7.2 Add 100 ml of 2% copper sulfate solution to the cadmium granules. Swirl for about 5 minutes, then decant the liquid and repeat the process with a fresh portion of 2% copper sulfate solution. Continue this process until the blue color of the copper sulfate solution persists.

8.7.3 Decant off the copper sulfate solution and rinse the copper granules with at least 5 portions of ammonium chloride buffer to remove the colloidal copper. The cadmium should be black or dark gray at this point and can be stored in a capped bottle under ammonium chloride buffer solution.

8.7.4 Open one end of a column, removing the colored lead and the foam plug, and clamp the column so that the open end is pointing up. Fill the column with ammonium chloride buffer. Pour the prepared cadmium granules into the column and tap the column lightly so that the granules settle to the bottom of the column. Fill the column to about 5 mm from the open end. Make sure that there are no air bubbles. Push in the foam plug and screw on the cap. Rinse the outside of the column with DI water.

8.7.5 Insert the column into the manifold by first pumping all reagents into the manifold. Then turn the pump off. Connect the column to the appropriate tubing, making sure that no air is in the tubing. Then return the pump to its normal speed.

8.8 Stock nitrate solution, 1000 mg/l. Dissolve 7.218 g of KNO_3 and dilute to 1 liter with DI water in a 1 liter volumetric flask. Preserve with 2 ml of chloroform per liter. This solution is stable for 6 months.

8.9 Standard nitrate solution, 100 mg/l. Dilute 10.0 ml of 1000 mg/l nitrate solution to 100 ml with DI water in a volumetric flask.

8.10 Standard nitrate solution, 10.0 mg/l. Dilute 10.0 ml of 1000 mg/l nitrate solution to 1000 mg/l with DI water in a volumetric flask.

8.11 Nitrate Calibration Standards. Calibration standards should be made from the above standard solutions as shown below. Class A volumetric pipettes and flasks should be used for all dilutions. A calibration check standard should also be prepared that is at or near the mid-point of the calibration curve.

NOTE: Other calibration standards may be used if necessary. Bring all standards to 100 ml final volume with DI water.

Ml of 8.11	Ml of 8.10	Final Conc.(mg/l)
0.00		0.00
1.00		0.10
3.00		0.30
5.00		0.50
8.00		0.80
10.0		1.00
	2.00	2.00
	5.00	5.00

8.12 Stock nitrite solution, 1000 mg/l. Dissolve 6.072 g of KNO_2 in 500 ml of DI water and dilute to 1 liter in a 1 liter volumetric flask. Preserve with 2 ml of chloroform and keep under refrigeration.

8.13 Standard nitrite solution, 10.0 mg/l. Dilute 1.0 ml of 1000 mg/l nitrite solution (8.13) to 100 ml with DI water in a volumetric flask.

8.14 2.0 ppm Standard nitrite solutions. The nitrite solution is used to check the efficiency of the cadmium reduction column, by comparing a nitrite standard directly with a nitrite standard of the same concentration. Dilute 20 ml of 10 ppm nitrite solution (8.14) to 100 ml with DI water in a volumetric flask.

8.15 Spike solution 100 Mg/L. Dilute 10 ml of 1000 mg/l nitrate solution (8.9) to 100 ml with DI water in a volumetric flask.

9.0 INTERFERENCES

9.1 Build up of suspended matter in the reduction column will restrict sample flow. However, samples can be filtered through a 0.45 um membrane filter to avoid this interference.

9.2 High concentrations of iron, copper, or other heavy metals can cause low results, but this can be avoided by adding EDTA to the samples to complex the metals.

9.3 Residual chlorine can produce a negative interference. This can be eliminated by dechlorinating the sample with sodium thiosulfate.

9.4 Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. This interference is eliminated by pre-extracting the sample.

10.0 PROCEDURE

10.1 Below is a step by step procedure for the analysis of samples for the determination of nitrate/nitrite and nitrate only. At the end of this SOP is a short summary outlining the overall procedure.

10.2 Install the nitrate reaction manifold, excluding the cadmium column. Check all tubing and change any tubing that is flat, dirty, etc. Install the appropriate sample loop and the appropriate filter. Place the tubing in the bottles for the sulfanilamide color reagent, the ammonia buffer solution, and the degassed DI water carrier. Also make sure that the waste container is in place. Refer to the manual for additional information.

10.3 For soil samples, follow the digestion procedure described below. The matrix spike should be prepared by adding 4.0 ml of 100 mg/l nitrate solution directly to the soil and mixing well before the acid digestion. The spike blank should also be prepared by digesting 4.00 ml of the 100 mg/l standard. Make sure to prepare a method blank with each batch of samples.

10.3.1 Weigh out 1.0 g of sample (dry weight) into a 200 ml Erlenmeyer flask. Add 50 ml of DI water and 4 drops of concentrated sulfuric acid. Add another 50 ml of DI water and then boil the sample on a hot plate for 15 minutes.

NOTE: This procedure is operationally defined, so make sure that the same heating time is used for all samples.

10.3.2 Transfer the sample to a centrifuge tube and centrifuge for 5 to 10 minutes. Decant the wash into a 200 ml volumetric flask.

10.3.3 Add 50 ml of DI water to the solids in the centrifuge tube and mix well. Then centrifuge the sample for 5 to 10 minutes and decant the wash into the volumetric flask.

10.3.4 Repeat the above step a second time and again decant the wash into the volumetric flask.

10.3.5 Bring the sample to a final volume of 200 ml with DI water. Filter the sample through a 0.45 um filter before analysis.

10.4 For water samples no preparation is necessary unless the sample is turbid. If the sample is turbid, filter before analysis through a 0.45 um membrane filter paper. If the pH of the sample is below 5 or above

9, adjust to between 5 and 9 with either con. HCl or conc NH_4OH. The matrix spike should be prepared by adding 0.2 ml of 100 mg/l nitrate solution to approximately 10 ml of sample. The spike blank should be prepared by diluting 0.2 ml of 100 mg/l nitrate solution to a final volume of 10 ml with DI water. Make sure to analyze a method blank for each batch of samples.

10.5 On the desk top open the lachat software by clicking on the "**Omni"** icon, and then click on "**OPEN"** on top of the tool bar. The "**OPEN"** window will now be on the screen. The templates, specific to each methods, are stored in the data file. Open the appropriate data file (ie., NO3). Click on the template.

10.6 Three windows will open on screen, **("the run worksheet", "run properties", and "channel one**). "**Run worksheet"** will contain the appropriate standards. To extend the worksheet (adding samples and QC, etc), right click on the bottom line of the worksheet (CalBlk), and click on "**append many".** The appended rows window will now be open and the appropriate number of rows needed should be entered, click ""**ok**". The work sheet must now be sequenced to direct the auto-sampler to the correct sample locations.

10.7 Click and drag by starting in the gray sample No. column down to the last sample to highlight the rows (not including STD's). Right click, then go to columns, then to "**Auto Number Cups"** and click. The run should now be in numerical sequence.

10.8 In the **"Run Properties"** window, click on the Run tab and check "**Export Data as CSV file"** There are other areas of the "**Run Properties"** window that contain method specific information such as timing. These settings must not be adjusted without consulting the area lab supervisor, or an experienced analyst.

10.9 Allow the instrument to warm up for 30 minutes.

10.10 Start pumping reagents through the system. When reagents are pumped through the manifold, then the cadmium column can be installed.

10.11 To begin the analysis, click on "START" on toolbar. The instrument will begin to calibrate. The acceptance calibration criteria for correlation coefficient of 0.995 are set within the software. If the criteria is met, the instrument will proceed with sample analysis.

10.12 Observe the peaks in "**Channel One"** window. The baseline should be smooth and peaks must be well shaped and smooth. If peaks look abnormal, that may indicate the chemistry problems, such as pH differences. Small spikes are indicative of air bubbles in the system.

10.13 The run maybe stopped at anytime by clicking **"Stop"** in the top toolbar. It should be noted that every time the run has been stopped and started, a new file is created. If dilutions are required, the dilution factor needs to be entered in the "**Run Worksheet"** window. On **MDF** column, click on the box and enter the dilution factor.

10.14 When the run is completed the file is automatically exported to " **Lachat CSV files**" locally under "My Document" directory. Click on **"Lachat CSV Files**". All generated files are listed based on the following format: **OM_date_time Am or PM** (**OM_4-11-2006_12-10-34PM**). Drag the generated files for that run/day to the current Month/Year directory. For the ease of search later on, at the

beginning of each month, create a directory to save the runs for the entire month, and name it based on the month, and the year (ie, **OCT 2006**). Once you have moved your file to the month/year directory, copy this file to" **Lacha**t" directory located on the server **Mafile1\WC_DATA** , rename the file to the format which is acceptable to LIMS. This naming scheme will be based on date, the matrix, no. of the run for that day, and finally the test code extension, (ie, **050206W1.NO3**). Once the files have been renamed, drag the file to Server **LIMS_WC**. Server **LIMS_WC** is the processing branch of the LIMS for Wet Chemistry. Once the Run is processed in LIMS, go to GNAPP, and review the run. Package all raw data, and logbook copies in a folder, and turn the package to the area manager for data review, and quality control check.

10.15 To obtain a print out of the sample run, click on Tools in the top toolbar and then click on custom report. To format the report to contain the calibration curve and dilutions, click on report, then format in the custom report window.

10.16 Make sure to check the cadmium reduction efficiency at the beginning of the run. If the efficiency is outside of the range of 85-115%, then the column should be reactivated.

10.17 At the end of the run, make sure to pump ammonia buffer into the cadmium column and cap off the column, making sure that no air is entrained. Rinse out the remainder of the system with DI water.

10.18 Results exceeding the upper range of the calibration curve must be diluted and re-analyzed. The diluted result should be within the upper range of the calibration curve.

11.0 QUALITY ASSURANCE

11.1 Calibration curve. The correlation coefficient of the calibration curve must be 0.995 or greater. The curve must be verified using a standard source independent from the calibration standards (second source). Only the low and high points of the curve may be removed to meet correlation coefficient criteria. If a middle point is removed, it must be approved by the supervisor and documented in the analysis logbook. Removing the low point raises the reporting limit, and removing the high point reduces the calibration range.

11.2 Quality Control Sample (also referred to as Initial Calibration Verification Standard (ICV) a standard from a different source than the calibration standard must be analyzed with each initial calibration. Normally this is analyzed at the beginning of the run after the CCV and CCB checks. For this method, the ICV should be within 10% of the true value.

NOTE: It is recommended that this standard be analyzed with each run.

11.3 Method Blank. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 10 samples. The method blank must not contain the analyte greater than the reporting limit. If the method blank contains over that limit, the samples must be re-analyzed (if the samples are non-detected they may be reported without qualification).

11.4 Spike Blank. The laboratory must digest and analyze a spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 10 samples. Assess laboratory performance against the control limits of 90-110%. In house limits should also be

generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). In house limits must equal or better than the required limits. If the lab control is outside of the control limits for a parameter, all samples must be redigested or redistilled and reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag.

11.5 MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 10 samples. The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits of 90-110%. In house limits are generated once sufficient matrix spike data is available to generate limits (usually a minimum of 20 to 30 analyses). If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect

$$\frac{(Spiked\ Sample\ Result\ -\ Sample\ Result)}{(Amount\ Spiked)}\ x\ 100\ =\ MS\ Recovery$$

11.6 Matrix Duplicate. The laboratory must analyze a duplicate sample for a minimum of 1 in 10 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. The duplicate RPD should be assessed using in house limits. Until these limits can be generated, then default limits of 20% RPD should be applied. If a duplicate is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control.

11.8.1The duplicate RPD should be calculated as shown below:

$$\frac{(Sample\ Result\ -\ Duplicate\ Result)\ x\ 100}{(Sample\ Result\ +\ Duplicate\ Result)\ x\ 0.5}\ =\ \%RPD$$

11.9 Continuing Calibration Verification. (Also known as the instrument performance check solution). Analyze the continuing calibration verification solution and the continuing calibration blank after the initial calibration, after every tenth sample, and at the end of the sample run. If the CCV solution is not within 10% of the true value, then no samples can be reported in the area bracketed by that CCV.

NOTE: **The exception is if the CCV is biased high and the samples are less than the detection limit. In that case, the samples can be reported with no flag.**

The CCV concentration should be at or near the mid-range of the calibration curve.

11.10 Continuing Calibration Blank. Analyze the CCV solution and the CCB after the initial calibration, after every tenth sample, and at the end of the sample run. If the CCB is not less than the reporting limit, then no samples can be reported in the area bracketed by the failing CCB.

11.11 A Precision and accuracy (P&A) study is performed as an initial determination of capability, on an annual basis (continued demonstration of capability – a successful PT result may be used in place of a P&A for continued DOC), and if any significant changes have been made to the instrument. In general, 4 replicates or blank spikes are analyzed using the same procedures and conditions for sample analysis. The percent recoveries are compared to either default limits of 80-120% or in-house control limits once established. The standard deviation of the 4 replicate percent recoveries are compared to either ±20 or to in-house limits once established. If percent recovery or standard deviation criteria are not met, corrective action must be taken to bring the system back into control. The P&A study must be performed using a source independent from the calibration standards (second source).

11.12 Quality Control data is generated (control charts) and reviewed on an annual basis by Quality Assurance (blank spike/ matrix spike recoveries and matrix duplicate RPDs).

12.0 DOCUMENTATION

12.1 The analytical logbook is a record of the analysis sequence; the logbook must be completed daily. Each instrument will have a separate logbook.

12.2 If samples require reanalysis, a brief explanation of the reason should be documented in this log.

12.3 The standard preparation logbook application must be completed for all standard preparations. All information requested must be completed; the page must be signed and dated by the respective person.

12.4 The Accutest lot number must be cross-referenced on the standard vial/container.

12.5 The instrument Maintenance logbook must be completed when any type of maintenance is performed on the instrument. Each instrument will have a separate log.

12.6 All laboratory logbooks must be routinely reviewed and initialed or signed by the lab manager.

12.7 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

13.0 DATA REVIEW

13.1 The analyst conducts the primary review of all data. This review begins with a check of all Instrument and method quality control and progresses through sample quality control concluding with a check to assure that the client's requirements have been executed. The analyst has the authority and responsibility to perform corrective action for any out-of-control parameter of non-conformance.

13.2 A secondary review is performed by department managers, and it includes review of the data produced by their department. All manual calculations, QC criteria, and a comparison of the data package to client specified requirements are checked. The department manager may reject data, initiate reanalysis, take additional corrective action, or reprocess data.

13.3 The laboratory director performs a full tertiary review of the data package following its assembly. This review includes an evaluation of QC data against acceptance criteria and a check of the data package contents to assure that all analytical requirements and specifications were executed.

13.4 Spot-check reviews are performed by the Quality Assurance Officer focusing on all elements of the deliverable including the client's specifications and requirements, analytical quality control, sample custody documentation and sample identification.

14.0 DATA REPORTING

14.1 A results page including positive results and/or RLs, units, methodology, preparation and/or analysis dates, and data qualifiers are reported. Additional quality control data including calibration summaries, MS/duplicate percent recoveries and RPDs, blank spike recoveries, and method blank results may be reported upon request of the client. Additionally, raw data including any instrument printouts, laboratory logbooks, etc. may be reported to the client.

14.2 Data may be submitted to the client in a specified electronic format (EDD).

14.3 Data may be submitted to the client electronically as a PDF (e-hardcopy).

14.4 Once the data is approved by the laboratory manager, it may be accessed by clients via LabLink™.

14.5 Procedures for handling non-conforming data.

14.5.1 If quality control data does not meet criteria the non-conformance must be discussed in a case narrative and footnoted on the applicable quality control report summary.

14.5.2 If preservation or holding time criteria is not met and the samples are analyzed the result page must be footnoted with this information, and the non-conformance must be discussed in a case narrative or other suitable communication (telephone conversation log or email). Client notification documentation should be included with the data (telephone conversation log, fax, or email).

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Pollution Prevention. Users of this method must perform all procedural steps that controls the creation and/or escape of wastes of hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids, or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 15.2.

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the Sample and Waste Disposal SOP. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

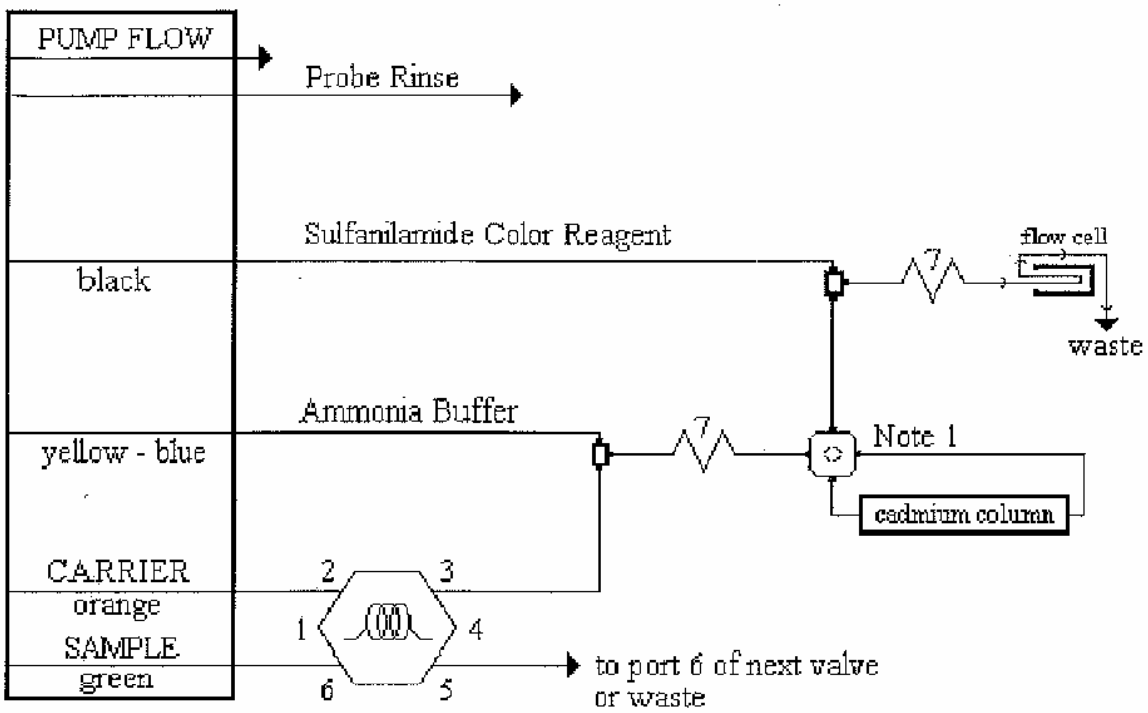
15.2.1 Non-hazardous aqueous wastes
15.2.2 Hazardous aqueous wastes
15.2.3 Chlorinated organic solvents
15.2.4 Non-chlorinated organic solvents
15.2.5 Hazardous solid wastes
15.2.6 Non-hazardous solid wastes
15.2.7 Microbiological wastes

16.0 METHOD PERFORMANCE

16.1 Method performance is evaluated by the annual QC limits (control charts) generated by QA, and the annual MDL study results. Refer to section 3.5 for MDLs, and section 11.12 for QC limits.

17.0 ADDITIONAL REFERENCES

17.1 Lachat QuickChem Method 10-107-04-1-C

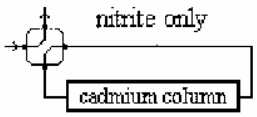


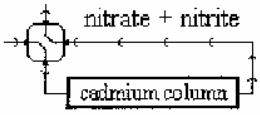
Carrier: Helium Degassed DI water
Manifold Tubing: 0.8 mm (0.032 in) i.d. This is 5.2 µL/cm.
AE Sample Loop: 17 cm x 0.8 mm i.d.
QC8000 Sample Loop: 22.5 cm x 0.8 mm i.d.
Interference Filter: 520 nm

Apparatus: An injection valve, a 10 mm path length flow cell , and a colorimetric detector module is required.

7: 135 cm of tubing on a 7 cm coil support

Note 1: This a 2 state switching valve used to place the cadmium column in-line with the manifold





Lab Manager: Brad Madadian

QA Officer: Robert Treggiari

TITLE: SULFIDE

TEST METHOD REFERENCE: 4500-S F . Standard Methods for the Examination of Water and Wastewater 21th Edition, 2005

REVISED SECTION: Section 8.0 notation

1.0 SCOPE & APPLICATION

1.1 This method is applicable to total and dissolved sulfides in drinking water and surface waters, sewage and industrial wastes. Acid insoluble sulfides are not measured by the use of this test.

1.2 A modification of this method is used to determine water- soluble sulfides in soil samples.

2.0 SUMMARY

2.1 Excess iodine is added to sample which may or may not have been treated with zinc acetate to produce zinc sulfide. The iodine oxidizes the sulfide to sulfur upon addition of HCL. The excess iodine is back titrated with sodium thiosulfate.

3.0 METHOD REPORTING LIMIT AND DETECTION LIMIT

3.1 The normal reporting limit for sulfide in waters is 2 mg/l and 4 mg/kg for soils.

3.2 The Method Detection Limit (MDL) represents the lowest reportable concentration of an individual analyte that meets the method qualitative identification criteria.

3.3 Method Detection limits (MDLs) are experimentally determined using the procedures described in 40 CFR, Part 136, Appendix B. Actual reported MDLs incorporate the sample volume analyzed and sample dilutions if needed, which may cause MDL variations from sample to sample.

3.4 In general, MDLs are determined through the analysis of at least 7 replicate blank spikes (using the same procedures for sample analysis). The MDL is calculated by multiplying the standard deviation of the replicate concentrations by the appropriate Student's t value (3.143 for 7 replicates). If more than 7 replicates are analyzed refer to 40 CFR, Part 136, Appendix B for the appropriate student's t value. MDLs are determined initially (prior to analysis), on an annual basis, and after major maintenance to equipment. MDL data is archived with Quality Assurance. Refer to the most recent study for current MDLs. For additional detail regarding MDL studies, refer to the MDL SOP MQA245.

3.5 The MDL represents the lowest reportable concentration of an individual analyte that meets the method qualitative identification criteria.

3.6 Current MDL studies are filed with Quality Assurance. Obsolete MDL studies are archived with the QA files. Electronic MDL data is found in the annual "MDL" folder on the QA server (LINUXMA1).

4.0 DEFINITIONS

4.1 ALIQUOT - a measured portion of a sample, or solution, taken for sample preparation and/or analysis.

4.2 BATCH – A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20 (or 10 for certain methods), then each group of 20 samples (or 10 samples for certain methods) or less will all be handled as a separate batch.

4.3 DRY WEIGHT – the weight of a sample based on percent solids. The weight after drying. See Percent Moisture.

4.4 CONTAMINATION - a component of a sample or an extract that is not representative of the environmental source of the sample. Contamination may stem from other samples, sampling equipment, while in transit, from laboratory reagents, laboratory environment, or analytical instruments.

4.5 FIELD SAMPLE - a portion of material to be analyzed that is contained in single or multiple containers and identified by a unique sample number.

4.6 FIELD BLANK – this is any sample that is submitted from the field and is identified as a blank. This includes trip blanks, rinsates, equipment blanks, etc.

4.7 HOLDING TIME – the elapsed time expressed most commonly in days from the date of sampling until the date of its analysis.

4.8 INSUFFICIENT QUANTITY - when there is not enough volume (water sample) or weight (soil/sediment) to perform any of the required operations: sample analysis or extraction, percent moisture, MS/DUP, etc.

4.9 MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

4.10 Matrix Spike: The laboratory must add a known amount of each analyte to a minimum of 1 in 10 samples. The matrix spike recovery is calculated and assessed against the control limits that are generated in house. If control limits are not available, then a default limits of 75 to 125 percent should be applied.

4.11 MATRIX DUPLICATE: A duplicate sample is analyzed at a minimum of 1 in 10 samples. The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate

RPD is calculated as shown below. Assess laboratory performance against the control limits. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified, use default limits of ± 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2} = \text{Duplicate RPD}$$

4.12 METHOD BLANK. The laboratory must analyze a method blank with each set of samples. A minimum of one method blank is required for every 10 samples. The method blank must contain the parameter of interest at levels of less that the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

4.13 PERCENT MOISTURE - an approximation of the amount of water in a soil/sediment sample made by drying an aliquot of the sample at 105 °C. The percent moisture determined in this manner also includes contributions from all compounds that may volatilize at or below 105 °C, including water. Percent moisture may be determined from decanted samples and from samples that are not decanted.

4.14 RELATIVE PERCENT DIFFERENCE (RPD) - To compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero. In contrast, see percent difference.

4.15 REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents that conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

4.16 REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. Water in which an interferant is not observed at or above the minimum quantitation limit of the parameters of interest. Accutest uses deionized water (municipal water which passes through Accutest's DI treatment system).

4.17 REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

4.18 SPIKE BLANK OR LAB CONTROL SAMPLE. Analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 10 samples. Assess laboratory performance against the control limits. In house limits should also be generated once sufficient data is available to generate limits (usually a minimum of 20 to 30 analyses). If the lab control is outside of the control limits for a parameter, all samples must be reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of

the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag. Note: If control limits are not specified, then default limits of 80 to 120 percent should be used.

5.0 HEALTH & SAFETY

5.1 All safety practices must be followed as outlined in the Accutest Laboratories Employee Safety Handbook and Chemical Hygiene Plan. Safety glasses, gloves, and lab coats must be worn. All samples, solutions, and extracts must be treated as unknown and potentially hazardous.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level.

6.0 COLLECTION, PRESERVATION, AND HOLDING TIMES

6.1 Water samples should be collected in two 250-300 ml containers. Soil samples should be collected in one 250-300ml glass container.

6.2 Water samples should be preserved with zinc acetate and sodium hydroxide. Water and soil samples should be kept under refrigeration at 4° ± 2° C until they are analyzed.

6.3 All samples should be analyzed within 7 days of the date of collection.

7.0 APPARATUS & MATERIALS

The following items are needed for the analysis of samples following the method outlined below:

7.1 Burette.
7.2 Graduated glass or plastic beakers.
7.3 Stir bars.
7.4 Stir plates.
7.5 Class A Volumetric pipettes.
7.6 Filtering Apparatus with 934 AH Whatman Glass Fibers or equivalent.

8.0 STANDARDS & REAGENTS

NOTE: All chemicals listed below are reagent grade unless otherwise specified. Distilled, deionized water should be used whenever water is required. All applicable standard/reagent preparation information, including vendor, lot number, date of preparation, calculations, and initials must be entered in the appropriate standard/reagent preparation logbook. Vendors typically used by Accutest include Fisher Scientific, VWR, Accustandard, Absolute Standards, Supelco, Chemservices, Ultra, and ERA. Additional vendors may be utilized as necessary.

8.1 Hydrochloric Acid, HCL, (6 N). Add 100 ml of concentrated HCL to 100 ml of DI water. Cool, mix.

8.2 Standard Iodine Solution (0.025 N). Dissolve 20 to 25g of anhydrous potassium iodide (KI) and 3.2 g of iodine in 400 ml of DI water and dilute to 1000 ml in a volumetric flask. Standardize this solution against 0.025 N sodium thiosulfate.

8.3 Sodium Thiosulfate solution (0.025N). Dissolve 6.205 g of Na2S2O3.5H2O in approximately 500 ml of DI water. Add 9 ml of 1 N NaOH and dilute to a final volume of 1000 ml in a volumetric flask. Note: this solution is commercially available. Request the certificate of the analysis from the vendor and keep in file.

8.4 Starch Indicator solution. This solution is also commercially available.

8.5 Zinc acetate solution. Dissolve 220 g of zinc acetate (Zn(C2H3O2)2)2H2O in 870 ml of DI water.

8.6 Sodium Hydroxide, (6N). Dissolve 24 g of sodium hydroxide in 50 ml of DI water. Dilute to 100 ml with DI water.

8.7 Sodium Hydroxide, (1N). Dissolve 40 g of sodium hydroxide in 500 ml of DI water. Dilute to 1000 ml with DI water.

8.8 Sulfide 537 mg/L Stock Solution. Dissolve 4.02 g of sodium sulfide nonahydrate, Na2S.9H2O, in approximately 980 ml of DI water. Adjust the PH of this solution to >9 and < 11 with 1 N sodium hydroxide solution (8.7). Dilute to 1000 ml with DI water in a volumetric flask. Note: Sodium sulfide nonahydrate is extremely hydroscopic. Make sure that the compound is dry before weighing (Excess moisture can be removed by rinsing the solid with a small amount of ether). Prepare weekly.

9.0 INTERFERENCES

9.1 Reduced sulfur compounds, which decompose in acid, such as sulfite and thiosulfate, may yield erratic results. Volatile iodine consuming substances will give high results. Oxidation may also affect sample results and samples should be taken with a minimum of aeration.

10.0 PROCEDURE

10.1 Below is a step by step procedure for analysis of samples for sulfide. The automated spreadsheet is used for documentation, calculation of standardization, and the analysis. The application can be found on the server. Before starting on the samples, standardize the iodine solution daily, using the following procedure.

10.1.1 Volumetrically pipet 5.00 ml of the Iodine solution into the beaker. Place the beaker on stir plate and add 2 to 4 mls of 6 N HCL to bring the PH< 2. Measure out 200 ml of DI water into beaker with a stir bar. This solution should now be an amber color.

10.1.2 Fill a burette with 0.025 N Sodium thiosulfate solution. Titrate the iodine solution with sodium thiosulfate until the amber color fades to yellow, then add enough starch solution to

obtain a blue color. Slowly continue to titrate until blue color disappears. Record the volume used. Repeat this procedure in duplicate.

10.1.3 Calculate the normality of the iodine as shown below. The iodine normality used should be the average of the normalities for the two standardizations of the DI water blanks.

$$\text{N of iodine sloution} = \frac{\text{(ml of Na thiosulfate) x (0.025)}}{\text{(5.00 ml,of iodine)}}$$

10.2 For soil samples, weigh out 25 g and dilute to 250 ml with DI water. Mix well. Let settle and filter through Whatman 934 AH or equivalent filter paper. Measure out 200 ml to use for analysis. Make sure to prepare a matrix spike, duplicate sample, a method blank, and a spike blank.

Note: The soil sample should be prepared immediately before the titration is to be done.

10.3 For water samples that **are not preserved with NaOH/zinc acetate,** mix and, measure out 200 ml of sample to use for analysis. Follow step 10.5.

10.4 For water samples that **are preserved with NaOH/zinc acetate,** mark the side of the original sample bottle at the level of the sample meniscus.

10.5 Pipet 5 ml of the iodine solution into a 400 ml beaker and add 2 to 4 mls of 6 N HCl (to bring the PH less than 2) for most soils and water samples that are not preserved with NaOH/Zinc Acetate, and 20 ml of 6N HCl for samples preserved with NaOH/Zinc Acetate. Swirl to mix. Gently transfer the contents of the original sample bottle to the beaker (or the 200 ml from step 10.3) with minimum agitation under the iodine surface. Rinse the sample bottle with adequate DI water to the beaker to make sure all zinc sulfides have been transferred to the beaker. **If the Iodine color disappears, add more Iodine immediately to the sample**. Add a stir bar and start stirring slowly, check the pH to be less than 2. Titrate the sample slowly with sodium thiosulfate solution until the solution changes to a lighter yellow (straw) color. Then add a small amount of starch solution and the solution should turn blue. Continue to titrate until the last bluish tint disappears and the solution appears clear.

10.6 Set up quality control samples for each batch, including a method blank, a spike blank, matrix spike and a duplicate sample. The spike blank and matrix spike should be spiked with 5 ml of 537 mg/l sulfide spiking solution (8.8). Follow step 10.5.

Note: For MS and SB use 20 ml of Iodine

10.7 For samples that are preserved with NaOH/ zinc acetate, measure sample volume used by filling the sample bottle with water to the line marked at the meniscus and then measuring the amount of water used in a class A graduated cylinder.

10.8 If interferences are suspected, the sample may be taken through a pretreatment step as described below:

10.8.1 If the sample was not treated with zinc acetate and sodium hydroxide, then shake the sample well and measure out 200 ml of sample. Add 0.30 ml of zinc acetate solution and 4 to 5 drops of 6N NaOH solution to bring the PH to above 9. Mix gently. Let the precipitate settle until the sample can be readily filtered. Follow 10.8.3.

10.8.2 If the sample was treated with zinc acetate and sodium hydroxide, verify the PH is above 9. mark the side of the original sample bottle at the level of the sample meniscus. Then follow 10.8.3. Additional zinc acetate may be added to ensure complete precipitation.

10.8.3 Filter the sample (200 ml from step 10.8.1 or the entire sample from step 10.8.2) through glass filter paper(Whatman 934AH or equivalent). Place the filter paper in the original sample container (i.e. the container to which the zinc acetate and NaOH were added), and add approximately 200 ml of DI water to the container and proceed with the titration starting at step 10.5. If a lower detection limit of 0.2 mg/l is requested, concentrate the sample by a factor of 10 to 1 (filter 1000 ml of sample and return to original battle with addition of 100 ml and titrate).

10.9 Calculations The calculations to be used are shown below

WATER $$\frac{\{ (Vi)\ (Ni) - (Vt)\ (Nt) \} \times 16000}{Vti} = \text{Mg Sulfide/L}$$

SOIL $$\frac{\{ (Vi)\ (Ni) - (Vt)\ (Nt) \} \times 16000 \times Vf}{Vti \times \text{sample weight in g} \times \%sol/100} = \text{Mg Sulfide/Kg}$$

Where Vi= Volume of iodine solution in Ml
Ni = Normality of iodine solution
Vt = Volume of sodium thiosulfate in Ml

Nt = Normality of sodium thiosulfate
Vti= Volume of sample titrated in Ml
Vf = Final volume of sample after preparation in Ml

11.0 QUALITY ASSURANCE

11.1 Below is a summary of the quality control requirements for this method. Make sure to check with the laboratory supervisor or manager for any additional client specific quality control requirements.

11.2 Method Blank. The laboratory must analyze method blank with each set of samples. A minimum of one method blank is required for every 10 samples. The method blank must not contain the analyte at more

than the reporting limit. If the method blank contains an analyte level over that limit, the samples must be reanalyzed.

11.3 Laboratory control sample/Spike Blank. The laboratory must analyze a spike blank with each set of samples. A minimum of one LCS (SB) is required for every 10 samples. In house limits should be generated once, sufficient data is available (usually a minimum of 20 to 30 analysis). If the lab control is outside of the control limits for a parameter, all samples must be reanalyzed. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limits. In that case, the sample results can be reported with no flag. Note; If control limits are not available, then a default limits of 80 to 120 percent should be used.

11.4 An external QC sample (ICV) is analyzed every 10 samples. The acceptance criteria are 90-110% recovery. If the ICV is outside of the control limits, all samples must be reanalyzed. The exception is if the ICV recovery is high and the results for the samples are non-detected. In that case the sample results can be reported with no flag.

11.5 Matrix Spike. The Laboratory must add a known amount of each analyte to a minimum of 1 in 10 samples. The spike recovery should be assessed using in house limits. Until these limits can be generated, then default limits of 75 to 125 percent recovery should be applied. If insufficient sample is available to prepare a matrix spike, then blank spike may be substituted.

$$\frac{(\text{spiked sample Result} - \text{sample Result}) \times 100}{(\text{Amount spiked})} = \text{Ms Recovery}$$

11.6 Matrix duplicate. The laboratory must prepare a duplicate sample for a minimum of 1 in 10 samples. If insufficient sample is available to prepare a duplicate, then a duplicate blank spike maybe substituted. The RPD between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below.

11.6.1 The duplicate RPD should be assessed using in house limits. Until these limits can be generated, then default limits of 20 percent should be applied. If a duplicates out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control.

11.6.2 The duplicate RPD should be calculated as shown below.

$$\frac{(\text{I Sample results} - \text{Duplicate results I})}{(\text{Sample results} + \text{Duplicate results})} = \%\text{RPD}$$

11.7 A Precision and accuracy (P&A) study is performed as an initial determination of capability, on an annual basis (continued demonstration of capability – a successful PT result may be used in place of a P&A for continued DOC), and if any significant changes have been made to the instrument. In general, 4 replicates or blank spikes are analyzed using the same procedures and conditions for sample analysis. The percent recoveries are compared to either default limits of 80-120% or in-house control limits once established. The standard deviation of the 4 replicate percent recoveries

are compared to either ±20 or to in-house limits once established. If percent recovery or standard deviation criteria are not met, corrective action must be taken to bring the system back into control.

11.8 Quality control data are generated at least on an annual basis by QA using an in-house program. Blank spike and MS/Dup data are pooled for the previous year (or other specified time frame) and the data is processed and evaluated by QA. The annual QC data is filed with QA.

12.0 DOCUMENTATION

12.1 If samples require reanalysis, a brief explanation of the reason should be documented.

12.2 The standard preparation logbook application must be completed for all standard preparations. All information requested must be completed; the page must be signed and dated by the respective person.

12.3 The Accutest lot number must be cross-referenced on the standard vial.

12.4 All laboratory logbooks must be reviewed and initialed or signed by the lab manager.

12.5 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

13.0 DATA REVIEW

13.1 The analyst conducts the primary review of all data. This review begins with a check of all method quality control and progresses through sample quality control concluding with a check to assure that the client's requirements have been executed. The analyst has the authority and responsibility to perform corrective action for any out-of-control parameter of non-conformance.

13.2 A secondary review is performed by department managers, and it includes review of the data produced by their department. All manual calculations, QC criteria, and a comparison of the data package to client specified requirements are checked. The department manager may reject data, initiate reanalysis, take additional corrective action, or reprocess data.

13.3 The laboratory director performs a full tertiary review of the data package following its assembly. This review includes an evaluation of QC data against acceptance criteria and a check of the data package contents to assure that all analytical requirements and specifications were executed.

13.4 Spot-check reviews are performed by the Quality Assurance Officer focusing on all elements of the deliverable including the client's specifications and requirements, analytical quality control, sample custody documentation and sample identification.

14.0 DATA REPORTING

14.1 A results page including positive results and/or RLs, units, methodology, preparation and/or analysis dates, and data qualifiers are reported. Additional quality control data duplicate RPDs, blank spike recoveries, and method blank results may be reported upon request of the client. Additionally, raw data including any instrument printouts, laboratory logbooks, etc. may be reported to the client.

14.2 Data may be submitted to the client in a specified electronic format (EDD).

14.2 Once the data is approved by the laboratory manager, it may be accessed by clients via LabLink™.

14.3 Procedures for handling non-conforming data.

14.3.1 If quality control data does not meet criteria the non-conformance must be discussed in a case narrative and footnoted on the applicable quality control report summary.

14.3.2 If preservation or holding time criteria is not met and the samples are analyzed the result page must be footnoted with this information, and the non-conformance must be discussed in a case narrative or other suitable communication (telephone conversation log or email). Client notification documentation should be included with the data (telephone conversation log, fax, or email).

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Pollution Prevention. Users of this method must perform all procedural steps that control the creation and/or escape of wastes of hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids, or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 15.2.

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the Sample and Waste Disposal SOP. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

15.2.1 Non-hazardous aqueous wastes
15.2.2 Hazardous aqueous wastes
15.2.3 Chlorinated organic solvents
15.2.4 Non-chlorinated organic solvents
15.2.5 Hazardous solid wastes
15.2.6 Non-hazardous solid wastes
15.2.7 Microbiological wastes

16.0 METHOD PERFORMANCE

16.1 Method performance is evaluated by the annual QC limits (control charts) generated by QA, and the annual MDL study results. Refer to section 3.0 for MDLs, and section 11 for QC limits.

17.0 ADDITIONAL REFERENCES

17.1 No additional references are required for this method.

Lab Manager: Brad Madadian
QA Officer: Robert Treggiari

TITLE: ALKALINITY, TOTAL (pH 4.5)

TEST METHOD REFERENCE: 2320 B. Standard Methods for the Examination of Water and Wastewater 21th Edition, 2005

REVISED SECTIONS: Section 8.0 notation

1.0 SCOPE AND APPLICATION

1.1 Alkalinity is the measure of the acid-neutralizing capacity of a water sample, as the sum of all titratable bases. Since the alkalinity of surface waters is primarily a function of carbonate, bicarbonate, and hydroxide content, it may be used as an indicator for the concentration of these constituents. The measured value will also include some borates, phosphates, silicates and other bases if they are present. The sample is not to be diluted, filtered, or altered in any way.

1.2 For samples of low alkalinity (<20 mg $CaCO_3$/l) an extrapolation technique is used. The amount of acid to lower the pH exactly 0.3 pH units is measured, after the initial endpoint has been attained. Because this corresponds to an exact doubling of the hydrogen ion concentration, an extrapolation may be made to the equivalence point.

1.3 This method is applicable to surface water, and saline waters, domestic and industrial waste.

1.4 Test code: ALK

2.0 SUMMARY

2.1 An unaltered sample is titrated to an electrometrically determined end point of PH 4.5. The sample must not be filtered, diluted, concentrated, or altered in any way.

3.0 METHOD REPORTING AND DETECTION LIMIT

3.1 The reporting limit for this analysis is 5.0 Mg/L.

3.2 The Method Detection Limit (MDL) represents the lowest reportable concentration of an individual analyte that meets the method qualitative identification criteria.

3.3 Method Detection limits (MDLs) are experimentally determined using the procedures described in 40 CFR, Part 136, Appendix B. Actual reported MDLs incorporate the sample volume analyzed and sample dilutions if needed, which may cause MDL variations from sample to sample.

3.4 In general, MDLs are determined through the analysis of at least 7 replicate blank spikes (using the same procedures for sample analysis). The MDL is calculated by multiplying the standard deviation of the replicate concentrations by the appropriate Student's t value (3.143 for 7 replicates). If more than 7 replicates are analyzed refer to 40 CFR, Part 136, Appendix B for the appropriate student's t value. MDLs are determined initially (prior to analysis), on an annual basis, and after major maintenance to equipment. MDL data is archived with Quality Assurance. Refer to the most recent study for current MDLs. Refer to the SOP for MDLs

(MQA245) for additional detail regarding MDL study procedures. The MDL represents the lowest reportable concentration of an individual analyte that meets the method qualitative identification criteria.

3.5 Current MDL studies are filed with Quality Assurance. Obsolete MDL studies are archived with the QA files. Electronic MDL data is found in the annual "MDL" folder on the QA server (LINUXMA1).

4.0 DEFINITION

4.1 ALIQUOT - a measured portion of a sample, or solution, taken for sample preparation and/or analysis.

4.2 BATCH – A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 10, then each group of 10 samples or less will all be handled as a separate batch.

4.3 CONTAMINATION - a component of a sample or an extract that is not representative of the environmental source of the sample. Contamination may stem from other samples, sampling equipment, while in transit, from laboratory reagents, laboratory environment, or analytical instruments.

4.4 EXTERNAL CHECK STANDARD - The external check standard that is used to verify the accuracy of the calibration standards. An external check must be run with each analytical batch. The laboratory should initially assess laboratory performance of a check standard using the control limits generated by the external check supplier. Refer to the quality control section for each SOP. If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

4.5 FIELD SAMPLE - a portion of material to be analyzed that is contained in single or multiple containers and identified by a unique sample number.

4.6 HOLDING TIME – the elapsed time expressed in days from the date of sampling until the date of its analysis.

4.7 INTERFERENTS – substances which affect the analysis for the element of interest.

4.8 MATRIX - the predominant material of which the sample to be analyzed is composed. For the purpose of this SOP, a sample matrix is either water or soil/sediment. Matrix is not synonymous with phase (liquid or solid).

4.9 MATRIX DUPLICATE - a second aliquot of the original sample prepared and analyzed in order to determine the precision of the method.

4.10 MATRIX SPIKE- aliquot of a matrix(water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

4.11 RELATIVE PERCENT DIFFERENCE (RPD) - As used in this SOP to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero.

4.12 REAGENT WATER - water in which an interferant is not observed at or above the minimum quantitation limit of the parameters of interest. Accutest uses deionized water (municipal water, which passes through Accutest's DI treatment system).

5.0 HEALTH AND SAFETY

5.1 The analyst should follow normal safety procedures as outlined in the Accutest Laboratories Chemical Hygiene Plan, which includes the use of lab coat and safety glasses. In addition, all acids are corrosive and should be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

6.0 COLLECTION, PRESERVATION & HOLDING TIMES

6.1 The sample must be stored at 4 C.

6.2 All samples must be analyzed within 14 days from sampling date.

7.0 APPARATUS

7.1 pH meter with glass electrode capable of reading 0.05 pH unit.
7.2 Titration vessel, 100 ml or 200 ml beaker.
7.3 Magnetic stirrer; stirbars.
7.4 Pipettes, class A.
7.5 Volumetric flasks, class A.
7.6 Burets, 50 ml and 10 ml micro.

8.0 STANDARDS AND REAGENTS

NOTE: All chemicals listed below are reagent grade unless otherwise specified. Distilled, deionized water should be used whenever water is required. All applicable standard/reagent preparation information, including vendor, lot number, date of preparation, calculations, and initials must be entered in the appropriate standard/reagent preparation logbook. Vendors typically used by Accutest include Fisher Scientific, VWR, Accustandard, Absolute Standards, Supelco, Chemservices, Ultra, and ERA. Additional vendors may be utilized as necessary.

8.1 Sodium Carbonate solution, approximately 0.05 N:Place 2.5 + or - 0.2 g (weigh to nearest 0.1 mg) of sodium carbonate (Na_2CO_3, dried at 250^{o} C for 4 hours and cooled in a desiccator) into a 1 liter flask and dilute to the mark. Do not store for more than 1 week.

8.2 Standard Acid, 0.1 N:

8.2.1 Sulfuric acid: Add 3.0 ml of concentrated H_2SO_4 to 500 ml of DI water in a 1 liter volumetric flask. Dilute to 1 liter with water.

or

8.2.2 Hydrochloric Acid: Add 8.3 ml of concentrated HCl to 500 ml DI water in a 1 liter volumetric Flask. Dilute to 1 liter with water.

8.3 Standard Acid 0.02 N: Dilute 200.0 ml of 0.1 N Standard Acid (use 8.2.1 or 8.2.2) to 1 liter with distilled water.

8.4 Sodium Phosphate, dibasic: 0.10 M Weigh 26.81 g of sodium phosphate dibasic heptahydrate ($Na_2HPO_4 \cdot 7H_2O$). Dissolve in approximately 600 ml of DI water in a 1000 ml volumetric flask. Dilute to 1

liter. Alkalinity value is 5000 mg/l as $CaCO_3$. Add 5 ml of this solution to 100 ml of DI water for blank spike and also 5 ml to 100 ml of sample for matrix spike. This solution must be discarded after 6 months.

8.5 All applicable standard/reagent preparation information, including vendor, lot number, date of preparation, expiration date, calculations, and initials must be entered in the appropriate standard/reagent preparation logbook. Vendors typically used by Accutest include Fisher Scientific, VWR, Accustandard, Supelco, Chemservices, Ultra, and ERA. Additional vendors may be utilized as necessary.

9.0 INTERFERENCES

9.1 Samples that contain oil, soaps or suspended solids may coat the electrode and cause a sluggish electrode response. Allow additional time between measurements to reach equilibrium at the electrode.

10.0 PROCEDURE

Below is a step by step procedure for the analysis of samples for ALK. The automated spreadsheet is used for Documentation, calculations of Standardization, and the analysis. This application can be found on the server.

10.1 **Standardizing acid solutions: 0.10 N**

10.1.1 Calibrate the pH meter according to manufacture's instructions, and document the calibration in the pH meter log book.

10.1.2 Rinse the 50 ml buret with approximately 20 ml of standard acid, then fill it.

10.1.3 Add 40.0 ml of 0.05N Sodium Carbonate Solution to approximately 60 ml of distilled water in a 250 ml beaker.

10.1.4 Add a stir bar and place on a magnetic stirrer. Mix gently.

10.1.5 Place pH probe in the sodium carbonate solution and titrate to a pH of approximately 5. Record the pH after every 0.50 to 2 ml acid addition. Remove electrode and rinse with DI water into the beaker.

10.1.6 Cover the beaker with a watch glass and boil the solution for 3- 5 minutes. Allow to cool. Rinse watch glass with DI water into beaker.

10.1.7 Continue the titration to the pH inflection point and record the pH after every 0.050 ml addition . Continue the titration to pH 3.0.

10.1.8 Plot the pH of the sodium carbonate vs. ml of acid added around the inflection point, starting a few mls prior to boiling the solution, and continuing to pH 3.

10.1.9 Calculate the normality of the acid as follows;

$$\text{Normality N} = \frac{A \times B}{53.00 \times C}$$

Where: A = g Na_2CO_3 weighed
B = ml Na_2CO_3 solution
C = ml Acid used at inflection point.

10.2 **Standardizing Acid solution, 0.02 N**: Repeat steps 10.1.1 through 10.1.9 using 15 ml of Sodium Carbonate Solution and 0.020N standard acid.

10.3 **Sample analysis**

An automated Alkalinity spreadsheet is located on MAFILE!\APPS server. Use this application to record all measurments.

10.3.1 Samples above 20 mg/l and less than 1000 mg/l

10.3.2 Place 100 ml of the sample in the titration vessel (beaker or flask), with minimal agitation. Place a stir bar in the titration vessel.

10.3.3 While stirring gently but thoroughly, measure the pH of the sample. Record the pH on the analysis log.

10.3.4 Slowly add 0.02 N standard acid allowing the pH meter to equilibrium between additions.

10.3.5 Titrate the sample to pH 4.5. Record the volume of titration on the analysis log.

10.4 **Samples below 20 mg/l**

10.4.1 Titrate the sample as described in 10.3.1 through 10.3.4, using a 10 ml microburette and 0.02 N titrant. Stop titration at a pH in range of 4.3-4.7. Record the volume of titration and exact pH.

10.4.2 Very carefully add titrant to lower the pH 0.3 pH units and again record the volume.
Note: Samples above 1000 mg/l follow steps 10.3.1 to 10.3.5 using 0.10N titrant

10.5 **Calculations**.

10.5.1 Samples above 20 mg/l:

Alkalinity , mg/l $CaCO_3$ = $\frac{A \times N \times 50000}{\text{ml sample}}$

Where: A = ml of standard acid
N = Normality of standard acid

10.5.2 Samples below 20 mg/l

Alkalinity, mg.l $CaCO_3$ = $\frac{(2A-C) \times N \times 50000}{\text{ml sample}}$

Where: A = ml titrant to first pH
C = total ml titrant to reach pH 0.3 units lower
N = Normality of Acid.

11.0 QUALITY ASSURANCE

11.1 Below is a summary of the quality control requirements for this method. Make sure to check with laboratory supervisor or manager for any additional client specific quality control requirements.

11.2 **Method Blank**. The laboratory must analyze a method blank with each set of samples. A minimum of one method blank is required for every 10 samples. The method blank must contain the analyte at less than the reporting limit (1/2 the RL for some clients). If the method blank contains an analyte level over that limit the problem must be identified and corrected prior to sample analysis.

11.3 **Matrix Duplicate.** The laboratory must prepare a duplicate sample for a minimum of 1 in 10 samples. The relative percent difference (RPD) between the duplicate sample and the original should be assessed. The Duplicate RPD should be calculated as shown below

$$\frac{\text{(Original Sample Result – Duplicate Result) x 100}}{\text{(Original Sample Result + Duplicate Result) x 0.5}} = \%\ \text{RPD}$$

The Duplicate RPD should be assessed using in house limits. Until these limits can be generated, then the default limit of 20 percent RPD should be applied. If a duplicate RPD is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control.

11.4 **Matrix spike.** The laboratory must add a known amount of each analyte to a minimum of 1 in 10 samples. The spike recovery should be assessed using in house limits. Until these limits can be generated, default limits of 75-125 % recovery should be applied. If a matrix recovery is out of control, then the recovery should be flagged with the appropriate footnote. If a matrix spike amount is less than one fourth of the sample amount, then the sample can be assessed against the control limits and should be footnoted to that effect.

$$\frac{\text{(Matrix Spike Result – Original Result) x 100}}{\text{Amount of Spike}}$$

11.5 **Spike Blank.** The laboratory must analyze a spike blank with each set of samples. A minimum of one spike blank is required for every 10 samples. The net recovery should be within 20 percent of the true value. If the spike blank is outside of this range, the problem must be identified and corrected before sample analysis can proceed.

11.6 **External Standard.** An external standard is analyzed with each analytical batch. The net recovery should be within 10% of the true value (if the external is prepared in house) or within the manufacturer's acceptance criteria if purchased from an outside vendor. If the external is outside this range, the problem must be identified and corrected before sample analysis can proceed.

11.7 A Precision and accuracy (P&A) study is performed as an initial determination of capability, on an annual basis (continued demonstration of capability – a successful PT result may be used in place of a P&A for continued DOC), and if any significant changes have been made to the instrument. In general, 4 replicates or blank spikes are analyzed using the same procedures and conditions for sample analysis. The mean percent recovery is compared to the spike blank control limits of 20%. The standard deviation (of the percent recovery of the 4 spike blanks) is compared to the control limit of $\pm$20. If percent recovery or standard deviation criteria are not met, corrective action must be taken to bring the system back into control.

11.8 Quality Control data is generated (control charts) and reviewed on an annual basis by Quality Assurance (blank spike/ matrix spike recoveries and matrix duplicate RPDs).

12.0 DOCUMENTATION

12.1 The Standard preparation log application must be completed for all standard preparations. All information requested must be completed.

12.2 The Accutest lot number must be cross-referenced on the standard vial/container.

12.3 Any comments or observations concerning the sample that may influence the analytical procedure.

12.4 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of corrections must appear next to the correction.

12.5 All laboratory logs must be reviewed and initialed or signed by the lab manager.

13.0 DATA REVIEW

13.1 The analyst conducts the primary review of all data. This review begins with a check of all method quality control and progresses through sample quality control concluding with a check to assure that the client's requirements have been executed.

13.2 A secondary review is performed by department managers, and it includes review of the data produced by their department. Manual calculations, QC criteria, and a comparison of the data package to client specified requirements are checked. The department manger may reject data, initiate reanalysis, and take additional corrective action, or process data.

13.3 The laboratory director performs a full tertiary review of the data package following its assembly. This review includes an evaluation of QC data against acceptance criteria and a check of the data package contents to assure that all analytical requirements and specifications were executed.

13.4 Spot-check reviews are performed by the Quality Assurance Officer focusing on all elements of the deliverable including the client's specifications and requirements, analytical quality control, sample custody documentation and sample identification.

14.0 DATA REPORTING

14.1 A results page including positive results and/or RLs, units, methodology, analysis dates, and data qualifiers are reported. Additional quality control data including matrix duplicate RPDs, matrix spike recovery, blank spike and method blank results may be reported upon request of the client.

14.2 Data may be submitted to the client in a specified electronic format (EDD).

14.3 Once the data is approved by the laboratory manager, it may be accessed by clients via LabLink™.

14.4 Procedures for handling non-conforming data.

14.4.1 If quality control data does not meet criteria the non-conformance must be discussed in a case narrative and footnoted on the applicable quality control report summary.

14.4.2 If preservation or holding time criteria is not met and the samples are analyzed the result page must be footnoted with this information, and the non-conformance must be discussed in a case narrative or other suitable communication (telephone conversation log or email). Client notification documentation should be included with the data (telephone conversation log, fax, or email).

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Pollution Prevention. Users of this method must perform all procedural steps that control the creation and/or escape of wastes of hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids, or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 15.2.

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the Sample and Waste Disposal SOP. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

15.2.1 Non-Hazardous aqueous wastes
15.2.2 Hazardous aqueous wastes
15.2.3 Chlorinated organic solvents
15.2.4 Non-chlorinated organic solvents
15.2.5 Hazardous solid wastes
15.2.6 Non-hazardous solid wastes
15.2.7 Microbiological waste

16.0 METHOD PERFORMANCE

16.1 Method performance is evaluated by the annual QC limits (control charts) generated by QA, and the annual MDL study results. Refer to section 3.0 for MDLs, and section 11.8 for QC limits.

17.0 ADDITIONAL REFERENCES

17.1 No additional references are required for this method.

ACCUTEST LABORATORIES
STANDARD OPERATING PROCEDURE

Lab Manager: Brad Madadian
QA Manager: Robert Treggiari

TITLE: TOTAL DISSOLVED SOLIDS (TOTAL FILTERABLE RESIDUE).

TEST METHOD REFERENCE: 2540 C. Standard Methods for the Examination of Water and Wastewater 21th Edition, 2005

REVISED SECTIONS: 11.2

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the amount of solids in a sample which are capable of passing through a glass fiber filter. The method is based on EPA Method 160.1 and is applicable to all waters, drinking and wastewaters.

1.2 Test code:TDS

2.0 SUMMARY

A well mixed aliquot of the sample is filtered through a standard glass fiber filter (Gelman 934-AH). The filtrate is evaporated and dried to constant weight at 180 Deg C.

3.0 METHOD DETECTION LIMIT

3.1 The reporting limit (RL) is based on the lowest calibration standard. RL's may vary depending on matrix difficulties, sample volumes or weights, and percent moisture. Detected concentrations below this concentration cannot be reported without qualification. The RL for this test is 10 mg/L.

3.2 The Method Detection Limit (MDL) represents the lowest reportable concentration of an individual analyte that meets the method qualitative identification criteria.

3.3 Method Detection limits (MDLs) are experimentally determined using the procedures described in 40 CFR, Part 136, Appendix B. Actual reported MDLs incorporate the sample volume analyzed and sample dilutions if needed, which may cause MDL variations from sample to sample.

3.4 In general, MDLs are determined through the analysis of at least 7 replicate blank spikes (using the same procedures for sample analysis). The MDL is calculated by multiplying the standard deviation of the replicate concentrations by the appropriate Student's t value (3.143 for 7 replicates). If more than 7 replicates are analyzed refer to 40 CFR, Part 136, Appendix B for the appropriate student's t value. MDLs are determined initially (prior to analysis), on an annual basis, and after major maintenance to equipment. MDL data is archived with Quality Assurance. Refer to the most recent study for current MDLs. Refer to the most recent study for current MDLs. Refer to the MDL SOP (MQA245) for additional detail of procedures.

3.5 Current MDLs may be entered into the LIMS, and can be viewed by printing out the compound list from the LIMS. Additionally, MDLs are reported on the result page upon client request. Current MDL studies are filed with Quality Assurance. Obsolete MDL studies are archived with the QA files. Electronic MDL data is found in the annual "MDL" folder on the QA server (LINUXMA1).

4.0 DEFINITIONS

4.1 ALIQUOT - a measured portion of a sample, or solution, taken for sample preparation and/or analysis.

4.2 BATCH – A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 10, then each group of 10 samples or less will all be handled as a separate batch.

4.3 CONTAMINATION - a component of a sample or an extract that is not representative of the environmental source of the sample. Contamination may stem from other samples, sampling equipment, while in transit, from laboratory reagents, laboratory environment, or analytical instruments.

4.4 FIELD SAMPLE - a portion of material to be analyzed that is contained in single or multiple containers and identified by a unique sample number.

4.5 HOLDING TIME – the elapsed time expressed in days from the date of sampling until the date of its analysis.

4.6 MATRIX - the predominant material of which the sample to be analyzed is composed. For the purpose of this SOP, a sample matrix is either water or soil/sediment. Matrix is <u>not</u> synonymous with phase (liquid or solid).

4.7 MATRIX DUPLICATE - a second aliquot of the original sample prepared and analyzed in order to determine the precision of the method.

4.8 METHOD BLANK - an analytical control consisting of all reagents that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background, and reagent contamination.

4.9 REAGENT WATER - water in which an interferant is not observed at or above the minimum quantitation limit of the parameters of interest. Accutest uses deionized water (municipal water which passes through Accutest's DI treatment system).

4.10 RELATIVE PERCENT DIFFERENCE (RPD) - As used in this SOP to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero.

5.0 HEALTH AND SAFETY

5.1 All safety practices must be followed as outlined in the Accutest Laboratories Employee Safety Handbook and chemical Hygiene Plan. Safety glasses, gloves, and lab coats must be worn. All samples, solutions, and extracts must be treated as unknown and potentially hazardous.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level.

6.0 COLLECTION, PRESERVATION & HOLDING TIMES

6.1 The sample must be stored at 4° C ± 2.0° C.

6.2 At least 500 ml of sample should be collected in a plastic sample container.

6.3 All samples must be prepared and analyzed within 7 days from the time sampled.

7.0 APPARATUS

7.1 Whatman 934-AH glass fiber filters.

7.2 Filter holder with filtering flask.

7.3 100 ml evaporating dishes.

7.4 Steam baths or hot plates.

7.5 Drying oven to be set at 180°C.

7.6 Desiccator.

7.7 4-place analytical balance.

8.0 REAGENTS

8.1 DI water.

8.2 500 mg/L KCl – Dissolve 0.5 g of pre-dried KCl to 1000 ml DI water. This solution is used for 2nd source verification (ICV).

9.0 INTERFERENCES

9.1 Waters containing significant amounts of calcium, magnesium, chloride, and/or sulfate may be hygroscopic and will require prolonged drying, desiccation, and rapid weighing.

9.2 Samples containing high concentrations of bicarbonate will require prolonged drying at 180 C to ensure that all of the bicarbonate is converted to carbonate.

9.3 Total residue in a drying dish should be limited to approximately 200 mg. If there is too much residue in a dish, water may become trapped below the residue and give an artificially high TDS number.

10.0 PROCEDURE

10.1 Prepare evaporating dishes by heating the clean dish to 180°C for 1 hour. Cool in dessicator, and store until needed. Weigh immediately before use. Open the TDS automated spreadsheet, and record the weights, temperature, and time. This application will automatically calculate and stores all data related to this analysis. This application is connected to the balance for direct readings of the weights.

10.2 Place a clean filter in the filter holder and place the filter holder on the filtering flask. Pour

three 20 ml portions of DI water through the filter. Continue to apply a vacuum to the filter for additional 3 minutes until no traces of water remain. Discard the rinsing water.

10.3 Shake the sample well and measure out 100 ml in a 100 ml graduated cylinder. Turn on the vacuum.o'

NOTE: **A smaller sample size may be used if a very high TDS value is expected (results > 2,000 mg/L). For Method Blanks, use a 100 ml portion of DI water.**

10.4 Filter the sample through the glass fiber filter. With suction on, wash the graduated cylinder, filter, non-filterable residue and filter funnel wall with three 10 mL portions of DI water allowing complete drainage between washing. Continue suction for about 3 minutes after filtration is complete.

10.5 Transfer the filtrate into the 100 ml evaporating dish and lightly cover the dish with foil.

NOTE: If the sample cannot be evaporated at once or if all of the sample will not fit into the evaporating dish put the extra sample into a labeled plastic beaker and cover with a lid.

10.6Evaporate the sample to dryness in the oven set at approximately 103-105°C.

10.7 Dry the evaporated sample for at least one hour at 180°C ($\pm$ 2 C). Cool in a desiccator and weigh. Repeat drying cycle until a constant weight can be obtained or until weight change is less than 4% of the previous weighing or 0.5 mg, whichever is less.

10.8 For samples with results greater than 2000 mg/l, repeat steps 10.1 to 10.7 using a smaller sample size.

NOTE: All of the samples should be redried until a constant weight is obtained or until weight loss is less than 0.5 mg.

10.9 CALCULATIONS

The following calculations are used.

$$\frac{(A-B) * 1000 \text{ ml/l}}{\text{(sample volume in ml)}}$$

where A = Weight of evaporating dish + dried sample in mg
B = Tare weigh of evaporating dish in mg

11.0 QUALITY ASSURANCE

11.1 **Method Blank**. The laboratory must analyze a method blank with each set of samples. A minimum of one method blank is required for every 10 samples. The method blank must contain the analyte at less than the reporting limit (1/2 the RL for some clients). If the method blank contains an analyte level over that

limit the problem must be identified and corrected prior to sample analysis.

11.2 **Matrix Duplicate.** The laboratory must prepare a duplicate sample for a minimum of 1 in 10 samples. The relative percent difference (RPD) between the duplicate sample and the original should be assessed. The Duplicate RPD should be calculated as shown below

$$\frac{\text{(Original Sample Result – Duplicate Result) x 100}}{\text{(Original Sample Result + Duplicate Result) x 0.5}} = \% \text{ RPD}$$

The Duplicate RPD should be assessed using in house limits. Until these limits can be generated, then the default limit of 5 percent RPD should be applied. If a duplicate is out of control, then the results should be flagged with the appropriate footnote.

11.3 KCL second source (ICV).

11.3.1 A 500 mg/L KCL solution is analyzed with each analytical batch to verify accuracy of the test. The percent recovery should be ±10%. If this criteria is not met corrective action should be taken to determine and resolve the problem before samples can be analyzed.

11.4 A Precision and accuracy (P&A) study is performed as an initial determination of capability, on an annual basis (continued demonstration of capability – a successful PT result may be used in place of a P&A for continued DOC), and if any significant changes have been made to the instrument. A 100 mg/L sodium chloride solution is prepared and analyzed in quadruplicate using the same procedures and conditions for sample analysis. The percent recoveries are compared to 80-120%. If percent recovery criteria are not met, corrective action must be taken to bring the system back into control.

11.5 Quality control limits are generated at least on an annual basis by QA using an in-house program. Duplicate data are pooled for the previous year (or other specified time frame) and the data is processed and evaluated by QA. The annual QC control limit data is filed with QA.

12.0 DOCUMENTATION

12.1 If samples require reanalysis, a brief explanation of the reason should be documented.

12.2 The standard preparation logbook application must be completed for all standard preparations.

12.3 The Accutest lot number must be cross-referenced on the standard vial/container.

12.4 All laboratory logbooks must be routinely reviewed and initialed or signed by the lab manager.

12.5 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

13.0 DATA REVIEW

13.1 The analyst conducts the primary review of all data. This review begins with a check of all method

quality control and progresses through sample quality control concluding with a check to assure that the client's requirements have been executed.

13.2 A secondary review is performed by department managers, and it includes review of the data produced by their department. Manual calculations, QC criteria, and a comparison of the data package to client specified requirements are checked. The department manger may reject data, initiate reanalysis, take additional corrective action, or process data.

13.3 The laboratory director performs a full tertiary review of the data package following its assembly. This review includes an evaluation of QC data against acceptance criteria and a check of the data package contents to assure that all analytical requirements and specifications were executed.

13.4 Spot-check reviews are performed by the Quality Assurance Officer focusing on all elements of the deliverable including the client's specifications and requirements, analytical quality control, sample custody documentation and sample identification

14.0 DATA REPORTING

14.1A results page including positive results and/or RLs, units, methodology, preparation and/or analysis dates, and data qualifiers are reported. Additional quality control data including calibration summaries, MS/duplicate percent recoveries and RPDs, blank spike recoveries, and method blank results may be reported upon request of the client. Additionally, raw data including any instrument printouts, laboratory logbooks, etc. may be reported to the client.

14.1.1 Data may be submitted to the client in a specified electronic format (EDD).

14.1.2 Data may be submitted to the client electronically as a PDF (e-hardcopy).

14.1.3 Once the data is approved by the laboratory manager, it may be accessed by clients via LabLink™.

14.2Procedures for handling non-conforming data.

14.2.1 If quality control data does not meet criteria the non-conformance must be discussed in a case narrative and footnoted on the applicable quality control report summary.

14.2.2 If preservation or holding time criteria is not met and the samples are analyzed the result page must be footnoted with this information, and the non-conformance must be discussed in a case narrative or other suitable communication (telephone conversation log or email). Client notification documentation should be included with the data (telephone conversation log, fax, or email).

15.0POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Pollution Prevention. Users of this method must perform all procedural steps that controls the creation and/or escape of wastes of hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices

designed to limit the escape of vapors, liquids, or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 15.2.

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the Sample and Waste Disposal SOP. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

15.2.1 Non-Hazardous aqueous wastes
15.2.2 Hazardous aqueous wastes
15.2.3 Chlorinated organic solvents
15.2.4 Non-chlorinated organic solvents
15.2.5 Hazardous solid wastes
15.2.6 Non-hazardous solid wastes
15.2.7 Microbiological wastes

16.0METHOD PERFORMANCE

16.1Method performance is evaluated by the annual quality control limits generated by QA, and the annual MDL study results. Refer to section 3.0 for MDLs, and section 11.5 for QC limits.

17.0ADDITIONAL REFERENCES

17.1No additional references are required for this method.

ACCUTEST LABORATORIES
STANDARD OPERATING PROCEDURE

Lab Manager: Brad Madadian
QA Manager: Robert Treggiari

TITLE: TOTAL SUSPENDED SOLIDS (NON-FILTERABLE RESIDUE)

TEST METHOD REFERENCE: 2540 D. Standard Methods for the Examination of Water and Wastewater, 21th Edition, 2005

REVISED SECTIONS: 10.4.1

1.0 SCOPE & APPLICATION

1.1 This method is used to determine the amount of residue/solids in a sample, which are retained on a glass fiber filter. The method is based on Method 2540D from the 21th Edition of Standard Methods for the Examination of Water and Wastewater.

1.2 Test Codes: TSS

2.0 SUMMARY

2.1 A well mixed sample is filtered through a glass fiber filter, and the residue retained on the filter is dried to constant weight at 103-105 Deg. C.

3.0 METHOD DETECTION LIMIT

3.1 The reporting limit (RL) is based on the lowest calibration standard. RL's may vary depending on matrix difficulties, sample volumes or weights, and percent moisture. Detected concentrations below this concentration cannot be reported without qualification. The RL for this test is 4.0 mg/L.

3.2 The Method Detection Limit (MDL) represents the lowest reportable concentration of an individual analyte that meets the method qualitative identification criteria.

3.3 Method Detection limits (MDLs) are experimentally determined using the procedures described in 40 CFR, Part 136, Appendix B. Actual reported MDLs incorporate the sample volume analyzed and sample dilutions if needed, which may cause MDL variations from sample to sample.

3.4 In general, MDLs are determined through the analysis of at least 7 replicate blank spikes (using the same procedures for sample analysis). The MDL is calculated by multiplying the standard deviation of the replicate concentrations by the appropriate Student's t value (3.143 for 7 replicates). If more than 7 replicates are analyzed refer to 40 CFR, Part 136, Appendix B for the appropriate student's t value. MDLs are determined initially (prior to analysis), on an annual basis, and after major maintenance to equipment. MDL data is archived with Quality Assurance. Refer to the most recent study for current MDLs. For additional detail regarding MDL studies, refer to the MDL SOP MQA245

3.5 Current MDLs may be entered into the LIMS. Additionally, MDLs are reported on the result page upon client request. Current MDL studies are filed with Quality Assurance. Obsolete MDL studies are archived with the QA files. Electronic MDL data is found in the annual "MDL" folder on the QA server (LINUXMA1).

4.0 DEFINITIONS

4.1 ALIQUOT - a measured portion of a sample, or solution, taken for sample preparation and/or analysis.

4.2 BATCH – A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 10, then each group of 10 samples or less will all be handled as a separate batch.

4.3 CONTAMINATION - a component of a sample or an extract that is not representative of the environmental source of the sample. Contamination may stem from other samples, sampling equipment, while in transit, from laboratory reagents, laboratory environment, or analytical instruments.

4.4 EXTERNAL CHECK STANDARD/INITIAL CALIBRATION VERIFICATION(ICV). The external check standard or ICV is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards. An external check must be run a minimum of once per quarter for most analyses where a check is commercially available. The laboratory should initially assess laboratory performance of a check standard using the control limits generated by the external check supplier. Refer to the quality control section for each SOP. If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

4.5 FIELD SAMPLE - a portion of material to be analyzed that is contained in single or multiple containers and identified by a unique sample number.

4.6 HOLDING TIME – the elapsed time expressed most commonly in days from the date of sampling until the date of its analysis.

4.7 INTERFERENTS – substances which affect the analysis for the analyte of interest.

4.8 MATRIX - the predominant material of which the sample to be analyzed is composed. For this SOP, the matrix is water.

4.9 MATRIX EFFECT - in general, the effect of a particular matrix (water) on the constituents with which it contacts.

4.10 MATRIX DUPLICATE - a second aliquot of the original sample analyzed in order to determine the precision of the method.

4.11 METHOD BLANK - an analytical control consisting of all reagents that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background, and reagent contamination.

4.12 RELATIVE PERCENT DIFFERENCE (RPD) - used to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero.

4.13 REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. Water in which an interferant is not observed at or above the minimum quantitation limit of the parameters of interest. Accutest uses deionized water (municipal water which passes through Accutest's DI treatment system).

5.0 HEALTH & SAFETY

5.1 All safety practices must be followed as outlined in the Accutest Laboratories Employee Safety Handbook and Chemical Hygiene Plan. Safety glasses, gloves, and lab coats must be worn. All samples, solutions, and extracts must be treated as unknown and potentially hazardous.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level.

6.0 PRESERVATION & HOLDING TIME

6.1 The samples should be stored at 4° C ± 2°C.

6.2 Samples should be analyzed within 7 days from the date of collection.

7.0 APPARATUS & MATERIALS

7.1 Glass micro fiber filters Whatman 934-AH (prepared as described below).
7.2 100 ml graduated cylinder
7.3 Analytical balance (4 place)
7.4 Vacuum pump apparatus, with filter support
7.5 1000 ml flask attached to vacuum
7.6 Desiccator
7.7 Tweezers
7.8 Trays with grates for drying
7.9 Oven at 103-105 Deg. C

8.0 INTERFERENCES

8.1 Filtration apparatus, filter material, pre-washing, post-washing, and drying temperature are specified because these variables have been shown to affect the results.

8.2 Samples high in dissolved solids, such as saline waters, brines and some wastes, may be subject to a positive interference. Care must be taken in **washing step to minimize this effect**.

9.0 PROCEDURE

9.1 An automated TSS spreadsheet is located on the server. Use this application to record all data. Using tweezers, place filter with wrinkled side up in the filtration apparatus. Rinse with three 20 ml portions of DI water. Dry in a 103-105 Deg.C oven for at least one hour. Cool in desiccator and weigh. Repeat the drying cycle until a constant weight can be obtained or until weight change is less than 4% of the previous weighing or 0.5 mg, whichever is less. **Note:** It is recommended to prepare more filters for samples that may need less aliquot. See the note in section 9.6.

9.2 Immediately before the analysis, obtain the weight of the dried glass filter using a 4 place analytical balance. Record the data in the analysis log book.

9.3 Using tweezers, carefully place the prepared filter in Buchner funnel, which is attached to a 250 ml or larger filtering flask. Wet filter with a small volume of DI water to seat it.

9.4 Shake the sample vigorously and measure a 100 ml aliquot using a graduated cylinder. Pour the aliquot into the Buchner funnel.

9.5 Turn on vacuum.

9.6 Wait until all liquid has gone through filter. With suction on, wash the graduated cylinder, filter, non-filterable residue and filter funnel wall with three 10 mL portions of DI water allowing complete drainage between washing. Continue suction for about 3 minutes after filtration is complete.

NOTE: If during filtration of this initial volume, filtration time exceeds 5 to 10 minutes, you may use 75, 50 or 25 ml of sample. If there is still a problem, consult your laboratory supervisor.

9.7 Using forceps, remove filter paper and place on drying grate being careful not to tear or damage the filter. Place the filters sequentially on the drying grate to assure proper identity.

NOTE: Small aluminum drying tins may be marked with the sample identification and used to hold the filter while drying.

9.8 Place the drying grate in oven for at least one hour at 103-105 Deg.C.

9.9 Remove the drying grate from oven and place filters in desiccator for one hour to cool.

9.10 Weigh filter and residue and record weight. Redry the samples by placing the drying grates in the oven at 103-105 Deg C for 15 minutes. Cool and reweigh the filters. Repeat the redrying cycle until a constant weight can be obtained or until weight change is less than 4% of the previous weighing or 0.5 mg, whichever is less. Use the final redry for calculation.

10.0 QUALITY ASSURANCE

10.1 Below is a summary of the quality control requirements for this method. Make sure to check with the laboratory supervisor or manager for any additional client specific quality control requirements.

10.2 **Method Blank.** The laboratory must analyze a method blank with each set of samples. A minimum of one method blank is required for every 10 samples. The method blank must contain the analyte at less that the reporting limit. If the method blank contains an analyte level over that limit, the samples must be reanalyzed.

10.3 **External Check Sample.** An external check standard is analyzed with each batch. The limits supplied by the external check manufacturer should be applied. If an in-house ICV is used, the results must be within ±10 % of the true value. If results for the external QC check sample are outside of the range, do not continue analysis. Consult the laboratory supervisor. Do not analyze samples until the problem is solved.

10.4 **Matrix Duplicate.** The laboratory must prepare a duplicate sample for a minimum of 1 in 10 samples. The relative percent difference (rpd) between the duplicate and the sample should be assessed. The duplicate rpd is calculated as shown below. Check with the laboratory supervisor for specific state or client requirements.

10.4.1 The duplicate RPD should be assessed using in house limits. Until these limits can be generated, then default limits of 5 percent RPD should be applied If a duplicate is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control.

10.5 The duplicate RPD should be calculated as shown below.

$$\frac{(\text{Sample Result} - \text{Duplicate Result}) \times 100}{(\text{Sample Result} + \text{Duplicate Result}) \times 0.5} = \%\ \text{RPD}$$

10.6 A Precision and accuracy (P&A) study is performed as an initial determination of capability, on an annual basis (continued demonstration of capability – a successful PT result may be used in place of a P&A for continued DOC), and if any significant changes have been made to the instrument. In general, 4 replicates or blank spikes are analyzed using the same procedures and conditions for sample analysis. The percent recoveries are compared to either default limits of 80-120% or in-house control limits once established. The standard deviation of the 4 replicate percent recoveries are compared to either ±20 or to in-house limits once established. If percent recovery or standard deviation criteria are not met, corrective action must be taken to bring the system back into control.

10.7 Quality control data are generated at least on an annual basis by QA using an in-house program. Duplicate data are pooled for the previous year (or other specified time frame) and the data is processed and evaluated by QA. The annual QC data is filed with QA.

11.0 DOCUMENTATION

11.1 All data regarding the analysis must be recorded on the automated TSS spreadsheet. Make sure that all sample information is included. Any unusual characteristics of the samples should be noted in the comment section.

11.2 The standard preparation logbook application must be completed for all standard preparations.

11.3 The Accutest lot number must be cross-referenced on the standard vial/container.

11.4 All laboratory logbooks must be routinely reviewed and initialed or signed by the lab manager.

11.5 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

12.0 DATA REVIEW

12.1 The analyst conducts the primary review of all data. This review begins with a check of all Instrument and method quality control and progresses through sample quality control concluding with a check to assure that the client's requirements have been executed. The analyst has the authority and responsibility to perform corrective action for any out-of-control parameter of non-conformance.

12.2 A secondary review is performed by department managers, and it includes review of the data produced by their department. All manual calculations, QC criteria, and a comparison of the data package to client specified requirements are checked. The department manager may reject data, initiate reanalysis, take additional corrective action, or reprocess data.

12.3 The laboratory director performs a full tertiary review of the data package following its assembly. This review includes an evaluation of QC data against acceptance criteria and a check of the data package contents to assure that all analytical requirements and specifications were executed.

12.4 Spot-check reviews are performed by the Quality Assurance Officer focusing on all elements of the deliverable including the client's specifications and requirements, analytical quality control, sample custody documentation and sample identification.

13.0 DATA REPORTING

13.1 A results page including positive results and/or RLs, units, methodology, preparation and/or analysis dates, and data qualifiers are reported. Additional quality control data including calibration summaries, MS/duplicate percent recoveries and RPDs, blank spike recoveries, and method blank results may be reported upon request of the client. Additionally, raw data including any instrument printouts, laboratory logbooks, etc. may be reported to the client.

13.1.1 Data may be submitted to the client in a specified electronic format (EDD).

13.1.2 Data may be submitted to the client electronically as a PDF (e-hardcopy).

13.1.3 Once the data is approved by the laboratory manager, it may be accessed by clients via LabLink™.

13.2 Procedures for handling non-conforming data.

13.2.1 If quality control data does not meet criteria the non-conformance must be discussed in a case narrative and footnoted on the applicable quality control report summary.

13.2.2 If preservation or holding time criteria is not met and the samples are analyzed the result page must be footnoted with this information, and the non-conformance must be discussed in a case narrative or other suitable communication (telephone conversation log or email). Client notification documentation should be included with the data (telephone conversation log, fax, or email).

14.0 POLLUTION PREVENTION & WASTE MANAGEMENT

14.1 Pollution Prevention. Users of this method must perform all procedural steps that controls the creation and/or escape of wastes of hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids, or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 14.2

14.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the Sample and Waste Disposal SOP. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

14.2.1 Non-hazardous aqueous wastes
14.2.2 Hazardous aqueous wastes
14.2.3 Chlorinated organic solvents
14.2.4 Non-chlorinated organic solvents
14.2.5 Hazardous solid wastes
14.2.6 Non-hazardous solid wastes
14.2.7 Microbiological wastes

15.0 ADDITIONAL REFERENCES

15.1 No additional references are required for this method.

TITLE: TOTAL ORGANIC CARBON IN AQUEOUS SAMPLES

TEST METHOD REFERENCES: - SW846 9060A Modified,
-5310 B, Standard Methods for the Examination of Water and Wastewater 21st Edition, 2005

REVISED SECTIONS: 1.2; 7.2; 8.5.1 – 4; 8.6.2; 8.6.3; added 8.8 and 8.9; revised 10.1; 10.2; 10.3; 10.4; 10.5 and sections 10.5.1 – 3; 10.6; 10.7; 10.8; 10.9.5; 10.9.6; added 10.9.7 and 10.9.8; revised 10.12.8

1.0 SCOPE AND APPLICATION

1.1 This method can be used to determine total organic carbon or dissolved organic carbon in any aqueous matrix. The total organic carbon is actually being determined as non-purgable organic carbon. Volatile compounds are lost during the sparging process to remove inorganic carbon.

1.2 The product for total organic carbon is TOC and the product for dissolved organic carbon is DOC. TOC work groups require prep and analytical work groups. DOC product requires analytical work group only.

1.3 Samples containing high levels of particulates may need to be run using the boat sampler normally used for soil samples. When analyzing these samples using the boat sampler, all steps of the soil SOP, including acidification and heating to remove inorganic carbonates, must be followed. (Acidification and sparging may also be used to remove inorganic carbonates.)

1.4 The modification to method 9060A is that water samples are not homogenzied in a blender.

2.0 SUMMARY

2.1 Total organic carbon is determined by combusting an acidified sample and quantitating the carbon dioxide released using infrared analysis. The quantitation is done by comparison to a linear calibration curve. Dissolved organic carbon is determined following the same method, but the sample is filtered through a 0.45 filter before analysis.

3.0 REPORTING LIMIT AND METHOD DETECTION LIMIT

3.1 The reporting limit (RL) is based on the lowest calibration standard. RL's may vary depending on matrix difficulties, sample volumes or weights, and percent moisture. Detected concentrations below this concentration cannot be reported without qualification. The normal reporting limit for TOC and DOC in aqueous samples is 1.0 mg/l.

3.2 The Method Detection Limit (MDL) represents the lowest reportable concentration of an individual analyte that meets the method qualitative identification criteria.

3.3 Method Detection limits (MDLs) are experimentally determined using the procedures described in 40 CFR, Part 136, Appendix B. Actual reported MDLs incorporate the sample volume analyzed and sample dilutions if needed, which may cause MDL variations from sample to sample.

3.4 In general, MDLs are determined through the analysis of at least 7 replicate blank spikes (using the same procedures for sample analysis). The MDL is calculated by multiplying the standard deviation of the replicate concentrations by the appropriate Student's t value (3.143 for 7 replicates). If more than 7 replicates are analyzed refer to 40 CFR, Part 136, Appendix B for the appropriate student's t value. MDLs are determined initially (prior to analysis), on an annual basis, and after major maintenance to equipment. MDL data is archived with Quality Assurance. Refer to the most recent study for current MDLs. For additional detail regarding MDL studies, refer to the MDL SOP MQA245.

3.5 Current MDL studies are filed with Quality Assurance. Obsolete MDL studies are archived with the QA files. Electronic MDL data is found in the annual "MDL" folder on the QA server (LINUXMA1).

4.0 DEFINITIONS

4.1 ALIQUOT - a measured portion of a sample, or solution, taken for sample preparation and/or analysis.

4.2 BATCH: A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

4.3 CALIBRATION CHECK STANDARD (CCV). The calibration check standard is a mid-range calibration standard. It is recommended that the calibration check standard be run at a frequency of approximately 10 percent. (For some methods this is mandatory and for some it is a recommendation only. Refer to individual method SOP's) For most methods, the mid-level calibration check standard criteria is $\pm$ 10 percent of the true value. The exception to this rule is if the recovery on the calibration check standard is high and the samples to be reported are less than the detection limit.

4.4 EXTERNAL CHECK STANDARD (ICV). The external check standard is a standard from a separate source than the calibration curve that is used to verify the accuracy of the calibration standards (also called an initial calibration verification – ICV). An external check must be run a minimum of once per quarter for all analyses where a check is commercially available. The laboratory should initially assess laboratory performance of a check standard using the control limits

generated by the external check supplier. In house limits should also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

4.5 SPIKE BLANK OR LAB CONTROL SAMPLE. Digest and analyze a laboratory control sample or spike blank with each set of samples. A minimum of one lab control sample or spike blank is required for every 10 or 20 samples (refer to quality assurance section). Assess laboratory performance against the control limits specified in the SOP. In house limits should also be generated once sufficient external check standard data is available to generate limits (usually a minimum of 20 to 30 analyses). If the lab control is outside of the control limits for a parameter, all samples must be reanalyzed for that parameter. The exception is if the lab control recovery is high and the results of the samples to be reported are less than the reporting limit. In that case, the sample results can be reported with no flag. Note: If control limits are not specified in the SOP, then default limits of 80 to 120 percent should be used.

4.6 MATRIX: The component or substrate (e.g., water, soil) which contains the analyte of interest.

4.7 MATRIX DUPLICATE: A duplicate sample is analyzed at a minimum of 1 in 10 or 20 samples (refer to quality assurance section). The relative percent difference (RPD) between the duplicate and the sample should be assessed. The duplicate RPD is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient duplicate data is available to generate limits (usually a minimum of 20 to 30 analyses). If a duplicate is out of control, flag the results with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control. Note: If control limits are not specified in the SOP, use default limits of $\pm$ 20% RPD.

$$\frac{(|\text{Sample Result} - \text{Duplicate Result}|) \times 100}{(\text{Sample Result} + \text{Duplicate Result})/2)} = \text{Duplicate RPD}$$

4.8 MATRIX SPIKE: The laboratory must add a known amount of each analyte to a minimum of 1 in 10 or 20 samples (refer to quality assurance section). The matrix spike recovery is calculated as shown below. Assess laboratory performance against the control limits that are specified in the SOP. In house limits are generated once sufficient matrix spike data is available to generate limits (usually a minimum of 20 to 30 analyses). If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect. Note: If control limits are not specified in the SOP, then default limits of 75 to 125 percent should be used.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{} \times 100 = \text{Matrix Spike Recovery}$$

(Amount Spiked)

4.9 MATRIX SPIKE DUPLICATES: Intra-laboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

4.10 METHOD BLANK. The laboratory must digest and analyze a method blank with each set of samples. A minimum of one method blank is required for every 10 or 20 samples (refer to quality assurance section). The method blank must contain the parameter of interest at levels of less than the reporting limit for that parameter. If the method blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

4.11 METHOD DETECTION LIMITS (MDLS). MDLs should be established for all appropriate methods, using a solution spiked at approximately 3 times the estimated detection limit. To determine the MDL values, take seven replicate aliquots of the spiked sample and process through the entire analytical method. The MDL is calculated by multiplying the standard deviation of three replicate analyses by 3.14, which is the student's t value for a 99% confidence level. MDLs should be determined approximately once per year for frequently analyzed parameters.

4.12 REAGENT BLANK: The reagent blank is a blank that has the same matrix as the samples, i.e., all added reagents, but did not go through sample preparation procedures. The reagent blank is an indicator for contamination introduced during the analytical procedure. The concentration of the analyte of interest in the reagent blank must be less than the reporting limit for that analyte. If the reagent blank contains levels over the reporting limits, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the reagent blank level. In addition, if all the samples are less than a client required limit and the reagent blank is also less than that limit, then the results can be reported as less than that limit.

4.13 REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

4.14 REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water. Accutest uses deionized water (municipal water which passes through Accutest's DI treatment system).

4.15 REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analyti-cal process.

4.16 STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

4.17 TRIP BLANK: A sample of analyte-free media taken from the laboratory to the sampling site and returned to the laboratory unopened. A trip blank is used to document contamination attributable to shipping and field handling procedures. This type of blank is useful in documenting contamination of volatile organics samples.

5.0 HEALTH & SAFETY

5.1 All safety practices must be followed as outlined in the Accutest Laboratories Employee Safety Handbook and Chemical Hygiene Plan. Safety glasses, gloves, and lab coats must be worn. All samples, solutions, and extracts must be treated as unknown and potentially hazardous.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level.

6.0 COLLECTION, PRESERVATION, AND HOLDING TIME

6.1 Collection and Preservation

6.1.1 Containers: Samples should be collected in 40 ML VOA, zero headspace glass containers.

6.1.2 Preservation: Samples should be preserved with H_3PO_4 , H_2SO_4 or HCl to a pH of < 2. Samples should be stored at $4°C \pm 2°C$.

Note: Total carbon preservation is not directly addressed in the methods. Normally an unpreserved sample is used . Acid preserved sample is used for Total Organic Carbon.

6.2 Holding Time: Samples should be analyzed within 28 days from the date of collection.

7.0 APPARATUS

7.1 The following items are needed for the analysis of samples following the method outlined below:

7.2 Shimadzu TOC L analyzer with an auto-sampler.

7.2.1 Every day, the humidifier should be checked to ensure that the water level is within the two white lines on the side of the humidifier.

7.2.2 Whenever calibration check recoveries are low or blank results are high, the flow and the condition of the catalyst should be checked. Refer to the instrument manual for additional information. Never change the catalyst without first checking with the area supervisor or manager.

7.3 Analytical balance, capable or weighing to 0.1 mg. The calibration of the analytical balance should be verified each day before use.

7.4 Volumetric glassware, class A. For standards and reagent preparation.

7.5 Filter paper, 0.45 um pore size. (For DOC only)

7.6 40 ml VOC bottles with septum.

8.0 REAGENTS

8.1 All chemicals listed below are reagent grade unless otherwise specified. Deionized water should be used whenever water is required. Make sure to properly label all reagents and record the reagent preparation in the reagent log book.

8.2 Potassium hydrogen phthalate (KHP), Calibration stock solution, 1000 mg carbon/L. Dissolve 2.125 g of potassium hydrogen phthalate (primary standard grade, dried to a constant weight, approximately 1 hour at 105^0 C) in approximately 800 ml of DI water. Add concentrated HCl or H_3PO_4 to bring the pH to less than 2 and dilute to a final volume of 1000 ml with DI water. Prepare this solution quarterly.

8.3 Carbonate-Bicarbonate Stock solution, 1000 mg/l. Weigh 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate into a 100 ml volumetric flask. Dissolve in DI water and dilute to a final volume of 100 ml. Prepare this solution quarterly.

8.4 Sparger Check Solution (Carbonate-Bicarbonate Standard solution, 50 mg/l). Dilute 5.00 ml of the 1000 mg/l carbonate-bicarbonate stock solution to 100 ml with DI water.

Note: Do not use Sparger for TCAR determinations.

8.5 Potassium hydrogen phthalate (KHP) calibration stock solutions. All standards should be made up in volumetric flasks using volumetric pipets.

Note: The concentrations shown below are suggested levels. Alternate calibrations may be constructed in the TOC method file and used.

8.5.1 40 PPM Calibration. Std., Dilute 4.0 ml of solution 8.2, and 5 drops of 1:1 H_3PO_4 or HCl to 100 ml with DI water.

8.5.2 30 PPM Calibration. Std., Dilute 3.0 ml of solution 8.2, and 5 drops of 1:1 H_3PO_4 or HCl 100 ml with DI water.

8.5.3 10 PPM Calibration. Std., Dilute 1.0 ml of solution 8.2, and 5 drops of 1:1 H_3PO_4 or HCl to 100 ml with DI water.

8.5.4 1.0 PPM Calibration. Std., Dilute 10 ml of 10 PPM solution 8.5.3, and 5 drops of 1:1 H_3PO_4 or HCl 100 ml with DI water.

Place the reagent blank (DI water plus 5 drops of 1:1 HCl or H_3PO_4), and calibration stock standards 8.5.1, 8.5.2, 8.5.3 8.5.4 in position 1, 2, 3, 4 respectively, and the auto-sampler will dilute and make the following calibration standards: 0.0,1.0, 5.0, 10.0, 20.0, 30.0, 40.0 ppm.

Note: For pH adjustment of calibration stock standards and the reagent blanks, it is recommended to use the same type of acid as was used for sample preservation.

Note: Do not add acid to calibration standards for TCAR determinations.

8.6 Potassium hydrogen phthalate (KHP), Initial & Continuing Calibration Verification Standard, 1000 mg carbon/L. Dissolve 2.125 g of potassium hydrogen phthalate (primary standard grade, dried to a constant weight, approximately 1 hour at 105º C) in approximately 800 ml of DI water. Add concentrated HCl or H3PO4 to bring the pH to less than 2 and dilute to a final volume of 1000 ml with DI water. Prepare this solution quarterly and from a **different lot or manufacturer than the KPH calibration standards used in 8.5. Also this standard is available already made from Absolute Standards Inc.**.

8.6.1 Initial Calibration Verification Solution, 30 Mg C/L. Dilute 3 ml of solution 8.6 into 100 ml volumetric flask containing 80 ml of DI water. Add concentrated HCl to bring the pH to less than 2. Mix well and bring to final volume of 100 ml.

8.6.2 Continuing Calibration Verification (CCV) **SW846 9060A**, Dilute 2.0 ml of 8.6 solution and 5 drops of 1:1 HCl or H_3PO_4 to 100 ml with DI water.

8.6.3 Continuing Calibration Verification (CCV) **SM 5310B,** Dilute 2 ml of 8.2 solution and 5 drops of 1:1 HCl or H_3PO_4 to 100 ml with DI water

8.7 2 Molar HCL solutions. Add 36.5 ml of concentrated HCl in 300 ml of DI water, dilute to 500 ml with DI water. Mix well.

Note: Do not use for TCAR determinations.

8.8 1:1 Phosphoric Acid: Add 50.0 ml of Conc. H_3PO_4 to 50.0 ml of DI water. Mix and Cool.

8.9 1:1 Hydrochloric Acid: Add 50.0 ml of Conc. HCL to 50.0 ml of DI water. Mix and Cool.

9 INTERFERENCES

9.1 High results may be obtained if the inorganic carbon is not completely removed from the sample before analysis. The sample must be acidified to a pH of less than 2 and sparged for at least 1 minute to remove the inorganic carbon.

9.2 Large particulates in the sample may not be pulled into the needle during the sample injection and may result in a low bias.

9.3 Filtration can result in loss or gain of DOC, depending on the physical properties of the carbons containing compounds and the adsorption of carbonaceous material on the filter or its desorption from it.

10 PROCEDURE

10.1 Below is the procedure to be followed for the analysis of aqueous samples for total organic carbon using the Shimadzu TOC L analyzer. All standards and samples must be analyzed using a minimum of duplicate injections.

Note: If **SW846 9060** method is being used, all standards and samples must be analyzed in quadruple injections.

10.2 Turn on the Oxygen. The oxygen pressure at the tank regulator must be at 200 KPA to maintain pressure at the instrument. Check to make sure that the humidifier contains sufficient DI water. It should be filled to HI line on the side of the humidifier (Humidifier is located inside the water analyzer at the front right side of the instrument).

10.3 Turn on the instrument using the main power switch on the right backside towards the top of the TOC instrument and the left side of the autosampler. After a few seconds the TOC instrument will shut down which means the instrument ready condition is not established. Turn on the power switch on the left of the instrument front door. The lit power switch will change from orange to green when ready.

10.4 On the desktop, double click on **TOC-Control L** icon and double click on the sample table editor icon. User name and password window will appear. Type **Wetchem** in the user name space and **TOC2012** for the password. Please note that this software is case sensitive.

10.5 Go to **H/W Setting** on the sample table and double click on it. TOC AQ and TOC SO will appear below the **H/W Setting.** If AQ samples are to be analyzed choose TOC AQ. Using a right click on the mouse, choose the TOC AQ icon and a menu will appear that follows:

Line1: Connect
Line2: Background Monitor Setting
Line3: Shutdown
Line4: Maintenance

Line5: Instrument Setting

10.5.1 Click on Connect, a **Sequence** window will pop up. It indicates the sequence which is currently in progress. Also the open port in this window should indicate at 100% otherwise the Instrument and PC isn't communicating.

Note: If the open port is not at 100%, shutdown the software and instrument then boot up the PC. Restart the process 10.3 through 10.5 again.

10.5.2 Once the communication is established, click on the **Instrument Setting** in the 10.5 menu and **Instrument Properties** window will appear. Go to the **TOC** tab in **Instrument Properties** and click on the 680 Deg C option button. This will heat up the TC furnace for TOC AQ.

10.5.3 While the furnace is heating up, go to the 10.5 menu and click on **Background Monitor Setting.** A window will come into view that is called the **peak view window**. Set the view setting at 50x and monitor the baseline. Let the instrument warm up for 30 to 45 minutes. Once the instrument is ready the baseline will be flat or in a slight seesaw motion.

10.6 Verify the carrier gas flow rate displayed on the TOC tab in the Background Monitor window reads 150 ml/min. Never allow the carrier gas supply pressure to exceed 250 KPA.

10.7 Check the levels in the Rinse, Diluent and HCL solution bottles. Make sure the transfer lines are well below the liquid levels. If any of these are not, refill as necessary.

10.8 On the tool bar, go to the file tab, then go to open, and last go to sample table. Choose TOC AQ up to 40ppm.tlx file (TC AQ up to 40ppm.tlx for TCAR). Go to file in tool bar and save the file as a new file name. The new name scheme must be as follows: TOC, month, day, year, matrix, and the number of the run for that day. For example: TOC092812W1, which would be the TOC run on September 28, 2012 water run number 1 for that day. TOC092812W2 would be the second run for that day.

10.9 The template contains all the information regarding the calibration curve, sparge time, etc.

10.9.1 First line of the template contains the calibration curve.

10.9.2 Enter the sample sequence starting from second line as follows:

Line 2 CCV
Line 3 CCB
Line 4 Spargerchkconf
Line 5 ICV

Continue and enter the sample sequence including the quality control, etc.

10.9.3 Pour out the standards and the samples (section 10.12). Label each bottle and place on auto-sampler.

10.9.4 Remove any unused rows/lines by high lighting and cutting. Again, save the file under the proper name before starting the analysis.

10.9.5 On the tool bar, go to the **Instrument** tab and then go to **Maintenance** and finally choose **Replace Flow Line Content.** Select start in the flow content window. This will fill in the lines with the diluents, DI water and HCL solution. Once this is finished close the window. .

10.9.6 The vial ID's in the PC must be matched to the sample positions in the auto sampler. To do this, select the **View Vial Settings** icon in the left hand corner of the sample table window. The **View Vial dialog box** will open showing the standards and samples lined up in a row with the **Vial** column used for vial ID's. Check each position entered against the actual position on the auto sampler and verify the sequence. Once they match select OK.

10.9.7 Select the **Start** icon on the tool bar. Selecting **Instrument – Start Measurement** after connection is established can also start analysis. The **Measurement Start** window will pop up with three options. Select the appropriate process that will take place after analysis is complete.

10.9.8 After the calibration is completed, the instrument will check the coefficient of correlation to be 0.995 or greater. If these criteria are not established, the instrument will stop. A corrective action must be taken to correct any problems, and the calibration curve must be reanalyzed prior to sample analysis.

10.10 After the calibration is completed, Monitor CCV, CCB, Sparger chk, and ICV standard. ICV standard must agree within 10 percent of the true value. If it is not within this range, determine the source of the problem before proceeding.

10.11 After every 10 samples and at the end of the run, a continuing calibration check sample and a continuing calibration blank should be analyzed. The continuing calibration check should be a standard near the mid-range of the curve. It is recommended that a check standard at 20 mgC/l be used as the continuing calibration check standard. The continuing calibration check should agree within 10 percent of the true value. The result for the continuing calibration blank must be less than the reporting level. If either the CCV or the CCB do not meet criteria, then all samples bracketed by this QC must be reanalyzed.

10.12 Sample log and handling

10.12.1 All samples and check standards must be analyzed with duplicate injections (quadruple for **SW 8469060**).

10.12.2 Shake the samples well to make sure they are completely homogenized.

10.12.2.1 If a sample contains a high level of particulates, check with the lab supervisor before proceeding. The sample may need to be analyzed using the soil module.

10.12.3 Using SM5310B with each batch of 20 samples or less, a matrix spike, matrix duplicate method blank, and spike blank must be analyzed. If SW846 9060A is used, then with each batch of 10 samples or less, a matrix spike, matrix spike duplicate, method blank and spike blank must be analyzed. All of these quality control points must be analyzed using duplicate injections (quadruple injections for SW846 9060A).

10.12.3.1 Prepare the matrix spike and matrix spike duplicate by adding 0.500 ml of 1000 mgC/l standard solution to 50 ml of acidified sample. (use matrix spike and matrix duplicate using SM5310B)

10.12.3.2 The spike blank may be prepared by adding 0.500 ml of 1000 mgC/l standard solution to 50 ml of DI blank. Alternatively, the external check may be used as the spike blank.

10.12.4 Analyze continuing calibration checks and continuing calibration blanks as outlined in 10.11 above.

10.12.4.1 The software may not accept large dilution factors (>100). In that case, enter in the dilution in the column to the right of the sample ID and correct the final result in the LIMS system for the sample dilution. The instrument will dilute samples automatically, although a sample with suspected high concentration should be diluted prior to analysis to protect the instrument. The instrument will attempt a dilution by reducing the injection volume. This information could be accessed in

the "Sample View Window" and on the sample report. If the TOC concentration is still too high, the sample will be diluted with dilution water. The "Auto – dilution factor" is only available in the sample view window and will not be included in the sample report.

10.12.5 Use sample window to view the peaks as the analysis is in process. With the cursor positioned on the autosampler window click on any row to be highlighted, the result for the completed samples will show in the view window.

10.12.6 Make sure the sparger check result is less than reporting detection limit of 1 PPM and preferably less than half the reporting detection limit.

10.12.7 After the analysis is complete, check through the data to make sure that all QC is within criteria, that samples are within the curve, and that good reproducibility is obtained for all injections. If the sample injections have a coefficient of variation (CV) of greater than 2 percent, then verify the repeated analysis with additional replicate injection (Parameters for CV already programmed in the template). If, on the repeated analysis, a high rpd is still obtained, then the sample results should be reported with a flag due to possible sample non-homogeneity.

$$CV = (\text{Std Dev}_{n-1} / \text{mean}) \times 100$$

Note: Measure and record in the logbook the pH of samples after analysis using pH paper strips. The pH of samples must be <2. If the sample is not properly preserved, this information must be communicated to the client.

10.12.8 Review the run for completeness and data and quality control problems. Go to "File" (in the tool bar of the sample table window) select "ASCII export." The "Save As" window will now open. Save the file in the location "C:/TOCL/Data" using the same naming procedure as seen in section 10.8. This file can be accessed through windows explorer and should be transferred to LIMS. Make any necessary corrections in GNAPPR such as entering the spike amounts. Approve in batch in GNAPP and provide the data to the supervisor for additional review. See the area supervisor or manager for further details.

11 QUALITY ASSURANCE

11.1 Below is a summary of the quality control requirements for this method. Make sure to check with the laboratory supervisor or manager for any additional client specific quality control requirements.

11.2 Method Blank. The laboratory must prepare and analyze a method blank with each analysis. When using method ***SW846 9060A***, a minimum of one method blank is required for every 10

samples (20 samples if ***SM 5310B*** is used). The method blank must contain the analyte at less that the reporting limit. If the method blank contains over that limit, the samples must be reanalyzed. The exception to this rule is when the samples to be reported contain greater than 10 times the method blank level. In addition, if all the samples are less than a client required limit and the method blank is also less than that limit, then the results can be reported as less than that limit.

11.3 Spike Blank. The laboratory must prepare and analyze a spike blank with each analysis. When using method ***SW846 9060A***, a minimum of one spike blank is required for every 10 samples (20 samples if ***SM 5310B*** is used). The laboratory should assess laboratory performance of the spike blank against recovery limits of 80 to 120 percent. If the lab control recovery is high and the results of the samples to be reported are less than the reporting limit, then the sample results can be reported with no flag. In all other situations, all samples associated with a spike blank outside of recovery limits must be reanalyzed.

11.4 Matrix Spike. The laboratory must add a known amount of analyte to a minimum of 1 in 10 samples when using method ***SW846 9060A*** (20 samples if ***SM 5310B*** is used).

11.4.1 The spike recovery should be assessed using in house limits. Until these limits can be generated, then default limits of 75 to 125 percent recovery should be applied. If a matrix spike is out of control, then the results should be flagged with the appropriate footnote. If the matrix spike amount is less than one fourth of the sample amount, then the sample cannot be assessed against the control limits and should be footnoted to that effect.

11.4.2 The matrix spike recovery should be calculated as shown below.

$$\frac{\text{(Spiked Sample Result - Sample Result)}}{\text{(Amount Spiked)}} \times 100 = \text{MS Recovery}$$

11.5 Matrix Duplicate/Matrix Spike Duplicate. The laboratory should analyze a Matrix Spike duplicate sample for a minimum of 1 in 10 samples when using method ***SW846 9060A***, and a Matrix duplicate sample for a minimum of 1 in 20 samples if ***SM 5310B*** is used. The relative percent difference (rpd) between the duplicate and the sample should be assessed. Matrix spike duplicates may be used in place of matrix duplicates. The duplicate rpd is calculated as shown below.

11.5.1 The duplicate RPD should be assessed using in house limits. Until these limits can be generated, then default limits of 20 percent RPD should be applied. If a duplicate is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control.

11.5.2 The duplicate RPD should be calculated as shown below.

$$\frac{\text{(Sample Result - Duplicate Result) x 100}}{\text{Result + Duplicate Result) x 0.5}} = \text{\% RPD}$$

11.6 Quality Control Sample (also referred to as Initial Calibration Verification Standard, (ICV). It is recommended that a standard from a separate source than the calibration should be run at the beginning of each run. This ICV should be within 10 percent of the true value. If it is not, the problem must be resolved before any samples can be analyzed.

11.7 Analyze the continuing calibration verification solution after every tenth sample and at the end of the sample run. If the CCV solution is not within 10 percent of the true value, then no samples can be reported in the area bracketed by that CCV. (Note: the exception is if the CCV is biased high and the samples are less than the detection limit. In that case, the samples can be reported with no flag.) The CCV concentration should be at or near the mid-range of the calibration curve.

11.8 Analyze the continuing calibration blank solution after every CCV check (every tenth sample and at the end of the sample run). The continuing calibration blank must be less than the reporting limit. If the CCB solution is not less than the reporting limit, then no samples can be reported in the area bracketed by that CCB. (Note: the exception is if the CCB is biased high and the samples are less than the detection limit. In that case, the samples can be reported with no flag.).

11.9 Minimum Reporting Limit (MRL) check. A blank spike at the concentration of the minimum reporting limit (MRL) must be prepared and analyzed with each sample batch for drinking water samples. The acceptance criteria are 50-150% recovery. If the acceptance criteria is not met then corrective action must be taken to correct the exceedence and all associated samples must be reanalyzed with a satisfactory MRL check.

11.10 A Precision and accuracy (P&A) study is performed as an initial determination of capability, on an annual basis (continued demonstration of capability – a successful PT result may be used in place of a P&A for continued DOC), and if any significant changes have been made to the instrument. In general, 4 replicates or blank spikes are analyzed using the same procedures and conditions for sample analysis. The percent recoveries are compared to either default limits of 90-110% or in-house control limits once established. The standard deviation of the 4 replicate percent recoveries are compared to either $\pm$20 or to in-house limits once established. If percent recovery or standard deviation criteria are not met, corrective action must be taken to bring the system back into control.

11.11 Quality control data are generated at least on an annual basis by QA using an in-house program. Blank spike and MS/Dup data are pooled for the previous year (or other specified time frame) and the data is processed and evaluated by QA. The annual QC data is filed with QA.

12 DOCUMENTATION

12.1 All sample ID's, dilution, weights and any other information should be recorded. Make sure to record any comments regarding unusual sample appearance or any other problems or observations.

12.2 The instrument Maintenance logbook must be completed when any type of maintenance is performed on the instrument. Each instrument will have a separate log.

12.3 All laboratory logbooks must be routinely reviewed and initialed or signed by the lab manager.

12.4 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

13 DATA REVIEW

13.1 Primary Review. All samples should be updated to both prep (GP) and analysis (GN) batches in the LIMS system. The analyst should calculate all matrix spike, duplicate, external, and CCV recoveries and review the results of all blanks.

13.2 All documentation must be completed, including reagent references and spike amounts and spiking solution references.

13.3 A final report should be printed out from the TOC software. Make sure to check that all samples meet replication requirements (< 2% CV) and that the samples are within the range of the calibration curve.

13.4 A data file should be exported to the LIMS system and the spike amounts should be entered into the file at the GNAPP process step.

13.5 A final data package, consisting of the raw data (TOC printout), copy of the TOC analysis runlog and workgroup printout, should be turned into the area supervisor for review.

13.6 Department managers perform a secondary review, and it includes review of the data produced by their department. All manual calculations, QC criteria, and a comparison of the data package to client specified requirements are checked. The department manager may reject data, initiate reanalysis, take additional corrective action, or reprocess data.

13.7 The laboratory director performs a full tertiary review of the data package following its assembly. This review includes an evaluation of QC data against acceptance criteria and a

check of the data package contents to assure that all-analytical requirements and specifications were executed.

13.8 Spot-check reviews are performed by the Quality Assurance Officer focusing on all elements of the deliverable including the client's specifications and requirements, analytical quality control, sample custody documentation and sample identification.

14 DATA REPORTING

14.1 A results page including positive results and/or RLs, units, methodology, preparation and/or analysis dates, and data qualifiers are reported. Additional quality control data including calibration summaries, MS/duplicate percent recoveries and RPDs, blank spike recoveries, and method blank results may be reported upon request of the client. Additionally, raw data including any instrument printouts, laboratory logbooks, etc. may be reported to the client.

14.1 Data may be submitted to the client in a specified electronic format (EDD).

14.2 Data may be submitted to the client electronically (e-hardcopy) in PDF.

14.3 Once the data is approved by the laboratory manager, it may be accessed by clients via LabLink™.

14.2 Procedures for handling non-conforming data.

14.2.1 If quality control data does not meet criteria the non-conformance must be discussed in a case narrative and footnoted on the applicable quality control report summary.

14.2.2 If preservation or holding time criteria is not met and the samples are analyzed the result page must be footnoted with this information, and the non-conformance must be discussed in a case narrative or other suitable communication (telephone conversation log or email). Client notification documentation should be included with the data (telephone conversation log, fax, or email).

15 POLLUTION PREVENTION & WASTE MANAGEMENT.

15.1 Users of this method must perform all procedural steps in a manner that controls the creation and/or escape of wastes or hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 15.2.

15.2 Waste Management. Individuals performing this method must follow established waste

management procedures as described in the waste management SOP. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

15.2.1 Non hazardous aqueous wastes.
15.2.2 Hazardous aqueous wastes
15.2.3 Chlorinated organic solvents
15.2.4 Non-chlorinated organic solvents
15.2.5 Hazardous solid wastes
15.2.6 Non-hazardous solid wastes
15.2.7 Microbiological wastes

16 ADDITIONAL REFERENCES

16.1 Shimadzu TOC L instrument manual.

ACCUTEST LABORATORIES
STANDARD OPERATING PROCEDURE

Lab Manager: Brad Madadian
QA Officer: Robert Treggiari

TITLE: CHEMICAL OXYGEN DEMAND

TEST METHOD REFERENCE: Method 5220C, Standard Methods for the Examination of Water and Wastewater, 21th Edition 2005,

REVISED SECTIONS: Section 8.0 notation

1.0 SCOPE AND APPLICATION

1.1 This method is used as a measure of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. This procedure is written to incorporate the use of both the low level and mid- level Hach COD kits.

1.1 This method is applicable to surface water, and saline waters, domestic and industrial waste. Modified version of this test could be utilized for measuring COD in solids.

1.2 Test code: COD

1.0 SUMMARY

1.2 A sample is refluxed for 2 hours in a strong acid solution with a known excess of potassium dichromate(K2Cr2O7). After digestion, the remaining unreduced K2Cr2O7 is titrated with ferrous ammonium sulfate to determine the amount of K2Cr2O7 consumed and the oxidizable organic matter is calculated in terms of oxygen equivalent.

10.0 METHOD REPORTING AND DETECTION LIMIT

10.2 The reporting limit for this analysis is 20 Mg/L for waters, and 100 Mg/Kg for soils.

10.3 The Method Detection Limit (MDL) represents the lowest reportable concentration of an individual analyte that meets the method qualitative identification criteria.

10.4 Method Detection limits (MDLs) are experimentally determined using the procedures described in 40 CFR, Part 136, Appendix B. Actual reported MDLs incorporate the sample volume analyzed and sample dilutions if needed, which may cause MDL variations from sample to sample.

10.5 In general, MDLs are determined through the analysis of at least 7 replicate blank spikes (using the same procedures for sample analysis). The MDL is calculated by multiplying the standard deviation of the replicate concentrations by the appropriate Student's t value (3.143 for 7 replicates). If more than 7 replicates are analyzed refer to 40 CFR, Part 136, Appendix B for the appropriate student's t value. MDLs are determined initially (prior to analysis), on an annual basis, and after major maintenance to equipment. MDL data is archived with Quality Assurance. Refer to the most recent study for current MDLs. Refer to the SOP for MDLs (MQA245) for additional detail regarding MDL study procedures.

11.0 DEFINITION

11.2 ALIQUOT - a measured portion of a sample, or solution, taken for sample preparation and/or analysis.

11.3 BATCH – A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20 (or 10 for certain methods), then each group of 20 samples (or 10 samples for certain methods) or less will all be handled as a separate batch.

11.4 CONTAMINATION - a component of a sample or an extract that is not representative of the environmental source of the sample. Contamination may stem from other samples, sampling equipment, while in transit, from laboratory reagents, laboratory environment, or analytical instruments.

11.5 EXTERNAL CHECK STANDARD - The external check standard that is used to verify the accuracy of the calibration standards. An external check must be run with each analytical batch. The laboratory should initially assess laboratory performance of a check standard using the control limits generated by the external check supplier. Refer to the quality control section for each SOP. If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

11.6 FIELD SAMPLE - a portion of material to be analyzed that is contained in single or multiple containers and identified by a unique sample number.

11.7 HOLDING TIME – the elapsed time expressed in days from the date of sampling until the date of its analysis.

11.8 INTERFERENTS – substances which affect the analysis for the element of interest.

11.9 MATRIX - the predominant material of which the sample to be analyzed is composed. For the purpose of this SOP, a sample matrix is either water or soil/sediment. Matrix is not synonymous with phase (liquid or solid).

11.10 MATRIX DUPLICATE - a second aliquot of the original sample prepared and analyzed in order to determine the precision of the method.

11.11 MATRIX SPIKE- aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

11.12 RELATIVE PERCENT DIFFERENCE (RPD) - As used in this SOP to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero.

11.13 REAGENT WATER - water in which an interferant is not observed at or above the minimum quantitation limit of the parameters of interest. Accutest uses deionized water (municipal water which passes through Accutest's DI treatment system).

5.0 HEALTH AND SAFETY

5.1 The analyst should follow normal safety procedures as outlined in the Accutest Laboratories Chemical Hygiene Plan, which includes the use of lab coat and safety glasses. In addition, all acids are corrosive and should be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

10.0 COLLECTION, PRESERVATION & HOLDING TIMES

10.4 Aqueous samples must be preserved with H2SO4 to pH less than 2, and stored at 4 Deg. C.

10.5 Soil samples must be stored at 4°C ± 2°C.

10.6 All samples must be analyzed within 28 days from sampling date.

11.0 APPARATUS AND MATERIALS

11.4 Heating block
11.5 Microburette with a teflon stopcock
11.6 Magnetic stirrer; stirbars.
11.7 Pipettes, class A.
11.8 Volumetric flasks, class A.

12.0 STANDARDS AND REAGENTS

NOTE: All chemicals listed below are reagent grade unless otherwise specified. Distilled, deionized water should be used whenever water is required. All applicable standard/reagent preparation information, including vendor, lot number, date of preparation, calculations, and initials must be entered in the appropriate standard/reagent preparation logbook. Vendors typically used by Accutest include Fisher Scientific, VWR, Accustandard, Absolute Standards, Supelco, Chemservices, Ultra, and ERA. Additional vendors may be utilized as necessary.

8.1 Hach Test Kit Reagents, Low Level (0.00 - 150 mg/L):

8.1.1 Standard Potassium Dichromate Digestion Solution, 0.025 N (0.00417M): Add to about 500 ml water 1.2259 g of potassium dichromate, primary standard grade, previously dried at 103 C for 2 hr.. Dissolve, cool to room temperature, and dilute to 1000 ml. Note: This solution is to be used for standardization of the FAS only and should not be used as a digestion reagent

8.1.2 Sulfuric Acid, Concentrated

8.1.3 Ferroin Indicator Solution: Dissolve 1.485 g of 1,10 phenanthroline monohydrate and 695 mg of $FeSO_4$ $7H_2O$ in water and dilute to 100 ml. This indicator solution may also be purchased already prepared.

8.1.4 Hach prepared digestion tubes containing pre-made and pre-measured reagents. The pre-made reagents include the catalysts and chloride compensator.

8.1.5 Standard Ferrous Ammonium Sulfate Titrant (FAS), approximately 0.0125 N: Dissolve 4.90 g $Fe(NH_4)_2(SO_4)_2$ $6H_2O$ in water. Add 20 ml concentrated sulfuric acid, cool, and dilute to 1000 ml. Standardize solution daily against standard potassium dichromate solution.

1.1.1 Potassium Hydrogen Phthalate (KHP) Stock Standard: Weigh 4.250 g (previously dried at 120 C to a constant weight) of potassium hydrogen phthalate and dilute to 500 ml with DI water. This solution has a theoretical COD of 10,000 mg of oxygen per l of solution. This solution is stable when refrigerated for up to 3 months in the absence of visible biological growth.

1.1.2 1000ppm KHP solution, Dilute 10ml of 10000ppm solution (8.1.6) to 100ml of DI water.

8.1.8 Potassium Hydrogen Phthalate Calibration Standards. With each batch of low level samples that are digested, check standards at the levels of 20 and 50 mg/l should be prepared. The calibration standards can be made as shown below.

ml of 1000 mg/l	Final Volume (ml)	Final Conc. Mg/l
5.0	100	50.0
1.0	100	20.0

8.2 Hach Test Kit Reagents, Mid Level (0.00 - 1500 mg/L):

8.2.1 Standard Potassium Dichromate Digestion Solution, 0.25 N (0.0417M): Add to about 500 ml water 12.259 g of potassium dichromate, primary standard grade, previously dried at 103 Deg C for 2 hr.. Dissolve, cool to room temperature, and dilute to 1000 ml. Note: This solution is to be used for standardization of the FAS only and should not be used as a digestion reagent

8.2.2 Sulfuric Acid, Concentrated

8.2.3 Ferroin Indicator Solution: Dissolve 1.485 g of 1,10 phenanthroline monohydrate and 695 mg of $FeSO_4$ $7H_2O$ in water and dilute to 100 ml. This indicator solution may also be purchased already prepared.

8.2.4 Hach prepared digestion tubes containing pre-made and pre-measured reagents. The pre-made reagents include the catalysts and chloride compensator.

8.2.5 Standard Ferrous Ammonium Sulfate Titrant (FAS), approximately 0.125 N: Dissolve 49.0 g $Fe(NH_4)_2(SO_4)_2$ $6H_2O$ in water. Add 20 ml concentrated sulfuric acid, cool, and dilute to 1000 ml. Standardize solution daily against standard potassium dichromate solution.

8.2.6 Potassium Hydrogen Phthalate (KPH) Stock Standard: Weigh 4.250 g (previously dried at 120 C to a constant weight) of potassium hydrogen phthalate and dilute to 500 ml with DI water. This solution has a theoretical COD of 10,000 mg of oxygen per l of solution. This solution is stable when refrigerated for up to 3 months in the absence of visible biological growth.

1.1.1 With each batch of high level samples that are digested, check standards at the levels of 150 and 750 mg/l must be prepared.

ml of 10000 Mg/l	Final Vol.(ml)	Final Conc. Mg/l
1.50	100	150
7.50	100	750

13.0 INTERFERENCES

13.4 Positive interferences can be caused by the oxidation of reduced inorganic species such as ferrous iron, sulfide, and manganous manganese. Nitrite can also cause interferences, but nitrite levels in samples are generally low and this is normally an insignificant interference. Negative interferences can be caused by volatile straight-chain aliphatic compounds that are not oxidized to any appreciable extent. The use of mercuric sulfate and silver sulfate can improve the oxidation of the straight chain aliphatics. In addition, this method should not be used for samples containing more than 20000 mg/l of chloride.

14.0 PROCEDURE

Below is a step by step procedure for the analysis of samples for COD. Use the automated spreadsheet for documentation, and calculations of Standardization, and the analysis. This application can be found on server.

10.1 COD DIGESTION PROCEDURE

Below is a step-by-step procedure to digest the samples before titrating them for determination of COD.

The low level Hach kit should initially be used for most sample analysis, unless the sample has a history of a higher COD level. If you are preparing a dilution for the mid-level kit, make sure that the dilution will yield a result above the 50 mg/L level. For emergency or rush samples, it is suggested that digestions be done with both the high and the low level kits.

10.2 Low Level Hach kit digestion procedure:

CAUTION: When adding sample aliquots to the reagent vials, always add them along the side of the tube, such it forms a layer on top of the reagent mix. This must be performed in a hood with appropriate protective gear. After the sample aliquot has been added, cap the tube, verify the cap is tight, and invert the sample. This must be performed behind the hood sash. Verify the cap seal is not leaking. Invert the sample two more times and place in the digestion block. Do not use any tubes that do not seal or are cracked. **CAUTION:** The sample/reagent mix will be very hot.

1.1.1 Pipette 2.0 mL of liquid sample into the pre-prepared Hach digestion tubes (0 - 150 mg/L). If the sample is solid, stir the sample well and then add 0.40 g of sample to the digestion tube, along with 2.0 ml of water. Prepare one duplicate and one matrix spike for each set of 20 samples. Prepare two blanks with 2.0 ml of water each. An external check standard should also be prepared with each batch. A 20 and a 50 mg/L standard should also be prepared. Make sure that each of the tubes is clearly labeled.

Note: Larger dilutions will be required for most solid samples and in most cases they will be run using the mid-level Hach kit. Water samples that require dilution should also be analyzed using the mid-level kit.

1.1.2 Place capped tubes in a block digester preheated to 150 Deg. C and reflux for 2 hours. Cool to room temperature and place the vessels in a test tube rack.

Note: If samples turn green either prior to digestion or within the first 15 minutes of digestion a dilution (using DI water) should be prepared.

10.3 Mid Level Hach kit digestion procedure:

1.1.1 Pipette 2.0 mL of liquid sample into the pre-prepared Hach digestion tubes (50 - 1500 mg/L). If the sample is solid, stir the sample well and then add 0.40 g of sample to the digestion tube, along with 2.0 ml of water. Prepare one duplicate and one matrix spike for each set of 20 samples. Prepare two blanks with 2.0 ml of water each. An external check standard should also be prepared with each batch. A 150 and a 750 mg/L standard should also be prepared. Make sure that each of the tubes is clearly labeled.

Note: Larger dilutions will be required for most solid samples.

1.1.2 Place capped tubes in a block digester preheated to 150 C and reflux for 2 hours. Cool to room temperature and place the vessels in a test tube rack.

10.4 COD TITRATION PROCEDURE

Below is a step-by-step procedure for the titration of samples for the determination of COD. This procedure is shown for both the low and the mid-level Hach COD kits.

1.1.1 Low Level Hach Kit. If you are using the low level Hach kit (0 - 150 mg/L), pipette 2.00 mL of Potassium Dichromate solution, 0.025 N (0.00417 M), into two clean empty vials. Add 3 mL of sulfuric acid to each of the vials and swirl gently to mix, cool. Add a drop of Ferrion Indicator Solution and titrate with the FAS standard solution, 0.0125 N, until the color changes from greenish-blue to orange-brown. Make sure that the sample is continuously stirred during the titration. Record the number of ml used. Calculate the molarity of the FAS solution using the following equation:

$$\text{Molarity of FAS solution} = \frac{\text{Volume of 0.00417 M dichromate digestion solution, ml}}{\text{Volume of FAS solution,ml}} \times 0.025$$

The molarity to be used for the final calculations should be the average of the molarity calculated for each of the undigested blanks. Record the standardization data on the top of the COD analysis form as indicated.

10.4.2 Titrate each of the digested samples and blanks as follows: Take the digested sample or blank and add a small Teflon coated stir bar. Add 1 to 2 drops of ferrion indicator and stir rapidly on a magnetic stirrer while titrating with the standardized FAS solution from a burette. As in the FAS standardization, the end point is reached when there is a sharp color change from blue-green to reddish brown. Again, this color change is not permanent and the blue-green color may quickly reappear. Record the starting and ending volumes of FAS solution on the COD analysis form as indicated.

Note: The molarity of the FAS solution decreases over time and more FAS will be required to titrate the calibration blanks as the FAS solution ages.

10.5 Mid Level Hach Kit

1.1.1 If you are using the mid level Hach kit (0.00 -1500 mg/L), pipette 2.00 mL of Potassium Dichromate solution, 0.25 N (0.0417 M), into two clean empty vials. Add 3 mL of sulfuric acid to each of the vials and swirl gently to mix. Add a drop of Ferrion Indicator Solution and titrate with the FAS standard solution, 0.125 N, until the color changes from greenish-blue to orange-brown. Make sure that the sample is continuously stirred during the titration. Record the number of ml used. Calculate the molarity of the FAS solution using the following equation:

Note: The calculation used is dependent upon the molarity of the dichromate solution used. The factor applied should be equal to 6 times the molarity of the dichromate solution.

$$\text{Molarity of FAS Solution} = \frac{\text{Volume of 0.0417 M dichromate digestion solution, ml} \times 0.25}{\text{Volume of FAS solution, ml}}$$

The molarity to be used for the final calculations should be the average of the molarity calculated for each of the undigested blanks. Record the standardization data on the top of the COD analysis form as indicated.

10.5.2 Titrate each of the digested samples and blanks as follows: Take the digested sample or blank and add a small Teflon coated stir bar. Add 1 drop of ferrion indicator and stir rapidly on a magnetic stirrer while titrating with the standardized FAS solution from a burette. As in the FAS standardization, the end point is reached when there is a sharp color change from blue-green to reddish brown. Again, this color change is not permanent and the blue-green color may quickly reappear. Record the starting and ending volumes of FAS solution on the COD analysis form as indicated.

Note: The molarity of the FAS solution decreases over time and more FAS will be required to titrate the calibration blanks as the FAS solution ages.

11.0 QUALITY ASSURANCE

1.1 Below is a summary of the quality control requirements for this method. Make sure to check with laboratory supervisor or manager for any additional client specific quality control requirements.

1.2 **Calibration Standards.** The laboratory must digest and analyze a 20 ppm and 50 ppm calibration standards for low level kits or (150 ppm and 750 ppm standards for mid level kits, when used) with each batch of 20 or less samples. The 20 ppm standard results must be within ± 30% recovery. The 50 ppm , 150 ppm,and 750 ppm standard results must be within ± 10% recovery. If this criteria is not met corrective action must be taken and the problem resolved (as indicated by passing calibration standards) prior to sample analysis.

1.3 **Method Blank**. The laboratory must analyze a method blank with each set of samples. A minimum of one method blank is required for every 20 samples. The method blank must contain the analyte at less than the reporting limit (1/2 the RL for some clients). If the method blank contains an analyte level over that limit the problem must be identified and corrected prior to sample analysis.

1.4 **Matrix Duplicate.** The laboratory must prepare a duplicate sample for a minimum of 1 in 20 samples. The relative percent difference (RPD) between the duplicate sample and the original should be assessed. The Duplicate RPD should be calculated as shown below

$$\frac{\text{(Original Sample Result – Duplicate Result)} \times 100}{\text{(Original Sample Result + Duplicate Result)} \times 0.5} = \%\ \text{RPD}$$

The Duplicate RPD should be assessed using in house limits. Until these limits can be generated, then the default limit of 20 percent RPD should be applied. If a duplicate RPD is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of ± the reporting limit, then the duplicate is considered to be in control.

1.5 **Matrix spike.** The laboratory must add a known amount of each analyte to a minimum of 1 in 20 samples. The spike recovery should be assessed using in house limits. Until these limits can be generated, default limits of 75-125 % recovery should be applied. If a matrix recovery is out of control, then the recovery should be flagged with the appropriate footnote. If a matrix spike amount is less than one fourth of the sample amount, then the sample can be assessed against the control limits and should be footnoted to that effect.

$$\frac{(\text{Matrix Spike Result} - \text{Original Result}) \times 100}{\text{Amount of Spike}}$$

1.6 **Spike Blank.** The laboratory must analyze a spike blank with each set of samples. A minimum of one spike blank is required for every 20 samples. The net recovery should be within 20 percent of the true value. If the spike blank is outside of this range, the problem must be identified and corrected before sample analysis can proceed.

1.7 **External Standard.** An external standard is analyzed with each analytical batch. The net recovery should be within 10% of the true value (if the external is prepared in house) or within the manufacturer's acceptance criteria if purchased from an outside vendor. If the external is outside this range, the problem must be identified and corrected before sample analysis can proceed.

1.8 A Precision and accuracy (P&A) study is performed as an initial determination of capability, on an annual basis (continued demonstration of capability – a successful PT result may be used in place of a P&A for continued DOC), and if any significant changes have been made to the instrument. In general, 4 replicates or blank spikes are analyzed using the same procedures and conditions for sample analysis. The mean percent recovery is compared to the spike blank control limits of 20%. The standard deviation (of the percent recovery of the 4 spike blanks) is compared to the control limit of 20. If percent recovery or standard deviation criteria are not met, corrective action must be taken to bring the system back into control. The P&A study replicates must be prepared from a source independent from the calibration standards.

1.9 Quality Control data is generated (control charts) and reviewed on an annual basis by Quality Assurance (blank spike/ matrix spike recoveries and matrix duplicate RPDs).

12.0 DOCUMENTATION

1.1 The Standard preparation log application must be completed for all standard preparations. All information requested must be completed.

1.2 The Accutest lot number must be cross-referenced on the standard vial/container.

1.3 Any comments or observations concerning the sample that may influence the analytical procedure.

1.4 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of corrections must appear next to the correction.

1.5 All laboratory logs must be reviewed and initialed or signed by the lab manager.

13.0 DATA REVIEW

13.1 The analyst conducts the primary review of all data. This review begins with a check of all method quality control and progresses through sample quality control concluding with a check to assure that the client's requirements have been executed.

1.1 A secondary review is performed by department managers, and it includes review of the data produced by their department. Manual calculations, QC criteria, and a comparison of the data package to client specified requirements are checked. The department manger may reject data, initiate reanalysis, take additional corrective action, or process data.

1.2 The laboratory director performs a full tertiary review of the data package following its assembly. This review includes an evaluation of QC data against acceptance criteria and a check of the data package contents to assure that all analytical requirements and specifications were executed.

1.3 Spot-check reviews are performed by the Quality Assurance Officer focusing on all elements of the deliverable including the client's specifications and requirements, analytical quality control, sample custody documentation and sample identification.

1.0 DATA REPORTING

1.1 A results page including positive results and/or RLs, units, methodology, analysis dates, and data qualifiers are reported. Additional quality control data including matrix duplicate RPDs, matrix spike recovery, blank spike and method blank results may be reported upon request of the client.

1.2 Data may be submitted to the client in a specified electronic format (EDD).

1.3 Once the data is approved by the laboratory manager, it may be accessed by clients via LabLink™.

2.0 POLLUTION PREVENTION & WASTE MANAGEMENT

1.3 Pollution Prevention. Users of this method must perform all procedural steps that control the creation and/or escape of wastes of hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids, or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 15.2.

1.4 Waste Management. Individuals performing this method must follow established waste management procedures as described in the Sample and Waste Disposal SOP. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

1.3.1 Non-Hazardous aqueous wastes
1.3.2 Hazardous aqueous wastes
1.3.3 Chlorinated organic solvents
1.3.4 Non-chlorinated organic solvents
1.3.5 Hazardous solid wastes
1.3.6 Non-hazardous solid wastes
1.3.7 Microbiological waste

3.0 METHOD PERFORMANCE

1.3 Method performance is evaluated by the annual QC limits (control charts) generated by QA, and the annual MDL study results. Refer to section 3.5 for MDLs, and section 11.8 for QC limits.

4.0 ADDITIONAL REFERENCES

14.1 No additional references are required for this method.

Lab Manager: Brad Madadian

QA Officer: Robert Treggiari

TITLE: **METALS BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY SW846 6010C**

TEST METHOD REFERENCE: SW846 6010C, Revision 3, February 2007

REVISED SECTIONS: 8.15, 11.10

1.0 SCOPE & APPLICATION

1.1 This method is applicable for the determination of Total metals in ground waters, domestic and industrial wastes, TCLP leachates, sludges, soils, sediments, and various other wastes.

NOTE: **Dissolved elements are determined after filtration with 0.45 micron filter paper and preserved with Nitric acid for 24 hours prior to analysis.**

1.2 Test Codes: A variety of metals can be analyzed by ICP. These include: Al, Sb, As, Au, B, Ba, Be, Cd, Ca, Cr, Cu, Co, Fe, Pb, Pd, Pt, Li, Mn, Mg, Mo, Ni, K, Se, Ag, Na, Si, Sn, Sr, Ti, Tl, V, W, Zn Zr.

2.0 SUMMARY

2.1 Prior to analysis, samples must be digested using the appropriate digestion method. When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

2.2 This method describes multi-elemental determinations by ICP/AES using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency ICP. Background correction is required for trace element determination.

3.0 METHOD DETECTION AND REPORTING LIMITS

3.1 Reporting limits are established at the lowest concentration standard. RL's may vary depending on matrix difficulties, sample volumes or weight, percent moisture. Detected concentrations below this concentration cannot be reported without qualification. See below table for analytes' RL:

Analyte	RL (ug/L)	Analyte	RL (ug/L)
Al	200	Mo	100
Sb	6	Ni	40
As	4	Pd	50
Ba	50	Pt	50
Be	4	K	5000
B	100	Se	10
Cd	4	Si	100
Ca	5000	Ag	5
Cr	10	Na	5000
Co	50	Sr	10
Cu	25	Tl	5
Au	50	Sn	100
Fe	100	Ti	50
Pb	5	W	100
Li	5000	V	10
Mg	5000	Zn	20
Mn	15	Zr	50

3.2 Method Detection Limits

3.2.1 Detection limits are experimentally determined using the procedures described in 40 CFR, Part 136, Appendix B. Actual reported MDLs incorporate the sample weight or volume analyzed and sample dilutions if needed, which may cause MDL variations from sample to sample.

3.2.2 In general, MDLs are determined through the analysis of at least 7 replicate blank spikes (using the same procedures for sample analysis). The MDL is calculated by multiplying the standard deviation of the replicate concentrations by the appropriate Student's t value (3.143 for 7 replicates). If more than 7 replicates are analyzed refer to 40 CFR, Part 136, Appendix B for the appropriate student's t value. MDL studies are performed on an annual basis or after any major changes to the instrumentation. For additional detail regarding MDL studies, refer to the MDL SOP MQA245.

3.2.3 The MDL represents the lowest reportable concentration of an individual analyte that meets the method qualitative identification criteria.

3.2.4 Current MDL studies are filed with Quality Assurance. Obsolete MDL studies are archived with the QA files. Electronic MDL data is found in the annual "MDL" folder on the QA server (LINUXMA1).

4.0 DEFINITIONS

4.1 ALIQUOT - a measured portion of a sample, or solution, taken for sample preparation and/or analysis.

4.2 BACKGROUND CORRECTION – a technique to compensate for variable background contribution to the instrument signal in the determination of trace elements.

4.3 BATCH – a group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 20 (or 10 for certain methods), then each group of 20 samples (or 10 samples for certain methods) or less will all be handled as a separate batch.

4.4 CALIBRATION – the establishment of an analytical curve based on the absorbance, emission intensity, or other measured characteristic of known standards. The calibration standards must be prepared using the same type of acid or concentration of acids as used in the sample preparation.

4.5 CALIBRATION BLANK - a volume of acidified deionized/distilled water.

4.6 CALIBRATION STANDARDS – a series of known solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve).

4.7 CONTINUING CALIBRATION – analytical standard run every 10 samples or 2 hours, whichever is more frequent, to verify the calibration of the analytical system.

4.8 DISSOLVED METALS – elements in an aqueous sample which will pass through a 0.45 um filter.

4.9 DRY WEIGHT – the weight of a sample based on percent solids. The weight after drying in an oven.

4.10 FIELD SAMPLE - a portion of material to be analyzed that is contained in single or multiple containers and identified by a unique sample number.

4.11 FIELD BLANK – this is any sample that is submitted from the field and is identified as a blank. This includes trip blanks, rinsates, equipment blanks, etc.

4.12 HOLDING TIME – the elapsed time expressed in days from the date of sampling until the date of its analysis.

4.13 INDUCTIVELY COUPLED PLASMA (ICP) – a technique for the simultaneous or sequential multi-element determination of elements in solution. The basis of the method is the measurement

of atomic emission by an optical spectroscopic technique. Characteristic atomic line emission spectra are produced by excitation of the sample in a radio frequency ICP.

4.14 INSTRUMENT CHECK SAMPLE – a solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors.

4.15 INSTRUMENT CHECK STANDARD – a multi-element standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis.

4.16 INTERFERENTS – substances which affect the analysis for the element of interest.

4.17 MATRIX - the predominant material of which the sample to be analyzed is composed. For the purpose of this SOP, a sample matrix is either water or soil/sediment. Matrix is not synonymous with phase (liquid or solid).

4.18 MATRIX EFFECT - in general, the effect of a particular matrix (water or soil/sediment) on the constituents with which it contacts. This is particularly pronounced for clay particles which may adsorb chemicals and catalyze reactions. Matrix effects may prevent extraction of target analytes, and may affect surrogate recoveries. In addition, non-target analytes may be extracted from the matrix causing interferences.

4.19 MATRIX SPIKE - aliquot of a matrix (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery. The matrix spike recovery is calculated as shown below.

$$\frac{(\text{Spiked Sample Result} - \text{Sample Result})}{(\text{Amount Spiked})} \times 100 = \text{Matrix Spike Recovery}$$

4.20 MATRIX SPIKE DUPLICATE - a second aliquot of the original sample that is spiked in order to determine the precision of the method. The matrix spike duplicate RPD is calculated as shown below.

$$\frac{(|\text{MS Result} - \text{MSD Result}|) \times 100}{(\text{MS Result} + \text{MSD Result})/2} = \text{MSD RPD}$$

4.21 METHOD BLANK- an analytical control consisting of all reagents, that is carried throughout the entire analytical procedure. The method blank is used to define the level of laboratory, background, and reagent contamination.

4.22 PERCENT DIFFERENCE (%D) - as used in this SOP to compare two values, the percent difference indicates both the direction and the magnitude of the comparison, i.e., the percent difference may be either negative, positive, or zero.

4.23 REAGENT WATER- water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. Water in which an interferant is not observed at or above the minimum quantitation limit of the parameters of interest. Accutest uses deionized water (municipal water which passes through Accutest's DI treatment system).

4.24 SERIAL DILUTION – the dilution of a sample by a factor of five. When corrected by the dilution factor, the diluted sample must agree with the original undiluted sample within specified limits. Serial dilution may reflect the influence of interferents.

4.25 SOIL - used herein synonymously with soil/sediment and sediment.

4.26 TOTAL METALS – analyte elements which have been digested prior to analysis.

4.27 Linear Dynamic Range (Linearity studies) -the concentration range over which the instrument response to an analyte is linear.

5.0 HEALTH & SAFETY

5.1 All safety practices must be followed as outlined in the Accutest Laboratories Employee Safety Handbook and Chemical Hygiene Plan. Safety glasses, gloves, and lab coats must be worn. All samples, solutions, and extracts must be treated as unknown and potentially hazardous. In addition, all acids are corrosive and should be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level.

6.0 COLLECTION, PRESERVATION, & HOLDING TIMES

6.1 Preservation. All aqueous samples should be preserved with nitric acid at the time of collection. Both soils and aqueous samples should be kept under refrigeration at $4^{o} \pm 2°C$.

6.2 Holding Time. All samples should be analyzed within 6 months of the time of collection.

7.0 APPARATUS and MATERIALS

7.1 Currently there is one solid state ICP (Thermo 6500 ICP. Software iTEVA, Issue 8) available for use in the laboratory. The unit has been optimized to obtain low detection limits for a wide range of elements. Since it is solid state system, different lines may be included for elements to obtain the best analytical results. See below table for the lines in use.

Element	Wavelength	View	Internal	Wavelength
Ag	328	Axial	Yttrium	360.0
Al	396.1	Radial	Yttrium	371.0
As	189	Axial	Yttrium	224.3
Au	242.7	Axial	Yttrium	360.0
B	208.9	Axial	Yttrium	224.3
Ba	455.4	Radial	Yttrium	371.0
Be	313	Radial	Yttrium	371.0
Ca	317.9	Radial	Yttrium	371.0
Cd	228.8	Axial	Yttrium	224.3
Co	228.6	Axial	Yttrium	224.3
Cr	267.7	Axial	Yttrium	360.0
Cu	324.7	Axial	Yttrium	360.0
Fe	259.9	Radial	Yttrium	371.0
Li	610.3	Radial	Yttrium	371.0
K	766.4	Radial	Yttrium	371.0
Mg	279	Radial	Yttrium	371.0
Mn	257.6	Axial	Yttrium	360.0
Mo	202	Axial	Yttrium	224.3
Na	589.5	Radial	Yttrium	371.0
Ni	231.6	Axial	Yttrium	224.3
Pb	220.3	Axial	Yttrium	224.3
Pd	340.4	Axial	Yttrium	360.0
Pt	265.9	Axial	Yttrium	360.0
Sb	206.8	Axial	Yttrium	224.3
Se	196	Axial	Yttrium	224.3
Si	212.4	Axial	Yttrium	224.3

Sn	189.9	Axial	Yttrium	224.3
Sr	407.7	Radial	Yttrium	371.0
Ti	334.9	Axial	Yttrium	360.0
Tl	190.8	Axial	Yttrium	224.3
V	292.4	Axial	Yttrium	360.0
W	239.7	Axial	Yttrium	360.0
Zn	206.2	Axial	Yttrium	224.3
Zr	339.1	Axial	Yttrium	224.3

7.2 Peristaltic pump

7.3 Auto-sampler

7.4 Volumetric flasks of suitable precision and accuracy

7.5 Argon gas supply - Liquid, high purity grade (99.995%) supplied by Air Products, Inc.

7.6 Instrument maintenance

7.6.1 Recommended periodic maintenance includes the items outlined below. All maintenance should be recorded in the instrument maintenance log.

7.6.2 Change the pump tubing weekly or as needed.

7.6.3 Clean the filter on the re-circulating pump every one to two weeks and dust off the power supply vents every one to two weeks.

7.6.4 Clean the nebulizer, torch, and injector tube every week or more often as required.

7.6.5 Clean the pump once per month.

7.6.6 Change the sampler tip as needed.

7.6.7 Clean the recirculating pump lines as needed.

8.0 STANDARDS AND REAGENTS

8.1 All chemicals listed below are reagent or trace grade unless otherwise specified. Distilled, deionized water from Accutest's DI system should be used whenever water is required.

8.2 Concentrated hydrochloric acid, trace metal grade.

8.3 Concentrated nitric acid, trace metal grade.

8.4 Stock metals standard solution (generally 1000 Mg/L or 10000 Mg/L), ICAP grade.

NOTE: Combined stock standards can be ordered or made from ICAP purity standards.

8.5 Hydrochloric acid (1:1) - Add 500 ml conc. HCl to 400 ml of DI. Cool and dilute to 1 liter.

8.6 Nitric acid (1:1) - Add 500 ml of conc. HNO_3 to 400 ml of DI. Cool and dilute to 1 liter.

8.7 Rinse solution - To 800 ml DI water, add 50 ml of conc. HNO_3 and 50 ml of conc. HCl. Dilute to 1 liter.

8.8 Calibration Blank - To 800 ml DI, add 50 ml of conc. HNO_3 and 50 ml of conc. HCl. Dilute to 1 liter.

8.9 Calibration Standards

8.9.1 Premixed stocks purchased from Absolute standards and other vendors are used in this section along with individual standards and subsequent dilutions.

8.9.2 Calibration Std # 1 contains the following analytes and concentration:

Analyte	Conc. (Mg/L)
Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Tl, Zn	**1000**
Ag	**12.5**

8.9.3 Calibration Std # 2 contains the following analytes and concentration:

Analyte	Conc. (Mg/L)
Al, Ca, Fe, Mg, K, Na	**1000**

8.10.4 Calibration Std # 3 contains the following analytes and concentration:

Analyte	Conc. (Mg/L)
Sr, Sn, Ti, V	**1000**

8.10.5 Individual 1000 ppm analytes.

8.10.6 In general there are 3 different standards are recommended to be used for calibration. Other combinations and concentrations may be used.

STANDARD#1:

Analyte	Conc. (Mg/L)
Sb, As. Ba, Be, B, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Tl, Zn	4.0
Ag	0.50

STANDARD#2:

Analyte	Conc. (Mg/L)
Al, Ca, Fe, Mg, K, Na, Li	20

STANDARD #3:

Analyte	Conc. (Mg/L)
Sr, Sn, Ti, V, Au, Pd, Pt, Si, W, Zr	4.0

NOTE: 1) Since addition of silver may result in an initial precipitation, you may warm the flask until solution clears. Cool to room temperature and use.

8.11 Continuing Calibration Verification (CCV)

Prepare mixed CCV solution by combining appropriate volumes of the individual stock standards or by using the premixed stock purchased from Absolute Standard and subsequent dilutions. The CCV must be prepared in the same acid matrix using the same standards used for calibration at a concentration near the mid point of the calibration curve. Below are the recommended concentrations of CCV to use with the above calibration standards.

NOTE: Since addition of silver may result in an initial precipitation, you may warm the flask until the solution clears. Cool to room temperature and use.

The CCV will contain the following analytes and concentrations:

Analyte	Conc. (Mg/L)
Sb, As. Ba, Be, B, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Tl, Zn, Sr, Sn, Sr, Ti, V, Si, W, Au, Pd, Pt, Zr	2.0
Al, Ca, Fe, Mg, K, Na, Li	10
Ag	0.25

8.12 Initial Calibration Verification/ Quality Control Standard (ICV/QCS)- This standard is prepared by combining compatible elements from a standard source different than the calibration standards and the concentrations should be at or near the mid-range of the calibration curve.

Below are the recommended concentrations of ICV. Dilute the individual stocks, and premixed standards such as ICQ500-19 or the equivalents. (ICQ500-19 is a multi element standard purchased and contains multiple analytes). The ICV will contain the following analytes and concentrations:

Analyte	Conc. (Mg/L)
Sb, As. Ba, Be, B, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Tl, Zn, Sr, Sn, Ti, V, Si, W, Au, Pd, Pt, Zr	3.0
Al, K, Na, Li	15
Ca, Fe, Mg	18
Ag	0.50

8.13 Spectral Interference Check I (ICSA) - Dilute the following listed aliquot volumes of individual stock standards to 1 Liter with calibration blank (8.8).

Analyte	Stock Conc. (Mg/L)	Aliquot Vol. (Ml)	Final Conc. (Mg/L)
Al, Ca, Mg	10000	50	500

Fe	**10000**	**20**	**200**

8.14 Spectral Interference Check II (ICSAB) - Dilute the following listed aliquot volumes of individual stock standards and 10 ml of CLPILM 030 Analytes B standard to 1 Liter with calibration blank (8.8).

- CLPILM030 Analytes B standard contains the following analytes and concentrations:

Analyte	Conc. (Mg/L)
Ag, Cd, Ni, Pb, Zn	**100**
Ba, Be, Co, Cr, Cu, Mn, V	**50**

ICSAB solution contains the following analytes and concentrations:

Analyte	Stock Conc. (Mg/L)	Aliquot Vol. (Ml)	Final Conc. (Mg/L)
Al, Ca, Mg	**10000**	**50**	**500**
Fe	**10000**	**20**	**200**
As, Se, Tl, Sb	**1000**	**2.0**	**2.0**
Ag, Cd, Ni, Pb, Zn	**100**	**10**	**1.0**
Ba, Be, Co, Cr, Cu, Mn, v	**50**		**0.50**
Mo, Sr, Sn, B	**1000**	**1.0**	**1.0**
Ti, Au*, Pd*, Pt*	**1000**	**0.50**	**0.50**
Si*, W *	**1000**	**2.0**	**2.0**
Zr*	**1000**	**0.5**	**0.5**

*When the element is requested ICSAB will be made accordingly. Internal Standard/Ionization suppressant solution (5 ppm Yttrium, 1000 ppm Lithium) In a 1000 ml volumetric flask, dilute 5 ml of 1000 ppm Yttrium standard and 100 ml of 10000 ppm Lithium standard to the mark with calibration blank (8.8)

Note: If Na, Ca, Mg and K are not being analyzed Li can be excluded in the internal standard mix. If Li requested, use 5 ppm Yttrium and 50 ppm Indium solution mix as internal standard.

8.15 Low level Check (CRI). The CRI standard contains the elements of interest at levels near the low end of the curve. Typically the concentration of CRI is at the reporting limits. Check with the metals supervisor or the client tech specs, to see which CRI needs to be analyzed. The acceptance criteria of 70 to 130percent will be applied unless there are specific instructions set by client or program.

Program/Client	CRI Concentration Level	CRI Acceptance Criteria	Non Conformance
6010C	At the RL	+/- 30%	Re-calibrate & re-analyze
DoD	At the RL	+/- 20%	Re-calibrate & re-analyze
RCP	At the RL	+/- 30% *	Re-calibrate & re-analyze

* Except +/-50% for As, Sb, Tl, Co

. See below table for CRI solution preparation and the final concentration at the instrument.

Low Levels Check Solution	Element	Stock Conc. in mg/l	Amt of Stock used in ml	Final Vol. of CRI Stock Solution in ml	Conc. of CRI Stock Solution in ug/l	Amt of CRI Stock Solution used in ml	Final Vol. of CRI Solution in ml	Final Conc. at the instrument in ug/l
ICP CRI 6010C	Sb	6.00	0.50	500.00	N/A	N/A	N/A	6.00
	As	4.00			N/A			4.00
	Ba	50.00			N/A			50.00
	Be	4.00			N/A			4.00
	B	100.00			N/A			100.00
	Cd	4.00			N/A			4.00
	Cr	10.00			N/A			10.00
	Co	50.00			N/A			50.00
	Cu	25.00			N/A			25.00
	Pb	5.00			N/A			5.00
	Mn	15.00			N/A			15.00
	Mo	100.00			N/A			100.00
	Ni	40.00			N/A			40.00
	Se	10.00			N/A			10.00

	Ag	5.00			N/A		5.00
	Sr	10.00			N/A		10.00
	Tl	5.00			N/A		5.00
	Sn	100.00			N/A		100.00
	Ti	50.00			N/A		50.00
	V	10.00			N/A		10.00
	Zn	20.00			N/A		20.00
ICP CRI MINERAL	Al	20.00	5.00	500.00	N/A	N/A	200.00
	Fe	10.00					100.00
	Ca	500.00					5000.00
	Mg	500.00					5000.00
	K	500.00					5000.00
	Na	500.00					5000.00
ICP CRI OTHER	Au	1000.00	0.10	100.00	1000.00	5.00	50.00
	Pd	1000.00	0.10		1000.00		50.00
	Pt	1000.00	0.10		1000.00		50.00
	Sl	1000.00	0.20		2000.00		100.00
	W	1000.00	0.20		2000.00		100.00
	Zr	1000.00	0.10		1000.00		50.00
ICP CRI LI	Li	10000.00	0.05	100.00	N/A	N/A	5000.00

9.0 INTERFERENCES

9.1 Several types of interference effects may cause inaccuracies in the determination of an analyte in this method. These interferences can be summarized as follows:

9.1.1 Spectral Interferences: Spectral interferences are caused by overlap of a spectral line from another element, unresolved overlap of molecular band spectra, background contribution from stray light from the line emission of high concentration elements. Corrections for these interferences can be made by using interfering element corrections, by choosing an alternate analytical line, and/or by applying background correction points.

9.1.2 Physical Interferences: Physical interferences are generally considered to be effects associated with the sample introduction (nebulization and transport processes). Such properties as change in viscosity or surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids and/or high acid concentrations. The use of a peristaltic pump, sample dilution and/or utilization of standard addition techniques will reduce these interferences.

9.1.3 Chemical Interferences: Chemical interferences are not pronounced with the ICAP techniques due to the high temperature of plasma, however, if they are present, they can be reduced by optimizing the analytical condition (i.e. power level, torch height).

9.1.4 Memory Interferences: Memory interferences result when analytes in a previous sample contribute to the signal measured in the new sample. This result from sample builds up in the plasma torch spray chamber. This can be reduced by flushing the system between samples with rinse solution (8.7). A minimum of 60 seconds rinse time must be applied.

9.2 The occurrence of interferences described above are primarily attributed to the sample matrix. To ensure the absence of any type of interferences, the following precautions may be taken:

9.2.1 Serial Dilution: See section 11.9.

9.2.2 Analyte Addition (Post Digestion Spike – PDS): An analyte spike added to a portion of prepared sample, or its dilution, should be recovered to within 80% to 120% (Note, some cleints or programs (i.e., DoD), the recovery is 75% to 125%) of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the IDL for that element.

9.2.3 Method of Standard Addition (MSA). If the PDS does not meet criteria, the MSA may be used. Standards are added at one or more levels to portions of a prepared sample. This technique compensates for enhancement or depression of an analyte signal by a matrix. It will not correct for additive interferences, such as contamination, interelement interferences, or baseline shifts. This technique is valid in the linear range when the interference effect is constant over the range, the added analyte responds the same as the endogenous analyte, and the signal is corrected for additive interferences. The simplest version of this technique is the single addition method. This procedure calls for two identical aliquots of the sample solution to be taken. To the first aliquot, a small volume of standard is added; while to the second aliquot, a volume of acid blank is added equal to the standard addition. The sample concentration is calculated by: multiplying the intensity value for the unfortified aliquot by the volume (Liters) and concentration (mg/l or mg/kg) of the standard addition to make the numerator; the difference in intensities for the fortified sample and unfortified sample is multiplied by the volume (Liters) of the sample aliquot for the denominator. The quotient is the sample concentration.

9.2.4 An alternative to using the method of standard addition is the internal standard technique. Add yttrium to the standards, samples, and blanks at a concentration to be sufficient for optimum precision, but not so high as to alter the salt concentration of the matrix. The element intensity is used by the instrument as an internal standard to ratio the analyte intensity signals for both calibration and quantitiation.

9.2.5 Wavelength Scanning: Wavelength scanning of the sample can be performed and compared to the scan of the analyte to detect potential spectral interferences.

10.0 PROCEDURE

General procedure on how to operate the SS6500 is described below. Refer to the Thermo 6500 operation manual for further details.

10.1 Before bringing up the instrument, make sure that the sample tubings, the nebulizer, and the spray chamber are clean and that there are no leaks in the torch area.

10.2 Turn on the recirculating cooler.

10.3 Engage the peristaltic pump.

10.4 Make sure reagent reservoirs (rinse solution and internal std solution) are filled with enough solution to last for a full days run. The rinse reservoir is filled with rinse solution (8.7) and internal standard solution (8.14).

NOTE: If the internal standard solution runs out during the run, instrument must be recalibrated with the new standard.

10.5 Ignite the plasma and let the instrument warm up for 30 minutes before starting analysis. New tubing may need an hour to stabilize.

10.6 Type up the auto sampler sequence, and set up the trays.

10.7 CALIBRATION

10.7.1 Prior to calibration, make sure a minimum of 60-second rinse time and 60 seconds up take time is set up in the method/auto-sampler.

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10.7.2 Calibrate the instrument using calibration blank, standard #1, standard #2, and standard #3.

10.8 DAILY CALIBRATION

10.8.1 Calibrate the instrument using calibration blank (8.8) and calibration standards (8.10.5).

10.8.2 When calibration is complete, a printout of slopes will be printed for each line and calibration is automatically approved.

10.9 Dilutions.

10.9.1 The pH of all aqueous samples must be verified to be <2 prior to aliquot for processing. If samples have a pH of >2 add additional nitric acid and wait 24 hours before rechecking the pH. If a sample result exceeds the upper linear range, a dilution must be made using rinse solution (8.7). The diluted result should be within the upper linear dynamic range.

10.10 Filtration.

10.10.1 If particulate were observed in the samples, then they should be re-filtered along with the associated blanks.

11.0 QUALITY ASSURANCE

NOTE: 1) The system must be rinsed with the calibration blank solution between each sample analysis for a minimum of 60 seconds.

11.1 Set up the auto-sampler sequence as described below.

11.2 Analyze the mid-level initial calibration verification (ICV - 8.12). The analyzed value of each analyte for the mid-level ICV must be within 90%-110% of its expected value and the RPD between replicates should be less than 5%. If not, recalibrate.

11.3 Analyze the Initial Calibration Blank (ICB - 8.8). The ICB results should be less than the reporting limits for an element). If not, re-calibrate.

11.4 Analyze the Continuing Calibration Verification (CCV - 8.11) and Continuing Calibration Blank (CCB - 8.8). Also analyze the CCV and CCB after every 10 samples and at the end of the sample run. The analyzed value of each analyte in the CCV should be within 90% to 110% of its true value and the RPD between replicates should be less than 5%. If not, rerun one more time. If an analyte value is still outside the range, the instrument should be recalibrated and all samples following the last acceptable CCV should be reanalyzed. All CCBs should be less than the reporting limits for each element. If not, it can be reanalyzed one more time, if still out, no samples can be reported in the area bracketed by the failing CCB for the failing elements.

11.5 Analyze the CRI check standards at the beginning and the end of the run with each new calibration.

11.5.1 The low-level initial calibration verification (LLICV) is used as CRI check standard at the beginning of the run. The analyzed value of each analyte for the LLICV must be within 70%-130% of its expected value. Note, for some clients or programs (i.e., DoD), the recovery is 80%-120%, check with Dept. manager for specific project requirement. It acceptance criteria not met, reanalyze once. If acceptance criteria not met after second analysis perform corrective action and recalibrate. The LLICV can be prepared by using the same source as the calibration standards, but must at a concentration expected to be at the RL.

11.5.2 The low-level continuing calibration verification (LLCCV) is used as CRI check standard at the end of the run. It is recommended that a LLCCV be analyzed after every 10 samples and at the end of each analysis batch. The acceptance criteria for LLCCV should be within 70%-130% of its true value. Note, for some clients or programs (i.e., DoD), the

recovery is 80%-120%, check with Dept. manager for specific project requirement. It acceptance criteria not met, reanalyze once. If acceptance criteria not met after second analysis, no samples for failed analyte in LLCCV can be reported. The LLCCV should be prepared from the same source as the initial calibration standards at a concentration of the RL.

11.6 Analyze the Spectral Interference Check I (ICSA) and Spectral Interference Check II (ICSAB)

11.6.1 The analyzed value of Al, Ca, Mg, and Fe must be between 80-120%. The analyzed value of each remaining analyte in ICSA should be less than twice the reporting limit, unless specified by client or program. If not, rerun one more time, if still not, either recalibrate or no sample for failed analyte in ICSA can be reported. You may have to perform inter-element correction of interfering elements.

11.6.2 The analyzed value of each analyte in ICSAB should be within ± 20% of its expected value. If not, repour and reanalyze. If still outside the limit, recalibrate. If after recalibration ICSAB is still outside the limit, you may have to perform inter-element correction of interfering elements and recalibrate.

11.6.3 The ICSA and ICSAB should be run prior to sample analysis and at the end of the run.

11.7 If all initial quality control steps mentioned above were satisfied, you may start the analysis of the samples.

11.8 For each analysis run a laboratory reagent blank (method blank), laboratory fortified blank (spike blank), laboratory control sample (LCS – for soil samples), laboratory fortified sample (matrix spike), a matrix spike duplicate must be analyzed. If samples that were prepared on several different days are analyzed, make sure that the method blanks and spike blanks from all of the preparation dates are also analyzed. (A matrix spike, a matrix spike duplicate, a spike blank, and a method blank are prepared with each set of 20 samples).

Analyte recovery: Until sufficient data becomes available the following limits should be exercised:

Spike Blank Recovery	± 20%
Spike Blank Duplicate RPD	≤ 20% (AQ) ≤ 30% (SO)
Matrix Spike Recovery	± 25% *
RPD	± 20%

Note: The Spike Blank Duplicate is an MCP/RCP requirement. A project-specific matrix duplicate or matrix spike duplicate may be used in lieu of the spike blank duplicate for MCP.

* If the % Recovery of an analyte falls outside the ± 25% limit (Note, for some clients or programs (i.e., DoD), the Matrix Spike recovery is +/- 20%, check with Dept. manager for project specific requirement) but spike blank recovery falls within the accepted range, then the recovery problem is judged to be matrix related, not system related. Sample results

need to be footnoted and a post spike must be analyzed. (Analyze the post digestion spike according to section 9.2.2) Note, for some clients , the unspiked aliquot of the sample should be spiked at two –times the indigenous level or two times their specific required detection limit, which ever is greater. The results of post spike must be reported in their summary report (check with Dept. manager for client specific lists) If post spike recoveries are not within the 80%-120% criteria, a matrix effect should be suspected. Follow step 11.9.

For the soil LCS – the manufacturer QC limits should be used for evaluation.

The method blank results must be less than the reporting limit for an element. Note, for some clients the method blank results must be less then ½ of the RL. If not, any sample results in the associated batch has a positive result for that element, the batch must be re-digested and reanalyzed.

11.9 Serial Dilution- The analysis of a (1:5) dilution should agree within 10% of the original sample result. If the analyte concentration is not high enough and the serial dilution is not within 10 % of the original sample but less than 50 times the IDL for that analyte, serial dilution results are acceptable. In addition, serial dilution should be done on every sample that is significantly different matrix or if a matrix interference is suspected. If analysis of the dilution does not meet the 10% criteria, a matrix interference may be suspected. For some clients or programs (i.e., DoD), if 1:5 dilution does not agree within +/- 10% of the original measurement for samples with concentrations greater than 50 times of LOD, perform post digestion spike (check with Dept. manager for project specific requirement for post spike criteria).

11.10 Internal standard-Internal standard is added to all standards and samples. Acceptance criteria for the internal standard are ±30% as compared to the Calibration Blank.

11.11 A Precision and accuracy (P&A) study is performed as an initial determination of capability, on an annual basis, and if any major changes have been made to the instrument. Four replicates or blank spikes are analyzed using the same conditions for sample analysis. The percent recoveries are compared to limits as described in section 11.8 (spike blank). The standard deviation results of the 4 blank spike recoveries should be ≤ 20%. If percent recovery or standard deviation criteria are not met, corrective action must be taken to bring the system back into control.

11.12 Linearity studies should be determined quarterly and whenever there is significant change in instrument response. The study must be performed using minimum 5 different concentration standards across the range, and 1 standard must be near the upper limit. The acceptance criteria for linearity studies should be within ±10% of its true value.

11.13 MDLs are determined annually, or if significant maintenance has been performed on the instrument. Refer to the MDL SOP (MQA245) for details.

11.14 IDLs are performed quarterly. The IDLs can be estimated by calculating the average of the standard deviations of three runs on three non-consecutive days from the analysis of a reagent

blank solution with seven consecutive measurements per day. The IDL concentration must be ≤ the MDL concentration. The study must be repeated for any analytes that do not meet this criteria.

11.15 The lower limit of quantitation sample (LLQC) should be analyzed after establising the lower laboratory reporting limits and on an as needed basis to demonstrate the desired detection capability. The LLQC must be prepared at the same concentrations as the RL, and the LLQC must be carried through the entire preparation and analytical procedure. The lower quantitation limits are verfied when all analytes in the LLQC are detected within ±30% of their true value. This check should be used to both establish and confirm the lowest quantitation limit.

11.16 Interelement spectral interference determination routine must be verified every 6 months.

11.17 Quality control data are generated at least on an annual basis by QA using an in-house program. Blank spike and MS/Dup data are pooled for the previous year (or other specified time frame) and the data is processed and evaluated by QA. The annual QC data is filed with QA.

11.18 All NELAC-accredited target compounds must be spiked in the blank spike and matrix spike within a two-year period. All target compounds reported for a project are spiked and evaluated in the blank spike and MS/MSD

12 DOCUMENTATION

12.1 Make sure that all sample ID's and standard lot# are recorded in analysis log book. All comments and edits MUST BE clearly documented and initialed. Generate run logs from the LIMS system along with all quality control data.

12.2 Each analyst should review all data and assemble a data package consisting of :

- Print out of automated digestion prep sheet
- Print out of automated analysis runlog
- LIMS generated run log
- Raw data
- LIMS generated batch list

12.3 If samples require reanalysis, a brief explanation of the reason should be documented in this log.

12.4 The Accutest lot number must be cross-referenced on the standard bottle. Expiration date must be noted on standard bottle.

12.5 The instrument Maintenance logbook must be completed daily. Each instrument will have a separate log.

12.6 All laboratory logbooks must be reviewed and initialed or signed by the lab manager. A signed or initialed copy of the logbook page filed with the daily batch is sufficient.

12.7 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of correction must appear next to the correction.

12.8 The inter-element spectral interference determination routine must be kept on file.

12.9 Linearity studies must be kept on file.

13 DATA REPORTING

13.1 A results page including positive results and/or RLs for all target elements, units, methodology, dates of digestion and analysis, data qualifiers, are reported. Additional quality control data including calibration summaries, MS/MSD percent recoveries and RPDs, blank spike recoveries, method and calibration blank results, and any associated raw support data may be reported upon request of the client.

13.2 Data may be submitted to the client in a specified electronic format (EDD).

13.3 Data may be submitted to the client in PDF via e-hardcopy.

13.4 Once the data is approved by the laboratory manager, it may be accessed by clients via LabLink™.

13.5 Procedures for handling non-conforming data.

13.5.1 If quality control data does not meet criteria the non-conformance must be discussed in a case narrative and footnoted on the applicable quality control report summary.

13.5.2 If preservation or holding time criteria is not met and the samples are analyzed the result page must be footnotes with this information, and the non-conformance must be discussed in a case narrative or other suitable communication (telephone conversation log or email). Client notification documentation should be included with the data (telephone conversation log, fax, or email).

14.0 DATA REVIEW

14.1 The analyst conducts the primary review of all data. This review begins with a check of all Instrument and method quality control and progresses through sample quality control concluding with a check to assure that the client's requirements have been executed. The analyst has the authority and responsibility to perform corrective action for any out-of-control parameter of non-conformance.

14.2 A secondary review is performed by department managers, and it includes review of the data produced by their department. All manual calculations, QC criteria, and a comparison of the data package to client specified requirements are checked. The department manager may reject data, initiate reanalysis, take additional corrective action, or reprocess data.

14.3 The laboratory director performs a full tertiary review of the data package following its assembly. This review includes an evaluation of QC data against acceptance criteria and a check of the data package contents to assure that all analytical requirements and specifications were executed.

14.4 Spot-check reviews are performed by the Quality Assurance Officer focusing on all elements of the deliverable including the client's specifications and requirements, analytical quality control, sample custody documentation and sample identification

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Pollution Prevention. Users of this method must perform all procedural steps that control the creation and/or escape of wastes of hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids, or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 15.2.

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the Sample and Waste Disposal SOP. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

15.2.1 Non-hazardous aqueous wastes
15.2.2 Hazardous aqueous wastes
15.2.3 Chlorinated organic solvents
15.2.4 Non-chlorinated organic solvents
15.2.5 Hazardous solid wastes
15.2.6 Non-hazardous solid wastes

16.0 METHOD PERFORMANCE

16.1 Method performance is evaluated by the annual quality control data generated by QA, and the annual MDL study results. Refer to section 3.0 for MDLs, and section 11.9.10 for QC data.

17.0 ADDITIONAL REFERENCES

17.1 None.

Lab Manager: Brad Madadian
QA Officer: Robert Treggiari

TITLE: HARDNESS AS CaCO3

TEST METHOD REFERENCE: 2340 C. Standard Methods for the Examination of Water and Wastewater 21th Edition, 2005

REVISED SECTIONS: Section 8.0 notation

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

1.2 The method is suitable for all concentration ranges of hardness

1.3 Test code: HRD

2.0 SUMMARY

2.1 Calcium and magnesium ions in the sample are sequestered upon the addition of disodium ethylenediamine tetraacetate (Na2EDTA). The end point of the reaction is detected by means of Calmagite or Eriochrome Black indicator, which has a red color in the presence of calcium and magnesium and a blue color when the cations are sequestered.

3.0 METHOD REPORTING AND DETECTION LIMIT

3.1 The reporting limit for this analysis is 4.0 Mg/L.

3.2 The Method Detection Limit (MDL) represents the lowest reportable concentration of an individual analyte that meets the method qualitative identification criteria.

3.3 Method Detection limits (MDLs) are experimentally determined using the procedures described in 40 CFR, Part 136, Appendix B. Actual reported MDLs incorporate the sample volume analyzed and sample dilutions if needed, which may cause MDL variations from sample to sample.

3.4 In general, MDLs are determined through the analysis of at least 7 replicate blank spikes (using the same procedures for sample analysis). The MDL is calculated by multiplying the standard deviation of the replicate concentrations by the appropriate Student's t value (3.143 for 7 replicates). If more than 7 replicates are analyzed refer to 40 CFR, Part 136, Appendix B for the appropriate student's t value. MDLs are determined initially (prior to analysis), on an annual basis, and after major maintenance to equipment. MDL data is archived with Quality Assurance. Refer to the most recent study for current MDLs. Refer to the SOP for MDLs (MQA245) for additional detail regarding MDL study procedures. For additional detail regarding MDL studies, refer to the MDL SOP MQA245.

3.5 Current MDL studies are filed with Quality Assurance. Obsolete MDL studies are archived with the QA files. Electronic MDL data is found in the annual "MDL" folder on the QA server (LINUXMA1).

4.0 DEFINITION

4.1 ALIQUOT - a measured portion of a sample, or solution, taken for sample preparation and/or analysis.

4.2 BATCH – A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit. For QC purposes, if the number of samples in a group is greater than 10, then each group of 10 samples or less will all be handled as a separate batch.

4.3 CONTAMINATION - a component of a sample or an extract that is not representative of the environmental source of the sample. Contamination may stem from other samples, sampling equipment, while in transit, from laboratory reagents, laboratory environment, or analytical instruments.

4.4 EXTERNAL CHECK STANDARD - The external check standard that is used to verify the accuracy of the calibration standards. An external check must be run with each analytical batch. The laboratory should initially assess laboratory performance of a check standard using the control limits generated by the external check supplier. Refer to the quality control section for each SOP. If the external check is outside of the control limits for a given parameter, all samples must be reanalyzed for that parameter after the problem has been resolved.

4.5 FIELD SAMPLE - a portion of material to be analyzed that is contained in single or multiple containers and identified by a unique sample number.

4.6 HOLDING TIME – the elapsed time expressed in days from the date of sampling until the date of its analysis.

4.7 INTERFERENTS – substances which affect the analysis for the element of interest.

4.8 MATRIX - the predominant material of which the sample to be analyzed is composed. For the purpose of this SOP, a sample matrix is either water or soil/sediment. Matrix is <u>not</u> synonymous with phase (liquid or solid).

4.9 MATRIX DUPLICATE - a second aliquot of the original sample prepared and analyzed in order to determine the precision of the method.

4.10 MATRIX SPIKE- aliquot of a matrix(water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

4.11 RELATIVE PERCENT DIFFERENCE (RPD) - As used in this SOP to compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero.

4.12 REAGENT WATER - water in which an interferant is not observed at or above the minimum quantitation limit of the parameters of interest. Accutest uses deionized water (municipal water which passes through Accutest's DI treatment system).

5.0 HEALTH AND SAFETY

5.1 The analyst should follow normal safety procedures as outlined in the Accutest Laboratories Chemical Hygiene Plan, which includes the use of lab coat and safety glasses. In addition, all acids are corrosive and should be handled with care. Flush spills with plenty of water. If acids contact any part of the body, flush with water and contact the supervisor.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level.

6.0 COLLECTION, PRESERVATION & HOLDING TIMES

6.1 The sample must be acidified to a pH of less than 2 by addition of 1:1 Nitric acid, and kept under refrigeration at 4 Deg C.

6.2 All samples must be analyzed within 180 days from sampling date.

7.0 APPARATUS AND MATERIALS

7.1 Titration vessel, 50 ml or 100 ml beaker.
7.2 Magnetic stirrer; stirbars.
7.3 Pipettes, class A.
7.4 Volumetric flasks, class A.
7.5 Burets, 50 ml and 10 ml micro.

8.0 REAGENTS AND STANDARDS

NOTE: All chemicals listed below are reagent grade unless otherwise specified. Distilled, deionized water should be used whenever water is required. All applicable standard/reagent preparation information, including vendor, lot number, date of preparation, calculations, and initials must be entered in the appropriate standard/reagent preparation logbook. Vendors typically used by Accutest include Fisher Scientific, VWR, Accustandard, Absolute Standards, Supelco, Chemservices, Ultra, and ERA. Additional vendors may be utilized as necessary.

8.1 Buffer solution. Dissolve 1.179 g of disodium EDTA (analytical grade) and 780 mg of MgSO4 $7H_2O$ (or 644 mg $MgCl_2$ $6H_2O$) in 50 ml of DI water. Add this solution to a 250 ml volumetric flask containing 16.9 g of ammonium chloride (NH_4Cl) and 143 ml concentrated ammonium hydroxide (NH_4OH) with mixing and dilute to the mark with DI water. Store in a plastic bottle for no longer than 1 month.

8.2 Inhibitor solution. These are to be used only if interferences are evident during the titration (Please check with lab supervisor or lab manager first).

8.2.1 Inhibitor II: Dissolve 5.0 g of Na_2S $9H_2O$ in 100 ml of DI water. Cover with tightly fitted rubber stopper. This inhibitor deteriorates through air oxidation. It produces a sulfide precipitate that obscures the end point when appreciable concentration of heavy metals are present.

8.3 Indicator solutions. A Calgamite indicator solution can be purchased commercially or by dissolving 0.10 g calgamite in 100 ml DI water. Use 4 to 5 drops per 50 ml solution to be titrated. Adjust the number of drops if necessary.

8.4 Standard EDTA titrant, 0.01M. Place 3.723 g of analytical reagent grade disodium ethylenediamine tetraacetate dihydrate, $Na_2H_2C_{10}H_{12}O_8N2$ $2H_2O$ in a 1 liter volumetric flask and dilute to the mark with DI

water. Check with standard calcium solution by titration. (See section 1 under procedure.) Store in polyethylene.

8.5 Standard calcium solution. Place 1.000 g of anhydrous calcium carbonate in a 500 ml flask. Slowly add 1:1 HCl (<10 ml) until all of the $CaCO_3$ has dissolved. Add 200 ml distilled water to the flask and mix. Boil this solution for a few minutes to expel CO_2. Cool. Add a few drops of methyl red indicator and adjust to intermediate orange color by adding dropwise, 3N NH_4OH or 1+1 HCl as required. Quantitatively transfer to a 1 Liter volumetric flask and dilute to mark with DI water.

8.6 Hydrochloric acid solution, 1:1. Add 100 mls of concentrated HCl to 100 mls of DI. Mix and cool.

8.7 Methyl red indicator. Dissolve 0.10 g methyl red in DI water in a 100 ml volumetric flask and dilute to the mark.

8.8 Ammonium hydroxide solution, 3 N. Dilute 210 ml of concentrated ammonium hydroxide (NH_4OH) to 1 liter with DI water.

8.9 Ammonium hydroxide solution, 1 N. Dilute 70 ml of concentrated ammonium hydroxide to 1 liter with DI water.

8.10 NaOH, 0.1 N. In a 1000 ml volumetric flask, dissolve 4 grams of NaOH in 750 ml of DI water. Cool, and bring to volume with DI water.

9.0 INTERFERENCES

9.1 Some metal ions interfere by causing fading or indistinct endpoints or by stoichiometric consumption of EDTA. These interferences can be reduced by adding certain inhibitors before titration.

9.2 Conduct titrations at or near normal room temperature. The color change will be impractically slow as the The sample temperature approaches freezing temperatures.

10.0 PROCEDURE

Below is a step by step procedure for the analysis of samples for HRD. Use the automated spreadsheet for documentation, and calculations of Standardization, and the analysis. This application can be found on server. Before starting on the samples, standardize the EDTA solution following the procedure outlined below.

10.1 Place 10.0 ml of standard calcium solution in a vessel containing about 50 ml of DI water. Add 1 to 2 ml of buffer solution. Usually 1 ml will be sufficient to give a pH of 10.0 $\pm$ 0.1. Record the pH. Add 4 to 5 drops of calgamite indicator. Titrate slowly with continuous stirring with the EDTA until the last reddish tinge disappears. Add the last few drops at 3 to 5 second intervals. At the end point the color is blue. Total titration duration should be 5 minutes from the time of the buffer addition. Calculate the normality of the EDTA as shown below, and document the result in the analysis log book.

N of EDTA = (0.20)/(ml of EDTA added)

10.2 Start the titration of samples by measuring 25 ml of sample into a 50 ml titration vessel. Add 25 ml of DI water, and mix. Note: Select a sample size that requires less than 15 ml of EDTA titrant. For quality control sample, measure 3 aliquots. One will be the duplicate sample, one will be the original sample

analysis, and one will be the matrix spike sample. Set up a preparation blank and a spike blank by placing 50 mls of DI water into the titration vessels. Add 1 ml of standard calcium carb. solution (8.5) to spike blank and matrix spike. The final concentration of the spike will be 40 mg/l.

NOTE: Highly polluted samples (industrial waste, organic contaminants, etc.) should first go through a metal digestion step before analysis. Please check with lab supervisor or manager.

10.3 Neutralize the samples with 1N ammonium hydroxide and dilute to a final volume of approximately 50 ml.

10.4 Add 1 to 2 ml of buffer solution to each sample.

10.5 Add 4 to 5 drops of calgamite indicator solution to each sample.

10.6 Titrate the sample slowly with continuous stirring with the standard EDTA titrant until the last reddish tint disappears. The solution is normally blue at the end point. Total titration duration should be 5 minutes from the time of buffer addition.

NOTE: Completion of the titration within 5 minutes minimizes the tendency for CaCO3 to precipitate.

NOTE: If it appears that interferences are present, repeat the titration as above, but add inhibitor immediately after step 10.4.

10.7 Calculations.

10.7.1

$$\text{Hardness , mg/l } CaCO_3 = \frac{(A - B) \times N \times 50000}{\text{ml sample}}$$

Where: A = ml of EDTA titrant.
B= ml of EDTA used for Method Blank
N = Normality of EDTA titrant.

11.0 QUALITY ASSURANCE

11.1 Below is a summary of the quality control requirements for this method. Make sure to check with laboratory supervisor or manager for any additional client specific quality control requirements.

11.2 **Method Blank**. The laboratory must analyze a method blank with each set of samples. A minimum of one method blank is required for every 10 samples. The method blank must contain the analyte at less than the reporting limit (1/2 the RL for some clients). If the method blank contains an analyte level over that limit the problem must be identified and corrected prior to sample analysis.

11.3 **Matrix Duplicate.** The laboratory must prepare a duplicate sample for a minimum of 1 in 10 samples. The relative percent difference (rpd) between the duplicate sample and the original should be assessed. The Duplicate RPD should be calculated as shown below

$$\frac{\text{(Original Sample Result – Duplicate Result) x 100}}{\text{(Original Sample Result + Duplicate Result) x 0.5}} = \%\ \text{RPD}$$

The Duplicate RPD should be assessed using in house limits. Until these limits can be generated, then the default limit of 20 percent RPD should be applied. If a duplicate RPD is out of control, then the results should be flagged with the appropriate footnote. If the sample and the duplicate are less than 5 times the reporting limits and are within a range of $\pm$ the reporting limit, then the duplicate is considered to be in control.

11.4 **Matrix spike.** The laboratory must add a known amount of each analyte to a minimum of 1 in 10 samples. The spike recovery should be assessed using in house limits. Until these limits can be generated, default limits of 75-125 % recovery should be applied. If a matrix recovery is out of control, then the recovery should be flagged with the appropriate footnote. If a matrix spike amount is less than one fourth of the sample amount, then the sample can be assessed against the control limits and should be footnoted to that effect.

$$\frac{\text{(Matrix Spike Result – Original Result) x 100}}{\text{Amount of Spike}}$$

11.5 **Spike Blank.** The laboratory must analyze a spike blank with each set of samples. A minimum of one spike blank is required for every 10 samples. The net recovery should be within 20 percent of the true value. If the spike blank is outside of this range, the problem must be identified and corrected before sample analysis can proceed.

11.6 **External Standard.** An external standard is analyzed with each analytical batch. The net recovery should be within 10% of the true value (if the external is prepared in house) or within the manufacturer's acceptance criteira if purchased from an outside vendor. If the external is outside this range, the problem must be identified and corrected before sample analysis can proceed.

11.7 A Precision and accuracy (P&A) study is performed as an initial determination of capability, on an annual basis (continued demonstration of capability – a successful PT result may be used in place of a P&A for continued DOC), and if any significant changes have been made to the instrument. In general, 4 replicates or blank spikes are analyzed using the same procedures and conditions for sample analysis. The mean percent recovery is compared to the spike blank control limits of 20%. The standard deviation (of the percent recovery of the 4 spike blanks) is compared to the control limit of 20. If percent recovery or standard deviation criteria are not met, corrective action must be taken to bring the system back into control. The P&A study replicates must be prepared from a source independent from the calibration standards (as applicable).

11.8 Quality Control data is generated (control charts) and reviewed on an annual basis by Quality Assurance (blank spike/ matrix spike recoveries and matrix duplicate RPDs).

12.0 DOCUMENTATION

12.1 Which method was used.

12.2 The sample ID, duplicate as necessary.

12.3 The initial volume aliquoted.

12.4 Any comments or observations concerning the sample that may influence the analytical procedure.

12.5 The date the analysis performed.

12.6 Any corrections to laboratory data must be done using a single line through the error. The initials of the person and date of corrections must appear next to the correction.

12.7 All laboratory logbooks must be reviewed and initialed or signed by the lab manager.

13.0 DATA REVIEW

13.1 The analyst conducts the primary review of all data. This review begins with a check of all method quality control and progresses through sample quality control concluding with a check to assure that the client's requirements have been executed.

13.2 A secondary review is performed by department managers, and it includes review of the data produced by their department. Manual calculations, QC criteria, and a comparison of the data package to client specified requirements are checked. The department manger may reject data, initiate reanalysis, take additional corrective action, or process data.

13.3 The laboratory director performs a full tertiary review of the data package following its assembly. This review includes an evaluation of QC data against acceptance criteria and a check of the data package contents to assure that all analytical requirements and specifications were executed.

13.4 Spot-check reviews are performed by the Quality Assurance Officer focusing on all elements of the deliverable including the client's specifications and requirements, analytical quality control, sample custody documentation and sample identification.

14.0 DATA REPORTING

14.1 A results page including positive results and/or RLs, units, methodology, analysis dates, and data qualifiers are reported. Additional quality control data including matrix duplicate RPDs, matrix spike recovery, blank spike and method blank results may be reported upon request of the client.

14.2 Data may be submitted to the client in a specified electronic format (EDD).

14.3 Once the data is approved by the laboratory manager, it may be accessed by clients via LabLink™.

14.4 Procedures for handling non-conforming data.

14.4.1 If quality control data does not meet criteria the non-conformance must be discussed in a case narrative and footnoted on the applicable quality control report summary.

14.4.2 If preservation or holding time criteria is not met and the samples are analyzed the result page must be footnoted with this information, and the non-conformance must be

discussed in a case narrative or other suitable communication (telephone conversation log or email). Client notification documentation should be included with the data (telephone conversation log, fax, or email).

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Pollution Prevention. Users of this method must perform all procedural steps that control the creation and/or escape of wastes of hazardous materials to the environment. The amounts of standards, reagents, and solvents must be limited to the amounts specified in this SOP. All safety practices designed to limit the escape of vapors, liquids, or solids to the environment must be followed. All method users must be familiar with the waste management practices described in section 15.2.

15.2 Waste Management. Individuals performing this method must follow established waste management procedures as described in the Sample and Waste Disposal SOP. This document describes the proper disposal of all waste materials generated during the testing of samples as follows:

15.2.1 Non-Hazardous aqueous wastes
15.2.2 Hazardous aqueous wastes
15.2.3 Chlorinated organic solvents
15.2.4 Non-chlorinated organic solvents
15.2.5 Hazardous solid wastes
15.2.6 Non-hazardous solid wastes
15.2.7 Microbiological waste

16.0 METHOD PERFORMANCE

16.1 Method performance is evaluated by the annual QC limits (control charts) generated by QA, and the annual MDL study results. Refer to section 3.5 for MDLs, and section 11.8 for QC limits.

17.0 ADDITIONAL REFERENCES

17.1 None.

Project Specific SOP Addendum

SOP Title or Method Number: SOP/03-03. Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) 8260B, Issue 12, September 9, 2010.

Reference Documents:

Method 8260 B, SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update III, December 1996.

Method 5035, Closed System Purge &Trap and Extraction for Volatile Organics in Soil and Waste Samples. SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update III, December, 1996.

Method 5030B, Purge & Trap for Aqueous Samples. SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update III, December, 1996.

MassDEP CAM QC Requirements and Performance Standards for the Analysis of Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 1, July 1, 2010.

Client: Various

Project Name: All Massachusetts Contingency Plan Projects

Project No.: Various

The following modifications need to be made to the referenced SOP for all samples applicable to this project:

Section 1. The following compounds can be determined by this method:

8260B MCP LIST OF ANALYTES		
dichlorodifluoromethane	benzene	1,2,3-trichloropropane
chloromethane	trichloroethene	n-propylbenzene
vinyl chloride	1,2-dichloropropane	bromobenzene
chloroethane	bromodichloromethane	2-chlorotoluene
bromomethane	dibromomethane	1,3,5-trimethylbenzene
trichlorofluoromethane	4-methyl-2-pentanone	4-chlorotoluene
ethyl ether	cis-1,3-dichloropropene	tert-butylbenzene
acetone	toluene	1,2,4-trimethylbenzene
1,1-dichloroethene	trans-1,3-dichloropropene	sec-butylbenzene
carbon disulfide	1,1,2-trichloroethane	p-isopropyltoluene
methylene chloride	2-hexanone	1,3-dichlorobenzene
methyl-tert-butyl ether	1,3-dichloropropane	1,4-dichlorobenzene
trans-1,2-dichloroethene	tetrachloroethene	n-butylbenzene
1,1-dichloroethane	chlorodibromomethane	1,2-dichlorobenzene

2-butanone	1,2-dibromoethane	1,2-dibromo-3-chloropropane
2,2-dichloropropane	chlorobenzene	1,2,4-trichlorobenzene
cis-1,2-dichloroethene	1,1,1,2-tetrachloroethane	hexachlorobutadiene
chloroform	ethyl benzene	naphthalene
bromochloromethane	p/m xylene	1,2,3-trichlorobenzene
tetrahydrofuran	o xylene	Diisopropyl Ether
1,1,1-trichloroethane	styrene	Ethyl-tert-butyl-ether
1,1-dichloropropene	bromoform	Tertiary-amyl methyl ether
carbon tetrachloride	isopropylbenzene	1,4-Dioxane
1,2-dichloroethane	1,1,2,2-tetrachloroethane	

Section 9.2.5 Immediately after each calibration before the analysis of samples, an Initial Calibration Verification (ICV) must be analyzed at or near the midpoint of the curve. The ICV must be prepared using a different source than the Initial Calibration and must contain all target analytes. The percent recoveries must be between 70% and 130% for target analytes except for “difficult” analytes, which must exhibit percent recoveries between 40% and 160%. Corrective action is required if greater than 10% of all analytes are outside the prescribed criteria.

Section 9.3.5.1 The percent difference or drift for each target analyte must be less than or equal to 20%. If greater than 20% of target analytes exceed the %D criteria corrective action must be taken prior to the analysis of samples. If less than or equal to 20% of compounds exceed the criteria, corrective action is not required as long as the %D is less than 40%.

Section 10.2 Method Blank

Analyze a reagent water blank each day prior to sample analysis to demonstrate that interferences from the analyical system are under control. The reagent blank must contain the internal standards and surrogates.

Analyze the reagent water blank from the same lot of water used for preparing the standards, QC samples and sample dilutions. Target analytes must be below the reporting limit except for common laboratory contaminants (acetone, methylene chloride and MEK) which must be less than 5x the reporting limit. If concentration of the contaminants in sample is less than 10x the concentration of the contaminants in the method blank, the method blank and samples must be reanalyzed. No corrective action is required if the concentration of the contaminant in the sample is 10x the concentration in the method blank.

Section 10.3 Laboratory Control Sample (LCS) and LCS Duplicate (LCSD)

A laboratory control sample is analyzed at the beginning of each analytical sequence. Since the LCS contains the same compounds at the same concentrations as the continuing calibration check standard, the same analysis is used to satisfy both QC elements. A laboratory control sample duplicate is also analyzed in every analytical sequence, usually following the LCS.

Recoveries for all analytes in the LCS and LCSD must be between 70 – 130%, with an allowance of less than or equal to 10% of all analytes outside of criteria. An additional allowance is also made for “difficult” analytes (as noted in Table 7), which must exhibit percent recoveries between 4-% and 160%. If less than 10% of compounds are outside the acceptance criteria, reanalysis is not required as long as recoveries are greater than 10%. Furthermore, if greater than 10% of

compounds are above the acceptance criteria of 130%, reanalysis is not required if affected compounds were not detected in associated compounds. RPDs calculated between the LCS and LCSD must be less than or equal to 20% for waters and solids. RPD exceedences for non-conforming compounds must be noted in the laboratory narrative.

Section 10.4 Matrix Spike/Matrix Spike Duplicates (MS/MSD)

A MS/MSD is not performed unless specifically requested by the client. Recovery must be between 70% and 130%. RPD must be less than 20% for liquid samples and 30% for solid samples. Exceedences are noted in the laboratory narrative.

Table 1: Standard Reported Detection Limits MCP Method 8260B

Analyte	RDL (µg/L)	RDL(µg/KG)[1]	RDL (µg/KG) [2]
Acetone	5.0	36.0	1800
Benzene	1.0	1.0	50
Bromobenzene	2.0	5.0	250
Bromochloromethane	2.0	4.0	200
Bromodichloromethane	1.0	1.0	50
Bromoform	2.0	4.0	200
Bromomethane	2.0	2.0	100
2-Butanone	5.0	10.0	500
n-Butyl benzene	2.0	1.0	50
sec-Butyl benzene	2.0	1.0	50
tert-Butyl benzene	2.0	4.0	200
Carbon disulfide	2.0	4.0	200
Carbon tetrachloride	1.0	1.0	50
Chlorobenzene	1.0	1.0	50
Chloroethane	2.0	2.0	100
Chloroform	1.0	1.5	75
Chloromethane	2.0	4.0	200
o-Chlorotoluene	2.0	4.0	200
p-Chlorotoluene	2.0	4.0	200
Dibromochloromethane	1.0	1.0	50
1,2-Dibromo-3-chloropropane	2.0	4.0	200
1,2-Dibromoethane	2.0	4.0	200
Dibromomethane	2.0	4.0	200
1,2-Dichlorobenzene	1.0	4.0	200
1,3-Dichlorobenzene	1.0	4.0	200
1,4-Dichlorobenzene	1.0	4.0	200
Dichlorodifluoromethane	2.0	10.0	500
1,1-Dichloroethane	1.0	1.5	75
1,2-Dichloroethane	1.0	1.0	50
1,1-Dichloroethene	1.0	1.0	50
cis-1,2-Dichloroethene	1.0	1.0	50

trans-1,2-Dichloroethene	1.0	1.5	75
1,2-Dichloropropane	1.0	3.5	180
1,3-Dichloropropane	2.0	4.0	2050
2,2-Dichloropropane	2.0	5.0	250
1,1-Dichloropropene	2.0	4.0	200

Table 1 (continued): Standard Reported Detection Limits MCP Method 8260B

Analyte	RDL (µg/L)	RDL(µg/KG)[1]	RDL (µg/KG)[2]
cis-1,3-Dichloropropene	0.5	1.0	50
trans-1,3-Dichloropropene	0.5	1.0	50
Ethylbenzene	1.0	1.0	50
Ethyl ether	2.0	5.0	250
Hexachlorobutadiene	0.6	4.0	200
2-Hexanone	5.0	10.0	500
Isopropylbenzene	2.0	1.0	50
p-Isopropyltoluene	2.0	1.0	50
Methylene chloride	2.0	10.0	500
4-Methyl-2-pentanone	5.0	10.0	500
Methyl-tert-butyl-ether	2.0	2.0	100
Naphthalene	5.0	4.0	200
n-Propylbenzene	2.0	1.0	50
Styrene	1.0	2.0	100
1,1,1,2-Tetrachloroethane	1.0	1.0	50
1,1,2,2-Tetrachloroethane	1.0	1.0	50
Tetrachloroethene	1.0	1.0	50
Tetrahydrofuran	10.0	4.0	200
Toluene	1.0	1.5	75
1,2,3-Trichlorobenzene	2.0	4.0	200
1,2,4-Trichlorobenzene	2.0	4.0	200
1,1,1-Trichloroethane	1.0	1.0	50
1,1,2-Trichloroethane	1.0	1.5	75
Trichloroethene	1.0	1.0	50
Trichlorofluoromethane	2.0	4.0	200
1,2,3-Trichloropropane	2.0	4.0	200
1,2,4-Trimethylbenzene	2.0	4.0	200
1,3,5-Trimethylbenzene	2.0	4.0	200
Vinyl chloride	1.0	2.0	100
m/p-Xylenes	2.0	2.0	100
o-Xylene	1.0	2.0	100
Diisopropyl Ether	2.0	4.0	200
Ethyl-tert-butyl Ether	2.0	4.0	200
Tertiary-Amyl Methyl Ether	2.0	4.0	200
1,4-Dioxane	250	500	25000

(1) Detection Limits are for Low-level Sodium Bisulfate preserved samples.
(2) Detection Limits are for High-level Methanol preserved samples.

Table 4: Stock Standard Concentrations and Calibration Concentration Levels

Target Compounds	Stock (µg/mL)	Level 1 (ug/L)	Level 2 (ug/L)	Level 3 (ug/L)	Level 4 (ug/L)	Level 5 (ug/L)	Level 6 (ug/L)	Level 7 (ug/L)	Level 8 (ug/L
Acetone	2000	0.5	2	10	20	30	50	100	200
Benzene	2000	0.5	2	10	20	30	50	100	200
Bromobenzene	2000	0.5	2	10	20	30	50	100	200
Bromochloromethane	2000	0.5	2	10	20	30	50	100	200
Bromodichloromethane	2000	0.5	2	10	20	30	50	100	200
Bromoform	2000	0.5	2	10	20	30	50	100	200
Bromomethane	2000	0.5	2	10	20	30	50	100	200
2-Butanone	2000	0.5	2	10	20	30	50	100	200
n-Butyl benzene	2000	0.5	2	10	20	30	50	100	200
sec-Butyl benzene	2000	0.5	2	10	20	30	50	100	200
tert-Butyl benzene	2000	0.5	2	10	20	30	50	100	200
Carbon disulfide	2000	0.5	2	10	20	30	50	100	200
Carbon tetrachloride	2000	0.5	2	10	20	30	50	100	200
Chlorobenzene	2000	0.5	2	10	20	30	50	100	200
Chloroethane	2000	0.5	2	10	20	30	50	100	200
Chloroform	2000	0.5	2	10	20	30	50	100	200
Chloromethane	2000	0.5	2	10	20	30	50	100	200
o-Chlorotoluene	2000	0.5	2	10	20	30	50	100	200
p-Chlorotoluene	2000	0.5	2	10	20	30	50	100	200
Dibromochloromethane	2000	0.5	2	10	20	30	50	100	200
1,2-Dibromo-3-chloropropane	2000	0.5	2	10	20	30	50	100	200
1,2-Dibromoethane	2000	0.5	2	10	20	30	50	100	200
Dibromomethane	2000	0.5	2	10	20	30	50	100	200
1,2-Dichlorobenzene	2000	0.5	2	10	20	30	50	100	200
1,3-Dichlorobenzene	2000	0.5	2	10	20	30	50	100	200
1,4-Dichlorobenzene	2000	0.5	2	10	20	30	50	100	200
Dichlorodifluoromethane	2000	0.5	2	10	20	30	50	100	200
1,1-Dichloroethane	2000	0.5	2	10	20	30	50	100	200
1,2-Dichloroethane	2000	0.5	2	10	20	30	50	100	200
1,1-Dichloroethene	2000	0.5	2	10	20	30	50	100	200
cis-1,2-Dichloroethene	2000	0.5	2	10	20	30	50	100	200
trans-1,2-Dichloroethene	2000	0.5	2	10	20	30	50	100	200
1,2-Dichloropropane	2000	0.5	2	10	20	30	50	100	200
1,3-Dichloropropane	2000	0.5	2	10	20	30	50	100	200

Table 4 (continued): Stock Standard Concentrations and Calibration Concentration Levels

Target Compounds	Stock (µg/mL)	Level 1 (ug/L)	Level 2 (ug/L)	Level 3 (ug/L)	Level 4 (ug/L)	Level 5 (ug/L)	Level 6 (ug/L)	Level 7 (ug/L)	Level 8 (ug/L)
2,2-Dichloropropane	2000	0.5	2	10	20	30	50	100	200
1,1-Dichloropropene	2000	0.5	2	10	20	30	50	100	200
cis-1,3-Dichloropropene	2000	0.5	2	10	20	30	50	100	200
trans-1,3-Dichloropropene	2000	0.5	2	10	20	30	50	100	200
Ethylbenzene	2000	0.5	2	10	20	30	50	100	200
Ethyl ether	2000	0.5	2	10	20	30	50	100	200
Hexachlorobutadiene	2000	0.5	2	10	20	30	50	100	200
2-Hexanone	2000	0.5	2	10	20	30	50	100	200
Isopropylbenzene	2000	0.5	2	10	20	30	50	100	200
p-Isopropyltoluene	2000	0.5	2	10	20	30	50	100	200
Methylene chloride	2000	0.5	2	10	20	30	50	100	200
4-Methyl-2-pentanone	2000	0.5	2	10	20	30	50	100	200
Methyl-tert-butyl-ether	2000	0.5	2	10	20	30	50	100	200
Naphthalene	2000	0.5	2	10	20	30	50	100	200
n-Propylbenzene	2000	0.5	2	10	20	30	50	100	200
Styrene	2000	1	4	20	40	60	100	200	400
1,1,1,2-Tetrachloroethane	2000	0.5	2	10	20	30	50	100	200
1,1,2,2-Tetrachloroethane	2000	0.5	2	10	20	30	50	100	200
Tetrachloroethene	2000	0.5	2	10	20	30	50	100	200
Tetrahydrofuran	2000	0.5	2	10	20	30	50	100	200
Toluene	2000	0.5	2	10	20	30	50	100	200
1,2,3-Trichlorobenzene	2000	0.5	2	10	20	30	50	100	200
1,2,4-Trichlorobenzene	2000	0.5	2	10	20	30	50	100	200
1,1,1-Trichloroethane	2000	0.5	2	10	20	30	50	100	200
1,1,2-Trichloroethane	2000	0.5	2	10	20	30	50	100	200
Trichloroethene	2000	0.5	2	10	20	30	50	100	200
Trichlorofluoromethane	2000	0.5	2	10	20	30	50	100	200
1,2,3-Trichloropropane	2000	0.5	2	10	20	30	50	100	200
1,2,4-Trimethylbenzene	2000	0.5	2	10	20	30	50	100	200
1,3,5-Trimethylbenzene	2000	0.5	2	10	20	30	50	100	200
Vinyl chloride	2000	0.5	2	10	20	30	50	100	200
m/p-Xylenes	2000	1	4	20	40	60	100	200	400
o-Xylene	2000	1	4	20	40	60	100	200	400
Diisopropyl Ether	2000	0.5	2	10	20	30	50	100	200
Ethyl-tert-butyl Ether	2000	0.5	2	10	20	30	50	100	200
Tertiary-Amyl Methyl Ether	2000	0.5	2	10	20	30	50	100	200
1,4-Dioxane	10000	100	400	1000	1500	2000	3000	5000	10000

Table 4 (continued): Stock Standard Concentrations and Calibration Concentration Levels

Target Compounds	Stock (µg/mL)	Level 1 (ug/L)	Level 2 (ug/L)	Level 3 (ug/L)	Level 4 (ug/L)	Level 5 (ug/L)	Level 6 (ug/L)	Level 7 (ug/L)	Level 8 (ug/L)
Internal Standards									
Fluorobenzene	2500	10	10	10	10	10	10	10	10
Chlorobenzene-d5	2500	10	10	10	10	10	10	10	10
1,4-Dichlorobenzene-d4	2500	10	10	10	10	10	10	10	10
Surrogates									
Dibromofluoromethane	2500	10	10	10	10	10	10	10	10
1,2-Dichloroethane-d4	2500	10	10	10	10	10	10	10	10
Toluene-d8	2500	10	10	10	10	10	10	10	10
4-Bromofluorobenzene	2500	10	10	10	10	10	10	10	10

TABLE 5

MCP 8260B Volatile Internal Standards with Corresponding Target Compounds and Surrogates Assigned for Quantitation

Fluorobenzene	Chlorobenzene-d5	1,4-Dichlorobenzene-d4
dichlorodifluoromethane	toluene-d8 surr	bromoform
chloromethane	toluene	1,1,2,2,-tetrachloroethane
vinyl chloride	trans-1,3-dichloropropene	4-bromofluorobenzene surr
bromomethane	1,1,2-trichloroethane	1,2,3-trichloropropane
chloroethane	2-hexanone	trans-1,4-dichloro-2-butene
trichlorofluoromethane	1,3-dichloropropane	n-propylbenzene
ethyl ether	tetrachloroethene	bromobenzene
Freon 113	chlorodibromomethane	1,3,5-trimethybenzene
acetone	1,2-dibromoethane	2-chlorotoluene
1,1,-dichloroethene	chlorobenzene	4-chorotoluene
carbon disulfide	1,1,1,2-tetrachloroethane	tert-butylbenzene
methylene chloride	ethyl benzene	1,2,4-trimethylbenzene
acrylonitrile	p/m xylene	sec-butylbenzene
methyl tert butyl ether	o xylene	p-isopropyltoluene
Hexane	styrene	1,3-dichlorobenzene
trans-1,2-dichloroethene	isopropylbenzene	1,4-dichlorobenzene
Diisopropyl Ether		n-butylbenzene
1,1-dichloroethane		1,2-dichlorobenzene
Ethyl-Tert-Butyl-Ether		1,2-dibromo-3-chloropropane
2-butanone		1,2,4-trichlorobenzene
2,2-dichloropropane		hexachlorobutadiene
cis-1,2-dichloroethene		naphthalene
chloroform		1,2,3-trichlorobenzene
bromochloromethane		
tetrahydrofuran		
dibromofluoromethane		
1,1,1-trichloroethane		
1,1-dichloropropene		
carbon tetrachloride		
Tertiary-Amyl Methyl Ether		
1,2-dichloroethane-d4 surr		
1,2-dichloroethane		
benzene		
trichloroethene		
1,2-dichloropropane		
bromodichloromethane		
1,4-Dioxane		
dibromomethane		

TABLE 6

MCP 8260B Quantitation Ions

Compound	Quantitation Ion	Compound	Quantitation Ion
Dichlorodifluoromethane	85	toluene	92
Chloromethane	50	trans-1,3-dichloropropene	75
Vinyl Chloride	62	2-hexanone	43
Bromomethane	94	1,1,2-trichloroethane	83
Chloroethane	64	tetrachloroethene	166
Trichlorofluoromethane	101	chlorodibromomethane	129
Ethyl ether	74	1,2-dibromoethane	107
Acetone	43	chlorobenzene	112
1,1-Dichloroethene	96	1,1,1,2-tetrachloroethane	131
Methylene Chloride	84	ethyl benzene	91
Carbon disulfide	76	p/m xylene	106
Methyl tert butyl ether	73	o xylene	106
Trans-1,2-dichloroethene	96	styrene	104
Diisopropyl ether	45	bromoform	173
1,1-dichloroethane	63	isopropylbenzene	105
Ethyl-tert-butyl-ether	59	1,1,2,2-tetrachloroethane	83
2-butanone	43	1,2,3-trichloropropane	75
2,2-dichloropropene	77	n-propylbenzene	91
Cis-1,2-dichloroethene	96	bromobenzene	156
Chloroform	83	2-chlorotoluene	91
bromochloromethane	128	1,3,5-trimethylbenzene	105
tetrahydrofuran	42	4-chlorotoluene	91
1,1,1-trichloroethane	97	tert-butylbenzene	119
1,1-dichloropropene	75	1,2,4-trimethylbenzene	105
Tertiary-amyl methyl ether	73	sec-butylbenzene	105
carbon tetrachloride	117	p-isopropyltoluene	119
1,2-dichloroethane	62	1,3-dichlorobenzene	146
benzene	78	1,4-dichlorobenzene	146
trichloroethene	95	n-butylbenzene	91
1,2-dichloropropane	63	1,2-dichlorobenzene	146
bromodichloromethane	83	1,2-dibromo-3-chloropropane	75
1,4-dioxane	88	1,2,4-trichlorobenzene	180
dibromomethane	93	hexachlorobutadiene	225
4-methyl-2-pentanone	58	naphthalene	128
cis-1,3-dichloropropene	75	1,2,3-trichlorobenzene	180

Table 7: Difficult Analyte List

2-Butanone
Acetone
4-Methyl-2-Pentanone
2-Hexanone
Bromomethane
Bromoform
Dichlorodifluoromethane
1,2-Dibromo-3-Chloropropane
1,4-Dioxane
Chloromethane
2,2-Dichloropropane
Carbon Disulfide

Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)

References: **Method 8260C**, SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, 2005.

Method 5035A, Closed System Purge &Trap and Extraction for Volatile Organics in Soil and Waste Samples. SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update IV, Draft, July 2002.

Method 5030B, Purge & Trap for Aqueous Samples. SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update III, December, 1996.

1. Scope and Application

- **Matrices:** Method 8260 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including various air sampling trapping media, ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.
  Definitions: Refer to Alpha Analytical Quality Manual.

The following compounds may be determined by this method:

8260C LIST OF ANALYTES		
Dichlorodifluoromethane	Carbon tetrachloride	Isopropylbenzene
Chloromethane	1,2-Dichloroethane	1,4-Dichloro-2-butane
Vinyl chloride	Benzene	1,1,2,2-Tetrachloroethane
Chloroethane	Trichloroethene	Trans-1,4-dichloro-2-butene
Bromomethane	1,2-Dichloropropane	1,2,3-Trichloropropane
Trichlorofluoromethane	Bromodichloromethane	n-Propylbenzene
Ethyl ether	Dibromomethane	Bromobenzene
Acetone	4-Methyl-2-pentanone	2-Chlorotoluene
1,1-Dichloroethene	cis-1,3-Dichloropropene	1,3,5-Trimethylbenzene
Carbon disulfide	Toluene	4-Chlorotoluene
Methylene chloride	Trans-1,3-dichloropropene	Tert-butylbenzene
Acrylonitrile	Ethyl-methacrylate	1,2,4-Trimethylbenzene
Methyl-tert-butyl ether	1,1,2-Trichloroethane	Sec-butylbenzene
Trans-1,2-dichloroethene	2-Hexanone	p-Isopropyltoluene
1,1-Dichloroethane	1,3-Dichloropropane	1,3-Dichlorobenzene
Vinyl acetate	Tetrachloroethene	1,4-Dichlorobenzene
2-Butanone	Chlorodibromomethane	n-Butylbenzene
2,2-Dichloropropane	1,2-Dibromoethane	1,2-Dichlorobenzene
Cis-1,2-dichloroethene	Chlorobenzene	1,2-Dibromo-3-chloropropane
Chloroform	1,1,1,2-Tetrachloroethane	1,2,4-Trichlorobenzene
Bromochloromethane	Ethyl benzene	Hexachlorobutadiene
Tetrahydrofuran	p/m Xylene	Naphthalene
1,1,1-Trichloroethane	o Xylene	1,2,3-Trichlorobenzene

1,1-Dichloropropene	Styrene	Bromoform
Acrolein	2-Chloroethylvinyl ether	Ethanol
Cyclohexanone		

There are various techniques by which these components may be introduced into the GC/MS system. Purge-and-trap, by Methods 5030 (aqueous samples) and 5035A (solid and waste oil samples), is the most commonly used technique for volatile organic analytes. However, other techniques are also appropriate and necessary for some analytes. One technique is direct injection of an aqueous sample (concentration permitting).

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one or more of the following laboratory personnel before performing the modification: Area Supervisor, Department Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of analysts experienced in the operation of the gas chromatograph/mass spectrometers and in the interpretation of mass spectra and their use as a quantitative tool. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability, analyzing a proficiency test sample and completing the record of training.

After initial demonstration, ongoing demonstration is based on acceptable laboratory performance of at least a quarterly laboratory control sample or acceptable performance from an annual proficiency test sample. A major modification to this procedure requires demonstration of performance. The identification of major method modification requiring performance demonstration is directed by the Quality Assurance Officer and/or Laboratory Director on a case-by-case basis.

2. Summary of Method

The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by direct injection. The analytes are introduced to a narrow-bore capillary column for analysis. The Gas Chromatograph (GC) is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced to the GC.

Analytes eluted from the capillary column are introduced into the mass spectrometer via a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard, comparing sample response to the calibration standards.

2.1 Method Modifications from Reference

None.

3. Reporting Limits

Table 1 lists our typical reporting limits.

4. Interferences

4.1 Impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be free from contamination under the conditions of the analysis. Running laboratory reagent blanks as described in Section 10.3 and 9.1 demonstrates the system is free of contamination. The use of non-Teflon plastic tubing, non-Teflon thread sealants, or flow controllers with rubber components in the purge and trap system must be avoided.

4.2 Sample contamination occurs by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during shipment and storage. A trip blank or a field reagent blank prepared from reagent water and carried through the sampling and handling protocol serves as a check on such contamination.

4.2.1 Storage blanks shall be analyzed if contamination is suspect. If contamination is confirmed by positive detections in the sample storage blanks, all data from samples contained in the relative refrigerator or freezer shall be evaluated for possible contamination. If the samples contain suspected contamination, the Client Services department shall be notified in order to contact the necessary clients regarding the contamination. Samples shall be reanalyzed if so desired by the client. If suspected contamination is not confirmed by storage blanks, no further action shall be pursued concerning said blanks. It is recommended that further action be taken to determine the possible cause of suspected contamination.

4.3 Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. Whenever a highly concentrated sample is being encountered, it should be followed by an analysis of reagent water (instrument blank) to check for potential contamination. If carry-over is suspected, then numerous instrument blanks may be required; additionally all affected samples are rerun for confirmation.. In case of severe contamination, preventive maintenance of the entire system may be required.

5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichloroethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5.1 Lab coats, safety glasses, and gloves must be worn when handling samples, standards, or solvents.

5.2 All stock solution standard preparation must be performed in the volatiles hood. Initial calibration, continuing calibration, laboratory control sample and client sample dilutions do not need to be performed in the hood.

5.3 All expired standards must be placed into the waste bucket in the lab, for future disposal. The container must be labeled properly with hazard warning labels indicating the container contents.

5.4 Bottles containing Methanol must be stored in the flammables cabinet.

6. Sample Collection, Preservation, Storage, Shipping and Handling

6.1 Sample Collection and Preservation

6.1.1 Aqueous Samples

Grab samples are collected in standard 40mL amber glass screw-cap vials with Teflon lined silicon septa (VOA vial). Two or more VOA vials should be filled per sample location. EPA Method 8260 requires that samples be acidified to eliminate the possibility of biological degradation. Unless otherwise directed for project-specific reasons, all VOA vials are delivered to the client with approximately 2 – 4 drops of 1:1 HCl added to the vial, which is sufficient to adjust the pH of the sample to < 2. Prepared trip blanks are provided to the client to accompany field samples for QC purposes.

Fill the sample vial to the point of overflowing so that no headspace is contained within. Samples must be introduced into the vials gently to reduce agitation, which might drive off volatile compounds or cause loss of the HCl preservative.

Seal the bottle so that no air bubbles are in the VOA vial. If preservative has been added, shake vigorously for one minute. Invert the bottle and tap to check for air bubbles. Recollect the samples if any air bubbles are present.

Maintain the hermetic seal on the VOA vial until time of analysis.

6.1.2 Soil Samples

The recommended sampling method for soil samples is EPA 5035A. Method 5035A provides for two distinct sampling procedures, depending on the required reporting limits and suspected or known concentration levels of target analytes. These methods are referred to as the High Level and Low Level methods. Both are listed below, but depending on the samples only one of the methods may be required. If concentration levels are unknown, it is recommended that samples be collected using both procedures. The Lab will analyze the high level sample first, followed by the low level sample if the results from the high level analysis show that the sample is clean or contains analytes at low levels. The typical reporting levels of the two methods are listed in Table 1.

6.1.2.1 High Level Soil Samples

Collect sample in a standard 40mL amber glass screw-cap vial with Teflon lined silicon septa (VOA vial). The vial is provided containing 15mL of Purge and Trap Grade methanol, and is labeled and weighed prior to addition of sample. Record the weight of the vial with methanol on the vial label. Prepared trip blanks are provided to the client to accompany field samples for QC purposes.

Approximately 15g of soil is added to the vial in the field, making sure that the sample is completely covered by the methanol.

Maintain the hermetic seal on the VOA vial until the time of analysis.

An additional sample of the soil must also be obtained (without methanol) to be used for the determination of soil moisture content to allow for the calculation of the dry weight results, and to calculate the methanol dilution effect. (See Sections 11.1.2.2.2 and 11.1.2.2.3)

6.1.2.2 Low Level Soil Samples

Collect sample in a standard 40mL amber glass screw-cap vials with Teflon lined silicon septa (VOA vial). Two samples should be taken per sample location. Vials are provided containing a magnetic stirring bar and 5 mL of either 200g/L sodium bisulfate solution or water, prepared by a certified vendor. These vials are labeled and weighed prior to addition of sample. Record the weight of the vial with the stirring bar and preservative on the vial label.

Approximately 5g of soil is added to the vial in the field, making sure that the sample is completely covered by the sodium bisulfate solution or water.

Maintain the hermetic seal on the VOA until the time of analysis.

6.2 Sample Handling and Storage

Document client specific sample handling, preservation and collection criteria in the project file. The laboratory Log-in staff documents sample temperature at the time of receipt.

Record deviations from this SOP or client specific criteria on the chain of custody form.

Record holding time exceedence, improper preservation and observed sample headspace on the nonconformance report form.

6.2.1 Aqueous Samples

Ice or refrigerate all samples from the time of collection until analysis, maintaining the sample temperature between 1 and 4 °C. Sample receiving personnel note on the sample delivery group form when samples received at the laboratory are not within the temperature criteria. If more than one vial is received for a sample the vials are stored in separate refrigerators. Storing the vials apart provides a useful check if laboratory contamination of a sample is suspected. Samples must be analyzed within 14 days of collection. Unpreserved samples requiring aromatic analysis must be analyzed within 7 days of collection.

6.2.2 High Level Soil Samples

Ice or refrigerate all samples from the time of collection until analysis, maintaining the sample temperature between 2 and 6 °C. Sample receiving personnel note on the nonconformance report form when samples received at the laboratory are not within the temperature criteria.

6.2.3 Low Level Soil Samples

Ice or refrigerate samples preserved with water or sodium bisulfate from the time of collection until analysis, maintaining the sample temperature between 2 and 6 °C. Samples preserved with water are to be immediately frozen after sampling. Sample receiving personnel note on the nonconformance report form when samples received at the laboratory are not within the temperature criteria.

6.3 Sample Shipping

Samples requiring shipment to the laboratory are shipped in ice-packed coolers via an overnight delivery service in accordance with applicable Department of Transportation regulations.

7. Equipment and Supplies

7.1 Purge and Trap System (For Aqueous samples and High Level Soils): The purge-and-trap system consists of two separate pieces of equipment: a purging device (autosampler) (Varian Archon/8100, Tekmar Solatek, EST Centurion) coupled to the desorber (concentrator) (Tekmar Velocity or EST Encon).

7.1.1 Purge gas = Helium, analytical grade (99.999%).

7.1.2 The purging device is configured with 25 mL sample purge tubes, and the helium purge gas is introduced at the bottom of the water column as finely divided bubbles

7.1.3 The trap used in the desorber is typically a Supelco "K" trap. Different traps may be used if equivalent performance is demonstrated.

7.1.4 The desorber is capable of rapidly heating the trap to 260^{o}C. The trap is not heated above manufacturer's specifications

7.2. Purge and Trap System (For Low Level Soil Samples): The purge and trap system consists of two separate pieces of equipment: a purging device (autosampler) coupled to the desorber (concentrator) (Varian Archon/8100, Tekmar Solatek, EST Centurion with EST Encon, Tekmar Velocity, or equivalents).

7.2.1. Purge gas = Helium, analytical grade (99.999%).

7.2.2. The autosampler purging device is a closed system, designed to accept the 40mL VOA vials. The VOA vial, containing the soil sample, water (or sodium bisulfate), and stirring bar is placed into the autosampler tray. The instrument automatically adds reagent water, internal standards, and surrogates to the unopened VOA vial. The vial is heated to 40 °C, and the helium purge gas is introduced into the aqueous portion to purge the volatile components onto the trap.

7.2.3. The trap used in the desorber is typically a Supelco "K" trap. Different traps may be used if equivalent performance is demonstrated.

7.2.4. The desorber is capable of rapidly heating the trap to 260 °C. The trap is not heated above manufacturer specifications.

7.3 Gas Chromatography/Mass Spectrometer/Data System:

7.3.1 Gas Chromatograph, Hewlett Packard 6890/7890 or equivalent: An analytical system complete with a temperature-programmable gas chromatograph with appropriate interface for sample introduction device. The system includes all required accessories, including syringes, analytical columns, and gases. The capillary column is directly coupled to the source of the GC/MS system.

7.3.2 Typical Gas Chromatographic Columns:

7.3.2.1 Column 1: Restek 502.2, 40 meter, 0.18mm ID, or equivalent.
7.3.2.2 Column 2: Restek RTX-VMS, 30 meter, 0.25mm ID, or equivalent

7.3.3 Mass Spectrometer, Hewlett Packard 5973/5975 or equivalent: Scanning from 35 to 300 amu every 2 seconds or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for 4-Bromofluorobenzene (BFB) which meets all of the criteria in Table 3, when 50ng of the GC/MS tuning standard (BFB) are injected through the GC.

7.3.4 Data System: Hewlett-Packard EnviroQuant software is used for data acquisition, and allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program.

Thruput Target 4.12 software is used for data processing, and allows searching of any GC/MS data file for ions of a specified mass, and plotting such ion abundances versus time or scan-number.

The most recent version of the EPA/NIST Mass Spectral Library is loaded onto the Target data system.

7.4 Wiretrol or Microsyringes: 10µL - 1,000µL.

7.5 Syringes: 5mL, 10mL, or 25mL, glass with Luerlock tip.

7.6 Balances: Top-loading, capable of weighing 0.1g.

7.7 Vials: 2mL, 4mL.

7.8 Disposable Pipets.

7.9 Volumetric Flasks: Class A, appropriate sizes, with ground-glass stoppers.

7.10 Eppendorf Pipets

8. Reagents and Standards

Reagent grade organic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all organic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

Great care must be taken to maintain the integrity of all standard solutions. Standards in methanol are stored at –10ºC or less, in amber vials with PTFE-lined screw-caps.

8.1 Organic-free Reagent Water:

All references to water in this method refer to organic-free reagent water, which is tap water passed through activated carbon and air bubbled through.

8.2 Methanol:

Purge and Trap Grade or equivalent. Store in flammables cabinet.

8.3 Stock Solutions:

All stock standard solutions are purchased from commercial vendors as ampulated certified solutions. When an ampulated stock solution is opened, it is transferred to a labeled amber screw-cap vial with minimal headspace. The expiration date of the stock solution is either the vendor specified expiration date or 6 months from the date the ampule was opened, whichever is sooner. Typical stock standard concentrations are listed in Table 4.

8.4 Intermediate Standards: Intermediate standards are prepared volumetrically by diluting the appropriate stock standard(s) with methanol. Initial Calibration solutions expire 2 months from the date of preparation, or sooner if daily continuing calibration checks do not achieve the method acceptance criteria. If the Intermediate Standards are used as a second source to verify a valid Initial Calibration solution, there is no expiration date.

8.4.1 Internal Standard Solutions:

The internal standards are Fluorobenzene, Chlorobenzene-d_5, and 1,4-Dichlorobenzene-d_4. The intermediate IS solution is prepared by diluting the stock solution(s) with methanol to a concentration of100 µg/mL. The appropriate amount of IS solution is added to the water or soil sample or QC sample to achieve a final concentration of 100 ng/sample or standard. Internal standard is added at the same concentration to all standards, samples, and QC samples.

8.4.2 Surrogate Standard Solutions:

The surrogate standards are Dibromofluoromethane, 1,2-Dichloroethane-d_4, Toluene-d_8, and 4-Bromofluorobenzene. The intermediate surrogate solutions is prepared by diluting the stock solution(s) with methanol to a concentration of 100 µg/mL. The appropriate amount of surrogate solution is added to the water or soil sample or QC sample to achieve a final concentration of 100 ng/sample.

8.4.3 Target Compound Solutions:

The target analytes routinely reported by this method are listed in Table 4. The intermediate target compound solutions are prepared by diluting the stock solution(s) with methanol. This set of solutions, at concentrations of 200 µg/mL, is used for preparation of the calibration standards at the concentrations listed in Table 4.

8.4.4 4-Bromofluorobenzene (BFB) Tune solution:

A solution containing BFB at a concentration of 25 µg/mL is prepared by volumetrically diluting the BFB stock solution. 2 µL of this solution is direct-injected or purged into the GC/MS system to verify system performance prior to any standard or sample analysis.

8.5 Calibration Standards:

There are two types of calibration standards used for this method – initial calibration standards and calibration verification standards.

8.5.1 Initial Calibration Standards:

Initial calibration standards are prepared at the levels listed in Table 4. Prepare these solutions in organic-free reagent water. The standards correspond to the range of concentrations found in typical samples and do not exceed the working range of the GC/MS system. Initial calibration should be mixed from fresh stock standards and dilution standards when generating an initial calibration curve.

8.5.2 Initial Calibration Verification Standard (ICV):

The initial calibration verification standard is at the same concentration as the level 3 initial calibration standard. This standard is made from a second source than the Initial Calibration Standards.

8.5.3 Continuing Calibration Verification Standard:

The continuing calibration verification standard, or calibration check standard, is at the same concentrations as the level 3 initial calibration standard. This standard is run at the beginning of each analytical sequence, following the BFB tune standard, to verify system performance.

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blank(s)

Blank samples must be matrix specific, i.e. methanol samples need to have methanol in the blank; sodium bisulfate samples need to have a sodium bisulfate blank analyzed; TCLP samples need a TCLP blank.

Analyze a matrix-specific blank each day prior to sample analysis to demonstrate that interferences from the analytical system are under control. The blank must contain the internal standards and surrogates.

Analyze the reagent water blank from the same source of water used for preparing the standards, QC samples and making sample dilutions. The method blank must not contain any target analytes at or above the compound reporting limits.

9.2 Laboratory Control Sample (LCS)/ Laboratory Control Sample Duplicate (LCSD)

A LCS/LCSD pair is analyzed at the beginning of each analytical sequence. Since the LCS contains the same compounds at the same concentrations as the continuing calibration check standard, the same analysis is used to satisfy both QC elements. The LCS/LCSD acceptance criteria are based on in-house control limits.

9.3 Initial Calibration Verification (ICV)

Refer to Section 10.4

9.4 Continuing Calibration Verification (CCV)

Refer to Section 10.4.

9.5 Matrix Spike/ Matrix Spike Duplicate

Upon Client Request, a matrix spike/matrix spike duplicate pair may be analyzed with each batch of 20 or less samples. The MS/MSD are sample aliquots spiked with the target compounds at the same concentration as the continuing calibration standard. The MS/MSD acceptance criteria are based on in-house control limits. If the MS/MSD does not meet the criteria, but the LCSD does, the failure may be attributed to sample matrix. Report the MS/MSD, including a narrative sheet for inclusion with the client report.

9.6 Laboratory Duplicate

Not applicable.

9.7 Method-specific Quality Control Samples

9.7.1 Internal Standards

Area counts of the internal standard peaks in all samples and QC samples must be between 50-200% of the areas of the internal standards in the QC check standard.

If any individual percent recovery falls outside the range, that parameter has failed the acceptance criteria. For calibration standards, CCVs, LCS/LCSD or blanks the internal standard must be within the range for data to be reported to the clients. For samples, matrix spikes and duplicates: if the data is not within the range, the sample is rerun to confirm that the failure is due to sample matrix. A nonconformance report form is completed to ensure client notification and reporting if matrix effect is confirmed.

9.7.2 Surrogates

Surrogates are added to each field sample and QC sample. The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. The surrogate acceptance criteria are listed in Table 2.

9.8 Method Sequence

In a 12-hour period, the typical analytical sequence is as follows:

- BFB
- QC Check Standard/Laboratory Control Sample/LCSD
- Method Blank
- Samples
- MS/MSD (upon Client request, may be run anytime after the Method Blank)

10. Procedure

10.1 Equipment Set-up

Typical instrument operating conditions are listed below. Alternate conditions are allowed, as long as method performance criteria can be met.

10.1.1 GC Conditions:

Temperature 1:	35°C	Carrier gas:	Helium, 99.999%
Hold Time 1:	4 minutes	Carrier mode:	Constant flow
Ramp 1:	6°C/minute	Carrier flow:	1 mL/minute
Temperature 2:	150°C		
Hold Time 2:	0 minutes		
Ramp 2:	8°C/minute		
Temperature 3:	220°C		
Final Time:	1 minute		

10.1.2 MS Conditions:

Mass scan range:	35 – 260 amu
Scan time:	0.5 minutes/scan
Source temperature:	230°C

10.1.3 Velocity Concentrator Purge and Trap Conditions:

Purge time:	11 minutes
Dry purge:	2 minutes
Desorb preheat:	250°C
Desorb temp:	255°C
Desorb time:	2 minutes
Bake temp:	290°C
Bake time:	10 minutes

10.1.4 Encon Concentrator Purge and Trap Conditions:

Purge time:	11 minutes
Dry purge:	1 minute
Desorb preheat:	245°C
Desorb temp:	255°C
Desorb time:	1 minute
Bake temp:	270°C
Bake time:	10 minutes

10.2 Initial Calibration

10.2.1 The initial calibration is performed at a minimum of five (5) concentration levels listed in Table 4, the low level of the either at or below the reporting limit. The calibration is performed using instrument conditions listed in Section 10.1.

BFB must be analyzed prior to analysis of the initial calibration standards, and must pass the criteria listed in Table 3. The mass spectrum of BFB should be acquired in the following manner:

(1) Three scans (the peak apex scan, the scan immediately preceding the apex and the scan immediately following the apex) are acquired and averaged.
(2) Background subtraction is performed using a single scan of no more than 20 scans prior to the elution of BFB.

This is done automatically with the ThruPut Target software.

10.2.1.1 **Low Level/High Level Soil Curve on Archon or Centurion:** To prepare a calibration standard, add the appropriate volume of standard solution(s) to a 50mL volumetric flask using a microsyringe. Remove the needle quickly and mix by inverting the flask 3 times. Pour several mLs of the aqueous standard into the waste vessel, then gently fill a 5mL syringe with standard and transfer to a 40mL VOA vial containing a magnetic stir bar. Load the vial onto Archon Autosampler.

10.2.1.2 **Aqueous/High Level Soil Curve on Solatek or Centurion:** To prepare a calibration standard, add the appropriate volume of standard solution(s) to a 100mL volumetric flask using a microsyringe. Remove the needle quickly and mix by inverting the flask 3 times. Pour several mLs of the aqueous standard into the waste vessel, then gently fill a 40mL VOA vial to the top. Load the vial onto the Autosampler.

10.2.2 Establish the GC operating conditions by loading the appropriate GC method. Typical instrument conditions are listed in Section 10.1. The same operating conditions are used for calibration and sample analyses. Create the analytical sequence using the HP Enviroquant data acquisition software.

Relative Response Factors: The internal standard calibration technique is used. In each calibration standard, calculate the relative response factor for each analyte and the relative standard deviation (RSD) of the response factors using the Target data processing software. The response factors are calculated using the areas of the characteristic (quantitation) ion for each target analyte and internal standard. The calculations are performed automatically using the Target software, using the formulae listed in Alpha's Quality Manual.

10.2.3 **Initial Calibration Criteria:** The following sections outline the method acceptance criteria for an initial calibration curve. All criteria must be met for the calibration to be deemed acceptable, and for sample analysis to proceed.

10.2.3.1 **Relative Standard Deviation Criteria:** If the RSD for each target analyte is less than or equal to 20%, then the response for this compound is considered linear over the calibration range and the mean calibration factor can be used to quantitate sample results. If the 20% RSD criterion is not met for an analyte linear regression may be used if $\mathbf{r} \geq 0.990$, weighted linear with a weighting factor of 1/SD2 and $r > 0.990$, or quadratic fit if $\mathbf{r^2} \geq 0.995$. A minimum of six points is required and the low point of the calibration must be re-quantitated and recover within 70-130% to be deemed acceptable. The calibration must be repeated for any compounds that fail. If more than 10% of the compounds exceed the 20% RSD limit and do not achieve the minimum correlation coefficient for alternative curve fits, sample analysis cannot proceed.

10.2.3.2 **Minimum Response Factors:** Table 1 lists the minimum response factors for the most common analytes. Each calibration level must be evaluated against the specified criteria. Analytes that fall below the criteria, but are greater than or equal to 0.05, are narrated for inclusion on the final report. If an analyte falls below 0.05, then corrective action must be taken to resolve the problem before analysis can proceed.

10.2.4 Evaluation of Retention Times: The relative retention times used for identification of target analytes are +/- 0.06 RRT (Relative Retention Time) units, based on the most recent standard run. It has been determined that these limits work well, being wide enough to eliminate false-negative results while being tight enough to eliminate false positive results. Due to the selectivity of the mass spectrometer, compound identification is more definitive than when using a less selective detector.

10.2.5 Initial Calibration Verification: Immediately after each calibration before the analysis of samples, an ICV must be analyzed at or near the midpoint of the curve. The ICV must be prepared using a different source than the Initial Calibration and must contain all target analytes. The percent recoveries must be between 70% and 130% for target analytes except for "difficult" analytes (Table 7), which must exhibit percent recoveries between 40% and 160%. Corrective action is required if greater than 10% of all analytes are outside the prescribed criteria.

10.3 Equipment Operation and Sample Processing

The same GC, MS, and Purge and Trap conditions used for the initial calibration must be employed for sample analysis. After verification of system performance by analysis of BFB, the continuing calibration standard and method blank, samples are analyzed and processed as described below.

10.3.1 Analysis of Samples

Retrieve sample VOA vials from the sample bank refrigerator just prior to loading onto the purge and trap system. High level soil samples must be shaken for 1 – 2 minutes to extract the volatile components into the methanol. Let sample settle prior to taking methanol aliquot. Low level soil sample should be shaken briefly to ensure that the stir bar is loose, and will spin on the Archon or Centurion unit.

10.3.1.1 Low level soil samples: (Archon or Centurion)
Take the low level VOA vial and place directly into the rack of the Archon sampling unit. Surrogate and internal standards are added automatically by the Archon prior to sample purging.

10.3.1.2 Aqueous samples: (Solatek or Centurion)
Load the VOA vial directly on the sampling rack. Dilutions may be prepared volumetrically and poured into VOA vials ensuring there is no headspace left in the vial. The auto-sampler will then sample 10mL from the VOA vial.

10.3.1.3 High level soil samples: (Archon/Solatek/Centurion)

Shake for 2 minutes, ensuring the methanol has completely penetrated the soil in the vial.

10.3.1.3.1 Through liquid path
Load a maximum of 430µL or appropriate dilution of the methanol into a half-full VOA vial. Fill the VOA vial up to the top with water and cap with no headspace. Allow the auto-sampler to sample 10mL out of the VOA vial which would be equivalent to injecting 100µL of the methanol extract. Prepare dilutions accordingly.

10.3.1.3.2 Through soil path

Into a VOA vial with a stir bar added, load 4.9mL of water plus a maximum of 100 μL of methanol or appropriate dilution of methanol extract from a 5mL luerlock syringe. Cap the vial and load onto the auto-sampler.

10.3.2 Qualitative Analysis:

10.3.2.1 The qualitative identification of each compound is based on retention time and on comparison of the sample mass spectrum with the reference mass spectrum. The reference mass spectrum must be generated by the laboratory on the same GC/MS system. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met:

10.3.2.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. The Target data system is configured to make this check.

10.3.2.1.2 The relative retention time (RRT) of the sample component is within ±0.06 RRT units of the RRT of the standard component.

10.3.2.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

10.3.2.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs (i.e., m and p-xylene).

10.3.2.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

10.3.2.1.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

10.3.2.2 For samples containing non-target analytes, a library search will be performed at client request. Compound identification will be classified as “tentative”, and the concentration will be reported as an estimate as no quantitative standards are run for these compounds.

1) Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

2) The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%.)

3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks.

10.3.3 Quantitative Analysis:

10.3.3.1 Quantitation of a target compound detected in a sample is performed automatically by the Target data processing software, using the formulae found in Alpha's Quality Manual. Either the average response factor or calibration curve will be used for sample quantitation, depending on how the particular analyte was processed in the initial calibration curve.

If non-target compounds are to be reported, the quantitation is performed automatically by the Target software using the total area of the compound and the nearest internal standard, and assuming a relative response factor of 1.0.

10.4 Continuing Calibration

Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

10.4.1 Prior to the analysis of samples or calibration standards, inject or purge 2 µL (50 ng) of the 4-Bromofluorobenzene standard (Section 8.4.4) into the GC/MS system. The resultant mass spectra for the BFB must meet the criteria given in Table 3 before sample analysis begins.

10.4.2 The initial calibration curve for each compound of interest must be verified once every 12 hours prior to sample analysis. This is accomplished by analyzing the continuing calibration check standard (Section 8.5.2). The results from the calibration standard analysis must meet the verification acceptance criteria provided in Section 10.5.

10.4.3 A method blank must be analyzed prior to any samples, typically immediately following the continuing calibration check standard, to ensure that the analytical system is free of contaminants. The method blank must not contain any target analytes at or above the required compound reporting limits.

10.4.4 The percent difference or drift for each target analyte must be less than or equal to 20%. If greater than 20% of target analytes exceed the %D criteria corrective action must be taken prior to the analysis of samples. If less than or equal to 20% of compounds exceed

the criteria, corrective action is not required as long as the %D is less than 40% and less than 60% for difficult analytes.

10.4.5 The continuing calibration standard must also be evaluated for the minimum response factor criteria, as specified in section 10.2.3.2

10.4.6 Internal Standard Retention Time:

The retention times of the internal standards in the calibration verification standard are evaluated after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

10.4.7 Internal Standard Response:

If the area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to +100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, re-analysis of samples analyzed while the system was malfunctioning is required.

10.5 Preventive Maintenance

Routine preventive maintenance should be performed on the analytical system. This includes replacement of GC septa and periodic rinsing or replacement of purge and trap tubes and sparge needles. The trap should be replaced every six months, or sooner if performance criteria cannot be met. Periodic cleaning (typically twice per year) of the mass spectrometer ion source is required. More frequent source cleaning may be needed, especially if dirty samples are analyzed.

If system performance deteriorates, additional maintenance may be required. This includes replacement of injector ports and seals, clipping several inches off of the front end of the GC column, or in extreme cases the replacement of the GC column. Flushing or replacement of purge and trap lines may be necessary if they become contaminated or develop active sites.

Perform routine preventative maintenance as described throughout this SOP. Record all maintenance in the instrument logbook.

11. Data Evaluation, Calculations and Reporting

11.1.1 LIMS Data Corrections

Please note that the Laboratory Information Management System (LIMS) automatically adjusts soil sample results to account for the % Total Solids of the sample (as determined per Alpha SOP/07-38) and the methanol preservation dilution effect.

11.1.2 Data Calculations

11.1.2.1 Results of Aqueous Sample Analysis:

$$concentration\ (ug/L) = \frac{(Conc.)\ (Vp)\ (DF)}{(Vs)}$$

where:

Conc. = On-column concentration obtained from the quantitation report.
Vp = Volume purged, 10 mL is standard
Vs = Volume of sample purged
DF = Dilution factor, for manually prepared dilutions, not instrumental "dilutions".

11.1.2.2 Results of Sediment/Soil, Sludge, and Waste Analysis: All solids including soils, sediments, and sludges must be reported on a dry-weight basis.

11.1.2.2.1 Low-Level Samples:

$$concentration\ (ug/Kg) = \frac{(Conc.)\ (Vp)\ (DF)}{(W)\ (\%S)}$$

11.1.2.2.2 High-Level Samples:

$$concentration\ (ug/Kg) = \frac{(Conc.)\ (Vp)\ (5000)\ (DF)}{(W)\ (Ve)\ (\%S)}$$

where:

Conc. = On-column concentration obtained from the quantitation report.
DF = Dilution factor, for manually prepared dilutions, not instrumental "dilutions".
Ve = Extract volume, mL
Vp = Volume purged, 5 mL is standard
W = Aliquot of sample (wet), g
%S = Sample % solid
5000 = Constant representing the final volume of the methanol extraction.

11.1.2.2.3 High-Level Samples Corrected for Total Water/Solvent Mixture (V_t):

Samples that are extracted prior to analysis in a water miscible solvent such as methanol are diluted by the total volume of the water/solvent mixture. The total mixture volume can only be calculated based on the sample moisture present as determined by the % moisture calculation.

$$\%\ moisture = \frac{g\ of\ sample - g\ of\ dry\ sample}{g\ of\ sample} \times 100$$

$$V_t = \frac{[mL\ of\ solvent + (\%moisture \times g\ of\ sample)]}{100} \times 1000mL/mL$$

The calculated V_t value is now added to the volume of methanol in the sample (typically 5000µL), and the corrected concentration is calculated using the equation below:

$$\textit{Corrected concentration (mg/Kg)} = \frac{\textit{(Conc.) (}V_t\textit{ + methanol vol.) (Vp) (DF)}}{\textit{(W) (Ve) (\%S)}}$$

12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

All batch and sample specific QC criteria outlined in section 10 are evaluated by the analyst prior to approval of the data. When any QC criteria fail, the cause for the failure must be identified and corrected. This may include instrument recalibration followed by sample reanalysis, sample cleanup, or sample re-extraction. If it is determined that the failure is due to sample matrix effects, a project narrative report is written by the analyst for inclusion in the data report. If there is insufficient sample volume to perform the re-analysis for confirmation, this is also noted in the narrative and included in the client report.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/08-05. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP/08-12 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

SOP/08-05 MDL/LOD/LOQ Generation

SOP/08-12 IDC/DOC Generation

SOP/14-01 Waste Management and Disposal SOP

16. Attachments

TABLE 1: 8260 REPORTING LIMITS

TABLE 2: 8260 QC ACCEPTANCE CRITERIA

TABLE 3: BFB TUNING CRITERIA

TABLE 4: STANDARD SOLUTIONS

TABLE 5: 8260C Volatile Internal Standards with Corresponding Target Compounds and Surrogates Assigned for Quantitation

TABLE 6: 8260C Quantitation Ions

Table 1
Standard Reported Detection Limits
US EPA METHOD 8260C and 5035A/8260C

Analyte	Minimum Response Factor	RDL (µg/L)	RDL(µg/KG)[1]	RDL (µg/KG)[2]
Acetone [3,4,5]	0.100	5.0	10	250
Acrolein [5]		5.0	25	1250
Acrylonitrile [3,4]		5.0	5	200
Benzene [3,4,5]	0.500	0.5	1	50
Bromobenzene [3,4]		2.5	5	250
Bromochloromethane [3,4,5]		2.5	5	250
Bromodichloromethane [3,4,5]	0.200	0.5	1	50
Bromoform [3,4,5]	0.100	2.0	4	200
Bromomethane [3,4,5]	0.100	1.0	2	100
2-Butanone [3,4,5]	0.100	5.0	10	500
n-Butyl benzene [3,4]		0.5	1	50
sec-Butyl benzene [3,4]		0.5	1	50
tert-Butyl benzene [3,4]		2.5	5	250
Carbon disulfide [3,4,5]	0.100	5.0	10	500
Carbon tetrachloride [3,4,5]	0.100	0.5	1	50
Chlorobenzene [3,4,5]		0.5	1	50
Chloroethane [3,4,5]	0.100	1.0	2	100
2-Chloroethylvinyl ether [3]		10.0	20	1000
Chloroform [3,4,5]	0.200	0.75	1.5	75
Chloromethane [3,4,5]	0.100	2.5	5	250
o-Chlorotoluene [3,4]		2.5	5	250
Cyclohexane [5]	0.100	10	20	1000
Cyclohexanone		10	20	1000
p-Chlorotoluene [3,4]		2.5	5	250
Dibromochloromethane [3,4,5]	0.100	0.5	1	50
1,2-Dibromo-3-chloropropane [3,4,5]	0.050	2.5	5	250
1,2-Dibromoethane [3,4,5]	0.100	2.0	5	250
Dibromomethane [3,4]		5.0	10	500
1,2-Dichlorobenzene [3,4,5]	0.400	2.5	5	250
1,3-Dichlorobenzene [3,4,5]	0.600	2.5	5	250
1,4-Dichlorobenzene [3,4,5]	0.500	2.5	5	250
1,4-Dichlorobutane [3,4]		5.0	10	500
trans-1,4-Dichloro-2-butene [3,4]		2.5	5	250
Dichlorodifluoromethane [3,4,5]		5.0	10	500
1,1-Dichloroethane [3,4,5]	0.200	0.75	1.5	75
1,2-Dichloroethane [3,4,5]	0.100	0.5	1	50
1,1-Dichloroethene [3,4,5]	0.100	0. 5	1	50
cis-1,2-Dichloroethene [3,4,5]	0.100	0.5	1	50
trans-1,2-Dichloroethene [3,4,5]	0.100	0.75	1.5	75

Table 1 (continued)
Standard Reported Detection Limits
US EPA METHOD 8260C and 5035A/8260C

Analyte	Minimum Response Factor	RDL (µg/L)	RDL(µg/KG)[1]	RDL (µg/KG)[2]
1,2-Dichloropropane [3,4,5]	0.100	1.75	3.5	175
1,3-Dichloropropane [3,4]		2.5	5	250
2,2-Dichloropropane [3,4]		2.5	5	250
1,1-Dichloropropene [3,4]		2.5	2.5	250
cis-1,3-Dichloropropene [3,4,5]	0.200	0.5	1	50
p-Diethylbenzene [4]		2.0	4	200
Diisopropyl Ether [6]		2.0	4	200
1,4-Dioxane [5]		250	100	5000
trans-1,3-Dichloropropene [3,4,5]	0.200	0.5	1	50
Ethanol [7]		N/A	1000	50000
Ethylbenzene [3,4,5]	0.100	0.5	1	50
Ethyl ether [3,4]		2.5	5	250
4-Ethyltoluene [4]		2.0	4	200
Ethyl methacrylate [3,4]		5.0	10	500
Ethyl-Tert-Butyl-Ether [6]		2.0	4	200
Freon-113 [5]		10.0	20	1000
Hexachlorobutadiene [3,4]		0.5	5	250
2-Hexanone [3,4,5]	0.100	5.0	10	500
Isopropylbenzene [3,4,5]	0.100	0.5	1	50
p-Isopropyltoluene [3,4]		0.5	1	50
Methyl Acetate [5]	0.100	20	20	1000
Methylene chloride [3,4,5]	0.100	3.0	10	500
Methyl Cyclohexane [5]	0.100	20	4	200
4-Methyl-2-pentanone [3,4,5]	0.100	5.0	10	500
Methyl-tert-butyl-ether [3,4,5]	0.100	1.0	2	100
Naphthalene [3,4]		2.5	5	250
n-Propylbenzene [3,4]		0.5	1	50
Styrene [3,4,5]	0.300	1.0	2	100
Tert-Butyl Alcohol [5]		30	100	5000
Tertiary-Amyl Methyl Ether [6]		2.0	4	200
1,1,1,2-Tetrachloroethane [3,4]		0.5	1	50
1,2,4,5-Tetramethylbenzene [4]		2.0	4	200
1,1,2,2-Tetrachloroethane [3,4,5]	0.300	0.5	1	50
Tetrachloroethene [3,4,5]	0.200	0.5	1	50
Tetrahydrofuran [3]		10.0	20	1000
Toluene [3,4,5]	0.400	0.75	1	75
1,2,3-Trichlorobenzene [3,4,5]		2.5	5	250
1,2,4-Trichlorobenzene [3,4,5]	0.200	2.5	5	250

1,3,5-Trichlorobenzene (6)		2.0	5	250
1,1,1-Trichloroethane (3,4,5)	0.100	0.5	1	50
1,1,2-Trichloroethane (3,4,5)	0.100	0.75	1.5	75
Trichloroethene (3,4,5)	0.200	0.5	1	50
Trichlorofluoromethane (3,4,5)	0.100	2.5	5	250
1,2,3-Trichloropropane (3,4)		5.0	10	500
1,2,4-Trimethylbenzene (3,4)		2.5	5	250
1,3,5-Trimethylbenzene (3,4)		2.5	5	250
Vinyl acetate (3,4)		5.0	10	500
Vinyl chloride (3,4,5)	0.100	1.0	2	100
m/p-Xylenes (3,4,5)	0.100	1.0	2	100
o-Xylene (3,4,5)	0.300	1.0	2	100

(1) Detection Limits are for Low-level Aqueous preserved samples.
(2) Detection Limits are for High-level Methanol preserved samples.
(3) Analyte reported by standard 8260 reporting list.
(4) Analyte reported by New York TCL reporting list.
(5) Analyte reported by New Jersey TCL reporting list.
(6) Analyte reported for New Hampshire in addition to standard 8260 reporting list.
(7) Analyte only reported for New York TCL report upon client request.

Note: Reporting Limits are based on standard 8260 reporting list, RL's may vary for New York and New Jersey reporting lists.

Table 2

QUALITY CONTROL ACCEPTANCE CRITERIA

Surrogate Spike Percent Recovery	Aqueous Limits		Soil Limits	
	Lower Control Limit	Upper Control Limit	Lower Control Limit	Upper Control Limit
1,2-Dichloroethane-d_4	70%	130%	70%	130%
4-Bromofluorobenzene	70%	130%	70%	130%
Toluene-d_8	70%	130%	70%	130%
Dibromofluoromethane	70%	130%	70%	130%

Table 3

BFB (4-BROMOFLUOROBENZENE) MASS INTENSITY CRITERIA

m/z	Required Intensity (relative abundance)
50	15 to 40% of m/z 95
75	30 to 60% of m/z 95
95	Base peak, 100% relative abundance
96	5 to 9% of m/z 95
173	Less than 2% of m/z 174
174	Greater than 50% of m/z 95
175	5 to 9% of m/z 174
176	Greater than 95% but less than 101% of m/z 174
177	5 to 9% of m/z 176

Table 4

Stock Standard Concentrations and Calibration Concentration Levels

Target Compound	Stock (µg/mL)	Level 1 (µg/L)	Level 2 (µg/L)	Level 3 (µg/L)	Level 4 (µg/L)	Level 5 (µg/L)	Level 6 (µg/L)	Level 7 (µg/L)	Level 8 (µg/L)
Acetone	2000	0.5	2	10	20	30	50	100	200
Acrolein	2000	0.5	2	10	20	30	50	100	200
Acrylonitrile	2000	0.5	2	10	20	30	50	100	200
Benzene	2000	0.5	2	10	20	30	50	100	200
Bromobenzene	2000	0.5	2	10	20	30	50	100	200
Bromochloromethane	2000	0.5	2	10	20	30	50	100	200
Bromodichloromethane	2000	0.5	2	10	20	30	50	100	200
Bromoform	2000	0.5	2	10	20	30	50	100	200
Bromomethane	2000	0.5	2	10	20	30	50	100	200
2-Butanone	2000	0.5	2	10	20	30	50	100	200
n-Butyl benzene	2000	0.5	2	10	20	30	50	100	200
sec-Butyl benzene	2000	0.5	2	10	20	30	50	100	200
tert-Butyl benzene	2000	0.5	2	10	20	30	50	100	200
Carbon disulfide	2000	0.5	2	10	20	30	50	100	200
Carbon tetrachloride	2000	0.5	2	10	20	30	50	100	200
Chlorobenzene	2000	0.5	2	10	20	30	50	100	200
Chloroethane	2000	0.5	2	10	20	30	50	100	200
2-Chloroethylvinyl Ether	2000	0.5	2	10	20	30	50	100	200
Chloroform	2000	0.5	2	10	20	30	50	100	200
Chloromethane	2000	0.5	2	10	20	30	50	100	200
o-Chlorotoluene	2000	0.5	2	10	20	30	50	100	200
p-Chlorotoluene	2000	0.5	2	10	20	30	50	100	200
Cyclohexane	2000	0.5	2	10	20	30	50	100	200
Cyclohexanone	2000	0.5	2	10	20	30	50	100	200
Dibromochloromethane	2000	0.5	2	10	20	30	50	100	200
1,2-Dibromo-3-chloropropane	2000	0.5	2	10	20	30	50	100	200
1,2-Dibromoethane	2000	0.5	2	10	20	30	50	100	200
Dibromomethane	2000	0.5	2	10	20	30	50	100	200
1,2-Dichlorobenzene	2000	0.5	2	10	20	30	50	100	200
1,3-Dichlorobenzene	2000	0.5	2	10	20	30	50	100	200
1,4-Dichlorobenzene	2000	0.5	2	10	20	30	50	100	200
1,4-Dichlorobutane	2000	0.5	2	10	20	30	50	100	200
trans-1,4-Dichloro-2-butene	2000	0.5	2	10	20	30	50	100	200
Dichlorodifluoromethane	2000	0.5	2	10	20	30	50	100	200
1,1-Dichloroethane	2000	0.5	2	10	20	30	50	100	200
1,2-Dichloroethane	2000	0.5	2	10	20	30	50	100	200
1,1-Dichloroethene	2000	0.5	2	10	20	30	50	100	200
cis-1,2-Dichloroethene	2000	0.5	2	10	20	30	50	100	200
trans-1,2-Dichloroethene	2000	0.5	2	10	20	30	50	100	200
1,2-Dichloropropane	2000	0.5	2	10	20	30	50	100	200
1,3-Dichloropropane	2000	0.5	2	10	20	30	50	100	200

2,2-Dichloropropane	2000	0.5	2	10	20	30	50	100	200
1,1-Dichloropropene	2000	0.5	2	10	20	30	50	100	200
cis-1,3-Dichloropropene	2000	0.5	2	10	20	30	50	100	200
trans-1,3-Dichloropropene	2000	0.5	2	10	20	30	50	100	200
p-Diethylbenzene	2000	0.5	2	10	20	30	50	100	200
Diisopropyl Ether	2000	0.5	2	10	20	30	50	100	200
1,4-Dioxane	10000	100	400	1000	2000	3000	4000	5000	6000
Ethanol	10000	100	200	300	500	1000	2500	5000	N/A
Ethyl Acetate	2000	0.5	2	10	20	30	50	100	200
Ethylbenzene	2000	0.5	2	10	20	30	50	100	200
Ethyl ether	2000	0.5	2	10	20	30	50	100	200
Ethyl methacrylate	2000	0.5	2	10	20	30	50	100	200
Ethyl Tert-Butyl Ether	2000	0.5	2	10	20	30	50	100	200
4-Ethyltoluene	2000	0.5	2	10	20	30	50	100	200
Freon-113	2000	0.5	2	10	20	30	50	100	200
Halothane	2000	0.5	2	10	20	30	50	100	200
Hexachlorobutadiene	2000	0.5	2	10	20	30	50	100	200
2-Hexanone	2000	0.5	2	10	20	30	50	100	200
Isopropylbenzene	2000	0.5	2	10	20	30	50	100	200
p-Isopropyltoluene	2000	0.5	2	10	20	30	50	100	200
Methyl Acetate	2000	0.5	2	10	20	30	50	100	200
Methylene Chloride	2000	0.5	2	10	20	30	50	100	200
Methyl Cyclohexane	2000	0.5	2	10	20	30	50	100	200
4-Methyl-2-pentanone	2000	0.5	2	10	20	30	50	100	200
Methyl-tert-butyl-ether	2000	0.5	2	10	20	30	50	100	200
Naphthalene	2000	0.5	2	10	20	30	50	100	200
n-Propylbenzene	2000	0.5	2	10	20	30	50	100	200
Styrene	4000	1	4	20	40	60	100	200	400
Tert-Butyl alcohol	10000	2.5	10	50	100	150	250	500	1000
Tertiary-Amyl Methyl Ether	2000	0.5	2	10	20	30	50	100	200
1,1,1,2-Tetrachloroethane	2000	0.5	2	10	20	30	50	100	200
1,1,2,2-Tetrachloroethane	2000	0.5	2	10	20	30	50	100	200
Tetrachloroethene	2000	0.5	2	10	20	30	50	100	200
Tetrahydrofuran	2000	0.5	2	10	20	30	50	100	200
1,2,4,5-Tetramethylbenzene	2000	0.5	2	10	20	30	50	100	200
Toluene	2000	0.5	2	10	20	30	50	100	200
1,2,3-Trichlorobenzene	2000	0.5	2	10	20	30	50	100	200
1,2,4-Trichlorobenzene	2000	0.5	2	10	20	30	50	100	200
1,3,5-Trichlorobenzene	2000	0.5	2	10	20	30	50	100	200
1,1,1-Trichloroethane	2000	0.5	2	10	20	30	50	100	200
1,1,2-Trichloroethane	2000	0.5	2	10	20	30	50	100	200
Trichloroethene	2000	0.5	2	10	20	30	50	100	200
Trichlorofluoromethane	2000	0.5	2	10	20	30	50	100	200
1,2,3-Trichloropropane	2000	0.5	2	10	20	30	50	100	200
1,2,4-Trimethylbenzene	2000	0.5	2	10	20	30	50	100	200
1,3,5-Trimethylbenzene	2000	0.5	2	10	20	30	50	100	200

Vinyl acetate	2000	0.5	2	10	20	30	50	100	200
Vinyl chloride	2000	0.5	2	10	20	30	50	100	200
m/p-Xylenes	4000	1	4	20	40	60	100	200	400
o-Xylene	4000	1	4	20	40	60	100	200	400

Table 4 (continued)

Stock Standard Concentrations and Calibration Concentration Levels

Target Compounds	Stock (µg/mL)	Level 1 (µg/L)	Level 2 (µg/L)	Level 3 (µg/L)	Level 4 (µg/L)	Level 5 (µg/L)	Level 6 (µg/L)	Level 7 (µg/L)	Level 8 (µg/L)
Internal Standards									
Fluorobenzene	2500	10	10	10	10	10	10	10	10
Chlorobenzene-d5	2500	10	10	10	10	10	10	10	10
1,4-Dichlorobenzene-d4	2500	10	10	10	10	10	10	10	10
Surrogates									
Dibromofluoromethane	2500	10	10	10	10	10	10	10	10
1,2-Dichloroethane-d4	2500	10	10	10	10	10	10	10	10
Toluene-d8	2500	10	10	10	10	10	10	10	10
4-Bromofluorobenzene	2500	10	10	10	10	10	10	10	10

- For Low Level Soil analysis, the calibration levels are the same in µg/Kg units.
- For High Level Soil analysis, the calibration levels are at 50x the levels listed due to sample preparation requirements.

TABLE 5

8260C Volatile Internal Standards with Corresponding MCP Target Compounds and Surrogates Assigned for Quantitation

Fluorobenzene	Chlorobenzene-d5	1,4-Dichlorobenzene-d4
Dichlorodifluoromethane	Toluene-d8 (surr)	Isopropylbenzene
Chloromethane	Toluene	Bromoform
Vinyl Chloride	Ethyl Methacrylate	1,4-dichloro-2-butane
Bromomethane	Trans-1,3-dichloropropene	1,1,2,2,-tetrachloroethane
Chloroethane	1,1,2-trichloroethane	4-bromofluorobenzene (surr)
Trichlorofluoromethane	2-hexanone	1,2,3-trichloropropane
Ethyl Ether	1,3-dichloropropane	trans-1,4-dichloro-2-butene
Freon 113	Tetrachloroethene	n-propylbenzene
Acrolein	Chlorodibromomethane	Bromobenzene
Acetone	1,2-dibromoethane	4-ethyltoluene
Ethanol	Chlorobenzene	1,3,5-trimethybenzene
1,1,-dichloroethene	1,1,1,2-tetrachloroethane	2-chlorotoluene
Tert-Butyl Alcohol	Ethylbenzene	4-chorotoluene
Methyl Acetate	p/m xylene	tert-butylbenzene
Carbon Disulfide	o xylene	1,2,4-trimethylbenzene
Methylene Chloride	Styrene	sec-butylbenzene
Acrylonitrile		p-isopropyltoluene
Methyl Tert Butyl Ether		1,3-dichlorobenzene
Halothane		1,4-dichlorobenzene
Trans-1,2-dichloroethene		n-butylbenzene
Diisopropyl Ether		p-diethylbenzene
Vinyl Acetate		1,2-dichlorobenzene
1,1-dichloroethane		1,2,4,5-tetramethylbenzene
Ethyl-Tert-Butyl-Ether		1,2-dibromo-3-chloropropane
2-butanone		1,3,5-trichlorobenzene
2,2-dichloropropane		1,2,4-trichlorobenzene
Cis-1,2-dichloroethene		Hexachlorobutadiene
Chloroform		Naphthalene
Bromochloromethane		1,2,3-trichlorobenzene
Tetrahydrofuran		Cyclohexanone
Dibromofluoromethane (surr)		
1,1,1-trichloroethane		
Cyclohexane		
1,1-dichloropropene		
Carbon Tetrachloride		
Tertiary-Amyl Methyl Ether		
1,2-dichloroethane-d4 (surr)		
1,2-dichloroethane		
Benzene		
Trichloroethene		
Methyl Cyclohexane		
1,2-dichloropropane		
Bromodichloromethane		
1,4-Dioxane		
Dibromomethane		
2-Chloroethylvinyl Ether		
4-methyl-2-pentanone		
Cis-1,3-dichloropropene		

TABLE 6
8260C Quantitation Ion

Analyte	Quantiation Ion	Analyte	Quantiation Ion
Dichlorodifluoromethane	85	Ethyl Methacrylate	69
Chloromethane	50	Trans-1,3-dichloropropene	75
Vinyl Chloride	62	1,1,2-trichloroethane	83
Bromomethane	94	2-hexanone	43
Chloroethane	64	1,3-dichloropropane	76
Trichlorofluoromethane	101	Tetrachloroethene	166
Ethyl Ether	74	Chlorodibromomethane	129
Freon 113	101	1,2-dibromoethane	107
Acrolein	56	Chlorobenzene	112
Acetone	43	1,1,1,2-tetrachloroethane	131
1,1,-dichloroethene	96	Ethylbenzene	91
Tert-Butyl Alcohol	59	p/m xylene	106
Methyl Acetate	43	o xylene	106
Carbon Disulfide	84	Styrene	104
Methylene Chloride	76	Isopropylbenzene	105
Acrylonitrile	53	Bromoform	173
Methyl Tert Butyl Ether	73	1,4-dichloro-2-butane	55
Halothane	117	1,1,2,2,-tetrachloroethane	83
Trans-1,2-dichloroethene	96	1,2,3-trichloropropane	75
Diisopropyl Ether	45	Trans-1,4-dichloro-2-butene	53
Vinyl Acetate	43	n-propylbenzene	91
1,1-dichloroethane	63	Bromobenzene	156
Ethyl-Tert-Butyl-Ether	59	4-ethyltoluene	105
2-butanone	43	1,3,5-trimethybenzene	105
2,2-dichloropropane	77	2-chlorotoluene	91
Cis-1,2-dichloroethene	96	4-chorotoluene	91
Chloroform	83	tert-butylbenzene	119
Bromochloromethane	128	1,2,4-trimethylbenzene	105
Tetrahydrofuran	42	sec-butylbenzene	105
1,1,1-trichloroethane	97	p-isopropyltoluene	119
Cyclohexane	56	1,3-dichlorobenzene	146
1,1-dichloropropene	75	1,4-dichlorobenzene	146
Carbon Tetrachloride	117	n-butylbenzene	91
Tertiary-Amyl Methyl Ether	73	p-diethylbenzene	119
1,2-dichloroethane	62	1,2-dichlorobenzene	146
Benzene	78	1,2,4,5-tetramethylbenzene	119
Trichloroethene	95	1,2-dibromo-3-chloropropane	75
Methyl Cyclohexane	83	1,3,5-trichlorobenzene	180
1,2-dichloropropane	63	1,2,4-trichlorobenzene	180
Bromodichloromethane	83	Hexachlorobutadiene	225
1,4-dioxane	88	Naphthalene	128
Dibromomethane	93	1,2,3-trichlorobenzene	180
2-Chloroethylvinyl Ether	63	Ethanol	45
4-methyl-2-pentanone	58	Cyclohexanone	55

Cis-1,3-dichloropropene	75		
Toluene	92		

Volatile Organic Compounds - Non Potable Water

Reference Method No.: **EPA 624**

Reference: **40 CFR Part 136, Appendix A**

1. Scope and Application

Matrices: Wastewater, Water

Definitions: See Alpha Laboratories Quality Manual Appendix A

Regulatory Analyte List 624

Parameter	CAS No.	Parameter	CAS No.
Benzene	71-43-2	1,2 – Dichloropropane	78-87-5
Bromodichloromethane	75-27-4	cis- 1,3 - Dichloropropene	10061-01-5
Bromoform	75-25-2	trans- 1,3 - Dichloropropene	10061-02-6
Bromomethane	74-83-9	1,4-Dioxane	123-91-1
Carbon tetrachloride	56-23-5	Ethyl benzene	100-41-4
Chlorobenzene	108-90-7	Methylene chloride	75-09-2
Chloroethane	75-00-3	Methyl tert-butyl ether	1634-04-4
2 - Chloroethylvinyl ether	110-75-8	tert-Butyl alcohol	75-65-0
Chloroform	67-66-3	Tertiary- amyl methyl ether	994-05-8
Chloromethane	74-87-3	1,1,2,2- Tetrachloroethane	79-34-5
Dibromochloromethane	124-48-1	Tetrachloroethene	127-18-4
1,2 - Dichlorobenzene	95-50-1	Toluene	108-88-3
1,3 - Dichlorobenzene	541-73-1	1,1,1 - Trichloroethane	71-55-6
1,4 - Dichlorobenzene	106-46-7	1,1,2 - Trichloroethane	79-00-5
1,1 - Dichloroethane	75-34-3	Trichloroethene	79-01-6
1,2 - Dichloroethane	107-06-2	Trichlorofluoromethane	75-69-4
1,1 - Dichloroethene	75-35-4	Vinyl chloride	75-01-4
trans- 1,2 - Dichloroethene	156-60-5	cis-1,2-dichloroethene	156-59-2

Extended Analyte List:

Parameter	CAS No.	Parameter	CAS No.
Acrolein	107-02-8	4-Methyl-2-pentanone	108-10-1
Acrylonitrile	107-13-1	2-Hexanone	591-78-6
Acetone	67-64-1	m/p- Xylene	1330-20-7
Carbon Disulfide	75-15-0	o-Xylene	1330-20-7
Vinyl Acetate	108-05-4	Styrene	100-42-5
2-Butanone	78-93-3	Dibromomethane	74-95-3

This method covers the determination of a number of purgeable organics regulated under the Clean Water Act. This is a purge and trap gas chromatographic/mass spectrometer (GC/MS) method applicable to the determination of the parameters listed above in municipal and industrial discharges as provided under 40 CFR Part 136.1. The compound list is extended to add analytes

commonly requested by clients for water samples such as groundwater, surface water and process waters. The procedure is based on **EPA Method 624**.

Any modification to this method, must be documented in the data report package. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results when applied to relevant wastewaters and other non-potable waters. Method modifications must be approved by one of the following laboratory personnel before performing any modification: area supervisor, organics manager, laboratory services manager, laboratory director, or quality assurance officer

This method is restricted to use by or under the supervision of analysts experienced in the operation of a purge and trap system and a gas chromatograph/mass spectrometer and in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability, analyzing a proficiency test sample and completing the record of training.

After initial demonstration, ongoing demonstration is based on acceptable laboratory performance of at least a quarterly laboratory control sample or acceptable performance from an annual proficiency test sample. Major modification to this procedure requires demonstration of performance. The identification of major method modifications requiring performance demonstration is directed by the QA Officer and Laboratory Director on a case-by-case basis.

2. Summary of Method

Helium is bubbled through a 10mL water sample contained in a specially designed purging chamber at ambient temperature. The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent trap where the purgeables are trapped. After purging is completed, the trap is heated and backflushed with helium gas to desorb the purgeables onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the purgeables, which are then detected with a mass spectrometer.

2.1 Method Modifications from Reference

2.1.1 The following capillary column is substituted for the columns referenced in the method:

RTX 502.2, 40m, 0.18μm df or equivalent.

3. Detection Limits

The laboratory reporting limits are listed in Table 1. The laboratory reporting limits are adjusted on a sample specific basis to account for dilutions required for target analyte concentrations that exceed the calibration range or sample matrix interference purposes.

4. Interferences

Impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be free from contamination under the conditions of the analysis. Running laboratory reagent blanks as described in Section 9.4 and 10.2 demonstrates the system is free of contamination. The use of non-Teflon plastic tubing, non-Teflon thread sealants, or flow controllers with rubber components in the purge and trap system must be avoided.

Sample contamination occurs by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during shipment and storage. A trip blank or a field reagent blank prepared from reagent water and carried through the sampling and handling protocol serves as a check on such contamination.

Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. To reduce carry-over, the sample syringe must be rinsed with reagent water between sample analyses. Each autosampler position is also monitored for positive hits and subsequent sample analyses are checked for potential carry-over. If carry-over is suspected, the sample is rerun for confirmation. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high purgeable levels, it may be necessary to wash the purging device with a detergent solution, rinse it with reagent water, and then dry it in a 105°C oven between analyses. The trap and other parts of the system are subject to contamination; therefore, frequent bakeout and purging of the entire system may be required.

When the sample foams, antifoam is added. One drop of antifoam is use per 10 mls of sample. The same amount is added to the QC. If the sample is too foamy and one drop per 10 mls cannot eliminate the foam, then the sample is diluted and then one drop of antifoam per 10 mls of sample is added. Continue to dilute as necessary keeping the 1 drop per 10 mls constant. This foam check is done on the screen sample to preserve the integrity of the other vials.

5. Safety

The toxicity or carcinogenity of each reagent and standard used in this method is not precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

The following parameters covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, chloroform, 1,4-dichlorobenzene, and vinyl chloride. Pure standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn if the analyst handles pure (undiluted) materials of these toxic compounds.

6. Sample Collection, Preservation, Shipping, and Handling

6.1 Sample Collection

Grab samples in standard 40mL glass screw-cap vials with Teflon lined silicon septa (VOA vial). Three VOA vials are filled per sample location.

Fill the sample bottle just to overflowing. Samples must be introduced into the vials gently to reduce agitation, which might drive off volatile compounds.

Seal the bottle so that no air bubbles are in the sample container. If preservative has been added, shake vigorously for one minute. Invert the bottle and tap to check for air bubbles. Recollect the samples, if any air bubbles are present.

Maintain the hermetic seal on the sample bottle until time of analysis.

Ice or refrigerate all samples from the time of collection until analysis.

Cool and maintain the sample temperature between 1 and 6 °C. Sample receiving personnel note on the nonconformance form when samples received at the laboratory are not within the temperature criteria.

6.2 Sample Preservation

Experimental evidence indicates that some aromatic compounds, notably benzene, toluene, and ethyl benzene are susceptible to rapid biological degradation under certain environmental conditions. Refrigeration alone may not be adequate to preserve these compounds in waters for more than seven days.

Samples suspected of containing residual chlorine are preserved differently. The sample vials are preserved with sodium thiosulfate and the vials are filled completely with the sample.

The analyte Acrolein has a three day hold time if it is not preserved to a pH between 4 and 5 pH units. Additionally, the analyte 2-Chloroethyl vinyl ether is known to degrade quickly in a low pH environment.

Considering the above preservation issues, Alpha's standard protocol is to preserve all samples with sodium thiosulfate and complete the analysis within 3 days.

The sampling procedure is then completed as per Section 6.1.

6.3 Sample Shipping

Samples requiring shipment to the laboratory are shipped in coolers packed in ice via an overnight delivery service in accordance with applicable Department of Transportation regulations.

6.4 Sample Handling

The laboratory routine practice is to collect three 40mL glass vials and transport the sample with ice in coolers. The three sample vials that make up each sample are then split between the two VOC sample storage refrigerators at the laboratory. Storing the vials apart provides a useful check if laboratory contamination of a sample is suspected.

Note: Samples requiring analysis for Acrolein must be analyzed within three (3) days of sample collection.

Document client specific sample handling, preservation and collection criteria in the project file. The laboratory Login staff documents sample temperature at the time of receipt.

Record deviations from this SOP or client specific criterion on the chain of custody form.

Record holding time exceedances, improper preservation and observed sample headspace on the nonconformance report form.

7. Equipment and Supplies

7.1 Vial: 40mL capacity equipped with a screw cap with a hole in the center. Purchased pre-leaned to EPA specifications.

7.2 Septum: Teflon-faced silicone. Purchased pre-cleaned to EPA specifications.

7.3 Purge and Trap System: The purge and trap system consists of two separate pieces of equipment: a purging device coupled to the desorber (Tekmar Solatek, with Tekmar 2000/3000, or equivalents).

7.3.1 Purge gas = Helium, analytical grade (99.999%).

7.3.2 The purging device accepts 5mL of sample. The 5mL of sample must have a water column at least 3cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3mm at the origin. The purge gas must be introduced no more than 5mm from the base of the water column.

7.3.3 The Tekmar Solatek purging device is a closed system, designed to accept the 40mL VOA vials. The instrument automatically adds internal standards and surrogates when transferring the 5 mls of sample to the purge vessel. The helium purge gas is introduced into the aqueous portion to purge the volatile components onto the trap.

7.3.4 The trap used in the desorber is typically a Supelco "K" trap. Different traps may be used if equivalent performance is demonstrated.

7.3.5 The desorber is capable of rapidly heating the trap to 260 °C. The trap is not heated above manufacturer specifications.

7.4 Gas chromatograph: An analytical system complete with a temperature programmable gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, and gases. Agilent 6890 or equivalent, Column - RTX 502.2, 40m, 0.18μm df, or equivalent.

7.5 Mass spectrometer: Capable of scanning from 35-260 amu every seven seconds or less, utilizing 70V (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the criteria in Table 2 when 50ng of 4-bromofluorobenzene (BFB) is injected through the GC inlet. The GC/MS interface is direct capillary. Agilent 5973 or equivalent.

7.6 Data system: A computer system is interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer software allows searching any GC/MS data file for specific m/z (masses) and plotting such m/z abundance versus time or scan number**.** HP ChemServer software is used for data acquisition and Throughput Systems Target 3.0 is used for data reduction. Approved data is electronically transferred to the laboratory wide LIMS for final client reporting.

7.7 Syringes: 5mL and 10mL, glass with Luerlock tip.

7.8 Micro syringes: 10, 25, 100, 250, 500, and 1000µL.

7.9 Syringe valve: Two-way, with Luer ends.

7.10 Disposable Pasteur pipets.

7.11 Volumetric flasks: 10mL, 100mL, Class A with ground glass stoppers.

7.12 Vials: 2mL, 4mL with Teflon-lined screw caps.

7.13 Autopipet: 1mL

7.14 Antifoam A: Sigma Catalog #A-6582

8. Standards and Reagents

8.1 Reagent water: Reagent water in the GC/MS volatiles laboratory is municipal water, passed through a reverse osmosis system. The reagent water after treatment with activated carbon does not contain interferents or the parameters of interest at the reporting limit.

8.2 Sodium Thiosulfate: ACS Reagent Grade or equivalent, Granular.

8.3 Methanol, MeOH: ACS Purge and Trap grade quality or equivalent.

8.4 Trap: Tekmar purge trap K, Vocarb3000 or equivalent.

8.5 Stock standard solutions: Certified stock standard solutions in methanol. The certification includes the concentration, uncertainty and traceability to NIST if available. Stock standards include calibration standards, calibration verification, internal, surrogates and spiking solutions. 2 sources are necessary: one utilized for Initial Calibration Standard preparation and the other utilized for ICV Standard preparation.

Select the certified stock standards containing the parameters of interest. Record the concentration of the certified stock standards, lot number, supplier, standard name, catalog number, expiration date, solvent vendor, solvent lot number, preparation date and preparer's initials in the standards logbook. Record the number of containers prepared and the identifier for the stock standard.

Transfer the opened stock standard solution into a Teflon-sealed screw-cap vial. Store, with minimal headspace, at -10 to -20°C and protect from light. Store according to the manufacturer's documented holding time and storage temperature recommendations.

Stock Standard Solutions (or equivalent)

Initial Calibration, Continuing Calibration, QC Check, LCS, MS, primary source:

624 Orange: Accustandard - Custom VOC Standard; Catalog # S24310-01; varied concentrations

624 Yellow: Accustandard – Purgeables-EPA Method 624; Catalog # M-624; 0.2 mg/ml

ICVS, secondary source:

A-Mix: Accustandard— Custom ketone mix
Catalog # S-8082B 5000µg/mL

B-Mix: Accustandard– Custom VOC mix
Catalog # S-8082A varied conc.

C-Mix: Accustandard–Acrolein + Acrylonitrile
Catalog # M-603-10X 10.0 mg/mL

1,4-Dioxane: Restek—1,4-Dioxane
Catalog # 30287 2000µg/mL

D-Mix:
Accustandard—MTBE
Catalog # S-078-10V 2000 µg/mL

Restek—Vinyl Acetate
Catalog # 30216 2000µg/mL

Accustandard – Dibromomethane
Catalog # M-502-20-10X 2000ug/mL

Oxygenates:

Restek—Custom Oxygenates
Catalog # 559744 varied conc.

8.6 Primary dilution standards: Using the stock standard solutions listed above, prepare the Primary dilution standards in methanol that contain the parameters of interest.

Primary dilution standards are stored with minimal headspace at -10 to -20°C and protected from light. Check for signs of degradation or evaporation, before preparing calibration standards from them. ICVS A -, C -, and D -Mix standards should be replaced when it is suspected that the standard has degraded or by comparison with the check standard or every three months. The B -Mix standard, which contains the gaseous compounds, must be prepared on a monthly basis. The 624 Orange and 624 Yellow standards must be prepared every two months or when degradation is suspected.

Record the stock standard identifier, expiration date for primary dilution standard, solvent vendor, solvent lot number, preparation date and preparer's initials in the standards logbook. Record the number of containers prepared and the identifier for the secondary standard.

8.6.1 ICVS Calibration A (ICA): 400µL of A-Mix brought to 10mL volume with MeOH.

8.6.2 ICVS Calibration B (ICB): 100µL of B-Mix brought to 1mL volume with MeOH.

8.6.3 ICVS Calibration C (ICC): 160µL of C-Mix brought to 10mL volume with MeOH.

8.6.4 ICVS Calibration D (ICD): 500µL D-Mix MTBE, 500µL D-Mix 2-CEVE and 1mL D-Mix Vinyl Acetate brought to 10mL volume with MeOH.

8.6.5 ICVS Oxygenates: 100µL of Oxy mix brought up to 1mL volume with MeOH.

8.6.6 624 Orange A: 500µL brought to 10 ml with MeOH

8.6.7 624 Yellow: Transfer to a vial

8.7 Calibration standards and Matrix Spiking Solutions: The primary dilution standards (Sections 8.6.1 – 8.6.7) are used to prepare the aqueous calibration standards. Prepare the calibration standards using a microliter syringe (µL) to transfer the appropriate volume of primary dilution standard into a 100 mL volumetric flask containing lab reagent water (mL). Five mLs of this aqueous solution is the calibration standard. The aqueous standards can be stored for up to 24 hours at 4 ± 2 °C, if held in sealed vials with zero headspace.

Record the primary standard identifier, expiration date for primary dilution standard, preparation date and preparer's initials in the standards logbook. Record the exact preparation steps and the identifier for the calibration standards.

Initial Calibration Standard Preparation / ICVS Standard Preparation:

- **Level 1 Standard (all: 5ng; Acrolein, Acrylonitrile, Vinyl acetate, m,p-Xylene: 10ng; Acetone, 2-Butanone, 4-Methyl-2-pentanone, 2-Hexanone: 12.5ng; Total Xylene: 15ng; TBA: 25ng; 1,4-Dioxane: 1000ng):** Add 12.5 mL of Level 2 Standard (below) into a 50 mL volumetric flask. Bring to volume with reagent water. Transfer into a 40mL vial. For use with the Solatek autosampler, add 10µL IS/SS (Section 8.10).
- **Level 2 Standard (4X the Level 1):** Add 4µL of 624 Orange A and 2 µL of 624 Yellow into a 100mL volumetric flask. Bring to volume with reagent water. Transfer into a 40mL vial. For use with the Solatek autosampler, add 10µL IS/SS (Section 8.10).
- **Level 3 Standard (20X the Level 1):** Add 20µL of 624 Orange A and 10 µL of 624 Yellow into a 100mL volumetric flask. Bring to volume with reagent water. Transfer to a 40mL vial. For use with the Solatek autosampler, add 10µL IS/SS (Section 8.10).

- **Level 4 Standard (40X the Level 1):** Add 40µL of 624 Orange A and 20 µL 624 Yellow into a 100mL volumetric flask. Bring to volume with reagent water. Transfer to a 40mL vial. For use with the Solatek autosampler, add 10µL IS/SS (Section 8.10).
- **Level 5 Standard (60X the Level 1):** Add 60µL of 624 Orange A and 30 µL 624 Yellow into a 100mL volumetric flask. Bring to volume with reagent water. Transfer to a 40mL vial. For use with the Solatek autosampler, add 10µL IS/SS (Section 8.10).
- **Level 6 Standard (100X the Level 1):** Add 100µL of 624 Orange A and 50 µL 624 Yellow into a 100mL volumetric flask. Bring to volume with reagent water. Transfer to a 40mL vial. For use with the Solatek autosampler, add 10µL IS/SS (Section 8.10).
- **Level 7 Standard (200X the Level 1):** Add 200µL of 624 Orange A and 100 µL 624 Yellow into a 100mL volumetric flask. Bring to volume with reagent water. Transfer to a 40mL vial. For use with the Solatek autosampler, add 10µL IS/SS (Section 8.10).
- **Level 8 Standard (400X the Level 1):** Add 400 µL of 624 Orange A to a 100mL volumetric flask. Bring to volume with reagent water. Transfer to a 40mL. For use with the Solatek autosampler, add 10µL IS/SS (Section 8.10).
- **ICVS (same concentration as the Level 3):** Add 20µL of Oxygenates Standard, 25µL of ICA, 10µL of ICB, 25µL of ICC, 20µL ICD and 100 µL of the 1,4-Dioxane standard into a 100mL volumetric flask. Bring to volume with reagent water. Transfer to a 40mL vial. For use with the Solatek autosampler, add 10µL IS/SS (Section 8.10).

Continuing Calibration Standard / QC Check / LCS / Matrix Spiking (MS) Solution (for GC/MS with Solatek): Follow instructions above for Level 3 Standard using the primary source stock standards. Set the Solatek to "624.MSVW". Set the sample volume to 10mL, and set the dilution to 1:2.

8.8 Internal standard spiking solution: Restek 624 Internal standard mix, catalog # 30023, or equivalent, 1500µg/mL. Store with minimal headspace at -10 to -20°C and protect from light. Expires 6 months from the date the vial was opened.

- Add 100µL stock standard to approximately 10mLs MeOH in a 25mL volumetric flask. Fill to volume to give a final concentration of 15µg/mL.
- Add 10µL to each sample, standard and blank to give a concentration of 30µg/L in the 10mL gas tight syringe.

Record the stock standard identifier, expiration date for the internal standard, preparation date and preparer's initials in the standards logbook. Record the exact steps for preparing the standard and the identifier for the internal standard.

8.9 Surrogate standard spiking solution: Restek 624 Surrogate standard mix, catalog # 30243, or equivalent, 2000µg/mL. Store with minimal headspace at -10 to -20°C and protect from light. Expires 6 months from the date the vial was opened.

- Add 75µL stock standard to approximately 10mLs MeOH in a 25mL volumetric flask. Fill to volume to give a final concentration of 15µg/mL.
- Add 10µL to each sample, standard and blank to give a concentration of 30µg/L.

Record the stock standard identifier, expiration date for the surrogate, preparation date and preparer's initials in the standards logbook. Record the exact steps for preparing the surrogate and the surrogate identifier.

8.10 Internal Standard/Surrogate Standard Mixed Solution (IS/SS):

100µL of Internal Standard Spiking Solution (Section 8.8) and 75µL Surrogate Standard Spiking Solution (Section 8.9) brought up to 10mL with reagent water. Final concentration is 15µg/L. Store with minimal headspace at -10 to -20°C and protect from light. Expires 6 months from the date the vials were opened.

8.11 Tune standard: Ultra Scientific Catalog # STS-110N, Bromofluoromethane (BFB) in methanol, 2000µg/mL or equivalent.
Add 250µL stock standard to approximately 5mLs Methanol in a 10mL volumetric flask. Fill to volume to give a final concentration of 50µg/mL. Transfer to screw-cap vials, cap tightly and store amber vials with minimal headspace in freezer at -10 to -20°C. Expires 6 months from the date of preparation.

Record the stock standard identifier, expiration date for the tune solution, preparation date and preparer's initials in the standards logbook. Record the exact steps for preparing the tune solution and the identifier.

9. Procedure

9.1 GC/MS Tune

At the beginning of every 12 hours of instrumental analysis, tune the GC/MS system to demonstrate acceptable performance for BFB. The tune must pass before proceeding with the analysis of any samples, blanks, or standards.

Inject 1µL of BFB tune solution directly on to the column.

Analyze the solution using the same mass spectrometer conditions as used for the sample analyses.

Obtain a background-corrected mass spectrum of BFB and confirm that all the key m/z criteria in Table 2 are achieved. The mass spectrum of BFB should be acquired in the following manner:

(1) Three scans (the peak apex scan, the scan immediately preceding the apex and the scan immediately following the apex) are acquired and averaged.
(2) Background subtraction is performed using a single scan of no more than 20 scans prior to the elution of BFB.

If the criteria are not achieved, the analyst must perform needed maintenance, retune the mass spectrometer and repeat the test until all criteria are achieved.

9.2 Initial Calibration

Prepare the instrumental system to meet the specifications in Section 9.4. For new systems or systems not in use on a daily basis, condition the trap overnight at 180°C by backflushing with an inert gas flow of at least 20mL/min. The internal standard calibration procedure is used for quantifying all samples. The internal standards are specified in Section 8 and are listed in Table 3.

Calibration standards are prepared as specified in Section 8.7. Prepare calibration standards at seven concentration levels for each parameter to achieve the final concentrations of 1µg/L, 4µg/L, 20µg/L, 40µg/L 60µg/L, 100µg/L and 200µg/L. The calibration standards define the working range of the GC/MS system. Fill the 5mL syringe the same as the sample (Section 9.4).

Surrogates and Internal Standards are added by the autosampler at a constant concentration in the calibration standard analyses.

Analyze each calibration standard according to Section 9.4.

Record the calibration standards identifier, internal standard identifier, surrogate standard identifier, concentration, analyst initials and any deviations to this procedure in the instrument analysis logbook.

Tabulate the area response of the characteristic m/z against concentration for each compound and internal standard, and calculate response factors (RF) for each compound as follows:

$$RF = \frac{(A_s \times C_{is})}{(A_{is} \times C_s)}$$

Where:

RF = Response Factor
A_s = Area of the characteristic m/z for the parameter to be measured.
A_{is} = Area of the characteristic m/z for the internal standard.
C_{is} = Concentration of the internal standard.
C_s = Concentration of the parameter to be measured.

If the RF value over the working range is < 35% RSD, the RF can be assumed to be linear and the average RF is used for calculations. Average RF = Sum of RF values from the calibration curve/ Number of RF values

If the % RSD is > 35%, remake the standard and repeat the calibration. Alternatively, a calibration curve may be generated plotting response factor vs. analyte concentration. If the problem persists, perform maintenance and any other corrective action. Perform a full initial calibration to standardize the system if any other system changes are made.

9.3 Standardization (Continuing Calibration Verification)

The average RF must be verified on each working day by the measurement of a calibration verification standard. Verification is based on the percent recovery results being within the acceptance criteria listed in Table 5.

Analyze the calibration verification according to Section 9.4.

Record the calibration verification standard identifier, internal standard identifier, surrogate standard identifier, concentration, analyst initials and any deviations to this procedure in the instrument analysis logbook.

9.4 Equipment Operation and Sample Analysis

Changes in acquisition parameters, equipment, conditions and tune criteria require written authorization from management. Demonstration of method performance based on method modifications must be on file before sample analysis.

The following are the routine instrumental parameters:

Electron Energy = 70 V (nominal)
Mass Range = 35-260 amu
Scan Time = At least five scans/peak but not to exceed seven seconds/scan
Carrier Gas = Helium
Acquisition mode = Scan
Resulting Voltage = 2370

The following are purge parameters:

Purge gas flow rate	= 40 mL/min
Purge time	= 11.0 min
Purge temperature	= 40 °C
Dry purge time	= 4 min
Desorb temperature	= 255 °C
Desorb time	= 4 min
Bake out temperature	= 280°C
Bake out time	= 10 min

After achieving the key m/z abundance criteria for the BFB, calibrate or verify the calibration of the system daily as described in Sections 9.2 and 9.3. If the performance criteria are achieved continue the analysis. If performance criteria are not achieved take corrective action as defined in Section 12.

Analyze a reagent water blank containing 10.0μL surrogate spiking solution and 10.0μL internal standard spiking solution. If no target parameters are above the reporting limit and the chromatography is acceptable continue the analysis. If poor chromatography or target parameters are above the reporting limit, take appropriate corrective action as defined in Section 12. The purging vessel must be rinsed twice with organic free water between each analysis.

Record the sample number (standard or QC sample identifier), dilution, analyst initials, deviations from this procedure and visual observations in the instrument analysis logbook.

Perform a preliminary data review of the sample, internal standard and surrogate performance at the time of analysis or when the sequence is complete. Note any obvious problems in the instrument analysis logbook. If the concentration for any analyte exceeds the working range of the system, the sample must be reanalyzed at the appropriate dilution.

9.5 Qualitative Identification

Perform first level data review. Obtain the primary m/z (Table 4) and at least two secondary masses for each parameter of interest. The following criteria must be met to make a qualitative identification:

- Compare the background subtracted mass spectra for the sample to the reference spectra. The characteristic masses of each parameter of interest must maximize in the same or within one scan of each other.
- The retention time must fall within +/- 0.1 minutes of the retention time of the compound in the analytical standard. However, analyst experience should be used in making the qualitative identification.
- The relative peak heights of the three characteristic masses must fall within 20% of the relative intensities of the masses in a reference mass spectrum. The reference spectrum is obtained from a standard analyzed in the GC/MS system.

Structural isomers that have very similar mass spectra are identified only if the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved

if the baseline to valley height between the isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

9.6 Calculations

When a parameter is identified, the quantitation of that parameter should be based on the integrated abundance of the quantitation characteristic m/z given in Table 4. If the sample produces an interference for the primary m/z, use a secondary characteristic m/z to quantitate.

Calculate the concentration in the sample using the average response factor (RF) from the initial calibration curve as follows:

$$Concentration(\mu g / L) = D\left(\frac{A_x \times C_{is}}{A_{is} \times \overline{RF}}\right)$$

where:

D = Dilution Factor (sample aliquot mL/ 5 mL)
A_x = Area of the characteristic m/z for the compound to be measured
A_{is} = Area of the characteristic m/z for the internal standard
C_{is} = Concentration of the internal standard
$\overline{RF}$ = Average RF (Section 9.2)

Report results in µg/L without correction for blank and recovery data. Record all QC data and report with the sample results as required by client specifications. Reported detection limits must be corrected for the sample dilution factor.

10. Quality Control and Data Assessment

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a QC check standard is used to confirm the measurements were performed in an in-control mode of operation.

10.1 Demonstration of Capability

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. Each time a method modification is made, the analyst is required to repeat the procedure.

Prepare the QC check standard according to the specifications in Section 9.3.

Analyze four 5mL aliquots of the well-mixed QCS according to the method beginning in Section 9.4.

Calculate the result for each aliquot in µg/L, the relative standard deviation of the four results in µg/L, the average result for the four aliquots in µg/L, and the percent recovery in % for each parameter of interest using the four results.

For each parameter, compare the average percent recovery of the four results with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 5. All parameters of interest must meet the acceptance criteria before actual sample analysis begins. If

any individual parameter exceeds the precision limit or any individual falls outside the range for accuracy, the system performance is unacceptable for that parameter.

NOTE: The large number of parameters in Table 5 present a substantial probability that one or more will fail at least one of the acceptance criteria when all parameters are analyzed.

When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must locate and correct the source of the problem and repeat the test for failed parameters of the method.

Repeated failure confirms a general problem with the measurement system or analytical technique of the analyst. If the failure repeats, locate and correct the source of the problem and repeat the test for all parameters listed in the method.

10.2 Blank

Analyze a reagent water blank each day to demonstrate that interferences from the analytical system are under control. The reagent blank must contain the internal standards.

Analyze the reagent water blank from the same lot of water used for preparing the standards, QC samples and making sample dilutions. If the lot of reagent water is changed during the analysis perform an additional blank to ensure the analytical system is not contaminated.

The Blank results must be less than the RL for the analyte. If failure occurs, the Blank is reanalyzed. If failure continues, maintenance should be performed and the system recalibrated if necessary.

10.3 QC Check Standard or Laboratory Control Sample (LCS)

Demonstrate through the analyses of the QC check standard or LCS that the operation of the measurement system is in control. The frequency of the analyses is once every 12 hours of analytical run time.

Analyze the QC check standard to determine the concentration measured of each parameter. Calculate each percent recovery. For each parameter listed in Table 5, compare the percent recovery with the corresponding calibration acceptance criteria found in Table 5. If the responses for all parameters of interest fall within the designated ranges, analysis of actual samples can begin. If any individual recovery falls outside the range, proceed according to Section 12.

10.4 Internal Standards

Area counts of the internal standard peaks in all samples and QC samples must be between 50-200% of the areas of the internal standards in the QC check standard.

If any individual percent recovery falls outside the range, that parameter has failed the acceptance criteria. For calibration standards, CV or blanks the internal standard must be within the range for data to be reported to the clients. For samples, matrix spikes and duplicates: if the data is not within the range, the sample is rerun to confirm that the failure is due to sample matrix. A nonconformance report form is completed to ensure client notification and reporting if matrix effect is confirmed.

10.5 Matrix Spike

Spike and analyze a minimum of 5% of all samples to monitor and evaluate laboratory data quality.

The concentration of the spike should be at one to five times higher than the sample concentration or at the client requested action level. Due to the large number of unknown samples performed, the concentration of the matrix spike is at 20μg/L unless otherwise requested by the client. Refer to Section 8.7 for matrix spike preparation.

Calculate the matrix spike recovery. Compare the percent recovery for each parameter with the corresponding QC acceptance criteria found in Table 5.

If any individual percent recovery falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A nonconformance report form is completed to ensure client notification and reporting.

The EPA reference Method 624 allows the reporting of the data from a failed MS if the LCS is within the QC acceptance criteria. All acceptance and rejection data is based on a 20μg/L concentration.

10.6 Duplicates

Analyze a duplicate sample at a minimum of 5% of all samples. The percent RPD is determined. The laboratory generated limits for RPD must be met. Acceptance criteria of ≤ 30% will be used until in-house criteria can be generated. If acceptance criteria are not met, the duplicate sample is reanalyzed. If failure continues, a narrative is submitted with the data to be included with the final report.

10.7 Surrogates

The laboratory must spike all samples with surrogate standards to monitor continuing laboratory performance. Calculate the percent recovery of each surrogate compound. The recovery for the surrogate compounds must be within the 80-120% acceptance criteria.

If surrogate recovery fails to meet criteria, sample must be reanalyzed. The only exception to this rule is, if sample shows no detection of target compounds and any surrogate exceeds acceptance range, no further action is required. If the reanalysis also fails, a narrative is submitted for inclusion on the Client report.

10.8 Control Limits

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained.

Control charts for the method parameters are generated by the QC staff. The control limits are based on in-house performance data.

10.9 Analytical Sequence

In a 12-hour period, the analytical sequence is as follows:

BFB Tune Standard

QC Check Standard

Method Blank

Samples

MS (as required)

Duplicate (as required)

11. Method Performance

11.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/08-05. These studies performed by the laboratory are maintained on file for review.

11.2 Demonstration of Capability Studies

11.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

11.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

12. Corrective Actions

Holding time exceedances, improper preservation and observed sample headspace are noted on the nonconformance report form.

Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

Review of internal standard, surrogates and QC check standard response for acceptable performance occurs for each batch of samples. Record any trends or unusual performance on a nonconformance action form.

If the QC check standard or LCS recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected prior to analysis of samples.

Manual integration must be minimized. Routine manual integration of the same parameters indicates a system performance problem. Correct this problem or note in the instrument analysis logbook the suspected causes for routine manual integration. Sign and date all quantitation reports, which require manual integration.

13. Pollution Prevention

See Chemical Hygiene Plan for pollution prevention operations.

14. Waste Management

See Chemical Hygiene Plan for waste handling and disposal.

15. Attachments

Table 1: Reporting Limits

Table 2: BFB Key m/z Abundance Criteria

Table 3: Suggested Surrogate and Internal Standards

Table 4: Characteristic Masses for Purgeable Organics

Table 5: EPA 624 Calibration and QC Acceptance Criteria

Table 6: 624 Quantitation Ions

Table 7: 624 Volatile Internal Standards with Corresponding Target Compounds and Surrogates Assigned for Quantitation

Table 1: Reporting Limits

Parameter	Reported Detection Limits (µg/L)
Chloromethane	10.0
Bromomethane	5.0
Vinyl chloride	2.0
Chloroethane	2.0
Methylene chloride	5.0
Trichlorofluoromethane	5.0
1,1- Dichloroethene	1.0
1,1- Dichloroethane	1.5
Trans- 1,2- Dichloroethene	1.5
Chloroform	1.5
1,2- Dichloroethane	1.5
1,1,1- Trichloroethane	2.0
Carbon tetrachloride	1.0
Bromodichloromethane	1.0
1,2- Dichloropropane	3.5
cis- 1,3- Dichloropropene	1.5
Trichloroethene	1.0
Benzene	1.0
Dibromochloromethane	1.0
1,1,2- Trichloroethane	1.5
trans- 1,3- Dichloropropene	1.5
2- Chloroethylvinyl ether	10.0
Bromoform	1.0
1,1,2,2- Tetrachloroethane	1.0
Tetrachloroethene	1.5
Toluene	1.0
Chlorobenzene	3.5
Ethyl benzene	1.0
1,3- Dichlorobenzene	5.0
1,2- Dichlorobenzene	5.0
1,4- Dichlorobenzene	5.0
Xylenes	2.0
Styrene	1.0
Acetone	10.0
Carbon Disulfide	5.0
2-Butanone	10.0
Vinyl acetate	20.0
4-Methyl-2-pentanone	10.0
2-Hexanone	10.0
Acrolein	8.0
Acrylonitrile	10.0
cis-1,2-dichloroethene	1.0
Tert-butyl alcohol	20.0

MTBE	20.0
Tertiary amyl methyl ether	1.0
1,4-Dioxane	2000
Dibromomethane	1.0

Table 2

BFB Key m/z Abundance Criteria

Mass m/z	Abundance criteria
50	15-40% of Mass 95.
75	30-60% of Mass 95.
95	Base Peak, 100% Relative Abundance.
96	5-9% of Mass 95.
173	<2% of Mass 174.
174	>50% of Mass 95.
175	5-9% of Mass 174.
176	>95% but 101% of Mass 174.
177	5-9% of Mass 176.

Table 3

Suggested Surrogate and Internal Standards

Compound	Primary/Secondary Masses (m/z)	Routine Surrogates and Internal Standards
4-Bromofluorobenzene	95 174, 176	S
Fluorobenzene	96 70	S
Pentafluorobenzene	168	S
Bromochloromethane	128 130	I
2-Bromo-1-chloropropane	77 79, 156	I
1,4-Dichlorobutane	55 90, 92	I

Table 4: Characteristic Masses for Purgeable Organics

Parameter	Primary	Secondary
Chloromethane	50	52
Bromomethane	94	96
Vinyl chloride	62	64
Chloroethane	64	66
Methylene chloride	84	49, 86
Trichlorofluoromethane	101	103
1,1-Dichloroethene	96	61, 98
1,1-Dichloroethane	63	65, 85
trans-1,2-Dichloroethene	96	61, 98
Chloroform	83	85, 47
1,2-Dichloroethane	62	64, 98
1,1,1-Trichloroethane	97	99
Carbon tetrachloride	117	119, 121
Bromodichloromethane	83	85,127
1,2-Dichloropropane	112	65, 112
trans-1,3-Dichloropropene	75	77
Trichloroethene	130	95, 132
Benzene	78	
Dibromochloromethane	129	127
1,1,2-Trichloroethane	97	83, 99
cis-1,3-Dichloropropene	75	77
2-Chloroethylvinyl ether	106	65, 106
Bromoform	173	171, 175
1,1,2,2-Tetrachloroethane	83	131, 168
Tetrachloroethene	166, 164	129, 164
Toluene	92	91
Chlorobenzene	112	114
Ethyl benzene	91	106
1,3-Dichlorobenzene	146	148, 113
1,2-Dichlorobenzene	146	148, 113
1,4-Dichlorobenzene	146	148, 113
Xylenes	106	91
Styrene	104	78, 51
Acetone	43	58
Carbon Disulfide	76	78
2-Butanone	43	72
Vinyl acetate	43	
4-Methyl-2-pentanone	58	43
2-Hexanone	43	42, 58
Acrolein	56	55
Acrylonitrile	53	52
cis-1,2-dichloroethene	96	

Tert-butyl alcohol	59	
MTBE	73	
Tertiary amyl methyl ether	73	
1,4-Dioxane	88	
Dibromomethane	95	

Table 5 : EPA 624 Calibration and QC Acceptance Criteria

Parameter	Range for CCV (%)	Range for LCS/MS (%)
Benzene	64 - 136	37 - 151
Bromodichloromethane	66 – 134	35 - 155
Bromoform	71 – 129	45 - 169
Bromomethane	60 – 140	D - 242
Carbon tetrachloride	73 – 127	70 - 140
Chlorobenzene	66 – 134	37 - 160
Chloroethane	60 – 140	14 - 230
2- Chloroethylvinyl ether	40 – 140	D - 305
Chloroform	68 – 132	51 - 138
Chloromethane	60 – 140	D - 273
Dibromochloromethane	68 – 132	53 - 149
1,2- Dichlorobenzene	63 – 137	18 - 190
1,3- Dichlorobenzene	73 – 127	59 - 156
1,4- Dichlorobenzene	63 – 137	18 - 190
1,1-Dichloroethane	73 – 127	59 - 155
1,2- Dichloroethane	68 – 132	49 - 155
1,1- Dichlorothene	60 – 140	D - 234
cis- 1,2- Dichloroethene	60 – 140	60 - 140
trans- 1,2- Dichloroethene	70 – 131	54 - 156
1,2- Dichloropropane	60 – 140	D - 210
cis- 1,3- Dichloropropene	60 – 140	D - 227
trans- 1,3- Dichloropropene	60 – 140	17 - 183
1,4-Dioxane	60 – 140	60 – 140
Ethyl benzene	60 – 140	37 - 162
Methylene chloride	61 – 139	D - 221
MTBE	60 – 140	60 – 140
Tert-butyl alcohol	300 – 700	300 – 700
Tertiary amyl methyl ether	60 – 140	60 – 140
1,1,2,2- Tetrachloroethane	61 – 139	46 - 157
Tetrachloroethene	74 – 126	64 - 148
Toluene	75 – 125	47 - 150
1,1,1- Trichloroethane	75 – 125	52 - 162
1,1,2- Trichloroethane	71 – 129	52 - 150
Trichloroethene	67 – 133	71 - 157
Trichlorofluoromethane	40 – 140	17 - 181
Vinyl chloride	60 - 140	D - 251
cis-1,2-dichloroethene	60 – 140	60 - 140

Acrolein	40 – 160	40 - 160
Acrylonitrile	60 – 140	40 - 160
Acetone	40 – 160	40 - 160
Carbon Disulfide	60 – 140	40 - 160
Vinyl Acetate	60 – 140	40 - 160
2-Butanone	60 – 140	40 - 160
4-Methyl-2-pentanone	60 – 140	40 - 160
2-Hexanone	60 – 140	40 - 160
m/p- Xylene	60 – 140	40 - 160
o-Xylene	60 – 140	40 - 160
Styrene	60 – 140	40 - 160
Dibromomethane	70 - 130	70 - 130

D = Detected; result must be greater than zero. Criteria were calculated assuming a QC check sample concentration of 20 µg/L.

TABLE 6

624 Quantitation Ions

Compound	Quantitation Ion	Compound	Quantitation Ion
Benzene	78	Methyl tert-butyl ether	73
Bromodichloromethane	83	tert-Butyl alcohol	59
Bromoform	172	Tertiary- amyl methyl ether	73
Bromomethane	94	1,1,2,2- Tetrachloroethane	83
Carbon tetrachloride	117	Tetrachloroethene	166
Chlorobenzene	112	Toluene	92
Chloroethane	64	1,1,1 - Trichloroethane	97
2 - Chloroethylvinyl ether	63	1,1,2 - Trichloroethane	97
Chloroform	83	Trichloroethene	130
Chloromethane	50	Trichlorofluoromethane	101
Dibromochloromethane	129	Vinyl chloride	62
1,2 - Dichlorobenzene	146	cis-1,2-dichloroethene	96
1,3 - Dichlorobenzene	146	Acrolein	56
1,4 - Dichlorobenzene	146	Acrylonitrile	53
1,1 - Dichloroethane	63	Acetone	43
1,2 - Dichloroethane	62	Carbon Disulfide	76
1,1 - Dichloroethene	96	Vinyl Acetate	43
trans- 1,2 - Dichloroethene	96	2-Butanone	43
1,2 – Dichloropropane	63	4-Methyl-2-pentanone	58
cis- 1,3 - Dichloropropene	75	2-Hexanone	43
trans- 1,3 - Dichloropropene	75	m/p- Xylene	106
1,4-Dioxane	88	o-Xylene	106
Ethyl benzene	91	Styrene	104
Methylene chloride	84	Dibromomethane	95

TABLE 7

624 Volatile Internal Standards with Corresponding Target Compounds and Surrogates Assigned for Quantitation

Bromochloromethane	2-Bromo-1-Chloro-Propane	1,4-Dichloro-Butane
Chloromethane	2-Chloroethylvinyl ether	Chlorobenzene
Vinyl Chloride	4-Methyl-2-pentanone	Ethylbenzene
Bromomethane	cis-1,3-Dichloropropene	p/m-Xylene
Chloroethane	Toluene	o-Xylene
Trichlorofluoromethane	Trans-1,3-Dichloropropene	Styrene
Acrolein	2-Hexanone	Bromoform
Acetone	1,1,2-Trichloroethane	1,1,2,2-Tetrachloroethane
1,1-Dichloroethene	Tetrachloroethene	4-Bromofluorobenzene (surr)
tert-butyl alcohol	Dibromochloromethane	1,3-Dichlorobenzene
Methylene Chloride		1,4-Dichlorobenzene
Carbon Disulfide		1,2-Dichlorobenzene
Acrylonitrile		Xylenes (Total)
Methyl-tert-butyl-ether		
Trans-1,2-Dichloroethene		
Vinyl Acetate		
1,1-Dichloroethane		
2-Butanone		
cis-1,2-Dichloroethene		
Chloroform		
Pentafluorobenzene (surr)		
1,1,1-Trichloroethane		
Carbon Tetrachloride		
Tertiary-Amyl Methyl Ether		
1,2-Dichloroethane		
Benzene		
Fluorobenzene (surr)		
Trichloroethene		
1,2-Dichloropropane		
Bromodichloromethane		
1,4-Dioxane		
Dibromomethane		

Separatory Funnel Liquid-Liquid Extraction

Reference Method: **EPA 3510C (EPA 608, EPA 625, EPA 8151A and MA-DEP EPH)** SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update III, December 1996.

1. Scope and Application

Matrices: This method is applicable to aqueous samples.

Definitions: Refer to Alpha Analytical Quality Manual.

This method describes the procedure for extracting water-insoluble and lightly water-soluble organic compounds from aqueous samples. The method also describes concentration and extract clean-up techniques suitable for preparing the extract for the various determinative methods listed in Table 1.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one or more of the following laboratory personnel before performing the modification: Area Supervisor, Department Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability, analyzing a proficiency test sample and completing the record of training.

After initial demonstration, ongoing demonstration is based on acceptable laboratory performance of at least a quarterly laboratory control sample or acceptable performance from an annual proficiency test sample. A major modification to this procedure requires demonstration of performance. The identification of major method modification requiring performance demonstration is directed by the Quality Assurance Officer and/or Laboratory Director on a case-by-case basis.

2. Summary of Method

A measured volume of sample, typically 1 liter, is serially extracted with methylene chloride using a separatory funnel. Depending on the analytes to be detected, it may be necessary to adjust the pH of the aqueous sample prior to extraction (Table 1).

Any water is removed from the sample extract by filtering through a powder funnel containing approximately 20g of baked anhydrous sodium sulfate. The extract is then concentrated and, as needed, exchanged into a solvent compatible with the cleanup or determinative step being employed. The various cleanup methods used summarized in Table 1.

2.1 Method Modifications from Reference

None.

3. Reporting Limits

Reporting Limit information can be found in the analytical method SOPs.

4. Interferences

4.1 The most common cause of contamination is from improperly cleaned glassware and lab supplies. All glassware and re-useable extraction equipment must be scrupulously cleaned, following the Organic Extraction Glassware Cleaning and Handling SOP/1953.

4.2 Impurities in solvents and reagents may also yield artifacts and/or interferences that may compromise the results of sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of extract preparation and analysis by preparing method blanks with each extraction batch. The same solvents and reagents are used for the method blank and the associated samples.

4.3 Phthalate esters contaminate many types of products used in the laboratory. Plastic materials must not contact the samples or extracts, as phthalates could be easily leached from the plastic. The exception is in the use of various pre-packed reagent cartridges (Florisil, Silica gel) used in the extract cleanup steps. Each new lot of cartridges is checked for contamination, and is monitored on an on-going basis through the analysis of method blanks.

4.4 Additional specific interference or contamination concerns are addressed in the various analytical SOPs.

5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

5.1 Lab coats, safety glasses, and gloves must be worn when handling samples, extracts, standards or solvents and when washing glassware.

5.2 All extract concentration steps must be performed in the extraction hoods. All solvent and extract transfers must also be handled in the hood.

5.3 All expired stock standards, working standards, and spent sample extracts must be placed into the waste bucket in the lab, for future disposal by the Hazardous Waste Manager. The container must be properly labeled with hazard warning labels indicating the container contents.

5.4 Bottles containing flammable solvents must be stored in the flammables cabinet or in the vented cabinets found under the hoods.

5.5 All waste solvents must be transferred to the satellite waste storage containers located in the extraction lab. Separate containers are provided for chlorinated and non-chlorinated solvents and must be used accordingly. Under no circumstances are solvents to be poured down the sink drains.

5.6 Inspect all glassware prior to use. Do not use any glassware that is chipped, cracked or etched if it could present a safety hazard. Damaged glassware is put aside for repair, otherwise discard the piece.

5.7 All Field Samples must be opened and handled in a hood.

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

Sample collection and preservation requirements are described in the various analytical method SOPs.

6.2 Sample Preservation

None.

6.3 Sample Shipping

See applicable Sample Custody SOP.

6.4 Sample Handling

All aqueous samples are stored, refrigerated, in the Organic Extraction Custody Refrigerators. Samples are removed from the refrigerator by the Chemist immediately prior to sample extraction. The Chemist must take custody of the samples by signing them out utilizing the LIMS, see Work Instruction 2517 ELN Procedure and Work Instruction 2421 Labeling and Generating Work Groups and Batches.

Visually inspect the samples prior to starting the extraction process, as described in Section 10.1. Typically the entire content of the 1L amber jar is used for extraction. After the sample or sample aliquot is measured, the samples or empty sample containers are scanned to “empty” or returned to the Refrigerator.

7. Equipment and Supplies

7.1 Separatory Funnel: 2-Liter, glass or Teflon, with polytetrafluoroethylene (PTFE) stopcock and cap.

7.2 Erlenmeyer Flasks: 250 and 500 mL.

7.3 Centrifuge Tubes.

7.4 Syringes: 1mL, 250µL

7.5 Disposable Borosilicate Transfer Pipets.

7.6 Sodium Sulfate glass filtering funnels. Add a plug of glass wool to the base of the 75mm glass funnel. Add approximately 20grams of baked sodium sulfate.

7.7 Glass wool.

7.8 Water Bath: Heated, with concentric ring cover, with variable temperature control.

7.9 Kuderna-Danish (KD) Apparatus: Assemble by attaching the Concentrator Tube to the Evaporation Flask using the Plastic clip. Add the Macro column to the Evaporation

Flask. The Micro Snyder Column is attached directly to the Concentrator Tube using the Plastic Clip.

7.9.1 Evaporation Flask: 500mL KD flask.

7.9.2 Concentrator Tube: 15mL, 25mL, graduated.

7.9.3 3-Ball Macro Snyder Column.

7.9.4 Micro Snyder Column.

7.9.5 Plastic Kek clips.

7.10 Boiling Chips: Solvent extracted, approximately 10/40 mesh (silicon carbide, or equivalent).

7.11 Graduated Cylinders: 25, 50, 250 and 1000 mL, class "A".

7.12 N-EVAP: Organomation; utilized for micro blow down.

7.13 TURBO-VAP II: Auto-concentrator, Caliper Life Sciences.

7.14 Zymark Tubes: 50mL and 200mL.

7.15 pH Paper: Multibanded, wide range.

7.16 Filter Paper: Whatman #4 150mm

7.17 Screw-top vials: 22mL volume.

7.18 Automatic Separatory Funnel Shaker

7.19 KI Paper Strips: 0.05mg/L residual chlorine sensitivity.

7.20 Multi-Colored "DOTS"- Used to assist in Labeling Separatory Funnels.

7.21 Multi-Position Stirring Plates.

7.22 Magnetic Stirring Bars.

7.23 250mL Volumetric Flask.

8. Reagents and Standards

Pesticide or reagent grade chemicals are used in all tests. All reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.1 Reagent Water: All references to water in this method refer to reagent water from Alpha's DI water treatment system.

8.2 Sodium hydroxide solution (25%), NaOH: Dissolve 245g NaOH in reagent water and dilute to 1000mL. For basification of samples. Reagent expires one year after preparation.

8.3 Sulfuric acid solution (1:1 v/v), H_2SO_4: Prepare by slowly adding 500mL of concentrated H_2SO_4 to 500mL of reagent water, in a 1-Liter beaker placed in an ice water bath. For acidification of all non-EPH samples. Reagent expires one year after preparation.

8.4 Hydrochloric Acid, 6N, 2:1: Place a 2000mL Beaker or equivalent in an ice water bath. Add 50mL of DI water to the beaker. Slowly add 100mL of Concentrated HCL. Mix with a stirring rod and allow to cool in a hood. Used for the acidification of EPH samples. No expiration date needed.

8.5 Sodium Sulfate (Na_2SO_4): Granular anhydrous; purified by baking at 400ºC for 4 hours in a shallow tray. Store in closed glass containers. All references to sodium sulfate in this method refer to this prepared reagent.

8.6 Methylene Chloride: Pesticide quality or equivalent. No expiration date listed.

8.7 Hexane: Pesticide quality or equivalent. No expiration date listed.

8.8 Acetone: Pesticide quality or equivalent. No expiration date listed.

8.9 Spiking Solutions: The various surrogate and LCS/MS spiking solutions used in the extraction steps are listed in Table 2. The preparation and expiration dates of these solutions are described in the analytical SOPs.

8.10 Sodium Thiosulfate Crystals ($Na_2S_2O_3$): J.T. Baker; 5-Hydrate crystal.

8.11 Silica Gel: VWR, Cat# TX4694MAAA. 60 - 200 mesh, chromatography grade. Activated by baking at 140 °C for a minimum of 14 hours in a shallow tray. The silica gel is stored in the oven or desiccator until ready for use. All references to silica gel in this method refer to this prepared reagent.

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

Each extraction batch contains various QC samples used to ensure the validity of the sample results. The particular QC elements performed for a given extraction batch are determined by the requirements of the determinative method. The purpose and definition of the QC samples performed are listed below. The specific QC requirements of the analytical methods are listed in Table 2.

9.1 Blank

Blanks, or method blanks, are measured aliquots of reagent water (for aqueous extractions) that are treated identically to the associated samples. Surrogates are added, and the blanks are

carried through all stages of the sample extraction, concentration, and cleanup procedures. Blanks serve to ensure that no systematic contamination exists. A blank is extracted with each batch of 20 or less samples. For 608 and 625 a blank is extracted with each batch of 10 or less samples.

9.2 Laboratory Control Sample (LCS/LCSD)

LCS samples are measured aliquots of reagent water (for aqueous extractions) that are spiked with a solution containing known amounts of target compounds, in addition to the surrogate solution. The LCS is carried through all stages of the sample extraction, concentration, and cleanup procedures. LCS samples serve as batch specific quantitative checks of the extraction. An LCS is extracted with each batch of 20 or less samples. For samples to be analyzed by EPA 608 and 625, a LCS is extracted with each batch of 10 or less samples.

An LCSD is performed in addition to an LCS for most methods, as well as in lieu of the MS/MSD or Duplicate when there is insufficient sample volume available. The required solutions and volumes are listed in Table 2.

9.3 Initial Calibration Verification (ICV)

Not Applicable.

9.4 Continuing Calibration Verification (CCV)

Not Applicable.

9.5 Matrix Spike

MS and MSDs are field samples spiked with a known quantity of the target analyte(s). They are prepared by taking additional sample aliquots, and adding the appropriate amounts of surrogate and spiking solutions. The MS/MSD are carried through all stages of the sample extraction, concentration, and cleanup procedures. MS samples serve as a measure of extraction accuracy, by allowing the comparison of the found amount(s) of target analyte(s) with the spiked amount(s). An MS/MSD set also allows for the calculation of the extraction precision, by comparing the results of the two samples.

For samples to be analyzed by EPA 608 and 625, a MS is extracted with batch of 10 samples or less.

9.6 Laboratory Duplicate

Duplicates are laboratory selected replicate samples, prepared by taking an additional sample aliquot of a sample. The duplicate is carried through all stages of the sample extraction, concentration, and cleanup procedures. Duplicates serve as a measure of the extraction precision, by comparing the results of the sample and duplicate. For samples to be analyzed by EPA 608 and 625, a DUP is extracted with batch of 10 samples or less.

9.7 Method-specific Quality Control Samples

9.7.1 Surrogates

Surrogates are compounds specified by the analytical method that are added to all samples and QC samples prior to beginning the extraction process. Surrogate recoveries are calculated and serve as a sample specific quantitative check of the extraction. The various spiking solutions are prepared according to the directions found in the analytical SOPs. The required solutions and volumes used are listed in Table 2.

9.8 Method Sequence

See Section 10.

10. Procedure

All glassware and Separatory Funnels must be cleaned following the procedure described in the glassware washing SOP/1953. In addition, the glassware must be rinsed with acetone and methylene chloride, or baked at 400C for four hours just prior to use. The Separatory Fuunnels are rinsed with acetone, followed by DCM.

All water extractions follow the LEAN "one-piece flow". All extraction information is recorded by the chemist performing the work in the ELN (Electronic Lab Notebook) see WI/2517. In addition to recording the extraction, concentration, clean-up and vialing information, the analyst must note any anomalies during the extraction procedure in the comments section of the ELN. Generating Work Groups, Batches and Labeling is described in Work Instruction WI/2421.

10.1 Sample Extraction

10.1.1 Carefully examine the sample prior to beginning the extraction process. The sample should be a single phase, with minimal or no sediment or solid material present. If this is not the case, contact the Extraction Lab Supervisor or Manager to determine how to handle the sample. The supervisor may need to contact login or the project manager to determine how the client would like the sample handled. Generally 1000mL,1200mL or 2000mL of sample is extracted to meet reporting limits. If 1200mL is required, this will be specified by the client

10.1.2 If the sample volume is less than the top of the sample collection bottle, if additional sample volume exists, use another bottle to top it off. If additional volume is not available, mark the current volume level on the sample bottle using a permanent marker for later volume determination.

10.1.3 Field and QC samples being analyzed for either EPA 625 or EPA 608 must be checked for residual chlorine prior to any pH adjustments or extraction. Invert the sample several times to ensure that sample is well mixed, then dip one KI test strip into sample for 10 seconds with a gentle constant back and forth motion. Wait 30 seconds and then refer to the chart on the KI strip container, if chlorine is detected at a level less than 0.1mg/L proceed with the extraction. Otherwise, record in the ELN that the TRC is positive (+). Then add sodium thiosulfate to the sample, mix and re-check, repeat until the chlorine level is less than 0.1mg/L. Record in the ELN.

10.1.4 For One-piece flow sample processing and labeling, see Labeling and Generating Work Groups and Batches Work Instruction WI/2421.

10.1.5 Using a 1-Liter Class "A" Graduated Cylinder, measure 1 liter of reagent water for blanks and LCSs. For QC requirements, see Table 2 and Form 02-58. For samples, use the entire sample bottle (See10.1.2). Unless high analyte concentrations are anticipated, a smaller sample volume may be taken and diluted to 1L with reagent water. On occasion, the client may provide smaller sample volumes, note this in the ELN. If the sample volume is higher than 750 mLs, then mark the water level on the amber and use the entire contents. If the sample volume is less than 750mL, add reagent water to reach a final volume of 1000mL. Notate in the ELN the sample volume extracted and addition of DI water. If the sample was prepared as a TCLP, use only 200 mLs for the sample volume and QC. The TCLP fluid is used instead of DI water for the QC. For SPLPs samples, extract a full 1000 mL for all samples and QC. QC will require the use of SPLP fluid.

NOTE: For samples to be analyzed for Alpha 8082 NY Products, a total of 1200mL of sample is extracted. Use a 250mL Class "A" Graduated Cylinder to measure the additional 200mL sample volume and combine in the Separatory Funnel.

10.1.6 Transfer the sample from the sample container or graduated cylinder into a labeled 2L separatory funnel.

10.1.7 Adjust the pH, if necessary, to the pH indicated in Table 1, using the base and acid solutions listed in Sections 8.2-8.4. (**NOTE:** Do not alter the pH for neutral extractions.) The amount of acid or base required to achieve the desired pH is highly sample dependant, but is typically 3-20 mL.

10.1.8 Add the appropriate volume(s) of the spiking solutions; see Table 2, to the LCS, LCSD, MS, and/or MSD samples, as required. Using a syringe, add the appropriate volume(s) of the surrogate solution(s), listed in Table 2, into each sample and QC sample(See WI/2421).

10.1.9 If there was no significant sediment or non-aqueous material present in the sample container, use 60mL of methylene chloride to rinse the sample cylinder (or bottle) and transfer this rinseate into the separatory funnel**.**

If the sample did contain sediment or solid material that is not considered part of the sample, add 60mL of methylene chloride directly into the separatory funnel.

If the sample was transferred directly from the sample bottle, refill the bottle with water to the mark made in Section 10.1.2 and measure the volume using a graduated cylinder. Record the volume of sample that was in the bottle into the ELN.

10.1.10 Tightly cap the separatory funnel and vent each separatory funnel into a hood. Place the funnel into the holders on the Automatic Shaker, cap downward. Secure the locks.

10.1.11 Turn the unit on. Press 'Select' three times to open the timing menu. Press the 'up arrow' to set the number of minutes to be equal to '2'.

NOTE: For EPH extractions set the number of minutes to be equal to '3'.

10.1.12 Press "Start". By pressing the 'up arrow' set the rpm to be equal to '170'.

10.1.13 When the Automatic Shaker stops, remove the separatory funnel and align in the hood over the appropriate KD Setup (see WI/2421). Allow the organic layer to separate from the water phase. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, addition of sodium chloride, or other physical methods.

10.1.14 **Before decanting the solvent layer**, check the pH of the sample with wide-range pH paper and record the value in the ELN. If the pH of the sample has not been satisfied as required by the determative method, re-adjust the pH as indicated in Table1, using the base and acid solution. Repeat sections 10.1.10-10.1.13 until the appropriate pH is reached.

10.1.15 Filter the extract through a funnel packed with glass wool and approximately 20 grams of sodium sulfate, collecting the filtrate in a KD Apparatus with the appropriate sample label. Alternatively, the sample may be filtered directly into a Zymark Tube for Turbovap concentration (See Section 10.3).

10.1.16 For all analyses repeat the extractions two more times for two minutes each, using fresh portions of solvent (Section 10.1.9-10.1.15). Collect all three solvent extract portions in the same labeled KD Apparatus.

10.1.17 If additional pH adjustment during extraction is required, adjust the pH of the aqueous phase to the desired pH indicated in Table 1. Repeat the extraction process Section 10.1.9-10.1.15).

10.1.18 For EPH analysis, repeat the extractions two more times for three minutes each, using fresh portions of solvent (Section10.1.9-10.1.15). Collect all three solvent extract portions in the same labeled KD Apparatus.

10.1.19 For ETPH Analysis, the sample extract is collected into a 250mL Erlenmeyer Flask. Add 3 grams of activated Silica Gel and a stir bar to the extract. Place the sample on a stirring plate and stir for 5 minutes. Filter the extract through a glass funnel containing filter paper and approximately 20 grams of sodium sulfate, collecting the filtrate in a Zymark Tube for Turbovap concentration. Alternatively, the sample may be filtered directly into a KD-Setup and concentrated using the KD Technique (See Section 10.2).

10.1.20 The extract is now ready for concentration proceed to section 10.2

10.2 Sample Concentration: KD Technique

10.2.1 Attach a three-ball Snyder column to the top of the flask. Place the KD apparatus on a hot water bath (heated to approximately 75^{o}C for samples extracted in Methylene Chloride and 95^{o}C for samples extracted in Hexane) so that the concentrator tube is partially immersed in the hot water, and so that the entire lower rounded surface of the flask is bathed in hot water vapor. Adjust the position of the apparatus as required to complete the concentration in 30 to 40 minutes. At the proper rate of distillation, the balls in the column will actively chatter, but the chambers will not flood with solvent. Periodically rinse the internal walls of the concentrator tubes with DCM.

10.2.2 If a Hexane exchange is required (see Table 1), add 30 to 35mL of hexane, when the sample volume reaches approximately 5-10mLs. Add the hexane to the top of the Snyder column while the concentrator is still on the water bath. Continue with the concentration until the extract volume is reduced to below 10mL. Periodically rinse the internal walls of the synder column with 5-10mLs of Hexane. Remember to switch the extract to the higher temperature bath after the addition of hexane.

10.2.3 Remove the KD apparatus from the water bath. Rinse the flask and its lower ground glass joint with 1 to 2 mL of acetone to remove any moisture from the outside of the glassware. Allow to cool for 15 minutes. Disassemble the KD apparatus. Move the label from the K-D Flask to the concentrator tube (See WI/2421).

10.2.4 Place the Concentrator tube on the N-EVAP. The N-EVAP is set at 37°C for samples extracted in Methylene Chloride and 65 °C for samples extracted in Hexane with the nitr**o**gen flow at 5 - 7. Samples remain on N-EVAP until they are reduced to 1mL. **Pesticide Extracts:** Using a syringe or volumetric flask, adjust final volume to 10 mL with hexane.

10.2.5 The extract is now ready for sample cleanup or vialing (See Table 1). Refer to the relevant Clean-up SOP or proceed with extract vialing (See WI/3827, Extract Vialing Procedure, WI/2426, GC Extract Vialing Procedure and WI/2423, GC/MS Extract Vialing Procedure).

10.3 Alternate Concentration Technique

The equipment used for alternate sample concentration is the Zymark TurboVap II, which is a self-contained water bath and nitrogen blow-down. It is equipped with sensors to allow for

automatic shutdown when the extract volume goes below 1mL. This technique is generally used for concentration of TPH samples.

10.3.1 The TurboVap is set at 37°C for samples extracted in Methylene Chloride. The nitrogen pressure is set to 10-15 psi and the endpoint concentration is set to 'Sensor'. The Zymark tube is labeled with the sample I.D.

10.3.2 Place the labeled Zymark tube containing sample into the TurboVap II concentration unit. Start the nitrogen blow-down by pressing the button on the front panel of the unit.

10.3.3 When the concentration is complete, the nitrogen stream will be automatically shut off. The light on the front panel will flash, and the instrument will beep. Remove the tube from the Zymark concentrator; the final extract volume is 1mL. Refer to the relevant Clean-up SOP or proceed with extract vialing (Extract Vialing Procedure, WI/3827, GC Extract Vialing Procedure and WI/2426, GC/MS Extract Vialing Procedure WI/2423).

10.4 Preventive Maintenance

10.4.1 Turbovap II Concentrators

10.4.1.1 Maintain the level of the water bath by adding water daily.

10.4.1.2 Keep the unit clean. Avoid solvent spills on or around unit. Clean periodically with a damp cloth.

10.4.2 Water Bath

10.4.2.1 The water bath should be kept full at all times. Add reagent water as necessary.

10.4.2.2 Keep unit clean. Avoid solvent spills on or around unit. Clean periodically with a damp cloth.

10.4.3 Automatic Shaker

10.4.3.1 The Automatic Shaker should be lubricated according to the manufacturer's instructions.

11. Data Evaluation, Calculations and Reporting

Not Applicable.

12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

Holding time exceedence, improper preservation and observed sample headspace are noted on the nonconformance report form.

When analysis of samples indicates possible extraction problems, such as poor surrogate recoveries, poor LCS/MS/MSD recoveries, or suspected contamination in blanks or samples, re-extractions are required. Depending on the particular failure, the re-extraction may be of a specific sample or the entire extraction batch.

The analyst that determines the need for re-extraction must fill out a sample re-extract request form. This form notes the reason for the re-extraction request along with any special requirements, and the date and time that the re-extract is needed. Re-extraction request forms are maintained on file to help track the cause for re-extractions, and to be used as a tool in improving systems to minimize the need for re-extractions.

Depending on the results of the re-extraction, the first, second, or both sets of results may be reported to the client, along with a narrative report detailing the problems encountered and the resolution.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/1732. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP/1739 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

SOP/1732 DL/LOD/LOQ Generation

SOP/1739 DOC Generation

SOP/14-01 Waste Management and Disposal SOP

SOP/1953 Organic Extraction Glassware Cleaning and Handling

Form 02-50 Sample Cleanup and Vialing Guide

WI/2421 Labeling and Generating Work Groups and Batches

WI/2517 LIMS Electronic Laboratory Notebook Procedure

WI/2423 GC Mass Spec Extract Vialing Procedure

WI/2426 GC Extract Vialing Procedure

WI/3827 Extract Vialing Procedure

Form 02-58 Sample Extraction Guide

16. Attachments

Table 1

Specific Extraction Conditions for Various Determinative Methods

Determinative Method	Initial Extraction pH	Secondary Extraction pH	Extraction Solvent	Exchange Solvent Required	Final Volume	Appropriate Cleanup Technique
Pest/8081	5 – 9	None	DCM	Hexane	10 mL	Florisil [b]
PCB/8082	5 – 9	None	DCM	Hexane	1 mL	Sulfuric acid
608	5 – 9	None	DCM	Hexane	1 mL	Florisil [b]
8270	< 2	> 11	DCM	n/a	1 mL	n/a
625	< 2	> 11	DCM	n/a	1 mL	n/a
TPH-DRO	As received	None	DCM	n/a	1 mL	n/a
NJ TPH	As received	None	DCM	n/a	1 mL	n/a
MA-EPH	< 2	None	DCM	Hexane	1 mL	Silica Gel Fractionation
NJ-EPH	<2	None	DCM	Hexane	1mL	Silica Gel Fractionation
CT-ETPH	As received	None	DCM	n/a	1 mL	Silica Gel
Herbicide	See relevant SOP					

- 8270 and 625 methods are for extraction of both acidic and base/neutral compounds.
- Sample extracts may require additional cleanup by Method 3660A to remove elemental sulfur, as determined by the sample extract appearance once florisil cleanup has been performed.
- The TPH-DRO method includes the products TPH-DRO and TPH-DRO-D.

For additional product QC, Solvent, Surrogate and Spike solutions, see Form "Sample Extraction Guide".

Table 2

Liquid Extraction Guide

Analytical Method	QC	Surrogate Solution	LCS/LCSD MS/MSD Solution	Solvent	pH (Acid/Base/Neutral)
625	WB, LCS, MS, Dup	1mL ABN	1mL MCP ABN Spike #1/ Spike #2	DCM	A/B
625-AEXT	WB, LCS, MS, Dup	1mL ABN	1mL MCP ABN Spike #1/ Spike #2	DCM	A/B
625-BNEXT	WB, LCS, MS, Dup	1mL ABN	1mL MCP ABN Spike #1/ Spike #2	DCM	A/B
625-PHT	WB, LCS, MS, Dup	1mL ABN	1mL MCP ABN Spike #1/ Spike #2	DCM	A/B
PEST-608	WB, LCS, MS, Dup	250µL PCB/PEST	250µL PEST 608	DCM	N
NYPCB-608	WB, LCS, MS, Dup	250µL PCB/PEST	250uL PCB-608	DCM	N
PCB-608	WB,LCS,MS,Dup	250µL PCB/PEST	250µL PCB-608	DCM	N
PCB/PEST-608	WB, LCS, MS, Dup	250µL PCB/PEST	250µL PEST 608	DCM	N
8270	WB, LCS, LCSD	1mL ABN	1mL MCP ABN Spike #1/ Spike #2	DCM	A/B
PAH	WB, LCS, LCSD	1mL ABN	1mL MCP ABN Spike #1/ Spike #2	DCM	A/B
PHT	WB, LCS, LCSD	1mL ABN	1mL MCP ABN Spike #1/ Spike #2	DCM	A/B
AEXT	WB, LCS, LCSD	1mL ABN	1mL MCP ABN Spike #1/ Spike #2	DCM	A/B
BNEXT	WB, LCS, LCSD	1mL ABN	1mL MCP ABN Spike #1/ Spike #2	DCM	A/B
PAH-Low	WB, LCS, LCSD	1mL ABN	1mL MCP PAHLOW Spike #1/Spike #2	DCM	A/B
MCP 8270	WB, LCS, LCSD	1mL ABN	1mL MCP ABN Spike #1/ Spike #2	DCM	A/B
MCP-8270SIM	WB,LCS,LCSD	1mL ABN	1mL MCP PAHLOW Spike #1/Spike #2	DCM	A/B
MCP PAH	WB, LCS, LCSD	1mL ABN	1mL MCP ABN Spike #1/ Spike #2	DCM	A/B
MCP-PHT	WB, LCS, LCSD	1mL ABN	1mL MCP ABN Spike #1/ Spike #2	DCM	A/B
MCP PAH-LOW	WB, LCS, LCSD	1mL ABN	1mL MCP PAHLOW	DCM	A/B
PEST (8081)	WB, LCS, LCSD	250µL PCB/PEST	250µL PEST	DCM	N
PCB (8082)	WB, LCS, LCSD	250µL PCB/PEST	250µL PCB	DCM	N
MCP PEST (8081)	WB, LCS, LCSD	250µL PCB/PEST	250µL PEST	DCM	N
MCP PCB (8082)	WB, LCS, LCSD	250µL PCB/PEST	250µL PCB	DCM	N
EPH/PAH-LOW	WB, LCS, LCSD	1mL EPH	1mL EPH	DCM	A-Use 6N HCL
EPH-DELUX	WB, LCS, LCSD	1mL EPH	1mL EPH	DCM	A-Use 6N HCL
EPH	WB, LCS, LCSD	1mL EPH	1mL EPH	DCM	A-Use 6N HCL
NJEPH	WB,LCS,LCSD,MS,DP	1mL NJEPH	1mL NJEPH	DCM	A-Use 6N HCL
TPH-DRO	WB, LCS, Dup	1mL DRO	1mL ETPH	DCM	N

TPH-DRO-D	WB, LCS, Dup	1mL DRO	1mL ETPH	DCM	N
ETPH	WB, LCS, MS, Dup	1mL DRO	1mL ETPH	DCM	N
NJEPH/TPH	WB, LCS,LCSD, MS, Dup	1mL NJEPH	1mL NJEPH	DCM	A-Use 6N HCL
ME-4125	WB, LCS, MS, Dup	1mL DRO	1mL ETPH	DCM	N
ABN-TCLP*	WB, LCS, LCSD	1mL ABN	1mL MCP ABN Spike #1/ Spike #2	DCM	A/B
PEST-TCLP*	WB, LCS, LCSD	250uL PCB/PEST	250uL PEST	DCM	N
PCB-TCLP*	WB, LCS, LCSD	250uL PCB/PEST	250uL PCB	DCM	N
ABN-SPLP	WB, LCS, LCSD	1mL ABN	1mL MCP ABN Spike #1/ Spike #2	DCM	A/B
Pest-SPLP	WB, LCS, LCSD	250uL PCB/Pest	250uL PCB	DCM	N
PCB-SPLP	WB, LCS, LCSD	250uL PCB/Pest	250uL PCB	DCM	N

*Note- All TCLP extractions are 200mL of sample.
** For additional QC requirements see Form 02-58.

Semivolatile Organic Compounds by Gas Chromatography/ Mass Spectrometry (GC/MS)

Reference Method No.: **EPA 625**

Reference: Test Procedures for the Analysis of Organic Pollutants. Appendix A, Part 136, Code of Federal Regulations. July 1, 1985 edition.

1. Scope and Application

Matrices: This method is used to determine the concentration of semivolatile organic compounds in extracts prepared from aqueous samples.

This method is used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted, without derivatization, as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone.

The following compounds may require special treatment when being determined by this method:

- Benzidine may be subject to oxidative losses during solvent concentration and its chromatographic behavior is poor.
- Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition.
- n-Nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described.
- Pentachlorophenol, 2,4-dinitrophenol, nitrophenol, benzoic acid, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one of the following laboratory personnel before performing the modification: Area Supervisor, Laboratory Services Manager, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of analysts experienced in the operation of a gas chromatograph/mass spectrometer and in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability (Section 10.1), analyzing a proficiency test sample and completing the record of training. After initial demonstration, ongoing demonstration is based on acceptable laboratory performance of at least a quarterly laboratory control sample or acceptable performance from an annual proficiency test sample.

2. Summary of Method

The samples are introduced into the GC/MS by injecting 1µL of the sample extract into a gas chromatograph (GC) with a narrow-bore fused-silica capillary column. The GC is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the gas chromatograph.

Analytes eluted from the capillary column are introduced into the mass spectrometer via direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of standards run on the same GC/MS system. Quantitation is accomplished by comparing the response of the quantitation ion relative to an internal standard using a five-point calibration curve.

2.1 Method Modifications from Reference

None.

3. Detection Limits

Table 6 lists our routine reporting limits. Whenever MDL studies are performed, the MDL results are compared with our reporting limits to ensure that the calculated MDLs are equal to or below our reporting limits.

4. Interferences

4.1 Instrumental

4.1.1 Only high purity helium is used in the GC system to eliminate this source of possible contamination. The helium (carrier gas) is certified by the gas supplier.

4.1.2 Preventive instrument maintenance is performed routinely, and whenever highly contaminated extracts are analyzed that could result in chromatographic interferences or result in degradation of system performance. Section 9.5 details the maintenance steps.

4.1.3 Glassware must be scrupulously cleaned. This procedure is detailed in the extraction SOPs. Store dry glassware in a clean environment.

4.2 Parameters

4.2.1 Contaminated solvents or reagents are also possible sources or contamination. All solvents used are pesticide grade or equivalent, and reagents are purchased as certified contaminant free. All of these materials are routinely determined to be free of interferences by analysis of extraction blanks with every extraction batch performed.

4.2.2 Contamination by carry-over can occur whenever high-concentration and low-concentration samples are sequentially analyzed. Whenever an unusually concentrated sample is encountered, it must be followed by the analysis of a solvent blank to check for possible carryover.

5. Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound must be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

5.1 Lab coats, safety glasses, and gloves must be worn when handling samples, extracts, standards or solvents.

5.2 All solvent and extract transfers must be handled in the vented bench area in the GC/MS laboratory.

5.3 All stock standards, working standards, and vialed sample extracts must be placed into the waste bucket in the lab for future disposal by the Health and Safety Officer. The container must be labeled properly with hazard warning labels indicating the container contents.

5.4 Flammable solvent bottles must be stored in the flammables cabinet.

6. Sample Collection, Preservation, and Handling

6.1 Sample Collection

Samples are collected in two 1L amber glass jars with teflon-lined lids. All containers are purchased pre-cleaned and certified from commercial vendors.

6.2 Sample Preservation

Samples are preserved by packing in coolers with ice or ice packs, to maintain a temperature of $\leq$ 4ºC. Upon receipt at the laboratory, the samples are transferred into sample storage refrigerators to maintain at a temperature of $\leq$ 4ºC.

6.3 Sample Handling

Samples must be extracted within 7 days of sample collection. Once extracted, the samples must be analyzed within 40 days of the extraction date.

7. Equipment and Supplies

7.1 Gas Chromatograph/Mass Spectrometer System:

7.1.1 Gas Chromatograph: A nanalytical system complete with a temperature-programmable gas chromatograph configured for split/splitless-injection and all required accessories, including syringes, analytical columns, and gases. The capillary column is directly coupled to the source.

7.1.2 Column: 30m x 0.32mm ID, 0.25 µm film thickness silicone-coated, fused-silica capillary column (RXi-5Sil MS w/5m Integra Guard, Restek), or equivalent.

7.1.3 Mass Spectrometer: Scanning from 35 to 500 amu every 1 second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer is capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets the criteria in Table 1 when 1 µL of the GC/MS tuning standard is injected through the GC (50ng of DFTPP).

7.1.4 Data System: A computer system is interfaced to the Mass Spectrometer. The system allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer software allows the analyst to search any GC/MS data file for ions of specific mass and plot such ion abundances versus time. *HP ChemServer* software

is used for data acquisition and *Target/NT Revision 4.12* software is used for data reduction.

7.1.5 Syringes: 10 µL – 1mL.

7.1.6 Volumetric Flasks, Class A: Appropriate sizes with ground-glass stoppers.

7.1.7 Vials: Glass autosampler vials with polytetrafluoroethylene (PTFE)-lined crimp top caps

8. Standards and Reagents

8.1 Stock Standard Solutions

Certified stock standard solution in dichloromethane (DCM). Stock standards include calibration standards, calibration verification, and internal standard.

All stock standards, lot number, catalog number, expiration date, preparation date and initials are recorded in a logbook.

All stock standard solutions must be transferred into bottles with PTFE-lined screwcaps. Store, protected from light, at –10ºC or less. Stock standard solutions are checked for signs of degradation or evaporation, especially just prior to preparing secondary dilution standards.

Stock standard solutions are all replaced after 6 months or sooner if comparison with quality control check samples indicates a problem.

Vendor	Standard	Catalog Number	Concentration
Restek			
	8270 Mega Mix	31850	1000ug/ml
	605 Benzidines Mix	31030	2000ug/ml
	Benzoic Acid Mix	31879	2000ug/ml
	Acid Surrogate Mix	31025	2000ug/ml
	BN Surrogate	31024	1000ug/ml
	Custom SV Standard	562843	2000ug/ml
	Custom ABN Additionals Standard	562538	2000ug/ml
	Benzaldehyde Standard	33017	2000ug/ml
	Alpha-Terpineol Standard	33912	2000ug/ml
	8270 Benzidines Mix#2	31852	2000ug/ml
Absolute	Atrazine Solution	70023	1000ug/ml
AccuStandard	Parathion	M-622-19	1000ug/ml

8.1.1 ABN Mega Mix Standard, 200ug/mL

Use 1mL of each of the following:

605 Benzidines Mix
Benzoic Acid Mix
Acid Surrogate Mix

and use 2mL of each of the following:

8270 Mega Mix
BN Surrogate

and bring up to 10mL volume with DCM.

8.1.2 AP9 Additional Compounds Standard, 200ug/mL

Use 1mL of each of the following:

Custom SV Standard
Custom ABN Additionals Standard
Benzaldehyde Standard
Alpha-Terpineol Standard

and bring up to 10mL volume with DCM

8.1.3 Atrazine, 3,3-Dimthylbenzidine, Parathion 200ug/ml

Use 2 ml of each of the following:
Atrazine Solution
Parathion
And Use 1 ml of 8270 Benzidine Mix#2 and bring up to 10ml with DCM.

8.1.4 Calibration Standard

A minimum of 5 calibration standards for each analyte

Level	***Concentration (ug/ml)***
L1	1
L2	2
L3	3
L4	5
L5	10
L6	20
L7	50
L8	100
L9	150
L10	200

8.1.5 Continuing Calibration Standard

The initial Calibration Verification Standard Solution (secondary source) is used for the Continuing Calibration Standard.

The standards used for the secondary source (except surrogates) **MUST** be of a different vendor production lot than those used to prepare the initial calibration standards.

8.2 Internal Standard Solution

The internal standards are:

1,4-dichlorobenzene-d_4
naphthalene-d_8
acenaphthene-d_{10}
phenanthrene-d_{10}
chrysene-d_{12}
perylene-d_{12}

This is a premixed, certified solution from Supelco, 2000ng/mL in DCM, catalog #4-8902. Store, protected from light, at –10ºC or less. Solution is replaced after 6 months.

Each 500µL of standards, blank and sample extracts are spiked with 10µL of Internal Standard Solution, resulting in a concentration of 40ng/ µL.

8.3 GC/MS Tuning Standard

A methylene chloride solution containing 50ng/µL of decafluorotriphenylphosphine (DFTPP). The standard also contains 50ng/µL each of 4,4'DDT, pentachlorophenol, and benzidine to verify injection port inertness and GC column performance. Store at –10ºC or less when not in use. Standard is replaced after 6 months

This working standard is prepared from a stock solution, purchased from Ultra Scientific, Catalog# GCM-150.

Prepare the GC/MS Tuning Standard with 25µL GCM-150 and 475µL Dichloromethane. Store in the refrigerator at 4 ± 2ºC. Standard expires 6 months from date of preparation.

8.4 Surrogate Spiking Solution

During extraction of samples, add 1mL of the surrogate spiking solution to each sample, blank and QC samples. See extraction SOP(s) for details.

Record the preparation, analyst's initials, preparation date, expiration date and identifier in a logbook. Store, protected from light, at –10ºC or less. Solution is replaced after 6 months.

Vendor	Standard	Catalog Number	Concentration
Restek			
	Base-Neutrals Surrogate Standard Mix	31086	5000µg/mL
	Acid Surrogate Standard Mix	31087	10000µg/mL

8.4.1 Extraction Surrogate Preparation

In a 1000mL volumetric flask, add 5ml of 31086 and 31087. Bring up to volume with Acetone. The final concentration is 50µg/mL for the acid surrogates and 25µg/mL for the B/N surrogates.

8.5 Spike Solution (LCS, MS, MSD)

Record the preparation, preparation date, analyst's initials, expiration date and identifier in a logbook.

ABN SPKI:

Vendor	Standard	Catalog nr	Concentration
Restek			
	8270 Mega Mix	31850	500-1000ug/ml
	Benzoic Acid Mix	31879	2000ug/ml
	Custom SV Standard	562843	2000ug/ml
	Custom ABN Additionals Standard	562538	2000ug/ml
	Benzaldehyde Standard	33017	2000ug/ml
	Alpha-Terpineol Standard	33912	2000ug/ml

ABN SPK2:

Ultra	Atrazine	EPA-1176A	1000ug/ml
AccuStandard	Parathion	M-622-19	1000ug/ml
Restek	8270 Benzidine Mix#2	31852	2000ug/ml

Spike Solution Preparation

ABN SPK1:
In a 200ml volumetric flask add 8ml of 8270 Mega Mix; 4ml of Benzoic Acid Mix, Custom SV Standard, Custom ABN Additionals Standard, Benzaldehyde Standard, Alpha-Terpineol Standard; Bring up to volume with Acetone. The final concentration is 40ug/ml. The Spike Solution is stored in the refrigerator at 4 ± 2ºC and expires 6 months from date of preparation.

ABN SPK2:
In a 250ml volumetric flask add 10ml of Atrazine and Parathion; 5ml of 8270 Benzidine Mix#2; Bring up to volume with Acetone. The final concentration is 40ug/ml. The Spike Solution is stored in the refrigerator at 4 ± 2ºC and expires 6 months from date of preparation.

8.6 Secondary Source Standards

Record the preparation, analyst's initials, preparation date, expiration date and identifier in a logbook. The Secondary Source Standards are stored in the refrigerator at 4 ± 2ºC and expire 6 months from date of preparation.

Vendor	Standard	Catalog Number	Concentration
Restek			
	8270 Mega Mix	31850	1000ug/ml
	605 Benzidines Mix	31030	2000ug/ml
	Benzoic Acid Mix	31879	2000ug/ml
	Custom SV Standard	562843	2000ug/ml
	Custom ABN Additionals Standard	562538	2000ug/ml
	Benzaldehyde Standard	33017	2000ug/ml
	Alpha-Terpineol Standard	33912	2000ug/ml
	8270 Benzidines Mix#2	31852	2000ug/ml

*__NOTE__: The standards used for the secondary source (except surrogates) **MUST** be of a different vendor production lot than those used to prepare the initial calibration standards.

8.6.1 Second Source Standard

The standards used for the secondary source (except surrogates) **MUST** be of a different vendor production lot than those used to prepare the initial calibration standards.

8.7 Dichloromethane (DCM): Pesticide quality.

8.8 Acetone: Pesticide quality.

9. Procedure

9.1 SET-UP

9.1.1 GC/MS Operating Conditions:

Typical GC/MS operating conditions are listed below, but may be altered as long as method performance criteria are met.

Mass range:	35 – 500 amu
Scan time:	3.15 scans/second
Initial temperature:	50°C, hold for 1.5 minutes
Temperature program:	282°C/minute to 250°C then 9°C/minute to 320°C
Final temperature:	320°C for 0.58 min
Injector temperature:	300°C
Transfer line temperature:	280°C
Source temperature:	230ºC
Injector:	split ratio 5:1, 11.7mL/min
Injection volume:	1µL
Carrier gas:	helium at 523 cm/second (2.0 mL/min) constant flow

After achieving the key ion abundance criteria for DFTPP, calibrate or verify the calibration of the system daily as described in Sections 9.2 and 9.3. If performance criteria are not achieved, take corrective action as defined in Section 12.

9.1.2 GC/MS Tune:

At the beginning of every 12 hour sequence, analyze the 50µg/L DFTPP tuning solution (Section 8.3).

The resultant mass spectrum for DFTPP must meet the criteria given in Table 1 before sample analysis begins. The mass spectrum of DFTPP should be acquired in the following manner:

(1) Three scans (the peak apex scan, the scan immediately preceding the apex and the scan immediately following the apex) are acquired and averaged.
(2) Background subtraction is performed using a single scan of no more than 20 scans prior to the elution of DFTPP.

The GC/MS tuning standard is also used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD must not exceed 20%. Benzidine and pentachlorophenol must be present at their normal responses and no peak tailing must be visible.

The tailing factor for benzidine and pentachlorophenol must be calculated in every DFTPP run. (See Table 4.)

If degradation is excessive and/or poor chromatography is noted, the system needs maintenance (see Section 9.5).

9.2 Initial Calibration

9.2.1 Prepare calibration standards for all target analytes at the five concentration levels specified in Section 8.1.4.

9.2.2 Add 10µL of Internal Standard to each calibration standard directly into the autosampler vial containing 500µL of standard. Analyze each calibration standard according to Section 9.1.1.

9.2.3 Record the calibration standard, unique lab identifier code (lot), concentration, and analyst's initials in the analytical sequence list.

9.2.4 In each standard, calculate the response factor (RF) for each analyte, the average RF, and the relative standard deviation (RSD) of the RFs, using the Target data processing software. The calculations are performed automatically, using the formulae listed in Alpha's Quality Manual.

The minimum acceptable average RF for all analytes is 0.050.

Some of the target analytes (2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitrocresol and hexachlorocyclopentadiene) have a tendency to decrease in response as the chromatographic system begins to deteriorate or standard materials begin to deteriorate.

They are usually the first to show poor performance, therefore they must be monitored as indicators of degrading system performance.

If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

9.2.5 Initial Calibration RF Criteria:

For all analytes, including the compounds listed above, the RSD must be $\leq$ 15% for the mean response factor to be used for sample quantitation. If the RSD is > 15%, then linearity through the origin cannot be assumed. An alternate calculation may be performed by using the linearity, provided that the correlation coefficient is $\geq$ 0.995. If both quantitation methods fail the acceptance criteria for any compound in the initial calibration, then the system must be re-evaluated and a new calibration curve must be analyzed.

9.2.6 Evaluation of Retention Times:

The relative retention time (RRT) of each target analyte in each calibration standard must agree within 0.06 RRT units. Late-eluting target analytes usually have much better agreement.

9.2.7 Initial Calibration Verification (Second Source Verification)

9.2.7.1 The initial calibration (Section 9.2) for each compound of interest must be verified prior to sample analysis. This is accomplished by analyzing second source calibration standards (Section 8.7) at a concentration near the midpoint concentration for the calibrating range of the GC/MS.

9.2.7.2 Analyze the standards and calculate the % Difference for each analyte according to the formula in Alpha's Quality Manual.

If the % Difference for each analyte is $\leq$ 20%, then the calibration is assumed to be valid. If this criterion is not met, then corrective action must be taken prior to the analysis

9.2.7.3 If this criterion is exceeded, inspect the gas chromatographic system to determine the cause and perform whatever maintenance is necessary before verifying calibration and proceeding with sample analysis.

9.2.7.4 If routine maintenance does not return the instrument performance to meet the QC requirements (Section 10) based on the last initial calibration, then a new initial calibration must be performed.

9.3 Continuing Calibration Verification

9.3.1 Continuing calibration verification is performed at the beginning of each 12 hour analytical sequence.

9.3.2 The criteria given in Table 1 for DFTPP must be met for each 12-hour shift during which samples are analyzed.

9.3.3 The initial calibration (Section 9.2) for each compound of interest must be verified once every 12 hours prior to sample analysis. This is accomplished by analyzing calibration standards at a concentration near the midpoint concentration for the calibrating range of the GC/MS.

9.3.4 Analyze the standards and calculate the % Difference for each analyte according to the formula in Alpha's Quality Manual.

If the % Difference for each analyte is $\leq$ 20%, then the calibration is assumed to be valid. If this criterion is not met, then corrective action must be taken prior to the analysis samples.

9.3.5 If this criterion is exceeded, inspect the gas chromatographic system to determine the cause and perform whatever maintenance is necessary before verifying calibration and proceeding with sample analysis.

If routine maintenance does not return the instrument performance to meet the QC requirements (Section 10) based on the last initial calibration, then a new initial calibration must be performed. Due to the large number of analytes present, allowances may be made for a RF that drifts out high, as long as there are no positive hits for that particular analyte in any of the associated samples. Any QC failures must be written up by the analyst on narrative sheets for inclusion with the sample data.

9.3.6 Internal Standard Retention Time

The retention times of the internal standards in the calibration verification standard is evaluated after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the mid-point standard of the most

recent initial calibration, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

9.3.7 Internal Standard Response

If the area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to +100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

9.4 Sample Analysis

9.4.1 Preparation of extracted samples for analysis

All extracted samples in K-D tubes need to be brought up to 1mL volume with DCM. Transfer exactly 500µL of the extract into 1mL vials with crimp top. Cap the vials with crimper, using 11mm aluminum crimp caps with red septa. If extract dilutions are needed, perform the dilution and then transfer 500µL to the vial.

Record the sample number (standard or QC sample identifier), dilution and analyst's initials in the analytical sequence list. Note any deviations from this procedure or visual observations on a sample narrative sheet.

9.4.2 GC/MS Analysis of Samples

9.4.2.1 Allow the sample extracts to warm to room temperature.

9.4.2.2 Add 10µL of the internal standard (Section 8.2) to the 500µL of sample extract.

9.4.2.3 The autosampler is programmed to inject 1µL aliquot of the sample extract into the GC/MS system, using the same instrument conditions that were used for calibration (Section 9.1.1). The injection volume of the sample must be the same as the volume used for the calibration standard.

9.4.2.4 If the response of any quantitation ion exceeds the initial calibration range of the GC/MS system, the sample extract must be diluted and reanalyzed.

9.5 Maintenance

Additional maintenance may be required if system performance degrades. GC injector ports are of critical concern. Injectors that are contaminated or chemically active can cause poor sensitivity for the compounds listed in Section 9.2.4

When poor sensitivity is observed, replacement of the injector liner and seal may solve the problem. If not, clip approximately 3 – 6 inches from the injector end of the GC column. If the sensitivity does not improve it may be necessary to replace the split line or the injector weldment assembly. If the problem persists, it may be necessary to replace the GC column.

Periodic cleaning (typically twice per year) of the mass spectrometer ion source is required. More frequent source cleaning may be needed, especially if dirty samples are analyzed. In addition, semi-annual preventive maintenance is provided by the instrument manufacturer as part of our service agreement.

9.6 Qualitative Identification

Perform first level data review. Obtain the primary m/z (Table 4) masses for each parameter of interest. The following criteria must be met to make qualitative identification:

- Compare the background subtracted mass spectra for the sample to the reference spectra. The characteristic masses of each parameter of interest must maximize in the same or within one scan of each other.

- The retention time must fall within ± 0.1 minutes of the retention time of the compound in the analytical standard. However, analyst experience must be used in making the qualitative identification.

- The relative peak height of the one characteristic mass must fall within 20% of the relative intensity of the mass in a reference mass spectrum. The reference spectrum is obtained from a standard analyzed on the GC/MS system.

Structural isomers that have very similar mass spectra are identified only if the resolution between authentic isomers in a standard mix is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

9.7 Calculations

9.7.1 When a parameter is identified, the quantitation of that parameter must be based on the integrated abundance of the quantitation characteristic m/z given in Table 5. If the sample produces an interference for the primary m/z, use a secondary characteristic m/z to quantitate.

9.7.2 Calculate the concentration in the sample using the average response factor (RF) from the initial calibration curve according to the formulae in Alpha's Quality Manual.

$$\text{Concentration } (\mu g/L) = \frac{C \times DF \times Vf \times 1000}{Vo}$$

where:

C = Extract concentration (µg/mL)
DF = Dilution factor
Vf = Final extract volume (mL)
Vo = Sample volume (mL)

9.7.3 Results for positive hits in samples are reported in µg/L units. After performing technical data review, validating that all QC criteria have been met and confirming all positive hits, the data report is sent electronically to the LIMS computer for generation of the client report. There are two levels of review of the data in the LIMS system prior to release of data. These reviews must be done by two separate individuals.

10. Quality Control and Data Assessment

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

10.1 Demonstration of Capability

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. Each time a method modification is made, the analyst is required to repeat the procedure.

Analyze four QC check samples spiked with all analytes at 10 – 50 times the MDL.

Calculate the result for each aliquot in µg/L, the relative standard deviation of the four results, and the average percent recovery for each analyte.

The average percent recovery must be 70 – 130%. However, due to poor extraction efficiencies of several target analytes this may not be achievable for all compounds.

NOTE: The large number of parameters in Table 5 present a substantial probability that one or more will fail at least one of the acceptance criteria when all parameters are analyzed. The majority of compounds must meet the 70 – 130% recovery criteria for the IDC to be acceptable.

10.2 Blank

Extraction blanks are performed with each extraction batch of 10 or less samples, according to the extraction SOPs. The extraction blank must not contain any of the reportable analytes above the reporting limit. If any reportable analytes are detected in the blank, the entire extraction batch is suspect and re-extraction of all associated samples is required. The surrogate recoveries must also be within the acceptance criteria listed in section 10.6. If surrogate acceptance criteria are exceeded, the extraction batch must be evaluated to determine if re-extraction or re-analysis is necessary.

10.3 Laboratory Control Sample (LCS)

A Laboratory Control Sample (LCS) is extracted with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The spike compounds and levels are listed in Section 8.5. The recovery acceptance criteria are listed in Table 3. If any recovery criteria are not met, the extract must be reanalyzed. If the criteria are still not met, the entire batch must be re-extracted. If this is not possible, due to insufficient sample or holding time exceedence, the analyst must write up the failure on a narrative sheet for inclusion in the client report.

10.4 Matrix Spike (MS)

A matrix spike is extracted and analyzed for each batch of 10 or less samples. The spike compounds and levels are listed in Section 8.5. The recovery acceptance criteria are listed in Table 3. If the recovery criteria are not met, but are met in the LCS, this must be noted on a narrative sheet for inclusion in the client report.

10.5 Duplicates

Analyze a duplicate sample for each batch of 10 samples or less. The percent RPD is determined. The laboratory generated limits for RPD must be met. Acceptance criteria of ±40% will be used until in-house criteria can be generated.

10.6 Surrogates

All extracted samples and associated QC are spiked with surrogate at the levels listed in Section 8.4. The laboratory must evaluate surrogate recovery data from individual samples and QC samples versus the surrogate control limits listed in Table 2. If the surrogate limits are not met, the extract must be reanalyzed to determine if the failure was due to an instrument problem. If the criteria are still not met, the affected samples must be re-extracted to confirm that the failure was due to sample matrix. If matrix effect is confirmed, this must be noted on a narrative sheet for inclusion in the client report.

10.7 Control Limits

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained.

Control charts for the method parameters are generated by the QC staff and distributed to the analysts. The control limits are based on in-house performance data, and are compared to the control limits found in the reference method.

10.8 Analytical Sequence

In a 12-hour period, the typical analytical sequence is:

- Degradation Check
- DFTPP
- Continuing or Daily Standards (1 – 3)
    (1) ABN 50ppm
    (2) AP9 50ppm
- Method Blank
- Samples
- QC (as required)

11. Method Performance

11.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/08-05. These studies performed by the laboratory are maintained on file for review.

11.2 Demonstration of Capability Studies

11.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

11.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

12. Corrective Actions

Holding time exceedence and improper preservation are noted on the nonconformance report form.

Perform instrument maintenance as described throughout this SOP as needed when instrument calibration criteria are not met. Record all maintenance in the instrument logbook.

All batch and sample specific QC criteria outlined in section 10 are evaluated by the analyst prior to approval of the data. When any QC criteria fail, the cause for the failure must be identified and corrected. This may include instrument recalibration followed by sample reanalysis, sample cleanup, or sample re-extraction. If it is determined that the failure is due to sample matrix effects, a project narrative report is written by the analyst for inclusion in the data report. If there is insufficient sample volume to perform the re-analysis for confirmation, this is also noted in the narrative and included in the client report.

13. Pollution Prevention

See Chemical Hygiene Plan for pollution prevention operations.

14. Waste Management

See Chemical Hygiene Plan for waste handling and disposal.

15. Attachments

Table 1: DFTPP Key Ions and Ion Abundance Criteria

Table 2: Acceptable Surrogate Spike Recovery Limits

Table 3: Acceptable Matrix Spike Recovery Limits

Table 4: Tailing Factor Calculation

Table 5: Characteristic Ions for Semivolatile Compounds

Table 6: Reported Detection Limits

Table 7: Semivolatile Internal Standards with Corresponding Target Compounds and Surrogates Assigned for Quantitation

TABLE 1

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	40-60% of mass 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	> 40% of mass 198
443	17-23% of mass 442

TABLE 2

ACCEPTABLE SURROGATE SPIKE RECOVERY LIMITS

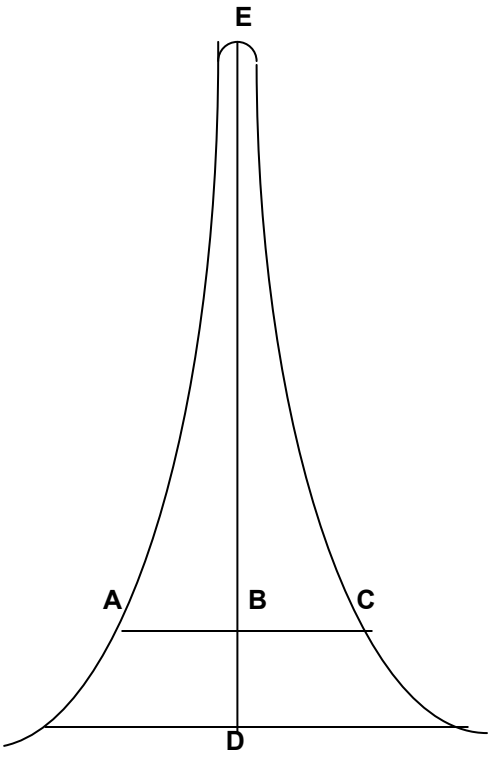
Analytical Fraction	Surrogate Compound	Water
BN-625	Nitrobenzene-d_5	23-120%
BN-625	2-Fluorobiphenyl	43-120%
BN-625	p-Terphenyl-d_{14}	33-120%
Acid-625	Phenol-d_6	10-120%
Acid-625	2-Fluorophenol	21-120%
Acid-625	2,4,6-Tribromophenol	10-120%

TABLE 3

ACCEPTABLE LCS AND MATRIX SPIKE RECOVERY LIMITS

Analytical Fraction	Spike Compound	Water
BN-625	**1,2,4-Trichlorobenzene**	**39-98%**
BN-625	**Acenaphthene**	**46-118%**
BN-625	**2,4-Dinitrotoluene**	**24-96%**
BN-625	**2,6-Dinitrotoluene**	**40-140%**
BN-625	**Pyrene**	**26-127%**
BN-625	**n-Nitroso-di-n-propylamine**	**41-116%**
BN-625	**Hexachloropropene**	**40-140%**
BN-625	**2-Chloronaphthalene**	**40-140%**
BN-625	**4-Chlorophenyl phenyl ether**	**40-140%**
BN-625	**Anthracene**	**40-140%**
BN-625	**Fluoranthene**	**40-140%**
BN-625	**Butyl benzyl phthalate**	**40-140%**
Acid-625	**Pentachlorophenol**	**9-103%**
Acid-625	**Phenol**	**12-110%**
Acid-625	**2-Chlorophenol**	**27-123%**
Acid-625	**4-Chloro-3-methylphenol**	**23-97%**
Acid-625	**2-Nitrophenol**	**30-130%**
Acid-625	**4-Nitrophenol**	**10-80%**
Acid-625	**2,4-Dinitrophenol**	**30-130%**

TABLE 4



Tailing Factor = $\frac{BC}{AB}$

Example calculation:

Peak Height = DE = 100mm
10% Peak Height = BD = 10mm
Peak Width at 10% Peak Height = AC = 23mm

AB = 11mm
BC = 12mm

Therefore: Tailing Factor = $\frac{12}{11}$ = 1.1

Tailing factor for benzidine < 3.0

Tailing factor for pentachlorophenol < 5.0

TABLE 5

CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Primary Ion	Secondary Ion(s)
Acenaphthene	**154**	**153, 152**
Acenaphthylene	**152**	**151, 153**
Aniline	**93**	**66, 65**
Anthracene	**179**	**176, 179**
Benzidine	**184**	**92, 185**
Benzo(a)anthracene	**228**	**229, 226**
Benzo(a)pyrene	**252**	**253, 125**
Benzo(b)fluoranthene	**252**	**253, 125**
Benzo(g,h,i)perylene	**276**	**138, 277**
Benzo(k)fluoranthene	**252**	**253, 125**
Benzoic acid	**122**	**105, 77**
Benzyl alcohol	**108**	**79, 77**
Bis (2-chloroethoxy) methane	**93**	**95, 123**
Bis (2-chloroethyl) ether	**93**	**63, 95**
Bis (2-chloroisopropyl) ether	**45**	**77, 121**
Bis (2-ethylhexyl) phthalate	**149**	**167, 279**
4-Bromophenyl phenyl ether	**248**	**250, 141**
Butyl Benzyl phthalate	**149**	**91, 206**
Carbazole	**166**	
4-Chloro-3-methylphenol	**107**	**144, 142**
4-Chloroaniline	**127**	**129, 65, 92**
2-Chloronaphthalene	**162**	**127, 164**
2-Chlorophenol	**128**	**64, 130**
Chrysene	**228**	**226, 229**
Dibenz(a,h)anthracene	**278**	**139, 279**
Dibenzofuran	**168**	**139**
3,3'-Dichlorobenzidine	**252**	**254, 126**
2,4-Dichlorophenol	**162**	**164, 98**
Diethyl phthalate	**149**	**177, 150**
2,4-Dimethylphenol	**122**	**107, 121**
Dimethyl phthalate	**163**	**194, 164**
4,6-Dinitro-2-methylphenol	**198**	**51, 105**

TABLE 5 (continued)

CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Primary Ion	Secondary Ion(s)
2,4-Dinitrophenol	184	63, 154
2,6-Dinitrophenol	162	164, 126, 98, 63
2,6-Dinitrotoluene	165	63, 89
2,4-Dinitrotoluene	165	63, 89
Di-n-butyl phthalate	149	150, 104
Di-n-octyl phthalate	149	167, 43
Fluoranthene	202	101, 203
Fluorene	166	165, 167
Hexachlorobenzene	284	142, 249
Hexachlorobutadiene	225	223, 227
Hexachlorocyclopentadiene	237	235, 272
Hexachloroethane	117	201, 199
Hexachloropropene	213	211, 215, 117, 106, 141
Indeno(1,2,3-cd)pyrene	276	138, 227
Isophorone	82	95, 138
2-Methylnaphthalene	142	141
2-Methylphenol	107	108, 77, 79, 90
3,4-Methylphenol	107	108, 77, 79, 90
4-Methylphenol	107	108, 77, 79, 90
Naphthalene	128	129, 127
NDPA/DPA	169	168, 167
Nitrobenzene	77	123, 65
n-Nitrosodimethylamine	42	74, 44
n-Nitrosodi-n-propylamine	70	42, 101, 130
2-Nitroaniline	65	92, 138
3-Nitroaniline	138	108, 92
4-Nitroaniline	138	65, 108, 92, 80, 39
2-Nitrophenol	139	109, 65
4-Nitrophenol	139	109, 65
Pentachlorobenzene	250	252, 108, 248, 215, 254
Pentachlorophenol	266	264, 268
Phenanthrene	178	179, 176
Phenol	94	65, 66
Pyrene	202	200, 203

TABLE 5 (continued)

CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Primary Ion	Secondary Ion(s)
1,2,4-Trichlorobenzene	180	182, 145
2,4,5-Trichlorophenol	196	198, 97, 132, 99
2,4,6-Trichlorophenol	196	198, 200
Acenaphthene-d_{10} (IS)	164	162, 160
Chrysene-d_{12} (IS)	240	120, 236
1,4-Dichlorobenzene-d_4 (IS)	152	150, 115
Naphthalene-d_8 (IS)	136	68
Perylene-d_{12} (IS)	264	260, 265
Phenanthrene-d_{10} (IS)	188	94, 80
2-Fluorobiphenyl (Surrogate)	172	171
2-Fluorophenol (Surrogate)	112	64
Nitrobenzene-d_5 (Surrogate)	82	128, 54
Phenol-d_6 (Surrogate)	99	42, 71
Terphenyl-d_{14} (Surrogate)	244	122, 212
2,4,6-Tribromophenol (Surrogate)	330	332, 141

TABLE 6
REPORTED DETECTION LIMITS
FOR SEMIVOLATILE ORGANIC COMPOUNDS

Analyte	RDL (µg/L)
Acenaphthene	5.0
Acenaphthylene	5.0
Aniline	20.0
Anthracene	5.0
Azobenzene	5.0
Benzidine	50.0
Benzo(a)anthracene	5.0
Benzo(b)fluoranthene	5.0
Benzo(k)fluoranthene	5.0
Benzo(ghi)perylene	5.0
Benzo(a)pyrene	5.0
Benzoic acid	50.0
Benzyl alcohol	10.0
Bis(2-chloroethyl)ether	5.0
Bis(2-chloroisopropyl)ether	5.0
Bis(2-chloroethoxy)methane	5.0
Bis(2-ethylhexyl)phthalate	5.0
4-Bromophenyl phenyl ether	5.0
Butyl benzyl phthalate	5.0
Carbazole	5.0
4-Chloroaniline	5.0
p-Chloro-m-cresol	5.0
2-Chloronaphthalene	5.0
2-Chlorophenol	5.0
4-Chlorophenyl phenyl ether	5.0
Chrysene	5.0
m/p-Methylphenol	5.0
o-Methylphenol	5.0
Dibenzo(a,h)anthracene	5.0
Dibenzofuran	5.0
Di-n-butylphthalate	5.0
3,3-Dichlorobenzidine	50.0
2,4-Dichlorophenol	10.0
Diethyl phthalate	5.0
2,4-Dimethylphenol	10.0
Dimethyl phthalate	5.0

TABLE 6 (continued)

REPORTED DETECTION LIMITS

FOR SEMIVOLATILE ORGANIC COMPOUNDS

Analyte	RDL (µg/L)
4,6-Dinitro-o-cresol	20.0
2,4-Dinitrophenol	30.0
2,4-Dinitrotoluene	5.0
2,6-Dinitrotoluene	5.0
Di-n-octylphthalate	5.0
Fluoranthene	5.0
Fluorene	5.0
Hexachlorobenzene	5.0
Hexachlorobutadiene	10.0
Hexachlorocyclopentadiene	30.0
Hexachloroethane	5.0
Indeno(1,2,3-cd)pyrene	5.0
Isophorone	5.0
1-Methylnaphthalene	5.0
2-Methylnaphthalene	5.0
Naphthalene	5.0
2-Nitroaniline	5.0
3-Nitroaniline	5.0
4-Nitroaniline	5.0
Nitrobenzene	5.0
2-Nitrophenol	10.0
4-Nitrophenol	10.0
n-Nitrosodimethylamine	50.0
n-Nitrosodiphenylamine	5.0
n-Nitrosodi-n-propylamine	5.0
Pentachlorophenol	10.0
Phenacetin	10.0
Phenanthrene	5.0
Phenol	5.0
Pyrene	5.0
1,2,4-Trichlorobenzene	5.0
2,4,5-Trichlorophenol	5.0
2,4,6-Trichlorophenol	5.0

Table 7
Semivolatile Internal Standards with Corresponding
Target Compounds and Surrogates Assigned for Quantitation

1,4-dichlorobenzene-d4	Naphthalene-d8	Acenaphthene-d10	Phenanthrene-d10	Chrysene-d12	Perylene-d12
N-Nitrosodimethylamine	Nitrobenzene	Dimethyl phthalate	2,4,6-Tribromophenol, surr	3,3'-Dichlorobenzidine	Benzo(b)fluoranthene
2-Fluorophenol, surr	Naphthalene	3-Nitroaniline	Pentachlorophenol	Benzo(a)Anthracene	Benzo(k)fluoranthene
Phenol	4-Chloroaniline	Acenaphthene	Phenanthrene	Chrysene	Benzo(a)pyrene
Aniline	Hexachlorobutadiene	2,4-Dinitrophenol	Anthracene	Bis(2-ethylhexyl) phthalate	Indeno(1,2,3-cd)pyrene
Phenol-d6, surr	4-Chloro-3-Methylphenol	Dibenzofuran	Carbazole	Di-n-octylphthalate	Dibenzo(a,h)anthracene
Bis(2-chloroethyl)ether	2-Methylnaphthalene	4-Nitrophenol	Di-n-Butylphthalate		Benzo(g,h,i)perylene
2-Chlorophenol	1-Methylnapthalene	2,4-Dinitrotoluene	Fluoranthene		
	Hexachlorocyclo-pentadiene	Fluorene	Benzidine		
	2,4,5-Trichlorphenol	Diethyl phthalate	Pyrene		
Benzyl Alcohol	2,4,6-Trichlorophenol	4-Chlorophenyl-phenylet	Terphenyl-d14, surr		
	2-Fluorobiphenyl, surr	4-Nitroaniline	Benzyl butyl phthalate		
2-Methylphenol	2-Chloronaphthalene	4,6-Dinitro-2-methylphe			
bis(2-Chloroisopropyl)ether	2-Nitroaniline	NDPA/DPA			
3-Methylphenol/4-ethyl	2,6-Dinitrotoluene	Azobenzene			
N-Nitrosodi-n-propylamine	Acenaphthylene	4-Bromophenyl-phenyleth			
Hexachloroethane	Benzoic Acid	Hexachlorobenzene			
Nitrobenzene-d5, surr	2,4-Dichlorophenol				
Isophorone	1,2,4-Trichlorobenzene				
2-Nitrophenol					
2,4-Dimethylphenol					
Bis(2-chloroethoxy)methane					

Organochlorine Pesticides and PCBs By Capillary Column Gas Chromatography

Reference Method No.: **608**

Reference: Test Procedures for the Analysis of Organic Pollutants. Appendix A, Part 136, Code of Federal Regulations. July 1, 1985 edition.

1. Scope and Application

Method 608 is used to determine the concentrations of various organochlorine pesticides and Polychlorinated Biphenyls (PCBs) as Aroclors in extracts from liquid matrices. This SOP details the analysis using fused-silica, open-tubular, capillary columns with electron capture detectors (ECD).

Matrices: Extracts from liquid matrices.

Definitions: See Alpha Analytical Quality Manual Appendix A

Regulatory Parameter List: The compounds listed below are determined by this method:

Parameter	CAS
Aldrin	309-00-2
Alpha-BHC	319-84-6
Beta-BHC	319-85-7
Gamma-BHC	58-89-9
Lindane	58-89-9
Delta-BHC	319-86-8
Alpha-chlordane	5103-71-9
Gamma-chlordane	5103-74-2
4,4'-DDD	72-54-8
4,4'-DDE	72-55-9
4,4'-DDT	50-29-3
Dieldrin	60-57-1
Endosulfan I	959-98-8
Endosulfan II	33213-65-9
Endosulfan Sulfate	1031-07-8
Endrin	72-20-8
Endrin Aldehyde	7421-93-4
Endrin Ketone	53494-70-5
Heptachlor	76-44-8
Heptachlor Epoxide	1024-57-3
Methoxychlor	72-43-5
Toxaphene	8001-35-2
Technical Chlordane	57-74-9
Aroclor 1016	12674-11-2
Aroclor 1221	11104-28-2
Aroclor 1232	11141-16-5
Aroclor 1242	53469-21-9
Aroclor 1248	12672-29-6
Aroclor 1254	11097-69-1
Aroclor 1260	11096-82-5

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one of the following laboratory personnel before performing the modification: Area Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of analysts experienced in the operation of the gas chromatograph (GC) and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability (see section 13.2), analyzing a proficiency test sample and completing the record of training.

After initial demonstration, ongoing demonstration is based on acceptable laboratory performance of at least a quarterly laboratory control sample or acceptable performance from an annual proficiency test sample. A major modification to this procedure requires demonstration of performance. The identification of major method modification requiring performance demonstration is directed by the QA Officer and/or Laboratory Director on a case-by-case basis.

2. Summary of Method

A measured volume of sample (approximately 1L) is extracted using the separatory funnel extraction technique. (Refer to Separatory Funnel Extraction SOP/02-02).

A variety of cleanup steps may be applied to the extract, depending on the nature of the matrix interferences and the target analytes to be determined. Routine cleanups used include Florisil (Method 3620), Method 3660 for the removal of elemental sulfur from sample extracts, and sulfuric acid cleanup for PCB only extracts.

After cleanup, the extract is analyzed by injecting a 1µL sample into a gas chromatograph equipped with narrow-bore fused silica capillary columns and electron capture (GC/ECD) detectors.

2.1 Method Modifications from Reference

Internal standard calibration is used for all analytes. The internal standard used is 1-bromo-2-nitrobenzene.

Extract cleanup techniques are selected based upon the analytes to be determined. If only PCBs are to be reported, the sulfuric acid cleanup procedure is used. If pesticides are also to be determined, the florisil cleanup procedure is used instead. See extraction SOPs for details concerning the extract cleanup procedures.

3. Reporting Limits

Table 1 lists our routine reporting limits.

4. Interferences

4.1 Instrumental

4.1.1 Only high purity gases are used in the GC system to eliminate this source of possible contamination. Both the helium (carrier gas – 99.999%) and argon-methane (detector make-up gas) are certified by the gas supplier.

4.1.2 Preventive instrument maintenance is performed routinely, and whenever highly contaminated extracts are analyzed that could result in chromatographic interferences or result in degradation of system performance. Section 10.5 details the maintenance steps.

4.1.3 Glassware must be scrupulously cleaned. This procedure is detailed in the extraction SOPs. Store dry glassware in a clean environment.

4.2 Parameters

4.2.1 All solvents used are pesticide grade or equivalent, and reagents are purchased as certified contaminant free. All of these materials are routinely determined to be free of interferences by analysis of extraction blanks with every extraction batch performed.

4.2.2 Certain compounds (i.e. phthalates) can be extracted from the sample matrix and be detected by the ECD that could possibly result in false positive results or complicate the data interpretation. The use of the cleanup procedures mentioned in Section 2.1 and detailed in the extraction SOPs minimize these possible interferences. Analyst experience is also crucial in making compound determinations.

4.2.3 Interferences co-extracted from the samples will vary considerably from waste to waste. While general cleanup techniques are referenced or provided as part of the method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation.

4.2.4 Interferences by phthalate esters introduced during sample preparation can pose a major problem in pesticide determinations.

4.2.4.1 Common flexible plastics contain varying amounts of phthalate esters, which are easily extracted or leached from such materials during laboratory operations.

4.2.4.2 Cross-contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled.

4.2.4.3 Interferences from phthalate esters are minimized by avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination.

4.2.5 The presence of elemental sulfur will result in broad peaks that interfere with the detection of early-eluting organochlorine pesticides. Sulfur contamination is often seen in sediment and some soil samples. Method 3660 is used for removal of sulfur.

4.2.6 Other halogenated pesticides or industrial chemicals may interfere with the analysis of pesticides. Coeluting chlorophenols are eliminated by using Method 3620 (florisil).

5. Health and Safety

The toxicity or carcinogenity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. The following analytes covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: 4,4-DDT, 4,4-DDD, BHC's, and the PCBs. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

5.1 Lab coats, safety glasses, and gloves must be worn when handling samples, extracts, standards or solvents.

5.2 All solvent and extract transfers must be handled in the vented bench area in the GC laboratory.

5.3 All stock standards, working standards, and vialed sample extracts must be placed into the waste bucket in the lab, for future disposal by the Hazardous Waste Manager. The container must be labeled properly with hazard warning labels indicating the container contents.

5.4 Bottles containing flammable solvents must be stored in the flammables cabinet.

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

Aqueous samples are collected in two 1L amber glass jars with lined-lined lids.

6.2 Sample Preservation

Upon receipt, samples must be tested for residual chlorine. Refer to the Sample Receipt and Login Qualtrax ID 1559 and the Separatory Funnel Liquid-Liquid Extraction SOP/02-02 for further information.

Also upon receipt, samples must have a pH within the range of 5.0 – 9.0 pH units. If the sample is not within this range, it is adjusted using either NaOH to increase the pH or with H_2SO_4 to decrease the pH. A record is made on the Sample Delivery Group form to indicate the volume of acid or base that was added to the sample.

The samples are transferred into sample storage refrigerators to be maintained at a temperature of 4 ±2 ^{o}C.

6.3 Sample Shipping

No special shipping requirements.

6.4 Sample Handling

Aqueous samples must be extracted within 7 days of sample collection. Once extracted, the samples must be analyzed within 40 days of the extraction date.

7. Equipment and Supplies

7.1 Gas Chromatograph: An analytical system complete with gas chromatograph configured for split-splitless injection and all required accessories including syringes, analytical columns, gases, electron capture detectors (ECD), and data system.

7.2 GC Columns: Alpha utilizes dual-column analyses. The dual-column approach involves dual injections of the split extract on a single GC equipped with two columns. Typical column pairs used are listed below. Other columns may be used as long as method performance criteria can be met.

7.2.1 Column pair 1

30m x 0.32mm ID fused silica capillary column (RTX-CLP) 0.32µm film thickness.

30m x 0.32mm ID fused silica capillary column (RTX-CLPII) 0.25µm film thickness.

7.2.2 Column pair 2

30m x 0.32mm ID fused silica capillary column (STX-CLP) 0.32µm film thickness.

30m x 0.32mm ID fused silica capillary column (STX-CLPII) 0.25µm film thickness.

7.3 Volumetric Flasks: 10mL and 25mL, for the preparation of standards.

7.4 Microsyringes/Wiretrol syringes: 10 µL – 1000 µL

7.5 Disposable Borosilicate Pipets

7.6 Vials: 2 mL clear glass, crimp-top and screw-cap.

8. Reagents and Standards

Reagent grade or pesticide grade chemicals are used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficient high purity to permit its use without lessening the accuracy of the determination.

NOTE: Store the standard solutions (stock, composite, calibration, internal, and surrogate) at 4 ±2°C in Teflon(R)-sealed containers in the dark. When a lot of standards is prepared, aliquots of that lot are stored in individual small vials. All stock standard solutions must be replaced after one year or sooner if routine QC tests indicate a problem. All other standard solutions must be replaced after six months or sooner if routine QC indicates a problem.

8.1 n-Hexane: Pesticide quality or equivalent.

8.2 Acetone: Pesticide quality or equivalent.

8.3 Methylene chloride: Pesticide quality or equivalent.

8.4 Organic-free Reagent Water: All references to water in this method refer to organic-free reagent water from Alpha's RO water treatment system.

8.5 Stock Standard Solutions: All stock standard solutions are purchased from commercial vendors as ampulated certified solutions. Store all vendor solutions per vendor specifications. When an ampulated stock solution is opened, it is transferred to a labeled amber screw-cap vial. The expiration date of the stock solution is either the vendor specified expiration date, or 6 months from the date the ampule was opened, whichever is sooner. Record all solvent lot numbers whenever a solution is made. Typical stock standard concentrations are listed in Table 1.

8.6 Calibration Standards: Calibration standards are prepared volumetrically by diluting the appropriate stock standard(s) with hexane. Calibration standards expire 6 months from the date of preparation, or on the earliest expiration date of any of the stock solutions used to prepare the calibration standard. Calibrations are typically performed at the 6 concentration levels listed in Table 1, and always at a minimum of 3 Levels.

8.7 Internal Standard Solution: 1-Bromo-2-nitrobenzene is used as the internal standard, and is added to all single-component calibration standards and sample extracts to achieve a concentration of 0.25 µg/mL.

8.8 Surrogate Standards: Tetrachloro-m-xylene and decachlorobiphenyl are used as surrogates. They are added to the pesticide calibration standards at the concentrations listed in Table 1, and are spiked into all samples and QC samples prior to extraction. The spiking solution is prepared in acetone at the concentrations listed in Table 1.

8.9 LCS/MS Spiking Solutions: The LCS/MS spiking solutions are prepared volumetrically by diluting the appropriate stock standards in acetone. The spiking solution concentrations are listed in Table 1.

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blank(s)

Extraction blanks are performed with each extraction batch of 10 or less samples, according to the extraction SOPs. The extraction blank must not contain any of the reportable analytes above the reporting limit. If any reportable analytes are detected in the blank, the entire extraction batch is suspect and re-extraction of all associated samples is required. The surrogate recoveries must also be within the acceptance criteria listed in Table 2. If surrogate acceptance criteria are exceeded, the extraction batch must be evaluated to determine if re-extraction or re-analysis is necessary.

9.2 Laboratory Control Sample (LCS)

A Laboratory Control Sample (LCS) is extracted with each batch of 10 or less samples. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the single component pesticide analytes if the associated samples are being analyzed for pesticides or pesticides and PCBs. The LCS is spiked with Aroclor 1016 and 1260 if the samples are only being analyzed for PCBs. The concentrations of the spiking solutions are listed in Table 1. The recovery acceptance criteria are listed in Table 1. If any recovery criteria are not met, the extract should be reanalyzed. If the criteria are still not met, the entire batch should be re-extracted. If this is not possible, due to insufficient sample or holding time exceedances, the analyst must write up the failure on a narrative sheet for inclusion in the client report.

9.3 Initial Calibration Verification (ICV)

Refer to Section 10.2.

9.4 Continuing Calibration Verification (CCV)

Refer to Section 10.4.

9.5 Matrix Spike

For pesticide and combined Pesticide/PCB analyses, a matrix spike is extracted and analyzed utilizin pesticide spike for each batch of 10 or less samples. The spike compounds and levels are listed in Table 1. For PCB only analyses, a matrix spike is extracted and analyzed with each batch of 10 or less samples. The PCB spike compounds and concentrations are listed in Table 1. The recovery acceptance criteria are listed in Table 3. If the recovery criteria are not

met, but are met in the LCS, the failure may be attributed to sample matrix effects and must be noted on a narrative sheet for inclusion in the client report.

9.6 Laboratory Duplicate

For pesticide analyses, a sample duplicate is extracted and analyzed for each batch of 10 or less samples. For PCB only analyses, a sample duplicate is extracted and analyzed with each batch of 10 or less samples. The RPD acceptance criteria are listed in Table 2. If the recovery criteria are not met, but the LCS is acceptable, the failure may be attributed to sample matrix effects and must be noted on a narrative sheet for inclusion in the client report.

9.7 Method-specific Quality Control Samples

9.7.1 Surrogates

All extracted samples and associated QC are spiked with surrogates at the levels listed in Table 1. The laboratory must evaluate surrogate recovery data from individual samples and QC samples versus the surrogate control limits listed in Table 2. If the surrogate limits are not met, the extract should be reanalyzed to determine if the failure was due to an instrument problem. If the criteria are still not met, the affected samples should be re-extracted to confirm that the failure was due to sample matrix. If matrix effect is confirmed, this must be noted on a narrative sheet for inclusion in the client report.

9.8 Method Sequence

Initial calibration:

1. Degradation Standard (Not required for PCB ICAL)
2. Pest Standard Level 1 (or Aroclor Standard Level 1)
3. Pest Standard Level 2 (or Aroclor Standard Level 2)
4. Pest Standard Level 3 (or Aroclor Standard Level 3)
5. Pest Standard Level 4 (or Aroclor Standard Level 4)
6. Pest Standard Level 5 (or Aroclor Standard Level 5)
7. Pest Standard Level 6 (or Aroclor Standard Level 6)
8. ICV

Repeat lines 3-9 for other mixes until curve is complete.

(Note: The ICVs may be grouped at the end of the sequence after all the ICAL standards have been injected. Place a degradation standard [required for pesticides] prior to the ICVs.)

Pesticide-608 only Daily sequence:

1. Degradation Standard
2. Pesticide Cal Check
3. Chlordane/Toxaphene Cal Check
4. Extraction Blank
5. Laboratory Control Sample
6. Matrix Spike
7. Duplicate
8. Samples (6)
9. Pesticide Cal Check

Repeat 5-9 as needed (Note: Lines 1-4 need to be repeated every 12 hours)

PCB-608 only Daily sequence:

1. Aroclor 1016/1260 Cal Check
2. Extraction Blank
3. Laboratory Control Sample
4. Matrix Spike
5. Duplicate
6. Samples (6)
7. Cal Check (Alternate the other Aroclors)

Repeat 2-7 as needed.

PCB/Pesticide-608 Daily sequence:

1. Degradation Standard
2. Pesticide Cal Check
3. Chlordane/Toxaphene Cal Check
4. Aroclor 1016/1260 Cal Check
5. Extraction Blank
6. Laboratory Control Sample
7. Matrix Spike
8. Duplicate
9. Samples (6)
10. Pesticide Cal Check
11. PCB Cal Check (Alternate the other Aroclors)

Repeat 6-12 as needed. (Note: Lines 1-5 need to be repeated every 12 hours.)

10. Procedure

10.1 Equipment Set-up

10.1.1 Sample Extraction

Water samples are extracted at a neutral pH with methylene chloride using a separatory funnel (Method 3510). See extraction SOP for details.

10.1.2 Extract Cleanup

Cleanup procedures may not be necessary for a relatively clean sample matrix, but most extracts from environmental and waste samples will require additional preparation before analysis. The specific cleanup procedure used will depend on the nature of the sample to be analyzed and the data quality objectives for the measurements. See extraction SOPs for details.

10.1.3 GC Conditions:

The dual-column / dual-detector approach involves the use of the columns listed in section 7.2. The columns are connected to an injection tee or dual injection GC, and separate electron capture detectors. Typical GC conditions are listed below, but may be altered as long as method performance criteria are met.

Temperature 1:	120 °C
Time 1:	0 minutes
Ramp 1:	45 °C/minute
Temperature 2:	200 °C
Time 2:	0 minutes
Ramp 2:	15 °C/minute
Final temperature:	230 °C
Time 3:	0 minutes
Ramp 3:	30 °C/minute
Final temperature:	330 °C/minute
Final time:	2.00 minutes

10.1.4 DDT and Endrin Breakdown

When pesticide analysis is required, the breakdown of DDT and Endrin is measured before samples are analyzed and at the beginning of each 12-hour shift. Injector maintenance is completed if the breakdown in greater than 15% for either compound. (See Section 10.5.2)

10.2 Initial Calibration

10.2.1 Prepare calibration standards using the procedures in Section 8.6 and Table 2. The calibration standards are aliquoted into autosampler vials and capped prior to loading onto the autosampler tray.

10.2.2 Establish the GC operating conditions by loading the appropriate GC method. Typical instrument conditions are listed in section 10.1.3. The same operating conditions are used for calibrations and sample analyses. Create the analytical sequence using the Turbochrom data acquisition software.

10.2.2.1 Record the calibration standard, unique lab identifier code (lot), concentration, and analyst's initials in the analytical sequence list.

10.2.3 A 1µL injection volume of each calibration standard is typically used. Other injection volumes may be employed, provided that the analyst can demonstrate adequate sensitivity for the compounds of interest. The same injection volume must be used for all standards and samples.

10.2.4 Because of the low concentration of pesticide standards injected on a GC/ECD, column adsorption may be a problem when the GC has not been used for a day or more or after system maintenance. The GC column may be primed (or deactivated) by injecting a pesticide or PCB standard mixture approximately 20 times more concentrated than the mid-concentration standard. Inject this standard mixture prior to beginning the initial calibration or calibration verification.

Several analytes may be observed in the injection just following this system priming. Always run an instrument blank after system priming.

10.2.5 Calibration Factors

Internal standard calibration techniques are employed in this method.

Internal Standard Procedure. In each standard, calculate the response factor (RF) for each analyte, the average RF, and the relative standard deviation (RSD) of the RFs, using the Target data processing software. The calculations are performed automatically, using the formulae listed in Alpha's Quality Manual.

10.2.6 Initial Calibration Criteria

If the RSD for an analyte is $\leq$ 10%, then the response of the instrument for this compound is considered linear over the range and the mean calibration factor can be used to quantitate sample results. If the RSD for any analyte is > 10%, then linearity through the origin cannot be assumed. The calibration must be repeated for any compounds that fail, or a calibration curve may be generated for this compound and used for sample quantitation instead of the mean calibration factor. If a calibration curve is used, the correlation coefficient must be $\geq$ 0.995.

10.2.7 Retention Time Windows

10.2.7.1 The retention time windows used for the identification of target analytes are calculated using the procedure recommended in Method 608 and were found to be $\pm$ 0.015 minutes.

10.2.8 The windows listed above are used as guidance; however the experience of the analyst weighs heavily in the interpretation of the chromatograms. For example, it has been observed that certain oil matrices can cause the retention times to shift more dramatically. Additionally, if any positive results are questionable and at sufficiently high concentration, GC/MS analysis is used for confirmation.

10.3 Equipment Operation and Sample Processing

10.3.1 The same GC operating conditions used for the initial calibration must be employed for sample analyses, including sample injection volume (Section 10.1.3).

10.3.2 Tentative identification of an analyte occurs when a peak from a sample extract falls within the retention time window for the compound. Each tentative identification is confirmed using a second GC column of dissimilar stationary phase. In particularly difficult matrices, confirmation by GC/MS may be advisable (see Section 10.3.10).

10.3.3 The concentration reported for an identified target analyte in an extract is calculated using the Target data processing software. The Target methods have been configured to utilize the quantitation formulas found in Alpha's Quality Manual. Proper quantitation requires the appropriate selection of a baseline from which the peak area or height can be determined. See the Manual Integration SOP for integration guidelines.

10.3.3.1 If the responses exceed the calibration range of the system, dilute the extract and reanalyze.

10.3.4 Each sample analysis must be bracketed with an acceptable initial calibration, calibration verification standard(s) (each 12-hour analytical shift), or calibration standards interspersed within the samples. When a calibration verification standard fails to meet

the QC criteria, all samples that were injected after the last standard that met the QC criteria must be re-injected.

Calibration verification standards that are interspersed throughout the analytical sequence are varied to verify performance of all analytes.

10.3.5 Sample injections may continue for as long as the calibration verification standards and standards interspersed with the samples meet instrument QC requirements. Standards are analyzed after every 4 – 8 samples to minimize the number of samples that must be re-injected when the standards fail the QC limits. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

10.3.6 Use the calibration standards analyzed during the sequence to evaluate retention time stability. The retention time windows are established using the absolute retention time of each analyte in the mid-concentration standard during the initial calibration as the mid-point of the window. The widths of the windows are defined in Section 10.2.7.

10.3.7 Each subsequent injection of a standard during the 12-hour analytical shift (i.e., those standards injected every 10 samples, or more frequently) must be checked against the retention time windows. If any of these subsequent standards fall outside their absolute retention time windows, the GC system is out of control. Determine the cause of the problem and correct it. If the problem cannot be corrected, a new initial calibration must be performed.

10.3.8 Identification of mixtures (i.e. Chlordane and Toxaphene) is based on the characteristic 'fingerprint' retention time and shape of the indicator peak(s); and quantitation is based on the area under the characteristic peaks as compared to the area under the corresponding calibration peaks(s) of the same retention time and shape generated using internal calibration procedures.

10.3.9 If compound identification or quantitation is precluded due to interference (e.g., broad, rounded peaks or ill-defined baselines are present) cleanup of the extract may be needed. If instrument problems are suspected, rerun the extract on another instrument to determine if the problem results from analytical hardware or the sample matrix. Refer to the extraction SOPs for the procedures to be followed in sample cleanup.

10.3.10 GC/MS Confirmation

GC/MS confirmation may be used in conjunction with either single-column or dual-column analysis if the concentration is sufficient for detection by GC/MS.

10.3.10.1 Full-scan GC/MS will normally require a concentration of approximately 10ng/µL in the final extract for each single-component compound.

10.3.10.2 The GC/MS must be calibrated for the specific target pesticides when it is used for quantitative analysis.

10.3.10.3 GC/MS may not be used for confirmation when concentrations are below the sensitivity of the instrument.

10.3.10.4 GC/MS confirmation should be accomplished by analyzing the same extract that is used for GC/ECD analysis.

10.3.10.5 The base/neutral/acid extract and the associated blank may be used for GC/MS confirmation if the surrogates and internal standards do not interfere and if it is demonstrated that the analyte is stable during acid/base partitioning. However, if

the compounds are not detected in the base/neutral/acid extract, then GC/MS analysis of the pesticide extract should be performed.

10.3.11 A QC reference sample containing the compound should also be analyzed by GC/MS. The concentration of the QC reference sample must demonstrate that those pesticides identified by GC/ECD can be confirmed by GC/MS.

10.4 Continuing Calibration

10.4.1 Verify calibration each 12-hour shift by injecting calibration verification standards prior to conducting any sample analyses. High and low concentration mixtures of single-component analytes and multi-component analytes may be alternated for calibration verification. A calibration standard must also be injected at intervals of not less than once every 10% of all samples analyzed but may be reduced if spike recoveries from samples meet all specified quality control criteria.

10.4.1.1 The response factor (for internal standard compounds) for each analyte to be quantitated must not exceed a ± 15% difference when compared to the initial calibration curve. An alternative calculation may be done by the use of linearity provided that the correlation coefficient is $\geq$ 0.995. If both of these quantitation methods fail acceptance criteria for any compound in the initial calibration, then the system must be re-evaluated and a new calibration curve must be analyzed. The Target data processing software automatically calculates the %D for all analytes according to the formulae in Alpha's Quality Manual.

10.4.1.1.1 PCBs and multi-component Pesticides: The average %D for all quantitation peaks must be less than 15%, for the CC to be considered acceptable.

10.4.1.2 If this criterion is exceeded, inspect the gas chromatographic system to determine the cause and perform whatever maintenance is necessary before verifying calibration and proceeding with sample analysis.

10.4.1.3 If routine maintenance does not return the instrument performance to meet the QC requirements (Section 10) based on the last initial calibration, then a new initial calibration must be performed. Due to the large number of analytes present, allowances may be made for a CF or RF that drifts out high, as long as there are no positive hits for that particular analyte in any of the associated samples. Any QC failures must be written up by the analyst on narrative sheets for inclusion with the sample data.

10.4.2 Compare the retention time of each analyte in the calibration standard with the absolute retention time windows described in section 10.2.7. The center of the absolute retention time window for each analyte is its retention time in the mid-concentration standard analyzed during the initial calibration. Each analyte in each standard must fall within its respective retention time window. If not, the gas chromatographic system must either be adjusted so that a second analysis of the standard does result in all analytes falling within their retention time windows, or a new initial calibration must be performed and new retention time windows established.

10.5 Preventive Maintenance

10.5.1 Preventive Maintenance

Routine preventive maintenance should be performed to maintain GC system performance. This includes periodic replacement of injector septa, replacement of injector liner(s), and replacement of injector seals.

10.5.2 Other Maintenance

Additional maintenance may be required if system performance degrades. GC injector ports are of critical concern, especially in the analysis of DDT and Endrin. Injectors that are contaminated or chemically active can cause the degradation ("breakdown") of the analytes. Endrin and DDT breakdown to Endrin aldehyde, Endrin ketone, DDD, or DDE.

Check for degradation problems by injecting a standard containing only 4,4'-DDT and Endrin. Presence of 4,4'-DDE, 4,4'-DDD, Endrin ketone or Endrin indicates breakdown. If degradation of either DDT or Endrin exceeds 15%, take corrective action before proceeding with calibration.

When such breakdown is observed, replacement of the injector liner and seal may solve the problem. If not, clip approximately 3 – 6 inches from the injector end of the GC column. If the problem persists, replacement of the "Y" splitter (if used) may be necessary. If the degradation does not improve, it may be necessary to replace the column(s).

10.5.2.1 Calculate percent breakdown as follows:

$$\%\ \text{breakdown of DDT} = \frac{\text{sum of degradation peak areas (DDD+DDE)}}{\text{sum of all peak areas (DDT+DDE+DDD)}} \times 100$$

$$\%\ \text{breakdown of Endrin} = \frac{\text{sum of degradation peak areas (aldehyde+ketone)}}{\text{sum of all peak areas (Endrin+aldehyde+ketone)}} \times 100$$

10.5.3 ECD detectors may also become contaminated, requiring bake out at elevated temperatures, or repair by the manufacturer.

11. Data Evaluation, Calculations and Reporting

11.1 Quantitation of Single Component Pesticides

The single component pesticide compounds are calculated as described in Section 10.3.3, and reported in µg/L units. After performing technical data review, validating that all QC criteria have been met and confirming all positive hits, the data report is sent electronically to the LIMS computer for generation of the client report. There are two levels of review of the data in the LIMS system prior to release of data. These reviews should be done by two separate individuals.

11.2 Quantitation of Multiple-Component Analytes

11.2.1 **Toxaphene**

Toxaphene is quantitated by the internal standard method, using the five largest peaks found in the standard and averaging the resulting concentrations.

11.2.2 **Chlordane**

Chlordane is a technical mixture of at least 11 major components and 30 or more minor components. Trans- and cis-Chlordane (alpha and gamma, respectively), are the two major components of technical Chlordane. However, the exact percentage of each in the technical material is not completely defined, and is not consistent from batch to batch.

11.2.2.1 The GC pattern of a Chlordane residue may differ considerably from that of the technical standard. Depending on the sample substrate and its history, residues of Chlordane can consist of almost any combination of constituents from the technical Chlordane, plant and/or animal metabolites, and products of degradation caused by exposure to environmental factors such as water and sunlight.

11.2.2.2 Whenever possible, when Chlordane residue does not resemble technical Chlordane, the analyst should quantitate the peaks of alpha-Chlordane, gamma-Chlordane, and Heptachlor separately against the appropriate reference materials, and report the individual residues.

11.2.2.3 When the GC pattern of the residue resembles that of technical Chlordane, the analyst may quantitate Chlordane residues by comparing the total area of the Chlordane chromatogram using the three major peaks.

12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

Holding time exceedances and/or improper preservation are noted on the nonconformance report form.

Perform instrument maintenance as described throughout this SOP as needed when instrument calibration criteria are not met. Record all maintenance in the instrument logbook.

All batch and sample specific QC criteria outlined in Section 9 are evaluated by the analyst prior to approval of the data. When any QC criteria fail, the cause for the failure must be identified and corrected. This may include instrument recalibration followed by sample reanalysis, sample cleanup, or sample re-extraction. If it is determined that the failure is due to sample matrix effects, a project narrative report is written by the analyst for inclusion in the data report. If there is insufficient sample volume to perform the re-analysis for confirmation, this is also noted in the narrative and included in the client report.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Qualtrax ID 1732. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Qualtrax ID 1739 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

Qualtrax ID 1732 MDL/LOD/LOQ Generation

Qualtrax ID 1739 IDC/DOC Generation

SOP/14-01 Waste Management and Disposal SOP

16. Attachments

Table 1: REPORTING LIMITS

Table 2: STANDARD SOLUTIONS

Table 3: QC ACCEPTANCE CRITERIA

TABLE 1
STANDARD SOLUTIONS

	Stock solution	Level 6	Level 5	Level 4	Level 3	Level 2	Level 1	Spike Solution
Alpha-BHC	1000	0.4	0.2	0.01	0.05	0.01	0.005	0.625 µg/mL
Lindane	1000	0.4	0.2	0.01	0.05	0.01	0.005	0.625 µg/mL
Heptachlor	1000	0.4	0.2	0.01	0.05	0.01	0.005	0.625 µg/mL
Endosulfan I	1000	0.4	0.2	0.01	0.05	0.01	0.005	0.625 µg/mL
Dieldrin	1000	0.4	0.2	0.01	0.05	0.01	0.005	0.625 µg/mL
Endrin	1000	0.4	0.2	0.01	0.05	0.01	0.005	0.625 µg/mL
4, 4'-DDD	1000	0.4	0.2	0.01	0.05	0.01	0.005	0.625 µg/mL
4, 4'-DDT	1000	0.4	0.2	0.01	0.05	0.01	0.005	0.625 µg/mL
Methoxychlor	1000	0.4	0.2	0.01	0.05	0.01	0.005	0.625 µg/mL
Tetrachloro-m-Xylene	200	0.64	0.32	0.16	0.08	0.04	0.02	2.0 µg/mL
Decachloro-Biphenyl	200	1.28	0.64	0.32	0.16	0.08	0.04	2.0 µg/mL
Aldrin	1000	0.4	0.2	0.01	0.05	0.01	0.005	0.625 µg/mL
Beta-BHC	1000	0.4	0.2	0.01	0.05	0.01	0.005	0.625 µg/mL
Delta-BHC	1000	0.4	0.2	0.01	0.05	0.01	0.005	0.625 µg/mL
Heptachlor Epoxide	1000	0.4	0.2	0.01	0.05	0.01	0.005	0.625 µg/mL
Trans-Chlordane	1000	0.4	0.2	0.01	0.05	0.01	0.005	0.625 µg/mL
Cis-Chlordane	1000	0.4	0.2	0.01	0.05	0.01	0.005	0.625 µg/mL
4, 4'- DDE	1000	0.4	0.2	0.01	0.05	0.01	0.005	0.625 µg/mL

Endosulfan II	1000	0.4	0.2	0.01	0.05	0.01	0.005	0.625 µg/mL
Endrin Aldehyde	1000	0.4	0.2	0.01	0.05	0.01	0.005	0.625 µg/mL
Endosulfan Sulfate	1000	0.4	0.2	0.01	0.05	0.01	0.005	0.625 µg/mL
Endrin Ketone	1000	0.4	0.2	0.01	0.05	0.01	0.005	0.625 µg/mL
Technical Chlordane	100 µg/mL	0.1 µg/mL	5.0 µg/mL	2.5 µg/mL	1.0 µg/mL	0.5 µg/mL	0.25 µg/mL	
Toxaphene	100 µg/mL	0.2 µg/mL	10 µg/mL	5.0 µg/mL	2.5 µg/mL	1.0 µg/mL	0.50 µg/mL	
PCB 1016/1260 Mix								
Aroclor 1016	100 µg/mL	0.1 µg/mL	10 µg/mL	5.0 µg/mL	2.5 µg/mL	1.0 µg/mL	0.5 µg/mL	4.00 µg/mL
Aroclor 1260	100 µg/mL	0.1 µg/mL	10 µg/mL	5.0 µg/mL	2.5 µg/mL	1.0 µg/mL	0.5 µg/mL	4.00 µg/mL
PCB 1221/1254 MIX								
Aroclor 1221	100 µg/mL	0.1 µg/mL	10 µg/mL	5.0 µg/mL	2.5 µg/mL	1.0 µg/mL	0.5 µg/mL	
Aroclor 1254	100 µg/mL	0.1 µg/mL	10 µg/mL	5.0 µg/mL	2.5 µg/mL	1.0 µg/mL	0.5 µg/mL	
Aroclor 1248	100 µg/mL	0.1 µg/mL	10 µg/mL	5.0 µg/mL	2.5 µg/mL	1.0 µg/mL	0.5 µg/mL	
Aroclor 1242	100 µg/mL	0.1 µg/mL	10 µg/mL	5.0 µg/mL	2.5 µg/mL	1.0 µg/mL	0.5 µg/mL	
Aroclor 1232	100 µg/mL	0.1 µg/mL	10 µg/mL	5.0 µg/mL	2.5 µg/mL	1.0 µg/mL	0.5 µg/mL	
Internal Standard								
1-Bromo-2-Nitrobenzene	5000 µg/mL	0.25 µg/mL	0.25 µg/mL	0.25 µg/mL	0.25 µg/mL	0.25 µg/mL	0.25 µg/mL	

TABLE 2

QC ACCEPTANCE CRITERIA

Surrogate % Recovery	**Lower Control Limit**	**Upper Control Limit**
2,4,5,6-Tetrachloro-m-xylene	30%	150%
Decachlorobiphenyl	30%	150%

	% Recovery	**Duplicate and/or MSD**

MS/MSD and LCS	Lower Control Limit	Upper Control Limit	Aqueous RPD
Lindane	56%	123%	30%
Heptachlor	40%	111%	30%
Aldrin	40%	120%	30%
Dieldrin	52%	126%	30%
Endrin	56%	121%	30%
4,4'-DDT	38%	127%	30%
Aroclor 1016	40%	126%	30%
Aroclor 1260	40%	127%	30%
Heptachlor Epoxide	37%	142%	30%
Alpha-BHC	37%	134%	30%
Beta-BHC	17%	147%	30%
Delta-BHC	19%	140%	30%
4,4'-DDD	31%	141%	30%
4,4'-DDE	30%	145%	30%
Endosulfan I	45%	153%	30%
Endosulfan II	0.1%	202%	30%
Endosulfan Sulfate	26%	144%	30%
Endrin Aldehyde	42%	122%	30%

Chloride

References: **Method SM 4500Cl-E,** Standard Methods for the Examination of Water and Wastewater, APHA-AWWA-WPCF, 21st Edition, 1997.

Method 9251, SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update III, 1997.

Method 10-117-07-1-B, Chloride in Water, Lachat Instruments, 6645 West Mill Road, Milwaukee, WI 53218 (1993).

1. Scope and Application

Matrices: The method is applicable to potable water, surface water, saline water, domestic and industrial wastewaters. The concentration range can be varied by using the colorimeter controls. Soil samples can be analyzed following water extraction.

Definitions: See Alpha Laboratories Quality Manual Appendix A.

Chloride, in the form of chloride (Cl-) ion, is one of the major inorganic anions in water and wastewater. In potable water, the salty taste produced by chloride concentrations is variable and dependent on the chemical composition of water. Some waters containing 250mg Cl-/L may have a detectable salty taste if the cation is sodium. On the other hand, the typical salty taste may be absent in waters containing as much as 1000mg/L when the predominant cations are calcium and magnesium. The chloride concentration is higher in wastewater than in raw water because sodium chloride (NaCl) is a common article of diet and passes unchanged through the digestive system. Along the seacoast, chloride may be present in high concentrations because of leakage of salt water into the sewerage system. It also may be increased by industrial processes. A high chloride content may harm metallic pipes and structures, as well as growing plants.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one of the following laboratory personnel before performing the modification: Area Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability, analyzing a proficiency test sample and completing the record of training.

After initial demonstration, ongoing demonstration is based on acceptable laboratory performance of at least a quarterly laboratory control sample or acceptable performance from an annual proficiency test sample. A major modification to this procedure requires demonstration of performance. The identification of major method modification requiring performance demonstration is directed by the QA Officer and/or Laboratory Director on a case-by-case basis.

2. Summary of Method

Thiocyanate ion is liberated from mercuric thiocyanate by the formation of soluble mercuric chloride. In the presence of ferric iron, free thiocyanate ion forms the highly colored ferric thiocyanate, of which the absorbance is proportional to the chloride concentration. Samples are analyzed directly against a nonlinear calibration curve.

2.1 Method Modifications from Reference

None.

3. Detection Limits

The reported detection limit is 1.0mg Cl^-/L for water samples or 10.0 mg/kg for soils.

4. Interferences

4.1 Turbid samples and samples containing suspended solids are filtered through a 0.45µm filter.

4.2 Substances, which reduce iron (III) to iron (II) and mercury (II) to mercury (I), (e.g. sulfite, thiosulfate), will interfere.

4.3 Halides which also form strong complexes with mercuric ion (e.g. Br-, I-) give a positive interference.

4.4 Calcium and Magnesium ion may precipitate if present in sufficient concentration.

5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

Samples are collected in clean, chemically resistant glass or plastic bottles. The maximum sample portion required is 100mL. Soil samples may be collected in glass or plastic containers.

6.2 Sample Preservation

Refrigerate at 4 ± 2 ºC until analysis.

6.3 Sample Shipping

No special shipping requirements.

6.4 Sample Handling

The maximum holding time is 28 days from collection.

7. Equipment and Supplies

7.1 Automated Ion Analyzer: Lachat Instruments.

7.2 Volumetric Flasks: Various volumes.

7.3 Volumetric Pipets: Various volumes.

7.4 Filtering Apparatus

7.5 0.45 µm Filters

7.6 Data Station

7.7 Analytical balances

7.8 Stirring plate

7.9 Plastic cups.

7.10 Ottawa sand.

7.11 10 ml syringes

8. Reagents and Standards

8.1 Stock Calibration Standard, 1000mg Cl^-/L: Commercially prepared. A Certificate of Analysis is kept on file. Stored at room temperatures and expires per manufacturer's expiration date.

8.1.1 Working Calibration Standards: Stable for period of six months. Store at room temperature.

8.1.1.1 100ppm Working Standard: To a 200mL volumetric flask, pipet 20.0mL of 1000ppm stock standard, (Section 8.1). Bring to volume with DI.

8.1.1.2 80ppm Working Standard: To a 100mL volumetric flask, pipet 8.0mL of 1000ppm stock standard, (Section 8.1). Bring to volume with DI.

8.1.1.3 20ppm Working Standard: To a 200mL volumetric flask, pipet 4.0mL of 1000ppm stock standard, (Section 8.1). Bring to volume with DI.

8.1.1.4 10ppm Working Standard: To a 200mL volumetric flask, pipet 2.0mL of 1000ppm stock standard, (Section 8.1). Bring to volume with DI.

8.1.1.5 5ppm Working Standard: To a 200mL volumetric flask, pipet 1.0mL of 1000ppm stock standard, (Section 8.1). Bring to volume with DI.

8.1.1.6 1ppm Working Standard: To a 200mL volumetric flask, pipet 2.0mL of 100ppm working standard, (Section 8.1.1.1). Bring to volume with DI.

8.1.1.7 Calibration Blank: DI water.

8.2 Stock Mercuric Thiocyanate Solution: In a 1L volumetric flask, dissolve 4.17g mercuric thiocyanate ($Hg(SCN)_2$) in about 500mL methanol. Dilute to the mark with methanol and stir for 20 minutes until dissolved. **CAUTION!** Mercury is a very toxic metal. Work under a hood and wear gloves! Solution is prepared every six months, and stored at room temperature.

8.2.1 Mercuric Thiocyanate, $Hg(SCN)_2$: Purchase ACS Grade. Store at room temperature. Expires upon manufacturer's expiration date.

8.2.2 Methanol: Reagent grade. Store at room temperature. Expires upon manufacturer's expiration date.

8.3 Stock Ferric Nitrate Reagent 0.5M: In a 1L volumetric flask, dissolve 202g ferric nitrate $Fe(NO_3)_3 \times 9H_2O$ in approximately 800mL water. Add 25mL concentrated nitric acid and dilute to the mark. Stir until dissolved. Reagent is prepared every 6 months, and stored at room temperature.

8.3.1 Ferric Nitrate, $Fe(NO_3)_3 \times 9H_2O$: Purchase ACS Grade. Store at room temperature. Expires upon manufacturer's expiration date.

8.3.2 Concentrated Nitric Acid, HNO_3: Reagent Grade. Store at room temperature. Expires upon manufacturer's expiration date.

8.4 Combined Color Reagent: In a 500mL volumetric flask, mix 75mL stock mercuric thiocyanate solution (Section 8.2) with 75mL stock ferric nitrate reagent (Section 8.3) and dilute to the mark with water. Invert three times to mix. Solution is prepared monthly, and stored at room temperature.

8.5 Stock LCS Standard, 1000mg Cl/L: Commercially prepared. A Certificate of Analysis is kept on file. The LCS Stock Standard must be from a different source than the Calibration Stock Standard. Store at room temperature, expires per manufacturer's expiration date.

8.5.1 5ppm (Low-level) LCS: Pipet 1mL of the 1000ppm stock LCS into a 200mL volumetric flask and bring to volume with DI. Standard is stable for six months. Store at room temperature.

8.5.2 30ppm (Mid-range) LCS: Pipet 3mL of the 1000ppm stock LCS into a 100mL volumetric flask and bring to volume with DI. Standard is stable for six months. Store at room temperature.

8.5.3 80ppm (High-level) LCS: Pipet 8mL of the 1000ppm stock LCS into a 100mL volumetric flask and bring to volume with DI. Standard is stable for six months. Store at room temperature.

8.5.4 Soil LCS: weigh 5 g(record exact weight) of Ottawa sand into plastic cup, pipet 2 ml of 1000 ppm stock LCS and add 48 ml of DI. Stir for 30 min, analyze water portion.

Final LCS concentration @ 400 mg/kg.

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blank(s)

9.1.1 Method Blank / ICB

Analyze one DI Blank per batch of 20 samples or less. An Initial Calibration Blank is analyzed at the start of each analytical sequence. The ICB consists of DI that has been filtered through a 0.45µm filter.
For soil samples: weigh 5 g of Ottawa sand (record exact weight in Log book), add 50 ml of DI, stir for 30 min, and filter. Analyze water portion.

Results must be less than the RL. If the ICB fails, re-run the ICB. If it passes criteria, the analysis can continue. If the ICB fails again, re-filter the ICB. If failure continues, analyze the ICB without filtering the DI, to determine if the contamination is coming from the filter or the water. If the ICB passes criteria, then check the filters. Any contaminated filters must be discarded; samples are only filtered through clean filters. Samples that don't have any trace of turbidity may be analyzed without filtering.

9.2 Laboratory Control Sample (LCS)

The calibration curve is verified at three concentrations at the start of each analytical run (ICV standards) . Middle standard (30 mg/L) used for reportable LCS. The LCS must fall between 90-110% of the true value.

If the LCS falls outside acceptance criteria, reprepare the solution and reanalyze. If the LCS falls outside for a second time, re-calibrate the system.

9.3 Initial Calibration Verification (ICV)

Refer to Section 9.2.

9.4 Continuing Calibration Verification (CCV)

The calibration curve is verified at 20 mg/l standard after every 10^{th} sample, and at the end of the analytical run. Recovery for the CCV must be within ±10% of the true value.

If the CCV fails criteria, reanalyze the CCV. If it passes criteria, then continue with the analytical run. If the CCV fails for a second time, reprepare the CCV and reanalyze. If it passes criteria, reanalyze all samples that were analyzed since the last acceptable CCV.

9.5 Matrix Spike

Pipet 0.5mL of the 1000ppm Calibration Stock Standard (Section 8.1) into a 25mL volumetric flask and bring to volume with sample. The spike concentration will be 20ppm. Analyze one spike per batch of 20 samples or less.

For soil samples: weigh 5 g of sample (record exact weight), pipet 2 ml of 1000 ppm stock LCS and add 48 ml of DI. Stir for 30 min, analyze water portion. Final spike concentration @ 400 mg/kg.

The MS recovery must fall within in-house control limits. If the MS falls outside of the recovery criteria, re-analyze both the MS and the associated sample. If the % recovery is still outside acceptance criteria, narrate the nonconformance due to sample matrix.

9.6 Laboratory Duplicate

Analyze one sample in duplicate per batch of 20 samples or less.

The duplicate must be within in-house control limits. If the RPD is outside acceptance limits, re-run both the duplicate and out of control sample. If the RPD is still outside acceptance criteria, narrate the nonconformance.

9.7 Method-specific Quality Control Samples

Not applicable.

9.8 Method Sequence

- Calibration of the instrument
- ICV/LCS analysis (5, 30, 80ppm standards)
- Curve verification (DI blank and 20ppm calibration standard)
- Sample analysis, up to ten samples
- Curve verification (DI blank and 20ppm calibration standard) after every tenth sample and at the end of the analytical run.

10. Procedure

10.1 Equipment Set-up

Turn on instrument and connect appropriate board.

10.2 Initial Calibration

10.2.1 Calibrate the Lachat flow injection analyzer according to the manufacturer's instructions.

10.2.2 Connect the chloride board in the appropriate channel position.

10.2.3 Using the six calibration standards and a DI blank (see Section 8.1.1.1 to 8.1.1.7), calibrate the instrument. A correlation coefficient ≥ 0.995 must be achieved using a second order quadratic calibration, otherwise recalibration will be necessary. This can be done by re-analyzing the standards used previously, or preparing the standards again. The calibration curve is prepared by plotting the peak areas of each standard processed through the manifold against the true chloride concentrations in each standard.

10.2.4 **Initial Calibration Verification (ICV/LCS):** Prior to sample analysis, the calibration curve is checked at low, mid and high ends of the curve with 5ppm LCS, 30ppm LCS and 80ppm LCS respectively (Sections 8.5.1 through 8.5.3). Recovery for each standard must be within ±10% of their true value, otherwise recalibration is necessary.

10.3 Equipment Operation and Sample Processing

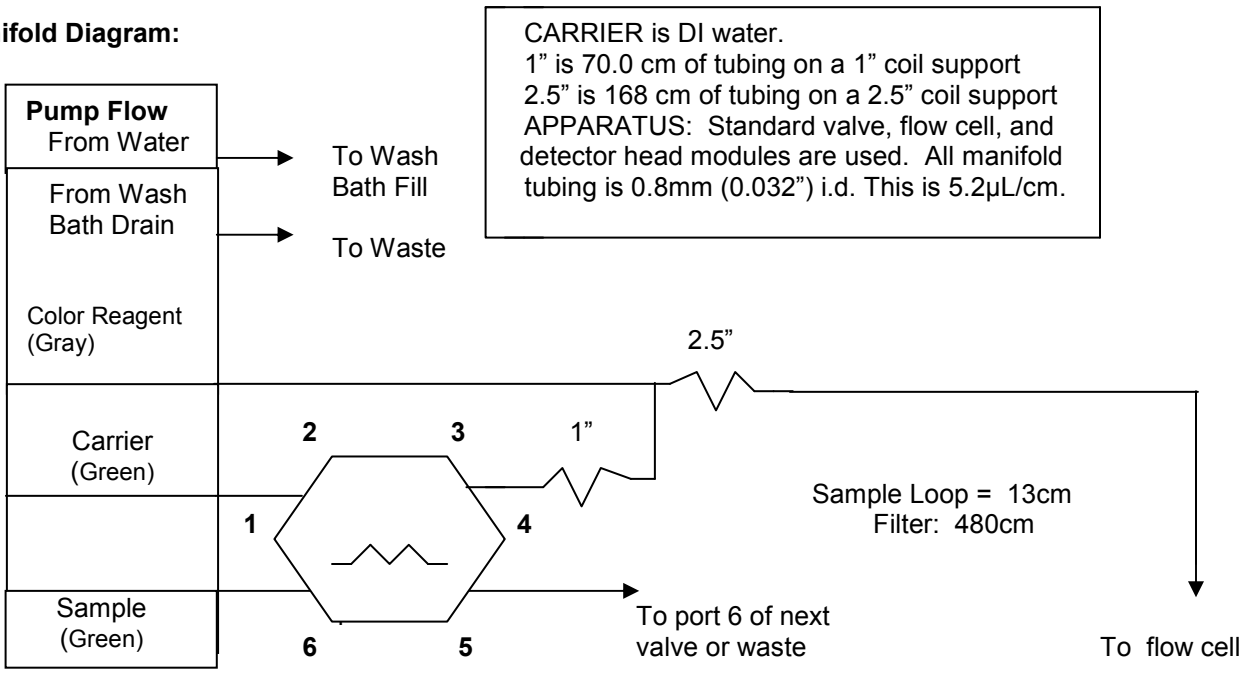
10.3.1 Follow the instrument manual for instrument operating instructions. Water samples should be poured in sample tubes for analysis. If sample is turbid or has sediment, sample has to be filtered prior analysis using 0.45 nm acrodisk filters. For soil samples: weigh 5 g of sample (record exact weight in log book), add 50 ml of Di stir for 30 min, filter and analyze water portion.

Note: 1:10 ratio should be used for soil:water extraction

10.3.2 The following are the specific parameters for this method:

Sample throughput:	120 samples/h; 30 s/sample
Pump speed:	35
Cycle period:	30 s
Inject to start of peak period:	8 s
Inject to end of peak period:	30 s
System IV Gain Setting	149 x 1
Presentation, Data Window	
Top Scale Response:	1.00
Bottom scale response:	0.00

Manifold Diagram:



10.3.3 A volumetric dilution is performed on any sample that has a result greater than 100ppm (the highest point on the calibration curve), so that the sample concentration is near the midpoint of the curve. All dilution factors are recorded.

10.3.4 Any sample with a result >1ppm, that follows a sample with a result of 100ppm or greater, should be considered suspect due to possible carry-over contamination and must be reanalyzed.

10.4 Continuing Calibration

Before sample analysis begins, after every 10 samples, and at the end of the sample run, the following must be analyzed:

- DI blank (Section 8.1.1.7)
- 20ppm calibration working standard (CCV) (Section 8.1.1.3)

The blank must yield a non-detectable result and the standard must be recovered within ±10% of its true value. If recoveries fall outside of this range, the cause for the failure is determined and corrected. When the CCV fails low, the CCV is re-made and re-analyzed. If failure continues, all samples analyzed since the last valid CCV, are considered invalid and must be re-analyzed. However, prior to re-analysis, a new calibration curve must be generated. If the CCV fails high, and all sample are considered ND, then the failure is narrated.

10.5 Preventative Maintenance

10.5.1 All lines are flushed with DI at the end of each run.

10.5.2 Tubing is replaced as necessary.

10.5.3 All equipment is kept clean.

10.5.4 All maintenance is recorded in the Instrument Maintenance Logbook.

11. Data Evaluation, Calculations and Reporting

Prepare standard curves by plotting peak heights of standards processed through the manifold against chloride concentrations in standards. The Lachat software will compute the sample chloride concentration by comparing the sample peak height with the standard curve.

The analyst has two options for final calculation: 1) Manually multiply the Lachat result times the dilution factor, if any, or 2) Input the dilution factor into the Lachat software and allow it to compute the corrected results.

12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

Holding time exceedence and improper preservation are noted on the nonconformance report form.

Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

Review of standards, blanks and standard response for acceptable performance occurs for each batch of samples. Record any trends or unusual performance on a nonconformance action form.

If the CV or LCS recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked samples is suspect and is only reported for regulatory compliance purposes with the appropriate nonconformance action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/1732. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP/1734 and 1739 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

SOP/1732 MDL/LOD/LOQ Generation

SOP/1734,1739 IDC/DOC Generation

SOP/1728 Waste Management and Disposal SOP

16. Attachments

None.

Hot Block Digestion

For Aqueous Samples

Reference Methods: **EPA 200.7,** Code of Federal Regulations 40, Part 141 and Part 136, Revision 4.4, May 1994; **EPA 200.8,** Environmental Monitoring Systems Laboratory Office of Research and Development U.S. EPA Cincinnati, OH Rev 5.4; **Method 3005A,** SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update I, 1992. **EPA 6010B,** SM2340B, Hardness by Calculation, Standard Methods for the Examination of Water and Wastewater. APHA-AWWA-WPCF, 18th Edition. 1992; Method **6020** Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846 Draft Update UVA, May 1998.

1. Scope and Application

Matrices: This method is appropriate for the digestion of all influents, effluents, surface waters, monitoring wells, liquids, drinking waters, furnace metals and soluble metals.

Definitions: See Alpha Laboratories Quality Manual Appendix A.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one of the following laboratory personnel before performing the modification: Area Supervisor, Metals Manager, Laboratory Services Manager, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability, analyzing a proficiency test sample and completing the record of training.

After initial demonstration, ongoing demonstration is based on acceptable laboratory performance of at least a quarterly laboratory control sample or acceptable performance from an annual proficiency test sample. A major modification to this procedure requires demonstration of performance. The identification of major method modification requiring performance demonstration is directed by the QA Officer and/or Laboratory Director on a case-by-case basis.

2. Summary of Method

Aqueous samples and appropriate QC samples are poured into 50mL digestion cups. Acid is added to the cup and the samples are reduced at 90-95 °C for approximately 3 hours. The samples are then brought up to a final volume of 50mL, and are ready for analysis by ICP or ICP-MS.

2.1 Method Modifications from Reference

Using 50mL for sample volume and final volume, not 100mL.

3. Reporting Limits

Reporting Limit information may be found in the analytical method SOPs.

4. Interferences

Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents. This includes wearing personal protective equipment such as a lab coat, safety glasses, gloves and respirator (as necessary).

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

Samples are collected in plastic bottles.

6.2 Sample Preservation

If samples are for soluble metals analysis, filtration must take place prior to preservation with 1:1 HNO_3 to a pH < 2. Soluble samples must be held at pH < 2 for at least 24 hours prior to digestion.

Samples for total metals analysis are preserved with 1:1 HNO_3 to a pH < 2. Non-potable water samples must be held at pH <2 for at least 24 hours prior to digestion.

6.3 Sample Shipping

No special shipping requirements.

6.4 Sample Handling

Samples are stored at room temperature. Samples for soluble metals analysis should be filtered and preserved within 24 hours of collection.

6.4.1 Sample Filtration for soluble metals: Obtain a 250mL plastic bottle for each sample to be filtered plus one for the filter blank. Put preprinted labels on each bottle and place in glass jars of filtration apparatus. Screw caps on and attach filter funnel. Pour desired amount of sample into filter funnel and turn vacuum on. Filter blank uses DI water. Preserve samples and blank with 1:1HNO3 to a pH<2. Record in Sample Handling logbook.

7. Equipment and Supplies

7.1 Hot Block Apparatus: Calibrated quarterly by outside vendor to maintain sample temperature of 95°C.

7.2 Digestion cups: 50mL volume, polypropylene

7.3 Watch Glass: Polypropylene to cover the digestion cups during digestion.

7.4 Threaded Caps: To cover digestate following digestion

7.5 Volumetric Glassware: Various sizes of volumetric flasks and pipets, as needed

7.6 Filter Mate Push Plunger Filter

7.7 pH Indicator Strips

7.8 Vacuum Filtration Apparatus: For filtering samples for soluble metals

7.9 0.45um Filter Funnel: 100mL volume

7.10 250mL plastic bottles

8. Reagents and Standards

8.1 Analytical Standards: All standards shall be prepared according to the appropriate method of analysis.

8.2 Trace Nitric Acid ($tHNO_3$)

8.2.1 Trace-grade $tHNO_3$: Acid expires one year from date it was opened. Store at room temperature in hood.

8.2.2 1:1$tHNO_3$: 500mL $tHNO_3$ diluted to 1 liter with DI water. Store at room temperature in hood. Expires 1 year from date of prep.

8.3 Trace Hydrochloric Acid (tHCl)

8.3.1 Trace-grade tHCl: Acid expires one year from date it was opened. Store at room temperature in hood.

8.3.2 1:1tHCl: 500mL tHCl diluted to 1 liter with DI water. Store at room temperature in hood. Expires 1 year from date of prep.

8.4 Deionized Water (DI)

8.5 Standard Spiking Solutions

Store at room temperature. Standards expire upon manufacturer's specified date.

8.5.1 IPS: To a 500mL volumetric flask, add 100mL DI water and 25mL of tHNO3. Add 50.0mL of the well-shaken, room temperature, ICP Spike Standard #1 (Section 8.5.5), 25.0mL of 1000ppm Antimony standard, and 2.5mL of 1000ppm Cadmium standard. Bring to volume with DI water.

0.5mL of this solution per 50mL of sample volume will yield the following concentrations in the spiked sample: 2ppm Aluminum, 2ppm Barium, 0.05ppm Beryllium, 0.2ppm

Chromium, 0.5ppm Cobalt, 0.25ppm Copper, 1.0ppm Iron, 0.5ppm Manganese, 0.5ppm Nickel, 0.05ppm Silver, 0.5ppm Vanadium, 0.5ppm Zinc.

8.5.2 **FPS**: To a 500mL volumetric flask, add 200mL of DI water and 25mL of tHNO3. Add 3mL of the well-shaken, room temperature ICP Spike Standard #3 (Section 8.5.6) and add 25mL of1000ppm Lead standard. Bring to volume with DI water.

0.5mL of this solution per 50mL of sample volume will yield the following concentrations in the spiked sample: 0.12ppm Arsenic, 0.05ppm Cadmium, 0.12ppm Selenium, 0.12ppm Thallium, and 0.51ppm Lead.

8.5.3 **MIX:** To a 500mL volumetric flask add 50mL of DI water and 25mL of tHNO3. Add50mL of each of the following stock standards: 1000ppm Boron, 10,000ppm Calcium, 10,000ppm Magnesium, 1000ppm Molybdenum, 10,000ppm Potassium, 1000ppm Strontium, 10,000ppm Sodium, 1000ppm Titanium, and 1000ppm Tin. Bring to volume with DI water.

0.5mL of this solution per 50mL of sample volume will yield the following concentrations in the spike sample: 1.0ppm Boron, 10ppm Calcium, 10ppm Magnesium, 1.0ppm Molybdenum, 5ppm Potassium, 1.0ppm Strontium, 10ppm Sodium, 1.0 Titanium.

8.5.4 **1000ppm Standards of individual metals**

8.5.5 ICP Spike Standard #1: Purchased commercially prepared, with a certificate of analysis. Contains the following: 2000ppm Aluminum, 2000ppm Barium, 50ppm Beryllium, 200ppm Chromium, 500ppm Cobalt, 250ppm Copper, 1000ppm Iron, 500ppm Manganese, 500ppm Nickel, 50ppm Silver, 500ppm Vanadium, 500ppm Zinc.

8.5.6 ICP Spike Standard #3: Purchased commercially prepared, with a certificate of analysis. Contains the following 2000ppm Arsenic, 50ppm Cadmium, 500ppm Lead, 2000ppm Selenium, 2000ppm Thallium.

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blank(s)

A minimum of one blank must be digested for every sample batch.

9.2 Laboratory Control Sample (LCS)

Use 50mL of DI water. Add 0.5mL each of IPS Spiking Solution (Section 8.5.1), FPS Spiking Solution (Section 8.5.2), and MIX Spiking Solution (Section 8.5.3). If the desired metal is not included in the spiking solution, add 50uL of desired metal standard stock 1000ppm solution.

9.3 Initial Calibration Verification (ICV)

Not applicable to this preparatory method.

9.4 Continuing Calibration Verification (CCV)

Not applicable to this preparatory method.

9.5 Matrix Spike

A matrix spike is performed for each sample matrix. A minimum of one matrix spike must be analyzed for each batch of ten (10) or less wastewater or drinking water samples to be digested for methods 200.7 and 200.8. A minimum of one matrix spike shall be performed for

each batch of twenty (20) or less groundwater or monitoring well samples. Add 0.5mL each of IPS Spiking Solution (Section 8.5.1), FPS Spiking Solution (Section 8.5.2), and MIX Spiking Solution (Section 8.5.3). If the desired metal is not included in the spiking solution, add 50uL of desired metal standard stock 1000ppm solution.

9.6 Laboratory Duplicate

Each batch of ten (10) or less wastewater or drinking water samples to be digested for methods 200.7 and 200.8 will include a duplicate sample. A minimum of one sample duplicate shall be performed for each batch of twenty (20) or less groundwater or monitoring well samples.

9.7 Method-specific Quality Control Samples

None.

9.8 Method Sequence

- Determine which samples will be used for batch QC
- Record sample pH for those samples to be analyzed for Methods 200.7 and/or 200.8
- Pour 50mL sample into a digestion cup
- Add spike solution to samples, as appropriate
- Add 1 mL of 1:1 tHNO_3 and 0.5 mL of 1:1 tHCl
- Heat on hot block for 3 hours
- Bring samples to 50mL volume with DI water. Filter any digestates containing sediment.

10. Procedure

10.1 Equipment Set-Up

10.1.1 Inspect all samples and determine QC duplicate (dp) and spike (ms). This decision is normally based upon client sample content history and analytes requested. The ideal sample for QC is one that has both ample volume and the most requested analytes of all the samples in the batch.

10.1.2 One spike and one duplicate must be performed per batch of twenty (20) or less groundwater or monitoring well samples. One spike and one duplicate must be performed for every ten (10) or less samples to be digested for Methods 200.7 and 200.8.

10.1.3 Each batch must have a Prep Blank Water (PBW) and a Laboratory Control Sample Water (LCS).

10.1.4 Sample Preparation for Digestion

10.1.4.1 Obtain one 50mL polypropylene digestion cup for each sample and QC sample to be digested. Label the cups with the last 5 digits of the sample number across the top 1/3 of the cup and at the bottom write “T” for total metals, “S” for soluble metals. Additionally, if the sample is being re-prepped, note this with a “II” on the cup. All matrix spikes and LCSs get a black line on top of tube to indicate that it will be spiked.

10.1.4.2 Using the Preprinted Hot Block lab notebook, fill in appropriate spaces for date, analyst, products, acid type(s), ms/lcs spiking information. Place a pre-printed label with the lot numbers on the top right hand corner.

Samples to be analyzed by Methods 200.7 and 200.8 must have the pH verified as being <2 prior to digestion. Using a clean disposable transfer pipet, place a drop of sample onto a pH strip.

NOTE: Under no circumstances shall the pH strip be put directly into the original sample container.

The pH results are recorded in the logbook with a checkmark for those below 2 and "no" for those that are not. If sample pH is above 2 preserve sample with HNO3 and wait 24 hours before digesting for 200.7 and 200.8.

10.1.4.2.1 Place all samples on the lab bench from left to right in rows of 5 samples. Note the number of samples on the bottom right hand corner of logbook page.

10.1.4.2.2 Shake and pour 50mL of each sample into the appropriate cup. 50mL of DI water is used for the Blank (PBW) and LCS..

10.1.4.2.3 Note the Color and Clarity of each sample in the appropriate columns in the laboratory notebook. Clarity is used to describe any sediment the sample may contain cloudiness or opaqueness.

10.1.4.2.4 Hardness: If samples require Hardness analysis then perform the following:

10.1.4.2.4.1 Determine if there is any sediment in the sample. If there is none, then simply decant the sample into the cup without shaking.

10.1.4.2.4.2 If the sample does contain sediment and the only requested analyte is Hardness, then let the sample settle and decant only the top layer, avoiding the sedimentary layer.

10.1.4.2.4.3 If other analytes are requested on the sample, first decant 50mL off the top layer into a tube marked with the sample number and “Ha” below. Then shake the sample and pour it into a second tube labeled with the sample number. The first tube will be used for the Hardness analysis, and the second tube will be used for the analysis of the other analytes requested.

10.1.4.2.5 Any sample dilutions must be performed based upon initial knowledge of sample concentration or if the sample is either soapy, opaque, darkly colored or foamy. Dilutions up to 10x are prepared directly in the digestion cup, utilizing the graduated markings as a guide. Otherwise, for dilutions > 10x, volumetric glassware is used.

Count all matrix spikes and LCSs on page. Using a spiking tray pull out all samples to be spiked and confirm that it matches count from page. Spike all matrix spikes and LCSs with 0.5mL IPS, FPS, and MIX .

10.1.4.2.6 50µL of the individual 1000ppm metal standard is used, if the requested metal is not included in the other spike mixes. All Hot Block samples are brought up

to a 50mL final volume, replacing any volume that has evaporated on the hotblocks.

10.1.4.2.7 Once spiked return spiked samples to the hotblock rack and add 1 mL of 1:1 HNO3 and 0.5 mL of 1:1 HCl.

10.2 Initial Calibration

Not applicable to this preparatory method.

10.3 Equipment Operation and Sample Processing

10.3.1 Sample Digestion

10.3.1.1 The sample cups are placed on the hot block set to a temperature of 96.5 °C. Each cup is covered with a ribbed polypropylene watch glass and remains on the hot block for 3 hours. Record in the laboratory notebook the time sample digestion began and the time the samples are taken off the Hot Block unit. Record the hot block temperature in the logbook

10.3.1.2 Upon completion of the digestion, the samples are removed from the hot block and allowed to cool to room temperature. For each tube, the ribbed watch glass cover must be rinsed with a small amount of DI water to incorporate any condensate back into the digestate. Samples are then brought up to a final volume of 50mL using DI water.

All digestates that are sediment-free are capped and are ready for instrumental analysis. If any samples contain sediment, they are filtered using a filter mate push plunger filter. The filter is clipped onto the plunger and then pushed into the tube gently, but with enough force to move it downward through the tube. The sample is then capped and is ready for instrumental analysis.

10.4 Continuing Calibration

Not applicable to this preparatory method.

10.5 Preventative Maintenance

The Hot Block temperature is calibrated on a quarterly basis by an instrument service company. Certificates are kept on file.

11. Data Evaluation, Calculations and Reporting

Refer to the analytical method SOPs.

12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

Holding time exceedence and improper preservation are noted on the nonconformance report form.

Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

Review of standards, blanks and standard response for acceptable performance occurs for each batch of samples. Record any trends or unusual performance on a nonconformance action form.

If any QC parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/08-05. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP/08-12 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

SOP/08-05 MDL/LOD/LOQ Generation

SOP/08-12 IDC/DOC Generation

SOP/14-01 Waste Management and Disposal SOP

16. Attachments

None.

Inductively Coupled Plasma - Atomic Emission Spectrometry

Reference Method No.: **Method 6010C**

Reference: SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update IV, February 2007.

SM 2340B, Hardness by Calculation, Standard Methods for the Examination of Water and Wastewater, APHA-AWWA-WPCF, 18th Edition, 1992.

1. Scope and Application

Matrices: Digestate from all matrices.

Definitions: See Alpha Laboratories Quality Manual Appendix A

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) determines trace elements, including metals, in solution. The method is applicable to all of the elements listed in Table 1. All matrices, excluding filtered groundwater samples but including ground water, aqueous samples, TCLP and EP extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis. Groundwater samples that have been prefiltered and acidified will not need acid digestion. Samples which are not digested must either use an internal standard or be matrix matched with the standards. Refer to Metals Preparation SOPs for the appropriate digestion procedures.

Table 1 lists the elements for which this method is applicable. Detection limits, sensitivity, and the optimum and linear concentration ranges of the elements can vary with the wavelength, spectrometer, matrix and operating conditions. Table 1 lists the recommended analytical wavelengths for the elements in clean aqueous matrices. Table 3 lists the Reported Detection Limits. The reported detection limit data may be used to estimate instrument and method performance for other sample matrices. Elements other than those listed in Table 1 may be analyzed by this method if performance at the concentration levels of interest (see Section 9) is demonstrated.

Users of the method should state the data quality objectives prior to analysis and must document and have on file the required initial demonstration performance data described in the following sections prior to using the method for analysis.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is made by one of the following laboratory personnel before performing the modification: Area Supervisor, Metals Manager, Laboratory Services Manager, Laboratory Director, or Quality Assurance Officer.

Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences described in this method. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability, analyzing a proficiency test sample and completing the record of training.

After initial demonstration, ongoing demonstration is based on acceptable laboratory performance of at least a quarterly laboratory control sample or acceptable performance from an annual proficiency test sample. A major modification to this procedure requires demonstration of performance. The identification of major method modification requiring performance demonstration is directed by the QA Officer and Laboratory Director on a case-by-case basis.

2. Summary of Method

Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods. When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

This method describes multielemental determinations by ICP-AES using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. In one mode of analysis the position used must be as free as possible from spectral interference and must reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in Section 4.0 must also be recognized and appropriate corrections made; tests for their presence are described in Section 9.4.4. Alternatively, users may choose multivariate calibration methods. In this case, point selections for background correction are superfluous since whole spectral regions are processed.

This SOP includes the manual calculations for Total Hardness and Calcium Hardness, according to SM 2340B.

2.1 Method Modifications from Reference

None.

3. Reporting Limits

Refer to Table 3 for method Reporting Limits.

4. Interferences

4.1 Spectral

Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

4.1.1 Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may

indicate when alternate wavelengths are desirable because of severe spectral interference. These scans will also show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by measured emission on only one side. The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The locations used for routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak. For multivariate methods using whole spectral regions, background scans must be included in the correction algorithm. Off-line spectral interferences are handled by including spectra on interfering species in the algorithm.

4.1.2 To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the analyst must determine and document both the overlapping and nearby spectral interference effects from all method analytes and common elements and provide for their automatic correction on all analyses. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 100 mg/L single element solutions are sufficient; however, for analytes such as iron that may be found at high concentration, a more appropriate test would be to use a concentration near the upper analytical range limit.

4.1.3 Spectral overlaps may be avoided by using an alternate wavelength or can be compensated by equations that correct for interelement contributions. Instruments that use equations for interelement correction require the interfering elements be analyzed at the same time as the element of interest. When operative and uncorrected, interferences will produce false positive determinations and be reported as analyte concentrations. More extensive information on interferant effects at various wavelengths and resolutions is available in reference wavelength tables and books. Users may apply interelement correction equations determined on their instruments with tested concentration ranges to compensate (off line or on line) for the effects of interfering elements. For multivariate methods using whole spectral regions, spectral interferences are handled by including spectra of the interfering elements in the algorithm. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature are listed. These overlaps were observed with a single instrument having a working resolution of 0.035 nm.

4.1.4 When using interelement correction equations, the interference may be expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that As is to be determined (at 193.696 nm) in a sample containing approximately 10 mg/L of Al. 100 mg/L of Al would yield a false signal for As equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for As equivalent to approximately 0.13 mg/L. The user is cautioned that each instrument may exhibit somewhat different levels

of interference. The interference effects must be evaluated for each individual instrument since the intensities will vary.

Major known interferences are Fe, Al, Ca, Mg, V, Ni, Cu, and Cr. To minimize any of these interferences, every analyte is analyzed on each instrument at or near its linear range and corrected for these interferences. This is done on an annual basis, and data is kept on file.

4.1.5 Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating, the entrance and exit slit widths, and by the order of dispersion. Interelement corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear must be avoided when practical. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Users must not forget that some samples may contain uncommon elements that could contribute spectral interferences.

4.1.6 The interference effects must be evaluated for each individual instrument whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths, the analyst is required to determine and document for each wavelength the effect from referenced interferences as well as any other suspected interferences that may be specific to the instrument or matrix. The analyst is encouraged to utilize a computer routine for automatic correction on all analyses.

4.1.7 The primary wavelength for each analyte is based upon the instrument manufacturer's recommendations. An alternate wavelength is chosen if there is an indication of elevated background or overlap of another spectral wavelength. The wavelength for each analyte must be as free from interferences as possible.

4.1.8 If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution must fall within a specific concentration range around the calibration blank. The concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and divided by 10. If after the subtraction of the calibration blank the apparent analyte concentration falls outside of this range in either a positive or negative direction, a change in the correction factor of more than 10% should be suspected. The cause of the change must be determined and corrected and the correction factor updated. The interference check solutions must be analyzed more than once to confirm a change has occurred. Adequate rinse time between solutions and before analysis of the calibration blank will assist in the confirmation.

4.1.9 When interelement corrections are applied, their accuracy must be verified, daily, by analyzing spectral interference check solutions. If the correction factor or multivariate correction matrices tested on a daily basis (by running a check solution on each analytical run) are found to be within 20% criteria for 5 consecutive days, analysis may be extended to a weekly basis. Also, if the nature of the samples analyzed is such that they do not contain concentrations of the interfering elements greater than the reported detection limit, daily verification is not required. All interelement spectral correction factors or multivariate correction matrices are verified and updated on an annual basis

or when an instrumentation change, such as in the torch, nebulizer, injector, or plasma conditions occurs. The standard solution must be inspected to ensure that there is no contamination that may be perceived as a spectral interference.

4.1.10 When interelement corrections are not used, verification of absence of interferences is required.

4.1.10.1 One method is to use a computer software routine for comparing the determinative data to limits, files for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration, (i.e., greater than) the analyte instrument detection limit, or false negative analyte concentration, (i.e., less than the lower control limit of the calibration blank defined for a 99% confidence interval).

4.1.10.2 Another method is to analyze an Interference Check Solution(s) which contains similar concentrations of the major components of the samples (>10 mg/L) on a continuing basis to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the check solution confirms an operative interference that is >20% of the analyte concentration, the analyte must be determined using (1) analytical and background correction wavelengths (or spectral regions) free of the interference, (2) by an alternative wavelength, or (3) by another documented test procedure.

4.2 Physical

Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, using a peristaltic pump, use of an internal standard or by using a high solids nebulizer. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, affecting aerosol flow rate and causing instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, using a high solids nebulizer or diluting the sample. Also, it has been reported that better control of the argon flow rate, especially to the nebulizer, improves instrument performance: this may be accomplished with the use of mass flow controllers. The test described in Section 10.3.4.1 will help determine if a physical interference is present.

4.3 Chemical

Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique, but if observed, can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

4.4 Memory

Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the build up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized

by flushing the system with a rinse blank between samples. The possibility of memory interferences must be recognized within an analytical run and suitable rinse times must be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements at a concentration ten times the usual amount or at the top of the linear dynamic range. The aspiration time for this sample must be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of two of the method detection limit must be noted. Until the required rinse time is established, this method suggests a rinse period of at least 60 seconds between samples and standards. If a memory interference is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Alternate rinse times may be established by the analyst based upon their DQOs.

4.5 Other Interferences

4.5.1 Users are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests. If the instrument does not display negative values, fortify the interference check solution with the elements of interest at 0.5 to 1 mg/L and measure the added standard concentration accordingly. Concentrations must be within 20% of the true spiked concentration or dilution of the samples will be necessary. In the absence of measurable analyte, overcorrection could go undetected if a negative value is reported as zero.

5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound must be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

Samples are collected in plastic bottles.

6.2 Sample Preservation

Samples for Total Metals are preserved with 1:1 Nitric acid to a pH of <2.

If samples are for Soluble Metals, they must not be preserved prior to filtration. They are preserved with 1:1 Nitric acid to a pH of <2 post-filter.

6.3 Sample Shipping

No special shipping requirements.

6.4 Sample Handling

Samples to be analyzed for soluble metals, that have not been filtered, must be filtered and preserved within 24 hours of sample collection.

Preserved samples have a hold time of 6 months, and are stored under refrigeration at 4°C.

7. Equipment and Supplies

7.1 Inductively coupled argon plasma emission spectrometer:

- **Thermo Jarrell Ash 61E Trace Analyzer (Trace3)**
- **ThermoFisher Scientific ICAP Duo 6500 (Trace4)**

7.1.1 Computer-controlled emission spectrometer with background correction.

7.1.2 Radio-frequency generator compliant with FCC regulations.

7.1.3 Optional mass flow controller for argon nebulizer gas supply.

7.1.4 Optional peristaltic pump.

7.1.5 Optional Autosampler.

7.1.6 Argon gas supply - high purity.

7.2 Volumetric flasks of suitable precision and accuracy.

7.3 Volumetric pipets of suitable precision and accuracy.

8. Standards and Reagents

Reagent semiconductor and/or trace grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question, analyze for contamination. If the concentration of the contamination is less than the MDL then the reagent is acceptable.

8.1 Hydrochloric acid (conc), HCl. Stored at room temperature in acid resistant cabinet. Expiration date as defined by vendor.

8.2 Hydrochloric acid (1:1), HCl. Add 500 mL concentrated HCl to 400 mL DI water and dilute to 1 liter in an appropriately sized beaker. Stored at room temperature in polypropylene bottle, expiration one month from date of preparation.

8.3 Nitric acid (conc), HNO_3. Stored at room temperature in acid resistant cabinet. Expiration date as defined by vendor.

8.4 Nitric acid (1:1), HNO_3. Add 500 mL concentrated HNO_3 to 400 mL DI water and dilute to 1 liter in an appropriately sized beaker. Stored at room temperature in polypropylene bottle, expiration one month from date of preparation.

8.5 Reagent Water. All references to water in the method refer to reagent water unless otherwise specified. Reagent water will be interference free. Refer to Chapter One for a definition of reagent water.

8.6 Standard stock solutions may be purchased or prepared from ultra- high purity grade chemicals or metals (99.99% pure or greater). All stock standards are ordered through ISO and American Association for Lab Accreditation vendors. All standards are in aqueous solutions and are at concentrations of 1000ppm and 10,000ppm.

8.7 Mixed calibration standard solutions

Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. Add the appropriate types and volumes of acids so that the standards are matrix matched with the sample digestates. Care must be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards must be prepared, as needed, with the realization that concentration can change on aging.

NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of water and warm the flask until the solution clears. Cool and dilute to 100 mL with water. For this acid combination, the silver concentration must be limited to 2 mg/L. Silver under these conditions is stable in a tap-water matrix for 30 days. Higher concentrations of silver require additional HCl.

8.8 Blanks

Two types of blanks are required for the analysis for samples prepared by any method other than 3040. The calibration blank is used in establishing the analytical curve, and the method blank is used to identify possible contamination resulting from varying amounts of the acids used in the sample processing.

8.8.1 The calibration blank is prepared by acidifying reagent water to the same concentrations of the acids found in the standards. Prepare a sufficient quantity to flush the system between standards and samples. The calibration blank will also be used for all initial (ICB) and continuing calibration blank (CCB) determinations (see Sections 10.2 and 10.4). Refer to Section 10.4.1.2 for acceptance criteria and/or corrective actions.

8.8.2 The method blank must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis. Refer to Section 9.1 for acceptance criteria and/or corrective actions.

8.9 The Initial Calibration Verification Standard (ICV) and the Continuing Calibration Verification Standard (CCV)

These Standards are prepared by the analyst by combining compatible elements from a standard source different than that of the calibration standard and within the mid-point of the calibration curve.

8.10 Interference Check Solution

These solutions are prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

8.11 CRI

The CRI is an ICP standard that is analyzed at a concentration of 2 - 5 times each element's RDL. The CRI must be recovered within 70-130% of its true value. If the CRI does not meet these criteria, it is remade and reanalyzed. If the CRI fails a second time, the analysis is terminated, the problem determined and corrected. The instrument is then recalibrated.

CRI solutions are made for each type of instrument.

8.11.1 CRI Stock Standard Solution, for the TJA Trace instruments

To a 500mL volumetric flask, add 200mL DI water and 50mL of 1:1 HNO_3. Add the following volumes of each certified 1000ppm stock standard:

Pb	0.9 mL	Ni	1.6 mL
Se	0.4 mL	Ag	0.4 mL
Sb	2.0 mL	Tl	0.4 mL
As	0.4 mL	V	2.0 mL
Ba	0.8 mL	Zn	0.8 mL
Be	0.2 mL	Al	8.0 mL
Cd	0.2 mL	Ca	8.0 mL
Co	2.0 mL	Mg	8.0 mL
Cr	0.4 mL	B	2.0 mL
Cu	1.0 mL	Sr	0.4 mL
Fe	4.0 mL	Ti	0.4 mL
Mn	0.6 mL	Sn	0.4 mL
Mo	2.0 mL		

And the following volumes of each certified 10000ppm stock standard:

K	10.0 mL
Na	10.0 mL
Si	2.0 mL

Bring to volume of 500mL with DI water. This solution expires 12 months after the date of preparation.

8.11.1.1 CRI Working Standard Solution

To a 1L volumetric flask, add 25mL of CRI Stock Standard Solution (Section 8.11.1). Bring to volume with DI water. This solution will contain elements in the following concentrations:

Pb	0.045 ppm	Ag	0.02 ppm
Se	0.02 ppm	Tl	0.02 ppm
Sb	0.10 ppm	V	0.10 ppm
As	0.02 ppm	Zn	0.04 ppm
Ba	0.04 ppm	Al	0.40 ppm
Be	0.01 ppm	Ca	0.40 ppm
Cd	0.01 ppm	Mg	0.40 ppm
Co	0.10 ppm	B	0.10 ppm
Cr	0.02 ppm	Sr	0.02 ppm
Cu	0.05 ppm	Ti	0.02 ppm
Fe	0.20 ppm	Sn	0.02 ppm
Mn	0.03 ppm	K	5.0 ppm
Mo	0.10 ppm	Na	5.0 ppm
Ni	0.08 ppm	Si	1.0 ppm

8.12 Reporting Limit (RL) Standard

The RL standard consists of a series of standards that are analyzed after the initial calibration verification. The following standards are analyzed. This standard does not have to be a second source. Typically the calibration standard is serially diluted. The acceptance criteria is 70-130%.

0.0025 mg/L Cd,Be

0.005 mg/L As,Ag,Tl

0.010 mg/L Pb,Se,Ba,Co,Cr,Cu,Mn,,Ni,V,Sr,Ti,B, Mo

0.050 mg/L Al,Sb,Fe,Zn, Ca, Mg Sn,Si

2 mg/L Na(added to 0.050 mg/L standard)

2.5 mg/L K(added to 0.050 mg/L standard)

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blank(s)

Employ a minimum of one method blank per sample batch to determine if contamination or any memory effects are occurring. A method blank is a volume of reagent water carried through the same preparation process as a sample.

The method blank results must be less than the reported detection limit (RDL) for all analytes of concern. If the results of the method blank exceed the RDL for any analyte, perform re-analysis of a new aliquot of the method blank.

If the results continue to exceed the RDL, proceed as follows:

If all of the samples for the analyte are non-detected, and the method blank is at or above the RDL, no action is required.

If one or more associated samples for that analyte have positive results at or above the RDL, those samples must be considered to be out of control, and are re-digested and reanalyzed.

9.2 Laboratory Control Sample (LCS)

Analyze one LCSW/LCSS per sample batch. A LCS/LCSW sample is a spiked volume of reagent water that is brought through the entire preparation and analytical process. The LCSW must have a % Recovery of ± 20% within the actual value or within the documented historical limits for each matrix.

If the LCSW % Recovery is outside the acceptable limits as stated in Table 2, or outside any historical documentation, the LCS is rerun once. If upon reanalysis the LCS is still out of control, the failed analytes are re-prepped and re-analyzed. Otherwise, a nonconformance report form is raised to document the exact problem and this form is then authorized by the QA/QC Director and/or the Laboratory Manager(s).

9.3 Initial Calibration Verification (ICV)

For all analytes and determinations, the laboratory must analyze an ICV (Section 8.9), and a calibration blank (ICB, Section 8.8.1), immediately following daily calibration. The results of the ICV are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and recalibrate the instrument.

9.4 Continuing Calibration Verification (CCV)

A calibration blank (CCB, Section 8.8.1) and a calibration verification standard (CCV, Section 8.9) must be analyzed after every tenth sample and at the end of the sample run. Analysis of the calibration verification (CCV) must verify that the instrument is within 10% of the calibration with the relative standard deviation < 5% from replicate (minimum of two) integrations.

Immediate corrective action for a failing CCV/CCB includes reanalyzing the failing standard. If the standard passes the second time then the analysis may be continued. The raw data is noted. If the standard fails again, the problem must be found and corrected. The CCV/CCB standard is remade and reanalyzed. If the standard passes, then the data that had failed up to

the previous passing standard is reanalyzed. The raw data is noted and all data associated with the failing standard must have one line drawn through the data, indicating its unusability.

If the standard fails after instrument maintenance, the instrument is recalibrated. A new ICV/ICB is performed, and all previous data that had failed up to the previous passing CCV/CCB is reanalyzed.

9.5 Matrix Spike

Analyze matrix spike samples at a frequency of one per matrix batch. A matrix spike sample is a sample brought through the entire sample preparation and analytical process.

9.5.1 The percent recovery is to be calculated as follows:

$$\% \text{ Recovery} = \frac{MS - S}{C} \times 100$$

where:

MS = Matrix Spike value
S = Sample value.
C = Concentration of the Spiking solution.

9.5.2 If the Matrix Spike falls outside of the limits as stated in Table 2, or outside any historical documentation, the failed analytes are either re-prepped and re-analyzed, or a post analytical spike is performed. The acceptable % Recovery of the post analytical spike is 80-120%. A nonconformance report form is raised and is attached to the data package. This form is then authorized by the QA/QC Director and/or the Laboratory Manager.

9.6 Laboratory Duplicate

A duplicate sample is analyzed once per matrix batch. This sample is brought through the entire sample preparation and analytical process.

9.6.1 The relative percent difference between duplicate determinations is to be calculated as follows:

$$RPD = \frac{|D_1 - D_2|}{(|D_1 + D_2|)/2} \times 100$$

where:

RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (replicate).

9.6.2 If the Duplicate falls outside of the limits as stated in Table 2, or outside any historical documentation, the failed analytes are re-prepped and re-analyzed. A nonconformance report form is raised and is attached to the data package. This form is then authorized by the QA/QC Director and/or the Laboratory Manager.

If re-digestion is not available or applicable, a nonconformance report form is raised and is attached to the data package. This form is then authorized by the QA/QC Director and/or the Laboratory Manager.

9.7 Method-specific Quality Control Samples

9.7.1 Interference Check Standards

A check solution is analyzed twice per each calibration curve. One solution has only elevated concentrations of Fe, Al, Ca, Mg to ensure no interferences occur. The other check solution is the same solution spiked with a known amount of each analyte. These solutions are analyzed at the beginning and at the end of each analytical run.

If the Interference Check Solution falls outside the acceptable limits of 80 – 120% of the true value, the failed analytes are re-analyzed. Otherwise, a Nonconformance Report form is raised to document the exact problem and this form is then forwarded to the Department Supervisor and/or the QA Department.

9.7.2 Reporting Limit (RL) Standard

The RL standard is actually a series of standards that are analyzed after the CRI. The lowest of the RL standards may be used to evaluate the sensitivity of reportable elements under method 6010. This may be a low level client-specific analysis, or it may be the standard reporting limits for an aqueous sample or a soil/solid material. The standards must have a % Recovery of 70-130%. If an element fails the acceptance criteria, the RL standard may be re-analyzed. If the element failure continues, then either re-calibrate the instrument or analyze the sample on another instrument.

9.8 Method Sequence

- Calibration of instrument
- Initial Calibration Verification Standard
- Initial Calibration Blank
- RL Limit Check Standards
- Interference Check Solution A
- Interference Check Solution AB
- CRI
- Continuing Calibration Verification Standard
- Continuing Calibration Blank
- samples
- Continuing Calibration Verification Standard
- Continuing Calibration Blank

10. Procedure

10.1 Equipment Set-up

10.1.1 Sample Preparation

Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Groundwater samples which have been prefiltered and acidified will not need acid digestion. Samples which are not digested must either use an internal standard or be matrix matched with the standards. Solubilization and digestion procedures are presented in Sample Preparation Methods (Chapter Three, Inorganic Analytes).

10.1.2 Instrument Set-Up

Set up the instrument with proper operating parameters established as detailed below. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 minutes of operation prior to calibration).

Startup Procedures

For the TJA Trace 61E ICP(Trace3)

- Turn on the main power switch
- Turn on the power to the chillers
- Push the re-set switch on the front of the spectrometers
- Turn on the computer
- Click on the “Thermo-Spec” software icon
- Click on “Set-Up”
- Choose “Plasma Control Panel”
- Click on F1. This is the automated start-up sequence.
- Escape back to the Main Menu and move the cursor over to “Operations” and type in (ALL02) in the method box. This will automatically set up the instrument with the correct method Parameters.
- Wait 30 minutes for the instrument to come to equilibrium
- Enter F5 then F3 (Profile)
- Profile instrument with 1.0 mg/L As standard. When acceptable profile has been performed, enter profile intensity in instrument logbook, and press F9. This will bring you back to the Main Menu.
- Select “ Auto Sampler Set-up”
- Input batch #s and sample ID’s
- Select “Analyze

For the iCAP Duo 6500(Trace4)

- Turn on the main power switch
- Turn on power to the chiller

- Click on ThermoSpec Icon; enter analyst initials in login screen
- Click on Flame icon to start instrument
- Allow to warm up for 30 minutes
- In the iTeva Analyst screen, select the Instrument menu; click on the Optimize Spectrometer option
- Enter analytical workgroup number (obtained from LIMS) globally under the Instrument menu by selecting Tools, then Options, then Analyst.
- Click on the Sequence tab and enter the sequence by selecting New Autosampler Table, Add Sequence, Add # of spaces.
- Enter the sample locations and IDs
- Press Run Auto-Session button (►)in menu bar.

10.1.2.1 Specific wavelengths are listed in Table 1. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality to the program and data user.

Operating conditions for axial plasma will vary from 1100 – 1500 watts forward power, 15-19 Liters/min argon coolant flow, 0.5 – 0.7 L/min argon nebulizer flow, 140 – 200 rpm pump rate and a 1 minute preflush time and 10 second measurement time is recommended for all simultaneous instruments.

10.1.2.1.1 The essential peak quality control acceptance criteria listed below must be met, otherwise the problem must be found and corrected:

Peak position in terms of wavelength: <1

Peak width at half-height: 10 +/- 10%

Peak intensity : < ½ the intensity since the instrument was last serviced

10.1.2.2 The plasma operating conditions need to be optimized prior to use of the instrument. This routine is not required on a daily basis, but only when first setting up a new instrument or following a change in operating conditions. The following procedure is recommended or follow manufacturer's recommendations. The purpose of plasma optimization is to provide a maximum signal to background ratio for some of the least sensitive elements in the analytical array. The use of a mass flow controller to regulate the nebulizer gas flow or source optimization software greatly facilitates the procedure.

10.1.2.2.1 The TJA ICP's use a Meinhard Nebulizer. The nebulizer flow for each instrument is listed below:

- TJA Trace (Purge): 0.65 L/min

10.1.2.2.2 Profiles on the TJA Trace ICP's use a 1.0mg/L solution of Arsenic. Peak position on the TJA instruments have a tolerance of 0.1. If the tolerance is

not met, the computer program automatically corrects and re-profiles. Profile intensity is recorded in the instrument notebook. Dramatic loss of intensity must be a signal that there is a problem with the instrument. Usually this entails checking and cleaning the nebulizer, and making sure that the nebulizer flows are correct.

10.1.2.2.3 The instrument operating condition finally selected as being optimum must provide the lowest reliable instrument detection limits and method detection limits.

10.1.2.2.4 If either the instrument operating conditions, such as incident power or nebulizer gas flow rate are changed, or a new torch injector tube with a different orifice internal diameter is installed, the plasma and viewing height must be reoptimized.

10.1.2.2.5 After completing the initial optimization of operating conditions, but before analyzing samples, the laboratory must establish and initially verify an interelement spectral interference correction routine to be used during sample analysis. A general description concerning spectral interference and the analytical requirements for background correction in particular are discussed in the section on interferences. Criteria for determining an interelement spectral interference is an apparent positive or negative concentration for the analyte that falls within ± the RDL. The upper control limit is the analyte instrument detection limit. Once established, the entire routine is periodically verified annually. In between that time, IEC's are done on a need be basis per analyte. Only a portion of the correction routine must be verified more frequently or on a daily basis. Initial and periodic verification of the routine must be kept on file. Special cases where continual verification is required are described elsewhere.

10.1.2.3 Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on each particular instrument. All measurements must be within the instrument linear range where the correction equations are valid.

10.1.2.3.1 Method detection limits must be established for all wavelengths utilized for each type of matrix commonly analyzed. The matrix used for the MDL calculation must contain analytes of known concentrations within 3-5 times the anticipated detection limit.

10.1.2.3.2 Determination of limits using reagent water MDLs represent a best case situation and do not represent possible matrix effects of real world samples.

10.1.2.3.3 If additional confirmation is desired, reanalyze the seven replicate aliquots on two more non-consecutive days and again calculate the method detection limit values for each day. An average of the three values for each analyte may provide for a more appropriate estimate.

10.1.2.3.4 The upper limit of the linear dynamic range must be established for each wavelength utilized by determining the signal responses from a minimum for three, preferably five, different concentration standards across the

range. One of these must be near the upper limit of the range. The ranges which may be used for the analysis of samples must be judged by the analyst from the resulting data. The data, calculations and rationale for the choice of range made must be documented and kept on file. The upper range limit must be an observed signal no more than 10% below the level extrapolated from lower standards. Determined analyte concentrations that are above the upper range limit must be diluted and reanalyzed. The analyst must also be aware that if an interelement correction from an analyte above the linear range exists, a second analyte where the interelement correction has been applied may be inaccurately reported. New dynamic ranges must be determined whenever there is a significant change in instrument response. The linear dynamic range is checked on an annual basis. For those analytes that are known interferences, and are present at above the linear range, the analyst must ensure that the interelement correction has not been inaccurately applied.

NOTE: Many of the alkali and alkaline earth metals have non-linear response curves due to ionization and self-absorption effects. These curves may be used if the instrument allows; however the effective range must be checked and the second order curve fit must have a correlation coefficient of 0.995 or better. Third order fits are not acceptable. These non-linear response curves must be revalidated and recalculated every six months. These curves are much more sensitive to changes in operating conditions than the linear lines and must be checked whenever there have been moderate equipment changes.

10.1.2.4 The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.

10.2 Initial Calibration

Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Section 8.7. Flush the system with the calibration blank (Section 8.8.1) between each standard or as the manufacturer recommends. (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.) The calibration curve consists of a calibration blank and a high level standard. Calibration curve verification is accomplished through the analysis of the ICV and CRI standards.

10.3 Equipment Operation and Sample Processing

10.3.1 For all analytes and determinations, the laboratory must analyze an ICV (Section 8.9), and a calibration blank (ICB, Section 8.8.1), immediately following daily calibration.

A calibration blank (CCB, Section 8.8.1) and a calibration verification standard (CCV, Section 8.9) must be analyzed after every tenth sample and at the end of the sample run. Analysis of the calibration verification (CCV) must verify that the instrument is within 10% of the calibration with the relative standard deviation < 5% from replicate (minimum of two) integrations.

If the calibration cannot be verified within the specified limits, the sample analysis must be discontinued, the cause determined and the instrument recalibrated. All samples

following the last acceptable ICB, ICV, CRI, CCV or CCB must be reanalyzed. The analysis data for the calibration blank, check standard, and ICV or CCV must be kept on file with the sample analysis data.

10.3.2 Rinse the system with the calibration blank solution (Section 8.8.1) before the analysis of each sample. The rinse time will be one minute. Each laboratory may establish a reduction in this rinse time through a suitable demonstration.

10.3.3 Dilute and reanalyze samples that exceed the linear calibration range or use an alternate, less sensitive line for which quality control data is already established.

10.3.4 A series of tests is performed prior to reporting concentration data for analyte elements. These tests, as outlined in Sections 10.3.4.1 and 10.3.4.2, will ensure that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

10.3.4.1 Dilution Test: If the analyte concentration is sufficiently high (minimally, a factor of 50 above the detection limit before dilution), an analysis of a 1:5 dilution must agree within ± 10% of the original determination. If not, a chemical or physical interference effect must be suspected.

10.3.4.2 Post Digestion Spike Addition: An analyte spike added to a portion of a prepared sample, or its dilution, must be recovered to within 80% to 120% of the known value. The spike addition must produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect must be suspected.

10.3.5 **CAUTION:** If spectral overlap is suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

10.4 Continuing Calibration

10.4.1 Verify calibration with the Continuing Calibration Verification (CCV) Standard (Section 8.9) immediately following daily calibration, after every ten samples, and at the end of an analytical run. Check calibration with an ICV following the initial calibration (Section 8.9). At the laboratory's discretion, an ICV may be used in lieu of the continuing calibration verifications. If used in this manner, the ICV must be at a concentration near the mid-point of the calibration curve. Use a calibration blank (Section 8.8.1) immediately following daily calibration, after every 10 samples and at the end of the analytical run.

A CRI (Section 8.11) must be analyzed after the ICSAB. The concentration of the CRI is 2 – 5 times that of each element's RDL. The linearity of the instrument is determined on an annual basis by linear ranges.

10.4.1.1 The results of the ICV are to agree within 10% of the expected value, and CCVs are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and recalibrate the instrument.

10.4.1.2 The results of the calibration blank are to agree within three times the IDL. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples. If the blank is less than 1/10 the concentration of the action level of interest, and no sample is within ten percent of the action limit, analyses need not be rerun and recalibration need not be performed before continuation of the run.

10.4.1.3 The results of the CRI must be within 30% of the true value. If they are not, correct the problem and recalibrate the instrument. (Any element may be analyzed on a different ICP that has passed the CRI.)

10.4.2 Verify the interelement and background correction factors at the beginning of each analytical run. Do this by analyzing the interference check sample (Section 8.10). Results must be within 80 – 120% of the true value.

10.4.3 When low-level sensitivity is required, a check standard at the requested limit of quantitation is analyzed to confirm the reported detection limit (RDL). This is performed on a project-by-project basis.

10.5 Preventive Maintenance

Whenever instrument maintenance is performed, it is noted in the instrument's Maintenance Logbook.

10.5.1 Daily

Change the nebulizer pump tubing from the Autosampler to the Nebulizer.

10.5.2 Monthly or as needed

Remove the torch, nebulizer and spray chamber. Clean each with 10% Nitric Acid and 5% Hydrochloric Acid. Soak the torch and spray chamber for one hour, then rinse well with DI water. Soak the nebulizer in an ultrasonic bath for 30 minutes, then rinse with DI water.

10.5.3 Every 6 months

Preventive Maintenance is performed by the Vendor as follows:

- clean the lenses
- check/replace the power tube
- check the cooling system
- refill the chiller with distilled water
- clean the instrument to regain intensity
- clean/replace air filters on the rear of the instruments.

11. Data Evaluation, Calculations and Reporting

11.1 If dilutions were performed, the appropriate factors must be applied to sample values. All results must be reported with up to three significant figures.

11.2 Soil samples

Soil samples are calculated as follows:

$$\mathbf{A} = \frac{\text{Sample weight (grams)}}{\text{Final Volume (mL)}}$$

$$\mathbf{B}\ (\text{concentration in mg/Kg}) = \frac{\text{Concentration of analyte (mg/L)}}{\mathbf{A}}$$

11.2.1 Dry weight correction

The LIMS calculates the dry weight correction, however it is calculated as follows:

$$\text{Final concentration in mg/Kg dry weight} = \frac{\mathbf{B}}{\text{\% Solids}}$$

11.3 Liquid samples

Liquid samples are calculated as follows:

$$\text{Dilution Factor} = \frac{\text{Final Volume (mL)}}{\text{Sample Volume (mL)}}$$

$$\text{Final concentration in mg/L} = \text{Concentration of analyte (mg/L)} \times \text{Dilution Factor}$$

11.4 Calculations for Hardness

The method for determining hardness is to compute it from the results of separate determinations of Calcium and Magnesium on aqueous samples.

11.4.1 Total Hardness

Total Hardness, mg equivalent $CaCO_3$/L = [2.497 (Ca, mg/L)] + [4.118 (Mg, mg/L)]

11.4.2 Calcium Hardness

Calcium Hardness, mg equivalent $CaCO_3$/L = [2.497 (Ca, mg/L)]

12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

Also refer to Section 9 for Quality Control and acceptance criteria.

If the ICSA or ICSAB is outside of the 80 – 120% recovery window, then the standard is reanalyzed. If the standard failure continues, the IECs for the element/elements in question are reviewed and recalculated if necessary.

Immediate corrective action for a failing CCV/CCB includes reanalyzing the failing standard. If the standard passes the second time then the analysis may be continued. The raw data is noted. If the standard fails again, the problem must be found and corrected. The CCV/CCB standard is remade and reanalyzed. If the standard passes, then the data that had failed up to the previous passing standard is reanalyzed. The raw data is noted and all data associated with the failing standard must have one line drawn through the data, indicating its unusability.

If the standard fails after instrument maintenance, the instrument is recalibrated. A new ICV/ICB is performed, and all previous data that had failed up to the previous passing CCV/CCB is reanalyzed.

The procedure outline above is also conducted for a failing LCS or Method Blank.

If the Matrix Spike does not meet acceptance criteria, an analytical spike is performed. The recovery must be within 80-120% of the true value for aqueous samples and within 80-120% of the true value for soil samples. If this criteria is met, then the Matrix Spike data is reported, with the post spike narrated on the final report. If the post spike fails the acceptance criteria, the Department Manager is notified to determine what type of matrix interferent is present, and whether a serial dilution must be performed.

If sample Duplicates are outside of the acceptance criteria, the analyst examines the sample for homogeneity. If the sample is not homogenous, this is narrated on the final report. Clean, homogenous samples are redistilled and reanalyzed within holding time.

Sample nonconformance regarding a Matrix Spike recovery or a duplicate %RSD is narrated on the final report along with the corrective action(s) taken.

If the ICSA or the ICSAB are outside of the 80-120% window then the standard in question must be re-analyzed. If the standard failure continues, then check the IECs for the element(s) in question and re-calculate and recalibrate the instrument. The ICSA and the ICSAB are then re-analyzed. If the standard failure repeats, then a fresh standard is prepared and re-analyzed. If failure continues notify the Department Supervisor.

The RL standards must have a % Recovery of 70-130%. If an element fails the acceptance criteria, the RL standard may be re-analyzed if the element must be included in the analytical event. If the element failure continues, then either re-calibrate the instrument or analyze the sample on another instrument.

If the CRI (low level check standard), is recovered outside of the 70-130% window, the standard may be re-analyzed if the element must be included in the analytical event. If the element failure continues, then either re-calibrate the instrument or analyze the sample on another instrument.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/08-05. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP/08-12 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

SOP/08-05 MDL/LOD/LOQ Generation

SOP/08-12 IDC/DOC Generation

SOP/14-01 Waste Management and Disposal SOP

16. Attachments

TABLE 1: Element Wavelengths

TABLE 2: Precision and Accuracy Acceptance Criteria

TABLE 3: Reporting Limits

TABLE 1
ELEMENT WAVELENGTHS

Element	Trace 3 wavelength (nm)	Trace 4 wavelength (nm)
Pb	220.3	220.3
Se	196.0	196.0
Sb	206.8	206.8
As	189.0	189.0
Ba	493.4	455.4
Be	313.0	313.0
Cd	226.5	214.4
Co	228.6	228.6
Cu	324.7	324.7
Cr	267.7	267.7
Fe	271.4	259.9
Mn	257.6	257.6
Mo	202.0	202.0
Ni	231.6	231.6
Ag	328.0	328.0
Tl	190.8	190.8
V	292.4	292.4
Zn	213.8	206.2
Al	308.2	396.1
Ca	317.9	315.8
Mg	279.0	279.0
B	249.6	208.9
Si	288.1	212.9
Sn	189.9	189.9
Sr	421.5	421.5
Ti	337.2	334.9
Bi	223.0	223.0
Na	330.2	589.5
K	766.4	766.4

TABLE 2
PRECISION AND ACCURACY ACCEPTANCE CRITERIA

	Aqueous % Recovery LCS		Aqueous % Recovery MS		TCLP and Soil % Recovery LCS / MS		Duplicate	
Element	**Lower Control Limit**	**Upper Control Limit**	**Lower Control Limit**	**Upper Control Limit**	**Lower Control Limit**	**Upper Control Limit**	**Aqueous %RPD**	**Soil %RPD**
Aluminum	80	120	80	120	80	120	20	20
Antimony	80	120	80	120	80	120	20	20
Arsenic	80	120	80	120	80	120	20	20
Barium	80	120	80	120	80	120	20	20
Beryllium	80	120	80	120	80	120	20	20
Boron	80	120	80	120	80	120	20	20
Cadmium	80	120	80	120	80	120	20	20
Calcium	80	120	80	120	80	120	20	20
Chromium	80	120	80	120	80	120	20	20
Cobalt	80	120	80	120	80	120	20	20
Copper	80	120	80	120	80	120	20	20
Iron	80	120	80	120	80	120	20	20
Lead	80	120	80	120	80	120	20	20
Lithium	80	120	80	120	80	120	20	20
Magnesium	80	120	80	120	80	120	20	20
Manganese	80	120	80	120	80	120	20	20
Molybdenum	80	120	80	120	80	120	20	20
Nickel	80	120	80	120	80	120	20	20
Phosphorus	80	120	80	120	80	120	20	20
Potassium	80	120	80	120	80	120	20	20
Selenium	80	120	80	120	80	120	20	20
Silica (SiO_2)	80	120	80	120	80	120	20	20
Silver	80	120	80	120	80	120	20	20
Sodium	80	120	80	120	80	120	20	20
Strontium	80	120	80	120	80	120	20	20
Thallium	80	120	80	120	80	120	20	20
Tin	80	120	80	120	80	120	20	20
Titanium	80	120	80	120	80	120	20	20
Vanadium	80	120	80	120	80	120	20	20
Zinc	80	120	80	120	80	120	20	20

TABLE 3
REPORTING LIMITS

Element	Aqueous (mg/L)	Soil (mg/Kg)
ALUMINUM	0.10	4.0
ANTIMONY	0.05	2.0
ARSENIC	0.005	0.40
BARIUM	0.01	0.40
BERYLLIUM	0.005	0.20
BORON	0.03	1.2
CADMIUM	0.005	0.40
CALCIUM	0.10	4.0
CHROMIUM	0.01	0.40
COBALT	0.02	0.80
COPPER	0.01	0.40
IRON	0.05	2.0
LEAD	0.01	2.0
MAGNESIUM	0.10	4.0
MANGANESE	0.01	0.40
MOLYBDENUM	0.05	2.0
NICKEL	0.025	1.0
POTASSIUM	2.5	100
SELENIUM	0.01	0.80
SILICON	0.50	20
SILVER	0.007	0.40
SODIUM	2.0	80
STRONTIUM	0.01	2.0
THALLIUM	0.02	0.80
TIN	0.05	4.0
TITANIUM	0.01	0.40
VANADIUM	0.01	0.40
ZINC	0.05	2.0

Inductively Coupled Plasma - Mass Spectrometry

Reference Methods: **Method 6020,** Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update II, September 1994.

Method 6020A, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Draft Update IVA, May 1998.

1. Scope and Application

Matrices: Groundwaters, aqueous samples, industrial waste, soils, sludges, sediments, and other solid wastes.

Definitions: See Alpha Laboratories Quality Manual Appendix A

Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of sub µg/L concentrations of a large number of elements in water samples, waste extracts or digestates.

ICP-MS has been applied to the determination of over 60 elements in various matrices. Elements for which EPA has determined the acceptability of Method 6020 in a mulit-laboratory study on solid wastes are listed below and in Table 1.

If method 6020 is used to determine any analyte not listed in Table 1 below, it is the responsibility of the analyst to demonstrate the accuracy and precision of the method in the waste to be analyzed. The analyst is always required to monitor potential sources of interferences and take appropriate action to ensure data of known quality.

Use of this method is restricted to spectroscopists who are knowledgeable in the recognition and in the correction of spectral, chemical, and physical interferences in ICP-MS.

An appropriate internal standard is required for each analyte determined by ICP-MS. Recommended Internal standards are ^{6}Li, ^{45}Sc,^{89}Y,^{103}Rh,^{115}In,^{159}Tb,^{165}Ho, and ^{209}Bi. The Lithium internal standard must have an enriched abundance of 6Li, so that interference from Lithium native to the sample is minimized. Other elements may need to be used as internal standards when samples contain significant amounts of the recommended internal standards. The internal standard used in this method is as follows: ^{6}Li,^{45}Sc, ^{74}Ge,^{115}In, ^{209}Bi

TABLE 1

Parameter	CAS
Aluminum	7429-90-5
Antimony	7440-36-0
Arsenic	7440-38-2
Barium	7440-39-3
Beryllium	7440-41-7
Cadmium	7440-43-9
Calcium	7440-70-2
Chromium	7440-47-3
Cobalt	7440-48-4
Copper	7440-50-8
Iron	7439-89-6
Lead	7439-92-1

Parameter	CAS
Magnesium	7439-95-4
Manganese	7439-96-5
Mercury	7439-97-6
Molybdenum	7439-98-7
Nickel	7440-02-0
Potassium	7440-09-7
Selenium	7782-49-2
Silver	7440-22-4
Sodium	7440-23-5
Thallium	7440-28-0
Vanadium	7440-62-2
Zinc	7440-66-6

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one of the following laboratory personnel before performing the modification: Area Supervisor, Metals Manager, Laboratory Services Manager, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of analysts experienced in the operation of the ICP-MS and in the interpretation of ICP-MS data. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability, analyzing a proficiency test sample and completing the record of training.

After initial demonstration, ongoing demonstration is based on acceptable laboratory performance of at least a quarterly laboratory control sample or acceptable performance from an annual proficiency test sample. A major modification to this procedure requires demonstration of performance. The identification of major method modification requiring performance demonstration is directed by the QA Officer and/or Laboratory Director on a case-by-case basis.

2. Summary of Method

When dissolved constituents are required, samples must be filtered and acid-preserved prior to analysis. No digestion is required prior to analysis for dissolved elements in water samples. Acid digestion prior to filtration and analysis is required for groundwater, aqueous samples, industrial waste, soils, sludge's, sediments, and other solid wastes for which total (acid-leachable) elements are required.

Method 6020 describes the multi-elemental determination of analytes by ICP-MS. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of an interface, into the mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratio and quantified with a channel electron multiplier. Interferences must be assessed and valid corrections applied or the data flagged to indicate a problem. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

2.1 Method Modifications from Reference

This method is performed in a 1% Nitric Acid matrix for the calibration curve and standards and a 2% Nitric Acid matrix for the rinse.

3. Detection Limits

The laboratory follows the procedure found in 40CFR Part 136 to determine the MDL on an annual basis. The method detection limits determined by the laboratory are on file for review.

Instrument detection limits, sensitivities, and linear ranges will vary with the matrices, instrumentation and operating conditions. In relatively simple matrices, detection limits will generally be below 20 µg/L.

4. Interferences

4.1 Isobaric Elemental Interference

Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Since commercial ICP-MS instruments nominally provide unit resolution at 10% of the peak height, very high ion currents at adjacent masses can also contribute to ion signals at the mass of interest. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require resolution improvement, matrix separation, or analysis using another verified and documented isotope, or use of another method.

4.2 Isobaric Molecular and Doubly Charged Ion Interference

Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that could affect ICP-MS determinations have been identified in the literature. Examples include $ArCl^+$ ions on the ^{75}As signal and MoO^+ ions on the Cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below using the natural isotope abundances form the literature, the most precise coefficients for an instrument can be determined form the ratio of the net isotope signals observed for a standing solution at a concentration providing suitable (<1 percent) counting statistics. Because the ^{35}Cl natural abundance of 75.77 percent is 3.13 times the ^{37}Cl abundance of 24.23 percent, the chloride correction for arsenic can be calculated (approximately) as follows (where the $^{38}Ar^{37}Cl^+$ contribution at m/z 75 is a negligible 0.06 percent of the $^{40}Ar^{35}Cl^+$ signal):

Corrected arsenic signal (using natural isotopes abundances for coefficient approximations) = (m/z 75 signal) – (3.13) (m/z 77 signal) + (2.73) (m/z) (82 signal), (where the final term adjust for any selenium contribution at 77 m/z)

Note: Arsenic values can be biased high by this type of equation when the net signal at m/z 82 is caused by ions other than $^{82}Se^+$, (e.g. $^{81}BrH^+$ from bromine waste)

Similarly, corrected cadmium signal (using natural isotopes abundances for coefficient approximations) = (m/z 114 signal) – (0.027) (m/z 118 signal) – (1.63) (m/z 108 signal), (where the last two terms adjust for any tin or MoO^+ contributions at m/z 114).

> **Note:** Cadmium values will be biased low by this type of equation when $^{92}ZrO^+$ ions contribute at m/z 108, but use of the m/z 111 for Cd is even subject to direct ($^{94}ZrOH^+$) and indirect ($^{90}ZrO^+$) additive interferences when Zr is present.
>
> **Note**: As for the arsenic equation above, the coefficients in the Cd equation are for only illustrative purposes. The most appropriate coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 percent) counting precision.

The accuracy of these types of equations is based upon the constancy of the OBSERVED isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the “parent” ion have not been found to be reliable, e.g. oxide levels can vary. If a correction for an oxide ion is based upon the ratio of parent –to-oxide ion intensities, the correction must be adjusted for the degree of outside formation by the use of an

appropriate oxide internal standard previously demonstrated to form a similar level of oxide as the interferant. This type of correction has been reported for oxide-ion corrections using ThO^+/Th for the determination of rare earth elements. The use of aerosol desolvation and/or mixed plasmas has been shown to greatly reduce molecular interferences. These techniques can be used provided that method detection limits, accuracy, and precision requirements for analysis of the samples can be met.

4.3 Physical Interference

Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000mg/L) have been currently recommended to minimize solid deposition. An internal standard can be used to correct for the physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by the matrix change. When the intensity level of an internal standard is less than 30 percent or greater than 120 percent of the intensity of the first standard used during calibration, the sample must be reanalyzed after a fivefold (1+4) or greater dilution has been performed.

4.4 Memory Interference

Memory interferences can occur when there are large concentration differences between samples or standards which are analyzed sequentially. Sample deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affect the extent of the memory interferences which are observed. The rinse period between samples must be long enough to eliminate significant memory interferences.

5. Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound must be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

6. Sample Collection, Preservation, and Handling

6.1 Sample Collection

Only Polyethylene or fluorocarbon (PFA or TFE) containers are recommended. Alpha uses polyethylene bottles. 0.5L is the recommended size.

6.2 Sample Preservation

Samples for total metals are preserved with (1:1) Nitric Acid to a pH<2.

Samples for soluble metals must be preserved with (1:1) Nitric Acid to a pH of <2 **after** filtration through a 0.45 um filter.

6.3 Sample Handling

Samples that are to be analyzed for soluble metals, and have not been field filtered, must be filtered through a 0.45um filter as soon as possible. Samples are then preserved with 1:1 Nitric Acid to a pH<2, and then held for 18 hours. After the 18 hours the pH must be re-checked. If after 18 hours the pH is still >2, then the sample must be re-acidified and held again for 18 hours. If the pH is till >2 after this 18 hour period , then the Inorganics Manager must be told.

Samples preserved with Nitric Acid to a pH<2, and are not being analyzed for Mercury, have a hold time of 6 months.

Samples are stored at room temperature.

7. Equipment and Supplies

7.1 Agilent 7500a ICP-MS:

The ICP features a wide-diameter ICP torch injector for improved resistance to clogging with samples containing high dissolved solids levels. A high energy 27.12 MHz plasma, a solid state RF generator. Torch alignment is performed by auto-tuning software. The sample is introduced using an Agilent High Solids Nebulizer.

The MS features dual extraction lenses and a compound ion lens system that ensures a mass range from Li-U (masses 6-240). It also features the enhanced Omega II off-axis ion lens which gives mean random background of typically <2cps. The quadrapole rods produce an ideal true hyperbolic field, with digitally synthesized drive circuits to ensure faster scan speeds and greater stability to operate at high frequency –3MHz. The detector is a new electron multiplier operating simultaneously in pulse counting mode and analog mode. The log amplifier circuit extends dynamic range to 9 orders of magnitude with a high speed analog mode (minimum dwell time 100µsec) designed specifically for transient signal analysis. The software is ChemStation, it controls all instrument operations including tuning, data question, data analysis and reporting. The software provides the capability for qualitative, semiquantitive and quantitive analysis, as well as time-resolved, isotope ratio and isotope dilution analysis. A comprehensive array of autotune functions provide hands-free optimization of torch alignment, ion lenses, mass calibration and resolution, and detector calibration.

7.2 CETAC ASX-510 Autosampler: Delivers sample and internal standard to the torch

7.3 Edwards E2M18 Rotary Pump: Creates the necessary vacuum to operate the MS

7.4 Neslab M-75 Chiller: Cools the torch and the MS

7.5 Eppendorf pipets: Accurate means to make trace standards

8. Standards and Reagents

8.1 Nitric Acid (HNO_3), Trace metals grade: 18M Concentrated

8.2 1% Nitric Acid (v/v): 10mL of 18M HNO_3 diluted to 1L using Type I water

8.3 Type I De-Ionized Water

8.4 Calibration Standard: Agilent #5183-4688 (Table 4). Store at room temperature. Expires upon manufacturer's specified date.

8.5 Internal Standard: Agilent #5188-6525. 0.5 mL of internal standard diluted to 50mL in 5% HNO_3 (Table 8). Store at room temperature. Expires upon manufacturer's specified date.

8.6 Tune Stock: Agilent #5188-6564 10 µg/mL each of ^{7}Li,^{89}Y,^{140}Ce,^{205}Tl. Dilute 0.2mL to 200mL (Table 9). Store at room temperature. Expires upon manufacturer's specified date.

8.7 ICV/CCV: Agilent #5183-4682 stock (Table 10). Store at room temperature. Expires upon manufacturer's specified date.

8.8 ICSA: High-Purity Standards Cat. #ICP-MS-ICS-2 A stock. Dilute 5 mL to 50 mL (Table 11). Store at room temperature. Expires one week from date of preparation.

8.9 ICSB: High-Purity Standards Cat. #ICP-MS-ICS-2 B. Dilute 0.5 mL to 50mL (Table 11). Store at room temperature. Expires one week from date of preparation.

8.10 ICSAB: Dilute 30 uL of ICSB stock in 3.0 mL of working ICSA solution (Table 11). Store at room temperature. Made fresh daily.

8.11 Argon Gas: 0.9995 or better grade. Plumbed into the lab.

8.12 1 ppm High Standard: Dilute 5 mL of ICV/CCV standard(Section 8.7) to a final volume of 50 mL in 1%(v/v) HNO_3. Made fresh daily.

9. Procedure

9.1 Set-Up

9.1.1 Sample Preparation

Prior to analysis, samples which require total (acid-leachable) values must be digested using appropriate sample preparation methods, such as Methods 3005A, 3015, 3051 and 3050B.

9.1.2 Turning the instrument on from Stand By

- Tighten the peristaltic pump windings for the sample, Internal standard and spray chamber drain.
- Turn on the Argon gas supply and Neslab M-75 chiller under the bench.
- Turn on the computer, monitor and printer. Make sure that the printer is loaded with paper. Once the computer has booted, the Agilent ICP-MS top page will be shown. At this page select "**Instrument control"** (Note: Standby mode is indicated here and also by a yellow light on the front of the instrument.) From the "**Instrument control"** select "**Plasma"**. From "**Plasma**" select "**Plasma On"**.
- The instrument will start automatically and go into **"Analysis Mode"** which will be indicated on the instrument control page and on the instrument when the yellow light turns green. The autosampler probe must be in the autosampler rinse at position #1, and the internal standard must be blank. The autosampler can be positioned by selecting **"ALS"** from the **"Instrument control"**.
- Allow the instrument to warm up for **30 minutes.**

- For improved performance in calibration stability of the instrument, it is recommended that the analyst run an exposure of the ICSA solution, especially after any cleaning of the sampler and skimmer cones, prior to calibration.

9.2 Tuning

9.2.1 After the 30 minute warm up period has passed, a daily tune must be performed and a report generated. This tuning solution (Section 8.6) must be analyzed **four** times with relative standard deviations of **less than or equal to 5%** for the analytes contained in the tuning solution (^{7}Li, ^{89}Y, ^{205}Tl). The tuning solution also acts as a **Daily Performance Check Solution**, and serves as a **check on oxide interferences and double charged ion interferences; the criteria is <3% Note**: Precautions must be taken to protect the channel electron multiplier from high ion currents. The channel electron multiplier suffers from fatigue after being exposed to high ion currents. This fatigue can last form several seconds to hours depending on the extent of exposure. During this time period, response factors are constantly changing, which invalidates the calibration curve, causes instability, and invalidates sample analysis.

9.2.2 The mass calibration and resolution check is also performed during the tuning. The mass calibration and resolution parameters are required criteria which must be met prior to any samples being analyzed. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration must be adjusted to the correct value. The resolution must also be verified to be less than 0.9 amu full width at 10 percent peak height.

9.2.3 The stock tune solution (Section 8.6) is a 10 µg/L solution of **Li, Y, Ce** and **Tl** and is located at position #3 on the **"ALS"** which is accessed from the **"Instrument control"**

9.2.3.1 When the solution has been introduced to the plasma, select **"Instrument Control"** and then **"Tune".**

9.2.4 The **Sensitivity Tuning Page** will come up on the screen showing masses **7, 89** and **205**. Click **"START"** to begin the tuning. ***Caution:*** Typical tune parameters and a sample tune report are shown below to be an example. However, a detailed explanation of the tuning is found in the Agilent Users Manual pages 4.2 through 4.19. This chapter introduces the theory and mechanics of the tune. The physics involved in the tune and the effects of the tune on the calibration. This chapter must be read and understood by any operator before going any further. This manual will be found next to the computer near the spectrophotometer. When the analyst is satisfied that the tune has passed all of the quality control measures, then a tune report is generated and kept on file. To generate the report do the following from the **"Instrument Control"** page: go to **"Tune"** and then to **"Autotune"** and then **"Run"**. Make sure that these items are selected for the report: EM, ADJUST DISCRIMINATOR, RESOLUTION / AXIS, TUNING REPORT. The remaining autotune parameters such as TORCH VERTICAL / HORIZONTAL and LENS / PLASMA are easier to perform manually prior to running autotune and must not be selected.

9.2.5 The Analytical Sequence can now be started. In most instances, an analytical sequence will be set up and run automatically from an autosampler table and will consist of the following blocks: **CALIBRATION**: for the calibration standards. **SAMPLES:** Unknown samples with periodic QC checks (ICV, ICB, ICSA, ICSB, CCV, CCB). **TERM:** Termination block which instructs the instrument to perform certain functions when the analysis is complete. Usually this will consist of a final CCV/CCB and either shutdown or wait for further instruction.

9.2.6 When an acceptable tune has been achieved, a **pulse/analog** tune must be performed. This helps prevent damage to the detector by establishing the switching point between pulse mode and the analog mode. This tune is also necessary to achieve accurate

quantification of result. From the **ALS** page move the autosampler to the 100 µg/L Calibration Standard. The internal standards must be present. From **"Instrument Tune"** select **"P/A Factor"** then select **"Run".** A new list of factors will be shown on the monitor. Close this screen and it will ask if you would like to save these new factors. Select **"Yes"**.

Typical values of tuning parameters

Parameter	Typical Conditions	Adjustment
RF Power (W)	1300	1200 to 1600
Sampling Depth (mm)	6	4 to 8
Carrier gas (L/min)	1.2	0.8 to 1.3
Makeup gas (L/min)	0	0 to 0.4
Peri-pump 1 (rps)	0.1	0.06 TO 0.15
S/C Temp (°C)	2	Normally used at 2 °C
Extraction	-150	-200 to -100
Extraction	-70	-150 to -10
Einzel 1.3 (V)	-100	-130 to -40
Einzel 2(V)	7	-20 to +70
Omega Bias (V)	-35	-40 to 0
Omega (+)(V)	5	0 to +30

Typical value of Sensitivity and RSD (Using the normal torch)

Mass	Counts / 10ppb Integ. Time = 0.1 sec	RSD
^{7}Li	>6400	<5%
^{89}Y	>16000	<5%
^{205}Tl	>9600	<5%

9.3 Initial Calibration (ICV / ICB)

Mixed calibration standard solutions are prepared by diluting the stock-standard solutions to levels within the linear range for the instrument in a solvent consisting of 5% HNO_3 (v/v) in reagent water. The calibration standard solutions must contain a suitable concentration of an appropriate internal standard for each analyte. Internal standards are added at the time of analysis using a second channel of the peristaltic pump and an appropriate mixing manifold. The **CETAC ASX-510 Autosampler** handles this task of the operation. Generally, an internal standard must be no more than 50amu removed from the analyte. Alpha employs the following internal standards: ^{6}Li, ^{45}Sc, ^{74}Ge, ^{115}In and ^{209}Bi.

Prior to preparing the mixed standards, each stock solution must be analyzed separately to determine possible spectral interferences or the presence of impurities. Care must be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to freshly acid-cleaned FEP fluorocarbon bottles for storage. Fresh mixed standards must be prepared as needed with the realization that concentrations can change upon aging. Calibration standards must be initially verified using a quality control standard (ICV), and monitored weekly for stability.

Calibrate the instrument for the analytes of interest (recommended isotopes for the analytes in Table 1 are provided in Table 3), using the calibration blank (Section 10.4.1) and the set of 5 standards (see Table 4.). The analytical range brackets an RDL of 0.1 µg/L to 200 µg/L with the exceptions of Fe, K, Na, Ca and Mg which bracket the range of 10µg/L to 20,000µg/L. All solutions and standards are prepared in a 1% Nitric Acid matrix. The calibration is defined as the calibration blank and five standards. The only standards that may be discarded in the calibration are the first standard (the low standard) and the fifth standard (the high standard). The only instance when the standard may be discarded is if the linearity of the element in question does not meet the correlation coefficient acceptance criteria of 0.995 or greater. No mid-level standards are ever discarded. All standards, QC samples and samples are to be integrated three times and then averaged. The calibration block is part of the analytical sequence and includes an ICV and an ICB immediately following the analysis of the calibration standards. The calibration block can also contain a pause so that the analyst can evaluate the calibration prior to sample analysis. The calibration sequence is as follows:

Blank #1
Cal blank #2
0.1 µg/L std (10 µg/L Fe, K, Na, Ca, Mg)
0.2 ug/L std (20ug/L Fe, K, Na, Ca, Mg)
1.0 µg/L std (100 µg/L Fe, K, Na, Ca, Mg)
10.0 µg/L std (1000 µg/L Fe, K, Na, Ca, Mg)
100.0 µg/L std (10,000 µg/L Fe, K, Na, Ca, Mg)
200.0 µg/L std (20,000 µg/L Fe, K, Na, Ca, Mg) this standard is optional in the calibration, it extends the linear range.

When the calibration standards have finished running then the analyst may choose to delete certain standards entirely or certain elements from either the high or low standard in order to produce an acceptable correlation coefficient. To view the calibration data sheet go to **"Off Line Data Analysis"** then **"Calibrate"** then **"Cal Graph". "Cal Graph"** will produce a graph of each element in the calibration. Data points can be rejected or restored from this screen. If a standard is found to be made incorrectly it can be deleted entirely by accessing **"Calibrate"** then **"Std Data Files".**

The quality control standard is the Initial Calibration Verification solution (ICV), which must be prepared in the same acid matrix as the calibration standards. This solution must be an independent standard near the midpoint of the linear range at a concentration other than that used for instrument calibration. An independent standard is defined as a standard composed of analytes from a source other than that used for the standards for instrument calibration.

Immediately after the calibration has been established, the calibration must be verified and documented for every analyte by the analysis of the Initial Calibration Verification solution (ICV) (Section 8.7). The calibration is verified if the solution is within the 10% of the true value (Table 5.) for each element. See Section 12 for corrective action if the ICV fails. The ICB/CCB (10.4.1) are analyzed immediately following the ICV/CCV. The ICB/CCB must be no greater than ± |RL| for any analyte. See Sections 12.4, 12.5 and 12.6 for Corrective Actions.

9.4 Interference Check Solution (ICSA and ICSAB)

The interference check solution (ICS) is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interference and provide an adequate test of any corrections.

Chloride in the ICS provides a means to evaluate software corrections for chloride-related interferences such as $^{35}Cl^{16}O^{+}$ on $^{51}V^{+}$ and $^{40}Ar^{35}Cl^{+}$ on $^{75}As^{+}$.

Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese.

Molybdenum serves to indicate oxide effects on cadmium isotopes.

The other components are present to evaluate the ability of the measurement system to correct for various molecular-ion isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits. The ICSA solution (Section 8.8) contains 20,000mg/L of Cl^-, 3,000 mg/L of Ca, 2,500 mg/L of Fe and Na, 2,000 mg/L of C, 1,000 mg/L of Al, K , Mg, P, S and 20 mg/L of Mo and Ti. The ICSAB (Section 8.9) solution contains ICSA plus the addition of 0.1 mg/L of As, Cd, Zn, Se 0.2 mg/L Cu, Mn V, Cr, Ni, Co, 0.05 mg/L Ag.

The non-target analytes for the ICSA should have a recovery less than 10ppb, and the spiked analytes for the ICSAB should be recovered within ±20% of the true value. Narrate non-conformance.

9.5 Sample Analysis and Continuing Calibration Verification (CCV)

Sample analysis takes place from the **"Samples"** block. When filling out the autosampler table in the tuning section (Section 9.2.6), fill in the block for "Samples". This will run the ICV, ICB, ICSA, ICSAB, samples and CCV and CCB. After the initial Instrument QC has been analyzed and passed, then 10 samples will be analyzed. After the tenth sample has been analyzed, a CCV and a CCB will be analyzed. Analysis of standards and samples must only take place when the instrument has come to equilibrium. All masses which could affect data quality must be monitored to determine potential effects from matrix components on the analyte peaks. The recommended isotopes to be monitored are listed in Table 3. When the analysis is ready to start, flush the system with the rinse blank solution (Section 10.4.3) until the signal levels return to the method's level of quantitation (usually about 30 seconds) before the analysis of each sample. Nebulize each sample until a steady-state signal is achieved (usually in about 30 seconds) prior to collecting the data. Analyze the Continuing Calibration Verification solution (CCV) (Section 8.7) and the continuing Calibration blank (Section 10.4.1) at a frequency of at least once per ten analytical samples, and at the end of the analytical run. Flow injection systems may be used as long as they meet the performance criteria of this method. Dilute and reanalyze samples that are more concentrated than the linear range (or species needed for a correction) or measure an alternate less-abundant isotope. The linearity at the alternate mass must be confirmed by appropriate calibration.

9.6 Scheduled Maintenance

The scheduled maintenance is automatically tracked by the run time log for the following parameters. A message will appear on the computer screen reminding the analyst that a piece of maintance must be performed. An electronic log, along with a maintance notebook is kept. Below is a list what needs to be performed:

1. Check rough pump oil
2. Replace rough pump oil
3. Replace mist filter
4. Clean the Einzel lenses
5. Clean the extraction lenses
6. Clean the skimmer cone
7. Clean the sampling cone
8. Clean the nebulizer
9. Clean the spray chamber
10. Change pump tubing for the samples and the internal standards daily
11. The cones are cleaned using a 5% trace nitric acid solution followed by at least three rinses with deionized water, when carryover becomes a problem. All surface debris is removed with a cotton swab.

9.7 Calculations

The quantitative values are reported in appropriate units directly from the instrument: micrograms per liter (µg/L) for aqueous samples and milligrams per kilograms (mg/Kg) for solid samples. If dilutions were performed, the appropriate corrections must be applied to the sample values.

It is required that results for solids be reported on a dry weight basis as follows:

1. A separate determination of percent solids is performed by the Wet Chemistry Department and the result is loaded in the **LIMS**. To retrieve the result in the LIMS, go to **"Status"** and type in the sample ID. Click the sample number that is part of that sample ID, and click the product that says **TS-S**. The percent solids for the sample is there. LIMS will automatically correct the sample for percent solids after the metals analysis has been **Final Metals Reviewed.** This is the calculation:

   $$\text{Concentration (dry weight) (mg/Kg)} = \frac{C \times V}{W \times S}$$

   Where:
   C= Digest Concentration (mg/L)
   V= Final volume in Liters after sample preparation
   W= Weight in Kg of wet sample
   $S = \frac{\%\text{Solids}}{100}$

2. Calculations must include appropriate interference corrections (see Section 4.1 for examples), internal-standard normalization, and the summation of signals at 206, 207, and 208 m/z for Lead (to compensate for any differences in the abundances of these isotopes between samples and standards).

10. Quality Control and Data Assessment

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a calibration verification standard is used to confirm the measurements were performed in an in-control mode of operation.

10.1 Demonstration of Capability

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. Each time a method modification is made, the analyst is required to repeat the procedure.

When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must locate and correct the source of the problem and repeat the test for failed parameters of the method.

Repeated failure confirms a general problem with the measurement system or analytical technique of the analyst. If the failure repeats, locate and correct the source of the problem and repeat the test for all parameters listed in the method.

10.2 Instrument Detection Limits (IDLs)

Instrument Detection limits (in µg/L) can be estimated by calculating the average of the standard deviations of the three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e. each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs must be determined at least every three months and kept in the instrument log book.

10.3 Internal Standards

The intensities of all internal standards must be monitored for every analysis. When the intensity of any internal standard fails to fall between 60 and 125% of the intensity of that internal standard in the initial calibration, the following procedure is followed:

The sample must be diluted fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standards. This procedure must be repeated until the internal-standard intensities fall within the prescribed window.

See Section 12.15 for Corrective Action.

10.4 Blank

Three types of blanks are required for the analysis. The calibration blank, which is also the ICB/CCB, is used in establishing the calibration curve. The ICB/CCB is used to monitor carryover, signal noise, and drift. The preparation blank is used to monitor for possible contamination resulting from the sample preparation procedure. The rinse blank is used to flush the system between all samples and standards. See Section 12.3 for Corrective Action.

10.4.1 The Calibration blank, Initial Calibration Blank and the Continuing Calibration Blank consists of the same concentration of the same acid used to prepare the final dilution of the calibrating solutions of the analytes. This is a 1% HNO_3 solution (v/v) in Type I de-ionized water along with the selected concentrations of internal standard element for each of the analytes. The Calibration Blank is analyzed before the standards are analyzed. The Initial Calibration Blank must follow the Initial Calibration Verification standard (ICV) and the Continuing Calibration Blank must follow the Continuing Calibration Verification standard (CCV). These must be analyzed at a frequency of every 10 or less samples and at the end of the analytical run. The ICB/CCB must be no greater than ± |RL| for any analyte. See Section 12.11 for Corrective Action.

10.4.2 The preparation (or reagent) blank must be carried through the complete preparation procedure and contain the same volumes of reagents as the sample solutions. Results for the preparation blank must be less than the RL for any analyte. See Section 12.8 for Corrective Action.

10.4.3 The rinse blank consists of HNO_3 (1% or 2%) (v/v) in reagent water. Prepare a sufficient quantity to flush the system between standards and samples.

10.5 Calibration Verification (ICV/CCV) and Laboratory Control Samples (LCS)

The ICV and CCV must have a recovery that is within ±10% of the true value. The ICV and the CCV are from the same solution, and must contain all of the elements that are calibrated. The ICV/CCV is an independent source other than those standards used for the calibration of the

instrument. The ICV must be analyzed following the calibration. The CCV must be analyzed at a frequency of 10 samples or less and at the end of the analytical run. The Laboratory Control Sample (LCS) must be analyzed for each analyzed for each analyte using the same sample preparations, analytical methods and QA/QC procedures employed for the test samples. One LCS must be prepared and analyzed for each sample batch at a frequency of one LCS for each 20 samples or less. Aqueous LCS recoveries must be 80-120%, and soil LCS recoveries must be 70-130%. See Sections 12.9 and 12.10 for Corrective Actions.

10.6 Interference Check Standards

Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run or once every 12 hours, whichever is more frequent. Do this by analyzing the interference check solutions A and AB (9.4). The analyst must be aware that precipitation from solution AB may occur with some with some elements, specifically silver. Refer to Section 4.0 for a discussion on interferences and potential solutions to those interferences if additional guidance is needed. ICSAB must have a recovery of 80-120%. See Section 12.7 for Corrective Action.

10.7 Dilution Test

If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 times greater than the concentration of the reagent blank (10.4.2), an analysis of a fivefold (1+4) dilution must agree within ± 10% of the original determination. If not, interference must be suspected. One dilution test must be included for every twenty samples (or less) of each matrix. See Section 12.12 for Corrective Action.

10.8 Post Digestion Spike Addition

An analyte spike added to a portion of a prepared sample, or its dilution, must be recovered to within 75 to 125 percent of the known value or within the laboratory derived acceptance criteria. The spike addition must be based on the indigenous concentration of each element of interest in the sample. See 12.13 for Corrective Action.

10.9 Duplicates

Analyze one duplicate sample for every matrix in a batch at a frequency of one matrix duplicate for every 20 samples.

The relative percent difference (RPD) must be calculated as follows:

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100$$

Where:
RPD = relative percent difference
D_1 = first sample value
D_2 = second sample value (duplicate)

A control limit of 20% RPD must not be exceeded for analyte values greater than 100 times the instrument detection limit (Section 10.2). See Section 12.14 for Corrective Action.

10.10 Control Limits

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained. After the analysis of 20 spiked samples, and 20 laboratory control samples, calculate the average percent recovery (R) and the standard deviation of the percent recovery (S).

Control limits for the method parameters are generated by the QC staff and distributed to the analysts. The control limits are calculated based on in-house performance data. The limits are compared to the control limits found in the reference method.

10.11 Analytical Sequence

Performance Check Solution / Tuning Solution

PA Tune Solution

Calibration of instrument

Initial Calibration Verification Standard

Initial Calibration Blank

Interference Check Solution A

Interference Check Solution AB

Continuing Calibration Verification Standard

Continuing Calibration Blank

Samples (10)

Continuing Calibration Verification Standard

Continuing Calibration Blank

11. Method Performance

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations were obtained using reagent water in 5% HNO_3 (except for Antimony and Silver which use 3:1 HNO_3:HCl. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

Method performance data is on file in the laboratory QC department. Comparison of method performance data for the laboratory to the reference method criteria occurs when laboratory in-house acceptance limits are generated. In-house generated data must be within the specifications of the reference method or the analysis is not continued until corrective action is completed.

12. Corrective Actions

Holding time exceedence, improper preservation and observed sample headspace are noted on the nonconformance report form.

Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

Review of standards, blanks and standard response for acceptable performance occurs for each batch of samples. Record any trends or unusual performance on a nonconformance action form.

12.1 The performance check standard is included in the tuning solution. Ce is included with the tuning solution and monitors the formation of oxides and the effect of doubly-charged ions. If the solution fails >3% (Section 9.2.1) then instrument maintenance must be performed and the solution re-run.

12.2 For the Tune to pass, the mass calibration for the three tune elements (Section 9.2.1) must not differ by more than 0.1 amu from the true value and the resolution must be <0.9 amu full width at 10% peak height. Furthermore the RSD for the three tune elements must be <5% If any of these criteria fail then the mass calibration must be adjusted to the correct value. This is done by re-optimizing the instrument conditions and re-tuning.

12.3 The results of the calibration blank (Section 10.4.1) must be less than 3 times the current IDL for each element. If this is not the case, the reason for the out-of-control condition must be found and corrected, and affected samples must be reanalyzed. If the laboratory consistently has concentrations greater than 3 times the IDL, the IDL may be indicative of an estimated IDL and must be re-evaluated.

12.4 Calibration is performed after the tune passes. A five point calibration is performed (Section 9.3). If more than three points are to be used for the calibration, then the resultant curve must have a correlation coefficient (cc) of 0.995 or greater. If the cc is <0.995, then the instrument must be re-optimized and re-calibrated. The calibration must define the working linear range of the curve. The reporting RL must be the low standard, and the upper linear range must be defined by the high standard.

12.5 The ICV (Section 9.3) is performed immediately after an acceptable calibration has been produced. The acceptable range for this standard is 90-110%. If this standard fails then the analysis must be stopped and the instrument re-calibrated, and the ICV re-analyzed. Analysis cannot continue until this standard passes.

12.6 The ICB (Section 10.4.1) must be performed immediately after the ICV. The ICB must be < Reporting Limit. If the ICB fails then the analysis is terminated, sources of contamination are checked for, and the instrument is re-calibrated and the ICV and ICB are re-analyzed.

12.7 The Interference Check Solutions (Section 10.6), ICSA and ICSAB monitor how well the system is correcting for interference. The target elements in ICSA must be below the RL for those elements in question. Solution ICSAB must have a % recovery of 80-120% for the target elements. If the recovery of these solutions is outside of the control limits, the non-compliance must be narrated. There is no corrective action required because instrument corrections are based on natural isotope abundances that cannot be changed. If the IS is in compliance then the data is acceptable.

12.8 The Method (Preparation) Blank (Section 10.4.2) must be less than the RL for all of the elements that are being analyzed. If the element in question is non-detect, and the method blank is positive then the corrective action is a narration on the final report. If the samples associated with the method blank have “hits”, and they are 10x greater then the method blank, then the corrective action is a narration on the final report. If the method blank is not less than the RL, and the associated samples have results that are greater then the RL but less than 10x the method blank, then the samples must be re-digested and re-analyzed.

12.9 If the LCS (Section 10.5) fails, then all samples associated with that batch must be re-digested and re-analyzed. (Massachusetts recognizes that if the MS passes and the LCS fails then the data can be accepted. Narrate then non-compliance. This is only for MCP projects)

12.10 Failure of the CCV (Section 10.5) terminates the analysis immediately. Correct the problem, and re-calibrate and re-analyze all samples since the last compliant CCV.

12.11 Failure of the CCB (10.4.1) terminates the analysis immediately. Evaluate the data; if associated sample results are greater than 10x CCB level then the results are acceptable. Otherwise, re-calibrate and re-analyze all samples since last compliant CCB.

12.12 If the dilution test (Section 10.7) fails, then an interference must be suspected. There is no corrective action to be applied. Narrate the non-compliance on the final report.

12.13 If the Post–Digestion Spike (Section 10.8) fails, then the sample must be diluted and re-analyzed to compensate for the matrix effect. Narrate the non-compliance on the final report.

12.14 Failure of the duplicate sample (Section 10.9) must be investigated. If the sample is found to be non-homogeneous then the non-compliance must be narrated on the final report. If the sample is aqueous in nature or a homogenous soil, then the duplicates must be re-digested and re-analyzed and the non-compliance narrated on the final report.

12.15 If the Internal Standards (Section 10.3) fail the acceptance criteria, then dilute the samples until the IS passes. If the criteria are still not met, then terminate the analysis, re-calibrate, verify the new calibration, and reanalyze all of the affected samples.

13. Pollution Prevention

See Chemical Hygiene Plan for pollution prevention operations.

14. Waste Management

See Chemical Hygiene Plan for waste handling and disposal.

15. Attachments

Table 2: Detection Limits
Table 3: Interference Check Solution Concentrations
Table 4: Calibration Standards
Table 5: Recommended Isotopes for Selected Elements
Table 6: Precision and Accuracy Acceptance Criteria
Table 7: Metals LCS Concentrations
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Table 10: ICV / CCV Solution
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Table 2
Detection Limits

Element	Atomic Symbol	Mass (m/z)	Aqueous (µg/L)	Soil / Solid (ug/Kg)
Beryllium	Be	9	0.5	20
Sodium	Na	23	100	4000
Magnesium	Mg	24	100	4000
Aluminum	Al	27	10	400
Potassium	K	39	100	4000
Calcium	Ca	44	100	4000
Vanadium	V	51	0.50	20
Chromium	Cr	52	0.50	20
Manganese	Mn	55	0.50	20
Iron	Fe	57	50	2000
Cobalt	Co	59	0.50	20
Nickel	Ni	60	0.50	20
Copper	Cu	65	0.50	20
Zinc	Zn	66	5.0	100
Arsenic	As	75	0.50	20
Selenium	Se	82	0.50	20
Molybdenum	Mo	98	0.50	20
Silver	Ag	107	0.50	20
Cadmium	Cd	111	0.50	20
Antimony	Sb	121	0.50	20
Barium	Ba	137	0.50	20
Thallium	Tl	205	0.50	20
Lead	Pb	208	0.50	20
Internal Standards				
Lithium	Li	6		
Scandium	Sc	45		
Germanium	Ge	74		
Indium	In	115		
Bismuth	Bi	209		

ND = Not determined or listed in the reference method.
NL = Compound not listed in the reference method.
Calculated Method Detection Limits are on file in the QC Department.

Table 3
Interference Check Solution

Solution Component	Solution A Concentration (ug/L)	Solution AB Concentration (ug/L)
Al	100,000	100,000
Ca	300,000	300,000
Fe	250,000	250,000
Mg	100,000	100,000
Na	250,000	250,000
P	100,000	100,000
K	100,000	100,000
S	100,000	100,000
C	200,000	200,000
Cl	2,000,000	2,000,000
Mo	2,000	2,000
Ti	2,000	2,000
As	0.0	100
Cd	0.0	100
Cr	0.0	200
Co	0.0	200
Cu	0.0	200
Mn	0.0	200
Ni	0.0	200
Ag	0.0	50
Zn	0.0	100
Se	0.0	100
V	0.0	200

Table 4
Calibration Standards

Agilent Stock# 5183-4688 (Section 8.4)

Stock Standard B = 1000 mg/L of the following: Fe, K, Ca, Na, Mg, Sr

Stock Standard A = 10 mg/L of the following: Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn, Th, U

All Calibration Standards are prepared in 5% HNO3 (v/v) diluted to 50mL.

Standard #1 (0.1 µg/L of **B** and 10 µg/L of **A**): Dilute 5 mL of Standard #3 below, with 1% HNO_3 (v/v) to 50mL final volume.

Standard #2 (0.2µg/L of **B** and 20 µg/L of **A**): Dilute 10 mL of Standard #3 below, with 1% HNO_3 (v/v) to 50mL final volume.

Standard #3 (1.0 µg/L of **B** and 100 µg/L of **A**): Dilute 5 mL of Standard #3 below, with 1% HNO_3 (v/v) to 50mL final volume.

Standard #4 (10.0 µg/L of **B** and 1000 µg/L of **A**): Dilute 0.05 mL of Agilent Stock# 5183-4682, with 1% HNO_3 (v/v) to 50mL final volume.

Standard #5 (100 µg/L of **B** and 10000 µg/L of **A**): Dilute 0.5 mL of Agilent Stock# 5183-4682, with 1% HNO_3 (v/v) to 50mL final volume.

Standard #6 (200 µg/L of **B** and 20000 µg/L of **A**): Dilute 1.0 mL of Agilent Stock# 5183-4682, with 1% HNO_3 (v/v) to 50mL final volume.

Table 5: Recommended Isotopes for Selected Elements

Mass	Element of Interest
27	Aluminum
121, **123**	Antimony
75	Arsenic
138, 137, 136, **135**, 134	Barium
9	Beryllium
209	Bismuth (IS)
114, 112, **111**, 110, 113, 116, 106	Cadmium
42, 43, **44**, 46, 48	Calcium (I)
35, 37, (77, 82)[a]	Chlorine (I)
52, 53, **50**, 54	Chromium
59	Cobalt
63, **65**	Copper
165	Holmium (IS)
115, 113	Indium (IS)
56, 54, **57**, 58	Iron (I)
139	Lanthanum (I)
208, 207, **206**, 204	Lead
6[b], 7	Lithium (IS)
24**, 25**, **26**	Magnesium (I)
55	Manganese
98, 96, 92, **97**, 94 (108)[a]	Molybdenum (I)
58, **60**, 62, **61**, 64	Nickel
39	Potassium (I)
103	Rhodium (IS)
45	Scandium (IS)
80,**78**,**82**,**76**,**77**,74	Selenium
107, **109**	Silver
23	Sodium (I)
159	Terbium (IS)
205, 203	Thallium
51 ,50	Vanadium
120, **118**	Tin (I)
89	Yttrium (IS)
64, **66, 68**, **67**, 70	Zinc

NOTE: Method 6020 is recommended for only those analytes listed in Table 1. Other elements are included in this Table because they are potential interferents (I) in the determination of recommended analytes, or because they are commonly used internal standards (IS). Isotopes are listed in descending order of natural abundance. The most useful isotopes are underlined and in boldface, although certain matrices may require the use of alternative isotopes.

[a] These masses are also useful for interference correction (Section 4.2)
[b] Internal standard must be enriched in the 6Li isotope. This minimizes interference from indigenous Li.

Table 6
Precision and Accuracy Acceptance Criteria *

	Aqueous % Recovery LCS		Soil % Recovery LCS		Duplicate	
Element	**Lower Control Limit**	**Upper Control Limit**	**Lower Control Limit**	**Upper Control Limit**	**Aqueous %RPD**	**Soil %RPD**
Aluminum	80	120	70	130	20	20
Antimony	80	120	70	130	20	20
Arsenic	80	120	70	130	20	20
Barium	80	120	70	130	20	20
Berylium	80	120	70	130	20	20
Cadmium	80	120	70	130	20	20
Calcium	80	120	70	130	20	20
Chromium	80	120	70	130	20	20
Cobalt	80	120	70	130	20	20
Copper	80	120	70	130	20	20
Iron	80	120	70	130	20	20
Lead	80	120	70	130	20	20
Magnesium	80	120	70	130	20	20
Manganese	80	120	70	130	20	20
Molybdenum	80	120	70	130	20	20
Nickel	80	120	70	130	20	20
Potassium	80	120	70	130	20	20
Selenium	80	120	70	130	20	20
Silver	80	120	70	130	20	20
Sodium	80	120	70	130	20	20
Thallium	80	120	70	130	20	20
Vanadium	80	120	70	130	20	20
ZInc	80	120	70	130	20	20

* These are default limits. The limits are re-evaluated and updated as necessary pending compilation of the minimum number of data points.

Table 7
Metals LCS Concentrations

Analyte	Liquid Concentration (mg/L)	Soil Concentration (mg/Kg)
Antimony	0.5	20
Arsenic	0.12	4.8
Barium	2.00	80
Beryllium	0.05	2.0
Cadmium	0.051	2.04
Chromium	0.20	8.0
Copper	0.25	10
Lead	0.51	20.4
Nickel	0.50	20
Selenium	0.12	4.8
Silver	0.05	2.0
Thallium	0.12	4.8
Zinc	0.50	20
Iron	1.00	40
Manganese	0.50	20
Calcium	10.0	400
Magnesium	10.0	400
Potassium	10.0	400
Sodium	10.0	400
Aluminum	2.00	80
Cobalt	0.50	20
Vanadium	0.50	20

Table 8
Internal Standard

Agilent #5188-6525 (Section 8.5), 10mg/L of ^{6}Li,^{45}Sc, ^{74}Ge, ^{89}Y, ^{115}In, ^{209}Bi

Working Internal Standard (IS) Solution (1 mg/L of ^{6}Li,^{45}Sc, ^{74}Ge, ^{89}Y, ^{115}In, ^{209}Bi): Dilute 5.0 mL of Agilent Stock# 5188-6525, with 5% HNO_3 (v/v) to 50mL final volume.

Table 9
Tune Solution

Agilent Stock# 5188-6564 (Section 8.6), 10mg/L of ^{7}Li, ^{140}Ge, ^{89}Y, ^{204} Tl

Working Tune Solution (0.01 mg/L of ^{7}Li, ^{140}Ge, ^{89}Y, ^{204} Tl): Dilute 0.2 mL of Agilent Stock# 5188-6564, with 5% HNO_3 (v/v) to 200mL final volume.

Table 10
ICV / CCV Solution

Agilent Stock# 5183-4682 (Section 8.7): **1000mg/L** of K, Na, Ca, Mg, Fe, Sr
10mg/L of Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, An, Th, U

Working ICV/CCV Solution: Dilute 0.25 mL of Agilent Stock# 5183-4682, with 5% HNO_3 (v/v) to 50mL final volume. This will give the following concentrations:

5000µg/L of K, Na, Ca, Mg, Fe, Sr
50µg/L of Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, An, Th, U

Table 11
Interference Check Solutions

ICSA, High-Purity Standards Cat. #ICP-MS-ICS-2 A (Section 8.8):
20000 mg/L of Cl^-
3000 mg/L Ca
2500 mg/L Fe, Na
2000 mg/L of C
1000 mg/L of Al, K, Mg, P, S
20 mg/L of Mo, Ti

Working ICSA Solution: Dilute 5 mL of High-Purity Standards Cat. #ICP-MS-ICS-2 A, with 1% HNO_3 (v/v) to 50mL final volume. This will give the following concentrations:
2000 mg/L of Cl^-
300 mg/L Ca
250 mg/L Fe, Na
200 mg/L of C
100 mg/L of Al, K, Mg, P, S
2 mg/L of Mo, Ti

ICSB, High-Purity Standards Cat. #ICP-MS-ICS-2 B (Section 8.9): 20 mg/l Cu, Mn, V, Cr, Ni, Co. 10 mg/L As, Cd, Zn, Se. 5 mg/L Ag

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Working ICSAB Solution (Section 8.10): Dilute 30 uL of ICSB High-Purity Standards Cat. #ICP-MS-ICS-2 B with 3.0 mL of the working ICSA solution. This will give the following concentrations:
20000 mg/L of Cl^-
3000 mg/L Ca
2500 mg/L Fe, Na
2000 mg/L of C
1000 mg/L of Al, K, Mg, P, S
20 mg/L of Mo, Ti
0.2 mg/L Cu, Mn V, Cr, Ni, Co, 0.1 mg/L of As, Cd, Zn, Se 0.05 mg/L Ag.

Table 12

Interference Correction Equations

Correction equations are in the form: corrected signal for mass X=(signal from mass X) ± (signal from mass Y)*(correction factor).

6= (6) - ((7)*0.082)

44= (44) - ((88)*0.015)

51= (51) - ((53)*3.0)) + ((52)*0.34)

66= (66) - ((69)*0.00141)

75= (75) – ((77)*2.9) + ((82)*2.23) – ((83)*2.23)

82= (82) – (83)

98= (98) – ((99)*0.146)

111= (111) – ((108)*1.073) + ((106)*0.712)

114= (114) – ((118)*0.027)

115= (115) – ((118)*0.016)

208= (208) + (206) + (207)

Mercury in Liquid Waste

(Automated Cold-Vapor Technique)

Reference Method No.: **EPA 7470A**

Reference: SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update II, September 1994.

1. Scope and Application

Matrices: Method 7470 is a cold-vapor atomic absorption procedure approved for determining the concentration of mercury in mobility-procedure extracts, aqueous wastes, and ground waters. (Method 7470 can also be used for analyzing certain solid and sludge-type wastes; however, Method 7471 is usually the method of choice for these waste types.) All samples must be subjected to an appropriate dissolution step prior to analysis.

Definitions: See Alpha Laboratories Quality Manual Appendix A.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one or more of the following laboratory personnel before performing the modification: Area Supervisor, Department Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of analysts experienced in the operation of the Mercury Analyzer and in the interpretation of Mercury data. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability, analyzing a proficiency test sample and completing the record of training.

After initial demonstration, ongoing demonstration is based on acceptable laboratory performance of at least a quarterly laboratory control sample or acceptable performance from an annual proficiency test sample. A major modification to this procedure requires demonstration of performance. The identification of major method modification requiring performance demonstration is directed by the Quality Assurance Officer and/or Laboratory Director on a case-by-case basis.

2. Summary of Method

Prior to analysis, the liquid samples must be prepared according to the procedure discussed in this method.

Method 7470, a cold-vapor atomic absorption technique, is based on the absorption of radiation at 253.7-nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.1 Method Modifications from Reference

2.1.1 A smaller sample sized is prepared, and therefore proportionately less reagent volumes are used.

2.1.2 The original method does not address the automated instrument procedure.

3. Reporting Limits

The typical reporting limit for Mercury is 0.0002mg/L. This satisfies Massachusetts, GW1 and GW 2 criteria. Connecticut mobility criteria for SPLP is 0.0004mg/L, Rhode Island is 0.002mg/L, and the Drinking Water reporting limit is 0.0002mg/L.

4. Interferences

Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.

5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material safety data sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

Mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Analysis is conducted under a laboratory exhaust hood. The analyst must wear chemical resistant gloves when handling concentrated mercury standards.

The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Therefore, the acidification of samples is to be conducted under a laboratory exhaust hood.

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

Samples are collected in either glass or plastic containers.

6.2 Sample Preservation

Samples are preserved with HNO_3 to a pH of <2.

6.3 Sample Shipping

No special shipping requirements.

6.4 Sample Handling

Samples are stored under refrigeration at 4 ± 2°C and analyzed as soon as possible after collection. The samples have a 28-day holding time from the time of collection.

7. Equipment and Supplies

7.1 Perkin Elmer FIMS 100 Atomic absorption spectrophotometer: Use instrument settings recommended by the manufacturer. The PE FIMS is designed specifically for the measurement of mercury using the cold-vapor technique.

7.1.1 The FIMS has a PC that serves as a data station, collects and compiles the data, and the PC also contains the required software and hardware to operate the FIMS.

7.1.2 The FIMS employs a Plexiglass tube; it has an i.d. of 4mm, and an optical path length of 260mm. It has removable quartz windows on both ends of the tube. The cell is pre-aligned, so there is no need to align the cell for maximum throughput of energy.

7.1.3 The FIMS uses peristaltic pumps to transport the various reagents and sample through the system. The speed of the pumps is under software control: 20 – 120rpm or off.

7.1.3.1 Each pump accepts up to four magazines, which hold the pump tubing in place. There are different size magazines for different pump tubing sizes. Refer to the FIMS manual for replacement sizes. The pump tubing is available in different diameters depending on the reagent used. The different sizes have different colored collars. These can be ordered from Perkin Elmer.

7.1.4 The FIMS employs a 5-port Flow Injection Valve. The valve has two positions: fill and inject. The valve uses a sample loop to switch between fill and inject. The sample loops are made from PTFE. Alpha utilizes a 500µL loop. Sizes can range from 50 – 1000µL.

7.1.5 Sample and reagent are mixed in the manifold. The manifold has two purposes: to either initiate the reaction or to dilute one of the two mixing streams. The manifold blocks have three channels that are interconnected. The inlets of the channels have a ¼ -inch 28UNF internal screw thread. The blocks are made from inert, translucent plastic.

7.1.6 The gas/liquid separator is used in the mercury cold-vapor technique to separate the gas and liquid in the mixture as it leaves the manifold. It is connected to the manifold block by way of connector pegs.

7.1.7 An inert carrier gas is required for mercury determinations with FIMS. The FIMS is hard plumbed to accept Argon. The Argon is plumbed into the rear of the spectrometer, at the GAS IN connection. The gas outlet, flow regulator and flow gauge are on the front panel of the FIMS. Usable flows are between 40mL/minute and 250mL/minute at a recommended gas inlet pressure between 320kPa and 400kPa. The gas flow is off when the control knob is turned fully clockwise.

7.1.8 The radiation source is a low-pressure mercury lamp that is specific for the FIMS. This may be purchased from Perkin Elmer. The detector is a photocell with maximum sensitivity at 254nm.

7.1.9 Waste is pumped directly into a waste bottle. When the waste is full, it is emptied into the Metals/Wet Chem waste drum in the transfer room.

7.2 Graduated cylinder: Rinse once with 50% HNO_3 and then rinse with reagent water prior to use.

7.3 Volumetric Flasks, Class A, various volumes: Rinse once with 50% HNO_3 and then rinse with reagent water prior to use.

7.4 Water Bath: Fisher Isotemp Water Bath, 28L capacity, able to maintain 95°C.

7.5 Centrifuge Tubes: Capable of holding up to 50mL volume.

7.6 Centrifuge Tube Rack: Capable of submersion in 95°C water bath.

7.7 Pump tubing: Environmental Express, three stop (yellow/blue, red/red, and black/white).

7.8 PTFE membranes: Whatman TE37 disks.

7.9 Dilution vials: 20mL capacity, used to prepare analytical dilutions.

7.10 Kimwipes

7.11 Canned air

7.12 Whatman 41 filter paper

8. Reagents and Standards

8.1 Reagent Water: Reagent water is DI water shown to be interference free. All references to water in this method will refer to reagent water unless otherwise specified.

8.2 Sulfuric acid (H_2SO_4), concentrated: Reagent grade. Store at room temperature in an appropriately designated acid cabinet.

8.3 Hydrochloric acid, concentrated: Trace Metal grade. Store at room temperature in an appropriately designated acid cabinet.

8.4 Carrier, Hydrochloric Acid, 3%: This is the ***carrier*** for the PE FIMS Instrument. In a 1L volumetric flask, add 30mL concentrated trace grade HCl (Section 8.3). Bring to volume with reagent water. Store at room temperature, prepare daily as needed.

8.5 Reductant, Stannous Chloride in 3% HCl: This is the ***reductant*** for the PE FIMS Instrument. In a 1L volumetric flask, add 30mL concentrated trace grade HCl and 11g $SnCl_2 \cdot 2H_20$. Mix to dissolve the solid and bring to volume with reagent water. Store at room temperature, prepare daily as needed.

8.6 Nitric acid (HNO_3), concentrated: Trace metal grade of low mercury content. If a high reagent blank is obtained, it may be necessary to distill the nitric acid. Store at room temperature in an appropriately designated acid cabinet.

8.7 Sodium chloride-hydroxylamine hydrochloride solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine hydrochloride in reagent water and dilute to 100mL. Store at room temperature. Expires one month from date of preparation.

8.8 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of reagent water. Store at room temperature. Expires one month from date of preparation.

8.9 Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate in 100 mL of reagent water. Store at room temperature. Expires one month from date of preparation.

8.10 Mercury Stock Standard, 1000ppm: Purchased from a commercial source with a certificate of analysis. Purchase three different sources. Store at room temperature. Expires upon manufacturer's specification.

8.11 Mercury Stock Calibration Standard, 10ppm: To a 100mL volumetric flask, add 5mL of concentrated HNO_3 and 1mL of 1000ppm Mercury Stock Standard (Section 8.10, use one source). Bring to volume with reagent water. Store at room temperature. Expires one month from date of preparation.

8.12 Mercury Working Calibration Standard / Matrix Spike Solution, 0.1ppm: To a 500mL volumetric flask, add 25mL of concentrated HNO_3 and 5mL of 10ppm Mercury Stock Standard (Section 8.11). Bring to volume with reagent water. Store at room temperature. Expires one week from date of preparation.

8.13 Mercury Calibration Standards: All calibration standards are prepared daily.

8.13.1 0 ppm Calibration Standard: To a 200mL volumetric flask, add 10mL of concentrated HNO_3 (Section 8.6). Bring to volume with reagent water.

8.13.2 0.0002ppm Calibration Standard: To a 250mL volumetric flask, add 0.5mL of 0.1ppm Working Standard (Section 8.12) and 12.5mL of concentrated HNO_3 (Section 8.6). Bring to volume with reagent water.

8.13.3 0.0005ppm Calibration Standard: To a 100mL volumetric flask, add 0.5mL of 0.1ppm Working Standard (Section 8.12) and 5.0mL of concentrated HNO_3 (Section 8.6). Bring to volume with reagent water.

8.13.4 0.001ppm Calibration Standard: To a 100mL volumetric flask, add 1.0mL of 0.1ppm Working Standard (Section 8.12) and 5.0mL of concentrated HNO_3 (Section 8.6). Bring to volume with reagent water.

8.13.5 0.002ppm Calibration Standard: To a 100mL volumetric flask, add 2.0mL of 0.1ppm Working Standard (Section 8.12) and 5.0mL of concentrated HNO_3 (Section 8.6). Bring to volume with reagent water.

8.13.6 0.005ppm Calibration Standard/Continuing Calibration Verification Standard: To a 200mL volumetric flask, add 10mL of 0.1ppm Working Standard (Section 8.12) and 10mL of concentrated HNO_3 (Section 8.6). Bring to volume with reagent water.

8.13.7 0.010ppm Calibration Standard / Post Analytical Spike Solution: To a 100mL volumetric flask, add 10mL of 0.1ppm Working Standard (Section 8.12) and 5.0mL of concentrated HNO_3 (Section 8.6). Bring to volume with reagent water.

8.14 Mercury Stock LCS Standard, 10ppm: To a 100mL volumetric flask add 25mL of reagent water and 5mL of concentrated HNO_3 (Section 8.6). Add 1mL of 1000ppm Mercury Stock Standard (Section 8.10, use alternate source than that used for the calibration standards). Bring to volume with reagent water. Store at room temperature. Expires one month from date of preparation.

8.15 Mercury Working LCS Standard, 0.1ppm: To a 100mL volumetric flask add 25mL of reagent water and 5mL concentrated HNO_3 (Section 8.6). Add 1mL of 10ppm Stock LCS Standard (Section 8.14). Bring to volume with reagent water. Store at room temperature. Expires one week from date of preparation.

8.16 Mercury LCS Standard, 0.001ppm: Prepare daily with each batch of samples. To a 100mL volumetric flask add 25mL of reagent water and 5mL concentrated HNO_3 (Section 8.6). Add 1mL of 0.1ppm Working LCS Standard (Section 8.15). Bring to volume with reagent water. A 25mL aliquot of this standard is treated for the LCS as in Section 10.1.1.

8.17 Mercury Stock ICV Standard, 10ppm: To a 100mL volumetric flask add 25mL of reagent water and 5mL of concentrated HNO_3 (Section 8.6). Add 1mL of 1000ppm Mercury Stock Standard (Section 8.10, use alternate source than that used for both the calibration standards and the LCS Stock Standard). Bring to volume with reagent water. Store at room temperature. Expires one month from date of preparation.

8.18 Mercury Working ICV Standard, 0.3ppm: To a 100mL volumetric flask add 25mL of REAGENT water and 5mL of concentrated HNO_3 (Section 8.6). Add 3mL of 10ppm Stock ICV Standard (Section 8.17). Bring to volume with reagent water. Store at room temperature. Expires one week from date of preparation.

8.19 Mercury ICV Standard, 0.003ppm: Prepare daily with each batch of samples. To a 100mL volumetric flask add 25mL of reagent water and 5mL of concentrated HNO_3 (Section 8.6). Add 1mL of 0.3ppm Working ICV Standard (Section 8.18). Bring to volume with reagent water. A 25mL aliquot of this standard is treated for the ICV as in Section 10.1.1.

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blank(s)

The ICB, CCB, and Preparatory Blank: A 25mL aliquot of 0ppm calibration standard brought through the preparation procedure as outlined in Section 10.1.1 . Blank results must be <RL. See Section 12.1 for corrective action.

9.2 Laboratory Control Samples (LCS)

The LCS Standard consists of a 25mL aliquot of 0.001ppm Mercury LCS Standard (Section 8.16). This standard is brought through the preparation procedure as outlined in Section 10.1.1. The LCS Standard must be recovered within ± 20% of the true value. See Section 12.3 for corrective action.

9.3 Initial Calibration verification (ICV)

The ICV Standard consists of a 25mL aliquot of 0.003ppm Mercury ICV Standard (Section 8.19). This standard is brought through the preparation procedure as outlined in Section 10.1.1. The ICV must be recovered within 10% of the true value. See Section 12.2 for corrective action.

9.4 Continuing Calibration Verification (CCV)

The CCV Standard consists of a 25mL aliquot of 0.005ppm calibration standard (Section 8.13.6). This standard is brought through the preparation procedure as outlined in Section 10.1.1. The CCV must be recovered within 20% of the true value. See Section 12.2 for corrective action.

9.5 Matrix Spike

To perform the matrix spike, add 0.25mL of the 0.1ppm Working Calibration/Matrix Spike Standard (Section 8.12), to a 25mL aliquot of sample. The final concentration of the matrix spike is 0.001mg/L.

The matrix spike sample is brought through the preparation procedure as outlined in Section 10.1. A matrix spike is analyzed once per batch of samples. A batch consists of 20 samples for monitoring wells and surface waters. The recovery of the matrix spike must be between 70 – 130% (using the calculation in Section 11.2).

If the recovery of the matrix spike is out of range, a post-analytical spike is analyzed. Prepare the post analytical spike by adding 5mL of 0.010ppm Calibration Standard / Post Analytical Spike Solution (Section 8.13.7) and 5mL of the sample digestate to a 50mL centrifuge tube for a final concentration of 0.005mg/L. Analyze the post spike as outlined in Section 10.3.5.

Calculate the post spike concentration as follows:

Post Analytical Spike Sample Concentration (mg/L) =

[Sample Concentration (mg/L) x (0.5)] + 0.005mg/L

The percent recovery of the post-analytical spike must be between 75 – 125%. See Section 12.4 for corrective action.

9.6 Laboratory Duplicate

A sample is analyzed in duplicate once per batch of samples. A batch consists of 20 samples for monitoring wells and surface waters. The RPD between the sample and its duplicate must be 20% or less (using the calculation in Section 11.3), See Section 12.5 for corrective action.

9.7 Method-specific Quality Control Samples

Not applicable.

9.8 Method Sequence

- Calibration Blank
- 0.0002 ppm Calibration Standard
- 0.0005 ppm Calibration Standard

- 0.001 ppm Calibration Standard
- 0.002 ppm Calibration Standard
- 0.005 ppm Calibration Standard
- 0.010 ppm Calibration Standard
- ICV
- ICB
- Ten analytical samples
- CCV
- CCB
- Ten analytical samples
- CCV
- CCB
- Etc.

10. Procedure

10.1 Equipment Set-up

10.1.1 Preparation and Digestion

Samples, Standards and All Batch QC

Transfer 25mL of well-homogenized sample (or an aliquot of the sample diluted to 25mL with reagent water) or standards (Sections 8.13.1 through 8.13.7, 8.16 and 8.19) to a 50mL centrifuge tube.

Add 1.25mL of concentrated H_2SO_4 (Section 8.2), 0.625mL of concentrated HNO_3 (Section 8.6), 2mL of Potassium Persulfate Solution (Section 8.9), and 3.75mL of Potassium Permanganate Solution (Section 8.8).

Heat samples for 2 hours in a 95°C waterbath. Cool, and add 1.5mL of Sodium Chloride-Hydroxylamine hydrochloride solution (Section 8.7).

Filter the sample if needed to remove any sediment or particulate.

Analyze samples using the PE FIMS 100 as outlined in Section 10.4. The digested calibration standards (Sections 8.13.1 through 8.13.7) are used in Section 9.2 to generate a calibration curve on the PE FIMS Instrument.

10.2 Initial Calibration

Construct a calibration curve by plotting the absorbances of prepared standards (Section 10.1.1) versus micrograms of mercury. Determine the peak height of the unknown from the absorbance maxima on the spectrometer, and read the mercury value from the standard curve. (See Section 11.)

The curve correlation coefficient (cc) must be greater than or equal to 0.995 in order for the curve to be linear. If the correlation coefficient is less than 0.995, find and correct the problem. When the problem has been corrected, re-analyze either the previous standards or new standards. When the curve has generated an acceptable cc then the analysis can continue with the ICV/ICB.

10.3 Equipment Operation and Sample Processing

Sample and standard analysis using the Perkin Elmer FIMS 100:

10.3.1 Instrument Setup

10.3.1.1 Turn the instrument on by flipping the power switch on the face of the instrument. The autosampler will initialize itself.

10.3.1.2 Choose AA Winlab Analyst from the START menu. The autosampler will initialize again.

NOTE: The instrument must be turned on before the application is started. Otherwise, an error message will result.

10.3.1.3 Click the button next to "open a custom workspace".

10.3.1.4 Select "startup.fms" from the list and click OPEN. This will open the "FIAS Control" and "Automated Analysis" windows.

10.3.1.5 Click on the "Analyze" tab in the Automated Analysis window, then click on the "Select Location" button. Click OK and the probe will go to the autosampler rinse.

10.3.1.6 Fill the carrier and reductant bottles.

10.3.1.6.1 The Carrier is 3% HCl (Section 8.4).

10.3.1.6.2 The Reductant is 1.1% $SnCl_2$ in 3% HCl (Section 8.5).

10.3.1.7 Allow the instrument to warm up while clearing samples. Samples that are cloudy or with particulate present after clearing must be filtered through Whatman 41 filter paper (Section 7.12) before analysis.

10.3.1.8 Place carrier uptake line (blue/yellow tubing, Section 7.7) and reductant uptake line (red/red tubing. Section 7.7) into graduated cylinders containing reagent water.

10.3.1.9 Load carrier and reductant lines into pump magazines above the roller so that the long ends come out on the right side. The carrier line goes into the inner magazine, and the reductant line goes into the outer magazine.

10.3.1.10 Load the two waste lines into the pump magazines below the roller.

10.3.1.10.1 The blue/yellow line goes into the inner two-channel magazine so that the long end comes out on the left side.

10.3.1.10.2 The black line goes into the outer magazine so that the long end comes out on the right side

10.3.1.11 Lock both the top and bottom magazines into place.

10.3.1.12 Unscrew the fitting from the sample absorption cell leading to the liquid vapor separator and place it into an empty dilution-vial (Section 7.9).

10.3.1.13 Click the "Pump1" button in the "FIAS Control" window to start the roller.

10.3.1.14 Adjust the tension on the lower pump magazine using the thumbscrews until a steady (but not too fast) stream of bubbles comes out of the liquid vapor separator and through the black tubing.

10.3.1.15 Adjust the tension on the upper pump magazines to obtain the following flow rates:

10.3.1.15.1 Carrier = 9 – 11 mL/minute

10.3.1.15.2 Reductant = 5 – 7 mL/minute

10.3.1.16 When the flow rates are set, click on the "Pump1" button to stop the roller.

10.3.1.17 Place carrier uptake line in the carrier bottle and reductant line in the reductant bottle.

10.3.1.18 Click the "Pump1" button to restart the roller. Allow to run for a couple of minutes to flush the reagent water from the lines. Click on the "Fill/Inject" button several times to flush the sample loop.

10.3.1.19 With the "Fill/Inject" button in the "Fill" position, (button not depressed), click the "Pump1" button to stop the roller.

10.3.1.20 Remove the cap from the liquid/vapor separator and wipe dry with a KimWipe (Section 7.10). Blow canned air (Section 7.11) through the vapor transfer line to dry it out.

10.3.1.21 Place a PTFE membrane (Section 7.8), rough side up, in the liquid/vapor separator; replace the cap and reattach the vapor transfer line to the sample absorption cell.

10.3.1.22 Click on the "Pump1" button to start the roller.

10.3.1.23 Adjust the gas flow by turning the black knob below the air flow meter to obtain a reading of just over 50.

10.3.1.24 Click on the "Pump1" button to stop the roller.

10.3.2 Creating a Sample Information File and Loading the Sample Tray

10.3.2.1 Click the "SampInfo" button on the toolbar.

10.3.2.2 In the description line, type "prep date MM/DD/YY".

10.3.2.3 In the analyst line, type the analyst's initials.

10.3.2.4 Drag the scroll bar so that the autosampler location 12 is showing.

10.3.2.5 Double-click the "Sample Units" cell in line 12.

10.3.2.6 Select "µg/L" from the list and enter the range of locations (12 up to 44) and click OK.

10.3.2.7 Starting with position 12, type in the sample ID

10.3.2.8 When finished, choose "Save As" from the "File" menu, then choose the "Sample Information" file.

10.3.2.9 Save the file as MMDDYYA

10.3.2.10 Load the samples into the tray as follows:

Position 1	Calibration Blank
Position 2	0.2ppb Standard
Position 3	0.5ppb Standard
Position 4	1.0ppb Standard

Position 5 2.0ppb Standard

Position 6 5.0ppb Standard

Position 7 10.0ppb Standard

Position 8 ICV

Position 9 ICB

Position 10 CCV

Position 11 CCB

Position 12 PBW listed in the sample information file.

Position 13 LCSW listed in the sample information file.

Positions 14 – 44 Samples as listed in the sample information file.

10.3.2.11 Click the "Load Tray" button.

10.3.2.12 Replace the empty tray with the tray containing the standards and samples.

10.3.2.13 Click the "Load Tray" button.

10.3.2.14 Click the "Select Location" button and click OK to lower the probe into the autosampler rinse.

10.3.3 Instrument Calibration

10.3.3.1 Click the "Workspace" button in the toolbar.

10.3.3.2 Select daves.fms and click OK.

10.3.3.3 Click on the Setup tab in the automated analysis window.

10.3.3.4 Click the "Browse" button under "Sample Information File"

10.3.3.4.1 Select the sample information file that you want to open and click OK.

10.3.3.5 Click the "Browse" button under "Results Data Set Name".

10.3.3.5.1 Type in the data set name in the format MMDDYYA and click OK.

10.3.3.6 Click the "X" under the "Use Entire Sample Info File" so that it disappears.

10.3.3.7 Under the "Use Autosampler Locations Listed Below", enter the order of samples to be run. NOTE: Do not include standards and QC checks.

10.3.3.8 Click the "Analyze" tab.

10.3.3.9 Click the "Calibrate' button

10.3.3.9.1 The instrument will run the calibration curve.

10.3.3.9.2 Watch the calibration blank run; if the readings vary widely, stop the run by clicking the "Calibrate" button.

10.3.4 Initial Calibration Verification

10.3.4.1 When the calibration is complete (6 – 7 minutes) and has a r^2 of 0.995 or better, click the "Analyze Samples" button.

10.3.4.1.1 The instrument will run the ICV and ICB. If the recoveries of these are within the proper ranges (Sections 9.3 and 9.1), the instrument will continue with analysis of samples as outlined in Section 10.3.5.

10.3.4.1.2 If the recoveries of the ICV and/or ICB are not within the proper ranges (Sections 9.3 and 9.1), the problem must be found and corrected, and the instrument recalibrated per Section 10.3.3.

10.3.5 Sample Analysis

10.3.5.1 The instrument will now run ten analytical samples, a CCV and CCB, ten analytical samples, CCV, CCB, etc. The CCBs and CCVs must be recovered within the proper ranges (Sections 9.1 and 9.4) for analysis to continue.

10.3.5.2 If the recoveries of the CCB and/or CCV are not within the proper ranges (Sections 9.1 and 9.4), the instrument must be recalibrated per Section 10.3.3. The samples that were analyzed after the last valid CCV/CCB must be re-analyzed.

10.3.5.3 If the sample result is beyond the concentration of the highest point on the calibration curve, dilute the sample extract with a portion of one of the prepared blanks (ICB, CCB or PWB) to produce an analytical result that is within the calibration range.

10.3.6 Instrument Shut Down

10.3.6.1 When analysis is complete, click the “Workspace” button in the toolbar.

10.3.6.2 Place reagent uptake lines in a beaker of reagent water.

10.3.6.3 Click on the “Analyze” tab.

10.3.6.4 Click on the “Pump1” button to start the roller

10.3.6.4.1 Allow to run for several minutes to flush reagents out of the lines.

10.3.6.4.2 Click on the “Fill/Inject” button several times to rinse the sample loop.

10.3.6.5 Click the “Move Probe Up/Down” button to raise the probe out of the autosampler rinse.

10.3.6.6 Pull the reagent uptake lines out of the reagent water beaker to allow the pump to draw air through the lines.

10.3.6.7 Click “Fill/Inject” button several times to pull air through the sample loop.

10.3.6.8 With the “Fill/Inject’ button in the “Fill” position, click “Pump1” button to stop roller.

10.3.6.9 Unlock the top and bottom pump magazines and remove tubing from the magazines.

10.3.6.10 Return the reagent uptake lines to the reagent water beaker.

10.3.6.11 Click the “Move Probe Up/Down” button to lower the probe into the rinse beaker.

10.3.6.12 Select “EXIT” from the File menu to exit the WinLab application.

10.3.6.12.1 A “Shutting Down System” message will display.

10.3.6.13 When the desktop appears, turn off the power switch on the instrument.

10.3.6.14 Dump the samples and instrument waste in the Metals/WetChem waste drum located in the transfer room.

10.4 Continuing Calibration

Continuing calibration verification samples are analyzed after every 10 samples in the sample run, as outlined in Section 10.3.5.

10.5 Preventative Maintenance

Preventative maintenance is conducted per the manufacturer's instructions. All preventative maintenance is recorded in the Instrument Maintenance Logbook.

11. Data Evaluation, Calculations and Reporting

11.1 Calculate Mercury concentration

Calculate Mercury concentration from the daily calibration curve. The curve is generated utilizing a straight-line equation defined as:

$$A = k_1 + k_2C$$

Where:

A = Average peak height of the sample/standard integrations
C = Sample/Standard Concentration, µg/L
k_1 = y-intercept
k2 = slope

The instrument will plot peak height against concentration (µg/L). The result is generated in µg/L . This value is divided by 1000 to convert the units to mg/L. If the sample is diluted (DF), the result is multiplied by the DF to generate the final result.

Result, mg/L = (concentration, µg/L) x (1mg/1000µg) x (DF)

11.2 Matrix Spike Calculation

Calculate percent recovery for the Matrix Spike corrected for concentrations measured in the unfortified sample. Percent recovery is calculated using the following equation:

$$\% \text{ Recovery} = \frac{(Cm - C)}{s} \times 100$$

Where:

Cm = measured Mercury in the fortified sample
C = measured native mercury sample concentration
S = concentration equivalent of spike added to sample

11.3 Relative Percent Difference (RPD) Calculation

Calculate the Relative Percent Difference (RPD) for each Duplicate of the initial quantitated concentration (IC) and duplicate quantitated concentration (Dc) using the following formula:

$$RPD = \frac{|(IC - Dc)|}{\{(IC + Dc) / 2\}} \times 100$$

12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

12.1 Method Blank Failure: When a prep blank mercury level constitutes 10% or more of analyte level determined for any sample in the batch, or is greater than 2.2x the MDL value (whichever is greater), the associated samples in the batch must be redigested (Section 10.1).

For method blanks that have concentrations greater than the RL, the data is rejected and the associated samples sent back for redigestion unless the associated sample concentrations are greater than 10x the blank concentration. In this case the blank is narrated and the results are reported without qualification.

12.2 ICV / CCV Failure: If the ICV %Recovery is outside of acceptance criteria, the ICV is reinjected immediately. If the %Recovery is outside the acceptance criteria, the analysis is terminated until the problem is found and corrected. If the CCV %Recovery is outside of acceptance criteria, the CCV is reinjected immediately. If the % Recovery is outside the acceptance criteria, all samples analyzed since the last acceptable CCV must be reanalyzed following correction of the problem.

12.3 LCS Failure: If the LCS is not recovered within acceptance criteria, the LCS is reinjected. If the % Recovery is still outside the acceptance criteria, the associated batch and another LCS must be redigested (Section 10.1).

12.4 Matrix Spike / Post Digestion Spike Failure: If the recovery of the matrix spike is outside of the acceptance criteria, a post digestion spike is performed (Section 9.54). If the post digestion spike is beyond 75 – 125%, the sample and its spike are redigested (Section 10.1).

12.5 Duplicate Failure: If the RPD between the sample and its duplicate is greater than 20%, visually evaluate the sample matrix. If the sample matrix appears clean, the sample and its duplicate are removed from the batch and redigested (Section 10.1). If the matrix appears problematic, the sample digestate may be diluted and reanalyzed, or a narrative included with the data to explain the matrix problem.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/08-05. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP/08-12 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

SOP/08-05 MDL/LOD/LOQ Generation

SOP/08-12 IDC/DOC Generation

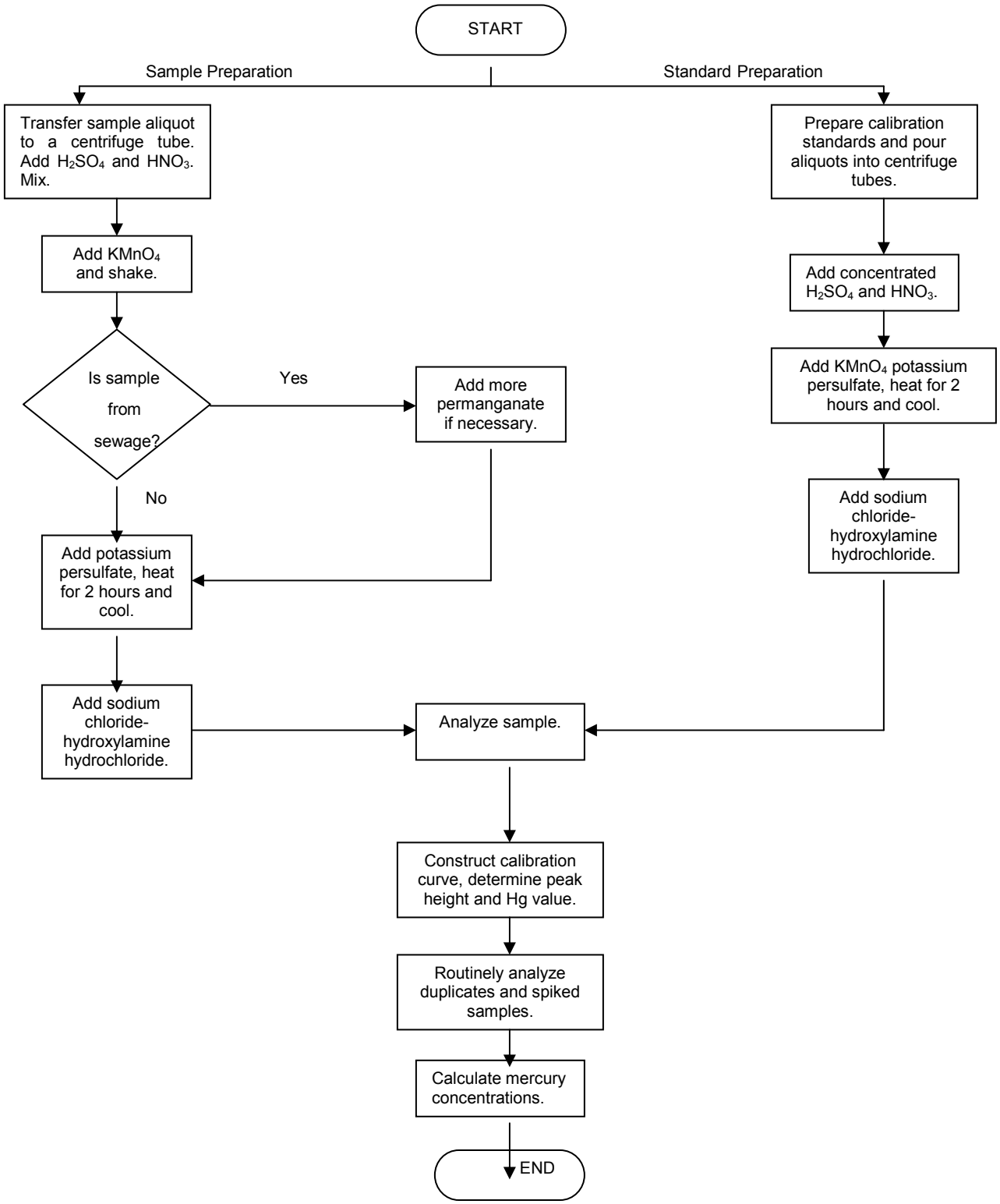
SOP/14-01 Waste Management and Disposal SOP

16. Attachments

Figure 1: Method 7470A Flow Chart

Figure 1

Method 7470A Flow Chart



Nitrate, Nitrite and Nitrate/Nitrite Nitrogen

Automated Cadmium Reduction Method

References: **Methods 353.2:** Methods for the Determination of Inorganic Substances in Environmental Samples, EPA 600/ R-93/ 100. August, 1993.

Methods 4500NO_3-F, 4500NO_2-B: Standard Methods for the Examination of Water and Wastewater, APHA-AWWA-WPCF, 21st Edition, 2000.

Method 10-107-04-1, Lachat Instruments, 6645 West Mill Road, Milwaukee, WI 53218, 1992.

1. Scope and Application

Matrices: This method is limited to optically clear water samples with a total concentration of nitrite and nitrate below 8mg N/L.

Definitions: See Alpha Laboratories Quality Manual Appendix A

In waters and wastewaters, the forms of nitrogen of greatest interest are, in order of decreasing oxidation state, nitrate, nitrite, ammonia, and organic nitrogen. All these forms of nitrogen, as well as nitrogen gas (N_2), are biochemically interconvertible and are components of the nitrogen cycle. They are of interest for many reasons.

Organic nitrogen is defined functionally as organically bound nitrogen in the trinegative oxidation state. It does not include all organic nitrogen compounds. Analytically, organic nitrogen and ammonia can be determined together and have been referred to as “kjeldahl nitrogen,” a term that reflects the technique used in their determination. Organic nitrogen includes such natural materials as proteins and peptides, nucleic acids and urea. Numerous concentrations vary from a few hundred micrograms per liter in some lakes to more than 20mg/L in raw sewage.

Total oxidized nitrogen is the sum of nitrate and nitrite nitrogen. Nitrate generally occurs in trace quantities in surface water but many attain high levels in some groundwater. In excessive amounts, it contributes to the illness known as methemoglobinemia in infants. A limit of 10mg nitrate as nitrogen/L has been imposed on drinking water to prevent this disorder. Nitrate is found only in small amounts in fresh domestic wastewater but in the effluent of nitrifying biological treatment plants, nitrate may be found in concentrations of up to 30mg nitrate as nitrogen/L. It is an essential nutrient for many photosynthetic autotrophs and has been identified as a growth-limiting nutrient.

Nitrite is an intermediate oxidation state of nitrogen, both in the oxidation of ammonia to nitrate and in the reduction of nitrate. Such oxidation and reduction may occur in wastewater treatment plants, water distribution systems, and natural waters. Nitrite can enter a water supply system through its use as a corrosion inhibitor in industrial process water. Nitrite is the actual etiologic agent of methemoglobinemia. Nitrous acid, which is formed from nitrite in acidic solution, can react with secondary amines (RR’NH) to form nitrosamines (RR’N-NO), many of which are known to be carcinogens. The toxicologic significance of nitrosation reactions in vivo and in the natural environment is the subject of much current concern and research.

Within this SOP, organic nitrogen is referred to as organic N, nitrate nitrogen as NO_3^--N, and nitrite nitrogen as NO_2^--N.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the

laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one of the following laboratory personnel before performing the modification: Area Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of analysts experienced in the operation of the Lachat Analyzer and in the interpretation of Lachat data. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability, analyzing a proficiency test sample and completing the record of training.

After initial demonstration, ongoing demonstration is based on acceptable laboratory performance of at least a quarterly laboratory control sample or acceptable performance from an annual proficiency test sample. A major modification to this procedure requires demonstration of performance. The identification of major method modification requiring performance demonstration is directed by the QA Officer and/or Laboratory Director on a case-by-case basis.

2. Summary of Method

Nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl)ethylenediamine dihydrochloride. The resulting water-soluble dye has a magenta color, which is read at 520nm. Nitrite alone can be determined by removing the cadmium column. The nitrate is calculated as the difference between the reduced and non-reduced sample.

2.1 Method Modifications from Reference

Soils can be analyzed using 1:10 ratio soil to water extraction, following filtration.

3. Detection Limits

This method has an analytical range of 0.1 to 8.0mg N/L in the form of nitrate, and 0.05 to 8.0mg N/L in the form of nitrite.

The Reporting Limit is 0.1mg/L for Nitrate and 0.05 mg/L for Nitrite. Reporting limit is 1.0 mg/kg for soils.

4. Interferences

4.1 Suspended matter in the column will restrict sample flow.

4.2 For turbid samples, filter through 0.45µm membrane filter prior to analysis.

4.3 Low results would be obtained for samples that contain high concentrations of iron, copper or other metals. In this method, EDTA is added to the buffer to reduce this interference.

4.4 Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. In this case, only the water phase of the sample is used for analysis and a narrative is submitted with the data. Dilutions are performed as necessary.

4.5 Residual chlorine can interfere by oxidizing the Cd column, reducing its efficiency. Prior to analysis, check wastewater and drinking water samples for residual chlorine and record results in the Laboratory Notebook. If residual chlorine is present, and the samples are preserved with H_2SO_4, the sample may be analyzed for NO_3/NO_2 determination. However,

NO_2 must be performed by a manual method. If it is not possible to analyze NO_2 by a manual method, the result is reported as NA and a narrative is submitted.

4.6 Sample color interferes if it is absorbed at about 540nm.

5. Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

6. Sample Collection, Preservation, and Handling

6.1 Sample Collection

Samples are collected in glass or plastic bottles; 250mL minimum volume. Soils can be collected in plastic or glass containers.

6.2 Sample Preservation

Refrigerate samples at 4 ± 2 °C.

For Nitrate/Nitrite analysis, the samples are preserved with 1:1 H_2SO_4.

6.3 Sample Handling

Begin NO_3^- and/or NO_2^- determinations promptly after sampling. If storage is necessary, store for up to 48 hours at 4 ± 2 °C.

NOTE: If the 48-hour hold time cannot be met, the sample is to be handled as follows, only in an emergency situation. These instructions are not to be used on a regular basis.

Prior to the expiration of the 48-hour hold time, the following three steps are executed:

1. A manually colored Nitrite test is performed by Method 354.2. Results are recorded in the Laboratory Notebook.
2. A 50mL aliquot of the sample is preserved to a pH of <2 with concentrated H_2SO_4. Preservation is recorded in the Laboratory Notebook.

Prior to analysis, within 14 days of preservation, the preserved sample is neutralized using 6N NaOH. The sample is analyzed using only the Lachat Instrument.

CAUTION! Samples must NOT be preserved with mercuric chloride or thiosulfate because this will degrade the cadmium column.

7. Equipment and Supplies

7.1 Lachat 8000 Automated Ion Analyzer

7.2 Nitrate+Nitrite Lachat Board

7.3 Nitrite Lachat Board

7.4 Pre-packed Cadmium Columns: Available from Lachat.

7.5 Ottawa sand.

8. Standards and Reagents

8.1 Stock Nitrate Standard, 1000mg N/L as NO_3^-: Purchased commercially prepared with certificate of analysis. Expires upon manufacturer's expiration date. There must be different manufacturers for calibration stock and ICV/LCS stock.

8.1.1 Stock Nitrate Standard, 200.0mg N/L as NO_3^-: Pipet 50mL of 1000ppm standard (Section 8.1) into 250mL volumetric flask and bring to volume with DI.

Alternately, in a 1L volumetric flask, dissolve 1.444g potassium nitrate (KNO_3) in about 600mL DI. Add 2mL chloroform. Dilute to the mark with DI and invert to mix. Refrigerate at 4±2°C. This solution is stable for six months.

8.2 Stock Nitrite Standard, 1000mg N/L as NO_2^-: Purchased commercially prepared with certificate of analysis. Expires upon manufacturer's expiration date. There must be different manufacturers for calibration stock and ICV/LCS stock.

8.2.1 Stock Nitrite Standard, 200.0mg N/L as NO_2^-: Pipet 50mL of 1000ppm standard (Section 8.2) into 250mL volumetric flask and bring to volume with DI.

Alternately, in a 1L volumetric flask, dissolve 0.986g sodium nitrite ($NaNO_2$) or 1.214g potassium nitrite (KNO_2) in approximately 800mL DI. Add 2mL chloroform. Dilute to the mark with DI and invert to mix. Refrigerate at 4±2°C. This solution is stable for six months.

8.3 Intermediate Nitrate Working Standard, 20 mg N/L as Nitrate: To a 250mL volumetric flask, add 25.0mL of the 200mg N/L NO_3^- stock standard. Dilute to the mark with DI and invert to mix. These solutions are stable for two weeks. Refrigerate at 4±2°C.

8.4 Intermediate Nitrite Working Standard, 20 mg N/L as Nitrite: To a 250mL volumetric flask, add 25.0mL of the 200mg N/L NO_2^- stock standard. Dilute to the mark with DI and invert to mix. These solutions are stable for two weeks. Refrigerate at 4±2°C.

8.5 Set of Six Calibration NO_3^- Standards, 8.0, 4.0, 1.00, 0.40, 0.20 and 0.1mg N/L as Nitrate: These standards are stable for 2 weeks. Refrigerate at 4±2°C.

To four 200mL volumetric flasks, add respectively: 8.0, 4.0, 1.0 and 0.4mL of the 200mg N/L NO_3^- stock standard. Bring to volume with DI water.

To two 200mL volumetric flasks, add respectively: 2.0 and 1.0mL of the 20mg N/L NO_3^- intermediate standard. Bring to volume with DI water.

Alternatively, an autodiluter can be used to make the standards during calibration, in which case only 8.0ppm and 1.0 ppm need to be manually prepared. If an autodiluter is used then it must be checked in an analytical tray by autodiluting 8.0mg N/L as Nitrite. The recovery for NO2 must be within 10% of the true value.

8.6 Set of Six Calibration NO_2^- Standards, 8.0, 4.0, 1.00, 0.40, 0.10 and 0.05mg N/L as Nitrite: These standards are stable for 2 weeks. Refrigerate at 4±2°C.

To three 200mL volumetric flasks, add respectively: 8.0, 4.0 and 1.0 of the 200mg N/L NO_2^- stock standard. Bring to volume with DI water.

To three 200mL volumetric flasks, add respectively:4.0, 1.0mL and 0.5mL of the 20mg N/L NO_2^- intermediate standard. Bring to volume with DI water.

Alternatively, an autodiluter can be used to make the standards during calibration, in which case only 8.0ppm and 1.0 ppm need to be manually prepared.

8.7 Ammonium Chloride Buffer, pH 8.5: In a 2L volumetric flask, dissolve 170g ammonium chloride (NH_4Cl) and 2.0g disodium ethylenediamine tetraacetic acid dihydrate ($Na_2EDTA•2H_2O$) in about 800mL water. Dilute to the mark with DI water and invert to mix. Adjust the pH to 8.5 with concentrated ammonium hydroxide. This solution is prepared monthly and stored at room temperature.

8.8 Sulfanilamide Color Reagent: To a 2L volumetric flask add about 1200mL water. Then add 200mL of 85% phosphoric acid (H_3PO_4), 80.0g sulfanilamide, and 2.0g N^-(1-naphthyl)ethylenediamine dihydrochloride (NED). Shake to wet, and stir to dissolve for 30 minutes. Dilute to the mark with DI water and invert to mix. Store in a dark bottle. This solution is stable for one month. Store at room temperature.

8.9 200ppm Nitrate Stock Standard, (for ICV/LCS): Pipet 50mL of 1000ppm standard (Section 8.1) into 250mL volumetric flask and bring to volume with DI. Store refrigerated at 4±2°C. Expires six months from preparation or upon manufacturer's expiration date.

8.10 200ppm Nitrite Stock Standard: Pipet 50mL of 1000ppm standard (Section 8.2) into 250mL volumetric flask and bring to volume with DI. Store refrigerated at 4±2°C. Expires six months from preparation or upon manufacturer's expiration date.

8.11 Initial Calibration Verification Standard (ICV)/Laboratory Control Sample (LCS): Store refrigerated at 4±2°C. Expiration is 2 weeks from date of preparation.

8.11.1 Nitrate LCS, 5.0ppm: Pipet 5.0mL of 200ppm stock (Section 8.9) into a 200mL volumetric flask and bring to volume with DI.

8.11.2 Nitrate ICV, 0.5ppm: Pipet 10.0mL of 5.0ppm standard (Section 8.11.1) into a 100mL volumetric flask and bring to volume with DI.

8.11.3 Nitrite LCS, 5.0ppm: Pipet 5.0mL of 200ppm stock (Section 8.9) into a 200mL volumetric flask and bring to volume with DI.

8.11.4 Nitrite ICV, 0.5ppm: Pipet 10.0mL of 5.0ppm standard (Section 8.11.3) into a 100mL volumetric flask and bring to volume with DI.

8.12 DPD Free Chlorine Reagent Powder Pillows: HACH brand, for 25mL sample. Store at room temperature. Expires upon manufacturer's expiration date.

9. Procedure

9.1 SET-UP

9.1.1 Preparation

9.1.1.1 Place the Nitrate+Nitrite board (containing the cadmium column) in Channel 1. Place the Nitrite board in Channel 2. Make sure the valve to the cadmium column is closed prior to starting to pump the reagents.

9.1.1.2 Commence pumping of reagents.

9.1.1.3 Once the lines are full of reagent and free of gas bubbles, open the valve to allow reagent to flow through the cadmium column.

NOTE: Be sure to switch the valve back before rinsing the manifold with DI water at the completion of the run.

NOTE: DO NOT LET AIR ENTER THE CADMIUM COLUMN.

9.1.2 Column Efficiency Procedure

9.1.2.1 Visually inspect the column. Check for air bubbles in the column or lines, gaps in the column or any change in the cadmium surface characteristics, (cadmium granules should be dark gray). If air bubbles are present in column, connect the column into the manifold, turn the pump on maximum and tap firmly with a screwdriver handle, being careful not to break the column, working up the column until all air is removed. If air cannot be removed, the column should be repacked. Cadmium columns should be stored filled with buffer. If air enters the column, efficiency will decrease. Check the flow efficiency by disconnecting the cadmium column from the manifold and reconnecting to a green pump tube. Pump buffer through the packed column and collect in a graduated cylinder. The flow rate with the column connected should be greater than 4.0 mL/minute.

9.1.2.2 **Column Efficiency – Slope Ratio Method:** Calibrate with the mid-range NO_3 –N standards. Calibrate with a matching concentration range of NO_2–N standards. The column efficiency is determined by the equation:

$$E = \frac{S_{NO3\text{-}N}}{S_{NO2\text{-}N}} \times 100$$

where:

$S_{NO3\text{-}N}$ = slope of NO_3 calibration
$S_{NO2\text{-}N}$ = slope of NO_2 calibration
E = % efficiency

9.1.2.3 **Column Efficiency – Concentration Ratio Method:** Calibrate with the mid-range NO_2-N and NO_3-N standards. Run a known concentration NO_2-N standard. Run a matching concentration NO_3-N standard. The column efficiency is determined by the following equation:

$$E = \frac{C_{NO3\text{-}N}}{C_{NO2\text{-}N}} \times 100$$

where:

$C_{NO3\text{-}N}$ = concentration of NO_3 standard
$C_{NO2\text{-}N}$ = concentration of NO_2 standard
E = % efficiency

9.1.2.4 Column Efficiency Result: If the efficiency is <75%, the column is repacked. All results are recorded and maintained on file in the QC department.

9.1.3 Residual Chlorine Screening

Check all wastewater and drinking water samples for residual chlorine prior to analysis.

9.1.3.1 Add 1 DPD Free Chlorine powder pillow (Section 8.12) to 25mL of sample in a centrifuge tube. An immediate color change to pink indicates residual chlorine is present. If residual chlorine is present, add a small amount of ascorbic acid to a sample aliquot (record this in logbook) and check for residual chlorine presence again. If residual chlorine remains, notify the Department Manager and/or the Laboratory Director. Results will be reported as Not Applicable (N/A).

If residual chlorine is not present, continue with sample analysis.

9.2 Initial Calibration

Calibrate the Lachat ion analyzer according to manufacturer's instructions.

9.2.1 Calibration

Two boards are used to calibrate the Lachat instrument. Each curve has seven calibration points. The correlation coefficient of each curve must be $\geq$0.995, otherwise recalibration is necessary. Prepare standard curves by plotting the peak areas of standards processed through the manifold against NO_3+NO_2 as N and NO_2 as N concentrations in standards.

9.2.1.1 Channel 1 is used to generate a calibration curve for Nitrate/Nitrite ranging from 0 to 8.0ppm.

9.2.1.2 Channel 2 is used to generate a calibration curve for Nitrite ranging from 0 to 8.0ppm.

9.2.2 Initial Calibration Verification (ICV)

9.2.2.1 Prior to sample analysis, the following ICVs must be analyzed to verify both calibration curves.

9.2.2.1.1 Nitrate ICV, 0.5ppm (Section 8.12.2)

9.2.2.1.2 Nitrate ICV, 5.0ppm (Section 8.12.1)

9.2.2.1.3 Nitrite ICV, 0.5ppm (Section 8.12.4)

9.2.2.1.4 Nitrite ICV, 5.0ppm (Section 8.12.3)

9.2.2.2 The results must be within ±10% of the true value, otherwise re-calibration is required.

9.3 Continuing Calibration Verification

9.3.1 Continuing Calibration Verification, (CCV) and Continuing Calibration Blank, (CCB)

9.3.1.1 At the beginning of the first tray, after every ten samples and at the end of every analytical sequence, a CCV and a CCB pair must be analyzed to verify both calibration curves.

9.3.1.1.1 1.0ppm Nitrate CCV (Section 8.5)

9.3.1.1.2 1.0ppm Nitrite ICV (Section 8.6)

9.3.1.1.3 Calibration Blank (DI)

9.3.1.2 The results of the CCVs must be within ±10% of the true value, otherwise re-calibration is required.

9.3.1.3 The results of the CCBs must be less than our standard limit of detection, otherwise the analysis is stopped and the problem corrected.

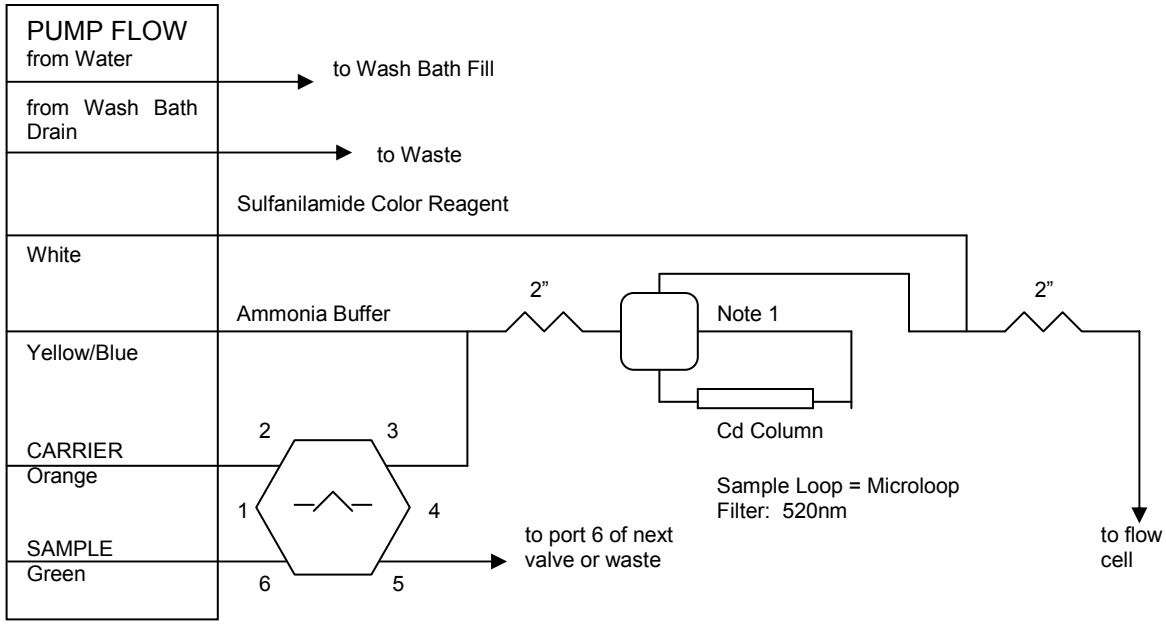
9.4 Equipment Operation and Sample Analysis

Follow the manufacturer's directions for the operation of the Lachat 8000.

All samples have to be expected prior to analysis. Samples that are turbid or have sediment have to be filtered prior to analysis.
For soils: extract soils samples prior to analysis: take 5g of sample, add 50 ml of DI, extract for 30 min, then filter thorough 0.45 nm filter. Record all weights for calculations.

Note: if samples are filtered, then Method blank also have to be filtered

The Manifold Diagram follows:



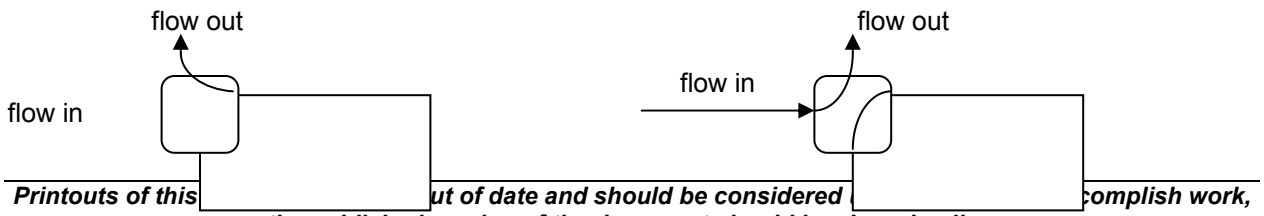
CARRIER is water.

2" is 135cm of tubing on a 2-inch coil support.
APPARATUS: Standard valve, flow cell, and detector head modules are used.

All manifold tubing is 0.8mm (0.032") i.d. This is 5.2µL/cm.

NOTE 1: This is a two-state switching valve used to place the cadmium column in line with the manifold.

State 1: Nitrate + Nitrite **State 2: Nitrite Only**



9.5 Preventative Maintenance

Tubing is changed monthly or as needed.

At the end of each analytical sequence, the valve to the column is closed. DI is rinsed through the Lachat for five minutes followed by five minutes of air.

All maintenance is documented in the Instrument Maintenance Logbook.

9.6 Calculations

9.6.1 **Nitrate/Nitrite:** When the software is set up according to the manufacturer's recommendations, the concentration of nitrate plus nitrite in mg NO_3/NO_2-N/L is reported directly when the Cd column is included in the sample train in Channel 1.

9.6.2 **Nitrite:** When the software is set up according to the manufacturer's recommendations, the concentration nitrite in mg NO_2-N/L is reported directly when the Cd is not included in the sample train in Channel 2.

9.6.3 **Nitrate:** The concentration of nitrate is determined by the subtraction of the nitrite concentration, (Section 9.6.2 above), from the nitrate-nitrite concentration, (Section 9.6.1 above).

9.6.3.1 If the sample was preserved initially as described in Section 6.3, subtract the Nitrite value generated manually from the Nitrate/Nitrite value generated by the Lachat Instrument. This value is reported as the Nitrate result.

When the sample is preserved initially as described in Section 6.3, the value generated by the Lachat instrument for Nitrite is invalid and therefore disregarded.

9.6.4 If any sample exceeds a concentration of 8.0 mg/L, the sample must be diluted and re-analyzed. All sample concentrations must fall within the calibration curve.

10. Quality Control and Data Assessment

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a calibration verification standard is used to confirm the measurements were performed in an in-control mode of operation.

10.1 Demonstration of Capability

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. Each time a method modification is made, the analyst is required to repeat the procedure.

When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must locate and correct the source of the problem and repeat the test for failed parameters of the method.

Repeated failure confirms a general problem with the measurement system or analytical technique of the analyst. If the failure repeats, locate and correct the source of the problem and repeat the test for all parameters listed in the method.

10.2 Method Blank

One Method Blank is analyzed per batch of 20 samples or less The Method Blank consists of DI.
For soils: 5g of Ottawa sand extracted with 50 ml of DI. Results must be < 0.1mg/L. If this criterion is not met, the blank is re-analyzed. If there is still failure, the problem must be found and corrected prior to any sample analysis.

10.3 Calibration Verification and Laboratory Control Samples (LCS)

Two ICVs are analyzed at the beginning of the analytical sequence. One is at a concentration of 0.5ppm, and the other is at a concentration of 5.0ppm.

Both must be recovered within ± 10% of the true value. If these criteria are not met, the ICVs must be re-analyzed. If failure continues, the ICVs are to be re-made and/or a new calibration curve is to be generated.

The 5ppm ICV is reported as the LCS for the batch.

For soil LCS: 5g of Ottawa sand extracted with 0.25 ml of 1000 mg/l nitrate (8.1) (or 1000 mg/l Nitrite standard (8.2)) and 50 ml DI. The nitrate standard is used for spikes for Nitrate-N as well as Nitrate/Nitrite-N. LCS recoveries must be recovered within ± 10% of the true value. If these criteria are not met, LCS's must be re-analyzed. If failure continues, the batch has to be re-extracted and re-analyzed.

10.4 Matrix Spike

One Matrix Spike is analyzed per batch of 20 samples or less. Separate spikes are performed for Nitrate and Nitrite. In a 25mL volumetric flask, 0.5mL of 200ppm stock calibration standard (Section 8.1 or 8.2) is added to the sample. The final concentration of the matrix spike is 4.0ppm. The nitrate standard is used for spikes for Nitrate-N as well as Nitrate/Nitrite-N. The nitrite standard is used for spikes for Nitrite-N.

For soils: weigh 5.0 g of sample, add 2.0 ml of 200 mg/l Nitrate or Nitrite standard and 48 ml of DI. The final concentration of the matrix spike is 80.0 mg/kg. The nitrate standard is used for spikes for Nitrate-N as well as Nitrate/Nitrite-N. The nitrite standard is used for spikes for Nitrite-N.

% Recovery for the Matrix Spike must be within in-house control limits. If acceptance criteria are not met, the Matrix Spike is reanalyzed. If failure continues, a narrative is included with the data for inclusion on the Client report.

10.5 Duplicates

One Duplicate sample is analyzed per batch of 20 samples or less. A separate aliquot of the sample is analyzed for this purpose.

% RPD for the Duplicate must be within in-house control limits. If acceptance criteria are not met, the Duplicate is reanalyzed. If failure continues, a narrative is included with the data for inclusion on the Client report.

10.6 Control Limits

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained.

Control limits for the method parameters are generated by the QC staff. The control limits are calculated based on in-house performance data. The limits are compared to the control limits found in the reference method.

10.7 Analytical Sequence

- Calibration
- ICV/LCS – both levels
- Sample analysis
- CCV – every ten samples and at the end of the analytical sequence

11. Method Performance

11.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/1732. These studies performed by the laboratory are maintained on file for review.

11.2 Demonstration of Capability Studies

Refer to Alpha SOP/1734 and 1739 for further information regarding IDC/DOC Generation.

11.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

11.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

12. Corrective Actions

Holding time exceedence and improper preservation are noted on the nonconformance report form.

Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

Review of standards, blanks and standard response for acceptable performance occurs for each batch of samples. Record any trends or unusual performance on a nonconformance action form.

If the CV or LCS recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked samples is suspect and is only reported for regulatory compliance purposes with the appropriate nonconformance action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time.

13. Pollution Prevention

See Chemical Hygiene Plan for pollution prevention operations.

14. Waste Management

See Chemical Hygiene Plan for waste management and disposal.

Determination of Inorganic Anions by Ion Chromatography

Reference Methods: **EPA 300.0,** Methods for the Determination of Inorganic Substances in Environmental Samples, EPA/600/R-93/100, August, 1993.

Method 9056, SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update III, 1997.

1. Scope and Application

Matrices: Drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, solids (after extraction) leachates (when no acetic acid is used).

Definitions: See Alpha Laboratories Quality Manual Appendix A.

Regulatory Parameter List:

Parameter
Bromide
Chloride
Fluoride
Nitrate – N
Sulfate

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one of the following laboratory personnel before performing the modification: Area Supervisor, Laboratory Services Manager, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of analysts experienced in use of ion chromatography and in the interpretation of ion chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability, analyzing a proficiency test sample and completing the record of training.

After initial demonstration, ongoing demonstration is based on acceptable laboratory performance of at least a quarterly laboratory control sample or acceptable performance from an annual proficiency test sample. A major modification to this procedure requires demonstration of performance. The identification of major method modification requiring performance demonstration is directed by the QA Officer and Laboratory Director on a case-by-case basis.

2. Summary of Method

A small volume of sample is introduced into an ion chromatograph. The anions are separated and measured, using a system comprised of a guard column, analytical column, suppressor device, and conductivity detector.

2.1 Method Modifications from Reference

Use of other eluents that improve method performance are minor modifications of the method and are considered by the method to be acceptable.

3. Detection Limits

The laboratory follows the procedure found in 40CFR Part 136 to determine the MDL on a semi-annual basis. The method detection limits determined by the laboratory are on file for review.

4. Interferences

4.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to solve most interference problems associated with retention times.

4.2 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

4.3 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

4.4 Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Known coelution is caused by carbonate and other small organic anions. At concentrations of fluoride above 1.5mg/L, this interference may not be significant, however, it is the responsibility of the user to generate precision and accuracy information in each sample matrix.

4.5 The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

4.6 The quantitation of unretained peaks should be avoided, such as low molecular weight organic acids (formate, acetate, propionate, etc.) which are conductive and coelute with or near fluoride and would bias the fluoride quantitation in some drinking and most waste waters.

4.7 Any residual chlorine dioxide present in the sample will result in the formation of additional chlorite prior to analysis. If any concentration of chlorine dioxide is suspected in the sample, purge the sample with an inert gas (argon or nitrogen) for about five minutes or until not chlorine dioxide remains.

5. Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

Sulfuric acid used in this method has the potential to be highly toxic or hazardous.

6. Sample Collection, Preservation, and Handling

6.1 Sample Collection

Samples are collected in glass or plastic bottles of sufficient volume to allow replicate analyses of the anions of interest.

6.2 Sample Preservation

Samples are refrigerated at 4°C.

6.3 Sample Handling

The sample holding time is 48 hours for the following anions: Nitrate –N.

The sample holding time is 28 days for the following anions: Bromide, Chloride, Fluoride, and Sulfate.

7. Equipment and Supplies

7.1 Balance: Analytical, capable of weighing to 0.0001g.

7.2 Ion Chromatograph: Analytical system (Dionex ICS-2000) complete with ion chromatograph and all required accessories including syringes, autosampler, analytical columns, compressed gasses and detectors.

7.2.1 Anion guard column: AG-18 (Dionex PN 060551) A protector of the separator column. If omitted from the system the retention times will be shorter. Usually packed with a substrate the same as that in the separator column.

7.2.2 Anion analytical column: AS-18 (Dionex PN 060549). This column produces the separation shown in Figure 1.

7.2.3 Anion supressor: ASRS Ultra II 4mm (PN 061561). The supressor column is packed with a high capacity cation exchange resin that is capable of converting the eluent and separated anions to their respective acid forms.

7.2.4 Detector: DS6 (PN 057985) Temperature controlled, heated conductivity cell

7.2.5 Eluent Generator: EG40 (Dionex PN 058900) Prepares the eluent electronically, controlled by the software; equipped with KOH cartridge.

7.3 Software: The Dionex IC Instrument uses Chromeleon Software.

7.4 0.45µm Membrane Filter Syringes.

7.5 Volumetric Flasks: Various volumes.

7.6 Volumetric Pipets: Various volumes.

7.7 0.5mL Vials with Caps: Dionex PN 038142.

8. Standards and Reagents

Note: All analytical standards used for calibration and calibration verification must be traceable to NIST. Each standard is recorded in a Logbook and unique ID is assigned to each standard. The unique IDs must also be included in all analytical sequences.

8.1 Reagent Water: Deionized water, free of the anions of interest. Water should contain particles no larger than 0.20 microns.

8.2 Eluent Solution: 32mM KOH, Prepared by the Eluent Generator.

8.3 Stock Calibration / ICV Standard Solutions, 1000mg/L (1mg/mL): Stock standards for all analytes are usually purchased as certified solutions. Certificates of analysis are kept on file.

However, if it is necessary, the Stock Solutions may be prepared from ACS reagent grade materials (dried at 105°C for 30 minutes) as listed below. The ICV Standards must be prepared from a different source than the calibration standards.

NOTE: Stock calibration/ ICV standards are stable for at least six months when stored at 4°C. Dilute working standards are prepared fresh daily.

8.3.1 Standard 1: Fluoride Stock Standard, 1000mg F^-/L

In a 250mL volumetric flask, dissolve 0.5526g of sodium fluoride (NaF, CASRN 7681-49-4) in about 200mL reagent water. Dilute to the mark with reagent water, and invert to mix.

8.3.2 Standard 2: Fluoride Stock Standard, 100mg F^-/L

In a 250mL volumetric flask, pipet 25mL of Standard 1, dilute to the mark with reagent water, and invert to mix.

8.3.3 Standard 3: Chloride Stock Standard, 1000mg Cl^-/L

In a 250mL volumetric flask, dissolve 0.4121g of sodium chloride (NaCl, CASRN 7647-14-5) in about 200mL reagent water. Dilute to the mark with reagent water, and invert to mix.

8.3.4 Standard 4: Bromide Stock Standard, 1000mg Br^-/L

In a 250mL volumetric flask, dissolve 0.3219g of sodium bromide (NaBr, CASRN 7647-15-6) in about 200mL reagent water. Dilute to the mark with reagent water, and invert to mix.

8.3.5 Standard 5: Bromide Stock Standard, 100mg Br^-/L

In a 250mL volumetric flask, pipet 25mL of Standard 4, dilute to the mark with reagent water, and invert to mix.

8.3.6 Standard 8: Nitrate Stock Standard, 1000mg NO_3^--N /L

In a 250mL volumetric flask, dissolve 1.5170 g of sodium nitrate ($NaNO_3$, CASRN 7631-99-4) in about 200mL reagent water. Dilute to the mark with reagent water, and invert to mix.

8.3.7 Standard 9: Nitrate Stock Standard, 100mg NO_3^--N /L

In a 250mL volumetric flask, pipet 25mL of Standard 8, dilute to the mark with reagent water, and invert to mix.

8.3.8 Standard 12: Sulfate Stock Standard, 1000mg SO_4^{2-}/L

In a 250mL volumetric flask, dissolve 0.4535 g of anhydrous dibasic, potassium sulfate (K_2SO_4, CASRN 7778-80-5) in about 200mL reagent water. Dilute to the mark with reagent water, and invert to mix.

8.3.9 Stock Bromide Standard, 1000ppm

Commercially available. Certificate of analysis required and kept on file. Use separate sources for the ICV and Calibration standards listed below.

8.3.9.1 ICV Bromide Standard, 100ppm

In a 100mL volumetric flask, add 1mL of Stock 1000ppm Bromide standard (Section 8.4.13). Bring to volume with reagent water.

8.4 Working Mixed Stock Standard A (Calibration Stock)

In a 200mL volumetric flask, transfer using volumetric pipets, 2mL each of Standards Bromide 1000ppm and Nitrate 1000ppm; 20mL of Chloride 1000ppm and Fluoride 100ppm (Section 8.3). Dilute to the mark with reagent water and invert to mix. Store at 4 ± 2°C for up to one month.

This makes Standard A containing F^-, Cl^-, NO_2^- -N, Br^-, NO_3^- -N and SO_4^{2-} at the concentrations of 10, 100, 10, 10 and 200ppm respectively.

8.4.1 Analyte Matrix Spike Solution

Volumetrically prepare the spike solution by bringing 1.0 mL of the calibration stock standard (Section 8.4) up to a 25mL final volume with the sample.

8.5 Working Mixed Standards B through G (Calibration Curve)

Working mixed standards B through F are prepared by diluting Standard A as summarized in the following Table. These are prepared fresh as needed for calibration.

Std.	Std. A (mL)	Final Vol. (mL)	F^-	Cl^-	Br	NO_3^- -N	SO_4^{2-}
B	5	10	5.0	50.0	5.0	5.0	100.0
C	5.0	25	2.0	20.0	2.0	2.0	40.0
D	1.25	25	0.5	5.0	0.5	0.5	10.0
E	0.5	25	0.2	2.0	0.2	0.2	4.0
F	1 of Std D	10	0.05	0.5	0.05	0.05	1.0
G	0.5 of Std D	10	0.025	0.25	0.025	0.025	0.5

Example: To make up Standard B, take 25mL of Standard A in a 10mL volumetric flask and dilute to the mark with reagent water.

Note: The dynamic range for the method is two orders of magnitude. The concentrations for the standards could be changed to bracket the concentrations of the samples to be analyzed.

8.6 ICV Stock Standard (Second Source Verification)

To a 200mL volumetric flask add 20mL of the following standards: Chloride 1000ppm and Sulfate 1000ppm, and 2mL of Fluoride 1000ppm, Bromide 1000ppm and Nitrate 1000ppm (Section 8.3). Dilute to volume with reagent water.

8.6.1 ICV Working Standard / LCS Solution

In a 25mL volumetric flask, add 1mL of the ICV Stock Standard. Bring to volume with reagent water. Store at 4 ± 2°C. Prepare weekly.

ICV working standard will have the following concentrations: 0.4 mg/L for Fluoride, Nitrate and Bromide; 4.0 mg/L for Chloride and Sulfate.

8.7 CCV Working Solution

The CCV Working Solution is the equivalent of Standard D above in Section 8.5. Store at 4 ± 2°C. Prepare weekly.

9. Procedure

9.1 SET-UP

9.1.1 Determination of Linear Calibration Range (LCR)

The LCR must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to ensure that the resulting curve is linear. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by ± 10%, linearity must be reestablished. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

9.1.2 **Prime Pump:** The pump must be primed prior to analysis, to ensure that there is no gas entering the column.

9.1.3 **Monitor Baseline:** From the main Panel screen, press the “Startup” Button. This will turn on, in order, the pump, the eluent generator, and the conductance cell. Allow the instrument to warm up for 10 – 20 minutes to ensure the baseline is stable and flat.

9.1.4 While the baseline stabilizes, the sample sequence can be written and the autosampler may be loaded.

9.1.5 When the baseline is stabilized, the sample sequence may be loaded into the analytical run, and started from the Chromeleon software.

9.1.6 Operating Conditions: Dionex IC Instrument

Eluent Concentration: 32mM KOH

Flow rate: 1.0mL / minute

Injection volume: 100µL

ASRS: ON

Conductivity Cell Temperature: 30 °C

9.1.7 Monitor instrument stability: Prior to QC sample and sample analysis, analyze a DI water blank to ensure the instrument is stable.

9.1.8 Sample filtration: Autosampler vials are equipped with a filter. If additional filtration is necessary, samples may be filtered through a 0.45µm membrane filter attached to a syringe. **NOTE:** If samples require filtration, all associated batch QC samples must also be filtered.

9.1.9 Extraction of solid materials : Add a volume of reagent water equal to 10 times the weight of dry solid material taken as a sample. This slurry is mixed for 10 minutes using a magnetic stirring device. Filter the resulting slurry before injecting using a 0.45µ membrane filter attached to a syringe. Care should be taken to show that good recovery and identification of peaks is obtained with the user's matrix through the use of matrix spikes (Section 10.5).

9.2 Calibration Curve Generation

For each analyte of interest, prepare calibration standards at a minimum of three concentration levels and a blank by adding accurately measured volumes of one or more stock standards (Section 8.5) to a volumetric flask and diluting to volume with reagent water. If a sample analyte concentration exceeds the calibration range, the sample may be diluted to fall within the range.

Using injections of 100µL of each calibration standard, tabulate peak height or area responses against the concentration. The results are used to prepare a calibration curve for each analyte. During this procedure, retention times must be recorded.

The calibration curve for each analyte is prepared by plotting instrument response against the standard concentration. A correlation coefficient of 0.995 or greater is considered acceptable for all analytes.

9.2.1 Initial Calibration Verification (ICV/LCS): The calibration curve must be verified on each working day, and after every 20 samples. The ICV/LCS sample is prepared from a different source than that used for the calibration standards (Section 8.6). If the response or retention time for any analyte varies from the expected values by more than ± 10%, the analysis must be repeated, using fresh calibration standards. If the results are still more than ± 10%, a new calibration curve must be prepared for that analyte.

9.3 Standardization (Continuing Calibration Verification)

This standard (Standard D: Section 8.5) is prepared weekly. The CCV is analyzed at the beginning of each run, after every tenth sample, and at the end of the sample run. The % Recovery of this standard must be within ± 10% of the calibration standard. Refer to Section 10.3 if % Recovery falls outside of the acceptance range.

9.4 Equipment Operation and Sample Analysis

9.4.1 An automated constant volume injection system is used. Load and inject a fixed amount of well-mixed sample. Flush injection loop thoroughly, using each new sample. Use the same size loop for standards and samples. Record the resulting peak size in area or peak height units.

9.4.2 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for each analyte. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

9.4.3 If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

9.4.4 If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, fortify the sample with an appropriate amount of standard and reanalyze.

Note: Retention time is inversely proportional to concentration. Nitrate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. In some cases this peak migration may produce poor resolution or identification.

9.5 Preventative Maintenance

Follow the Preventative Maintenance Schedule as outlined on the Dionex ICS-2000 CDROM.

As Needed

- Check the eluent reservoir to see if it needs to be refilled.

Daily

- Check the ICS-2000 component mounting panel for leaks or spills. Wipe up spills. Isolate and repair leaks. Rinse off any dried eluent with reagent water.
- Check the waste container daily and empty when needed.

Weekly

- Once a week, check fluid lines for crimping or discoloration. Relocate any pinched lines. Replace damaged lines.
- Check the junctions between the pump heads and the pump casting for evidence of liquid leaks. If piston seal wash tubing is not connected, check the drain tubes at the rear of the pump heads for evidence of moisture. Normal friction and wear may gradually result in small liquid leaks around the piston seal. If unchecked, these leaks can gradually contaminate the piston housing, causing the pump to operate poorly. If leaks occur, replace the piston seals.

- Check the end-line filter (PN 045987) and change if needed. When new, end-lline filters are pure white. If the system is in continuous operation, change the end-line filter weekly, or whenever it becomes discolored. Replace the filter more often if bacterial buildup is visible or if the eluent does not contain solvent.

NOTE: It is especially important to regularly replace end-line filters when using aqueous eluents, which may contaminate the filter with bacteria or algae. The bacterial buildup may not be visible.

Yearly (performed by Dionex technician)

- Calibrate the cell.
- Calibrate the vacuum degas assembly
- Replace the pump piston rinse seals and piston seals.

9.6 Calculations

9.6.1 Compute the sample concentration by comparing sample response with the standard curve. Multiply the result by the appropriate dilution factor.

9.6.2 Report only those values that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

10. Quality Control and Data Assessment

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a calibration verification standard is used to confirm the measurements were performed in an in-control mode of operation.

10.1 Demonstration of Capability

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. Each time a method modification is made, the analyst is required to repeat the procedure.

When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must locate and correct the source of the problem and repeat the test for failed parameters of the method.

Repeated failure confirms a general problem with the measurement system or analytical technique of the analyst. If the failure repeats, locate and correct the source of the problem and repeat the test for all parameters listed in the method.

10.2 Method Blank

One Method Blank consisting of an aliquot of reagent water is analyzed with each batch of 20 samples or less. Data produced are used to assess contamination from the laboratory environment. Method Blank results must be less than the Reporting Limit (RL) for the analyte.

Note: If samples have to be filtered prior to analysis, all associated batch QC must also be filtered.

10.3 Continuing Calibration Verification (CCV) Standard

The CCV Standard is the equivalent of Standard D in Section 8.5. Store at 4 ± 2°C. Prepare weekly. The CCV is analyzed at the beginning of each run, after every tenth sample, and at the end of the sample run. The % Recovery of this standard must be within ± 10% of the calibration standard.

10.4 Initial Calibration Verification (ICV) Standard / Laboratory Control Sample (LCS)

The ICV/LCS is analyzed at the beginning of each run, but after the CCV standard. This standard is prepared from a different source than that used to prepare the calibration standards (Section 8.6). The % Recovery of this standard must be within ± 10% of the calibration standard.

10.5 Matrix Spike

Prepare and analyze one spiked sample per batch of 20 samples or less (Section 8.4.1). Recovery of the Matrix Spike must be within the Laboratory defined control limits (Section 10.7).

10.6 Duplicates

Prepare and analyze one duplicate sample per batch of 20 samples or less. The RPD for the duplicate measurements must be within the Laboratory defined control limits (Section 10.7).

10.7 Control Limits

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained. After the analysis of 20 spiked samples, and 20 laboratory control samples, calculate the average percent recovery (R) and the standard deviation of the percent recovery (S).

Control limits for the method parameters are generated by the QC staff and distributed to the analysts. The control limits are calculated based on in-house performance data. The limits are compared to the control limits found in the reference method.

10.8 Analytical Sequence

- Instrument calibration
- DI Blank
- CCV
- ICV
- Ten samples
- CCV
- Blank
- Shut-down

11. Method Performance

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations were obtained using reagent water. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

MDL's must be established for all analytes, using reagent water (blank) fortified at a concentration of two to three times the estimated calculated detection limit.

Method performance data is on file in the laboratory QC department. Comparison of method performance data for the laboratory to the reference method criteria occurs when laboratory in-

house acceptance limits are generated. In-house generated data must be within the specifications of the reference method or the analysis is not continued until corrective action is completed.

12. Corrective Actions

If the Method Blank result exceeds the Reporting Limit (RL) for the analyte, the Blank is reanalyzed. If the second result remains > RL, notify the Laboratory Manager to ensure maintenance is performed on the water filtration system and seek an alternate reagent water source within the laboratory. If the alternate reagent water source is acceptable, this source must be utilized for all blanks, standards and sample dilutions for the sample batch. If the second source reagent water also fails, the Laboratory Manager is notified.

If the Continuing Calibration cannot be verified within the specified limits, reanalyze the CCV solution. Record the reason for re-injection. If the second analysis of the CCV solution confirms calibration to be outside the limits, sample analysis must be discontinued, the cause determined and/or in the case of drift, the instrument recalibrated. All samples following the last acceptable CCV solution must be reanalyzed. The analysis data of the calibration blank and CCV solution must be kept on file with the sample analyses data.

If the ICV/LCS acceptance criterion cannot be met, reanalyze the standard. If failure continues, the instrument is recalibrated.

If the Matrix Spike acceptance criteria is not met, the spiked sample is reanalyzed (if possible). If failure continues and if all other QC performance criteria are met, the data is reported and a narrative is included with the final report.

If the RPD for the Duplicate measurements falls outside the Laboratory defined control limits (Section 10.7), the sample is reanalyzed (if possible). If failure continues, and if all other QC performance criteria are met, the data is reported and a narrative is included with the final report.

Holding time exceedence and improper preservation are noted on the nonconformance report form.

Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

Review of standards, blanks and standard response for acceptable performance occurs for each batch of samples. Record any trends or unusual performance on a nonconformance action form.

If the CCV or LCS recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked samples is suspect and is only reported for regulatory compliance purposes with the appropriate nonconformance action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time.

13. Pollution Prevention

See Chemical Hygiene Plan for pollution prevention operations.

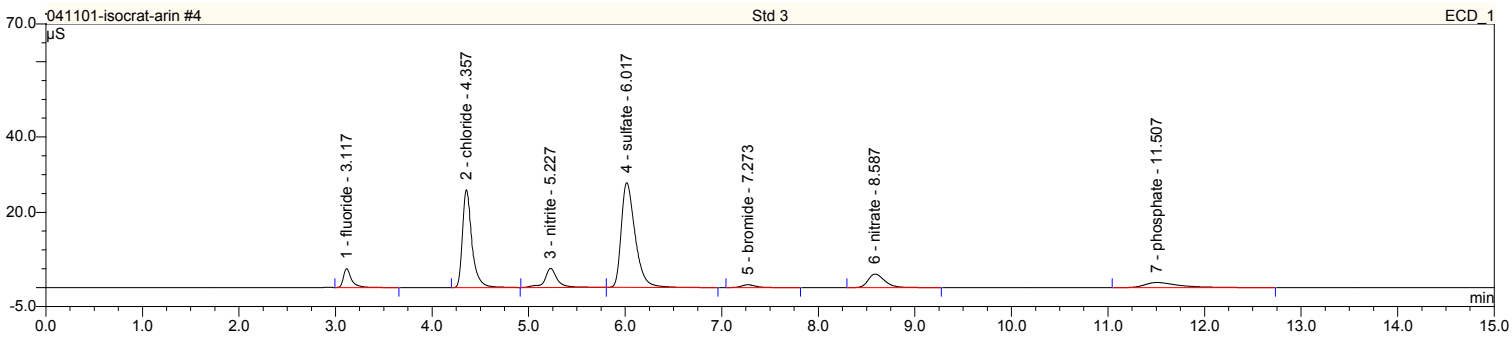
14. Waste Management

See Chemical Hygiene Plan for waste handling and disposal.

15. Attachments

Figure 1: Isocratic Anion Standard Separation

Figure 1
Isocratic Anion Standard Separation



Oil and Grease
Total Petroleum Hydrocarbons by
n-Hexane Extraction and Gravimetric Method

Reference Method No.: 1664A

Reference: Method 1664, Revision A: N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGTHEM; Non-polar Material) by Extraction and Gravimetry. EPA-821-R-98-002. February 1999.

1. Scope and Application

Matrices: This method, as outlined, is limited to liquid samples. This method is suitable for surface waters, saline waters and industrial and domestic aqueous wastes.

Definitions: See Alpha Analytical Quality Manual Appendix A

This method is for the determination of n-hexane extractable material (HEM) in surface and saline waters and industrial and domestic aqueous wastes. Extractable materials that may be determined are relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases and related materials.

This method is not applicable to measurement of materials that volatilize at temperatures below approximately 85ºC. Petroleum fuels from gasoline through #2 fuel oil may be partially lost in the solvent removal operation.

Some crude oils and heavy fuel oils contain a significant percentage of materials that are not soluble in n-hexane. Accordingly, recoveries of these materials may be low.

This method is capable of measuring HEM in the range of 2 to 1000mg/L and may be extended to higher levels by analysis of a smaller sample volume collected separately.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one of the following laboratory personnel before performing the modification: Area Supervisor, Laboratory Director, or Quality Assurance Officer.

Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability, analyzing a proficiency test sample and completing the record of training.

After initial demonstration, ongoing demonstration is based on acceptable laboratory performance of at least a quarterly laboratory control sample or acceptable performance from an annual proficiency test sample. A major modification to this procedure requires demonstration of performance. The identification of major method modification requiring performance demonstration is directed by the QA Officer and/or Laboratory Director on a case-by-case basis.

2. Summary of Method

A 1L sample is acidified to pH <2.

The sample is set in its original container onto the SPE extractor and is automatically filtered through a conditioned SPE disk, which retains the oil and grease from the sample.

Through a series of hexane rinses, the oil and grease is eluded from the disk to a collector vial.

The hexane from the collector vial is dried in a tared dish. The amount of oil and grease is calculated gravimetrically.

For TPH-1664 determination, an amount of silica gel proportionate to the oil and grease result is added to the solution containing the redissolved oil and grease. The solution is then stirred and filtered through sodium sulfate. The solution is then dried and the amount of TPH is calculated gravimetrically.

2.1 Method Modifications from Reference

In place of evaporating the extract in a waterbath, the use of a Speedvap 9000 has been substituted. MDL Studies utilizing the Speedvap 9000 show no quantitative difference with the boil-down in a waterbath. Using Speedvap technology, the laboratory proved that samples have constant weight during one drying cycle; laboratory doesn't repeat drying, cooling, desiccating and weighing process multiple times.

3. Reporting Limits

The reporting limit is 4.0mg/L when analyzing a 1L sample.

4. Interferences

4.1 Instrumental

Improperly prepared glassware may result in interferences.

Sodium sulfate may cause interferences, if it is powder form instead of granular.

4.2 Parameters

Samples containing particulates or detergents may cause interferences. Smaller sample volumes may need to be collected in these cases.

5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

The Hexane used in this method is hazardous, as well as flammable. This chemical should be used under a laboratory hood and stored in a flammables cabinet.

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

A 1 liter representative grab sample should be collected in a glass bottle with PTFE lined caps. (Do not overfill the sample container, and do not subdivide the sample in the laboratory.)

If high oil and grease results are suspected, collect a smaller volume of sample and acidify appropriately.

6.2 Sample Preservation

Acidify to pH <2 with 1:1 HCl and refrigerate at 4 ± 2 ºC.

6.3 Sample Shipping

No special shipping requirements.

6.4 Sample Handling

Analyze within 28 days of sample collection.

7. Equipment and Supplies

7.1 SPE System

7.2 SPE Disks

7.3 SPE Prefilters

7.4 Vacuum Pressure Pump

7.5 Speedvap Evaporator: With spark-proof pump.

7.6 Aluminum Weighing Dishes: Disposable.

7.7 Nitrogen: Low grade.

7.8 Fume Hood

7.9 Desiccator

7.10 Analytical Balance: Capable or weighing to 0.1mg.

7.11 Food Coloring

7.12 Transfer Pipets: Disposable.

7.13 Pipets: 5mL and 10 mL

7.14 Erlenmeyer flasks: 125mL, 250mL

7.15 Oil and Grease SPE flasks

7.16 Glass Stirring Rod

7.17 Glass funnel

7.18 pH Paper: Range 1 – 12 pH units

7.19 Magnetic Stirring Bar

7.20 Filter Paper

7.21 Stirring Plate

8. Reagents and Standards

8.1 Hexadecane / Stearic Acid Stock 4mg/mL and 8 mg/mL (LCS Standard and Spiking Solution): Commercially prepared and purchased. (Available from Environmental Express and Horizon.) Maintain capped and stored in the dark at room temperature. Expires upon manufacturer's specified date

NOTE: The LCS Standard must be from a different source than that used for the Spiking Solution.

8.2 Acetone: ACS residue less than 1mg/L. Store in flammables cabinet. Expires upon manufacturer's specified date.

8.3 Hydrochloric Acid: HCl, 1:1. Store in flammables cabinet. Expires upon manufacturer's specified date.

8.4 n-Hexane: 85% purity, residue less than 1mg/L. Store in flammables cabinet. Expires upon manufacturer's specified date.

8.5 Sodium Sulfate: Na_2SO_4, anhydrous granular crystals. Store in flammables cabinet. Expires upon manufacturer's specified date.

8.6 Methanol: MeOH. Store in flammables cabinet. Expires upon manufacturer's specified date.

8.7 Silica Gel: JT Baker 60-200 mesh, chromatography grade. Activated by baking at 140 °C for a minimum of 14 hours in a shallow tray. Stored in closed glass containers, in a desiccator. All references to silica gel in this method refer to this prepared reagent.

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blank(s)

Analyze one Blank per batch of 20 samples or less. The method blank must be <4.0 mg/L. If the method blank does not meet this criterion, the entire batch is suspect and must be re-extracted.

9.2 Laboratory Control Sample (LCS)

Analyze one LCS per batch of 20 samples or less. The percent recovery must be within the acceptance range of 79-114% for oil and grease, and 64 – 132% for TPH, per the reference method. If this criterion is not met the LCS is reanalyzed. If failure continues a narrative is submitted with the data for inclusion on the Client report.

9.3 Initial Calibration Verification (ICV)

Not applicable.

9.4 Continuing Calibration Verification (CCV)

Not applicable.

9.5 Matrix Spike

Analyze one matrix spike sample per batch of 20 samples or less. A matrix spike concentration must be approximately 1-5 times greater than the concentration of the sample being spiked. The percent recovery must be within the acceptance range of 79% to 114% for oil and grease, and 64 – 132% for TPH, per the reference method. If the percent recovery is outside of these limits, a narrative is submitted with the data for inclusion on the Client report.

9.6 Laboratory Duplicate

Analyze one sample in duplicate per batch of 20 samples or less. The relative difference must be equal or less than 18% for oil and grease, and equal or less than 34% for TPH. If the %RPD is outside of this criterion, a narrative is submitted with the data for inclusion on the Client report.

9.7 Method-specific Quality Control Samples

Not applicable.

9.8 Method Sequence

1. Record the sample pH in the laboratory notebook or use excel format for recording.
2. Extract the sample with Hexane.
3. Weigh an empty aluminum dish for each sample.
4. Pour a sample portion into a weighed aluminum dish.
5. Evaporate the sample using the Speedvap 9000.
6. Place the aluminum dishes in a desiccator for 10 minutes.
7. Re-weigh the aluminum dishes.
8. Calculate sample results.
9. TPH-1664
   - Clean-up the sample and QC sample extracts with silica gel.
   - Repeat steps 5 – 8.

10. Procedure

10.1 Equipment Set-up

10.1.1 Turn on main power switch found on the back right side of the controller. Then turn on vacuum pump.

10.1.2 Check stoppers and fittings to ensure tightness.

10.1.3 Turn on Nitrogen gas.

10.1.4 Check the solvent bottles for sufficient reagents, if needed add to the bottle. Solvents are as follows:

- Bottle # 1 is n-Hexane
- Bottle # 2 is Methanol
- Bottle # 3 is n-Hexane
- Bottle # 4 is Methanol

Bottles 1 and 2 are used for pre-wetting filter. Bottle 3 and 4 are for rinsing.

10.1.5 Check waste bottles to ensure proper capacity for collection of waste, if needed empty the bottles.

10.1.6 Purge the system as follows: Put an empty sample bottle on the bottle holder of each extractor to be purged. Place a purge gasket where the filter disk would ordinarily go during a regular sample extraction. Install an empty collector vial.

10.1.7 Press <Status> and enter the number of the extractor to be purged. Press <Drain>. Press <Elute> .

NOTE: Generally, one purge is sufficient, but if the instrument has not run for several days or is being cleaned after a dirty sample, a second purge may be necessary.

10.1.8 Watch the extractors during the purge cycle to ensure the following steps have run correctly:

10.1.8.1 The Prewet solvent is dispensed through the solvent ring and fills the disk holder assembly to the top sensor. The solvent is then pulled out of the Teflon tubing

located on the left side of the disk holder assembly. All the solvent should be pulled out to waste.

10.1.8.2 This step will be repeated for the total number of Prewet steps used in the purge method.

10.1.8.3 The rinse solvent should spray into the bottle, reaching the top, hitting the center and providing a thorough rinse action. The rinse solvent is then pulled into the collection tube. (The rinse step should be repeated a second time.)

10.1.8.4 If at any time, no solvent flows to the waste, see SPE-DEX manual.

10.1.8.5 It is recommended to rerun the purge method a second time to remove all air from solvent lines and to make sure the desired volume of rinse solvent is being collected.

NOTE: Only during an actual sample run will consistent volumes of final extracting solvent be collected.

10.2 Initial Calibration

Not applicable.

10.3 Equipment Operation and Sample Processing

10.3.1 Bring samples to room temperature.

10.3.2 Mark meniscus level of sample on sample container. This is for the later determination of the volume of sample which was extracted (Section 11).

10.3.3 Check pH of samples. Using a piece of pH paper and the glass stirring rod, dip the rod into the sample and blot onto the pH paper. Rinse the glass rod with hexane back into sample container that will be extracted to prevent the loss of extractable material. The pH must be <2. If not, lower the pH with concentrated HCl. The pH result for each sample is recorded in the laboratory notebook or in the Excel spreadsheet. Ensure all pH values are recorded.

10.3.4 Preparation of QC Samples:

10.3.4.1 **Blank:** Add 1000mL of DI to a clean sample bottle. Adjust the pH to < 2 using 1:1 HCl.

10.3.4.2 **LCS:** Add 1000mL of DI to a clean sample bottle. Adjust the pH to < 2 using 1:1 HCl. Slowly add 5mL of LCS Stock Standard (Section 8.1), by touching the pipet tip to the side of the sample bottle. Release the contents of the pipet very slowly so that the LCS Solution floats on top of the DI. (For best recoveries, use chilled DI and warmed LCS Solution.)

10.3.4.3 **Matrix Spike:** To an entire second bottle of a chosen sample, slowly add 10mL of the Spiking Solution (Section 8.1) directly into the sample bottle. Use the same procedure described above in Section 10.3.4.2.

10.3.5 On the controller of the SPE system, push <Status> button, and then enter the # of the extractor used.

10.3.6 Press Method, and then enter <15>.

10.3.7 Load an SPE disk into position on the extractor and place an empty collection vial in position.

10.3.8 Next, perform the sample test check procedure. At the extractor keypad, press the <Start> key.

10.3.9 While the extractor is running, watch for the following events: The Prewet solvent is dispensed through the solvent ring and fills the disk holder assembly to the top sensor. Upon reaching the top sensor, the solvent is pulled out of the tubing. (Actual flow rate depends on setting of regulator. Regulator should be set to 15" Hg.)

10.3.10 The solvent will reach the bottom sensor and the vacuum valve will turn off, soaking the disk. Next, the air-dry step will occur.

10.3.11 Sections 10.3.9 and 10.3.10 will repeat for the number of cycles specified in the actual method.

10.3.12 The "Water In" valve will open, allowing the water sample to fill up the disk holder assembly. When the water reaches the top sensor, the valve will close and the "Water to Waste" valve will open pulling water out of the tube.

10.3.13 When the water sample reaches the bottom sensor, the "Water In" valve will open, repeating step 10.3.12. This process will continue until all of the water sample has been introduced to the SPE disk.

10.3.14 When all of the water has been filtered, the air-dry filter step will begin to remove most of the residual water from the disk. (The unit will then perform an automatic 5-minute dry and stabilize.)

10.3.15 The rinse solvent will spray into the bottle and will then be pulled into the collection tube. Rinse a second time.

10.3.16 Repeat Section 10.3.15 for all extractors.

10.3.17 Download the desired analytical extraction method to each extractor and prepare each unit for use, such as, new SPE disk, new collection tube, vial, and the actual sample. Use the following loading techniques:

10.3.17.1 Center the disk in the lower case of the holder. If a prefilter is being used for dirty samples, place this directly on top of the SPE disk.

10.3.17.2 Close the disk assembly and firmly squeeze the assembly to ensure a leak tight seal.

10.3.17.3 Visually inspect the disk assembly and align the two halves.

10.3.17.4 Load the collection vessel by gently lifting and twisting the vessel and adapter. The final sample extract will only be collected if the vessel is on tightly.

10.3.18 Remove collector vial from extractor and add a few drops of food coloring to more clearly define the hexane phase from the water phase.

10.3.19 With a transfer pipet, remove the water phase (the lower phase) and discard in the laboratory sink.

10.3.20 Filter the hexane phase through a filter funnel lined with filter paper that contains sodium sulfate, and into an Erlenmeyer flask. Rinse the collector vial with hexane and add to the filter funnel. Rinse the filter funnel with hexane.

NOTE: Sometimes a slightly cloudy white layer will appear between the hexane layer and the colored water layer. Do not transfer this layer to the weighing dish.

10.3.21 Pre-weigh an empty aluminum weighing dish to the nearest 0.0001g. Record weight in the Laboratory Notebook. Transfer the filtered hexane sample into the weighed aluminum dish.

10.3.22 Turn Speedvap 9000. (Switch is on back of instrument.) Turn dial all the way to the right. Push <Release Cover> button and put weighing dishes containing the extracted oil and grease in hexane in the Speedvap.

10.3.23 Allow the evaporator to continue to run at 35ºC until the dish reaches dryness. This takes about 8-10 minutes. **Do Not Over-dry. Do this in a fume hood.**

10.3.24 Turn off Speedvap using button on back. Place the dishes in a desiccator for about 10 minutes.

10.3.25 Re-weigh the aluminum dishes and record weight in the Laboratory Notebook.

Note 1: Record lot numbers for SPE disks, reagents and solvents used for extraction in Laboratory Notebook.

Note 2: On each day of use, the laboratory balances are verified to be accurate at weights that bracket the weight of use. The balance verification performed both before and after a sample batch must pass within the acceptance criteria outlined in the Balance Calibration Verification SOP (SOP ID 1730). If the balance verification is outside of acceptance criteria, the problem must be corrected and the sample extracts re-weighed.

10.3.26 Clean-up Procedure for TPH-1664 Analysis

Using Hexane, rinse the oil and grease from the aluminum dish into a 250mL Erlenmeyer flask. Add a stir bar and silica gel. The amount of silica gel is dependent upon the concentration of oil and grease determined in the sample. For every 100ppm of oil and grease, add 3 grams of silica gel. Place the flask on the stirplate and stir for 5 minutes. Repeat Sections 10.3.20 – 10.3.25.

NOTE: All QC samples in the batch must be treated in the same manner as samples. Therefore, if TPH-1664 is to be determined, the Blank, LCS, matrix spike and duplicate must also go through the TPH-1664 clean-up procedure along with the samples.

10.4 Continuing Calibration

Not applicable.

10.5 Preventive Maintenance

Preventative maintenance is conducted per the manufacturer's instructions. All maintenance is recorded in the Instrument Maintenance Logbook. Rinsing of the lines with a 50/50 Acetone and Hexane mixture is done daily to keep the lines clean.

11. Data Evaluation, Calculations and Reporting

$$\text{mgHEM / L} = \frac{\text{Final weight of dish – tared weight}}{\text{V}} \times 1000$$

Where V = volume of sample in liters, determined by taking original bottle and fill to mark with water (Section 10.3.2). Pour into a 1L graduated cylinder to measure volume and record in logbook.

12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

Holding time exceedence and improper preservation are noted on the nonconformance report form.

Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

Review of standards, blanks and standard response for acceptable performance occurs for each batch of samples. Record any trends or unusual performance on a nonconformance action form.

If the LCS recovery falls outside the designated acceptance range, the laboratory performance is judged to be out of control, and the problem must be immediately identified and corrected. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/1732. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP/1734, 1739 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

Chemical Hygiene Plan

SOP/1732 MDL/LOD/LOQ Generation

SOP/1734, 1739 IDC/DOC Generation

SOP/1728 Waste Management and Disposal SOP

16. Attachments

None

Dissolved Gases

References: US EPA REGION 1: Technical Guidance for the Natural Attenuation Indicators: Methane, Ethane, and Ethene. Revision 1, 2/21/2002.

EPA RSKSOP-175: Sample Preparation and Calculations for Dissolved Gas Analysis in Water Samples Using a GC Headspace Equilibration Technique, Revision 2, May 2004.

1. Scope and Application

Matrices: Aqueous samples

Definitions: See Alpha Analytical Quality Manual.

Regulatory Parameter List:

Parameter	CAS	Reporting Limit, ug/L
Methane	74-82-8	5.0
Ethane	74-84-0	0.5
Ethene	74-85-1	0.5
Propane	74-98-6	1.0
Butane	106-97-8	1.0
Carbon Dioxide	124-38-9	1200

This standard operating procedure (SOP) presents the methods that are used for the analysis of aqueous samples for dissolved gaseous volatile organic compounds in the GC laboratory.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one of the following laboratory personnel before performing the modification: Area Supervisor, Laboratory Services Manager, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of analysts experienced in the operation of the GC and in the interpretation of GC data. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability, analyzing a proficiency test sample and completing the record of training.

After initial demonstration, ongoing demonstration is based on acceptable laboratory performance. A major modification to this procedure requires demonstration of performance. The identification of major method modification requiring performance demonstration is directed by the QA Officer and/or Laboratory Director on a case-by-case basis.

2. Summary of Method

An inert gas is injected into the VOA vial containing the water sample to create headspace. After equilibration, the headspace is analyzed for the target gases. The concentration of the gases in the water is calculated using Henry's law. The concentration of the gas in the liquid is proportional to the partial pressure of the gas above the liquid.

2.1 Method Modifications from Reference

The method calibration procedure consists of calibrating the analytical system using gaseous phase calibration standards and then calculating the concentration in the aqueous phase using Henry's Law. The calibration standards in this SOP are prepared by spiking known quantities of target analytes into VOA vials containing the same headspace/ aqueous phase ratio as the samples. The calibration standards are then agitated in an identical manner as the samples and an aliquot of headspace is injected into the gas chromatograph. This modification lessens the effect of moisture on the calibration procedure and allows for a more simplistic approach to the calculation of results. A comparison of both calibration procedures is maintained on file. See Appendix B for a detailed calculation of the calibration standard true values.

3. Detection Limits

Reporting Limits are listed in Section 1.

4. Interferences

4.1 The carrier and reagent gases used must be free of target analyte contamination. Interference could occur if the ambient air or the De-ionized water in the laboratory is contaminated with the analytes of interest.

4.2 Moisture on the analytical column could create a negative effect on the chromatography of the samples, possibly rendering the column useless.

4.3 The sample matrix may cause interferences by one of several processes, including the biological activity and/or the actual composition of the sample.

5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

Gloves, safety glasses and lab coats should be worn whenever handling standards and preparing samples.

6. Sample Collection, Preservation, Shipping and Handling

6.1 Sample Collection

Samples should be collected in duplicate to enable the analysis of a quality control samples and re-analysis of samples if needed.

6.2 Sample Preservation

Samples to be analyzed for methane, ethane, ethene, propane, and butane must be preserved to a pH < 2 with hydrochloric or sulfuric acid. Samples to be analyzed for carbon dioxide must be collected in vials with no preservative.

6.3 Sample Shipping

Samples requiring shipment to the laboratory are shipped in ice-packed coolers via an overnight delivery service in accordance with applicable Department of Transportation regulations.

6.4 Sample Handling

Samples should be received on ice; at 4°C. Samples should be stored in a refrigerator at the same temperature until analysis. Hold time for samples that are preserved to a pH < 2 is 14 days. For non-preserved samples, the hold time is 7 days.

7. Equipment and Supplies

7.1 Haysep S Column: 2 meter by 0.95 mm" OD, packed column, 100/120 mesh (Restek part number 19011) or a similar type column capable of separating the compounds of interest.

7.2 HP7890A GC: Or similar model GC, with flame ionization detector (FID) and thermal conductivity detector (TCD).

Oven program: 40 °C for 3 min: then 25 °C/min to 220 °C; final time = 1.00 min.
Column flow: 20 mL/min
Inlet pressure: 20 psig
TCD reference gas flow rate: 48 mL/min
TCD make up flow rate: 10 mL/min
Air flow rate FID: 300 mL/min
Hydrogen flow rate FID: 60 mL/min
TCD & FID temperature: 250° C
Injection port temperature: 70° C

7.2.1 Enviroquant Data system (version G1701AA version E.02.00 or equivalent) to acquire data and process data.

7.3 LEAP Headspace Autosampler: capable of injecting headspace in vials and performing sample heating and/or agitation.

Syringe Temperature: 40 °C
Syringe Size: 2.5 mL
Injection Volume: 0.5 mL

Agitation Program: Incubation Temperature: 45 °C
Incubation Time: 3 min.
Agitation Speed: 700 RPM
On Time: 10 sec
Off Time: 2 sec

7.4 Single stage regulator: 0-200 psig

7.5 20 mL open-top septa vials: For preparation of calibration standards, QA/QC samples, and samples, MicroLiter pt# 16-6000 (vials) and 16-0030M (caps).

7.6 Assorted gas-tight microliter syringes : 100 uL to 1.0 mL sizes

7.7 Side port needles: For gas tight luer tip syringes, 22 gauge; (Hamilton part # 90222)

7.8 Syringe adapters: For Scotty II cylinders (Restek part #21118)

7.9 Purging vessel (carboy): One-liter capacity

7.10 pH test strips: Capable of measuring pH values from 0-14.

8. Reagents and Standards

8.1 GC/FID support gases: UHP Helium carrier, Ultra Zero Air, UHP Hydrogen

8.2 UHP Helium: To be used for dilutions

8.3 Calibration gas cylinders:

8.3.1 Restek part #34511, concentration of 1.0% by mole in nitrogen for methane, ethane, ethene, and acetylene.

8.3.2 Restek part #34454, concentration of 99% by mole in for methane.

8.3.3 Restek part # 34452, 99% for carbon dioxide.

8.3.4 Butane, 99% - Sigma Aldrich pt# 494402-170g

8.3.5 Propane, 99% - Sigman Aldrich pt# 295655-100g

8.3.6 Linde Custom second source standard – all analytes of interest at 1.0% in nitrogen.

8.4 Laboratory DI Water or Carbon-filtered tap water: Free of any target analytes.

Purge laboratory DI water or carbon filtered tap water with helium for approximately 20 minutes in the one-liter carboy.

8.5 Calibration Standards: Calculate and record the amount of calibration gas mix needed to prepare a minimum of five calibration standards for the target analytes. The calibration

standards must bracket the expected concentration of the analytes in the sample. Record all working standard preparation in the Standard preparation logbook. See **Table 1** and **Table 2** for an example of typical volumes of stock standards injected and typical concentrations of a working standard.

8.5.1 Prepare a 1.0% calibration gas standard by spiking 20 mL each of butane and propane into the 1.0% Restek standard #34511. This is done by allowing the Restek standard to flow into a 1.0 L canister, and the butane and propane is spiked into the gas stream via an injection port. Final pressure in the 1.0 L cylinder is then brought to 30 psia.

8.5.2 Prepare a secondary gas standard by injecting 20 mL of the 1.0% calibration gas cylinder into a 1.0 L canister. Pressurize the canister to 30 psia. Final concentration of the secondary gas standard is 0.01%.

8.5.3 Fill a 20 mL vial completely with DI water. There should be no bubbles or headspace present when capped and inverted.

8.5.4 Remove the plunger from the 10 mL gas tight syringe and insert into 20 mL vial. Insert the helium supply through the septa of the 20 mL vial. Remove 5 mL of DI water through the septa by pressurizing the vial with helium. The helium will pressurize the vial and displace the water into the 10 mL syringe, creating a headspace of helium gas. The resulting standard volume is 5 mL.

8.5.5 Using a gas tight microliter syringe, remove the calculated amount of headspace from the vial through the septa (this volume is the same as the calculated amount of calibration gas added).

8.5.6 Next, remove the calculated amount (see Table 1 and Table 2 for appropriate volumes) of calibration gas (stock standard) from the gas cylinder via the syringe adapter. Inject the calculated amount of calibration gas through the septa into the vial, bubbling the gas through the DI water. Place vial on autosampler tray.

8.5.7 Repeat steps 8.5.2 through 8.5.5 for each calibration level.

8.5.8 Program the autosampler software and GC instrument software to inject the calibration standards. All calibration standards must be injected using the “DISSGAS” method of the LEAP autosampler. This method will perform the sample vial heating and agitation prior to sample injection. The GC acquisition method is also “DISSGAS”.

9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1 Blank(s)

A laboratory method blank should be prepared and analyzed daily for each batch of 20 aqueous samples. It should be prepared in a similar manner as the calibration standards and LCS, without injecting any stock standards. The method blank is considered acceptable when the target analytes are less than one half the detection limit. Sample analysis may begin when the blank QA/QC requirements are met. If the method blank QA/QC requirements are not met, re-inject the blank.

9.2 Laboratory Control Sample (LCS)

A laboratory control sample (LCS) should be analyzed immediately after the initial calibration or daily continuing calibration standard to assess the accuracy of the initial calibration. The LCS should be prepared and analyzed daily for each batch of 20 aqueous samples. It should be prepared using a different stock standard (different lot number of a purchased gas cylinder) in a similar manner as the calibration standards, with the true value of the LCS around the midpoint of the calibration range. The LCS is considered acceptable when the percent recovery is 80-120%. If LCS QA/QC requirements are not met, re-inject the LCS. If criteria are still not met, recalibrate the instrument. The LCS may also be used as the continuing calibration check.

9.3 Initial Calibration Verification (ICV)

Refer to Section 9.2.

9.4 Continuing Calibration Verification (CCV)

Refer to Section 9.2.

9.5 Matrix Spike

Matrix spike analysis is used to test for matrix interferences and should be prepared in the same manner as other samples, using separate sample vials. The spiked amount should be around the midpoint of the calibration range. The spiking of calibration standard into the sample should be conducted in the same manner as the spiking of the laboratory check standard. Calculate the matrix spike percent recoveries (See Sections 11.7). The matrix spike analysis is considered valid if the matrix spike percent recovery is 80-120%.

9.6 Laboratory Duplicate

Duplicate samples are used to test the reproducibility of preparation and analysis and should be prepared in the same manner as other samples, using a separate sample vial if possible. A minimum of one duplicate sample per 20 samples should be analyzed. If possible, it is preferable for a sample with a detected value to be used as the duplicate sample, as opposed to a sample that has no detected analytes. Calculate the relative percent difference (RPD) of the sample values (See Section 11.6). A duplicate is considered acceptable if the RPD is less than 25%.

9.7 Method-specific Quality Control Samples

The following field QC is required per the reference method: field blanks and field duplicates (one per Sample Delivery Group).

9.8 Method Sequence

The analytical sequence is:

- Calibration Standards (initial) or mid-range Calibration Check Standard (daily check of initial calibration) (REQUIRED)
- Laboratory Method Blank (REQUIRED)
- Laboratory Control Sample (may also be used as Continuing Calibration Check Standard) (REQUIRED)
- Samples
- Mid-sequence Continuing Calibration Check Standard (as REQUIRED in Section 10.4)
- Sample Duplicate Analysis (REQUIRED)
- Sample Matrix Spike Analysis (REQUIRED)
- Post-sequence Continuing Calibration Check Standard (REQUIRED)

10.Procedure

10.1 Equipment Set-up

10.1.1 Sample Preparation

Each sample is prepared by removing 5 mL of headspace through the septa of the vial as in section 8.5.3.

Measure the pH of each sample using the 5 mL aliquot removed from the vial. Record the pH of the sample on the instrument runlog (Form 117-09). Any deviation of pH from expected values must be included in the case narrative.

10.2 Initial Calibration

Separation of the analytes of interest should be greater than or equal to resolution between peaks (See Section 11.1).

Calibration standards prepared in sect. 8.5 are analyzed using the LEAP autosampler which agitates the sample via the parameters listed in Section 7.4. Agitation of the sample vial volatilizes the target analytes from the aqueous phase into the headspace of the vial. An aliquot of the headspace (0.5 mL) is then injected into the GC. Analyze all calibration level standards in the same manner.

Calculate the response factor (RF) for each analyte at each concentration. Note that this is done automatically in the Enviroquant software (method file DGASxxxx.m [xxxx = Date Calibrated] for methane, ethane, ethene, propane, and butane and method file dgas_CO2.m for carbon dioxide). (See Section 11.2 for manual calculation.)

Use a linear regression curve, forced through the origin. The R^2 value (correlation coefficient) must be greater than 0.995 to be considered valid.

If the R^2 criteria is not achieved, remake the standards and recalibrate the instrument until the R^2 criteria are achieved. The linear regression curve is used to quantitate all samples and associated QC samples.

Use the Enviroquant software to determine retention time windows (refer to sect. 11.4).

10.3 Equipment Operation and Sample Processing

10.3.1 Program the autosampler software to inject the CCV, method blank and samples. All calibration standards, method blanks, and samples must be injected using the "DISSGAS" method of the LEAP autosampler. This method will perform the sample vial heating and agitation prior to sample injection.

10.3.2 Program the GC software (Chemstation) to acquire data using the "DISSGAS" acquisition method and begin the analytical sequence.

10.3.3 Examine the chromatogram for each sample run. Determine which peaks fall within the retention time windows of the target analytes. Note the sample concentration as calculated by the software. Refer to the manual integration SOP 08-03 for rules on performing manual integrations on any peak.

10.3.4 If the sample concentration exceeds the highest calibration level, dilute the sample so that the sample concentration falls within the calibration range.

10.3.4.1 For dilutions 2-fold and under, a syringe dilution may be used; for dilutions over 10-fold, direct injection of a secondary dilution must be used.

10.3.4.1.1 A syringe dilution consists of using an alternate LEAP autosampler method (DGAS-DIL) which is programmed to withdraw and inject only 0.25 mL.

10.3.4.1.2 A gas sampling bulb dilution consists of filling a gas-sampling bulb or other vessel with UHP Helium and injecting the appropriate amount (usually 1-10 mL) of sample into the bulb via the half hole septa. The resulting dilution factor must be factored into sample calculations (See Section 11.9).

10.3.5 For duplicate or matrix spike duplicates, a second agitation of the vial is not necessary. If a second agitation of the vial is not needed, use the DGAS-QC method for the LEAP autosampler. This method will only heat the vial to setpoint temperature but will not agitate.

10.3.6 All injections (QC samples, samples, dilutions, etc.) need to be recorded on the instrument runlog (form 117-09).

10.4 Continuing Calibration

Analyze the midpoint calibration standard (continuing calibration) as the first and last analytical run of the day, as well as after every 10 sample analyses. At a minimum, a calibration check standard needs to be run every 4 hours.

Calculate the percent recovery for each target analyte (See Section 11.5). The percent recovery must be within 80-120% to be considered valid. If the continuing calibration does not meet these criteria, re-inject the standard. If it fails again, recalibrate the instrument and re-analyze the samples associated with that continuing calibration.

The retention time (RT) for the target analytes must be within the current retention time window. If any of the target analytes are outside the window, the cause of the shift must be determined before sample analysis resumes.

10.5 Preventative Maintenance

Standard preventative maintenance: (a) Change septa before run, or when a shift in retention times is observed. (b) Change injector port before run if degradation in chromatography is evident.

11. Data Evaluation, Calculations and Reporting

11.1 Peak Resolution Calculation

$$\% \text{ Resolution} = \frac{\text{Peak height of valley}}{\text{Peak height of smaller peak}} \text{ X } 100$$

11.2 Response Factor (RF) Calculations

11.2.1 Individual Response Factor:

$$RF = \frac{A_1}{C_1}$$

where:
A_1 = peak area of the compound of interest
C_1 = concentration of the compound interest

11.2.2 Mean Response Factor:

$$RF_{avg} = \frac{RF_1+RF_2+RF_3 \ldots RF_n}{n}$$

where:
RF_x = Individual response factor
n = number of calibration standards

11.3 Relative Standard Deviation (RSD)

$$\%RSD = \frac{SD}{RF_{avg}} \times 100$$

where:
SD = Standard Deviation (see below for formula)
RF_{avg} = Mean Response Factor from calibration curve

$$SD = \sqrt{\frac{n\sum x^2 - \left(\sum x\right)^2}{n(n-1)}}$$

11.4 RT Windows Calculations

11.4.1 Mean Retention Time:

$$RT_{avg} = \frac{\sum_{i=1}^{n} RT_i}{n}$$

where:

n = number of compound calibration standard levels
RT = compound retention time from each calibration level

11.4.2 Retention Time Windows:

Retention Time Window = SD X 3

where:

SD = standard deviation of compound retention times (see 11.3 for equation)
n = number of standards injected for the compound

note: retention time window calculations often produce a window that is narrower than the width of the peak. If this is the case, use a default window of 0.3 min.

11.5 Percent Recovery

$$\% \text{ Recovery} = \frac{C_x}{C_t} \text{ X } 100$$

where:
C_x = measured concentration of compound
C_t = true concentration of compound

11.6 Relative Percent Difference (RPD)

$$\%RPD = \frac{ABS(C_{x1}-C_{x2})}{Average(C_{x1},C_{x2})} \text{ x } 100$$

where:
C_{x1} = concentration of target analyte from initial injection
C_{x2} = concentration of target analyte from second injection

11.7 Matrix Spike Percent Recovery

$$\% \text{ Recovery} = \frac{C_{ms}-C_x}{C_{spk}} \text{ X } 100$$

where:
C_{ms} = measured analyte amount in Matrix Spiked Sample (ug/L)
C_x = measured analyte amount in Matrix sample (ug/L)
C_{spk} = amount of analyte spiked onto matrix (ug/L)

11.8 Sample Concentration

$$ug/L = \frac{A_x}{RF_{avg}} \text{ X DF}$$

where:
A_x = area of target analyte peak

RF_{avg} = average response factor for target analyte
DF = Dilution Factor (see Section 9.6.9)

11.9 Dilution Factor (DF)

$$DF = \frac{V_t}{V_s}$$

where:

V_t = Total volume of dilution vessel, mL
V_s = Volume of sample added to dilution volume, mL

12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

Holding time exceedence, improper preservation and observed sample headspace are noted on the nonconformance report form.

Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

Review of standards, blanks and standard response for acceptable performance occurs for each batch of samples. Record any trends or unusual performance on a nonconformance action form.

If the CV or LCS recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked samples is suspect and is only reported for regulatory compliance purposes with the appropriate nonconformance action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time.

13. Method Performance

13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/08-05. These studies performed by the laboratory are maintained on file for review.

13.2 Demonstration of Capability Studies

Refer to Alpha SOP/08-12 for further information regarding IDC/DOC Generation.

13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

14. Pollution Prevention and Waste Management

Refer to Alpha's Chemical Hygiene Plan and Waste Management and Disposal SOP for further pollution prevention and waste management information.

15. Referenced Documents

SOP/08-05 MDL/LOD/LOQ Generation

SOP/08-12 IDC/DOC Generation

SOP/14-01 Waste Management and Disposal SOP

SOP/08-03 Manual Integration SOP

Form 117-09 Air Lab Instrument Runlog

16. Attachments

Table 1: Recommended Calibration Levels-C1-C4

Table 2: Recommended Calibration Levels-Carbon Dioxide

Appendix A: Procedure for transferring samples received in 40 mL VOA vials

Appendix B: Example calculation of method modification to perform dynamic calibration

Table 1

Recommended Calibration Levels-Methane, Ethane, Ethene

Calibration Level	Amount of gas standard added, uL	Methane True Value, ug/L	Ethene True Value, ug/L	Ethane True Value, ug/L	Propane True Value, ug/L	Butane True Value, ug/L
1 *	65	0.28	0.50	0.53	0.78	1.03
2 *	250	1.09	1.91	2.05	3.00	3.96
3 *	500	2.18	3.82	4.10	6.01	7.92
4	50	21.9	38.2	41.0	60.1	79.2
5	125	54.6	95.5	102	150	198
6	250	109	191	205	300	396
7	500	219	382	410	600	792
8 **	200	8740	NA	NA	NA	NA

* utilize secondary gas standard (see section 8.5.2) for spiking these calibration standards.

** gas standard used for spiking must be 100% methane.

Table 2

Recommended Calibration Levels-Carbon Dioxide

Calibration Level	Amount of gas standard added *, uL	Carbon Dioxide True Value, ug/L
1	10	1200
2	50	6000
3	100	12000
4	250	30000
5	500	60000
6	1000	120000

* gas standard used must be 100% carbon dioxide

Appendix A

Procedure for transferring samples received in 40 mL VOA vials

13.2.3 Samples inadvertently sampled in 40 mL VOA vials can be transferred to a 20 mL vial that is able to be injected into the GC via the LEAP autosampler. This transfer needs to conducted while the sample is cold (i.e. 4 ^{o} C) and under pressurized conditions to minimize loss of the target analytes.

13.2.4 Discharge all ambient air from an empty 20 mL vial by flushing for 1 minute with a high flow helium stream.

13.2.5 Using the vial utilized as the method blank for a template, mark the line of the start of the headspace on the now flushed empty 20 mL vial.

13.2.6 Insert a transfer line consisting of 1/32" tubing into both the 20 mL empty vial and the 40 mL sample vial. Insert a syringe tip into the 20 mL vial to serve as a vent line.

13.2.7 Insert the helium gas line into the 40 mL vial. Allow gas to flow into the 40 mL vial, pushing the water from the 40 mL vial into the 20 mL vial. Fill the vial to the mark.

13.2.8 The sample is now ready for analysis via the LEAP autosampler. Proceed to section 10.1 for sample analysis.

Appendix B

Example calculation of method modification to perform dynamic calibration

As noted in the method modification section, the calculation noted in the reference method has been simplified by performing a calibration using aqueous-phase standards. This appendix will show an example calculation for methane to demonstrate how the true value of the continuing calibration standard is determined.

B-1) convert the concentration of the gas standard from % to ug/L:

$$ug/L = \frac{(\%)(10000)(MW)}{24.47} = \frac{(1.0\%)(10000)(16.04)}{24.47} = 6555 \text{ ug/L}$$

Where:

24.47 = molar gas constant @ ambient temperature and pressure
MW = molecular weight of compound
10000=conversion factor from % to ppmV

B-2) determine total ng of analyte injected into vial containing 5 mL headspace and 15 mL of water:

$$\text{Total ng} = (ug/L)(1000) \times \frac{(\text{mLs of gas injected})}{1000} = (6555 \text{ ug/L})(1000) \times (0.125 \text{ mL} / 1000) = 819.37 \text{ ng}$$

B-3) determine final ug/L of calibration standard

ug/L = total ng added / total mL of water extra

Attachment B

Permit No. 020

MASSDEVELOPMENT

33 Andrews Parkway
Devens, MA 01434

LANDFILL DISCHARGE PERMIT

Permittee Name:	U.S Army Corp of Engineers
Mailing Address:	50 MacArthur Avenue Box 90 Devens, MA 01434
Facility Address:	Shepley's Hill Landfill Devens, Massachusetts 01434
Contact Name:	Robert Simeone, BRAC Environmental Coordinator
Contact Address:	30 Quebec St., Box 100 Devens, MA 01434
Contact Phone:	(978) 796-2205

The above permittee is authorized to discharge treated groundwater from the Shepley's Hill Landfill to the Devens Sewerage System in compliance with the *Sewer Rules and Regulations for the Devens Sewerage Service Area*, as adopted by MassDevelopment (MDFA), including any applicable provisions of Federal or Commonwealth of Massachusetts laws or regulations, and in accordance with discharge point(s), effluent limitations, monitoring requirements and other conditions set forth herein.

Effective Date of Permit: June 28, 2010

Expiration Date of Permit: June 28, 2013

Issued by: _____

Mark Cohen
Devens Utilities Dept
MassDevelopment

PART I - Wastewater Discharge Limitations and Monitoring Requirements

A. The permittee shall comply with all Local Effluent Limitations and monitor the discharge as specified below:

Parameter	Limitations	Type	Frequency
Arsenic	0.20 mg/l*	Composite	Monthly
Chromium (total)	0.40 mg/l	Composite	Quarterly
Cadmium	0.045 mg/l	Composite	Quarterly
Copper	0.75 mg/l	Composite	Quarterly
Lead	0.20 mg/l	Composite	Quarterly
Silver	0.30 mg/l	Composite	Quarterly
Selenium	0.03 mg/l	Composite	Quarterly
Mercury	0.001 mg/l	Composite	Quarterly
Total Toxic Organics	5.0 mg/l	Composite	Annually
Total Petroleum Hydrocarbons	100 mg/l	Composite	Annually
pH (units)	5.5 - 9.5	Meter	Continuous

annual as of 12/16/10

* Maximum daily loading for Arsenic shall not exceed 0.10 pounds per day.

B. The permittee shall comply with the additional effluent monitoring requirements specified below:

Parameter	Type	Frequency
Flow (MGD)	Meter	Continuous
Barium	Composite	Quarterly
Manganese	Composite	Quarterly
Magnesium	Composite	Quarterly
Chloride	Composite	Quarterly
Nitrate	Composite	Quarterly
Sulfate	Composite	Quarterly

Notes:

(1) A flow meter shall be used for recording effluent discharge into the Devens sewer system. The flowmeter shall be properly maintained in accordance with the manufacturer's requirements and it shall be calibrated at least annually by a certified and qualified manufacturer's representative. A copy of the "Certificate of Calibration" shall be submitted to MDFA following each calibration.

(2) A pH meter shall be used to continuously measure the pH of the discharge. The pH meter shall be a continuous monitoring instrument with a chart recorder. All charts shall be maintained on file onsite for a minimum of 3 years. At a minimum, the pH meter shall be calibrated weekly and a calibration log maintained on file onsite for a minimum of 3 years. The pH meter shall be properly maintained in accordance with the manufacturer's requirements and it shall be calibrated at least every six months by a certified and qualified manufacturer's representative. A copy of the "Certificate of Calibration" shall be submitted to the MDFA following each calibration.

(3) Spill protection shall be provided for all chemicals stored at the site. Adequate spill protection must be capable of containing all chemical spills and preventing them from entering the sewer or harming the environment.

C. Samples shall be obtained from the discharge of individual extraction wells or the discharge of a pretreatment system installed to reduce pollutant levels. The location of the sampling point and discharge pipeline are shown on the attached drawing.

(1) Composite Sample - A composite sample shall be the collection of individual grab samples obtained at regular intervals either based on time intervals or flow intervals. Each individual grab sample is either combined with the others or analyzed individually and the results averaged. In time composite sampling the samples are collected after equal time intervals and combined in proportion to the rate of flow when the sample was collected. Flow composite sampling can be produced by varying the volume of the aliquot collected in proportion to the amount of flow that passed over the time interval which the sample represents. Composite samples are designed to be representative of the effluent conditions by reflecting the average conditions during the entire sampling period.

(2) Grab Sample - A grab sample shall be a sample, which is taken from a wastestream without regard to the flow in the wastestream and over a period of time not to exceed 15 minutes.

(3) Representative Sample - A representative sample shall mean a sample taken from a wastestream that is nearly identical in composition to that in the larger volume of wastewater being discharged during a normal production day as approved by MDFA.

D. Approved flow for the permittee :

The maximum anticipated flow is 72,000 gallons per day (50 gallons per minute). If the Permittee desires to exceed this flow, he shall request an increase from the Devens Utilities Dept.

E. Automatic Re-sampling: If the results of the permittee's wastewater analyses indicate that a violation of this permit has occurred, the permittee must:

(1) Inform the Industrial Pretreatment Coordinator and the Utilities Supervisor of MDFA/Devens of the violation within 24 hours; and,

(2) Repeat the sampling and pollutant analysis for the parameters that exceeded the permit limit and submit, in writing to MDFA, the results of the second analysis within 30 days of the first violation; and,

(3) If the re-sample results still exceed the permit limit, submit an explanation for the violation and an action plan to prevent a recurrence of the non-compliance event within 30 days of the violation.

Part II - Special Conditions

A. **The Army shall take all reasonable steps to prevent any adverse impact to the Devens wastewater treatment facility or the environment due to the operation of the facility and shall assure the proper operation of the facility as specified in the treatment system manufacturer specifications and operating manual. If the arsenic concentration in the effluent exceeds 75 ug/l for a monthly sample event, the permittee shall, within 7 days of receiving the exceedance results, commence weekly sampling of arsenic until the concentration does not exceed 75 ug/l.**

If the weekly samples exceed 75 ug/l for more than 4 consecutive weeks, the permittee shall shut down plant operation and submit a Corrective Action Plan to MDFA for review and comment. Resumption of operation and discharge to the Devens wastewater treatment facility will require written authorization of MDFA.

B. **The Industrial Pretreatment Coordinator and MDFA Devens Utilities Department staff will review the facility Self-Monitoring data, and Devens wastewater treatment facility influent, effluent and sludge monitoring "baseline" data and operational data on an ongoing basis to determine whether there is any potential adverse affect on the Devens wastewater treatment facility influent, effluent or sludge quality, or any adverse impact on the Devens wastewater treatment facility operation or environment due to the operation of the Army's treatment facility. In the event that MDFA determines the data analysis indicates that an adverse affect has taken place, MDFA shall notify the Army and the Army shall immediately cease all discharge and shall disconnect from the Devens sewer system. (Initial notification may be made verbally with a written notice to follow.) For the purpose of this section, cessation of discharge and disconnection is required if:**

(1) The arsenic concentration in the effluent from the Shepley's Hill treatment system is greater than 75 ug/l, and
(2) The arsenic concentration in the Devens wastewater treatment facility effluent is greater than 10 ug/l or sludge is greater than 40 mg/kg, or
(3) There is some other indication of adverse environmental impact resulting from the Shepley's Hill discharge.

C. **The permittee, at no cost to the MDFA, shall be responsible for paying for additional laboratory tests for arsenic required to monitor the arsenic concentrations at the Devens wastewater treatment facility. MDFA's wastewater contract operator will arrange to have samples collected for these additional tests to be performed quarterly on the wastewater influent, effluent and sludge. All analytical costs associated with this arsenic sampling shall be included in the permittee's regular sewer discharge fee and shall be billed along with such. (Billing is currently done on a quarterly cycle.)**

Part III - Monitoring Requirements

A. The permittee shall provide monthly, quarterly and annual sampling and analysis for the parameters listed in Part I, Section A and Section B of this Permit.

B. All sampling and analysis shall be performed in accordance with 40 CFR Part 136 and amendments thereto.

C. All sample analysis required by this permit shall be performed by an independent laboratory certified by the MADEP for the parameters being analyzed. The use of a laboratory with provisional MADEP certification is prohibited.

D. The permittee shall submit a copy of the "Massachusetts Certification for Chemical Analysis of Water" for each laboratory that performs an analysis submitted to MassDevelopment by or on behalf of the permittee.

E. The Self-Monitoring results shall be submitted to MDFA/Devens within 30 days of the analysis.

F. Each Self-Monitoring Report shall be signed by an authorized representative of the permittee submitting the Report, and shall be certified as accurate. An authorized representative shall be an individual described in 40 C.F.R. Part 403.12(I). The Self Monitoring Report shall contain a certification statement consistent with the following:

"I certify under the penalty of law that this document and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gather and evaluate the information submitted. Based on my inquiry of the person or persons who manage the system or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations."

Part IV - Reporting Requirements

A. As required in the MDFA *Sewer Use Rules and Regulations*, Section 1.012, the permittee shall notify MDFA/Devens and the MADEP immediately by telephone of any accidental or slug discharge to the sewer. Formal written notification addressing the circumstances and remedies shall be submitted to MDFA/Devens within 5 days of the occurrence. Furthermore, a notice shall be permanently posted on the permittee's bulletin board or other prominent location advising employees whom to call in the event of an accidental, slug or dangerous discharge. The permittee shall instruct all necessary employees of the emergency notification procedure.

B. The permittee shall notify MDFA/Devens prior to the introduction of new wastewater or pollutants or any substantial change in volume or characteristics of the wastewater being introduced to the sewer from the permittee's industrial process. Formal written notification shall follow within thirty (30) days of such introduction.

C. The permittee shall submit a monitoring report that tabulates the flow and sample analysis results for the composite samples and grab samples required in Part I. The monitoring quarters and due dates are as follows:

Quarter	Report Due Date	Data
January 1 - March 31	April 5th	Quarterly Sampling, Flows
April 1 - June 30	July 5th	Quarterly Sampling, Flows
July 1 - September 30	October 5th	Quarterly/Annual Sampling, Flows
October 1 - December 31	January 5th	Quarterly Sampling, Flows

The monthly analysis results for arsenic samples required in Part I are due no later than the 5th of the month following the month the sample was taken.

D. All reports shall be submitted to the following address:

Utilities Supervisor
MassDevelopment
33 Andrews Parkway
Devens, Massachusetts 01434

With copy to: Industrial Pretreatment Coordinator
United Water
85 Walker Rd
Shirley MA, 01464

E. Emergency notifications shall be made to:

Devens Dispatch
Phone: (978) 772-7200

-and-

United Water – Devens Wastewater Operations
Phone: (978) 772-4250

Part V - Standard Conditions

A. *General Prohibitions.* The permittee shall comply with all general and specific prohibitive discharge standards described in Sections 1.021, 1.022 and 1.023 of the MassDevelopment, *Sewer Use Rules and Regulations.*

B. *Right of Entry.* The permittee shall, in accordance with Section 1.011 (3) of the Sewer Use Rules and Regulations, allow MassDevelopment or their representatives to enter upon the premises of the permittee, at any time, for the purpose of inspection, sampling or records inspection.

C. *Records Retention.* The permittee shall retain and preserve for no less than three (3) years, any records, books, documents, memoranda, reports, correspondence and any and all summaries thereof, relating to monitoring, sampling and chemical analyses made by or in behalf of the permittee in connection with its discharge. All records that pertain to matters that are the subject of special orders or any other enforcement or litigation activities brought by MassDevelopment shall be retained and preserved by the permittee until all enforcement activities have concluded and all periods of limitation with respect to any and all appeals have expired. Copies must be provided as required by MassDevelopment.

D. *Confidential Information.* Information and data on a permittee obtained from reports, questionnaires, permit applications, permits and monitoring programs and from inspections shall be available to the public or other governmental agency without restriction unless the permittee specifically requests and is able to demonstrate to the satisfaction of MassDevelopment that the release of such information would divulge information, process or methods of production entitled to protection as trade secrets of the permittee.

When requested by the person furnishing a report, the portions of a report which might disclose trade secrets or secret processes shall not be made available for inspection by the public, but shall be made available upon written request to governmental agencies for uses related to the Rules and Regulations, the Devens wastewater treatment facility's Groundwater Discharge Permit, State Disposal System permit and/or the Pretreatment Programs and also provided that such portions of a report shall be available for use by the State or any State agency in judicial review, or enforcement proceedings involving the person furnishing the report. Wastewater constituents and characteristics will not be recognized as confidential information. Information accepted by MassDevelopment as confidential shall not be transmitted to the general public until notice is given to the permittee. EPA officials shall have unrestricted and immediate access to all information

collected by MassDevelopment.

E. *Recording of Results.* For each measurement or sample taken pursuant to the requirements of this permit, the permittee shall have the following information recorded:

1. The exact place, date, time of sampling and the person performing the sampling;
2. The dates the analyses were performed;
3. The person(s) who performed the analyses;
4. The analytical techniques or methods used;
5. Sample preservation; and,
6. The results of all required analyses.

F. *Dilution.* The permittee shall not increase the use of potable water or process water or, in anyway, attempt to dilute a discharge as a partial or complete substitute for adequate treatment to achieve compliance with the limitations contained in this permit.

G. *Proper Disposal of Pretreatment Sludges and Spent Chemicals.* The disposal of sludges and spent chemicals generated shall be done in accordance with Section 405 of the Clean Water Act and Subtitles C and D of the Resource Conservation and Recovery Act.

H. *Signatory Requirements.* All applications, reports, or information submitted to MassDevelopment, must contain the following certification statement and be signed as required in Sections 1, 2, 3, or 4 below:

"I certify under penalty of law that this document and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gather and evaluate the information submitted. Based on my inquiry of the person or persons who manage the system or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations."

Authorized Representative of the Permittee:

1. If the permittee is a corporation, a responsible corporate officer means:

   a. The president, secretary, treasurer, or a vice-president of the corporation in charge of a principle business function or any other person who performs similar policy or decision-making functions for the corporation; or

   b. The manager of one or more manufacturing, production, or operation facilities employing more than two hundred fifty (250) persons or having a gross annual sales or expenditures exceeding twenty five (25) million dollars, if authority to sign documents has been assigned or delegated to the manager in accordance with corporate procedures.

2. If the permittee is a partnership or sole proprietorship: a general partner or proprietor, respectively.

3. If the permittee is a Federal, State or local governmental facility: a director or highest official appointed or designated to oversee the operation and performance of the activities of the government facility, or their designee.

4. The individuals described in paragraphs 1 through 3 above may designate another authorized representative if the authorization is in writing, the authorization specifies the individual or person responsible for the overall operation of the facility from which the discharge originates or having overall responsibility for the environmental matters for the company, and the written authorization is submitted to MassDevelopment.

5. If the authorization under paragraph 4 above is no longer accurate because a different individual or position has responsibility for the overall operation of the facility or company, a new authorization satisfying the requirements of paragraph 4 of this section must be submitted to MassDevelopment prior to or together with any reports to be signed by an authorized representative.

I. *Revocation of Permit.* The permit issued to the permittee by MassDevelopment may be revoked when, after inspection, monitoring or analyses it is determined that the discharge of wastewater to the sanitary sewer is in violation of Federal, State or Local laws, ordinances or regulations. Additionally, falsification or intentional misrepresentation of data or statements pertaining to the permit application or any other required reporting form, shall be cause for permit revocation and possible criminal prosecution.

J. *Limitation of Permit Transfer.* Wastewater discharge permits are issued to a specific permittee for a specific operation and are not assignable to another user or transferable to any other location without the prior written approval of MassDevelopment. Sale of a permitted facility shall obligate the purchaser to seek prior written approval of MassDevelopment for continued discharge to the Devens Regional Wastewater Treatment Facility.

K. *Falsifying Information or Tampering With Monitoring Equipment.* Any person who knowingly makes any false statements, representation or certification in any application, record, report, plan or other document filed or required to be maintained pursuant to the *Sewer Use Rules and Regulations*, or permit, or who falsifies, tampers with or knowingly renders inaccurate, any monitoring device or method required under these Rules and Regulations, may, upon conviction, be punished by fine of up to $10,000 per day and imprisonment up to six months, or by both.

L. *Civil Penalties.* Any permittee who is found to have violated an Order of MassDevelopment or who failed to comply with any provision of the Rules and Regulations, and the orders, rules, regulations and permits issued hereunder, may be fined up to $10,000 for each offense. Each day on which a violation shall occur or continue shall be deemed a separate and distinct offense. In addition to the penalties provided herein, MassDevelopment may recover reasonable attorney's fees, court costs, court reporters' fees and other expenses of litigation by

appropriate suit at law against the person found to have violated the Rules and Regulations or the orders, rules, regulations and permits issued hereunder. Nothing in the permit shall be construed to relieve the permittee from civil and/or criminal penalties for noncompliance under these Rules and Regulations or State or Federal laws or regulations.

M. *Recovery of Cost Incurred.* In addition to civil and criminal liability, the permittee violating any of the provisions of this permit or causing damage to or otherwise inhibiting the Agency's wastewater disposal system shall be liable to the Agency for any expenses, loss, or damage caused by such violation or discharge. The Agency shall assess the permittee for the cost incurred by the Agency for any cleaning, repair, or replacement work caused by the violation or discharge.

N. *Duty to Comply.* The permittee must comply with all conditions of this permit. Failure to comply with the requirements of this permit may be grounds for administrative action, or enforcement proceedings including civil or criminal penalties, injunctive relief and summary abatements.

O. *Duty to Mitigate.* The permittee shall take all reasonable steps to minimize or correct any adverse impact to the public treatment plant or to the environment resulting from noncompliance with this permit, including such accelerated monitoring as necessary to determine the nature and impact of the noncompliance discharge.

P. *Duty to Halt or Reduce Activity.* Upon reduction of efficiency of operation, or loss or failure of all or part of the treatment facility, the permittee shall, to the extent necessary to maintain compliance with its permit, control the production or discharges, or both, until operation of the treatment facility is restored or an alternate method of treatment is provided.

Q. *Modification or Revision of the Permit.* The terms and conditions of this permit may be subject to modifications by MassDevelopment at any time as limitations or requirements are modified or other just cause exists. This permit may be modified for other just cause. This permit may also be modified to incorporate special conditions resulting from the issuance of a special order promulgating a new pretreatment standard. Any permit modifications which result in new conditions in the permit shall include a reasonable time schedule for compliance.

R. *Duty to Reapply.* The permittee shall apply for permit renewal a minimum of sixty (60) days prior to the expiration of the Permittee's existing permit.

S. *Severability.* The provisions of this permit are severable, and if any provision of this permit, or the application of any provision of this permit are deemed invalid, the remainder of this permit shall not be affected thereby.

T. *Property Rights.* The issuance of this permit does not convey any property rights in either real or personal property, or any exclusive privileges, nor does it authorize any invasion of personal rights, nor any infringement of Federal, State or Local regulations.

MassDevelopment

SHEPLEY'S HILL LANDFILL DISCHARGE PERMIT

Please complete this page, keep a copy with your Landfill Discharge Permit and return the original to the following address:

MassDevelopment
Attn: Utilities Supervisor
33 Andrews Parkway
Devens, MA 01434

Acknowledgment of permit terms, conditions and limitations:

The undersigned acknowledges receipt of a renewal of Permit Number 020 authorizing a discharge of treated landfill wastewater to the Devens Wastewater Treatment Facility sewer system. The permittee also acknowledges that this permit is issued at its request based upon the application for the permit and the information provided and acknowledges the conditions and limitations set forth in said permit, **including the requirement for the permittee to pay for additional arsenic tests at the Devens wastewater treatment facility as described in Special Conditions paragraph II.C of this permit.** All information and data contained in this document may be made available to the public without restriction.

U.S Army Corp of Engineers
Permittee Name

50 MacArthur Ave.
Box 90
Devens, MA 01434
Permittee Address

By: _____
Authorized Representative - Please Print or Type

_____
Signature

_____
Title

_____
Date

APPENDIX D

ANNUAL LANDFILL INSPECTION
Shepley's Hill Landfill
Devens, Massachusetts

Date of Inspection:
Inspector/Company:
Site Location:

Weather Conditions:
Temperature:
Weather:

Type of Inspection: ☐ Annual
☐ Post-Major Weather Event
☐ Re-Inspection of Deficiencies
☐ Other

Landfill Attribute & Observations	Comments and Recommendations	SAT	UNSAT
Cover Surface			
		☐	☐
		☐	☐
Vegetative Growth			
		☐	☐
		☐	☐
Landfill Gas Vents & Monitoring Wells			
		☐	☐
		☐	☐
Drainage Swales			
		☐	☐
		☐	☐
Settlement			
		☐	☐
		☐	☐

ANNUAL LANDFILL INSPECTION
Shepley's Hill Landfill
Devens, Massachusetts

Landfill Attribute & Observations	Comments and Recommendations	SAT	UNSAT
Erosion			
		☐	☐
		☐	☐
Access Roads			
		☐	☐
		☐	☐
Culverts and Catch Basins			
		☐	☐
		☐	☐
Security/Fencing			
		☐	☐
		☐	☐
Wetland Encroachment			
		☐	☐
		☐	☐
Other Observations			
		☐	☐
		☐	☐

APPENDIX E

Annual Landfill Gas Monitoring
Shepley's Hill Landfill
Devens, Massachusetts

Date: **Weather:** **Field Team:**

		Initial Readings									Post Purge Readings							
ID	**Time**	**VOC (ppm)**	**0_2 (%)**	**H_2S (ppm)**	**LEL (%)**	**CO (ppm)**	**$C0_2$ (%)**	**CH_4 (%)**	**Purge Rate (lpm)**	**Purge Time (sec)**	**VOC (ppm)**	**0_2 (%)**	**H_2S (ppm)**	**LEL (%)**	**CO (ppm)**	**$C0_2$ (%)**	**CH_4 (%)**	**Bar. Pres.("Hg)**
GV-1																		
GV-2																		
GV-3																		
GV-4																		
GV-5																		
GV-6																		
GV-7																		
GV-8																		
GV-9																		
GV-10																		
GV-11																		
GV-12																		
GV-13																		
GV-14																		
GV-15																		
GV-16																		
GV-17																		
GV-18																		
LGP-01-01X																		
LGP-09-01XA																		
LGP-09-01XB																		
LGP-01-02X																		
LGP-09-02X																		
LGP-01-03X																		
LGP-09-03X																		
LGP-01-04X																		
LGP-09-04X																		
LGP-05-05X																		
LGP-09-05X																		
LGP-05-06X																		
LGP-09-06X																		
LGP-05-07X																		
LGP-05-08X																		
LGP-09-08X																		
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LGP-05-10X																		
LGP-09-10X																		
LGP-05-11X																		
LGP-09-11X																		
LGP-05-13X																		
LGP-05-14X																		
LGP-09-15X																		

APPENDIX F

Permit No. 020

MASSDEVELOPMENT

33 Andrews Parkway
Devens, MA 01434

LANDFILL DISCHARGE PERMIT

Permittee Name:	U.S Army Corp of Engineers
Mailing Address:	50 MacArthur Avenue Box 90 Devens, MA 01434
Facility Address:	Shepley's Hill Landfill Devens, Massachusetts 01434
Contact Name:	Robert Simeone, BRAC Environmental Coordinator
Contact Address:	30 Quebec St., Box 100 Devens, MA 01434
Contact Phone:	(978) 796-2205

The above permittee is authorized to discharge treated groundwater from the Shepley's Hill Landfill to the Devens Sewerage System in compliance with the *Sewer Rules and Regulations for the Devens Sewerage Service Area*, as adopted by MassDevelopment (MDFA), including any applicable provisions of Federal or Commonwealth of Massachusetts laws or regulations, and in accordance with discharge point(s), effluent limitations, monitoring requirements and other conditions set forth herein.

Effective Date of Permit: June 28, 2013

Expiration Date of Permit: June 28, 2016

Issued by: Mark Cohen

Mark Cohen
Devens Utilities Dept
MassDevelopment

PART I - Wastewater Discharge Limitations and Monitoring Requirements

A. The permittee shall comply with all Local Effluent Limitations and monitor the discharge as specified below:

Parameter	Limitations	Type	Frequency
Arsenic	0.20 mg/l*	Composite	Monthly
Chromium (total)	0.40 mg/l	Composite	Annually
Cadmium	0.045 mg/l	Composite	Annually
Copper	0.75 mg/l	Composite	Annually
Lead	0.20 mg/l	Composite	Annually
Silver	0.30 mg/l	Composite	Annually
Selenium	0.03 mg/l	Composite	Annually
Mercury	0.001 mg/l	Composite	Annually
Total Toxic Organics	5.0 mg/l	Composite	Annually
Total Petroleum Hydrocarbons	100 mg/l	Composite	Annually
pH (units)	5.5 - 9.5	Meter	Continuous

* Maximum daily loading for Arsenic shall not exceed 0.10 pounds per day.

B. The permittee shall comply with the additional effluent monitoring requirements specified below:

Parameter	Type	Frequency
Flow (MGD)	Meter	Continuous
Barium	Composite	Quarterly
Manganese	Composite	Quarterly
Magnesium	Composite	Quarterly
Chloride	Composite	Quarterly
Nitrate	Composite	Quarterly
Sulfate	Composite	Quarterly

Notes:

(1) A flow meter shall be used for recording effluent discharge into the Devens sewer system. The flowmeter shall be properly maintained in accordance with the manufacturer's requirements and it shall be calibrated at least annually by a certified and qualified manufacturer's representative. A copy of the "Certificate of Calibration" shall be submitted to MDFA following each calibration.

(2) A pH meter shall be used to continuously measure the pH of the discharge. The pH meter shall be a continuous monitoring instrument with a chart recorder. All charts shall be maintained on file onsite for a minimum of 3 years. At a minimum, the pH meter shall be calibrated weekly and a calibration log maintained on file onsite for a minimum of 3 years. The pH meter shall be properly maintained in accordance with the manufacturer's requirements and it shall be calibrated at least every six months by a certified and qualified manufacturer's representative. A copy of the "Certificate of Calibration" shall be submitted to the MDFA following each calibration.

(3) Spill protection shall be provided for all chemicals stored at the site. Adequate spill protection must be capable of containing all chemical spills and preventing them from entering the sewer or harming the environment.

C. Samples shall be obtained from the discharge of the pretreatment system installed to reduce pollutant levels. The location of the sampling point and discharge pipeline are shown on the attached drawing.

(1) Composite Sample - A composite sample shall be the collection of individual grab samples obtained at regular intervals either based on time intervals or flow intervals. Each individual grab sample is either combined with the others or analyzed individually and the results averaged. In time composite sampling the samples are collected after equal time intervals and combined in proportion to the rate of flow when the sample was collected. Flow composite sampling can be produced by varying the volume of the aliquot collected in proportion to the amount of flow that passed over the time interval which the sample represents. Composite samples are designed to be representative of the effluent conditions by reflecting the average conditions during the entire sampling period.

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(3) Representative Sample - A representative sample shall mean a sample taken from a wastestream that is nearly identical in composition to that in the larger volume of wastewater being discharged during a normal production day as approved by MDFA.

D. Approved flow for the permittee :

The maximum anticipated flow is 72,000 gallons per day (50 gallons per minute). If the Permittee desires to exceed this flow, he shall request an increase from the Devens Utilities Dept.

E. Automatic Re-sampling: If the results of the permittee's wastewater analyses indicate that a violation of this permit has occurred, the permittee must:

(1) Inform the Industrial Pretreatment Coordinator and the Utilities Supervisor of MDFA/Devens of the violation within 24 hours; and,

(2) Repeat the sampling and pollutant analysis for the parameters that exceeded the permit limit and submit, in writing to MDFA, the results of the second analysis within 30 days of the first violation; and,

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If the weekly samples exceed 75 ug/l for more than 4 consecutive weeks, the permittee shall shut down plant operation and submit a Corrective Action Plan to MDFA for review and comment. Resumption of operation and discharge to the Devens wastewater treatment facility will require written authorization of MDFA.

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(1) The arsenic concentration in the effluent from the Shepley's Hill treatment system is greater than 75 ug/l, and
(2) The arsenic concentration in the Devens wastewater treatment facility effluent is greater than 10 ug/l or sludge is greater than 40 mg/kg, or
(3) There is some other indication of adverse environmental impact resulting from the Shepley's Hill discharge.

C. **The permittee, at no cost to the MDFA, shall be responsible for paying for additional laboratory tests for arsenic required to monitor the arsenic concentrations at the Devens wastewater treatment facility. MDFA's wastewater contract operator will arrange to have samples collected for these additional tests to be performed quarterly on the wastewater influent, effluent and sludge. All analytical costs associated with this arsenic sampling shall be included in the permittee's regular sewer discharge fee and shall be billed along with such. (Billing is currently done on a quarterly cycle.)**

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C. All sample analysis required by this permit shall be performed by an independent laboratory certified by the MADEP for the parameters being analyzed. The use of a laboratory with provisional MADEP certification is prohibited.

D. The permittee shall submit a copy of the "Massachusetts Certification for Chemical Analysis of Water" for each laboratory that performs an analysis submitted to MassDevelopment by or on behalf of the permittee.

E. The Self-Monitoring results shall be submitted to MDFA/Devens within 30 days of the analysis.

F. Each Self-Monitoring Report shall be signed by an authorized representative of the permittee submitting the Report, and shall be certified as accurate. An authorized representative shall be an individual described in 40 C.F.R. Part 403.12(I). The Self Monitoring Report shall contain a certification statement consistent with the following:

"I certify under the penalty of law that this document and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gather and evaluate the information submitted. Based on my inquiry of the person or persons who manage the system or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations."

Part IV - Reporting Requirements

A. As required in the MDFA *Sewer Use Rules and Regulations*, Section 1.012, the permittee shall notify MDFA/Devens and the MADEP immediately by telephone of any accidental or slug discharge to the sewer. Formal written notification addressing the circumstances and remedies shall be submitted to MDFA/Devens within 5 days of the occurrence. Furthermore, a notice shall be permanently posted on the permittee's bulletin board or other prominent location advising employees whom to call in the event of an accidental, slug or dangerous

discharge. The permittee shall instruct all necessary employees of the emergency notification procedure.

B. The permittee shall notify MDFA/Devens prior to the introduction of new wastewater or pollutants or any substantial change in volume or characteristics of the wastewater being introduced to the sewer from the permittee's industrial process. Formal written notification shall follow within thirty (30) days of such introduction.

C. The permittee shall submit a monitoring report that tabulates the flow and sample analysis results for the composite samples and grab samples required in Part I. The monitoring quarters and due dates are as follows:

Quarter	**Report Due Date**	**Data to be Reported**
January 1 - March 31	April 5th	Quarterly Sampling, Flows
April 1 - June 30	July 5th	Quarterly Sampling, Flows
July 1 - September 30	October 5th	Quarterly/Annual Sampling, Flows
October 1 - December 31	January 5th	Quarterly Sampling, Flows

The monthly analysis results for arsenic samples required in Part I are due no later than the 5th of the month following the month the sample was taken.

D. All reports shall be submitted to the following address:

Utilities Supervisor
MassDevelopment
33 Andrews Parkway
Devens, Massachusetts 01434

With copy to: Industrial Pretreatment Coordinator
United Water
85 Walker Rd
Shirley MA, 01464

E. Emergency notifications shall be made to:

Devens Dispatch
Phone: (978) 772-7200

-and-

United Water – Devens Wastewater Operations
Phone: (978) 772-4250

Part V - Standard Conditions

A. *General Prohibitions.* The permittee shall comply with all general and specific prohibitive

discharge standards described in Sections 1.021, 1.022 and 1.023 of the MassDevelopment, *Sewer Use Rules and Regulations*.

B. *Right of Entry.* The permittee shall, in accordance with Section 1.011 (3) of the Sewer Use Rules and Regulations, allow MassDevelopment or their representatives to enter upon the premises of the permittee, at any time, for the purpose of inspection, sampling or records inspection.

C. *Records Retention.* The permittee shall retain and preserve for no less than three (3) years, any records, books, documents, memoranda, reports, correspondence and any and all summaries thereof, relating to monitoring, sampling and chemical analyses made by or in behalf of the permittee in connection with its discharge. All records that pertain to matters that are the subject of special orders or any other enforcement or litigation activities brought by MassDevelopment shall be retained and preserved by the permittee until all enforcement activities have concluded and all periods of limitation with respect to any and all appeals have expired. Copies must be provided as required by MassDevelopment.

D. *Confidential Information.* Information and data on a permittee obtained from reports, questionnaires, permit applications, permits and monitoring programs and from inspections shall be available to the public or other governmental agency without restriction unless the permittee specifically requests and is able to demonstrate to the satisfaction of MassDevelopment that the release of such information would divulge information, process or methods of production entitled to protection as trade secrets of the permittee.

When requested by the person furnishing a report, the portions of a report which might disclose trade secrets or secret processes shall not be made available for inspection by the public, but shall be made available upon written request to governmental agencies for uses related to the Rules and Regulations, the Devens wastewater treatment facility's Groundwater Discharge Permit, State Disposal System permit and/or the Pretreatment Programs and also provided that such portions of a report shall be available for use by the State or any State agency in judicial review, or enforcement proceedings involving the person furnishing the report. Wastewater constituents and characteristics will not be recognized as confidential information. Information accepted by MassDevelopment as confidential shall not be transmitted to the general public until notice is given to the permittee. EPA officials shall have unrestricted and immediate access to all information collected by MassDevelopment.

E. *Recording of Results.* For each measurement or sample taken pursuant to the requirements of this permit, the permittee shall have the following information recorded:

1. The exact place, date, time of sampling and the person performing the sampling;
2. The dates the analyses were performed;
3. The person(s) who performed the analyses;
4. The analytical techniques or methods used;
5. Sample preservation; and,
6. The results of all required analyses.

F. *Dilution.* The permittee shall not increase the use of potable water or process water or, in anyway, attempt to dilute a discharge as a partial or complete substitute for adequate treatment to achieve compliance with the limitations contained in this permit.

G. *Proper Disposal of Pretreatment Sludges and Spent Chemicals.* The disposal of sludges and spent chemicals generated shall be done in accordance with Section 405 of the Clean Water Act and Subtitles C and D of the Resource Conservation and Recovery Act.

H. *Signatory Requirements.* All applications, reports, or information submitted to MassDevelopment, must contain the following certification statement and be signed as required in Sections 1, 2, 3, or 4 below:

"I certify under penalty of law that this document and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gather and evaluate the information submitted. Based on my inquiry of the person or persons who manage the system or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations."

Authorized Representative of the Permittee:

1. If the permittee is a corporation, a responsible corporate officer means:

   a. The president, secretary, treasurer, or a vice-president of the corporation in charge of a principle business function or any other person who performs similar policy or decision-making functions for the corporation; or

   b. The manager of one or more manufacturing, production, or operation facilities employing more than two hundred fifty (250) persons or having a gross annual sales or expenditures exceeding twenty five (25) million dollars, if authority to sign documents has been assigned or delegated to the manager in accordance with corporate procedures.

2. If the permittee is a partnership or sole proprietorship: a general partner or proprietor, respectively.

3. If the permittee is a Federal, State or local governmental facility: a director or highest official appointed or designated to oversee the operation and performance of the activities of the government facility, or their designee.

4. The individuals described in paragraphs 1 through 3 above may designate another authorized representative if the authorization is in writing, the authorization specifies the individual or person responsible for the overall operation of the facility from which the discharge originates or having overall responsibility for the environmental

matters for the company, and the written authorization is submitted to MassDevelopment.

5. If the authorization under paragraph 4 above is no longer accurate because a different individual or position has responsibility for the overall operation of the facility or company, a new authorization satisfying the requirements of paragraph 4 of this section must be submitted to MassDevelopment prior to or together with any reports to be signed by an authorized representative.

I. *Revocation of Permit.* The permit issued to the permittee by MassDevelopment may be revoked when, after inspection, monitoring or analyses it is determined that the discharge of wastewater to the sanitary sewer is in violation of Federal, State or Local laws, ordinances or regulations. Additionally, falsification or intentional misrepresentation of data or statements pertaining to the permit application or any other required reporting form, shall be cause for permit revocation and possible criminal prosecution.

J. *Limitation of Permit Transfer.* Wastewater discharge permits are issued to a specific permittee for a specific operation and are not assignable to another user or transferable to any other location without the prior written approval of MassDevelopment. Sale of a permitted facility shall obligate the purchaser to seek prior written approval of MassDevelopment for continued discharge to the Devens Regional Wastewater Treatment Facility.

K. *Falsifying Information or Tampering With Monitoring Equipment.* Any person who knowingly makes any false statements, representation or certification in any application, record, report, plan or other document filed or required to be maintained pursuant to the *Sewer Use Rules and Regulations*, or permit, or who falsifies, tampers with or knowingly renders inaccurate, any monitoring device or method required under these Rules and Regulations, may, upon conviction, be punished by fine of up to $10,000 per day and imprisonment up to six months, or by both.

L. *Civil Penalties.* Any permittee who is found to have violated an Order of MassDevelopment or who failed to comply with any provision of the Rules and Regulations, and the orders, rules, regulations and permits issued hereunder, may be fined up to $10,000 for each offense. Each day on which a violation shall occur or continue shall be deemed a separate and distinct offense. In addition to the penalties provided herein, MassDevelopment may recover reasonable attorney's fees, court costs, court reporters' fees and other expenses of litigation by appropriate suit at law against the person found to have violated the Rules and Regulations or the orders, rules, regulations and permits issued hereunder. Nothing in the permit shall be construed to relieve the permittee from civil and/or criminal penalties for noncompliance under these Rules and Regulations or State or Federal laws or regulations.

M. *Recovery of Cost Incurred.* In addition to civil and criminal liability, the permittee violating any of the provisions of this permit or causing damage to or otherwise inhibiting the Agency's wastewater disposal system shall be liable to the Agency for any expenses, loss, or damage caused by such violation or discharge. The Agency shall assess the permittee for the cost incurred by the Agency for any cleaning, repair, or replacement work caused by the violation or discharge.

N. *Duty to Comply.* The permittee must comply with all conditions of this permit. Failure to comply with the requirements of this permit may be grounds for administrative action, or enforcement proceedings including civil or criminal penalties, injunctive relief and summary abatements.

O. *Duty to Mitigate.* The permittee shall take all reasonable steps to minimize or correct any adverse impact to the public treatment plant or to the environment resulting from noncompliance with this permit, including such accelerated monitoring as necessary to determine the nature and impact of the noncompliance discharge.

P. *Duty to Halt or Reduce Activity.* Upon reduction of efficiency of operation, or loss or failure of all or part of the treatment facility, the permittee shall, to the extent necessary to maintain compliance with its permit, control the production or discharges, or both, until operation of the treatment facility is restored or an alternate method of treatment is provided.

Q. *Modification or Revision of the Permit.* The terms and conditions of this permit may be subject to modifications by MassDevelopment at any time as limitations or requirements are modified or other just cause exists. This permit may be modified for other just cause. This permit may also be modified to incorporate special conditions resulting from the issuance of a special order promulgating a new pretreatment standard. Any permit modifications which result in new conditions in the permit shall include a reasonable time schedule for compliance.

R. *Duty to Reapply.* The permittee shall apply for permit renewal a minimum of sixty (60) days prior to the expiration of the Permittee's existing permit.

S. *Severability.* The provisions of this permit are severable, and if any provision of this permit, or the application of any provision of this permit are deemed invalid, the remainder of this permit shall not be affected thereby.

T. *Property Rights.* The issuance of this permit does not convey any property rights in either real or personal property, or any exclusive privileges, nor does it authorize any invasion of personal rights, nor any infringement of Federal, State or Local regulations.

MassDevelopment

SHEPLEY'S HILL LANDFILL DISCHARGE PERMIT

Please complete this page, keep a copy with your Landfill Discharge Permit and return the original to the following address:

MassDevelopment
Attn: Utilities Supervisor
33 Andrews Parkway
Devens, MA 01434

Acknowledgment of permit terms, conditions and limitations:

The undersigned acknowledges receipt of a renewal of Permit Number 020 authorizing a discharge of treated landfill wastewater to the Devens Wastewater Treatment Facility sewer system. The permittee also acknowledges that this permit is issued at its request based upon the application for the permit and the information provided and acknowledges the conditions and limitations set forth in said permit, **including the requirement for the permittee to pay for additional arsenic tests at the Devens wastewater treatment facility as described in Special Conditions paragraph II.C of this permit**. All information and data contained in this document may be made available to the public without restriction.

U.S Army Corp of Engineers
Permittee Name

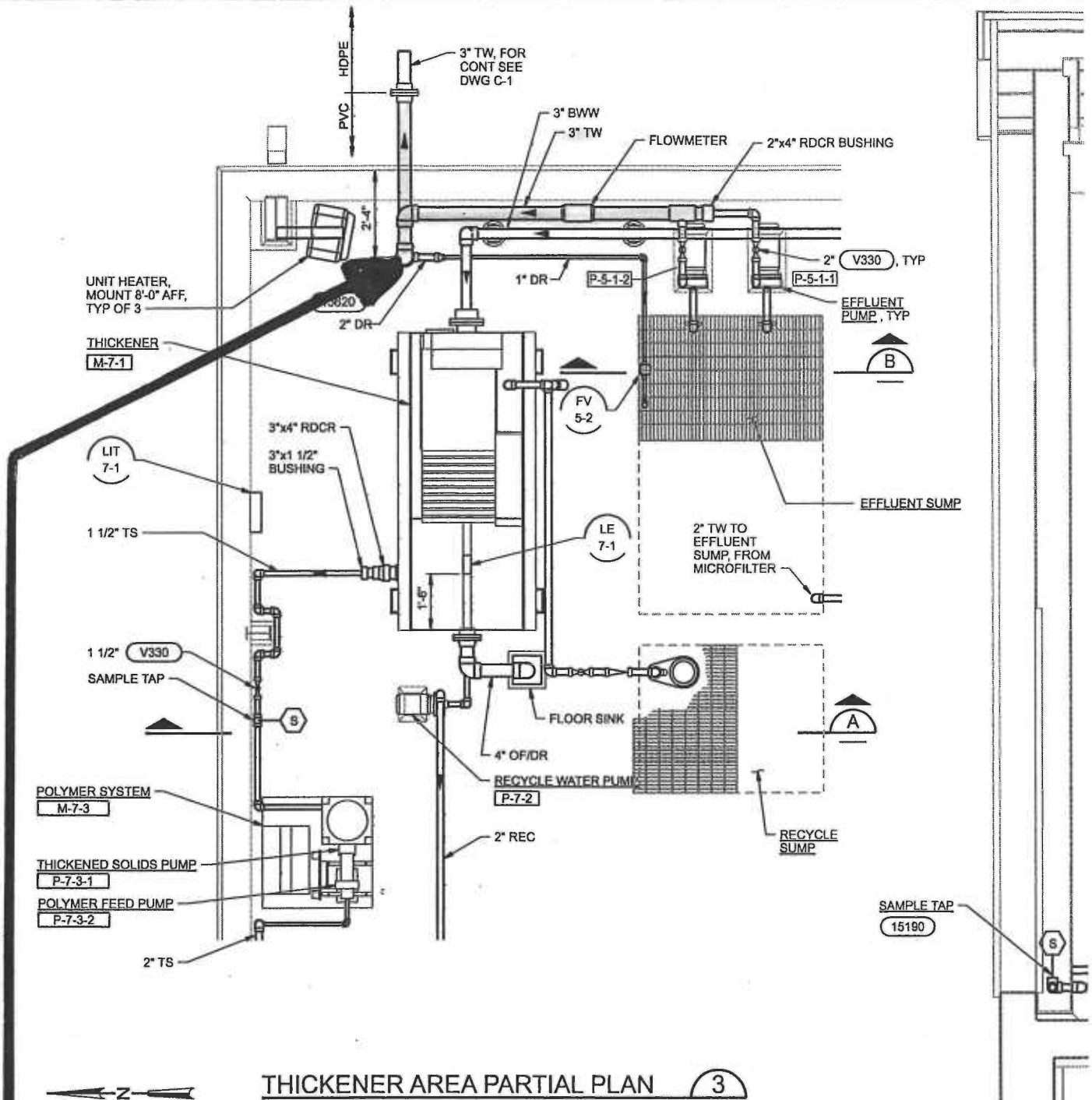
50 MacArthur Ave.
Box 90
Devens, MA 01434
Permittee Address

By:_____
Authorized Representative - Please Print or Type

_____
Signature

_____
Title

_____
Date



Z

THICKENER AREA PARTIAL PLAN 3

1/2"=1'-0" M-1

SAMPLES TO BE OBTAINED FROM EFFLUENT DISCHARGE PIPING

(see piping labeled 3" TW above)

DSGN S BUECKER							VERIFY SCALE
DR C WORRALL							BAR IS ONE INCH ON ORIGINAL DRAWING. 0 1"
CHK S KADER							IF NOT ONE INCH ON THIS SHEET, ADJUST SCALES ACCORDINGLY.
APVD S KADER	NO.	DATE	REVISION		BY	APVD	

APPENDIX G
(CD)

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION I

LOW STRESS (low flow) PURGING AND SAMPLING PROCEDURE FOR THE COLLECTION OF GROUNDWATER SAMPLES FROM MONITORING WELLS

Quality Assurance Unit
U.S. Environmental Protection Agency – Region 1
11 Technology Drive
North Chelmsford, MA 01863

Prepared by: Charles Porfert 1/19/10
(Charles Porfert, Quality Assurance Unit) Date

Approved by: Gerard Sotolongo 1-19-10
(Gerard Sotolongo, Quality Assurance Unit) Date

Revision Page

Date	Rev #	Summary of changes	Sections
7/30/96	2	Finalized	
01/19/10	3	Updated	All sections

TABLE OF CONTENTS

USE OF TERMS

Equipment blank: The equipment blank shall include the pump and the pump's tubing. If tubing is dedicated to the well, the equipment blank needs only to include the pump in subsequent sampling rounds. If the pump and tubing are dedicated to the well, the equipment blank is collected prior to its placement in the well. If the pump and tubing will be used to sample multiple wells, the equipment blank is normally collected after sampling from contaminated wells and not after background wells.

Field duplicates: Field duplicates are collected to determine precision of the sampling procedure. For this procedure, collect duplicate for each analyte group in consecutive order (VOC original, VOC duplicate, SVOC original, SVOC duplicate, etc.).

Indicator field parameters: This SOP uses field measurements of turbidity, dissolved oxygen, specific conductance, temperature, pH, and oxidation/reduction potential (ORP) as indicators of when purging operations are sufficient and sample collection may begin.

Matrix Spike/Matrix Spike Duplicates: Used by the laboratory in its quality assurance program. Consult the laboratory for the sample volume to be collected.

Poteniometric Surface: The level to which water rises in a tightly cased well constructed in a confined aquifer. In an unconfined aquifer, the potentiometric surface is the water table.

QAPP: Quality Assurance Project Plan

SAP: Sampling and Analysis Plan

SOP: Standard operating procedure

Stabilization: A condition that is achieved when all indicator field parameter measurements are sufficiently stable (as described in the "Monitoring Indicator Field Parameters" section) to allow sample collection to begin.

Temperature blank: A temperature blank is added to each sample cooler. The blank is measured upon receipt at the laboratory to assess whether the samples were properly cooled during transit.

Trip blank (VOCs): Trip blank is a sample of analyte-free water taken to the sampling site and returned to the laboratory. The trip blanks (one pair) are added to each sample cooler that contains VOC samples.

SCOPE & APPLICATION

The goal of this groundwater sampling procedure is to collect water samples that reflect the total mobile organic and inorganic loads (dissolved and colloidal sized fractions) transported through the subsurface under ambient flow conditions, with minimal physical and chemical alterations from sampling operations. This standard operating procedure (SOP) for collecting groundwater samples will help ensure that the project's data quality objectives (DQOs) are met under certain low-flow conditions.

The SOP emphasizes the need to minimize hydraulic stress at the well-aquifer interface by maintaining low water-level drawdowns, and by using low pumping rates during purging and sampling operations. Indicator field parameters (e.g., dissolved oxygen, pH, etc.) are monitored during purging in order to determine when sample collection may begin. Samples properly collected using this SOP are suitable for analysis of groundwater contaminants (volatile and semi-volatile organic analytes, dissolved gases, pesticides, PCBs, metals and other inorganics), or naturally occurring analytes. This SOP is based on Puls, and Barcelona (1996).

This procedure is designed for monitoring wells with an inside diameter (1.5-inches or greater) that can accommodate a positive lift pump with a screen length or open interval ten feet or less and with a water level above the top of the screen or open interval (Hereafter, the "screen or open interval" will be referred to only as "screen interval"). This SOP is not applicable to other well-sampling conditions.

While the use of dedicated sampling equipment is not mandatory, dedicated pumps and tubing can reduce sampling costs significantly by streamlining sampling activities and thereby reducing the overall field costs.

The goal of this procedure is to emphasize the need for consistency in deploying and operating equipment while purging and sampling monitoring wells during each sampling event. This will help to minimize sampling variability.

This procedure describes a general framework for groundwater sampling. Other site specific information (hydrogeological context, conceptual site model (CSM), DQOs, etc.) coupled with systematic planning must be added to the procedure in order to develop an appropriate site specific SAP/QAPP. In addition, the site specific SAP/QAPP must identify the specific equipment that will be used to collect the groundwater samples.

This procedure does not address the collection of water or free product samples from wells containing free phase LNAPLs and/or DNAPLs (light or dense non-aqueous phase

liquids). For this type of situation, the reader may wish to check: Cohen, and Mercer (1993) or other pertinent documents.

This SOP is to be used when collecting groundwater samples from monitoring wells at all Superfund, Federal Facility and RCRA sites in Region 1 under the conditions described herein. Request for modification of this SOP, in order to better address specific situations at individual wells, must include adequate technical justification for proposed changes. All changes and modifications must be approved and included in a revised SAP/QAPP before implementation in field.

BACKGROUND FOR IMPLEMENTATION

It is expected that the monitoring well screen has been properly located (both laterally and vertically) to intercept existing contaminant plume(s) or along flow paths of potential contaminant migration. Problems with inappropriate monitoring well placement or faulty/improper well installation cannot be overcome by even the best water sampling procedures. This SOP presumes that the analytes of interest are moving (or will potentially move) primarily through the more permeable zones intercepted by the screen interval.

Proper well construction, development, and operation and maintenance cannot be overemphasized. The use of installation techniques that are appropriate to the hydrogeologic setting of the site often prevent "problem well" situations from occurring. During well development, or redevelopment, tests should be conducted to determine the hydraulic characteristics of the monitoring well. The data can then be used to set the purging/sampling rate, and provide a baseline for evaluating changes in well performance and the potential need for well rehabilitation. Note: if this installation data or well history (construction and sampling) is not available or discoverable, for all wells to be sampled, efforts to build a sampling history should commence with the next sampling event.

The pump intake should be located within the screen interval and at a depth that will remain under water at all times. It is recommended that the intake depth and pumping rate remain the same for all sampling events. The mid-point or the lowest historical midpoint of the saturated screen length is often used as the location of the pump intake. For new wells, or for wells without pump intake depth information, the site's SAP/QAPP must provide clear reasons and instructions on how the pump intake depth(s) will be selected, and reason(s) for the depth(s) selected. If the depths to top and bottom of the well screen are not known, the SAP/QAPP will need to describe how the sampling depth will be determined and how the data can be used.

Stabilization of indicator field parameters is used to indicate that conditions are suitable for sampling to begin. Achievement of turbidity levels of less than 5 NTU, and stable drawdowns of less than 0.3 feet, while desirable, are not mandatory. Sample collection

may still take place provided the indicator field parameter criteria in this procedure are met. If after 2 hours of purging indicator field parameters have not stabilized, one of three optional courses of action may be taken: a) continue purging until stabilization is achieved, b) discontinue purging, do not collect any samples, and record in log book that stabilization could not be achieved (documentation must describe attempts to achieve stabilization), c) discontinue purging, collect samples and provide full explanation of attempts to achieve stabilization (note: there is a risk that the analytical data obtained, especially metals and strongly hydrophobic organic analytes, may reflect a sampling bias and therefore, the data may not meet the data quality objectives of the sampling event).

It is recommended that low-flow sampling be conducted when the air temperature is above 32°F (0°C). If the procedure is used below 32°F, special precautions will need to be taken to prevent the groundwater from freezing in the equipment. Because sampling during freezing temperatures may adversely impact the data quality objectives, the need for water sample collection during months when these conditions are likely to occur should be evaluated during site planning and special sampling measures may need to be developed. Ice formation in the flow-through-cell will cause the monitoring probes to act erratically. A transparent flow-through-cell needs to be used to observe if ice is forming in the cell. If ice starts to form on the other pieces of the sampling equipment, additional problems may occur.

HEALTH & SAFETY

When working on-site, comply with all applicable OSHA requirements and the site's health/safety procedures. All proper personal protection clothing and equipment are to be worn. Some samples may contain biological and chemical hazards. These samples should be handled with suitable protection to skin, eyes, etc.

CAUTIONS

The following cautions need to be considered when planning to collect groundwater samples when the below conditions occur.

If the groundwater degasses during purging of the monitoring well, dissolved gases and VOCs will be lost. When this happens, the groundwater data for dissolved gases (e.g., methane, ethene, ethane, dissolved oxygen, etc.) and VOCs will need to be qualified. Some conditions that can promote degassing are the use of a vacuum pump (e.g., peristaltic pumps), changes in aperture along the sampling tubing, and squeezing/pinching the pump's tubing which results in a pressure change.

When collecting the samples for dissolved gases and VOCs analyses, avoid aerating the groundwater in the pump's tubing. This can cause loss of the dissolved gases and VOCs in

the groundwater. Having the pump's tubing completely filled prior to sampling will avoid this problem when using a centrifugal pump or peristaltic pump.

Direct sun light and hot ambient air temperatures may cause the groundwater in the tubing and flow-through-cell to heat up. This may cause the groundwater to degas which will result in loss of VOCs and dissolved gases. When sampling under these conditions, the sampler will need to shade the equipment from the sunlight (e.g., umbrella, tent, etc.). If possible, sampling on hot days, or during the hottest time of the day, should be avoided. The tubing exiting the monitoring well should be kept as short as possible to avoid the sun light or ambient air from heating up the groundwater.

Thermal currents in the monitoring well may cause vertical mixing of water in the well bore. When the air temperature is colder than the groundwater temperature, it can cool the top of the water column. Colder water which is denser than warm water sinks to the bottom of the well and the warmer water at the bottom of the well rises, setting up a convention cell. "During low-flow sampling, the pumped water may be a mixture of convecting water from within the well casing and aquifer water moving inward through the screen. This mixing of water during low-flow sampling can substantially increase equilibration times, can cause false stabilization of indicator parameters, can give false indication of redox state, and can provide biological data that are not representative of the aquifer conditions" (Vroblesky 2007).

Failure to calibrate or perform proper maintenance on the sampling equipment and measurement instruments (e.g., dissolved oxygen meter, etc.) can result in faulty data being collected.

Interferences may result from using contaminated equipment, cleaning materials, sample containers, or uncontrolled ambient/surrounding air conditions (e.g., truck/vehicle exhaust nearby).

Cross contamination problems can be eliminated or minimized through the use of dedicated sampling equipment and/or proper planning to avoid ambient air interferences. Note that the use of dedicated sampling equipment can also significantly reduce the time needed to complete each sampling event, will promote consistency in the sampling, and may reduce sampling bias by having the pump's intake at a constant depth.

Clean and decontaminate all sampling equipment prior to use. All sampling equipment needs to be routinely checked to be free from contaminants and equipment blanks collected to ensure that the equipment is free of contaminants. Check the previous equipment blank data for the site (if they exist) to determine if the previous cleaning procedure removed the contaminants. If contaminants were detected and they are a concern, then a more vigorous cleaning procedure will be needed.

PERSONNEL QUALIFICATIONS

All field samplers working at sites containing hazardous waste must meet the requirements of the OSHA regulations. OSHA regulations may require the sampler to take the 40 hour OSHA health and safety training course and a refresher course prior to engaging in any field activities, depending upon the site and field conditions.

The field samplers must be trained prior to the use of the sampling equipment, field instruments, and procedures. Training is to be conducted by an experienced sampler before initiating any sampling procedure.

The entire sampling team needs to read, and be familiar with, the site Health and Safety Plan, all relevant SOPs, and SAP/QAPP (and the most recent amendments) before going onsite for the sampling event. It is recommended that the field sampling leader attest to the understanding of these site documents and that it is recorded.

EQUIPMENT AND SUPPLIES

A. Informational materials for sampling event

A copy of the current Health and Safety Plan, SAP/QAPP, monitoring well construction data, location map(s), field data from last sampling event, manuals for sampling, and the monitoring instruments' operation, maintenance, and calibration manuals should be brought to the site.

B. Well keys.

C. Extraction device

Adjustable rate, submersible pumps (e.g., centrifugal, bladder, etc.) which are constructed of stainless steel or Teflon are preferred. Note: if extraction devices constructed of other materials are to be used, adequate information must be provided to show that the substituted materials do not leach contaminants nor cause interferences to the analytical procedures to be used. Acceptance of these materials must be obtained before the sampling event.

If bladder pumps are selected for the collection of VOCs and dissolved gases, the pump setting should be set so that one pulse will deliver a water volume that is sufficient to fill a 40 mL VOC vial. This is not mandatory, but is considered a "best practice". For the proper operation, the bladder pump will need a minimum amount of water above the pump; consult the manufacturer for the recommended submergence. The pump's recommended submergence value should be determined during the planning stage, since it may influence well construction and placement of dedicated pumps where water-level fluctuations are significant.

Adjustable rate, peristaltic pumps (suction) are to be used with caution when collecting samples for VOCs and dissolved gases (e.g., methane, carbon dioxide, etc.) analyses. Additional information on the use of peristaltic pumps can be found in Appendix A. If peristaltic pumps are used, the inside diameter of the rotor head tubing needs to match the inside diameter of the tubing installed in the monitoring well.

Inertial pumping devices (motor driven or manual) are not recommended. These devices frequently cause greater disturbance during purging and sampling, and are less easily controlled than submersible pumps (potentially increasing turbidity and sampling variability, etc.). This can lead to sampling results that are adversely affected by purging and sampling operations, and a higher degree of data variability.

D. Tubing

Teflon or Teflon-lined polyethylene tubing are preferred when sampling is to include VOCs, SVOCs, pesticides, PCBs and inorganics. Note: if tubing constructed of other materials is to be used, adequate information must be provided to show that the substituted materials do not leach contaminants nor cause interferences to the analytical procedures to be used. Acceptance of these materials must be obtained before the sampling event.

PVC, polypropylene or polyethylene tubing may be used when collecting samples for metal and other inorganics analyses.

The use of 1/4 inch or 3/8 inch (inside diameter) tubing is recommended. This will help ensure that the tubing remains liquid filled when operating at very low pumping rates when using centrifugal and peristaltic pumps.

Silastic tubing should be used for the section around the rotor head of a peristaltic pump. It should be less than a foot in length. The inside diameter of the tubing used at the pump rotor head must be the same as the inside diameter of tubing placed in the well. A tubing connector is used to connect the pump rotor head tubing to the well tubing. Alternatively, the two pieces of tubing can be connected to each other by placing the one end of the tubing inside the end of the other tubing. The tubing must not be reused.

E. The water level measuring device

Electronic "tape", pressure transducer, water level sounder/level indicator, etc. should be capable of measuring to 0.01 foot accuracy. Recording pressure transducers, mounted above the pump, are especially helpful in tracking water levels during pumping operations, but their use must include check measurements with a water level "tape" at the start and end of each sampling event.

F. Flow measurement supplies

Graduated cylinder (size according to flow rate) and stopwatch usually will suffice.

Large graduated bucket used to record total water purged from the well.

G. Interface probe

To be used to check on the presence of free phase liquids (LNAPL, or DNAPL) before purging begins (as needed).

H. Power source (generator, nitrogen tank, battery, etc.)

When a gasoline generator is used, locate it downwind and at least 30 feet from the well so that the exhaust fumes do not contaminate samples.

I. Indicator field parameter monitoring instruments

Use of a multi-parameter instrument capable of measuring pH, oxidation/reduction potential (ORP), dissolved oxygen (DO), specific conductance, temperature, and coupled with a flow-through-cell is required when measuring all indicator field parameters, except turbidity. Turbidity is collected using a separate instrument. Record equipment/instrument identification (manufacturer, and model number).

Transparent, small volume flow-through-cells (e.g., 250 mLs or less) are preferred. This allows observation of air bubbles and sediment buildup in the cell, which can interfere with the operation of the monitoring instrument probes, to be easily detected. A small volume cell facilitates rapid turnover of water in the cell between measurements of the indicator field parameters.

It is recommended to use a flow-through-cell and monitoring probes from the same manufacturer and model to avoid incompatibility between the probes and flow-through-cell.

Turbidity samples are collected before the flow-through-cell. A "T" connector coupled with a valve is connected between the pump's tubing and flow-through-cell. When a turbidity measurement is required, the valve is opened to allow the groundwater to flow into a container. The valve is closed and the container sample is then placed in the turbidimeter.

Standards are necessary to perform field calibration of instruments. A minimum of two standards are needed to bracket the instrument measurement range for all parameters except ORP which use a Zobell solution as a standard. For dissolved oxygen, a wet sponge used for the 100% saturation and a zero dissolved oxygen solution are used for the calibration.

Barometer (used in the calibration of the Dissolved Oxygen probe) and the conversion formula to convert the barometric pressure into the units of measure used by the Dissolved Oxygen meter are needed.

J. Decontamination supplies

Includes (for example) non-phosphate detergent, distilled/deionized water, isopropyl alcohol, etc.

K. Record keeping supplies

Logbook(s), well purging forms, chain-of-custody forms, field instrument calibration forms, etc.

L. Sample bottles

M. Sample preservation supplies (as required by the analytical methods)

N. Sample tags or labels

O. PID or FID instrument

If appropriate, to detect VOCs for health and safety purposes, and provide qualitative field evaluations.

P. Miscellaneous Equipment

Equipment to keep the sampling apparatus shaded in the summer (e.g., umbrella) and from freezing in the winter. If the pump's tubing is allowed to heat up in the warm weather, the cold groundwater may degas as it is warmed in the tubing.

EQUIPMENT/INSTRUMENT CALIBRATION

Prior to the sampling event, perform maintenance checks on the equipment and instruments according to the manufacturer's manual and/or applicable SOP. This will ensure that the equipment/instruments are working properly before they are used in the field.

Prior to sampling, the monitoring instruments must be calibrated and the calibration documented. The instruments are calibrated using U.S Environmental Protection Agency Region 1 *Calibration of Field Instruments (temperature, pH, dissolved oxygen, conductivity/specific conductance, oxidation/reduction [ORP], and turbidity),* January 19, 2010, or latest version or from one of the methods listed in 40CFR136, 40CFR141 and SW-846.

The instruments shall be calibrated at the beginning of each day. If the field measurement falls outside the calibration range, the instrument must be re-calibrated so that all measurements fall within the calibration range. At the end of each day, a calibration check is performed to verify that instruments remained in calibration throughout the day. This check is performed while the instrument is in measurement mode, not calibration mode. If the field instruments are being used to monitor the natural attenuation parameters, then a calibration check at mid-day is highly recommended to ensure that the instruments did not drift out of calibration. Note: during the day if the instrument reads zero or a negative number for dissolved oxygen, pH, specific conductance, or turbidity (negative value only), this indicates that the instrument drifted out of calibration or the instrument is malfunctioning. If this situation occurs the data from this instrument will need to be qualified or rejected.

PRELIMINARY SITE ACTIVITIES (as applicable)

Check the well for security (damage, evidence of tampering, missing lock, etc.) and record pertinent observations (include photograph as warranted).

If needed lay out sheet of clean polyethylene for monitoring and sampling equipment, unless equipment is elevated above the ground (e.g., on a table, etc.).

Remove well cap and if appropriate measure VOCs at the rim of the well with a PID or FID instrument and record reading in field logbook or on the well purge form.

If the well casing does not have an established reference point (usually a V-cut or indelible mark in the well casing), make one. Describe its location and record the date of the mark in the logbook (consider a photographic record as well). All water level measurements must be recorded relative to this reference point (and the altitude of this point should be determined using techniques that are appropriate to site's DQOs.

If water-table or potentiometric surface map(s) are to be constructed for the sampling event, perform synoptic water level measurement round (in the shortest possible time) before any purging and sampling activities begin. If possible, measure water level depth (to 0.01 ft.) and total well depth (to 0.1 ft.) the day before sampling begins, in order to allow for re-settlement of any particulates in the water column. This is especially important for those wells that have not been recently sampled because sediment buildup in the well may require the well to be redeveloped. If measurement of total well depth is not made the day before, it should be measured after sampling of the well is complete. All measurements must be taken from the established referenced point. Care should be taken to minimize water column disturbance.

Check newly constructed wells for the presence of LNAPLs or DNAPLs before the initial sampling round. If none are encountered, subsequent check measurements with an interface probe may not be necessary unless analytical data or field analysis signal a worsening situation. This SOP cannot be used in the presence of LNAPLs or DNAPLs. If NAPLs are present, the project team must decide upon an alternate sampling method. All project modifications must be approved and documented prior to implementation.

If available check intake depth and drawdown information from previous sampling event(s) for each well. Duplicate, to the extent practicable, the intake depth and extraction rate (use final pump dial setting information) from previous event(s). If changes are made in the intake depth or extraction rate(s) used during previous sampling event(s), for either portable or dedicated extraction devices, record new values, and explain reasons for the changes in the field logbook.

PURGING AND SAMPLING PROCEDURE

Purging and sampling wells in order of increasing chemical concentrations (known or anticipated) are preferred.

The use of dedicated pumps is recommended to minimize artificial mobilization and entrainment of particulates each time the well is sampled. Note that the use of dedicated sampling equipment can also significantly reduce the time needed to complete each

sampling event, will promote consistency in the sampling, and may reduce sampling bias by having the pump's intake at a constant depth.

A. Initial Water Level

Measure the water level in the well before installing the pump if a non-dedicated pump is being used. The initial water level is recorded on the purge form or in the field logbook.

B. Install Pump

Lower pump, safety cable, tubing and electrical lines slowly (to minimize disturbance) into the well to the appropriate depth (may not be the mid-point of the screen/open interval). The Sampling and Analysis Plan/Quality Assurance Project Plan should specify the sampling depth (used previously), or provide criteria for selection of intake depth for each new well. If possible keep the pump intake at least two feet above the bottom of the well, to minimize mobilization of particulates present in the bottom of the well.

Pump tubing lengths, above the top of well casing should be kept as short as possible to minimize heating the groundwater in the tubing by exposure to sun light and ambient air temperatures. Heating may cause the groundwater to degas, which is unacceptable for the collection of samples for VOC and dissolved gases analyses.

C. Measure Water Level

Before starting pump, measure water level. Install recording pressure transducer, if used to track drawdowns, to initialize starting condition.

D. Purge Well

From the time the pump starts purging and until the time the samples are collected, the purged water is discharged into a graduated bucket to determine the total volume of groundwater purged. This information is recorded on the purge form or in the field logbook.

Start the pump at low speed and slowly increase the speed until discharge occurs. Check water level. Check equipment for water leaks and if present fix or replace the affected equipment. Try to match pumping rate used during previous sampling event(s). Otherwise, adjust pump speed until there is little or no water level drawdown. If the minimal drawdown that can be achieved exceeds 0.3 feet, but remains stable, continue purging.

Monitor and record the water level and pumping rate every five minutes (or as appropriate) during purging. Record any pumping rate adjustments (both time and flow rate). Pumping rates should, as needed, be reduced to the minimum capabilities of the pump to ensure stabilization of the water level. Adjustments are best made in the first fifteen minutes of pumping in order to help minimize purging time. During pump start-up, drawdown may exceed the 0.3 feet target and then "recover" somewhat as pump flow adjustments are made. Purge volume calculations should utilize stabilized drawdown value, not the initial drawdown. If the initial water level is above the top of the screen do not allow the water level to fall into the well screen. The final purge volume must be greater than the stabilized drawdown volume plus the pump's tubing volume. If the drawdown has exceeded 0.3 feet and stabilizes, calculate the volume of water between the initial water level and the stabilized water level. Add the volume of the water which occupies the pump's tubing to this calculation. This combined volume of water needs to be purged from the well after the water level has stabilized before samples are collected.

Avoid the use of constriction devices on the tubing to decrease the flow rate because the constrictor will cause a pressure difference in the water column. This will cause the groundwater to degas and result in a loss of VOCs and dissolved gasses in the groundwater samples.

Note: the flow rate used to achieve a stable pumping level should remain constant while monitoring the indicator parameters for stabilization and while collecting the samples.

Wells with low recharge rates may require the use of special pumps capable of attaining very low pumping rates (e.g., bladder, peristaltic), and/or the use of dedicated equipment. For new monitoring wells, or wells where the following situation has not occurred before, if the recovery rate to the well is less than 50 mL/min., or the well is being essentially dewatered during purging, the well should be sampled as soon as the water level has recovered sufficiently to collect the volume needed for all anticipated samples. The project manager or field team leader will need to make the decision when samples should be collected, how the sample is to be collected, and the reasons recorded on the purge form or in the field logbook. A water level measurement needs to be performed and recorded before samples are collected. If the project manager decides to collect the samples using the pump, it is best during this recovery period that the pump intake tubing not be removed, since this will aggravate any turbidity problems. Samples in this specific situation may be collected without stabilization of indicator field parameters. Note that field conditions and efforts to overcome problematic situations must be recorded in order to support field decisions to deviate from normal procedures described in this SOP. If this type of problematic situation persists in a well, then water sample collection should be changed to a passive or no-purge method, if consistent with the site's DQOs, or have a new well installed.

E. Monitor Indicator Field Parameters

After the water level has stabilized, connect the "T" connector with a valve and the flow-through-cell to monitor the indicator field parameters. If excessive turbidity is anticipated or encountered with the pump startup, the well may be purged for a while without connecting up the flow-through-cell, in order to minimize particulate buildup in the cell (This is a judgment call made by the sampler). Water level drawdown measurements should be made as usual. If possible, the pump may be installed the day before purging to allow particulates that were disturbed during pump insertion to settle.

During well purging, monitor indicator field parameters (turbidity, temperature, specific conductance, pH, ORP, DO) at a frequency of five minute intervals or greater. The pump's flow rate must be able to "turn over" at least one flow-through-cell volume between measurements (for a 250 mL flow-through-cell with a flow rate of 50 mLs/min., the monitoring frequency would be every five minutes; for a 500 mL flow-through-cell it would be every ten minutes). If the cell volume cannot be replaced in the five minute interval, then the time between measurements must be increased accordingly. Note: during the early phase of purging emphasis should be put on minimizing and stabilizing pumping stress, and recording those adjustments followed by stabilization of indicator parameters. Purging is considered complete and sampling may begin when all the above indicator field parameters have stabilized. Stabilization is considered to be achieved when three consecutive readings are within the following limits:

Turbidity (10% for values greater than 5 NTU; if three Turbidity values are less than 5 NTU, consider the values as stabilized),
Dissolved Oxygen (10% for values greater than 0.5 mg/L, if three Dissolved Oxygen values are less than 0.5 mg/L, consider the values as stabilized),
Specific Conductance (3%),
Temperature (3%),
pH (± 0.1 unit),
Oxidation/Reduction Potential (±10 millivolts).

All measurements, except turbidity, must be obtained using a flow-through-cell. Samples for turbidity measurements are obtained before water enters the flow-through-cell. Transparent flow-through-cells are preferred, because they allow field personnel to watch for particulate build-up within the cell. This build-up may affect indicator field parameter values measured within the cell. If the cell needs to be cleaned during purging operations, continue pumping and disconnect cell for cleaning, then reconnect after cleaning and continue monitoring activities. Record start and stop times and give a brief description of cleaning activities.

The flow-through-cell must be designed in a way that prevents gas bubble entrapment in the cell. Placing the flow-through-cell at a 45 degree angle with the port facing upward can help remove bubbles from the flow-through-cell (see Appendix B Low-Flow Setup Diagram). All during the measurement process, the flow-through-cell must remain free of any gas bubbles. Otherwise, the monitoring probes may act erratically. When the pump is turned off or cycling on/off (when using a bladder pump), water in the cell must not drain out. Monitoring probes must remain submerged in water at all times.

F. Collect Water Samples

When samples are collected for laboratory analyses, the pump's tubing is disconnected from the "T" connector with a valve and the flow-through-cell. The samples are collected directly from the pump's tubing. Samples must not be collected from the flow-through-cell or from the "T" connector with a valve.

VOC samples are normally collected first and directly into pre-preserved sample containers. However, this may not be the case for all sampling locations; the SAP/QAPP should list the order in which the samples are to be collected based on the project's objective(s). Fill all sample containers by allowing the pump discharge to flow gently down the inside of the container with minimal turbulence.

If the pump's flow rate is too high to collect the VOC/dissolved gases samples, collect the other samples first. Lower the pump's flow rate to a reasonable rate and collect the VOC/dissolved gases samples and record the new flow rate.

During purging and sampling, the centrifugal/peristaltic pump tubing must remain filled with water to avoid aeration of the groundwater. It is recommended that 1/4 inch or 3/8 inch (inside diameter) tubing be used to help insure that the sample tubing remains water filled. If the pump tubing is not completely filled to the sampling point, use the following procedure to collect samples: collect non-VOC/dissolved gases samples first, then increase flow rate slightly until the water completely fills the tubing, collect the VOC/dissolved gases samples, and record new drawdown depth and flow rate.

For bladder pumps that will be used to collect VOC or dissolved gas samples, it is recommended that the pump be set to deliver long pulses of water so that one pulse will fill a 40 mL VOC vial.

Use pre-preserved sample containers or add preservative, as required by analytical methods, to the samples immediately after they are collected. Check the analytical methods (e.g. EPA SW-846, 40 CFR 136, water supply, etc.) for additional information on preservation.

If determination of filtered metal concentrations is a sampling objective, collect filtered water samples using the same low flow procedures. The use of an in-line filter (transparent housing preferred) is required, and the filter size (0.45 μm is commonly used) should be based on the sampling objective. Pre-rinse the filter with groundwater prior to sample collection. Make sure the filter is free of air bubbles before samples are collected. Preserve the filtered water sample immediately. Note: filtered water samples are not an acceptable substitute for unfiltered samples when the monitoring objective is to obtain chemical concentrations of total mobile contaminants in groundwater for human health or ecological risk calculations.

Label each sample as collected. Samples requiring cooling will be placed into a cooler with ice or refrigerant for delivery to the laboratory. Metal samples after acidification to a pH less than 2 do not need to be cooled.

G. Post Sampling Activities

If a recording pressure transducer is used to track drawdown, re-measure water level with tape.

After collection of samples, the pump tubing may be dedicated to the well for re-sampling (by hanging the tubing inside the well), decontaminated, or properly discarded.

Before securing the well, measure and record the well depth (to 0.1 ft.), if not measured the day before purging began. Note: measurement of total well depth annually is usually sufficient after the initial low stress sampling event. However, a greater frequency may be needed if the well has a "silting" problem or if confirmation of well identity is needed.

Secure the well.

DECONTAMINATION

Decontaminate sampling equipment prior to use in the first well and then following sampling of each well. Pumps should not be removed between purging and sampling operations. The pump, tubing, support cable and electrical wires which were in contact with the well should be decontaminated by one of the procedures listed below.

The use of dedicated pumps and tubing will reduce the amount of time spent on decontamination of the equipment. If dedicated pumps and tubing are used, only the initial sampling event will require decontamination of the pump and tubing.

Note if the previous equipment blank data showed that contaminant(s) were present after using the below procedure or the one described in the SAP/QAPP, a more vigorous procedure may be needed.

Procedure 1

Decontaminating solutions can be pumped from either buckets or short PVC casing sections through the pump and tubing. The pump may be disassembled and flushed with the decontaminating solutions. It is recommended that detergent and alcohol be used sparingly in the decontamination process and water flushing steps be extended to ensure that any sediment trapped in the pump is removed. The pump exterior and electrical wires must be rinsed with the decontaminating solutions, as well. The procedure is as follows:

Flush the equipment/pump with potable water.

Flush with non-phosphate detergent solution. If the solution is recycled, the solution must be changed periodically.

Flush with potable or distilled/deionized water to remove all of the detergent solution. If the water is recycled, the water must be changed periodically.

Optional - flush with isopropyl alcohol (pesticide grade; must be free of ketones {e.g., acetone}) or with methanol. This step may be required if the well is highly contaminated or if the equipment blank data from the previous sampling event show that the level of contaminants is significant.

Flush with distilled/deionized water. This step must remove all traces of alcohol (if used) from the equipment. The final water rinse must not be recycled.

Procedure 2

Steam clean the outside of the submersible pump.

Pump hot potable water from the steam cleaner through the inside of the pump. This can be accomplished by placing the pump inside a three or four inch diameter PVC pipe with end cap. Hot water from the steam cleaner jet will be directed inside the PVC pipe and the pump exterior will be cleaned. The hot water from the steam cleaner will then be pumped from the PVC pipe through the pump and collected into another container. Note: additives or solutions should not be added to the steam cleaner.

Pump non-phosphate detergent solution through the inside of the pump. If the solution is recycled, the solution must be changed periodically.

Pump potable water through the inside of the pump to remove all of the detergent solution. If the solution is recycled, the solution must be changed periodically.

Pump distilled/deionized water through the pump. The final water rinse must not be recycled.

FIELD QUALITY CONTROL

Quality control samples are required to verify that the sample collection and handling process has not compromised the quality of the groundwater samples. All field quality control samples must be prepared the same as regular investigation samples with regard to sample volume, containers, and preservation. Quality control samples include field duplicates, equipment blanks, matrix spike/matrix spike duplicates, trip blanks (VOCs), and temperature blanks.

FIELD LOGBOOK

A field log shall be kept to document all groundwater field monitoring activities (see Appendix C, example table), and record the following for each well:

Site name, municipality, state.

Well identifier, latitude-longitude or state grid coordinates.

Measuring point description (e.g., north side of PVC pipe).

Well depth, and measurement technique.

Well screen length.

Pump depth.

Static water level depth, date, time and measurement technique.

Presence and thickness of immiscible liquid (NAPL) layers and detection method.

Pumping rate, drawdown, indicator parameters values, calculated or measured total volume pumped, and clock time of each set of measurements.

Type of tubing used and its length.

Type of pump used.

Clock time of start and end of purging and sampling activity.

Types of sample bottles used and sample identification numbers.

Preservatives used.

Parameters requested for analyses.

Field observations during sampling event.

Name of sample collector(s).

Weather conditions, including approximate ambient air temperature.

QA/QC data for field instruments.

Any problems encountered should be highlighted.

Description of all sampling/monitoring equipment used, including trade names, model number, instrument identification number, diameters, material composition, etc.

DATA REPORT

Data reports are to include laboratory analytical results, QA/QC information, field indicator parameters measured during purging, field instrument calibration information, and whatever other field logbook information is needed to allow for a full evaluation of data usability.

Note: the use of trade, product, or firm names in this sampling procedure is for descriptive purposes only and does not constitute endorsement by the U.S. EPA.

REFERENCES

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Robert W. Puls and Michael J. Barcelona, *Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures*, April 1996 (EPA/540/S-95/504).

U.S. Environmental Protection Agency, 1992, *RCRA Ground-Water Monitoring: Draft Technical Guidance*; Washington, DC (EPA/530-R-93-001).

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U.S Environmental Protection Agency, Region 1, *Calibration of Field Instruments (temperature, pH, dissolved oxygen, conductivity/specific conductance, oxidation/reduction [ORP], and turbidity),* January 19, 2010 or latest version.

U.S Environmental Protection Agency, EPA SW-846.

U.S Environmental Protection Agency, 40 CFR 136.

U.S Environmental Protection Agency, 40 CFR 141.

Vroblesky, Don A., Clifton C. Casey, and Mark A. Lowery, Summer 2007, Influence of Dissolved Oxygen Convection on Well Sampling, *Ground Water Monitoring & Remediation* 27, no. 3: 49-58.

APPENDIX A
PERISTALTIC PUMPS

Before selecting a peristaltic pump to collect groundwater samples for VOCs and/or dissolved gases (e.g., methane, carbon dioxide, etc.) consideration should be given to the following:

- The decision of whether or not to use a peristaltic pump is dependent on the intended use of the data.
- If the additional sampling error that may be introduced by this device is NOT of concern for the VOC/dissolved gases data's intended use, then this device may be acceptable.
- If minor differences in the groundwater concentrations could effect the decision, such as to continue or terminate groundwater cleanup or whether the cleanup goals have been reached, then this device should NOT be used for VOC/dissolved gases sampling. In these cases, centrifugal or bladder pumps are a better choice for more accurate results.

EPA and USGS have documented their concerns with the use of the peristaltic pumps to collect water sample in the below documents.

- "Suction Pumps are not recommended because they may cause degassing, pH modification, and loss of volatile compounds" *A Compendium of Superfund Field Operations Methods*, EPA/540/P-87/001, December 1987.
- "The agency does not recommend the use of peristaltic pumps to sample ground water particularly for volatile organic analytes" *RCRA Ground-Water Monitoring Draft Technical Guidance*, EPA Office of Solid Waste, November 1992.
- "The peristaltic pump is limited to shallow applications and can cause degassing resulting in alteration of pH, alkalinity, and volatiles loss", *Low-flow (Minimal drawdown) Ground-Water Sampling Procedures*, by Robert Puls & Michael Barcelona, April 1996, EPA/540/S-95/504.
- "Suction-lift pumps, such as peristaltic pumps, can operate at a very low pumping rate; however, using negative pressure to lift the sample can result in the loss of volatile analytes", USGS Book 9 Techniques of Water-Resources Investigation, Chapter A4. (Version 2.0, 9/2006).

APPENDIX B

SUMMARY OF SAMPLING INSTRUCTIONS

These instructions are for using an adjustable rate, submersible pump or a peristaltic pump with the pump's intake placed at the midpoint of a 10 foot or less well screen or an open interval. The water level in the monitoring well is above the top of the well screen or open interval, the ambient temperature is above 32°F, and the equipment is not dedicated. Field instruments are already calibrated. The equipment is setup according to the diagram at the end of these instructions.

1. Review well installation information. Record well depth, length of screen or open interval, and depth to top of the well screen. Determine the pump's intake depth (e.g., mid-point of screen/open interval).

2. On the day of sampling, check security of the well casing, perform any safety checks needed for the site, lay out a sheet of polyethylene around the well (if necessary), and setup the equipment. If necessary a canopy or an equivalent item can be setup to shade the pump's tubing and flow-through-cell from the sun light to prevent the sun light from heating the groundwater.

3. Check well casing for a reference mark. If missing, make a reference mark. Measure the water level (initial) to 0.01 ft. and record this information.

4. Install the pump's intake to the appropriate depth (e.g., midpoint) of the well screen or open interval. Do not turn-on the pump at this time.

5. Measure water level and record this information.

6. Turn-on the pump and discharge the groundwater into a graduated waste bucket. Slowly increase the flow rate until the water level starts to drop. Reduce the flow rate slightly so the water level stabilizes. Record the pump's settings. Calculate the flow rate using a graduated container and a stop watch. Record the flow rate. Do not let the water level drop below the top of the well screen.

If the groundwater is highly turbid or colored, continue to discharge the water into the bucket until the water clears (visual observation); this usually takes a few minutes. The turbid or colored water is usually from the well being disturbed during the pump installation. If the water does not clear, then you need to make a choice whether to continue purging the well (hoping that it will clear after a reasonable time) or continue to

the next step. Note, it is sometimes helpful to install the pump the day before the sampling event so that the disturbed materials in the well can settle out.

If the water level drops to the top of the well screen during the purging of the well, stop purging the well, and do the following:

> Wait for the well to recharge to a sufficient volume so samples can be collected. This may take awhile (pump maybe removed from well, if turbidity is not a problem). The project manager will need to make the decision when samples should be collected and the reasons recorded in the site's log book. A water level measurement needs to be performed and recorded before samples are collected. When samples are being collected, the water level must not drop below the top of the screen or open interval. Collect the samples from the pump's tubing. Always collect the VOCs and dissolved gases samples first. Normally, the samples requiring a small volume are collected before the large volume samples are collected just in case there is not sufficient water in the well to fill all the sample containers. All samples must be collected, preserved, and stored according to the analytical method. Remove the pump from the well and decontaminate the sampling equipment.

If the water level has dropped 0.3 feet or less from the initial water level (water level measure before the pump was installed); proceed to Step 7. If the water level has dropped more than 0.3 feet, calculate the volume of water between the initial water level and the stabilized water level. Add the volume of the water which occupies the pump's tubing to this calculation. This combined volume of water needs to be purged from the well after the water level has stabilized before samples are be collected.

7. Attach the pump's tubing to the "T" connector with a valve (or a three-way stop cock). The pump's tubing from the well casing to the "T" connector must be as short as possible to prevent the groundwater in the tubing from heating up from the sun light or from the ambient air. Attach a short piece of tubing to the other end of the end of the "T" connector to serve as a sampling port for the turbidity samples. Attach the remaining end of the "T" connector to a short piece of tubing and connect the tubing to the flow-through-cell bottom port. To the top port, attach a small piece of tubing to direct the water into a calibrated waste bucket. Fill the cell with the groundwater and remove all gas bubbles from the cell. Position the flow-through-cell in such a way that if gas bubbles enter the cell they can easily exit the cell. If the ports are on the same side of the cell and the cell is cylindrical shape, the cell can be placed at a 45-degree angle with the ports facing upwards; this position should keep any gas bubbles entering the cell away from the monitoring probes and allow the gas bubbles to exit the cell easily (see Low-Flow Setup Diagram). Note,

make sure there are no gas bubbles caught in the probes' protective guard; you may need to shake the cell to remove these bubbles.

8. Turn-on the monitoring probes and turbidity meter.

9. Record the temperature, pH, dissolved oxygen, specific conductance, and oxidation/reduction potential measurements. Open the valve on the "T" connector to collect a sample for the turbidity measurement, close the valve, do the measurement, and record this measurement. Calculate the pump's flow rate from the water exiting the flow-through-cell using a graduated container and a stop watch, and record the measurement. Measure and record the water level. Check flow-through-cell for gas bubbles and sediment; if present, remove them.

10. Repeat Step 9 every 5 minutes or as appropriate until monitoring parameters stabilized. Note at least one flow-through-cell volume must be exchanged between readings. If not, the time interval between readings will need to be increased. Stabilization is achieved when three consecutive measurements are within the following limits:

Turbidity (10% for values greater than 5 NTUs; if three Turbidity values are less than 5 NTUs, consider the values as stabilized),
Dissolved Oxygen (10% for values greater than 0.5 mg/L, if three Dissolved Oxygen values are less than 0.5 mg/L, consider the values as stabilized),
Specific Conductance (3%),
Temperature (3%),
pH (± 0.1 unit),
Oxidation/Reduction Potential (±10 millivolts).

If these stabilization requirements do not stabilize in a reasonable time, the probes may have been coated from the materials in the groundwater, from a buildup of sediment in the flow-through-cell, or a gas bubble is lodged in the probe. The cell and the probes will need to be cleaned. Turn-off the probes (not the pump), disconnect the cell from the "T" connector and continue to purge the well. Disassemble the cell, remove the sediment, and clean the probes according to the manufacturer's instructions. Reassemble the cell and connect the cell to the "T" connector. Remove all gas bubbles from the cell, turn-on the probes, and continue the measurements. Record that the time the cell was cleaned.

11. When it is time to collect the groundwater samples, turn-off the monitoring probes, and disconnect the pump's tubing from the "T" connector. If you are using a centrifugal or peristaltic pump check the pump's tubing to determine if the tubing is completely filled with water (no air space).

All samples must be collected and preserved according to the analytical method. VOCs and dissolved gases samples are normally collected first and directly into pre-preserved sample containers. However, this may not be the case for all sampling locations; the SAP/QAPP should list the order in which the samples are to be collected based on the project's objective(s). Fill all sample containers by allowing the pump discharge to flow gently down the inside of the container with minimal turbulence.

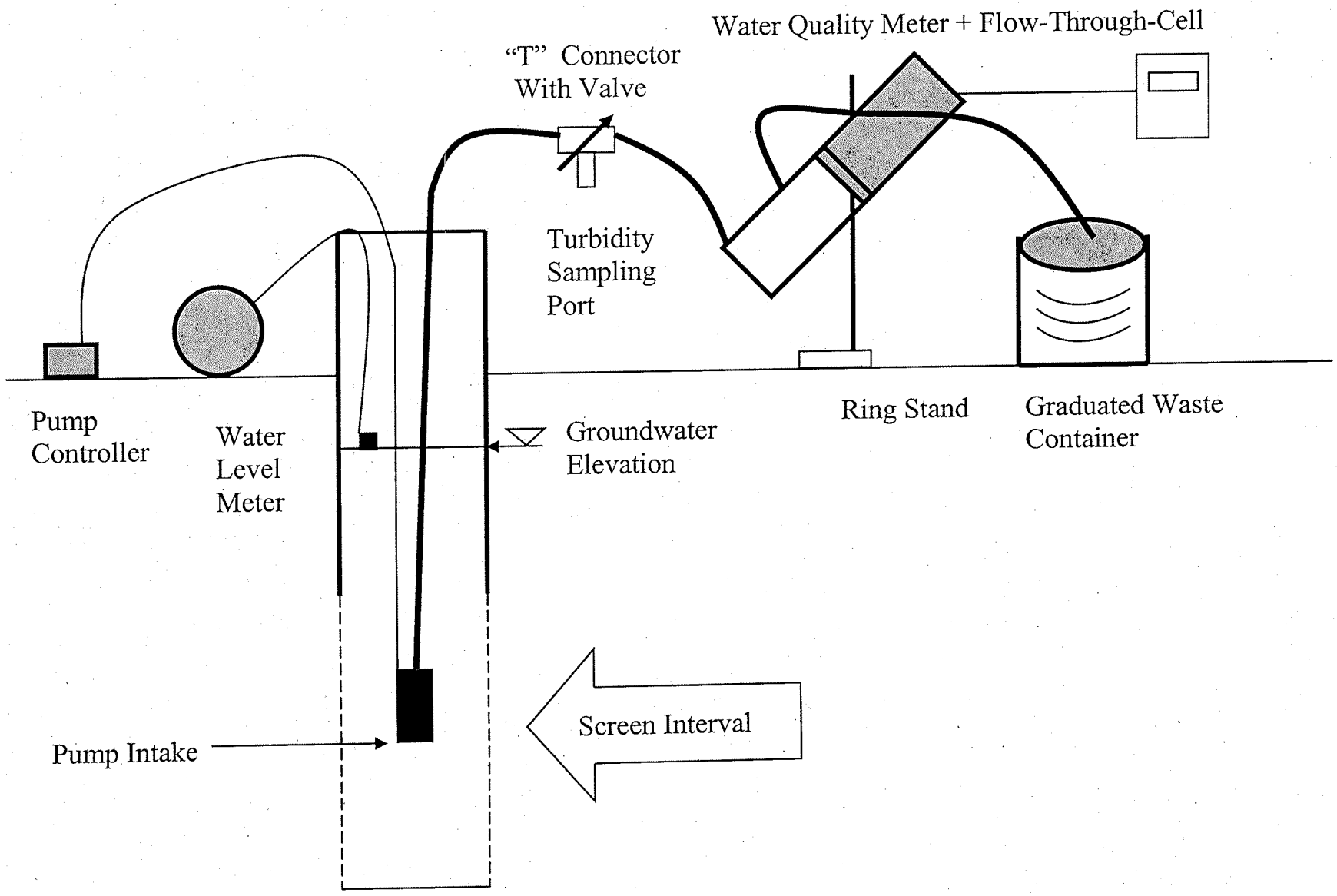
If the pump's tubing is not completely filled with water and the samples are being collected for VOCs and/or dissolved gases analyses using a centrifugal or peristaltic pump, do the following:

> All samples must be collected and preserved according to the analytical method. The VOCs and the dissolved gases (e.g., methane, ethane, ethene, and carbon dioxide) samples are collected last. When it becomes time to collect these samples increase the pump's flow rate until the tubing is completely filled. Collect the samples and record the new flow rate.

12. Store the samples according to the analytical method.

13. Record the total purged volume (graduated waste bucket). Remove the pump from the well and decontaminate the sampling equipment.

Low-Flow Setup Diagram



APPENDIX C
EXAMPLE (Minimum Requirements)
WELL PURGING-FIELD WATER QUALITY MEASUREMENTS FORM

Location (Site/Facility Name)_____
Well Number_____ Date_____
Field Personnel_____
Sampling Organization_____
Identify MP_____

Depth to _____/_____ of screen
(below MP) top bottom
Pump Intake at (ft. below MP)_____
Purging Device; (pump type)_____
Total Volume Purged _____

Clock Time 24 HR	Water Depth below MP ft	Pump Dial[1]	Purge Rate ml/min	Cum. Volume Purged liters	Temp. °C	Spec. Cond.[2] µS/cm	pH	ORP[3] mv	DO mg/L	Turb-idity NTU	Comments
Stabilization Criteria					3%	3%	±0.1	± 10 mv	10%	10%	

1. Pump dial setting (for example: hertz, cycles/min, etc).
2. µSiemens per cm(same as µmhos/cm)at 25 °C.
3. Oxidation reduction potential (ORP)

APPENDIX H

MONITORING WELL SAMPLING LOG

Low Flow Sampling

PROJECT NAME:	PROJECT LOCATION:			DATE:	WELL ID:
PROJECT NUMBER:	WELL DIAMETER: (inches)	DEPTH TO WATER: (feet)	DEPTH TO BOTTOM: (feet)		PID READING: (ppmv)

PURGING DATA

TUBING DIAMETER (inches):	TUBING MATERIAL CODE: (see below)	PURGE PUMP TYPE:	PUMP EQUIPMENT MODEL & SERIAL #s:	
WELL VOLUME PURGE: 1 WELL VOLUME = (TOTAL WELL DEPTH – STATIC DEPTH TO WATER) X WELL CAPACITY			GALLONS:	LITERS:
WELL CAPACITY (Gallons Per Foot): 0.75" = 0.02; 1" = 0.04; 1.25" = 0.06; 2" = 0.16; 3" = 0.37; 4" = 0.65; 5" = 1.02; 6" = 1.47; 12" = 5.88			1 GALLON = 3.785 LITERS	TOTAL VOLUME PURGED:
WELL SCREEN INTERVAL DEPTH (feet):	INITIAL PUMP OR TUBING DEPTH IN WELL (feet):	FINAL PUMP OR TUBING DEPTH IN WELL (feet):	PURGING INITIATED AT:	PURGING ENDED AT:	GALLONS: LITERS:

WATER LEVEL STABLIZATION DEPTH TO WATER WITH PUMP: (feet)

TIME INTERVAL (min)	FLOW RATE (mL/min)	PUMP SETTINGS	DEPTH TO WATER (feet) START	DEPTH TO WATER (feet) END	Water Level Stable (Yes or No)	VOLUME PURGED DURING INTERVAL (mL)

TIME (min)*	FLOW RATE (mL/min) (100-500 mL/min)**	DEPTH TO WATER (feet) (+/- 0.3')**	TURBIDITY (NTU) (+/- 10%)or <5**	DISSOLVED OXYGEN (mg/L) (+/- 10%)or <0.5**	pH (+/- 0.1)**	TEMP (°C) (+/- 3%)**	SPECIFIC CONDUCTIVITY (µS/cm) (+/- 3%)**	ORP (mV) (+/- 10mV)**	COLOR (describe) -	ODOR (describe) -

* every 5 or more minutes, depending on volume of flow-through cell, from EPA Region 1 Low-Flow SOP version 3: 1-19-2010

** EPA stabilization parameters from EPA/540/S-95/504 April 1996

SAMPLING DATA

SAMPLED BY (PRINT) / AFFILIATION:	SAMPLER(S) SIGNATURES:	SAMPLING INITIATED AT:	SAMPLING ENDED AT:
PUMP OR TUBING DEPTH IN WELL (feet):	SAMPLE PUMP FLOW RATE (mL per minute):	FIELD PARAMETER MONITORING EQUIPMENT MODEL & SERIAL #s:	
FIELD DECONTAMINATION: Y N	FIELD-FILTERED: Y N FILTER SIZE: _____ µm Filtration Equipment Type:	DUPLICATE: Y N	

MATERIAL CODES: **AG** = Amber Glass; **CG** = Clear Glass; **PE** = Polyethylene; **PP** = Polypropylene; **S** = Silicone; **T** = Teflon; **O** = Other (Specify)

WELL CONDITION CHECKLIST (circle appropriate item(s), cross out if not applicable)

Type: Flush Mount / Stand Pipe General Condition: Good / Needs Repair Well Caps: Good / Broken / None Lock: Good / Broken / None

Evidence of Rain Water Between Steel & PVC? Y / N Is Well Plumb?: Y / N PVC Riser: Good / Damaged / None

Evendence of Ponding Around Welll? Y / N Concrete Collar: Good / Cracked / Leaking / None

REMARKS:

APPENDIX I

DEPARTMENT OF THE ARMY
ASSISTANT CHIEF OF STAFF FOR INSTALLATION MANAGEMENT
600 ARMY PENTAGON
WASHINGTON, DC 20310-0600

December 31, 2014

Reply to the order of
BRAC Environmental Office
DAIM-BO-DV
30 Quebec Street, Unit 100
Devens, MA 01432

Ms. Carol Keating
U.S. Environmental Protection Agency
5 Post Office Square, Suite 100
Boston, MA 02109-3912

RE: Former Fort Devens Army Installation – Shepley's Hill Landfill (SHL) – Long-Term Monitoring and Maintenance Plan (LTMMP) Update (Draft Version dated Oct 2013); Army Response to EPA Comments dated September 29, 2014 (Final Comment Package).

Dear Ms. Keating:

I am writing in response to the subject letter in which EPA provided a compilation of technical review comments on the subject document. The EPA's letter also presented an overall assessment of "*big picture*" issues affecting the current SHL remedy and proposed a long-term remediation strategy. This letter provides a general response to these issues and addresses all elements in EPA's proposed remediation strategy moving forward. The attachment to this letter provides the Army's detailed responses to the EPA's final comment package dated 29 September 2014. Also included in the attachment are responses to the MassDEP comments (dated 06 December 2013) and PACE comments (dated 25 November 2013) on the draft LTMMP Update.

The EPA's letter identified five (5) elements to address a proposed long-term remediation strategy that "*effectively contains (and/or treats) high-arsenic groundwater at the north end of the landfill and achieve cleanup goals for the "impacted" area (i.e., within the NIA or some other, downgradient location)*". This proposed strategy was based on EPA's determination that "*the current SHL remedy (i.e., extraction and treatment of arsenic contaminated groundwater) is inadequate for purposes of achieving the RAOs and cleanup levels set forth in the 1995 SHL ROD*". The Army agrees with this determination and provides the following path forward to address the task elements in the EPA's proposed long-term remediation strategy such that an alternate groundwater remedy can be implemented and the current Arsenic Treatment Plant (ATP) can cease operation.

(1) optimization of the current ATP (to achieve its designed, fully operational capacity);

The Army will complete ATP optimization/upgrades by January 30, 2015. These ATP modifications will increase the average effective pumping rate of the system to 50 gpm. However, these changes will have a limited effect on overall remedy performance in

achieving aquifer restoration throughout the NIA and will further increase the operational costs of an already costly and "*inadequate*" remedial approach. No additional ATP upgrades are planned at this time.

(2) development of an overarching, comprehensive Conceptual Site Model (CSM) (that encompasses a number of critical elements including topography, geology, groundwater-surface water interactions, geochemistry, etc.;

While refinement of the CSM is an ongoing process, the Army believes that all critical elements of the current CSM are sufficient for both the evaluation of the current remedy and development of an alternate SHL remedy (see attached general response to EPA's draft LTMMP comments).

The Army proposes to resolve any major differences between Army and EPA interpretations of the CSM through a series of BCT technical meetings so that a focused feasibility study can be performed and an alternate remedy selected.

(3) continued, frequent collection of groundwater samples from an expanded monitoring well network (to supplement (and compare to) historical datasets, evaluate short- and long-term trends (in contaminant concentrations and geochemical parameters), and monitor remedy component performance)

The Army is currently revising the draft SHL LTMMP Update based on BCT comments. A draft final SHL LTMMP Update will be submitted to the BCT by February 20, 2015. This document will continue to include sampling requirements from the expanded monitoring well network. In addition, the LTMMP will include sampling requirements for development of an arsenic background data set and value. Regarding the evaluation of data and remedy performance, the draft final LTMMP Update will include a revised set of DQOs (see Army response to EPA comment #7 attached). The Army will schedule BCT technical meeting(s) prior to submittal of the draft final LTMMP Update to reach consensus on these specific elements noted above and in the specific comments on the draft LTMMP.

(4) development of a SHL specific, arsenic background value (and/or some unacceptable "range" from which to gauge remedy performance), and

The Army has provided comments on the EPA's proposal for development of a background arsenic concentration (see Army response to EPA comment #1). While the Army generally supports this effort, the development of an arsenic background value as proposed is unlikely to modify remediation goals sufficiently to reflect limitations of the current Response Action or any future alternate remedy. Therefore, in addition to an arsenic background value (and/or range), the Army proposes that alternative strategies be considered such as defining the SHL groundwater point of compliance by considering factors such as the proximity of the sources (i.e., the sources of arsenic extend beyond the landfill area within the bedrock and overburden material), the technical practicability of ground-water remediation at the site (i.e., the CSM indicates the current remedy has a

high level of uncertainty in achieving current remediation goals), the vulnerability of the groundwater and its possible uses, exposure and likelihood of exposure and similar considerations (i.e., exposure to groundwater within the NIA is unlikely given that this area has access to municipal drinking water and that land use control restrictions are in place). Such an approach can be consistent with EPA's long-term remediation strategy to achieve cleanup goals *"within the NIA or some other, downgradient location"* and has the potential to establish more realistic cleanup goals within the NIA and other downgradient locations.

The Army appreciates EPA's support on the development of an arsenic background value and looks forward to discussing the specific scope and schedule for these efforts during a series of BCT technical meeting in the near future.

(5) an improved, updated groundwater flow model.

The Army supports refinement of the current groundwater flow model and appreciates EPA's technical input and comprehensive review of the SHL groundwater model. The SHL groundwater model has undergone several major revisions and peer reviews over the years (with significant coordination and input from EPA and MassDEP) and as a result is a useful tool for evaluating the SHL remedy performance and any future remedy alternatives. However, we do not believe that reliance on a groundwater model is a *"primary line of evidence"* to support remedial decisions and disagree that there are *"deficient components"* that would significantly affect the model's application in evaluating the SHL remedy.

The Army will perform necessary groundwater model improvements based on the EPA's comments and through a series of BCT technical meeting to be scheduled in the near future.

In summary, the Army will schedule BCT technical meetings in early 2015 to address the stated issues and to better define the long-term remediation strategy for the SHL. Following resolution of these issues, the BCT can then initiate discussion on the scope and schedule for performing a focused feasibility study from which a more sustainable and achievable alternate remedy can be selected. We look forward to EPA's continued support as we work toward implementing a long-term sustainable remedy. Please contact me at (978) 796-2205 or at robert.j.simeone.civ@mail.mil should you have any questions.

Sincerely,

SIMEONE.ROBERT.J.1242822893

Digitally signed by SIMEONE.ROBERT.J.1242822893
DN: c=US, o=U.S. Government, ou=DoD, ou=PKI, ou=USA, cn=SIMEONE.ROBERT.J.1242822893
Date: 2014.12.29 14:02:34 -05'00'

Robert J. Simeone
BRAC Environmental Coordinator

Attachments:

1. Response to 29 September 2014 USEPA Comments on the Draft LTMMP Update
2. Response to 07 February 2014 USEPA Preliminary Recommendations for Additional Monitoring Locations and Objectives, Nonacoicus Brook as part of the Draft LTMMP Update
3. Response to the 06 December 2013 MassDEP Comments on the Draft LTMMP Update
4. Response to the 25 November 2013 PACE Comments on the Draft LTMMP Update

Cc: Dave Chaffin, MassDEP
Ron Ostrowski, MassDevelopment
Richard Doherty, ECR Consulting, Inc.
Laurie Nehring, PACE
Julie Corenzwit, PACE

Response to 2014 USEPA Comments on
DRAFT LTMMP UPDATE
SHEPLEY HILL LANDFILL
Former Fort Devens Army Installation

General Response to Comments

The LTMMP Update was the Army's attempt to propose Data Quality Objectives (DQOs) for the existing remedial actions as it continues to work with the BCT to address its concerns on perceived data gaps and disagreement over the Conceptual Site Model (CSM). Discussions and agreement on the CSM and DQOs are critical to a path forward and to establishing a basis to measuring the performance on any remedial action, including, but not limited to the Arsenic Treatment Plant (ATP). Without a consensus on the CSM and the DQOs, there can be no consensus on attainable remedial outcomes and/or remedial timeframes.

With respect to the BCT's continuing concerns for the need for additional data, we reiterate that in accordance with the CERCLA guidance for RI/FS uncertainties are a part of the Superfund process and that the desire to remove all uncertainties competes with the Superfund Program's mandate to perform cleanups within designated schedules. Therefore, the objective of data collection is not to achieve the unobtainable goal of removing all uncertainty, but rather to gather information sufficient to support an informed risk management decision. To this point the Army believes that the existing data is more than sufficient to establish the CSM and determine the appropriate remedial actions.

Based on the comments below it is evident that the need for agreement and consensus on the CSM is imperative and we believe that given the available data and the length of time the groundwater pump and treat system has operated, in conjunction with investigations performed over the past decades there is more than enough data for both parties to come to an agreement on the CSM. Therefore, the Army proposes to resolve any major differences between Army and EPA interpretations of the CSM through a series of BCT technical meetings so that a focused feasibility study can be performed and an alternate or modified remedy selected.

Response to Comments

USEPA Comments on the Draft LTMMP Update
29 September 2014

General Comments

Comment 1 - In several sections of the document, reference is made to secondary sources of information relative to a potential background concentration for arsenic in the aquifer impacted by Shepley's Hill Landfill (SHL). Establishment of a relevant background arsenic concentration for the site should be derived from analysis of chemistry from monitoring locations that lie outside of the influence of the plume emanating from the landfill. Guidance on establishing site-specific background/baseline concentration for contaminants is provided in the USEPA 2009 Unified Guidance (EPA/530/R-09-007), which is supported with the available computational tools in the USEPA ProUCL Software. Discussions should commence, as soon as possible, to develop a plan for establishing a site-specific background/baseline concentration for arsenic as derived from statistical analysis of existing monitoring locations with datasets supported from historical or on-going sampling programs. This technical evaluation of site-specific data is the most direct way to support establishment of a cleanup target and for designating wells within the monitoring program as lying within or outside the impact of SHL. It is anticipated that the revised groundwater flow model will also provide an important line of evidence to support designation of background/baseline wells. From this perspective, designation of well SHM-10-11 as a location "upgradient of source" (Table 1) is premature, given that it lies within the historical disposal footprint documented in aerial images of site operations. Based on physical location alone, it appears that wells SHL-12, SHL-17 and/or N7-P1/P2 may provide more reliable locations for defining groundwater chemistry flowing through the boundary of the historical disposal footprint.

Response: The Army believes that the establishment of a local background arsenic concentration for the site is appropriate, however, will be of limited value since existing data indicates that such a background arsenic concentration is still likely unattainable. Therefore, unless background values are set in the range found currently in the NIA, such an exercise will not change remedy performance or duration, as attainment throughout the NIA does not appear possible under the conditions with which the ATP operates (note the As concentration consistency measured between 2001 and 2013, a duration of 12 years which includes both several years prior and following ATP construction and operation). In addition, to come to an agreement on the appropriate background, discussions and an agreement on the conceptual site model are critical. Regarding the establishment of background, the USEPA provided the Army an outline for a field sampling effort designed to collect the data to calculate background in August 2014. The Army responded to USEPA in September 2014 with suggested changes and edits to this approach as the USEPA's proposal omitted the sampling of any of the monitoring wells USEPA installed on Shepley's Hill in the past years which contain elevated naturally occurring As and which groundwater flows into the landfill aquifer. To date, USEPA has not responded. The Army is awaiting EPA response to continue this discussion on finalizing a work plan designed to develop a background concentration, with the caveat that the Army does not anticipate such an exercise

will significantly change the view of the challenges posed by the arsenic impacted groundwater beneath and north of Shepley's Hill Landfill.

Regarding the location of upgradient wells, well SHM-10-11 has been re-designated as a landfill area well which will be sampled every 5 years. In its place, well SHL-12 has been designated as an upgradient well which will be sampled every 5 years.

Comment 3 - The monitoring plan includes wells to be sampled semi-annually, annually, and once every five years. In addition, many wells are proposed only for monitoring of hydraulic head. Some of the wells proposed for monitoring once every five years are in locations where hydraulic head data obtained more frequently would be useful for routine definition of the potentiometric surface. EPA recommends that hydraulic head be monitored at SHL-15, SHL-23, SHL-24, SHM-07-03, and SHM-10-11 at the same frequency as the locations currently proposed for hydraulic monitoring only. In addition, hydraulic head should be monitored at wells SHL-12 and SHL-17 to provide better control on the southern portion of the potentiometric surface maps and at well SHL-3 to provide additional control at the southern end of the slurry wall.

Response: All wells proposed for sampling, including those which will be sampled once every five years, are already included in the annual hydraulic monitoring program. The LTMMP Update will be revised to clarify this. In addition, wells SHL-3, SHL-12, and SHL-17 will be added to the hydraulic monitoring program as requested.

Page-Specific Comments

Comment 4 - Page 8, Section 2.2 – The estimated timeframes to "flush aqueous phase arsenic in the system to background conditions…" and to "flush residual carbon in the landfill footprint…" of 300 years and 500 years, respectively, seem excessive (especially given the monitoring wells upgradient of the ATP and within the landfill footprint show marked decreases in arsenic concentrations). Further discussion with regards to the SHL, as proposed in this section, is warranted.

Response: The Army is of the opinion that the available data supports the estimate, however, the Army agrees to continue discussions regarding this issue. Without a consensus on the CSM, there can be no consensus on attainable remedial outcomes and/or remedial timeframes. Therefore, the Army requests that discussions regarding the CSM continue before proceeding.

Comment 5 - Page 19, Section 3.1 – It is apparent, from statements made in this and preceding sections (regarding "conclusions" that may be drawn from the groundwater model update), that further discussion is warranted with regards to the interpretation of "RAOs stipulated in the ROD" for establishing and evaluating DQOs in the existing LTMMP and the "formulation" of revised RAOs to define DQOs proposed in the draft LTMMP update. The apparent disconnect between the RAOs (as identified in the 1995 ROD and those presented on page 16), will make it difficult for the BCT to develop the process by which the effectiveness and performance of "all of the remedial components underway at SHL" will be "evaluated" and "monitored" and to reach consensus on an updated "groundwater decision framework" for the SHL operable unit.

Response: The Army disagrees that there is a disconnect between the RAOs identified in the 1995 ROD and those formulated in the Draft LTMMP Update, but does agree that further discussion is warranted with regards to their interpretation and/or wording and presentation in the LTMMP. Also the need for coming to a consensus on those DQOs are critical to establishing a basis to measuring the performance on any remedial action, including, but not limited to the Arsenic Treatment Plant.

Comment 6 - Page 21, Section 3.1.2 - *"Statistically significant changes in the geochemical parameters within the capture zone (i.e., the landfill area) that indicate a shift in overall redox conditions necessary to decrease arsenic concentrations;"*

This decision statement assumes that arsenic concentrations will only decrease with the development of more oxidizing conditions within the aquifer. EPA recommends that this statement be revisited to account for the potential situation that arsenic concentrations show a statistically significant decline in the absence of statistically significant changes in "geochemical parameters" that might be used as indicators of redox conditions. For example, Figure 1(on the next page), shows long-term trends in arsenic, dissolved oxygen (DO) and oxidation-reduction potential (ORP) for wells upgradient of ATP, near ATP and downgradient of the ATP. These data show discernible trends in arsenic concentration with no apparent trend in DO and ORP, which are often used as "geochemical parameters" indicative of aquifer "redox conditions". Trends for other chemical parameters that may be influenced by changes in system "redox conditions" are shown in Figure 2 (iron, manganese, sulfate) (on the next page), along with the trend for chloride. Inspection of these data indicate that caution should be used when placing emphasis on "redox conditions" as the primary factor governing arsenic concentrations with different parts of the aquifer. However, these data indicate that the analytical parameters listed in Table 3 will likely provide the most critical context for understanding trends in arsenic concentrations.

Response: As presented in the LTMMP Update, conditions in the downgradient aquifer including the ongoing arsenic mobilization in the NIA demonstrate that it will take 100s of years to 'flush' residual carbon and remobilized arsenic in groundwater from the area of attainment. Further, there is conclusive evidence that the mechanisms for arsenic release and transport are complex geochemically and that dissolved arsenic at levels exceeding the MCL are also entering the groundwater system from natural sources. Source strength studies at the landfill suggest a significant continuing geochemical driver (anaerobic conditions and carbon sources) for the dissolution of arsenic rather than a source derived from a buried waste (i.e., a landfill leachate plume caused by arsenic leached from incinerator ash). Consequently, the evaluation of changes in the geochemical parameters within the capture zone that indicate a shift in overall redox conditions is appropriate as one of many factors indicating the performance of the ATP. All of these lines of evidence must be evaluated as part of the discussion designed to come to an agreement on the overall CSM.

Comment 7 - Page 23, Section 3.1.2 **–** *"If it is determined that the ATP remedy component is NOT having a beneficial impact as determined through the performance metrics specified below.."* **–** The

"decision rule" proposed in DQO Step 5 appears to be inconsistent with the goal of "restoring the aquifer to beneficial use," especially in light of the fact that "aquifer restoration goals" (other than MCLs) have not been clearly defined. EPA recommends that the identification and adoption of "DQOs for the Updated LTMMP" be postponed until BCT consensus can be reached on the specifics of the process "seven-step process," specifically as it relates to (1) the intended purpose and current relevance of the RAOs (as set forth in the 1995 ROD), (2) the designation of SHL "study boundaries", and (3) the criteria to be used to evaluate "remedy performance" for **all** SHL remedial system components, independently and collectively.

Response: *The DQO process outlined in the Draft LTMMP Update was presented in accordance with the January 2000 USEPA guidance document* Data Quality Objective Process for Hazardous Waste Site Investigations *(EPA QA/G-4HW) and is necessary to assure that the type, quantity, and quality of environmental data used in decision making will be appropriate for each remedy. Furthermore and as stated in the May 2014 USEPA guidance document* Groundwater Remedy Completion Strategy *(OSWER 9200.2-144), "the DQO process is designed to refine project information needs and focus monitoring efforts on collecting the appropriate type and amount of data so that data support key decisions. This strategy is intended to provide a technical and scientific process for evaluating when sufficient data have been obtained to assess the likelihood that a groundwater remedy has or will achieve the RAOs and associated cleanup levels in a reasonable timeframe." In addition, Army notes that "restoring the aquifer to beneficial use" must be achieved if it is reasonable and/or practicable, per EPA policy. There are several lines of evidence that suggest that it is neither reasonable nor practicable to achieve this goal in certain areas of this aquifer, which are related to the present disagreement on the CSM. Consequently, the identification and adoption of the proposed DQOs must be formalized in a document, and the LTMMP Update is the most appropriate at this time. Discussions with the BCT regarding the specifics of the seven-step process can be conducted parallel with the finalization of the LTMMP Update; however, we disagree that postponing the identification and adoption of the proposed DQOs is appropriate at this time.*

Comment 8 - Page 24, Section 3.1.2 - *"Due to the difficulties extrapolating bench scale conditions to the field, a 10-fold decrease may not be observed; however, a 30-50% reduction in arsenic concentrations in wells in the nearfield area should be expected."*

EPA agrees that extrapolating columns studies based on work with aquifer solids collected outside of the nearfield area would not give reliable projections for rates of concentration changes. However, it is not clear what technical basis is being used to propose that a "30-50% reduction" would occur over 5 years. EPA recommends that the technical basis for this projection be provided in order to clarify the purpose for proposing this alternative performance benchmark.

Response: *To measure and gauge the effectiveness of the extraction system, it will be necessary to establish a benchmark for estimating the amount of arsenic reduction. As stated in the LTMMP Update, the bench column studies suggest that as much as a 10-fold (or 90%) decrease in arsenic can occur in groundwater after 5 pore volumes of groundwater has been replaced if adsorbed arsenic does not leach back into the groundwater. Due to the difficulties extrapolating bench*

scale conditions to the field, a different, more conservative, approach for estimating arsenic reduction groundwater was evaluated. In the absence of a better benchmark, using the nearfield (closest to extraction system) wells in a time series analysis detail that natural fluctuation in well chemistry can range from 10% to 20% in any given season or sampling event. Based on the observed well chemistry and the raw interpretation of the column work, a more realistic reduction in contaminant concentration of 30% or more can be used for benchmarking reduction due to pumping. By using this approach, arsenic decreases of 30% or greater (above the 20% due to natural variability) should represent reductions due to pumping alone. As such, the Army maintains that the expectation of a 30% reduction throughout the NIA over the next five years or a definitive long-term downward trend in arsenic concentrations should be a target for considering the effectiveness of the ATP. The Army notes that the operation of the ATP is designed to reduce the concentrations of arsenic in groundwater and therefore it should be reasonable to expect to see a steady decline in arsenic concentration in groundwater directly affected by the ATP. If the ATP has no effect on groundwater, then the ATP, as a remedy, is ineffectual in meeting the RAOs stipulated in the ROD and should be evaluated for either upgrade, replacement, or decommissioning. Regardless, the Army is open to discussing and developing alternative performance benchmarks and criteria at proposed BCT technical meetings. However, it is imperative to develop decreasing concentration criteria or benchmarks to evaluate the ATP performance.

Comment 9 - Page 30, Section 3.2.2 - "*Groundwater Sampling Semiannual Events: The spring event will be focused on the arsenic-impacted area, where key wells are located for assessing the performance of the various remedies as detailed above. The semiannual events will be conducted for a minimum of three years (through 2016) to document seasonal fluctuations. Thereafter, the semiannual events will be discontinued, and the former semiannual wells will be sampled annually with alternating Spring and Fall sampling events to monitor seasonal variations.*"

EPA agrees that semiannual sampling of the proposed wells for a period of at least three years would be useful, given that at least half of the wells were installed recently. However, once the decision is made to transition these wells to annual sampling, EPA recommends that sampling be conducted in the fall, consistent with the current practice for wells sampled annually. This will allow for a more robust annual dataset and build on the existing historical dataset documenting chemistry trends in time. While well SHM-96-5B has appeared to display seasonal trends in the past, this has not been apparent in the trend for the past 2-3 years. Continued semiannual sampling for a period of three years should provide an adequate dataset to confirm the adequacy of annual sampling for this subset of wells.

Response: Agreed. The Army will revise the LMMP Update as appropriate.

Comment 10 - Page 30, Section 3.2.2 - "*Groundwater Sampling 5-Year Monitoring Events: Selected wells, considered less critical to performance evaluation but still of interest, will be included in the spring chemistry event every 5 years. This 5-year event will be designed to provide a larger scale snapshot of groundwater chemistry in all study areas including upgradient areas, landfill areas, barrier wall areas, extraction well area, and the NIA.*"

As previously stated, EPA recommends that sampling events to assess groundwater chemistry be conducted at similar times of the year to facilitate analysis of chemistry trends in time. As such, EPA recommends that sampling of wells designated for 5-year intervals be conducted during the fall. Also, please clarify that manganese analysis will be conducted on field filtered samples.

Response: Agreed. The Army will revise the LMMP Update as appropriate.

Comment 11 - Page 31, Section 3.2.2 & Table 4 *"The proposed list of wells and piezometers to be abandoned and the rationale for abandonment are included as Table 4."*

Well SHM-10-16 is recommended for abandonment based on its "…location near the SHM-05-41 series wells that have higher concentrations and better range of depths." As shown in Figure 3 (on the next page), arsenic concentrations that have been observed for this well are higher than concentrations observed for the past three years in the SHM-05-41 series wells. It should also be noted that SHM-10-16 is located in a portion of the aquifer north of the ATP extraction wells that appears critical for assessing the immediate downgradient impact of the extraction operation. From this perspective, EPA recommends that well SHM-10-16 be included for annual sampling for at least three additional years to better evaluate chemistry trends for this area within the NIA.

Response: Well SHM-10-16 will be removed from the abandonment list and will be incorporated into the annual groundwater hydraulic monitoring program. The LTMMP Update as well as Tables 2 and 4 will be revised to reflect this change.

Comment 12 - Figure 6 - The groundwater elevations measured in the pumping wells in Figure 6 do not appear to be representative of actual elevations in the aquifer immediately adjacent to the wells based on preliminary distance/drawdown analyses. The drawdown interpreted using these data appears to be a significant overestimate and, therefore, results in a biased interpretation of the potentiometric surface. This overestimate is likely due to a combination of well losses and the cyclic nature of the extraction from these wells. Data from a piezometer located in the aquifer near the pumping wells would be needed to accurately measure groundwater elevations in this area. EPA recommends that installation of such a piezometer be considered.

Response: Groundwater elevations were measured in extraction wells EW-01 and EW-04 on May 15, 2013 at the same time and utilizing the same standard operating procedures as the measurement of groundwater elevations in the surrounding monitoring wells. In June 2013, a complete horizontal and vertical survey of site wide wells, including the extraction wells, was conducted by a licensed surveyor. The survey was conducted horizontally on the Massachusetts State Plane Coordinate System and vertically North American Vertical Datum (NAVD) 1988. The revised reference elevations from the June 2013 survey were included in Table 3 of Appendix A of the Draft LTMMP Update and were used to generate the groundwater elevations presented on Figure 6. Consequently, it is the Army's opinion that these elevations are representative of actual elevations in the aquifer in the area of the extraction wells while the system is online and that they are not a significant overestimate due to well losses and the cyclic nature of the

extraction. Further, the typical drawdown water level at the extraction wells ranges from approximately 27 feet at EW-1 to 37 feet in EW-4 based on operation and maintenance data collected at the wells during the operation of the plant.

Regarding the installation of a piezometer near the extraction wells, the Army is installing transducers within both extraction wells to facilitate water level monitoring within the wells at all times and to allow the operators more control in optimizing flow rates. In this case, the installation of a piezometer near the extraction wells would be redundant and not necessary.

Comment 13 - Table 4 - Well SHL-3 is proposed for abandonment. As previously noted, it is recommended that this well be retained for monitoring of hydraulic head.

Response: Well SHL-3 will be removed from the abandonment list and will be incorporated into the annual groundwater hydraulic monitoring program. The LTMMP Update as well as Tables 2 and 4 will be revised to reflect this change.

Response to Comments

USEPA Comments on the Draft LTMMP Update
Appendix B – Model Update Report
29 September 2014

General Response to Model Comments

As discussed in the cover letter and within the LTMMP Update, the SHL groundwater model has undergone several major revisions and peer reviews since its initial development and with significant coordination and input from EPA and MassDEP, and as a result it is a useful tool for evaluating the SHL remedy performance and any future remedy alternatives. However, the Army does not believe that reliance on the groundwater model is a "primary line of evidence" to support remedial decisions. While there will be some uncertainty using the model, the model is one of many tools used to support an informed risk management decision and evaluate site conditions and activities. As such, it is impossible for any model to include every detail, known and unknown, and typically the time it takes to incorporate/interpret that detail is not rewarded by better results.

General Comments

Comment 1 – Purpose and Scope of Review - The review focused on assessing the ability of the revised model to accomplish its stated purpose as well as the adequacy of the report/documentation to support a technically feasible modeling approach and findings. The following comments are particularly directed to; (1) the assessment and validation of model data sets to ensure compatibility with the description of contents in the text of the report ((U.S. Army Corp of Engineers, 2013), (2) the assessment of the overall strategy of model simulation and processes invoked as specified in model input and the text, and (3) reexamination of selective model results from the simulations performed in the report.

Response: Comment noted.

Comment 2 - Structure of Review - EPA's review included documentation/verification of modeling software used, an assessment of model input, description of solution specifications and calibration approach. In addition, the modeling approach and results were evaluated in conjunction with the various critical elements of the overall site CSM (i.e., topography, geology, hydrology, groundwater-surface water interactions, and groundwater interactions) and a variety of engineered systems and site conditions resulting from human activities. Comment sections are divided into "General", "Page-Specific", "Summary and Conclusions," and "Recommendations". A number of accompanying figures are also provided (Attachment EPA 1).

Response: Comment noted.

Comment 3 - Source Materials for Model Review- Model files were checked against online help sources for MODFLOW located at: http://water.usgs.gov/nrp/gwsoftware/modtlow nwt/Guide/index.html?beginners guide to modflow.htm. Also, various reports on MODFLOW and its packages were consulted including Niswonger and others (2011), Harbaugh (2005), and Pollock (2012). A graphical interface modeling software developed by the USGS (Winston, 2009) was used for pre- and post-processing to assess model input and output. Geographic information (GIS) from MassGIS online http://www.mass.gov/anf/research-and-tech/it-serv-and-support/application-serv/officeof-geographic-information-massgis/online-mapping/ was compared to spatial data sets of the model. (The spatial data sets and other relevant model input data were obtained from digital files accessed via AMRDEC Safe Access File Exchange on February 10, 2014).

Response: Comment noted.

Comment 4 - Software Version - Verification and replication of modeling results could not be confirmed because the report fails to identify the software version used. Based on output from the listing file (Figure 1), EPA concluded that it is MODFLOW-NWT version 1.0.7 derived from MODFLOW-2005 version 1.9.01. Please confirm. (Please see Figure 1-Attachment EPA 1).

Response: MODFLOW-NWT version 1.0.7, released 15 January 2013, was used for the model. Version 1.0.8 was released on 24 September 2013, after the modeling was completed and the draft report was in development. According to release details from the USGS the difference between versions is inconsequential.

Comment 5 - Model Input - Model data files in "SHL200T2-Asparts-49reverse.lst" were evaluated in association with results reported in Figure 28 of the modeling report (U.S. Army Corp of Engineers, 2013). Model data input confirms that five model layers were simulated and all layers were specified with the convertible option. The convertible option allows layers to alternate between confined and unconfined conditions based on model-computed heads. The convertible option is a default option of MODFLOW. Rewetting of cells during the solution was specified as off but it is not needed in MODFLOW-NT (Niswonger and others, 2011). Hydraulic conductances between cells is calculated using the harmonic mean method. Harmonic mean is one of the default formulations for computing inter-cell flow in MODFLOW. No anisotropy was simulated in the bedrock; (the structural fabric of bedrock in New England can create preferred flow paths, often in the northeast direction). The active model grid terminates at the major river boundaries as indicated in the report. Grid cells are smaller by the landfill and coarsen outward.

Response: The model scenario reviewed (SHL200T2-ASparts-49reverse.lst) is a variation developed for reverse particle tracking and required the rewetting option be turned off. Consequently, this scenario is slightly different from the base model (SHL200T2), and the Army recommends that the base model be used when evaluating model inputs.

Comment 6 - River Stage Data - River stage data looks reasonable as compared to GIS data from MassGIS online. Riverbed hydraulic conductance shows a very high conductance by Red Cove in Plow Pond (simulated with the river package of MOD FLOW), which is not mentioned in any detail in the report. If the 2013 Red Cove excavation work resulted in a different (coarser) bed material · than the rest of the pond then the conductance could be a reasonable model specification. Low riverbed conductance is assigned to Grove Pond (simulated with the river package of MODFLOW), which is not fully explained in the report. Low conductance will reduce the amount of flow between the pond and aquifer. The two Town of Ayer wells are located adjacent to Grove Pond. Having a low conductance for Grove Pond may enhance flow to the town wells from other sources (distal rivers) to the east.

Response: As stated within the LTMMP Update, the riverbed conductance for the ponds were arrived at through calibration by comparing model predicted fluxes into the lake to seepage data presented in historical documents. Consequently, the Army maintains that the conductance values used for the river stage data are appropriate as presented.

Comment 7 - Layer and Cell Thicknesses - Layer and cell thicknesses vary spatially in the model. The topography of Shepley's Hill affects cell thicknesses. The cell thicknesses under the Hill are thin, which could result in some numerical solution problems such as dewatered cells.

Response: It is the Army's opinion that the layer and cell thicknesses used within the model are appropriate. Numerical solution problems due to dewatered cells were not an issue with the model due to the use of MODFLOW-NWT which can deal effectively with desaturated conditions. As noted in Comment 10 below, the model does not exhibit numerical solution problems.

Comment 8 - Horizontal Hydraulic Conductivity - Horizontal hydraulic conductivity (HK) from the model data sets compares to those illustrated in the report. However, insufficient information is presented to substantiate the use of zones for layers 1-3. How were they developed? Do the zones represent distinctive geologic units? For layer 4, why is the hydraulic conductivity under Nonacoicus Brook much higher than elsewhere. The report states that the weathered rock is absent at that location. However, other areas of unweathered rock are assigned a HK of 1.2 ft/d? Additional simulations should be performed to assess the effect of this high HK on model computed heads.

Response: The horizontal K zones were adopted from previous model versions and were adjusted during calibration to optimize to heads and fluxes under various seasonal and pumping conditions. For Layer 4, the K is higher under the brook because that layer, which represents weathered bedrock appears to be absent in the vicinity of the brook. A number of sensitivity simulations were performed including varying this high K zone, and the results are included in

the documentation presented within Appendix B of the LTMMP Update. The sensitivity analysis suggested that the K value used provided the best calibration results.

Comment 9 - Vertical hydraulic Conductivity - Vertical hydraulic conductivity (VK) was examined but not plotted in Attachment 1. Table 1 includes a summary of reported and identified VK, as assigned in model input data. No discussion in the report exists on VK regarding the higher values under the Brook for layer 4. The relatively high VK under the Hill promotes dewatering of cells in the upper model layers. It is not clear that these assigned values are realistic.

Response: As noted within the LTMMP Update, the model uses a horizontal to vertical K ratio of 10:1 which is a commonly used relationship. The exception is at Shepley's Hill where a higher vertical K is specified to represent the vertical fracturing which would accelerate downward movement of water.

During calibration it was apparent that this higher vertical K was necessary to facilitate the downward movement of water at the Hill which then ultimately upwells beneath the landfill, which is a process that has been discussed in previous documents. The April 2011 EPA Shepley's Hill Bedrock Investigation Report *(pg81), states that "It is apparent that significant recharge enters the fractured bedrock on Shepley's Hill, and that groundwater flows within the rock to the east, where some fraction of it discharges upward to the overburden material beneath the landfill. There is little evidence that there is a significant contribution of recharge to the overburden aquifer due to direct infiltration along the western margin of the landfill cap deriving from overland flow from the hill."*

Comment 10 - Model Solution Specifications - To ensure reliable model results, an accurate numerical solution should be obtained. Specification of numerical solution criteria controls, in part, the outcome of the numerical solution. The model uses the Newton Solver version 1.0.7 with the XMD solver (Attachment EPA 1 - Figure 1). Most values used appear to be within recommended levels (Niswonger and others, 2011). The report indicates that a good solution is achieved with a small closure error (0.002%). Examination of the model output file (SHL200T2-Asparts-49reverse.lst) indicates this is the case.

Response: Comment noted. In addition, the mass balance table in Attachment 2 of Appendix B of the LTMMP Update also shows that the model has a small closure error for each of the four seasonal quarters both pre and post-barrier wall.

Comment 11 - Model Calibration Approach - The report does not explicitly discuss the calibration approach. Because there were no model parameters specified in the model input, calibration appears to have been done using trial and error procedures. Therefore, automatic calibration and model parameterization were not done. The benefits of automatic calibration include an improved sensitivity analysis and a better understanding of model and parameter uncertainty. This should be considered, moving forward.

Response: The term "trial and error" for the calibration approach used is a little misleading as the process of adjusting parameters and evaluating the impact on calibration targets is the same whether or not auto-calibration is used. Calibration parameters can be adjusted either manually or automatically to improve overall calibration. During model development, parameter estimation (PEST) was used to help specify parameters, so an automated process was used to arrive at the completed model. A statement will be added to the text to better explain the calibration approach and indicate that PEST was used to specify parameters.

Comment 12 - Additional Calibration Issues - The Report acknowledges that " ... due to the short time since the barrier wall was installed, very few water level measurements were available to calculate quarterly average values for wells in the landfill area for model SHL200T2. It is important to keep this in mind when evaluating the model calibration, as quarterly average water levels at these wells are likely to change as additional data are collected in the future" (page 24). It is suggested that the landfill area of the model be re-evaluated (re-calibrated) once sufficient field data are available. Additionally, it would be prudent to increase the frequency of water level measurements for at least one year to facilitate model recalibration. Further, it is recommended that observed groundwater elevation maps be included in the modeling reports. Because the Pumping/Post-Wall Scenario represents the current conditions at the Site, the actual groundwater elevations should be used to create potentiometric maps for comparison with the model generated water elevation map. Modeled gradients should at least qualitatively match observed gradients. It should also be noted that a significant deficiency of the model calibration is a lack of supporting flux data. River seepage data are needed to improve upon model calibration even more so than additional head data (unless it is part of a pump test).

Response: It has been planned to update the model using additional data collected since it was presented in the LTMMP draft. That update would entail recalibration. In addition to the data collected by the Army, transducer data collected by the EPA, especially in the vicinity of the barrier wall, will also be used to enhance the calibration target dataset. The transducer data provides a more robust means to calculate quarterly average elevations than the spot measurements suggested.

The qualitative comparison of measured and model predicted groundwater elevation contours as suggested will be included in future model updates. In addition, the measurement of flow in the brook at staff gage locations is being evaluated. These flow data would allow an analysis of gain/loss and hence seepage over the reaches between the gages.

Comment 13 - Reported Model Results - The report indicates that a good calibration is achieved with small head residuals (small difference between observed and model heads). Calibration tables and maps of head residuals of the landfill area as shown in the report (report simulation) generally support this statement but the reliance on heads as the primary calibration data set and the absence of river leakage data as an additional calibration data set precludes the ability to obtain a robust model calibration. A robust

model calibration reduces the possibility of a non-unique solution. A non-unique solution can result in an unconstrained computation of flow but similar head patterns. In other words, the head difference between observed and model computed may be small but the difference in flow could be large. Flow is the key phenomenon that drives groundwater systems and contaminants. Further, spatial weights were applied to the observation based on location (distance from landfill) and not based on measurement error as should be the case.

Response: The model greatly reduces the possibility of non-uniqueness by comparing the head calibration targets to model predicted values for a variety of seasonal and pumping conditions. These conditions include the four-quarter seasonal variations, pre- and post-extraction well pumping, pre- and post-barrier wall, and specific pumping tests. Achieving a good calibration under each of these different conditions suggests non-uniqueness has been minimized. In addition to the head matching, flux measurements from Plow Shop Pond and Grove Pond were also used during the calibration process as noted in the documentation included within Appendix B of the LTMMP Update.

Comment 14 - Sensitivity Analysis - During sensitivity analysis, the input parameters were modified by assigning seven different multipliers ranging from 0.7 to 1.3 to each parameter. A large effort was invested in the sensitivity analysis; however, the same multipliers should not have been used for every parameter. For example, the hydraulic conductivity of 1 ft/d will not significantly affect the model results if modified by either a 0. 7 or 1.3 multiplier. It is suggested that each parameter have its own multiplier range, depending on the observed range of measured values or based on the known literature ranges of values.

Response: The purpose of a sensitivity analysis is to identify parameters the model is most sensitive to and to evaluate if the value specified for a particular parameter provides the best calibration. While varying a parameter such as K over a wide range may be useful in assessing how sensitive the model is to that parameter, it does not give an indication if the calibrated value is the better choice over using a narrower range. For future sensitivity analyses, the Army will evaluate if a different range of multipliers for a given parameter is warranted, perhaps including greater changes outside of the multiplier range used for this model version.

Comment 15 - Pumping Rates - The pumping rates vary significantly from month to month and from year to year. The combined extraction well pumping rate used for particle tracking (e.g., Figures 27 and 28) was 49 gpm. The representative pumping rates used during the model construction are significantly less, as presented in Attachment 1-6. From 2008 - 2012, the combined average quarterly pumping rate ranged from 36.2 gpm to 38.8 gpm, with an overall combined average extraction well pumping rate of37.8 gpm. These average values account for the temporal variations, including routine and non-routine system maintenance, repairs and upgrades. The use of the combined average quarterly pumping rates should be considered, rather than the higher value of 49 gpm, to account for system down time. Another option to more accurately evaluate groundwater flow and plume capture using the

model would be to simulate a simplified pumping schedule of the extraction system using a sub-model.

Response: As stated within the February 2014 EPA Capture Zone Analysis Memorandum, the effect of the brief pump-off periods is not significant, and water levels in the area of the extraction wells respond very quickly to changes in pumping. When the pumps are turned off the water levels recover to non-pumping levels rapidly, and when the pumps are turned back on, water levels decline to the pumping-influenced levels equally rapidly. That response appears to suggest that using a continuous pumping rate of 49 gpm does provide a reasonable representation of pumping conditions.

Comment 16 - Comparison of Model Results from an Independent Simulation - A simulation was run with the model-input data sets using model code MODFLOW-NWT version 1.0.8 derived from MODFLOW -2005 version 1.11.00. This model code is slightly newer than the code used in the report. Model heads from the new simulation show large areas of dry cells (EPA Attachment 1; Figure 3). Dry cells occurred in layers 2, 3, and 4. Maps of heads in the report show no dry cells. Possible reasons for the discrepancy include a unique model solution option not apparent in model input files that was not repeated in the new simulation, model code difference, initial head specifications too low, or error in reporting. Dry cells do not occur in the lowermost layer (5) in the new simulation. Note while running the model (new simulation), some initial heads fell below the bottom of the model layer, which could create solution problems. In contrast to heads, model budgets of inflows and outflows between the report simulation and the new simulation show good agreement. This suggests that the new simulation is generally replicating the results of the report simulation despite differences in dry cells.

Response: MODFLOW-NWT version 1.0.8 was released on 24 September 2013, after the modeling was completed and the draft LTMMP Update report was in development. According to release details from the USGS the difference between versions is inconsequential.

The model version reviewed is a variation of the base model, SHL200T2, which was developed to conduct reverse particle tracking. It is not clear why this model version was reviewed exclusively instead of, or in addition to the two base models (SHL200-T1 and SHL200T2). For the version reviewed, the rewetting option needed to be turned off because for MODPATH to work properly the desaturated cells have to be specifically coded as dry. This change does not alter the model results in comparison to the base model SHL200T2, but it is why dry cells are observed when running this model version. The presence of dry cells in the particle tracking variation does not affect results, as indicated by the noted match of model budgets.

Comment 17 - Transient Simulation Approach - The current model represents a significant improvement over past modeling efforts. One of the key differences is the change in simulation mode from steady-state to transient, "to be able to simulate seasonal changes in site conditions." This was accomplished by using quarterly stress periods. The same stresses for each quarter are repeated every year, resulting in a quasi-transient model consisting of

four steady-state quarters that are repeated year after year. While this method may capture some of the seasonal variability of site conditions representing an "average" year, it misses the significant variations in site conditions that occur on an annual basis, as indicated by the precipitation data presented in Figure 6. A significant level of effort was put into identifying the recharge zones based on the precipitation data, the land use, etc. The statement in the Report (page 5) that " ... Each quarter represents average conditions for those months and does not vary from year to year as that level of detail is not required to obtain an accurate model" is questionable if the objective of the model is to simulate transient conditions. Since the actual quarterly precipitation data are available, it is suggested that the "real" recharge data be applied to the corresponding stress periods (as the quarters represent the stress periods in the time discretization of the 2006-2012 simulation period).

Response: *The Army appreciates EPA acknowledging the current model represents a significant improvement. The model does incorporate "real" recharge data into the corresponding stress periods. The benefit of altering the model to represent specific years is questionable for a number of reasons:*

- *While there may be enough precipitation data to represent each year specifically, the data would still be averaged for each quarter;*
- *There isn't that level of data available for other parameters such as surface water elevations or even groundwater elevations. The resulting calibration datasets would be so dissimilar that comparing model calibration for each dataset would be questionable;*
- *Given the length of time of groundwater travel paths, incorporating the ups and downs of each actual year over the length of time that the simulations cover is essentially the same as using an average year throughout; and*
- *Since simulations of future conditions do not have real data, precipitation values for future years would use some sort of average value, similar to what is currently being used in the model.*

The model could be used to evaluate the effects of wet or dry years if there is a justifiable need for that, but altering the model to represent specific years does not seem warranted.

Comment 18 - Accuracy of Simulations near Slurry Wall and Red Cove - It appears that the current model may fail to approximate groundwater flow conditions in the area between the slurry wall and Plow Shop Pond. This is illustrated by comparing particle tracks presented in Figures 27 and 28 with flow lines interpreted from the attached potentiometric surface map for April24-25, 2013 (Attachment A, EPA Attachment 1). For this date, the shallow potentiometric surface map indicates that post-wall groundwater flow in much of the area between the wall and the pond is toward Red Cove. However, the particle tracks (Figures 27 and 28) show groundwater flow away from the pond in this area. Although additional data would be needed to define the average condition, this snapshot indicates a potentially significant discrepancy between observed and modeled results in this area.

Response: *The particle tracks show groundwater pathways over a number of years with associated seasonal variations. The comparison of particle paths to a single time event which may or may*

not vary at different times of the year is questionable. Regardless, as noted in the documentation included within Appendix B of the LTMMP Update, the post-wall data in this area of the model was limited at the time the model was developed, and this area will be reevaluated when the model calibration datasets are updated.

Comment 19 - Particle Tracking - The path line analysis in the report is inconclusive based on a limited number of particles tracked and the procedures tested. Additional discussion is needed to understand the results of the model and how the particle analysis was performed. Additional particle tracking analysis (both forward and backward) would help understand the flow system and potential landfill impacts. For example, it would be informative to seed a larger number of particles in various layers of interest in all areas beneath the landfill cap. This would provide a more meaningful assessment of the effective capture zone of the extraction system at various pumping rates. A technical meeting would be a useful forum to discuss potential, future particle tracking approaches.

Response: The Army is not clear on why there is confusion regarding how particle tracking was performed, or why it is considered to be inconclusive. The process used is discussed in the documentation included within Appendix B of the LTMMP Update, and the approach is the same as has been used and documented for previous model versions which have been included in previous Annual Reports that have been reviewed by EPA for many years without comment. The use of the same procedures that were used in the past allows comparison of the model versions, and was considered to be adequate because there has been no indication of past concerns with the procedure. The Army suggests continued discussion of this concern to better understand the benefit of a different particle tracking approach.

Comment 20 - Conceptual Site Model (CSM) - It is generally understood that a numerical model is predicated on a foundation created by an overarching comprehensive CSM. While technical discussions in recent years have been focused mainly to the geochemical aspects of the CSM, a robust CSM for a site of this level of complexity must encompass a number of critical elements including topography, geology, hydrology, groundwater-surface water interactions, geochemistry, etc. Additionally, the design, function, operation and performance of in-situ engineered systems in the site-specific setting also affect hydrology and therefore provide valuable insight and input which serve to refine the CSM. Such features include the impermeable landfill cover system, slurry wall, extraction system, surface and subsurface drainage systems, etc. It is essential that the model reflects these features appropriately given their importance to the overall water budget, the groundwater flow system, as well as to adequate remedial measures.

While most of the Appendix B-related comments focus on specifics of the model itself, there are several that relate to specific elements of the overarching CSM (such as geologic and hydrologic information, which in certain aspects, are insufficiently captured in the numerical model). While the reassessment of basic site data is often necessary for improving a numerical modeling approach, an in-depth, re-examination of the CSM is fundamental in

achieving remedial success. EPA recommends that the BCT begin this exercise once technical consensus on the underpinnings of the numerical flow model has been reached.

Response: Please see Army's cover letter response to similar EPA comment on the SHL CSM.

Comment 21 - Ground Surface Topography - The model uses representations of the ground surface topography and the bedrock surface topography as "fixed" reference points which are used to determine the relative positions of intermediate model layers based on a variety of factors. It is therefore critical that the ground surface and bedrock surface representations imported into the model are as accurate as current data allow. It is not clear that the MassGIS data layers are the best available in this regard. Please clarify how the ground surface layer was created, and which data were used. Clearly the layer imported into the model must honor the most up-to-date survey data at existing features such as monitoring well locations and other fixed points of reference. Please discuss the lateral and vertical accuracy of the site-specific survey data as compared to data available from MassGIS on a more regional scale. It may be advisable to reconfigure the surface topographic layer in order to insure the highest level of accuracy possible within the ' high-density' sub-grid in the central part of the model. In this regard, high accuracy topographic mapping from Mass Development should be evaluated to determine whether this data is superior to that used in the initial model construction of this layer. It may be beneficial to refine the ground surface topography map based on a composite of the best information for each subarea of the model. In this regard, it would be useful to prepare an index mosaic of the surface topographic layer indicating the data sources for various sub-regions of the layer.

Response: The Army disagrees with the benefit of producing a mosaic of surficial elevations from multiple datasets. Because MODFLOW does not simulate water movement in the unsaturated zone, the degree of accuracy of ground surface elevations is not critical as long as they are reasonable. The DEM/LiDAR resolutions used for ground surface topography are considered to be sufficient as surface elevations do not typically vary significantly over the resolution distance those coverages provide.

Comment 22 - Bedrock Surface Topography - As discussed in the previous comment, the bedrock surface topography is another critical building block of the model, yet it is not clear how this layer was established and what constraints were applied. Please prepare a separate file/figure which represents the top-of-bedrock surface used in the model. Please also post all hard data points (such as point data from monitoring well installations, refusal depths from slurry wall installations, bedrock outcrops, etc., with appropriate explanation) which are available to inform and constrain this layer. Given the lack of documentation on the preparation and modification of this layer in previous modeling efforts, it is essential to prepare and document the best possible representation of the bedrock surface topography for this version of the model. As discussed for the surface topography, above, it may be beneficial to refine the bedrock surface map based on a composite of the best information for each subarea of the model. In this regard, it would be useful to prepare an index mosaic of the bedrock surface layer indicating the data sources for various sub-regions of the layer.

Response: The bedrock topography defined in the model was adopted from the previous model version. For any future model updates the bedrock topography may be re-evaluated to determine if that surface needs to be re-contoured and updated in the model.

Comment 23 - Recharge at Southern Boundaries of the Landfill - On February 27, 2014, efforts were taken to field-locate a number of features in the southern and southeastern boundary regions of the landfill cap in order to better understand the accuracy of the present numerical model in representing actual conditions in this critical region. These features are presented on the attached Figures (EPA Attachment 1 - Figure 5, 6, and 7). Features mapped included:

- Large uncovered soil piles,
- Drainage ditches,
- Storm water detention basins,
- Outfall culverts,
- Areas of extensive impervious surfaces such as parking lots and rooftops
- Areas of ponded (frozen) water at the ground surface and
- A variety of engineered structures related to active and disused drainage systems.

Together, these features cover an area on the order of 40 acres and represent a potentially significant source of enhanced recharge to the aquifer which does not appear to be adequately represented by the model, as it is currently configured. Additional discussions are needed regarding the importance of these features individually and collectively in regards to recharge phenomena and magnitude in this southern (upgradient) portion of the landfill. It is likely that numerical model construction and supporting CSM development will need to be modified to address these features.

Specific questions that need to be addressed include the following:

a. What is the relationship of the large detention basin along the southern edge of the landfill to groundwater, if any? What are the construction specifications of this feature? Is it lined? What degree of exchange occurs (i.e., leakage) with the underlying aquifer?

b. The detention basin occupies an even larger topographic low area on the order of 10 acres. What is the magnitude in total of recharge focused to the aquifer in this area?

c. What is the total area of impervious surface (parking lots and rooftops) which drain into this detention basin and associated topographic depressions from the south? What is the magnitude of the input of storm water to recharge from these areas? Is the storm water system diverting water which would otherwise flow to the south, (and would therefore be of little relevance to flow beneath the landfill)? Is the overall effect to recharge one of amplification? Does the model capture this accurately?

d. A series of engineered drainage swales drain the southern portion of the landfill to the east and northeast, eventually discharging to the southwest corner of Plow Shop pond. What is the construction of these features? Are they lined? What degree of exchange occurs (i.e., leakage) with the underlying aquifer?

e. Two large soil piles and a large area of poorly vegetated coarse-grained sand deposits occur along the south-southeastern-eastern margin on the landfill. The coarse-grained nature of the materials, enhanced topographic relief and lack of vegetation all suggest that this area, which approaches 15-20 acres, contributes a significant degree of recharge to the groundwater system, particularly since these features are located beyond the limits of the landfill cover system. It is not clear that the model adequately represents this significant source of recharge.

f. A number of significant engineered features pertaining to active and/or disused storm water systems were identified along the south-southwestern edges of the landfill. Several interconnected catch basins appear to be located either on or near the southern edge of the cap here, and appear to discharge at a culvert near the western edge of the topographically depressed area. Additionally, disused remnants of a former large –scale engineered drainage system are located in this general vicinity? What is the current configuration of these features and systems? To what degree do they augment or modify the recharge picture in this part of the landfill as compared to the modeled simulation?

Response: The artificial drainage to the west of the landfill is included in the model. To be able to include all of the features noted in the model, a significant and long-term data collection effort would be needed, and it is not clear how this would be justified as the model shows good calibration as it is currently constructed. Due to the significant contribution of recharge from the bedrock to the unconsolidated material beneath the landfill, the low potential for the areas noted to significantly affect flow conditions makes a large data collection effort unwarranted. As stated above, the model is one of many tools used to evaluate site conditions. As such, it is impossible for any model to include every detail, known and unknown, and typically the time and effort and added complication to incorporate/interpret that detail is not rewarded by better results or improved understanding.

Comment 24 - Groundwater Divide South of Landfill - A groundwater divide has been observed from previous work in the general area between the southwestern corner of the landfill and the former site 32/43A property to the south. While the position of this feature has been observed to migrate somewhat with fluctuations in the seasonal water table, it is routinely observed in this general area. Attached are groundwater flow interpretations based on October 2004 head data which depict the position of the divide at that time. It is not clear that the model adequately captures this critical feature. (See attached Figures 18 and 19, EPA Attachment 1).

Response: The referenced divide is replicated in the model as indicated on Figure 24 in Appendix B of the LTMMP Update and appears to be in the vicinity of where it is interpreted from the October 2004 data.

Comment 25 - Residual Values, Group 9 (32/43A) -A number of measures point to subgroup 9 (32/43A) as one of the most poorly represented of the modeled sub-areas. For example, for simulation SHL200Tl, the residual mean (RM) values for individual groups ranged from -0.079 to 0.81, "with most of the groups having a RM within less than 0.5 ft of the observed." Subgroup 9 (32/43A) is a notable exception to this with a RM value of0.70 (Table 11). This is at the extreme end of the range, and is all the more problematic given the proximity of subgroup 9 (32/43A) to SHL. Similarly RM value reported for subgroup 9 (32/43A) for SHL200T2 is 2.63, the worst match of all of the subgroups, by a large margin. These residual head discrepancies are problematic given the location and hydraulic significance of the 32/43A area with respect to the landfill. As noted in the previous comments, the 32/43A area is immediately adjacent to the southern/southwestern margin of the landfill in a pivotal area which contains a number of features and characteristics important to the water balance beneath SHL. The CSM needs to be reconsidered here and the numerical model appropriately updated in an effort to improve calibration in this area.

Response: The 0.70 RM noted is within the stated range and is a good match. The RM of 2.3 for SHL200T2 is partly due to the fact the number of targets decreased from 22 to 11 as water level measurements occurred less frequently and at fewer wells. The decrease in measurement frequency also means the average water levels used as targets could be less reliable than those used for SHL200T1. The RM/Head Range for this subgroup is 3% and 11% for SHL200T1 and SHL200T2, respectively. The first value is indicative of a "well calibrated model". The second one is slightly about the 10% threshold for "adequately calibrated", which given the limitations of the target data could be argued to be adequate and certainly not problematic.

Comment 26 - Sub-landfill Stratigraphy (Overburden) - Ample stratigraphic data from boring logs and well installations exists to construct a more robust and representative model of the stratigraphic layers under the landfill footprint. The digital model should be constructed to honor the known geologic and geometric constraints of the defined geologic layering in the sub-landfill area. Discretization of these layers should at a minimum include a realistic level of detail with respect to the following units as defined and mapped through two decades of site characterization and remediation efforts:

- Landfill cap/cover system
- Waste deposits
- Discontinuous peat deposits
- Upper sand unit
- Lower fine sand unit
- Discontinuous localized glacial till lenses

Based on available data (e.g., boring and geophysical survey information, surface and thickness), maps for each unit should be constructed so that the true relative position, thickness, and geometry for each unit of interest may be inserted into the highest resolution portion of the model generally coinciding with the landfilled area.

Response: Because the model shows good calibration to a variety of conditions and for wells at various depths, it is not clear why additional discretization of the overburden material is necessary. The model is but one of many tools to evaluate site conditions and activities, and there is always less than perfect knowledge of the subsurface no matter how much data are collected. As such, it is impossible for any model to include every detail, known and unknown, and typically the time it takes to incorporate/interpret that detail is not rewarded by better results or enhanced understanding.

Comment 27 - Overburden Sand Unit Hydrostratigraphy -A majority of overburden thickness beneath the landfill is represented by thick sand deposits of glacial origin. Since the plume appears to be migrating principally in these units, and the extraction wells are also screened within these units, it is essential that the model accurately represents these key layers in terms of thickness, position, grain size, and hydraulic conductivity (lateral and vertical). A detailed examination of the logs near the two extraction wells (see Figure 4, EPA Attachment 1) shows that the sand deposits may be divided into two general layers as follows:

Layer 1 -the uppermost shallow overburden unit is approximately 50 feet thick in this part of the site. Logs consistently describe:

- Fine to medium sand grain-size
- Predominance of sand
- Brownish hues indicative of oxidizing conditions

Layer 2 - the deep overburden unit, is between 40 to 50 feet thick in the extraction well area. There seems to be a distinct contact between the two units which is defined by a color change from brownish hues in the upper unit to greenish gray colors in the lower unit, indicating a transition to more reducing conditions. Additional characteristics of this "lower sand" unit are as follows:

- Fine- to coarse-grained sand, but fine-grained sand is the predominant grain size
- Silt content is notable on logs, and these deposits appear to contain a significantly greater fraction of finer-grained material (i.e., very fine-sand, silt, and possibly clay-sized) as compared to the overlying "upper sand"
- Finely interbedded in some intervals
- Distinct darker interbeds noted.

The characteristics of the lower sand unit (proposed layer 2) are therefore more indicative of a unit with lower overall hydraulic conductivity unit than the upper sand. Additionally, vertical conductivities would be expected to be much lower in the lower sand given the

greater prevalence of finer-grained interbeds. The default value of K_h/K_v used for all sand units in the model needs to be reconsidered with a lower vertical hydraulic conductivity value for the lower sand applied to the model than is currently the case. An accurate representation of this distinction is critical given that the extraction wells are screened within the lower sand unit. Therefore, in the interest of improving the model with respect to the data-driven CSM, the contact between the "upper" and "lower" sand should be mapped in three dimensions. The thickness and relative position of the two units should be incorporated into the model, particularly in the fine-mesh detailed central region. Once the relative position and thicknesses of the two sand units are established, it will likely be necessary to adjust the model hydraulic conductivity values significantly.

Response: See Response to Comment 26 above. The Army notes that there appears to be a contradiction between this comment and Comment 26, as this comment indicates splitting the overburden into two basic units, yet the previous comment suggested that more units, some discontinuous, be included. It is impossible, and generally unnecessary in terms of the solution, to include every geologic unit into a model. Because the model shows good calibration to a variety of conditions and for wells at various depths, the existing model layering is appropriate and additional layers would have no beneficial result.

Comment 28 - Glacial Till/Weathered Bedrock - Existing data supports the presence of only spatially discontinuous lenses of till material. Similarly, weathered bedrock is encountered inconsistently, and is absent in many areas. The preponderance of data seems to suggest an abrupt transition from glacially derived sediments to relatively un-weathered bedrock in most locations. Therefore, there is little evidence for a uniform 5-ft thick weathered rock layer beneath the entire modeled area. It would therefore be more appropriate, particularly in the data-rich areas in the landfill's proximity, to map the locations, lateral extent, and associated thicknesses of these discontinuous units, as a first step towards determining whether their presence is significant enough to warrant specific inclusion in the model, and whether a continuous layer is technically justifiable.

Response: The weathered bedrock layer was included and documented as presented within the previous version of the model. There was no past indication that this layer was inappropriate or misrepresented. Additional discussion will be needed to assess the necessity and approach of this suggested revision. As stated in the response to Comment 26, the model is but one of many tools to evaluate site conditions and activities, and there is always less than perfect knowledge of the subsurface no matter how much data are collected. As such, it is impossible for any model to include every detail, known and unknown, and typically the time it takes to incorporate/interpret that detail is not rewarded by better results.

Comment 29 - Bedrock - The technical basis for the modeled representation of bedrock is inconsistent with what is known about the site. For example, detailed information presented in the Shepley's Hill Bedrock Investigation Report (SHL BRI; Gannett Fleming, 2012) presents considerable information supporting a different conceptualization of bedrock. This study generally concluded that there is a 40-50 foot thick interval in the upper bedrock with

hydraulic conductivity on the order of the glacial sand deposits beneath the adjacent landfilled area. The geometric mean from a number of slug tests from borings in this upper bedrock interval was determined to be 2 feet per day. There is little hydraulic conductivity data on the deeper bedrock, but available information suggests that fracturing is sparse compared to the upper interval. As such, a hydraulic conductivity of 0.2 feet per day, as applied in the current version of the model seems reasonable. It may be useful for reasons discussed in other comments to extend the deep bedrock model layer somewhat deeper than it is presently, e.g., total thickness of all bedrock should be on the order of 300 feet. In summary, it is suggested that the bedrock be re-conceptualized as follows:

- Upper Bedrock (layer 4); 45 feet thick; K= 2 ft/day
- Deep Bedrock (layer 5); 255 feet thick; K= 0.2 ft/day

Response: As with previous comments regarding revised discretization for the model, additional discussions regarding the benefit and nature of this revision are needed. Simply adding a uniformly thick upper bedrock layer with a higher K across the entire model domain may not be appropriate, as the justification for that is based on evaluations at the hill where shallow bedrock conditions may be different from those elsewhere in the model domain.

Comment 30 - Spatial Distribution of Hydraulic Conductivity Data - As stated above, the layer designation used to create the current version of the model need to be revised to better honor known geologic constraints. The current effort lacks resolution in the most important areas. For example, the sub-regional scale transmissivity map prepared by Harding ESE (2003) shown on Figure 8 was used as a general guidance for spatial distribution of K despite the fact that considerable additional data has been added since then. Figure 9 presents a number of data points, but the "lumping" of layers 1 through 3 hampers the ability to discriminate between higher and lower conductivity subunits within the 90+ thick interval of sandy deposits. As stated above, the upper and lower sand units have distinct geologic characteristics which undoubtedly relate to discernable K variations. Also, it is noted that the K data posted for Figure 9 does not include any of the points within the landfill. This needs to be updated/corrected. Similarly, Figures 10 and 11 are insufficiently resolved with respect to the actual vertical distribution of existing bedrock K data. Figure 1 0 shows a K distribution for a fictitious 5-ft thick weathered bedrock layer despite little evidence for this and no actual supporting K data. Figure 5 presents/plots a number of bedrock K values for layer 5. However, the overwhelming majority of these points are from the uppermost 50-feet or so of bedrock. As stated above, there is a strong case to be made for assigning the layer 4 bedrock layer to this uppermost 50 feet. In any case, Figure 11 omits additional data from within the landfilled footprint such as K-data resulting from the installation of test borings and/or monitoring points installed for the slurry wall project. This needs to be updated/corrected. Once layer designations are clarified, a table needs to be created which compiles all available K values on a layer specific basis. The table should contain separate columns for the well JD, well location (XY), elevation of the screened interval, geologic medium at screen, model assigned layer (revised), K-value, basis for K-value (test type and reference). The table should be used to prepare a series of revised layer-specific figures similar to Figures 8-11 in Appendix B, which plot the recorded K values in

their proper locations. Such a table and figures will be necessary to accurately reconstruct the model in conformance with available data.

Response: Before any additional discretization or revision of the model layers are conducted, the Army requests further discussing the usefulness and necessity of this change. The current model shows good calibration to a variety of conditions for data from points with good spatial distribution and a variety of depths, so it is not clear why the revisions are needed or what the benefit would be.

A revised table of K values can be developed for the next model update. It should be noted, however, that calculated K values typically vary based on the quality of the data and the method used to gather and analyze that data. Therefore the numbers are not precise but instead have a margin of error that varies, sometimes up to an order of magnitude. For example, K from pumping test data is typically more accurate than slug tests and grain size analyses. The zone values in the model use the K values as a starting point, but because the calculated values have error, the model values are altered during calibration but kept within reason based on the data. Consequently, K data are valuable but only as a guide during calibration.

Comment 31 - Bedrock - Landfill Interface at Shepley's Hill - A key conceptual issue concerns the nature of the hydraulic connection between the bedrock exposed on Shepley's hill and the landfilled area immediately to the east. Clearly, additional effort is needed in attempts to reconstruct the model in a manner which honors what has been learned regarding understanding of the nature, geometric constraints, and hydraulic properties of the bedrock fracture system. Both the magnitude and mechanism of recharge to the sub-landfill aquifer are critically important towards producing a representative flow model for SHL. While the Shepley's Hill Bedrock Investigation (Gannett Fleming, 2012) resulted in significant advances in our understanding of this interface, it is not clear that the model reflects these findings. As noted in the comments above, the uppermost 40-50 feet of bedrock was found to be highly fractured and contains many highly conductive zones. The prevalence of sheeting fractures inclined in the direction of the landfill may offer a direct recharge pathway from the bedrock to the sub-landfill sands via a process akin to "interflow". A potential effect of sheeting fractures is high focused recharge to the landfill but low recharge under the hill. The model simulates a high vertical hydraulic conductivity in this area whereas it is conceptually consistent to simulate the opposite. Further examination of this issue in the context of the model is needed. In this regard, a meeting should be convened to reach a technical consensus on appropriate modifications to the model. Once the geometric, physical and other constraints are built into the model, the model may be used to examine a range of recharge scenarios involving the bedrock-overburden interface along the western landfill boundary.

Response: While the potential impact of the sheet fracturing may be worth evaluating, the overwhelming evidence suggests vertical movement in the bedrock at the hill is extremely important. The bedrock report also indicates a significant volume of water flowing upward from the bedrock beneath and into the landfill, which suggests a high vertical K most likely indicative of vertical fracturing which would dominate the flow. In addition to the sheet fracturing, there

are also numerous vertical fractures that were mapped in the report. These would also suggest a high vertical K.

Page-Specific Comments

Comment 32 - Appendix B; Section 1.2 - Modeling Background - The absence of documentation from previous modeling revisions is troubling. It is incumbent on the Army to rectify this situation at the present juncture. In order to guide this effort, a table should be prepared which lists the missing documentation elements from previous efforts. This tabulation should be used to produce an outline of modeling documentation to be included with the current model updates. Ongoing updates should correct and document the previous omissions. A consensus from BCT modeling experts should be reached regarding the necessary elements of model documentation needed to insure that future revisions, if needed, will have the benefit of appropriate documentation.

Response: The development of a table that lists the missing documentation elements from previous and outdated modeling efforts is not necessary, since one of the primary goals of the latest model was to create a model wherein the basis and data for all parameters specified in the model are documented and described in the write up. As a result, the Army feels that a consensus on previous models is not needed. The documentation included as Appendix B in the LTMMP Update provides extensive detail on the current model and generally follows ASTM standards for model documentation. The description includes data used, procedures and basis for parameter specifications, and tables of data with explanations on analyses conducted.

Comment 33 - Appendix B; Section 1.2- Modeling Background, [Weathered bedrock layer in SHL-008], Page 3, 3rd - It is stated here that Model version SHL-008 added a new layer representing "weathered bedrock". Was this version of the model created before the additional drilling associated with the barrier wall? If so, it is likely that this conceptualization needs updating. It would therefore be useful to revisit the basis for the SHL-008 approach to bedrock (weathered and unweathered) and to compare this to more recent boring information. How does the "5- foot weathered layer" included in the current version of the model reflect this earlier thinking? Is this appropriate? Additional discussions are needed.

Response: See the responses to Comments 28 and 29 regarding the use of weathered and unweathered bedrock layers. Because the model shows good calibration to a variety of conditions and for wells at various depths, the existing model layering is appropriate and additional layers would have no beneficial result.

Comment 34 - Appendix B; Section 1.2 -Modeling Background, [in SHL-008], page 3, 2nd and 3rd - It is stated here that the representation of the bedrock surface, a key element of the model, was updated for model version SHL006, yet little documentation was provided. Similarly, it is stated that SHL-008 was revised in part by "reinterpreting the bedrock

surface." Given the importance of the bedrock surface to the model, it is necessary to reexamine the technical basis for the current iteration of the bedrock surface layer. Please submit a contoured plot of the bedrock elevation surface, with "hard" data points posted at the appropriate locations.

Response: The data used to develop the bedrock surface will be reevaluated for the next annual recalibration and the basis for the model assigned elevations will be provided.

Comment 35 - Appendix B: Section 1.3 - Coordinate and Elevation Datum, page 3, last - As discussed in "General Comments" above, the degree of potential horizontal error imported to the model due to "historical" practices is not clear. EPA recommends that a GPS with sub-meter accuracy be used to confirm that key features are adequately located horizontally.

Response: As noted in the model documentation, an extensive survey by Sovereign in 2013 provides accurate horizontal locations using NAD 83. Other data points and key features to the model at the site are also known to be accurate. The report comment refers largely to old and temporary data points from historical documents where either coordinates were not provided, or if they were the datum was not specified. An example of this is the seepage measurement points in Grove Pond. We do not believe that conducting a GPS survey as noted is necessary at this point, especially considering the considerable effort undertaken by the Army to move all relevant data points into NAD 83. However, what would be helpful for coordinating Army and EPA collected data would be for the EPA to use the NAVD 88 vertical datum, which is the current and most commonly used datum instead of NGVD 29 which is outdated and inconsistent with the work the Army is doing at the site.

Comment 36 - Appendix B; Section 2.1 - Model Domain, Grid, and Layers - The inclusion of three overburden layers provides the ability to employ some useful flexibility. However, increased vertical resolution and allowing for vertical variations in hydraulic conductivity are not the only appropriate objectives. As noted above, the actual geometries of the stratigraphic layers indicate lateral pinch-outs as well as vertical thickness variations. It will therefore be necessary to simulate these actual conditions. e.g., by varying hydraulic conductivity laterally within layers so as to produce a model which mimics the actual data to a greater degree. Please see General Comment 30, above.

Response: As noted previously in comments, the Army reiterates that there appears to represent no additional value in additional discretization of model layers. The model as it stands shows good calibration and is a useful tool to help evaluate site conditions and activities. It may not be possible or even appropriate to incorporate every variation in stratigraphy, and the benefit of significant model revisions is not clear.

Comment 37 - Appendix B. Section 2.3.1, and Figure 4, Layer Elevations - While the process by which the 5 layers were created is straightforward, it is not clear that the resulting 5-layer model adequately represents the actual conditions, particularly beneath the landfilled area. However, it is noted in Section 1.3 that, "in terms of the model, it will not affect the accuracy

if the spatial location of some points is off by a few feet, and it is much less important than the vertical accuracy." If so, is level of vertical resolution (DEM: 5 meter; LiDAR: 1 meter) sufficient, particularly given the lower resolution DEM coverage was most extensively relied on? Additionally, the assumption of layer continuity is inaccurate and may be problematic. For example, Figure 4 shows the 5 layers as being continuous over Shepley's Hill, albeit considerably thinner in that area. This representation is inaccurate as Shepley's Hill contains significant areas of minimally weathered bedrock outcrop (i.e., layer 5 only) where overburden materials are absent. Similarly, while the model contains a more highly discretized subarea in the core of the landfill, this additional resolution does not seem to account for layer geometries of the discontinuous peat deposits, till lenses, deep overburden fine sand deposits, etc., to the level of detail defined through the iterative site characterization process. A more accurate representation of the actual subsurface is needed, particularly beneath the landfill footprint where data density is high. Please see General Comments 29 and 30 above.

Response: The comment included with Appendix B of the LTMMP Update referring to points being off a few feet but not affecting the model is in reference to some well locations, in particular ones away from the landfill where the horizontal datum is unclear. The DEM/LiDAR resolutions used are considered to be sufficient as surface elevations do not typically vary significantly over the resolution distance those coverages provide.

Regarding layer continuity, there appears to be some confusion between model layers and units. In the example provided regarding Shepley's Hill, it is suggested the model is inaccurate because over burden layers are not present. As is shown on Figure 10 of Appendix B in the LTMMP Update report, layers 1-3 at the Hill are assigned K's reflective of the bedrock, so no overburden is simulated as being present at that location.

Regarding additional detail on the sand units and other discontinuous units, this has been discussed previously as part of responses to other comments above, and the need and benefit will need to be further discussed for future model updates.

Comment 38 - Appendix B. Section 2.5.2, Recharge, Page 9, 2nd - Please see general comments above concerning the spatial and temporal approach to recharge. Regarding recharge distribution, the area south of the landfilled area is particularly in need of additional consideration.

Response: See responses to Comments 9, 17, 23, and 31.

Comment 39 - Section 2.3 .3 and Figures 8-11, Hydraulic Conductivity - See General Comment 30 above.

Response: See response to Comment 30.

Comment 40 - Section 2.4.3 and Figure 12 and Table 6; Streams and Ponds - It is noted (page 16, 4th) at, "Three gages were recently installed on Nonacoicus Brook and are part of the L TMMP so gage data for the brook will increase as monitoring proceeds." While this is encouraging, EPA remains concerned regarding the overall integrity and spatial coverage of the existing staff gage network. For example, it is noted that gages 6, 7, 8, 9, and 10 are no longer existing. As such the entire reach downstream on the PSP dam to the main trunk to Nonacoicus Brook is not gaged. Moving forward, strong consideration should be given to improving the staff gage network with additional low-cost gages in key locations.

Response: In February 2014, an additional gage was installed downstream of the PSP dam to address this concern.

Comment 41 - Appendix B; Section 2.5.1 and Figure 15, Groundwater Elevations - It is noted here that, "to date there has not been a single repository or database for the historic and current well water level data [within the modeled area]." The Army's current efforts represent a significant step forward. Efforts should be made to archive and make this data available to the BCT so that the dataset may be improved and built upon as time goes on. Additionally, please see "General Comments" above regarding calibration and recharge issues at the southern boundary of the landfill (i.e., Areas "Other 32/43A" and "SHL2"). In particular, "Other 32/43A" appears to have a poor match between actual and modeled heads and therefore should be reexamined given the critical location just upgradient of SHL.

Response: The Army will expand on the current SHL database efforts to generate a single comprehensive database that will be available to BCT. Regarding recharge issues, see responses to Comments 9, 17, 23, and 31. Regarding the model calibration, see responses to Comments 11 and 12. In summary, it is believed the conclusion of a "poor match" is inaccurate as further elaborated in the referenced responses.

Comment 42 - Appendix B. Figures 10 and 11 - Figures 10 and 11 show the distribution of the hydraulic conductivity (K) in Layer 4 (weathered bedrock) and Layer 5 (bedrock), respectively. The Report states that "No K data were found for the weathered bedrock (layer 4) so that layer was assigned a K value of 1.2 ft/d~ which assumes the layer would contain clays that would result in a K similar to that of the assigned bedrock K of 1.3 ft/d. The vertical K for layer 4 is set at 0.12 ft/d. The K data for the bedrock (layer 5) show a fair amount of scatter, ranging from 0.2 to 100 ft/d. The model calibrated value of 1.3 ft/d falls within the range of the data" (page 14).

Response: See responses to Comments 8 and 9.

Comment 43 - Although the two values are identical from any practical hydrogeologic perspective, it may be unrealistic to expect that the weathered bedrock has a lower K value (1.2 ft/d) than the bedrock (1.3 ft/d). Furthermore, if the field data show a wide range for the bedrock between 0.2 and 100 ft/d, what is the basis for selecting a single value of 1.3

ft/d? The K values for Layers 4 and 5 should be re-examined. Please see general comments 28 and 29 above regarding weather bedrock and bedrock modeling approach.

Response: See responses to Comments 28 and 29.

Summary and Conclusions

Comment 44 - Spatial heterogeneity of the model is unsupported by a discussion of the conceptual flow model or available data. A representative model design is based on a sound conceptual model of the site. Spatial heterogeneity (variations in hydraulic properties of the aquifer), particularly when they affect flow paths from the landfill, should be substantiated by data and guided by the conceptual model. The report in some cases fails to present a reasonable argument for use of several model parameters.

Response: As stated above, the Army requests clarification regarding where the report fails to present a reasonable argument for "several model parameters". It is the Army's opinion that the documentation provided within Appendix B of the LTMMP Update is thorough and provides the basis for parameters used in the model.

Comment 45 - Several model parameters, which did not have a strong case for inclusion based on limited evidence or discussion, had the effect of enhancing flow into the nearby local streams and shortened flow paths in the model (reduced lateral flow). An example of such a parameter is the relatively high hydraulic conductivity of the bedrock under the Nonacoicus Brook in layer 4. The report specifies that the weathered rock is absent at that location but why is the conductivity so much higher than the conductivity of the bedrock in layer 5 that represents the same unweathered rock? Additional discussion is needed to support this assignment. Model sensitivity analysis could be used to support the assignment of a high hydraulic conductivity at that location but that was not presented in the report.

Response: This area of the model was included in the model sensitivity analysis, but for future updates the presentation of the results of sensitivity analyses for this zone will be enhanced.

Comment 46 - The report description of model design and model data sets were in good agreement in most cases. However, the replicated (from the report) USGS simulation produced large areas of dry cells in the upper layers of the model that were not presented in the report. Additional work is needed to identify the reason for the large areas of dry cells.

Response: The reason for the dry cells has been discussed as part of the response to Comment 16, and it is due to the fact the USGS simulation uses a version of the model where rewetting is turned off so that MODPATH works properly. It is purely visual, and the resulting head solution and mass balance is not affected.

Comment 47 - In several cases, the report omitted adequate discussion of some model input features like the high riverbed conductance at Red Cove. The relatively high vertical hydraulic conductivity under Shepley's Hill may promote dewatering of some cells in the model and inaccurate simulation in that area. This should be reexamined and confirmed with new wells. The bedrock layer thickness for layer 5 (100ft) could be extended to 300ft thickness to examine deeper zones in the bedrock that may be hydraulically active based on typical bedrock well depths in New England. The lack of a simulated anisotropy in the bedrock is contrary to some other areas of New England with strong anisotropy in the northeast direction. Upper model layers are too thin by Shepley's Hill that may cause solution dewatering and inaccurate simulation in that area.

Response: The high conductance at Red Cove was necessary to get fluxes to match measured values. The high vertical K at Shepley's Hill has been discussed as part of the responses to Comments 9 and 31 and supported by analyses in the area and no new wells are needed. The benefit or need for an extended bedrock thickness is not presented, so it is unclear why this is necessary. Model mass balance suggests there are no numerical instabilities that would support the contention that model results are inaccurate at Shepley's Hill.

Comment 48 - The path line analysis in the report is inconclusive based on a limited number of particles tracked and the procedures tested. Additional discussion is needed to understand the results of the model and how the particle analysis was performed. Additional particle analysis would help understand the flow system and potential landfill impacts.

Response: See response to Comment 19. The particle tracking procedure was specified in the report, and the comments regarding this do not provide any justification as to why the results are considered to be "inconclusive".

Recommendations

The model should be refined based on completion of the following tasks (many of which have been previously mentioned):

- Re-examination of the CSM- As an initial step, the CSM should be re-evaluated with an emphasis on developing a more highly resolved and realistic hydrostratigraphic representation for all defined bedrock and overburden units;

Response: See response to Comment 20.

- Reexamination of the thicknesses, and upper and lower boundaries, of the five layers;

Response: See response to Comment 7.

- Preparation of representations of the 3-dimensional surfaces of the top and bottom of each revised layers designation;

Response: Contour maps of the layer elevations can be provided as part of future model updates.

- Subdivision of the thick interval of overburden sand deposits in the central part of the site into at least 2 separate units based on the observed geologic and hydraulic characteristics;

Response: See responses to Comments 26 and 27.

- Re-conceptualization of the thick bedrock interval, according to observed characteristics, into a least two subunits, as follows: l) an upper 45-50 of highly fractured bedrock with localized discontinuous lenses of till/weathered bedrock in the uppermost region, and 2) a thick interval of lower bedrock with significantly lower hydraulic conductivity;

Response: See response to Comment 29.

- Once layer designations are clarified, a table needs to be created which compiles all available K values for each specific layer (by elevation and geologic medium); K-values assigned to the model should be corrected as needed;

Response: The K values used in the model will be tabulated as part of future model updates.

- Additional evaluation of the nature and magnitude of recharge in the upgradient areas to the south and west of the landfilled area;

Response: See response to Comment 23.

- Re-examination of the nature of the bedrock-overburden interface along the western margin of the cap;

Response: See response to Comment 31.

- Confirmation of model-computed high head under Shepley's Hill (based on monitoring well data);

Response: See response to Comment 29.

- Re-examination of boundary conditions by (town) extraction wells;

Response: The Army requests additional clarification regarding the necessity of this recommendation since these wells are a considerable distance from the area of interest.

- Re-evaluation (recalibration) of the landfill area of the model (once sufficient field data are available); EPA recommends that the frequency of water level measurements be increased for at least one year to facilitate model recalibration;

Response: See response to Comment 12. Recalibration will be conducted during the next model update and will incorporate additional water level data.

- Observed groundwater elevation maps should be included in the modeling reports. Because the Pumping/Post-Wall Scenario represents the current conditions at the Site, the actual groundwater elevations should be used to create potentiometric maps for comparison with the model generated water elevation map. Modeled gradients should at least qualitatively match observed gradients;

Response: This comparison will be included as part of future model updates.

- Employed of both head and flow as calibration targets in subsequent calibration efforts;

Response: Both head and flow data were used for calibration for the current model. The calibration datasets will continue to be updated as model updates are developed.

- Re-examination of specification of river conductance to ensure that it is conceptually realistic; collection of river leakage data (currently absent from the data set) as an additional calibration data set would improve calibration; the network of stream gages should be augmented;

Response: See response to Comment 6.

- Employment of automatic calibration and model parameterization methods during the next calibration effort;

Response: See response to Comment 11.

- For sensitivity analysis, it is suggested that each parameter have its own multiplier range, depending on the observed range of measured values or based on the known

literature ranges of values. A table summarizing these values should be created for BCT review prior to the next round of sensitivity analysis;

Response: See response to Comment 14.

- Moving forward, simulations should make use of the combined average quarterly pumping rates should be considered to more accurately account for system down time;

Response: See response to Comment 15.

- The actual quarterly precipitation data should be applied to the corresponding stress periods (as the quarters represent the stress periods in the time discretization of the 2006-2012 simulation period);

Response: See response to Comment 17.

- Additional particle tracking analysis (both forward and backward) would help understand the flow system and potential landfill impacts. For example, it would be informative to seed a large number of particles in various layers of interest in all areas beneath the landfill cap. This would provide a more meaningful assessment of the effective capture zone of the extraction system at various pumping rates;

Response: See response to Comment 19.

- Particle tracking of all extraction wells (Town wells, etc.) could assist in receptor risk assessment;

Response: The Army disagrees with the relevance of particle tracking to all extraction wells given the considerable distance from the area of interest and the repeated sampling data in the NIA that does not show As impacts migrating in a direction toward the Town Well.

- Model simulates Nonacoicus Brook as a strong sink: sensitivity analysis should examine other possibilities; and,

Response: As noted within the sensitivity analysis, the model shows good calibration when the Brook is a strong sink and not so good calibration when the Brook is not a strong sink. Future model recalibrations will continue to evaluate this characteristic of the Brook.

- All current and future modeling efforts need to be comprehensively documented and archived; these efforts should include creation of a single repository or database for the historic and current well water level data within the modeled area.

Response: This modeling effort is comprehensively documented and future updates will continue be as well. As stated in the response to Comment 41, the Army will expand on the current SHL database efforts to generate a single comprehensive database that will be available to BCT.

Response to Comments

USEPA Preliminary Recommendations
For Additional Monitoring Locations and Objectives, Nonacoicus Brook
07 February 2014

General Comments

Comment 1 – A large area of iron-stained sediment was observed in Nonacoicus brook in the general region between SHM-10-10 and SSHM-13-03. Numerous distinct areas of iron-staining and associated seepage were mapped in this area (referred to generally as "Area 1" on attachments). The location mapped as "Fe-1" on the figure appears to be located in the central portion of this zone. It should be noted that the actual area of staining in Area 1 is much greater than the mapped region would indicate, as deep water or unstable stream bottom prevented complete delineation. Abundant areas of stained sediments were readily observable on the north bank in all directions opposite "Fe-1". As such, this area appears to have the characteristics of a significant plume discharge zone.

The stained region appeared to extend eastward into the boggy area beyond SHM-13-03. The Army's proposed new monitoring well location SHM-13-15 appears to be targeted directly to this area, and as such appears to be well located. SHM-13-14S/D also appears to target an area where additional delineation would be useful, but the rationale for this location is somewhat unclear. It may serve as a useful monitoring point if determined to be in a minimally contaminated region cross-gradient of the plume axis/discharge. Since it is now 2014, it is presumed that the identifiers for these points will be revised. In any event, a review of previously modeled flow pathways leading to the NIA from SHL (see Attachment 3) highlight the current lack of delineation to the east of SHM-13-03 in the NIA area.

Response: This, and several of the comments below, discuss the visual observation of Fe-staining in and along Nonacoicus Brook. The location of the SHM-13-14S/D pair was requested and oversaw by MassDEP, who theorized that this wetland area might represent an As discharge area to Nonacoicus Brook in consideration of the As profiling points advanced along West Main Street upgradient of this area. Therefore, the rationale for location SHM-13-14S/D, as requested by MassDEP, was to measure vertical gradients in the eastern portion of the wetland located east of SHM-13-03. The EPA concurred with the location of SHM-13-14S/D in its 5 August 2013 comments on the Draft Addendum to the Work Plan for LTMMP Update. *Although SHM-13-14S/D and SHM-13-15 were installed beginning in January 2014 due to water levels prohibiting installation prior to the area freezing, the identifiers remain as originally proposed in the August 2013 Work Plan. Based on the results of groundwater profiling activities conducted in 2013 at SHM-13-03 and in 2014 at SHM-13-14S/D and SHM-13-15, arsenic-impacted groundwater was not encountered from 10 to 30 feet below grade at each location and was first encountered at a concentration of 17.6 µg/L at 30 feet below grade at SHM-13-03, 48.9 µg/L at 50 feet below grade in SHM-13-14S/D, and 35.5 µg/L at 60 feet below grade in SHM-13/15.*

It is critical to note that the visual presence of Fe-staining in a wetlands or brook area does not and has not correlated to the presence of arsenic in Nonacoicus Brook. The rationale for the installation of SHM-13-03, a location proposed and championed by USEPA, was for this same

purpose; evaluating Fe staining observed along the banks of Nonacoicus Brook in this area. The profiling and well sampling work in both the wetland area and in this area near many of these Fe-stained areas continue to only document arsenic concentrations at depths significantly below the brook elevation. Finally, a significant amount of surface water and sediment sampling has been conducted by the Army in the Brook since 2001 and these results also do not support a significant shallow arsenic discharge to the Brook.

Comment 2 – Groundwater conditions in a transect between SHM-10-10 and SHM-13-03 are insufficiently assessed, considering that the longitudinal axis of the plume core as it approaches Nonacoicus brook is likely to occur in the general area between DEP-08-03 and Fe-1. There is no permanent well control along this axis as DEP-08-03 has been destroyed. Further, while SHM-10-10 and SHM-13-03 provide useful monitoring points, it is possible that they are on the northern and southern fringes of the highest concentration part of the plume given the relatively narrow width of the "core" shown on upgradient transects (i.e., on the order of 100 feet; see Attachment 3). Furthermore, it is likely that the screened interval for SHM-13-03 is not optimal in that it overlooked a key zone from 30-40 feet. Rotasonic core samples from this interval indicate conductive sand and gravel materials which are highly stained with iron-oxide; in short, an obvious zone of interest. Attachment 3 includes a photograph I took of this zone while on site last spring. In summary, there is a strong case to be made for several additional shallow groundwater monitoring points in this area so that highest concentration core portion of the plume may be properly evaluated as it discharges to Nonacoicus brook in addition to the Army's present focus to the east of the area.

Response: The Army disagrees with the location of the longitudinal axis of the arsenic impacted groundwater located between West Main Street and Nonacoicus Brook. Based on groundwater profiling conducted in 2013, the longitudinal axis is located between SHM-13-06 and SHM-13-03. SHM-13-08 is located on the eastern edge of the impacted zone. It is the Army's opinion that the current monitoring well network provides adequate coverage in this area and that the installation of an additional well at the former location of DEP-08-03 is not necessary. Note that there are 3 additional wells within approximately 100 feet of this location, one of which is immediately downgradient of this location.

Regarding the screen interval of SHM-13-03, groundwater profiling data was utilized to determine the optimal depth of the screen. As identified during groundwater profiling activities, the zone of greatest impact at SHM-13-03 was at 50 feet below grade.

Comment 3 – It is clear from the locations of previous surface water and sediment (SW/SED) sampling that previous efforts were largely unsuccessful in targeting the most significant areas of contaminated groundwater discharge mapped in April 2013 as iron-stained/seepage areas (See Areas 1A, 1B, 1C, 2 and 3 on Attachment 3). As such previous risk assessments should be considered as preliminary in nature, and may present a biased-low picture of the actual risk range. It should also be noted that most of the previous surface water/sediment samples are approaching 15 years old and consideration should be given to updating the surface water/sediment database for that reason alone.

With the exception of SHW-07-01X, which appears to be peripheral to the "Area 1A" stained region, SW/SED conditions in the Fe-1 area and adjacent areas have not been evaluated, despite the evidence of significant discharge here.

The area of observed staining identified as "Area 1B" on Attachment 3 has not yet been evaluated with respect to SW/SED conditions or risk. For example the specific focused discharge/staining in the "Fe-2" area has not been evaluated.

SHW-01-08X and -09X appear to be located near the eastern/peripheral edge of "Area 1C". These data therefore, while useful, likely do not assess the most impacted portion of that region of Nonacoicus brook. Additional SW/SED sampling would appear to be necessary in the significant areas of seepage/discharge mapped in the region contained by seeps -7, -8, and -10.

Response: It is noted that the surface water and sediment sampling conducted in 2001 and 2007 targeted iron-stained areas of Nonacoicus Brook. Based on the groundwater profiling data collected from 2001 to 2013, the area of impacted groundwater is stable. Consequently, the age of the data is not relevant (note the significant consistency in arsenic concentrations in 2001 vs 2013 sampling work along West Main Street). In addition, the landfill had been emplaced for more than fifty years prior to the collection of surface water and sediment samples, so given the measured groundwater flow velocity, if there were impacts to the brook at concentrations representing a risk to human health or the environment, such impacts would have been detected during the 2001 and 2007 sampling events. Further and as stated above, arsenic-impacted groundwater was encountered at 50 to 60 feet below grade and has not been encountered from 10 to 40 feet below grade at each location based on the results of groundwater profiling activities conducted in 2013 at SHM-13-03 and in 2014 at SHM-13-14S/D and SHM-13-15. Consequently and due to the depth of impact, it is the Army's opinion that the iron-stained sediment in the area of SHM-13-03 is not an indicator of discharge of arsenic-impacted groundwater to the Nonacoicus Brook in this area that would cause unacceptable risk. Given this, the Army maintains that the previous assessments and risk evaluations are appropriate and complete.

Based on the figure titled "Reconnaissance of Nonacoicus Brook South Bank", Fe-1 appears to be located slightly upstream from SHW-07-01X and that SHW-07-01X would be a representative sample from this area. As stated previously, the depth of impacted groundwater identified in the area of SHM-13-03 is located approximately 50 feet below grade. Consequently, the iron-stained sediment in the area of SHM-13-03 should not be associated with the discharge of arsenic-impacted groundwater to the Nonacoicus Brook. The presence of Fe-staining in the brook or wetlands area does not always equate to the presence of arsenic.

Area Fe-2 is located northwest of SHM-10-10. Based on groundwater profiling data, arsenic impacted groundwater is located east of SHM-10-10 and at depths which are unlikely to impact Nonacoicus Brook. In addition, the highest concentration of dissolved arsenic detected during groundwater profiling activities conducted at SHM-10-10 was 2.47 µg/L.

Based on groundwater profiling and sampling data collected from 2001 to 2013, arsenic-impacted groundwater is located east of SHM-10-10. Groundwater profiling data from the profiling points

located west and southwest of SHM-10-10 (SHM-10-26, SHM-13-02, SHM-10-01, and SHM-13-12) do not indicate that arsenic-impacted groundwater is located or is discharging to the area of Seeps 7 through 10. Consequently, surface water and sediment sampling in this area is not necessary. Please refer to the Army's response to Comment #1.

Comment 4 – SHW-01-10X, -11X, -12X, and -13X do not appear to evaluated plume discharge and rather assess relatively un-impacted areas of the brook. Arsenic values in this part of the system have generally been extremely low, so the plume does not appear to be a discharging in this area.

Response: Comment noted.

Recommendations

Recommendation 1 – Consideration should be given to re-installing a shallow overburden monitoring point at the former DEP-08-03 location to duplicate the vertical interval associated with the highly-contaminated plume core.

Response: See the Army's response to Comment 2.

Recommendation 2 – Additional overburden monitoring points are needed along the plume axis downgradient from DEP-08-03, adjacent to Nonacoicus brook, so that plume conditions just prior to discharge to sediment and surface water may be evaluated over time. This will likely require at least two vertical screened intervals.

Response: See the Army's response to Comment 2.

Recommendation 3 – Additional evaluation of stream conditions is needed in areas identified to be impacted by the SHL plume.

Response: See Army's response to Comment 3 above.

Recommendation 4 – Additional surface water and sediment monitoring is needed in Area 1A, including seeps identified at "Fe-1", "Fe-2", Fe-5 and other areas of staining and seepage in order to assess current surface water and sediment conditions, perform risk assessment updates as necessary, and to establish appropriate monitoring stations to evaluate surface water and sediment trends moving forward.

Response: See Army's responses to Comments 1 and 3 above.

Recommendation 5 – Similarly, additional surface water and sediment monitoring is needed in Area1B, including "Fe-12", Seep 5, and perhaps other areas.

Response: See Army's response to Comment 3 above.

Recommendation 6 – Similarly, additional surface water and sediment monitoring is needed in Area1C, particularly in the area of staining associated with Seep 7, -8, -9, -10, and perhaps other areas.

Response: See Army's response to Comment 3 above.

Recommendation 7 – Data collected from the installation of SHM-13-15 and SHM-13-14S/D should be used to determine whether additional groundwater, surface water and sediment characterization is needed in this minimally characterized area east of the presently determined plume impacts.

Response: Data collected from the installation of SHM-13-14S/D and SHM-13-15 indicate that arsenic impacted groundwater is not located at a depth shallower than 50 feet below grade and that the core of arsenic impacted groundwater is located between SHM-13-07 and SHM-13-03. Consequently and due to this data and the depth of impact, it is the Army's opinion that additional surface water and sediment sampling is not warranted east of and in the area of SHM-13-03. The locations of the newly installed wells in reference to previous surface water and sediment sampling points will be depicted on Figure 2 of the LTMMP Update.

Response to 06 December 2013 MassDEP Comments on
DRAFT LTMMP UPDATE
SHEPLEY HILL LANDFILL
Former Fort Devens Army Installation
October 2013

General Response to Comments

The LTMMP Update was the Army's attempt to propose Data Quality Objectives (DQOs) for the existing remedial actions as it continues to work with the BCT to address its concerns on perceived data gaps and disagreement over the Conceptual Site Model (CSM). Discussions and agreement on the CSM and DQOs are critical to a path forward and to establishing a basis to measuring the performance on any remedial action, including, but not limited to the Arsenic Treatment Plant (ATP). Without a consensus on the CSM and the DQOs, there can be no consensus on attainable remedial outcomes and/or remedial timeframes.

With respect to the BCT's continuing concerns for the need for additional data, we reiterate that in accordance with the CERCLA guidance for RI/FS uncertainties are a part of the Superfund process and that the desire to remove all uncertainties competes with the Superfund Program's mandate to perform cleanups within designated schedules. Therefore, the objective of data collection is not to achieve the unobtainable goal of removing all uncertainty, but rather to gather information sufficient to support an informed risk management decision. To this point the Army believes that the existing data is more than sufficient to establish the CSM and determine the appropriate remedial actions.

Based on the comments below it is evident that the need for agreement and consensus on the CSM is imperative and we believe that given the available data and the length of time the groundwater pump and treat system has operated, in conjunction with investigations performed over the past decades there is more than enough data for both parties to come to an agreement on the CSM. Therefore, the Army proposes to resolve any major differences between Army and EPA interpretations of the CSM through a series of BCT technical meetings so that a focused feasibility study can be performed and an alternated remedy selected.

Response to Specific Comments

Comment 1 – Section 1.4: Characterization of the extraction system, treatment plant, and barrier wall as "remedies" is inconsistent with the meaning of the term under CERCLA. The contingency remedy does not refer to the particular hardware now installed and operating at the site; rather, it refers to the original remedy (landfill cover system) supplemented with a groundwater extraction system to prevent migration of contaminants from the landfill. The barrier wall is not a remedy; it is a supplemental component installed during a removal action to prevent migration of contaminants from the east side of the landfill.

Response: According to the Record of Decision (ROD) for the Shepley's Hill Landfill (1995) which was drafted in accordance with CERCLA, the selected remedy for the SHL is the completion of

the closure of the SHL in accordance with 310 CMR 19.000 and the monitoring and evaluation of the effectiveness of the landfill cover system. As further specified within the ROD, the selected remedy includes a contingency remedy, the construction and operation of a groundwater extraction and discharge facility, if the selected remedy proves ineffective at reducing contaminant concentrations. Consequently, the arsenic treatment plant (ATP) has been noted as the contingency remedy in the LTMMP Update to be consistent with the ROD. Further and as noted in the LTMMP Update, the barrier wall will be formalized as a remedy to mitigate arsenic-in-groundwater flux to Red Cove/Plow Shop Pond as part of a pending Explanation of Significant Differences (ESD).

Comment 2 - Section 2.1, 2.4, and 2.5: Data obtained from the recently installed EPA piezometers indicate that the capture zone of the extraction system is too small to prevent migration of contaminants from the landfill. More specifically, these data indicate that arsenic contamination emerges from the east side of the landfill, by-passes the capture zone of the extraction wells, and extends northward sustaining the arsenic plume in the NIA.

Water level measurements from the EPA piezometers are shown in Figure 6. Flow direction lines based on these data indicate that arsenic contamination emerges from the east side of the landfill (e.g., vicinity of SHM-10-06: As = 1,980 ug/L and SHM-11-06: As = 1,020 ug/L; Appendix A), by-passes the capture zone of the extraction wells, and extends from there northward toward West Main Street (see ATTACHMENT 1). The analytical results from groundwater samples collected by EPA from the deep piezometers in November 2012 confirm this interpretation and provide greater detail on the plume geometry in the vicinity of the extraction system. The distribution of arsenic in these samples and samples collected from nearby monitoring wells (SHM-96-5B: As = 1,400 ug/L; SHM-93-22B: As = 1,150 ug/L; and SHM-05-41B: As = 812 ug/L; Appendix A) indicates that the extraction system draws contaminated groundwater from the east side of the landfill westward toward the extraction wells but does not capture this groundwater; instead, this groundwater by-passes the extraction wells and extends northward toward West Main Street (see ATTACHMENT 2). Arsenic concentrations in the contaminated water that by-passes the extraction wells exceed 2,000 ug/L, sustaining the arsenic plume that extends across the NIA.

The actual size of the capture zone revealed by these data is smaller than predicted by the up-dated groundwater model and the extent of arsenic contamination not captured by the extraction system is larger than predicted by the model (Figure 4). The differences between the site data and the model predictions may not reflect a significant error in the design of the model; instead, the differences appear to be attributable to the difference between the modeled extraction pumping rate (49 gpm) and the actual extraction system pumping rates (e.g., 38.9 gpm in 2012; Appendix B, Attachment 1). The model could be re-run using the actual extraction rates to assess these differences.

In summary, these results indicate that the extraction system is not providing sufficient capture to prevent migration of contaminants from the landfill. Accordingly, the extraction system should be modified to prevent migration of contaminants from the landfill or an

alternative remedy should be developed to prevent migration of contaminants from the landfill.

Response: The Army disagrees with MassDEP's assessment of the data from the EPA piezometers. According to EPA's 29 October 2013 Draft Hydraulic Gradient Analysis of Pump and Treat System Performance Memorandum *(hereafter the EPA's Capture Zone Analysis), "[t]he data obtained do not indicate major seasonal changes in capture effectiveness or other major failures of the system with respect to plume capture." Further, "differences in the direction of hydraulic gradients related to changes in groundwater extraction system status (e.g., system on vs. system off) can be readily observed in the triangle established using wells SHM-93-22B, SHM-96-5B, and piezometer EPA-PZ-2012-3B." These wells are located northeast of the extraction system, and hydraulic gradient shifts are observable depending on extraction system status. This indicates that the extraction influences flowpaths east and northeast of the system.*

MassDEP's Attachment 1 was based on the 2-foot iso-contour plan presented as Figure 6 of the LTMMP Update. As part of the evaluation of Attachment 1, these contours were expanded to 0.5-foot iso-contours to evaluate flowpaths in the area of the extraction system. As presented on the attached figure, the influence of the extraction system can be observed as far southeast as monitoring well SHM-10-06, as far northeast as SHM-96-5B/C, and as far northwest as SHL-9. This suggests that groundwater from the east side of the landfill and from northeast of the extraction system is captured. The Army cautions MassDEP against drawing conclusions from only one line of evidence, especially when that line of evidence can be misinterpreted due to mapping constraints.

In addition and as part of the groundwater model update conducted in support of the LTMMP Update, forward and reverse particle tracking was completed to evaluate groundwater flowpaths. As illustrated on Figures 4 and 5 of the draft LTMMP Update, the forward and reverse particle tracking suggests that the capture zone for the extraction wells covers the landfill and extends eastward to the barrier wall.

A computer-generated dissolved arsenic iso-contour plan was developed using GIS and was compared to MassDEP's Attachment 2. The contours for both the arsenic iso-contour plan were generated using Fall 2013 dissolved arsenic data from wells which are screened between approximately 60 to 90 feet below grade, which is the zone of the greatest arsenic impacted groundwater. As indicated on the iso-contour plan, the 1,000 ppb contour as defined by SHM-10-06, SHM-11-06, SHM-96-5B, SHM-93-22B, and EPA-PZ-2012-6B, and EPA-PZ-2012-7B does not extend into the NIA and is drawn to the extraction wells. In the same manner as the results of the particle tracking analysis conducted as part of the model update, this indicates that groundwater from the east side of the landfill is captured by the extraction wells.

Consequently, the Army disagrees with the MassDEP's assessment of the flowpaths and concentration gradients in the area of the extraction wells. As indicated on the expanded iso-contour plan, the EPA's capture zone assessment, and the groundwater model update, the capture zone of the extraction system includes the east side of the landfill. It is important, as USEPA notes in their Capture Zone Analysis, to consider all available lines of evidence when considering capture analysis.

Regarding the actual extraction system pumping rate, the Army has responded to similar comments in the 2011, 2012, and 2013 Annual Reports and restates its response that brief periods of shutdown, on the order of one or two days, are a routine part of most groundwater extraction systems due to maintenance, power interruptions, etc. However, because maximum groundwater velocities are on the order of one half to less than one foot per day, such periods do not represent a significant 'escape' of plume mass. Rather such oscillations are consistent with recharge cycles, diurnal cycles, atmospheric pressure cycles, etc., which influence water table elevation, groundwater flow patterns, and velocities. Further and according to the EPA's Capture Zone Analysis, the extraction system has significant influence on the surrounding flow field, and groundwater elevations respond quickly to the operation of the system. While we note that 49 gpm is not the yearly average rate due to routine system maintenance, it is the appropriate rate that should be used for modeling purposes as it is the extent of capture while the system is operating, given the quick response of the aquifer and because it has been demonstrated that the short duration non-pumping conditions do not affect the effective capture zone as discussed in the EPA Capture Zone Analysis.

Comment 3 - Sections 2.1 and 2.2: Results from the long-term monitoring program indicate that much faster cleanup times than suggested in the plan (100s of years) are possible. In particular, the results from groundwater samples collected from well SHM-96-5B indicate that substantial reductions of arsenic concentrations can occur during a surprisingly short period of several of months. Well SHM-96-5B is located close to the eastern edge of the arsenic plume. As groundwater levels rise and fall due to seasonal variations, the arsenic plume shifts laterally through the portion of the aquifer sampled by this well, causing arsenic concentrations to oscillate annually between seasonal highs and lows (Appendix D, 2012 Annual Report). Seasonal declines during some years exceeded 50 percent (see ATTACHMENT 3). Evidently, the frequently cited study indicating that 100s of years would be required to "flush" carbon and arsenic from the aquifer is not representative of actual site conditions; it appears the carbon content of the samples used to conduct the study was much higher than the actual carbon content of the aquifer north of the landfill and/or the study did not account for other active carbon degradation processes that proceed at a much faster rate than mechanical flushing rates (e.g., microbial degradation).

Response: The data presented on MassDEP's Attachment 3 chart span November 1996 through October 2012, and seasonal variation in dissolved arsenic concentrations were observed since sampling began at this well. It is important to note that the extraction system was initialized in March 2006 and that approximately 10 years of seasonally influence data exists prior the initialization of the extraction system. Consequently, the observed seasonal trending in arsenic concentration existed both prior to and after the installation of the extraction system and is not an indicator of the effectiveness of the system. The seasonal fluctuations have nothing to do with the effectiveness or even the presence of the treatment system. Moreover, seasonal arsenic flux caused by oxic recharge (pre- and post-ATP) seems to further demonstrate the ineffectiveness of the remedy to shift redox conditions due to dissolved carbon and the number of pore volumes needed to begin a shift.

In addition, it is inappropriate to use the data from only one monitoring well in a statistical analysis to develop a conclusion on the effectiveness of the extraction system. However in

response to this comment, a Mann-Kendall statistical test was conducted on the data from SHM-95-5B to determine if a statistically significant trend can be interpreted from the data. The statistical test was conducted two data sets: The first set included the data collected before the initialization of the extraction system (November 1996 to January 2006), and the second set included the data collected from after the initialization of the extraction system to present (April 2006 to present). The entire data set was not tested as a whole because the initialization of the extraction system skews the data. Although arsenic concentrations initially decline between January 2006 and April 2006 due to system startup, statistical tests indicate that arsenic concentrations were increasing prior to the initialization of the extraction system but remain stable after the system was started. Consequently and although the extraction system caused an initial decline in concentration between January 2006 and April 2006 in SHM-96-5B, the Mann-Kendall analysis of the data set obtained since pumping began does not show a decline, therefore the data from this well does not indicate that cleanup of the NIA can be achieved in a reasonable timeframe as MassDEP asserts.

Comment 4 – Section 2.3.1 and 2.5: The LTMMP will not be complete until it includes provisions for monitoring the leading edge of the plume (i.e., monitoring longitudinal extent and stability). The plan suggests that the arsenic plume does not extend past Nonacoicus Brook, speculates about the presence of a redox boundary near the brook, and presents groundwater model results that indicate flowlines originating on the site terminate at the brook (Section 2.4); however, none of these ideas have been confirmed by data collected from the area between the brook and south side of the surrounding wetland. What is known, however, is that the arsenic concentrations in the core of the plume as it approaches the wetland exceed 1,000 ug/L (SHM 10-17: As = 1,860 ug/L; SHM 10-23: As = 1,100 ug/L; and SHM 10-27: As = 1,040 ug/L; Sovereign, 2011). In short, the location of the leading edge of the plume is not known. Additional field data should be acquired to determine where the leading edge of the plume is located so that the LTMMP can include provisions to monitor it, or remedial action that shortens the plume such that it does not extend beyond the existing well network should be conducted.

Response: *Data collected to date from groundwater profiling and sampling locations along the north side of Nonacoicus Brook (SHM-10-02, SHM-10-03, SHM-10-04, and SHM-10-08) does not indicate that arsenic impacted groundwater is located north of the brook. Further, hydraulic data gathered from these wells suggest a westerly/southwesterly flow of dissolved oxygen rich groundwater north of the brook that would create a redox boundary beneath Nonacoicus Brook as oxygen-depleted groundwater emanating from the landfill area migrates north and mixes with oxidized water from the north. In addition, work completed in Spring 2013 and January 2014 continues to document that arsenic remains at depth, tens of feet below the Brook elevation and, taken with the data collected north of the brook, indicates that the arsenic concentrations appear to decline rapidly at depth in proximity of the brook. As presented in the* 2013 Shepley's Hill Landfill Annual Report, *arsenic-impacted groundwater was encountered at 50 to 60 feet below grade south of the Brook and has not been encountered from 10 to 40 feet below grade at each location based on the results of groundwater profiling activities conducted in 2013 at SHM-13-03 and in 2014 at SHM-13-14S/D and SHM-13-15. Consequently, the existing data set does not suggest that arsenic is discharging to the Brook at appreciable concentrations and continues to suggest that a redox area is present which naturally precipitates arsenic into iron solids 10s of*

feet beneath Nonacoicus Brook as the low-dissolved oxygen groundwater mixes with oxidized water from the north and beneath the Brook. As stated in the General Response to Comments above, it is important for all parties to understand and accept that uncertainties are a part of the Superfund process and that the desire to remove all uncertainties competes with the Superfund Program's mandate to perform cleanups within designated schedules. Therefore, the objective of data collection is not to achieve the unobtainable goal of removing all uncertainty, but rather to gather information sufficient to support an informed risk management decision. To this point the Army believes that the existing data is more than sufficient to establish the CSM and determine the appropriate remedial actions.

Comment 5 – Section 2.6: Implementing the anticipated "second phase of operation (a 5-year period)…to more clearly evaluate the remedy performance" would be inconsistent with the EPA guidance cited here and inconsistent with the immediately preceding site-specific strategy: "For SHL, this phased approach includes the operation/implementation of the selected remedies, followed by an evaluation of each remedy performance. Adjustments to remedies are needed if any remedy component appears to be unable to meet RAOs." After 8 years of operation it is now apparent that the extraction system as operated currently is insufficient to prevent migration of contaminants from the landfill (refer to Comment 2); consequently, there is no reason to expect improvement during an additional 5-year period of operation. Instead, as suggested in the plan, the extraction system should be modified to prevent migration of contaminants from the landfill (e.g., reconfigure extraction wells and/or expand capacity), or an alternative remedy should be developed to achieve the RAOs.

Response: As stated in the response to MassDEP Comment 2, the Army disagrees with the MassDEP's assessment of the flowpaths and concentration gradients in the area of the extraction wells. As indicated on the expanded iso-contour plan, the EPA's capture zone assessment, and the groundwater model update, the capture zone of the extraction system includes the east side of the landfill. Further and according to the USEPA's July 2011 Groundwater Roadmap, Recommended Process for Restoring Contaminated Groundwater at Superfund Sites *(OSWER 9283.1-34), the "Operate, Monitor and Evaluate Remedy" stage typically involves five-year review periods to monitor the effectiveness of the subsurface remedy.*

Moreover and as stated in Appendix B of the July 1999 EPA guidance document A Guide to Preparing Superfund Proposed Plans, Records of Decision, and Other Remedy Selection Decision Documents *(OSWER 9200.1-23P), it is necessary to implement a phased approach toward the cleanup of a site where complex groundwater contamination problems are present. In a phased remedy, site response activities should be implemented in a sequence of steps so that the information gained in earlier phases can be used to refine subsequent objectives or actions. Further, groundwater response actions, in particular those using extraction and treatment, should generally be implemented in more than one phase. Ultimately, "performance data from an early phase of the remedy may show that attainment of the ultimate remediation objectives is not technically practicable, which would result in re-evaluation of the Selected Remedy and preclude implementation of later remedy phases."*

In addition, recent EPA Guidance on ***Groundwater Remedy Completion Strategy – May 2014 also details many of the LTMMP Update components including the development of remedy performance metrics.***

Consequently, a 5-year review period is not inconsistent with the stated evaluation of remedy performance following a period of operation/implementation. As stated within the LTMMP Update and within the USEPA guidance, adjustments to the remedies will be conducted upon completion of the evaluation period.

Comment 6 – Section 3.1: To facilitate evaluation of the proposed monitoring well network, the plan should include an updated map of the arsenic plume.

Response: An arsenic limit of impact plan will be included within the Draft Final LTMMP Update.

Comment 7 – Sections 3.1.1 and 3.3: The description of landfill closure requirements is incomplete. In addition to monitoring landfill gas, closure requires monitoring of downgradient groundwater and surface water. In particular, the state solid waste regulations require groundwater monitoring to ensure compliance with state water quality standards at a location no farther than 150 m from the edge of the landfill or the landfill property line, whichever is shorter (310 CMR 19.132). The LTMMP and site remedy should address these requirements.

Response: Media sampling at SHL is conducted in accordance with the existing LTMMP and its addendum which were previously reviewed and approved by the MassDEP in 2007 and 2009, respectively. The sampling rationale detailed in the LTMMP Update is consistent with these previous documents and agreements.

Comment 8 – Sections 3.1.2 and 3.4: The DQOs proposed to assess the performance of the extraction system should not be considered until the extraction system has been modified sufficiently to prevent migration of contamination from the landfill. Stated simply, the performance of a containment system in achieving cleanup of the NIA cannot be assessed until containment is achieved. Based on ample evidence indicating that the existing extraction system is not preventing migration of contaminants from the landfill (Comment 2) and will not prevent migration of contaminants from the landfill during an additional 5-year period (Comment 5), the DQOs for the NIA should be refocused to monitoring the installation and performance of a modified extraction system that prevents migration of contaminants from the landfill or supporting the development and implementation of an alternative remedy.

Response: As stated in the responses to MassDEP Comments 2 and 5, the Army disagrees with the MassDEP's assessment of the flowpaths and concentration gradients in the area of the extraction wells, the extent of the capture zone of the extraction system, and the applicability of the five-year review period to monitor the effectiveness of the subsurface remedy. Based on these responses, the

proposed DQOs for the NIA are appropriate as written and consensus on those DQOs are critical to establishing a basis to measuring the performance on any remedial action.

Comment 9 – Sections 3.1.3 and 3.5: To assess the long-term performance of the barrier wall, the plan should also include periodic collection and analysis of surface water and sediment samples from Red Cove.

Response: To assess the long-term performance of the barrier wall, long-term hydraulic monitoring of the barrier wall area will be conducted to collect hydraulic head data on either side of the barrier wall to verify the effectiveness of the barrier wall in diverting groundwater flow from Red Cove supplemented with periodic groundwater sampling of key indicator wells to verify a reduction in arsenic flux to Red Cove. In addition, post-excavation sediment samples were collected from Red Cove during the Plow Shop Pond Removal Action conducted in 2013, and additional sediment and surface water samples will be collected from Red Cove at the end of the 5-year evaluation period to assess if a statistically significant increase in concentrations from the post-excavation data has occurred. Previous modeling suggests that existing arsenic-impacted groundwater on the eastern side of the wall may require several years to flush from the aquifer; therefore, the statistically significant decrease in arsenic concentration on the eastern side of the wall is not expected to occur in the next 5 years. Future data collection optimization may be recommended in this area considering the long term life cycle of the barrier wall.

Comment 10 – Sections 3.1.4 and 3.6: The DQOs proposed to assess the performance of the remedy should be designed to monitor cleanup of the NIA, rather than monitoring the "stability" of contamination.

Response: The long-term monitoring program for the NIA detailed with the LTMMP will allow for not only the determination of the stability of the arsenic-impacted groundwater but also the effectiveness of the remedy to clean up the NIA. Consequently, the DQOs will be revised to include the monitoring of the cleanup of the NIA as well as the stability of the arsenic-impacted groundwater.

Comment 11 – Section 3.1.4: The meaning of "arsenic-impacted groundwater near the surface water elevation of Nonacoicus Brook" is uncertain. As explained in Comment 5, additional field data should be acquired to determine where the leading edge of the plume is located so that the LTMMP can include provisions to monitor it, or remedial action that shortens the plume such that it does not extend beyond the existing well network should be implemented.

Response: "Arsenic-impacted groundwater near the surface water elevation of Nonacoicus Brook" refers to the brook/aquifer interface located in the upper zone of the aquifer. As presented in the 2013 Shepley's Hill Landfill Annual Report, *arsenic-impacted groundwater was encountered at 50 to 60 feet below grade south of the Brook and has not been encountered from 10 to 40 feet below grade at each location based on the results of groundwater profiling activities conducted in*

2013 at SHM-13-03 and in 2014 at SHM-13-14S/D and SHM-13-15. Consequently, the existing data set does not suggest that arsenic is discharging to the Brook at appreciable concentrations and continues to suggest that a redox area is present which naturally precipitates arsenic into iron solids near or beneath Nonacoicus Brook as the low-dissolved oxygen groundwater mixes with oxidized water from the north and beneath the Brook.

Comment 12 – Section 3.1.4: Based on the 2010 and 2013 groundwater profile results, none of the monitoring wells proposed for sampling north of West Main Street intercepts the core of the plume as it approaches Nonacoicus Brook and the adjacent wetlands (SHM-13-03 appears to be located on the western edge of the plume). To monitor the core of the plume as it approaches Nonacoicus Brook and provide additional hydraulic control in the NIA, a monitoring well should be installed east of well SHM-13-03 (e.g., at profile locations SHM-10-23 or SHM-10-27) and sampled routinely during the long-term monitoring program.

Response: As presented in the 2013 Shepley's Hill Landfill Annual Report, m*onitoring wells SHM-13-14S/D and SHM-13-15 were installed east of SHM-13-03 beginning in January 2014. Data collected from the installation of SHM-13-14S/D and SHM-13-15 indicate that arsenic impacted groundwater is not located at a depth shallower than 50 feet below grade and that the core of arsenic impacted groundwater is located between SHM-13-07 and SHM-13-03.*

Comment 13 – Section 5.0: Should be revised to conform to the ESD and LUCIP after those documents are developed and approved.

Response: Section 5.0 of the LTMMP Update was prepared in consideration of the ESD and the LUCIP. If the final approved versions of these documents differ from what is presented in Section 5.0, then modifications to Section 5.0 will be made as appropriate. In the interim, Section 5.0 will be revised to state this contingency.

Comment 14 – Table 1: The near field monitoring program should include annual sampling of well SHM-10-06. This well is strategically located to monitor remedy performance; it can be used to monitor contaminant concentrations: (1) along the east side of the landfill (As = 1,980 ug/L), (2) downgradient of the recently installed barrier wall, which is expected to affect contaminant concentrations along the east side of the landfill, and (3) upgradient of the area where arsenic contamination by-passes the extraction system (refer to Comment 2).

Response: The nearfield monitoring program has been revised to include annual sampling of SHM-10-06.

Comment 15 –Tables 1 and 2: The NIA wells that will be sampled semi-annually should include SHM-13-04 (refer to Figure 7 and p. 25).

Response: As presented on Figure 7, Table 1, and page 25, SHM-13-04 is included as part of the semi-annual sampling program in the NIA.

Comment 16 – Tables 2 and 4: Well SHL-3 should not be abandoned; instead, it should be used for hydraulic monitoring. Measurements from this well may help demonstrate that the barrier wall has diverted landfill groundwater away from Red Cove.

Response: Well SHL-3 will be removed from the abandonment list and will be incorporated within the annual barrier wall hydraulic monitoring program. Tables 2 and 4 will be revised to reflect this change.

Comment 17 – Table 4: Monitoring well SHM-10-16 should not be abandoned; it can be used to monitor lateral shifts of the contaminant plume induced by seasonal variations and/or adjustments to the extraction system.

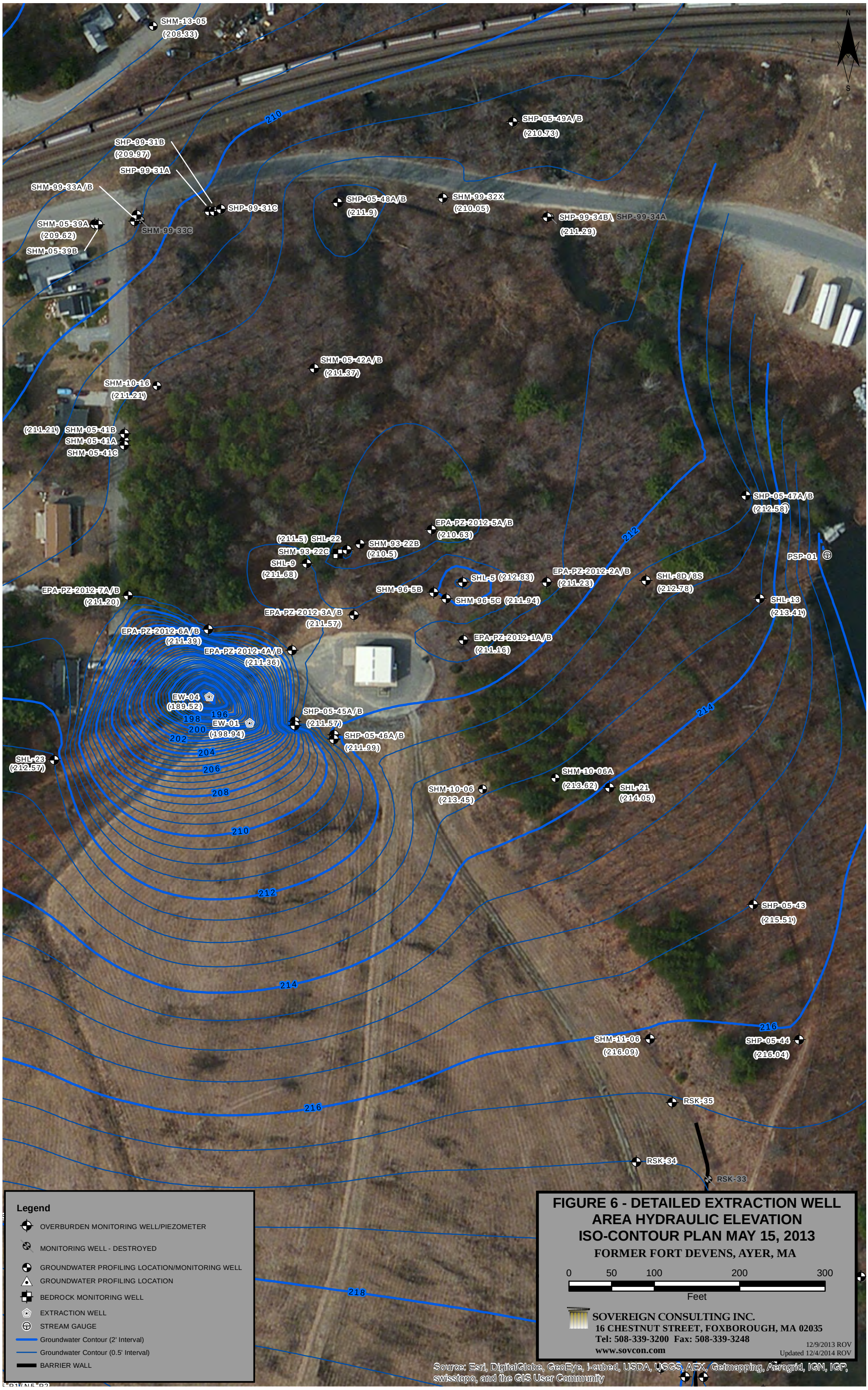
Response: Well SHM-10-16 will be removed from the abandonment list and will be incorporated into the annual nearfield groundwater hydraulic monitoring program. Tables 2 and 4 will be revised to reflect this change.

Comment 18 – Figure 7: Should indicate that groundwater samples will be collected annually from wells SHM-10-07, SHM-10-13, and SHM-10-14 (refer to Table 1 and p. 24). Also, as explained in Comment 14, Figure 7 should indicate that groundwater samples will be collected from well SHM-10-06.

Response: Figure 7 will be revised to indicate that groundwater samples will be collected annually from wells SHM-10-06, SHM-10-07, SHM-10-13, and SHM-10-14.

Comment 19 – Appendix E: The proposed landfill inspection form appears to be an abbreviated version of the inspection form currently used (e.g., refer to 2012 annual report). To ensure inspection continuity and completeness, the current form should be retained.

Response: The current landfill inspection form will be retained. The proposed landfill inspection form included within Appendix E will be replaced with the current form to ensure inspection continuity and completeness.


N
S
SHM-13-05
(208.33)
210
SHP-99-31B
(209.97)
SHP-99-31A
SHM-99-33A/B
SHP-99-31C
SHM-99-33C
SHM-05-39A
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(211.37)
SHM-10-16
(211.21)
(211.21)
SHM-05-41B
SHM-05-41A
SHM-05-41C
SHP-05-47A/B
(212.58)
EPA-PZ-2012-5A/B
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(211.5)
SHL-22
SHM-93-22B
(210.5)
SHM-93-22C
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(211.68)
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SHL-5
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SHM-96-5C
(211.94)
SHL-13
(213.41)
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(211.57)
EPA-PZ-2012-6A/B
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(189.52)
196
198
EW-01
(198.94)
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202
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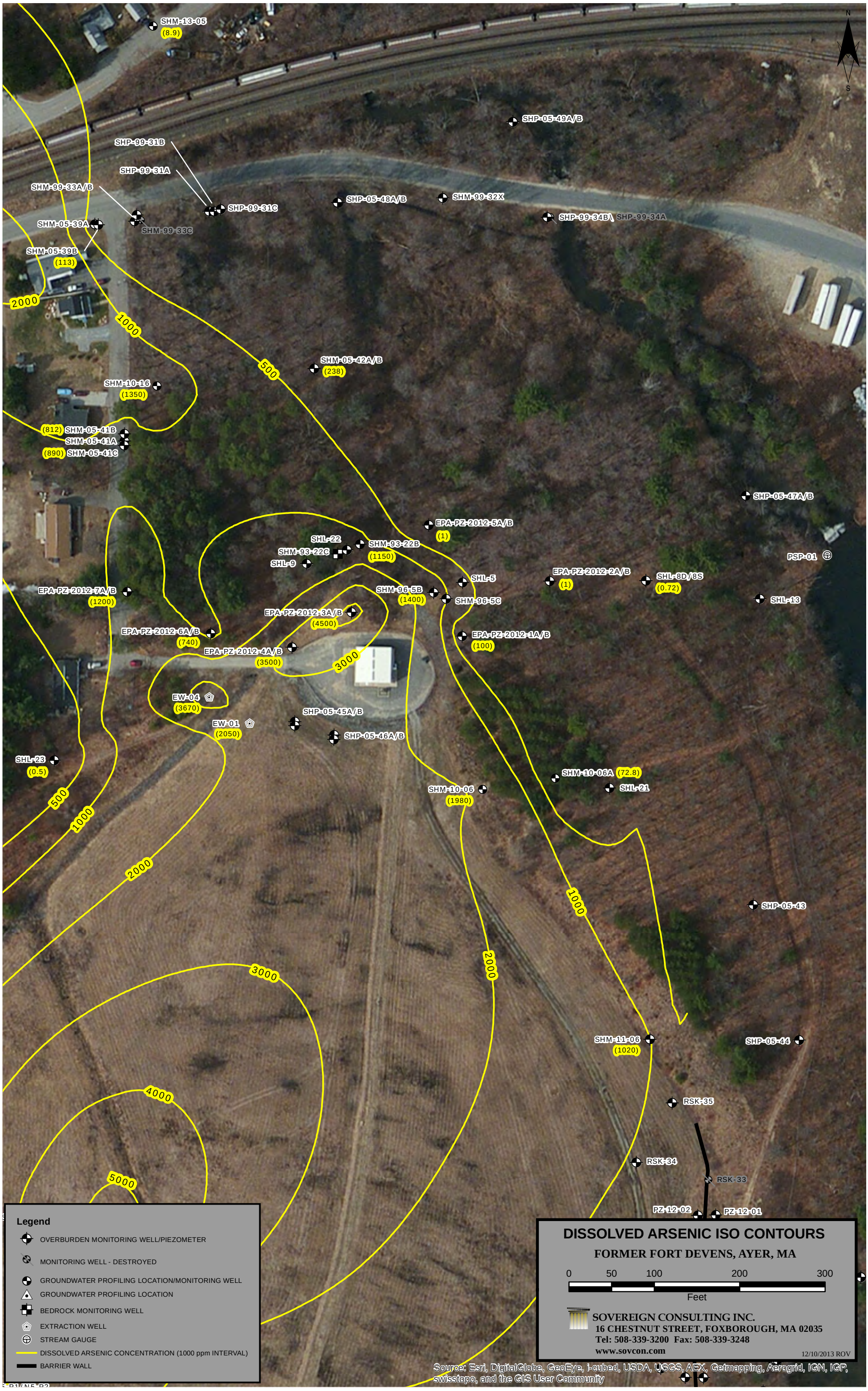
206
208
210
212
214
216
218
SHP-05-45A/B
(211.57)
SHP-05-46A/B
(211.99)
SHL-23
(212.57)
SHM-10-06A
(213.62)
SHM-10-06
(213.45)
SHL-21
(214.05)
SHP-05-43
(215.51)
SHM-11-06
(216.09)
SHP-05-44
(216.04)
RSK-35
RSK-34
RSK-33
Legend
OVERBURDEN MONITORING WELL/PIEZOMETER
MONITORING WELL - DESTROYED
GROUNDWATER PROFILING LOCATION/MONITORING WELL
GROUNDWATER PROFILING LOCATION
BEDROCK MONITORING WELL
EXTRACTION WELL
STREAM GAUGE
Groundwater Contour (2' Interval)
Groundwater Contour (0.5' Interval)
BARRIER WALL
FIGURE 6 - DETAILED EXTRACTION WELL AREA HYDRAULIC ELEVATION ISO-CONTOUR PLAN MAY 15, 2013
FORMER FORT DEVENS, AYER, MA
0 50 100 200 300
Feet
SOVEREIGN CONSULTING INC.
16 CHESTNUT STREET, FOXBOROUGH, MA 02035
Tel: 508-339-3200 Fax: 508-339-3248
www.sovcon.com
12/9/2013 ROV
Updated 12/4/2014 ROV
Source: Esri, DigitalGlobe, GeoEye, i-cubed, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community


N
S
SHM-13-05
(8.9)
SHP-05-49A/B
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SHM-99-32X
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SHP-99-34A
SHM-05-39A
SHM-99-33C
SHM-05-39B
(113)
2000
1000
500
SHM-05-42A/B
(238)
SHM-10-16
(1350)
(812) SHM-05-41B
SHM-05-41A
(890) SHM-05-41C
SHP-05-47A/B
EPA-PZ-2012-5A/B
(1)
SHL-22
SHM-93-22C
SHM-93-22B
(1150)
SHL-9
PSP-01
SHL-5
EPA-PZ-2012-2A/B
(1)
SHL-8D/8S
(0.72)
EPA-PZ-2012-7A/B
(1200)
SHM-96-5B
(1400)
SHM-96-5C
SHL-13
EPA-PZ-2012-3A/B
(4500)
EPA-PZ-2012-6A/B
(740)
EPA-PZ-2012-1A/B
(100)
EPA-PZ-2012-4A/B
(3500)
3000
EW-04
(3670)
SHP-05-45A/B
EW-01
(2050)
SHP-05-46A/B
SHL-23
(0.5)
500
1000
2000
SHM-10-06A (72.8)
SHL-21
SHM-10-06
(1980)
1000
SHP-05-43
2000
3000
SHM-11-06
(1020)
SHP-05-44
4000
RSK-35
RSK-34
RSK-33
5000
PZ-12-02
PZ-12-01
Legend
OVERBURDEN MONITORING WELL/PIEZOMETER
MONITORING WELL - DESTROYED
GROUNDWATER PROFILING LOCATION/MONITORING WELL
GROUNDWATER PROFILING LOCATION
BEDROCK MONITORING WELL
EXTRACTION WELL
STREAM GAUGE
DISSOLVED ARSENIC CONCENTRATION (1000 ppm INTERVAL)
BARRIER WALL
DISSOLVED ARSENIC ISO CONTOURS
FORMER FORT DEVENS, AYER, MA
0 50 100 200 300
Feet
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12/10/2013 ROV
Source: Esri, DigitalGlobe, GeoEye, i-cubed, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community

Response to 25 November 2013 PACE Comments on
DRAFT LTMMP UPDATE
SHEPLEY HILL LANDFILL
Former Fort Devens Army Installation
October 2013

General Response to Comments

The LTMMP Update was the Army's attempt to propose Data Quality Objectives (DQOs) for the existing remedial actions as it continues to work with the BCT to address its concerns on perceived data gaps and disagreement over the Conceptual Site Model (CSM). Discussions and agreement on the CSM and DQOs are critical to a path forward and to establishing a basis to measuring the performance on any remedial action, including, but not limited to the Arsenic Treatment Plant (ATP). Without a consensus on the CSM and the DQOs, there can be no consensus on attainable remedial outcomes and/or remedial timeframes.

With respect to the BCT's continuing concerns for the need for additional data, we reiterate that in accordance with the CERCLA guidance for RI/FS uncertainties are a part of the Superfund process and that the desire to remove all uncertainties competes with the Superfund Program's mandate to perform cleanups within designated schedules. Therefore, the objective of data collection is not to achieve the unobtainable goal of removing all uncertainty, but rather to gather information sufficient to support an informed risk management decision. To this point the Army believes that the existing data is more than sufficient to establish the CSM and determine the appropriate remedial actions.

Based on the comments below it is evident that the need for agreement and consensus on the CSM is imperative and we believe that given the available data and the length of time the groundwater pump and treat system has operated, in conjunction with investigations performed over the past decades there is more than enough data for both parties to come to an agreement on the CSM. Therefore, the Army proposes to resolve any major differences between Army and EPA interpretations of the CSM through a series of BCT technical meetings so that a focused feasibility study can be performed and an alternated remedy selected.

Response to Specific Comments

Comment 1 – Sections 2.1 and 2.2 reiterate the Army's opinions regarding the source of the arsenic at SHL and the effectiveness of groundwater extraction. For completeness, it should be noted in the text that regulators and technical reviewers have expressed fundamental disagreements with these opinions.

Response: The fundamental differences between the Army's conceptual site model (CSM) and that of regulators can be stated in their comments to the LTMMP. However, discussions and an agreement on the CSM are more critical to a path forward. Without a consensus on the CSM, there can be no consensus on attainable remedial outcomes and/or remedial timeframes. If necessary, the final LTMMP will acknowledge the disagreement; however, it is the Army's opinion that a LTMMP is a work plan and not the venue for this discussion.

Comment 2 – Section 2.2 highlights similarities between SHL and the Winthrop Landfill in Maine. Although similarities exist, the differences between these two sites are significant and need to be acknowledged in the text. Data from the 2012 five year review indicate that none of the monitored wells at the Winthrop landfill had an arsenic concentration above 1,000 parts per billion (ppb), and only one well has a concentration above 400 ppb. This contrasts markedly with SHL data where concentrations up to 6,000 ppb exist, and where several wells far downgradient of the source exhibit concentrations above 1,000 ppb. The Winthrop landfill's generally similar conditions but significantly lower arsenic concentrations support the premise that landfill waste is a significant contributor to dissolved arsenic concentrations at SHL. Section 2.2 should include a discussion of the magnitude of dissolved arsenic concentrations at SHL relative to other landfills in order to provide a more complete Conceptual Site Model.

Response: As stated within Section 2.2, the mechanisms responsible for the elevated arsenic at the SHL are the same as those at the Winthrop Landfill where arsenic contamination occurs. The difference between the concentrations of arsenic in groundwater at SHL and at the Winthrop Landfill is attributed to the difference in concentrations of naturally occurring arsenic located in the aquifer material beneath each landfill. The aquifer material at SHL contains an average of 14,000 µg/kg in the upper aquifer sands in contrast to the average of 4,900 µg/kg arsenic reported for aquifer material at Winthrop. More importantly, the bottom 10-20 feet of each boring at the SHL consisted of sand, glacial till or bedrock containing an average 38,000 µg/kg of arsenic. Thus a higher potentially soluble source of arsenic exists at SHL compared to Winthrop, and the SHL inventory of arsenic can be expected to be an order of magnitude greater than that found at the Winthrop Landfill. In addition, it is important to understand that the pump and treat system at the Winthrop Landfill was ultimately terminated, as it was determined to be not effective in remediating arsenic to achieve restoration of the aquifer, and that land use and institutional controls were sufficient to meet the RAO for receptor protection, are applicable and relevant to SHL, and therefore we believe that this has value/merit in evaluating and determining the performance and long term effectiveness of the ATP and necessary remedial action(s). The text of the LTMMP will be expanded to highlight both the differences and similarities.

Comment 3 – Section 2.4.2 states that the groundwater flow model was run using an extraction rate of 49 gallons per minute (gpm). To better evaluate the true extent of the capture zone, the model should be run using actual average flow rates which have ranged from approximately 39 to 43 gpm over the past several years. The results obtained should be compared with the 49 gpm model run, and any necessary revisions to the CSM should be made.

Response: See responses to MassDEP Comments 1 and 2 above.

Comment 4 – Section 2.5 states that data indicating elevated dissolved arsenic concentrations in new EPA piezometers "in close proximity to the downgradient limit of the ATP capture zone" support the Army's contention that natural sources of arsenic are

predominant. EPA's data could also support a contrary argument that the extent of the capture zone has been over-estimated as a result of using an extraction rate greater than the true rate. Running the model using the true extraction rate would help resolve this issue. Because the groundwater elevations at the EPA piezometers shown on Figure 6 appear to indicate minimal if any drawdown, it is unclear how the report can conclude that "significant pore volume flushing" will occur in this area. Further, because data on arsenic concentrations over time are lacking at these recently-installed EPA piezometers, it is very possible that arsenic concentrations at some or all of these locations have in fact decreased as a result of the ATP's operation.

Response: See response to MassDEP Comment No. 2 above.

Comment 5 – In Section 2.6 it is stated that a comparison of 2001 and 2013 arsenic transect data indicates "very stable" dissolved arsenic concentrations over time in downgradient areas. Discussion of results from specific sampling locations within the two transects, and references to appropriate sections of the table in Appendix C should be included to support this conclusion. Given that data from two sampling rounds spaced 12 years apart appears to be the primary basis for this conclusion, it should be considered preliminary, and the need for additional data should be acknowledged.

Response: The Army disagrees that additional data is required to conclude that arsenic concentrations are stable along the West Main Street transect. As presented in the 2013 Shepley's Hill Landfill Annual Report, *seventeen locations were profiled from 2001 to 2013, and approximately 100 groundwater samples were collected along this transect. In addition, this 12-year period, during which the ATP operated for half of that time, is a significant amount of time over which arsenic concentrations remained stable. Consequently, the Army maintains that it is appropriate to conclude based on the data that arsenic concentrations have remained stable over time in downgradient areas. In addition, it is further noted that the proposed LTMMP will continue to evaluate the effect of the arsenic-impacted groundwater over the next 5 years and beyond as part of the monitoring program until the RAOs are achieved.*

Comment 6 – Section 2.6 proposes revisions to the Remedial Action Objectives (RAOs) for SHL. While expansion of the RAOs beyond those specified in the Record of Decision may be appropriate at this time, the proposed RAOs should include a provision to address potential future expansion of the arsenic plume. Prevention of groundwater migration is one of the five key principles expressed in the National Contingency Plan (Summary of Key Existing EPA CERCLA Policies for Groundwater Restoration, OSWER Directive 9283.1-33, June 26, 2009). To address this key principle, the following additional RAO should be added:

Prevent further migration of the arsenic plume to areas including but not limited to areas north of the Nonacoicus Brook.

If, as the Army believes, the plume is not expanding, then this additional RAO would impose no burden on the Army

Response: As stated in Section 2.6, the RAOs that are formulated in the LTMMP include:

- *Control or minimize the migration of arsenic-impacted groundwater both north and east of the landfill to the extent necessary to:*
    - *Restore groundwater where practicable within a timeframe that is reasonable given the particular circumstances of the site; and*
    - *Prevent potential impact in excess of human health and ecological risk-based concentrations to the surface water and sediments of Plow Shop Pond and the Nonacoicus Brook/wetlands.*

It is the Army's opinion that these RAOs as written covers PACE's request and more.

Comment 7 – The Data Quality Objectives (DQOs) for the landfill cap in Section 3.1.1 contain several references to minimizing maintenance and repair of the cap. Because any necessary maintenance and repairs should be performed expeditiously in order to maintain cap integrity, making minimization of these activities a DQO is counter-productive to the primary purpose of the cap. Therefore, references to minimization of repair and maintenance should be removed from Section 3.1.1.

Response: The Army in no way meant to imply or suggest that these maintenance and repair items are of minimal importance. The Army and their contractors shall routinely inspect and repair the landfill cap as part of the annual inspection process, and those repairs and maintenance are detailed in the Annual Reports. Please note that the frequency of inspections and repairs has not been changed or modified in this LTMMP.

Comment 8 - The measures proposed in the LTMMP Update for evaluation of the ATP fail to consider or include management of migration as a remedial objective. If the ATP is shut down, large quantities of dissolved arsenic (roughly 500-600 pounds per year) will again be allowed to migrate from the landfill to the North Impact Area (NIA). DQO Step 1 in Section 3.1.2, and all of Section 3.4.3 need to be re-written to reflect the role of the ATP in preventing groundwater containing significantly elevated concentrations of dissolved arsenic from migrating from the landfill to the downgradient areas. Therefore, DQO Step 1 should read as follows:

Will the ATP remedy component help meet the overall SHL remedy objectives through the prevention of migration of arsenic-impacted groundwater from beneath the landfill to the downgradient areas?

If this "management of migration" goal is found to be met at each five-year review, then the ATP should continue operation.

Response: The RAOs applicable to the ATP and the NIA as stipulated in the ROD and further expanded as part of the update to the LTMMP include the protection of potential residential receptors from exposure to contaminated groundwater and the control or minimization of the migration of arsenic-impacted groundwater from the landfill. Consequently, the "management of migration" goal has been considered as one of the performance criteria for the ATP. Sections 3.1.2 and 3.4.3 will be revised for clarity. However, the Army notes that the As concentrations measured in 2001 in the NIA are effectively identical to the As concentrations measured in 2013 in the NIA along the West Main Street transect. These data challenge the comment above that "500-600 pounds per year…(of arsenic)…will again be allowed to migrate from the landfill to the NIA." If the As is sourced from reducing waters passing through As-enriched naturally occurring aquifer sands, as much of the data collected in the SHL study area suggests, the operation or non-operation of the ATP would have little effect on the concentrations of As in the NIA in the long term.

Comment 9 - All of Sections 3.1.2 and 3.4.3 need to be modified to include calculation and consideration of the total mass of arsenic removed by the ATP as an essential measure of system effectiveness. The fact that the ATP has prevented the migration of roughly 4,000 pounds of arsenic from the landfill to the NIA (the exact number is no longer being disclosed by the Army in their annual reports) is convincing evidence that the ATP is effective.

Response: As stated in its response to similar comments in the 2012 Annual Report, the Army is of the opinion that the requested calculation is not relevant to the remedy considering that the annual mass removal rate of the ATP is a small fraction of the overall mass available in the aquifer sands beneath the landfill. In addition and as stated within the updated LTMMP, the applicable performance metric for the ATP based on the stipulated RAOs is the statistically significant reduction in arsenic concentration in groundwater and improvement in geochemical parameters as determined by sampling data. The Army maintains that the calculation of total mass of arsenic is not a critical measure of the effectiveness of the extraction system.

Comment 10 - The first bulleted item under DQO Step 2 in Section 3.1.2 sets unrealistically high thresholds for evaluating the performance of the ATP. For example, it is clearly unrealistic to expect that groundwater extraction from one area near the toe of the landfill to significantly change redox chemistry throughout the entire NIA over the next five years. While none of the other project DQOs (except those for NIA data, discussed later in this letter) contains any requirement for proving statistical significance at the time of the first 5-year review, the proposed approach for the ATP requires five separate findings of statistical significance, all of which must be met to justify continued operation of the ATP. (Although the barrier wall DQO references a requirement for a statistically significant decrease in arsenic across the wall, the text states that such a decrease is not expected to occur in the next five years, effectively eliminating the requirement in the next five-year review.) Proving that a statistically significant trend exists can be difficult, but is especially so where the number of data points is small, as will be the case for arsenic data collected primarily on an annual basis over a period of five years. Under the proposed approach, future arsenic

concentrations could show substantial decreases over time, but, due to the statistical test's built-in bias toward concluding that a trend does not exist (the "null hypothesis"), the downward trend may not be identified as such by the method. Therefore, the DQO for Step 2 in Section 3.1.2 should be revised to be consistent with the burden of proof required for other components of the remedy, and the revised wording of DQO Step 1 proposed above. The revision should either (1) entirely remove the requirements for statistical significance, or (2) require the collection of data on a bi-monthly basis (6 times per year) so that sufficient data will be available to identify actual trends at the conclusion of the 5-year evaluation period, or (3) similar to the barrier wall DQO, acknowledge that the statistical significance test is unlikely to be met in the first five years, and extend the evaluation period to 10 years.

Response: Based on the ATP being operational since 2006 and accounting for an additional five year period of operation under this LTMMP Update (i.e., ATP operation through 2018), the time period associated with this DQO is 12 years. It is important to note that the Army is not stating that the ATP will be shutdown after this 12-year period only that there will be a representative amount of data available at the end of that period to conduct a statistical evaluation of the data. This is not without precedence as the groundwater extraction system at the Winthrop Landfill operated from 1995 to 2002, a 7-year period, at which time an evaluation of site data was conducted for that system.

The barrier wall was installed in 2012, and in 2018 half of the amount of available data for the ATP will be available for the barrier wall. Consequently, a statistical evaluation of the barrier wall data will not be appropriate at that time. With any active treatment system, it is important to have clear and definable operational parameters and clear and definable shutdown triggers.

Comment 11 - The proposed requirement under DQO Step 2 in Section 3.1.2 for statistically significant reduction in influent arsenic concentrations to the ATP is inappropriate and should be deleted because (1) the ATP influent is drawn largely from the landfill itself, which is not an attainment area, and (2) the requirement would allow shutdown of the ATP even if it is shown to be having a beneficial effect on the down-gradient areas.

Response: By 2018, the ATP will have operated for 12 years. If the primary source of the arsenic is the landfill itself as maintained by others and not the aquifer materials as maintained by the Army, then a statistically significant reduction in the influent of the ATP should be observed due to source removal over that period. Consequently, the Army maintains that this performance metric is appropriate and applicable. Please note that the influent As concentrations measured at the ATP are one consideration in the evaluation of the effectiveness, and it will not be the only determining criteria for the performance of the ATP. Therefore if there is a statistically significant new positive influence measured in the NIA, it shall be heavily considered in the performance evaluation.

Comment 12 - DQO Step 5 in Section 3.1.2 should be re-worded so that operation of the ATP will not cease until an alternative remedy component has been selected, approved, and fully implemented.

Response: If it is determined that the ATP is not having a beneficial impact, then an alternative remedial strategy will be evaluated.

Comment 13 - The text of DQO Step 5 in Section 3.1.2 states that "the performance metric for the landfill area is determined to be a minimum 30% reduction and/or a definitive downward trend in arsenic concentrations over this time period (12 years) ... " Because the landfill itself is not an attainment area where cleanup goals apply, this performance metric should be deleted both here and in Step 2, and the Study Boundaries in DQO Step 4 should be revised to delete the landfill area.

Response: The Army agrees that the landfill itself is not an attainment area. However, the ATP should have a demonstrable influence on arsenic concentrations within the landfill due to source removal over its period of operation as stated in response to Comment 11, and minimal reduction in arsenic concentrations from below the landfill would be consistent with the CSM and the Army's contention that the ATP will need to operate in perpetuity in order to maintain any perceived down-gradient improvements. Consequently, the Army maintains that the reduction or lack thereof of arsenic from the landfill area is an important consideration for remedy performance.

Comment 14 - The text of DQO Step 5 in Section 3.1.2 states that a 30-50% arsenic reduction in near-field wells and NIA is expected over the 12-year operating period ending in 2018. This expectation is based only on an arbitrary adjustment of a result from a bench scale test, and is therefore inappropriate for use in evaluating the effectiveness of the ATP. Given that arsenic data from 2001 and 2013 transects along West Main Street reportedly indicated stable concentrations, and given that the 2001-2013 time period included seven years of ATP operation, the expectation of a 30-50% reduction throughout the NIA over the next five years is clearly unrealistic. All references to this expected reduction should therefore be deleted from the LTMMP Update.

Response: To measure and gauge the effectiveness of the extraction system, it will be necessary to establish a benchmark for estimating the amount of arsenic reduction. As stated in the LTMMP Update, the bench column studies suggest that as much as a 10-fold (or 90%) decrease in arsenic can occur in groundwater after 5 pore volumes of groundwater has been replaced if adsorbed arsenic does not leach back into the groundwater. Due to the difficulties extrapolating bench scale conditions to the field, a different, more conservative, approach for estimating arsenic reduction groundwater was evaluated. Using the nearfield (closest to extraction system) wells in a time series analysis detail that natural fluctuation in well chemistry can range from 10% to 20% in any given season or sampling event. Based on the observed well chemistry and the raw interpretation of the column work, a more realistic reduction in contaminant concentration of 30% or more can be used for benchmarking reduction due to pumping. By using this approach, arsenic decreases of 30% or greater (above the 20% due to natural variability) should represent reductions due to pumping alone. As such, the Army maintains that the expectation of a 30% reduction throughout the NIA over the next five years or a definitive long-term downward trend

in arsenic concentrations should be a target for considering the effectiveness of the ATP. The Army notes that the operation of the ATP is designed to reduce the concentrations of As in groundwater and therefore it should be reasonable to expect to see reductions in As concentration in groundwater directly affected by the ATP. If the ATP has no effect on groundwater, then the ATP, as a remedy, is ineffectual in meeting the RAOs stipulated in the ROD and should be evaluated for either upgrade, replacement, or decommissioning.

Comment 15 - DQO Step 5 in Section 3.1.2 includes the evaluation of near-field decreases in dissolved arsenic concentrations. A complicating factor in evaluating such decreases is the lack of near-field monitoring wells between 2006 and 2013, before EPA installed piezometers in this area. This data gap needs to be taken into account when near-field data are evaluated. It is likely that additional time beyond five years will be needed to evaluate near-field effects of the ATP.

Response: The nearfield monitoring network includes those wells which are located in the vicinity of the ATP off the northern toe of the landfill and are more than just the EPA piezometers. See Table 1 for a complete list of nearfield monitoring wells. In some cases, data from these wells have been collected since 1993 (SHM-93-22C). However, the EPA-installed piezometers are slated for regular sampling as part of this LTMMP, and these data will be used to supplement near-field decrease conclusions. Consequently, it is the Army's opinion that a data gap does not exist and there are sufficient wells in the nearfield to conduct an evaluation of the data.

Comment 16 - The DQO in Section 3.1.4 for NIA monitoring requires that no new areas of the aquifer be impacted by dissolved arsenic. To avoid potential future confusion, this section should clarify how attainment of this DQO this will be evaluated. It is proposed that the MCL (or an appropriate background concentration greater than the MCL, if adopted) be used to evaluate whether or not a well is impacted. For wells where historic arsenic concentrations have been below the MCL or background, any future detection of arsenic above the MCL or background would result in a finding that a new area has been impacted.

Response: As stated in Section 3.1.4, the stability of the areas of arsenic-impacted groundwater in the NIA will be determined through statistically significant changes in dissolved arsenic concentrations and in geochemical parameters that indicate a shift in overall redox conditions necessary to change arsenic-impacted groundwater concentrations. If groundwater quality data indicate that the NIA arsenic-impacted groundwater concentrations are laterally stable and not appearing in other areas of the NIA which have not been impacted to date then the long-term monitoring of the NIA will be determined to be adequate. Section 3.1.4 of the LTMMP will be revised for clarity.

Comment 17 - Statistical significance is required in Section 3.1.4 for evaluation of upward trends in dissolved arsenic data from the North Impact Area. Please see the previous comments regarding the difficulty in identifying trends at SHL, given the built-in bias of the methods used and the lack of sufficient data points. The text should be revised to either

remove the requirement for statistical significance, or require the collection of data on a bi-monthly basis (6 times per year) so that actual trends, if any, are more likely to be identified at the conclusion of the 5-year evaluation period.

Response: Data collected over the next 5 years will expand the data set and is expected to be a representative amount of data sufficient to conduct a statistical evaluation of the data from the NIA. In 2018, approximately 20 years of data will be available for several wells located along Sculley and Mulomco Roads in the southern portion of the NIA. In addition, approximately 10 years of data will be available for several wells located throughout the northern portion of the NIA. Therefore, a sufficient data set for statistical analysis should be available within the next 5 years. Increasing the frequency of the sampling to 6 times per year is not expected to provide any new insight into the already significant 20 year dataset which will be available in 2018.

Comment 18 - DQO Step 2 in Section 3.1.4 should be modified to remove the requirement for evaluation of geochemical parameters. This requirement does not address any of the questions posed in DQO Step 1, and it is duplicative of requirements proposed in Section 3.1.2. Note that the questions in DQO Step 1 are focused on documenting stability of arsenic concentrations and assuring that new areas are not impacted. A requirement to show that geochemical parameters are changing is not germane to these objectives.

Response: Because arsenic is mobilized in reductive environments, evaluating geochemical parameters over time in the NIA is necessary to monitoring the stability of arsenic-impacted groundwater which is the subject of the first question presented in DQO Step 1 in Section 3.1.4. If geochemical parameters are found to be changing, then the behavior of arsenic and the stability of the arsenic-impacted groundwater can be expected to change in response, and therefore are deemed appropriate.

Comment 19 - The second bullet point under DQO Step 3 in Section 3.1.4 should be re-worded for clarity.

Response: The second bullet point under DQO Step 3 in Section 3.1.4 will be revised for clarity to state that arsenic-impacted groundwater will be collected from monitoring wells screened near the surface water/groundwater interface of Nonacoicus Brook.

Comment 20 - The text under DQO Step 4 of Section 3.1.4 envisions five additional years of monitoring of NIA wells. References to limitation of the NIA monitoring period should be deleted from the LTMMP Update, and decisions as to whether or not monitoring continues should be made based on data available at each future five-year review.

Response: As stated in Section 3.1.4, a sufficient data set for statistical analysis should be available within the next 5 years. This does not imply that monitoring will be discontinued after the next 5-year period in 2018. Section 3.1.4 will be revised for clarity.

Comment 21 - The list of wells to be monitored in Section 3.1.4 should require annual rather than 5-year monitoring of wells SHM-10-03 and SHM-10-04. The existing program does not include sufficient annual monitoring directly downgradient of the main body of the arsenic plume to meet the DQO of evaluating of whether or not the arsenic plume is stable.

Response: Wells SHM-10-03 and SHM-10-04 are located north of Nonacoicus Brook, and dissolved arsenic has not been detected in groundwater samples collected from these wells at a concentration above 1 parts per billion (ppb) in four sampling rounds conducted between 2010 and 2013. Consequently, it is the Army's opinion that the collection of groundwater samples from these wells every 5 years is appropriate to monitor the stability of arsenic-impacted groundwater in the NIA. An increase sampling frequency is not warranted for these wells at this time. As presented on Table 1, monitoring well SHM-13-03 will be sufficient to monitor the downgradient extent of the arsenic-impacted groundwater.

Comment 22 - Section 3.2.2 proposes elimination of semi-annual sampling after 2016. Semi-annual sampling should be continued until the next five-year review, and decisions on continued monitoring should be made based on the data available at that time.

Response: Semi-annual sampling has been conducted at monitoring wells located at SHL since 1996 and in the NIA since 1999. By 2016, approximately 20 years of data will be available to evaluate trends sufficiently. Therefore, the former semiannual wells will be sampled annually with alternating Spring and Fall sampling events to monitor seasonal variations.

Comment 23 - Section 3.4.3 contains detailed information on the procedures that will be used to evaluate the effectiveness of the ATP. Some of this information duplicates that found in Section 3.1.2, while other information is inconsistent with that found in 3.1.2. To simplify the document and help prevent ambiguity in future evaluations of the ATP, the procedure for ATP evaluation should be detailed in one and only one section, preferably Section 3.1.2. Similarly, Sections 3.3, 3.5. and 3.6 should be modified as needed to delete text referring to the procedures to evaluate monitoring data from the landfill, barrier wall, and NIA, respectively. Text deleted from these sections should be consolidated into the appropriate sub-sections of Section 3.1. Consistent with the titles of Sections 3.3 through 3.6, the text in these sections should be confined to discussion of what monitoring will be conducted rather than presenting additional text on how the data will be evaluated.

Response: Section 3.1 as a whole and specifically Section 3.1.2 outline the seven-step process used to specify DQOs for the collection of data for each remedy to ensure that the data collected for each remedy is of sufficient quality and quantity to evaluate the performance and/or protectiveness of the selected remedies and the ability for those remedies to meet the RAOs outlined in the ROD. This section was drafted in accordance with the Data Quality Objective Process for Hazardous Waste Site Investigations *(EPA QA/G-4HW)(USEPA, 2000). Section 3.4.3 details how the data gathered in accordance with Section 3.1.2 will be used to evaluate the effectiveness of the ATP and the decision parameters that will be employed based on the data. It is the Army's opinion that both sections are necessary to the LTMMP Update. Although the Army*

disagrees that the information presented therein is inconsistent, these sections will be streamlined for clarity. It is important to note that information from all data collected under each section/DQO is necessary to perform a thorough and complete evaluation for the performance of the ATP and consensus on those DQOs are critical to establishing a basis to measuring the performance on any remedial action, including, but not limited to the ATP.

Comment 24 - Section 3.5.2 states that calculation of arsenic flux around and across the barrier wall will be conducted at the end of the next 5-year review period. The text should specify that the flux will be separately calculated and documented for each annual monitoring event so that trends in flux can be evaluated.

Response: For the first evaluation of flux, it is necessary to wait 5 years since previous modeling suggests that existing arsenic-impacted groundwater on the eastern side of the wall may require several years to flush from the aquifer; therefore, the statistically significant decrease in arsenic concentration on the eastern side of the wall is not expected to occur in the next 5 years. At that time, the frequency of flux calculations will be evaluated and modified as necessary.

Comment 25 - Section 4.0 should include requirements and procedures for prompt re-collection of samples when results fail the data validation process due to exceedance of holding times, QC criteria, cross-contamination, or other data quality issues.

Response: Data that does not adhere to acceptable laboratory practices and data validation requirements will be flagged and/or rejected as appropriate. However, recollection of samples will not be conducted from these monitoring locations until the next scheduled monitoring event unless it was agreed by the BCT that the rejected data was critical and needs to be re-collected. Consequently, Section 4.0 will remain as presented.

Comment 26 - The LTMMP Update should include a requirement to determine a background value for dissolved arsenic that can potentially be used in place of the 10 parts per million Maximum Contaminant Level (MCL). If the background value is greater than the current cleanup goal, the LTMMP Update should use the background value to develop new estimates of cleanup time based on the achievement of background conditions in the areas of attainment. These estimates should be incorporated into the evaluation of the feasibility of achieving the goal of groundwater restoration.

Response: The Army believes that the establishment of a local background arsenic concentration for the site is appropriate, however, will be of limited value since existing data indicates that such a background arsenic concentration is still likely unattainable. Therefore, unless background values are set in the range found currently in the NIA, such an exercise will not change remedy performance or duration, as attainment throughout the NIA does not appear possible under the conditions with which the ATP operates (note the As concentration consistency measured between 2001 and 2013, a duration of 12 years which includes both several years prior and following ATP construction and operation).