ARCS V

Remedial Activities at Uncontrolled Hazardous Waste Sites in Region V

EPA United States Environmental Protection Agency

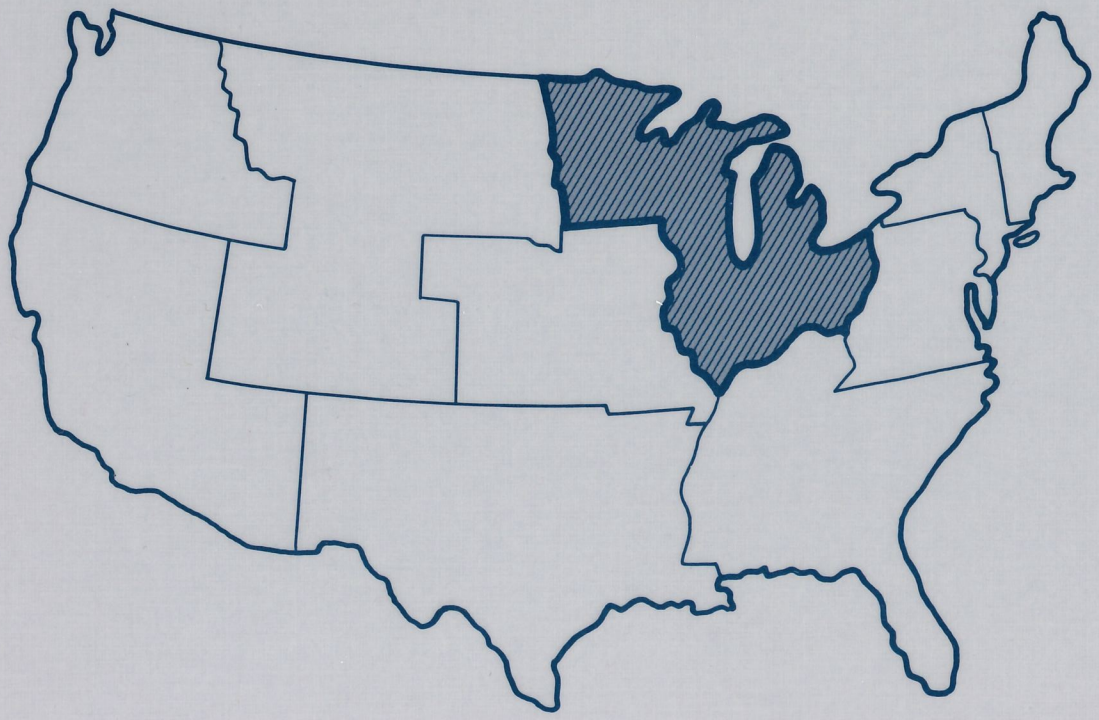
Agency Review Draft

IN SITU BIOREMEDIATION PRELIMINARY DESIGN REPORT

ONALASKA MUNICIPAL LANDFILL SITE
Onalaska, Wisconsin

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

January 31, 1992



CH2M HILL

Agency Review Draft

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ONALASKA MUNICIPAL LANDFILL SITE
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January 31, 1992

Engineers
Planners
Economists
Scientists

January 31, 1992

GLO65602.PD.H6

Mr. Kevin Adler
Work Assignment Manager
U.S. Environmental Protection Agency (5HS-RW67)
77 West Jackson
Chicago, IL 60604

Dear Mr. Adler:

Subject: In Situ Bioremediation Predesign Report
Onalaska Landfill Remedial Design, WA 38-5NL5

Enclosed are three copies of the In Situ Bioremediation Predesign Report. The report presents the proposed conceptual design for the in situ bioremediation system, and a predesign-level construction cost estimate.

As you are aware, we are in the process of designing the landfill cap and groundwater extraction and treatment systems. The decision as to whether the in situ system will be pursued will affect the ongoing designs, and for this reason, we hope to gain some direction from you on this matter as soon as possible. The ongoing designs have retained some flexibility to this date to accommodate the in situ system if it is to be designed as originally planned. The milestones for preparing the prefinal designs, however, are rapidly approaching, and direction is needed well in advance of the delivery dates.

CH2M HILL Milwaukee Office 310 West Wisconsin Avenue, Suite 700 414.272.2426
P.O. Box 2090 Milwaukee, Wisconsin 53201-2090 Fax 414.272.4408

The report also contains a summary of the bench-scale treatability test, which has been updated from what you received in December. We are looking forward to discussing the results of the test with you and Paul Kozol on February 3.

Sincerely,

CH2M HILL

Steve Keith

Steve Keith
Site Manager

eam/GLT272/025.51
Enclosure
cc: Steve Nathan/PO/U.S. EPA Region 5 (w/o enclosures)
Patricia Bamford/CO/U.S. EPA Region 5 (w/o enclosures)
Joe Dusek/U.S. EPA (w/o enclosure)
Paul Kozol/WDNR (2 copies)
Alpheus Sloan III/PM/GLO
Ike Johnson/APM-OPNS/GLO
John Fleissner/QAM/GLO
Phil Smith/RTL/GLO
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Tom Simpkin/QC RVW/DEN
Ellen Russell/GLO
Chris Ohland/GLO
Paul Boersma/ASM/GLO
Donna Navarro/PA/GLO
Elaine Steiner/GLO
Randy Videkovich/DAY

M E M O R A N D U M CH2M HILL

TO: In Situ Bioremediation Predesign Report
Agency Reviewers

FROM: Ellen Russell/CH2M HILL

DATE: February 3, 1992

SUBJECT: 90-Day Data

PROJECT: GLO65602.PD.H6

As you review the January 31, 1992 In Situ Predesign Report please be aware that the data reporting in Appendix A is not 100% complete. The final results from 92-day soil samples were received from the laboratory over this past weekend and therefore could not be reported. To avoid having to modify all tables and figures (Tables 4 through 6 and Figures 4 through 6) relevant to the soil results twice, only the data through 30 days of analysis has been presented in the report.

Attached you will find data through 92 days of analysis. All text discussions of biodegradation potential were made using data through 82 days of study. The additional 92-day data point does not change the overall conclusions of the report.

Table 3
Soil Hydrocarbon Results
Test Column BI--Background

Sample ID	Time (days)	Soil Weight (g)	HC (g)	Benzene (g)	Toluene (g)	Ethyl-benzene (g)	m&p-Xylene (g)	o-Xylene (g)
TCBLSS01A	0.0	20900	ND	ND	ND	ND	ND	ND
TCBLSS01B	0.0	20900	ND	ND	ND	ND	ND	ND
TCBLSS02A	0.3	20900	ND	ND	ND	ND	ND	ND
TCBLSS02B	0.3	20900	ND	ND	ND	ND	ND	ND
TCBLSS03A	1.1	20900	ND	ND	ND	ND	ND	ND
TCBLSS03B	1.1	20900	ND	ND	ND	ND	ND	ND
TCBLSS14A	92.0	20900	ND	ND	ND	ND	ND	ND
TCBLSS14B	92.0	20900	ND	ND	ND	ND	ND	ND

ND = Not Detected

Table 4
Soil Hydrocarbon Results
Test Column 2--Unamended

Sample ID	Time (days)	Soil Weight (g)	HC (g)	Benzene (g)	Toluene (g)	Ethyl-benzene (g)	m&p-Xylene (g)	o-Xylene (g)
TC02SS01A	0.0	22700	93	ND	1.3	1.0	1.8	0.7
TC02SS01B	0.0	22700	92	ND	1.1	1.0	1.7	0.7
TC02SS02A	0.3	22700	73	ND	0.1	0.1	0.6	0.6
TC02SS02B	0.3	22700	91	ND	0.9	0.9	0.7	0.7
TC02SS03A	1.1	22700	95	ND	0.2	0.1	1.9	0.8
TC02SS03B	1.1	22700	59	ND	0.1	0.6	1.1	0.4
TC02SS04A	4.3	22700	74	ND	1.6	1.2	2.3	1.0
TC02SS04B	4.3	22700	120	ND	1.0	0.9	1.7	0.7
TC02SS05A	10.1	22700	68	ND	0.9	0.7	1.3	0.6
TC02SS05B	10.1	22700	69	ND	1.2	0.8	1.4	0.6
TC02SS06A	14.2	22700	43	ND	0.2	0.4	0.6	0.2
TC02SS06B	14.2	22700	59	ND	0.5	0.6	0.4	0.4
TC02SS07A	18.2	22700	57	ND	0.1	0.1	0.8	0.6
TC02SS07B	18.2	22700	52	ND	0.1	0.1	0.8	0.6
TC02SS08A	22.2	22700	59	ND	0.1	0.1	1.1	0.5
TC02SS08B	22.2	22700	65	ND	0.1	0.1	1.0	0.8
TC02SS09A	26.1	22700	64	ND	0.7	0.7	1.2	0.5
TC02SS09B	26.1	22700	83	ND	0.1	0.1	1.7	0.7
TC02SS10A	32.1	22700	49	ND	0.1	0.5	0.9	4.1
TC02SS10B	32.1	22700	68	ND	0.8	0.7	1.4	0.6
TC02SS11A	46.0	22700	51	ND				
TC02SS11B	46.0	22700	69	ND				
TC02SS12A	60.1	22700	19	ND				
TC02SS12B	60.1	22700	66	ND				
TC02SS13A	82.0	22700	35	ND				
TC02SS13B	82.0	22700	23	ND				
TC02SS14A	92.1	22700	13	ND				
TC02SS14B	92.1	22700	41	ND				

ND = Not Detected

Table 5
Soil Hydrocarbon Results
Test Column 3--Unamended

Sample ID	Time (days)	Soil Weight (g)	HC (g)	Benzene (g)	Toluene (g)	Ethyl-benzene (g)	m&p-Xylene (g)	o-Xylene (g)
TC03SS01A	0.0	22200	84	ND	0.9	0.8	1.5	0.6
TC03SS01B	0.0	22200	91	ND	0.8	0.9	1.6	0.6
TC03SS02A	0.3	22200	105	ND	1.0	1.1	1.9	0.8
TC03SS02B	0.3	22200	124	ND	1.4	1.3	2.3	1.0
TC03SS03A	1.1	22200	94	ND	0.2	1.0	1.8	0.8
TC03SS03B	1.1	22200	148	ND	0.3	1.7	3.0	1.3
TC03SS04A	4.3	22200	89	ND	1.2	1.0	1.7	0.7
TC03SS04B	4.3	22200	101	ND	1.4	1.1	2.0	0.8
TC03SS05A	10.1	22200	77	ND	1.1	0.8	1.5	0.6
TC03SS05B	10.1	22200	97	ND	1.3	1.1	2.0	0.8
TC03SS06A	14.2	22200	57	ND	0.5	0.6	1.0	0.4
TC03SS06B	14.2	22200	112	ND	1.2	1.2	2.2	0.9
TC03SS07A	18.2	22200	90	ND	0.2	0.1	1.3	1.1
TC03SS07B	18.2	22200	71	ND	0.1	0.1	1.4	0.8
TC03SS08A	22.1	22200	72	ND	0.1	0.1	1.4	0.8
TC03SS08B	22.1	22200	65	ND	0.1	0.1	1.3	0.5
TC03SS09A	26.1	22200	51	ND	0.3	0.5	0.9	0.4
TC03SS09B	26.1	22200	71	ND	0.6	0.7	1.3	0.6
TC03SS10A	32.1	22200	93	ND	0.2	0.1	1.9	0.8
TC03SS10B	32.1	22200	107	ND	1.1	1.1	2.1	0.9
TC03SS11A	46.0	22200	75	ND				
TC03SS11B	46.0	22200	84	ND				
TC03SS12A	60.1	22200	60	ND				
TC03SS12B	60.1	22200	57	ND				
TC03SS13A	82.0	22200	36	ND				
TC03SS13B	82.0	22200	33	ND				
TC03SS14A	92.0	22200	28	ND				
TC03SS14B	92.0	22200	12	ND				

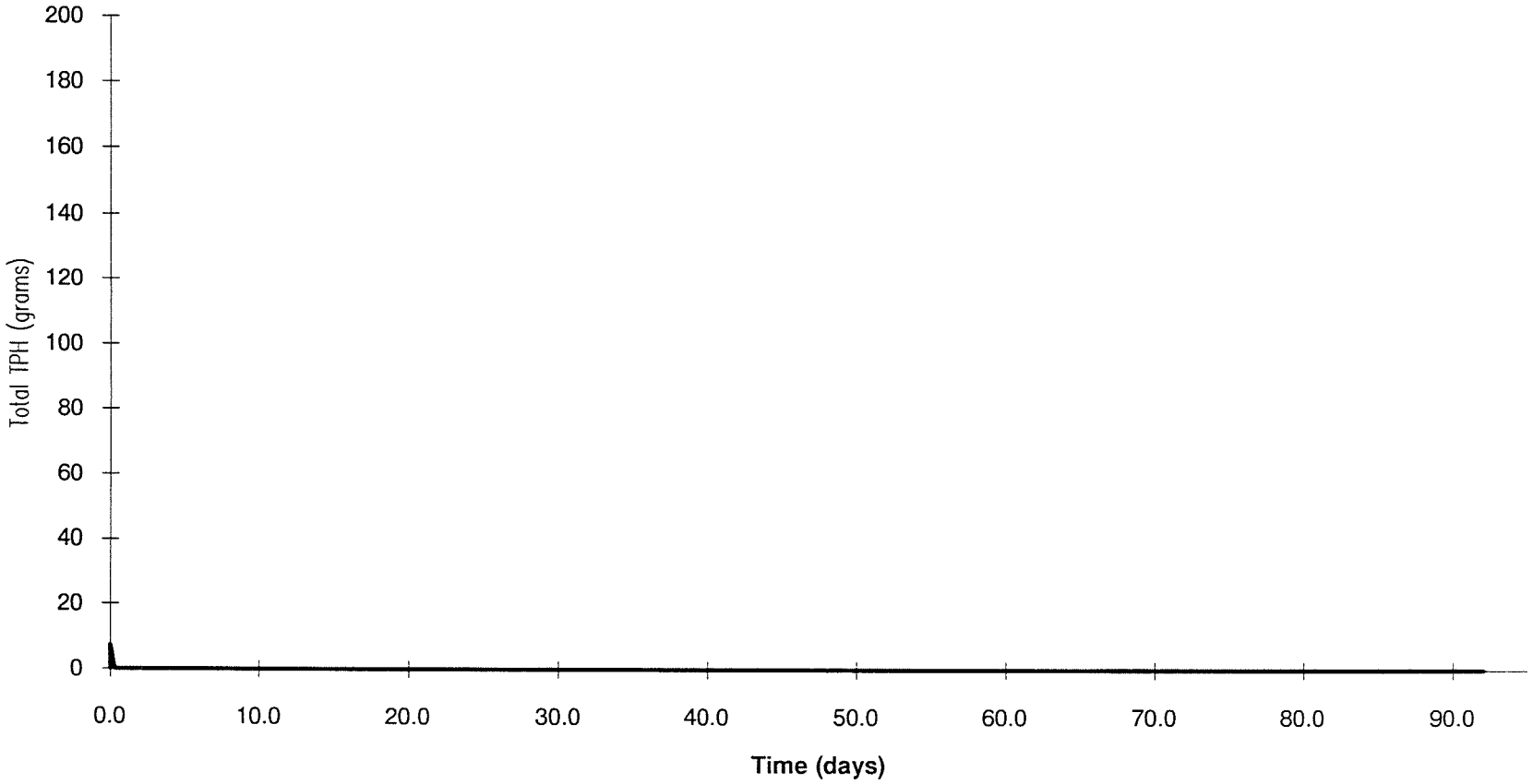
ND = Not Detected

Table 6
Soil Hydrocarbon Results
Test Column 4--Amended

Sample ID	Time (days)	Soil Weight (g)	HC (g)	Benzene (g)	Toluene (g)	Ethyl-benzene (g)	m&p-Xylene (g)	o-Xylene (g)
TC04SS01A	0.0	22700	103	ND	0.9	1.0	1.7	0.7
TC04SS01B	0.0	22700	65	ND	0.5	0.6	1.1	0.4
TC04SS02A	0.3	22700	173	ND	2.3	1.9	3.4	1.4
TC04SS02B	0.3	22700	191	ND	2.8	2.1	3.8	1.6
TC04SS03A	1.2	22700	140	ND	2.3	1.6	2.8	1.2
TC04SS03B	1.2	22700	77	ND	0.9	0.8	1.4	0.6
TC04SS04A	4.3	22700	103	ND	0.8	0.7	1.3	0.5
TC04SS04B	4.3	22700	83	ND	2.0	1.3	2.4	1.0
TC04SS05A	10.1	22700	86	ND	1.0	0.9	1.7	0.7
TC04SS05B	10.1	22700	116	ND	1.8	1.3	2.4	1.0
TC04SS06A	14.2	22700	57	ND	0.4	0.5	1.0	0.4
TC04SS06B	14.2	22700	75	ND	0.6	0.8	1.4	0.6
TC04SS07A	18.2	22700	48	ND	0.1	0.1	0.7	0.5
TC04SS07B	18.2	22700	83	ND	0.1	0.1	1.6	1.0
TC04SS08A	22.2	22700	57	ND	0.1	0.1	1.0	0.7
TC04SS08B	22.2	22700	76	ND	0.1	0.1	1.0	0.9
TC04SS09A	26.1	22700	73	ND	0.6	0.7	1.3	0.6
TC04SS09B	26.1	22700	61	ND	0.1	0.8	0.8	0.7
TC04SS10A	32.1	22700	65	ND	0.5	1.2	1.2	0.5
TC04SS10B	32.1	22700	60	ND	0.1	1.1	1.1	0.5
TC04SS11A	46.0	22700	27	ND				
TC04SS11B	46.0	22700	42	ND				
TC04SS12A	60.1	22700	44	ND				
TC04SS12B	60.1	22700	40	ND				
TC04SS13A	80.9	22700	13	ND				
TC04SS13B	80.9	22700	15	ND				
TC04SS14A	92.1	22700	53	ND				
TC04SS14B	92.1	22700	16	ND				

ND = Not Detected

Amount of TPH in Test Column Blank



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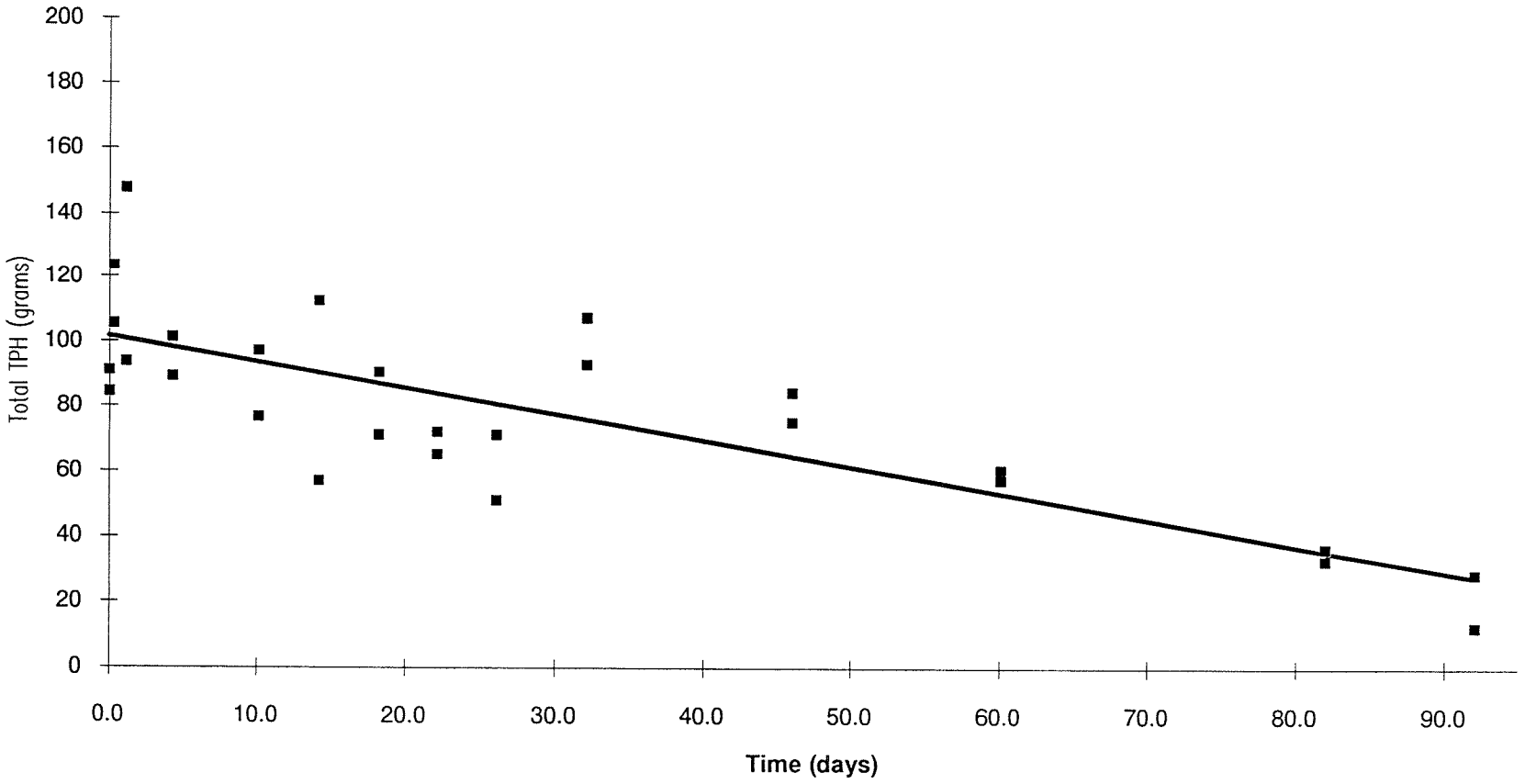

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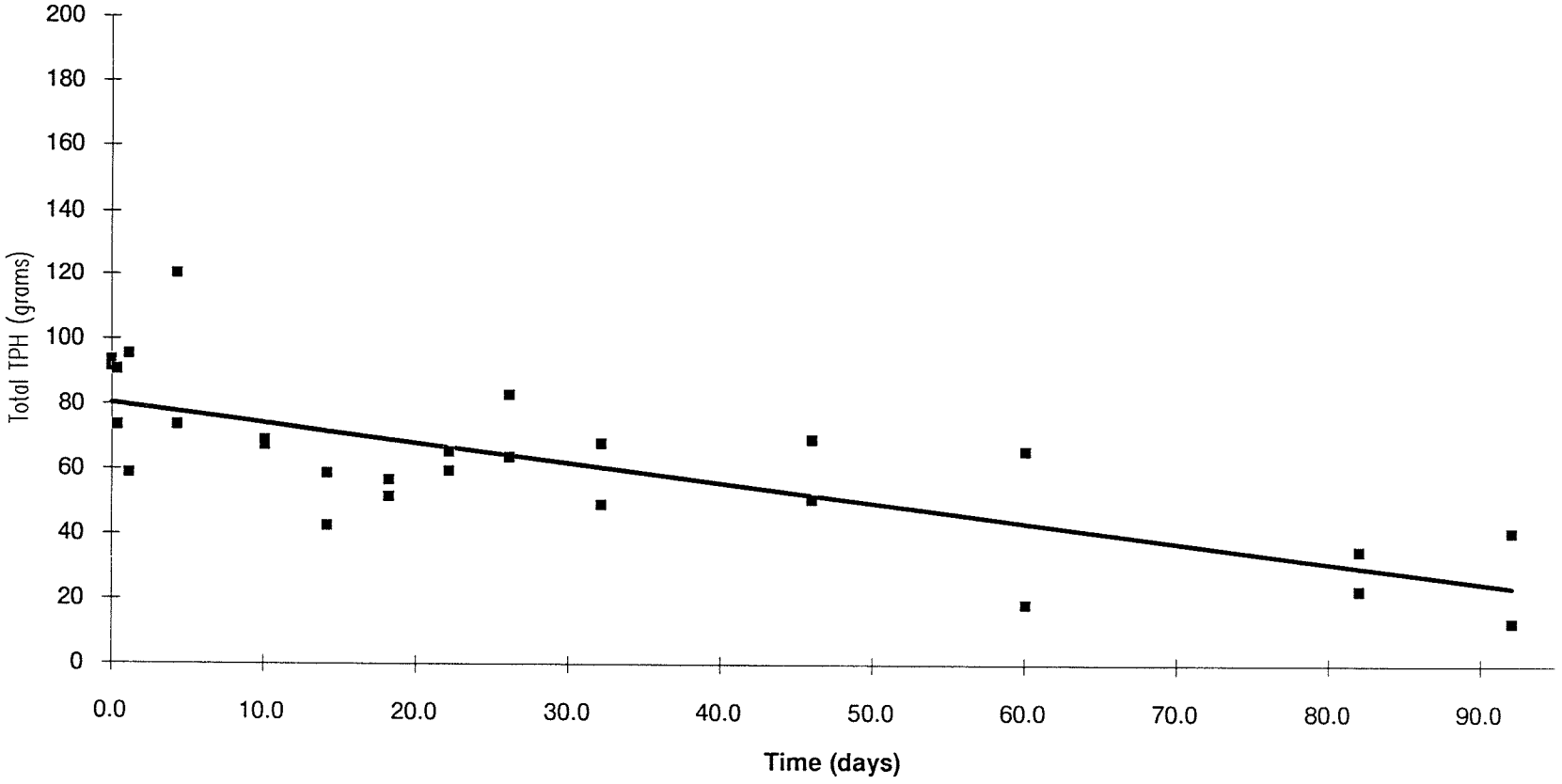

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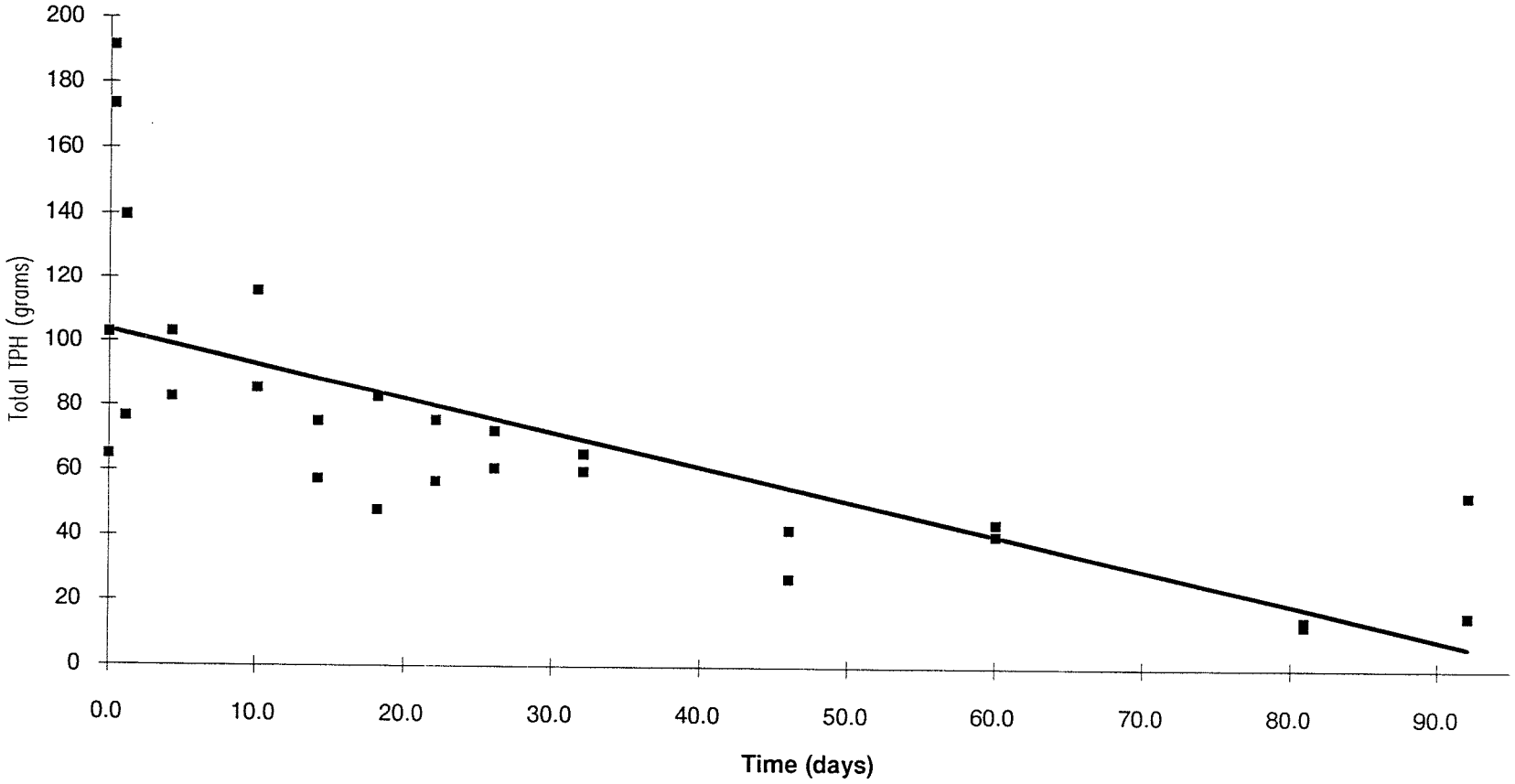


CONTENTS

FIGURES

GLT272/002.51

Section 1

Introduction

Background

Site Description and History

The Onalaska Municipal Landfill site is located in Onalaska Township, a rural area near La Crosse, Wisconsin. It consists of a former municipal landfill about 8 acres in area and 15 to 20 feet in thickness, and adjacent property where the groundwater contamination plume has migrated. The site was operated previously as a sand and gravel quarry from the 1960s to 1970s. Industrial wastes, including naphtha-based solvents, were disposed of at the site. Investigations conducted at the site in 1989 found that the groundwater is contaminated, primarily with volatile organic compounds (VOCs), and the groundwater contamination is migrating toward the Black River.

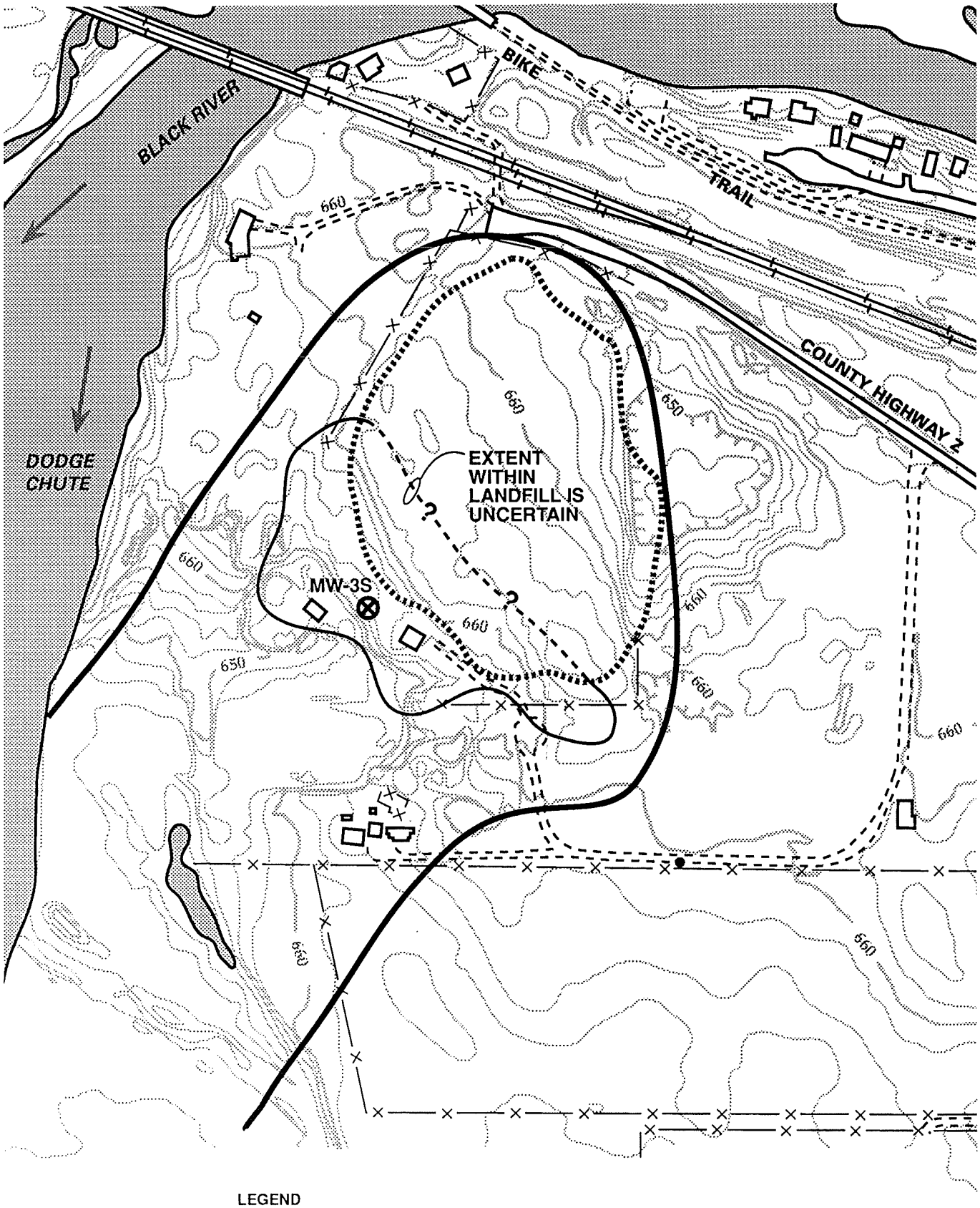
The investigations also determined that a 3- to 5-foot layer of soil in the vadose zone immediately above the water table is contaminated with petroleum hydrocarbon solvents. Much of the hydrocarbon contamination appears to be related to the naphtha disposed of at the site. The hydrocarbons migrated out of the disposal area and smeared through the vadose zone soil with changes in groundwater elevation. The zone of nonaqueous phase (ZNAP) contamination extends over an area estimated to be more than 4 acres within and immediately southwest of the landfill. The 2 to 2.5 acres of ZNAP contamination that extend beyond the landfill are targeted for in situ remediation. The depth to the ZNAP contamination is approximately 8 to 12 feet in this area. It was not considered technically feasible to address the contamination within the landfill through in situ methods because of the

potential for aerobic subsurface conditions to cause landfill smoldering. Figure 1-1 presents the estimated extent of the ZNAP contamination.

Proposed Remedial Actions

The Record of Decision (ROD) signed by the U.S. Environmental Protection Agency (EPA) on August 14, 1990, documents the selection of the remedial action for the site. The ROD requires:

- Implementation of an in situ bioremediation system to treat the zone of nonaqueous phase contamination
- Construction of a groundwater extraction system to extract the contaminants from the groundwater to meet federal drinking water standards and state groundwater quality standards
- Construction of a groundwater treatment system to treat the groundwater to meet the substantive requirements of the Wisconsin Pollution Discharge Elimination System.
- Discharge of the treated groundwater into the Black River
- Construction of a landfill cap to comply with NR 504.07
- Periodic monitoring of the groundwater contaminant plume
- Imposition of deed restrictions on the use of surface water and groundwater at the site



LEGEND

LIMITS OF LANDFILL AS DETERMINED BY GEOPHYSICAL SURVEY

ZONE OF NONAQUEOUS PHASE CONTAMINATION

GROUNDWATER REMEDIATION TARGET AREA

N

0 250

SCALE IN FEET

FIGURE 1-1
TARGET AREAS FOR GROUNDWATER REMEDIATION AND NONAQUEOUS PHASE CONTAMINATION
ONALASKA LANDFILL
Bioremediation-Preliminary Design

GLO65602.PD.H6 1-1 Targ Areas GW Remed 12-30-91mms

As described in the feasibility study (FS) for cleanup of the site, the in situ bioremediation system was to consist of the injection and extraction of air into and from the ZNAP contamination (and possibly nutrient and moisture addition) to stimulate the naturally-occurring microbes and so affect a higher rate of contaminant biodegradation. This technology is typically referred to as bioventing or enhanced biodegradation.

This preliminary design report was prepared for the EPA under authorization of EPA Contract Number 68-W8-0040 and Work Assignment Number WA 38-5NL5 as part of the overall remedial design for the Onalaska Municipal Landfill site. This report describes the proposed in situ bioremediation system, provides a preliminary design level cost estimate, and identifies regulatory and construction constraints involved in implementation. Following review and comment by the EPA and the Wisconsin Department of Natural Resources, the prefinal design (95 percent) will be prepared.

Report Overview

Section 1 presents background information about the project. Section 2 describes the remedial action goals of the treatment system and summarizes the results of the treatability study performed to examine the potential for bioremediation. The proposed treatment system is described in Section 3. A predesign cost estimate is provided in Section 4. Section 5 discusses implementation of the treatment system. Appendix A presents the detailed treatability study report submitted to the EPA as a separate memorandum. Appendix B contains detailed cost estimates.

GLT243/057.51

Section 2

Remedial Action Goals

Remedial Action Goals for the In Situ Treatment System

The in situ treatment system will be designed to enhance the degradation of organic contaminants in the vadose zone immediately downgradient from the landfill. This area is known as the zone of nonaqueous phase contamination (ZNAP). No treatment standards or health-based cleanup criteria have been established for contaminated soil. However, the ROD does defines a cleanup goal, as an 80-to 95-percent reduction of the organic contaminant mass in the soils. Organic contaminant mass refers to the petroleum-based and petroleum-related constituents in the soil. Because the ZNAP contamination could act as a source of benzene, toluene, ethylbenzene, and xylene (BTEX) contaminants in groundwater, a secondary goal of the treatment system will be to reduce the BTEX contaminant loading to the groundwater. No specific time period has been established for accomplishment of the remedial action goals, although the ROD specifies that in situ bioremediation would be performed for a minimum of two 200-day treatment seasons.

Treatability Study

Objectives

To assess if the cleanup goals could be achieved and to determine the time needed to achieve them and to develop site-specific design parameters, a bench-scale treatability study was undertaken that assessed the potential for contaminant biodegradation.

Four columns were designed to simulate in situ subsurface soil conditions during remediation. Specific objectives of the study were to:

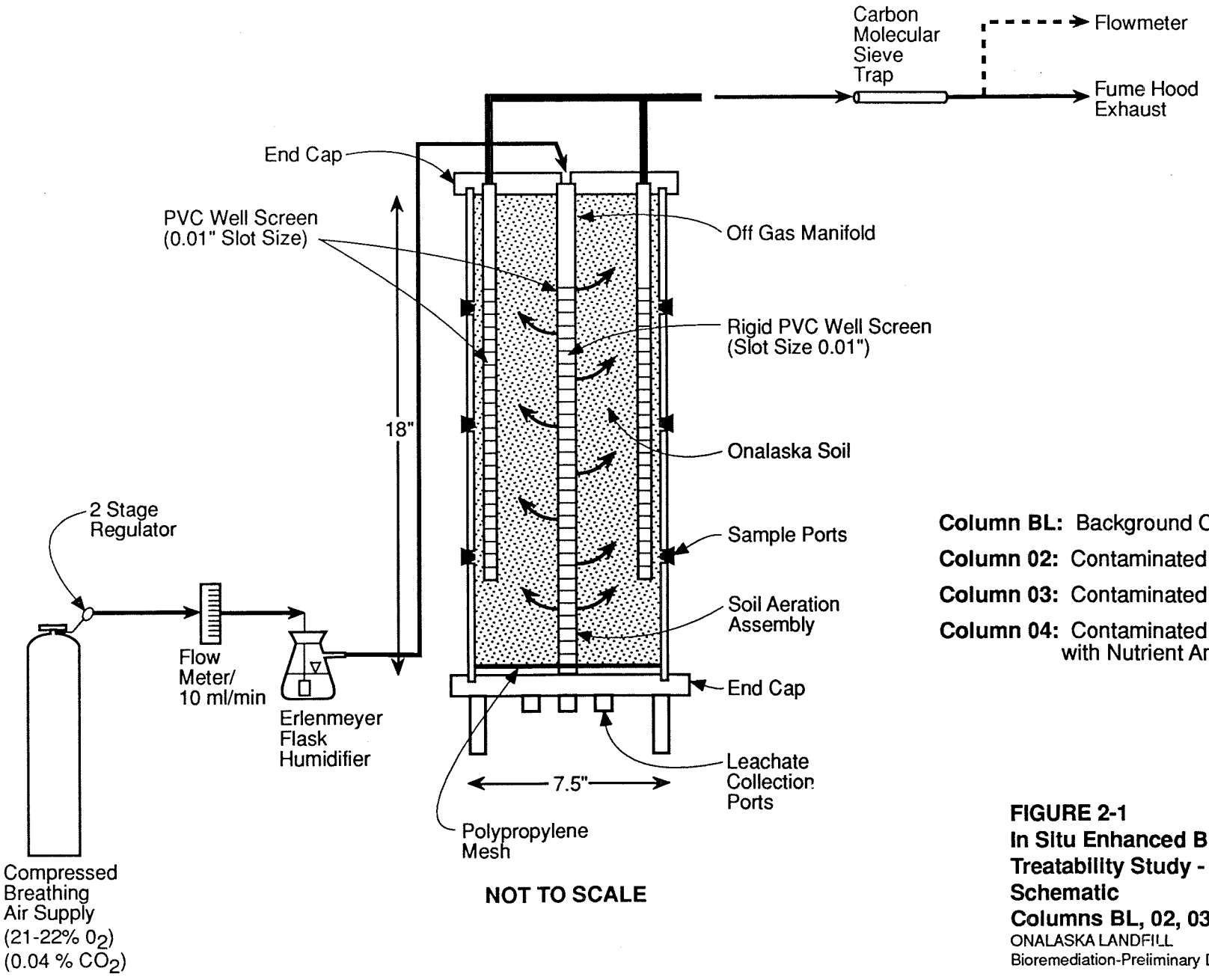
- Determine oxygen requirements that would allow in situ aerobic biodegradation of hydrocarbons to occur
- Determine the loss of hydrocarbons occurring because of volatilization of the volatile contaminant fraction
- Evaluate the percentages of hydrocarbon degradation achievable within the test simulation

A detailed report of the treatability study is presented in Appendix A. The following sections summarize the setup, operations, and results of the column study.

Column Construction and Operation

Four test columns were set up—one with "clean" sand to be used as a control, two with soil collected from the ZNAP, and one with soil collected from the ZNAP that had moisture and nutrients (nitrogen and phosphorous) added to the soil. The test columns were constructed of acrylic cylinders 7.5 inches in diameter and 18 inches tall (see Figure 2-1). A regulated air supply was fed into the column, and air was discharged through an offgas manifold. The offgas was sent through a carbon molecular trap to retain the vapor phase hydrocarbons. The columns were designed so that soil samples could be collected through sampling ports in the column walls. Offgas samples and hydrocarbons retained on the carbon trap could also be collected and analyzed.

Soil samples were collected at the site by excavating down to the ZNAP in the area of MW-3S (see Figure 1-1), removing a backhoe bucket of soil, and placing the soil into



NOT TO SCALE

Column BL: Background Control Soil

Column 02: Contaminated Soil

Column 03: Contaminated Soil

Column 04: Contaminated Soil with Nutrient Amendment

FIGURE 2-1
In Situ Enhanced Biodegradation Treatability Study - Equipment Schematic
Columns BL, 02, 03,04
ONALASKA LANDFILL
Bioremediation-Preliminary Design

the columns. Efforts were taken to minimize volatilization of organic compounds during soil handling. Attachment 1 to Appendix A provides details on the sample collection work.

During column operation, air was moved through the soil to maintain aerobic conditions, soil samples were collected for hydrocarbon analysis, offgas samples were collected and measured for oxygen and carbon dioxide, and the carbon trap was measured for volatile hydrocarbons removed from the offgas. Columns were kept in operation for a total of 3 months.

Initial Characterization of Soil and Soil Gas

Prior to setting up the column tests, in situ soil gas samples were collected from the ZNAP near MW-3S (at a distance of 25 feet from landfill) through a soil gas sampling probe and analyzed in the field. The oxygen concentration of the soil gas from the ZNAP was less than 1 percent, while the carbon dioxide and methane concentrations each ranged from 20 to 25 percent (Attachment 1, Appendix A). These concentrations indicate oxygen limited or anaerobic conditions, and possibly reflect landfill gases that have migrated beyond the land boundary.

Table 2-1 presents the results of the initial characterization of the soils in Column No. 2 (unamended) and Column No. 4 (amended with nutrients and water). The initial characterization shows that the soil at this sampling location is considerably more contaminated than the remedial investigation sampling results indicated. Concentrations of total petroleum hydrocarbons measured as part of the treatability study ranged from 10 to nearly 20 times the maximum observed in the remedial investigation (550 mg/kg). The soils were sufficiently contaminated with hydrocarbons such that pure phase liquids drained from the soil and pooled in the bottom of the columns. The area of the site believed to be most contaminated as determined during the remedial investigation was chosen as the sampling location for the study.

Table 2-1
Initial Soil Chemical and Physical Analyses
Onalaska In Situ Treatability Study

Parameter (mg/kg dry weight)	Unamended Test Column 02	Nutrient-Amended Test Column 04
Moisture, %	3.83	4.84
Loss on Ignition, %	0.53	0.63
Nitrogen Forms, as N Ammonia Total Kjeldahl	 17.0 64	 15.5 45.6
Total Phosphorus, as P	36.8	31.0
Total Organic Carbon	1,250	847
Total Petroleum Hydrocarbons	11,400	10,500
Benzene	< 4	< 4
Toluene	353	242
Ethylbenzene	26	20
Xylenes	235	212
Bacterial Number	10^8 cfus/g soil wet weight.	10^8 cfus/g soil wet weight.

Observations and Results

The key observations of the column test are as follows:

- Of the approximately 100 grams of hydrocarbon mass in each column, 50 grams were lost to draining of pure product from the soil, 12 grams to volatilization, and 10 grams to biodegradation. Roughly 25 grams of hydrocarbon remained as residual on the soil. These are mass estimates made using the data available after 3 months of column operation.

- The estimated hydrocarbon degradation rate was roughly 5 to 30 milligrams of hydrocarbon per kilogram of soil per day as determined using a mass balance approach and oxygen consumption/carbon dioxide production stoichiometric approach.

- Oxygen uptake during respiration studies (when oxygen flow to the columns was turned off) ranged from 0.68 to 1.58 micrograms of oxygen per gram of soil per hour or 0.004 to 0.011 percent oxygen consumed per minute. These rates are comparable to data from other studies that report 0.001 to 0.01 oxygen consumed per minute.

- The addition of nutrients and moisture had little observable effect on the rate of respiration or biodegradation.

- The soils are hydrophobic and can only retain up to 5 percent moisture, even after being wetted, thus limiting the ability to supply moisture and nutrients to the microorganisms.

- A flow of approximately 2 pore volumes of air per day was sufficient to maintain steady state oxygen concentrations in the 18-to 20-percent range. Lesser flows could have been supplied; however, as observed during the respiration studies, oxygen concentrations below 10 percent seemed to contribute to substantial fluctuation in respiration rates. Operation at lower oxygen concentrations was not desirable because these fluctuations made data interpretation difficult.

- Large variability was encountered in soil concentrations (at times, more than 50 percent for the same sampling event), even though the analytical precision was acceptable. This indicates a wide range of soil contaminant concentrations primarily due to differences in soil pore structure and surface tension forces.

- The absence of oxygen and presence of carbon dioxide and methane in the soil samples collected from the ZNAP near MW-3S verify that the soil in this zone is not aerobic, which in turn indicates that oxygen is a limiting factor to aerobic metabolism.

- The BTEX mass fraction of the soil-bound hydrocarbon was roughly 3 to 5 percent throughout the study. The BTEX mass fraction of the hydrocarbon trapped from the offgas was roughly 25 percent throughout the first 20 days of the study. During the latter days of the study, the percentage fell to 10 percent (and remained at this level throughout the study). The cumulative amount of volatile hydrocarbons, including the BTEX component trapped from the offgas, was roughly 10 percent of the total soil-bound hydrocarbon mass initially present before soil aeration.

Implications for the Bioremediation Design

The observations and conclusions listed above may have the following implications for establishing cleanup goals and designing the bioremediation system. These implications are discussed further in Section 3.

- Based on the observed degradation rates, it may take longer than the two 200-day treatment seasons estimated in the FS to achieve reductions in the range of 80 to 95 percent for the entire contaminant mass. The estimates that were incorporated into the ROD were made using lower average contaminant concentrations (250 mg/kg) as reported by the remedial investigation versus those found during treatability study (5,500 to 11,000 mg/kg). Some lesser contaminated areas of the ZNAP may achieve 80 to 90 percent reductions before other more highly contaminated areas.

- Respiration and contaminant degradation rates obtained during the treatability study emulate recent literature reports for in situ pilot studies of the bioventing technology which have demonstrated 40- to 55-percent removals by biodegradation in a 7-month period.

- The air injection system will be designed to inject up to two pore volumes of air per day. This rate of air supply was sufficient to maintain aerobic conditions throughout the treatability study. The flushing rate could be slower if good dispersion does not occur, or faster if pathways for short-circuiting of air are present in the field. To compensate for poor dispersion, the air supply blower will be sized two times larger than necessary.

- Initially, a system will not be built to provide nutrient and moisture addition. Rather, periodic control of the groundwater extraction system may allow for rewetting and exposure to groundwater-borne nutrients. Performance monitoring of the system will be implemented to assess moisture and nutrient limitation as operation proceeds.

- Most of the hydrocarbon mass is not easily volatilized as evidenced by the chromatographic profile of the free product and soil-bound hydrocarbons (predominantly C_{10} to C_{20} carbon containing compounds). For this reason, the attributes of a vapor extraction system coincident with the biodegradation component do not add much to potential contaminant removals. The mass that is volatile, however, could still be degraded. The proposed system will not include extraction of the soil vapor, but instead minimize the injected flow rates and attempt to biodegrade contaminants in situ.

- Because of the potential for large variability in the measured concentration of soil contaminants throughout the zone of remediation, it may be difficult to assess the progress of remediation from month to month. Use of more than one monitoring technique is considered the best approach for assessing the rate of remediation.

- The potential exists for biodegradation to mobilize hydrocarbon components either to the vapor or aqueous phase. Although the character of the soil-bound hydrocarbon chromatographic profile did not change over the course of the study, increased biological activity should degrade the lighter, more volatile components first, thereby reducing the mobility of the remaining hydrocarbons.

- Physical disruption of the soil matrix by forces associated with water table draw down or during well installation and air supply may allow additional drainage of free product material from the soil pore space.

- Finally, there is potential for the landfill to be an ongoing source of floating, nonaqueous phase pollutants. If the landfill acts as a long-term source of contaminants, then the period required to attain remedial action goals will be extended and the measurement of the effectiveness of the treatment system will be more complicated.

GLT243/058.51

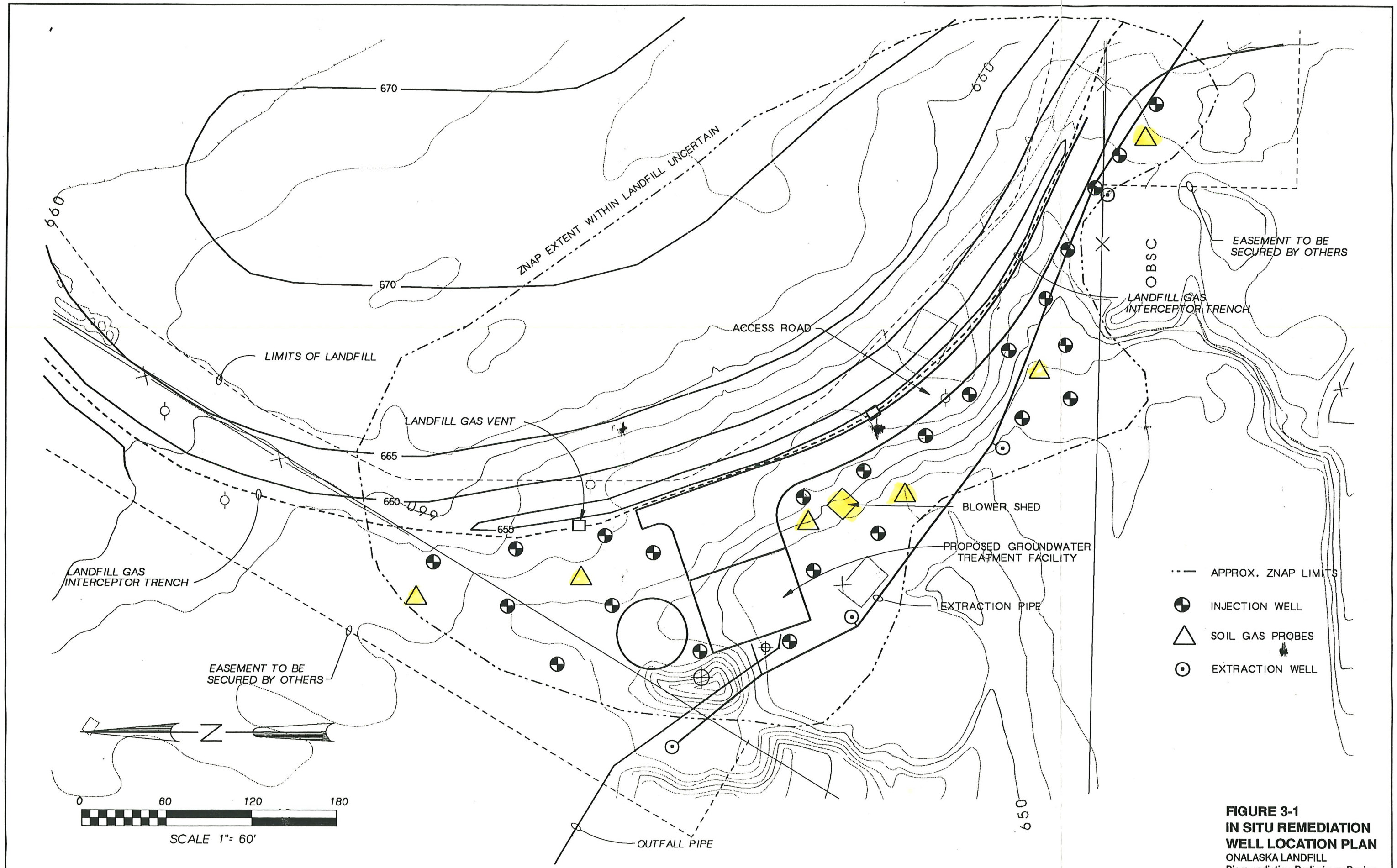
Section 3

Proposed Treatment System

Introduction

The object of the treatment system is to inject air into the ZNAP contamination at a rate that will maintain aerobic conditions within the soil. However, the air injection will be kept to a minimum to limit the potential for aeration of waste within the landfill, drying of the soil, or volatilization of organic contaminants. The system must not interfere with the cap or other facilities onsite such as roads or the treatment building, and must be adaptable to future modifications.

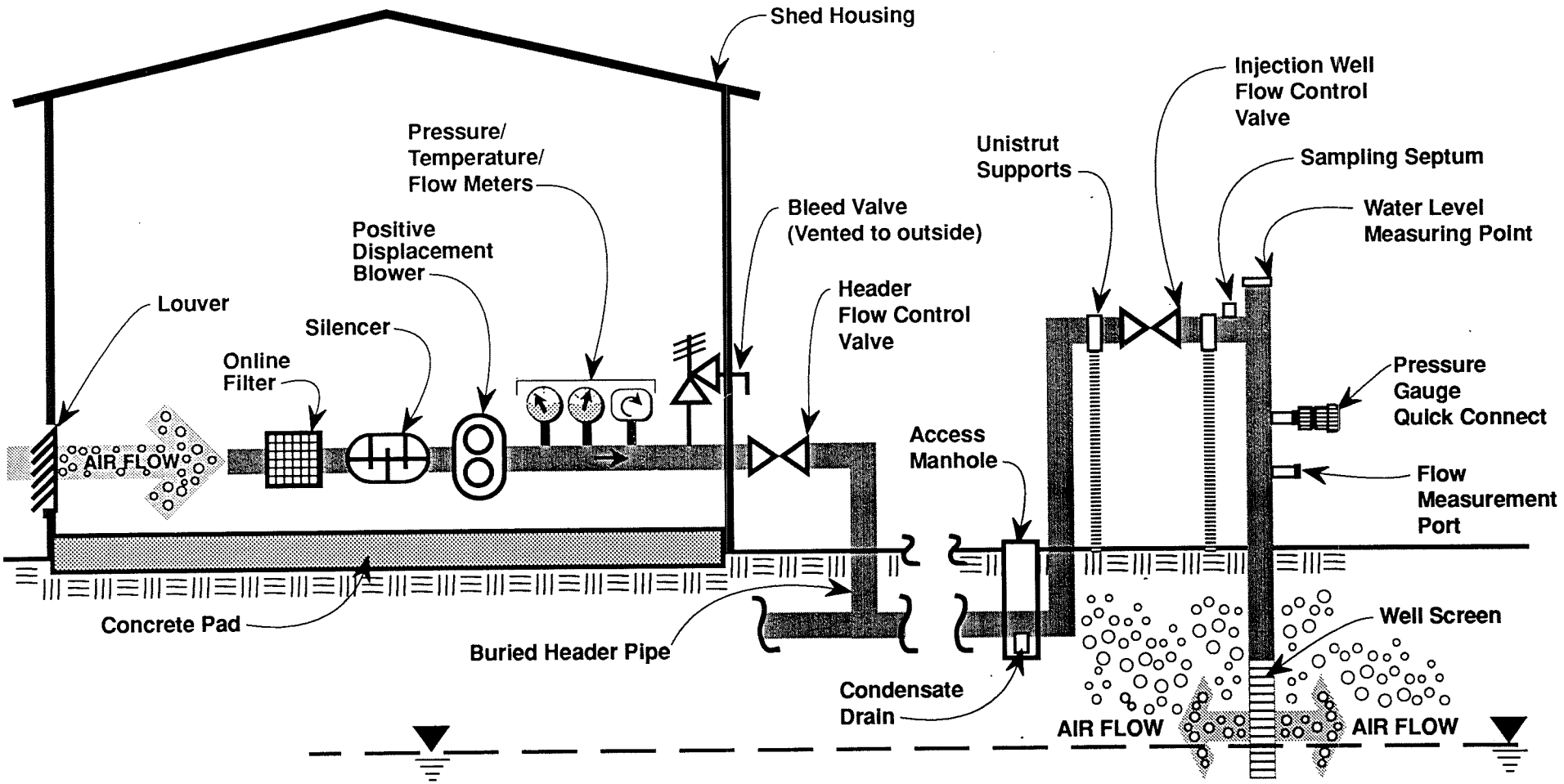
The proposed treatment system will consist of a series of vertical air injection wells, connected by a header piping network supplied with air from a single blower. The 2-inch-diameter air injection wells will be spaced on 40- to 50-foot centers throughout the ZNAP and installed with the screened interval spanning the 3-to-5-foot ZNAP layer. This spacing of wells is based upon experience with performance of soil vapor extraction systems in similar subsurface conditions. Each well will be connected to the header piping by a lateral pipe with a valve for controlling the amount of air introduced into the well, which will permit modulation of the air supply to specific areas in response to the rate of oxygen consumption in that area. Figure 3-1 is a preliminary layout of the treatment system. Figure 3-2 illustrates a conceptual diagram of the system.



GL065602.PD.H6 3-1 Border 1-31-92mms

FIGURE 3-1
IN SITU REMEDIATION
WELL LOCATION PLAN
ONALASKA LANDFILL
Bioremediation-Preliminary Design

GLO65602.PD.H6 3-2 Conc Biorem Flow Diag 1-28-92mms



NOT TO SCALE

FIGURE 3-2
CONCEPTUAL BIOREMEDIATION PROCESS FLOW DIAGRAM
ONALASKA LANDFILL
Bioremediation-Preliminary Design

System Design Criteria

Injection Wells

Air will be provided to the ZNAP layer by 24 vertical wells distributed throughout the plume area. The preliminary layout spaces the wells 40 to 50 feet apart which, for a sandy soil, gives a conservative radius of influence of at least 20 to 25 feet around each well. The preliminary layout also considers site constraints from the cap, building, access roads, and process equipment. The total number of wells and their final locations will be determined in the field during construction, based on observations of the extent of the ZNAP contamination during well installation, and the measured radius of influence around each injection well. Injection throughout the entire area shown may be limited in same areas by a high water table.

The conceptual design presented in the FS assumed the use of horizontal injection lines primarily because of a perceived cost advantage, with respect to installation; however, after additional consideration and experience with operation of soil vapor extraction systems, a vertical well system is proposed in this report because it has the following advantages:

- The system has the flexibility to deliver air to smaller areas and to adjust flow as required. The system will allow better control over oxygen mixing with landfill gases.

- The system is more amenable to construction using the observational approach, where additional wells are placed based on the radius of influence observed around the existing wells and the observed extent of contamination.

- There will be less exposure to VOCs and contaminated soil during construction.

- There will be less contaminated soil to manage.

- The system can be installed after the final cap and grading are completed, thus simplifying construction.

- A vertical well system will be less expensive to install.

The system is designed to provide 40 to 350 standard cubic feet per minute (scfm) of air to maintain aerobic conditions throughout the ZNAP contamination. A 300-scfm flow corresponds to two pore volume exchanges each day. At 300 scfm of flow, each well would deliver about 12 scfm of flow. The blower will be sized at 600 scfm to achieve greater flow should more aggressive aeration be determined necessary when monitoring system performance.

A typical well construction detail is shown in Figure 3-3. The wells will be constructed of 2-inch PVC pipe, with a 5-foot screen interval. The 5-foot slotted PVC well screen will be placed with about 2 feet of screen below, and 3 feet above the seasonal average static groundwater table. This will optimize coverage of the ZNAP and account for fluctuating groundwater levels from pumping and seasonal changes. The wells will be placed in 10-inch boreholes backfilled with pea gravel to the top of the well screen and backfilled with bentonite.

Each well riser will extend about 3 feet above ground level. A tee near the top of the riser will connect the lateral piping through a ball valve used to control the flow of air to the well. A sampling port with septum will be installed at the top of each well, as well as a tee for measurement of water levels within each well. A quick connect for pressure gauges and a flow measuring port will be installed on the side of each well.

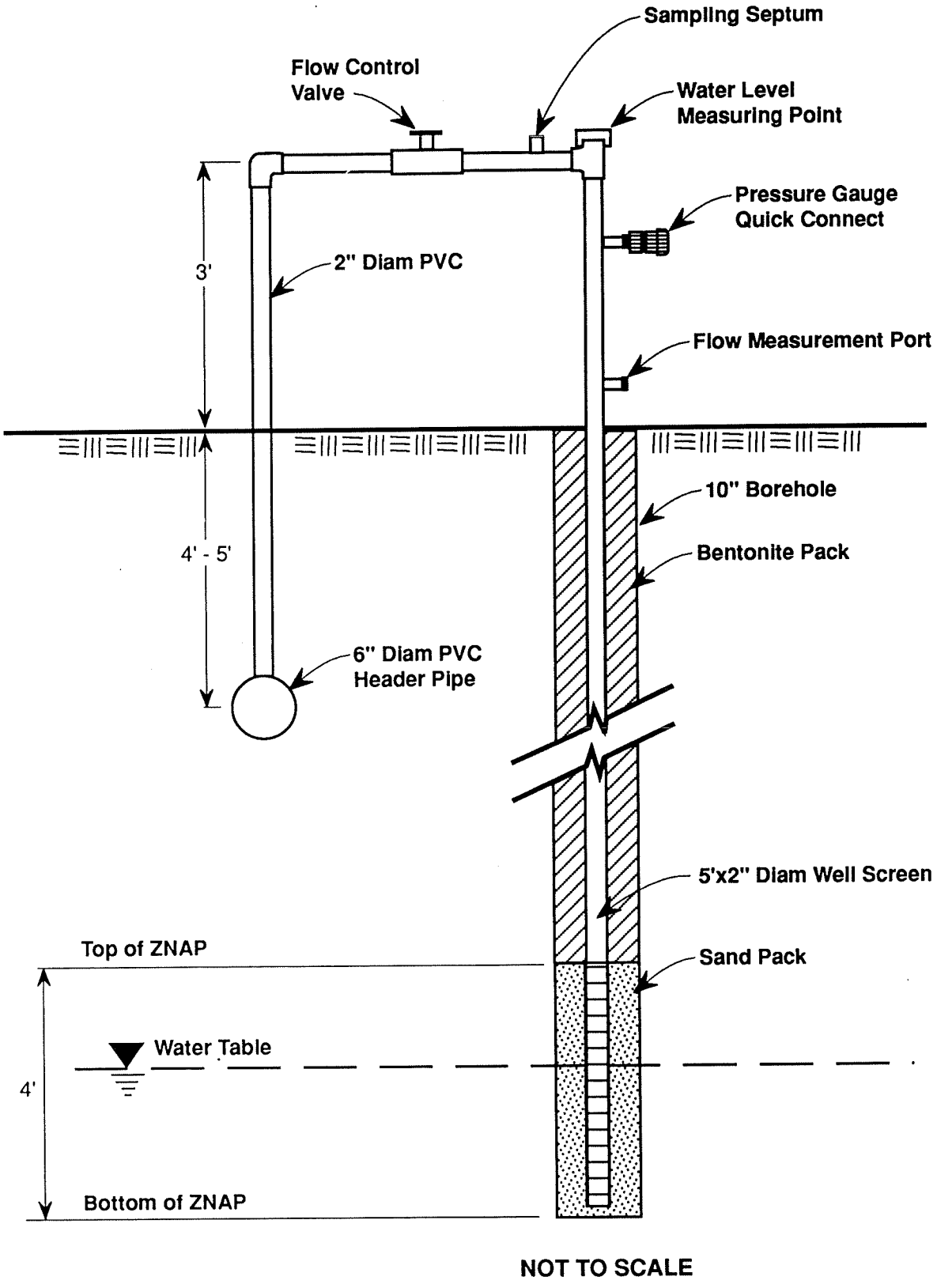


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FIGURE 3-3
INJECTION WELL CONSTRUCTION
ONALASKA LANDFILL
Bioremediation-Preliminary Design

GLO65602.PD.H6 3-3 Inject Well Construct 1-30-92mms

Header Piping

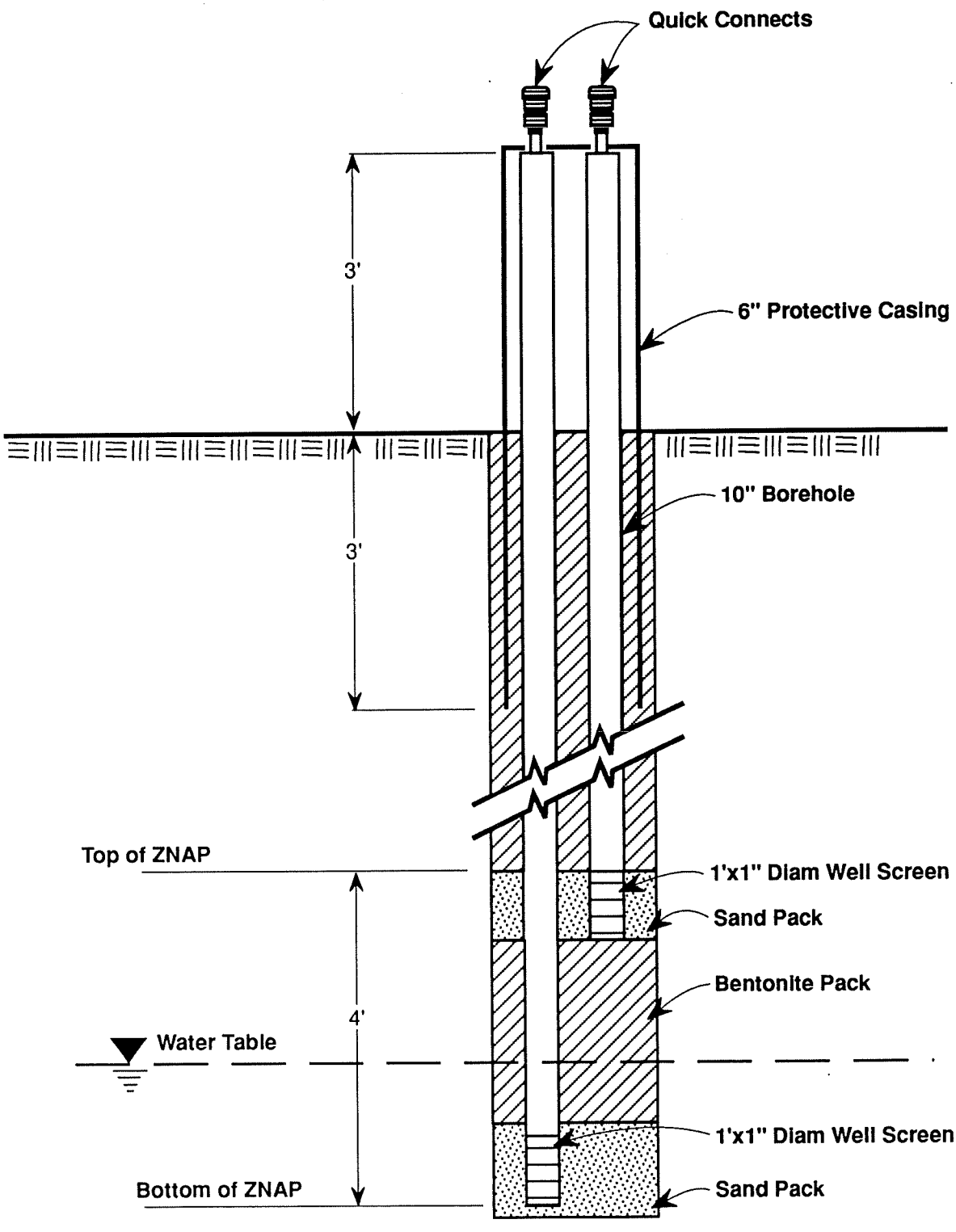
The option for burial of header pipe is included in this preliminary design. However, other than aesthetics, there is no technical rationale to bury the header network. A 2-inch PVC, Schedule 40 lateral pipe will extend from each well to a buried 6-inch header pipe. The header pipe will be buried about 4 feet below ground level. The header pipe will have a 2-percent slope for drainage of condensate to drains located every 200 feet of header run. Since the condensate will be moisture that condenses from ambient air, the condensate drains will open to the ground. Condensate drain valves will be accessible through a small manhole and valve pit. The exact layout of the header and lateral network will be determined during design.

Soil Gas Probes

Six soil gas probe nests (with two probes per nest) will be installed between the injection wells (Figure 3-1). The probes will be used to withdraw soil gas samples for oxygen, carbon dioxide, methane, and VOC analysis. They will be constructed of 1-inch diameter, Schedule 40 PVC pipe and will have 1 foot of well screen. At each nest, one probe will be placed at the bottom of the ZNAP and one at the top. Two probes will provide a better indication of the vertical differences in oxygen migration and availability. The bottom probe may be submerged at times during the year. To protect the probes, both probes of each nest will be encased in a 6-inch-diameter outer casing. A detail showing the probes construction is shown in Figure 3-4.

Blower

Air will be supplied to the distribution system by a single positive displacement blower (with silencer). The blower will be sized to deliver up to 600 scfm. The delivery pressure will vary depending on the actual air permeability of the soil. The air permeability of medium grained sands is often about 10 darcys. However, air



NOT TO SCALE

FIGURE 3-4
TYPICAL PROBE NEST CONSTRUCTION
ONALASKA LANDFILL
Bioremediation-Preliminary Design

GLO65602.PD.H6 3-4 Probe Nest Construct 1-30-92mms

permeability can easily vary by an order of magnitude. Assuming an air permeability of 2 darcys, the blower will deliver the 300 scfm at about 100 inches of water (4 psi). The actual flow needed by the system will be controlled by valves on the header lines and at each injection well. A bleed valve or pressure relief valve on the main header line will also be installed. The blower will be located in a separate shed, adjacent to the groundwater treatment facility. Controls for the blower also will be located inside the shed. Electrical service will be provided from the treatment facility. The blower shed is shown in Figure 3-1; this location may vary depending upon the final grading plan for the groundwater treatment facility and the required offset from the proposed outdoor propane storage tank.

Moisture Control

The column studies indicate that the soil tends to be hydrophobic, most likely because of the extent of petroleum contamination in the soil. The moisture content of the soil is 3 to 5 percent, even after wetting. However, respiration indicative of microbial activity still occurs despite the low moisture content.

The effect of air movement through the soil on the moisture content is difficult to quantify. It is possible that the soils could be dried further from the continual exchange of air. Air at 80°F with 40-percent relative humidity would be at 100-percent relative humidity when cooled to the 50°F temperature of the subsurface soil. Therefore, the injected air could be a source of some added moisture. At least during the warmer summer months, injected air would probably not dry the soils. Water would also be returned continually to the soil through percolation of rainfall and snowmelt, natural changes in the groundwater table, capillary rise from the groundwater, and diffusion from the groundwater. During winter months, the lowered air humidity could cause substantial drying of the soils, therefore, the system will be operated from April to October.

If it appears (through soil vapor and soil samples) that these mechanisms are not adequate to maintain minimal moisture requirements (3-5 percent as evidenced by treatability study), further moisture addition may be needed for the soil. The simplest method would be to turn off the groundwater extraction system for a few days during a period of high groundwater elevations. This would rewet a portion of the ZNAP. The amount of rise in water table could be as much as 2 feet near the wells to as little as 6 inches elsewhere. The rise will be monitored by water level measurement from each air injection well. Other options would be to grade toward the ZNAP area so that runoff from the cap would have more opportunity to infiltrate into the effected area. Finally, effluent from the groundwater treatment system could be used to irrigate the ZNAP area (this option would require special permitting).

Infiltration rates for sandy soils average about 0.5 inch per hour. For a 2-acre area, the rate would be 53,000 gallons each hour or about 900 gallons per minute. Diverting all the effluent from the treatment system to an irrigation system could bring the vadose zone soil to its field capacity (10-to 15-percent moisture content) within a couple of days.

Given the hydrophobic nature of the ZNAP, moisture addition may not be entirely effective. Because an irrigation system substantially increases the complexity and cost of the design, and its effectiveness is uncertain, it is not included. If irrigation would be needed at a future date, it could be implemented with agricultural irrigation equipment.

Nutrient Addition

During the treatability study, on the average approximately 15 mg/kg of NH_3 and 50 mg/kg of total organic nitrogen (TKN) was consumed. No measurable decline in phosphorous concentration was observed. The nutrient-amended column did not appear to demonstrate a significantly higher respiration rate or decrease in

hydrocarbon content due to biodegradation when compared to the unamended columns. This data indicates that although the column systems were not nutrient-limited, a full-scale system may become limited with extended operation.

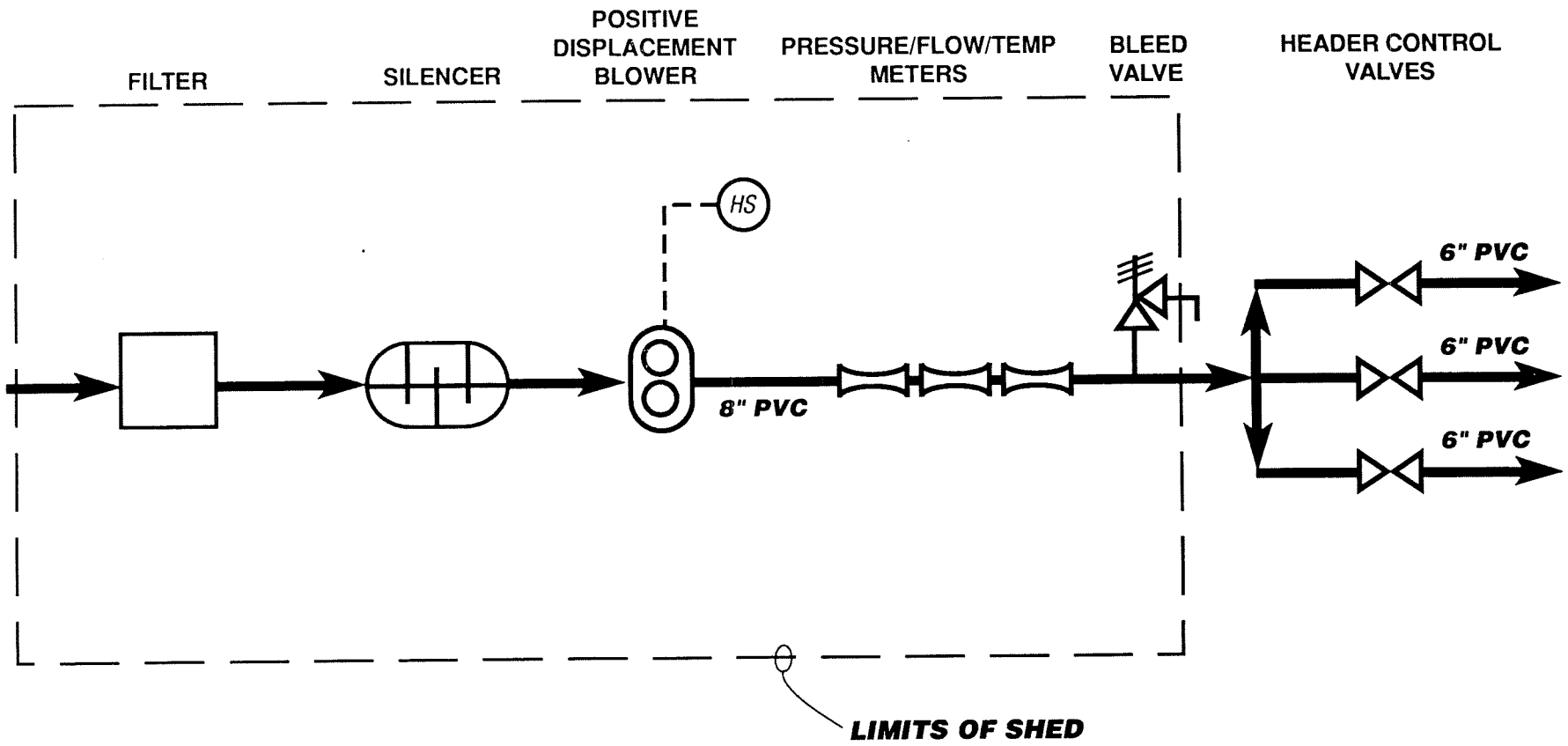
In the remedial investigation, the groundwater beneath the ZNAP was found to have an average ammonia concentration of 10 mg/L; thus, controlling the groundwater extraction system to allow for periodic wetting may also provide nutrients to the vadose zone. Landfill leachate, which may provide a continuous source of ammonia to the groundwater, has had measured ammonia concentrations of 80 mg/L. The effectiveness of this method of nutrient addition will be evaluated periodically through soil sampling and analysis.

If nutrient supply does not appear adequate after 2 years of review of the operational system, nitrogen supply through addition of aqueous ammonia could be adapted to the existing air injection supply system to remedy insufficient nutrient levels. Another option would be to provide nutrients through an irrigation system.

Instrumentation and Control

The blower will have a constant speed motor that will be controlled manually from a local control panel. The ON/OFF status of the blower will be indicated remotely in the groundwater treatment building. Thus, the operator of the treatment facility can notify the bioremediation contractor if the blower should trip off. No automatic shutdown features are provided in this system.

A pressure indicator, a thermometer, and a flowmeter will be mounted on the main header leaving the blower. A process flow diagram for the system is shown in Figure 3-5.



LEGEND

HS — Hand Switch

Gate Valve

NOT TO SCALE

FIGURE 3-5
P & ID
ONALASKA LANDFILL
Bioremediation-Preliminary Design

Vertical and Horizontal VOC Migration

Introducing air directly into the landfill could result in aerobic conditions in the refuse and, hence, composting of the waste. There would be a safety concern about the heat generated with composting and the potential for landfill fires. This question is addressed by the inclusion of a gas collection trench between the ZNAP and the landfill. The trench will be built during the landfill cap phase of construction, and its main function will be to prevent migration of landfill gas away from the landfill. Consequently, the trench also will act as a barrier to air flowing into the landfill from the in situ bioventing system. Figure 3-6 is a cross section of the area between the landfill and ZNAP area and the location of the trench. The exact trench location will not be finalized until review of the 60-percent landfill cap design is complete.

The vertical migration of VOCs through the vadose zone soil and into the atmosphere is also difficult to predict. Reliable prediction of an emission rate is nearly impossible because:

- Air flow patterns are difficult to predict.
- The degree of adsorption/desorption to soil as air rises through it to the ground surface is unknown.
- The amount of biodegradation of VOCs in the vadose zone between the ZNAP and ground surface is difficult to predict.
- A considerable amount of free product may be present.
- Analytical measurements of VOCs in the soil vary so widely that it is difficult to estimate contaminant mass reliably.

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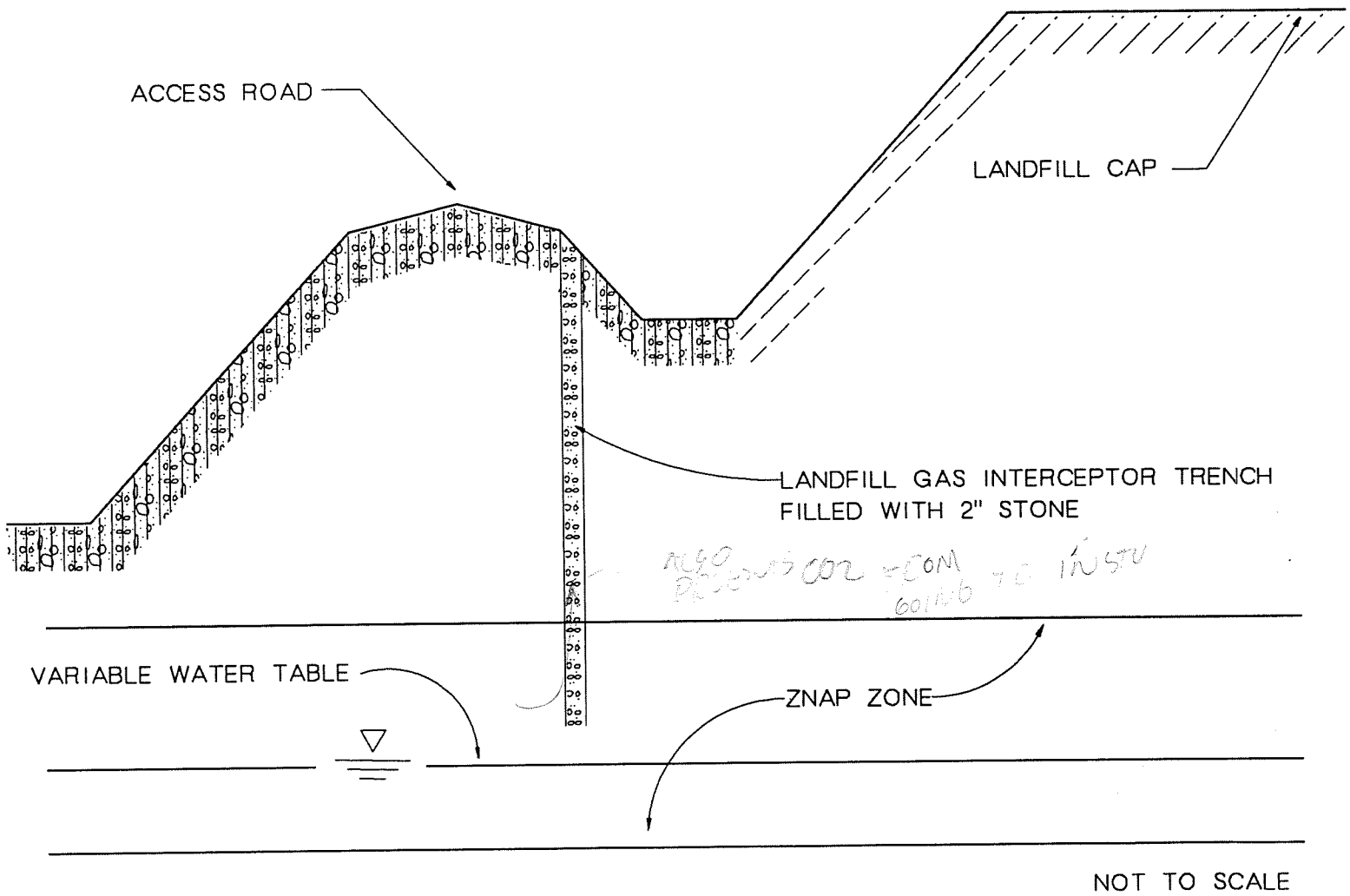

FIGURE 3-6
IN SITU REMEDIATION
LANDFILL GAS INTERCEPTOR TRENCH
ONALASKA LANDFILL
Bioremediation-Preliminary Design

The potential for release of VOCs will be minimized by controlling the flow rates of injected air to the minimum requirements to keep the ZNAP aerobic. The actual migration of vapor phase VOCs through the soil surface will be assessed after the system is started. Ambient air samples and shallow soil vapor samples can be collected over a period of several hours at several locations in the ZNAP. The shallow soil vapor samples (collected from 2 to 3 feet below ground) will be used to assess the extent that VOCs are migrating upward from the ZNAP.

Operating Requirements

It is assumed that the system will be operated from April through October, when the air temperatures and soil temperatures are warmest. The persons who will operate and maintain the facility have not yet been identified. Because of the relatively remote location of the facility, the design attempts to minimize the amount of operation and maintenance required.

In addition to routine operation, performance of the system will be evaluated from April through October. The purpose of the evaluations will be to gain some measure of understanding of the amount of biological degradation in the ZNAP layer. The following sections elaborate on the proposed approach to operating requirements and performance monitoring.

Duties of Operation

Routine

The routine requirements for effective operation and maintenance of the treatment system are to:

- Maintain aerobic conditions in the ZNAP layer
- Perform routine maintenance on the blower
- Drain condensate from the header lines
- Cut grass and weeds around distribution lines/wells

Special

Aerobic conditions throughout the ZNAP layer should be maintained if the radii of influence of the wells are greater than their spacing. The flow rate to the overall system and to each individual well will be manipulated based on observed oxygen concentrations in the soil gas probes during system startup. This will require a resident engineer onsite during the first one to two weeks of startup.

It is estimated that, after the system startup and determination of initial operating conditions, 1-day visits for a two-person crew would be needed each month (from April through October during system operation). During these visits, the crew will measure pressure, oxygen, carbon dioxide, and methane levels in each soil gas probe, and measure flow and pressure at each well. The visits should be followed with a 1- or 2-page operating report.

During the spring (April) of each operation period, when groundwater levels are ordinarily at their natural high level, the groundwater extraction and air injection systems will be turned off. The water level should reach its normal level within 1 day following cessation of pumping. This will be determined by measuring the water levels in the air injection wells. When the ZNAP indicates what appears to be its highest water table, the extraction and injection systems will be turned back on (approximately 2 days later).

Soil samples will be collected before and after the groundwater table is allowed to rise to determine the influence on soil moisture and nutrient concentration. Performance monitoring is described in more detail below.

Performance Monitoring

To determine whether the system is achieving the goals of the ROD, it will be necessary to measure system performance. Soil sampling is expensive and, as indicated in the column test, the amount of contaminants variability in the soil may result in sampling events that are difficult to compare. Further release of product from the landfill also may obscure performance monitoring results. Consequently, most soil performance monitoring will take place through soil gas sampling and in situ respiration studies. These methods have the advantages of:

- Ease of sample collection
- Immediate analysis
- Inexpensive collection of many samples, permitting development of a greater database and allowing better resolution of conditions

Under the proposed monitoring plan, in situ respiration studies would be conducted twice per year at two injection wells and two soil gas probes. The injection system would be shut down for a period of time necessary to consume the majority of oxygen present in the vadose zone (approximately 1 day). Field measurements of oxygen, carbon dioxide, and methane will be taken at each well and soil gas probe just before shutting the system down, and then every hour immediately thereafter, until the concentration of oxygen drops to less than 5 percent or until oxygen concentrations plateau and no additional decline is observed. Respiration tests will be compared to assess the demand for oxygen and the production of carbon dioxide, and thereby directly measure the rate of contaminant degradation.

Before conducting the respiration studies, soil gas samples will be collected in evacuated canisters and sent to an offsite laboratory for VOC analysis and percent moisture measurement. Successive analysis of the soil vapor will be compared for decreases in VOC concentrations and changes in relative humidity. It is estimated that the respiration studies and initial soil gas collection will take 2 days for a 2-person crew to complete for each sampling event.

Finally, 10 soil samples will be collected at the start of the remediation and at the beginning of each operating season. Soil samples will be measured for total petroleum hydrocarbons, VOCs, nutrients, and moisture to assess trends in soil concentrations, nutrient use, and moisture content. The results of the analysis will help guide decisions on the need for nutrient addition, moisture addition, and continuation of the treatment effort. Because of the large variability of the observed soil concentrations, it is suggested that only the center portion of the ZNAP be sampled. By sampling a smaller area (e.g., 100 square feet) lying directly between two injection wells more intensively and assuming that area is representative of the site as a whole, some variability in analytical results may be reduced. This soil sampling is estimated to take another 2 days for a 2-person crew (assuming collection with a hand auger).

Data from the respiration tests, soil gas sampling, and soil samples themselves, along with analytical data from shallow groundwater samples, will require collective review and should indicate the progress of remediation.

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Section 4

Estimated Capital and Operating Cost

The capital cost to construct the proposed in situ bioremediation system is estimated to be $114,000. Services during system startup are estimated at $15,000. The estimated annual operating cost is $36,000 with a present with worth over 10 years of operation equal to $278,000. Costs were estimated on the basis of the processes described in this report. Costs associated with the other aspects of site remediation such as the gas barrier trench are not included. Appendix B presents the detailed cost estimate tables.

The cost estimates are preliminary design cost estimates with an expected level of accuracy of +30 and -15 percent for the scope of work presented in Section 3. The final costs of the project will depend on actual labor and material costs, competitive market conditions, actual site conditions, final project scope, implementation schedule, continuity of personnel, and other variable factors. A final design cost estimate (expected +15 percent, -10 percent accuracy) will be submitted with the final design.

GLT243/060.51

Section 5

Implementation

Sequencing with Other Remedial Activities

The in situ bioremediation system is only part of the overall remedial action for the Onalaska Municipal Landfill site. In addition, a groundwater treatment facility will be constructed, as will a multilayer landfill cap on the site and over part of the ZNAP area of contamination. The preliminary construction schedule for the cap projects that its construction activities will be complete or nearly complete before construction of the in situ bioremediation system. Certain aspects of the bioventing system construction will be linked with groundwater treatment system construction. The bioventing system design and arrangement should adapt to anticipated changes in topography, roadways, and buildings.

Permits and Regulatory Requirements

The remedial action selected for any given site under the Comprehensive Environmental Response, Compensation, & Liability Act of 1980 (CERCLA) is required to attain the standards defined by the applicable or relevant and appropriate requirements (ARARs) established for the site by the U.S. EPA and Wisconsin Department of Natural Resources. The ARARs apply to environmental requirements. Permits and other administrative requirements that do not pertain to environmental regulation also must be followed.

CERCLA response actions conducted entirely onsite are not required to comply with the administrative requirements of ARARs. Administrative requirements include

fees, permitting, and reporting requirements. The onsite actions must meet the substantive technical requirements of the permits that would otherwise be required.

Because contaminated soil will be treated onsite, no permits are required. NR 445, which regulates the release of toxic organic compounds into the atmosphere, is potentially applicable. Because air will be injected into the zone of contaminated soil, this could result in some movement of injected air to the ground surface, and the potential for VOCs to be transported to the atmosphere. The rate of release cannot exceed the mass emission rates listed in NR 445.

As discussed in Section 4, the prediction of mass emission rates is made extremely difficult by several factors. Therefore, the actual mass emission rates will be made from field measurements of shallow soil gas and ambient air samples. Multiplying the concentrations of VOCs observed in the shallow soil gas times for flow of the injected air should yield an approximate mass emission rate.

Easements

An easement to the west of the ZNAP area is necessary. This easement is also necessary for construction of the groundwater treatment system and will be obtained. Some of the ZNAP area may extend beyond the landfill property limits, but this is a relatively small percentage of the overall area. No injection wells will be installed in that area extending beyond the landfill property limits.

Quality Assurance Project Plan

A construction quality assurance project plan will be prepared before construction. The plan will include procedures for inspection and documentation of the construction.

Community Relations

Before and during the course of construction, community relations activities will be undertaken to inform the community of the progress and schedule for construction and to facilitate communication with the U.S. EPA and the Wisconsin Department of Natural Resources. During previous public meetings, the community expressed concern over the effectiveness of the proposed system, considering it is an emerging technology, and the potential for airborne pollution from the system. These issues and others will be addressed during subsequent meetings with the community and through informal fact sheets.

Contracting Strategy

The scope of work for the final design assumes that bid documents will be prepared for the in situ biotreatment system and the groundwater extraction and treatment system. The advantages of bidding the two systems together are that:

- Drilling activities for air injection well and soil gas probes can be phased with monitoring well, piezometer, and extraction well installation.

- Routine operation of the bioventing system can be performed as a small supplemental task to the overall operation and maintenance of the groundwater treatment facility.

The main disadvantages of bidding the work separately is that additional in-field coordination efforts will be needed between the contractors and the duplication of a large portion of the general specifications for both projects would be necessary.

Preliminary Construction Schedule

The schedule for design and implementation of the bioventing system will depend upon the schedule for the groundwater treatment system since certain aspects such as well and soil gas probe installation will need to be coordinated with extraction and monitoring well installation. Construction of the bioventing system can be accomplished quickly and should be scheduled so as to not to interfere with the landfill cap or groundwater treatment facility. Since the schedule for groundwater treatment design and implementation is still uncertain, no schedule for bioventing has been prepared for this document.

GLT243/061.51

APPENDIX A
ENHANCED IN SITU BIODEGRADATION TREATABILITY STUDY

MEMORANDUM CH2MHILL

TO: Kevin Adler/U.S. Environmental Protection Agency Region 5

COPIES: Steve Keith/CH2M HILL Site Manager
Paul Boersma/CH2M HILL

FROM: Ellen Russell/CH2M HILL
Chris Ohland/CH2M HILL

DATE: January 31, 1992

SUBJECT: Onalaska Landfill Treatability Study—
Enhanced In Situ Biodegradation
WA38-5NL5

PROJECT: GLO65602.PD.H6

Introduction

This memorandum documents the objectives, experimental methods, and results of the Onalaska Landfill Enhanced In Situ Biodegradation Treatability Study. The scope of work for this study is outlined in the Quality Assurance Project Plan (QAPP) for the Onalaska Landfill [1]. The results of this study will be used to support planned predesign activities for implementation of in situ biodegradation as a remedial action at the site.

Detailed documentation of the site history can be found in the Remedial Investigation report [2]. Of particular importance to the in situ biodegradation remedial action is an approximate 2-acre area of contamination outside the delineated boundaries of the landfill. In that area, petroleum-based solvents have become distributed in a 4-foot-thick layer existing approximately 8 to 12 feet below ground and just above the groundwater table. The accumulation of those materials is the result of the practice of dumping quantities of Stoddard solvent, VM & P naphtha, high flash naphtha, mineral spirits, ethanol, toluol, asphaltum, paint formulas, and synthetic (amine-based) lubricants into the landfill and the subsequent leaching of those materials into the groundwater. The substances have low specific gravities and tend to float on top of the water table. Fluctuations in water table elevation have caused a smearing of compounds in a 4-foot-thick layer of the soil above the water table interface. The resulting zone of contamination is referred to as the zone of nonaqueous phase of contamination (ZNAP).

Objectives

As described in the Onalaska Landfill Feasibility Study (FS) report [3], enhanced in situ biodegradation was considered as a possible alternative for remediation of the primarily petroleum-based materials present in the subsurface ZNAP. This alternative was incorporated into the Record of Decision (ROD) because of its potential benefits over an alternative form of treatment (asphalt incorporation) [4]. Those benefits included the permanent destruction of the contaminants, meaning that transportation or excavation of the soils was not required.

Specifically, the ROD states that "Bioremediation . . . shall be implemented in the naphtha-contaminated soils (and in the southwestern portion of the landfill, if viable) for a minimum of two 200-day treatment seasons until the cleanup standard is met." The estimated cleanup goal was defined as an "80 to 95 percent reduction of the organic contaminant mass in the soils." No specific definition of organic contaminant mass was stated, but the term "organic contaminant mass" implies the petroleum-based and petroleum-related constituents within the soil.

In general, the objective of the treatability study was to determine whether added oxygen would enhance biodegradation in reducing total petroleum hydrocarbons (TPH) and benzene, toluene, ethylbenzene, and xylene (BTEX) in the ZNAP. A secondary objective was to estimate the amount of compound stripping/volatilization occurring so that estimates of biodegradation could be made.

Specific objectives, as outlined in the QAPP, were:

- 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 contaminant fraction within the test simulation
- To evaluate the percentages of hydrocarbon degradation achievable within the test simulation

Literature Review

As with most emerging and innovative technologies, the literature base covering the study of in situ biodegradation is constantly expanding. The literature review conducted during the FS indicated that in situ biodegradation had been demonstrated

with reductions in volatile compounds varying from 80 to 95 percent [5, 6, 7]. The studies evaluated biodegradation of gasoline, jet fuel, methylene chloride, isopropanol, acetone, tetrahydrofuran, and tetrachloroethene. Early studies were used in the FS to estimate the extent of achievable remediation for the contaminants at the Onalaska Landfill.

Recent investigations using the shake flask technique or equivalent serum vial studies have demonstrated that aerobic biodegradation is achievable for certain petroleum and volatile BTEX components [8, 9, 10]. Work in CH2M HILL laboratories has shown percent reductions ranging from 70 to 99 percent for these compounds [10]. Rates of degradation have varied anywhere from 1 to 52 mg compound degraded per liter of aquifer slurry material per day [9]. Of note is that lag periods of 5 to 22 days have been observed before rates became significant, which could indicate that study periods longer than 1 month would be preferable.

Within the past 2 years, there has been increasing focus placed on the remediation of petroleum contaminated sites using what is referred to as enhanced bioremediation or bioventing. The bioventing technology essentially involves injecting air to enhance biodegradation as well as extracting air to aid in the removal of volatile components. Studies have focused upon field pilot testing of the technology under actual site conditions and have demonstrated reductions of 55 percent hydrocarbon concentration over a 7-month period [11, 12].

Approach

Initial conceptual planning for this treatability study considered the use of shaker flask studies to determine the biodegradability of the ZNAP compounds under optimal mixing, aeration, and nutrient conditions. The experimental approach was modified when the literature base began to indicate that petroleum compounds were easily biodegradable under optimal conditions such as would be simulated in a shake flask study. It was no longer considered necessary to demonstrate that biodegradation under optimal conditions would occur, and it was felt that enough background literature to that effect was available.

Imitation of the subsurface physical system by column testing was considered to provide more valuable information than gained from a shaker flask study. The decision not to conduct a pilot-scale test of the technology also emphasized the need to simulate field conditions as closely as possible during the bench test. Therefore, soil enclosed within acrylic columns and supplied with forced air was used to simulate field subsurface conditions.

The parameters monitored routinely within the soil columns to reflect the ultimate disposition of hydrocarbon compounds were gas phase carbon dioxide and gas phase and soil bound hydrocarbons (C_2 to C_{32}). The soil bound and gas phase individual hydrocarbons quantified included not only BTEX, but also the other hydrocarbon components. Gas phase oxygen and soil bound nutrient concentrations were monitored to demonstrate that they were not limiting to the biological system. Oxygen and carbon dioxide were also monitored as indicators of respiration.

The treatability study was divided into preliminary and definitive studies as defined in the QAPP [2]. The preliminary study was conducted for 1 week to establish appropriate operating conditions for the soil columns and to develop procedures and methods for quantification of the aforementioned parameters. The definitive study was conducted under the refined operating conditions for a 90-day period to ascertain the project objectives.

Organization

This memorandum is organized into the five sections dealing with the methods and materials, preliminary study, definitive study, results and conclusions. Conclusions and points of discussion that are important to consider during design of any full-scale system are summarized at the end of the memorandum. Supporting information, including detailed analytical and sampling procedures, and data compilations are provided in Attachments 1 and 2.

Methods and Materials

Sample Collection

Attachment 1 provides the discussion and documentation of the procedures used for sample collection. Subsurface soil samples were collected from both contaminated and uncontaminated (background) locations at the Onalaska site and placed directly into test column assemblies. Treatability study and the bulk of the analytical work was performed at CH2M HILL's Treatability Laboratory in New Berlin, Wisconsin. Nutrient analysis and confirmatory TPH and BTEX testing was performed at CH2M HILL's Analytical Laboratory in Corvallis, Oregon.

System Construction and Operation

Columns

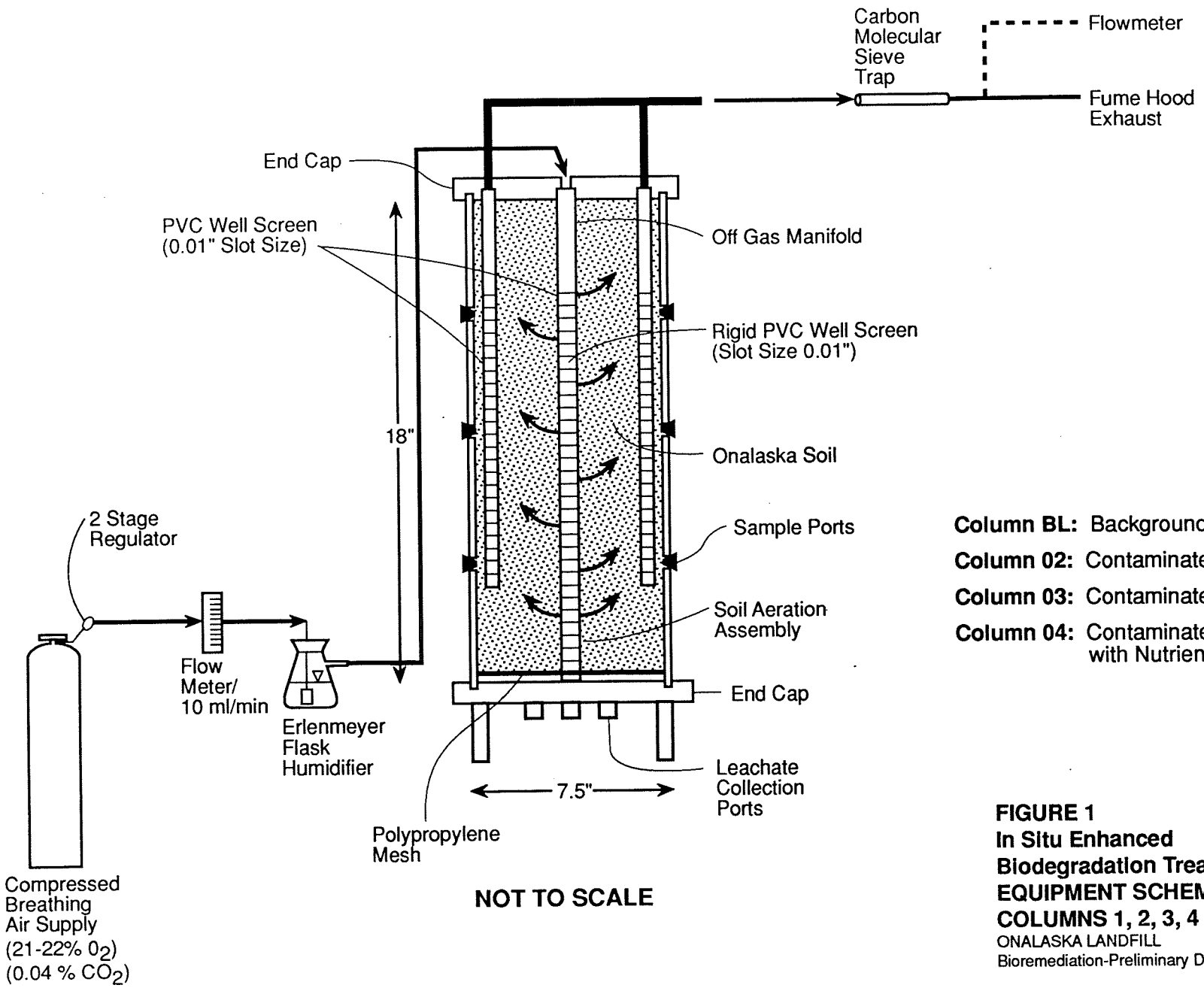
Four test columns were constructed. One column was used for the preliminary study and then later washed and used for the definitive study. The four columns used for the definitive study were designated as follows:

- TCBL—Background Control or Blank Column
- TC02—Test Column No. 2
- TC03—Test Column No. 3
- TC04—Test Column No. 4

The cylindrical column body was 18 inches tall and 7.5 inches in diameter and had walls that were 0.25 inch thick (Figure 1). The mass of soil within the preliminary column was 21.8 kg. Masses of soil within definitive test columns were 22.6 kg in TC02, 22.2 kg in TC03, 22.7 kg in TC04, and 20.9 kg in TCBL.

Top and bottom end caps were prepared from 0.75-inch acrylic flat stock. A 0.25-inch-deep groove was cut into each endcap to provide a firm fit for the cylindrical column. One endcap was permanently cemented in place using a methylene chloride-based adhesive, and the exterior surfaces were further sealed using silicone-based caulk. The other endcap was designed to be detachable. This would allow the test column to be filled with soil at the time of sample collection from the site. A rubber-based gasket was cut and fitted into the groove of the endcap. After the soil was added to the test column, the endcap was attached and held in place with 0.25-inch threaded rods installed through the top and bottom endcaps and tightened. The seal was completed by running a bead of silicone-based caulk along the exterior surfaces of the cut grooves.

An air inlet and exhaust manifold were constructed of 0.75- and 0.5-inch O.D. slotted PVC pipe, respectively. The slot was sized at 0.010 inch. An air intake manifold was positioned along the full length of the test column and fit snugly into 0.25-inch grooves cut into the center of the top and bottom endcaps. A silicone-based sealant was used to hold the inlet manifold in place at the bottom endcap and a rubber-based gasket was cut and fitted into the top endcap. Four exhaust manifolds were positioned at each 90° angle (i.e., 0°, 90°, 180°, and 270°) along the interior circumference of the test column. One end was capped and the other was fitted into the fixed endcap of the test column where holes had been drilled through the endcap to create an exhaust pathway. The four exhaust manifolds were connected into a single exhaust port constructed of Tygon™ tubing using wye connectors. To exclude



NOT TO SCALE

Column BL: Background Control Soil

Column 02: Contaminated Soil

Column 03: Contaminated Soil

Column 04: Contaminated Soil with Nutrient Amendment

FIGURE 1
In Situ Enhanced Biodegradation Treatability Study - EQUIPMENT SCHEMATIC COLUMNS 1, 2, 3, 4
ONALASKA LANDFILL
Bioremediation-Preliminary Design

preferential air pathways, the exhaust PVC pipe was not slotted in the 3.5-inch length nearest the endcaps.

A 0.25-inch layer of polypropylene mesh was placed between the test material and the detachable endcap of the test column. This layer served to exclude fine sized soil particles from the leachate (if leachate accumulated) and would allow for easy withdrawal of liquid material.

Test columns were tested for leaks by pressurizing the column with air and covering the fittings with SNOOP™ soap solution. Leaks would be detected using this method by observing the formation of an air bubble or by measuring a pressure drop within the test column. All leaks were repaired and the test columns retested. Testing for leaks was also performed after the test columns were filled with test material and returned to the laboratory and during the study. Leaks were repaired using silicone sealant.

Sample collection ports were initially installed in the fixed endcap. Because of sample handling constraints and a need to generate composite soil samples as determined from the preliminary study, alternate sample collection ports were installed before the definitive study. These ports were placed at 12 positions within the cylindrical body of the test column. Ports were positioned at three vertical points that mark the boundaries between the four quarters of the test column, located approximately 4.5, 9.0, and 13.5 inches from the bottom endcap. In addition, ports were positioned at each 90° angle (i.e., 0°, 90°, 180°, and 270°) along the circumference of the test column and staggered between the exhaust manifolds. The ports were made by drilling a $^{5}/_{16}$" hole through the wall of the column and were plugging with a tapered stopper.

Oxygen Supply

Breathing grade air (21 to 22 percent oxygen) was supplied to the test columns from a pressure regulated cylinder. Air pressure was controlled by a two-stage regulator to a final delivery pressure of 40 psi. Air was directed to a flow controller through a 0.125-inch I.D. copper line. Four independently controlled air supplies were established using a reconfigured gas chromatograph flow control panel. The panel consisted of two packed column flow controllers operating off an inlet pressure regulator and two hydrogen flow controllers operating off the supply line pressure.

The packed column flow controllers provided an acceptable flow rate in the range of the test system setup (5 mL/min during the preliminary study and 10 mL/min during the definitive study). During Day 0 of the definitive study, the hydrogen column flow

controllers were found to supply unacceptable flow rates in the required range. Precise flow control could not be achieved and ultimately the hydrogen flow controllers were replaced with high resolution flow restrictors that operate in the range of 0 to 30 mL/min.

Before the test column and after the flow controllers, the air was bubbled through a diffuser stone into reverse osmosis (RO) purified water contained in an Erlenmeyer side-arm flask to humidify the air. The humidified air was connected to the test column air intake manifold.

Hydrocarbon Trap

As described earlier, the four exhaust manifolds within the test column were directed into a single exhaust port on the outside of the column. Hydrocarbon traps constructed of 0.25- by 4-inch glass tubes containing 600 mg of coconut charcoal based adsorbent were appended to the exhaust port. Each tube was divided into a front and back region containing 400 and 200 mg of adsorbent, respectively, and separately by a polyurethane plug. During the early time intervals of the definitive study two tubes were connected in series. This practice was continued until the analytical results indicated that breakthrough from the first tube did not occur.

Daily Maintenance Activities

During both the preliminary and definitive studies, columns were kept upright. Columns were also kept dark in enclosed Coleman 80-quart coolers for the entire study period to avoid algal growth. Room temperature was kept constant at 20° ± 1.4°C. Air supply flow rates were controlled on the influent end of the column using the flowmeter and verified at the outlet end using a soap-bubble manometer calibrated for measurement of gas flow rates in gas.

Sampling Procedures

Soil, air (source air, interstitial air, and offgas), and hydrocarbon trap samples were collected from the test systems at various time intervals for the analysis of parameters discussed in the following sections. This section describes the general procedures used to collect the matrices. Sample preparation procedures are described in Attachment 2.

Soil. Soil subsamples were taken from sample containers filled during the field sampling event and from the test columns used during the preliminary and definitive studies.

transferred to glass containers, sealed with Teflon lined caps, and refrigerated until preparation for analysis.

Sample Nomenclature

All samples were labeled with an alphanumeric character set that identified the test column from which they were taken, the matrix of the sample, a sequential number in the order the samples was taken, and an identifier for sample duplicate, matrix spikes, or spike duplicates. For example:

> TC02HT01B: Test Column No. 2, hydrocarbon trap, series No. 1, sample replicate B
>
> TC03GP01: Test Column No. 3, gas phase, series No. 1
>
> TCBLSS01MSD: Test Column background/blank, subsurface soil, series No. 1, matrix spike duplicate
>
> TCXX = Test Column 01, 02, 03, 04, BL (Blank)
> GP = Gas Phase
> HT = Hydrocarbon Trap
> SS = Subsurface Soil
> A = Replicate A or front hydrocarbon trap
> B = Replicate B or back hydrocarbon trap
> MS = Matrix Spike
> MSD = Matrix Spike Duplicate

Chemical Analysis

Soil samples were collected on three occasions from test column materials and tested for outside laboratory analysis of TPH (using EPA Method 418.1–infrared spectrophotometer technique), BTEX, total Kjeldahl nitrogen (TKN), ammonia nitrogen, phosphate, total organic carbon, percent moisture, and total volatile solids concentrations (Table 1). Hydrocarbon trap and soil samples were collected routinely during the study and tested for hydrocarbon (HC) and BTEX using internally developed GC-FID techniques. Air supply and offgas samples were collected routinely and tested for oxygen and carbon dioxide concentrations at the treatability laboratory. The protocols for these methods, proposed in the Quality Assurance Project Plan [1], are listed in Table 1. A complete description of all methodologies is provided Attachment 2. Methods for the analysis of HC and BTEX in soil and

Table 1
Treatability Study
Analytical Methodologies
Onalaska RD QAPP

Medium	Analytical Result (units)	Analytical Method
Soil	HC (μg/g)	GC-Flame Ionization Detector (FID), Modified Method
	BTEX (μg/g)	GC-FID, Modified Method or GC-Photoionization Detection (PID), SW-8020
	TPH (mg/kg)	Infrared, EPA 418.1
	% Moisture (%)	MSA 21-2.2
	NH_3 as N (mg/kg)	Prep: MSA 33-3.2, 33-6.2 Analysis: SM 4500-F
	Phosphorus, total (mg/kg)	Prep: MSA 24-5.3 Analysis: SM 4500-PE
	Total Organic Carbon (TOC)	SM 2540-E
	Dry Weight and Total Volatile Solids (%)	SM 2540-E
	pH	MSA 12-2.6
Soil Vapor, Supply Air	HC (μg/tube)	GC-FID, Modified Method
	BTEX (μg/tube)	GC-FID, Modified Method or GC-PID, SW-8020
	O_2 (%)	GC-Thermal Conductivity Detector (TCD), SM 2720-C
	CO_2 (%)	GC-TCD, SM 2720-C

Note:
BETX = Benzene, Ethylbenzene, Toluene, and Xylene
HC = Petroleum Hydrocarbons using GC-FID
TPH = Total Petroleum Hydrocarbons using EPA Method 418.1
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., Seventeenth Edition
EPA = *Methods for Chemical Analysis of Water and Wastes*, U.S. EPA Environmental Monitoring and Support Laboratory, EPA-600/4-79-020, March 1983
Modified = Methods developed by CH2M HILL Applied Sciences Laboratory

hydrocarbon traps have been updated to reflect modifications incorporated after the preliminary study.

Biological Analysis

Bacterial enumeration was performed at the onset of the treatability testing because of initial concerns that the test sands would be devoid of an indigenous bacterial population. Standard plate counts were obtained using a non-selective Trypticase Soy Agar with dextrose medium (autoclaved for 20 min. at 121°C and 15 psi). A mass of soil (typically 5 grams) was aseptically collected from each column and suspended in 10 mL of sterile 0.01 M pH 7.5 phosphate buffered water. A sterile series dilution was performed on the suspension out to 10^{-7} and duplicate aliquots (0.05 mL) of each dilution were spread onto the surface of the agar media. Plates with only an aliquot of sterile buffered water were used as quality assurance controls. Plates were inverted and incubated at 25°C for 24 hours. After 24 hours, counts of colony forming units (CFUs) were made with the aid of a dissecting scope and handheld counting device.

Preliminary Study

Purpose

The preliminary study was conducted using the ZNAP soil to familiarize the analysts with handling of the test equipment, test material, and test instruments. The extractability of the BTEX and other hydrocarbon compounds from soil and carbon traps, and the chromatographic behavior of the contaminant compounds were also studied. An appropriate analytical standard for hydrocarbon analysis, preliminary rates of oxygen consumption and carbon dioxide evolution, air flushing rates, preliminary indications of volatilization of hydrocarbons, and characterization of potential nutrient limitation were to be identified as part of the preliminary study.

Findings

Test Equipment, Instruments and Materials

Once the preliminary column was removed from refrigeration and allowed to equilibrate to room temperature, a noticeable layer of organic liquid began to pool in the bottom of the column. The free product appeared as a black, non-viscous, hydrophobic layer that floated above the aqueous layer residing at the bottom of the column.

Initially, this accumulation was thought to be a temperature related phenomenon, but upon extraction from the column and refrigerating the pooled product, there appeared to be no observable change in viscosity. Therefore, it was concluded that removing the soil from refrigeration was not the entire cause of product pooling.

It was hypothesized that disturbance of the in situ soil matrix surface tension forces could have allowed for the release of this material. No dramatic evidence of free product was observed on the groundwater surface during the RI or subsequent phases other than sheens on soil samples and a slight sheen during pump test operations. This observation supports the theory that disruption of the soil matrix may be the cause of free product release and that ordinarily the free product is held in the soil matrix.

After the first week of preliminary study and before addition of the nutrient amendment, the aqueous layer and free product was removed from the column. Extraction was possible because the free product had pooled as a defined layer in the lower regions of the test column in the $^{3}/_{16}$-inch layer of polyethylene mesh material. The space created by this layer provided a cell for the drained fluids to pool into and flow freely. Removal was accomplished by inserting a syringe needle through a $^{1}/_{8}$-inch hole drilled into the column and drawing the fluids into the syringe barrel. The free product was determined to amount to 5 grams, or roughly 2 to 4 percent of the total estimated mass of soil contaminant and had accumulated over a 14-day period.

The contaminated soil and free product had an observable softening effect on the synthetic rubber material used for stoppers in each sampling port and on silicone sealant. Precautions were taken during the definitive study to avoid soil contact with sealant, replace rubber stoppers routinely, and test for system leaks throughout the study.

Extractability Assessment, Chromatographic Behavior, and Hydrocarbon Calibration

Contaminated soils collected from the ZNAP and free product collected from the preliminary test column were used to assess the extraction of contaminant from the soil matrix.

The contaminated soil was extracted with hexane, methylene chloride, and methanol using soxhlet extraction techniques. The three solvents span the range of polarity from nonpolar to polar and were selected to characterize the influence of solvent selectivity. An aliquot of each extract was introduced to the gas chromatographic

FIGURE 2.A SOIL EXTRACT, FREE PRODUCT APPEARANCE

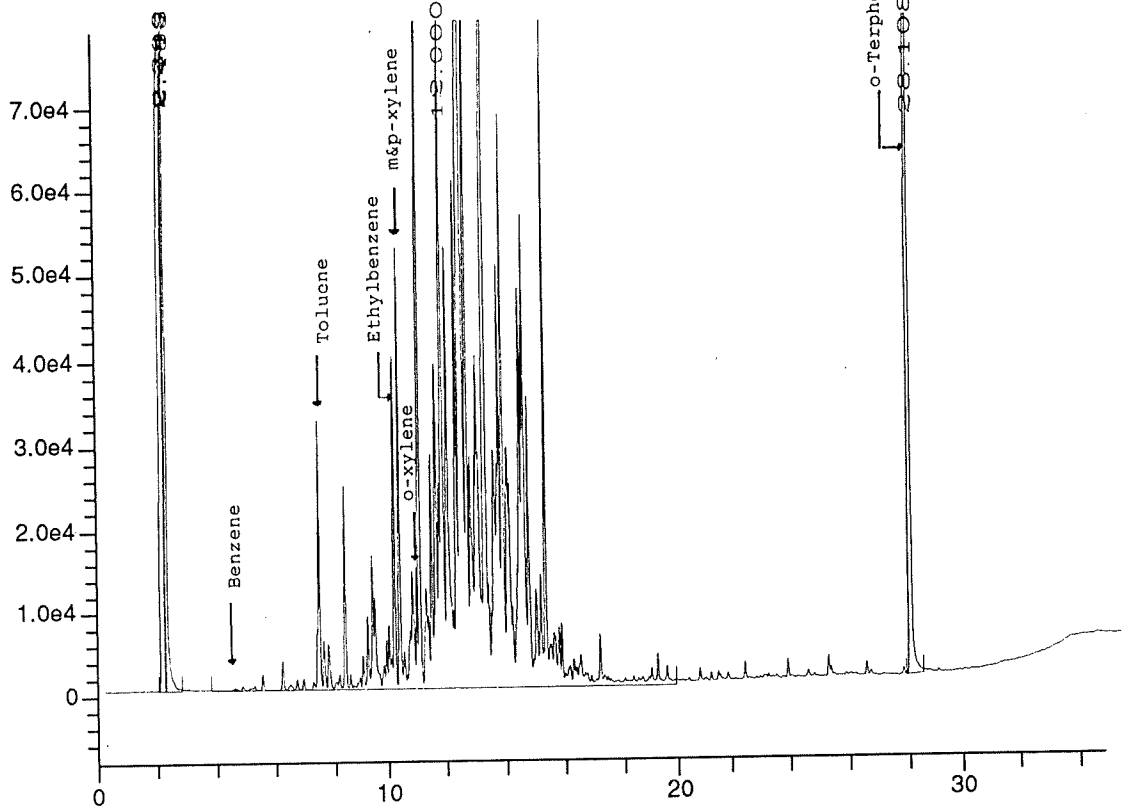


FIGURE 2.B HYDROCARBON TRAP EXTRACT

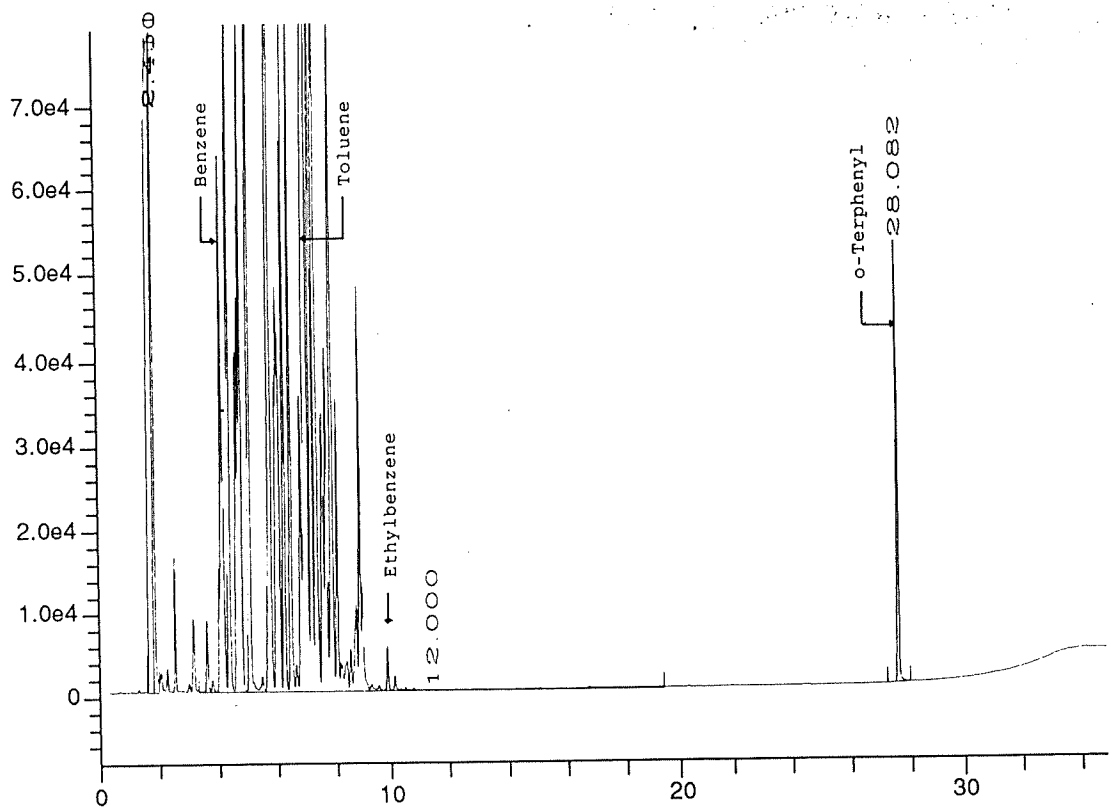


FIGURE 2
TPH Profiles
Onalaska Treatability Study

Preliminary Respiration and Air Flushing Measurements

Respiration. The preliminary column was supplied with an air flow rate of 5 mL/min. This flow rate was based on literature values of oxygen uptake rates (OUR) ranging from 0.2 to 10 μg of O_2 per hour per gram of soil for petroleum and gasoline contaminated soils and considered to satisfy the anticipated oxygen demand [10].

A respiration test on the preliminary column was conducted after 4 days of oxygen supply and following addition of a nutrient amendment solution to obtain information on rate of oxygen consumption. The air supply to the column was shut off and the changes in oxygen and carbon dioxide observed within the interstitial spaces of the column over a 48-hour time span. The respiration rate calculated from a linear regression of the data was 0.005 percent oxygen consumed per minute. The data appeared to demonstrate zero order kinetics. After 48 hours, only 1 percent O_2 remained and 8 percent CO_2 was being evolved.

Air Flushing. The interstitial space of the preliminary column had an initial gaseous composition of 3 to 7 percent CO_2, 1 to 5 percent O_2, 0.004 to 0.03 percent CO, 0.03 to 0.3 percent CH_4, and 73 to 83 percent N_2 prior to any air being supplied to the unit. Actual field in situ measurements showed 20 percent CO_2 and 20 percent CH_4 (Attachment 1). Once air supply began, it took 26 hours before the offgas from the system was observed to have an oxygen concentration that had increased to approximately 22 percent (equivalent to the source air supply), indicating that the system had been completely purged. Carbon monoxide and methane rapidly disappeared from the system and, as indicated by the first gas phase measurement, were not present in the column after purging.

The flushing rate finding corresponded to a previous purge test performed on the same system containing sterile sand where the column void space was filled with 100 percent CO_2 and then purged with air. The test took approximately 24 hours to approach supply oxygen percentages, and even after 24 hours the column had not been entirely purged as indicated by the remaining 35 percent CO_2.

The theoretical flushing rate or pore volume exchange rate for the soils within the column was 1 exchange per 12 hours assuming a porosity of 0.25 and an assumed dry bulk density of 90 lb/cu ft as representative of the medium grained sands in the column. Observed flushing rates were approximately twice as long as theoretical rates. These differences are due to dispersion or incomplete mixing that is likely occurring.

The 5 mL/min flow rate was doubled for the definitive study to 10 mL/min for the following reasons:

- The limited time span planned for the definitive test (initially planned for only 30 days) and the desire to observe changes in respiration rapidly
- The possibility that rapid oxygen uptake could occur (indicated by the preliminary respiration test showing oxygen levels at 1 percent within 48 hours)
- The small mass percentage of easily strippable hydrocarbons observed, indicating that volatilization did not play as great a role in hydrocarbon removal as initially estimated (A higher flow rate was not considered because of the possibility of drying the soil column since initial indications were that the soil had only 3 percent moisture.)

Preliminary Hydrocarbon Volatilization and Breakthrough Observations

Preliminary hydrocarbon trap measurements showed that the mass was less than 5 percent of the total soil bound hydrocarbon contamination after roughly 2 weeks of preliminary column operation. In addition, the character of hydrocarbons volatilized was markedly different (lighter) in appearance than the soil bound hydrocarbons (Figure 2).

Definitive Study

Purpose

Using the operating conditions established during preliminary study, the four test columns were used to study enhanced biodegradation under the following conditions.

- **TCBL**—Background/blank column, filled with soil collected from an uncontaminated area. Used to assess natural rates of respiration and correct for this rate, if necessary, in the contaminated columns.
- **TC02, TC03**—Non-nutrient amended. Columns filled with contaminated soil. Two columns were used to provide duplication of experimental results.

- **TC04**—Nutrient (nitrogen and phosphorus) amended column. Used to assess the possible enhancement of biodegradation as compared to TC02 and TC03.

No deviations from initial oxygen supply rates (other than two scheduled respiration tests), nutrients, or moisture content were planned for the definitive study once initial conditions were set.

Initial Characterization

Chemical and Physical Analysis Results

As described previously, several analyses were performed to establish and confirm initial conditions for the definitive study test columns. These tests were performed at CH2M HILL's Laboratory in Corvallis, Oregon. Measurements of nutrient concentrations (NH_3, PO_4, TKN) and carbon substrate (TOC, TPH, and BTEX) were performed. In addition, an estimate was made of biomass (total volatile solids) within the test soil. The results of these tests are listed in Table 2 for the two representative columns (TC02 and TC04).

Nutrients. Nutrient ratios varied anywhere from 100C:0.3N:0.5P to 100C:7:N:1.5P. Ratios varied depending upon whether total organic carbon or total petroleum hydrocarbon concentrations were used to determine the carbon contribution and whether TKN or ammonia results were used to calculate the nitrogen component of the ratio. Preferred ratios for heterotrophic growth would approximate a 20COD:1N ratio and a 100COD:1P ratio or a 100C:5N:1P ratio. The organic form (TKN) of nitrogen constituted the major percentage of the N present. If the organisms did not readily use the organic form of nitrogen, then some nutrient amendment might be warranted. Therefore, the treatability program was modified to include a nutrient amended column (TC04).

The nutrient amendment solution added to TC04 consisted of a 1-liter solution of ammonium chloride and pH 7.5 0.01 M phosphate buffer. When mixed with the column, this provided a nutrient ratio in the soil matrix of 100C:8N:4P using the TOC and ammonia concentrations. Phosphorous was proportionately added in greater quantity because laboratory results for P used to base the nutrient addition calculations on were initially incorrectly reported as phosphate. After nutrient addition had occurred, the error was noted and it was determined that phosphorous results had been initially reported as P; therefore more P was added to the system than necessary.

Table 2
Chemical and Physical Analyses
Oralaska In Situ Treatability Study

Parameter (mg/kg dry wt.)	Unamended Test Column 02			Nutrient Amended Test Column 04		
	Initial Pre-aeration	Day 20	Day 82	Initial Pre-aeration	Day 20	Day 82
Moisture, %	3.83	3.80	2.90	4.84	4.28	4.20
Loss on Ignition, %	0.53	0.63	0.87	0.63	0.79	0.82
Nitrogen Forms, as N						
Ammonia	17.0	5.86	0.32	15.5	7.67	0.29
Total Kjeldahl	64	34.0	3.45	45.6	46.7	4.11
Total Phosphorus, as P	36.8	79.5	47.1	31.0	95.1	52.1
Total Organic Carbon	1,250	1,010	1,180	847	878	1,190
Total Petroleum Hydrocarbons	11,400	3,790	8,980	10,500	7,220	7,820
Benzene	< 4	< 0.1	< 0.2	< 4	< 0.1	< 0.2
Toluene	353	18	0.3	242	5	0.2
Ethyl benzene	26	2	< 0.2	20	0.4	< 0.2
Xylenes	235	32	5.0	212	18	4.7
Bacterial Number	10^8 cfus/g soil wet wt.	NA	NA	10^8 cfus/g soil wet wt.	NA	NA

NA: Not analyzed

The nutrient solution was added through the air supply tube and mixed throughout the soil column by laying the column on its side and rotating the column 360° until all the soil had contacted the nutrient amendment. The solution was then allowed to drain to the bottom when the column was placed in its upright position. It occupied roughly one-third of the void space in TC04 during the entire definitive study.

Removal of the solution was not considered because of the coincident removal of hydrocarbon that would have occurred that would have had to be quantified in order to perform any mass balance on the system. The 1-liter volume of solution effectively occupied 1 liter of pore space, thus making this area of soil unavailable for biodegradation. This difference in effective volume was accounted for in all calculations (oxygen uptake and biodegradation rates) used to compare the amended and unamended systems. The purpose of this column was to evaluate whether the nutrient amendment made a marked difference in rate of respiration/biodegradation.

Moisture. Percent moisture measurements were performed as part of the initial characterization. Percent moisture tests were also scheduled for the middle and end of the definitive study. Across columns, percent moisture measurements varied from 3 to 5 percent. It is probable that because of the nutrient amendment solution, this column's percent moisture (4 to 5 percent) was slightly higher than unamended columns (3 to 4 percent). The low percent moisture, in general, is likely due to the hydrophobic nature of the soil bound petroleum hydrocarbons as well as the sandy soil type. The hydrophobic nature of the contaminants may also have limited nutrient transfer to the soil surface.

Carbon Substrate and Hydrocarbon Measurements. Results of outside TPH measurement indicated approximately 10,000 mg/kg using the outside infrared spectrophotometer technique and approximately 4,500 mg/kg HC using the internal free product standard and GC-FID technique. This difference is attributable to the bias produced by use of different calibration standards between the two methods. In both cases, concentrations of hydrocarbon were substantially different than those encountered during the RI. Concentrations ranged from 10 to 20 times higher than RI values. Total organic carbon values ranged from 847 to 1,250 mg/kg.

Total Volatile Solids. Total volatile solids measurement indicated a 0.53 percent loss of solids upon ignition at 550°C for initial samples from TC02 and 0.63 percent for TC04. The loss of solids takes into account losses due to driving off soil moisture and volatile hydrocarbons with boiling points less than 103°C. This mass translates to roughly 100 grams of solids initially present for the entire soil column. Increases in total volatile solids could indicate biomass addition to the column, therefore a mid and final test measurement was also scheduled.

Biological Analysis

Bacterial Enumeration. The results of the initial bacterial enumeration indicated approximately 10^8 colony forming units (CFUs)/g of soil (wet weight) in all test columns. This quantity is typical of a subsurface soil population of microorganisms [13, 14]. Two distinct colony morphologies were apparent. One colony type appeared to be a clear pinpoint with smooth margin, while the other predominant colony type was yellowish white and opaque with a furry or diffuse margin. Streaks were made from these colony types and the resulting organisms viewed under a light microscope. Both appeared to be highly motile rod-shaped organisms. The organisms from the white colony appeared at least 5 to 10 times longer than the short rod from the pinpoint colony.

After prolonged incubation, the organisms growing in the pinpoint colonies were surrounded by a fluorescent green pigment within the medium. This type of diffusible pigment production is characteristic of the genus Pseudomonas, members of which are common inhabitants of soil environments. Pseudomonades are also known for their ability to metabolize a wide variety of organic compounds as sole or principal carbon sources for growth [15]. From this testing, initial concerns regarding potential sterility of the subsurface soil samples were allayed.

Results of Definitive Study

QA/QC Measures

Gas Chromatographic Calibrations

HC/BTEX Calibration. Initial and continuing instrument calibrations were performed as indicated in the analytical methods. The measure of precision and accuracy of the calibrations met the required criteria and were acceptable.

Oxygen and Carbon Dioxide Calibration. The calibration of the instrument was performed using a single point concentration level at 5 percent. Using this approach, the linearity of the instrument could not be defined. The effect is that the accuracy of the quantification for oxygen and carbon dioxide at or near 5 percent is less bias than at the ranges measured in the samples, 1 percent for CO_2 and 22 percent for O_2. The accuracy bias can be seen in the data results for the source and ambient air. In these samples, the percentage of oxygen is about 22 and carbon dioxide is about 0.05. However, the known percent composition of oxygen in atmospheric air is 20.9 and carbon dioxide is 0.03.

Soil Measurement Variability

Duplicate soil samples were collected and analyzed. Precision as a measure of the percent difference (percent D) between hydrocarbon results for the two sample duplicate results ranged 2 to 48% D, 7 to 66% D, and 8 to 58% D for TC02, TC03 and TC04, respectively. The average percent difference and standard deviation of the percent difference results (percent D_{SD}) were 23% D, 17% D_{SD} for TC02; 25% D, 18% D_{SD} for TC03; and 30% D, 17% D_{SD} for TCO4. These results are extremely important when evaluating the loss of hydrocarbons in the test systems.

As an indication of the accuracy and precision of the soil hydrocarbon methodology a surrogate compound (o-terphenyl) was added to each sample before extraction and analysis. Average percent recoveries were 91 percent for TC02, TC03, and TCBL, and 90 percent for TCO4. The standard deviation of the recoveries were 6 percent for TC02, 7 percent for TC03 and TC04, and 9 percent for TCBL.

These results reflect the wide variability of the contamination within the soil matrix, whereas the variability of the analytical method was found to be acceptable.

Hydrocarbon Trap Variability

As an indication of the accuracy and precision of the hydrocarbon trap methodology a surrogate compound (o-terphenyl) was added to each sample prior to extraction and analysis. Average percent recoveries were 77 percent for TC02, 72 percent for TC03 and TC04, and 75 percent for TCBL. The standard deviation of the recoveries were 17 percent for TC02, 9 percent for TC03 and TCBL, and 8 percent for TC04.

These results indicate the variability of the analytical method, which was found to be acceptable.

Data Reduction

Conversion to Carbon Mass for Mass Balance

Soil and Hydrocarbon Traps Samples. To describe and compare the concentration of the contaminant mass between columns, the final concentration units were converted to mass of HC (in milligrams or grams). For the soil matrix, a total mass of HC or BTEX was determined for the entire test column and then converted to mass of carbon using a molecular formula for hydrocarbon of $C_{15}H_{32}$. For the hydrocarbon traps, a total mass of HC and BTEX for each hydrocarbon trap was also determined. A cumulative sum of HC in the hydrocarbon traps was provided to indicate the total

volatilized hydrocarbon mass. For mass balance purposes, the volatile trapped HC mass was converted to a mass of carbon using the molecular formula C_6H_{14}, since it is more representative of what would volatilize.

Gas Phase Samples. Data results for carbon dioxide were reported from the gas chromatograph as a percentage. In order to describe and compare the concentration of the respired carbon dioxide, percentage units were converted to cumulative mass of carbon (in milligrams) using the ideal gas law.

Linear Regression Analysis

Least squares linear regressions were fitted to the oxygen uptake results for the respiration studies and to the disappearance of soil bound hydrocarbons. The coefficients of correlation for all test columns exceeded 0.98 for the respiration studies but were less than 0.3 for all soil hydrocarbons results (Figure 3-10).

Data Interpretation

Hydrocarbon Degradation

Tables 3 through 6 and Figures 3 through 6 present the results of the soil bound hydrocarbon concentrations throughout study. Because of inherent soil variability as demonstrated by duplicate soil sample analyses results, the interpretation of the extent of loss of hydrocarbons becomes difficult. As discussed previously, linear regression of the data yielded poor correlation coefficients; however, a downward trend in the results appeared evident.

Relying on the linear fit of the data would indicate that the initial soil hydrocarbon concentration (roughly 100 grams for all test columns) declined by anywhere from 70 to 80 grams HC depending upon the column of interest. Since it had been documented that roughly 50 grams of HC are lost to free product settling and 12 grams lost to volatilization, then a decline of approximately 10 grams of HC is attributed to biodegradation. This translates to a hydrocarbon loss rate due to biodegradation of roughly 5 mg HC per kg of soil per day.

To perform a mass balance, it is also important to recognize that hydrocarbons lost by biodegradation would either undergo incorporation into biomass or metabolism to CO_2. Results of the Day 82 analyses (Table 2) show a 0.87 percent loss on ignition from TC02 and 0.82 percent from TC04. This translates to an increase in percent solids of approximately 0.3 percent or 3,000 mg/kg. Using a standard empirical formula for biomass of $C_5H_7O_2N$, roughly 30 grams of carbon have been incorporated

Table 3
Soil Hydrocarbon Results
Test Column BI--Background

Sample ID	Time (days)	Soil Weight (g)	HC (g)	Benzene (g)	Toluene (g)	Ethyl-benzene (g)	m&p-Xylene (g)	o-Xylene (g)
TCBLSS01A	0.0	20900	ND	ND	ND	ND	ND	ND
TCBLSS01B	0.0	20900	ND	ND	ND	ND	ND	ND
TCBLSS02A	0.3	20900	ND	ND	ND	ND	ND	ND
TCBLSS02B	0.3	20900	ND	ND	ND	ND	ND	ND
TCBLSS03A	1.1	20900	ND	ND	ND	ND	ND	ND
TCBLSS03B	1.1	20900	ND	ND	ND	ND	ND	ND

ND = Not Detected
Note: Further analysis considered unneccesary due to the absence of hydrocarbon content

Table 4
Soil Hydrocarbon Results
Test Column 2--Unamended

Sample ID	Time (days)	Soil Weight (g)	HC (g)	Benzene (g)	Toluene (g)	Ethyl-benzene (g)	m&p-Xylene (g)	o-Xylene (g)
TC02SS01A	0.0	22700	93	ND	1.3	1.0	1.8	0.7
TC02SS01B	0.0	22700	92	ND	1.1	1.0	1.7	0.7
TC02SS02A	0.3	22700	73	ND	0.1	0.1	0.6	0.6
TC02SS02B	0.3	22700	91	ND	0.9	0.9	0.7	0.7
TC02SS03A	1.1	22700	95	ND	0.2	0.1	1.9	0.8
TC02SS03B	1.1	22700	59	ND	0.1	0.6	1.1	0.4
TC02SS04A	4.3	22700	74	ND	1.6	1.2	2.3	1.0
TC02SS04B	4.3	22700	120	ND	1.0	0.9	1.7	0.7
TC02SS05A	10.1	22700	68	ND	0.9	0.7	1.3	0.6
TC02SS05B	10.1	22700	69	ND	1.2	0.8	1.4	0.6
TC02SS06A	14.2	22700	43	ND	0.2	0.4	0.6	0.2
TC02SS06B	14.2	22700	59	ND	0.5	0.6	0.4	0.4
TC02SS07A	18.2	22700	57	ND	0.1	0.1	0.8	0.6
TC02SS07B	18.2	22700	52	ND	0.1	0.1	0.8	0.6
TC02SS08A	22.2	22700	59	ND	0.1	0.1	1.1	0.5
TC02SS08B	22.2	22700	65	ND	0.1	0.1	1.0	0.8
TC02SS09A	26.1	22700	64	ND	0.7	0.7	1.2	0.5
TC02SS09B	26.1	22700	83	ND	0.1	0.1	1.7	0.7
TC02SS10A	32.1	22700	49	ND	0.1	0.5	0.9	4.1
TC02SS10B	32.1	22700	68	ND	0.8	0.7	1.4	0.6

ND = Not Detected

Table 5
Soil Hydrocarbon Results
Test Column 3--Unamended

Sample ID	Time (days)	Soil Weight (g)	HC (g)	Benzene (g)	Toluene (g)	Ethyl-benzene (g)	m&p-Xylene (g)	o-Xylene (g)
TC03SS01A	0.0	22200	84	ND	0.9	0.8	1.5	0.6
TC03SS01B	0.0	22200	91	ND	0.8	0.9	1.6	0.6
TC03SS02A	0.3	22200	105	ND	1.0	1.1	1.9	0.8
TC03SS02B	0.3	22200	124	ND	1.4	1.3	2.3	1.0
TC03SS03A	1.1	22200	94	ND	0.2	1.0	1.8	0.8
TC03SS03B	1.1	22200	148	ND	0.3	1.7	3.0	1.3
TC03SS04A	4.3	22200	89	ND	1.2	1.0	1.7	0.7
TC03SS04B	4.3	22200	101	ND	1.4	1.1	2.0	0.8
TC03SS05A	10.1	22200	77	ND	1.1	0.8	1.5	0.6
TC03SS05B	10.1	22200	97	ND	1.3	1.1	2.0	0.8
TC03SS06A	14.2	22200	57	ND	0.5	0.6	1.0	0.4
TC03SS06B	14.2	22200	112	ND	1.2	1.2	2.2	0.9
TC03SS07A	18.2	22200	90	ND	0.2	0.1	1.3	1.1
TC03SS07B	18.2	22200	71	ND	0.1	0.1	1.4	0.8
TC03SS08A	22.1	22200	72	ND	0.1	0.1	1.4	0.8
TC03SS08B	22.1	22200	65	ND	0.1	0.1	1.3	0.5
TC03SS09A	26.1	22200	51	ND	0.3	0.5	0.9	0.4
TC03SS09B	26.1	22200	71	ND	0.6	0.7	1.3	0.6
TC03SS10A	32.1	22200	93	ND	0.2	0.1	1.9	0.8
TC03SS10B	32.1	22200	107	ND	1.1	1.1	2.1	0.9

ND = Not Detected

Table 6
Soil Hydrocarbon Results
Test Column 4--Amended

Sample ID	Time (days)	Soil Weight (g)	HC (g)	Benzene (g)	Toluene (g)	Ethyl-benzene (g)	m&p-Xylene (g)	o-Xylene (g)
TC04SS01A	0.0	22700	103	ND	0.9	1.0	1.7	0.7
TC04SS01B	0.0	22700	65	ND	0.5	0.6	1.1	0.4
TC04SS02A	0.3	22700	173	ND	2.3	1.9	3.4	1.4
TC04SS02B	0.3	22700	191	ND	2.8	2.1	3.8	1.6
TC04SS03A	1.2	22700	140	ND	2.3	1.6	2.8	1.2
TC04SS03B	1.2	22700	77	ND	0.9	0.8	1.4	0.6
TC04SS04A	4.3	22700	103	ND	0.8	0.7	1.3	0.5
TC04SS04B	4.3	22700	83	ND	2.0	1.3	2.4	1.0
TC04SS05A	10.1	22700	86	ND	1.0	0.9	1.7	0.7
TC04SS05B	10.1	22700	116	ND	1.8	1.3	2.4	1.0
TC04SS06A	14.2	22700	57	ND	0.4	0.5	1.0	0.4
TC04SS06B	14.2	22700	75	ND	0.6	0.8	1.4	0.6
TC04SS07A	18.2	22700	48	ND	0.1	0.1	0.7	0.5
TC04SS07B	18.2	22700	83	ND	0.1	0.1	1.6	1.0
TC04SS08A	22.2	22700	57	ND	0.1	0.1	1.0	0.7
TC04SS08B	22.2	22700	76	ND	0.1	0.1	1.0	0.9
TC04SS09A	26.1	22700	73	ND	0.6	0.7	1.3	0.6
TC04SS09B	26.1	22700	61	ND	0.1	0.8	0.8	0.7
TC04SS10A	32.1	22700	65	ND	0.5	1.2	1.2	0.5
TC04SS10B	32.1	22700	60	ND	0.1	1.1	1.1	0.5

ND = Not Detected

FIGURE 3 TEST COLUMN 2

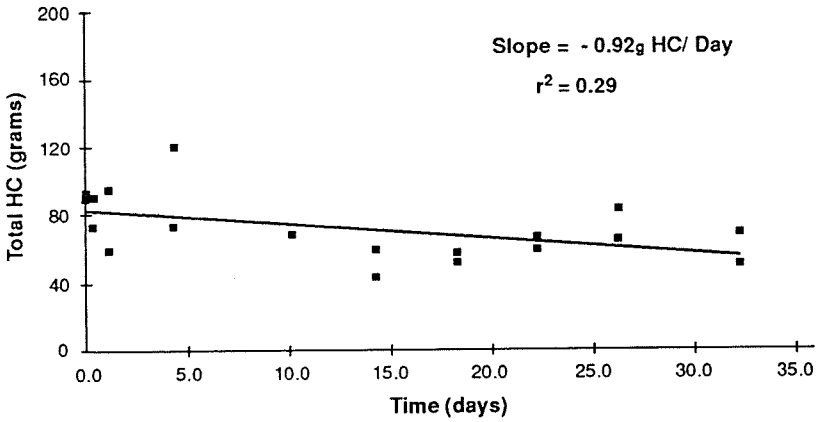


FIGURE 4 TEST COLUMN 3

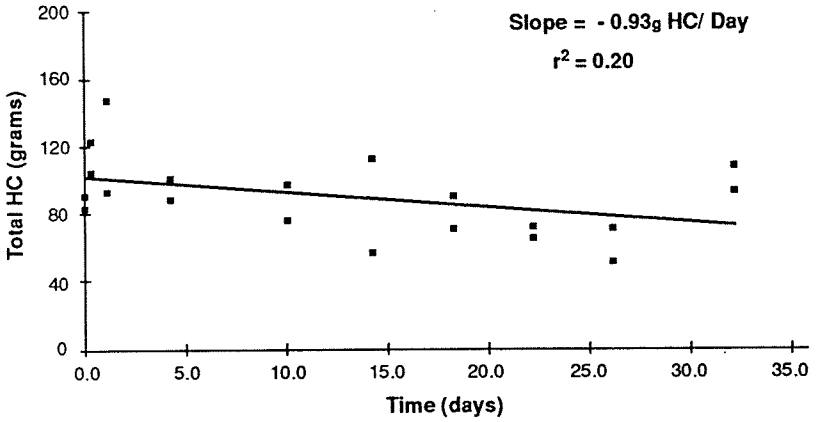


FIGURE 5 TEST COLUMN 4

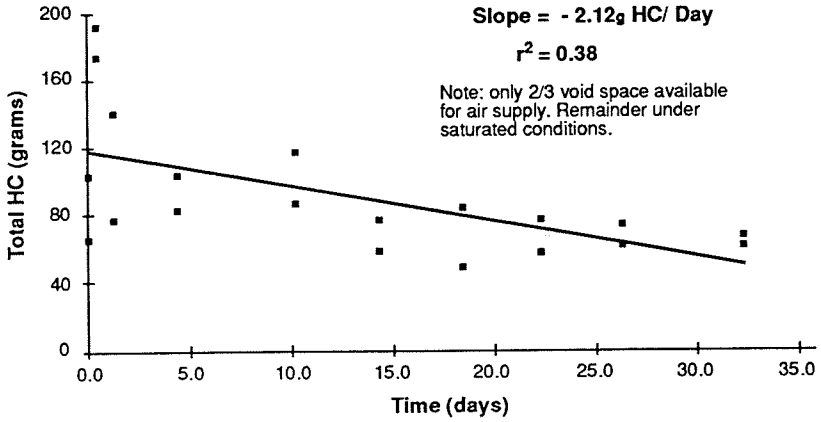
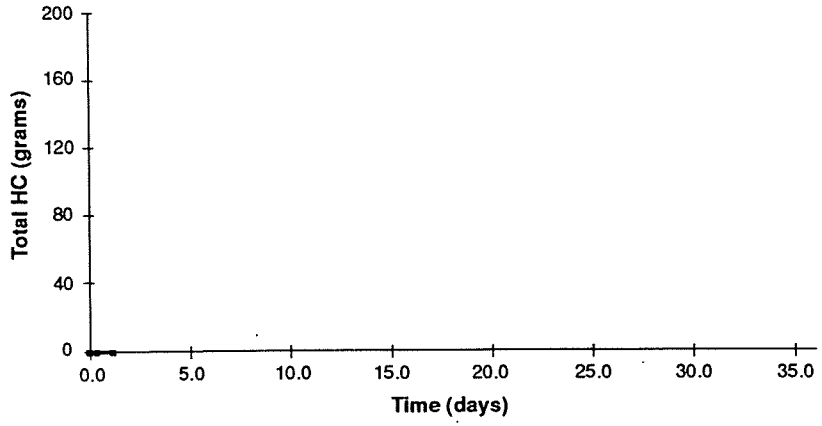


FIGURE 6 TEST COLUMN BLANK



FIGURES 3-6
Soil Bound Hydrocarbon (HC) Mass
Onalaska Treatability Study

into biomass. Cumulative carbon dioxide evolution over the study amounts to 10 grams of C for the columns. Using a rough mass balance approach, the decline in total hydrocarbon concentration can be accounted for as follows:

85 g	C (initial 100 g HC mass converted to carbon—MW $C_{15}H_{32}$)
-50 g	C (free product settling converted to carbon—MW $C_{15}H_{32}$)
-10 g	(cumulative volatilization mass converted to carbon—MW C_6H_{14})
-30 g	C (biomass conversion)
-10 g	C (cumulative carbon dioxide evolution)
-15 g	C (remaining HC) or considering an observed soil bound hydrocarbon remaining of approximately 25 g, a net 40 g of C in system not balancing

The 40 grams of C that cannot be explained through the mass balance approach is well within the range of measurement error associated with the soil bound hydrocarbons. Tables 4 through 6 show variation in soil measurements between duplicate samples as high as 63 grams.

Because of the variability in soil bound hydrocarbon concentrations, it was necessary to assess the rate of biodegradation through other conventional techniques. The following discusses the biodegradation rate in terms of oxygen consumption and carbon dioxide production.

Respiration Studies

Two respiration studies were conducted on the definitive columns. The first study was conducted on Day 22 (November 7, 1991) of operation and monitored the first 14 hours of oxygen uptake and CO_2 production following termination of air supply. The second study was conducted on Day 28 (November 13, 1991) and monitored hours 14 through 22 following termination of air supply.

Results of the first respiration study are presented in Figures 7 through 10. Respiration over the period observed appeared to follow zero order kinetics. No plateaus in oxygen uptake or O_2 production were observed. Carbon dioxide production mirrored oxygen consumption.

Respiration rates calculated for the columns ranged from 0.004 to 0.011 percent O_2 per minute or 0.68 to 1.58 μg of O_2 uptake per gram of soil per hour for both tests. These experimental rates are compared to other literature values for biodegradation of similar substrates in Table 7 [7, 8, 9, 10]. Rates for the second respiration study

Table 7
Experimental Oxygen Uptake Rate Comparison with Literature Values

Substrate	Oxygen Utilization Rate(s)	Source	Ref. No.
No. 2 Diesel Fuel	0.002–0.009 % O_2/min	Donney, et al., 1991	12
JP-4 Jet Fuel	0.001–0.01 % O_2/min	Hinchee and Miller, 1991	11
JP-4 Jet Fuel	0.124 μ mole O_2/g soil dry wt./day 0.165 μg O_2/g soil/hr	Aelion and Bradley, 1991	8
Diesel Fuel, BTEX, TPH	0.7–10.5 μg O_2/g soil dry wt./hr	CH2M HILL Dow Flora, 1991	10
Naphthas, Toluol, Mineral Spirits	0.004–0.011 % O_2/min 0.68–1.58 μg O_2/g soil/hr	CH2M HILL Onalaska, 1991	

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were similar, although substantial variation in O_2 and CO_2 results occurred when oxygen levels in the system fell below 10 percent. This indicating unstable system operation.

Oxygen consumption and carbon dioxide production rates during the 90-day period treatment remained fairly constant. In general, declines in oxygen percentages of 2 percent and increases in carbon dioxide concentrations of 2 to 3 percent were observed in amended and unamended columns. These observations are corrected for changes in gas concentrations measured in the background control column.

The following stoichiometric equation (based on a series of half reactions for aerobic metabolism) was used to predict hydrocarbon degradation from both steady state observations, as well as data collected during the respiration studies.

$$C_{15}H_{32} + 30\ H_2O + 11.5\ O_2 + 2.3\ NH_3 \rightarrow 2.3\ C_5H_7O_2N + 41\ H_2O + 3.5\ CO_2$$

A range of hydrocarbon biodegradation rates from 10 to 30 mg HC per kg soil per day were obtained using the appropriate stoichiometric relationships.

Assuming typical activation energies for this biological system, the van't Hoff-Arrhenius equation predicts a doubling of the rate constant with each temperature increase of 10°C. Conversely, the rate of degradation would be predicted to halve given a 10°C decrease in temperature from 20°C to 10°C as might be expected for the variation from bench test temperatures to those in the subsurface soils. Therefore, the more appropriate degradation rates to consider when predicting treatment times would be 5 to 15 mg HC/kg soil per day.

If the above rates are considered to represent zero order kinetics, then the estimated treatment times for when 80 to 95 percent removals are achieved could range from 2 to 5 years or 3 to 10 200-day treatment periods.

Nutrient Considerations

There does not appear to be a significant difference in rate of respiration or amount of hydrocarbon degradation between the duplicate columns or between the nutrient amended and non-amended columns over the 90-day period of operation. Although TC04 demonstrated what appeared to be higher respiration rates, when normalized to grams of soil actually exposed to oxygen (unsaturated zone) the rates of oxygen consumption per gram of contaminated soil were roughly equivalent with TC02 and TC03.

Results of nutrient analysis after 90 days of operation show an average decline in ammonia concentrations of 16.5 mg/kg soil and a decline in TKN concentrations of 50 mg/kg in both amended and unamended columns. On the average, phosphate concentrations remained approximately the same (60 mg/kg). These results indicate that nitrogen could become limiting over extended periods of treatment if no other source is provided.

Conclusions

For the 90-day treatment period, estimates are that 15 percent of hydrocarbon loss is due to biodegradation of hydrocarbons to CO_2, 14 percent due to volatilization, and 71 percent physical separation of phase from soil bound to free product. Problems with variability in hydrocarbon distribution within the soil account for the inability to obtain a definitive mass balance on the system. Incorporation of carbon into biomass was conservatively not used in order to obtain the temperature corrected mass balance derived biodegradation rate of 2.5 mg HC per kg soil per day.

Respiration rates were comparable to results for similar constituents as reported elsewhere [8, 10, 11, 12] for in situ systems that have exhibited up to 55 percent hydrocarbon loss due to biodegradation over a 7-month time frame. Steady state oxygen requirements for the 90-day treatment period appeared to approach 2 percent oxygen for two pore volume exchanges per day. These rates translate to temperature corrected stoichiometrically derived biodegradation rates of 5 to 15 mg HC/kg soil/ day or 2 to 5 years of treatment to reach remediation goals.

Nutrient amendment did not demonstrate a statistical increase in respiration rates, but final analysis indicates that the ammonia and organic forms of nitrogen may become exhausted as biodegradation continues. Respiration rates appear more favorable in amended than in unamended columns, however, this is due to the fact that roughly one-third less of the column was available for aerobic biodegradation.

Volatilization of hydrocarbons was a component of hydrocarbon loss (approximately 14 percent) at the air flow rates provided. Volatilization is a function of the equilibrium between air and contaminant. If flows through the full-scale system are increased, amounts of volatilized hydrocarbons will likely initially increase proportionately. Eventually, however, the amount of loss due to volatilization is likely to decrease with time as the easily volatilized compounds are stripped.

Recommendations

Additional testing is recommended to better identify the character of the volatile hydrocarbons and the free product. The gas chromatographic profile of the volatile hydrocarbons purged from the hydrocarbon traps differs from the profile of the free product material, and it is not clear whether this is because of microbial respiration changing the character of the hydrocarbon or due to concentrating effects occurring on the carbon traps. In addition, free product during the preliminary study should be tested for specific gravity, viscosity, and ignitability. Measurement of dissolved hydrocarbons should be measured in the liquid fraction of the nutrient amended column to confirm the initial mass balance approach presented in this report.

Predesign Issues

The principal considerations for preparation of the predesign for the bioremediation system and for its interface with other components of the Onalaska remedial alternative are as follows:

- Full-scale oxygen supply rates and corresponding hydrocarbon disappearance
- Vertical (well) air supply versus horizontal pipe supply
- Necessity for nutrient addition as treatment progresses
- Intermixing of oxygen with landfill gases and the potential for creating fires or explosive mixtures
- Physical constraints to placement of wells/horizontal headers imposed by location of the groundwater treatment system and landfill cap
- Effect of oxygen addition on extraction well biofouling/iron precipitation
- Accompanying air injection with air extraction, and the benefits/ detriments
- Amount of volatilization expected to occur

- The effect that air injection will have upon generation of free product and potential loading to the groundwater table

- Appropriate indicators of full-scale operation such as CO_2 or the use of scheduled respiration studies.

The predesign report documents assumptions and extrapolations of the treatability study results used to determine the above components of the design.

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ATTACHMENT 1
SOIL SAMPLING

MEMORANDUM CH2MHILL

TO: Kevin Adler/U.S. EPA, Region 5

COPIES: Steve Keith/CH2M HILL Site Manager
Paul Boersma/CH2M HILL

FROM: Chris Ohland/CH2M HILL Field Task Leader
Ellen Russell/CH2M HILL

DATE: January 10, 1992

SUBJECT: Onalaska Municipal Landfill Site
Treatability Study Activities

PROJECT: GLO65602.PD.H6

Introduction

This memorandum documents the activities performed from August and through October 1991 at the Onalaska Municipal Landfill site related to treatability testing of the in situ enhanced biodegradation technology. In situ soil gas measurements were taken in August. September activity involved the collection of subsurface soil samples for the treatability preliminary test. October activity involved the collection of subsurface soil samples for the treatability test. Individuals onsite for the events were as follows:

In Site Soil Gas Measurements	**Subsurface Soil Sampling**
Paul Boersma/CH2M HILL	Jeff Lamont/CH2M HILL
Steve Keith/CH2M HILL	Chris Ohland/CH2M HILL
	Aaron Petri/CH2M HILL
	McHugh Excavation Co.

This memorandum discusses the in situ soil vapor measurement, test pitting, subsurface soil sampling procedures, and the sample handling that occurred.

In Situ Soil Gas Measurements

A 7-foot-long soil vapor sampling probe was driven into the soil adjacent to MW3S. A vacuum pump was attached to the probe exit, and interstitial soil gas was withdrawn and collected in Tedlar bags.

Oxygen composition of the soil gas was measured using a hand-held LEL meter of the type typically used for health and safety monitoring. Oxygen was not present at measurable levels

using the device and was found to be less than the detection limit for the instrument (< 0.5 percent O_2).

Carbon dioxide was measured using a Ferrite Gas Meter and found to be in the range of 20 percent. Methane was measured using a hand-held methane detector and was also found in the 20 percent range.

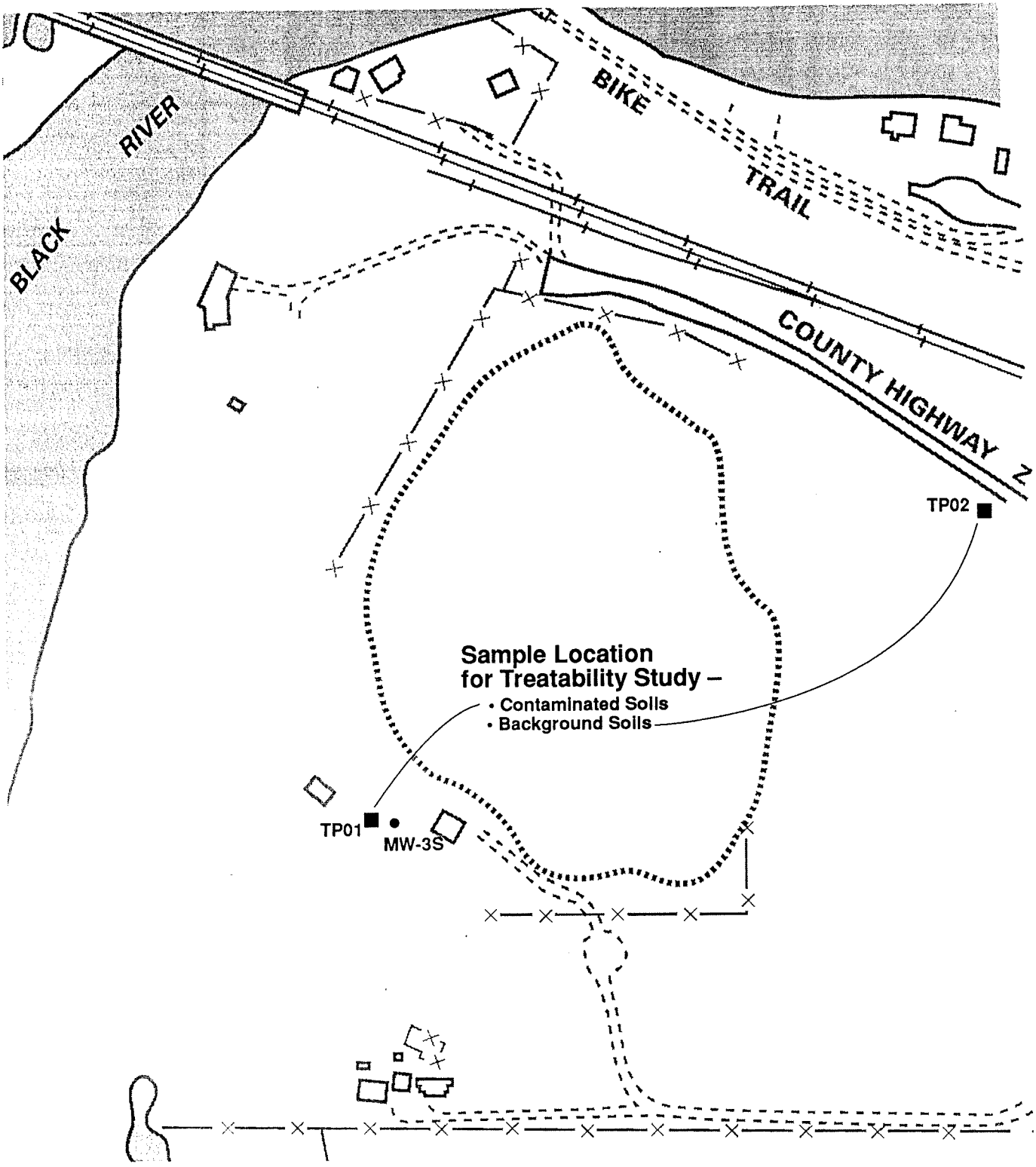
The gaseous composition of the soil vapor appeared to indicate anaerobic conditions as would be expected in the subsurface environment near a landfill. The presence of CO_2 and CH_4 (end products of anaerobic respiration) also indicate that biological activity was likely occurring. This finding had relevance to the treatability study in that it indicated conditions favorable for bacterial growth and that oxygen was likely a limiting factor to aerobic respiration in this subsurface environment.

Test Pitting Activities

McHugh Excavation Company provided an extended reach backhoe for excavation. Two pits were excavated (Figure 1). The location adjacent to MW3S represented the area that corresponded to the highest subsurface soil contamination encountered during the remedial investigation. The upgradient location represented background or uncontaminated subsurface conditions.

A portion of the first test pit (TP01) was excavated to observe the subsurface soil conditions and to identify the depth of the zone of nonaqueous phase contamination (ZNAP). The ZNAP was first encountered at a depth of 8 feet below ground. The ZNAP was present as a layer from 8 to 12 feet below ground surface to the groundwater table. No additional test pitting was attempted after encountering the water table. The soil within the ZNAP was discolored and grey with an oily sheen. A distinct boundary was present between the ZNAP and the overlying sandy soils. HNu readings from the soils in the area were as high as 200 to 300 ppm.

The excavation was backfilled and the backhoe was repositioned a short distance away from the backfilled area. TP01 was then extended and excavated to a depth of 1 foot above but not into the ZNAP. The vertical walls of the test pit were contoured to prevent surface soils from falling into the bottom of the test pit. The backhoe was then moved to the decontamination pad and steam cleaned. After cleaning, the backhoe was repositioned at the excavation. These activities were perform to prevent contamination of ZNAP soils collected for the test columns by non-ZNAP soils and to minimize the duration of time the soils would be exposed while packing the test columns.



LEGEND

LIMITS OF LANDFILL AS DETERMINED BY GEOPHYSICAL SURVEY

TP01 ■ TEST PIT LOCATION

● MONITORING WELL 3S LOCATION

N

0 200

SCALE IN FEET

FIGURE 1
SUBSURFACE SOIL SAMPLING LOCATIONS
ONALASKA RD
TREATABILITY STUDY

GLO65602.PD.H6 Subsurf Soil Samp 1-10-92mms

The test pit was excavated an additional 2 feet exposing the ZNAP, and one full bucket of contaminated soils was brought to the surface. Test columns 01 and 02 and additional glass jars were filled with material from the first bucket. A second full bucket was taken from the same depth and used to fill test columns 03 and 04 and additional glass jars.

After soils were packed into the columns, the test pit was backfilled. The grey soils were placed in the hole first, followed by the uncontaminated material that was filled to the surface. Compaction of the soil was performed by tamping the earth with the backhoe bucket.

The backhoe and bucket were decontaminated using a pressurized steam and hot water rinse before moving to the northeast corner of the site. Here the background soil sample was collected from test pit TP02 at a depth 8 feet below ground (Figure 1). The background soil was packed into a clean 5-gallon plastic bucket and sealed with an airtight cover. Additional soil was collected in a clean cooler. Despite efforts to locate this pit in an "uncontaminated" portion of the site, some landfill debris/trash was encountered within a layer 4 to 6 feet below ground.

The background pit was backfilled and compacted before the excavation crew left the site.

Subsurface Soil Sample Collection

Once the backhoe bucket was brought to the surface from TP01, sterilized soil sampling equipment was used to remove the soil directly from the bucket and placed into the prepared test columns. All columns were alcohol swabbed, weighed empty, and labeled. No sieving or screening of the soil was performed. All efforts were taken to minimize volatilization of volatile components and to collect samples as rapidly as possible. To ensure even distribution of soil within the columns, they were periodically lifted and dropped onto a hard surface. This caused soil to collapse and fill large voids. After filling the test columns, a polypropylene mesh was inserted at the end of the column and the test column was sealed with its removable end. Each test column was placed in a cooler for transport to the treatability laboratory.

Four soil columns were filled with the contaminated material as were four 4-oz wide-mouth glass sample jars. Soil samples collected from the background area (TP02) were placed into a cooler and 5-gallon bucket for transport to the treatability laboratory.

Sample Handling

After sampling, columns were laid on their side inside 80-quart coolers for transport to the laboratory. Coolers were kept upright during transport and while in cold storage at CH2M HILL's Treatability Laboratory in New Berlin, Wisconsin. Soil samples were sealed and kept on ice before being shipped for analysis at CH2M HILL's Laboratory in Corvallis, Oregon. All samples were handled using chain-of-custody procedures at all times.

GLT272/001.51

ATTACHMENT 2
ANALYTICAL METHODS

METHODS OF SOIL ANALYSIS

Part 2

Chemical and Microbiological Properties

Second Edition

A. L. Page, *Editor*

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METHOD FOR BETX AND TPH IN SOIL, WATER, AND AIR

CH2M HILL: Carbon Disulfide Extraction/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 whole soil and water samples and vapor phase samples captured on sorbent traps for benzene, ethyl benzene, toluene, and xylenes (BETX) and petroleum hydrocarbons (HC) parameters. This method was developed to support the Onalaska Site Remedial Design Treatability Study.

Target Constituents

Benzene
Ethylbenzene
Toluene
Xylene
Petroleum Hydrocarbons

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

1.3 Sample concentration techniques are utilize to lower the limits of detection.

2.0 SUMMARY OF METHOD

2.1 Vapor Phase Hydrocarbons: soil gas vapor is passed through coconut charcoal based sorbent tubes trapping vapor phase hydrocarbons. The hydrocarbon compounds are extracted with carbon disulfide from the sorbent tube and are analyzed by high resolution gas chromatography using flame ionization detection.

2.2 Soil: A quantity of soil is extracted with carbon disulfide and the extract is analyzed by high resolution gas chromatography using flame ionization detection.

2.3 Water: A quantity of water is extracted with carbon disulfide and the extract is 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 The 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 in order to avoid harmful exposure.

4.2 Lab 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 is comprised of a gas chromatograph equipped with flame ionization detection (FID), programmable thermal oven, electronic integration, report annotation, high resolution capillary chromatographic column.

5.6 Chromatographic Column——Restek Rt_x-5; 60m, 0.53mm ID, 3.0μm.

5.7 Coconut Base Charcoal Sorbant Tube——commercially available, 400mg/200mg packing configuration.

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

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

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

6.1 Stock Standards——benzene, ethyl benzene, toluene, xylenes and o-terphenyl are purchased neat or as commercially prepared standard mixtures traceable to the National Institute of Standards and Technology (NIST).

For total petroleum hydrocarbons the soil contamination which exists as a free product, will be isolated from the contaminated soil. Gravimetric standards will prepared from the isolated free product.

6.2 Working Standards——prepared from stock standards by precise dilution with carbon disulfide.

Surrogate Spike Solution prepared with o-terphenyl in carbon disulfide at 100—mg/ml

TPH Matrix Spiking Solution——prepared with isolated free product at 14,000—μg/mL

BETX Matrix Spiking Solution——prepared with benzene, ethyl benzene, toluene, xylenes at 10—μg/ml

6.3 Calibration Standards——calibration standards are prepared from stock standards by precise serial dilution. Five concentration levels should be used. The lowest standard should be a concentration level at or near the detection limit and the remaining standards should cover the linear range of concentration expected in the samples.

TPH Initial Calibration Solutions prepared with isolated free product in carbon disulfide at 175—μg/mL, 350—μg/mL, 700—μg/mL, 1400—μg/mL, 2800—μg/mL, and 5600—μg/mL

BETX Continuing Calibration Solution——prepared with benzene, ethyl benzene, toluene, and xylenes in carbon disulfide at 0.50—μg/mL, 3.0—μg/mL, 12.0—μg/mL, 30.0—μg/mL, and 60.0—μg/mL

TPH Continuing Calibration Solution prepared with isolated free product and o-terphenyl in carbon disulfide at 1400—μg/mL and 400—μg/mL, respectively.

BETX Continuing Calibration Solution——prepared with benzene, ethyl benzene, toluene, xylenes, and o-terphenyl in carbon disulfide at approximately 12—μg/ml and 400—μg/mL, respectively.

6.4 Sodium Sulfate——analytical grade dried in a oven for a minimum of 24-hours at a temperature that will drive off bound water.

6.5 Ultrapure helium——carrier gas.

6.6 Hydrocarbon free air——detector gas

6.7 Hydrogen——detector gas

7.0 SAMPLE PREPARATION and STORAGE

7.1 Soil Samples

7.1.1 Three 1-gram aliquots of soil are combined into a tared 25- by 300-mm glass test tube and the weight is recorded. Keep the test tube capped as often as possible.

7.1.2 A 3-gram aliquot of sodium sulfate is added to the tube, capped and shaken to mix the soil and sodium sulfate.

7.1.3 A 20—μL aliquot of surrogate spiking solution is added to all samples. A 100—μL aliquot of matrix spiking solution is added to the sample selected as a matrix spike.

7.1.4 A 3-ml portion of carbon disulfide is added to the soil sample. A small magnetic stir bar is also added and the mix is stirred for a minimum of 5-minutes. During this time the sample and position of the test tube may have to be manipulated to maintain the stirring action. This extract is transferred to a 10—mL culture tube and stored capped. The extraction sequence is repeated twice as described above and the extracts combined.

7.1.5 The final extract volume is adjusted to 7.0-ml. A gentle stream of air or helium may be used to reduce the volume of carbon disulfide; however, experience has shown that of the 9-ml carbon disulfide added during the preparation steps less than 7-ml is recovered. The loss is attributed to volatilization or remains within the soil pores.

7.1.6 A mark is scribed on the culture tube to monitor losses of the solvent during storage.

7.1.7 The prepared sample is ready for analysis. Add a 1—mL aliquot of the extract to a 2—mL auto—injection vial and crimp the top.

7.2 Water Samples (this extraction scheme has not been assessed)

7.2.1 A 3-ml aliquots of water are combined into a tared 25- by 300-mm glass test tube and the weight is recorded. Keep the test tube capped as often as possible.

7.2.2 The surrogate spiking solution is added to all samples. The matrix spiking solution is added to the sample selected as a matrix spike.

7.2.3 A 3-ml portion of carbon disulfide is added to the water sample. The tube is capped and shaken for 1-minute. After the organic phase has separated it is transferred to a 10- by 100-mm culture tube and stored capped. The extraction sequence is repeated twice as using 2-mL portion as described above and the extracts combined.

7.2.4 The final extract volume is adjusted to 7.0-ml. A gentle stream of air or helium may be used to reduce the volume of carbon disulfide.

7.2.5 A mark is scribed on the culture tube to monitor losses of the solvent during storage.

7.3 Charcoal Sorbant Samples

7.3.1 The glass ends of the sorbant tube are broken and the contents of the each end are transferred into separate glass auto-injection vials.

7.3.2 A 20—μL aliquot of surrogate spiking solution is added to all samples. A 100—μL aliquot of matrix spiking solution is added to the sample selected as a matrix spike.

7.3.3 A 980-μl (880—μL for matrix spike samples) portion of carbon disulfide is added to the charcoal sorbant sample and the vial is crimped with a Teflon™ lined septa cap. If a ultrasonic disrupter cell is available then the vial should be placed into the vial and agitated. Without the ultrasonic disrupter, the contents of the vial should be allowed to equilibrate for a period of 12 hours with continuous agitation.

7.3.4 A mark is scribed on the vial to monitor losses of the solvent during storage.

7.3.5 The prepared sample is diluted for analysis. Add 25—μL of extract to 975—μL of carbon disulfide in to a 2—mL auto—injection vial and crimp the top.

8.0 PREPARATION OF CHROMATOGRAPH CALIBRATION CURVE

8.1 Dynamic external calibration——five level calibration at approximately the expected range of the target constituents. 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.

8.1.2 For petroleum hydrocarbons analyses integrate the peak area in the time interval from 4 to 12 minutes.

8.2 Calibration Check——a calibration check shall be performed with the analysis of each working day's lot of samples or with each lot of 12 samples, whichever is more frequent. 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 re-calibration 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 The following instrument operating conditions are provided as a guide. Different instruments may require different operating conditions.

9.2.1 Oven temperature program

$$30°C\ (hold\ 10\ minutes) \xrightarrow{ramp\ 8°C\ per\ minute} 325°C\ (hold\ 5\ minutes)$$

9.2.2 GC temperature setpoints

Injector temperature = 150°C

Detector temperature = 250°C

9.2 For petroleum hydrocarbon measurements integrate the peak area from 4 to 20 minutes.

9.3 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 five levels plus a blank is performed on the GC-FID system. The calibration system uses standard reference materials. For the Onalaska Treatability Study the system will be calibrated with the free product which has been extracted from the contaminated soil. 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 . Matrix spikes are prepared in the same manner as calibration standards. 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 minutes, whichever is greater.

METHOD 8020

AROMATIC VOLATILE ORGANICS

1.0 SCOPE AND APPLICATION

1.1 Method 8020 is used to determine the concentration of various aromatic volatile organic compounds. Table 1 indicates compounds which may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8020 provides chromatographic conditions for the detection of aromatic volatile compounds. Samples can be analyzed using direct injection or purge-and-trap (Method 5030). Ground water samples must be determined using Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a photo-ionization detector (PID).

2.2 If interferences are encountered, the method provides an optional gas chromatographic column that may be helpful in resolving the analytes from the interferences and for analyte confirmation.

3.0 INTERFERENCES

3.1 Refer to Method 5030 and 8000.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A field sample blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph:

4.1.1 **Gas Chromatograph:** Analytical system complete with gas chromatograph suitable for on-column injections or purge-and-trap sample introduction and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS FOR AROMATIC VOLATILE ORGANICS

Compound	Retention time (min) Col. 1	Retention time (min) Col. 2	Method detection limit[a] (ug/L)
Benzene	3.33	2.75	0.2
Chlorobenzene	9.17	8.02	0.2
1,4-Dichlorobenzene	16.8	16.2	0.3
1,3-Dichlorobenzene	18.2	15.0	0.4
1,2-Dichlorobenzene	25.9	19.4	0.4
Ethyl Benzene	8.25	6.25	0.2
Toluene	5.75	4.25	0.2
Xylenes			

[a] Using purge-and-trap method (Method 5030).

TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-level soil	10
Water miscible liquid waste	500
High-level soil and sludge	1250
Non-water miscible waste	1250

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b]PQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

4.1.2 **Columns:**

4.1.2.1 Column 1: 6-ft x 0.082-in I.D. #304 stainless steel or glass column packed with 5% SP-1200 and 1.75% Bentone-34 on 100/120 mesh Supelcort or equivalent.

4.1.2.2 Column 2: 8-ft x 0.1-in I.D. stainless steel or glass column packed with 5% 1,2,3-Tris(2-cyanoethoxy)propane on 60/80 mesh Chromosorb W-AW or equivalent.

4.1.3 **Detector:** Photoionization (PID) (h-Nu Systems, Inc. Model PI-51-02 or equivalent).

4.2 Sample introduction apparatus: Refer to Method 5030 for the appropriate equipment for sample introduction purposes.

4.3 Syringes: A 5-mL Luerlok glass hypodermic and a 5-mL, gas-tight with shutoff valve.

4.4 Volumetric flask: 10-, 50-, 100-, 500-, and 1,000-mL with a ground-glass stopper.

4.5 Microsyringe: 10- and 25-uL with a 0.006-in I.D. needle (Hamilton 702N or equivalent) and a 100-uL.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit (MDL) of the parameters of interest.

5.2 Stock standards: Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standards in methanol using assayed liquids. Because of the toxicity of benzene and 1,4-dichlorobenzene, primary dilutions of these materials should be prepared in a hood.

5.2.1 Place about 9.8 mL of methanol in a 10-mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.2.2 Using a 100-uL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.2.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter (ug/uL) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction

to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store, with minimal headspace, at 4°C and protect from light.

5.2.5 All standards must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

5.3 Secondary dilution standards: Using stock standard solutions, prepare in methanol secondary dilution standards, as needed, that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Paragraph 5.4 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace for volatiles and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.4 Calibration standards: Calibration standards at a minimum of five concentration levels are prepared in reagent water from the secondary dilution of the stock standards. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Each standard should contain each analyte for detection by this method (e.g., some or all of the compounds listed in Table 1 may be included). In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

5.4.1 Do not inject more than 20 uL of alcoholic standards into 100 mL of reagent water.

5.4.2 Use a 25-uL Hamilton 702N microsyringe or equivalent (variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water).

5.4.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.4.4 Mix aqueous standards by inverting the flask three times only.

5.4.5 Fill the sample syringe from the standard solution contained in the expanded area of the flask (do not use any solution contained in the neck of the flask).

5.4.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.4.7 Aqueous standards are not stable and should be discarded after 1 hr, unless properly sealed and stored. The aqueous standards can be stored up to 24 hr, if held in sealed vials with zero headspace.

5.5 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples. The compound, alpha,alpha,alpha-trifluorotoluene recommended for use as a surrogate spiking compound (Paragraph 5.6) has been used successfully as an internal standards.

5.5.1 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest as described in Section 5.4.

5.5.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 5.2 and 5.3. It is recommended that the secondary dilution standard be prepared at a concentration of 15 ug/mL of each internal standard compound. The addition of 10 uL of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 ug/L.

5.5.3 Analyze each calibration standard according to Section 7.0, adding 10 uL of internal standard spiking solution directly to the syringe.

5.6 Surrogate standards: The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with surrogate compounds (e.g, alpha,alpha,alpha-trifluorotoluene) recommended to encompass the range of the temperature program used in this method. From stock standard solutions prepared as in Section 5.2, add a volume to give 750 ug of each surrogate to 45 mL of reagent water contained in a 50-mL volumetric flask, mix, and dilute to volume for a concentration of 15 ng/uL. Add 10 uL of this surrogate spiking solution directly into the 5-mL syringe with every sample and reference standard analyzed. If the internal standard calibration procedure is used, the surrogate compounds may be added directly to the internal standard spiking solution (Paragraph 5.5.2).

5.7 Methanol: pesticide quality or equivalent. Store away from other solvents.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Volatile compounds are introduced into the gas chromatograph either by direct injection or purge-and-trap (Method 5030). Method 5030 may be used directly on ground water samples or low-level contaminated soils and sediments. For medium-level soils or sediments, methanolic extraction, as described in Method 5030, may be necessary prior to purge-and-trap analysis.

7.2 Gas chromatography conditions (Recommended):

7.2.1 **Column 1:** Set helium gas flow at 36 mL/min flow rate. The temperature program sequences are as follows: For lower boiling compounds, operate at 50°C isothermal for 2 min; then program at 6°C/min to 90°C and hold until all compounds have eluted. For higher boiling range of compounds, operate at 50°C isothermal for 2 min; then program at 3°C/min to 110°C and hold until all compounds have eluted. Column 1 provides outstanding separations for a wide variety of aromatic hydrocarbons. Column 1 should be used as the primary analytical column because of its unique ability to resolve para-, meta-, and ortho-aromatic isomers.

7.2.2 **Column 2:** Set helium gas flow at 30 mL/min flow rate. The temperature program sequence is as follows: 40°C isothermal for 2 min; then 2°C/min to 100°C and hold until all compounds have eluted. Column 2, an extremely high-polarity column, has been used for a number of years to resolve aromatic hydrocarbons from alkanes in complex samples. However, because resolution between some of the aromatics is not as efficient as with Column 1, Column 2 should be used as a confirmatory column.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 Calibration must take place using the same sample introduction method that will be used to analyze actual samples (see Section 7.4.1).

7.3.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.4 Gas chromatographic analysis:

7.4.1 Introduce volatile compounds into the gas chromatograph using either Method 5030 (purge-and-trap method) or the direct injection method. If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to purging.

7.4.1.1 Direct injection: In very limited applications (e.g., aqueous process wastes), direct injection of the sample into the GC system with a 10 uL syringe may be appropriate. The detection limit is very high (approximately 10,000 ug/L); therefore, it is only permitted when concentrations in excess of 10,000 ug/L are expected or for water-soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

7.4.2 Follow Section 7.6 of Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

7.4.3 Table 1 summarizes the estimated retention times and detection limits for a number of organic compounds analyzable using this method. An example of the separation achieved by Column 1 is shown in Figure 1. Figure 2 shows an example of the separation achieved using Column 2.

7.4.4 Record the sample volume purged or injected and the resulting peak sizes (in area units or peak heights).

7.4.5 Calculation of concentration is covered in Section 7.8 of Method 8000.

7.4.6 If analytical interferences are suspected, or for the purpose of confirmation, analysis using the second GC column is recommended.

7.4.7 If the response for a peak is off-scale, prepare a dilution of the sample with reagent water. The dilution must be performed on a second aliquot of the sample which has been properly sealed and stored prior to use.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 8000 for gas chromatographic procedures. Quality control to ensure the proper operation of the purge-and-trap device is covered in Method 5030.

8.2 Mandatory quality control to validate the GC system operation is found in Method 8000, Section 8.6.

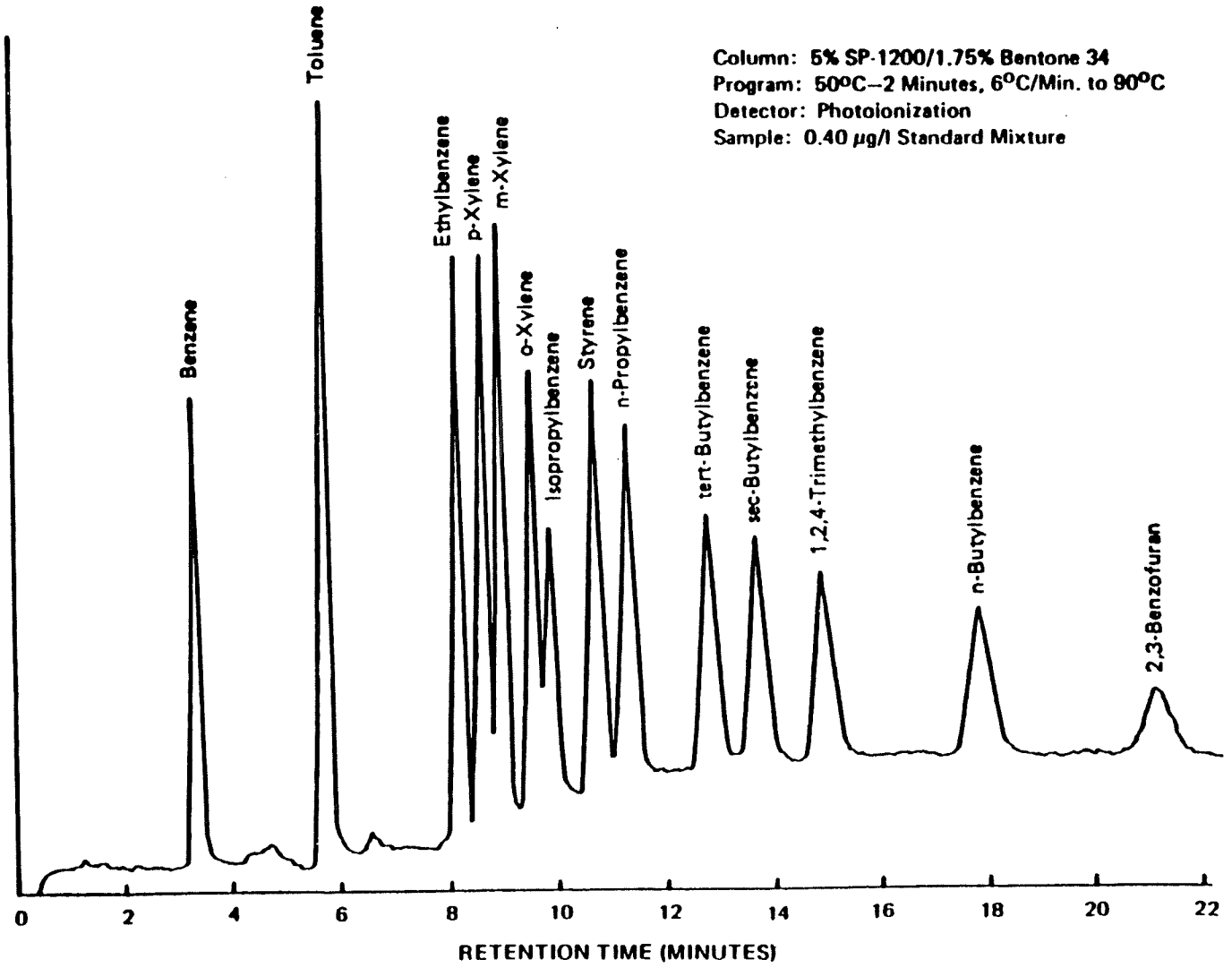

Figure 1. Chromatogram of aromatic volatile organics (column 1 conditions).

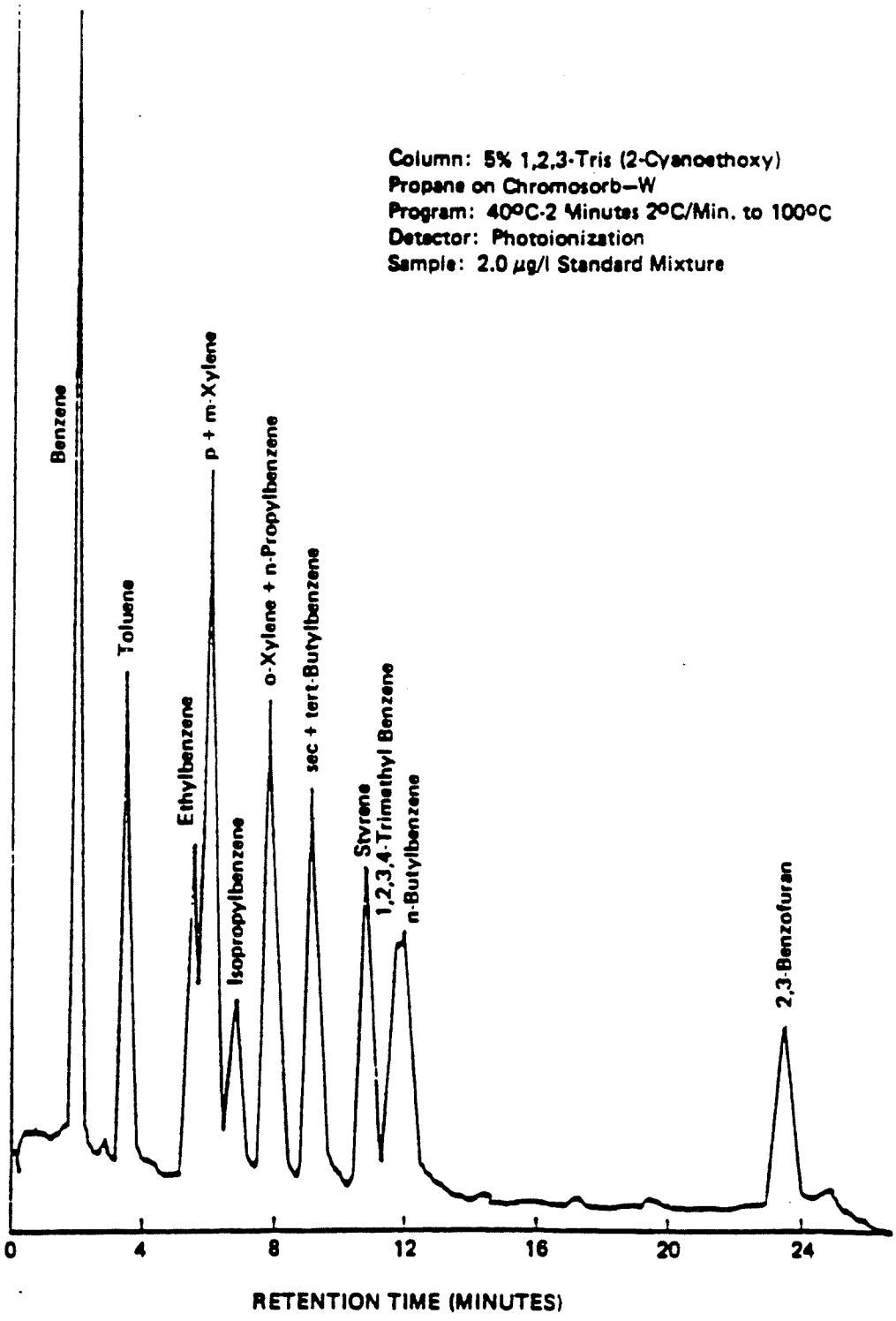

Figure 2. Chromatogram of aromatic volatile organics (column 2 conditions).

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each parameter of interest at a concentration of 10 ug/mL in methanol.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if recovery is within limits (limits established by performing QC procedure outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

9.0 METHOD PERFORMANCE

9.1 This method was tested by 20 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 2.1-500 ug/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample introduction technique, and by the calibration procedure used.

10.0 REFERENCES

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6. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

7. Provost, L.P., and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.

TABLE 3. CALIBRATION AND QC ACCEPTANCE CRITERIA[a]

Parameter	Range for Q (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range P, P_s (%)
Benzene	15.4-24.6	4.1	10.0-27.9	39-150
Chlorobenzene	16.1-23.9	3.5	12.7-25.4	55-135
1,2-Dichlorobenzene	13.6-26.4	5.8	10.6-27.6	37-154
1,3-Dichlorobenzene	14.5-25.5	5.0	12.8-25.5	50-141
1,4-Dichlorobenzene	13.9-26.1	5.5	11.6-25.5	42-143
Ethylbenzene	12.6-27.4	6.7	10.0-28.2	32-160
Toluene	15.5-24.5	4.0	11.2-27.7	46-148

Q = Concentration measured in QC check sample, in ug/L.

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

P, P_s = Percent recovery measured.

[a]Criteria are from 40 CFR Part 136 for Method 602 and were calculated assuming a QC check sample concentration of 20 ug/L. These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 1.

TABLE 4. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Benzene	0.92C+0.57	0.09$\bar{X}$+0.59	0.21$\bar{X}$+0.56
Chlorobenzene	0.95C+0.02	0.09$\bar{X}$+0.23	0.17$\bar{X}$+0.10
1,2-Dichlorobenzene	0.93C+0.52	0.17$\bar{X}$-0.04	0.22$\bar{X}$+0.53
1,3-Dichlorobenzene	0.96C-0.04	0.15$\bar{X}$-0.10	0.19$\bar{X}$+0.09
1,4-Dichlorobenzene	0.93C-0.09	0.15$\bar{X}$+0.28	0.20$\bar{X}$+0.41
Ethylbenzene	0.94C+0.31	0.17$\bar{X}$+0.46	0.26$\bar{X}$+0.23
Toluene	0.94C+0.65	0.09$\bar{X}$+0.48	0.18$\bar{X}$-0.71

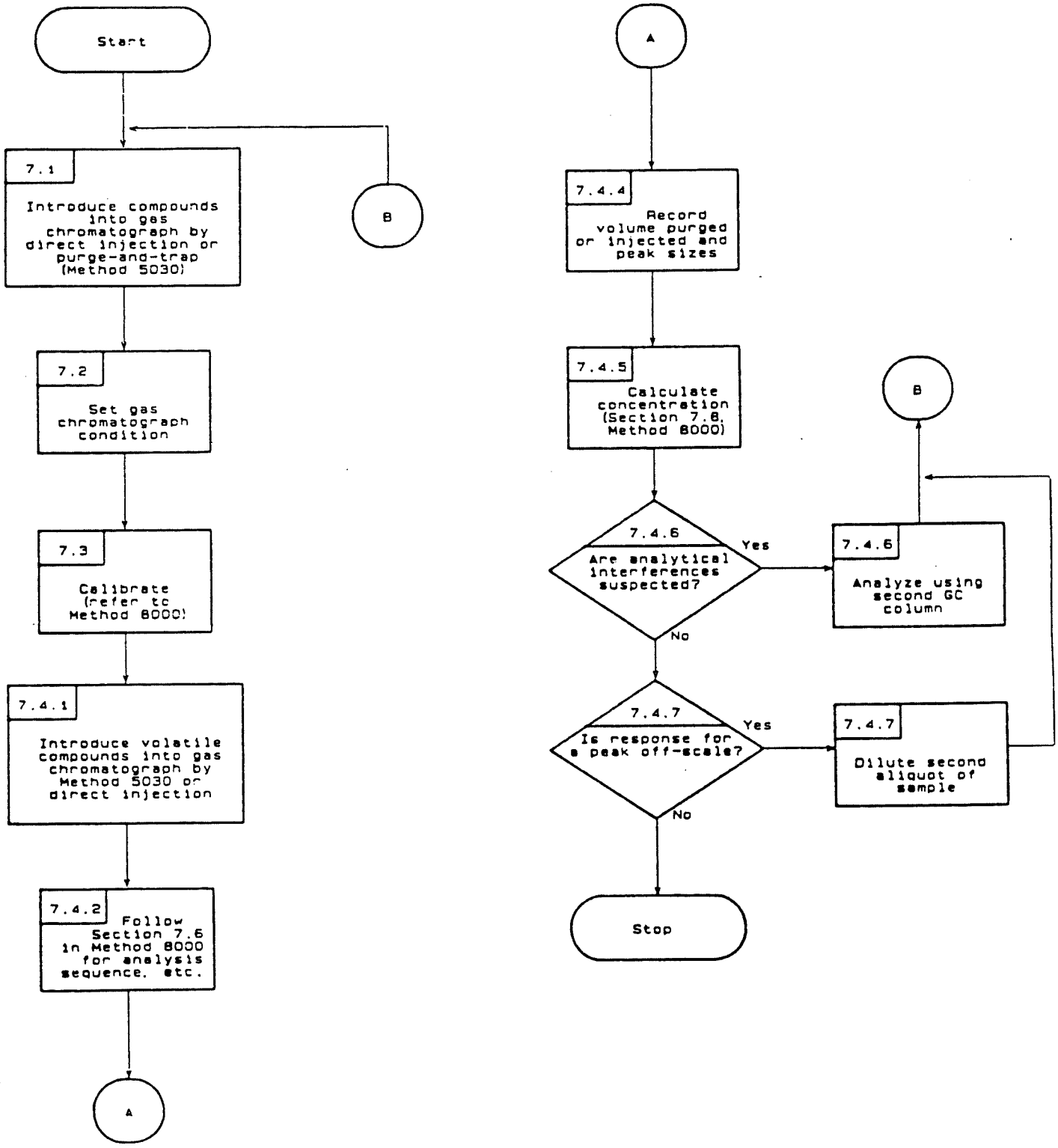
x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{X}$, in ug/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in ug/L.

C = True value for the concentration, in ug/L.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in ug/L.


Start
7.1
Introduce compounds into gas chromatograph by direct injection or purge-and-trap (Method 5030)
B
7.2
Set gas chromatograph condition
7.3
Calibrate (refer to Method 8000)
7.4.1
Introduce volatile compounds into gas chromatograph by Method 5030 or direct injection
7.4.2
Follow Section 7.6 in Method 8000 for analysis sequence, etc.
A
A
7.4.4
Record volume purged or injected and peak sizes
7.4.5
Calculate concentration (Section 7.8, Method 8000)
7.4.6
Are analytical interferences suspected?
Yes
No
7.4.6
Analyze using second GC column
B
7.4.7
Is response for a peak off-scale?
Yes
No
7.4.7
Dilute second aliquot of sample
Stop

METHOD FOR TOTAL PETROLEUM HYDROCARBONS IN SOIL

GLT175/079.51-13

PETROLEUM HYDROCARBONS, TOTAL RECOVERABLE

Method 418.1 (Spectrophotometric, Infrared)

STORET NO. 45501

1. Scope and Application
   - 1.1 This method is for the measurement of fluorocarbon-113 extractable petroleum hydrocarbons from surface and saline waters, industrial and domestic wastes.
   - 1.2 The method is applicable to measurement of light fuels, although loss of about half of any gasoline present during the extraction manipulations can be expected.
   - 1.3 The method is sensitive to levels of 1 mg/l and less, and may be extended to ambient monitoring.
2. Summary of Method
   - 2.1 The sample is acidified to a low pH (<2) and serially extracted with fluorocarbon-113 in a separatory funnel. Interferences are removed with silica gel adsorbant. Infrared analysis of the extract is performed by direct comparison with standards.
3. Definitions
   - 3.1 As in the case of Oil and Grease, the parameter of Petroleum Hydrocarbons is defined by the method. The measurement may be subject to interferences and the results should be evaluated accordingly.
   - 3.2 Oil and Grease is a measure of biodegradable animal greases and vegetable oils along with the relative non-biodegradable mineral oils. Petroleum hydrocarbons is the measure of only the mineral oils. Maximum information may be obtained using both methods to measure and characterize oil and grease of all sources.
4. Sampling and Storage
   - 4.1 A representative sample of 1 liter volume should be collected in a glass bottle. Because losses of grease will occur on sampling equipment, the collection of a composite sample is impractical. The entire sample is consumed by this test; no other analyses may be performed using aliquots of the sample.
   - 4.2 A delay between sampling and analysis of greater than 4 hours requires sample preservation by the addition of 5 ml HCl (6.1). A delay of greater than 48 hours also requires refrigeration for sample preservation.
5. Apparatus
   - 5.1 Separatory funnel, 2000 ml, with Teflon stopcock.
   - 5.2 Filter paper, Whatman No. 40, 11 cm.
   - 5.3 Infrared spectrophotometer, scanning or fixed wavelength, for measurement around 2950 cm^{-1}.
   - 5.4 Cells, 10 mm, 50 mm, and 100 mm pathlength, sodium chloride or infrared grade glass.
   - 5.5 Magnetic stirrer, with Teflon coated stirring bars.
6. Reagents
   - 6.1 Hydrochloric acid, 1:1. Mix equal volumes of conc HCl and distilled water.

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6.2 Fluorocarbon-113,(1,1,2-trichloro-1,2,2-trifluroethane), b.p. 48°C.

6.3 Sodium sulfate, anhydrous crystal.

6.4 Silica gel, 60–200 mesh, Davidson Grade 950 or equivalent. Should contain 1–2% water as defined by residue test at 130°C. Adjust by overnight equilibration if needed.

6.5 Calibration mixtures:

6.5.1 Reference oil: Pipet 15.0 ml n-hexadecane, 15.0 ml isooctane, and 10.0 ml chlorobenzene into a 50 ml glass stoppered bottle. Maintain the integrity of the mixture by keeping stoppered except when withdrawing aliquots.

6.5.2 Stock standard: Pipet 1.0 ml reference oil (6.5.1) into a tared 200 ml volumetric flask and immediately stopper. Weigh and dilute to volume with fluorocarbon-113.

6.5.3 Working standards: Pipet appropriate volumes of stock standard (6.5.2) into 100 ml volumetric flasks according to the cell pathlength to be used. Dilute to volume with fluorocarbon-113. Calculate concentration of standards from the stock standard.

7. Procedure

7.1 Mark the sample bottle at the water meniscus for later determination of sample volume. If the sample was not acidified at time of collection, add 5 ml hydrochloric acid (6.1) to the sample bottle. After mixing the sample, check the pH by touching pH-sensitive paper to the cap to insure that the pH is 2 or lower. Add more acid if necessary.

7.2 Pour the sample into a separatory funnel.

7.3 Add 30 ml fluorocarbon-113 (6.2) to the sample bottle and rotate the bottle to rinse the sides. Transfer the solvent into the separatory funnel. Extract by shaking vigorously for 2 minutes. Allow the layers to separate.

7.4 Filter the solvent layer through a funnel containing solvent-moistened filter paper into a 100 ml volumetric flask.

NOTE 1: An emulsion that fails to dissipate can be broken by pouring about 1 g sodium sulfate (6.3) into the filter paper cone and slowly draining the emulsion through the salt. Additional 1 g portions can be added to the cone as required.

7.5 Repeat (7.3 and 7.4) twice more with 30 ml portions of fresh solvent, combining all solvent into the volumetric flask.

7.6 Rinse the tip of the separatory funnel, filter paper, and the funnel with a total of 5–10 ml solvent and collect the rinsings in the flask. Dilute the extract to 100 ml. If the extract is known to contain greater than 100 mg of non-hydrocarbon organic material, pipet an appropriate portion of the sample to a 100 ml volumetric and dilute to volume.

7.7 Discard about 5–10 ml solution from the volumetric flask. Add 3 g silica gel (6.4) and a stirring bar; stopper the volumetric flask, and stir the solution for a minimum of 5 min on a magnetic stirrer.

7.8 Select appropriate working standards and cell pathlength according to the following table of approximate working ranges:

Pathlength	Range
10 mm	2–40 mg
50 mm	0.5–8 mg
100 mm	0.1–4 mg

Calibrate the instrument for the appropriate cells using a series of working standards (6.5.3). It is not necessary to add silica gel to the standards. Determine absorbance directly for each solution at the absorbance maximum at about 2930 cm^{-1}. Prepare a calibration plot of absorbance vs. mg petroleum hydrocarbons per 100 ml solution.

7.9 After the silica gel has settled in the sample extract, fill a clean cell with solution and determine the absorbance of the extract. If the absorbance exceeds 0.8 prepare an appropriate dilution.

NOTE 2: The possibility that the absorptive capacity of the silica gel has been exceeded can be tested at this point by adding another 3.0 g silica gel to the extract and repeating the treatment and determination.

7.10 Determine the concentration of petroleum hydrocarbons in the extract by comparing the response against the calibration plot.

8. Calculations

8.1 Calculate the petroleum hydrocarbons in the sample using the formula:

$$\text{mg/l Petroleum Hydrocarbons} = \frac{R \times D}{V}$$

where:

R = mg of Petroleum Hydrocarbons as determined from the calibration plot (7.10).
D = extract dilution factor, if used.
V = volume of sample, in liters.

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

METHOD FOR MOISTURE CONTENT AND TOTAL VOLATILE SOLIDS IN SOIL

GLT175/079.51-4

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.

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.

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.

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

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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.
2. MURPHY, J. & J. RILEY. 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta* 27:31.

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SLETTEN, O. & C.M. BACH. 1961. Modified stannous chloride reagent for orthophosphate determination. *J. Amer. Water Works Assoc.* 53:1031.

STRICKLAND, J.D.H. & T.R. PARSONS. 1965. A Manual of Sea Water Analysis, 2nd ed. Fisheries Research Board of Canada, Ottawa.

TOTAL ORGANIC CARBON

United States
Environmental Protection
Agency

Environmental Monitoring and
Support Laboratory
Cincinnati OH 45268

Research and Development

EPA

Test Method

Organic Carbon, Total (low level) (UV promoted, persulfate oxidation)—Method 415.2

1. Scope and Application

1.1 This method covers the determination of total organic carbon in drinking water and other waters subject to the limitations in 1.3 and 5.1.

1.2 This instrument is designed for a two-step operation to distinguish between purgeable and nonpurgeable organic carbon. These separate values are not pertinent to this method.

1.3 This method is applicable only to the carbonaceous matter which is either soluble or has a particle size of 0.2 mm or less.

1.4 The applicable range is from approximately 50 μg/L to 10 mg/L. Higher concentrations may be determined by sample dilution.

2. Summary of Method

A sample is combined with 1 mL of acidified persulfate reagent and placed in a sparger. The sample is purged with helium which transfers inorganic CO_2 and purgeable organics to a CO_2 scrubber. The CO_2 is removed with at least 99.9% efficiency with a 2.5-minute purge. The purgeable organics proceed through a reduction system where the gas stream is joined by hydrogen and passed over a nickel catalyst which converts the purgeable organic carbon to methane. The methane is measured by a flame ionization detector. The detector signal is integrated and displayed as the concentration of purgeable organic carbon.

The sample is then transferred to a quartz ultraviolet reaction coil where the nonpurgeable organics are subjected to intense ultraviolet illumination in the presence of the acidified persulfate reagent. The nonpurgeables are converted to CO_2 and transferred to a second sparger where a helium purge transfers the CO_2 to the reduction system and into the detector. The signal is integrated, added to the purgeable organic carbon value, and displayed as the concentration of total organic carbon.

3. Definitions

3.1. Total organic carbon measured by this procedure is the sum of the purgeable organic carbon and the nonpurgeable organic carbon as defined in 3.2 and 3.3.

3.2 Purgeable organic carbon is the organic carbon matter that is transferred to the gas phase when the sample is purged with helium and which passes through the CO_2 scrubber. The definition is instrument-condition dependent.

3.3 Nonpurgeable organic carbon is defined as that which remains after removal of the purgeable organic carbon from the sample containing acidified persulfate reagent and which

is converted to CO_2 under the instrument conditions.

3.4 The system blank is the value obtained in 8.2 for an irradiated, recirculated reagent distilled water sample.

4. Sample Handling and Preservation

4.1 Sampling and storage of samples must be done in glass bottles. Caution: Do not leave any headspace in the sample bottle as this may contribute to loss of purgeable organics.

4.2 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. Also, samples should be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

4.3 When analysis cannot be performed within two hours from time of sampling, the sample should be acidified to pH 2 with H_2SO_4. Note: HCl should not be used because it is converted to chlorine during the analysis. This causes damage to the instrument.

5. Interferences

5.1 If a sample is homogenized to reduce the size of the particulate matter, the homogenizing may cause loss of purgeable organic carbon, thus yielding erroneously low results.

6. Apparatus

6.1 Apparatus for blending or homogenizing samples: A household blender or similar device that will reduce particles in the sample to less than 0.2 mm.

6.2 Apparatus for Total Organic Carbon: The essential components for the apparatus used in this method are: A sparge assembly, flow switching valves, a pyrolysis furnace, quartz ultraviolet reactor coil, reducing column, flame ionization detector, electrometer and integrator. This method is based on the Dohrmann Envirotech DC-54 Carbon Analyzer. Other instruments having similar performance characteristics may be used.

6.3 Sampling Devices: Any apparatus that will reliably transfer 10 mL of sample to the sparger. A 50 mL glass syringe is recommended when analyzing samples with easily purgeable organics so as to minimize losses.

7. Reagents

7.1 Reagent Distilled Water: Distilled water used in preparation of standards and for dilution of samples should be ultra-pure to reduce the magnitude of the blank. Carbon dioxide-free, double distilled water is recommended. The water should be distilled from permanganate or be obtained from a system involving distillation and carbon treatment. The reagent distilled water value must be compared to a system blank determined on a recirculated distilled water sample. The total organic carbon value of the reagent distilled water should be less than 60 μg/L. Purgeable organic carbon values of the reagent distilled water should be less than 4 μg/L.

7.2 Potassium hydrogen phthalate, stock solution, 500 mg carbon/liter: Dissolve 1.063 g of potassium hydrogen phthalate (Primary Standard Grade) in reagent distilled water (7.1) and dilute to 1 liter.

7.3 Potassium hydrogen phthalate (2 mg/L): Pipet 4 mL of potassium hydrogen phthalate stock solution (7.2) into a one liter volumetric flask and dilute to the mark with reagent distilled water (7.1).

7.4 Potassium hydrogen phthalate (5 mg/L): Pipet 1 mL of potassium hydrogen phthalate stock solution (7.2) into a 100 mL volumetric flask and dilute to the mark with reagent distilled water (7.1).

7.5 Potassium hydrogen phthalate (10 mg/L): Pipet 2 mL of potassium hydrogen phthalate stock solution (7.2) into a 100 mL volumetric flask and dilute to the mark with reagent distilled water (7.1).

7.6 Acidified Persulfate Reagent: Place 100 mL of reagent distilled water (7.1) in a container. Add 5 g of potassium persulfate. Add 5 g (3 mL) of concentrated (85%) phosphoric acid.

7.7 Carbonate-bicarbonate, stock solution, 1000 mg carbon/liter: Place 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate in a 100 mL volumetric flask. Dissolve with reagent distilled water (7.1) and dilute to the mark.

7.8 Carbonate-bicarbonate, standard solution 50 mg/L: Place 5 ml of the carbonate-bicarbonate stock solution in a 100 mL volumetric flask and dilute to the mark with reagent distilled water (7.1).

8. Procedure

8.1 Allow at least 30 minutes warm-up time. Leave instrument console on continuously when in daily use, except for the ultraviolet light source, which should be turned off when not in use for more than a few hours.

8.2 Adjust all gas flows, temperatures and cycle times to manufacturer's specifications. Perform the "System Cleanup and Calibration" procedure in the manufacturer's specifications each day. Recirculate a sample of irradiated distilled water until two consecutive readings within 10% of each other are obtained. Record the last value for the system blank. This value is a function of the total instrument operation and should not vary significantly from previous runs. Reasons for significant changes in the value should be identified.

8.3 Check the effectiveness of the CO_2 scrubber by analyzing the carbonate-bicarbonate standard solution(7.8). Add 1 mL of acidified persulfate reagent (7.6) to 50 mL of the solution. Transfer 10 mL of the solution-with-reagent to the first sparger and start the analysis cycle. No response, or a very minor reading, should be obtained from this solution.

8.4 Add 1 mL of acidified persulfate reagent (7.6) to 50 mL of reagent distilled water (7.1) blank, standards 7.3, 7.4, and 7.5 and the samples.

8.5 Calibrate the analyzer as follows:

8.5.1 Run the reagent distilled water (7.1) and 5.0 mg/L standard (7.4): Transfer 10 mL of the solution-with-reagent to the first sparger and start analyzer cycle

Ignore the meter reading for the first cycle

Transfer a second 10 mL of the solution-with-reagent to the first sparger and start the analysis cycle

Record the meter reading (see 9.1) of the final carbon value for each of the reagent distilled water (7.1) and the standard (7.4).

If the meter reading is more than 25% above or below the calculated value of standard 7.4, reanalyze the standard

and set the calibration within 25% (8.5.4), reanalyze the system blank, and then begin 8.5.1 again. If the meter reading (see 9.1) is within 25% of the calculated value, continue to next step. The calculated value is defined in 8.5.2.

8.5.2 Calculate the factor for the deviation of the instrument reading (see 9.1) for the standard (7.4) from the calculated value by:

$$\frac{\text{standard reading - calculated value}}{\text{calculated value}} = \text{FACTOR}$$

where the calculated value is that value obtained by using the weight of potassium hydrogen phthalate and does not include the carbon contributed by the reagent distilled water (7.1) with which it has been diluted.

8.5.3 Calculate the adjusted reading by:
calculated value + (RDW - (FACTOR X RDW)) = ADJUSTED READING.
where RDW = mean reagent distilled water (7.1) value.

8.5.4 Push in CALIBRATE button after READY light comes on and adjust the SPAN control to the ADJUSTED READING calculated in 8.5.3.

8.6 Analyze the standards 7.3 and 7.5 in order to check the linearity of the instrument at least once each day:

Transfer 10 mL of the solution-with-reagent to the first sparger and start analyzer cycle

Ignore the meter reading for the first cycle

Transfer a second 10 mL of the solution-with-reagent to the first sparger and start the analyzer cycle

Record the meter reading (see 9.1) of the final carbon value for each of the standards 7.3 and 7.5.

The range of concentration used for calibrating the instrument and checking the linearity of the instrument should be ascertained from a knowledge of the range of concentrations expected from the samples. Standards for lower ranges can be prepared by diluting standards 7.2, 7.3, and 7.4.

8.7 Analyze the samples. Transfer 10 mL of sample with reagent to the first sparger and start the analysis cycle.

Transfer 10 mL of the solution-with-reagent to the first sparger and start analyzer cycle

Ignore the meter reading for the first cycle

Transfer a second 10 mL of the solution-with-reagent to the first sparger and start the analyzer cycle

Record the meter reading (see 9.1) of the final carbon value for each of the samples.

9. Calculations

9.1 The values are read off the final digital readout in μg/L. The system blank reading obtained in 8.2 must be subtracted from all reagent distilled water, standard and sample readings.

10. Precision and Accuracy

10.1 In a single laboratory (MERL), using raw river water, centrifuged river water, drinking water, and the effluent from a carbon column which had concentrations of 3.11, 3.10, 1.79, and 0.07 mg/L total organic carbon respectively, the standard deviations from ten replicates were $\pm$0.13, $\pm$0.03, $\pm$0.02, and $\pm$0.02 mg/L, respectively.

10.2 In a single laboratory (MERL), using potassium hydrogen phthalate in distilled water at concentrations of 5.0 and 1.0 mg/L total organic carbon, recoveries were 80% and 91%, respectively.

Bibliography

1. Proposed Standard Method for Purgeable and Nonpurgeable Organic Carbon in Water (UV-promoted, persulfate oxidation method). ASTM Committee D-19, Task Group 19.06.02.03 (Chairman R. J. Joyce), January 1978.

2. Operating Instruction Dohrmann Envirotech, 3420 Scott Boulevard, Santa Clara, California 95050.

3. Takahashi, Y., "Ultra Low Level TOC Analysis of Potable Waters." Presented at Water Quality Technology Conference, AWWA, Dec. 5-8, 1976.

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* $CaCl_2$.

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.

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*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.

APPENDIX B
DETAILED COST ESTIMATE

ONALASKA FACILITY SUMMARY

FACILITY NAME:	BIOVENTING PROCESS	ESTIMATE TYPE:	Facility Plan Analysis
FILE NAME:	BIOVENT.XLS	ESTIMATOR:	Jim Slattery
PROJECT NAME:	ONALASKA LANDFILL	DATE:	29-Jan-92
PROJECT NUMBER:	GLO65602.FD.EC	FACILITY TOTAL:	$114,000

DESCRIPTION	QTY	UNITS	UNIT COST	TOTAL COST	RESOURCE
DIVISION 01					
GENERAL COND./BONDS/INSUR/MOB					
% OF FACILITY TOTAL	5	%	$114,000	$6,000	Historical/Est. Judgement
DIVISION 02					
EARTHWORK/DEMO					
Header Pipe Trench Excavation	317	CY	$6.00	$1,900	Est Judgement
Imported Pipe Zone and Backfill	93	CY	$14.00	$1,301	Historical/Est Judgement
Injection Wells - Depth = #	24	EA	$480.00	$11,520	Means 026-704-0800
Soil Gas Probe Nests Depth = #	6	EA	$780.00	$4,680	Means 026-704-0800/E.J
Condensate Drain Manholes	6	EA	$750.00	$4,500	Engineer's Estimate
SUBTOTAL				$23,901	
CONTINGENCY	25	%		$5,975	
TOTAL DIVISION 02				$30,000	
DIVISION 03					
CONCRETE					
Concrete Equip Pads	1	EA	$1,500.00	$1,500	Historical/Est Judgement
SUBTOTAL				$1,500	
CONTINGENCY	25	%		$375	
TOTAL DIVISION 03				$2,000	
DIVISION 04					
MASONRY					
Pre- Engineered Treatment /Blower Building	144	SF	$50.00	$7,200	Historical/Est Judgement
SUBTOTAL				$7,200	
CONTINGENCY	25	%		$1,800	
TOTAL DIVISION 04				$9,000	
DIVISION 05					
METALS					
SUBTOTAL				$0	
CONTINGENCY	25	%		$0	
TOTAL DIVISION 05				$0	
DIVISION 06					
WOODS/PLASTIC	1	LS	$0.00	$0	
	1	EA	$0.00	$0	
SUBTOTAL				$0	
CONTINGENCY	25	%		$0	
TOTAL DIVISION 06				$0	

FACILITY NAME:	BIOVENTING PROCESS		ESTIMATE TYPE:	Facility Plan Analysis	
FILE NAME:	BIOVENT.XLS		ESTIMATOR:	Jim Slattery	
PROJECT NAME:	ONALASKA LANDFILL		DATE:	29-Jan-92	
PROJECT NUMBER:	GLO65602.FD.EC		FACILITY TOTAL:	$114,000	
DIVISION 07					
MOISTURE PROTEC.	0	SF	$0.00	$0	
	1	EA	$0.00	$0	
SUBTOTAL				$0	
CONTINGENCY	25	%		$0	
TOTAL DIVISION 07				$0	
DIVISION 08					
WINDOWS/DOORS					
SUBTOTAL				$0	
CONTINGENCY	25	%		$0	
TOTAL DIVISION 08				$0	
DIVISION 09					
PAINTING					
PERCENTAGE OF FACILITY TOTAL	2.00	%	$114,000	$2,000	Historical/Est. Judgement
DIVISION 10					
SPECIALTIES					
	1	EA	$0.00	$0	
	1	EA	$0.00	$0	
SUBTOTAL				$0	
CONTINGENCY	25	%		$0	
TOTAL DIVISION 10				$0	
DIVISION 11					
EQUIPMENT					
Blower Package	1	EA	$10,063	$10,063	Quote *1.25*1.15
SUBTOTAL				$10,063	
CONTINGENCY	15	%		$1,509	
TOTAL DIVISION 11				$12,000	
DIVISION 12					
FURNISHINGS	1	EA	$0.00	$0	
	1	EA	$0.00	$0	
SUBTOTAL				$0	
CONTINGENCY	25	%		$0	
TOTAL DIVISION 12				$0	
DIVISION 13					
I & C					
PERCENTAGE OF FACILITY TOTAL	5	%	$114,000	$6,000	Historical/Est. Judgement

FACILITY NAME:	BIOVENTING PROCESS	ESTIMATE TYPE:	Facility Plan Analysis
FILE NAME:	BIOVENT.XLS	ESTIMATOR:	Jim Slattery
PROJECT NAME:	ONALASKA LANDFILL	DATE:	29-Jan-92
PROJECT NUMBER:	GLO65602.FD.EC	FACILITY TOTAL:	$114,000

DIVISION 14					
CONVEYORS/HOISTS	1	EA	$0.00	$0	
SUBTOTAL				$0	
CONTINGENCY	25	%		$0	
TOTAL DIVISION 14				$0	
DIVISION 15					
MECHANICAL					
Pre-Engineered Building HVAC	144	SF	$10.00	$1,440	Historical/Est Judgement
6in Class 160 S.D.R. 26 PVC header pipe	1,140	LF	$10.00	$11,400	Means 026-678-2200
6 in Tees	30	EA	$65.00	$1,950	Means 026-678-8120
6 in Elbows	30	EA	$50.00	$1,500	Means 026-678-8020
2in Class 160 S.D.R. 26 PVC header pipe	420	LF	$4.25	$1,785	Means 026-678-2120
2 in Tees	30	EA	$15.00	$450	Est Judgement
2 in Elbows	60	EA	$20.00	$1,200	Est Judgement
2 in Flow Control Valve	24	EA	$75.00	$1,800	Means 151-975-3290/E.J.
6 in Flow Control Valve	1	EA	$300.00	$300	Means 151-975-3320/E.J.
Misc Fittings,Ports, Septums	48	EA	$25.00	$1,200	Est Allowance
Quick Connects	36	EA	$50.00	$1,800	Est Judgement
Condensate Drains	57	EA	$75.00	$4,275	Est Allowance
SUBTOTAL				$29,100	
CONTINGENCY	25	%		$7,275	
TOTAL DIVISION 15				$36,000	
DIVISION 16					
ELECTRICAL					
PERCENTAGE OF FACILITY TOTAL	10	%	$114,000	$11,400	Historical/Est. Judgement
TOTAL DIVISION 16				$11,000	
FACILITY TOTAL:				$114,000	

Onalaska Facility Summary
Operation and Maintenance Costs

Description	Annual O&M
Respiration Study	$16,000
Soil Gas Sampling and Analysis	4,400
Soil Sampling and Analysis	8,000
Electrical	
Blower power requirement	5,600
Mechanical	
Blower and motor maintenance	2,000
Total Annual O&M	**$36,000**

Present Worth O&M Analysis:
5% interest, 10-year operation = $278,000

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Onalaska Facility Summary
Preliminary Design Cost Estimate
In Situ Bioremediation

Capital Cost	$114,000
Services During Construction	15,000
	$129,000
Operation and Maintenance	($36,000/yr)
Present Worth O&M	$278,000
Total Estimate	**$407,000**

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