8/91

ARCS V

Remedial Activities at Uncontrolled Hazardous Waste Sites in Region V

EPA United States Environmental Protection Agency

QUALITY ASSURANCE PROJECT PLAN

ONALASKA MUNICIPAL LANDFILL
Onalaska, Wisconsin

Remedial Design Treatability Study

WA 38-5NL5/Contract No. 68-W8-0040

CH2M HILL

QUALITY ASSURANCE PROJECT PLAN

ONALASKA MUNICIPAL LANDFILL
Onalaska, Wisconsin

Remedial Design Treatability Study

WA 38-5NL5/Contract No. 68-W8-0040

August 14, 1991

Section 1
TITLE PAGE

REMEDIAL PLANNING ACTIVITIES
(ARCS V)
CONTRACT NO. 68-W8-0040
QUALITY ASSURANCE PROJECT PLAN (QAPP)

Project Title: Remedial Design
Treatability Study
Onalaska Municipal Landfill
Onalaska, Wisconsin

EPA No: WA 38-5NL5

EPA Remedial Project Officer: Stephen Nathan

Prepared by: CH2M HILL Date: August 14, 1991

Approved by: _____ Date: 8/15/91
Steven Keith
CH2M HILL Site Manager

Approved by: _____ Date: 8/15/91
Alpheus Sloan, III
Acting CH2M HILL Program Manager

Approved by: _____ Date: _____
Kevin Adler
EPA Region 5
Remedial Project Manager

GLT175/019.51

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Section 3
PROJECT DESCRIPTION

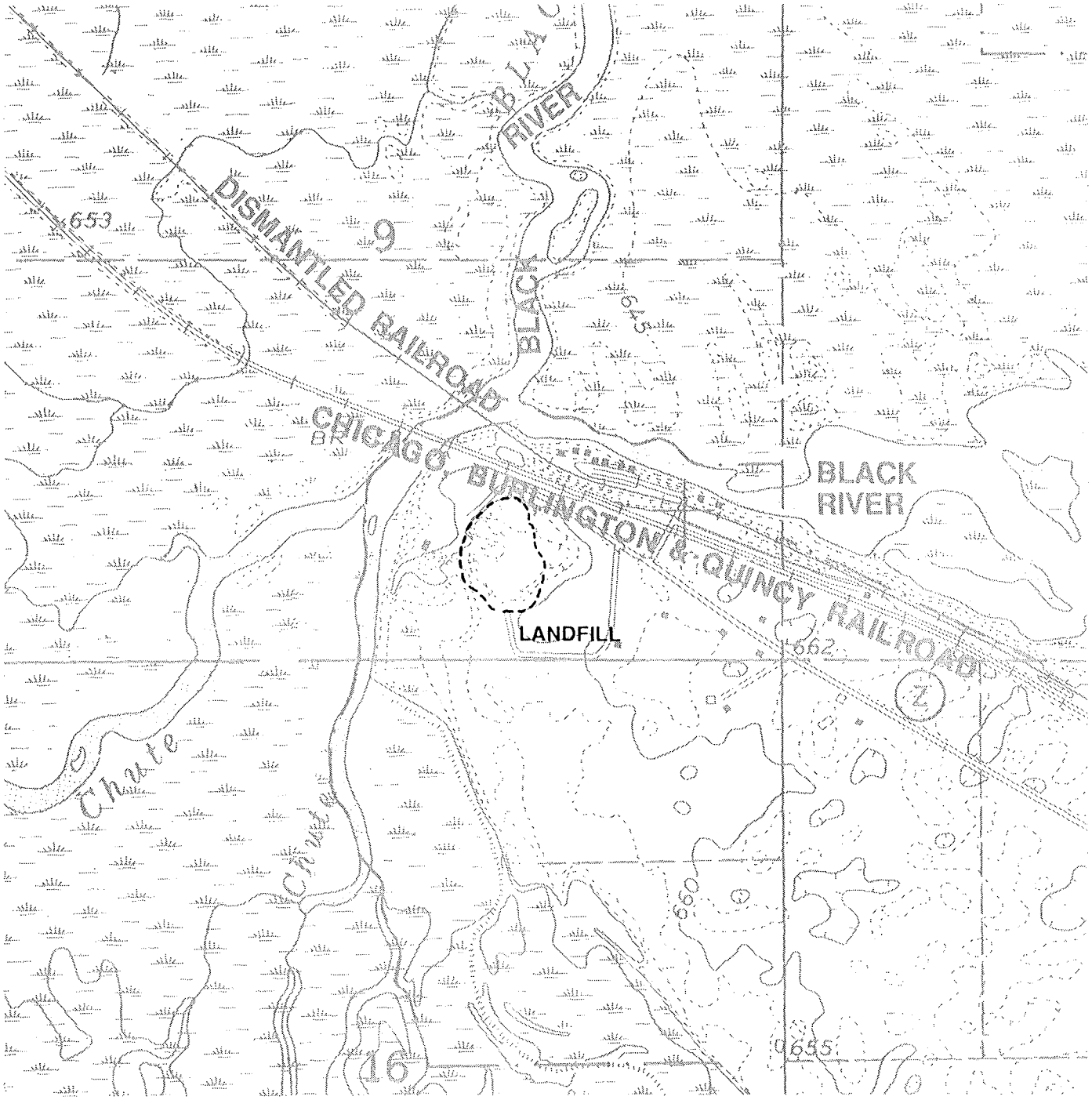
The United States Environmental Protection Agency (EPA) requires that all EPA contractors participate in a centrally managed quality assurance (QA) program. That requirement applies to all environmental monitoring and measurement efforts mandated or supported by the EPA. Each contractor generating data has the responsibility to implement minimum procedures to ensure that the precision, accuracy, completeness, and representativeness of its data are known and documented. To ensure that this responsibility is met uniformly, each EPA contractor must prepare a written Quality Assurance Project Plan (QAPP) addressing each project it is contracted to perform.

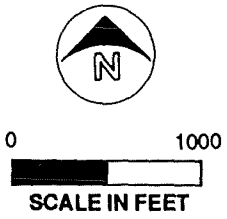
This QAPP is prepared as part of work assignment 38-5NL5 under ARCS V (Contract No. 68-W8-0040) which authorizes CH2M HILL to complete the remedial design for the Onalaska Municipal Landfill in Onalaska, Wisconsin. This QAPP presents the organization, objectives, functional activities, and specific QA/QC activities associated with bench-scale bioremediation treatability studies necessary to produce information and data pertinent to the remedial design. Specifically, it addresses the collection and handling of soil samples, and the subsequent treatment, sampling, and analysis activities to determine the amenability of contaminants for biodegradation.

3.1 SITE DESCRIPTION

The Onalaska Municipal Landfill is in La Crosse County, Wisconsin, about 10 miles north of the City of La Crosse near the confluence of the Mississippi River and within 400 feet of the Black River (Figure 1). Several homes are located within 500 feet of the site, and a subdivision of about 50 homes is located 1.25 miles southeast of the site. The area is generally rural and the sand and gravel aquifer is the water supply.

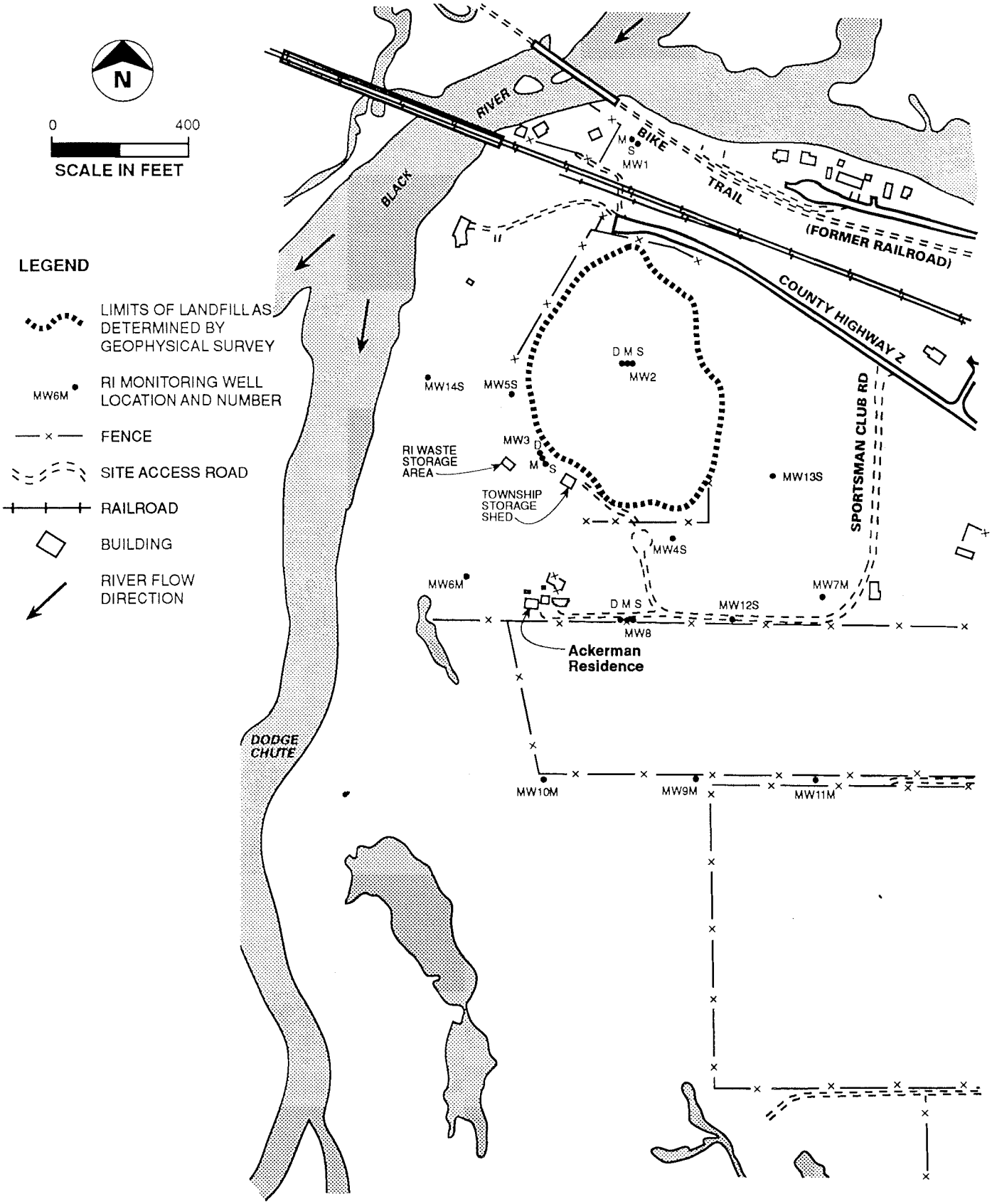
The 11-acre site was mined as a sand and gravel quarry in the early 1960s (see Figure 2). In the mid-1960s the quarry operation ceased, and the Town of Onalaska began using the quarry as a municipal landfill. Between 1969 and 1980, municipal trash and chemical wastes were disposed of in the landfill. The landfill was capped during the period of 1980 to 1982. The site is not fenced, but two gates restrict vehicular access to it.





SOURCE:
U.S. Geological Survey,
Trempealeau, 15' Quadrangle.

FIGURE 1
SITE LOCATION MAP
ONALASKA RD
TREATABILITY QAPP



GLO65550.FI FIG 2 site map 8-9-91

FIGURE 2
SITE MAP
ONALASKA RD
TREATABILITY QAPP

3.2 SITE HISTORY AND BACKGROUND

3.2.1 SITE HISTORY

The Town of Onalaska owned and was licensed to operate the Onalaska Landfill from 1969 to 1980 when the Wisconsin Department of Natural Resources (DNR) ordered its closure. During 11 years of operation, the Onalaska Landfill provided waste disposal for residential, commercial, and industrial generators located within the township and for nonresidents with a written permit. The landfill also accepted refuse from other townships.

Landfill operations were informal. During the first 3 years of operation, there was no attendant at the landfill. Later, operating hours were posted and an operator was present to cover incoming waste and measure the nonresidential waste for billing purposes. The landfill boundaries were defined by a cable or fence partially enclosing the site. A gate was installed at the site in early 1971 to restrict site access. However, keys were readily provided to clients who wished to use the landfill outside the posted operating hours.

Seven acres of the Onalaska Landfill were reportedly reserved for using the compaction and cover method of waste disposal. The landfill was regularly inspected by the DNR. Early DNR records indicate that open burning was practiced at the site in late 1970. The DNR prohibited all open burning in January 1971 after receiving several complaints about noxious odors and sooty, black smoke resulting from the burning of naphtha, an oily industrial solvent waste. Consequently, the DNR required an area be designated specifically for the disposal of industrial solvents and wastes delivered to the site. Several industrial firms are known to have used the landfill for waste disposal.

Outers Laboratories and Metallics, Inc., contributed significant quantities of industrial wastes to the site. Daily landfill operation reports indicate Outers and Metallics, at the time owned by the same individual, were disposing of industrial waste oils and solvents as early as July 7, 1970. Early DNR records report that Outers delivered liquid solvent residues to the site for burning. The waste solvents consisted primarily of naphtha, toluene, and paint residues. Initially, Outers and Metallics hauled solvent wastes in 55-gallon barrels. Once a week, 20 to 25 barrels of industrial wastes from both companies were hauled to the landfill. The barrels were emptied and the waste was burned. After burning was banned, the liquid waste was dumped in the designated area and poured into excavated holes for immediate burial. Occasionally, full barrels were left at the site if they could not be easily emptied or if they were damaged or leaking. In later years, the liquid waste was hauled in a 500-gallon truck instead of barrels. At that time, approximately 300 barrels were mass buried at the landfill.

On one occasion, when a tank truck hauling the waste could not be drained because the discharge outlet was plugged with hardened paint resin and solvent, the truck was reportedly buried in the south section of the landfill. In August 1975, the DNR recommended that Outers find alternative methods to dispose of its naphtha waste. Outers investigated and eventually implemented a reclamation process to recover some of the raw materials from the waste. In April 1976, Outers informed the DNR that it was no longer disposing of liquid wastes in the landfill.

On February 9, 1978, the DNR issued an order to the township to submit an infield conditions report for the landfill because the site did not meet Wisconsin solid waste codes. Warzyn Engineering investigated the site for the township and submitted a report to the DNR on April 17, 1978. Warzyn recommended phased abandonment of the site. In June 1978, the DNR reported that the average distance between the groundwater table and the base of the refuse pile at the site was 1 foot. Studies showed that the seasonal fluctuations in water levels sometimes allowed the groundwater to be in direct contact with a portion of the waste for extended periods of time.

On October 19, 1978, Warzyn Engineering submitted a plan of operation for phased abandonment of the landfill. On May 4, 1979, the DNR issued a plan approval and ordered the landfill closed by September 30, 1979. On May 30, 1980, the DNR modified the order to close the landfill by September 30, 1980. Closure proceeded in phases, and the final cap was placed in July 1982.

In September 1982, the DNR sampled monitoring wells and private wells for compliance with drinking water standards for organic and inorganic constituents. The investigations indicated groundwater contamination had occurred. The water in Cecil Miller's residential well south of the site exceeded the drinking water standards for barium and five organic compounds were detected above background levels. In January 1983, the Town of Onalaska replaced Mr. Miller's well with a deep well.

On May 2, 1983, an EPA Potential Hazardous Waste Site inspection report was submitted. In September 1984 the Onalaska Landfill was placed on the National Priorities list with a hazard ranking of 42.97.

3.2.2 BACKGROUND

The Onalaska Landfill used about 7 acres for open pit disposal. Records indicate that refuse was compacted and covered at the end of each collection day. Table 1 is a partial list of wastes disposed of at the landfill. There is little indication that the wastes were segregated, so industrial, commercial, and municipal wastes are considered to be mixed throughout the fill area. The industrial waste solvents from Outers and Metallics are an exception since a specific area was designated for liquid

Table 1
Characteristics of Chemicals Deposited
(Page 1 of 5)

NAPHTHA (VM & P)

Composed of 40 to 80 percent aliphatic hydrocarbons, 25 to 50 percent naphthenic hydrocarbons, 0 to 10 percent benzene, and 0 to 20 percent other aromatic hydrocarbons.

Observable Characteristics:

Watery liquid
Colorless
Gasoline-like odor

Physical and Chemical Properties:

Flash point: 103°F
Boiling point (1 atm): 266–311°F
Specific gravity: 0.84
Latent heat of vaporization: 103–150 Btu/lb
Heat of combustion: 18,200 Btu/lb
Immiscible in water, components slightly soluble in water

NAPHTHA (Stoddard Solvent)

Contains paraffins, naphthenes, alkylbenzenes, with a trace of benzene. Derived from petroleum.

Observable Characteristics:

Watery liquid
Colorless
Gasoline-like odor

Physical and Chemical Properties:

Flash point: 103°F
Boiling point (1 atm): 320–390°F
Specific gravity: 0.78
Latent heat of vaporization: 103–150 Btu/lb
Heat of combustion: 18,200 Btu/lb
Immiscible in water, components slightly soluble in water

Table 1
Characteristics of Chemical Deposited
(Page 2 of 5)

NAPHTHA (High Flash)

A coal tar derivative consisting of a mixture of aromatic hydrocarbons, principally toluene, xylene, cumene, and possibly benzene (depending on grade).

Observable Characteristics:

Watery liquid
Color: Crude—dark straw-colored
Refined—water-white
Hydrocarbon-like odor (like benzene, toluene, and xylene)
Produces irritating vapor

Physical and Chemical Properties:

Flash point: 107°F
Boiling point (1 atm): 200–500°F
Specific gravity: 0.86–0.88
Latent heat of vaporization: 101 Btu/lb
Heat of combustion: 18,200 Btu/lb
Immiscible in water, components slightly soluble in water

MINERAL SPIRITS

A naphtha composed of a fraction slightly lower in boiling point than Stoddard solvent (names are often used interchangeably). Fraction contains paraffins, naphthenes, olefins, and aromatics.

Observable Characteristics:

Watery liquid
Colorless
Gasoline-like odor

Physical and Chemical Properties:

Flash point: 105–140°F, depending on grade
Boiling point (1 atm): 310–395°F
Specific gravity: 0.78
Latent heat of vaporization: not available
Heat of combustion: not available
Immiscible in water, components slightly soluble in water

Table 1
Characteristics of Chemical Deposited
(Page 3 of 5)

Solvosol (a.k.a. Mineral Spirits)

Ethanol (ethyl alcohol) used as a solvent for resins, oils, hydrocarbons, surface cleaning preparations, surface coatings, etc.

Observable Characteristics:

Colorless, limpid, volatile liquid
Pungent taste
Ethereal, vinous odor

Physical and Chemical Properties:

Flash point: 55°F
Boiling point: 173°F
Specific gravity: 0.816
Miscible in water

TOLUENE (Toluol)

Methylbenzene (C_7H_8)

Observable Characteristics:

Mobile liquid
Colorless
Distinct aromatic odor, milder than benzene

Physical and Chemical Properties:

Flash point: 40°F
Boiling point: 110°F
Specific gravity: 0.866
Immiscible in water, components slightly soluble in water

ASPHALTUM

A dark brown to black oil liquid or semiliquid bituminous material resulting from the distillation of petroleum. Consists largely of asphaltic hydrocarbons that are a mixture of paraffinic and aromatic hydrocarbons and heterocyclic compounds containing sulfur, nitrogen, and oxygen. A.k.a. residual oil, liquid asphalt, black oil, petroleum tailings, and residuum.

Table 1
Characteristics of Chemical Deposited
(Page 4 of 5)

Observable Characteristics:

Oily liquid to semiliquid
Dark brown to black color
Tarry odor

Physical and Chemical Properties:

Flash point: 300–550°F
Boiling point: not pertinent
Specific gravity: 1.11 at 50°C (liquid)
Molecular weight range—290 to 630
Immiscible in water, components slightly soluble in water

PAINT FORMULAS

Proprietary formulas. Solvent components include high-flash petroleum and toluene. Substance is not water soluble.

SYNTHETIC LUBRICANT (PTL-1009)

Amine soap with chemical lubricity and extreme pressure additives.

Observable Characteristics:

Clear fluid
Mild odor

Physical and Chemical Properties:

Flash point: 220°F
Boiling point: 206°F
Specific gravity: 1.08
$PH_{2\%soln}$: 7.2
Saponification value: 24.8
Neutralization No.: 26.45 mg KOH/g
Cloud point: 60°F
Soluble in water

BARIUM

A silver white metal produced by the reduction of barium oxide. Does not occur free in nature. Barium compounds used in many commercial processes. Barium is not very mobile in soils because it forms water insoluble salts and is unable to form soluble complexes with humic and fulvic materials. In an aquatic environment, solubility of barium is controlled by the solubility product of barium carbonate.

Table 1
Characteristics of Chemical Deposited
(Page 5 of 5)

The properties of barium compounds vary with specific compounds. A few selected compounds are shown with their physical/chemical properties listed:

	Barium	**Barium Carbonate**	**Barium Chloride**	**Barium Oxide**	**Barium Sulfide**	**Barium Sulfate**
Chemical Formula	Ba	$BaCO_3$	$BaCl_2$	BaO	BaS	$BaSO_4$
Molecular Weight	137	197	208	153	169	233
Physical State	Silver White Solid	White Crystal/ Powder	White Solid	Colorless Crystals	In Aqueous Solution	Colorless Solid
Boiling Point	1630°C	N/A	1560°C	2,000°C	--	--
Melting Point	730°C	--	960°C	1,923°C	--	1,580°C
Density (g/cm^3)	3.5	4.43	3.9	5.72	4.25	4.5
Vapor Pressure	$1{,}810 \times 10^{-5}$ mmHg	N/A	N/A	N/A	N/A	N/A
Water Solubility (mg/l)	decomposes	2 (20°C)	31 (0°C)	3.5 (20°C)	decomposes	--

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industrial waste disposal according to DNR correspondence and license applications. However, the designated disposal area was not strictly limited to the industrial wastes from Outers and Metallics. Records indicate other commercial wastes were deposited simultaneously in the same area in October 1981 and October 1982. For a time, open burning occurred at the site. Until early 1971 when open burning was banned, the industrial solvents from Outers and Metallics were burned regularly at apparently random locations throughout the landfill. Some refuse was also burned bimonthly. Open burning reportedly continued, even though banned, as late as 1979.

Liquid wastes consisted primarily of naphtha-based solvents used in a metal cleaning process and solvent wastes from paint spray, gun cleaning, and machine shop cleaning fluids. At least two kinds of naphtha to the site—high-flash naphtha and VM&P or Stoddard naphtha. High-flash naphtha is a coal tar derivative consisting primarily of a mixture of aromatic hydrocarbons. It was probably used as a degreasing agent or a general solvent. The VM&P or Stoddard naphthas are slightly more volatile and are derived from petroleum. They consist of a mixture of aliphatic hydrocarbons, naphthenes, and alkyl benzenes. They are used as universal solvents for general cleaning and as paint thinners. These naphthas were probably used in a paint cleaning process at one of the plants and overall as general solvents. Both the petroleum and coal derived naphthas are less dense than water and would float on the water table if the waste reached the aquifer.

Some of the organic compounds detected in the groundwater from past analyses may be derived from the naphtha wastes floating on the water table. The liquid naphtha waste could generate a complex mixture of dissolved organic compounds in groundwater over a period of time. The two types of naphtha would each produce a different suite of degradation products of varying composition. It is impossible to predict the exact composition of each mixture, but generally the degradation products consist of aliphatic and aromatic carboxylic acids, toluene, and other complex mixtures of aromatic and aliphatic hydrocarbons.

3.3 TARGET COMPOUNDS

Of particular concern to the treatability portion of the Remedial Design are petroleum related organic compounds, referred to as the "naphtha" derived total petroleum hydrocarbons (TPHs) and the benzene, toluene, ethylbenzene, and xylene (BTEX) compounds. These compounds are located at the Onalaska site in a 2-acre area adjoining the landfill property and make up a 4-foot-thick subsurface layer known as the Zone of Non-Aqueous Phase (ZNAP) of contamination. (Feasibility Study Report, Onalaska Municipal Landfill, November 1989).

3.4 PROJECT OBJECTIVES

Based upon the results of the RI and FS, the objective of the bioremediation treatability study is to determine the ability of enhanced biodegradation to effect reduction of TPH and BTEX concentrations in the contaminated in situ ZNAP. While enhancement of biodegradation occurs, a secondary objective is to obtain estimates of the amount of compound stripping/volatilization occurring so that appropriate mass balances of contaminant removal due to biodegradation can be made. The bioremediation treatability study will focus on collecting representative soil samples to undergo biological treatment and then at designated intervals throughout the treatability study to determine the ability of biological treatment to effect reduction in concentration of TPH and BTEX compounds in the soil and to determine the role that stripping/volatilization plays in compound disappearance.

3.4.1 DATA QUALITY OBJECTIVES

Data quality objectives (DQO) define and specify the quality of data required for the intended use of the data. The degree of certainty of a data set with respect to precision, accuracy, representatives, completeness, and comparability is an indication of the data quality.

There are five defined levels of data quality:

1. Analytical Level I—Field Screening. The objective of this level of analysis is to generate data to be used in refining sampling plans and determining gross extent of contamination at this site. This type of data also provides real time monitoring for health and safety.

2. Analytical Level II—Field Analysis. The objective of this level of analysis is to provide real-time data for ongoing field activities or when initial data will provide the basis for selection of additional laboratory analyses. Analysis includes the use of an onsite close support laboratory.

3. Analytical Level III—Laboratory Analysis. This level of support is designed to provide laboratory analyses using standard EPA-approved procedures other than current CLP RAS. This level provides data for site characterization, environmental monitoring and confirmation of field data, and support of engineering studies.

4. Analytical Level IV—Contract Laboratory Programs (CLP) Routine Analytical Services (RAS). This level of analysis provides for the highest level of data quality with full CLP analytical, quality control, and

validation procedures in accordance with U.S. EPA protocols. The data are used for risk assessment and confirmation of lower level data and to obtain highly documented data.

5. Analytical Level V—Nonstandard Methods. The objective of this level of analysis is to provide data not obtained through standard avenues of analytical support. This usually involves modification of existing methods or method development. The level of quality control is usually similar to DQO Level IV data.

Analytical data of Levels I, III and V will be generated during this project. Level I data include field measurements of organic vapor using and HNu/OVA readings. HNu or OVA readings will be used to monitor the health and safety of the workers. The laboratory analyses requested include Levels III and V chemical analyses. Level III analyses will include those for percent moisture and nutrients parameters. Level V data are needed because modified EPA procedures are requested to analyze for gas phase oxygen and carbon dioxide and for BETX and TPH measurements in soil and air matrices.

3.4.2 INTENDED DATA USAGE

The data collected during the bioremediation treatability study will be used by CH2M HILL to support the development of the remedial design for a system designed to reduce toxicity, mobility, or volume of contaminated media. Table 2 itemizes specific data usage.

Table 2
Intended Data Usage

	Field Work			Laboratory Analytical Work		
Task/Field Activity	**Field Test and Measurement**	**Intended Data Usage**	**DQO Level**	**Laboratory Analysis**	**Intended Data Usage**	**DQO Level**
Soil sampling	HNu/OVA monitoring	Protect health and safety of workers	1	TPH, BTEX, nutrient parameters, percent moisture, measurements	Develop data on biodegradation and volatilization of target compounds	3 and 5
Gas sampling				O_2, CO_2 gas measurements	Develop data on in situ respiration of microorganisms	5

3.4.3 SPECIFIC PROJECT OBJECTIVES

Specific objectives of the bioremediation treatability study are to:

- Determine, if possible, the extent of treatment achievable
- Compare removal rates achieved by the treatment method studied
- Determine if biodegradation can be maintained while at the same time limiting the degree of compound stripping and volatilization.

A detailed discussion of project objectives can be found in Appendix A.

The treatability study will be performed by CH2M HILL Laboratory Services in Milwaukee, Wisconsin. Analyses for nutrients will be provided by CH2M HILL Laboratory Services in Corvallis, Oregon. Methods by which these analyses will be accomplished and SOPs for the bioremediation treatability study are included in Appendixes B and C.

3.5 SAMPLE NETWORK DESIGN AND RATIONALE

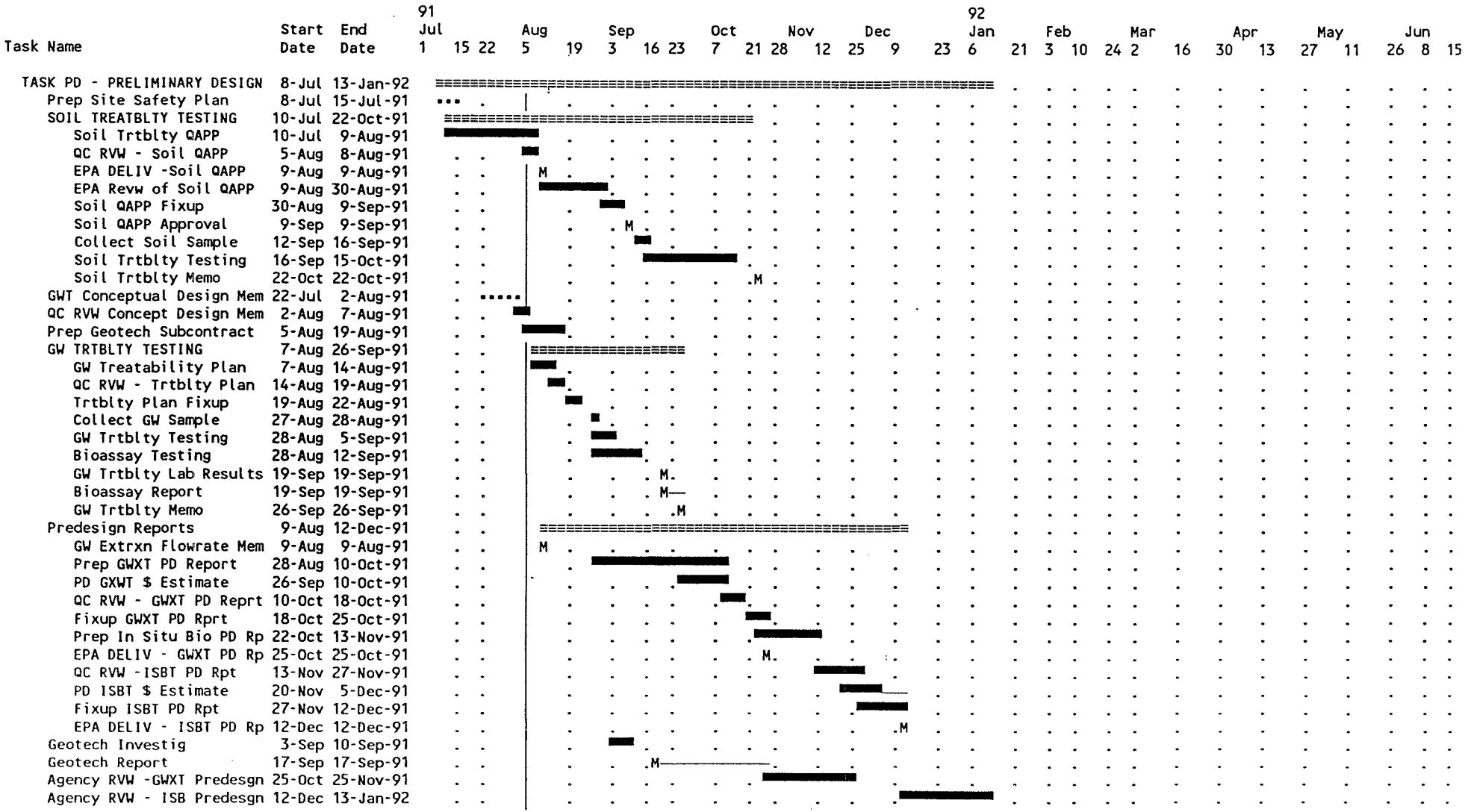
Complete descriptions of the field sampling tasks are included in Section 6 of this QAPP. Briefly, grab samples of soil will be taken for preliminary study characterization and use in the bioremediation treatability study. Each sample will be taken directly from a back-hoe and placed into sampling jars and the treatability study column and handled in accordance with Section 6. Sample locations are chosen to represent site conditions, giving consideration to past practices, existing analytical data, and physical constraints of the site.

Sampling of soil, liquids, gases, and offgas products during the bioremediation treatability study is discussed in Section 6 and Appendix A of this QAPP.

3.6 PROJECT SCHEDULE

The project schedule is presented in Figure 3.

ONALASKA REMEDIAL DESIGN SCHEDULE
Responsible : S. Keith
As-of Date : 5-Aug-91 9:00am Schedule File : RDSCHED2



Task Name	Start Date	End Date
TASK PD - PRELIMINARY DESIGN	8-Jul	13-Jan-92
Prep Site Safety Plan	8-Jul	15-Jul-91
SOIL TREATBLTY TESTING	10-Jul	22-Oct-91
Soil Trtblty QAPP	10-Jul	9-Aug-91
QC RVW - Soil QAPP	5-Aug	8-Aug-91
EPA DELIV -Soil QAPP	9-Aug	9-Aug-91
EPA Revw of Soil QAPP	9-Aug	30-Aug-91
Soil QAPP Fixup	30-Aug	9-Sep-91
Soil QAPP Approval	9-Sep	9-Sep-91
Collect Soil Sample	12-Sep	16-Sep-91
Soil Trtblty Testing	16-Sep	15-Oct-91
Soil Trtblty Memo	22-Oct	22-Oct-91
GWT Conceptual Design Mem	22-Jul	2-Aug-91
QC RVW Concept Design Mem	2-Aug	7-Aug-91
Prep Geotech Subcontract	5-Aug	19-Aug-91
GW TRTBLTY TESTING	7-Aug	26-Sep-91
GW Treatability Plan	7-Aug	14-Aug-91
QC RVW - Trtblty Plan	14-Aug	19-Aug-91
Trtblty Plan Fixup	19-Aug	22-Aug-91
Collect GW Sample	27-Aug	28-Aug-91
GW Trtblty Testing	28-Aug	5-Sep-91
Bioassay Testing	28-Aug	12-Sep-91
GW Trtblty Lab Results	19-Sep	19-Sep-91
Bioassay Report	19-Sep	19-Sep-91
GW Trtblty Memo	26-Sep	26-Sep-91
Predesign Reports	9-Aug	12-Dec-91
GW Extrxn Flowrate Mem	9-Aug	9-Aug-91
Prep GWXT PD Report	28-Aug	10-Oct-91
PD GXWT $ Estimate	26-Sep	10-Oct-91
QC RVW - GWXT PD Reprt	10-Oct	18-Oct-91
Fixup GWXT PD Rprt	18-Oct	25-Oct-91
Prep In Situ Bio PD Rp	22-Oct	13-Nov-91
EPA DELIV - GWXT PD Rp	25-Oct	25-Oct-91
QC RVW -ISBT PD Rpt	13-Nov	27-Nov-91
PD ISBT $ Estimate	20-Nov	5-Dec-91
Fixup ISBT PD Rpt	27-Nov	12-Dec-91
EPA DELIV - ISBT PD Rp	12-Dec	12-Dec-91
Geotech Investig	3-Sep	10-Sep-91
Geotech Report	17-Sep	17-Sep-91
Agency RVW -GWXT Predesgn	25-Oct	25-Nov-91
Agency RVW - ISB Predesgn	12-Dec	13-Jan-92

FIGURE 3
PROJECT SCHEDULE
ONALASKA RD
TREATABILITY QAPP

Section 4
PROJECT ORGANIZATION AND RESPONSIBILITY

At the direction of the Region 5 Remedial Project Manager, with final authority by the Region 5 Regional Project Officer, CH2M HILL has overall responsibility for all phases of the bioremediation treatability study, including field sampling, completion of study, laboratory analysis, and data reduction. Quality assurance and quality control are also provided by CH2M HILL. Figure 4 presents the project organization chart.

4.1 MANAGEMENT RESPONSIBILITIES

Project management will be conducted through CH2M HILL's regional office in Milwaukee. Contact will be maintained with the EPA's Remedial Project Manager during all phases of the project.

Monthly reports will be submitted to keep the EPA apprised of the technical, financial, and schedule status of the project. Other CH2M HILL responsibilities include controlling budgets and schedules; selecting, coordinating, and scheduling staff and subcontractors for task assignments; and maintaining project quality control and assurance programs.

Operational responsibilities involving execution and direct management of the technical and administrative aspects of this project have been assigned as follows:

- Regional Project Officer (RPO)
  Stephen Nathan (U.S. EPA Region 5)
- Remedial Project Manager (RPM)
  Kevin Adler (U.S. EPA Region 5)
- Site Manager (SM)
  Steven Keith (CH2M HILL)
- Program Manager (PM)
  John Fleissner (CH2M HILL)
  Acting—Alpheus Sloan (CH2M HILL)

As specified in the Work Plan, the SM accepts primary responsibility for all quality control activities. The SM is, in turn, supervised by the PM. All other positions of responsibility are filled by competent persons as assigned by the SM and PM.

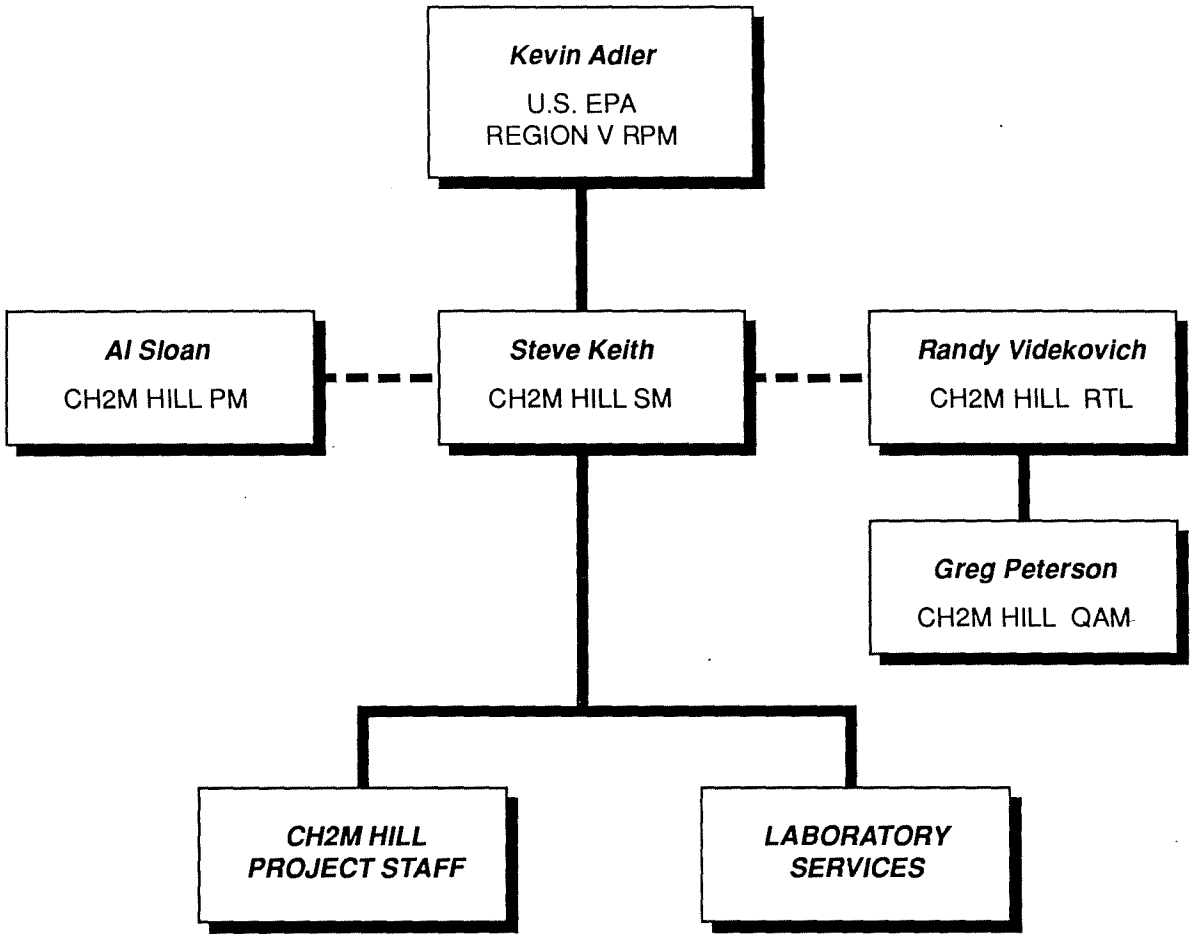


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FIGURE 4
PROJECT ORGANIZATION
ONALASKA RD
TREATABILITY QAPP

4.2 QUALITY ASSURANCE ORGANIZATION

Tasks	Responsible Organization/Personnel
• Final Review and Approval of QAPP	Kevin Adler (RPM)
• QA review of reports, SOPs, and field activities; auditing of reports, procedures, and activities for identifying and controlling non-conformance for corrective action	Quality Assurance Manager (QAM) Greg Peterson (CH2M HILL)

4.3 FIELD OPERATIONS

Responsibilities for field operations tasks, including both management and execution of the field work, are assigned as follows:

Tasks	Responsible Organization/Personnel
• Sample Collections	Steve Keith, CH2M HILL, SM
• External Field Audits	U.S. EPA Region 5 CRL
• Internal Field Audits	Randy Videkovich, CH2M HILL, RTL

4.4 LABORATORIES

All treatability study activities, including laboratory analysis and data reduction, will be completed by CH2M HILL's Applied Sciences Laboratory in Milwaukee, Wisconsin, or Corvallis, Oregon.

Tasks	Responsible Organization/Personnel
• Applied Science Laboratory Department Manager	Alpheus Sloan, CH2M HILL

Tasks	Responsible Organization/Personnel
• Applied Science Laboratory Department Manager	Mark Boedigheimer, CH2M HILL
• Chemistry Laboratory Operations Manager	Joe Sandrin, CH2M HILL
• Applied Science Laboratory QA Manager	Earl Hadfield, CH2M HILL

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Section 5
QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA IN TERMS OF PRECISION, ACCURACY, COMPLETENESS, REPRESENTATIVENESS, AND COMPARABILITY

5.1 QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

The overall QA objective is to develop and implement procedures for field sampling, chain-of-custody, laboratory analysis, and reporting that will provide results which are legally defensible in a court of law. Specific procedures for sampling, chain of custody, laboratory instrument calibration, laboratory analysis, reporting of data, internal quality control, audits, preventive maintenance of equipment, and corrective action are described in other sections of this QAPP. This section addresses specific objectives for accuracy, precision, completeness, representativeness, and comparability.

5.2 LEVEL OF QUALITY CONTROL EFFORT

The bioremediation treatability study is unlike typical remedial investigation activities where numerous samples are collected and analyzed to determine the nature and extent of site contamination. It differs from the typical remedial investigation activity in that a single soil sample is collected for use in a bench-scale treatability study, the analytical program does not use routine analytical procedures in a production setting, and the many analytical methods have been adopted specifically for the treatability study. Collection and analysis of field samples to assess the quality of data resulting from the field sampling activities is not required.

The specific objectives for accuracy, precision, completeness, representativeness, and comparability are considered, but the manner in which they are addressed is unique. The level of quality control required considers the project objectives of the treatability study. To meet the objectives of accuracy, precision, completeness, representativeness, and comparability the following factors were identified as quality assurance issues influencing the outcome of the treatability study:

- Collection of a soil sample representative of site conditions
- Maintenance of sample integrity in a sample containing large quantities of volatile organic constituents

- Determination of the hydrocarbon character of the contaminated soil so that an accurate quantification strategy can be implemented
- Collection of a subsample aliquot from the soil test column that is representative of the test system
- Evaluation of the contribution of uncontaminated (background) soil in the test system

A complete discussion of the goals of the treatability study is provided in Appendix A.

All soils will be analyzed in CH2M HILL Applied Sciences Laboratories. The analysis will be according to modified EPA protocols (Analytical Level V) for BETX, TPH, nutrients and conventional parameters. The level of laboratory QC effort for these analyses is specified in the methods included in Appendix B.

5.3 PRECISION, ACCURACY, AND SENSITIVITY OF ANALYSIS

The fundamental QA objective with respect to accuracy, precision, and sensitivity of laboratory analytical data is to achieve the QC acceptance criteria of the analytical protocols. SOPs for laboratory analyses are provided in Appendix B. These include the required accuracy, precision, and sensitivity of the analyses.

5.3.1 PRECISION

Precision of the data is a measure of the reproducibility or spread of the data when more than one measurement is taken on the same sample under prescribed similar conditions. Precision is the agreement between the set of replicate measurements without assumption or knowledge of the true value.

Precision comprises sampling precision and analytical precision. Sampling precision is a function of the operating procedures used to collect, store, and transport the sample and the variability or homogeneity of the media being sampled. Analytical precision is a function of the procedure used, the analyst's technique, and instrument performance.

Sampling and analytical precision are generally determined by collecting and analyzing duplicate samples. The samples are taken from the same source into separate containers and analyzed independently.

Analytical precision is determined by analyzing laboratory duplicate samples using ordinary duplicates or matrix spike/matrix spike duplicates (MS/MSD) as appropriate

to the analytical method. Analytical precision is also determined by the calibration linearity of the analytical instrument. Being dependent on analysis, sampling precision cannot be determined by itself but may be inferred as being related to the difference in precision of field duplicates and laboratory duplicates.

For duplicate measurements, precision can be expressed as the relative percent difference (RPD), the difference of duplicates as a percentage of the mean of the duplicates.

For instrument linearity, precision can be expressed as the relative standard deviation (RSD), the difference of response factors, as measured by the standard deviation, as a percentage of the mean of the duplicates. The precision of instrument linearity can also be measured by an evaluation of the least squares regression analysis, as measured by the coefficient of correlation and y-intercept.

5.3.2 ACCURACY

Accuracy of the data is a measure of the closeness or degree of agreement of a measured value (or mean of a set of values) to the true value. Accuracy is a measure of the bias of the measurement system. Since the true concentration of environmental samples cannot be known a priori, accuracy is usually inferred from recovery data.

An assessment is made by spiking samples with known standards or surrogate standards and calculating the average recovery by comparing results before and after spiking.

Unlike precision, accuracy is difficult to measure for field and laboratory activities. Sources of error that pertain to accuracy include the sampling method, field and laboratory contamination, preservation, handling, sample matrix, calibration, and analysis. Bias or systematic errors are inherent in the method or idiosyncratic in the measurement system. Temperature effects or extraction inefficiencies are examples of method errors; blanks, contamination, mechanical losses, and calibration shifts are examples of measurement errors.

Bias may be positive and negative, with several types concurrent such that the net result may be positive or negative. An accurate measurement system is capable of providing precise and unbiased results within acceptable limits. In practice, quality assessments actually determine the uncertainty of results data as inaccuracy and imprecision.

The potential for false positive results are assessed by laboratory and field blanks, which should be less than method or instrument detection limits. The potential for false negative results are assessed by spiking.

5.3.3 SENSITIVITY

Sensitivity of the data is a measure of the analytical detection or quantification limits. Sensitivity discussed here refers to minimum amounts measurable rather than minimum differences distinguishable between two samples having approximately the same amounts. Specific quantitation goals will be determined during the preliminary portion of the treatability study.

5.4 COMPLETENESS, REPRESENTATIVENESS, AND COMPARABILITY

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. Because the project team is involved in all aspects of the analytical program the amount of unvalid data will be assessed as it is generated and can be controlled through a process of corrective actions.

Following completion of the analytical testing, the percent completeness will be calculated by the following equation:

$$\text{Completeness (\%)} = \frac{\text{(number of valid data)}}{\text{(number of samples collected for each parameter analyzed)}} \times 100$$

Representativeness expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition. Representativeness is a qualitative parameter dependent upon the proper design of the sampling program and proper laboratory protocol. The sampling network was designed to provide data representative of site conditions. During development of this network, consideration was given to past waste disposal practices, existing analytical data, physical setting and processes, and constraints inherent to the Superfund program. The rationale of the sampling network is discussed in detail in Section 6—Field Sampling Procedures. Representativeness will be satisfied by insuring that sampling procedure is followed, proper sampling technique are used, proper analytical procedure are followed and holding times of the samples are not exceeded in the laboratory.

Comparability expresses the confidence with which one data set can be compared with another. The extent to which existing and planned analytical data will be comparable depends on the similarity of sampling and analytical methods. The procedures used to obtain the planned analytical data, as documented in the QAPP, are expected to provide comparable data. These new analytical data, however, may not be directly comparable to existing data because of difference in procedures and QA objectives.

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Section 6
FIELD SAMPLING PROCEDURES

To meet project objectives, special consideration is given to the procurement, preservation, transportation, and storage of samples to be analyzed. Detailed sampling procedures function to describe the sampling operation as it relates to the project justification, design, and implementation.

The objective of sampling is to collect a portion of material that accurately represents the material being sampled while being small enough in volume to be readily transported and conveniently handled in the laboratory. Consequently, procedures are followed to help ensure that the analyte originally present in the sample matrix has not undergone significant volatilization, biological or chemical degradation, or concentration, and that contaminants that might interfere with the analysis have not been added during the sampling process. Because of the wide variety of purposes and analytical methods, detailed sampling procedures must be described, implemented, and documented.

Field sampling procedures are prepared to provide the strategy for gathering soil at the Onalaska site for use in the treatability study. The following procedures were developed to address the intended data uses and data quality objectives (DQOs) described in the QAPP:

- Procedures, criteria, or guidelines used for sample point selection
- Specific sampling procedures to be used for collection of each sample
- Description of volumes, containers, holding temperatures, and reagents used for sample collection, preservation, transport, and storage
- Procedures for preparation of sampling containers and equipment
- Procedures for decontamination of sampling equipment between sampling times to reduce the potential for cross-contamination between samples
- Sample custody procedures, including a sample numbering system
- Forms, notebooks, logbooks, and procedures to be used to document sample history, sampling conditions, and analyses
- Coordination with the laboratory

6.1 SAMPLE LOCATIONS

Subsurface soil samples will be collected from the contaminated and background locations shown in Figure 5. These two locations represent the highest concentrations of TPH detected during the remedial investigation and a clean, uncontaminated area, respectively.

6.2 COLLECTION PROCEDURES

The strategy behind sample collection will be to minimize volatilization of compounds from the soil, to collect representative samples, and to prevent surface soils from collapsing into the treatability samples.

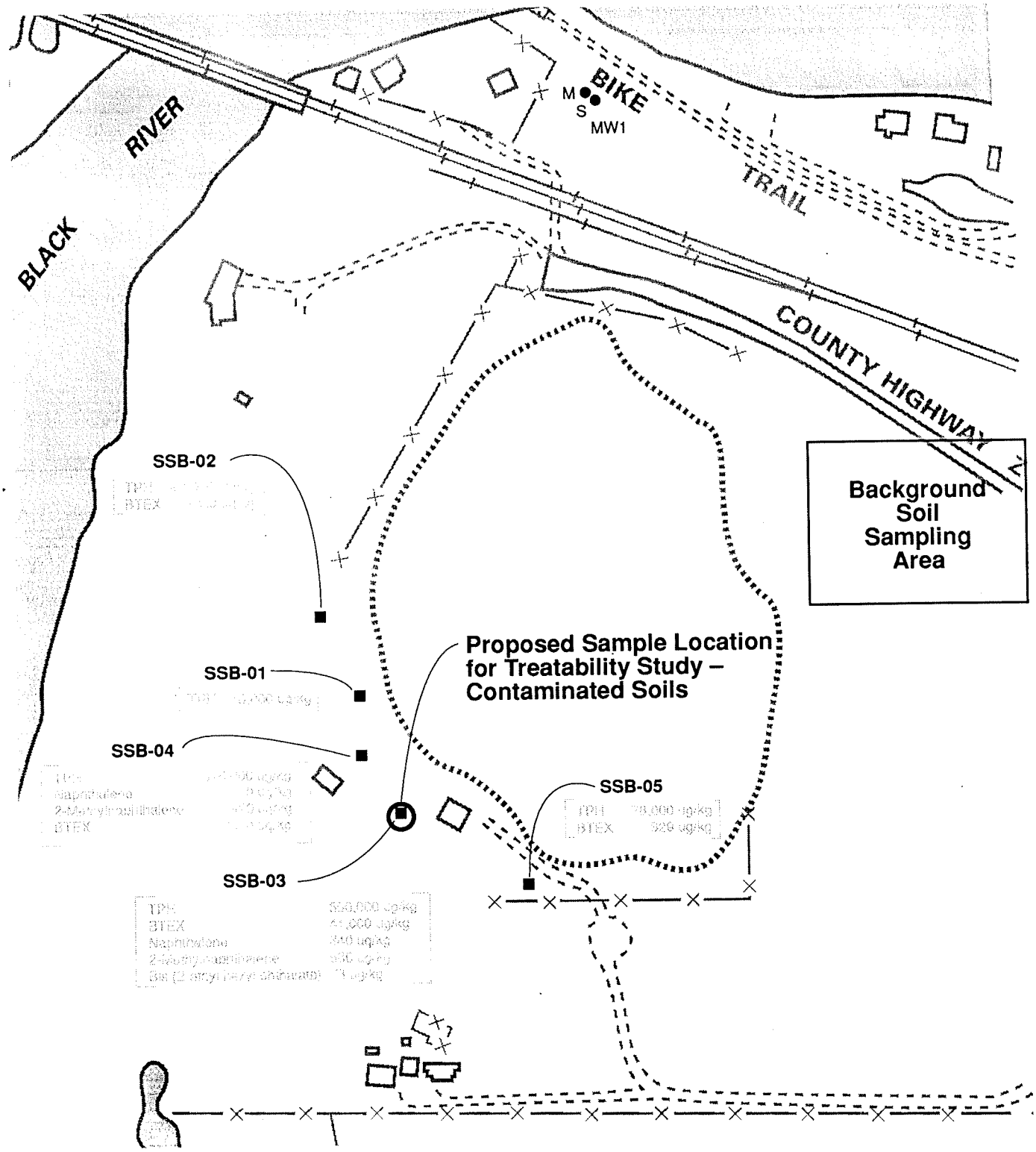
Using a backhoe, surface soils will be removed to a depth of roughly 6 to 8 feet at each of the two locations. At that depth, a stable bench plateau will be prepared before final excavation to the target depth of 10 feet. Creation of the intermediate level will minimize problems related to unstable slope conditions, the exposure of contaminated soils to ambient conditions, and entrainment of surface soils in the treatability samples.

Exact depths for sampling will be established in the field based upon the visual appearance of the soil and HNu measurements of soil sample headspace. Once the sampling depth is verified, one entire full backhoe bucket of soil will be used to pack the soil test columns and additional sampling jars. Only sterilized equipment will be used to manipulate the collected soil. Samples will not be composited. It will be left to the judgment of the field personnel as to whether the backhoe bucket contains enough soil of consistent appearance to be distributed through the three columns. The decision not to composite samples is based on the objectives of the treatability testing, which are to determine mass balances on the hydrocarbons in order to quantify biodegradation and stripping. Collecting the grab column samples will minimize disturbance of the soils and loss of volatile compounds.

Enough soil from a previously established clean area of the property (Figure 5) will be collected in the same manner as the contaminated soil to be used for assembly of the control column.

6.3 SAMPLE COLLECTION CONTAINERS AND EQUIPMENT

Soil test columns and sampling jars will be filled with soil samples and sealed. The type of material and configuration of the test column to be used is described in



LEGEND

- LIMITS OF LANDFILL AS DETERMINED BY GEOPHYSICAL SURVEY
- SUBSURFACE SOIL SAMPLING LOCATION
- ANALYTICAL RESULTS

Abbreviation Key

TPH = TOTAL PETROLEUM HYDROCARBONS

BTEX = TOTAL BENZENE, TOLUENE, ETHYL-BENZENE AND XYLENE

N

0 200

SCALE IN FEET

FIGURE 5
SOIL SAMPLING LOCATIONS
ONALASKA RD
TREATABILITY QAPP

GLO65550.FI SOIL SAMP. LOC. 8-14-91LML

Appendix A. Sampling jars will be 4-oz wide-mouth glass jars with Teflon seal caps supplied from a commercial vendor as EPA Protocol B washed.

Two test columns and four sampling jars should be collected from the contaminated soil location. From the background soil location, one test column and two sampling jars should be collected. Dedicated sampling equipment should be used at each location. Samples should be collected from the background location first before the contaminated location to prevent cross-contamination.

Sampling equipment including test columns, sampling jars, and tools that will be used to transfer the soil into the test column and sampling jars should be sterilized by autoclaving the equipment for 15 minutes at 121°C.

After sample collection, the test columns will be wrapped in aluminum foil to inhibit photolysis of contaminants and to deter algae growth. All samples will be stored in ice-filled coolers and maintained at the lowest possible temperature until the samples arrive at CH2M HILL laboratories. Samples from the contaminated location should not be stored with samples from the background location.

6.4 SAMPLE HANDLING, TRANSPORT, AND STORAGE

Subsurface soil samples will be collected as described above. Columns will be cushioned within the coolers with bubble wrap or other protective material and stored upright to minimize the effects of transportation to the laboratory. Columns will be transported to the Milwaukee laboratory by the field sampling team within 24 hours of the time of sample collection.

Measures will be taken to ensure the temperature of the samples and exposure to sunlight is minimized. Once the laboratory has received the samples, they are to be logged-in and stored under refrigeration. The CH2M HILL Applied Sciences Laboratory Manager should be notified at least 2 weeks before sampling to reserve time and space in the laboratory.

6.5 SAMPLE CUSTODY PROCEDURES AND SAMPLE DESIGNATION

6.5.1 SAMPLE CUSTODY

Sample custody and documentation procedures are further described in Section 7.

6.5.2 SAMPLE DESIGNATION

A two-character designation will be used to identify the site where the sample was collected (ON for Onalaska). The three-character designation SSB (subsurface soil) will be used to identify the sample type. It will be followed by either of the two two-digit sample location designations.

- CS—contaminated soil
- BS—background soil

All samples will have a two-digit number as the last component of the sample identifier. The sampling events will start with 01 and progress upward. For this single event, the identifier 01 will be used.

The sample collected from the contaminated area will be designated ON-SSB-CS-01 and the sample collected from the background area will be designated ON-SSB-BS-01.

Section 7
SAMPLE AND DOCUMENT CUSTODY PROCEDURES

It is U.S. EPA and Region 5 Policy to follow the U.S. EPA Region 5 sample custody, or chain-of-custody protocols as described in "NEIC Policies and Procedures" (EPA-330/9-78DDI-R, rev. June 1985). This custody is in three parts: sample collection, laboratory analysis, and final evidence files. Final evidence files, including all originals of laboratory reports and purge files, are maintained under document control in a secure area.

Sample custody procedures for this project will be in accordance with the U.S. EPA Region 5 Sample Custody Procedures. Modifications were made to the procedures to recognize that traffic reports are not generated and that the Central Regional Laboratory and Sample Management Office are not participants in this project.

A sample or evidence file is under your custody if one of the following applies:

- It is in your possession.
- It is in your view, after being in your possession.
- It is in your possession and you place it in a secured location.
- It is in a designated secure area.

7.1 FIELD CUSTODY PROCEDURES

The field samplers would collect only the number of samples needed to represent the media being sampled. As few people as possible should handle samples.

The field sampler is personally responsible for the care and custody of all samples collected until they are properly transferred or dispatched.

Sample labels shall be completed for each sample using waterproof ink unless prohibited by weather conditions. Each sample tag or label will contain the month, day, year, and time of sampling, the sample identification number, the location of the sample, the sampler's name, and the analyses requested.

The CH2M HILL site manager will determine whether proper custody procedures were followed during the field work and whether additional samples are required.

7.2 TRANSFER OF CUSTODY AND SHIPMENT

Samples must be accompanied by a chain-of-custody record. When transferring the possession of samples, both the individual relinquishing and receiving must sign, date, and note the time of custody transfer on the record. The chain-of-custody record documents sample custody transfer from the sampler, through another, to the analyst in the laboratory.

Samples must be packaged properly for shipment and dispatched to the laboratory for analysis, with a separate custody record accompanying each shipment. Shipping containers must be sealed for shipment to the laboratory. The method of shipment, courier name, and other pertinent information are entered in the "Remarks" section on the custody record.

All shipments will be accompanied by the chain-of-custody record identifying their contents. The original record will accompany the shipment, and the copy will be retained by the field team leaders.

Freight bills, Post Office receipts, and bills of lading will be retained as part of the permanent documentation.

7.3 CHAIN-OF-CUSTODY FORM

The CH2M HILL chain-of-custody form (Figure 6) will be used for shipment of samples and is filled out as follows:

1. SAMPLED BY AND TITLE—The person who took the samples signs this box and gives his title and the date and time he finished taking samples.

2. RELINQUISHED BY—The sampler signs this box when he gives the samples to someone else, and he fills in the date and time they left his possession.

3. RECEIVED BY—The person who receives the samples signs here and fills in the date and time he receives them. This date and time should be the same as the "relinquished by," unless the samples were shipped.

4. RELINQUISHED BY—The person who has custody of the samples signs here and fills in the date and time when he relinquishes them.

5. See instructions for 3.

CH2M HILL QUALITY ANALYTICS : FIGURE 6

CHAIN-OF-CUSTODY RECORD

PROJECT NUMBER (8)	PROJECT NAME (9)	# OF CONTAINERS	CLIENT ADDRESS AND PHONE NUMBER	LAB ID	FOR LAB USE ONLY
CLIENT NAME (10)			ANALYSES REQUESTED		LAB#
PROJECT MANAGER (11)	COPY TO: (12)				LAB#
REQUESTED COMP. DATE (13)	SAMPLING REQUIREMENTS: SDWA ☐ NPDES ☐ RCRA ☐ OTHER (26)				PROJECT NO.
					ACK / VERIFIED
					QUOTE# / BS
					NO. OF SAMP / PG / OF

STA NO. (15)	DATE (16)	TIME (17)	COMP (18)	GRAB (19)	SOIL	SAMPLE DESCRIPTIONS (12 CHARACTERS) (20)	# OF CONTAINERS (21)	ANALYSES REQUESTED (22)	LAB ID	REMARKS (24)

SAMPLED BY AND TITLE (1)	DATE/TIME	RELINQUISHED BY (2)	DATE/TIME	HAZWRAP/NEESA Y N	
RECEIVED BY: (3)	DATE/TIME	RELINQUISHED BY: (4)	DATE/TIME	QC LEVEL 1 2 3	
RECEIVED BY: (5)	DATE/TIME	RELINQUISHED BY: (6)	DATE/TIME	COC	ICE
RECEIVED BY LAB: (7)	DATE/TIME	SAMPLE SHIPPED VIA UPS BUS FED-EX HAND OTHER (27)	AIR BILL# (28)	ANA REQ	TEMP
				CUST SEAL	Ph
				SAMPLE COND.	

REMARKS (25) (14)

ENTERED INTO LIMS _____ COC REVIEWED _____

REV 6/89 FORM 340

6. See instructions for 4.

7. For laboratory use only, do not mark in this box.

8. PROJECT NUMBER—Applies only to samples submitted by CH2M HILL.

9. PROJECT NAME—Applies only to samples submitted by CH2M HILL.

10. CLIENT NAME—Name of the company requesting the analysis.

11. REPORT TO—Name of the person who receives the laboratory report.

12. COPY TO—Name of anyone else who should receive a copy of the report.

13. REQUESTED COMPLETION DATE—When the results are required. Additional charges may apply whenever requests are made for dates of less than 4 weeks turnaround time.

14. LABORATORY—The location of the laboratory to which the samples will be submitted.

15. STATION NO.—If the sample points are numbered, record the number here.

16. DATE—The date on which the sample was taken.

17. TIME—The time at which the sample was taken.

18. COMP—Check here if this is a composite sample.

19. GRAB—Check here if this is a grab sample.

20. SAMPLE DESCRIPTION—A short description of the sample point (for example, "Effluent from sand filter"). This description will appear on the report.

21. NUMBER OF CONTAINERS—The number of individual sample bottles containing portions of the same samples.

22. ANALYSES REQUESTED—Make one column for each parameter or group of parameters.

23. FOR LAB USE ONLY—Do not mark this area.

24. REMARKS—Record any comments about each sample on the same line as the sample description; e.g., "Wastewater contains VOCs."

25. REMARKS—Record any comments regarding the samples as a whole.

26. SAMPLING PROGRAM—The reason the samples were taken. For example, mark the NPDES box for samples taken for an NPDES DMAR.

27. SAMPLE SHIPPED VIA—How the samples are being shipped to the laboratory; e.g., "UPS."

28. AIR BUS BILL NUMBER—The number on the shipping papers by which the package can be traced.

7.4 LABORATORY CUSTODY

Laboratory custody procedures for the CH2M HILL Applied Sciences Laboratory will conform to the laboratory's conventional procedures. These procedures include:

- Designation of a sample custodian
- Correct completion by the custodian of the chain-of-custody record, sample tag, and laboratory request sheet (including documentation of sample condition upon receipt)
- Laboratory sample tracking and documentation procedures
- Secure sample storage in the appropriate environment (refrigerated, dry, etc.)
- Proper data logging and documentation procedures including custody of all original laboratory records
- Archiving of samples under refrigeration pending completion of the report, review of the data, and final instruction for disposal

7.5 DOCUMENT CUSTODY

7.5.1 FIELD LOGBOOK

All information pertinent to a field sampling effort will be recorded in a field log book or equivalent standardized form. Each page or form will be consecutively numbered and will be at least 4½ by 7 inches. All entries will be made in indelible ink, and all corrections will consist of line-out deletions that are initialed and dated. The log book will include at least the following:

- Purpose of sampling
- Location, description, and log of photographs of the sampling point
- Details of the specific site sampled (e.g., the elevation of the casing, casing diameter and depth, integrity of the casing, etc.)
- Name and address of field contact
- Documentation of procedures for preparation of reagents or supplies that become an integral part of the sample (e.g., filters and absorbing reagents)
- Identification of sampling crew members
- Type of sample (e.g., groundwater, soil, sludge, or wastewater)
- Suspected waste composition
- Number and volume of sample taken
- Sampling methodology, including distinction between grab and composite samples
- Information on the calibration of any field equipment used
- Sample preservation
- Date and time of collection
- Collector's sample identification numbers

- Sample distribution and how transported (e.g., name of the laboratory and cartage agent—Federal Express, United Parcel Service)
- References such as maps of the facility or site sampled
- Any field measurements made (e.g., pH, specific conductance, temperature, and water depth)
- Signature and date by the personnel responsible for observations
- Decontamination procedure

Sampling situations vary widely. No general rules can specify the extent of information that must be entered in a log book or standardized form. However, such records must contain sufficient information so that someone can reconstruct the sampling activity without relying on the collector's memory. The log book and standardized forms will be kept under strict chain-of-custody procedures.

7.5.2 CORRECTIONS TO DOCUMENTATION

Unless prohibited by weather conditions, all original data recorded on sample identification tags and chain-of-custody records must be written with waterproof ink. No accountable serialized documents are to be destroyed or thrown away, even if they are illegible or contain inaccuracies that require a replacement document. These documents will be archived as part of the project file.

If an error is made on the accountable document assigned to one individual, that individual shall make corrections by making a line through the error and entering the correct information. The erroneous information should not be obliterated. Any subsequent error discovered on an accountable document should be corrected by the person who made the entry. All corrections must be initialed and dated.

Final disposition of the completed documents is as follows:

- Shipped with samples:
  - Chain-of-custody form, white original
  - Sample tags
- Retained by site manager:
  - Sample identification matrix
  - Field log books (at completion of project)

- Sent to CH2M HILL documentation coordinator:
  - Chain-of-custody form, pink and yellow copies
  - Notice of transmittal

CH2M HILL will maintain files along with relevant records, reports, logs, field notebooks, and laboratory reports in a secured, limited access area under the custody of the site manager.

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Section 8
CALIBRATION PROCEDURES AND FREQUENCY

This section describes procedures for maintaining the accuracy of all the instruments and measuring equipment which are used for conducting field tests and laboratory analyses. These instruments and equipment should be calibrated prior to each use or scheduled periodically.

8.1 FIELD MEASUREMENTS

Instruments and equipment used to gather, generate, or measure environmental data will be calibrated with sufficient frequency and in such a manner that accuracy and reproducibility of results are consistent with the manufacturer's specifications.

Equipment to be used during the field sampling will be examined to ensure that it is in operating condition. This includes checking the manufacturer's operating manual and the instructions for each instrument to ensure that all maintenance requirements are being observed. Field notes from previous sampling trips will be reviewed so that the notation on any prior equipment problem is not overlooked and all necessary repairs to equipment have been carried out.

Calibration of field instruments is governed by the specific Standard Operating Procedure (SOP) for the applicable field analysis method given in Appendix C.

8.2 LABORATORY ANALYSIS

For the treatability study analyses, the specific calibration procedures and frequency are described in the analytical SOPs provided in Appendix B. Instruments will be operated and maintained in accordance with the manufacturer's guidelines and recommendations. This information is combined with the analytical method requirements to form specific calibration procedures.

8.2.1 INITIAL CALIBRATION

Initial calibration will consist of developing at least a three-point calibration curve covering a linear range of the instrument with the lowest standard at a concentration level near but above the previously determined reporting limit, using reference standards for each parameter analyzed plus a blank. Initial calibration is performed on a frequency schedule required by the analytical method.

8.2.2 CONTINUING CALIBRATION

Calibration is performed continually during the analytical process to verify that the initial calibration is still applicable. Continuing calibration is performed using check standards, though a replication of the initial calibration may be required instead. The check standard is a specific concentration, usually mid-level, used repeatedly.

Without perfect precision, calibration will change by some degree. Calibration criteria are applied to determine if the instrument is performing acceptably. The criteria are often expressed as a range of percent recovery of the initial calibration value. When continuing calibration meets the criteria, the normal measurement process continues. When criteria are not met, the problem is investigated, corrected, and verified before recalibrating and reanalyzing the samples since the last in-control, initial, or continuing calibration. Continuing calibration is performed on a frequency schedule required by the analytical method using the mid-point calibration standard.

Calibration standards will be procured from identified sources traceable to U.S. EPA or NIST standard reference materials. The purest grade of concentrated standard readily available will be used in preparing concentrated and diluted interim and working standards. Documentation of standards preparation will occur in the instrument log book or a standards log book containing most of the same essential information.

Section 9
ANALYTICAL PROCEDURES

Criteria for appropriate method selection are the project DQOs discussed in Section 3. The selected method must satisfy the objectives to produce data of suitable quality for its intended use. Analytical procedure requirements for this project are:

- Specify analytical procedures for treatability study data
- Specify analytical procedures for health and safety data

Samples taken during treatability study activities for the Onalaska RD will be analyzed by CH2M HILL's Applied Sciences Laboratories.

9.1 LABORATORY ANALYTICAL SERVICES

The selection and implementation of treatability study analytical methods is the product of careful analytical programming. The methods were developed to produce data of suitable quality for its intended use while considering other operation logistics. Selection of a particular method was based on the following considerations:

- Availability of analytical resources—qualified staff, equipment, instruments.
- Ability to reliably determine concentration of the analyte or parameter in air, soil, and water sample matrixes
- Methods that produce results consistent with the treatability study DQOs
- Recognition of the method as a standard method by the end users of the data, e.g., soil scientist, agronomists, and environmental scientists

Analytical methods included here have been selected from three reference manuals:

- *Test Methods for Evaluating Solid Waste*, SW-846, Third Edition. U.S. EPA Office of Solid Waste and Emergency Response, November 1986.

- *Methods of Soil Analysis*, Second Edition, Part 1—Physical and Mineralogical Methods, Part 2—Chemical and Microbiological Properties. American Society of Agronomy, Inc., et al., 1982.

- *Standard Methods For the Examination of Water and Wastewater*, Seventeenth Edition. American Public Health Association, et al., 1989.

Minor modifications to these standard methods are required. A decision to modify standard analytical methods is made jointly by the treatability task leaders and analysts. All procedural modifications will be documented.

The modified methods are generally validated prior to use to help assure that project objectives are met. Once the laboratory has been set up for operation, certain method validation procedures will be taken. Each SOP describes the minimum method validation steps that will be taken to ensure a properly operated measurement system.

Samples will be analyzed within the required EPA recommended holding times for each analyte or sooner if dictated by the task leader. When required, samples will be preserved and stored to maintain integrity.

Each SOP is based on published analytical methods and contains a description of:

- Procedures for sample preparation
- Instrument startup and performance check
- Procedures to establish the actual and required detection limits for each parameter
- Initial and continuing calibration check requirements
- Specific methods for each sample matrix type
- Required analyses and acceptance limits for quality control audit samples including method blanks, matrix spikes, matrix spike duplicates, and laboratory control samples (U.S. EPA or National Bureau of Standards (NBS) reference samples or laboratory prepared blank/spikes)

Table 3 summarizes the analyte group and method from which each SOP is derived for chemical analyses. Copies of the methods are contained in Appendix B.

Table 3
Analytical Methods

Analyte Group	Matrix		
	Soil	**Air**	**Water**
BTEX & TPH Preparation Analysis	 (CH) TDU (CH) FID	 (CH) TDU (CH) FID	 (CH) TDU (CH) FID
Nitrogen Preparation Analysis	 (MSA) 33-3.2 (SM) 4500-NH_3 F.	 not applicable not applicable	 not applicable not applicable
Phosphorus Preparation Analysis	 (MSA) 24-5.3 (SM) 4500-P E.	 not applicable not applicable	 not applicable not applicable
O_2 and CO_2	not applicable	(SM) 2720 C.	not applicable
Total Volatile Organics	(SM) 2540 E.	not applicable	not applicable
Water Content	(MSA) 21.2.2.2	not applicable	not applicable
Total Organic Carbon	(MSA) 29.3.5.3	not applicable	not applicable

Note:

BETX & TPH = Benzene, Ethylbenzene, Toluene, Xylene, and Total Petroleum Hydrocarbons

SW = *Test Methods for Evaluating Solid Waste*, U.S. EPA Office of Solid Waste and Emergency Response, SW-846, Third Edition.

MSA = *Methods of Soil Analysis*, Part 2, American Society of Agronomy, et al., Second Edition.

SM = *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, et al., Sixteenth Edition.

CH = Methods developed CH2M HILL Applied Science Laboratory.

9.2 FIELD INSTRUMENT MEASUREMENTS

The procedures for field measurement of health and safety monitoring using OVA and HNu equipment are described in the SOPs in Appendix C.

Section 10
INTERNAL QUALITY CONTROL

Internal QC checks help monitor and document the performance of sampling and laboratory activities. QC checks function as the QC process in place that establishes the quality of the data produced. The frequency and acceptance criteria are project-, matrix-, and parameter-specific. Project-specific QC checks and their frequency are dependent on DQOs and are described in the QAPP and the analytical methods.

10.1 FIELD MEASUREMENTS

Quality control procedures will be limited to checking reproducibility of measurements by taking multiple readings and by calibration of instruments.

10.2 LABORATORY ANALYSIS

The CH2M HILL Applied Science Laboratory monitors data quality with laboratory performance QA checks and matrix-specific QC checks as described throughout the QAPP. The QAPP provides rules and guidelines to ensure the reliability and validity of work conducted at the laboratory.

The stated objectives of the laboratory QA/QC Program are:

- To ensure that all procedures are documented, including any changes in administrative or technical procedures
- To ensure that all analytical procedures are conducted according to sound scientific principles and have been validated
- To monitor the performance of the laboratory by a systematic inspection program and to provide for a corrective action as necessary
- To ensure that all data are properly recorded and archived.

All laboratory procedures are documented in writing as either Standard Operating Procedures (SOP) or Method Procedures (MP). Internal quality control procedures for analytical services will be conducted by the laboratory in accordance with its standard operating procedures and individual method requirements.

The laboratory will document, in each data package provided, that both initial and ongoing instrument and analytical QC functions have been met. Any samples analyzed that do not conform with the QC criteria will be reanalyzed by the laboratory if sufficient sample volume is available. It is expected that sufficient volume of samples will be collected for reanalyses.

Analysis QC checks will be implemented through the following kinds of samples or procedures in the laboratory (if appropriate):

- Duplicates, replicates, or matrix spike duplicates
- Matrix spikes
- Laboratory or method blanks
- Instrument blanks
- Laboratory controls (EPA or NIST traceable reference samples)
- Multipoint calibration standards
- Check standards (low level or mid-range)
- Surrogate spikes
- Retention time markers during GC analysis

The internal quality control checks listed for the laboratory will be implemented during this project. A detailed description of the procedure performed for each of these checks is provided in the analytical method SOPs and previous sections of this QAPP.

Section 11
DATA REDUCTION, VALIDATION, AND REPORTING

The proper management of collected data is of equal importance to proper analysis and custody procedures in assuring that the data represent the environment from which the sample was taken. Data reduction, validation, and reporting procedures function to control data handling from field through laboratory and data processing to the point where data are turned over to the data user.

11.1 FIELD MEASUREMENTS

Raw data from field measurements and sample collection activities will be appropriately recorded in the field log book. If the data are to be used in the project reports, they will be reduced or summarized and the method of reduction will be documented in the report.

11.2 LABORATORY ANALYSIS

11.2.1 DATA REDUCTION

Each analyst is responsible for the recording and reduction of all raw data associated with the analyses. Equations and calculations for data reduction will be performed in accordance with the procedures detailed in the analytical methods. Computations and recorded results will report the typical units of measurement from the methods.

Data reduction will be performed using a programmable calculator or microcomputer. The computational algorithms will be periodically verified through cross-calculation (identical and reordered hand calculations). The units of the results will be verified using valueless units and canceling them during the progression of the calculation to see if the resulting units match the normal reporting units of concentration.

As part of the reduction process, the analyst will proofread all transcriptions to check the accuracy of data transfer, whether from handwritten form to handwritten form or to microcomputer form. After reduction, analytical values and qualifiers will be manually entered by the analyst into a program data base on a microcomputer. Data stored on floppy disk will be updated and copied for backup as necessary.

All data will be recorded in a clear and comprehensive manner. *Data* is defined as all analytical information in numerical and narrative form. This information will be recorded in ink in bound books having consecutively numbered pages or in instrument hard copy tracings or printouts. For reasons of traceability, entries in the bound books and instrument output will be dated and signed on each line, page, or book as appropriate. Errors will be lined out with a single line and corrections initialed and dated.

The bound books will include the following as the primary source of information:

- **Sample Logbook** containing information described in the sample management section.
- **Analysis Data Book** containing target parameters, sample identification numbers, standardizations, raw data, calculations, results, comments, and data qualifiers.
- **Daily Journal** containing a description of significant events, facility and analytical equipment breakdown repair comments, problems and solutions, requests for help, information from task leaders, and so on.
- **Instrument Logbook** containing a record of samples analyzed, calibration, hand-recorded digital or analog data, problems encountered, remedial and preventive maintenance, etc.

All raw, preliminary, and final data and instrument readouts (e.g., chromatograms, printed digital readouts, etc.) will be kept in the laboratory in the possession of the analysts for the duration of the treatability study. Upon request, copies of these data will be made available to the task leaders and managers for decision, review, and redundant storage purposes. Ultimately, all data will be archived along with other project records in accordance with contractual and legal requirements.

11.2.2 DATA REPORTING AND VALIDATION

Data will be summarized as they are generated and submitted to the project team. The data will be considered to be preliminary because they will not have been reviewed and validated (found suitable for their intended use).

Data from the treatability study will be reviewed and validated to determine whether

they have met the project DQOs and intended data uses. Data validation will be performed using criteria described in this QAPP and method SOPs.

The data review and validation process consists of two basic steps:

- Checking of sample and QC results to demonstrate that the analyses are within prescribed criteria for precision, accuracy, completeness, sensitivity, selectivity, blank contamination, understandability, and legibility. In addition to tabulated results, instrument readouts are checked (chromatograms, calibration curves, summary reports).

- Spot-checking of numerical computations to demonstrate freedom from mathematical errors, to confirm use of appropriate formulas, and to verify inclusion of factors related to dilution, concentration, or wet/dry sample weight basis.

Standard data qualifiers will be used as a means to classify data as to their conformance to QA/QC requirements. Where standard qualifiers are not applicable, other appropriate qualifiers will be defined. Where appropriate, the significance of the data qualifiers will be explained (i.e. low bias, poor precision, poor recovery, etc.). The following are examples of commonly used data qualifiers:

DATA QUALIFIERS:

U The material was analyzed for but was not detected. The associated numerical value is the sample quantitation limit or sample detection limit (approximate sample concentration necessary to be detected).

J The associated numerical value is an estimated quantity. (The analyte is present. The reported value may not be accurate or precise.)

K The analyte is present. The reported value may be biased high. The actual value is expected to be lower.

L The analyte is present. The reported value may be biased low. The actual value is expected to be higher.

R The data are unusable. (The compound may or may not be present.) Resampling and reanalysis (or supporting data) are necessary for verification.

UJ The material was analyzed for but was not detected. The sample quantitation limit is an estimated quantity. (The quantitation limit may be inaccurate or imprecise.)

UL The material was analyzed for but was not detected. The quantitation limit is probably higher.

B Not detected substantially above the level reported in laboratory or field blanks.

Q No analytical result.

Validated data will be considered final data. After data validation, the laboratory manager or designee will prepare reports containing the final data. The reports will have the following format:

- **Narrative** includes description of work and identification of all unusual circumstances related to the performance of the work.
- **Data Summary** includes data qualifiers.
- **QC Summary** includes (depending on the project) blanks, spike recoveries, surrogate recoveries, duplicate comparisons, control or check samples, calibration/standardization data, and so on.
- **Raw Data** includes (depending on the project) instrument tracings, hard copy printouts, handwritten bench sheets, sample logs, instrument logs, significant daily journal entries, and so on.

Reports will record the performance of all tasks and results. Missing data will be explained, and the validation of data will be demonstrated each time data are recorded, calculated, or transcribed. Internal checks will be made to uncover or avoid errors in the data collection, recording, or transfer process. The QAM may audit these data reviews at his or her discretion. The data reviews will be summarized in the final Remedial Design report.

Section 12
PERFORMANCE AND SYSTEMS AUDITS

Independent performance and systems audits may be conducted to evaluate the laboratory performance and operational procedures. These audits function to provide an overview for the following purposes:

- To determine whether the operation has the resources, capability, and capacity to perform the requisite work
- To verify that protocols in project documents are followed appropriately during the course of the work
- To detect and define problems so that corrective action can be implemented
- To confirm contract compliance

The audits may be internal or external. Internal audits at the laboratory are conducted by the laboratory manager, project manager, or designee, on a pre-determined frequency and schedule. At its discretion, Region 5 may also perform an external audit of the Milwaukee laboratory.

12.1 SYSTEMS AUDITS

Systems audits consist of an evaluation of all components of the measurement systems to determine their proper selection and use. They including field, laboratory, and data management QC procedures.

Laboratory systems audits are systematic qualitative inspections of all laboratory operations, including the quality assurance system and physical facilities for sample preparation, sample measurement, and data management, comparing them with the project SOP and good laboratory practices.

The laboratory systems audits will be performed under the direction of the project manager, project quality assurance officer, or designee, before or shortly after systems are operational on a given project, and also on a regularly scheduled basis during the lifetime of the project and program operation.

This audit will focus on the following areas:

- Qualification of personnel and organization
- Adequacy of facilities and equipment
- Completeness of documentation
- Applicability of analytical methodology
- Adequacy of quality control
- Acceptability of data handling and documentation

The audit will generally include the following sequence:

- Initial interview—introductions, discussion of audit objectives, review of personnel and equipment
- Inspection tour—trace the path from sample receipt to compilation, review, and distribution of sample data
- Mid-point interview—review of QA/QC data, review of previous systems and performance audits, discussion of user comments, review of nonconformance/corrective actions, etc.
- Documentation procedures review—chain-of-custody for sample and document control
- Debriefing session—discussion of identified strengths and weaknesses, solicitation of laboratory management response to identified items, summarization of items needing corrective action within a scheduled time frame

Documentation of the systems audit will be an audit report with an appended audit checklist. Audit reports will be distributed to appropriate project staff and filed in project records.

12.2 PERFORMANCE AUDITS

Performance audits consist of an evaluation of data and QC data from proficiency testing, which is the analysis of unknown samples to determine the accuracy of the measurement system. Performance audits verify the ability of the laboratory to correctly identify and quantify compounds in blind check samples submitted by the auditing agency.

Performance audits will take the form of blind samples submitted by a source external to the laboratories. These samples will be disguised as real samples or will be submitted so that the analyst will not know the audit type. The audit types may include known analyte concentrations (PE samples), blind field blanks, or blind field duplicates. Analyte concentrations of PE samples will vary over the course of the project. PE samples may be submitted to the laboratory if deemed necessary.

The data from the performance audit sample analysis may be compared with project quality assurance objectives. PE sample data will be compared with accuracy criteria. Duplicate sample data will be compared with precision criteria. Blank data will be compared with sensitivity criteria (instrument and method detection limits). Documentation of the performance audit will consist of an audit report including a statistical analysis and appended performance data. Audit reports will be distributed to appropriate program and project staff and will be filed in project records.

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Section 13
PREVENTIVE MAINTENANCE

Preventive and remedial maintenance procedures function to help maintain on-schedule operation of the laboratory and project through readiness of the equipment and supplies.

13.1 FIELD MEASUREMENTS

The field equipment to be used for this project includes an OVA and HNu. Specific preventive maintenance procedures for all equipment are referenced in the operators' manuals and will be conducted in accordance with manufacturers' specifications.

13.2 LABORATORY ANALYSIS

Maintenance will be performed in accordance with the directions and frequency detailed in instrument manufacturers' manuals. Dated and signed instrument logbooks will describe and document scheduled inspections, routine and nonroutine maintenance, and major repairs.

Normal preventive maintenance will be performed by the analysts on a scheduled routine and as-needed basis. Typical procedures involve cleaning, adjusting, and replacing easily serviced items. Specialized inspection, maintenance, and repair will be performed by trained personnel from the laboratory or the manufacturer, as appropriate. If needed, maintenance and repair will be provided through manufacturer's service contracts.

Remedial maintenance will be performed for real and potential out-of-control situations. Precision, accuracy, and sensitivity data are examined for trends and excursions toward or beyond limits described in the QAOs and the analytical methods, to detect evidence of equipment malfunction. Maintenance will be performed for decreases in resolution, shifts in calibration, decreased sensitivity, or failure to meet other QC criteria.

Instrument downtime will be minimized by having an adequate inventory of expendable supplies and critical instrument components available for use. Expendables are items considered to have a lifetime of less than 1 year.

Responsibility for performance of preventive and remedial maintenance lies with the laboratory operations manager, or designee (lead analyst, instrument operator, service technician).

Project-specific preventive maintenance requirements are detailed further in the analytical method SOPs.

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Section 14
SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA PRECISION, ACCURACY, AND COMPLETENESS

Data quality assessment procedures will be based in part on precision, outlier evaluation, accuracy, and completeness. Data assessment procedures function as the link between achieved quality and quality stipulated by the user and identified as DQOs and QAOs.

14.1 LABORATORY MEASUREMENTS

14.1.1 PRECISION

Precision will be assessed by comparing results of duplicate or replicate analyses. Both field and laboratory duplicate or replicate samples (more than two) are analyzed to determine precision.

Relative Percent Difference

Precision is evaluated by duplicate analyses of samples or matrix spike duplicate samples. (Matrix spikes are presented in the accuracy portion of this section.) The relative percent difference (RPD) is the difference between duplicates or matrix spike duplicates expressed as a percentage of the mean of the duplicates or matrix spike duplicates. The RPD is the most appropriate precision measure for this analytical data because of the limited precision data collected using project methods and matrixes. RPD is calculated by:

$$RPD = \frac{(X_1 - X_2) \times 100}{(X_1 + X_2)/2}$$

where, in terms of absolute quantity or concentration:

X_1 = sample result (or matrix spike)
X_2 = duplicate sample result (or matrix spike duplicate)

Standard Deviation

Precision is evaluated from replicate analyses with the statistically derived standard deviation, σ. Though applicable to replicated sample analyses (not duplicates), this

measure is more appropriate for often repeated analyses in statistically significant quantity such as control (reference) samples, check standards, blanks, and RPD results. The standard deviation (σ) is calculated by:

$$\sigma = \frac{[\sum(x - \bar{x})^2]^{1/2}}{n-1}$$

where:

$\bar{x}$ = $\frac{\sum x}{n}$, the arithmetic mean

n = number of replicates

Evaluation of Outliers

An outlier is an extreme high or low value that has observably questionable validity as a member of a set of measurements with which it is associated. Outliers may be rejected from the data set for the following reasons:

- A known experimental aberration occurred during the analysis, such as an instrument failure or other accidental event, or there was a specific documentable inconsistency in a significant procedure or analytical technique

- The Grubb's t value for the datum is larger than the tabulated Grubb's t value at 5 percent risk of false rejection for n number of data points when the t value is calculated by:

$$\bar{t} = \frac{(x_i - x)}{\sigma}$$

where:

x_i = extreme value being treated

$\bar{x}$ = mean of measurement set of n observations

σ = standard deviation associated with $\bar{x}$

14.1.2 ACCURACY

Analytical accuracy will be assessed by comparing concentration values with "true concentration values" in mathematical terms of recovery. The comparison is quantified by calculation of the percent recovery of the true value.

Accuracy can be evaluated in several ways. Commonly employed measures of accuracy include: matrix spike recovery, surrogate spike recovery, control sample recovery, check standard recovery or PE sample recovery, and overall accuracy.

Matrix Spike Recovery

Accuracy is evaluated by adding a known amount of compound (a spike) to a sample or duplicate samples and measuring the amount recovered by analysis. For a method or matrix spike, the compound is added prior to sample preparation (e.g., digestion or extraction, cleanup) and analysis. An analytical or post-preparation spike is added just prior to analysis (e.g. post-digestion spike for metals tests). Matrix spike percent recovery ($\%R_{ms}$) is calculated by:

$$\%R_{ms} = \frac{SSR\text{-}SR}{SA} \times 100$$

where, in terms of absolute quantity or concentration:

SSR = matrix spiked sample result
SR = sample result (unspiked)
SA = matrix spike added to sample

Surrogate Spike Recovery

Accuracy is evaluated by adding a known amount of a nontarget compound not normally found in the samples (a surrogate spike). Surrogates are similar to analytes or groups of analytes in composition. Surrogates mimic the analytes in preparation and analysis, e.g. organic extraction and chromatography. Surrogate spike recovery ($\%R_{ss}$) is calculated by:

$$\%R_{ss} = \frac{SSR}{SA} \times 100$$

where, in terms of quantity or concentration:

SSR = surrogate spiked sample result
SA = surrogate spike added to sample

Control, Check, or PE Recovery

Accuracy is evaluated by the recovery of the known or true value of the control (reference) sample, check standard, or PE sample (blind to CSL analyst). percent recovery ($\%R_{co,\ ch,\ or\ pe}$) is calculated by:

$$\%R_{co,\ ch,\ or\ pe} = \frac{SR}{TV} \times 100$$

where, in terms of quantity or concentration:

SR = result: control (co), check (ch), or PE (pe)
TV = true value

14.1.3 OVERALL ACCURACY

Accuracy is evaluated as the arithmetic mean of all of one kind of recovery measure: matrix spike, surrogate spike, control sample, check standard, or PE sample. Overall accuracy ($\bar{A}$) is calculated by:

$$\bar{A} = \frac{\sum_{i}^{n} A_i}{n}$$

where, in terms of recovery:

$\bar{A}$ = mean %R or overall accuracy for one recovery measure
A = individual %R for each accuracy measure

14.1.4 COMPLETENESS

Completeness will be assessed by comparing the number of samples having acceptable, valid, and usable data with the total samples collected having acceptable and unacceptable data. Percent completeness (%C) of the data is calculated by:

$$\%C = \frac{\text{number of samples having acceptable data}}{\text{number of samples collected}} \times 100$$

Routine procedures to assess data quality are discussed in detail within the analytical method SOPs.

14.1.5 CONTROL CHARTS

Precision, accuracy, and blank QC data may be plotted in control charts that graphically demonstrate statistical control, monitor performance, diagnose problems, document uncertainty, and aid in method development.

The laboratory measurement system is under statistical control when the assignable causes of variation have been detected, identified, and eliminated. Statistical control allows for normal, inherent variability, but assignable variability causes changes in the mean level or the variability about the mean level, or both, with respect to target levels. The statistics describe the system's current variability and provide a gauge for future data that is expected to be at a steady state under statistical control. The goal is to keep the system at a target level or improve it by reducing the variation about the target level. Control charts can be used to detect changes from target levels or changes in variability in the measurement process.

Laboratories often uses a type of Shewart control chart, the widely used x-bar. These control charts show time-plotted QC data distributed around the arithmetic mean along with some kind of control limits (boundaries for data quality). The control limits could be the non-statistical QAO criteria, e.g. ± 50% RPD, 60–140% spike recovery, and the MDL (for blanks). More often, the control limits are statistically derived warning and control limits. The warning limits are the mean plus and minus 2σ, which should include 95 percent of the data. The control limits are the mean plus and minus 3σ, which should include nearly all of the data. The production of control charts can be assisted by microcomputer software.

When σ is plotted along with the warning and control limits, the following rules help determine out-of-control points that are indicative of changes in the measurement process:

- One point greater than 3σ control limit
- Nine points in a row falling on one side of the central line
- Six points in a row either steadily increasing or decreasing

- Fourteen points in a row alternating up and down
- Two of three consecutive points more than 2σ from the central line
- Four of five points more than 1σ from the central line
- Fifteen points in a row within 1σ of the central line both above and below
- Eight points in a row on either side of the central line, none falling within 1σ of the central line

The preceding rules will maximize use of the control charts. On a practical basis, QC data that successively occur seven times on one side of the mean or exceed warning or control limits should trigger an investigation and subsequent corrective action.

Precision, accuracy, and completeness are defined in Section 5 of this QAPP. Equations for calculating precision, accuracy, and completeness are detailed below.

Precision is a measure of the reproducibility of field sampling and laboratory analyses. Both field duplicates (replicates) and laboratory duplicates are analyzed to determine data precision. The results are reported as the relative percent difference (RPD) and are calculated by:

$$RPD = \frac{D1 - D2}{(D1 + D2)/2} \times 100$$

where:

D1 = concentration of first duplicate
D2 = concentration of second duplicate

The accuracy of analytical results is a measure of the agreement between an experimental determination of the true value of the parameter being measured. Spike's sample analyses are used to determine the accuracy of analyses. A known quantity of the constituent of interest is added to a sample and analyzed. The amount of spiked compound recovered by analysis is compared to the amount added. Percent recovery is calculated by:

$$\%R = \frac{SSR-SR}{SA} \times 100$$

SSR = quantity measured in spike sample
SR = quantity measured in unspiked sample
SA = quantity of spike added

14.2 FIELD MEASUREMENTS

Field measurement data may be assessed by review of documentation of calibration, multiple readings, and analytical procedures to which field staff adhered. All data will be reviewed for completeness by the sample team leader.

Section 15
CORRECTIVE ACTION

Corrective action procedures are required as the result of audited or self-discovered nonconformance with predetermined QA/QC criteria. The nonconformance/ corrective action system functions to identify, document, address, and prevent recurrence of out-of-control situations requiring corrective action. The system applies to all situations that affect data quality, such as quality assurance objectives being exceeded, warning and action limits being approached, obvious outliers, deviations from normally expected results, divergence from SOPs, and abnormalities in sample handling.

15.1 LABORATORY ANALYSIS

The first level of responsibility for identifying nonconformances lies with the project staff. The lead analyst and other analysts will monitor their own performance and take actions as necessary. The second level of responsibility for identifying nonconformance lies with any person reviewing the data, including the laboratory manager, operations manager, laboratory QA officer, field task leader, and the project manager. The laboratory manager or task manager will be notified in all cases and will help develop and initiate corrective action. If problems continue, the laboratory manager or the task manager will notify the project manager.

Each nonconformance will be documented by recording the circumstances in the official contract laboratory records. Results of corrective actions will be recorded as well. Documentation of corrective action steps will include: problem identification, investigation responsibility assignment, investigation, action to eliminate the problem, increased monitoring of the effectiveness of the corrective action, and verification that the problem has been solved.

Examples of corrective actions include:

- Reanalysis of samples, if holding time criteria permit
- Resampling and reanalysis
- Examining and revising data or sample management procedures
- Evaluating and amending sampling or analytical procedures
- Acquiring additional training in sample preparation and analysis
- Reassigning analytical responsibilities
- Accepting data and acknowledging level of uncertainty (by use of flags or written explanations)

15.2 FIELD MEASUREMENTS

If nonconformance of field measurements are identified, field personnel will initiate corrective action in the following order, until satisfied of conformance:

- Repeat measurements
- Check adjustments
- Check batteries
- Check calibration
- Replace equipment
- Stop work

Stoppage of work may be implemented by field personnel if deemed necessary. However, the site manager should be immediately informed of such a measure. Further, corrective actions implemented in the field must be documented.

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Section 16
QUALITY ASSURANCE REPORTS TO MANAGEMENT

No separate QA report for this project is anticipated. Interim QA updates may be prepared, if found necessary, summarizing the status of the QA/QC program, documenting problematic conditions, and evaluating the attainment of QA/QC objectives of the program. Information will be presented in combinations of narrative text, tabular summaries, statistical charts, or schedules. The reports may include:

- Status of the program or project
- Assessment of analytical data quality for precision, accuracy, sensitivity, and completeness
- Results of performance audits and system audits
- Significant quality control problems and recommended solutions
- Corrective actions taken for any problems previously identified
- Recommendations for potential changes in the QAPP or other project documents

The reports will be given to the field task leader or project manager to be a part of the project records.

A data validation narrative summary and data quality assessment will be included as part of the final report. The report will contain QA sections that summarize data quality information collected during the project.

APPENDIX A
BIOTREATABILITY TESTING PROTOCOL

Appendix A
BIOTREATABILITY TESTING PROTOCOL

INTRODUCTION

As part of the remedial design for the Onalaska site it was desired to determine whether in situ biodegradation of contaminants within the lower portion of the unsaturated vadose zone could contribute to reducing the total amount of contamination at the site.

The particular zone of interest is defined as the zone of nonaqueous phase (ZNAP) contamination or the smear zone. This area of subsurface soil was created by the presence of petroleum product-related hydrocarbons floating on the groundwater surface. These hydrocarbons smeared over successive years along a 4- to 6-foot-thick zone that corresponds to seasonal fluctuations of the groundwater surface. Concentrations of total petroleum hydrocarbons (TPH) were found to be as high as 550 mg/kg in the ZNAP of contamination. Benzene, ethylbenzene, toluene, and xylene (BTEX) were found in the same region in summed concentrations of approximately 40 mg/kg.

To determine the effectiveness in situ biodegradation could play in an eventual remediation for the site, it was considered appropriate (given the lack of existing standardized engineering design parameters for operation of such a system) to obtain information from a bench-scale treatability study that simulated the ZNAP of contamination.

The treatability study objectives, soil sampling activities, equipment layout, sampling and analysis scheme, and mass balance data analysis of the bench studies are described in the following sections.

STUDY OBJECTIVES

The purpose for conducting bench scale treatability studies on the Onalaska site soil is three-fold: to determine oxygen requirements that will allow in situ aerobic biodegradation of hydrocarbons to occur within the test simulation; to determine the loss of hydrocarbons occurring because of volatilization of the volatile hydrocarbon fraction within the test simulation from forced addition of oxygen into the test medium; and to verify that a significant percentage of the hydrocarbons present are biodegradable.

The parameters that will be measured and tracked consistently throughout the treatability study are oxygen and carbon dioxide as indicators of biodegradation, vapor phase hydrocarbons in the offgas as indicators of volatilization, and soil bound hydrocarbons as an indicator of the undegraded contamination. Monitoring carbon dioxide as well as oxygen is necessary since oxygen may play a direct chemical oxidation role in conversion of certain contaminants. Thus, oxygen depletion may not be indicative of biodegradation only.

The purpose of treatability testing is to obtain a material balance of the test system throughout time. For this reason, consistency in analytical measurement and sample collection techniques are extremely important for the integrity of the project. Provisions have been built into the testing to minimize analytical error and conserve mass.

To address the above objectives in a scientifically controlled fashion and cost-effective manner the following operational parameters will **not** be manipulated (other than their initial establishment) over the course of the testing:

- Nutrient supply
- Moisture supply
- Temperature
- Microorganism content

The above components of the biological treatment system will be established at the beginning of the experiment, but not manipulated thereafter. Therefore, the assumption is made that nutrients and moisture will not become limiting factors to microorganism metabolism. Temperature variability is beyond engineering control for field applications. The other basic assumption made is that there are likely to be microorganisms present in the soil that will degrade the hydrocarbons. Therefore, the need to add an exogenous supply of microorganisms will not be assessed.

PRELIMINARY STUDY

A preliminary study will be conducted to familiarize the analyst with handling the test equipment, test material, and instruments, the extractability of BETX and total petroleum hydrocarbons from soil, the chromatographic behavior of the contaminants and standard compounds, the rates of O_2 uptake and CO_2 respiration, and rate of degradation.

Portions of the contaminated test soil will be analyzed for BETX and total petroleum hydrocarbons using traditional volatile organic techniques and the proposed CH2M HILL method to assess the extractability of hydrocarbons from the test soil (Appendix B).

After an acceptable extraction condition is found, two soil test columns will be prepared through which humid air will flow continuously (as described in "Test System" section). The test system will be kept in the dark at 25°C ± 5°C and connected to an apparatus containing a carbon molecular sieve for trapping volatile components. In the first test columns, the flow rate of air entering the column will be varied to optimized flow rates. In the second test column, subsamples of test soil will be removed and analyzed at Time 0 and at least three other intervals during a 7- to 10-day test period.

These data and procedures will be used in the final selection of chromatographic methods, extraction conditions, and sampling intervals for the definitive treatability study.

DEFINITIVE TREATABILITY STUDY

INITIAL CHARACTERIZATION

Test soil columns will be prepared with soil at the time of sample collection as described in Section 6 of the QAPP. Three soil columns will be prepared for the treatability study. One column containing clean background soil will be used as the control for the study and the other two columns will be used to duplicate treatability. Measures will be taken to ensure that the sample integrity of soil collected from the ZNAP of contamination is maintained.

Initial characterization of physical and chemical properties of the soil to be determined by CH2M HILL is as follows:

- BETX
- Total Petroleum Hydrocarbons
- Nutrients: Nitrogen and Phosphorus
- Moisture Content
- Total Organic Carbon
- Total Volatile Solids
- pH

If the measured C:N:P ratio is not sufficient to support the stoichiometric growth of microorganisms, the sample ports will be used for the injection of a nutrient amendment solution to establish initial nonlimiting conditions. Similarly, if soil pH measurements are not within the range of 6 to 8, a buffering amendment solution will be added. Percent moisture and dry weight measurements to determine moisture content and total volatile solids, respectively, will also be made on soil samples collected from the column material.

TEST SYSTEM

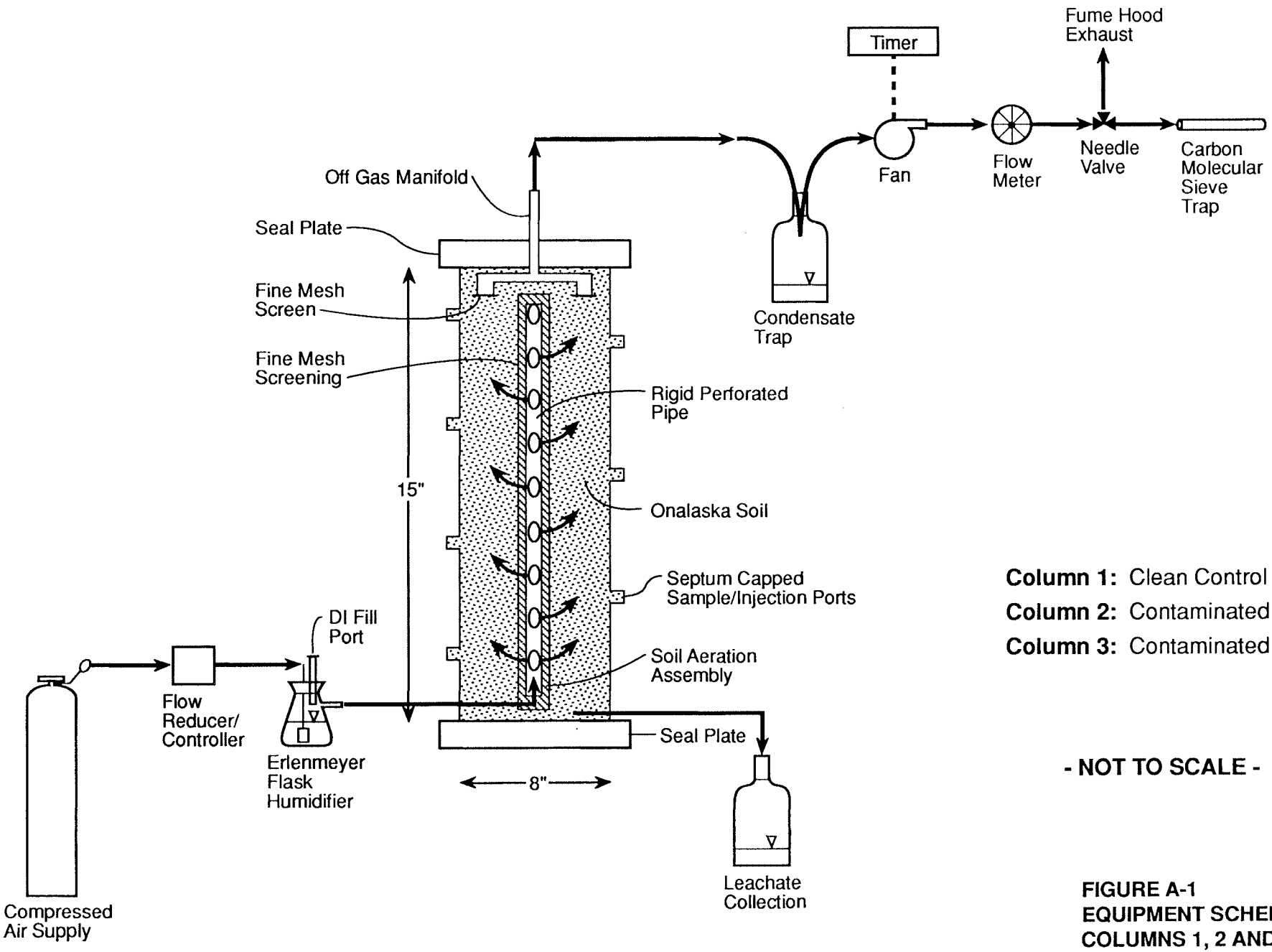
Figure A-1 depicts the equipment layout to be used for the treatability study. Components of the schematic will be fabricated from commonly available materials in-house or purchased preassembled from the appropriate manufacturers.

Once columns have been established with a fixed mass of soil, each column (having previously been tared when empty) will be weighed to the nearest 0.1 lb. Using an estimated soil density and knowing the volume of the column, the mass of soil collected for each column should translate to roughly 20 kg per column. The volume of each column will be approximately 0.5 cubic feet.

Compressed, oil-free air will be used to supply the sealed column system with a regulated amount of air flow. To avoid drying of the soil matrix during study, the supplied air will be humidified by passing the air through a porous diffuser that will bubble the air into distilled water. The humidified air will then be directed into a sealed column containing the soil to be treated.

Air will be supplied to the soil matrix through a perforated rigid supply line that will be in contact with the soil. To avoid clogging of the supply line, the line will be surrounded by a fine mesh screen to allow air transfer out, but limit sand particles

GLO65550.FI FIG. B-2 8-14-91LML



Column 1: Clean Control Soil
Column 2: Contaminated Soil
Column 3: Contaminated Soil

- NOT TO SCALE -

FIGURE A-1
EQUIPMENT SCHEMATIC
COLUMNS 1, 2 AND 3
ONALASKA RD
TREATABILITY QAPP

from entering the orifices. Initial flow rates for air supply will be determined using data from preliminary bench studies of a similar nature, stoichiometric oxygen requirements for hydrocarbon degradation, and pore volume exchange calculations. Ultimately, the lowest flow rate will be used that maintains aerobic conditions for the column.

The columns will be constructed of plexiglass with the approximate dimensions shown in Figure A-1. Columns will be surrounded by aluminum foil to inhibit photolysis of contaminants and to deter algae growth. Several sampling ports will be located along the length of the column. These ports will be covered with a septum to prevent loss of column soil gases. Offgas from the column will exit from the top of the column through a flowmeter and into a carbon molecular sieve trap for collection. The option for continuous offgas discharge from the column directly to a fume hood will also be available.

SAMPLING COLLECTION AND ANALYSIS SCHEME

Replicate soil samples will be removed from at least three areas of the soil column and combined. The soil samples will be analyzed as described in Section 9 of the QAPP at Time 0 and thereafter as dictated by the rate of volatilization and degradation and based on the results of the preliminary study, or both. Soil samples will be removed immediately before connection to the air flow supply to serve as the Time 0 interval. Table A-1 describes the anticipated sampling frequency and rationale for sampling at the intended intervals.

To provide analytical consistency, all phases of media (solid, liquid, and gas) will undergo the same analytical measurement using the same instrument and desorption method. This means that all hydrocarbon measurements can be directly related to one another and subtracted/summed to represent the true rate of hydrocarbon degradation to carbon dioxide and water.

All hydrocarbon measurements will be calibrated against a standard with known carbon range and compound structure. Since there is no true analytical standard for the weathered petroleum products present at the site, all hydrocarbon measurements and comparisons will be made relative to the standard of choice and each other. Quantification of the exact mass of every different component/fraction of the hydrocarbon waste is not achievable within the scope of this project. However, because compound specific air emission limits do exist for the aromatic BTEX hydrocarbon fraction and because these compounds have documented detrimental health effects when inhaled, these four compounds will be quantified individually. Table A-2 lists how each variable will be determined analytically.

Portions of soil will be collected through various sampling ports located along the length of the soil test column and the soil combined to form a single sample. After removing soil through the sampling ports, the column will be repacked by tapping the column. Filling the void spaces remaining after sampling will limit short circuiting of the air supply.

Soil samples will be analyzed for benzene, ethylbenzene, toluene, xylene, and total petroleum hydrocarbons using methods described in Section 9 of the QAPP.

Table A-1
Treatability Study
Sampling Frequency and Rationale
Onalaska RD QAPP
(Page 1 of 2)

Medium	Analytical Measurement	Sample Collection Point and Technique	Frequency of Sample Collection
Soil	Hydrocarbons	Column sample port using coring device	Time = 0 and estimated at one per 3 days thereafter
	BTEX	Column sample port using coring device	Time = 0 and estimated at one per 3 days thereafter
	% Moisture	Field/column shipped to Corvallis laboratory for analysis	Initial, mid-test, final
	Total Volatile Solids	Field/column shipped to Corvallis laboratory for analysis	Initial, mid-test, final
	Nitrogen	Field/column shipped to Corvallis laboratory for analysis	Initial, mid-test, final
	Total P	Field/column shipped to Corvallis laboratory for analysis	Initial, mid-test, final
	TOC	Field/column shipped to Corvallis laboratory for analysis	Initial, mid-test, final
	Dry Weight	Collected from column port at indicated frequency using coring device	Initial, mid-test, final
Offgas	Hydrocarbons	Offgas exit using CARBOTRAP™	Minimum frequency of once per pore volume residence time
	BTEX	Offgas exit using CARBOTRAP™	Maximum frequency to be determined following preliminary study
	O_2	Needle valve using syringe	Maximum frequency to be determined following preliminary study
	CO_2	Needle valve using syringe	Maximum frequency to be determined following preliminary study

Table A-1
Treatability Study
Sampling Frequency and Rationale
Onalaska RD QAPP
(Page 2 of 2)

Medium	Analytical Measurement	Sample Collection Point and Technique	Frequency of Sample Collection
Condensate and Leachate	Hydrocarbons	Respective traps using syringe	Frequency will be dictated by rate of formation
	BTEX	Respective traps using syringe	Frequency will be dictated by rate of formation
	O_2	Respective traps using syringe	Frequency will be dictated by rate of formation
	CO_2	Respective traps using syringe	Frequency will be dictated by rate of formation
	NH_3/Total P	Respective traps using syringe	Frequency will be dictated by rate of formation
Supplied Humidified Air	O_2	Humidifier exit port	Initial
	CO_2	Humidifier exit port	Initial
	Hydrocarbons	Humidifier exit port	Initial

Table A-2
Treatability Study
Analytical Data
Onalaska RD QAPP

Medium	Analytical Result (units)	Analytical Method
Soil	HC (μg/kg)	GC-Flame Ionization Detector (FID), Standard Methods 2720C.
	BTEX (μg/kg)	GC-FID, Standard Methods 2720C.
	% Moisture (%)	Methods of Soil Analysis 21-2.2
	N, NH_3 (mg/l)	Standard Methods 4500-NH_3 F Methods of Soil Analysis 33-3.2, 33-6.2
	Total P (mg/l)	Standard Methods 4500-PE. Methods of Soil Analysis 24-5.3
	Dry Weight/Total Volatile Solids (mg/kg)	Standard Methods 2540E.
	pH	Methods of Soil Analysis 12-2.6
Offgas	HC (μg/tube)	GC-FID, Standard Methods 2720C.
	BTEX (μg/tube)	GC-FID, Standard Methods 2720C.
	O_2 (μg/ml)	GC-Thermal Conductivity Detector (TCD)
	CO_2 (μg/l)	GC-TCD
Condensate and Leachate	HC (μg/tube)	GC-FID, Standard Methods 2720C.
	BTEX (μg/tube)	GC-FID, Standard Methods 2720C.
	O_2 (μg/ml)	GC-TCD
	CO_2 (μg/ml)	GC-TCD
Supplied Humidified Air	O_2 (μg/ml)	GC-TCD
	CO_2 (μg/ml)	GC-TCD
	HC (μg/ml)	GC-FID, Standard Methods 2720C.

Air that has passed through the soil column and into the carbon molecular trap will be analyzed for benzene, ethylbenzene, toluene, xylene, and total petroleum hydrocarbons using methods described in Section 9 of the QAPP.

Should condensate or leachate form, provisions will be made to sample the liquid condensate for benzene, ethylbenzene, toluene, xylene, and total petroleum hydrocarbons using methods described in Section 9 of the QAPP.

The concentration level of oxygen and carbon dioxide will be measured using gas chromatographic techniques described in Section 9 of the QAPP.

DATA INTERPRETATION

Obtaining quantification of the total amount of hydrocarbon degradation achievable is not an objective of this treatability study because of the limited study period (4 weeks) that may not allow for complete degradation to occur. The amount of biodegradation that does occur should not be directly extrapolated to cleanup goals for the ZNAP because the adjacent landfill provides an ongoing source of contamination whose characteristics may change over time. However, the test should verify that a significant percentage of the hydrocarbons are biodegradable.

A material balance on BETX and total petroleum hydrocarbons in the soil, water, and air emissions will be determined. The relationship between amount of oxygen supplied to the amount of hydrocarbon biodegraded and stripped will also be established.

GLT175/077.51

APPENDIX B
LABORATORY ANALYTICAL METHODS STANDARD OPERATING PROCEDURES

METHOD REFERENCES

METHODS OF SOIL ANALYSIS

Part 2

Chemical and Microbiological Properties

Second Edition

A. L. Page, *Editor*

R. H. Miller, *Associate Editor*

D. R. Keeney, *Associate Editor*

Number 9 (Part 2) in the series

AGRONOMY

American Society of Agronomy, Inc.
Soil Science Society of America, Inc.
Publisher
Madison, Wisconsin USA

1982

STANDARD METHODS

For the Examination of Water and Wastewater

SEVENTEENTH EDITION

Prepared and published jointly by:

AMERICAN PUBLIC HEALTH ASSOCIATION
AMERICAN WATER WORKS ASSOCIATION
WATER POLLUTION CONTROL FEDERATION

Publication Office:
American Public Health Association
1015 Fifteenth Street NW
Washington, DC 20005

METHOD FOR TOTAL VOLATILE SOLIDS IN SOIL

GLT175/079.51-4

2540 E. Fixed and Volatile Solids Ignited at 550°C

1. General Discussion

a. Principle: The residue from Method B, C, or D is ignited to constant weight at 550 ± 50°C. The remaining solids represent the fixed total, dissolved, or suspended solids while the weight lost on ignition is the volatile solids. The determination is useful in control of wastewater treatment plant operation because it offers a rough approximation of the amount of organic matter present in the solid fraction of wastewater, activated sludge, and industrial wastes.

b. Interferences: Negative errors in the volatile solids may be produced by loss of volatile matter during drying. Determination of low concentrations of volatile solids in the presence of high fixed solids concentrations may be subject to considerable error. In such cases, measure for suspect volatile components by another test, for example, total organic carbon (Section 5310).

2. Apparatus

See Sections 2540B.2, 2540C.2, and 2540D.2.

3. Procedure

Ignite residue produced by Method B, C, or D to constant weight in a muffle furnace at a temperature of 550 ± 50°C. Have furnace up to temperature before inserting sample. Usually, 15 to 20 min ignition are required. Let dish or filter disk cool partially in air until most of the heat has been dissipated. Transfer to a desiccator for final cooling in a dry atmosphere. Do not overload desiccator. Weigh dish or disk as soon as it has cooled to balance temperature. Repeat cycle of igniting, cooling, desiccating, and weighing until a constant weight is obtained or until weight loss is less than 4% of previous weight.

4. Calculation

$$\text{mg volatile solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

$$\text{mg fixed solids/L} = \frac{(B - C) \times 1000}{\text{sample volume, mL}}$$

where:

A = weight of residue + dish before ignition, mg,
B = weight of residue + dish or filter after ignition, mg, and
C = weight of dish or filter, mg.

5. Precision

The standard deviation was 11 mg/L at 170 mg/L volatile total solids in studies by three laboratories on four samples and 10 replicates. Bias data on actual samples cannot be obtained.

METHOD FOR OXYGEN AND CARBON DIOXIDE IN AIR

GLT175/079.51-5

2720 C. Gas Chromatographic Method

1. General Discussion

a. Principle: See Section 6630B for a discussion of gas chromatography.

b. Equipment selection: Many columns have been proposed for gas mixture analyses. Any that is capable of the desired separation is acceptable, provided that all of the exact conditions of analysis are reported with the calibration standards. The following directions are necessarily general. Follow the manufacturer's recommendations for the specific instrumentation.

2. Apparatus

a. Gas chromatograph: Use any instrument equipped with a thermal conductivity detector. With some column packings, ovens and temperature controls are necessary. Preferably use a unit with a gas sample valve.

b. Recorder: Use a 10-mV full-span strip chart recorder with the gas chromatograph. When minor components such as H_2 and H_2S are to be detected, a 1-mV full-span recorder is preferable.

*c. Column packing:** Some commercially available column packings useful for separating sludge gas components are listed below along with the routine separations possible at room temperature:[1,2]

1) Silica gel at room temperature: H_2, air (O_2 + N_2), CH_4, (CO_2-slow);

2) Molecular Sieve 13X: H_2, O_2, N_2, CH_4;

3) HMPA (hexamethylphosphoramide) 30% on Chromosorb P: CO_2 from (O_2, N_2, H_2, CH_4);

4) DEHS (di-2-ethylhexylsefacate) 30% on Chromosorb P: CO_2 from (O_2, N_2, H_2, CH_4).

Combinations of Columns 1 and 2, 3 and 2, or 4 and 2 when properly sized and used in the sequence: 1st column, detector, 2nd column, detector, readily will separate H_2, O_2, N_2, CH_4, and CO_2. Commercial equipment specifically designed for such operations is available.[2]

d. Sample introduction apparatus: An instrument equipped with gas-sampling valves is designed to permit automatic injection of a specific sample volume into the chromatograph. If such an instrument is not available, introduce samples with a 2-mL syringe fitted with a 27-gauge hypodermic needle. Reduce escape of gas by greasing plunger lightly with mineral oil or preferably by using a special gas-tight syringe.

3. Reagents

a. Carrier gases: Use helium for separating digester gases. If H_2 is to be determined, use argon as a carrier gas to increase the sensitivity greatly.

b. Calibration gases: Use samples of CH_4, CO_2, and N_2 of known purity, or mixtures of known composition, for calibration. Also use samples of O_2, H_2, and H_2S of known purity if these gases are to be measured.

4. Procedure

a. Preparation of gas chromatograph: Adjust carrier gas flow rate to 60 to 80 mL/min. Turn on oven heaters, if used, and detector current and adjust to desired values. The instrument is ready for use when the recorder yields a stable base line. Silica gel and molecular sieve columns gradually lose activity because of adsorbed moisture or materials permanently adsorbed at room temperature. If insufficient separations occur, reactivate by heating or repacking.

b. Calibration: For accurate results, prepare a calibration curve for each gas to be measured because different gas components do not give equivalent detector responses on either a weight or a molar basis. Calibrate with synthetic mixtures or with pure gases.

1) Synthetic mixtures—Use purchased gas mixtures of known composition or prepare in the laboratory. Inject a standard volume of each mixture into the gas chromatograph and note response for each gas. Compute detector response, either as area under a peak or as height of peak, after correcting for attenuation. Read peak heights accurately and correlate with concentration of component in sample. Reproduce operating parameters exactly from one analysis to the next. If sufficient reproducibility cannot be obtained by this procedure, use peak areas for calibration. Prepare calibration curve by plotting either peak area or peak height against volume percent for each component.

---

*Gas chromatographic methods are extremely sensitive to the materials used. Use of trade names in *Standard Methods* does not preclude the use of other existing or as-yet-undeveloped products that give *demonstrably* equivalent results.

2) Pure gases—Introduce pure gases into chromatograph individually with a syringe. Inject sample volumes of 0.25, 0.5, 1.0 mL, etc., and plot detector response, corrected for attenuation, against gas volume.

When the analysis system yields a linear detector response with increasing gas component concentration from zero to the range of interest, run standard mixtures along with samples. If the same sample size is used, calculate gas concentration by direct proportions.

c. Sample analysis: If samples are to be injected with a syringe, equip sample collection container with a port closed by a rubber or silicone septum. To take a sample for analysis, expel air from barrel of syringe by depressing plunger and force needle through the septum. Withdraw plunger to take gas volume desired, pull needle from collection container, and inject sample rapidly into chromatograph.

When samples are to be injected through a gas-sampling valve, connect sample collection container to inlet tube. Permit gas to flow from collection tube through the valve to purge dead air space and fill sample tube. About 15 mL normally are sufficient to clear the lines and to provide a sample of 1 to 2 mL. Transfer sample from loop into carrier gas stream by following manufacturer's instructions. Bring samples to atmospheric pressure before injection.

When calibration curves have been prepared with synthetic mixtures, use the same sample volume as that used during calibration. When calibration curves are prepared by the procedure using varying volumes of pure gases, inject any convenient gas sample volume up to about 2 mL.

5. Calculation

a. When calibration curves have been prepared with synthetic mixtures and the volume of the sample analyzed is the same as that used in calibration, read volume percent of each component directly from calibration curve after detector response for that component is computed.

b. When calibration curves are prepared with varying volumes of pure gases, calculate the percentage of each gas in the mixture as follows:

$$\text{Volume } \% = \frac{A}{B} \times 100$$

where:

A = partial volume of component (read from calibration curve) and
B = volume sample injected.

c. Where standard mixtures are run with samples and instrument response is linear from zero to the concentration range of interest:

$$\text{Volume } \% = \text{Volume } \% \text{ (std)} \times \frac{C}{D}$$

where:

C = recorder value of sample and
D = recorder value of standard.

6. Precision and Bias

Precision and bias depend on the instrument used and the techniques of operation. With proper care, a precision of 2% generally can be achieved. With digester gas the sum of the percent CH_4, CO_2, and N_2 should approximate 100%. If it does not, suspect errors in collection, handling, storage, and injection of gas, or in instrumental operation or calibration.

7. Reference

1. ANDREWS, J.F. 1968. Chromatographic analysis of gaseous products and reactants for biological processes. *Water Sewage Works* 115:54.
2. Column Systems for the Fisher Gas Partitioner. Tech. Bull. TB-154, Fisher Scientific Co., Atlanta, Ga. Catalog 77, Fisher Scientific Co.

METHODS FOR AMMONIA IN SOIL AND WATER

GLT175/079.51-6

Nitrogen—Inorganic Forms

33-3.2 Method

33-3.2.1 REAGENTS

1. Potassium chloride (KCl) solution, approximately 2*M*: Dissolve 1,500 g of reagent-grade KCl in 8 liters of water, and dilute the solution to 10 liters.

33-3.2.2 PROCEDURE

Place 10 g of soil in a 250-ml, widemouth bottle, and add 100 ml of 2*M* KCl. Stopper the bottle, and shake it on a mechanical shaker for 1 hour. Allow the soil-KCl suspension to settle until the supernatant liquid is clear (usually about 30 min), and perform the analyses described on aliquots of this liquid. If the KCl extract cannot be analyzed soon after its preparation (within 24 hours), filter the soil-KCl suspension (Whatman no. 42 filter paper), and store the filtrate in a refrigerator until analyses can be performed.

33-6.2 Determination of Ammonium by the Specific Ion Electrode

33-6.2.1 PRINCIPLES

Ammonium-nitrogen concentration is estimated by comparison of the electromotive force (emf, in millivolts) in the unknown with that obtained by analysis of NH_4^+-N standards by the same method. The sample or standard is made alkaline by the addition of NaOH (pH 11-12), because the electrode responds only to NH_3 activity.

33-6.2.2 METHOD

33-6.2.2.1 Special apparatus.

1. Ammonia electrode.
2. pH-millivolt meter with a sensitivity of ± 0.1 mV.

33-6.2.2.2 Reagents.

1. Sodium hydroxide (NaOH), 0.25*M*: Dissolve 10 g of NaOH in 800 ml of water, and dilute to 1,000 ml.
2. Standard NH_4^+-N solutions: Prepare a series of standards in 2*M* potassium chloride (KCl) ranging from 0.1 to 10 μg of NH_4^+-N/ml. If an extract other than 2*M* KCl is used, prepare the standards in this solution.

33-6.2.3 PROCEDURE (Modified from Banwart et al., 1972)

Place a 20-ml aliquot of the soil extract in a 30- to 50-ml beaker containing a Teflon-coated stirring bar. Place the beaker on a magnetic stirrer, add 2 ml of 0.25*M* NaOH, and insert into the solution an NH_3 electrode connected to a pH/millivolt meter. Stir the solution for 1 min, record the electrode potential value, and calculate NH_4^+-N in the sample by comparison of this value to a calibration curve prepared as described for determination of NH_4^+-N.

33-6.2.4 COMMENTS

The approach used to obtain the calibration curve and electrode potential readings will differ somewhat depending on the meter used; manufacturers instructions should be followed. The meter should be recalibrated immediately before each series of analyses. Non-Nernstain response (a marked deviation from a slope of 57 to 59 mV change per 10-fold concentration difference) or excessive drifting are indicative of need to replace the electrode membrane. Measurements must be made within 1 to 2 min after the addition of NaOH to ensure no loss of NH_3. If Hg^+ is present in the sample, NaI (15 g of NaI/liter) can be added to the 0.25*M* NaOH. Iodide forms complexes with Hg. Care must be taken to prevent air bubble entrapment under the electrode. This is easily accomplished by inserting the electrode at about a 20° angle with respect to vertical.

4500-NH_3 F. Ammonia-Selective Electrode Method

1. General Discussion

a. Principle: The ammonia-selective electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from an electrode internal solution of ammonium chloride. Dissolved ammonia ($NH_{3(aq)}$ and NH_4^+) is converted to $NH_{3(aq)}$ by raising pH to above 11 with a strong base. $NH_{3(aq)}$ diffuses through the membrane and changes the internal solution pH that is sensed by a pH electrode. The fixed level of chloride in the internal solution is sensed by a chloride ion-selective electrode that serves as the reference electrode. Potentiometric measurements are made with a pH meter having an expanded millivolt scale or with a specific ion meter.

b. Scope and application: This method is applicable to the measurement of 0.03 to 1400 mg NH_3-N/L in potable and surface waters and domestic and industrial wastes. High concentrations of dissolved ions affect the measurement, but color and turbidity do not. Sample distillation is unnecessary. Use standard solutions and samples that have the same temperature and contain about the same total level of dissolved species. The ammonia-selective electrode responds slowly below 1 mg NH_3-N/L; hence, use longer times of electrode immersion (5 to 10 min) to obtain stable readings.

c. Interference: Amines are a positive interference. Mercury and silver interfere by complexing with ammonia.

d. Sample preservation: Do not use $HgCl_2$ as a sample preservative. Refrigerate at 4°C for samples to be analyzed within 24 h. Preserve samples high in organic and nitrogenous matter, and any other samples for a prolonged period, by lowering pH to 2 or less with conc H_2SO_4.

2. Apparatus

a. Electrometer: A pH meter with expanded millivolt scale capable of 0.1 mV resolution between −700 mV and +700 mV or a specific ion meter.

*b. Ammonia-selective electrode.**

c. Magnetic stirrer, thermally insulated, with TFE-coated stirring bar.

*Orion Model 95-10 or 95-12, EIL Model 8002-2, Beckman Model 39565, or equivalent.

3. Reagents

a. Ammonia-free water: See Section 4500-NH_3.B.3*a*. Use for making all reagents.

b. Sodium hydroxide, 10N: Dissolve 400 g NaOH in 800 mL water. Cool and dilute to 1000 mL with water.

c. Stock ammonium chloride solution: See Section 4500-NH_3.C.3*d*.

d. Standard ammonium chloride solutions: See ¶ 4*a* below.

4. Procedure

a. Preparation of standards: Prepare a series of standard solutions covering the concentrations of 1000, 100, 10, 1, and 0.1 mg NH_3-N/L by making decimal dilutions of stock NH_4Cl solution with water.

b. Electrometer calibration: Place 100 mL of each standard solution in a 150-mL beaker. Immerse electrode in standard of lowest concentration and mix with a magnetic stirrer. Do not stir so rapidly that air bubbles are sucked into the solution because they will become trapped on the electrode membrane. Maintain the same stirring rate and a temperature of about 25°C throughout calibration and testing procedures. Add a sufficient volume of 10*N* NaOH solution (1 mL usually is sufficient) to raise pH above 11. Keep electrode in solution until a stable millivolt reading is obtained. CAUTION: Check electrode sensing element performance according to manufacturer's instructions to make sure that electrode is operating properly. Do not add NaOH solution before immersing electrode, because ammonia may be lost from a basic solution. Repeat procedure with remaining standards, proceeding from lowest to highest concentration. Wait for at least 5 min before recording millivolts for standards and samples containing ≤ 1 mg NH_3-N/L.

c. Preparation of standard curve: Using semilogarithmic graph paper, plot ammonia concentration in milligrams NH_3-N per liter on the log axis vs. potential in millivolts on the linear axis starting with the lowest concentration at the bottom of the scale. If the electrode is functioning properly a tenfold change of NH_3-N concentration produces a potential change of 59 mV.

d. Calibration of specific ion meter: Refer to manufacturer's instructions and proceed as in ¶s 4*a* and *b*.

e. Measurement of samples: Dilute if necessary to bring NH_3-N concentration to within calibration curve range. Place 100 mL sample in 150-mL beaker and follow procedure in ¶ 4*b* above. Record volume of 10*N* NaOH added in excess of 1 mL. Read NH_3-N concentration from standard curve.

5. Calculation

$$\text{mg } NH_3\text{-N/L} = A \times B \times \left[\frac{101 + C}{101}\right]$$

where:

A = dilution factor,
B = concentration of NH_3-N/L, mg/L, from calibration curve, and
C = volume of added 10*N* NaOH in excess of 1 mL, mL.

6. Precision and Bias

See Section 4500-NH_3.A.4.

7. Bibliography

BANWART, W.L., J.M. BREMNER & M.A. TABATABAI. 1972. Determination of ammonium in soil extracts and water samples by an ammonia electrode. *Comm. Soil Sci. Plant Anal.* 3:449.

MIDGLEY, C. & K. TERRANCE. 1972. The determination of ammonia in condensed steam and boiler feed-water with a potentiometric ammonia probe. *Analyst* 97:626.

BOOTH, R.L. & R.F. THOMAS. 1973. Selective electrode determination of ammonia in water and wastes. *Environ. Sci. Technol.* 7:523.

U.S. ENVIRONMENTAL PROTECTION AGENCY. 1979. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79-020, National Environmental Research Center, Cincinnati, Ohio.

METHODS FOR PHOSPHORUS IN SOIL AND WATER

GLT175/079.51-7

Phosphorus

24-5.3 Phosphorus Soluble in Water

24-5.3.1 PRINCIPLES

This method is useful in measuring the P concentration in water or dilute salt (i.e., 0.01*M* $CaCl_2$) extracts of the soil and in displaced soil solutions and saturation extracts of soil. With soils low in available P, root absorption of P and growth of plants increase as P concentration increases in the soil solution up to a limit. As an index of P availability, the objective of this method is to determine the P concentration level in the soil extract that limits growth of plants. In soil testing practices, the water or dilute salt extracts represent an attempt to approximate the soil solution P concentration. A research objective is to obtain the soil solution and determine its composition so that the chemical environment of the plant roots may be defined in quantitative terms (Adams, 1974).

24-5.3.2 METHOD

24-5.3.2.1 Reagents.

1. Ammonium paramolybdate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$]: Dissolve 12.0 g of ammonium paramolybdate in 250 ml of distilled water. Dissolve 0.2908 g of potassium antimony tartrate ($KSbO\cdot C_4H_4O_6$) in 100 ml of distilled water. Add these dissolved reagents to 1 liter of 5*N* sulfuric acid (H_2SO_4) (141 ml of conc H_2SO_4 diluted to 1 liter), mix thoroughly, and dilute with distilled water to 2 liters. Store in a Pyrex glass bottle in a dark and cool compartment (reagent A).
2. Ascorbic acid: Dissolve 1.056 g of ascorbic acid in 200 ml of reagent A, and mix. This ascorbic acid (reagent B) should be prepared as required because it does not keep more than 24 hours.

24-5.3.2.2 Procedure. Add 5 g of air-dry soil and 50 ml of distilled water to a flask suitable for continuous shaking. Shake the contents of the flask continuously for 5 min. Centrifuge the mixture until the solution is free of soil mineral particles. This usually occurs in 15 min in a high-speed Sorvall centrifuge at a setting of 100. Obtain clear extracts alternatively by repeated filtration through Whatman no. 42 filter paper. Return to the suspension the first portions coming through the filter paper.

Pipette aliquots containing 1 to 20 μg of P into 25-ml volumetric flasks. Add distilled water to increase the volume to 20 ml, and then add 4 ml of reagent B. Make to 25 ml volume and mix. The color is stable for 24 hours, and the maximum intensity develops in 10 min. The absorption maximum of the blue color formed in the presence of Sb is at 882 nm. Calibrate the method using a standard P solution. Prepare a blank with distilled water and 4 ml of reagent B.

24-5.3.2.3 Comments. Soils in California that showed more than 0.13 ppm of P in the water extract failed to respond in crop yields to P fertilization (Bingham, 1949; Martin & Buchanan, 1950; Martin & Mikkelsen, 1960). Thompson et al. (1960) found a high correlation between P uptake by sorghum (*Sorghum bicolor* L. Moench) and water-soluble P on 22 soils, most of which were acid. Fried and Shapiro (1956) observed a poor relation between water-soluble P and P uptake on eight acid soils for the initial extract but observed a much better correlation for the 14th successive extract. Olsen et al. (1954) observed a high correlation between water-soluble P and "A" values on some groups of soils.

Phosphorus concentration in solution usually increases as the amount of soil increases per unit volume of water. A saturation extract more nearly approaches the P concentration expected to be in a soil solution from which roots absorb P. Such an extract requires more time for preparation, and its analysis for P presents more difficulties. In some cases these factors may not be important, and the results from a saturation extract or the displaced soil solution may be most desirable. For more routine purposes and large numbers of samples, the 1:10 water extraction is more suitable.

The ascorbic acid method has proved to be reliable and less subject to interferences in color development than $SnCl_2$ methods, and the color is stable for 24 hours. A simple test of possible interference in the P analysis is provided by diluting the solution. If the diluted sample is proportionately greater or less in P concentration than indicated by the dilution factor, an interference is evident.

4500-P E. Ascorbic Acid Method

1. General Discussion

a. Principle: Ammonium molybdate and potassium antimonyl tartrate react in acid medium with orthophosphate to form a heteropoly acid—phosphomolybdic acid—that is reduced to intensely colored molybdenum blue by ascorbic acid.

b. Interference: Arsenates react with the molybdate reagent to produce a blue color similar to that formed with phosphate. Concentrations as low as 0.1 mg As/L interfere with the phosphate determination. Hexavalent chromium and NO_2^- interfere to give results about 3% low at concentrations of 1 mg/L and 10 to 15% low at 10 mg/L. Sulfide (Na_2S) and silicate do not interfere at concentrations of 1.0 and 10 mg/L.

c. Minimum detectable concentration: Approximately 10 μg P/L. P ranges are as follows:

Approximate P Range *mg/L*	Light Path *cm*
0.30–2.0	0.5
0.15–1.30	1.0
0.01–0.25	5.0

2. Apparatus

a. Colorimetric equipment: One of the following is required:

1) *Spectrophotometer,* with infrared phototube for use at 880 nm, providing a light path of 2.5 cm or longer.

2) *Filter photometer,* equipped with a red color filter and a light path of 0.5 cm or longer.

b. Acid-washed glassware: See Section 4500-P.C.2*b*.

3. Reagents

a. Sulfuric acid, H_2SO_4, 5*N:* Dilute 70 mL conc H_2SO_4 to 500 mL with distilled water.

b. Potassium antimonyl tartrate solution: Dissolve 1.3715 g $K(SbO)C_4H_4O_6 \cdot 1/2H_2O$ in 400 mL distilled water in a 500-mL volumetric flask and dilute to volume. Store in a glass-stoppered bottle.

c. Ammonium molybdate solution: Dissolve 20 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 500 mL distilled water. Store in a glass-stoppered bottle.

d. Ascorbic acid, 0.01*M:* Dissolve 1.76 g ascorbic acid in 100 mL distilled water. The solution is stable for about 1 week at 4°C.

e. Combined reagent: Mix the above reagents in the following proportions for 100 mL of the combined reagent: 50 mL 5*N* H_2SO_4, 5 mL potassium antimonyl tartrate solution, 15 mL ammonium molybdate solution, and 30 mL ascorbic acid solution. *Mix after addition of each reagent.* Let all reagents reach room temperature before they are mixed and mix in the order given. If turbidity forms in the combined reagent, shake and let stand for a few minutes until turbidity disappears before proceeding. The reagent is stable for 4 h.

f. Stock phosphate solution: See Section 4500-P.C.3*e*.

g. Standard phosphate solution: Dilute 50.0 mL stock phosphate solution to 1000 mL with distilled water; 1.00 mL = 2.50 μg P.

4. Procedure

a. Treatment of sample: Pipet 50.0 mL sample into a clean, dry test tube or 125-mL erlenmeyer flask. Add 0.05 mL (1 drop) phenolphthalein indicator. If a red color develops add 5*N* H_2SO_4 solution dropwise to just discharge the color. Add 8.0 mL combined reagent and mix thoroughly. After at least 10 min but no more than 30 min, measure absorbance of each sample at 880 nm, using reagent blank as the reference solution.

b. Correction for turbidity or interfering color: Natural color of water generally does not interfere at the high wavelength used.

TABLE 4500-P:II. COMPARISON OF PRECISION AND BIAS OF ASCORBIC ACID METHODS

Ascorbic Acid Method	Phosphorus Concentration, Dissolved Orthophosphate $\mu g/L$	No. of Laboratories	Relative Standard Deviation %		Relative Error %	
			Distilled Water	River Water	Distilled Water	River Water
13th Edition[1]	228	8	3.87	2.17	4.01	2.08
Current method[2]	228	8	3.03	1.75	2.38	1.39

For highly colored or turbid waters, prepare a blank by adding all reagents except ascorbic acid and antimonyl potassium tartrate to the sample. Subtract blank absorbance from absorbance of each sample.

c. Preparation of calibration curve: Prepare individual calibration curves from a series of six standards within the phosphate ranges indicated in ¶ 1*c* above. Use a distilled water blank with the combined reagent to make photometric readings for the calibration curve. Plot absorbance vs. phosphate concentration to give a straight line passing through the origin. Test at least one phosphate standard with each set of samples.

5. Calculation

$$\text{mg P/L} = \frac{\text{mg P (in approximately 58 mL final volume)} \times 1000}{\text{mL sample}}$$

6. Precision and Bias

The precision and bias values given in Table 4500-P:I are for a single-solution procedure given in the 13th edition. The present procedure differs in reagent-to-sample ratios, no addition of solvent, and acidity conditions. It is superior in precision and bias to the previous technique in the analysis of both distilled water and river water at the 228-μg P/L level (Table 4500-P:II).

7. References

1. EDWARDS, G.P., A.H. MOLOF & R.W. SCHNEEMAN. 1965. Determination of orthophosphate in fresh and saline waters. *J. Amer. Water Works Assoc.* 57:917.
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METHOD FOR BETX AND TPH IN SOIL, WATER, AND AIR

GLT175/079.51-8

CH2M HILL: THERMAL DESORPTION/GC-FID

APPLIED SCIENCES LABORATORY METHOD FOR DETERMINATION OF BETX AND PETROLEUM HYDROCARBONS

1.0 SCOPE AND APPLICATION

1.1 This method is being proposed for analysis of soil, air, and water samples generated from the Onalaska Site Remedial Design treatability study. Petroleum hydrocarbon and BTEX parameters will be captured on CARBOTRAP™ adsorbent traps.

Target Constituents

Benzene
Ethylbenzene
Toluene
Xylene
Petroleum Hydrocarbons

1.2 The method relies on techniques that have been derived from approved EPA methodology; however the specific configurations are not approved. Method development and validation are required to demonstrate the viability of the technique.

1.3 Sample concentration techniques are used to lower the limits of detection. As part of a method development and validation study, the actual MDLs will be determined as described in 40 CFR 136, Appendix B.

2.0 SUMMARY OF METHOD

2.1 Air: A known volume of vapor is passed through CARBOTRAP adsorbent tubes trapping volatile organic compounds. The volatile compounds are thermally desorbed from the adsorbent tube and are analyzed by high resolution gas chromatography using flame ionization detection.

2.2 Soil: A known mass of soil is combined with water in a sparging device and heated to a temperature near but below boiling. The heated headspace is swept with helium and passed through CARBOTRAP adsorbent tubes trapping volatile organic compounds. The volatile compounds are thermally desorbed from the adsorbent tube and are analyzed by high resolution gas chromatography using flame ionization detection.

2.3 Water: A quantity of water is placed in a sparging device and heated to a temperature near but below boiling. The heated headspace is swept with helium and passed through CARBOTRAP adsorbent tubes trapping volatile organic compounds. The volatile compounds are

thermally desorbed from the adsorbent tube and are analyzed by high resolution gas chromatography using flame ionization detection.

3.0 INTERFERENCES

3.1 Samples containing compounds that co-elute or overlap with the target constituents may cause a positive bias in the results.

3.2 The presence of compounds that closely match the retention times of the target constituents may result in false identifications.

3.3 Impurities in calibration standards, elution solvents, dilution solvents, and carrier gases are potential sources of interference.

4.0 SAFETY

4.1 Certain target constituents are either identified as or suspected of being **carcinogens. All samples are assumed to be hazardous.** All working calibration standards, as well as all samples, shall be handled with the utmost care using good laboratory techniques to avoid harmful exposure.

4.2 Laboratory analysts shall wear safety glasses and surgical gloves at all times when preparing and handling analytical standards.

4.3 Standards shall be prepared in a fume hood.

4.4 Standards prepared in flammable solvents shall be stored in an explosion proof refrigerator or in a cooler outside the laboratory.

4.5 Safety equipment, including a fire extinguisher, first aid kit, eye wash, and chemical spill cleanup kit, shall be available at all times.

5.0 APPARATUS AND MATERIALS

5.1 Sampling equipment as described in QAPP.

5.2 Glassware—volumetric pipets and flasks; beakers, vials, and miscellaneous glassware as necessary for preparation and handling of samples and standards.

5.3 Labware—necessary for preparation and handling of samples and standards.

5.4 Syringes—Hamilton glass type as required for injection of sample and standards, preparation of dilutions, and spiking of samples.

5.5 Gas chromatograph (GC)—The analytical system consists of a gas chromatograph equipped with flame ionization detection (FID), programmable thermal oven, electronic integration, report annotation, high resolution capillary chromatographic column.

5.6 Thermal Desorption Unit—designed to accept CARBOTRAP thermal desorption tubes.

5.7 Chromatographic Column—Restek Rt_x-1; 60m, 0.53mm ID, 3.0μm.

5.8 CARBOTRAP 300 Tube—commercially available from Supelco Inc. The three bed types contain sorbents for light hydrocarbons, C5-C8 compounds, and heavier compounds.

5.9 Cylinder pressure regulators—two-stage cylinder regulators with pressure gauges.

5.10 Gas purifiers—connected in-line to remove moisture and organic contaminants from the gas stream.

6.0 CHEMICALS, REAGENTS, AND GASES (use only chromatographic grade)

6.2 Standards—Purchased as commercially prepared standard mixtures traceable to a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) at approximately 1,000 μg/ml. If necessary, neat standards exceeding 99 percent purity may be used to prepare standards as described in this method.

6.3 Working standards—prepared from stock standard by precise dilution with hexane. Prepare working standards within the expected working range of calibration.

6.4 Ultrapure nitrogen or helium—carrier gas.

6.5 Hydrocarbon free air—detector gas

6.6 Hydrogen—detector gas

7.0 SAMPLE PREPARATION AND STORAGE

7.1 Trapping; Specific operating parameters will be optimized during method development.

7.1.1 Air: Collection of the vapor phase contaminants is accomplished by placing the CARBOTRAP tube in the test column offgas line. The tube is collected at previously defined intervals and stored in the glass container supplied with the tube until analysis.

7.1.2 Soil: A portion of the soil sample is combined with organic free water in a sparging device and heated to a temperature near but below boiling. The heated headspace is swept with helium and passed through CARBOTRAP adsorbent tubes trapping volatile organic compounds. The tube is collected and stored in the glass container supplied with the tube until analysis.

7.1.2 Water: A portion of the water is added to a sparging device and heated to a temperature near but below boiling. The heated headspace is swept with helium and passed through CARBOTRAP adsorbent tubes trapping volatile organic compounds. The tube is collected and stored in the glass container supplied with the tube until analysis.

7.2 Samples are to remain capped and placed out of direct sunlight. Perform the desorption step within 7 days of sample collection.

7.3 Preparation of Samples. Remove tube from storage sleeve and load the CARBOTRAP tube into the thermal desorption unit. Run desorption cycle and direct transfer through focusing tube to the GC injection port.

8.0 PREPARATION OF CHROMATOGRAPH CALIBRATION CURVE

8.1 Dynamic external calibration—three level calibration at approximately the expected range of the target constituents and a blank. Spike calibration standard directly onto a sample tube. Make a gas chromatographic measurement of each standard mixture using conditions identical with those used for samples.

8.1.1 Plot the concentration of the analyte versus the area of the peak response. Calculate the slope, intercept, and coefficient of correlation by linear regression analysis.

8.2 Working calibration—working calibration shall be performed with the analysis of each working day's lot of samples or with each lot of 10 samples, whichever is more frequent. Working calibration shall be verified by use of a mid-range standard mix.

8.2.1 If the response factors and retention times vary by more than ±30 percent or ±0.10 minutes from the initial calibration, then recalibration shall be performed on freshly prepared working standards.

9.0 SAMPLE ANALYSIS

9.1 The analytical system should be properly assembled in accordance to equipment manufacturer specifications and calibrated through dynamic standard calibration procedure.

9.2 Perform GC analysis on the adsorbent tube using the instrument conditions that were provided by the thermal desorption and chromatographic column manufacturers and demonstrated during method development and validation.

9.3 Load CARBOTRAP into thermal desorption unit and run program.

9.4 Check the retention values of sample peaks against target constituents retention time windows. Calculate an analyte concentration for those peaks that fall within the expected windows.

10.0 CALCULATIONS

10.1 Sample Concentrations: Quantification of the target compounds is based on the integrated areas of the samples in comparison to the integrated areas of the calibration standards for each analysis. Determine the mass (g) of analyte found in the adsorbent tube:

M_t (g) = M_s times DF

where;

M_t = Mass of analyte in adsorption tube (g)
M_s = Mass of analyte from calibration curve, (g)
DF = Dilution factor, if applicable

Calculate concentration, C_s, of analyte in the air volume sampled, V (l):

$$C_s \text{ (ppmv)} = \frac{M_t/10^3}{(k)\ (MW)\ (V)}$$

where;

M_t = Mass of analyte in adsorption tube (g)
k = constant, $(4.1 * 10^8)$
MW = Molecular mass of analyte, (a.m.u.)
V = Volume of air sampled, (l)

11.0 QUALITY ASSURANCE

11.1 Quality assurance measures shall include as a minimum:

- Recovery from collection media: It is necessary to verify that the analytical methodology used is accurately determining the quantity of material collected. A means for accomplishing this is fortification (spiking) of the sorbent material with a suitable solvent containing the target constituents. Spiking is accomplished by adding a solution containing the analytes directly onto the sorbent material. Recoveries greater than 75 percent are acceptable.

- Initially, a multipoint dynamic calibration at three levels plus a blank is performed on the GC-FID system. The calibration system uses standard reference materials. The correlation coefficient must be ≥ 0.9950 or the percent relative standard deviation of the individual response factors must be ≤ 25 percent.

- Daily mid-range calibration checks performed prior to the analysis of each day's batch of samples or with each batch of 10 samples, whichever is more frequent. The calculated response factor must agree ±25 percent difference of the slope calculated from the initial calibration. Retention times of each analyte must be within ±0.10 minutes of expected value.

- Analysis of laboratory blank samples at a rate of one per day. Should the results of the laboratory blanks show contamination greater than the MDL, the cause of contamination should be investigated and corrective action taken.

- Analysis of a mid-range matrix spike samples and a matrix spike duplicate at a frequency of 1 in 20 samples analyzed or 1/day, whichever is more frequent. Matrix spikes are prepared in the same manner as calibration standards except that the adsorbent tube is collected as an actual sample. A recovery of between 60 and 140 percent is expected for all targeted VOCs.

- Use of the retention time marker during the analysis of all samples and standards. Before analysis can be performed, the retention time windows must be established for each target VOC. Three injections of the standard containing all of the target VOCs will be made to determine retention time windows of the compounds of interest. The standard deviation of the three absolute retention times for each compound will be calculated. The retention time window is defined as the mean ±3 times the calculated standard deviation or 0.1 minute, whichever is greater.

GLT175/078.51

MOISTURE CONTENT

21 Water Content

21-2.2 Gravimetry With Oven Drying

21-2.2.1 INTRODUCTION

Water content measurements by gravimetric methods involve weighing the wet sample, removing the water, and reweighing the sample to determine the amount of water removed. Water content then is obtained by dividing the difference between wet and dry masses by the mass of the dry sample to obtain the ratio of the mass of water to the mass of the dry soil. When multiplied by 100, this becomes the percentage of water in the sample on a dry-mass (or, as often expressed, on a dry-weight) basis. Water content may be described in other ways as indicated in section 21-1. Water may be removed from the sample in any of a number of ways, the principal method in common use being the oven-drying method described here. Accuracy and reproducibility of water content measurements, assuming that weighing precision is consistent with desired precision of water content measurement, depend upon the drying technique and the care with which it is used. (See discussion in section 21-2.1).

21-2.2.2 METHOD

21-2.2.2.1 Special apparatus. Apparatus required for gravimetric determination of water content may be used in many different forms, and so exact specifications are not needed. Requirements include an auger or sampling tube or some other suitable device to take a soil sample, soil containers with tight-fitting lids, an oven with means for controlling the temperature to 100 to 110°C, a desiccator with active desiccant, and a balance for weighing the samples. In the field, if soil samples are taken under conditions where evaporation losses may be of sufficient magnitude to affect the desired accuracy of measurement, special equipment for weighing the samples immediately or reducing evaporative loss must be used. Both convective and forced-draft ovens are used, and for precise work a vacuum oven is of particular value. Balances used range all the way from analytical balances to rough platform scales, depending upon the size of the sample to be taken and the precision of measurement desired.

21-2.2.2.2 Procedure The procedure to be used must vary with the circumstances of measurement and the equipment. Since these vary widely it is impossible to specify a detailed standard procedure that will fit all of the many uses made of water content measurements. The procedure given here is intended for use in routine work where moderate precision (say, measurements having a precision of ± 0.5% water content) is desired. Replication must depend upon the nature of the sample and soil system for which water content is desired, but it is suggested that samples be run in duplicate as a minimum.

Place samples of 1 to 100 g of soil in weighing bottles or metal cans with tight-fitting lids. Weigh the samples immediately, or store them in such a way that evaporation is negligible. Refer to Fig. 21–2 to find the required weighing precision. (The balance need not be read to a precision greatly exceeding the standard deviation for the balance.) Place the sample in a drying oven with the lid off, and dry it to constant weight. Remove the sample from the oven, replace the cover, and place it in a desiccator containing active desiccant (e.g., magnesium perchlorate or calcium sulfate) until cool. Weigh it again, and also determine the tare weight of the sample container. Compute the water content by one of the following formulas:

$$\theta_{dw} = \frac{(\text{weight of wet soil + tare}) - (\text{weight of dry soil + tare})}{(\text{weight of dry soil + tare}) - (\text{tare})} \quad [23]$$

$$= \frac{(\text{weight of wet soil + tare}) - (\text{tare})}{(\text{weight of dry soil + tare}) - (\text{tare})} - 1 \quad [24]$$

$$= \frac{\text{weight of wet soil}}{\text{weight of dry soil}} - 1. \quad [25]$$

The third of these equations is useful where standardized cans are used and the tare weight is balanced out in the weighing process so that the sample weight is obtained directly. Multiplication by 100 gives the percentage of water in the sample on a dry-mass basis.

SOIL PH

12 Soil pH

12-2.6 Glass Electrode–Calomel Electrode pH Meter Method

Practically all laboratories use the glass (indicating) electrode paired with a calomel (Hg-Hg_2Cl)(reference) electrode for measuring soil pH. The electrodes are normally plugged into a regular commercial pH meter. Upon proper standardization with buffers of known pH, the meter indicates the pH of the soil suspension from the millivolts of potential generated when the two electrodes are placed in the soil suspension. The glass electrode is the H^+-sensing electrode, which develops changes in potential (voltage) proportional to the logarithm of changes in activity of H^+. Thus it is called the indicating electrode. The calomel electrode (i) contains a saturated KCl bridge that contacts the soil suspension and (ii) has a characteristic potential (voltage) relatively independent of the H^+ activity. Hence it is called the reference electrode.

Many companies make and market highly satisfactory glass and reference electrodes. Similarly, many different brands of pH meters that are quite satisfactory for measuring the soil pH are available. Selections are often made on the basis of such criteria as satisfactory performance, company service, and type of readout.

Individual laboratories differ on the details of soil and water solution measurement, soil/water or soil/solution ratio, containing solution, method of mixing, time of standing before reading, whether or not it is stirred during reading, etc. Some laboratories weigh the soil; others measure a volume of soil. Some use 5 g of soil and 5 g (or 5 ml) of water. Some use $0.01M$ $CaCl_2$ instead of water. Some measure the pH in water, add sufficient $CaCl_2$ to obtain $0.01M$ $CaCl_2$, and measure the pH again. Some laboratories stir the soil suspensions individually or by a manifold arrangement. Others use a time-controlled shaker to mix large numbers of samples simultaneously. A suggested procedure is described to minimize differences in results brought about by discretionary alternatives that often have more than minor influences.

12-2.6.1 STANDARDIZING pH METER

Set the pH meter at pH 7 with standard buffer solution of pH 7, and set the manual temperature compensator at the temperature of buffer. Check to see that the instrument reads very near pH 4 with standard pH 4 buffer. If necessary, adjust the reading to pH 4, using the temperature compensator knob. Repeat the above standardization procedure with both pH 7 and 4 buffers until the instrument reading agrees with both buffer pH's.

12-2.6.2 TROUBLESHOOTING pH METER PROBLEMS

Initial failure of the instrument to agree reasonably well with both buffers usually suggests malfunction of the glass electrodes or of the electrometer tube of the pH meter. The former may require cleaning or replacing, and the latter may require an electronics repair service. When the pH meter appears to be in proper operating condition, as indicated by initial agreement of pH readings of both buffers, or after the above adjustment, check the pH of a soil of known pH. If it gives the correct reading, proceed to the following section; if not, this usually indicates partial plugging of the microscopic opening in the reference electrode. This may be caused by improper venting of the electrode restricting free flow of the saturated KCl, excessive growth of KCl crystals around the fiber wick restricting normal flow of KCl, or plugging of capillary opening with soil particles. These problems may be solved by periodic uncovering or unplugging the air vent, washing out the KCl crystals with distilled water and replacing with several rinses of saturated KCl, and careful grinding of the tip of the electrode with fine emergy cloth or sand paper until the KCl flow shows slight wetting of the glass at the point of the capillary opening, respectively. Instability of the pH meter dial needle usually indicates excessive static electricity from the technician's clothing or floor or table covering. A creeping or sluggish pH meter dial needle may indicate a dirty glass electrode.[3]

12-2.6.3 MAINTAINING ELECTRODES

12-2.6.3.1 Glass Electrode. Glass electrodes frequently become sluggish in their operation, as evidenced by slow changes or drift of the indicated pH when the measurement is made. Such drift or slow response may be caused by a dried layer of clay or precipitated carbonate on the glass bulb that cannot be removed by ordinary washing with water. Or, sluggish response may be caused by an aging of the glass surface of the bulb. Rejuvenation of the glass surface by immersion in a dilute solution of HF for 10 to 15 sec usually corrects the problem.

12-2.6.3.2 Calomel Electrode. The most frequent source of error with calomel electrodes is caused by stoppage of flow of electrolyte through the wick, fiber, porous ceramic, or sleeve. Although the instrument may calibrate satisfactorily in the solutions used for this purpose, it does not give correct values of pH in soil systems. The error tends to be in the direction of soil pH values that are too low and of high pH values in mixtures of soils and buffer solution used for measuring lime requirement. It is essential that the calomel electrode be operated with a functional liquid junction.

Another source of error in this respect occurs when the calomel electrode is forced into soil at the bottom of the cup in which the measurement is made, which stops the free movement of salt from the liquid junction. A stop in the electrode holder, which will prevent the tip of the electrode from penetrating to the bottom of the sample cup, will generally prevent this error.

12-2.6.4 EQUIPMENT AND REAGENTS

1. pH meter equipped with glass (indicating and reference electrodes).
2. Automatic pipette, portable stirrer (optional).
3. Paper cups, 28 g (1 oz), Solo souffle cup (Solo Cup Co. Urbana, Ill.) (optional).
4. Calcium chloride ($CaCl_2$) solution, 1 or 0.01*M* (optional).
5. Standard buffers, pH 7 and 4.
6. Distilled water.

12-2.6.5 pH[4]

1. Weigh or measure 5 g of air-dry soil into a 28-g paper cup. (Other containers, such as 50-ml beakers, may be used, but this may require adjustments in the shaking procedure called for below.)
2. Place cups in a 20- or 40-unit tray designed to go into the mechanical shaker used in the lime requirement determination (described below).
3. With automatic pipette, add 5 ml of distilled water to each cup.
4. Mix thoroughly for 5 sec, preferably with portable mechanical stirrer. (A small stirrer motor, 1,550 rpm, mounted on a handle with a short, slightly bent plastic or glass rod agitator serves very well.)
5. Let stand for 10 min.
6. Insert the electrodes into the container, and stir the soil suspension by swirling the electrodes slightly. Protect the electrodes with a short glass rod attached to the electrode holder and extended just below the tips of the electrodes. If this method of agitation is used, it is not necessary to rinse the electrodes between successive samples.
7. Read the pH immediately on the standardized pH meter. Record as soil pH in water, or pH_w.
8. Optional test: To determine the soil pH in 0.01*M* $CaCl_2$, add 1 drop (0.05 ml) of 1*M* $CaCl_2$ solution to the soil water suspension.
9. Stir intermittently for 30 min.
10. Insert electrodes, and read the pH on the standardized pH meter. Record as soil pH in 0.01*M* $CaCl_2$, or pH_s. Alternatively, the soil pH in 0.01*M* $CaCl_2$ may be determined directly by substituting 0.01*M* $CaCl_2$ for water in no. 3 above.
11. If the lime requirement is to be determined on the samples, save them for this purpose after reading the pH in water or 0.01*M* $CaCl_2$.

TOTAL ORGANIC CARBON

29 Total Carbon, Organic Carbon, and Organic Matter[1]

29-3 ORGANIC CARBON

29-3.5.3 MODIFIED MEBIUS PROCEDURE

29-3.5.3.1 Special Apparatus.

1. Erlenmeyer flasks (125 ml) fitted with female standard-taper 24/40 ground-glass joints (Corning 5000 or Kimble 26510).
2. West condensers (30 cm) fitted with male standard-taper 24/40 ground-glass joints at the lower end (Corning 2800 or Kimble 18190).
3. Electric hot plate extraction unit (six plates per unit) fitted with individual rheostat controls (Labconco 60300, Precision 65500, Lab-Line Multi-Unit Extraction Heater, or equivalent).

29-3.5.3.2 Reagents.

1. Potassium dichromate solution ($K_2Cr_2O_7$), 0.5*N*: Dissolve 24.5125 g of $K_2Cr_2O_7$ (oven-dry) in 200 ml of deionized water, and dilute to 1 liter.
2. Sulfuric acid (H_2SO_4), concentrated, not less than 96%.
3. Ferrous ammonium sulfate hexahydrate solution [$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$], 0.2*N*: Dissolve 78.390 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in 50 ml of conc H_2SO_4, and dilute to 1 liter with deionized water (must be standardized daily because of slow oxidation).
4. Indicator solution: Dissolve 0.100 g of *N*-phenylanthranilic acid and 0.107 g of sodium carbonate (Na_2CO_3) in 100 ml of water.

29-3.5.3.3 Procedure. Weigh an amount of < 100-mesh soil (≤ 0.5 g) containing not greater than 8 mg of organic C into a 125-ml Erlenmeyer flask. Add exactly 10 ml of 0.5*N* $K_2Cr_2O_7$ solution and 15 ml of conc H_2SO_4 (H_2SO_4 may be added by burette). Attach the flask to the West condenser, and place on a preheated electric hot plate. Include a blank in each group of five soil samples to be heated and at least two unboiled blanks (unboiled blanks are unheated mixtures of 10 ml of 0.5*N* $K_2Cr_2O_7$ and 15 ml of conc H_2SO_4) for each day that analyses are performed. The normality of the $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ solution is determined by titrating the unboiled blank. Gently boil each sample for 30 min, and then insert an asbestos pad between the hot plate and bottom of the Erlenmeyer flask. Allow the flask to cool for about 15 min, and rinse the inside of the condenser with deionized water. Remove the flask from the condenser, and dilute the contents to about 60 ml with deionized water. Add about 0.2 ml of indicator solution, and titrate the samples, boiled blanks, and unboiled blanks with $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ solution using a magnetic stirrer and a lighted background. The color change at the endpoint is rapid and proceeds from violet to gray to bright green. It may be necessary to add additional indicator solution near the end of the titration to sharpen the endpoint.

ionized water. Remove the flask from the condenser, and dilute the contents to about 60 ml with deionized water. Add about 0.2 ml of indicator solution, and titrate the samples, boiled blanks, and unboiled blanks with $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ solution using a magnetic stirrer and a lighted background. The color change at the endpoint is rapid and proceeds from violet to gray to bright green. It may be necessary to add additional indicator solution near the end of the titration to sharpen the endpoint.

29-3.5.3.4 Calculations. The difference in titration values between the blank and the sample is proportional to the amount of organic C in soil. The blank minus titration (B − T) value must be corrected, however, for the amount of $Cr_2O_7^{2-}$ consumed during boiling. The correction is done by titrating the unboiled blank and determining the normality of the ferrous ammonium sulfate hexahydrate solution from this titration. The difference between the unboiled and boiled blank is then divided by the amount of ferrous ammonium sulfate hexahydrate solution required for the unboiled blank. This correction value (in the range of 0.04) is multiplied by the B − T value, and the product is added to the B − T value. This gives a corrected value A, or

$$A = (ml_{BB} - ml_{sample}) \times \left(\frac{ml_{UB} - ml_{BB}}{ml_{UB}}\right) + (ml_{BB} - ml_{sample})$$

where UB is unboiled blank, and BB is boiled blank.

Organic C concentration is then calculated by Eq. [14]:

$$\%\ \text{organic C} = \frac{(A) \times [N \text{ of } Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O] \times (0.003) \times (100)}{\text{g oven-dry soil}}. \quad [14]$$

29-3.5.3.5 Comments. Interferences noted in Walkley-Black procedures are also a problem with the Mebius procedure. However, the Mebius method gives complete decomposition of organic C compounds and thus does not require a factor to account for incomplete oxidation of organic matter. Organic C in soil extracts may be estimated by the Mebius procedure merely by carrying out the procedure with 5 ml of extract and 5 ml of $1N$ $K_2Cr_2O_7$ solution instead of 10 ml of $0.5N$ $K_2Cr_2O_7$ solution. When extracts are analyzed, it may be necessary to add glass beads to promote smooth boiling.

The ratio of the volumes of $K_2Cr_2O_7$ solution to H_2SO_4 is critical for accurate organic C measurements. Therefore, flasks should be clean and dry, and amounts of $K_2Cr_2O_7$ and H_2SO_4 added should be accurately measured. The ferrous ammonium sulfate hexahydrate solution must be standardized each day because of slow oxidation of Fe^{2+} to Fe^{3+}. The $K_2Cr_2O_7$ solution is the primary standard for the procedure, and therefore care should be taken in its preparation.

APPENDIX C
FIELD EQUIPMENT STANDARD OPERATING PROCEDURE: HNU MONITORING

Appendix C
FIELD EQUIPMENT STANDARD OPERATING PROCEDURE
HNu MONITORING

REFERENCES

HNu Model PI101 Portable Photoionization Analyzer Instruction Manual, HNu Systems, Inc., Newton, MA, December 1985.

HNu Model ISP1 101 Intrinsically Safe Portable Photoionization Analyzer Instruction Manual, HNu Systems, Inc., Newton, MA, January 1986.

SENSITIVITY

0 to 20 ppm at full-scale detection at span = 9.8 ppm, 10.2 eV Probe.

RANGE

0.1 to 2,000 ppm.

CALIBRATION GAS

Isobutylene at 100 ppm.

CALIBRATION

By analyzing a gas of known concentration, the HNu is easily calibrated. Isobutylene is typically used as the calibration gas with the instrument calibrated to benzene equivalents. When calibrating the HNu, always remember to:

- Deliver the calibration gas at ambient temperature and pressure.
- Handle gas cylinders with care.
- Calibrate every day.

Also:

- The calibration gas must be stable during the period of use.
- All gas cylinders must have proper regulators.

CALIBRATION PROCEDURE

1. Identify the probe by lamp label.

2. Attach the probe to the readout unit. Twist connector clockwise until locked.

3. Affirm the relative photoionization sensitivity (PS) of the calibration gas. The required reading for isobutylene to read in benzene equivalents is equal to:

$$\frac{\text{PS (Isob)}}{\text{PS (benzene)}}$$

4. Turn the function switch to the battery check position. The indicator should read within the green arc. If the indicator is below the green arc or if red LED comes on, the battery must be charged.

5. Zero the instrument by turning function switch to standby and rotate the potentiometer until the meter reads zero.

6. Connect the sampling hose to regulator outlet and the other end to sampling probe of HNu.

7. Crack the regulator valve.

8. Adjust the span of the potentiometer to obtain a proper reading.

9. If calibration cannot be achieved, clean the UV light source window using lense paper and HNu cleaning compound.

10. If it still cannot be calibrated, perform preventative maintenance. Return to factory if those procedures do not work.

CALIBRATION FREQUENCY

Calibrate daily or after maintenance. Recharge the battery after each use. Factory check out and calibration shall be conducted yearly or when malfunctioning.

GLT175/080.51