

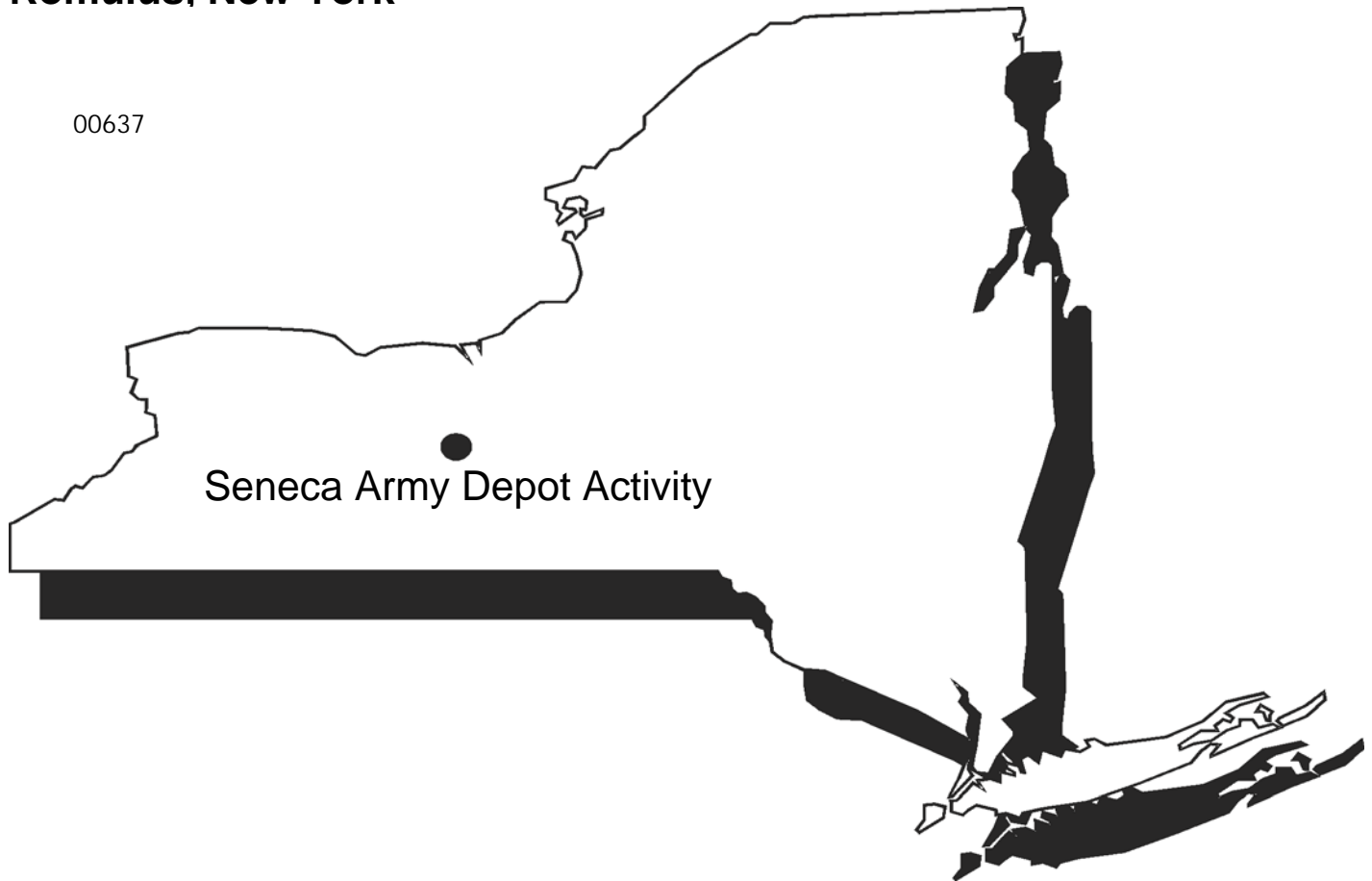
**US Army Corps of Engineers**

**Air Force Center for  
Environmental Excellence**



**Seneca Army Depot Activity  
Romulus, New York**

00637



**ASH LANDFILL BIOWALL  
PILOT STUDY WORK PLAN  
SENECA ARMY DEPOT ACTIVITY**

AFCEE CONTRACT NO. FA8903-04-D-8675

TASK ORDER NO. 0012

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EPA SITE ID# NY0213820830

NY SITE ID# 8-50-006

**PARSONS**

MAY 2005

**ASH LANDFILL BIOWALL PILOT STUDY WORK PLAN  
SENECA ARMY DEPOT ACTIVITY, ROMULUS, NY**

**May 2005**

**Prepared for:**

**AIR FORCE CENTER FOR ENVIRONMENTAL EXCELLENCE,  
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**SENECA ARMY DEPOT ACTIVITY  
ROMULUS, NY**

**Contract Number FA8903-04-D-8675 DO0012**

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## ACRONYMS AND ABBREVIATIONS

µg/L	micrograms per liter
AFB	Air Force Base
AFCEE	Air Force Center for Environmental Excellence
ARAR	Applicable or Relevant and Appropriate Requirement
ADQO	Analytical Data Quality Objectives
AWQS	Ambient Water Quality Criteria
bgs	below ground surface
bp	before present
BRAC	Base Realignment and Closure
CAHs	chlorinated aliphatic hydrocarbons
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
<i>cis</i> -DCE	<i>cis</i> -1,2-dichloroethene
cm/sec	centimeters per second
CME	Central Mining Equipment
DCE	Dichloroethene
°C	degrees Celsius
DO	dissolved oxygen
DQI	data quality indicator
DQAO	Data quality analytical objective
DQO	data quality objective
EPA	U.S. Environmental Protection Agency
ES	Engineering Science, Inc.
FFA	Federal Facilities Agreement
FSP	Field Sampling Plan
ft/day	feet per day
ft/yr	feet per year
H <sub>2</sub>	molecular hydrogen
HDPE	high density polyethylene
HSA	hollow stem auger
IDW	investigation-derived waste
IRM	Interim Remedial Measure
K	conductivity
LCS	laboratory control sample
LMB	laboratory method blank
MCLs	Maximum Contaminant Levels
mg/L	milligrams per liter
MNA	monitored natural attenuation
MS/MSD	matrix spike/matrix spike duplicate
N	nitrogen
NAD	North American Datum
NAVD	North American Vertical Datum
NGVD	National Geodetic Vertical Datum
NTCRA	Non Time Critical Removal Action
NTU	Nephelometric Turbidity Units

NYSDEC	New York State Department of Environmental Conservation
ORP	oxidation reduction potential
PARCC	Precision, accuracy, representativeness, completeness, comparability
PCE	Tetrachloroethene
PID	Photoionization Detector
POC	Point of Contact
PQL	Practicable Quantitation Limits
PVC	Polyvinyl Chloride
QA/QC	Quality Assurance/Quality Control
QAPP	Quality Assurance Project Plan
QC	Quality Control
RCRA	Resource Conservation and Recovery Act
Redox	Reduction Oxidation
RI	Remedial Investigation
RL	Reporting Limit
ROD	Record of Decision
SAP	Sampling and Analysis Plan
SEDA	Seneca Army Depot Activity
SOW	Statement of Work
SWMU	Solid Waste Management Unit
T	Transmissivity
TCE	Trichloroethene
TOC	Table of Contents
TOGS	Technical and Operational Guidance Series
USAEHA	U.S. Army Environmental Hygiene Agency
USCS	Unified Soil Classification System
VC	Vinyl Chloride
VOC	Volatile Organic Carbon
ZVI	Zero Valent Iron

## SECTION 1

### PROJECT DESCRIPTION

This pilot study work plan describes the methods that will be employed to assess the feasibility of promoting the *in-situ* bioremediation of chlorinated aliphatic hydrocarbons (CAHs, commonly referred to as chlorinated solvents) in groundwater using permeable biowalls at the Ash Landfill, Seneca Army Depot Activity (SEDA), Romulus, NY (**Figures 1-1 and 1-2**).

According to the Record of Decision (ROD) for this site, groundwater plume migration will be controlled by installing three *in situ* permeable barrier walls (Parsons, 2005). This pilot study is being performed to support the use of mulch within these walls to effectively control migration of groundwater contaminants at the site. Previous treatability testing supported the use of permeable barrier walls using iron filings, and a zero valent iron (ZVI) wall is currently providing some migration control at the site. In the interest of identifying a medium that will optimize cost effectiveness, a different treatment medium is being pursued for the full scale implementation of migration control. Permeable biowalls using mulch and sand are being developed as cost effective alternatives to other remedial technologies such as ZVI walls. To date, permeable biowalls have been installed by the Air Force at Offutt Air Force Base (AFB), Nebraska; Altus AFB, Oklahoma; Dover AFB, Delaware; and F.E. Warren AFB, Wyoming. Because this technology has been tested at other sites, a pilot study, rather than a bench scale study is deemed appropriate. Execution of a pilot-scale study will allow for more rapid design and implementation of a full-scale system at the site. As it is in the Army's interest to transfer this property within the next 18 months, the schedule of this study and full-scale implementation is critical.

#### 1.1 SCOPE OF WORK

The objective of this pilot study is to demonstrate whether mulch is essentially as effective as iron as a medium within a passive permeable wall in treating CAHs in shallow groundwater at the Ash Landfill. In addition, the pilot study will evaluate the constructability of a full-scale system. During this pilot study, two biowalls will be installed in series within close proximity to assess the effectiveness of a single wall and two walls in series. In addition, vegetable oil will be applied to the mulch in the upgradient wall to assess the ability of this amendment to degrade CAHs. Additional discussion of the biowall configuration and installation is provided in Section 4.3. Activities associated with this project include the following:

- Installation of two 150-foot long, 3.0-foot wide, and approximately 15-foot deep (to competent bedrock) permeable biowalls using conventional excavation methods;

- Installation and monitoring of up to 12 groundwater monitoring wells using hollow-stem augur (HSA) drilling technology;
- Baseline sampling of the biowall groundwater sampling network immediately following installation of the biowall;
- Performance monitoring of the biowall monthly for five months after installation; and
- Preparation of a report describing the biowall system construction and results of performance monitoring and providing recommendations regarding use of this remedial approach in a full-scale system.

The materials and methodologies that will be employed to accomplish these activities are described in subsequent sections of this work plan.

The work performed under this pilot study will conform to guidance provided in the following documents:

- *Air Force Center for Environmental Excellence (AFCEE) Model Field Sampling Plan, Version 1.2* (AFCEE, 2002).
- *AFCEE Quality Assurance Project Plan, Version 3.1* (AFCEE, 2001).
- *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater* (USEPA, 1998).
- *Draft SEDA Sampling and Analysis Plan* (Parsons, 2005)

These guidance documents are incorporated herein by reference. Any exceptions to these guidance documents are detailed in this pilot study work plan.

## **1.2 WORK PLAN ORGANIZATION**

This work plan consists of nine sections, including this project description, and an appendix. Section 2 provides an overview of the treatment technology for enhanced bioremediation of CAHs using permeable mulch biowalls. Section 3 defines the test objectives of this pilot study. Section 4 describes system design and installation. Section 5 provides a sampling and analysis plan (SAP) describing the procedures and protocols to be followed for data collection, and the data management and quality assurance/quality control (QA/QC) measures to be used during this project. Section 6 describes data analysis and interpretation, and reporting deliverables. Section 7 provides a list of AFCEE, SEDA, and Parsons project team members. Section 8 outlines the project schedule, and Section 9 contains reference citations used in preparing this document. The appendix contains copies of field forms and methods.

## **1.3 SITE BACKGROUND**

### **1.3.1 Site Location**

The SEDA is a former military facility, constructed in 1941, that has been undergoing Base Realignment and Closure (BRAC) since 1995. The depot is located approximately 40 miles south of Lake Ontario, near Romulus, New York as shown on **Figures 1-1** and **1-2**.

The Ash Landfill Operable Unit is situated on an upland area along the western border of the SEDA. Beyond the depot's western boundary, on Smith Farm Road and along Route 96A, are farmland and residences. A map identifying the location of the site on the depot is included as **Figure 1-2**. The Ash Landfill Operable Unit is located within the area that has been designated for use as a conservation/recreational area.

A site map of the Ash Landfill Operable Unit, identifying the locations of the Solid Waste Management Units (SWMUs), is provided as **Figure 1-3**. The Ash Landfill Operable Unit is comprised of five SWMUs including: the Incinerator Cooling Water Pond (SEAD-3), the Ash Landfill (SEAD-6), the Non-Combustible Fill Landfill (NCFL) (SEAD-8), the Refuse Burning Pits (SEAD-14), and the Abandoned Solid Waste Incinerator Building (SEAD-15). SEAD-14 is also known as the Debris Piles. A groundwater plume that emanated from the northern corner of the Ash Landfill area is depicted on **Figure 1-4**. The groundwater plume is shown following completion of a Non-Time Critical Removal Action (NTCRA) that was conducted by the Army in 1994-1995. Remediation of this groundwater plume is the focus of this pilot study.

### **1.3.2 Site Geology/Hydrogeology**

The site is underlain by a broad north-to-south trending series of rock terraces covered by a mantle of glacial till. As part of the Appalachian Plateau, the region is underlain by a tectonically undisturbed sequence of Paleozoic rocks consisting of shales, sandstones, conglomerates, limestones and dolostones. At the Ash Landfill site, these rocks (the Ludlowville Formation) are characterized by gray, calcareous shales and mudstones and thin limestones with numerous zones of abundant invertebrate fossils. Locally, the shale is soft, gray, and fissile. Pleistocene age (Late Wisconsin age, 20,000 years before present [bp]) till deposits overlie the shales, which have a thin (2 to 3 feet) weathered zone at the top. The till matrix varies locally but generally consists of of unsorted silt, clay, sand, and gravel. At the Ash Landfill Operable Unit, the thickness of the till generally ranges from 4 to 15 feet. At the location of the biowalls, the thickness of the till and weathered shale is approximately 10 to 15 feet.

Groundwater is present in both the shallow till/weathered shale and in the deeper competent shale. In both water-bearing units, the predominant direction of groundwater flow is to the west, toward Seneca Lake. Based on the historical data, the wells at the Ash Landfill site exhibit rhythmic, seasonal water table and saturated thickness fluctuations. The saturated interval is at its thinnest (generally between 1 and 3 feet thick) in the month of September and is the thickest (generally between 6 and 8.5 feet thick) between the months of December and March (Parsons ES, 1996).

The average linear velocity of the groundwater in the till/weathered shale was calculated using the following parameters: 1) an average hydraulic conductivity of  $4.5 \times 10^{-4}$  centimeters per second (cm/sec) (1.28 feet per day [ft/day]), 2) an estimated effective porosity of 15% (0.15) to 20% (0.20), and 3) a groundwater gradient of  $1.95 \times 10^{-2}$  foot per foot (ft/ft) (Parsons Engineering Science, Inc. [ES], 1994a). The average linear velocity was calculated to 0.166 ft/day or 60.7 feet per year (ft/yr) at 15% effective porosity and 0.125 ft/day or 45.5 ft/yr at 20% effective porosity. The actual velocity on-site may be locally influenced by more permeable zones possibly associated with differences in the actual porosity of the till/weathered shale.

The average linear velocity of the groundwater in the competent shale was calculated using the following parameters: 1) an average hydraulic conductivity of  $3.73 \times 10^{-5}$  cm/sec (0.106 ft/day), 2) an estimated effective porosity of 6.75% (0.0675), and 3) a groundwater gradient of  $2.5 \times 10^{-2}$  ft/ft. An average linear velocity of  $3.9 \times 10^{-2}$  ft/day or 14.3 ft/yr was calculated for the competent shale.

### **1.3.3. Site History**

Since its inception in 1941, SEDA's primary mission had been the receipt, storage, maintenance, and supply of military items. The SEDA was proposed for the National Priority List (NPL) in July 1989. In August 1990, SEDA was finalized and listed in Group 14 on the Federal Section of the NPL. The Environmental Protection Agency (EPA), New York State Department of Conservation (NYSDEC), and the Army entered into an agreement, called the Federal Facility Agreement (FFA), also known as the Interagency Agreement (IAG). This agreement determined that future investigations were to be based on Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) guidelines. The Resource Conservation and Recovery Act (RCRA) was considered to be an Applicable or Relevant and Appropriate Requirement (ARAR) pursuant to Section 121 of CERCLA. In October 1995, SEDA was designated as a facility to be closed under the provisions of the BRAC process.

Prior to the development of the Ash Landfill site, the land in this area was used for farming. From 1941 (the date SEDA was constructed) to 1974, uncontaminated trash was burned in a series of burn

pits near the abandoned incinerator building (Building 2207). According to a U.S. Army Environmental Hygiene Agency (USAEHA) Interim Final Report, Groundwater Contamination Survey No. 38-26-0868-88 (July 1987), the ash from the refuse burning pits was buried in the Ash Landfill (SEAD-6) from 1941 until the late 1950's or early 1960's.

The incinerator was built in 1974. Between 1974 and 1979, materials intended for disposal were transported to the incinerator. Nearly all of the approximately 18 tons of refuse generated per week on the depot were incinerated. The source for the refuse was domestic waste from depot activities and family housing. Large items that could not be burned were disposed of at the NCFL (SEAD-8). The NCFL has an area of approximately two acres and is located southeast of the incinerator building (immediately south of the SEDA railroad line). The NCFL was used as a disposal site for non-combustible materials, including construction debris, from 1969 until 1977.

Ash and other residue from the incinerator were temporarily disposed in an unlined cooling pond immediately north of the incinerator building. The cooling pond consisted of an unlined depression approximately 50 feet in diameter and approximately 6 to 8 feet deep. When the pond filled, the fly ash and residues were removed, transported, and buried in the adjacent ash landfill east of the cooling pond. The refuse was dumped in piles and occasionally spread and compacted. No daily or final cover was applied during operation. The active area of the Ash Landfill extended at least 500 feet north of the incinerator building, near a bend in a dirt road, based on an undated aerial photograph of the incinerator during operation. A fire destroyed the incinerator on May 8, 1979, and the landfill was subsequently closed. The landfill was apparently covered with native soils of various thicknesses but has not been closed with an engineered cover or cap. Other areas on the site were used for a grease pit and burning of debris.

An RI/FS investigation was completed in 1996. A Non-Time Critical Removal Action (NTCRA), also known as an Interim Removal Measure (IRM), was conducted by the Army between August 1994 and June 1995, under the requirements of the CERCLA, as amended. This source removal action involved the excavation of 63,000 cubic yards of soil and treatment using Low Temperature Thermal Desorption. The surface area involved approximately 1.5 acres.

The IRM thermal treatment project provided a positive benefit for the long-term remedial action by eliminating continued leaching of VOCs into groundwater and preventing further exposure to humans and wildlife. In the several years that have passed since the IRM, the positive benefits of the IRM have been observed as the concentration of groundwater in this area has decreased over 100-fold.

A ZVI treatability study was performed between 1998 and 2001 and showed that the permeable wall would degrade chlorinated ethenes to below NYSDEC Class GA standards if sufficient reaction time is allowed. A ROD for this site was subsequently issued in February 2005 and included the use of permeable walls as migration control for the groundwater contamination on site.

#### **1.3.4 Groundwater Use**

The site groundwater is classified as Class GA by NYSDEC, which means that it is designated as a suitable source of potable water, as is almost all groundwater in the State of New York. Seneca Lake, which is west of the site, is a source of drinking water for SEDA and many surrounding communities. A more comprehensive description of the site is presented in the Remedial Investigation (RI) Report (Parsons ES, 1994).

Regionally, four distinct hydrologic units have been identified within Seneca County (Mozola A.J., 1951). These include two distinct shale formations, a series of limestone units, and unconsolidated Pleistocene-age glacial drift. Overall, the groundwater in the county is very hard, and therefore the quality is minimally acceptable for use as potable water. There are no public water supply wells with a one-mile radius of the site. Approximately 95% of the wells in the county are used for domestic or farm supply and the average daily withdrawal is approximately 500 gallons, an average rate of 0.35 gallons per minute (gpm). About five percent of the wells in the county are used for commercial, industrial, or municipal purposes. Seneca Falls and Waterloo, the two largest communities in the county, are in the hydrogeologic region that is most favorable for the development of a groundwater supply. However, because the hardness of the groundwater is objectionable to the industrial and commercial establishments operating within the villages, both villages utilize surface water (Cayuga Lake and Seneca River, respectively) as their municipal supplies. The villages of Ovid and Interlaken, both of which are without substantial industrial establishments, utilize groundwater as their public water supply. Ovid obtains its supply from two shallow gravel-packed wells, and Interlaken is served by a developed seepage-spring area. The nearest off-site well to the Ash Landfill is a house located approximately 2,400 feet west of the landfill on West Smith Farm Road.



## SECTION 2

### TECHNOLOGY DESCRIPTION

#### 2.1 ENHANCED ANAEROBIC BIOREMEDIATION OF CHLORINATED SOLVENTS

Enhanced anaerobic bioremediation can be an effective method of degrading various forms of CAHs (chlorinated solvents) dissolved in groundwater. When anaerobic degradation of CAHs occurs naturally, it is considered a component of natural attenuation. Unfortunately, monitored natural attenuation (MNA) alone may not be sufficient to achieve remedial objectives in a timely manner at many sites contaminated with CAHs. The addition of an organic substrate to an aquifer has the potential to stimulate microbial growth and development, creating an anaerobic environment which may greatly enhance rates of anaerobic biodegradation. Therefore, a variety of organic substrates have been applied to the subsurface to promote anaerobic biodegradation of CAHs to innocuous end products.

Advantages of enhanced anaerobic bioremediation include complete mineralization of the contaminants *in situ* with little impact on infrastructure or the need for secondary treatment trains. Enhanced bioremediation can generally be implemented at relatively low cost compared to more active remedial systems (e.g., groundwater extraction, air sparging, permeable reactive iron barriers, or chemical oxidation).

Biodegradation of an organic substrate depletes the aquifer of dissolved oxygen (DO) and lowers the oxidation-reduction potential (ORP), thereby stimulating conditions conducive to anaerobic biodegradation processes. After the DO is consumed, anaerobic microorganisms typically use native electron acceptors (as available) in the following order of preference: nitrate, manganese oxides, ferric iron hydroxides and oxyhydroxides, sulfate, and finally carbon dioxide. Evaluation of the distribution of these electron acceptors can provide evidence of where and how biodegradation of CAHs may occur. Reductive dechlorination has been demonstrated under nitrate-, iron-, and sulfate-reducing conditions, but the most rapid biodegradation rates, affecting the widest range of CAHs, occur under methanogenic conditions (Bouwer, 1994).

Anaerobic reductive dechlorination is the degradation process targeted by enhanced anaerobic bioremediation. Three general reactions may degrade CAHs by reductive dechlorination and include the following:

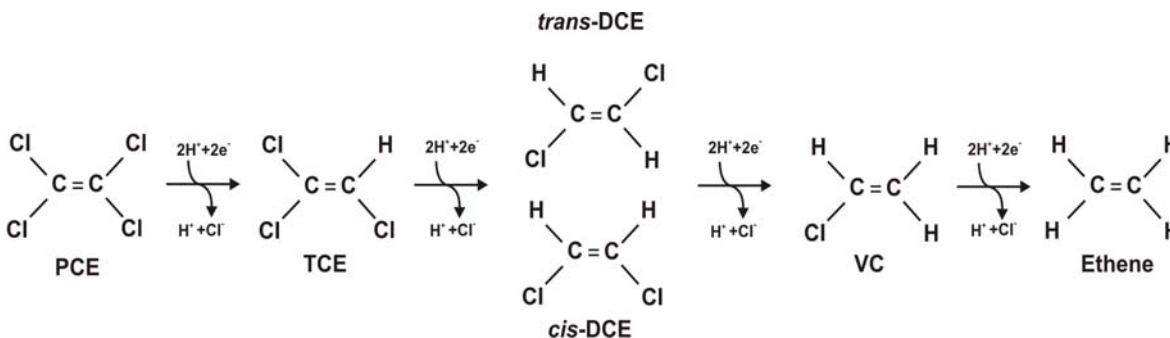
- **Direct Anaerobic Reductive Dechlorination** is a biological reaction in which bacteria gain energy and grow as one or more chlorine atoms on a CAH molecule are replaced with

hydrogen in an anaerobic environment. In this reaction, the chlorinated compound serves as the electron acceptor, and it appears that hydrogen serves as the direct electron donor. Hydrogen used in this reaction is typically supplied by fermentation of organic substrates. This reaction may also be referred to as halo-respiration or dehalorespiration (USEPA, 2000a).

- **Cometabolic Anaerobic Reductive Dechlorination** is a reaction in which a chlorinated compound is reduced by a non-specific enzyme or co-factor produced during microbial metabolism of another compound (i.e., the primary substrate) in an anaerobic environment. By definition, cometabolism of the chlorinated compound does not yield any energy or growth benefit for the microbe mediating the reaction (USEPA, 2000a). For the cometabolic process to be sustained, sufficient primary substrate is required to support growth of the transforming microorganisms.
- **Abiotic Reductive Dechlorination** is a chemical degradation reaction, not associated with biological activity, in which a chlorinated hydrocarbon is reduced by a reactive compound. Addition of an organic substrate and creation of an anaerobic environment may create reactive compounds, such as metal sulfides, that can degrade CAHs (e.g., Butler and Hayes, 1999; Lee and Batchelor, 2002). In this case, substrate addition may indirectly cause and sustain abiotic reductive dechlorination.

In practice, it may not be possible to distinguish among these three different reactions at the field scale; all three reactions may be occurring. Enhanced bioremediation applications to date have targeted biotic dechlorination processes. As used in this document, *anaerobic dechlorination* includes the biotic processes of direct and cometabolic anaerobic reductive dechlorination and abiotic reductive dechlorination.

In general, biotic anaerobic reductive dechlorination occurs by sequential removal of chlorine atoms. The most thoroughly studied anaerobic dechlorination pathway is the degradation of tetrachloroethene (PCE) to trichloroethene (TCE) to *cis*- and *trans*-dichloroethene (DCE) to vinyl chloride (VC), and finally to ethene. Sequential transformation from PCE to TCE to the DCE isomers (*cis*-DCE or *trans*-DCE) to VC to ethene is illustrated on **Figure 2-1**. Note that in highly reducing conditions, ethene may be further reduced to ethane.



**Figure 2-1 Sequential Reduction of PCE to Ethene by Anaerobic Reductive Dechlorination**

In this reaction, hydrogen is the electron donor, which is oxidized. The chlorinated ethene molecule is the electron acceptor, which is reduced. While other fermentation products (e.g., acetate) may serve as an electron donor, hydrogen appears to be the most important electron donor for anaerobic dechlorination of CAHs (Maymo-Gatell et al., 1997; Fennell and Gossett, 1998).

Anaerobic dechlorination of CAHs depends on many environmental factors (e.g., anaerobic conditions, presence of fermentable substrates, and appropriate microbial populations). Adding an organic substrate to the subsurface provides organic carbon that can be fermented to produce hydrogen, which may directly or indirectly stimulate anaerobic dechlorination reactions. Biodegradation of the organic substrate produces metabolic acids, primarily lactic, propionic, butyric, and acetic acids. Fermentation of these low-molecular-weight acids produces molecular hydrogen (H<sub>2</sub>), which is the primary electron donor used by microorganisms for reductive dechlorination of CAHs.

The most common approach utilized to date to stimulate reductive dechlorination has been addition of a carbon source dissolved in groundwater. This approach may prove effective in some applications, but in many cases may have difficulty competing with pump-and-treat remedial systems because some commonly-used carbon sources become exhausted in the subsurface relatively rapidly and must be periodically re-injected. Other approaches involving the emplacement of slowly-soluble and solid materials (e.g., mulch and compost) also are promising. This approach involves the emplacement of a slow-release carbon source which acts to stimulate anaerobic reductive dechlorination for many years.

## 2.2 PERMEABLE BIOWALLS

For this project, a mulch mixture will be emplaced as a solid slow-release carbon source in a one-time event by placing it in an excavated trench. The mulch will be emplaced in a contiguous wall by cutting a vertical trench and backfilling with the mulch/sand mixture. The use of permeable walls has

been studied at this site as an effective method of introducing a substrate to a generally low-permeability, heterogenous formation in an effort to destroy contaminants in groundwater. A treatability test was conducted in 1998-2001 using ZVI in a permeable reactive wall; the ZVI was shown to successfully decrease concentrations of chlorinated solvents in the groundwater. Permeable walls have been identified as a component of groundwater contaminant migration control at the Ash Landfill in the ROD. In an effort to maximize cost effectiveness, mulch, a relatively inexpensive substrate, is being considered for use with a permeable wall at this site. To date, the Air Force has installed permeable (mulch) biowalls at Offutt AFB, Nebraska; Altus AFB, Oklahoma; Dover AFB, Delaware; and F.E. Warren AFB, Wyoming.

Degradation of chlorinated ethenes at these sites occurs primarily by anaerobic reductive dechlorination, but may also occur by other processes including anaerobic oxidation or abiotic degradation by reactive metal-sulfides. Humic acids in the mulch and compost mixtures may also serve as electron acceptors in energy-yielding oxidation of *cis*-DCE under anaerobic conditions (Bradley and Chappelle, 1998).

***Advantages related to use of mulch biowalls include:***

- Effective for shallow groundwater plumes in very low to moderate permeability or highly heterogeneous formations. The continuity of the trench eliminates the potential for contaminant bypass problems due to preferential flow paths or inadequate delivery of substrate via injection wells.
- Trenches can be modified to include wells or perforated pipe for addition of liquid substrates to supplement carbon loading, if necessary. In addition, the relatively small treatment volume of the trench (relative to other substrate configurations) makes biowall systems ideal candidates for inoculation with bioaugmentation cultures, if necessary.

***Limitations of mulch biowalls include:***

- The depth that can be trenched in a practical and cost-effective manner is limited to approximately 35 feet below ground surface (bgs). Excavation of a bench for the trenching equipment may provide for an additional 8 to 10 feet of depth.
- Trenching may interfere with site infrastructure and utilities.
- The contaminant retention time in the trench and substrate loading capacity (i.e., rate at which organic carbon is added to the groundwater passing through the trench) may be insufficient to

treat concentrations of CAHs in excess of 10 to 100 milligrams per liter (mg/L). Use of wider trenches or multiple parallel trenches may be necessary to treat higher CAH concentrations.

The site conditions at the Ash Landfill are such that the limitations described above do not preclude use of a permeable mulch biowall for this treatability study.

### **2.3 PRELIMINARY ASSESSMENT FOR BIOREMEDIATION AT ASH LANDFILL**

Site-specific conditions and remedial objectives are evaluated in this work plan to determine if enhanced anaerobic bioremediation using a permeable mulch biowall is appropriate for the Ash Landfill. An evaluation of chlorinated solvents in groundwater at the Ash Landfill indicates that TCE persists with varying amounts of partial dechlorination to *cis*-DCE and/or VC observed in some locations, and complete dechlorination to ethene observed in isolated locations. The observation of intermediate degradation products suggests that the natural biodegradation of chlorinated solvents at the Ash Landfill is electron-donor (organic substrate) limited. Construction of a permeable mulch biowall will enhance the anaerobic degradation of CAHs in shallow groundwater by overcoming the observed electron donor limitation. For this treatability study, two types of organic carbon loading will be investigated at the field-scale. The first type of organic carbon loading will be the emplacement of a mixture of partially composted mulch and sand into the saturated zone using an excavator to open a trench and a front-end loader to push the backfill mix into the open trench. The second type of organic loading will be similar to the first, except that the mulch will be coated with food-grade vegetable oil prior to mixing with sand and inserting into the ground. It is anticipated that both backfill mixtures will provide sufficient organic substrate to drive anaerobic dechlorination for several years. The goal of applying a vegetable oil coating to the mulch in one trench is to evaluate whether this additional carbon loading provides a measurable increase in 1) the short-term magnitude of dissolved organic carbon released to the subsurface and 2) the longevity of performance effectiveness of the biowall over time.

As described in Section 1.3.2, the subsurface soils in the Ash Landfill pilot study area consist of gray, calcareous shales and mudstones and thin limestones. Pleistocene age (Late Wisconsin age, 20,000 years bp) till deposits overlie the shales, which have a thin (2 to 3 feet) weathered zone at the top. The till matrix varies locally but generally consists of unsorted silt, clay, sand, and gravel. The soils at the site contain varying amounts of inorganic clays, inorganic silts, and silty sands. At the Ash Landfill Operable Unit, the thickness of the till generally ranges from 4 to 15 feet. At the location of the biowalls, the thickness of the till and weathered shale is approximately 10 to 14 feet. This depth is within the depth obtainable by conventional excavation equipment and the bottom of the biowall will be “keyed” into the competent bedrock to mitigate the potential for contaminant bypass.

The average groundwater velocity at the study area was estimated to be approximately 61 ft/yr (Section 1.3.2) but may be locally influenced by more permeable zones possibly associated with differences in the actual porosity of the till/weathered shale. Based on an average groundwater velocity of 0.16 ft/day, the residence time for groundwater within a 3.0-foot wide biowall would be approximately 18 to 19 days, not accounting for differences in the effective porosity of the formation versus the biowall material.

Given current knowledge of site-specific geochemical characteristics, hydrogeological conditions, distribution of CAHs, and ability of conventional trenching equipment to open a trench through the overburden and down to the competent shale, the proposed approach of using an excavator and front-end loader to install permeable barriers containing a mulch/sand backfill at the Ash Landfill is deemed feasible and appropriate. In addition, there are no known or apparent site conditions that would limit the technical effectiveness of using biowall technology for treating TCE and its intermediate degradation products at this site.

## SECTION 3

### TEST OBJECTIVES

The objectives of this pilot study can be broken into two main categories: 1) assessment of technology treatment effectiveness and 2) evaluation of the constructability of the proposed full-scale remedy. This section describes specific objectives and goals for evaluating technology treatment effectiveness for this site.

The primary treatment objective of the proposed pilot study is to assess how well permeable walls filled with a mulch mixture (i.e., a biowall) enhance *in-situ* bioremediation of CAHs in groundwater at the Ash Landfill. One way to evaluate the effectiveness of each pilot study biowall is to compare the performance of the biowalls with previously-obtained results of a pilot study ZVI treatability study conducted at the site in 1998 and 1999 (Parsons, 2000). Specifically, the pilot study is intended to demonstrate that the emplacement of mulch substrate in a biowall trench will enhance anaerobic degradation and reduce concentrations of CAHs within the pilot study treatment area such that levels protective of human health and the environment may be reached on site (Section 3.1). Performance objectives have been developed to evaluate the ability of the mulch biowall to create geochemical conditions optimal for anaerobic dechlorination to occur, to increase rates of biodegradation, and to reduce concentrations of CAHs in groundwater (Section 3.2).

#### 3.1 SITE SPECIFIC CLEAN UP GOALS FOR GROUNDWATER

According to the ROD for this site, the remedial action objectives for groundwater are the following:

- Comply with New York State Class GA groundwater quality standards and federal Maximum Contaminant Levels (MCLs);
- Reduce and improve non-carcinogenic and cancer risk levels for current and intended future receptors; and
- Prevent exposure to off-site receptors through possible off-site migration of the VOC plume.

Land use controls will be set in place until remedial action objectives are attained.

Ambient Water Quality Standards (AWQS) have been established by the State of New York as published in the Division of Water Technical and Operational Guidance Series (TOGS), 1.1.1, Class GA Standards (June 1998). Clean-up goals for chlorinated solvents in groundwater at the Ash Landfill are based on these standards and are listed in **Table 3-1**.

**TABLE 3-1 CLEAN UP GOALS FOR GROUNDWATER**

Media	Chemical of Concern	Unit	Cleanup Level	Basis for Cleanup Level
Groundwater	trichloroethene	µg/L	5	NYSDEC AWQS
Groundwater	1,2-dichloroethene ( <i>cis</i> ) (Note 1)	µg/L	5	NYSDEC AWQS
Groundwater	1,2-dichloroethene ( <i>trans</i> ) (Note 1)	µg/L	5	NYSDEC AWQS
Groundwater	vinyl chloride	µg/L	2	NYSDEC AWQS

**Notes:**

µg/L = micrograms per liter.

Note 1: The NYSDEC AWQS Standard for 1,2-dichloroethene (*cis*) and 1,2-dichloroethene (*trans*) is based on the principal organic contaminant standard for groundwater of 5 µg/L. According to TOGS 1.1.1 and in reference to principal organic contaminants, "A less stringent guidance value for an individual substance may be substituted for this standard if so determined by the Commissioner of the New York State Department of Health."

The EPA has established a Maximum Contaminant Level for 1,2-dichloroethene (*cis*) of 70 µg/L and for 1,2-dichloroethene (*trans*) of 100 µg/L.

**3.2 PERFORMANCE OBJECTIVES**

Performance objectives have been developed to evaluate the effectiveness of the pilot study. The measures used to evaluate the performance of the proposed pilot study include the following:

- Achieve similar reduction of concentrations of TCE within each individual biowall as was demonstrated for the ZVI PRB described in the Feasibility Memorandum (Parsons, 2000).
- Demonstrate a reduction in total molar concentrations of CAHs in the biowalls and at monitoring locations downgradient of the biowalls. One metric used to evaluate biowall effectiveness in meeting this performance objective will be to demonstrate that the treatment efficiency achieved by the biowalls is equal to or greater than the percent molar reductions observed for the ZVI pilot-scale treatability study. The method used to evaluate this metric will be to compare total molar chlorinated ethene concentrations at upgradient monitoring wells with those observed in each individual biowall and at downgradient monitoring wells. Note that the performance monitoring well located in between the two proposed biowalls will serve as a downgradient monitoring well for one biowall, but an upgradient monitoring well for the other biowall. (See Section 4 for monitoring well locations relative to biowall alignments.) Results from this biowall pilot study will be compared to the molar reduction results that will be calculated from concentration measurements performed over time from monitoring wells in and around the ZVI PRB.
- Demonstrate that the biowalls create a treatment zone within and downgradient of the trenches that is favorable to the long-term enhancement of degradation of TCE and its regulated intermediate degradation products, *cis*-1,2-DCE and *trans*-1,2-DCE and VC. This



performance objective will be demonstrated through the evaluation of the groundwater geochemical conditions that are created within and downgradient of the biowall, and comparison of these conditions to sites where other biowalls have been installed. The long-term goal of constructing multiple biowalls is to degrade chlorinated ethenes to concentrations below the NYSDEC GA standards listed in **Table 3-1**.

- Demonstrate that no chlorinated solvents will exceed NYSDEC GA Standards at the Farm House west of the site at any time during the estimated remediation timeframe.
- Evaluate biowall design criteria (e.g., organic carbon generation, degradation rates, residence time) and constructability issues (e.g. trenching techniques, trench stability, oil application, and subsurface pipe placement) required for effective long-term operation.

The system design, installation methods, materials, and monitoring requirements to meet these performance objectives are described in the following sections. After biowall installation, groundwater in the pilot study area will be monitored for changes in groundwater geochemistry and reduction in contaminant concentrations over a period of at least 22 weeks.

## SECTION 4

### SYSTEM DESIGN, INSTALLATION, AND MONITORING

#### 4.1 FIELD ACTIVITIES

Field activities associated with this project will include installation of system components (i.e., biowall trench and groundwater monitoring wells), baseline characterization, and process monitoring. Specifically, these activities will include the following:

##### Installation of System Components

- Two 150-foot long, 3-foot wide pilot-scale biowalls will be installed using an excavator to open the trench and a front-end loader to place the backfill. The biowalls will be installed down to the competent shale which is approximately 15 feet bgs in this area. The pilot biowalls will be located downgradient of the Ash Landfill (in the vicinity of existing monitoring well PT-12A) and emplaced perpendicular to the general direction of groundwater flow.
- Eleven temporary groundwater monitoring wells will be installed using HSA drilling technology.

##### Baseline Characterization

- A groundwater monitoring network of consisting of 12 wells will be sampled immediately following (i.e., within one week of) completion of biowall system installation.

##### Process Monitoring

- The groundwater monitoring network (12 wells total) will be sampled during process monitoring events that will be conducted approximately 8, 15, and 22 weeks after completion of biowall system installation.

The proposed location for the pilot-scale biowall system is shown on **Figure 4-1**. As shown on this figure, the biowall system will be placed within one of the most contaminated areas of the dissolved chlorinated solvent plume. **Figure 4-2** is plan view of the location of the monitoring well network relative to the location of the biowalls. As shown on this figure, the hydraulically upgradient biowall will be referred to as the ‘East Biowall’ and hydraulically downgradient biowall will be referred to as the ‘West Biowall’. Monitoring wells will be installed in a series of two transects that are perpendicular to the alignment of the biowalls and along the path of groundwater flow. As shown on **Figure 4-2**, the monitoring well transects will be referred to as the ‘North Transect’ and ‘South

Transect'. The purpose of these monitoring well transects is to collect data on biowall performance. Each transect will be comprised of six wells. The monitoring well network for each biowall will start 13 feet upgradient (hydraulically) of the eastern edge of the East Biowall biowall and finish 21 feet downgradient of the western edge of the West Biowall. Each transect will consist of one well upgradient of the East Biowall, one monitoring well installed between the East and West Biowalls, one monitoring well installed inside each biowall, and two monitoring wells installed downgradient of the West biowall. Section 4.3.3 provides a detailed description of the placement and proposed sampling for the monitoring well network.

The pilot-scale biowall system has a dual purpose to 1) provide performance monitoring data on the effectiveness of the biowalls to degrade TCE and any intermediate degradation products that may be produced, and 2) evaluate site-specific constructability issues in preparation for a full-scale design and installation. The goals of process monitoring will be to 1) document the effectiveness of the biowalls in degrading influent chlorinated ethene concentrations, 2) evaluate the total molar reduction of these chlorinated ethenes, 3) observe the downgradient transport of organic carbon from the biowalls, and 4) provide data for estimation and comparison of biowall longevity with and without a vegetable oil coating on the mulch. The biowall performance monitoring well network will be sampled immediately following biowall installation to provide a baseline characterization that will be assumed to represent initial conditions.

Three process monitoring events are proposed at 8, 15, and 22 weeks following system installation. The locations of the downgradient monitoring wells are based primarily on the ability to observe the effects of the biowall on downgradient groundwater quality over this monitoring period. Assuming an estimated average groundwater velocity of 60 ft/yr, well spacings of 7.5 feet and 21.5 feet downgradient of the West Biowall correspond to travel times of approximately 6 to 7 weeks and 18 to 19 weeks, respectively. These travel time estimates assume that contaminant concentrations in groundwater and soil are already at equilibrium, which implies that there may be limited retardation effects on contaminant transport in this area. Therefore, effects of the biowall should be observed at the wells located 7.5 feet downgradient from the West Biowall during the first monitoring event at 8 weeks. Similarly, effects of the biowall at the wells located 21.5 feet downgradient from the West Biowall should be observed by the last monitoring event at 22 weeks.

The specific constructability issues that will be examined during the pilot test installation include 1) sidewall stability of the open trench, 2) methods for staging the sequential excavation and backfill of the trench, 3) methods for placing of a horizontal pipe (for future liquid organic injection) in the West

Biowall, and 4) the ability to add a coating of food grade vegetable oil to the mulch for the East Biowall prior to mixing with sand and placing in the trench.

## **4.2 SITE MANAGEMENT**

The following paragraphs outline site management requirements pertaining to the field activities to be conducted under this project, including SEDA support.

### **4.2.1 Seneca Army Depot Support**

Seneca Army Depot will provide the following support during field activities:

- **Site Access to Field Team Members.** The SEDA point of contact (POC) will arrange daily access to the site including procurement of all required personnel badges and vehicle passes. Project team members are listed in Section 7.
- **Scheduling Information.** The SEDA POC will notify Parsons of any Depot activities (such as hunting) that may adversely affect field activities and/or impact the sampling schedule. In turn, Parsons will provide the SEDA POC with advance notification of planned field activities.
- **Underground Utility Clearances.** Before commencing field activities, locations designated for intrusive activities (e.g., drilling, excavation) will be surveyed for the presence of underground utilities. Facility maps will be obtained from SEDA and consulted prior to commencing any intrusive work. Excavation or borehole sites will be positioned accordingly, marked with wooden stakes, and then cleared with SEDA. Excavation/drilling are to be done at the marked, cleared locations only.
- **Decontamination Area.** The SEDA POC will provide approval of an area to be designated for decontamination of drilling rigs and excavation equipment. The decontamination area will be large enough to allow storage of cleaned equipment and materials prior to use, as well as to stage storage containers of decontamination waste.
- **Storage Area.** The SEDA POC will provide approval of an area near the proposed biowall location for storage of mulch, sand, and other supplies.

### **4.2.2 Contingency Plans**

This subsection describes steps that will be taken by Parsons to minimize delays during the investigations. Potential problems that could be encountered during the field effort include:

- Access and coordination difficulties;
- Equipment breakdowns; and

- Abnormal site conditions (e.g., severe weather).

#### **4.2.2.1 Access and Coordination Contingencies**

Anticipated support needs are outlined in Section 4.2.1. In the event that site access difficulties arise, the Base POC will be contacted to resolve the problem. The Parsons site manager and field team leader will be responsible for notifying the Base POC of access or coordination difficulties.

#### **4.2.2.2 Equipment Contingencies**

Equipment to be employed on this project includes conventional construction equipment (i.e. backhoe, excavator) for installation of the proposed biowall, HSA drilling equipment for the installation of proposed monitoring wells, and field sampling and testing instruments for health and safety monitoring and field data collection.

Operational equipment problems identified during installation of the biowall and groundwater monitoring wells are to be directed to the Parsons site manager who will arrange for either the prompt repair or replacement of the affected equipment. The Base POC will be informed of any action or delay that impacts the project schedule.

In the event of operation problems with field sampling or testing instruments, field personnel will contact the Parsons field team leader and refer to the instrument's instruction manual for troubleshooting procedures and guidance. Field personnel are also encouraged to contact the instruments manufacturer and/or supplier. If necessary, backup instruments will be obtained. However, any such decisions will be made by the Parsons site manager or field team leader after consideration of other potential solutions. Equipment will be maintained and extra batteries and other standard replacement parts will be kept onsite in order to avoid downtime due to minor problems.

#### **4.2.2.3 Weather and Operational Contingencies**

Severe weather and Base operations could potentially impact field activities. Should severe weather (e.g., lightning) threaten the project site, the Parsons site manager or field team leader will temporarily suspend all field activities. When site activities are suspended due to severe weather, field team members will be notified immediately. Upon notification they will secure all equipment and the work area as quickly as possible, evacuate the work area, and gather at a pre-determined location. Work will resume when the threat of severe weather has past.

Additional guidance regarding other unidentified contingencies (e.g., spill responses, injuries, etc.) is provided in the Site-Specific Health and Safety Plan (Parsons, 2005).

### **4.3 BIOWALL SYSTEM DESIGN AND INSTALLATION**

System components that will be installed as part of this pilot-scale study will include two pilot-scale permeable mulch biowalls and 11 temporary groundwater monitoring wells.

#### **4.3.1 Proposed Biowall Locations**

The location of the pilot-scale biowalls will be within the dissolved chlorinated ethene plume that emanates from the Ash Landfill (**Figure 4-1**). The pilot-scale biowalls will be installed as two segments. Each segment will be approximately 150 feet long, 3.0 feet wide, and installed into the competent bedrock. The proposed pilot-scale biowalls will be installed perpendicular to the general direction of groundwater flow within the study area, approximately 13 feet west of existing groundwater monitoring well PT-12A (**Figure 4-2**). This area was selected because it contains some of the higher concentrations of TCE and DCE at the site and will provide a conservative test of the biowall's potential to treat site contaminants. Based on available historical hydrogeologic information and as shown on **Figure 4-2**, a north-south orientation of the biowall alignment will result in treatment zones that are perpendicular to the general direction of groundwater flow. The two segments will be placed parallel to each other, with the West Biowall installed approximately 12 feet west (hydraulically downgradient) of the East Biowall.

Two biowall segments, one downgradient of the other, are being installed for this pilot-scale study to assess the treatment efficiency of multiple biowalls in advance of a full-scale design where multiple barriers would be installed. Monitoring wells will be installed upgradient, within, between, and downgradient of the biowalls to assess the individual treatment efficiency of each biowall. The spatial location for the biowalls and monitoring wells in the proposed pilot-scale design was selected to facilitate evaluation of the effects of multiple treatment barriers within a relatively short (i.e., 5-month) monitoring period. Specifically, the relatively short monitoring period necessitates that the series of biowalls to be placed closer together than would typically be specified in a full-scale application. Based on the monitoring information obtained, the final configuration (i.e. location and spacing) of multiple biowalls will be determined. The full-scale design may consist of multiple biowalls that are spaced farther apart than specified in the proposed pilot-scale design.

#### **4.3.2 Proposed Backfill Composition and Biowall Installation**

Biowall installation will consist of excavating a linear trench into competent bedrock and backfilling this trench with a mixture of mulch and sand to approximately 1 foot bgs. The backfill mixture will be approximately 50 percent mulch and 50 percent coarse sand by volume. The ratio of mulch to sand is intended to maximize the amount of organic material, while still maintaining a permeability within the biowall that is greater than the surrounding formation. Previous biowall installations using

a mixture of 50 percent mulch and 50 percent sand have shown that this mixture is optimal for balancing ease of emplacement with the long-term maintenance of biowall permeability. At this ratio, the mulch is supported by a sand matrix that minimizes compaction and maintains permeability. Because sand fills much of the void space in the mulch, it will take approximately 400 cubic yards of mulch and 350 cubic yards of sand to create 500 cubic yards of the mixture. The top of the trench (above the mulch/sand mixture) will be backfilled with soil from the excavation.

The mulch for the East Biowall will be coated with food-grade vegetable oil prior to mixing with sand and emplacement in the trench. Mulch for the West Biowall will not be coated with vegetable oil prior to mixing and placement. The purpose of coating the East Biowall with vegetable oil prior to emplacement is to evaluate whether the vegetable oil coating will increase the potency and longevity of the organic carbon supply and chlorinated ethene removal, relative to uncoated mulch. The rationale behind using a vegetable oil coating on the mulch is that this oil has the potential to increase the duration of organic carbon release from the East Biowall.

**Figure 4-3** provides a cross-section of the biowall system components along one of the well transects. As shown on this figure, a slotted, high-density polyethylene (HDPE) pipe will be placed at the bottom of the trench for the West Biowall. The purpose of installing this piping in the West Biowall is to allow future testing of enhancements to biowall performance, as may eventually be required due to a change in desired performance criteria and/or due to the gradual depletion of the soluble organic carbon supply from the mulch. As shown on **Figure 4-3**, the ends of this pipe will extend to the ground surface at opposing ends of the West Biowall. Surface completions will consist of a 12-inch diameter flush-mounted well box encased in a 2-foot diameter bentonite collar. The surface completions are designed to protect the pipe access points. Potential liquid amendments that could be injected to “recharge” the biowall at a future date include 1) simple sugars, such as lactate or fructose, 2) emulsified vegetable oils, and 3) bioaugmentation microbial population cultures that can alter or enhance the degradation characteristics of the biowall (if needed).

In theory, biowall thickness would be specified using a site-specific calculation to determine the thickness required to maintain a sufficient residence time within the biowall for complete degradation to occur. This calculation would be performed using site-specific biodegradation half-lives, estimates of average influent concentrations, a target treatment concentration for the groundwater exiting the biowall, the highest groundwater velocity estimate along the biowall alignment, differences between porosity of the biowall versus the formation, and the sorption properties of the contaminants with the biowall material. In practice, however, biowall thickness is typically specified by selecting a trench

thickness that is consistent with available excavation equipment. The feasible widths for common trenching equipment range between 1 and 4 feet.

Based on previous site activities (e.g., test pits) and a review of local geology, an excavator with a 3-foot wide bucket is anticipated to be appropriate for constructing the trench for the Ash Landfill biowalls. The following discussion compares the conditions at the Ash Landfill site with those from a previous pilot-scale biowall at Altus AFB, Oklahoma to provide an assessment of whether a 3-foot thick biowall for treating CAH-impacted groundwater flowing out of the Ash Landfill is sufficient for this application.

Process monitoring data collected at Altus during the first 9 months after installation of the Altus biowall indicate that TCE concentrations have decreased by over 99 percent within the biowall. Similarly, the total molar concentration of chlorinated ethenes within the biowall decreased by over 80 percent during the first 9 months of installation. The dimensions of the Altus biowall were approximately 455 feet long, 24 feet deep, and 18 inches wide. In comparison, proposed dimensions of the pilot-scale biowalls for Ash Landfill are 150 feet long, approximately 15 feet deep (depending on the bedrock depth in the area), and 36 inches wide. Groundwater flow conditions at Altus (groundwater seepage velocity of 0.5 to 1.2 ft/day) are higher than those estimated for the dissolved CAH plume at the Ash Landfill (0.16 ft/day). Based on a comparison of wall thicknesses and local groundwater velocities between sites, the proposed design for the Ash Landfill biowalls is expected to result in a longer residence time within each Ash Landfill biowall than occurs at the Altus biowall. A longer residence time means that degradation processes within the Ash Landfill biowall are likely to have a longer period of time to impact influent CAH concentrations than is currently occurring at the Altus biowall.

A comparison of influent contaminant concentrations indicates that TCE concentrations flowing into the Ash Landfill biowall will be less than those flowing into the Altus biowall. Specifically, concentrations of TCE in groundwater at Altus AFB (as high as 8,000 µg/L) are greater than the highest concentration of TCE measured in PT-12A over the last five years (i.e., 1,000 µg/L in September 2001 and October 2003). Recall that PT-12A is the first monitoring well installed downgradient of the Ash Landfill, and is the monitoring well that is closest to the proposed locations for biowall installation as part of the current pilot-scale study. The most recent maximum TCE concentration measured within the Ash Landfill was 7,860 µg/L at PT-18 in October 2003, which was approximately equal to the highest TCE concentration observed upgradient of the Altus biowall test site. In summary, a single three-foot wide Ash Landfill biowall is expected to provide a significantly longer residence time (i.e., 18 days at the Ash Landfill versus 2 days at Altus AFB) and is expected to



be treating lower CAH concentrations than the Altus AFB biowall. As a result, a greater percentage of the CAH mass entering the Ash Landfill biowall should be degraded relative to the Altus AFB biowall.

The mulch backfill in the Ash Landfill biowalls will be a mixture of shredded plant material generated during seasonal landscaping/farming operations (i.e., tree/brush removal, silage). The mulch will be stockpiled and allowed to partially compost for a minimum period of 1 week prior to installation of the biowall. Poorly-graded, coarse or medium sand will also be stockpiled at the site in preparation for mixing with the mulch material. Examples of commonly available sands meeting this requirement include washed block sands and washed concrete sands. The mulch and sand mixture placed in the East Biowall will include a coating of food-grade vegetable oil (e.g., soybean oil), while the backfill mixture for the West Biowall will be comprised of sand and mulch only. The vegetable oil for the East Biowall backfill will be delivered to the site in either 55-gallon drums or as 220-gallon 'totes'. It is anticipated that the vegetable oil will be applied to the mulch for the East Biowall prior to mixing the mulch with sand. In the event that it is technically difficult or infeasible to sufficiently mix the oil-coated mulch with sand, the mulch will be mixed with the sand prior to application of vegetable oil to the backfill for the East Biowall.

The field engineer will evaluate the physical characteristics of the mulch and sand used for construction of the biowall, including visual descriptions of the mulch composition, point of origin, processing, range of particle size, and any signs of compositional decay. Two representative samples of sand and four representative samples of mulch will be collected and submitted for the analyses listed in **Table 4-1**. Note that two of the mulch samples will be collected from mulch coated with vegetable oil, while the remaining two mulch samples will be collected from non-coated mulch.

A descriptive log of all backfill mixing, trenching, and biowall installation activities will be recorded in the field. The field logs will include photo documentation and a written log. The written log will include daily setup and breakdown times, advancement rate, problems encountered in the field and corrective measures taken, as well as any other field observations. This log will form the basis for the development of guidelines for the full-scale implementation.

Soil generated during excavation of the biowall will be tested and disposed of as discussed in Section 4.4. The location and extent of the biowall will be marked with metal fence posts painted a high visibility color.

### 4.3.3 Proposed Groundwater Monitoring Locations

The locations of 11 proposed temporary groundwater monitoring wells, relative to the alignment of the biowalls, are shown on **Figure 4-4**. Construction details for these proposed monitoring wells are summarized in **Table 4-2**, and illustrated on the cross section provided as **Figure 4-3**. As shown on **Figure 4-4**, the proposed monitoring well network for the current pilot study consists of two transects (i.e., the North Transect and South Transect) of six wells each.

The North Transect will consist of six new temporary groundwater monitoring wells, with one well installed approximately 13 feet upgradient (east) of the East Biowall, one monitoring well installed between the East and West Biowalls, one monitoring well installed inside each biowall, one monitoring well installed 6.5 feet downgradient (west) of the West biowall, and a second downgradient monitoring well installed 21.5 feet downgradient of the West Biowall.

The South Transect will consist of five new temporary groundwater monitoring wells and one existing monitoring well (PT-12A). Existing monitoring well PT-12A will be used to define the position of the biowall trenches, in that centerline of the East Biowall trench will be specified as 14.5 feet west of PT-12A. As such, PT-12A will serve as the upgradient well for the South Transect. The remaining five wells in the South Transect will be placed in the same locations relative to the biowalls as was described above for the North Transect.

The monitoring wells in the network shown on **Figure 4-4** will be used to monitor groundwater geochemical conditions and contaminant concentrations upgradient, within, and immediately downgradient of the biowalls over time. Screened intervals for all new monitoring wells are planned to be 8 to 13 feet bgs. Final well installation configuration will be at the discretion of the field engineer, as the depth to competent shale and or the depth to piping in the West Biowall may require field adjustments to the final monitoring well depth and corresponding screen interval. The screened interval for PT-12A is currently unknown. A review of available records and/or a field evaluation of the screened interval for this well will be performed.

### 4.3.4 Proposed Drilling and Soil Sampling Procedures

Drilling for installation of groundwater monitoring wells will be accomplished using HSA drilling technology. Boreholes will be advanced to achieve the depths identified in **Table 4-2**. A Parsons field scientist will be responsible for field-classification of soil samples and maintaining a detailed descriptive log of all subsurface materials recovered during drilling. During borehole advancement, soil samples for visual description will be collected at a frequency sufficient to identify the depths of significant stratigraphic contacts or other soil properties at a minimum of three locations along the North Transect and two locations along the South Transect. Along the North Transect, the three

minimum locations for identification of soil properties will be the upgradient monitoring well (MWT-12), the monitoring well installed between the East and West Biowalls (MWT-14), and the furthest downgradient monitoring well (MWT-17). Along the South Transect, the two minimum locations for identification of soil properties will be the monitoring well installed between the East and West Biowalls (MWT-19) and the furthest downgradient monitoring well (MWT-22).

Soil samples will be collected using the procedures described in Section 5.1.1. The purpose of collecting these samples is to allow estimation of the effects of sorption on contaminant transport retardation in the immediate vicinity of the pilot-scale biowalls. At two borehole locations (**Table 4-3**), two soil samples will be collected and submitted to a fixed-base laboratory for analysis of total organic carbon (TOC) using USEPA Method SW9060-modified. At each of these boreholes, one sample will be collected from the till and a second will be collected from the weathered shale. The depth of sample collection for one of these samples will correspond to the screened interval for the newly installed monitoring well, and should be below the existing water table if encountered. Generated soil cuttings will be handled in accordance with the residuals management procedures discussed in Section 4.4.

#### **4.3.5 Proposed Temporary Groundwater Monitoring Well Installation**

This section describes the procedures to be used for installation of the 11 temporary groundwater monitoring wells.

##### **4.3.5.1 Pre-Installation Activities**

All underground utilities will be located, and proposed drilling locations will be cleared for utilities prior to any intrusive activities. Responsibilities for these clearances are discussed in Section 4.2.1.

Water to be used during well installation and equipment decontamination activities will be obtained from an onsite water supply. Water use approval will be verified by contacting the appropriate facility personnel. A Parsons field scientist will make the final determination as to the suitability of site water for these activities.

##### **4.3.5.2 Materials Decontamination**

All completion materials will be inspected by the field scientist and determined to be clean and acceptable prior to use. If not obtained in factory-sealed packages, riser, screen, end caps, and surface plugs will be cleaned prior to use with a high-pressure, steam/hot-water cleaner using approved water. Materials that cannot be cleaned to the satisfaction of the field scientist will not be used.

#### **4.3.5.3 Screen and Casing**

Groundwater monitoring wells will be installed using HSA drilling technology. Groundwater monitoring wells will be constructed of 2-inch nominal diameter, flush-threaded, Schedule 40 polyvinyl chloride (PVC) screen and riser. The screens will be factory slotted with 0.010-inch openings. Total depth and screen and riser length for each of the groundwater monitoring wells are summarized in **Table 4-2** and illustrated in **Figure 4-3**. The casing string will be fitted with a PVC bottom cap and a locking end cap.

The field scientist will verify and record the total depth of each monitoring well, the lengths of all casing sections, and the depth to the top of all completion materials. All lengths and depths will be measured to the nearest 0.1 foot.

#### **4.3.5.4 Groundwater Monitoring Well Completion**

Groundwater monitoring wells will be constructed with a number 20-40 sand pack that will be placed around the screen from the bottom of the borehole to approximately 2 feet above the top of the screened interval. A granular bentonite seal will be installed in 12-inch lifts from immediately above the sand pack to land surface. For the portion of the seal installed above the water table, each bentonite seal lift will be hydrated with potable water to ensure complete hydration of the seal. Surface completions will consist of a “stickup” well head protector set in bentonite and covered with a crushed rock and/or gravel collar (**Figure 4-3**).

During installation of monitoring wells within the biowall, the surrounding mulch and sand mixture will be allowed to collapse around the screen from the bottom of the screen to approximately 2 feet above the top of the screen. This will be done to preserve the effective treatment width of the biowall in the vicinity of the in-biowall wells. A bentonite chip seal will be installed in 12-inch lifts from the top of natural collapse to ground surface. Concrete grout will not be used during installation of monitoring wells installed in the biowalls to allow for potential settlement of the biowall backfill material following installation.

#### **4.3.6 Groundwater Monitoring Well Development**

All installed groundwater monitoring wells will be developed prior to sampling. Development removes sediment from inside the well casing and flushes fines from the portion of the formation adjacent to the screen. Groundwater development procedures and development records are included in the Field Sampling Plan (FSP) in Section 5.1. Development water will be handled in accordance with the residuals management procedures discussed in Section 4.4.

#### **4.3.7 Equipment Decontamination Procedures**

Prior to arriving at the site, and between each monitoring point, drill bits, drill pipe, drill casing, instrumented probes, samplers, tools, and other down-hole equipment will be decontaminated using the decontamination procedures described in the FSP (Section 5.1.1). Rinsate generated during decontamination operations will be handled in accordance with the residuals management procedures discussed in Section 4.4.

#### **4.3.8 Datum Survey**

The locations and elevations of the newly installed monitoring wells will be surveyed by a surveyor registered in the State of New York. The elevation of the ground surface adjacent to each monitoring well and measurement datum (top of the casing) will be measured relative to an existing benchmark location referencing the Base grid system. Survey of the new wells will take place as follows:

- Horizontal locations will be measured relative to Northing and Easting in State Planar Coordinates, North American Datum (NAD) 1983, accuracy  $\pm 0.1$  feet.
- The elevation of the ground surface adjacent to each monitoring well will be measured relative to North American Vertical Datum (NAVD) 1988, accuracy  $\pm 0.1$  feet at stake or pin in collar.
- The elevations of the top of the well protective casing and top of the well casing will be measured relative to NAVD 1988, accuracy  $\pm 0.01$ .

Monitoring wells will have three elevations with varying levels of accuracy; the first for the top of the well's PVC inner casing at a notch placed by the surveyor, a second for the top of the well's protective outer casing at the crown of the cap, and the last for the elevation at a pin placed in the collar of the well at the ground.

#### **4.4 RESIDUALS MANAGEMENT**

Investigation-derived waste (IDW) will include soil generated during the excavation of the biowall trenches, soil generated during installation of the proposed groundwater monitoring wells, purge water generated during development and sampling of proposed groundwater monitoring wells, and equipment decontamination rinsate. Water accumulation within the trench prior to placement of the mulch/sand media is not anticipated based on the tight formation and past observations during test pit excavations at the site.

Soil excavated from the trenches will be placed in a windrow parallel to the trench on the downgradient side of the trench for the East Biowall and the upgradient side of the trench for the

West Biowall. Once excavation activities have been completed, one discrete soil sample will be collected per 75 linear feet of trench excavated and analyzed for VOCs (Method SW8260 Medium level). The following table describes the fate of soils removed from the trench based on sampling results compared to NYSDEC Technical and Administrative Guidance Memorandum (TAGM) for soil cleanup levels.

<b>Sample Results</b>	<b>Acceptable Use</b>
TCE less than NYSDEC TAGM of 0.7 mg/kg.	Soil may be used on site for fill or grading material.
TCE greater than NYSDEC TAGM of 0.7 mg/kg.	Soil may be used as cover over the biowalls (a one-foot plug is required).

Soil cuttings generated during drilling activities will be added to the windrows created during the excavation of the biowall trenches above. Water generated during monitoring well development and sampling, and decontamination water generated during decontamination activities will be collected in a bulk storage tank or in 55-gallon drums. This water will be tested and disposed of according to test results.

Expendable sampling equipment and materials that may be generated during field activities (e.g., personal protective equipment) will be bagged and disposed of in an on-Base trash dumpster. Miscellaneous trash generated during field activities (e.g., empty sand bags) also will be placed in the dumpster.

#### **4.5 POST-COMPLETION ACTIVITIES**

##### **4.5.1 Baseline Characterization**

Immediately following well installation and development, baseline sampling will be conducted at the 11 new temporary groundwater monitoring wells (MWT-12 through MWT-22) and an existing groundwater monitoring well (PT-12A) that comprise the North and South Transects. Baseline characterization activities are summarized in **Table 4-3**, and will follow field sampling procedures described in the FSP and Quality Assurance Project Plan (QAPP) in Section 5.

##### **4.5.2 Process Monitoring**

To monitor system performance over time, sampling will be conducted at the 11 new groundwater monitoring wells (MWT-12 through MWT-22) and existing groundwater monitoring well (PT-12A)

at 8, 15, and 22 weeks after completion of the biowall system component installation. Activities that will be performed during the process monitoring events are summarized in **Table 4-4**.

#### **4.5.3 Aquifer Testing**

Slug tests will be conducted as part of baseline characterization activities to determine the hydraulic conductivity of natural aquifer materials surrounding the biowall and the materials installed within the biowall. The hydraulic conductivity estimates from these initial slug tests will be used to 1) document that the permeability in the trench is higher than the surrounding formation and 2) estimate local groundwater flow rates and corresponding residence times within the backfill of each trench. Aquifer testing will also be performed as part of the last process monitoring event proposed in this work plan. The purpose of this second aquifer testing event, which will be performed on the same wells as the initial aquifer test, will be to document whether there are measureable changes in permeability of the biowall or the surrounding aquifer over time. Potential phenomena that could cause changes in permeability that are related to a biowall installation include compaction of the backfill and biomass growth. Slug tests will be conducted at five of the proposed groundwater monitoring locations. The monitoring locations to be tested are identified in **Table 4-3**. Slug test procedures are described in Section 5.1.7.

## **SECTION 5**

### **SAMPLING AND ANALYSIS PLAN**

This SAP describes the field sampling procedures and QA/QC protocols that will be performed during the pilot study at the Ash Landfill, SEDA, Romulus, NY. This SAP is based on the scope of work outlined in Section 4, and consists of a FSP (Section 5.1) and a QAPP (Section 5.2). The following guidance documents were used in the preparation of this SAP:

- *Draft Sampling and Analysis Plan for Seneca Army Depot Activity* (Parsons, 2005);
- *Air Force Center for Environmental Excellence (AFCEE) Model Field Sampling Plan, Version 1.2* (AFCEE, 2002);
- *AFCEE Quality Assurance Project Plan, Version 4.0* (AFCEE, 2005); and
- *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater* (USEPA, 1998).

The *Draft Sampling and Analysis Plan for SEDA* is incorporated herein by reference. Unless described differently in the following sections, work performed under this pilot study will conform to the SEDA SAP.

#### **5.1 FIELD SAMPLING PLAN**

The purpose of this FSP is to establish field sampling protocols for a pilot study for bioremediation of chlorinated solvents in groundwater using a permeable mulch biowall at the Ash Landfill. This FSP includes procedures for sampling activities including decontamination procedures, equipment and instrument use, sample preservation and storage, maintenance of field records, and sample transport and chain-of-custody protocols.

##### **5.1.1 Soil Sampling Procedures**

Drilling for installation of the groundwater monitoring wells will be accomplished using HSA drilling technology (Section 4.3).

###### **5.1.1.1 Equipment Decontamination Procedures**

Prior to arriving at the site, and between each borehole, all downhole drilling equipment will be decontaminated using a high-pressure, hot water wash. Auger flights, rods, and bits will be decontaminated by cleaning with high pressure hot water at the beginning of the project, between boreholes, and before moving off site at the end of the field investigation. Only potable water will be used for decontamination. Rinse water generated during decontamination operations will be handled



in accordance with the IDW procedures discussed in Section 4.4. The field scientist will make the final determination as to the suitability of site water for these activities.

Instruments and hand tools may be decontaminated by hand by scrubbing all surfaces that may come in contact with contaminated soils or water with potable water and laboratory grade soap (Alconox™ or Liquinox™). After all visible foreign materials have been removed the decontaminated item will be thoroughly rinsed with distilled water.

#### **5.1.1.2 Borehole Advancement**

Boreholes will be advanced to achieve the depths identified in **Table 4-2**. During borehole advancement of a minimum of three locations along the North Transect and two locations along the South Transect, soil samples for visual description will be collected at a frequency sufficient to identify the depths of significant stratigraphic contacts and other soil properties. Along the North Transect, the three minimum locations for identification of soil characterization will be the upgradient monitoring well (MWT-12), the monitoring well installed between the East and West Biowalls (MWT-14), and the furthest downgradient monitoring well (MWT-17). Along the South Transect, the two minimum locations for identification of soil characterization will be the monitoring well installed between the East and West Biowalls (MWT-19) and the furthest downgradient monitoring well (MWT-22). Soil samples will be collected using split-spoon samplers at approximately 5-foot intervals from each borehole. A portion of each sample will be used to measure the total ionizable volatile organic compound (VOC) concentration in the soil headspace using a photoionization detector (PID).

At two borehole locations (**Table 4-3**), two soil samples will be collected and submitted to a fixed-base laboratory for analysis of total organic carbon (TOC) using USEPA Method SW9060-modified. At each of these boreholes, one sample will be collected from the till and a second will be collected from the weathered shale. The depth of sample collection for one of these samples will correspond to the screened interval for the newly installed monitoring well, and should be below the existing water table if encountered. Generated soil cuttings will be handled in accordance with the IDW procedures discussed in Section 4.4.

A Parsons field scientist will be responsible for 1) maintaining a detailed descriptive log of all subsurface materials recovered during drilling and any other relevant observations on borehole advancement and 2) recording field measurements. A boring log form is included in **Appendix C**. At a minimum, the descriptive log will contain:

- Sample interval (top and bottom depth) and sample recovery;

- Presence or absence of contamination (e.g., staining, odor, or elevated headspace screening readings);
- Soil description of the target sampling interval, including Unified Soil Classification System (USCS), relative density, color, major textural constituents, minor constituents, porosity, relative moisture content, plasticity of fines, cohesiveness, grain size, structure or stratification, relative permeability, and any other significant observations; and
- The depth of lithologic contacts and/or significant textural changes measured and recorded to the nearest 0.5 foot if present within the sampling intervals.

### **5.1.2 Groundwater Sampling Procedures**

Groundwater sampling activities are summarized in **Tables 4-3** and **4-4**. Groundwater sampling will be conducted by qualified scientists and technicians from Parsons who are trained in groundwater sampling, records documentation, and chain-of-custody procedures. All Site personnel will be 40-hour OSHA trained and subject to other training requirements as outlined in the Project Specific Health and Safety Plan (Parsons, 2005). In addition, sampling personnel will have thoroughly reviewed this work plan prior to sample collection and will have a copy of the work plan available onsite for reference. To maintain a high degree of quality control (QC) during this sampling event, the procedures described below will be followed.

#### **5.1.2.1 Monitoring Well Development**

All monitoring wells will require development prior to sampling. Development removes sediment from inside the well casing and flushes fines from the portion of the formation adjacent to the screen. Development will be accomplished using a bailer or a submersible pump. Newly installed wells will be developed after allowing a minimum of 48 hours for bentonite chips to set.

Development will be continued until 1) a minimum three casing volumes of water have been removed from the well 2) turbidity, pH, temperature, and specific conductance, have stabilized, and 3) the extracted water is visually clear. **Table 5-1** lists the stabilization criteria that will be used to define the acceptable ranges for parameter stabilization over three consecutive readings. Sets of readings will be collected every three to five minutes during purging. Development water will be managed in accordance with Section 4.4.

A development record will be maintained for each monitoring well. The development record will be completed in the field by the field scientist. Development records will include:

- Well number, date, and time of development;

- Development method;
- Pre- and post-development static water levels and total well depth;
- Volume of water removed and a qualitative description of the water produced (turbidity, color, and odor);
- Results of field analytical measurements for the parameters listed in **Table 5-1**.

At a minimum, the development record will include field analytical measurements collected at the start, during, and at the conclusion of the well development procedure described above.

#### **5.1.2.2 Sampling Equipment Decontamination**

All portions of sampling and test equipment that will contact the sample matrix will be thoroughly cleaned before each use. Clean, chemical-resistant gloves will be worn by persons decontaminating tools and equipment. Disposable sampling equipment will be used to the extent possible. All field equipment coming in contact with potentially contaminated soil or water, or used for sampling, will be decontaminated before and after use. Based on the types of sample analyses to be conducted, the following cleaning protocol will be used:

- Wash with potable water and phosphate-free laboratory detergent (e.g., Alconox<sup>TM</sup>);
- Rinse with potable water;
- Rinse with isopropyl alcohol;
- Rinse with distilled water; and
- Allow equipment to air dry prior to use (to the extent practical).

Potable water to be used in equipment cleaning and decontamination will be obtained on site. The Parsons field representative will make the final determination as to the suitability of site water for these activities.

Laboratory-supplied sample containers will be cleaned and sealed by the laboratory. The type of container provided and the method of container decontamination will be documented in the laboratory's permanent record of the sampling event. Any deviations from these procedures will be documented in the field notebook and on the groundwater sampling record.

#### **5.1.2.3 Preparation for Sampling and Equipment Calibration**

All equipment to be used for sampling will be assembled and properly cleaned and calibrated (if required) upon arrival in the field. In addition, all record-keeping materials will be gathered prior to mobilizing to the field.

As required, field analytical equipment will be calibrated according to manufacturers' specifications prior to field use. This applies to equipment used for onsite measurements of DO, pH, specific conductance, ORP, and other field parameters. Initial and daily calibrations will be recorded in the field notebook. In addition the reference electrode utilized for ORP and the appropriate conversion factor will be recorded in the field notebook.

#### **5.1.2.4 Water Level and Total Depth Measurements**

Prior to removing any water from the sampling well, the static water level will be measured. An electric water-level probe will be used to measure the depth to groundwater below the datum to the nearest 0.01 foot. After measuring the static water level, the water-level probe will be slowly lowered to the bottom of the well if the well depth is not known, and the depth will be measured to the nearest 0.01 foot. The water-level probe will be decontaminated using the procedure described in Section 5.1.1.1 prior to inserting the probe into each monitoring well.

#### **5.1.2.5 Low-Flow Purging**

The micropurging method described in the USEPA (1996) low-flow sampling protocol will be used to purge monitoring wells prior to collecting groundwater samples for field and laboratory analysis. The pump intake will be placed at the mid-point of the saturated screened interval prior to purging and sampling. Purging will be continued until a minimum 3 casing volumes of water have been removed from the well and until pH, temperature, specific conductance, DO, and ORP stabilize (**Table 5-1**). If the water remains turbid, purging will continue until the turbidity of the water produced has been stable after the removal of several additional casing volumes. Purge water will be collected and disposed of according to the IDW procedures described in Section 4.4.

A well purge record will be maintained for each monitoring well. The purge record will be completed in the field by the field scientist, and will include:

- Well number, date, and time of purging;
- Purge method and pumping rate;
- Pre-purging water level and well depth
- Water levels measured periodically during the purging process;
- Volume and description of water produced;
- Field analytical measurements, including pH, temperature, specific conductance, DO, and ORP.

#### **5.1.2.6 Sample Extraction**

A peristaltic pump, submersible sampling pump, or disposable bailer (if low-flow purging is not practical due to the low permeability of the formation) will be used to extract groundwater samples. Extracted groundwater will be transferred directly into the appropriate sample containers. The water will be carefully poured down the inner walls of the sample container to minimize aeration of the sample. Unless other instructions are given by the analytical laboratory, sample containers will be completely filled so that no air space remains in the container.

If a groundwater monitoring well is evacuated to a dry state during purging, the monitoring well will be allowed to recharge, and the sample will be collected as soon as sufficient water is present to obtain the necessary sample quantity. Sample compositing or sampling over a lengthy period by accumulating small volumes of water at different times to obtain a sample of sufficient volume will not be permitted.

#### **5.1.3 Sampling Procedures for Backfill Materials**

The sand and mulch that will be used to create the backfill mixture will be inspected by Parsons personnel before and after mixing as described below.

##### **5.1.3.1 Inspection of Backfill Materials**

Samples and gradation curves for washed sand will be procured from local suppliers to choose a suitable material that is poorly-graded, medium or coarse sand, with little or no fine-grained materials (i.e., fine sands, silts, clays). The Parsons field scientist will inspect sand delivered to the site and either approve or reject the sand for use in the use of this material in the backfill mixture. Gradation analysis of a minimum of two grab samples from the sand borrow pile(s) will be used to confirm that visual inspection of the sand is consistent with the specifications provided by the material supplier.

Samples of mulch will be procured from local suppliers to inspect the suitability of this material for inclusion in the backfill mixture. Characteristics that will be visually inspected include the approximate percentage of green material within the mulch mixture and the size distribution of mulch components. In the event that the percentage of green material appears to be insufficient (e.g. non-existent) to supply adequate quantities of nitrogen, phosphorous, potassium, iron, and other minerals, the mulch samples may be sent to a laboratory for analysis for TKN nitrogen using Method SM 4500 and iron, potassium, and phosphorous using Method SW-6010B. Alternately, locally available sources of green organic material (e.g., silage, alfalfa) may be identified and specified for mixing with the backfill material to increase its percentage up to 10 percent of the total volume of the backfill mixture.

### **5.1.3.2 Inspection of Mulch Mixture Homogenization**

Parsons personnel will visually inspect the backfill mixing process to determine when the mixture is adequately homogenized. Following a visual determination of homogenization, a minimum of three grab samples will be collected and analyzed in the field for the volume and weight ratio of sand to organic material. Note that organic material included in this analysis will include both mulch and any green organic material that is added to the backfill mixture. The target volumetric mulch mixture ratio of 50 percent organic material and 50 percent sand, with an allowable variation of  $\pm 10$  percent. Weight percentage will be used as a secondary criterion for evaluating mulch mixture homogeneity, with densities of individual mulch mixture components measured in the field as wet density. A target range for mulch mixture density will then be calculated using these wet densities and the range of acceptable volume ratios.

The mulch mixture QC will be performed by collecting approximately five liters sample of the mixture and passing it through a number 6 mesh sieve (0.132 inch opening). Material passing the number 6 mesh sieve is anticipated to be mostly sand, with some fine-grained organics from the mulch material. Material retained on the number 6 mesh sieve is anticipated to primarily be organic material. The volume and weight measurements for percent passing and percent retained on the number 6 mesh sieve will be recorded in the field. If either the volumetric or weight percentage of all samples is within the tolerances described above, the mulch mixture will be accepted as sufficiently mixed for placement as the backfill material. In the event that neither the volumetric or weight percentage of one or more samples is within the acceptable range of values, the mulch mixture will be mixed again to determine if insufficient mixing is the cause of this discrepancy. In the event that continued mixing does not result in the achievement of an acceptable mixture composition, addition of the material which is lean in the mixture will be performed to achieve an acceptable mixture ratio for the backfill material.

### **5.1.4 Laboratory Analyses**

Laboratory analyses will be performed on collected soil and groundwater samples as well as the QA/QC samples described in Section 5.2.4. The analytical methods for these sampling events are listed in **Table 5-2**. Prior to sampling, the laboratory will provide a sufficient number of analyte-appropriate sample containers for the samples to be collected. **Table 5-3** lists the appropriate sample containers and preservation for groundwater samples for laboratory analyses. All analytical samples will be immediately packed on ice and shipped to the appropriate lab for analysis.

Laboratory personnel will specify the necessary laboratory QC samples and prepare appropriate QC sample containers. For samples requiring chemical preservation, preservatives will be added to

containers by the laboratory. Containers and ice chests with adequate padding will be provided by laboratory personnel.

### **5.1.5 Groundwater Field Analyses**

As indicated in **Table 5-2**, many of the groundwater chemical parameters will be measured onsite by field personnel. Some of the measurements will be made with direct-reading meters (e.g., Horiba U-22XD), while others will be made using a Hach<sup>®</sup> portable colorimeter or titration kit in accordance with manufacturer-specified procedures. These procedures are described in the following subsections. User manuals and Hach analyses for direct-reading meters are included in the SEDA SAP. Additional Hach analyses specific to this work plan are included in **Appendix B**.

Samples will be collected after stable conditions have been obtained. All glassware or plasticware used in the field analyses will have been cleaned prior to sample collection by thoroughly washing with a solution of Alconox<sup>®</sup> and water, and rinsing with distilled water and isopropyl alcohol to prevent interference or cross contamination between measurements.

If concentrations of an analyte are greater than the range detectable by the titrimetric or colorimetric method, the analysis will be repeated by diluting the groundwater sample with distilled water until the analyte concentration falls to a level within the range of the method. All rinsate and sample reagents accumulated during groundwater analysis will be collected, combined with purge water, and disposed of according to the residuals management plan described in Section 4.4.

#### **5.1.5.1 Dissolved Oxygen Measurements**

DO measurements will be made using a meter with a sensor in a flow-through cell or a downhole oxygen sensor. Multiple measurements will be taken before groundwater sample acquisition during well purging, with the final measurement made immediately prior to completion of the well purge. DO measurements will be recorded on the groundwater sampling record (**Appendix C**). At a minimum of two monitoring well locations, the stabilized DO concentration will also be measured using a colorimetric indicator test (i.e., CHEMetrics Method K-7512 or equivalent) to confirm the accuracy of the DO meter. In the event that the concentration measurements by the DO meter and colorimetric test do not agree, the colorimetric test will be repeated and the calibration of the DO meter will be checked to identify and correct the reason for the discrepancy between readings.

#### **5.1.5.2 pH, Temperature, and Specific Conductance**

Because pH, temperature, and specific conductance of a groundwater sample can change significantly within a short time following sample acquisition, these parameters will be measured in the field in a

flow-through cell during the purging process. The measured values will be recorded in the groundwater sampling record.

#### **5.1.5.3 Carbon Dioxide Measurements**

Carbon dioxide is a byproduct of biological reactions and can be used to evaluate the bioactivity of the groundwater system. Carbon dioxide will be measured in the field via titrimetric analysis using USEPA-approved Hach<sup>®</sup> Method 8205 (0 to 1,000 mg/L), or equivalent. This method is included in **Appendix B**.

#### **5.1.5.4 Alkalinity Measurements**

Alkalinity in groundwater helps buffer the groundwater system against acids generated through both aerobic and anaerobic biodegradation processes. Alkalinity of the groundwater sample will be measured in the field via titrimetric analysis using USEPA-approved Hach<sup>®</sup> Method 8203 (0 to 40 mg/L, or 40 to 400 mg/L, as calcium carbonate), or equivalent. This method is included in **Appendix B**.

#### **5.1.5.5 Sulfate and Hydrogen Sulfide Measurements**

Sulfate in groundwater is a potential electron acceptor for biodegradation in anaerobic environments, and sulfide is produced during sulfate reduction. Sulfate will be measured in the laboratory (**Table 5-2**). Hydrogen sulfide concentrations will be measured in the field via colorimetric analysis with a Hach<sup>®</sup> DR/700 Portable Colorimeter or equivalent using USEPA-approved Hach<sup>®</sup> Method 8131 (0 to 0.60 mg/L hydrogen sulfide) or equivalent.

#### **5.1.5.6 Ferrous Iron Measurements**

Iron is an important trace nutrient for bacterial growth, and different states of iron can affect the ORP of the groundwater and act as an electron acceptor for biological metabolism under anaerobic conditions. Ferrous iron concentrations will be measured in the field via colorimetric analysis with a Hach<sup>®</sup> DR/700 Portable Colorimeter or equivalent after appropriate sample preparation. Hach<sup>®</sup> Method 8146, or equivalent, for ferrous iron (0 to 3.0 mg/L) will be used to prepare and analyze the samples. This method is included in **Appendix B**.

#### **5.1.5.7 Manganese Measurements**

Manganese is a potential electron acceptor in anaerobic environments. Manganese concentrations will be quantitated in the field using colorimetric analysis with a Hach<sup>®</sup> DR/700 Portable Colorimeter. USEPA-approved Hach<sup>®</sup> Method 8034 (0 to 20.0 mg/L), or equivalent, will be used to prepare the samples for quantitation of manganese concentrations. This method is included in **Appendix B**.



#### **5.1.5.8 Oxidation/Reduction Potential**

The ORP of groundwater is an indicator of the relative tendency of a solution to accept or transfer electrons. Reduction/oxidation (redox) reactions in groundwater are usually biologically mediated; therefore, the ORP of a groundwater system reflects the prevailing biogeochemical processes that are occurring. ORP measurements can be used to provide real-time data on biogeochemical conditions within the contaminant plume, especially in areas undergoing anaerobic biodegradation.

The ORP of a groundwater sample can change significantly within a short time following sample acquisition and exposure to atmospheric oxygen. Therefore, this parameter will be measured in a flow-through cell.

#### **5.1.6 Field Quality Assurance/Quality Control Procedures**

Field QA/QC procedures will include 1) collection of field duplicate and matrix spike/matrix spike duplicate (MS/MSD) samples, 2) decontamination of all non-dedicated equipment that contacts the sample medium before and after each use, 3) use of analyte-appropriate containers, and 4) use of chain-of-custody procedures for sample handling and tracking. All samples to be transferred to the laboratory for analysis will be clearly labeled to indicate sample number, location, matrix (e.g., groundwater), and analyses requested. Samples will be preserved in accordance with the analytical methods to be used, and water sample containers will be packaged in coolers with ice to maintain a temperature of 4 degrees Celsius (°C) or less.

Each field duplicate water sample will be collected concurrently with, and by the same method as, the primary sample. MS/MSDs will be prepared in the laboratory and used to establish matrix effects for samples analyzed for VOCs. Sufficient extra sample volume will be submitted to the laboratory to allow MS preparation and analysis.

All field sampling activities will be documented in a bound, sequentially-paginated field notebook in permanent ink. All sample collection entries will include the date, time, sample locations and numbers, notations of field observations, and the sampler's name and signature. Field QA/QC samples will be collected in accordance with the program described Section 5.2.4.

#### **5.1.7 Handling of Samples for Laboratory Analysis**

This section describes the handling of samples from the time of sampling until the samples are delivered to the laboratory.

##### **5.1.7.1 Sampling Records**

To provide complete documentation of the sampling event, detailed records will be maintained by the field scientist. At a minimum, these records will include the following information:

- Sample location (facility name) and sample station identification;
- Date and time of sampling;
- Sampling method;
- Field observations of sample appearance and odor;
- Weather conditions;
- Water level prior to purging (groundwater samples only);
- Monitoring well depth (groundwater samples only);
- Purge volume (groundwater samples only);
- Monitoring well condition (groundwater samples only);
- Sampler's identification;
- Field measurements; and
- Any other relevant information.

Groundwater sampling information will be recorded on a groundwater sampling form (**Appendix C**).

#### **5.1.7.2 Sample Preservation**

The laboratory will add any necessary chemical preservatives prior to shipping the sample containers to the field. Samples will be prepared for transportation to the analytical laboratory by placing the samples in a cooler containing ice to maintain a shipping temperature of 4 °C or lower.

#### **5.1.7.3 Sample Identification**

The field sample identification code provides the tracing of the sample from the location in the field, through laboratory analysis, and finally to data evaluation and presentation. Each sample will be assigned a unique field sample identification code and labeled accordingly. This field sample identification code will contain information traceable to the site, location, date, and other appropriate information (e.g., MS/MSD) unique to that sample. This code will be used for all references to this particular sample in all field and project documentation and reports.

Samples collected during this pilot study will each be assigned a unique field sample identification code using an alphanumeric system. Each sample identification number will consist of a segmented alphanumeric code that identifies the sampling location, the sample identifier, the type of sample, the date, and the QC identifier. Sample numbers will be assigned as described below.

- Location Designation. The first four characters represent the location within the sites where the samples are obtained. For example, a groundwater sample collected at monitoring well location MWT-12 would use the location identification of “MWT12.” Field duplicate samples will be given a fictitious number so that the laboratory is unaware which primary sample it is duplicating.
- Matrix Code. The next two characters indicate the sample matrix. The following are the codes that will be used during this investigation:

SO = Soil      GW = Groundwater      MU = Mulch

- Sample Depth. The next set of numerals will indicate the depth below the surface to the top of the soil sample collection interval in feet and tenths of feet (e.g., 2.5 or 17.5; this part of the code is used only for soil samples).
- Sample Date. The next set of characters represents the field sample date. A 6-digit code (MM-DD-YY) will be used for all samples during this investigation.
- Laboratory matrix spike and matrix spike duplicates. A sample submitted as a MS/MSD will be identified together with the primary sample, but designated as an MS/MSD sample type.

As an example, for a groundwater sample collected from well MW-12 on 15 June 2005, the sample number would be:

**MWT12-GW-061505**

A sample submitted as a MS/MSD would be identified by:

**MWT12-GW-061505 (MS/MSD)**

#### **5.1.7.4 Sample Container and Labels**

Sample containers will be filled and the container lids will be tightly closed. The sample label will be firmly attached to the container side, and the following information will be legibly and indelibly written on the label:

- Facility name and sample station identification;
- Sample type (e.g., groundwater, soil, mulch);
- Sampling date;
- Sampling time;
- Preservatives added;

- Sample collector's initials; and
- Analyses requested.

#### **5.1.7.5 Sample Shipment**

After the samples are sealed and labeled, they will be packaged for transport to the laboratory. The packaged samples will be delivered to the laboratory as soon as possible (within holding limits) after sample collection.

The following packaging and labeling procedures will be followed:

- Package sample so that it will not leak, spill, or vaporize from its container;
- Cushion samples to avoid breakage; and
- Add ice to container to keep samples cool.

#### **5.1.7.6 Chain-of-Custody Control**

For laboratory analysis, chain-of-custody forms will be completed for each shipment of samples to track the movement of samples and to provide a written record of all persons handling the samples. The chain-of-custody form will include sample information (sample identification, type, date, and time of collection), analyses requested, and the signature of each person receiving and relinquishing the samples.

The "Remarks" column of the chain-of-custody form will be used to record additional information which may be of use to the laboratory for prescreening the samples. When transferring samples, the individuals relinquishing and receiving the samples will sign, date, and note the time on the chain-of-custody form.

The original chain-of-custody form will accompany the samples to the laboratory. The laboratory will make and maintain a file copy, and the completed original will be returned to the project manager as a part of the final analytical report. This record serves to document sample custody transfer from the sampler to the shipper, and to the laboratory.

#### **5.1.8 Aquifer Testing**

To evaluate the impact of the bioremediation processes on the hydraulic conductivity of the aquifer and biowall, slug tests will be conducted at five of the proposed groundwater monitoring locations. A slug test is a single-well hydraulic test used to determine the hydraulic conductivity of an aquifer in the immediate vicinity of the screened interval of the tested well. Slug tests can be used for both confined and unconfined aquifers that have a transmissivity of less than 7,000 square feet per day.

Slug testing can be performed using either a rising head or a falling head test; at this site, both methods will be used in sequence.

Slug tests will be conducted immediately following development of newly installed monitoring wells to establish baseline conditions. An additional slug test will be performed during the 22-week monitoring event. The monitoring locations to that will be tested are identified in **Tables 4-3** and **4-4**.

#### **5.1.8.1 Definitions**

- **Hydraulic Conductivity (K).** A quantitative measure of the ability of porous material to transmit water; defined as the volume of water that will flow through a unit cross-sectional area of porous or fractured material per unit time under a unit hydraulic gradient.
- **Transmissivity (T).** A quantitative measure of the ability of a given thickness of an aquifer to transmit water. It is the product of the hydraulic conductivity and the saturated thickness of the water-bearing zone.
- **Slug Test.** Two types of tests are possible: rising head and falling head. A slug test generally consists of adding a slug of water or a solid cylinder of known volume to the well to be tested or removing a known volume of water or cylinder and measuring the rate of recovery of water level inside the well. The slug of a known volume acts to raise or lower the water level in the well.
- **Rising Head Test.** A test used in an individual well within the saturated zone to estimate the hydraulic conductivity of the surrounding formation adjacent to the screened interval by lowering the water level in the well and measuring the rate of recovery of the water level. The water level may be lowered by removing a quantity of water or a submerged solid slug from the well.
- **Falling Head Test.** A test used in an individual well to estimate the hydraulic conductivity of the surrounding formation adjacent to the screened interval by raising the water level in the well by insertion of a solid slug or quantity of water, and then measuring the rate of drop in the water level.

#### **5.1.8.2 Equipment and Materials**

The following equipment will be used to conduct a slug test:

- Teflon<sup>®</sup>, PVC, or metal slugs;
- Nylon or polypropylene rope;
- Electric water-level indicator;

- Pressure transducer/sensor;
- Field logbook/forms; and
- Automatic data recording instrument (e.g., Hermit Environmental Data Logger<sup>®</sup>, In-Situ, Inc. Model SE3000, or equivalent).

#### **5.1.8.3 General Test Methods**

Hydraulic testing will be completed on wells that have been properly developed and in which water levels have stabilized. During the slug test, the water level change should be influenced only by the introduction (or removal) of the slug volume. Other factors, such as inadequate well development or extended pumping, may lead to inaccurate results. The Parsons field scientist will determine when static equilibrium has been reached in the well. The pressure transducer, slugs, and any other downhole equipment will be decontaminated prior to and immediately after the performance of each slug test using the procedures described in Section 5.1.2.2. Because the aquifer that will be tested at the Ash Landfill site is unconfined, two rising head slug tests (rather than one rising head and one falling head slug test) will be performed to access hydraulic information.

#### **5.1.8.4 Rising Head Test**

Two rising head test will be performed at each selected monitoring location. The following steps describe the rising head slug test procedure:

1. Decontaminate all downhole equipment prior to initiating the test.
2. Open the well. Where wells are equipped with water-tight caps, the well should be unsealed at least 24 hours prior to testing to allow the water level to stabilize. The protective casing will remain locked during this time to prevent vandalism.
3. Prepare the aquifer slug test data form with entries for:
  - Well number, project number, and project name,
  - Aquifer testing team,
  - Climatic data,
  - Top of well casing elevation,
  - Identification of measuring equipment being used,
  - Static water level, and
  - Date.

4. Measure the static water level in the well to the nearest 0.01 foot.
5. Lower the decontaminated pressure transducer into the well and allow the displaced water to return to its static level. This can be determined by periodic water-level measurements until the static water level in the well is within 0.01 foot of the original static water level.
6. Lower a decontaminated or new, disposable bailer into the well and allow the bailer to completely fill with water.
7. Re-measure the static water level in the well to the nearest 0.01 foot to determine when the water level in the well has restabilized to within 10 percent of the original static water level.
8. Turn on the data logger and quickly lower the slug below the water table, being careful not to disturb the pressure transducer. Follow the user's manual for proper operation of the data logger.
9. Initiate data recording and quickly withdraw the bailer from the well.
10. Terminate data recording when the water level stabilizes in the well, and remove the pressure transducer from the well and decontaminate. The well will be considered stabilized for termination purposes when it has recovered to within 10 percent of the original static water level.

#### **5.1.8.5 Slug Test Data Analysis**

Data obtained during slug testing will be analyzed using the method of Bouwer and Rice (1976) and Bouwer (1989) for unconfined conditions.

## **5.2 QUALITY ASSURANCE PROJECT PLAN**

This QAPP is designed to provide data quality assurance objectives (DQAOs) specific to the pilot study for bioremediation of chlorinated solvents in groundwater using a permeable mulch biowall at the Ash Landfill, SEDA, Romulus, NY. This QAPP conforms to the requirements of the AFCEE QAPP Version 4.0.01 and was developed to address the AFCEE requirements for precision, accuracy, representativeness, completeness, and comparability (PARCC) of water, soil, and mulch data collected and generated during this pilot study. Data collection, field and laboratory analysis, and data management will be conducted in accordance with the procedures described in this QAPP, and in the following documents:

- *Seneca Army Depot Activity Sampling and Analysis Plan - Draft*, (Parsons 2005);
- *Air Force Center for Environmental Excellence Quality Assurance Plan, Revision 4.0.01* (AFCEE, 2005).

- *Data Quality Objectives Process for Hazardous Waste Site Investigations* (USEPA, 2000b).

Project-specific DQAOs are designed to ensure that data of adequate quality are collected to support project decisions. This section describes the project-specific requirements that ensure that the project and analytical DQAOs are met. Chemical data will be of sufficient quality to accurately evaluate the Ash Landfill Pilot Study. The chemical analyses to be performed under this project are listed in **Table 5-2**. The media to be sampled during implementation of this project include subsurface soil, groundwater, and the mulch backfill to be placed in the trenches. After all samples are analyzed, the Parsons project chemist will review the data for completeness and usability of the data.

### **5.2.1 Analytical Methods**

Laboratory analyses will be performed on collected soil and groundwater samples as well as the QA/QC samples described in Section 5.1.4. The analytical methods for these sampling events are listed in **Table 5-2**. The primary site-specific chemicals of concern are chlorinated solvents.

Prior to sampling, the laboratories will provide a sufficient number of analyte-appropriate sample containers for the samples to be collected. All containers, preservatives, and shipping requirements will be consistent with USEPA or other appropriate protocol. For samples requiring chemical preservation, preservatives will be added to containers by the laboratory. Containers and ice chests with adequate padding will be provided by laboratory personnel.

#### **5.2.1.1 Analytical Procedures**

The analytical program for this project will consist of both field-based screening analyses for groundwater, off-site (fixed-base) laboratory definitive analyses of subsurface soil, mulch, and groundwater samples, and associated QA/QC samples (e.g., field duplicates and trip blanks). **Table 5-2** lists the analytical parameters and analytical methods to be used for each of the environmental media to be sampled.

#### **5.2.1.2 Analytical Protocols for Analytes Not Listed in the Seneca SAP**

This section provides descriptions of analytical methods are not included in the Seneca SAP (Parsons, 2005). These methods are provided in **Appendix A** of this document.

##### **5.2.1.2.1 Methane, Ethane, and Ethane Microseeps SOP AM20-GAX**

Methane, ethane, and ethene samples collected as part of this study will be analyzed via the Microseeps, Inc. internal standard operating procedure (SOP) AM20-GAX. Method AM20-GAX is an analysis method that uses a gas chromatograph to analyze head space samples collected from the sample vials. The Microseeps SOPs will be utilized instead of the more common USEPA-approved RSK-175 method because the Microseeps methods are capable of detecting ethene and ethane at



much lower concentrations than the RSK-175 method. The AM20-GAX method SOP is available upon request. Very low detection limits are important for these compounds because ethene and ethane are produced in low concentrations during the reductive dechlorination of chlorinated ethenes.

The Microseeps methods are not USEPA approved and Microseeps does not possess the capability to produce all of the QC documentation and testing normally required for environmental samples. However, since methane, ethene, and ethane data will only be used to support conclusions arrived at through the analysis of VOC data, the lack of complete QC is of little consequence. The detection limits and project quantitation limits for methane, ethene, and ethane that the Microseeps methods are capable of attaining are summarized in **Table 5-4**.

#### **5.2.1.2.2 Volatile Fatty Acids by Microseeps SOPs**

Volatile fatty acids (VFAs) will be analyzed using Microseeps internal SOPs. The VFAs pyruvic, lactate, formate, acetate, propionate, and butyrate are used as biomarkers of anaerobic metabolism. Anaerobic bacteria produce these compounds through the fermentation of organic material. In the case of this pilot study the organic material will consist primarily of mulch.

VFAs are soluble and will tend migrate with advective groundwater flow. VFAs are also readily consumed by microbial activity. Analyzing the spatial and temporal distribution of VFA content in groundwater gives a good indication of microbial activity and impact of substrate addition to the treatment zone.

#### **5.2.1.2.3 Field Analyses Using USEPA-approved Field Methods**

Manganese, hydrogen sulfide, alkalinity, carbon dioxide, and ferrous iron will be analyzed in the field using various methods developed by the Hach<sup>®</sup> Company. These analytes will be analyzed in the field because they are indicator parameters that will be used only to support conclusions drawn from the other laboratory analytical data. The majority of these analytes also have short holding times that make them difficult to measure accurately by sample collection, storage, transport, and analysis in an offsite laboratory. The SOPs provided by Hach<sup>®</sup> are available upon request.

### **5.2.2 Data Quality Assurance Objectives**

The project scope and performance objectives are described in Section 3; analytical DQAOs are described in this section. This QAPP has been developed for use in conjunction with the environmental sampling activities for this project and describes the QA/QC procedures and protocols that will be used. The QAPP serves as a controlling mechanism during these investigations to ensure that all data collected are valid, reliable, and defensible. Analytical data quality levels, project QA

objectives, DQAOs and data quality indicators (DQIs) are described in this section. No criteria are set for geochemical analyses or measurements made directly in the field with field instruments.

The laboratory shall follow the appropriate method and program requirements so that the data quality is acceptable and can be used to support future decisions. The analytical DQAOs for this field investigation shall be met when the quality of the sample data meet the requirements defined in this QAPP. The analytical DQAOs for the site shall support the identification of chlorinated solvents in soil and groundwater, and characterization of site geochemical conditions.

#### **5.2.2.1 Analytical Data Quality Levels**

Analytical data quality is specified in terms of levels defined in the AFCEE QAPP, Version 4.0. The two general categories of data used by the AFCEE are defined as: (1) screening data and (2) definitive data. For this pilot study, the following analytical levels will be used as indicated:

- Screening data: Field screening analyses using portable instruments will be used for selected analyses including geochemical indicator parameters. These analytical methods will generate screening data of appropriate quality to support the intended data use. For example, screening level analytical methods will be used to determine the presence and concentration of groundwater geochemical parameters such as pH, ORP, DO, carbon dioxide, conductivity, temperature, alkalinity, ferrous iron, manganese, and hydrogen sulfide. These data will be used to monitor the whether geochemical conditions are appropriate for *in situ* bioremediation of CAHs.
- Definitive data: Definitive analyses will be performed in off-site analytical laboratories. These analytical methods will generate definitive data of appropriate quality to support the intended data use. The analytical laboratories will provide “definitive” data packages that would allow a definitive data validation process to be adequately completed. Laboratory data qualifiers are listed in the AFCEE QAPP Version 3.1. Definitive analytical methods will be used to determine concentrations of VOCs and certain geochemical parameters not practically determined using screening level analyses, such as TOC, nitrate + nitrite, sulfate, and chloride.

The QA program designed for this project addresses quality objectives for both sampling and laboratory methodology. Field QA efforts are aimed at assuring that samples are representative of the conditions in the various environmental media at the time of sampling. Laboratory QA efforts are aimed primarily at assuring that validated data packages provide sufficient PARCC to quantify contaminant levels in environmental samples.

### **5.2.2.2 Analytical Data Quality Objectives**

Analytical Data Quality Objectives (ADQOs) specify the data type, quality, quantity, and uses needed to make decisions and are the basis for designing data collection activities. ADQOs are based on the use of the data and include consideration of PARCC DQIs. The process of establishing and evaluating achievement of the project-specific ADQOs is a systematic process for generating environmental data that will be sufficient for their intended use. The analytical parameters and rationale that support the project ADQOs are defined in **Table 5-5**.

### **5.2.2.3 Data Quality Assessment**

The data assessment activities incorporated into this project will be used to maintain the accuracy, precision, comparability, and representativeness of data collected during this pilot study. These activities include frequent equipment calibration, blind duplicate analyses, MS/MSD analyses, and laboratory blank and duplicate analyses. Data quality will be determined by measuring data accuracy, precision, and completeness.

### **5.2.3 Sample Custody and Sample Management**

The following subsections describe sample custody and handling procedures. Sample custody documentation procedures described in this section will be followed throughout all sample collection activities during this pilot study. Components of sample custody procedures include the use of field logbooks, sample labels, and chain-of-custody forms.

#### **5.2.3.1 Sample Containers, Volumes, Preservation, and Holding Times**

All physical samples obtained at the site will be placed in an appropriate sample container for preservation and shipment to the designated laboratory. Section 5.1.4 of this project SAP discusses, and **Table 5-3** summarizes, the appropriate type and number of sample containers, preservatives, and holding times for soil and aqueous samples.

#### **5.2.3.2 Sample Identification**

Section 5.1.6.3 of this project SAP summarizes the project sample identification procedures.

#### **5.2.3.3 Sample Packaging and Shipping**

Sections 5.1.6.4 and 5.1.6.5 of this project SAP summarize the project sample packaging and shipping procedures.

#### **5.2.3.4 Sample Custody**

Chain-of-custody records provide a means of tracing each sample from the time of collection through shipment and final analysis, producing a written record of all persons handling the samples. A sample is defined as being under one's custody if it is in one's possession or in view after being in

one's possession or if that person locked the sample up or put it in a designated secure area. Section 5.1.6.6 of this project work plan summarizes sample custody procedures.

#### **5.2.4 Quality Control Samples**

Field QA/QC procedures will include collection of field duplicates and trip blanks; decontamination of all equipment that contacts the sample medium before and after each use; use of analyte-appropriate containers; and chain-of-custody procedures for sample handling and tracking. Field QC samples will be collected in accordance with the program summarized in **Table 5-6**. QA/QC sampling will include collection and analysis of duplicate groundwater samples, trip blanks, and MS/MSD samples. Internal laboratory QC procedures will involve the analysis of laboratory control samples (LCSs) and laboratory method blanks (LMBs).

##### **5.2.4.1 Field Duplicates**

A field duplicate sample is a second sample collected at the same location as the original sample. Duplicate samples are collected simultaneously or in immediate succession, using identical recovery techniques, and treated in an identical manner during storage, transportation, and analysis. Duplicate sample results are used to assess precision of the sample collection process. The duplicate sample is submitted to the primary laboratory as a “blind” duplicate and also serves the purpose of measuring the primary laboratory’s precision for a specific method and matrix.

Duplicate groundwater samples will be collected at a frequency of 1 for every 20 or fewer samples of similar matrix. Each duplicate water sample will be collected concurrently with, and by the same method as, the primary sample. Duplicate water samples will be analyzed for VOCs and geochemical parameters (i.e., methane, ethane, and ethene; TOC; nitrate + nitrite; dissolved inorganics; chloride; sulfate; and mobile field analyses).

##### **5.2.4.2 Matrix Spike and Matrix Spike Duplicates**

Matrix spikes will be prepared in the laboratory and used to establish matrix effects for samples analyzed for VOCs. Sufficient extra sample volume will be submitted to the laboratory to allow matrix spike preparation and analysis. MS and MSD analyses will be performed at a frequency of one per every twenty VOC samples. Field personnel will designate on the chain of custody the particular samples the laboratory is to perform these analyses on.

##### **5.2.4.3 Trip Blanks**

Trip blanks are used to assess the potential introduction of contaminants from sample containers or during the transportation and storage procedures. A trip blank will be analyzed to assess the effects of ambient conditions on sampling results during the transportation of samples. The water trip blank

will consist of a VOC sample vial filled in the laboratory with ASTM Type II reagent grade water, transported to the sampling site, handled like an environmental sample and returned to the laboratory for analysis. Trip blanks are not opened in the field. Trip blanks are prepared only when VOC samples are taken and are analyzed only for VOCs. One trip blank will be transported inside each sample shipment containing samples for VOC analysis.

#### **5.2.4.4 Laboratory Control Spikes and Laboratory Method Blanks**

LCSs and LMBs will be prepared internally by the laboratory and will be analyzed each day samples that from the sites are analyzed. Samples will be reanalyzed in cases where the LCS or LMB are out of the control limits. Control charts for LCSs and LMBs will be developed by the laboratory and monitored for the analytical methods used.

#### **5.2.5 Data Quality Assessment**

Upon completion of all field and analytical work, the quality of data generated as part of this pilot study will be assessed. This includes a review of field and analytical data. Formal data validation will not be performed.

##### **5.2.5.1 Review of Field Data**

The Parsons field team leader, project chemist, and project manager shall ensure that all field records are evaluated for the following:

- Completeness of field records. A check of field record completeness will ensure that all requirements for field activities in the statement of work (SOW) have been fulfilled, complete records exist for each field activity, and that the procedures specified in this QAPP have been followed. Field documentation will ensure sample integrity and provide sufficient technical information to recreate each field event.
- Identification of anomalous field test data. Anomalous field data shall be identified and explained to the extent possible. For example, headspace readings obtained at one boring location that are significantly higher than at any other boring shall be explained in the technical report.
- Accuracy and precision of field data and measurements. The assessment of the quality of field measurements shall be based on instrument calibration records and a review of any field corrective actions. The accuracy and precision of field measurements shall be discussed in the technical report.

Field record review is an ongoing process. Field team leaders will be responsible for ensuring that proper documentation is recorded during each site's sampling activities.

### **5.2.5.2 Review of Laboratory Data**

All laboratory data shall be reviewed by laboratory personnel. The establishment of method detection and control limits shall be documented and verified. Any data outside the acceptable range specified in the analytical methods shall be identified. Any trends or problems with the data shall be evaluated. The absence of records supporting the establishment of control criteria and detection limits shall also be noted. Analytical batch quality control, calibration check samples, method calibrations, continuing calibration verifications, corrective action reports, the results of reanalysis, sample holding times, sample preservations, and any re-sampling and analysis shall all be evaluated by the laboratory.

Samples associated with out-of-control QC data will be identified in the technical report, and an assessment of the utility of such analytical results will be made. The check of laboratory data completeness shall ensure that complete records exist for each analysis and the associated QC samples, and procedures specified in the laboratory QAP have been implemented.

An analyst (lab review analyst) other than the original data processor will be responsible for reviewing all steps of the laboratory data processing. Each page of checked data shall be signed and dated by the verifier.

### **5.2.5.3 Data Reporting**

This subsection describes the processes that will be used to review and report the analytical data.

#### **5.2.5.3.1 Field Reporting**

Field reporting procedures are described in Section 5.1 of this SAP.

#### **5.2.5.3.2 Laboratory Data Verification and Reporting**

All analytical data will be verified prior to being released by the laboratory. Laboratory data verification will consist of reviewing the data for technical validity. Reporting of analytical results for this project will include environmental and QC sample analysis data in hard copy format, as well as a computer disk containing Environmental Resources Program Information Management System (ERPIMS)-formatted data. Analytical hardcopy reports will contain the following items:

- Case narrative,
- Laboratory name,
- Client name,
- Date of issue,
- Parsons project identification number,
- Field sample identification,

- Laboratory assigned sample number,
- Sample matrix description,
- Analytical method description and reference citation,
- Individual parameter results (including second column and primary results where appropriate),
- Date of analysis (extraction dates, first run, and any subsequent runs),
- Method detection limits achieved,
- Concentration units,
- Dilution or concentration factors,
- Corresponding QC report, and
- Corrective action report.

Laboratory QA/QC deliverables include two hardcopies and an electronic deliverable in ERPIMS format. QC data are recorded on the QC report forms for the appropriate tests and correlated to the analysis results by the laboratory lot control numbers. QC reports will contain the following items:

- Narrative describing any noncompliant samples,
- Initial and continuing calibration results,
- Method blank,
- LCS,
- Surrogate results, and
- MS/MSD results.

The Parsons project chemist will review all laboratory data packages. Any reports that are rejected as incomplete or in error will be returned to the laboratory for correction. The laboratory shall submit a revised, corrected report within two weeks of notification of a rejected report.

#### **5.2.5.4 Parsons Data Review and Reporting**

Using the reviews of field records and laboratory analyses, the data collected will be reviewed for any results that are not representative of environmental conditions (because they were generated through poor field or laboratory practices), and these samples shall not be used in the site evaluation process. This determination shall be made using the professional judgment of a multidisciplinary team (e.g.,

chemists, hydrologists, other scientists, and engineers), and other personnel having direct experience with the data collection effort. This coordination is essential for the proper evaluation of that data. The usefulness of historical data will also be evaluated.

Formal validation of the laboratory data using AFCEE QAPP guidelines for review and validation for definitive data will not be performed under this project's scope of work. The data will be collected, analyzed, and reported in a format that will allow a data review. Field screening data will be evaluated in a manner suitable for the intended data uses.

The project-specific data review will include evaluation of:

- Case narrative information,
- Chain-of-custody forms,
- Holding times,
- Method calibration limits,
- Laboratory-established detection limits and reporting limits (RLs) or practical quantitation limits (PQLs),
- Method blanks,
- Laboratory QC sample results (LCS, replicate samples)
- Analytical batch control records, including recoveries for spike and spike duplicate results,
- Surrogate spike results,
- Internal standards recovery,
- Corrective actions, and
- Completeness of data.

#### **5.2.6 Data Deliverables**

The data deliverables required for this project are to be provided in both hard-copy and electronic format. The laboratory will be required to provide two copies of each hard-copy data reporting package.

To facilitate data handling and management, laboratory data will be entered into electronic format. All data will be delivered from the laboratory in the database format specified in the *AFCEE Environmental Resources Program Information Management System (ERPIMS) Data Loading*



*Handbook*, Version 4.0. The laboratory will be responsible for running the ERPTools<sup>®</sup> software on the analytical data files prior to delivery.

## **SECTION 6**

### **DATA ANALYSIS, INTERPRETATION, AND REPORTING**

#### **6.1 DATA ANALYSIS AND INTERPRETATION**

Parsons will compile, analyze, and interpret field test data after the 5-month process monitoring event. Parsons will evaluate and provide defensible conclusions regarding, but not limited to: the efficiency of electron donor utilization for reductive dechlorination as compared to metabolic (e.g., sulfate reduction, methane production) and anabolic (i.e., biomass growth) processes; growth and development of microbial populations; magnitude and composition of TOC in the biowall; effective zone of influence; apparent electron donor requirements; observed changes in site-geochemistry; actual/significant changes in contaminant concentrations and mass (considering volatilization, dilution, degradation, and daughter product formation and persistence); reaction kinetics and residence time; and feasibility and cost-effectiveness of full-scale implementation when compared to the use of ZVI.

#### **6.2 REPORTING**

At the conclusion of the pilot study, a report will be incorporated into a preliminary design and will document the results of the Ash Landfill biowall pilot study to determine if the permeable biowall is effective at reducing concentrations of CAHs to levels protective of human health and the environment. The report will include a summary of field activities, analytical data, recommendations, and conclusions. Based upon the results of the field application, continued monitoring and the need for any system modification or optimization will be evaluated. In addition, other information that will be provided includes any site photographs, field notes, laboratory data, and waste disposal documentation.

## SECTION 7

### MANAGEMENT AND STAFFING

Contact information for the project management and staffing team is listed below.

<b>Name</b>	<b>Title</b>	<b>Address</b>	<b>Phone and Fax</b>	<b>E-mail</b>
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Mr. Todd Heino	Parsons Project Manager	Parsons 150 Federal St. Suite 800 Boston, MA 02110	617-449-1405 617-946-9777 (fax)	Todd.Heino @parsons.com
Mr. Doug Downey	Parsons Technical Director	Parsons 1700 Broadway, Suite 900 Denver, CO 80290	303-764-1915 303-831-8208 (fax)	doug.downey @parsons.com
Mr. Ben McAllister	Parsons Field Task Manager	Parsons 150 Federal St. Suite 800 Boston, MA 02110	617-449-1592 617-946-9777 (fax)	Benedict.McAllister @parsons.com
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## SECTION 8

### SCHEDULE

The following schedule is proposed for implementation of the permeable biowall pilot study.

<b>Activity</b>	<b>Deliverable</b>	<b>Start Date</b>	<b>End (Due) Date</b>
Work Plan	Biowall Pilot Study Work Plan	02 May 2005	25 May 2005
Work Plan Review/Subcontractor Selection (30 days)	--	25 May 2005	27 June 2005
Respond to Comments (5 days) and Mobilize to Field	Comment Response Letter	27 June 2005	8 July 2005
System Installation and Baseline Characterization	--	11 July 2005	23 July 2005
Process Monitoring Event 1 (8 weeks)	--	12 September 2005	16 September 2005
Process Monitoring Event 2 (15 weeks)	--	31 October 2005	4 November 2005
Process Monitoring Event 3 (22 weeks)	--	19 December 2005	23 December 2005
Remedial Design Work Plan and Preliminary Design Report	Preliminary Design Report	09 January 2006	28 February 2006
RD WP and Preliminary Design Review (30 days)	--	28 February 2006	28 March 2006
Final Design Report Revisions and Approval	Final Design Report	28 March 2006	28 August 2006
Full Scale Installation	--	28 August 2006	28 September 2006

The biowall pilot study results will be presented within 60 days of the last process monitoring event. The biowall pilot study results will be incorporated into a preliminary design report and remedial design work plan for full scale implementation. The preliminary design report will include recommendations for additional performance monitoring and evaluate the need for any system modification or optimization (Section 6) prior to, or as part of, full-scale design and installation.

The Army's goal is to transfer the Ash Landfill property by January 31, 2007. The schedule above allows for the completion of the full scale installation by the end of September 2006 and sufficient time to submit and gain approval on a site completion report prior to the Army's target transfer date of January 31, 2007.

## SECTION 9

### REFERENCES

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**TABLE 4-1**  
**SUMMARY OF SAMPLING ACTIVITIES FOR BIOWALL BACKFILL**  
**BIOWALL PILOT STUDY WORKPLAN**  
**ASH LANDFILL**  
**SENECA ARMY DEPOT, NEW YORK**

Identifier	Backfill Analysis <sup>a/</sup>			
	Total Nitrogen TKN (SM 4500)	Iron Phosphorous Potassium (SW6010B)	Percent Organic Carbon (SW9060M)	Percent Solids (EPA 160.3)
Mulch Sample 1 <sup>b/</sup>	1	1	1	1
Mulch Sample 2 <sup>b/</sup>	1	1	1	1
Mulch Sample 3 <sup>c/</sup>	1	1	1	1
Mulch Sample 4 <sup>c/</sup>	1	1	1	1
Sand Sample 1		1		1
Sand Sample 2		1		1
	4	6	4	6

<sup>a/</sup> Representative samples will be collected at from indicated backfill component prior to combining materials.

<sup>b/</sup> Mulch sample will be collected prior to application of food-grade soybean oil.

<sup>c/</sup> Mulch sample will be collected after application of food-grade soybean oil but before mixing with sand.

**TABLE 4-2**  
**PROPOSED GROUNDWATER MONITORING WELL CONSTRUCTION SUMMARY**  
**BIOWALL PILOT STUDY WORK PLAN**  
**ASH LANDFILL**  
**SENECA ARMY DEPOT, NEW YORK**

<b>Monitoring Well Identifier</b>	<b>Location Description</b>	<b>Well Diameter (inches)</b>	<b>Total Well Depth (feet bgs)<sup>a/</sup></b>	<b>Screened Interval (feet bgs)</b>	<b>Length of Riser (feet)</b>	<b>Length of Screen (feet)</b>
<b>North Transect</b>						
MWT-12	Upgradient of East Biowall	2.0	15 <sup>c/</sup>	8-13	10	5
MWT-13 <sup>b/</sup>	Within East Biowall	2.0	15 <sup>c/</sup>	8-13	10	5
MWT-14	Between East and West Biowalls	2.0	15 <sup>c/</sup>	8-13	10	5
MWT-15 <sup>b/</sup>	Within West Biowall	2.0	15 <sup>c/</sup>	8-13	10	5
MWT-16	Downgradient of West Biowall	2.0	15 <sup>c/</sup>	8-13	10	5
MWT-17	Downgradient of West Biowall	2.0	15 <sup>c/</sup>	8-13	10	5
<b>South Transect</b>						
PT-12A (Existing)	Upgradient of East Biowall	2.0	13	Unknown, to be determined in field		
MWT-18 <sup>b/</sup>	Within East Biowall	2.0	15 <sup>c/</sup>	8-13	10	5
MWT-19	Between East and West Biowalls	2.0	15 <sup>c/</sup>	8-13	10	5
MWT-20 <sup>b/</sup>	Within West Biowall	2.0	15 <sup>c/</sup>	8-13	10	5
MWT-21	Downgradient of West Biowall	2.0	15 <sup>c/</sup>	8-13	10	5
MWT-22	Downgradient of West Biowall	2.0	15 <sup>c/</sup>	8-13	10	5

<sup>a/</sup> feet bgs indicates depth in feet below ground surface.

<sup>b/</sup> Monitoring well located inside biowall.

<sup>c/</sup> approximate well depth is 15 feet bgs. Wells will be installed to competent bedrock.



**TABLE 4-3**  
**SUMMARY OF BASELINE CHARACTERIZATION ACTIVITIES**  
**BIOWALL PILOT STUDY WORK PLAN**  
**ASH LANDFILL**  
**SENECA ARMY DEPOT, NEW YORK**

Location Identifier	Location Description	Aquifer Test Analysis	Water Level Measurement	Soil		Groundwater Analyses						
				Total Organic Carbon (SW9060M)	VOCs <sup>a/</sup> (SW8260B)	Methane, Ethane, Ethene (Microseeps)	Nitrate + Nitrite (E300.1)	Sulfate, Chloride (E300.1)	Total Organic Carbon (SW9060M)	Volatile Fatty Acids (Microseeps)	Well Head Analyses <sup>b/</sup>	Mobile Lab Analyses <sup>c/</sup>
<b>North Transect</b>												
MWT-12	Upgradient of East Biowall	1	1	2	1	1	1	1	1	1	1	1
MWT-13	Within East Biowall	1	1		1	1	1	1	1	1	1	1
MWT-14	Between East and West Biowalls	1	1		1	1	1	1	1	1	1	1
MWT-15	Within West Biowall	1	1		1	1	1	1	1	1	1	1
MWT-16	Downgradient of West Biowall	1	1		1	1	1	1	1	1	1	1
MWT-17	Downgradient of West Biowall		1	2	1	1	1	1	1	1	1	1
<b>South Transect</b>												
PT-12A	Upgradient of East Biowall		1		1	1	1	1	1	1	1	1
MWT-18	Within East Biowall		1		1	1	1	1	1	1	1	1
MWT-19	Between East and West Biowalls		1		1	1	1	1	1	1	1	1
MWT-20	Within West Biowall		1		1	1	1	1	1	1	1	1
MWT-21	Downgradient of West Biowall		1		1	1	1	1	1	1	1	1
MWT-22	Downgradient of West Biowall		1		1	1	1	1	1	1	1	1
<b>SUBTOTALS</b>		5	12	4	12	12	12	12	12	12	12	12
<b>QA/QC</b>												
Duplicates					1	1	1	1	1	1		1
MS					1							
MSD					1							
Trip Blanks					1							
<b>TOTAL NUMBER OF SAMPLES DURING BASELINE SAMPLING</b>				4	16	13	13	13	13	13	12	13

<sup>a/</sup> Volatile organic compounds (VOCs) to include aromatic and chlorinated aliphatic hydrocarbons.

<sup>b/</sup> Well head analyses include dissolved oxygen, oxidation-reduction potential, pH, temperature, conductivity, and turbidity.

<sup>c/</sup> Mobile lab analyses include carbon dioxide, alkalinity, ferrous iron, hydrogen sulfide, and manganese.

**TABLE 4-4**  
**SUMMARY OF PROCESS MONITORING ACTIVITIES<sup>a/</sup>**  
**BIOWALL PILOT STUDY WORK PLAN**  
**ASH LANDFILL**  
**SENECA ARMY DEPOT, NEW YORK**

Location Identifier	Location Description	Aquifer Test Analysis <sup>c/</sup>	Water Level Measurement	Groundwater Analyses						
				VOCs <sup>b/</sup> (SW8260B)	Methane, Ethane, Ethene (Microseeps)	Sulfate, Chloride (E300.1)	Total Organic Carbon (SW9060M)	Volatile Fatty Acids <sup>c/</sup> (Microseeps)	Well Head Analyses <sup>d/</sup>	Mobile Lab Analyses <sup>e/</sup>
<b>North Transect</b>										
MWT-12	Upgradient of East Biowall	1	1	1	1	1	1	1	1	1
MWT-13	Within East Biowall	1	1	1	1	1	1	1	1	1
MWT-14	Between East and West Biowalls	1	1	1	1	1	1	1	1	1
MWT-15	Within West Biowall	1	1	1	1	1	1	1	1	1
MWT-16	Downgradient of West Biowall	1	1	1	1	1	1	1	1	1
MWT-17	Downgradient of West Biowall		1	1	1	1	1	1	1	1
<b>South Transect</b>										
PT-12A	Upgradient of East Biowall		1	1	1	1	1	1	1	1
MWT-18	Within East Biowall		1	1	1	1	1	1	1	1
MWT-19	Between East and West Biowalls		1	1	1	1	1	1	1	1
MWT-20	Within West Biowall		1	1	1	1	1	1	1	1
MWT-21	Downgradient of West Biowall		1	1	1	1	1	1	1	1
MWT-22	Downgradient of West Biowall		1	1	1	1	1	1	1	1
<b>SUBTOTALS</b>		<b>5</b>	<b>12</b>	<b>12</b>	<b>12</b>	<b>12</b>	<b>12</b>	<b>12</b>	<b>12</b>	<b>12</b>
<b>QA/QC</b>										
Duplicates				1	1	1	1	1		1
MS				1						
MSD				1						
Trip Blanks				1						
<b>TASK TOTAL</b>				<b>16</b>	<b>13</b>	<b>13</b>	<b>13</b>	<b>13</b>	<b>12</b>	<b>13</b>
<b>TOTAL NUMBER OF SAMPLES OVER THREE EVENTS</b>				<b>48</b>	<b>39</b>	<b>39</b>	<b>39</b>	<b>13</b>	<b>36</b>	<b>39</b>

<sup>a/</sup> Summary of monitoring activities that will be performed approximately 8 weeks, 15 weeks, and 22 weeks after complete installation of biowall system components, unless otherwise noted.

<sup>b/</sup> Volatile organic compounds (VOCs) to include aromatic and chlorinated aliphatic hydrocarbons.

<sup>c/</sup> Monitoring activity will only be performed during final sampling event only.

<sup>d/</sup> Well head analyses include dissolved oxygen, oxidation-reduction potential, pH, temperature, conductivity, and turbidity.

<sup>e/</sup> Mobile lab analyses include carbon dioxide, alkalinity, ferrous iron, sulfide, and manganese.

**TABLE 5.1**  
**STABILIZATION CRITERIA FOR WATER QUALITY PARAMETERS**  
**ASH LANDFILL BIOWALL PILOT STUDY**  
**SENECA ARMY DEPOT ACTIVITY**

<b>Parameter</b>	<b>Stabilization Criteria</b>
Turbidity	+/- 10 NTU
pH	+/- 0.2
Specific Conductance	+/- 5%
Temperature	+/- 1.0 °C

mg/L = milligrams per liter.

mV = millivolts.

°C = degrees Centigrade

**TABLE 5-2**  
**ANALYTICAL PROTOCOLS FOR MULCH, SOIL, AND GROUNDWATER**  
**ASH LANDFILL PILOT STUDY WORK PLAN**  
**SENECA ARMY DEPOT ACTIVITY**

Matrix/Analyte	Method	Field (F) or Lab (L)	Screening (S) or Definitive (D)	Addressed in SEDA QAPP (Parsons, 2005)
<b>Mulch</b>				
Total Organic Carbon	Lloyd Kahn	L	D	Yes
TKN	SM4500	L	D	Yes
Iron, Phosphorus, Potassium	SW6010B	L	D	Yes
Percent Solids	EPA 160.3	L	D	Yes
<b>Boring Soil</b>				
Total Organic Carbon	Lloyd Kahn	L	D	Yes
<b>Residual Soils</b>				
VOCs	SW 8260B	L	D	Yes
<b>Water</b>				
<i>Field-measured Analyses</i>				
Dissolved Oxygen	Direct-reading meter; CHEMetrics K-7512	F	S	Yes
Oxidation-Reduction Potential	Direct-reading meter	F	S	Yes
pH	Direct-reading meter	F	S	Yes
Specific Conductance	Direct-reading meter	F	S	Yes
Turbidity	Direct reading meter	F	S	Yes
Temperature	Direct-reading meter	F	S	Yes
Ferrous Iron	Colorimetric, Hach Method 8146	F	S	No
Manganese	Colorimetric, Hach Method 8034	F	S	No
Hydrogen Sulfide	Colorimetric, Hach Method 8131	F	S	No
Alkalinity (as carbonate [CO <sub>3</sub> <sup>-2</sup> ])	Titrimetric, Hach Method 8203 (or similar)	F	S	No
Carbon Dioxide	Titrimetric, Hach Method 8205 (or similar)	F	S	No
<i>Fixed-Laboratory Analyses</i>				
VOCs <sup>a/</sup>	SW8260B	L	D	Yes
Methane, Ethane, Ethene	AM-20GAX <sup>b/</sup>	L	D	No
Nitrate + Nitrite [as Nitrogen]	E353.1	L	D	Yes
Sulfate and Chloride	E300.1 or SW846 9056	L	D	Yes
Total Organic Carbon	SW9060A	L	D	Yes
Volatile Fatty Acids	Microseeps SOP <sup>c/</sup>	L	S	No

<sup>a/</sup> VOCs = volatile organic compounds.

<sup>b/</sup> AM-20GAX = Microseeps, Inc. laboratory standard operating procedure.

<sup>c/</sup> SOP = Internal laboratory standard operating procedure.

**TABLE 5-3**  
**ANALYTICAL METHODS AND REQUIREMENTS FOR CONTAINERS, PRESERVATION**  
**TECHNIQUES, SAMPLE VOLUMES, AND HOLDING TIMES**  
**ASH LANDFIL PILOT STUDY WORK PLAN**  
**SENECA ARMY DEPOT ACTIVITY**

Name	Matrix	Analytical Methods	Container	Preservation <sup>a/</sup>	Minimum Sample Volume or Weight	Maximum Holding Time
Total Organic Carbon	Soil	Lloyd Kahn	G	4°C	1 x 4 oz jar	28 days
Alkalinity	Water	Hach <sup>®</sup> Field Analysis	Provided with Hach Kit	None	100 ml	14 days <sup>a/</sup>
Carbon Dioxide	Water	Hach <sup>®</sup> Field Analysis	Provided with Hach Kit	None	100 ml	at well head <sup>a/</sup>
Ferrous Iron	Water	Hach <sup>®</sup> Field Analysis	Provided with Hach Kit	None	100 ml	at well head <sup>a/</sup>
Manganese	Water	Hach <sup>®</sup> Field Analysis	Provided with Hach Kit	None	100 ml	at well head <sup>a/</sup>
Sulfide	Water	Hach <sup>®</sup> Field Analysis	Provided with Hach Kit	None	100 ml	at well head <sup>a/</sup>
Methane/ Ethane/ Ethene	Water	AM20GAX	G, Teflon <sup>®</sup> septum	4°C	3 x 40 ml	14 days
Nitrate and Nitrite	Water	E353.1	P,G	4°C, H <sub>2</sub> SO <sub>4</sub> to pH < 2	500 ml	28 days
Sulfate and Chloride	Water	E300.1 or SW9056	P	4°C	250 ml	28 days
Total Organic Carbon	Water	SW9060 modified	P	4°C, H <sub>2</sub> SO <sub>4</sub> to pH < 2	250 ml	28 days
Volatile Organic Compounds	Water	SW8260B	G, Teflon <sup>®</sup> septum	4°C, HCl to pH < 2	3 x 40 ml	14 days
Volatile Fatty Acids	Water	Microseeps SOP	G, Teflon <sup>®</sup> septum	4°C	2 x 40 ml	7 days
Dissolved Inorganics	Water	SW6010B/SW6020	P,G	4°C, HNO <sub>3</sub> to pH < 2	500 ml	180 days

**Acronyms:**

P - Polyethylene

G - Glass

H<sub>2</sub>SO<sub>4</sub> – Sulfuric acid

HNO<sub>3</sub> – Nitric Acid

HCl - Hydrochloric acid

<sup>a/</sup> Note: Hach field analysis should be completed as soon as possible after collection of the sample. The holding times indicated are the maximum times the samples may be held before analysis and still be considered valid.

**TABLE 5-4**  
**LABORATORY DETECTION AND PROJECT QUANTITATION LIMITS FOR**  
**ANALYTES THAT ARE NOT ADDRESSED BY THE SENECA QAPP**  
**ASH LANDFILL PILOT STUDY**  
**SENECA ARMY DEPOT ACTIVITY**

Analyte	Analytical Method	Method Detection Limit	Project Quantitation Limit	Units
Methane	AM20-GAX <sup>a/</sup>	0.002	0.015	µg/L <sup>b/</sup>
Ethane	AM20-GAX	1.0	5.0	ng/L <sup>b/</sup>
Ethene	AM20-GAX	3.0	5.0	ng/L
Manganese	Hach Method 8034	100	300	µg/L
Ferrous Iron	Hach Method 8146	10	30	µg/L
Sulfide	Hach Method 8131	10	30	µg/L
Alkalinity	Hach Method 8203	1.0	30	mg/L <sup>b/</sup>
Carbon Dioxide	Hach Method 8205	10	30	mg/L
Volatile Fatty Acids (VFAs)	Microseeps SOP	0.3	1.0 <sup>c/</sup>	mg/L

<sup>a/</sup> Internal Microseeps Inc. SOP

<sup>b/</sup> µg/L = micrograms per liter; ng/L = nanograms per liter; mg/L = milligrams per liter.

<sup>c/</sup> Project Quantitation Limit for all reported VFA acids other than pyruvic acid is 1 mg/L. The Project Quantitation Limit for pyruvic acid is 4 mg/L.

**TABLE 5-5**  
**ANALYTICAL PROTOCOLS FOR SOIL AND GROUNDWATER**  
**ASH LANDFILL BIOWALL PILOT STUDY**  
**SENECA ARMY DEPOT ACTIVITY**

Parameter	Rationale
<b>Soil</b>	
Total Organic Carbon (TOC)	Used to calculate sorption of contaminants to the soil matrix.
<b>Groundwater</b>	
Dissolved Oxygen	Determination whether aerobic or anaerobic conditions exist. Concentrations less than about 0.5 mg/L generally indicate an anaerobic degradation pathway.
Oxidation-reduction potential (ORP)	The ORP of groundwater reflects the relative oxidizing or reducing nature of the groundwater system. ORP is influenced by the nature of the biologically mediated degradation of organic carbon.
pH	Aerobic and anaerobic processes are pH-sensitive
Conductivity	Well development and purging parameter.
Temperature	Well development and purging parameter.
Ferrous Iron	Indication of iron reduction during microbial degradation of organic compounds in the absence of dissolved oxygen and nitrate.
Manganese	Indication of manganese reduction during microbial degradation of organic compounds in the absence of dissolved oxygen and nitrate.
Sulfide	Byproduct of sulfate reduction.
Alkalinity	Indicator of biodegradation and buffering capacity of the aquifer.
Carbon Dioxide	Byproduct of both aerobic and anaerobic biodegradation processes.
Methane, ethane, and ethene	The presence of methane indicates fermentation via methanogenesis. The presence of ethane and ethene are indicative of reductive dechlorination of chlorinated solvents.
Nitrate	Electron acceptor for microbial respiration in the absence of oxygen
Nitrite	A byproduct of denitrification of nitrate.
Sulfate	Indication of sulfate reduction by microbial biodegradation.
Chloride	General water quality parameter. Byproduct of dechlorination of chlorinated solvents.
Total Organic Carbon (TOC)	Indication of organic substrate available for biological metabolism.
VOCs (chlorinated solvents)	Contaminant of concern, byproducts of anaerobic dechlorination.
Volatile Fatty Acids (VFAs)	Biodegradation breakdown products and fermentation substrates. Indicator of substrate distribution.

**TABLE 5-6**  
**QA/QC SAMPLING PROGRAM**  
**ASH LANDFILL BIOWALL PILOT STUDY**  
**SENECA ARMY DEPOT ACTIVITY**

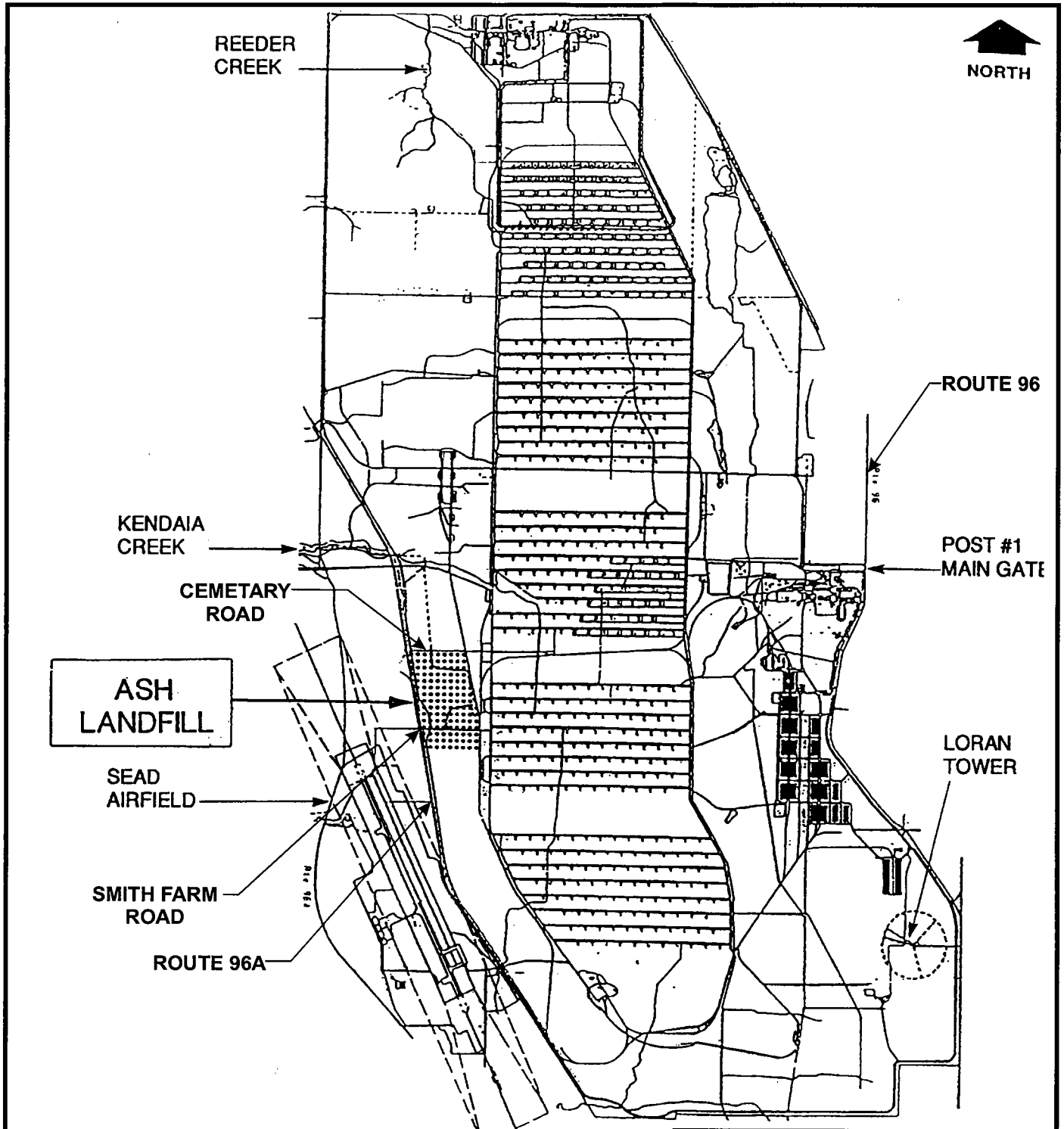
<b>QA/QC Sample Type</b>	<b>Minimum Frequency to be Collected and Analyzed <sup>a/</sup></b>	<b>Analytes</b>
Field Duplicate	5 to 10 percent of groundwater and soil samples	VOCs; methane, ethane, and ethene; TOC; nitrate; chloride; sulfate; mobile lab analyses
Trip Blank	One per sample shipment containing VOCs	VOCs
Matrix Spike and Matrix Spite Duplicate	5 percent of groundwater and soil samples	VOCs
Laboratory Control Sample	One per method per medium per analytical batch	Laboratory control charts (Method Specific)
Laboratory Method Blank	One per method per medium per analytical batch	Laboratory control charts (Method Specific)

a/ Actual frequency of QA/QC samples may be altered by the Parsons field scientist, but will not be less than minimum QA/QC sampling frequency.





<b>PARSONS</b>	
CLIENT/PROJECT TITLE	
<b>SENECA ARMY DEPOT ACTIVITY</b>	
ASH LANDFILL BIOWALL PILOT STUDY WORK PLAN	
DEPT.	DWG NO.
ENVIRONMENTAL ENGINEERING	744538-01100
<b>FIGURE 1-1</b>	
<b>LOCATION MAP</b>	
SCALE	DATE
1" = 8 MILES APPROX.	MAY 2005



**PARSONS**

CLIENT/PROJECT TITLE

SENECA ARMY DEPOT ACTIVITY  
 ASH LANDFILL BIOWALL PILOT  
 STUDY WORK PLAN

DEPT.

ENVIRONMENTAL ENGINEERING

DWG NO.

744538-01100

FIGURE 1-2

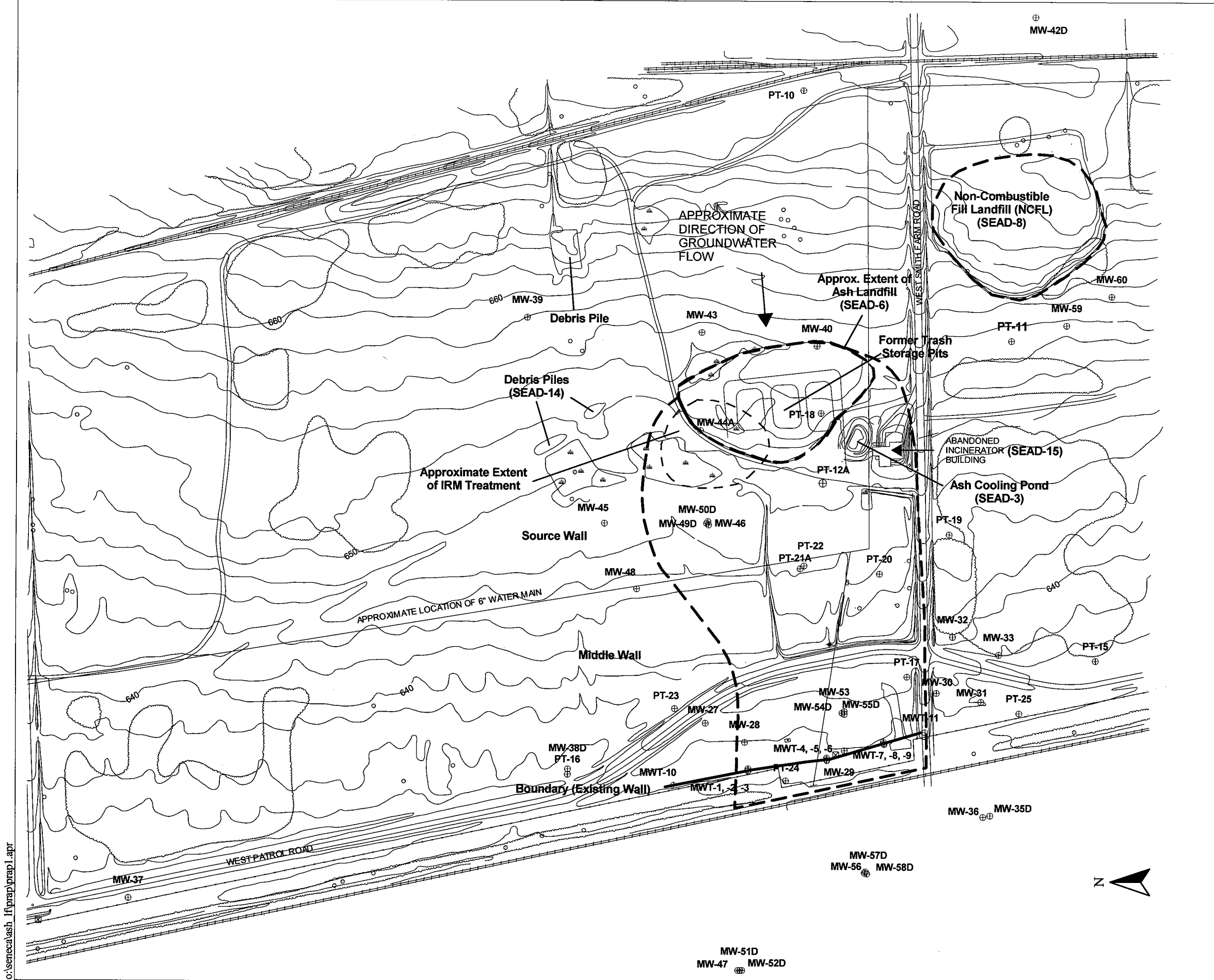
LOCATION OF ASH LANDFILL  
 AT SEDA

SCALE

NA

DATE

May 2005



**LEGEND**

- PAVED ROAD
- GROUND CONTOUR AND ELEVATION
- WETLAND
- OUTLINE OF FORMER TRASH PITS (IDENTIFIED FROM AERIAL PHOTO)
- APPROXIMATE EXTENT OF DEBRIS PILE
- BRUSH
- CHAIN LINK FENCE
- UTILITY POLE
- APPROXIMATE LOCATION OF FIRE HYDRANT
- MONITORING WELL AND DESIGNATION
- RAILROAD
- 6" WATER MAIN
- EXISTING TREATMENT WALL
- APPROX. AREA REQUIRING LAND USE CONTROLS
- APPROX. EXTENT OF IRM SOIL TREATMENT

**PARSONS**

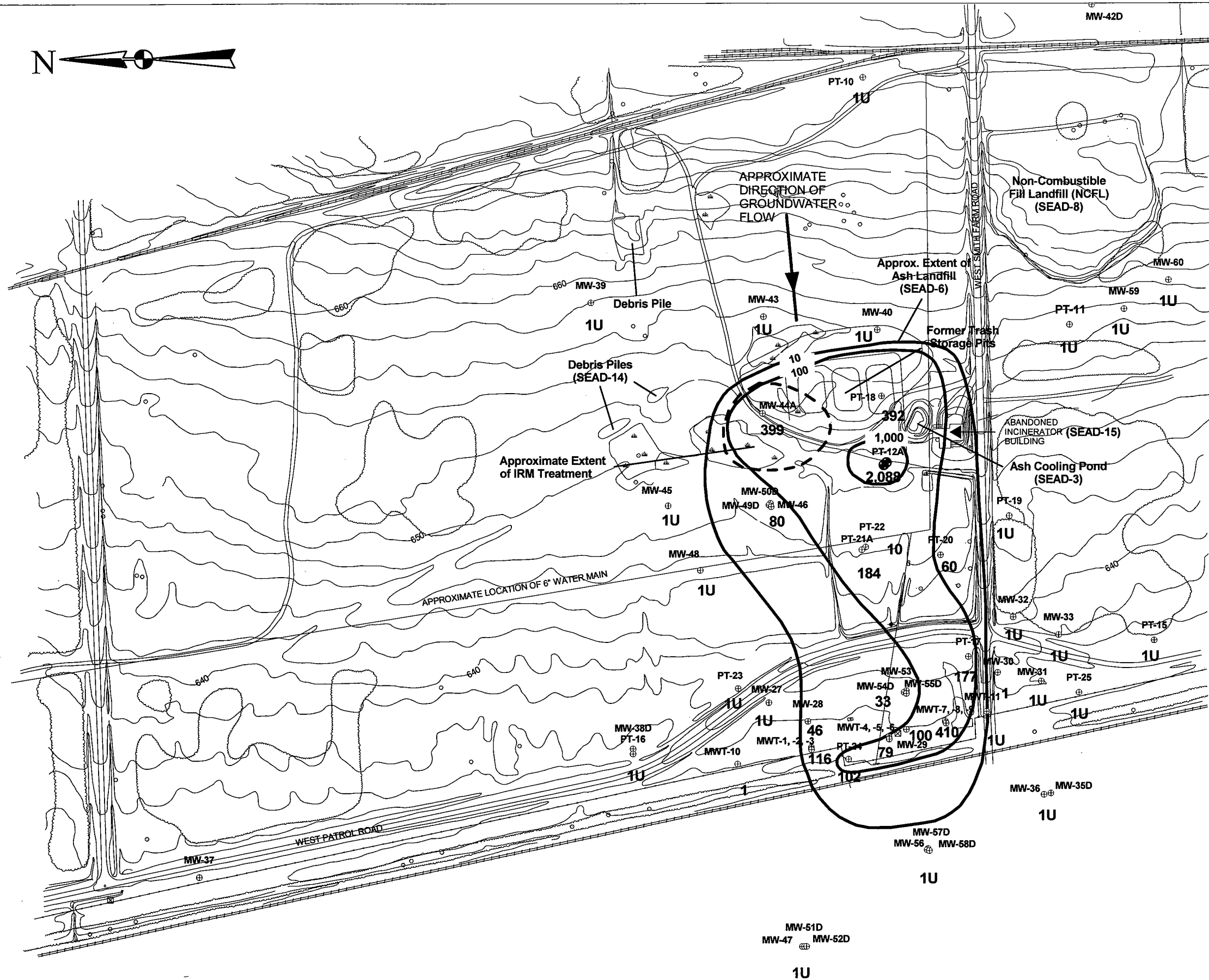
**SENECA ARMY DEPOT ACTIVITY  
ASH LANDFILL BIOWALL PILOT  
STUDY WORK PLAN**

**FIGURE 1-3  
ASH LANDFILL  
SITE MAP**

SCALE: 1" = 250'

MAY 2005

c:\senecash\ifrap\rap1.apr



**LEGEND**

- PAVED ROAD
- GROUND CONTOUR AND ELEVATION
- WETLAND & DESIGNATION
- OUTLINE OF FORMER TRASH PITS (IDENTIFIED FROM AERIAL PHOTO)
- APPROXIMATE EXTENT OF DEBRIS PILE
- BRUSH
- CHAIN LINK FENCE
- UTILITY POLE
- APPROXIMATE LOCATION OF FIRE HYDRANT
- PT-22 MONITORING WELL AND DESIGNATION
- MW-37 MONITORING WELL AND DESIGNATION
- RAILROAD
- 6" WATER MAIN
- GROUNDWATER ISOCONTOUR (ug/L)
- 1,000
- 75
- 10U

1,000 TOTAL CHLORINATED ETHENES (ug/L) FROM SAMPLES COLLECTED IN JANUARY 2000

75 TOTAL CHLORINATED ETHENES (ug/L) FROM SAMPLES COLLECTED IN JANUARY 2000

10U NO CHLORINATED ETHENES DETECTED

NOTE:  
THE CONCENTRATIONS SHOWN ON THIS FIGURE ARE FOR WELLS SCREENED IN THE TILLED/WEATHERED SHALE AQUIFER.

SCALE: 1" = 250'



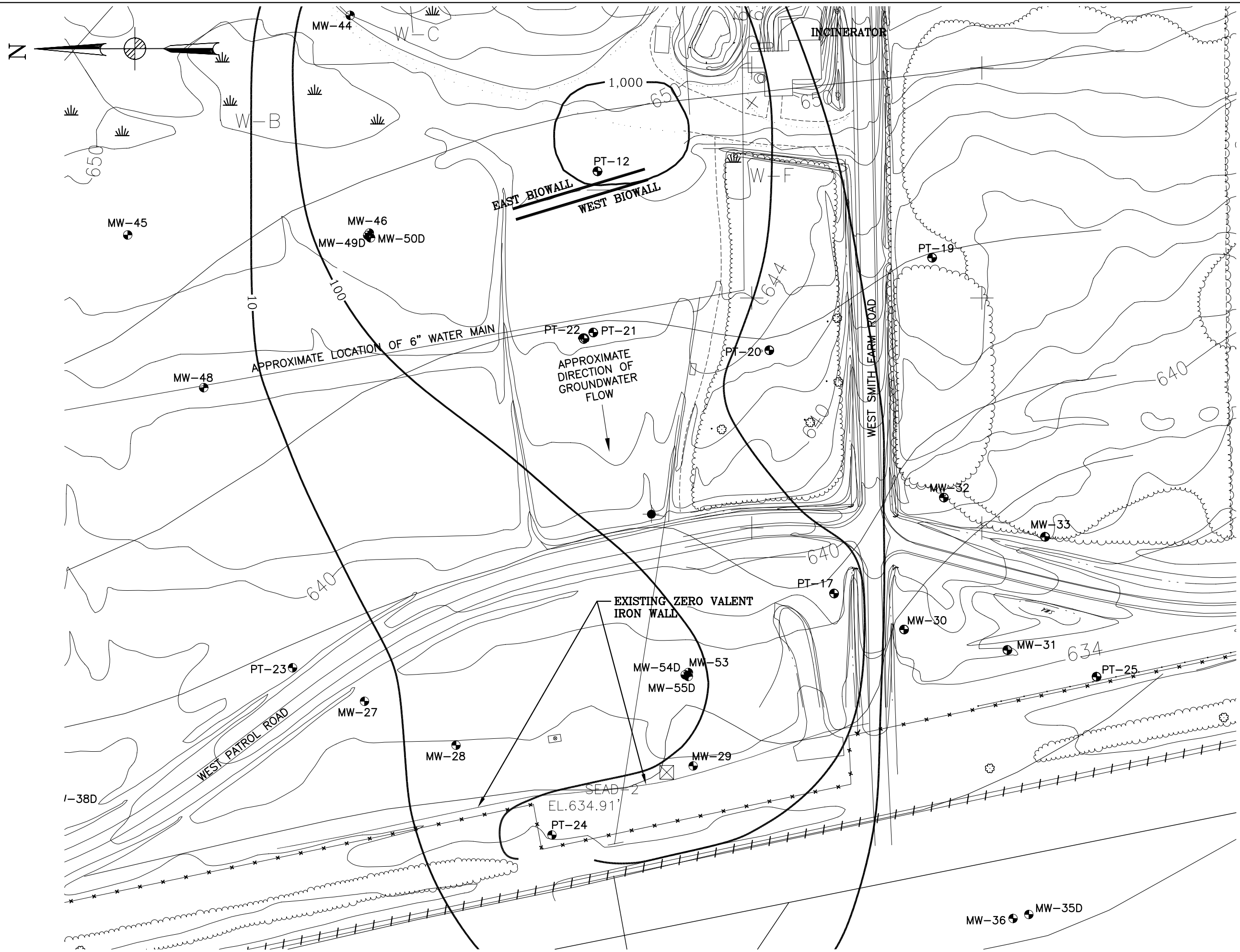
SENECA ARMY DEPOT ACTIVITY  
ASH LANDFILL BIOWALL PILOT  
STUDY WORK PLAN

ENVIRONMENTAL ENGINEERING 744538-01100

**FIGURE 1 - 4**  
TOTAL CHLORINATED ETHENES  
IN GROUNDWATER  
JANUARY 2000

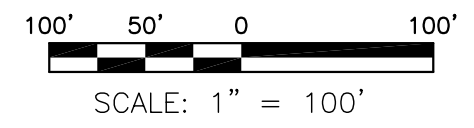
SCALE: 1 INCH = 250 FEET MAY 2005

c:\arcview\seneca\ash\_1\biowp.apr



**LEGEND:**

- PAVED ROAD
- DIRT ROAD
- GROUND CONTOUR AND ELEVATION
- TREE
- WETLAND & DESIGNATION
- APPROXIMATE EXTENT OF FILL
- OUTLINE OF FORMER TRASH PITS (IDENTIFIED FROM AERIAL PHOTO)
- APPROXIMATE EXTENT OF DEBRIS PILE
- BRUSH
- CHAIN LINK FENCE
- UTILITY POLE
- APPROXIMATE LOCATION OF FIRE HYDRANT
- FUEL OR UNDERGROUND STORAGE TANK
- SURVEY MONUMENT
- MONITORING WELL AND DESIGNATION
- RAILROAD TRACKS
- TREATMENT WALL
- 6" WATER MAIN
- 10 GROUNDWATER ISO CONTOUR (UG/L)

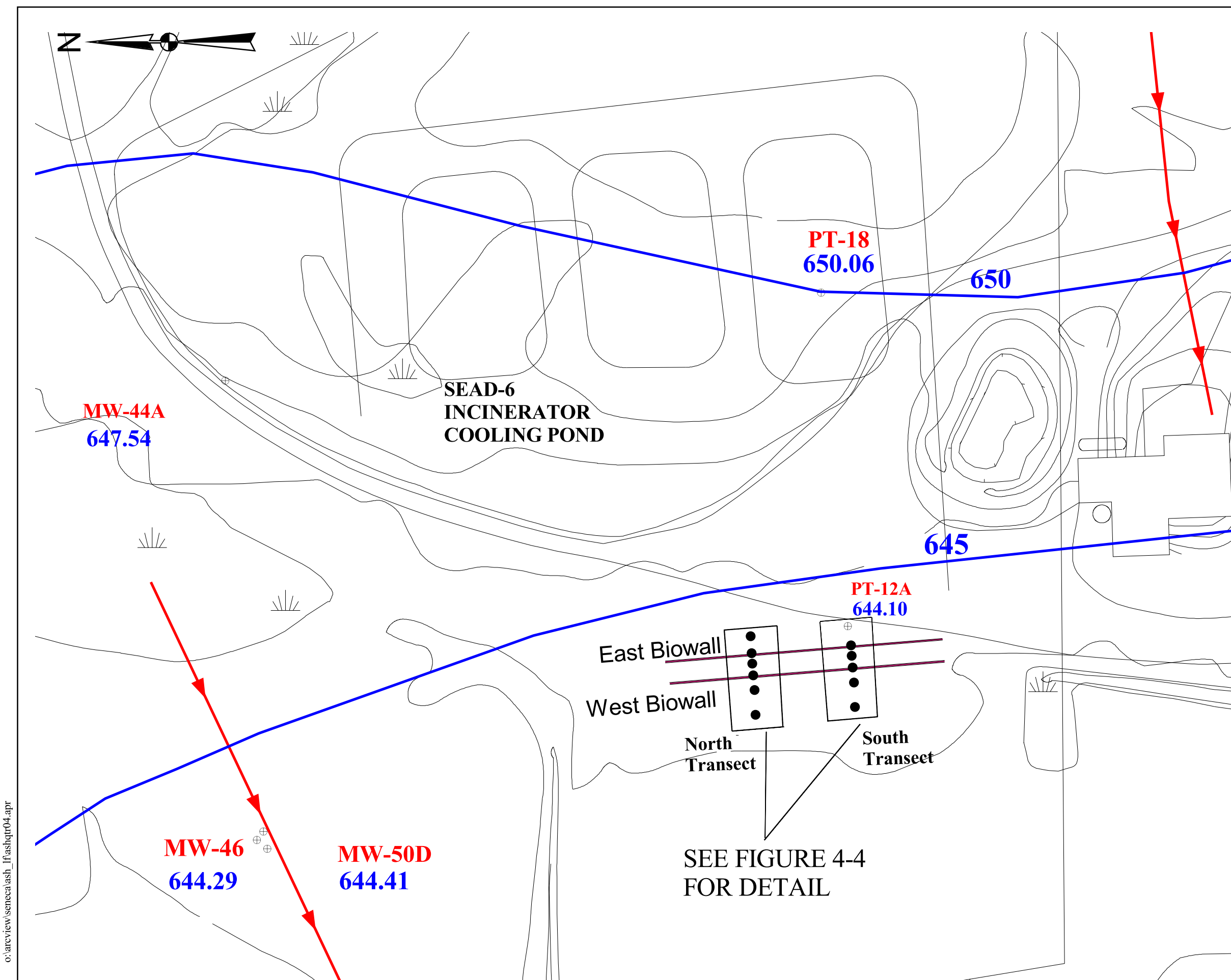


**PARSONS**


















SENECA ARMY DEPOT ACTIVITY  
ASH LANDFILL  
BIOWALL PILOT STUDY  
WORKPLAN

ENVIRONMENTAL ENGINEERING 744538-01100

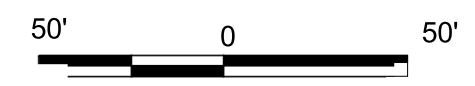
FIGURE 4-1  
APPROXIMATE LOCATION OF  
BIOWALLS AND TOTAL  
CHLORINATED ETHENES  
IN GROUNDWATER



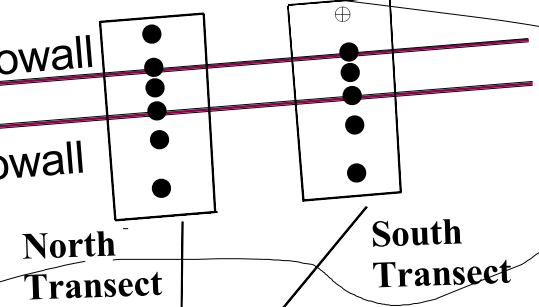
**LEGEND**

-  PAVED ROAD
-  GROUND CONTOUR AND ELEVATION
-  WETLAND & DESIGNATION
-  OUTLINE OF FORMER TRASH PITS (IDENTIFIED FROM AERIAL PHOTO)
-  APPROXIMATE EXTENT OF DEBRIS PILE
-  BRUSH
-  CHAIN LINK FENCE
-  UTILITY POLE
-  APPROXIMATE LOCATION OF FIRE HYDRANT
-  RAILROAD
-  6" WATER MAIN
-  **MW-1** ⊕
-  637.51
-  **640**
-  
-  ●

NOTES:  
 GROUNDWATER MEASUREMENTS TAKEN AUGUST 23, 2004  
 GROUNDWATER ELEVATIONS CONTOURS BASED ON CONDITIONS AT THE TIME OF MEASUREMENT. GROUNDWATER CONDITIONS AT OTHER TIMES MAY VARY.



SCALE: 1" = 50'



SEE FIGURE 4-4 FOR DETAIL

**PARSONS**

SENECA ARMY DEPOT ACTIVITY  
 ASH LANDFILL  
 BIOWALL PILOT STUDY  
 WORKPLAN

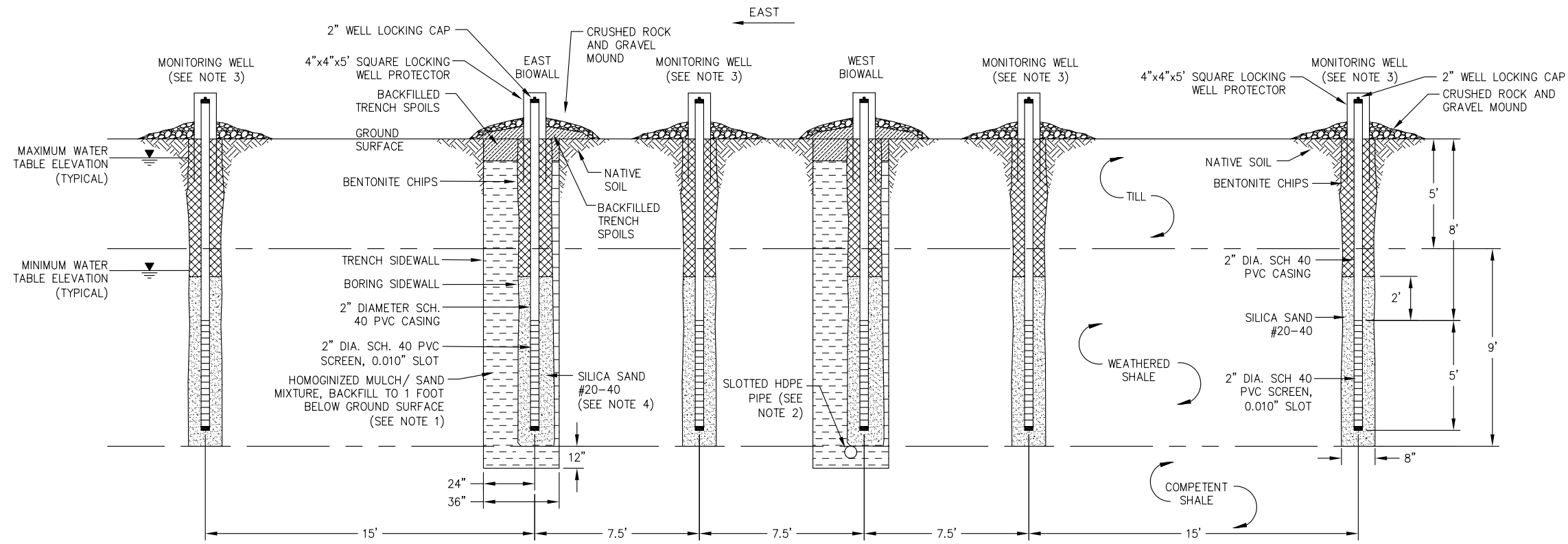
ENVIRONMENTAL ENGINEERING | 744538-01100

**FIGURE 4-2**  
 APPROXIMATE LOCATION OF  
 BIOWALLS AND GROUNDWATER  
 ELEVATION CONTOURS  
 ROUND 23 - AUGUST 2004

SCALE: 1 INCH = 50 FEET | MAY 2005

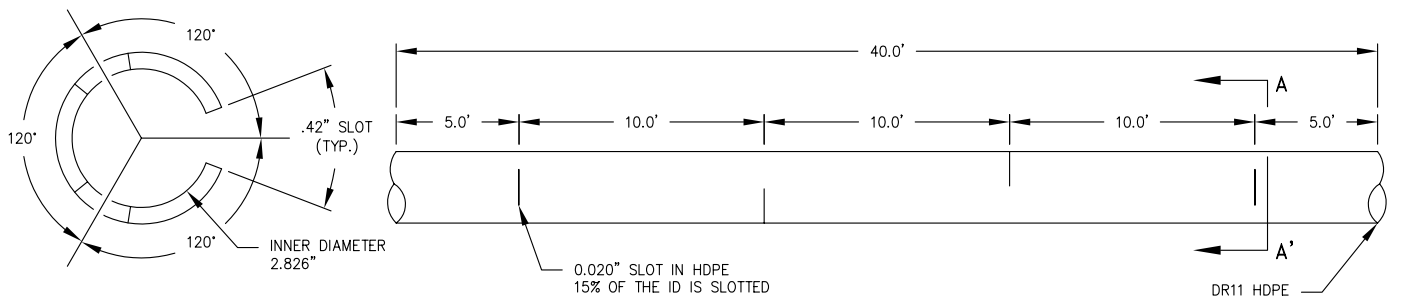
o:\arcview\seneca\ash\_if\ashqr04.apr



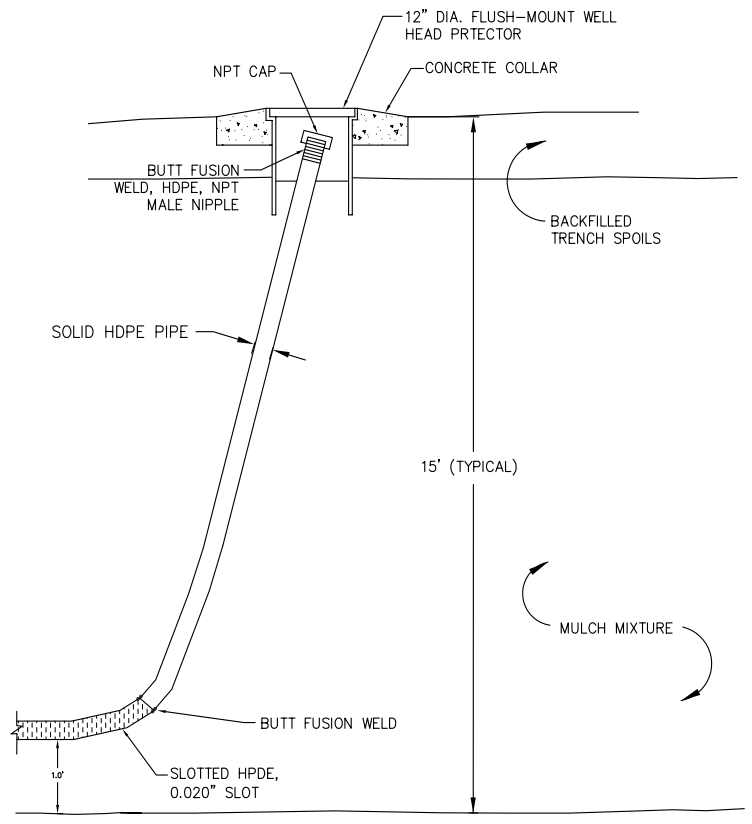


TYPICAL CROSS SECTION ALONG MONITORING WELL TRANSECT  
N.T.S.

- NOTES:
- MULCH FOR EAST BIOWALL SHALL BE COATED WITH FOOD-GRADE VEGETABLE OIL (2 TO 5 PERCENT BY VOLUME) PRIOR TO MIXING MULCH WITH SAND.
  - SLOTTED HDPE PIPE SHALL BE ROLLED INTO BOTTOM OF TRENCH FOR THE WEST BIOWALL PRIOR TO EMPLACEMENT OF MULCH OR AS DIRECTED BY SITE ENGINEER.
  - CONSTRUCTION DETAIL SHOWN FOR WESTERNMOST MONITORING WELL IS TYPICAL FOR ALL PROPOSED MONITORING WELLS.
  - THE REACTIVE BACKFILL MIXTURE SHALL BE ALLOWED TO COLLAPSE AROUND THE SCREENED INTERVAL OF MONITORING WELLS INSTALLED INSIDE THE BIOWALL TO A MAXIMUM HEIGHT OF APPROXIMATELY TWO FEET ABOVE THE TOP OF THE SCREEN. SILICA SAND SHALL BE USED TO FILL VOIDS LEFT BY NATURAL COLLAPSE.



TYPICAL SLOTTED HDPE PIPE AT BOTTOM OF BIOWALL  
N.T.S.



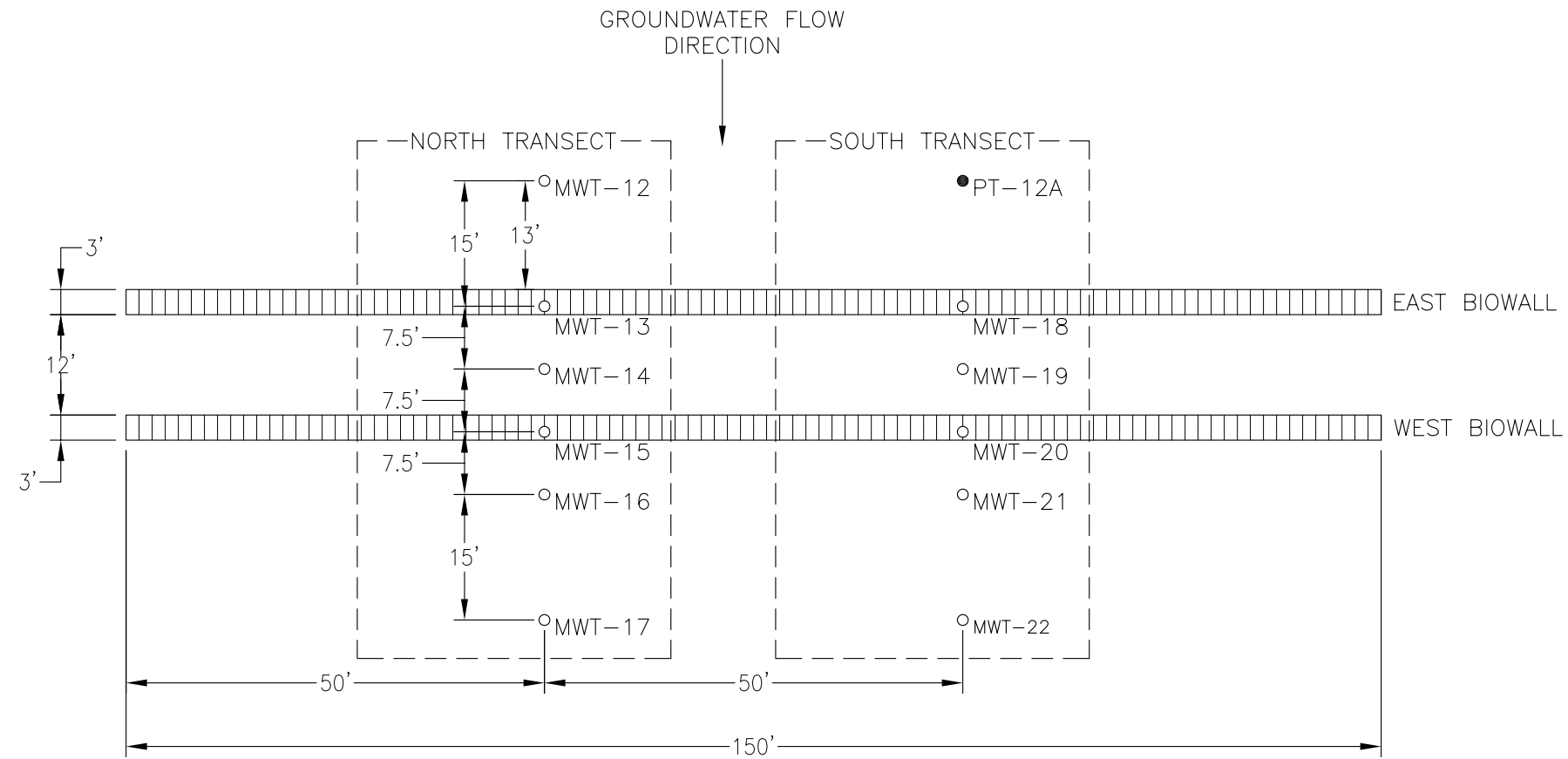
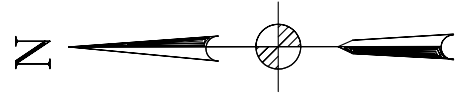
SURFACE COMPLETION OF DISTRIBUTION PIPE  
N.T.S.

**PARSONS**

SENECA ARMY DEPOT ACTIVITY  
ASH LANDFILL  
BIOWALL PILOT STUDY  
WORKPLAN

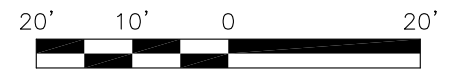
ENVIRONMENTAL ENGINEERING 744538-01100

FIGURE 4-3  
BIOWALL AND GROUNDWATER  
MONITORING WELL  
CONSTRUCTION DETAILS



**LEGEND**

- PT-12A EXISTING 2" GROUNDWATER MONITORING WELL
- MWT-17 PROPOSED 2" GROUNDWATER MONITORING WELL
- ▤ PROPOSED BIOWALL



SCALE: 1" = 20'

**PARSONS**

SENECA ARMY DEPOT ACTIVITY  
ASH LANDFILL  
BIOWALL PILOT STUDY  
WORKPLAN

ENVIRONMENTAL ENGINEERING 744538-01100

FIGURE 4-4  
APPROXIMATE LAYOUT OF  
BIOWALLS



**Appendix A**  
**Microseeps Standard Operating Procedure for Site Specific**  
**Analyses**

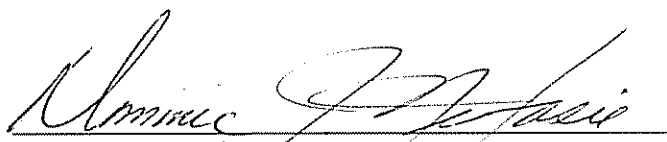
# Microseeps, Incorporated

## Standard Operating Procedure For the Analyses of Low Level Volatile Fatty Acids by Ion Chromatography

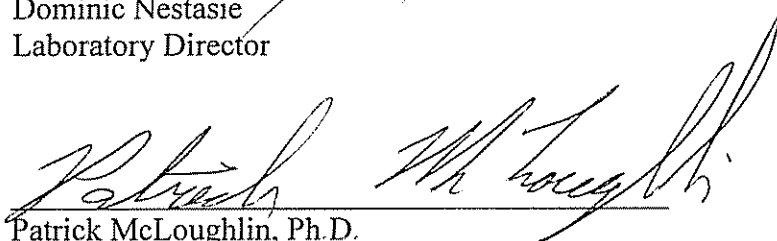
(Reference: SW846-9056 & 9056A; Standard Methods 429; ASTM D3427)

Controlled Copy No. \_\_\_\_\_

### Signatures of Final Approval:



Dominic Nestasie  
Laboratory Director



Patrick McLoughlin, Ph.D.  
Technical Director

8-30-04  
Date

SOP Review Date: August 30, 2004

Controlled Document

## **1.0 Purpose and Application**

When microbes are carrying on reductive dechlorination, they do not use the chlorinated compounds as food. Instead, they use other sources, such as BTEX or natural organic carbon. When food is unavailable, an attempt to enhance the biodegradation by addition of a carbon substrate is a viable option. Once these substrates enter the groundwater and the microbes begin using them as a food source, they rapidly take the form of Volatile Fatty Acids (VFAs). As the groundwater travels down gradient from the injection point, VFA concentrations rapidly drop below the 1-ppm level, however there is still evidence of reductive dechlorination. This suggests that microbes can utilize VFAs at concentrations lower than 1-ppm.

This Standard Operating Procedure addresses the sequential determination of low level VFAs in groundwater. The method used for this procedure is a modification of SW846-9056A.

### **1.1 Analyte List**

**Table 1.1  
Analyte List**

<b>Low Level VFA</b>	<b>CAS Number</b>
Lactic acid	50-21-5
Hydroxy-isobutyric acid (HIBA)	594-61-6
Acetic acid	64-19-7
Propionic acid	79-09-4
Butyric acid	107-92-6
Formic acid	64-18-6
Pyruvic acid	127-17-3
i-Pentanoic	503-74-2
n-Pentanoic acid	109-52-4
i-Hexanoic	646-07-1
n-Hexanoic acid	142-62-1
Heptanoic acid	111-14-8

### **1.2 Matrix**

This method is applicable to groundwater.

## **2.0 Method Summary**

Samples are pretreated to remove potential interference. The pretreated samples are then spiked with a mix of compounds that serve as preservatives and internal retention time markers.

Samples are then analyzed by ion exchange in an ion chromatograph (IC). In the alkaline solutions of the IC, the acids ionize to their conjugate anions. The anions are separated on an ion chromatograph and chemically converted to their acid form in an anion self-regenerating suppressor (ARSR). The volatile fatty acids pass through an electrical conductivity detector. The instrument responds by producing peaks that correspond to the individual VFA concentration.

## 2.1 Definitions

**Analytical Batch:** a group of twenty samples or fewer that are prepared and analyzed together.

**Laboratory Control Sample:** sample matrix free from analytes of interest, spiked with verified known amounts of analytes. A LCS is used to assess the performance of the measurement system.

**Matrix Spike/Matrix Spike Duplicate:** samples prepared by adding a known concentration of target analyte to a specific amount of sample. Matrix spikes are used to determine the effect of sample matrix on a method's recovery efficiency.

**Method Blank:** a sample of similar matrix that is free from the analytes of interest that is processed through all the steps of the analysis with other samples.

## 2.2 Method Limitations

Lactic acid (2-hydroxy propionic acid) co-elutes with hydroxy-iso-butyric acid (HIBA, 2 hydroxy-2 methyl propionic acid). Either of these may be a target analyte, but it is unlikely that they would both be found at detectable levels in the same well. Studies have shown that the two compounds respond equally, and the Laboratory Information System (LIMS) is set so that the client report reflects that any observed peak may be lactic acid, HIBA, or both.

The anion exchange chromatography used in this procedure produces considerable retention time shifts. Further confidence can be provided by the use of an analytical spike.

Retention time shifts are due to variations in the pH and the ionic strength of the treated sample. Any increase in ionic strength will shift retention times and may degrade the chromatography. For this reason, surrogates are not used in this method because they would increase the ionic strength of the sample.

Dichloroacetic acid, nitrate and bromide co-elute. Inadvertent introduction of carbonate or carbon dioxide can adversely affect the samples. Additionally, latex gloves must be worn throughout the preparation procedure to minimize the introduction of sulfate and chloride.

### **3.0 Apparatus, Materials, and Operating Conditions**

#### **3.1 Apparatus**

- Sample pre-treatment rack
- Dionex<sup>®</sup> Ion Chromatograph DX-500:
  - Chromatography Oven: LC 25
  - Conductivity Detector: CD 20
  - Gradient Pump: GP 40
  - Ion Trap Column: Ion Pac ATC-3, 9 x 24 mm
  - Analytical Column: Ion Pac ASII-HC, 4 x 250 mm
  - Sample Loop: 500  $\mu$ l
  - Suppressor: ASRS Ultra II, 4 mm
  - Guard Column: Ion Pac AG11-HC, 4 x 50 mm
  - Data collection system: IBM-compatible PC with Dionex Chromeleon software.

#### **3.2 Materials**

- Type II deionized degassed water

#### **3.3 Operating Conditions**

- Oven temperature: 35°C
- Reservoir pressure: 7psi
- Suppressor current: 50 mA

### **4.0 Reagents**

All reagents are prepared from water with a resistivity of 18-mega ohm/cm (Mohm); obtained from the Ultra-pure water system in Microseeps wet chemistry laboratory. Reagent grade chemicals are used in preparing all reagents. All standards are labeled and documented in accordance with Microseeps Standard Operating Procedure for Standards and Reference Materials SOP-ADM 15. The following reagents are used:

- IC Grade 50% Sodium Hydroxide (NaOH)
- Benzalkonium chloride (BAK)
- Degassed deionized water
- UHP Helium
- Formic acid
- HIBA
- Lactic acid
- Pyruvic acid

## 4.1 Standard Preparation Procedures

Standards are purchased as a custom mix from Supelco for the simple alkanolic acids and spiked with a mixture of Lactic acid, Pyruvic acid and HIBA. Initial calibration standards are prepared at five concentrations: low, medium low (MLow), medium (mid-range), medium high (MHigh) and high using 15,000X, 10,000X, 5000X, 1000X and 500X dilutions of the purchased standard mix. This is listed in Table 4.1.

### 4.1.1 Initial Calibration Verification (ICV)

Standards for initial calibration are prepared at a 1 ppm concentration from purchased stock standards. The acceptance criterion for the ICV is a percent drift of  $\pm 20\%$  from the initial calibration.

**Corrective Action:** If the initial calibration verification falls outside of the acceptance criterion, a new initial calibration is performed.

**Table 4.1**  
**Calibration Mix Concentrations**

Acid	Concentration in ppm	Low 15,000X	MLow 10,000X	Medium 5000X	MHigh 1000X	High 500X
Lactic acid	1000	0.667	0.100	0.200	1.00	2.00
Acetic	610.0	0.0406	0.0610	0.122	0.610	1.22
Propionic	777.1	0.0518	0.0776	0.155	0.776	1.55
Formic	499.4	-	-	-	-	-
i-Butyric <sup>1</sup>	886.4	-	-	-	-	-
Butyric	888.1	0.0591	0.0887	0.177	0.887	1.77
Pyruvic	1000	0.0667	0.100	0.200	1.00	2.00
i-Pentanoic	1054.1	0.0702	0.105	0.211	1.1	2.11
Pentanoic	1054.1	0.0702	0.105	0.211	1.1	2.11
i-Hexanoic	1161.6	0.0773	0.116	0.232	1.16	2.32
Hexanoic	1165.1	0.0776	0.116	0.233	1.16	2.33

<sup>1</sup> I-Butyric acid is only used as an internal retention time marker.

## 4.2 Eluent Preparation

The method on the computer uses 3 eluent solutions. The eluent solutions are de-gassed, de-ionized water (DDI) based sodium hydroxide (NaOH) solutions. The DDI water, and all solutions, must be degassed prior to use (see Appendix A). The greatest source of noise is

carbonate that has formed in the eluent. The higher the pH of the eluent, the more likely it is to sequester carbon dioxide and convert it into carbonate.

### **4.3 Preservative Solution Preparation**

#### **BAK field Preservative**

BAK is an extremely viscous liquid that is completely water soluble (it is a soap). Dissolve 12 grams of BAK into 1 liter of DI water.

### **4.4 Quality Control Sample Preparation**

#### **4.4.1 Laboratory Control Sample**

The laboratory control sample (LCS) is prepared at a 1 ppm concentration from purchased stock standards by adding 1ml of the standard solution to 9ml of deionized water.

#### **4.4.2 Matrix Spike/Matrix Spike Duplicate**

The matrix spike and spike duplicates are prepared using a 1000x dilution of the same standard used for initial calibration by adding 0.5ml of the standard solution to 9.5ml of deionized water.

#### **4.4.3 Continuing Calibration Verification**

The CCV is prepared at a concentration of 1 ppm from purchased stock standards by adding 0.25ml of the standard to 4.75ml deionized water.

### **4.5 Glassware and Storage Requirements for Reagents and Standards**

All standards are stored in tightly sealed glass containers and cooled to between 2°C and 6°C when not in use.

## **5.0 Procedure**

Samples are collected in 40 ml glass VOA vial and preserved with the BAK solution described in section 4.3.1. Preserved but further unprepared samples may be stored for up to 14 days at 4°C ± 2°C.

Analysts who use this method have been certified for the method by running Initial Demonstration of Proficiency (IDOP) Samples in accordance with Microseeps Standard Operating Procedure for Administering and Documenting Training in Laboratory Procedures and Instrumentation (SOP ADM 02). IDOP's are run any time there is significant change to an instrument, method, or in the training procedure for training a new analyst.

## 5.1 Sample Preparation

Prepare the sample bottles by adding 4 drops of prepared BAK solution to a clear glass 40 ml vial. Be sure that the full preservative name of benzalkonium chloride is written on the bottle labels.

## 5.2 Calibration

The calibration occurs in two parts: establishing a calibration curve (5.2.1) and verifying that curve (5.2.2).

### 5.2.1 Establishing the Calibration Curve

The calibration proceeds via three steps: standard sample preparation, peak identification and calibration calculation.

#### 5.2.1.1 Standard Sample Preparation

The standards are prepared according to the following procedure:

- Insure that the instrument is setup as specified in section 3.
- Prepare calibration standards and a blank by labeling six vials with the concentrations specified in section 4.1.
- Cap the vials, being sure to completely insert the filter-cap into the vials (the cap depression tool may be used to facilitate this).
- Load the calibration standards into an autosampler rack and begin a sequence file that identifies each bottle and its contents.

#### 5.2.1.2 Peak Identification

Initially, the order of elution must be measured from the analysis of single component standards. For a Dionex<sup>®</sup> AG11-HC/AS11-HC, that order has been found to be the same order in which the acids are listed in table 4.1, with HIBA exactly co-eluting with lactic acid.

With that information, the position and width of the retention time window used to make identifications should be based on 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 a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

#### 5.2.1.3 Calibration Calculations

The standards are analyzed as samples and then the Chromeleon software is used to combine the calibration and the method file. The calibration points (instrument response vs. concentration) are fit to a line without intercept via a least-squared-error type regression routine in the software.



For further procedural details, please see the Chromeleon software documentation. The correlation of determination must be at least 0.995. If this criterion is failed, the system should be inspected and the calibration repeated.

### **5.2.2 Initial Calibration Verification**

After initial calibration, the calibration curve must be verified by use of an ICV standard prepared at or near the mid-range of the calibration curve as specified in Section 4.1.

#### **5.2.2.1 ICV Acceptance Criteria**

The acceptance criteria for the ICV standard must be no greater than  $\pm 20\%$  of its true value.

#### **5.2.2.2 Corrective Action**

If the calibration curve cannot be verified within the specified limits, the cause must be determined and the instrument recalibrated before samples are analyzed.

### **5.3 Sample Analysis**

Instrument runs employing the autosampler should always start off with two blanks. The purpose of the first is to establish the baseline conditions discussed above and to clean the entire instrument. The data produced from this first analysis is of no use. This run is typically called the "blank XX". The second analysis is a true blank. The data it produces can be used to verify the cleanliness of the system at the start of the run. To insure that no analytes or samples are left in the analytical path, the last analysis should also be a blank. A method called "shutdown.met" was written to turn off the pump and the ASRS. It should always be in a schedule, and should always be last.

#### **5.3.1 Instrument Run Procedure**

For a new calibration, a new sequence file should be set up per 5.3.1.1. For a run that is using a pre-existing calibration, the current sequence should simply be appended to the existing sequence file, per 5.3.2.2.

##### **5.3.1.1 Setting Up and Using a New Sequence**

- With Chromeleon running, make sure the program is available and note the name of the program.
- On the IC computer, using Chromeleon and the timebase Semiv013, choose File>New>Sequence
- Use the Wizard to set up the sequence, responding to the prompts.

### 5.3.1.2 Using an Existing Sequence

- Select a sequence on the IC computer.
- Scroll to the last sample and append another below that by selecting the sample, right clicking on it, and choosing "Append".
- In the appended sample, change the sample type (standard or unknown, the last being for QC samples and client samples), the sample name and check the method and program.
- You can always add to a sequence after it has started.
- From the VFA panel choose "Batch" and "Start"

The method is already set up to synchronize the autosampler, IC injection valve, and the data acquisition system.

## 5.4 Quality Control Requirements

The following quality control samples must be run with each analytical batch or more frequently, if noted.

### 5.4.1 Continuing Calibration Verification

In order to verify the working calibration curve, a CCV shall be run at the beginning of each day, and after every twenty samples. The CCV should be made from the same material as the initial calibration standards at or near mid-range. If the instrument response has changed more than  $\pm 20\%$ , the instrument should be recalibrated.

**Corrective Action:** If the calibration cannot be verified within the specified limits, discontinue sample analysis, determine the cause, and recalibrate the instrument. All samples analyzed after the last acceptable CCV/CCB must be reanalyzed.

### 5.4.2 Continuing Calibration Blank

The CCV must be followed by a continuing calibration blank (CCB). The calibration blank must not contain target analytes above the PQL indicated in table 7.0.

Every instrument run must include an acceptable analysis of the following samples:

### 5.4.3 Performance/Method Blank

A performance (PBW) or method blank (18 Mohm water) shall be analyzed for each analytical batch. Any analytes detected in this blank must not be present in concentrations greater than that analyte in the lowest standard.

**Corrective Action:** If this criterion is not met, inspect all glassware, etc. and then prepare and analyze another blank. Blanks shall be run until this criterion is met. If three blanks are analyzed in succession and this criterion is still not met, the laboratory director shall be notified.

#### 5.4.4 Laboratory Control Sample (LCS)

A Laboratory Control Sample (LCS) as a second source QC reference sample shall be analyzed every twenty samples. The LCS should be spiked with each analyte of interest between the low and mid-level standards and must be carried throughout the entire sample preparation and analytical process. Acceptance criterion is a percent recovery between 70% and 130%.

**Corrective Action:** If the percent recovery for this sample is not between 70% & 130%, a fresh LCS solution should be made, and the LCS should be run again. If it fails again, all samples analyzed after the last acceptable LCS must be prepared again and reanalyzed.

#### 5.4.5 Matrix Spike and Matrix Spike Duplicate

Matrix spike and matrix spike duplicate (MS) samples shall be run for each analytical batch. The percent recovery must be between 70% and 130% and the relative percent difference (RPD) must be  $\leq 30\%$ .

**Corrective Action:** If this criterion fails, but all other instrument run criteria are passed, then it is simply noted in the case narrative for the instrument run and the analysis proceeds. Acceptance criteria shall be modified as in-house data is compiled.

#### 5.4.6 Contingency for Handling Out of Control or Unacceptable Data

All samples associated with out of control quality control samples must be reanalyzed. If quality control acceptance criteria cannot be met using the corrective action above, a detailed check of the de-ionized water and chemical purity is made. Reagents, standards, and other quality control samples are re-prepared and analyzed. If problems persist, sample analysis will be halted and the Technical Director shall be contacted immediately to determine the cause and implement corrective action.

Any data submitted with unacceptable quality control sample results shall be qualified in a case narrative. The narrative should indicate the out of control event that occurred, the corrective action that was taken, and any other pertinent information to inform the client of exactly what occurred.

### 5.5 Capturing and Submitting Data

After the anions are separated on the IC column, they are chemically converted to their acid form. The anion most prevalent in the column eluent is hydroxide ( $\text{OH}^-$ ). The acid form of hydroxide is water. Water has no measurable conductivity. The other acids all have measurable conductivity, so they produce peaks in the conductivity cell as they pass through it.

The peaks are maximized and the noise is minimized if the conversion is perfectly efficient. The conversion occurs in the suppressor (ASRS, or anion self regenerating suppressor).

The ASRS uses an electrical current to generate the hydronium ions ( $H^+$ ) that acidify the anions. If this current is too low, the ASRS cannot efficiently neutralize all of the hydroxide. If the current is too high, the useful lifetime of the ASRS is reduced. The minimum setting is 50 mA, and that is the present setting. If the baseline becomes noisier, this can be increased in the method, but such increases should generally be a last resort, and would require a recalibration.

Acquisition of data for all standards, samples, blanks, and laboratory control samples is done using a Windows based personal computer outfitted with Dionex Chromeleon software. The software collects data, plots the peaks, integrates the peaks, calculates the calibration curve associated with the target analytes, and calculates the concentrations of the analytes in mg/L. After review from the analyst, a standard report containing a chromatogram is printed.

The raw data from all analyses, including initial calibration, calibration verification, and method blanks are stored by the analyst in the laboratory where the analyses are performed.

#### **Formula:**

The formula used for calculating concentrations is as follows:

$$c = \frac{A}{c_{ii}}$$

Where:  $c$  = concentration.  
 $c_{ii}$  = first coefficient for compound  $i$ , determined from the calibration (5.2.1).  
 $A$  = area count or instrument response.

### **6.0 Secondary Data Review**

The analyst is responsible for insuring that all calibrations, calibration checks, and quality control samples are within the specifications outlined in this SOP.

All data are validated by the analyst and the Lead Analyst. Both signatures are required on the case narrative sheets that are turned in for each analytical batch.

The analyst checks all raw data and calculations for reasonableness and accuracy, making sure that sample dilutions are taken into account. Quality control results are rechecked for compliance with acceptance criteria. If any acceptance criteria cannot be met or if any atypical conditions are encountered, a Case Narrative detailing the conditions is written and handed in with the results.

## 6.1 Peer Review

All data derived from this method undergoes peer data review prior to being turned into the assistant laboratory director. This review served to catch potential errors prior to the data's entry into the Laboratory Information Management System. This review may only be done by another analyst who is certified in this method or the Group Lead Analyst.

## 6.2 Laboratory Director Review

The Laboratory Director reviews 10% of all laboratory data and calculations. This review includes sample results, quality control acceptance limits, and a review of the level of quality control required for the project.

## 6.3 Performance Evaluation Studies

Performance evaluation samples are currently not available. When they become available, they will be analyzed twice annually using this method.

## 7.0 Reporting Limits

Method detection limit studies are run annually in accordance with Microseeps Standard Operating Procedure for the Determination of Method Detection Limits and PQLs (SOP-ADM 18). Reporting limits for the VFAs are shown in table 7.0 below:

**Table 7.0**  
**Volatile Fatty Acid PQLs**

VFA	PQL in mg/L
Lactic Acid	0.07
Hydroxy-isobutyric acid (HIBA)	0.07
Acetic acid	0.07
Propionic acid	0.07
Formic acid	0.07
i-Butyric acid	0.07
Butyric acid	0.07
Pyruvic acid	0.07
i-Pentanoic	0.07
Pentanoic acid	0.10
i-Hexanoic	0.10
Hexanoic acid	0.10

## **8.0 Safety**

Safety glasses are required in all laboratory areas. Samples and reagents should always be handled with caution. For other safety concerns, consult Microseeps' Chemical Hygiene Plan. Material Safety Data Sheets (MSDS) for all compounds used in this procedure are available in the Microseeps' conference room.

## **9.0 Waste**

Unused portions of samples are kept for thirty days following analysis. The samples are then removed from the laboratory and stored until disposal according to Microseeps Standard Operation Procedure for Waste Disposal (SOP-ADM 14).

### **9.1 Waste Minimization**

Where possible, Microseeps takes steps to minimize the amount of waste generated by substitution and good chemical handling procedures. For specific information on waste minimization consult SOP-ADM 14.

## **10.0 References**

U.S. Environmental Protection Agency, 1996, Test Methods for Evaluating Solid Waste, SW-846, Office of Solid Waste and Emergency Response, Washington D.C. Method 9056 and Method 9056A.

Annual Book of ASTM Standards, Volume 11.01 Water D4327, Standard Test Method for Anions in Water by Ion Chromatography, pp. 696-703, 1988.

Standard Methods for the Examination of Water and Wastewater, Method 429, "Determination of Anions by Ion Chromatography with Conductivity Measurement," 16<sup>th</sup> Edition of Standard Methods.

# Appendix A

## **Contents:**

**Procedure for Degassing Water**

**Procedure for Regeneration of the ATC and cleaning of the ASRS**

**Instructions for priming the pump**

## Procedure for Degassing Water

To degas the water use the following procedure:

- Place the water to be degassed into a 4L side-arm vacuum Erlenmeyer flask with a clean, 18 Mohm water rinsed stir bar. Stopper the top of the flask.
  - Set the flask atop a stir plate. With the rotation initially at zero, gradually increase it so that the water throughout the entire flask is well stirred.
  - Attach the side arm to mechanical vacuum pump inlet and turn on the pump. Make sure that there is a liquid trap between the flask and the pump.
  - Pump-on and mix the solution for ~ 10 minutes. Bubbles will continue to come out of the water as the water boils under vacuum, but the rate of bubbling should slow dramatically by the time pumping is ceased.
  - Clamp the line from the sidearm to the trap closed and break the connection after the clamp. Turn off the stir plate. Be sure to handle the water with a minimum of agitation and atmospheric exposure.
-



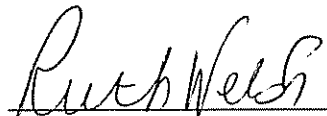
**Microseeps, Incorporated**

**Analytical Method AM20Gax**

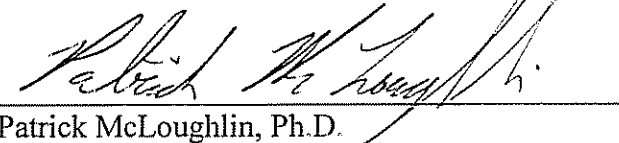
**Standard Operating Procedure for the**

**Analysis of Biodegradation Indicator Gases**

Controlled Copy No. \_\_\_\_\_

  
\_\_\_\_\_  
Ruth Welsh  
Laboratory Manager

Signature of Final Approval:

  
\_\_\_\_\_  
Patrick McLoughlin, Ph.D.  
Technical Director

3-1-05  
Date

SOP Review Date: March 1, 2005

## **1.0 Scope and Application**

Method AM20Gax is used to determine the concentration of biodegradation indicator gases in vapor samples. Specifically, Method AM20Gax is used to determine the dissolved concentration of the following gases:

<b>Gases</b>	<b>CAS Number</b>
Acetylene	74-86-2
Carbon dioxide	124-38-9
Oxygen	7782-44-7
Nitrogen	7727-37-9
Hydrogen	1333-74-0
Methane	74-82-8
Ethane	74-84-0
Ethene	74-85-1
Propane	74-98-6
Propene	115-07-1
n-Butane	106-97-8
i-Butane	75-28-5
Carbon Monoxide	630-08-0
Total Inorganic Carbon*	

\*Total inorganic carbon (TIC) is converted to carbon dioxide using the steps outlined in SOP-PM01. The sample is then analyzed for carbon dioxide according to this SOP. Any differences in method are specified in the appropriate section.

This method is recommended for use by, or under the supervision of, analysts experienced in sample preparation, the operation of gas chromatographs and in the interpretation of chromatograms.

## **2.0 Method Summary**

The sample gas is analyzed with a gas chromatograph capable of simultaneous analysis of all of the target analytes from a single 10 mL gas sample. A single injection of gas from integral, simultaneously filled sample loops is used to assure consistent injection volume. The permanent gases are analyzed using a thermal conductivity detector (TCD). The light hydrocarbons are analyzed using a flame ionization detector (FID). Hydrogen is analyzed using a reduction gas detector (RGD). The data are transferred to a microcomputer, converted to digital format, stored, and processed using a chromatography data system.

## 2.1 Definitions

**Batch:** A sample batch consists of twenty or fewer samples run during an eight-hour work shift.

**Instrument Flush:** The front end of the sample loop is flushed with ultra high purity helium injected into the loop directly from the cylinder to remove possible interference by ambient air and to avoid cross contamination between samples.

**Method Blank:** A sample analyzed by all three detectors that consists of ultra high purity helium. The method blank is free from the analytes of interest

**Laboratory Control Sample:** A sample spiked with verified known amounts of analytes. A LCS is used to assess the performance of the measurement system.

**Matrix Spike and Matrix Spike Duplicate:** A sample prepared by adding a known concentration of target analyte to a specific amount of sample. Matrix spikes are used to determine the effect of sample matrix on a method's recovery efficiency.

## 3.0 Apparatus and Materials and Operating Conditions

### 3.1 Apparatus

Gas Chromatograph: The chromatographs designed and built by Microseeps are equipped with multiple packed columns and multi-port valves, a TCD, a FID, a RGD, and multiple sample loops. The FIDs, which were also built by Microseeps, are of a special design that allows considerably more sensitivity than commercially available models. To increase the working range of the system, there are two outputs to the FID. Thus, it is a four-channel system: (1) FID low; (2) TCD; (3) RGD; and (4) FID high. As discussed in Section 5.3, each channel is calibrated separately. This instrument provides rapid turn-around for consecutive analyses and a clean baseline for accurate, reproducible results.

#### 3.1.1 Column Specifications

- **Column 1:** 80/100 mesh alumina packing material; 6' length, 3/16" OD; stainless steel, pre-washed (for hydrocarbon analysis).
- **Column 2:** 80/100 mesh Molesier 5A packing material; 12' length, 1/8" OD; stainless steel, pre-washed, preconditioned (for dissolved gas analysis).
- **Column 3:** 80/100 mesh Hayesep Q packing material; 12' length; 1/8" OD; stainless steel, pre-washed, preconditioned (for dissolved gas analysis).

### 3.2 Materials

- Sample vials (Supelco, Inc, Bellefonte, PA or equivalent)
- Syringe: locking gas tight

### 3.3 Operating Conditions

#### Gas Chromatograph:

- Sample Loop Temperature: ambient
- Thermal Conductivity Detector Temperature: 100°C
- Flame Ionization Detector Temperature: ambient
- Reduction Gas Detector Temperature: 280°C
- Oven Temp.: 100 °C. isothermal
- TCD Signal Range: 1
- FID Signal Range: variable depending on concentrations
- RGD Signal Range: 1
- He Carrier Gas Regulator Pressure: 60 psig
- Sample carrier flow: 30 mL/min.
- Reference flow: 30 mL/min.
- N2 Carrier Gas Regulator Pressure: 25 psig
- Sample carrier flow: 25 mL/min
- Valve Air Pressure: 60 psig.

#### 3.3.1 Interferences

The most likely source of "interference" is ambient air. Due to the relatively high concentrations of oxygen and nitrogen, a very small amount of air as a contaminant will dramatically affect the results. The analyst must take great care to ensure that air is flushed from the gas tight syringe before sample preparation and that no air has entered the syringe or needle prior to injection of the sample into the gas chromatograph.

Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. An unrestricted flow (Instrument flush) of pure carrier gas from a 10 psig source should be allowed to flow through each sample loop for 30 seconds prior to each analysis.

As required, the analyst should demonstrate the absence of carryover contamination by analysis of the contents of the sample loop when purged with carrier gas. This demonstration should be performed when carryover contamination is suspected (after high samples). In the event that 'ghost peaks' (peaks similar to previous sample) appear when a pure carrier gas sample is analyzed (method blank), measures should be taken to eliminate the carryover contamination.

## **4.0 Reagents**

- Helium (UHP Gas)
- Nitrogen (UHP Gas)
- Certified Commercial Gas Standards
- Benzalkonium chloride (BAK) solution – Prepared by dissolving 12.08 g into 1L DI water.
- Tri-sodium phosphate (TSP) – purchased as the dodecahydrate

### **4.1 Standard Preparation Procedures**

Calibration standards are prepared by using the procedures below:

#### **4.1.1 Vial Preparation**

Headspace vials used for instrument calibration standards for this method are prepared as follows:

- Crimp and cap each vial, with stopper septa.
- Evacuate each vial to vacuum below 100 milli torr.
- Flush each vial to atmospheric pressure with the vial preparation gas. The gas used depends upon the detector that is being calibrated and is specified in Table 4.1 below:

**Table 4-1**

<b>Detector</b>	<b>Vial Balance Gas</b>	<b>Standard Mix Vendor</b>
FID	Nitrogen	Spectra
TCD	Helium	Scotty
RGD	Nitrogen	Spectra and Scotty

#### **4.1.1 Preparing Calibration Standards**

Instrumentation is calibrated using dilutions of custom certified gas mixes. (Refer to Table 4.1.1 for the correct amounts of standard mix and vial preparation gas to inject into prepared vials.)

- Prepare the correct number of vials for the detector being calibrated.
- Inject the specified amount of standard by extracting it from the standard mix gas cylinder using a gas-tight syringe and injecting it into a prepared vial.
- Then the specified amount of vial balance gas is added to the same vial.

The dilution factor of one is achieved by directly injecting the standard gas mix from the cylinder into the GC.

**Table 4.1.1**  
**Standard Gas and Balance Gas Injection Volumes in ml**

Dilution Levels	Standard Gas Mix	Balance Gas	Final Gas Volume
1	N/A	N/A	N/A
2	21	21	42
5	10	40	50
10	5	45	50
25	2	48	50
100	2	198	200
250	1	249	250
2500	20 (of 250x)	180	200

#### 4.1.2 Calibration Standard Concentrations

Calibration standards are made up in the following concentrations as specified in Tables 4.1.2 A, B, and C. The true values of the calibration standards vary slightly from cylinder to cylinder. The values below are very close approximations. All standards are prepared using 22 cc headspace vials with stopper septum or 160cc serum bottles.

**Table 4.1.2 A**  
**FID Calibration**  
**In PPMV**

Compound	1X	5X	25X	250X	2500X
Methane	500	100	20	2	0.2
Ethane	500	100	20	2	0.2
Ethene	500	100	20	2	0.2
Propane	500	100	20	2	0.2
Propene	500	100	20	2	0.2
n-Butane	500	100	20	2	0.2
i-Butane	500	100	20	2	0.2
Compound	1X	2X	10X	50X	250X
Acetylene	100	50	10	2	0.4

**Table 4.1.2 B  
 TCD Calibration  
 In PPMV**

<b>Compound</b>	<b>1X</b>	<b>2X</b>	<b>10X</b>	<b>25X</b>	<b>100X</b>
Carbon Dioxide	150,000	75,000	15,000	6,000	1,500
Oxygen	70,000	35,000	7,000	2,800	700
Nitrogen	665,000	332,500	66,500	26,600	6650
Methane	45,000	22,500	4,500	1,800	450
Carbon Monoxide	70,000	35,000	7,000	2,800	700

**Table 4.1.2 C  
 RGD Calibration  
 In PPMV**

<b>Compound</b>	<b>10X</b>	<b>25X</b>	<b>100X</b>	<b>250X</b>	<b>2500X</b>
Hydrogen	50	20	5	2	0.2

## 4.2 Quality Control Sample Preparation

Quality control samples are prepared as indicated below.

### 4.2.1 Laboratory Control Sample (LCS) and LCS Duplicate (LCSD)

The LCS and LCSD are prepared at a mid-calibration range and are made from the same source as the matrix spike and spike duplicate. The type of LCS/LCSD depends upon the original matrix of the sample. For samples that arrive as vapors, the LCS/LCSD is injected as a gas. For samples that arrive as waters, DI water is spiked with a gas mixture of target analytes and prepared the same as the samples. Water that is free of the principle atmospheric components of nitrogen and oxygen is very difficult to make and similarly difficult to store. Toward that end, LCS/LCSD results for nitrogen will not be reported with client data. Table 4.2.2 below gives the true values of both the LCSs and MS/MSDs.

#### 4.2.1.1 Total Inorganic Carbon LCS

Mix approximately 0.20g NaHCO<sub>3</sub> into 200ml H<sub>2</sub>O, prepare according to the TIC procedures outlined in PM01 and analyze in duplicate as a sample. The true value of the spike is calculated as follows:

$$\text{Mg/L CaCO}_3 = \frac{\text{Mass}(g)\text{NaHCO}_3}{\text{H}_2\text{O}(L)} \times \frac{100.09}{84.01} \times (1,000,000)$$

#### 4.2.2 Matrix Spike (MS) and Matrix Spike Duplicate (MSD)

MS and MSDs are prepared, analyzed, and reported when clients' request and send sufficient numbers of aliquots to prepare them (e.g. one 40 ml vial each for the MS and the MSD). They are prepared, one at a time, as follows:

- Using a clean 50ml gas-tight locking syringe, withdraw a volume of water from the bottom of the sample vial.
- Withdraw 10 cc of the certified standard gas used for preparing the LCSs and lock the syringe.
- Shake the syringe by hand (for use a wrist action shaker) for five minutes.
- The equilibrated MS and/or MSD is/are now ready to be analyzed.

**Table 4.2.2**  
**LCS/MS/MSD True Values**

Compound	Vapor (ppmv)	Water
Methane	300	65.84 µg/L
Ethane	100	41,700 ng/L
Ethene	100	38,540 ng/L
Propane	100	60,560 ng/L
Propene	100	57,810 ng/L
iso-Butane	100	79,830 ng/L
n-Butane	100	79,830 ng/L
Carbon dioxide	50,000	30.22 mg/L
Oxygen	20,000	8.720 mg/L
Nitrogen	balance gas	balance gas
Hydrogen	25	344.1 nM

#### Notes on Table 4.2.2

- MS/MSD not performed on vapor samples and results are corrected for water samples.
- Actual values vary slightly from lot to lot of cylinders of calibration gases.
- MS/MSD prepared by using 10cc of standard instead of 10cc He in the headspace prep. procedure.



#### 4.2.2.1 Total Inorganic Carbon MS and MSD

Mix approximately 0.04g NaHCO<sub>3</sub> directly into client samples (when provided and requested), prepare according to the TIC procedures outlined in PM01 and analyze in duplicate as a sample. The true value of the spike is calculated as follows:

$$\text{Mg/L CaCO}_3 = \frac{\text{Mass}(g)\text{NaHCO}_3}{\text{H}_2\text{O}(L)} \times \frac{100.09}{84.01} \times (1,000,000)$$

#### 4.2.3 Method Blank

Method blanks are made up of ultra high purity helium injected into a vial and then into the instrument.

##### 4.2.3.1 Total Inorganic Carbon Method Blank

The method blank for TIC is made up of deionized water in a 40 ml vial, prepared according to the TIC procedures outlined in PM01, and analyzed as a sample.

#### 4.3 Glassware and Storage Requirements for Reagents and Standards

Reagents are stored at room temperature (70°F ±5°) and all standards are prepared fresh for each use immediately prior to each analysis. Standards are made up from compressed gas cylinders. Those standards expire after 2 years.

### 5.0 Procedure

Water samples should be cooled upon shipment and stored at a temperature of 4°C ±2°. Gas samples are shipped and received at a positive pressure, which eliminates a cross-contamination issue during sample shipment. It is preferable that gas samples be shipped without cooling. However, it is not a sample receipt non-conformance if received packed in ice (sample may experience slight loss in pressure.) Gas samples are stored in the laboratory at room temperature (70°F ±5°). The pressure in gas vials is not checked upon receipt in the laboratory because of the inherent risk of losing sample, or inadvertently introducing atmospheric gases, when the septum is pierced. The number of times the septum is pierced should be as few as absolutely possible. See Section 5.2.2 for a discussion on how the laboratory checks and documents vial pressure. Holding time for both gas and water samples is fourteen days.

Water samples for light hydrocarbon analyses only (methane, ethane, ethane, propane, propene, n-butane, i-butane, acetylene) are collected in 40ml VOA vials with zero headspace and preserved with tri-sodium phosphate (TSP). TSP is added as the dodecahydrate at 200 mg/40 ml vial. This results in a sample pH > 10. Water samples collected for either permanent gases only

or permanent gases and light hydrocarbon analyses are collected in 40ml amber VOA vials with zero headspace and preserved with four drops of BAK solution.

Analysts who use this method have been certified for the method by running Initial Demonstration of Proficiency (IDOP) Samples in accordance with Microseeps Standard Operating Procedure for Administering and Documenting Training in Laboratory Procedures and Instrumentation (SOP ADM 02). IDOPs are run any time there is significant change to an instrument, method, or in the training procedure for training a new analyst.

## **5.1 Sample Preparation**

Samples that are collected using the Bubble Strip Sampling Technique, Microseeps Sampling Method SM9, do not require additional preparation prior to analysis.

Samples that are collected as waters and are to be analyzed for dissolved gases (methane, ethane, ethene, acetylene, CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, propane, propene, iso-butane, n-butane, TIC), must be prepared using Microseeps Standard Operating Procedure PM01G.

Samples that are collected as gases, for example from a soil gas survey or from the headspace of a microcosm sample, need not be collected by a Microseeps sampling method, nor do they require additional preparation.

## **5.2 Analysis**

**5.2.1** If the sample is prepared via SOP-PM 01, it can be injected from the gastight syringe in which it is prepared by inserting the needle of the syringe through the septum on the "sample in" port. If the sample is a calibration standard, a bubble strip sample (SM9), or a gas, the septum inlet to the "sample in" port of the GC must be removed and a luer-lock needle receptacle is plumbed to the "sample in" port in place of the needle. A needle is attached to the luer-lock receptacle and inserted through the septa of the calibration standard, bubble stripped sample, or gas sample.

**5.2.2** In order to initiate analysis and introduce the sample into the GC sample loop, a needle is attached to the entry port on the GC and inserted through the sample septum. The flow through the sample loop is monitored by a flow meter connected to the sample-loop vent-port on the gas chromatograph.

When a vial is sufficiently filled, the ball in the flow meter will shoot to the top of the column. This indicates that there is sufficient pressure in the vial to fill the sample loop. If the loop is not properly pressurized, this is reflected on the flow meter immediately. The ball in the flow meter will go up the column part way and drop back to the bottom. This indicates there is not sufficient pressure in the sample vial. If this happens, the analyst will remove the vial from the inlet port as quickly as possible and withdraw 10 – 12ccs of sample from the sample vial using a locking

syringe. This is then injected into the instrument. The lack of sufficient pressure in the vial and the means of sample injection are then documented on the case narrative.

**5.2.3** Once the flow out of the sample loop ceases (3 seconds if SOP-PM 01 is used) the sample loop valves are activated.

**5.2.4** Once the sample loop valves are activated, the ports to and from the sample loop are flushed with ultra high purity helium injected into the loop directly from the cylinder to remove any interference from ambient air and to avoid cross contamination between samples.

### **5.3 Calibration and Results**

**5.3.1** The standard calibration gas should be introduced in the same manner as described in section 5.2.1 above. Measured peak areas are converted to concentrations using certified commercial gas standards. Dilutions are made to achieve multi-point calibration curves for each detector.

Methane can be detected on both the FID and the TCD. If the methane concentration causes an FID signal output level of 8000 millivolts, then any output exceeding that is quantified on the TCD.

**5.3.2** Initial calibration is accomplished by analyzing multiple standards of appropriate calibration ranges.

**Note:** Due to the nature of preparing custom gas standards, the component concentration can fluctuate between purchased lots. This is accounted for during method/calibration development. These results will be used to establish a multi-point calibration curve.

**Acceptance Criteria:** A linear fit to an area response versus concentration plot is formed with the origin forced to zero, and the calibration is accepted for use if  $r^2$ , the coefficient of determination is  $\geq 0.995$ .

**Corrective Action:** If the acceptance criteria specified above is not met, the reason is determined and a new set of calibration standards are analyzed.

**5.3.3** An Initial Calibration Verification (ICV) standard immediately follows the initial calibration. The ICV is made up from a second source and is identical to the LCS used for the analysis of vapors. Acceptance criterion for the ICV is an instrument response of  $\leq$  (less than or equal to) 20% (%D).

**Acceptance Criteria and Corrective Action:** If the instrument response for the ICV standard varies by more than 20% (%D), the analyst will not analyze samples until, either the reason is determined and the problem is corrected, or a new multi-point calibration is analyzed.

**5.3.4** An initial calibration blank follows the ICV. The blank is made up of the carrier gas. Compounds must not be detected above the reporting limits.

**Corrective Action:** If the blank does not meet the acceptance criterion, another blank is injected until the results are within the acceptance criterion.

**5.3.5** The analytes of this method are indicators. Every attempt to achieve and deliver precise results is made. However, it is realized that for indicator parameters measuring the range of the analyte concentration (*i.e.* is the concentration of methane gas >1 mg/l or < 0.1 mg/l) is the primary goal of employing these analyses. The calibration range is chosen to extend over most of the bio-indicator concentration range. If the concentration of an analyte exceeds that of the highest calibration standard, but does not saturate the instrument response, the concentration is calculated by assuming detector response linearity and using an extrapolation of the calibration plot. If the instrument response is saturated the sample is diluted to bring the analyte concentration into the calibration range.

## **5.4 Quality Control**

The following quality control samples shall be analyzed with each analytical batch of twenty or fewer samples.

**5.4.1 A Continuing Calibration Verification:** The CCV is made up from a source other than what was used to make up the initial calibration. The acceptance criterion for the CCV is a percent drift of  $\pm 20\%$ .

**Corrective Action:** If the CCV fails, the instrument shall be recalibrated, and all samples since the last acceptable calibration shall be reanalyzed, provided sufficient sample volume is present and the samples have not been compromised by exposure to air.

**5.4.2 A Continuing Calibration Blank:** A CCB follows each CCV. The blanks are made up of the carrier gas. The acceptance criterion for the blank is the result must be less than the reporting limits for all compounds.

**Corrective Action:** If the blank does not meet the acceptance criterion, another blank is injected until the results are within the acceptance criterion.

**5.4.3 Laboratory Control Sample and Laboratory Control Sample Duplicate:** The LCS and LCSD are prepared and analyzed at a mid-calibration range.

**Acceptance Criteria:** Percent recovery is required to be between 75% and 125%, inclusive. Acceptance criterion is based upon the percent recovery and the RPD as calculated by:

$$\text{Percent Recovery} = \frac{\text{Measured Value}}{\text{True Value}} \times 100\%$$

$$\text{RPD} = \frac{|C1 - C2|}{\frac{C1 + C2}{2}} \times 100\%$$

Where: C1=LCS  
C2=LCSD

RPD (Relative Percent Difference) is required to be less than or equal to 20%.

**Corrective Action:** If the LCS fails, a new LCS is prepared and analyzed. If the new LCS fails within the acceptance criterion, analysis continues. If the new LCS fails, analysis is stopped and the instrument is checked with a series of standards to determine the cause. Once the cause is determined and the instrument repaired, calibration is conducted and analysis continues.

**5.4.4 Matrix Spike and Matrix Spike Duplicate:** Matrix spikes and spike duplicates are analyzed for water samples only when requested by a client and sufficient sample aliquots are provided. Acceptance criterion is a percent recovery between 70% and 130%, and a relative percent difference of less than or equal to 20%.

**Corrective Action:** If the matrix spike and spike duplicate fail but all the other quality control samples are within the acceptance criteria, matrix interference is noted in the Case Narrative.

**5.4.5 Method Blank:** A method blank is analyzed with each sample batch. The blanks are made up of UHP helium for all of the gases except for blanks for TIC. TIC blanks are made up of deionized water. The acceptance criterion for the blank is the result must be less than the reporting limits for all compounds.

**Corrective Action:** If the blank does not meet the acceptance criterion, another blank is injected until the results are within the acceptance criterion.

#### **5.4.6 Contingency for Handling Out of Control or Unacceptable Data**

If the requirements set forth in section 5.4 are not met, the analytical program will be terminated until the cause is determined and a solution is affected. All samples associated with out of control quality control samples (with the exception of matrix interference) must be reanalyzed provided another vial of sample has been provided by the client. If quality control acceptance criteria cannot be met using the corrective action above, a detailed check of the analytical system is made. Reagents, standards, and other quality control samples are re-prepared and analyzed. If problems persist, sample analysis will be halted and the Laboratory Manager shall be contacted immediately to determine the cause and implement corrective action.

Any data submitted with unacceptable quality control sample results shall be qualified in a case narrative. The narrative should indicate the out of control event that occurred, the corrective action that was taken, and any other pertinent information to inform the client of exactly what occurred.

**5.4.7** An experienced analyst shall examine all chromatograms.

**5.4.8** Through out analysis the gas samples are injected mechanically into the GC flow path utilizing a sample loop to achieve a uniform sample size from a flow directly from the sample preparation syringe. The uniform sample size achieved using the sample loop assures consistent and accurate results. Table 5.4.8 (see next page) gives example data from a study performed via this analysis. That data can also be used for accuracy and precision estimates.

**Table 5.4.8**  
**Example Data for Precision and Accuracy Studies**

REP. #	Carbon Dioxide (%v)	Oxygen (%v)	Nitrogen (%v)	Methane (%v)	Hydrogen (PPMV)	Methane (PPMV)	Ethane (PPMV)	Ethylene (PPMV)	Propane (PPMV)	Propylene (PPMV)	Iso-Butane (PPMV)	N-Butane (PPMV)
1	0.1221	0.0670	0.5744	0.0410	0.1118	0.2512	0.0525	0.0453	0.0461	0.0581	0.0473	0.0358
2	0.1267	0.0690	0.6020	0.0428	0.1122	0.2608	0.0518	0.0468	0.0521	0.0465	0.0439	0.0407
3	0.1207	0.0657	0.5838	0.0446	0.1247	0.2812	0.0509	0.0485	0.0529	0.0588	0.0436	0.0405
4	0.1193	0.0667	0.6036	0.0444	0.1244	0.2779	0.0549	0.0460	0.0461	0.0536	0.0549	0.0476
5	0.1261	0.0703	0.5860	0.0439	0.1120	0.2894	0.0551	0.0497	0.0520	0.0549	0.0417	0.0460
6	0.1193	0.0665	0.5861	0.0478	0.0943	0.2970	0.0515	0.0467	0.0458	0.0542	0.0435	0.0514
7	0.1227	0.0732	0.5748	0.0353	0.1296	0.3053	0.0532	0.0473	0.0485	0.0584	0.0483	0.0535
AVERAGE	0.1224	0.0683	0.5872	0.0428	0.1156	0.2804	0.0528	0.0472	0.0491	0.0549	0.0462	0.0451
KNOWN	0.1500	0.0700	0.6649	0.0450	0.0999	0.1500	0.0500	0.0500	0.0500	0.0500	0.0500	0.0500
STD. DEV.	0.003	0.003	0.012	0.004	0.012	0.019	0.002	0.001	0.003	0.004	0.004	0.006

**5.4.9** The gas matrix for this analysis minimizes the opportunity for matrix effects. If the gas is prepared from a matrix other than that which is injected into the GC (*e.g.* prepared through headspace extraction via Microseeps SOP-PM01), the client should request that matrix spike (MS) and matrix spike duplicate (MSD) analyses be conducted and should supply sufficient sample volume. Since matrix effects are extremely site dependent, the MS and MSD are not part of the regular analytical quality assurance program.

**5.4.10** All of the target analytes are gases at room temperature so the opportunity for carry over is negligible. Because of the configuration of the GC used in this analysis, any possible carryover would only manifest itself as a ghost peak, well out of the RT windows of any analytes and thus never misinterpreted. For these reasons, samples that have high concentrations of analytes do not need to be followed by a blank analysis.

## **5.5 Capturing and Submitting Data**

The output of the chromatograph is directed to a microcomputer where the signal is converted to digital format, stored, and processed using a chromatography data system.

Automated valve control: Digital control is provided by the microcomputer through the chromatography data-system software. This control provides constant start and stop times for directing carrier gas flow. The event times are programmed and saved using the method editor module of the software.

### **5.5.1 Total Inorganic Carbon Result Calculation**

The total inorganic carbon result is calculated as follows:

$$\text{TIC as mg/L CaCO}_3 = (\% \text{CO}_2) \times (\text{Volume headspace}) \times (2.08) + 43.3$$

This analysis produces concentration of the analyzed gas in PPMV or % V. If the sample was collected via the bubble-strip method (Microseeps SOP SM9) or prepared through static headspace preparation (Microseeps SOP DGPM 01), the gas phase concentrations can be used to specify sample water concentrations via the calculations presented in those Standard Operating Procedures.

### **5.5.2 Retention Time Windows**

Retention time studies have been conducted for this analysis. These studies are kept on file in the Quality Systems Office. The retention times in Table 5.5.2 below are examples. The exact retention times will vary as a function of column type, column age, and column history. For the instruments that use this method, true retention times and retention time windows are taken from the most recent retention time window study conducted.



**Table 5.5.2**  
**Retention Time Windows**

Compound	RT Window (Min.)	RT Window (Min.)	RT Window (Min.)	RT Window (Min.)
	BioRem I Unit		BioRem II Unit	
Carbon Dioxide	5.171	5.340	4.058	4.635
Oxygen	6.537	7.015	5.686	5.721
Nitrogen	7.200	7.626	6.510	6.570
Methane	9.523	9.933	8.874	8.999
Carbon Monoxide	10.475	10.841	10.938	11.302
Methane	0.586	0.609	0.420	0.420
Ethane	0.809	0.835	0.730	0.730
Ethene	1.027	1.050	1.029	1.064
Propane	1.545	1.570	1.871	1.962
Propene	2.822	2.850	3.942	4.225
iso-Butane	3.763	3.807	5.804	6.230
n-Butane	4.351	4.399	6.855	7.379
Hydrogen	4.404	4.480	NA	NA

## **6.0 Secondary Data Review**

All analytical data must undergo a minimum of a two-tiered review. The analyst first reviews the data for completeness and accuracy. The data is then submitted to the Group Lead Analyst for final review and the data is entered into the LIMS. Once approved at this level, the data is released as a final report.

## **7.0 Reporting Limits**

The reporting limits for this analysis are listed in Table 7.0 below. Method detection limit studies are run annually in accordance with Microseeps Standard Operating Procedure for the Determination of Method Detection Limits and PQLs (SOP-ADM 18).

Those MDLs must be less than the reporting limits specified below. MDL studies are also performed when there is reason to suspect that method sensitivity has changed. The MDL studies are kept on file in the Quality Systems Office.

**Reporting Limits  
 Table 7.0**

Parameter	Reporting Limit	Units
Carbon Dioxide	0.02	%V
Oxygen	0.02	%V
Nitrogen	0.04	%V
Hydrogen	0.02	ppmv
Acetylene	0.34	ppmv
Methane	0.06	ppmv
Ethane	0.01	ppmv
Ethene	0.01	ppmv
Propane	0.01	ppmv
Propene	0.01	ppmv
n-butane	0.01	ppmv
i-butane	0.02	ppmv
Acetylene	500	ng/L

### 7.1 Conversion Factors

This procedure is used to measure the volume concentration of the analytes in a gas. Two methods are used to extract that gas from the groundwater. The conversion factors that are used to convert the concentration of the analytes in the water from the concentration of the analytes as they are measured using this method, are specific to the collection or preparation method and can be found in either SOP-SM9 or SOP-PM 01.

### 8.0 Safety

Gloves, proper eye protection, and a laboratory coat shall be worn when handling samples and standards. The major hazard in this laboratory area is stick from needles. All needles must be capped when not in use and when moving about the laboratory. The proper way of capping a needle is to place the cap on the laboratory bench and direct the needle into the cap. A needle is never to be directed into a cap while the cap is being held.

All compressed gases are to be moved using a dolly made for transporting gases and shall be chained in place when in the laboratory. The chain shall be tightened sufficiently to keep the cylinder upright if jostled.

## **9.0 Laboratory Waste**

Samples are kept for 30 days following analysis. Samples are disposed according to Microseeps Standard Operation Procedure for Waste Disposal (SOP-ADM 14).

### **9.1 Waste Minimization**

Where possible, Microseeps takes steps to minimize the amount of waste generated in the laboratory by using substitution, where possible, and good chemical handling procedures. For specific information on waste minimization consult SOP-ADM 14.

## **10.0 References**

Citing a reference does not imply that all of the recommendations and/or requirements in those cited methods is required in this Standard Operating Procedure. This section simply refers to sources that were consulted to gather information or knowledge in order to write an informed technical procedure.

U.S. Environmental Protection Agency, Test Methods for Evaluating Solid Waste. SW-846, 3<sup>rd</sup> ed., Office of Solid Waste and Emergency Response, Washington, DC. 1986.

Newel, B.S., RSKSOP-175, Sample Preparation and Calculations for Dissolved Gas Analysis in Water Samples using a GC Headspace Equilibration Technique. Revision No. 0, August 1994.

Newel, B.S., RSK-SOP-147, Gas Chromatographic Analysis of Gaseous Samples for Part-Per-Million Levels of Nitrous Oxide, Methane, Ethylene, and Ethane. Revision No. 0, August 1993.

American Society for Testing and Materials, Standard Practice for Analysis of Reformed Gas by Gas Chromatography. Annual Book of ASTM Standards. Vol. 14.02, 1994.

Kampbell, D.H. and Vandegrift, S.A., Analysis of Dissolved Methane, Ethane, and Ethylene in Ground Water by a Standard Gas Chromatographic Technique. Journal of Chromatographic Science. Vol. 36, May 1998.

**Appendix B**  
**Site-Specific Field Analyses Standard Operating Procedures**

✓ **Method 8034**

Periodate Oxidation Method\*

**Powder Pillows**

HR (0.2 to 20.0 mg/L)

**Scope and Application:** For soluble manganese in water and wastewater; USEPA approved for reporting wastewater analyses (digestion required)\*\*

\* Adapted from *Standard Methods for the Examination of Water and Wastewater*

\*\* *Federal Register*, 44(116) 34193 (June 14, 1979)



## Tips and Techniques

- Digestion required. See *Section 4 Sample Pretreatment by Digestion*.
- If only dissolved manganese is to be determined, filter the sample before acid addition.
- For more accurate results, determine a reagent blank value for each new lot of reagent. Follow the procedure using deionized water in place of the sample. Subtract the reagent blank value from the final results or perform a reagent blank adjust. See the instrument manual for more information on *Running a Reagent Blank*.

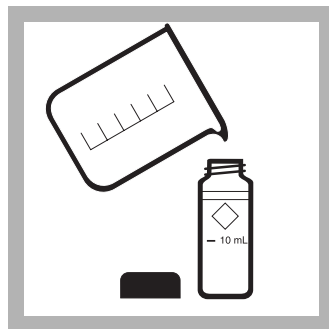


## Powder Pillows

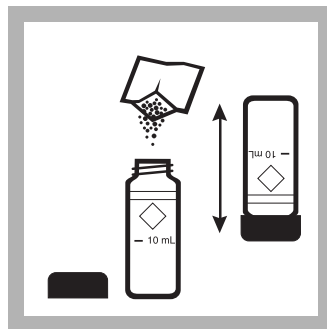
## Method 8034



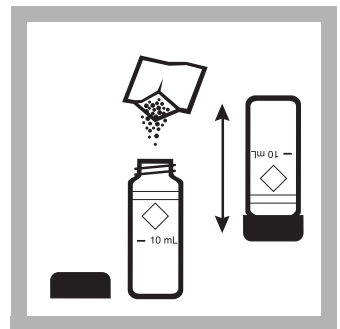
1. Touch **Hach Programs**.  
Select program **295 Manganese HR**.  
Touch **Start**.



2. Fill a round sample cell with 10 mL of sample.

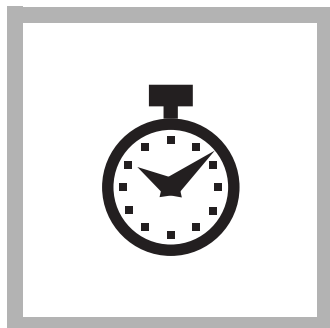


3. Add the contents of one Buffer Powder Pillow, Citrate Type for Manganese. Cap and invert gently to mix.

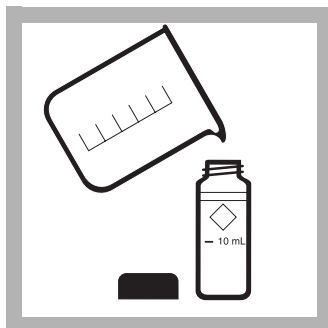


4. Add the contents of one Sodium Periodate Powder Pillow to the sample cell. Cap and invert gently to mix.  
A violet color will develop if manganese is present.

# Manganese



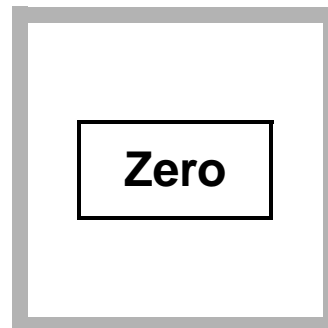
**5.** Touch the timer icon.  
Touch **OK**.  
A two-minute reaction period will begin.



**6.** Fill another round sample cell with 10 mL of sample.



**7.** When the timer beeps, place the blank into the cell holder.



**8.** Touch **Zero**.  
The display will show:  
**0.0 mg/L Mn**



**9.** Within eight minutes of the timer beep, place the sample into the cell holder.

Results will appear in mg/L Mn.

## Interferences

Interfering Substance	Interference Levels and Treatments
Calcium	700 mg/L
Chloride	70,000 mg/L
Iron	5 mg/L
Magnesium	100,000 mg/L
pH	Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see <i>Section 3.3 Interferences</i> on page 30.

## Sample Collection, Storage and Preservation

Collect samples in acid-washed plastic bottles. Do not use glass containers due to possible adsorption of Mn to glass. If samples are acidified, adjust the pH to 4–5 with 5.0 N Sodium Hydroxide (Cat. No. 2450-32) before analysis. Do not exceed pH 5, as manganese may precipitate. Correct the test result for volume additions; see *Section 3.1.3 Correcting for Volume Additions* on page 23.

## Accuracy Check

### Standard Additions Method (Sample Spike)

1. After reading test results, leave the sample cell (unspiked sample) in the instrument. Verify the chemical form.
2. Touch **Options**. Touch **Standard Additions**. A summary of the standard additions procedure will appear.
3. Touch **OK** to accept the default values for standard concentration, sample volume, and spike volumes. Touch **Edit** to change these values. After values are accepted, the unspiked sample reading will appear in the top row. See *Standard Additions* in the instrument manual for more information.
4. Snap the neck off a Manganese Voluette<sup>®</sup> Ampule Standard, 250-mg/L Mn (Cat. No. 14258-10).
5. Prepare three sample spikes. Fill three Graduated Mixing Cylinders (Cat. No. 1896-40) with 10 mL of sample. Use the TenSette<sup>®</sup> Pipet (Cat. No. 19700-01) to add 0.1 mL, 0.2 mL, and 0.3 mL of standard, respectively, to each sample and mix thoroughly. This will result in a 2.5 mg/L increase in manganese in each sample spike.
6. Analyze each sample spike as described in the procedure above, starting with the 0.1 mL sample spike. Accept each standard additions reading by touching **Read**. Each addition should reflect approximately 100% recovery.
7. After completing the sequence, touch **Graph** to view the best-fit line through the standard additions data points, accounting for matrix interferences. Touch **View: Fit**, then select **Ideal Line** and touch **OK** to view the relationship between the sample spikes and the “Ideal Line” of 100% recovery.

See *Section 3.2.2 Standard Additions* on page 26 for more information.

### Standard Solution Method

1. Prepare a 10.0-mg/L manganese standard solution by pipetting 10.0 mL of Manganese Standard Solution, 1000-mg/L, into a 1000-mL volumetric flask. Dilute to the mark with deionized water. Prepare this solution daily. Perform the manganese periodate oxidation procedure as described above.
2. The calibration curve can be adjusted to account for variability in laboratory technique. To adjust the calibration curve using the reading obtained with the 10.0 mg/L standard solution, touch **Options** on the current program menu. Touch **Standard Adjust**.
3. Touch **On**. Touch **Adjust** to accept the displayed concentration (the value depends on the selected chemical form). If an alternate concentration is used, touch the number in the box to enter the actual concentration, then touch **OK**. Touch **Adjust**.

# Manganese

## Method Performance

### Precision

Standard: 10.0 mg/L Mn

Program	95% Confidence Limits of Distribution
295	9.8–10.2 mg/L Mn

See *Section 3.4.3 Precision* on page 33 for more information, or if the standard concentration did not fall within the specified range.

### Sensitivity

Portion of Curve	$\Delta$ Abs	$\Delta$ Concentration
0.010 abs	0.010	0.13 mg/L Mn
10 mg/L	0.010	0.14 mg/L Mn
18 mg/L	0.010	0.15 mg/L Mn

See *Section 3.4.5 Sensitivity* on page 34 for more information.

## Summary of Method

Manganese in the sample is oxidized to the purple permanganate state by sodium periodate, after buffering the sample with citrate. The purple color is directly proportional to the manganese concentration. Test results are measured at 525 nm.

## Required Reagents

Description	Quantity Required per test	Unit	Cat. No.
High Range Manganese Reagent Set (100 Tests).....			24300-00
Includes:			
Buffer Powder Pillows, citrate type for manganese.....	1 pillow.....	100/pkg.....	21076-69
Sodium Periodate Powder Pillows, for manganese.....	1 pillow.....	100/pkg.....	21077-69

## Required Apparatus

Sample Cells, 10 mL, w/cap .....	2 .....	6/pkg.....	24276-06
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## Required Standards

Manganese Standard Solution, 1000-mg/L Mn.....	100 mL.....	12791-42
Manganese Standard Solution, 10-mL Voluette® Ampule, 250-mg/L Mn.....	16/pkg.....	14258-10
Metals Drinking Water Standard, HR for Cu, Fe, Mn.....	500 mL.....	28336-49
Water, deionized .....	4 liters.....	272-56



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HACH COMPANY  
WORLD HEADQUARTERS  
Telephone: (970) 669-3050  
FAX: (970) 669-2932



## Method 8146

1, 10 Phenanthroline Method\*

### Powder Pillows or AccuVac® Ampuls

(0.02 to 3.00 mg/L)

**Scope and Application:** For water, wastewater, and seawater

\* Adapted from *Standard Methods for the Examination of Water and Wastewater*, 15th ed. 201 (1980)



## Tips and Techniques

- Analyze samples as soon as possible to prevent air oxidation of ferrous iron to ferric iron, which is not determined.
- For more accurate results, determine a reagent blank value for each new lot of reagent. Follow the procedure using deionized water in place of the sample. Subtract the reagent blank value from the final results or perform a reagent blank adjust. See the instrument manual for more information on *Running a Reagent Blank*.
- If ferrous iron is present, an orange color will form after adding the reagent.

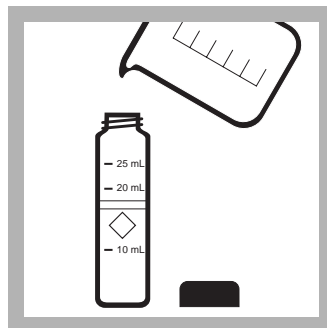


## Powder Pillows

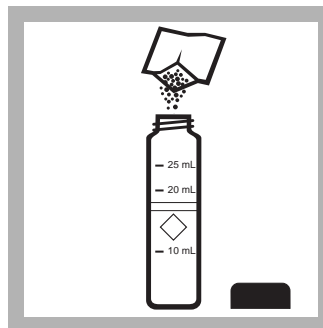
## Method 8146



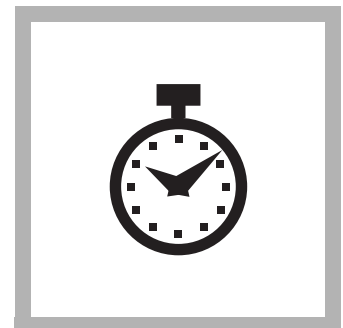
- Touch **Hach Programs**.  
Select program **255 Iron, Ferrous**.  
Touch **Start**.



- Fill a clean, round sample cell with 25 mL of sample.

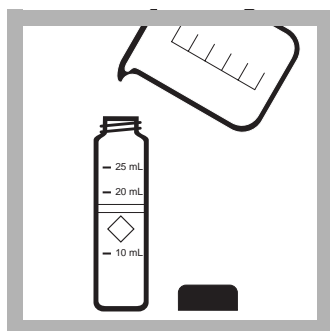


- Add the contents of one Ferrous Iron Reagent Powder Pillow to the sample cell (the prepared sample). Swirl to mix.

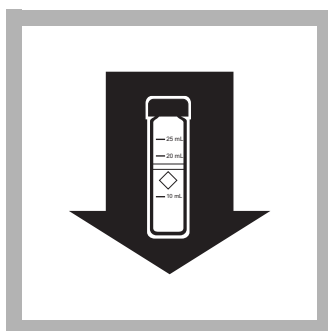


- Touch the timer icon. Touch **OK**.  
A three-minute reaction period will begin.

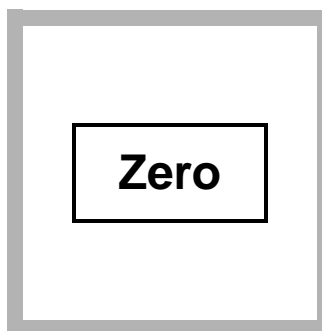
# Iron, Ferrous



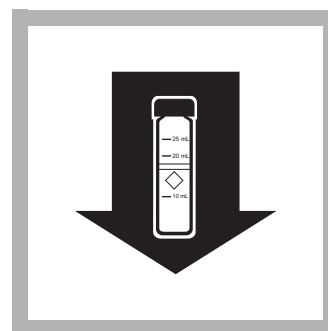
5. Fill a second round sample cell with 25 mL of sample (the blank).



6. When the timer beeps, place the blank into the cell holder.



7. Touch **Zero**.  
The display will show:  
**0.00 mg/L Fe<sup>2+</sup>**



8. Place the prepared sample into the cell holder.

Results will appear in mg/L Fe<sup>2+</sup>.

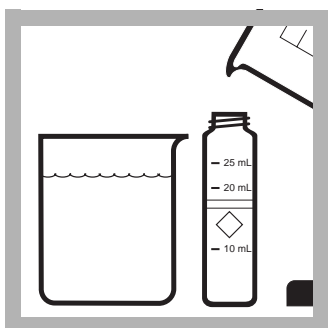


## AccuVac Ampul

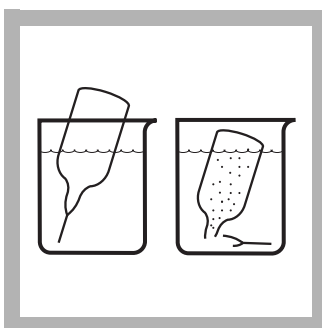
## Method 8146



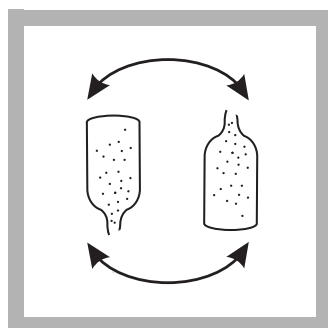
1. Touch  
**Hach Programs**.  
Select program  
**257 Iron, Ferrous AV**.  
Touch **Start**.



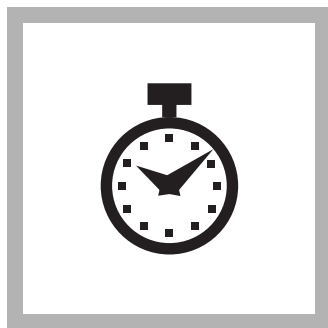
2. Fill a sample cell with 25 mL of sample (the blank). Collect at least 40 mL of sample in a 50-mL beaker.



3. Fill a Ferrous Iron AccuVac® Ampul with sample. Keep the tip immersed while the ampule fills completely.



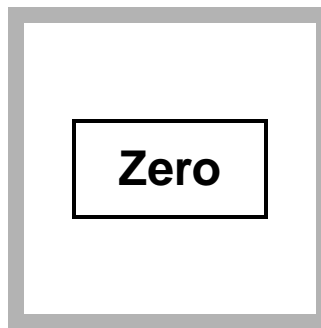
4. Quickly invert the ampule several times to mix. Wipe off any liquid or fingerprints.



**5.** Touch the timer icon. Touch **OK**. A three-minute reaction period will begin.



**6.** When the timer beeps, place the blank into the cell holder.



**7.** Touch **Zero**. The display will show:  
**0.00 mg/L Fe<sup>2+</sup>**



**8.** Place the AccuVac Ampul into the cell holder. Results will appear in mg/L Fe<sup>2+</sup>.

## Sample Collection, Storage and Preservation

Collect samples in plastic or glass bottles. Analyze samples as soon as possible after collection.

## Accuracy Check

### Standard Solution Method

1. Prepare a ferrous iron stock solution (100-mg/L Fe<sup>2+</sup>) by dissolving 0.7022 grams of Ferrous Ammonium Sulfate, hexahydrate, in deionized water. Dilute to one liter in a Class A volumetric flask. In a 100-mL Class A volumetric flask, dilute 1.00 mL of this solution to 100 mL with deionized water to make a 1.0-mg/L standard solution. Prepare this solution immediately before use. Perform the iron procedure as described above.
2. To adjust the calibration curve using the reading obtained with the 1.0-mg/L Fe<sup>2+</sup> Standard Solution, touch **Options** on the current program menu. Touch **Standard Adjust**.
3. Touch **On**. Touch **Adjust** to accept the displayed concentration. If an alternate concentration is used, touch the number in the box to enter the actual concentration, then touch **OK**. Touch **Adjust**.

See *Section 3.2.4 Adjusting the Standard Curve* on page 49 for more information.

## Method Performance

### Precision

Standard: 1.000 mg/L Fe

Program	95% Confidence Limits of Distribution
255	0.989–1.011 mg/L Fe
257	0.977–1.023 mg/L Fe

See *Section 3.4.3 Precision* on page 53 for more information, or if the standard concentration did not fall within the specified range.

# Iron, Ferrous

## Sensitivity

Program	Portion of Curve	$\Delta$ Abs	$\Delta$ Concentration
255	Entire range	0.010	mg/L Fe
257	Entire range	0.010	0.023 mg/L Fe

See Section 3.4.5 Sensitivity on page 54 for more information.

## Summary of Method

The 1,10 phenanthroline indicator in the Ferrous Iron Reagent reacts with ferrous iron in the sample to form an orange color in proportion to the iron concentration. Ferric iron does not react. The ferric iron ( $\text{Fe}^{3+}$ ) concentration can be determined by subtracting the ferrous iron concentration from the results of a total iron test. Test results are measured at 510 nm.

## Required Reagents

Description	Quantity Required per test	Unit	Cat. No.
Ferrous Iron Reagent AccuVac <sup>®</sup> Ampuls.....	1 ampul.....	25/pkg.....	25140-25
<i>or</i>			
Ferrous Iron Reagent Powder Pillows.....	1 pillow.....	100/pkg.....	1037-69

## Required Apparatus

Beaker, 50-mL.....	1.....	each.....	500-41H
Sample Cells, 10-20-25 mL, w/cap.....	2.....	6/pkg.....	24019-06

## Required Standards

Ferrous Ammonium Sulfate, hexahydrate, ACS.....	113 g.....	11256-14
Water, deionized.....	4 liters.....	272-56



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## Method 8203

## Phenolphthalein and Total using Sulfuric Acid Method

### Digital Titrator

(10 to 4000 mg/L as CaCO<sub>3</sub>)

**Scope and Application:** For water, wastewater, and seawater



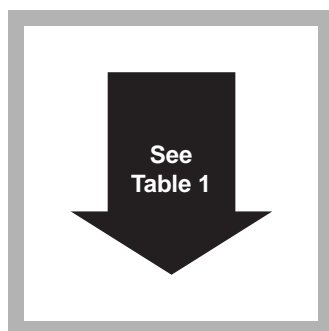
### Tips and Techniques

- For added convenience when stirring, use the TitraStir® apparatus (Cat. No. 19400-00, -10).
- Four drops of Phenolphthalein Indicator Solution (Cat. No. 162-32) may be substituted for the Phenolphthalein Indicator Powder Pillow.
- Four drops of Bromcresol Green-Methyl Red Indicator Solution (Cat. No. 23292-32) may be substituted for the Bromcresol Green-Methyl Red Indicator Powder Pillow.
- meq/L Alkalinity = mg/L as CaCO<sub>3</sub> ÷ 50

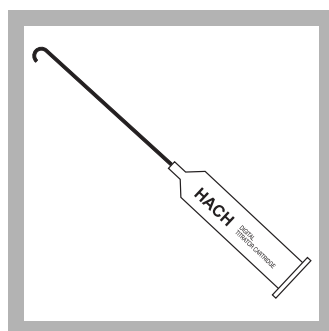


### Digital Titrator

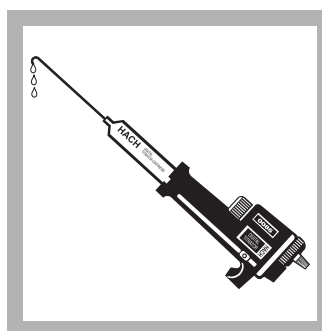
### Method 8203



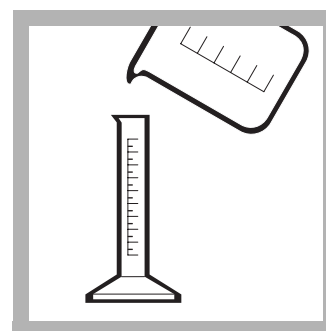
**1.** Select the sample volume and Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>) Titration Cartridge that correspond to the expected alkalinity concentration as mg/L calcium carbonate (CaCO<sub>3</sub>) from *Table 1*.



**2.** Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body.

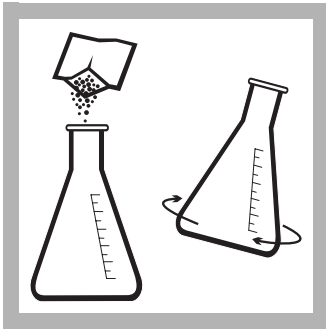


**3.** Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

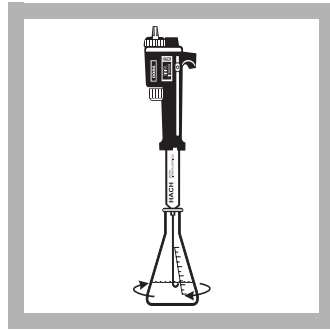


**4.** Use a graduated cylinder or pipet to measure the sample volume from *Table 1*. Transfer the sample into a clean, 250-mL Erlenmeyer flask. Dilute to the 100-mL mark with deionized water, if necessary.

# Alkalinity

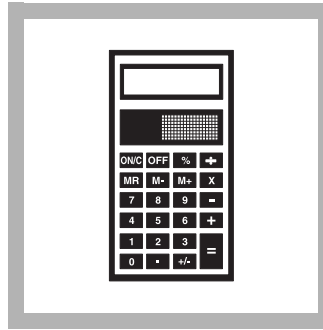


5. Add the contents of one Phenolphthalein Indicator Powder Pillow and swirl to mix.



6. If the solution turns pink, titrate to a colorless end point. Place the delivery tube tip into the solution and swirl the flask while titrating with sulfuric acid. Record the number of digits required.

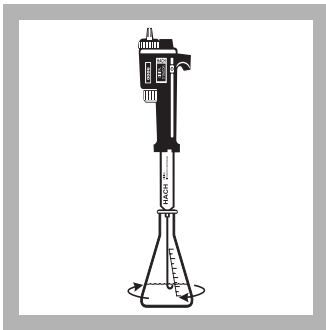
If the solution is colorless before titrating with Sulfuric acid, the Phenolphthalein (P) alkalinity is zero. Proceed to step 8.



7. Calculate:  
 Digits Required X  
 Digit Multiplier =  
 mg/L as CaCO<sub>3</sub> P Alkalinity



8. Add the contents of one Bromcresol Green-Methyl Red Indicator Powder Pillow to the flask. Swirl to mix.



9. Continue the titration with sulfuric acid to a light pink (pH 4.5) color as required by sample composition. Record the number of digits required.

**Note:** A pH meter may be used to titrate to a specific pH as required by sample composition. See Table 2.



10. Calculate:  
 Digits Required X  
 Digit Multiplier =  
 mg/L as CaCO<sub>3</sub> Total (T or M)  
 Alkalinity

Carbonate, bicarbonate, and hydroxide concentrations may be expressed individually using the relationships shown in Table 3.

Table 1

Range (mg/L as CaCO <sub>3</sub> )	Sample Volume (mL)	Titration Cartridge (N H <sub>2</sub> SO <sub>4</sub> )	Catalog Number	Digit Multiplier
10–40	100	0.1600	14388-01	0.1
40–160	25	0.1600	14388-01	0.4
100–400	100	1.600	14389-01	1.0
200–800	50	1.600	14389-01	2.0
500–2000	20	1.600	14389-01	5.0
1000–4000	10	1.600	14389-01	10.0

**Table 2 End Point pH**

Sample Composition	End Point	Phenolphthalein Alkalinity
Alkalinity about 30 mg/L	pH 4.9	pH 8.3
Alkalinity about 150 mg/L	pH 4.6	pH 8.3
Alkalinity about 500 mg/L	pH 4.3	pH 8.3
Silicates or phosphates present	pH 4.5	pH 8.3
Industrial wastes or complex system	pH 4.5	pH 8.3
Routine or Automated Analyses	pH 4.5	pH 8.3

## Sampling and Storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Avoid excessive agitation or prolonged exposure to air. Samples should be analyzed as soon as possible after collection but can be stored at least 24 hours by cooling to 4 °C (39 °F) or below. Warm to room temperature before analyzing.

## Alkalinity Relationship Table

Total alkalinity primarily includes hydroxide, carbonate and bicarbonate alkalinities. The concentration of these alkalinities in a sample may be determined when the phenolphthalein and total alkalinities are known (see *Table 3*).

**Table 3 Alkalinity Relationship**

Row	Result of Titration	Hydroxide Alkalinity Equals:	Carbonate Alkalinity Equals:	Bicarbonate Alkalinity Equals:
1	Phenolphthalein Alkalinity = 0	0	0	Total Alkalinity
2	Phenolphthalein Alkalinity equal to Total Alkalinity	Total Alkalinity	0	0
3	Phenolphthalein Alkalinity less than one-half of Total Alkalinity	0	Phenolphthalein Alkalinity times 2	Total Alkalinity minus two times Phenolphthalein Alkalinity
4	Phenolphthalein Alkalinity equal to one-half of Total Alkalinity	0	Total Alkalinity	0
5	Phenolphthalein Alkalinity greater than one-half of Total Alkalinity	2 times Phenolphthalein Alkalinity minus Total Alkalinity	2 times the difference between Total and Phenolphthalein Alkalinity	0

To use the table follow these steps:

- a. Does the phenolphthalein alkalinity equal zero? If yes, use Row 1.
- b. Does the phenolphthalein alkalinity equal total alkalinity? If yes, use Row 2.
- c. Divide the total alkalinity by 2 to give one-half the total alkalinity.
- d. Select Row 3, 4, or 5 based on comparing the result of step c (one-half total alkalinity) with the total alkalinity.
- e. Perform the required calculations in the appropriate row, if any.
- f. Check your results. The sum of the three alkalinity types will equal the phenolphthalein alkalinity.

**For example:**

A sample has 170 mg/L as CaCO<sub>3</sub> phenolphthalein alkalinity and 250 mg/L as CaCO<sub>3</sub> total alkalinity. What is the concentration of hydroxide, carbonate and bicarbonate alkalinities?

The phenolphthalein alkalinity does not equal 0 (it is 170 mg/L), see step a.

The phenolphthalein alkalinity does not equal total alkalinity (170 mg/L vs. 250 mg/L), see step b.

One-half of the total alkalinity (250 g/L) equals 125 mg/L. Because the phenolphthalein alkalinity (170 mg/L) is greater than one-half the total alkalinity (125 mg/L), select Row 5.

**The hydroxide alkalinity is equal to:**

$$2 \times 170 = 340$$

$$340 - 250 = 90 \text{ mg/L hydroxide alkalinity}$$

**The carbonate alkalinity is equal to:**

$$250 - 170 = 80$$

$$80 \times 2 = 160 \text{ mg/L carbonate alkalinity}$$

**The bicarbonate alkalinity equals 0 mg/L.**

Check: (See step f)

$$90 \text{ mg/L hydroxide alkalinity} + 160 \text{ mg/L carbonate alkalinity} + 0 \text{ mg/L bicarbonate alkalinity} = 250 \text{ mg/L}$$

The above answer is correct; the sum of each type equals the total alkalinity.

## Accuracy Check

**End Point Confirmation**

A solution of one pH 8.3 Buffer Powder Pillow (Cat. No. 898-68) and one Phenolphthalein Powder Pillow in 50 mL of deionized water is recommended as a comparison for determining the proper end point color.

A solution of one Bromcresol Green-Methyl Red Powder Pillow and one pH 4.5 Buffer Powder Pillow (895-68) in 50 mL of deionized water is recommended as a comparison for judging the pH 4.5 end point color.



## Standard Additions Method (Sample Spike)

This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Snap the neck off an Alkalinity Voluette<sup>®</sup> Ampule Standard, 0.500 N.
2. Use a TenSette Pipet (Cat. No. 19700-01) to add 0.1 mL of standard to the sample titrated in steps 6 or 9. Resume titration back to the same end point. Record the number of digits needed.
3. Repeat, using two more additions of 0.1 mL. Titrate to the end point after each addition.
4. Each 0.1 mL addition of standard should require 25 additional digits of 1.600 N titrant or 250 digits of 0.1600 N titrant. If these uniform increases do not occur, refer to *Section 3.4 Method Performance* to determine the cause.

## Interferences

Highly colored or turbid samples may mask the color change at the end point. Use a pH meter (Cat. No. 51700-10) for these samples, titrating to a pH 8.3 for phenolphthalein alkalinity and the appropriate pH (see *Table 2*) for total alkalinity.

Chlorine at levels above 3.5 mg/L may cause a yellow-brown color upon the addition of the Bromocresol Green-Methyl Red Powder Pillow. Add one drop of 0.1 N Sodium Thiosulfate (Cat. No. 323-32) to eliminate this interference.

## Summary of Method

The sample is titrated with sulfuric acid to a colorimetric end point corresponding to a specific pH. Phenolphthalein alkalinity is determined by titration to a pH of 8.3, as evidenced by the color change of phenolphthalein indicator, and indicates the total hydroxide and one half the carbonate present. M (methyl orange) or T (total) alkalinity is determined by titration to a pH between 3.7 and 5.1, and includes all carbonate, bicarbonate and hydroxide. Alternatively, total alkalinity end points may be determined by using a pH meter and titrating to the specific pH required for the sample composition.

# Alkalinity

---

## Required Reagents

Description	Unit	Cat. No
Alkalinity Reagent Set (about 100 tests) (varies with sample characteristics).....		22719-00
Includes:		
Bromcresol Green-Methyl Red Powder Pillows.....	100/pkg.....	943-99
Phenolphthalein Powder Pillows.....	100/pkg.....	942-99
Sulfuric Acid Titration Cartridge, 1.600 N.....	each.....	14389-01
Sulfuric Acid Titration Cartridge, 0.1600 N.....	each.....	14388-01
Water, demineralized.....	4 L.....	272-56

## Required Apparatus

Select one or more based on sample concentration

Cylinder, graduated, 10-mL.....	each.....	508-38
Cylinder, graduated, 25-mL.....	each.....	508-40
Cylinder, graduated, 50-mL.....	each.....	508-41
Cylinder, graduated, 100-mL.....	each.....	508-42
Digital Titrator.....	each.....	16900-01
Flask, Erlenmeyer, 250-mL.....	each.....	505-46

## Required Standards

Alkalinity Standard Solution, Voluette® Ampule 0.500 N Na <sub>2</sub> CO <sub>3</sub> , 10-mL.....	16/pkg.....	14278-10
Buffer Powder Pillows, pH 4.5.....	25/pkg.....	895-68
Buffer Powder Pillows, pH 8.3.....	25/pkg.....	898-68



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## Method 8205

## Digital Titrator Method Using Sodium Hydroxide

### Digital Titrator

(10 to 1000 mg/L as CO<sub>2</sub>)

**Scope and Application:** For water and seawater



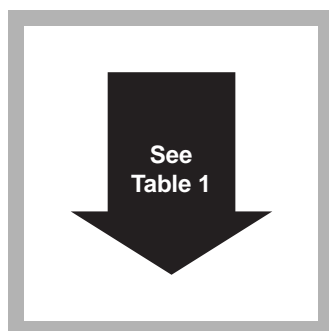
### Tips and Techniques

- For added convenience when stirring, use the TitraStir apparatus (Cat. No. 19400-00, -10).
- For more accurate results, check the calibration of the Erlenmeyer flask. Fill a graduated cylinder with the sample volume of deionized water. Pour the water into the Erlenmeyer flask and mark the proper level with a wax pencil or permanent marker.
- Four drops of Phenolphthalein Indicator Solution (Cat. No. 162-32) can be substituted for the Phenolphthalein Indicator Powder Pillow.
- Minimize agitation of the sample to avoid loss of carbon dioxide.

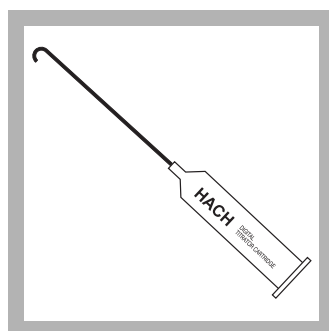


### Digital Titration

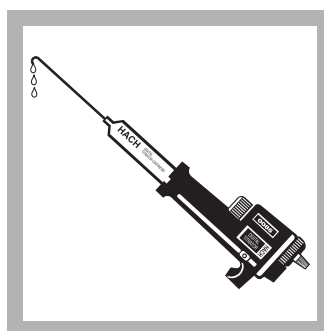
### Method 8205



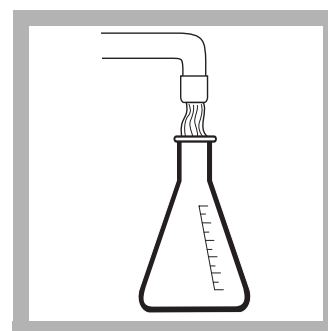
**1.** Select a sample size and a Sodium Hydroxide (NaOH) Titration Cartridge in *Table 1* that correspond to the expected carbon dioxide (CO<sub>2</sub>) concentration.



**2.** Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body.

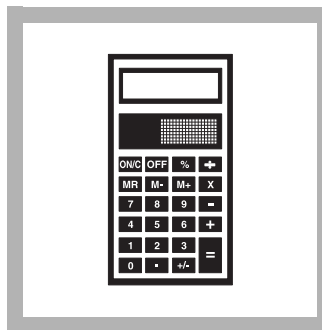
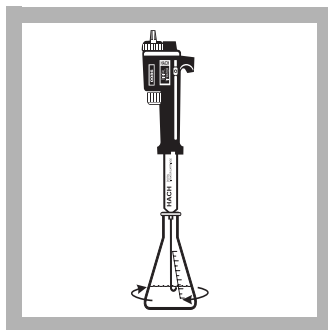


**3.** Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.



**4.** Collect a water sample directly into the titration flask by filling to the appropriate mark.

# Carbon Dioxide



5. Add the contents of one Phenolphthalein Indicator Powder Pillow and mix.

If a pink color forms, no carbon dioxide is present.

6. Place the delivery tube into the solution and swirl the flask gently while titrating with sodium hydroxide from colorless to a light pink color that persists for 30 seconds (pH 8.3). Record the number of digits required.

7. Calculate:

$$\text{Total Digits Required} \times \text{Digit Multiplier} = \text{mg/L as CO}_2$$

Table 1

Range (mg/L as CO <sub>2</sub> )	Sample Volume (mL)	Titration Cartridge (N NaOH)	Catalog Number	Digit Multiplier
10–50	200	0.3636	14378-01	0.1
20–100	100	0.3636	14378-01	0.2
100–400	200	3.636	14380-01	1.0
200–1000	100	3.636	14380-01	2.0

## Interferences

Highly colored or turbid sample may mask the color change of the end point. Use a pH meter (Cat. No. 51700-10) for these samples, titrating to pH 8.3. Other acid components in the sample will be titrated and interfere directly in this determination.

Sodium hydroxide standard solutions tend to lose strength slowly with age and should be checked periodically by titrating a known standard. Check the solution frequently (monthly) by titrating 50 mL of Potassium Acid Phthalate Standard Solution, 100 mg/L CO<sub>2</sub>, using Phenolphthalein Indicator Solution. The titration should require 5.00 mL of titrant. If the volume required for this titration is greater than 5.25 mL, discard the sodium hydroxide and replace it with a fresh supply.

## Sampling and Storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Avoid excessive agitation or prolonged exposure to air. Analyze samples as soon as possible after collection. If immediate analysis is not possible, the samples may be stored for at least 24 hours by cooling to 4 °C (39 °F) or below. Before analysis, warm the samples to room temperature.

## Accuracy Check

### Standard Additions Method

This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Snap the neck off a Carbon Dioxide Voluette Ampule Standard for Carbon Dioxide, 10,000 mg/L CO<sub>2</sub>.
2. Use a TenSette Pipet (Cat. No. 19700-01) to add 0.1 mL of standard to the sample titrated in step 6. Resume titration back to the same end point. Record the number of digits required.
3. Repeat, using additions of 0.2 mL and 0.3 mL. Titrate to the same end point after each addition.
4. Each 0.1 addition of standard should require 50 additional digits of 0.3636 N titrant or five digits of 3.636 N titrant. If these uniform increases do not occur, refer to *Section 3.2.2 Standard Additions* on page 46.

## Summary of Method

Acidity due to carbon dioxide in a sample is titrated with sodium hydroxide to a phenolphthalein end point. Strong acids are assumed to be absent or of insignificant concentration. See *Appendix A, Chemical Procedures Explained*.

### Required Reagents (varies with sample characteristics)

Description	Unit	Cat. No.
Carbon Dioxide Reagent Set (about 100 tests) .....		22727-00
Includes:		
Phenolphthalein Powder Pillows .....	100/pkg.....	942-99
Sodium Hydroxide Titration Cartridge, 0.3636 N.....	each .....	14378-01
Sodium Hydroxide Titration Cartridge, 3.636 N.....	each .....	14380-01
Water, deionized .....	4 L .....	272-56

### Required Apparatus

Digital Titrator.....	each.....	16900-01
Select one or more based on sample concentration:		
Flask, Erlenmeyer, 250-mL.....	each.....	505-46
Flask, Erlenmeyer, 125-mL.....	each.....	505-43

### Required Standards

Carbon Dioxide Standard Solution, Voluette® Ampule, 10,000-mg/L as CO <sub>2</sub> , 10-mL.....	16/pkg.....	14275-10
Phenolphthalein Indicator Solution, 5-g/L .....	100 mL MDB.....	162-32
Potassium Acid Phthalate Standard Solution, 100-mg/L as CO <sub>2</sub> .....	100 mL.....	2261-42



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**Appendix C**  
**Field Forms**

# OVERBURDEN BORING REPORT

<b>PARSONS</b>	CLIENT:	BORING NO.:
----------------	---------	-------------

PROJECT :	START DATE:
SWMU # (AREA) :	FINISH DATE:
SOP NO.:	CONTRACTOR:

### DRILLING SUMMARY

DRILLING METHOD	HOLE DIA.(ft)	DEPTH INTERVAL (ft)	SAMPLER		HAMMER	
			SIZE	TYPE	TYPE	WT/FALL

DRILLER:	
INSPECTOR:	
CHECKED BY:	
CHECK DATE:	
BORING CONVERTED TO MW?	Y    N

### DRILLING ACRONYMS

HSA	HOLLOW-STEM AUGERS	HMR	HAMMER	SS	SPLIT SPOON
DW	DRIVE-AND-WASH	SHR	SAFETY HAMMER	CS	CONTINUOUS SAMPLING
MRS LC	MUD-ROTARY SOIL-CORING	HHR	HYDRAULIC HAMMER	5I	5 FT INTERVAL SAMPLING
CA	CASING ADVANCER	DHR	DOWN-HOLE HAMMER	NS	NO SAMPLING
SPC	SPIN CASING	WL	WIRE-LINE	ST	SHELBY TUBE
				3S	3 INCH SPLIT SPOON

### MONITORING EQUIPMENT SUMMARY

INSTRUMENT TYPE	DETECTOR TYPE/ENERGY	RANGE	BACKGROUND			CALIBRATION		WEATHER (TEMP., WIND, ETC.)
			READING	TIME	DATE	TIME	DATE	

### MONITORING ACRONYMS

PID	PHOTO - IONIZATION DETECTOR	BGD	BACKGROUND	DGRT	DRAEGER TUBES
FID	FLAME - IONIZATION DETECTOR	CPM	COUNTS PER MINUTE	PPB	PARTS PER BILLION
GMD	GEIGER MUELLER DETECTOR	PPM	PARTS PER MILLION	MDL	METHOD DETECTION LIMIT
SCT	SCINTILLATION DETECTOR	RAD	RADIATION METER		

### INVESTIGATION DERIVED WASTE

DATE			
SOIL AMOUNT : (fraction of drum)			
DRUM #, LOCATION:			

#### COMMENTS:

#### SAMPLES TAKEN:

SAMPLES	
DUPLICATES	
MS/MSD	
MRD	





# OVERBURDEN MONITORING WELL COMPLETION REPORT & INSTALLATION DETAIL PROTECTIVE RISER COMPLETION

<b>PARSONS</b>		CLIENT: _____	WELL #: _____
PROJECT: _____		PROJECT NO: _____	
LOCATION: _____		INSPECTOR: _____	
		CHECKED BY: _____	
DRILLING CONTRACTOR: _____		POW DEPTH: _____	
DRILLER: _____		INSTALLATION STARTED: _____	
DRILLING COMPLETED: _____		INSTALLATION COMPLETED: _____	
BORING DEPTH: _____		SURFACE COMPLETION DATE: _____	
DRILLING METHOD(S): _____		COMPLETION CONTRACTOR/CREW: _____	
BORING DIAMETER(S): _____		BEDROCK CONFIRMED (Y/N?): _____	
ASSOCIATED SWMU/AOC: _____		ESTIMATED GROUND ELEVATION: _____	
PROTECTIVE SURFACE CASING:			
DIAMETER: _____		LENGTH: _____	TOR: _____
RISER:			
TOC: _____		TYPE: _____	LENGTH: _____
SCREEN:			
TSC: _____		TYPE: _____	LENGTH: _____
		DIAMETER: _____	SLOT SIZE: _____
POINT OF WELL: (SILT SUMP)			
TYPE: _____		BSC: _____	POW: _____
GROUT:			
TG: _____		TYPE: _____	LENGTH: _____
SEAL:			
TBS: _____		TYPE: _____	LENGTH: _____
SAND PACK:			
TSP: _____		TYPE: _____	LENGTH: _____
SURFACE COLLAR:			
TYPE: _____		RADIUS: _____	THICKNESS CENTER: _____
		THICKNESS EDGE: _____	
CENTRALIZER DEPTHS			
DEPTH 1: _____		DEPTH 2: _____	DEPTH 3: _____
		DEPTH 4: _____	
COMMENTS:			
* ALL DEPTH MEASUREMENTS REFERENCED TO GROUND SURFACE			

SEE PAGE 2 FOR SCHEMATIC







SAMPLING ORDER		PRESERVATIVES		BOTTLES		SAMPLE NUMBER	TIME	CHECKED BY/ DATE
				COUNT/ VOLUME	TYPE			
1	VOC -CLP(Low Level) 8260B	4 deg. C	HCL	3/ 40 ml	VOA			
2	SVOC 8270C	4 deg. C		1 x 1L	Am G			
3	PESTICIDES 8081	4 deg. C		1 x 1L	Am G			
4	PCBs 8082			1 x 1L				
5	METALS 6010 & 7###	4 deg. C	HNO3	1 x 500 mL	HDPE			
6	CYANIDE 9012	4 deg. C	NaOH	1 x 500 mL	HDPE			
7	Total Pet Hydrocarbon	4 deg. C	HCl	1 x 1L	Am G			

**COMMENTS: (QA/QC?)**

**IDW INFORMATION:**







