ON-SITE ENGINEERING REPORT OF THE SLURRY-PHASE BIOLOGICAL REACTOR FOR PILOT-SCALE TESTING ON CONTAMINATED SOIL

by

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Technical Project Officer

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory (RREL) is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This report describes the results of a pilot-scale test of slurry-phase bioremediation technology for treatment of creosote-contaminated soil. The data will be used to develop best demonstrated available technology (BDAT) standards for contaminated soil in support of the land disposal restrictions under the 1984 Resource Conservation and Recovery Act (RCRA) Hazardous and Solid Waste Amendments (HSWA).

E. Timothy Oppelt, Director
Risk Reduction Engineering Laboratory

ABSTRACT

The EPA's Office of Solid Waste and Emergency Response (OSWER) is currently developing land disposal restrictions (LDRs) for contaminated soil and debris (CS&D). The Office of Research and Development, through its Risk Reduction Engineering Laboratory (RREL), is providing support to OSWER by supplying technical data on the performance of selected types of technologies for CS&D treatment. Based on the technical data supplied by RREL and other data obtained from independent sources, OSWER will prepare a regulatory package that establishes BDAT standards for the level of CS&D treatment required prior to land disposal.

IT Environmental Programs (ITEP), is providing the U.S. Environmental Protection Agency's (EPA's) Risk Reduction Engineering Laboratory (RREL) with technical data on the bioslurry treatment technology. The technology uses a slurry-phase bioreactor in which the soil is mixed with water to form a slurry. Microorganisms and nutrients are added to the slurry to enhance the biodegradation process, which converts organic wastes into relatively harmless byproducts of microbial metabolism and inorganic salts.

A pilot-scale test of the slurry-phase bioremediation technology was performed by ECOVA Corporation (ECOVA) at the U.S. EPA Test and Evaluation (T&E) facility from May 8 through July 10, 1991 (12 weeks). The slurry-phase bioreactors were tested on a creosote-contaminated soil from the Burlington Northern Superfund Site in Brainerd, Minnesota. The results of the bench-scale study (performed by ECOVA prior to the pilot-scale study) were used to optimize a pilot-scale bioreactor system containing 64 liters of 30 percent slurry (soil:water, w/v). The pilot-scale phase utilized an inoculum of indigenous polynuclear aromatic hydrocarbon (PAH) degraders (9.3×10^7 per gram of soil), an inorganic nitrogen supplement in the form of NH_4-N, and a media broth containing potassium, phosphate, magnesium, calcium, and iron to achieve an overall reduction. During the study, levels of soil-bound and liquid-phase PAHs, total petroleum hydrocarbons (TPHs), nutrients, pH, dissolved oxygen, temperature, toxicity, and microbial activity were monitored. The total percent reduction of soil-bound PAHs achieved over 9 weeks of testing ranged from >44.2 to >97.1 percent. The total percent reduction of PAHs achieved over 12 weeks ranged from >74.2 to >90.6 percent. This report presents detailed information concerning the operation, sampling and analysis, and results achieved with the pilot-scale slurry-phase bioremediation system.

This report was submitted in fulfillment of Contract No. 68-C9-0036 by IT Environmental Programs, Inc., under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from 1 October 1989 to 31 March 1992, and work was completed as of 31 March 1992.

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ACKNOWLEDGMENT

This report was prepared for the U.S. Environmental Protection Agency, Office of Research and Development, Risk Reduction Engineering Laboratory, Cincinnati, Ohio, by IT Environmental Programs (ITEP) under Contract No. 68-C9-0036. Mr. Richard P. Lauch was the EPA Technical Project Monitor. The principal authors of this report were Mr. Majid Dosani of ITEP and Dr. Alan Jones of ECOVA Corporation. Other personnel contributing to the project were Ms. Judy Hessling (ITEP), Mr. Michael Smith (ITEP), Mr. Ernie Grossman (U.S. EPA), Dr. William Mahaffey (ECOVA), Ms. Madonna Brinkman (ECOVA), and Mr. Christopher Krauskopf (ECOVA).

ACRONYMS (continued)

RPD	Relative percent difference
RREL	Risk Reduction Engineering Laboratory
SAP	Sampling and Analysis Plan
SOP	Standard Operating Procedure
TCL	Target Compound List
TCLP	Toxicity characteristic leaching procedure
T&E	Test and evaluation (facility)
THC	Total hydrocarbons
TKL	Total Kjeldahl nitrogen
TOC	Total organic carbon
TOX	Total organic halogens
TPH	Total petroleum hydrocarbons
TRPH	Total recoverable petroleum hydrocarbons (by infrared spectroscopy)
TS	Total solids
TSS	Total suspended solids
TVS	Total volatile solids
TVSS	Total volatile suspended solids
WCAP	Waste Characteristic Approval Plan

TABLES (continued)

LIST OF ACRONYMS

BDAT	Best demonstrated available technology
BN	Burlington Northern
BNA	Base neutral and acids
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CFU	Colony-forming unit
CLP	Contract Laboratory Program
CS&D	Contaminated soil and debris
CMC	Critical micelle concentration
CSTR	Continuously stirred tank reactor
EPA	Environmental Protection Agency
GC-MS	Gas chromatography - mass spectrometry
GPC	Gel permeation chromatography
HSWA	Hazardous and Solid Waste Amendments
IDL	Instrument detection limit
IT	IT Corporation
ITAS	IT Analytical Services
ITEP	IT Environmental Programs
LDR	Land disposal restrictions
LOD	Limits of detection
LTTD	Low-temperature thermal desorption
MDL	Method detection limit
MS/MSD	Matrix spike/matrix spike duplicate
O&G	Oil and grease
OER	Onsite Engineering Report
ORD	Office of Research and Development
OSW	Office of Solid Waste
OSWER	Office of Solid Waste and Emergency Response
PAH	Polynuclear aromatic hydrocarbon
PCA	Plate count agar
PCB	Polychlorinated biphenyl
PMS	PAH mineral salts (plates)
PMSS	PMS (plates) with 0.05% salicylate
PQL	Practical quantitation limit
QA/QC	Quality assurance/quality control
RCRA	Resource Conservation and Recovery Act
ROD	Record of Decision

SECTION 1

INTRODUCTION

The 1984 Hazardous and Solid Waste Amendments (HSWA) to the Resource Conservation and Recovery Act (RCRA) prohibit the continued land disposal of untreated hazardous wastes beyond specified dates. The statute requires the U.S. Environmental Protection Agency (EPA) to set "levels or methods of treatment, if any, which substantially diminish the toxicity of the waste or substantially reduce the likelihood of migration of hazardous constituents from the waste so that short-term and long-term threats to human health and the environment are minimized." The legislation sets forth a series of deadlines beyond which further disposal of untreated wastes is prohibited. Land disposal restrictions (LDRs) have been set for solvents and dioxins; the California List; and first-, second-, and third-third hazardous wastes. These LDRs establish concentration- or technology-based treatment standards that must be met prior to land disposal of RCRA-regulated hazardous wastes. These treatment standards are also applicable to soil and debris contaminated with these wastes at uncontrolled hazardous waste sites under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA or Superfund) and at RCRA corrective-action and closure sites.

Contaminated soil and debris (CS&D) pose a special problem because of their complexity and high degree of variability. Therefore, the EPA has determined the need for a detailed evaluation of treatment technologies for CS&D to develop separate LDR standards applicable to their disposal. These standards are being developed through the evaluation of best demonstrated available technologies (BDATs). Once these LDRs are promulgated, only CS&D wastes that meet the LDR standards will be permitted to be disposed of in land disposal units unless a treatability variance is issued.

The EPA's Office of Solid Waste and Emergency Response (OSWER) is currently developing LDRs for CS&D. The Office of Research and Development (ORD), through its Risk Reduction Engineering Laboratory (RREL) in Cincinnati, Ohio, is supporting OSWER by providing technical data on the performance of various technologies used to treat CS&D. Based on the technical data provided by RREL, along with other data obtained from independent sources, OSWER will prepare a regulatory package that establishes BDAT standards for the level of CS&D treatment required prior to land disposal.

In support of the CS&D program, RREL is developing data on biological treatment of contaminated soil. Biodegradation involves the biooxidation of organic compounds by microorganisms. The ultimate goal of biodegradation is to convert organic wastes into biomass and relatively harmless byproducts of microbial metabolism such as carbon dioxide (CO_2), methane (CH_4), and inorganic salts. Several biodegradation technologies are available for the remediation of soils and sludges contaminated with organic compounds. These technologies include composting, in situ biodegradation, solid-phase treatment, and slurry-phase treatment. In slurry-phase bioremediation (bioslurry), contaminated soil is excavated and treated in a bioreactor in which the soil is mixed with water to form a slurry. If necessary, nutrients, microorganisms, or surfactants are added to the slurry to enhance the biodegradation process.

IT Environmental Programs (ITEP), in conjunction with RREL, evaluated the performance of pilot-scale bioslurry treatment on creosote-contaminated soil from the Burlington Northern (BN) Superfund site in Brainerd, Minnesota. ECOVA Corporation, performed the testing on the contaminated soil at the U.S. EPA Test and Evaluation (T&E) facility in Cincinnati, Ohio. Routine monitoring and analysis were performed by ECOVA either on site or at their laboratory in Redmond, Washington. All critical measurements were performed by IT Analytical Services (ITAS) in Cincinnati, Ohio.

This onsite engineering report (OER) describes the operation, sampling and analysis, and results achieved during the pilot-scale bioslurry treatment conducted on the contaminated soil at the T&E facility. The sampling procedures followed during the treatment study are outlined in the Sampling and Analysis Plan (SAP), which is

included as Appendix A. Any deviations from the original SAP are noted in this OER. The information presented in this OER will assist the CS&D group in evaluating the bioslurry treatment technology.

The OER was prepared in accordance with the guidelines established by the Office of Solid Waste (OSW) in their "Quality Assurance Project Plan for Characterization Sampling and Treatment Tests Conducted for the Contaminated Soil and Debris (CS&D) Program" (Appendix B). Sections 2 and 3 of this report describe the contaminated soil and the treatment technology under evaluation, respectively. Section 4 addresses the sampling and analysis activities, and Section 5 addresses treatment technology design and operating data collection. Section 6 presents data on all analyses performed on the treatment test samples. Section 7 discusses the quality assurance/quality control (QA/QC) measures associated with the analytical data. Any correspondence critical to the performance or evaluation of the treatment test is presented in Section 8.

The pilot-scale bioslurry test was performed from May 8 through July 10, 1991, at the T&E facility. Representatives of the U.S. EPA, ITEP, ECOVA, and S-Cubed (technical systems auditor) were present to observe the treatment technology in operation. Key personnel in attendance during the test or involved with the sampling or analytical activities are listed in Table 1-1.

TABLE 1-1. KEY PERSONNEL INVOLVED IN THE PILOT-SCALE BIOSLURRY TEST

Treatment Test Facility:	U.S. EPA Test and Evaluation Facility 1600 Gest Street Cincinnati, Ohio 45204
Test Facility Coordinator:	Mr. Frank Evans, Director U.S. EPA T&E Facility 1600 Gest Street Cincinnati, Ohio 45204 (513) 684-2621
Date of Treatment Test:	May 8 through July 31, 1991
EPA Personnel:	Richard P. Lauch Technical Project Monitor
Contract Personnel:	Judy Hessling, ITEP, CS&D Project Manager Majid Dosani, ITEP, Bioslurry Work Assignment Manager Michael Smith, ITEP, Soil Sampling Coordinator Dr. Alan Jones, ECOVA, Project Manager Dr. William Mahaffey, ECOVA, Technical Principal Madonna Brinkmann, ECOVA, Project Scientist Christopher Krauskopf, ECOVA, Project Scientist Burt Blackburn, S-Cubed, Technical Systems Auditor Greg Swanson, S-Cubed, Technical Systems Auditor
OER Preparation:	Majid Dosani, ITEP Alan Jones, ECOVA
Laboratory Manager:	Richard Gurley IT Analytical Services 11499 Chester Road Cincinnati, Ohio 45246

SECTION 2

CONTAMINATED SOIL UNDER EVALUATION

The BN Superfund Site is located on the border between Baxter and Brainerd, Minnesota. State Highway 371 is approximately 800 to 1000 feet north of the site, and the Mississippi River flows about 3000 feet east of the plant. Residential areas are located within 1000 feet to the northeast and southeast of the site. Burlington Northern has owned and operated the railroad tie treatment plant on this site since 1907. The plant uses creosote mixtures to preserve railroad ties. During the 1950s, BN began blending creosote with No. 5 fuel oil in a 1:1 ratio. At some undetermined time, this mixture was changed to creosote and coal tar, which are currently being used at the plant in the ratio of 7:3.

Historically, wastewater generated from the wood-treating process was sent to shallow, unlined surface impoundments for disposal. The first impoundment, which covered an area of approximately 60,000 ft^2, eventually became filled with sludge; and in the 1930s, it was buried under clean fill. A second impoundment was used until October 1982, when a wastewater pretreatment plant was completed. The discharge of wastewater to the disposal ponds generated a sludge that contaminated both the soil and groundwater beneath both ponds. As a result, the site was included on the proposed National Priorities List issued by the U.S. EPA in December 1982. Figure 2-1 is a map of the BN Superfund Site.

All wastewater and creosote have been removed from the second impoundment. The wastewater was transported to BN's Northtown, Minnesota, wastewater treatment plant for pretreatment and subsequent discharge to the sanitary sewer. Creosote was pumped from the pond for reuse or recycling at the BN plant. The

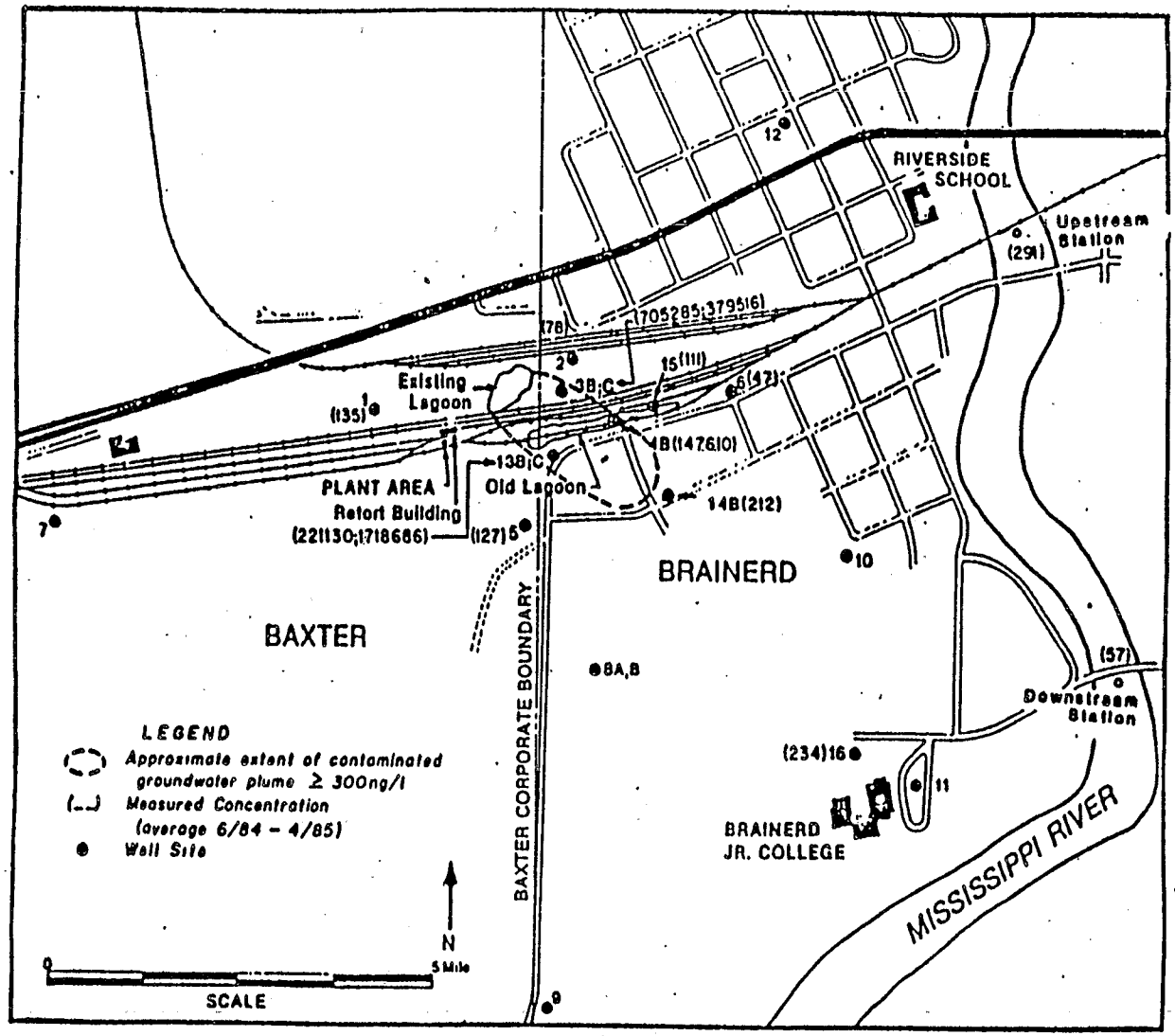

Figure 2-1. Burlington Northern Superfund Site, Brainerd, Minnesota.

Source: Summary of Remedial Alternative Selection, Burlington Northern Hazardous Waste Site, Brainerd, Minnesota. U.S. Environmental Protection Agency (Region V). 1985.

removal of wastewater and creosote left behind a heavy sludge layer approximately 6 inches to 1 foot thick in localized areas of the impoundment.

The Record of Decision (ROD) for the BN Superfund Site was signed by the Regional Administrator on June 4, 1986. The recommended alternative for treatment of the contaminated sludges and soils was onsite land treatment. Land treatment is a managed technology that involves the controlled application of a waste on a soil surface and the incorporation of the waste into the upper soil zone. Aerobic microorganisms in the top layer of the soil then break down and transform the organic contaminants into harmless byproducts and aid in the immobilization of other organic and inorganic contaminants. The annual waste application rate is expected to be less than 6 inches/year. At this rate, the last waste application should be in the fifth year after the system startup, which occurred in 1986.

The ROD specifies that only visibly contaminated soils and sludges will be excavated from the site for onsite treatment. Visibly contaminated soil was characterized as being heavily stained, dark brown to black in color, visibly oily, and usually having a pronounced creosote odor. The second impoundment from which wastewater and creosote were removed contained an estimated 6000 yd^3 of contaminated soil and 1000 yd^3 of contaminated sludge. The first impoundment, which was closed in the 1930s, contained an additional 2500 yd^3 of contaminated soil. Together, the two impoundments contained an estimated 9500 yd^3 of contaminated material.

Initial sampling showed the primary constituents of concern to be polynuclear aromatic hydrocarbons (PAHs), heterocyclic compounds, and phenols. Concentrations of these contaminants ranged from 34,388 mg/kg total PAHs and heterocyclics and 16 mg/kg total phenols in the old impoundment to 134,044 mg/kg total PAHs and heterocyclics and 130 mg/kg total phenols in the second impoundment. Groundwater monitoring results indicated that the groundwater contamination is restricted to a relatively small area downgradient from the site. All contaminated soils have been excavated from the lagoon areas and are currently stored in a waste pile on site, which is just east of the existing lagoon area. Each spring a new layer of waste from the

covered waste stockpile is placed on the adjacent landfarm designed for biological degradation of organic contaminants.

On November 7, 1989, ITEP sent a sampling team to the BN site to characterize the stockpiled soil and to find the hot spot for PAHs. Six soil samples were taken from the waste pile at the locations shown in Figure 2-2. The sampling depths for these locations are listed in Table 2-1. The soil under investigation is a fine, sandy soil, of which 75 percent has a grain size between 0.1 and 0.4 mm in diameter. Figure 2-3 presents a graphical display of grain-size distribution. The soil has a relatively low moisture content (10 percent) and a heat value below 500 Btu/lb. A review of the analytical data indicated that Sampling Point 4 contains the highest levels of PAHs detected. Table 2-2 summarizes the concentrations of PAHs and other semivolatile organics detected in the soil. Appendix C contains complete characterization data for Burlington Northern soil.

TABLE 2-1. SAMPLING DEPTHS FOR BURLINGTON NORTHERN CHARACTERIZATION SAMPLES

Sampling point	Depth of sample, in.
1	6-24
2	0-19
3	21-48
4	25-48
5	12-40
6	0-24

On November 20, 1989, ITEP returned to the site to excavate soil for the CS&D treatment studies. Although Sampling Point 4 showed the highest levels of PAHs, Sampling Point 5 was chosen for the excavation site. The Site Coordinator, James Brown, believed that Sampling Point 5 posed the least threat with regard to liner damage by the backhoe and offered more area for maneuverability of the backhoe.

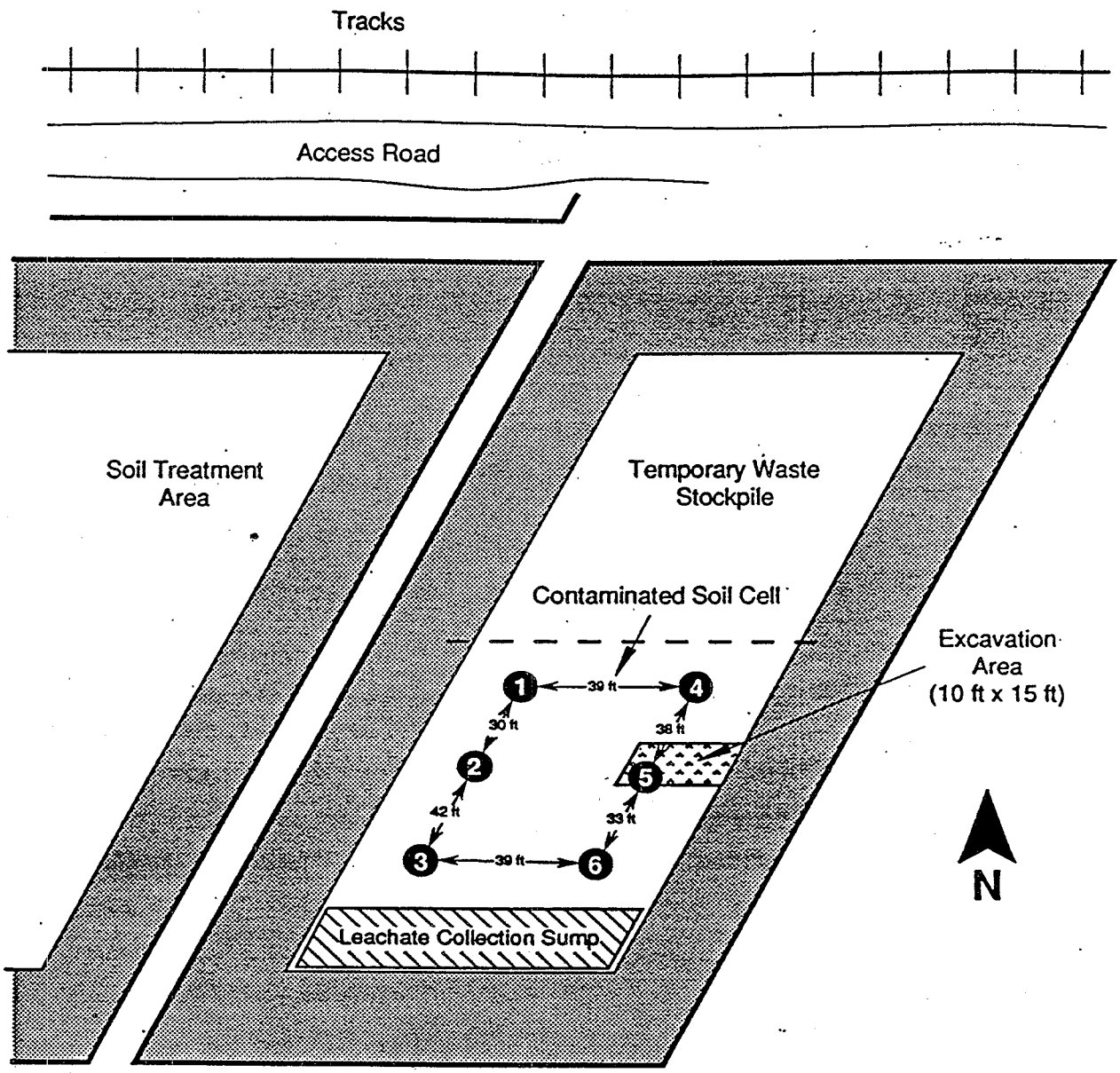

Figure 2-2. Waste pile sampling locations.

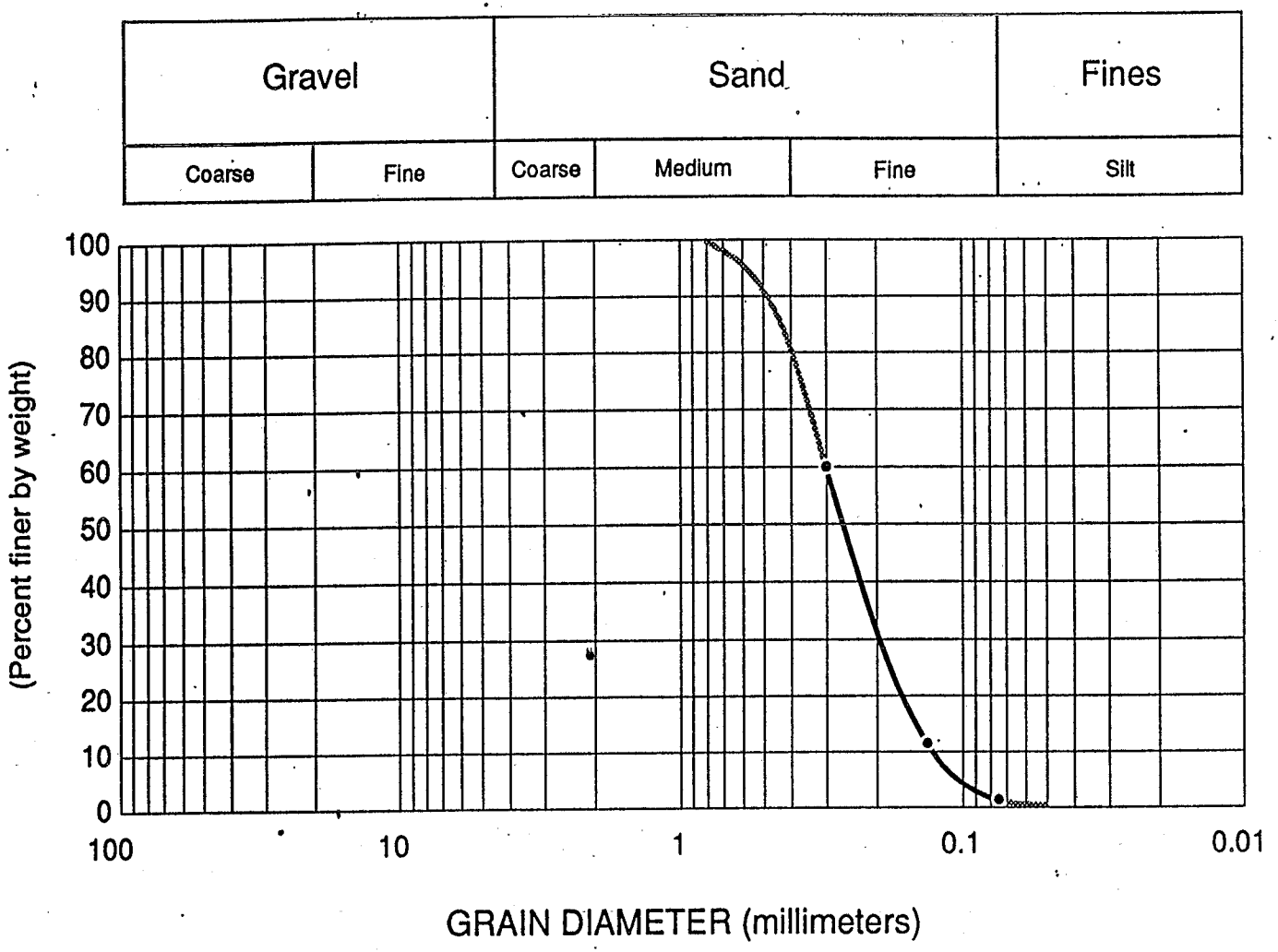

Figure 2-3. Grain-size distribution for Burlington Northern soil.

TABLE 2-2. CONCENTRATIONS OF SEMIVOLATILE ORGANICS IN BURLINGTON NORTHERN CHARACTERIZATION SAMPLES (mg/kg)

Analyte	Sampling point 1	2	3	4	5	6
Semivolatile organics						
Naphthalene	110	170	860	5200	1200	2300
2-Methylnaphthalene	56	81	260	1200	310	590
Acenaphthylene	11 J[a]	14 J	16 J	18 J	41	70
Acenaphthene	120	130	370	1900	320	600
Dibenzofuran	91	90	250	1100	270	480
Fluorene	150	120	360	1500	380	630
Phenanthrene	420	360	1000	4000	1000	1800
Anthracene	880	120	340	560	540	840
Fluoranthene	350	350	570	1800	580	1000
Pyrene	410	330	370	1400	370	760
Benzo(a)anthracene	130	91	110	350	150	330
Chrysene	340	120	120	350	160	350
Benzo(b)fluoranthene	150	120	77	120	120	300
Benzo(a)pyrene	82	70	41	84	7 J	150
Indeno(1,2,3-cd)pyrene	41	35 J	16 J	28 J	ND[b]	64
Dibenzo(a,h)anthracene	19 J	18 J	7 J	ND	6 J	16 J
Benzo(g,h,i)perylene	32 J	34 J	12 J	10 J	22 J	38 J
Phenol	ND	ND	ND	28 J	ND	4 J
2-Methylphenol	ND	ND	ND	24 J	3 J	8 J
4-Methylphenol	ND	ND	ND	58	ND	10 J
2,4-Dimethylphenol	ND	ND	ND	39 J	6 J	18 J
Total semivolatile constituents	3392	2253	4779	19769	5485	10358

[a] J = Estimated value for constituent detected below the established detection limit of 40 mg/kg.

[b] ND = Compound not detected above established detection limit of 40 mg/kg.

A 10-by-15-ft cut was made in the liner to the north side of Sampling Point 5, and the liner was pulled back to the west. The north side of the cut was excavated to a width of about 5 ft, and the upper 2 ft was pulled back. Soil was then removed to a depth of 2 to 6 ft and placed in 55-gallon drums. Seven drums were filled by the backhoe, and three drums were filled by hand from the excess backhoed material. The drums were then sealed with lids, labeled, covered, and stored on site. Table 2-3 lists the key personnel present at the site during the excavation of the contaminated soil into the drums.

The drummed soil from the original excavation was stored at the BN site for one year. On October 15, 1990, ITEP returned to the site to repackage two drums and collect four pails of contaminated soil for the CS&D treatment studies. The drums were repackaged to ensure that samples used for the treatment tests were thoroughly homogenized.

The sampling crew emptied the entire contents of two drums of soil and half of a third drum onto a plastic liner. Over the course of the year, most of the heavy sludge from the site had settled to the bottom of the drums. Shovels were used to mix (homogenize) the soil manually. When the soil was thoroughly homogenized (based on the evenness in soil color throughout the pile), the crew began to fill two drums and four pails of soil. Leftover soil in the pile was placed back in the third drum, which was then returned to the covered waste stockpile at the BN site. One drum was shipped to the T&E facility for pilot-scale bioslurry tests, and three pails were shipped to ECOVA for bench-scale bioslurry tests. The other drum and pail were shipped to IT-Knoxville for low-temperature thermal desorption (LTTD) treatment tests. Key personnel involved with repackaging and shipment of the drums are listed in Table 2-4.

TABLE 2-3. KEY PERSONNEL INVOLVED IN THE EXCAVATION OF TREATMENT SOIL FROM THE BURLINGTON NORTHERN SUPERFUND SITE

Excavation Site Facility:	Burlington Northern Superfund Site West City Limits Brainerd, Minnesota 56401
Excavation Location:	Temporary Waste Stockpile Sampling Point 5 (as shown in Figure 2-2)
Site Remediation Coordinator:	James Brown Remediation Technologies, Inc. 602 Ninth Avenue Brainerd, Minnesota 56401 (218) 829-9756
Date of Excavation:	November 20, 1989
Contract Personnel:	Philip Utrecht, ITEP, Sampling Team Leader Steve Giti-Pour, ITEP, Sampling Team Member Wade Johnson, Dust Coating, Inc., Backhoe Operator

TABLE 2-4. KEY PERSONNEL INVOLVED IN THE REPACKAGING OF DRUMS FOR THE CS&D TREATMENT STUDIES

Excavation Site Facility:	Burlington Northern Superfund Site West City Limits Brainerd, Minnesota 56401
Repackaging Location:	Concrete pad adjacent to site's work shed
Site Remediation Coordinator:	James Brown Remediation Technologies, Inc. 602 Ninth Avenue Brainerd, Minnesota 56401 (218) 829-9756
Date of Repackaging:	October 15, 1990
Contract Personnel:	Philip Utrecht, ITEP, Sampling Team Leader Michael Smith, ITEP, Sampling Team Member
Transport Company:	Hyman Freightways, Baxter, Minnesota

SECTION 3

TREATMENT SYSTEM UNDER EVALUATION

3.1 Description of Treatment System

Since 1986, landfarming has been conducted on contaminated soil and sludges at the Burlington Northern site. Although this work has resulted in significant reductions in 2- and 3-ring PAHs, the degradation of 4-ring and larger PAHs and benzene-extractable hydrocarbons has been less successful.

Biodegradation rates of 4-ring and larger PAHs could be improved appreciably through the use of slurry-phase biological treatment. In this process, the soil is suspended to obtain a pumpable slurry, which is fed to a large-capacity, continuously stirred tank reactor (CSTR). The reactor is then supplemented with oxygen, nutrients, and when necessary, a specific inoculum of microorganisms to enhance the biodegradation process. This treatment method has several advantages because the engineering and biotechnology required to provide an optimal environment for biodegradation of the organic contaminants can be controlled with a high degree of confidence. Biological reactions can be accelerated in a slurry system because of the increased contact efficiency that can be achieved between contaminants and microorganisms by successfully maintaining higher bacterial populations (10^8/mL). A slurry-phase process can also be operated as a continuous-flow system, which reduces the impact of toxic waste levels by instantaneously diluting the feed stream as it enters the reactor. In addition, toxic end products of microbial metabolism, which may repress bacterial activity, do not accumulate to inhibitory levels.

ECOVA, in conjunction with ITEP, conducted pilot-scale process studies at the U.S. EPA T&E facility in Cincinnati, Ohio, using a slurry-phase biotreatment design to

evaluate bioremediation of PAHs in creosote-contaminated soil. The treatment program was initially designed to evaluate six replicate batch slurry-phase reactors; however, mechanical difficulties encountered during startup caused this number to be reduced to five.

The EIMCO Biolift™ Reactor (60-liter) was selected for this study. These reactors are made of stainless steel and equipped with agitation, aeration, and temperature controls. Agitation is provided by three mechanical methods. First, a rake mechanism moves the settled material from the bottom of the reactor to the second agitation mechanism, an airlift circulation system that circulates the material to the top of the reactor. The third agitation mechanism is a low-sheer impeller located approximately in the middle of the central shaft of the reactor. Aeration is supplied by a set of air diffusers that are attached to the rake arm at the bottom of the reactor. Temperature is controlled by a heat tape system with a digital readout.

The EIMCO Biolift™ Reactor can be sampled in two ways. An opening at the front top of the reactor allows access at the top surface of the liquid. This permits visual inspection of the mechanical actions within the reactor as well as data collection with hand-held instruments that can be inserted into the slurry from the top. Samples are collected from the three sampling ports located along the side of the reactor at three vertical penetrations through the reactor wall. Samples collected from each of the three ports represent three distinct zones of the slurry. The bottom sampling ports provide sample material from within the rake mixing zone, where the heaviest particles are likely to be present. The middle sampling port provides sample material from within the most well-mixed zone of optimal grain size. Finally, the top sampling port provides sample material from the finest mixing distribution. These three ports are crucial in the evaluation of the mechanical efficiency of the reactor as well as collection of samples of the contaminated material. An EIMCO Biolift™ Reactor Diagram is presented in Figure 3-1.

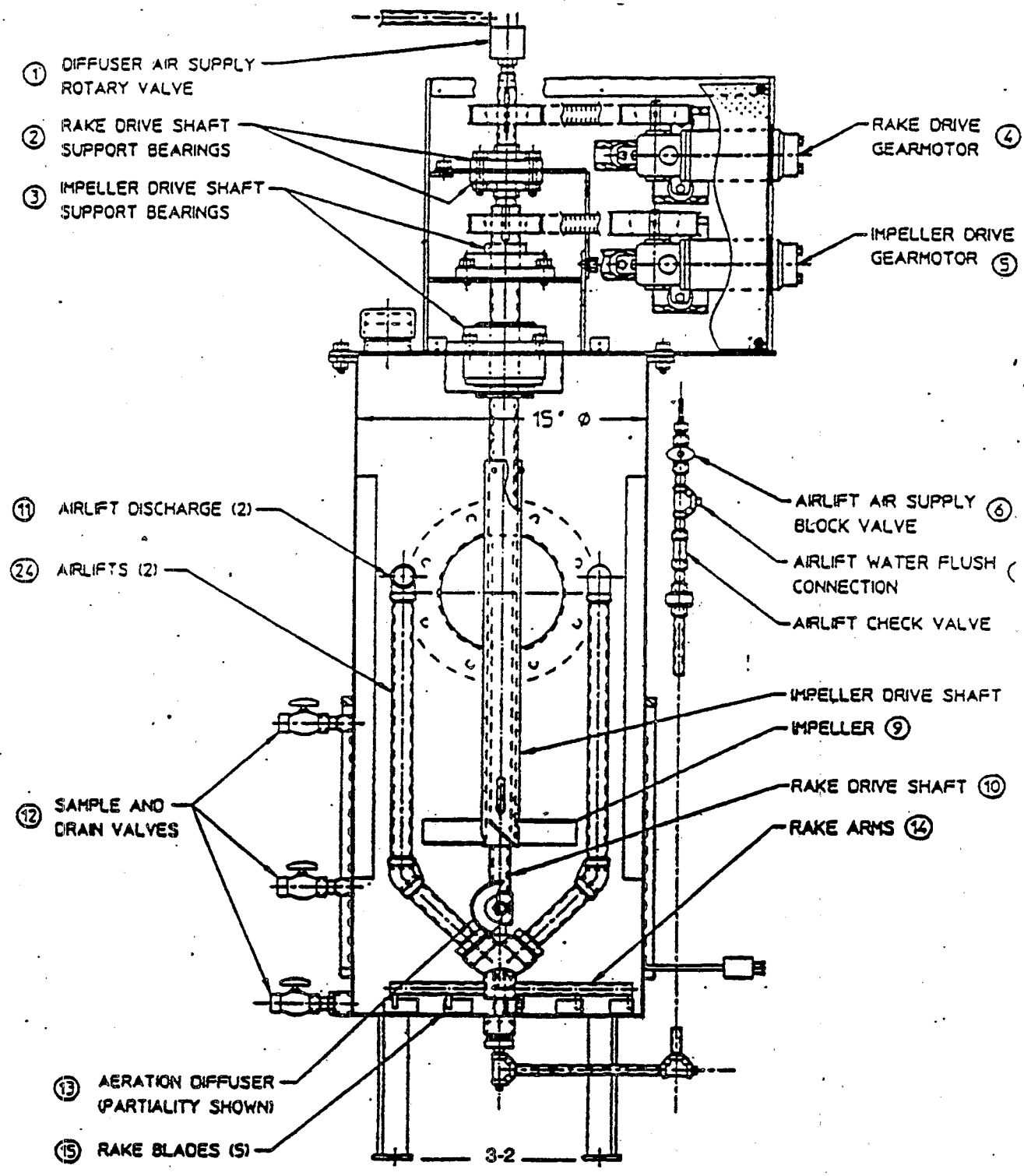

Figure 3-1. EIMCO Biolift™ Reactor.

3.2 Bench-Scale Flask Study

In January 1991, ECOVA conducted bench-scale process development studies using 250 mL Erlenmeyer flasks to evaluate bioremediation of PAHs in creosote-contaminated soil collected from the Burlington Northern site. The objective of the bench-scale studies was to develop the data necessary to determine the optimum process conditions for the pilot-scale treatment, which will use a 60-liter EIMCO Biolift™ reactor.

Physical, chemical, and microbial characterization of site soils was performed. The information generated was used to evaluate the soil characteristics and to assist in the development of an appropriate treatability study design. Physical characterization was performed to determine the particle size distribution of the soil by using standard sieve analysis and to estimate terminal settling velocities of soil particles. This information was used to determine appropriate slurry concentrations and to estimate energy requirements for the slurry-phase bioreactor. Chemical and microbial characterizations were performed to determine the levels of target contaminants, to determine required inorganic nutrients that may limit microbial growth, and to ensure that specific microbial degrader populations were present.

At the end of the bench-scale flask study, a physical characterization of the site soils was performed for the scale-up exercise from the bench-scale flask study to the single 64-liter EIMCO Biolift™ reactor. The results of this study indicated that there was a substantial amount of heavy, coarse-grained particulates comprising this soil. The volume percentage of soil fines less than 100 mesh in size was only 9 percent of the total soil volume, with 72.4 percent greater than 100 mesh in size. These data suggested that there would be significant difficulties encountered in generating a manageable slurry from this soil. Hence, it was clear that an additional step would be necessary to prepare the soil for use in the bioslurry reactor. The soil was subjected to a milling process to pulverize the coarse-grained material and creosote inclusions to yield a final material that was enriched in the -200-mesh particle fraction. This procedure was quite useful for generating a material amenable to the formation of a manageable slurry.

For the purpose of the BDAT program effort, U.S. EPA program managers from the Office of Solid Waste, in conjunction with representatives from the U.S. EPA RREL in Cincinnati and various support contractors, reviewed the above options and decided to endorse the soil milling option as a pretreatment step prior to pilot-scale processing. While this type of pretreatment step would not be efficient for a full-scale processing option, it provides the information necessary to evaluate bioslurry treatment under some of the most difficult technical and materials handling conditions.

Based on the scale-up exercise using the single 64-liter reactor, it was determined that to maintain efficient mechanical operation of the bioreactors during the pilot-scale testing, a 30 percent solids slurry with an airflow of 50 standard cubic feet per hour (scfh) to the diffusers and airlift mechanisms should be used.

Based on the bench-scale results and observations, it was also concluded that the pilot-scale slurries should be amended with inorganic nutrients and a concentrated inoculum of indigenous microorganisms selected for their ability to metabolize or co-oxidize PAHs to ensure an optimal rate of bioprocessing. Supplementation with a surfactant such as Tween 80 would be necessary if degradation rates appeared lower than expected on the basis of the bench-scale studies. To ensure a sufficiently active surfactant-enabled desorption, the surfactant concentration should always remain far above the critical micelle concentration (CMC). However, lacking a specific assay to evaluate surfactant concentration, it was generally concluded that it would be best to use the surfactant only after the BDAT data requirements had been satisfied.

A report describing the results of the bench-scale development of the slurry-phase process is included in Appendix D.

3.3 Pilot-Scale Testing of Bioslurry Reactors

The pilot-scale slurry-phase testing program started on May 8, 1991, at the U.S. EPA T&E facility. The six reactors selected for this study were the reactors (60-liter EIMCO Biolift™ reactor) were identical to the one used in the scale-up exercise at ECOVA following the completion of the bench-scale flask study. Representatives of U.S. EPA, IT Corporation, and ECOVA Corporation were involved in conducting the

pilot-scale testing. All pilot-scale study activities described in this document were governed by the U.S. EPA-approved Health and Safety Plan (Appendix E).

The operational volume of the EIMCO Biolift™ Reactor is 64 liters. Because of the large volumes of slurry to be removed at the initial T_0 time point, however, it was concluded that the reactors should initially be loaded to a volume of 66 liters. This volume was immediately decreased after the collection of the first sample set, which allowed for the maximum loading of the batch slurry reactor. Nutrient and inoculum calculations were based on a 66-liter initial reactor volume at 30 percent slurry.

3.3.1 Soil Screening

A temporary enclosure was constructed at the T&E facility to house the soil screening and milling activities. (Figure 3-2 shows the layout of the containment area.) Soil was shoveled from a 55-gallon drum in which it had been transported from the site, and then passed through a ½-in. screen to remove any debris and oversized material. The soil was worked through the screen by hand and with a trowel.

The screened soil was shoveled from the collection area below the screen onto a plastic-wrapped board to form the stockpile. The rejected material was diverted into a 5-gallon pail. Most of the rejected material consisted of wood fragments, pieces of brick, and coarse gravel (>½-in.). In general, the soil was brown to black, fine- to medium-grained sand with some minor gravel content, and it was somewhat resilient and greasy. The color and texture of the soil suggested it was highly contaminated.

The screened material formed a pile approximately 3 feet high and 4 feet in diameter. The pile was spread out on the board, leveled off, and mixed by quartering. This splitting process took place twice. (Figure 3-3 shows the splitting sequence.) Several samples were taken of the material during these activities, and the rejected material was returned to the original 55-gallon drum.

3.3.2 Soil Milling

After the soil was screened, a 5-gallon bucket was half-filled with soil and water and mixed into a slurry. The original plan was to pump the slurry into a ball mill by

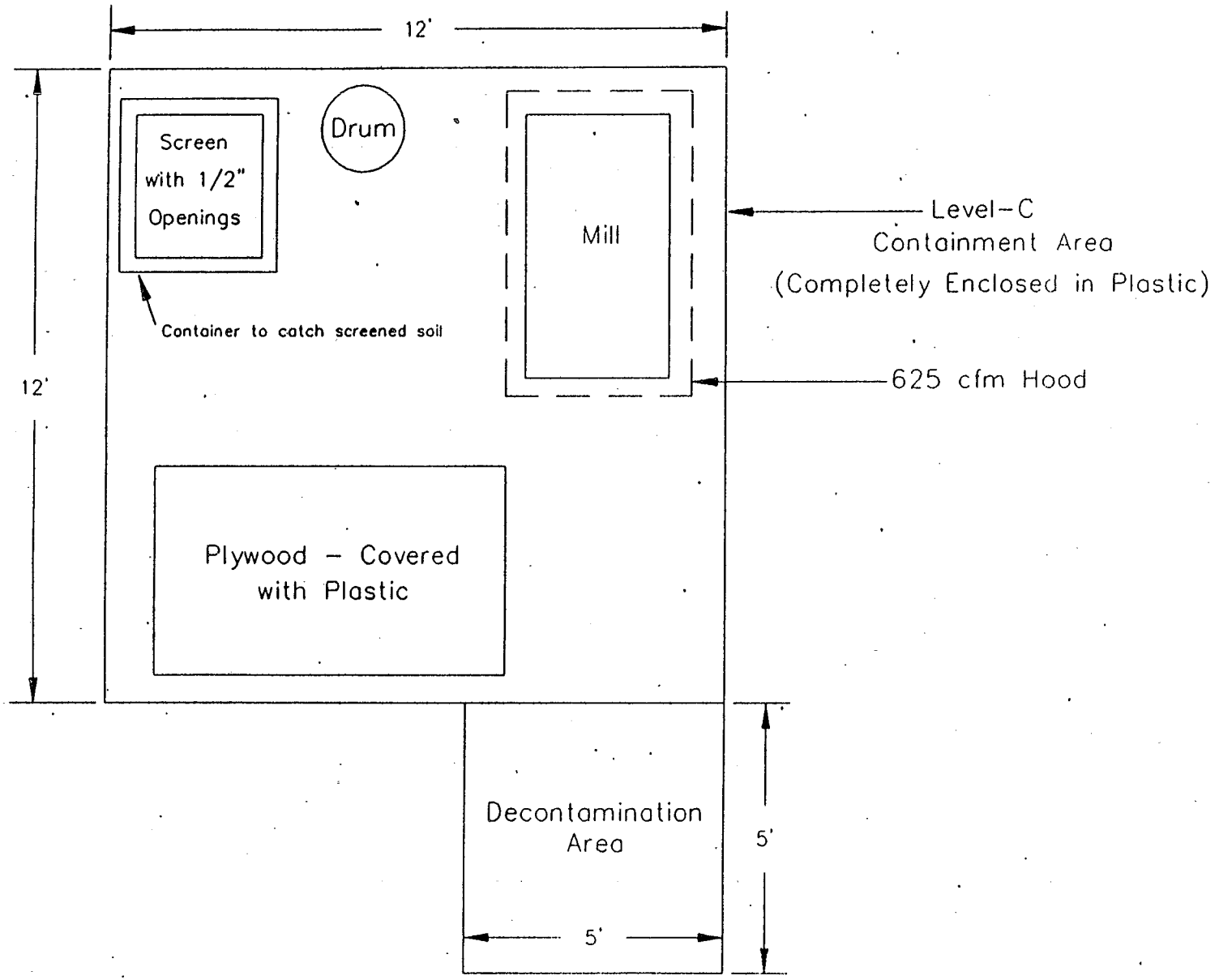

Figure 3-2. Containment area layout.

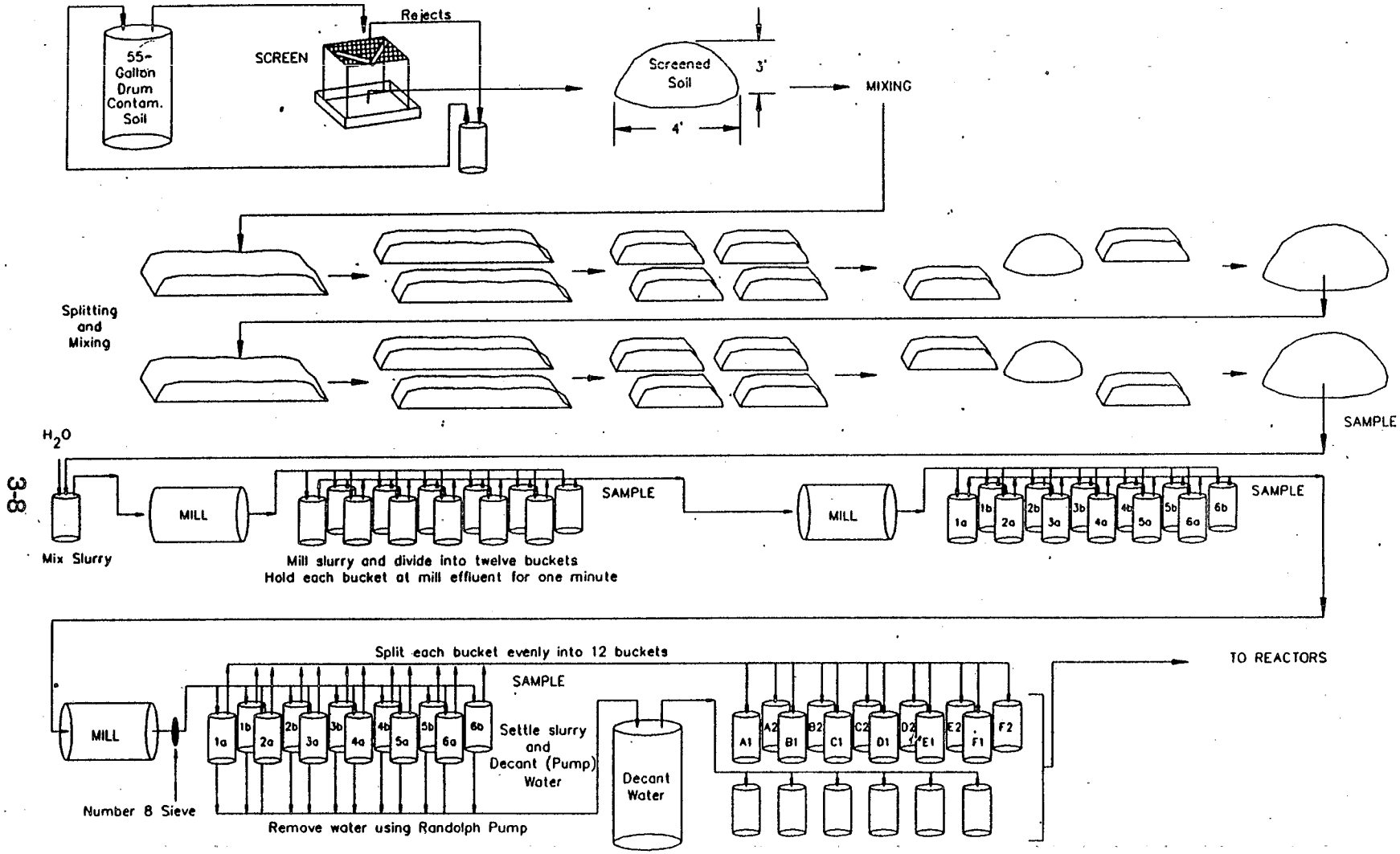

Figure 3-3. Screening, mixing, and milling flow diagram.

using a 2-gpm Randolph peristaltic pump. When this method failed because the gravel in the slurry repeatedly plugged the pump, it was decided to pour the slurry into the mill through a flexible funnel. A number of buckets were used for continuously mixing the slurry and feeding it into the ball mill. Fourteen buckets were used to collect the slurry at the mill outlet. The slurry was caught in the buckets at 1-minute intervals until all of the soil had been processed. Samples were collected at the outlet of the mill as the slurry was being milled for postmilling analysis for PAHs.

The slurry was milled a second time, after which a wet-sieve analysis was performed to determine if the particles would pass through a No. 10 sieve. The slurry was collected in two sets of six buckets each, marked 1 through 6 and 1a through 6a, respectively. Abundant siliceous gravel still remained in the slurry, and it was clear that a third milling was necessary before the material could be added to the reactors. Another round of sampling was performed during the second milling.

During the third milling, the slurry was added at a slower rate to allow for a longer retention time and better pulverization of the gravel. Also, the slurry was continuously screened with a No. 8 sieve at the outlet of the mill. After passing through the sieve, the effluent appeared to be well-mixed and was sampled again. Another sieve analysis showed that the third milling, combined with screening, produced a slurry with a grain size distribution suitable for charging to the reactors.

The next step in the process was to allow the slurry to settle, to decant the liquid, and to take samples for percent solids analysis. After one hour, the slurry had not settled enough to produce an obvious liquid-sediment interface. At this point, the buckets were sealed and left overnight. The following day, the liquid was decanted from all 12 buckets into a 55-gallon drum by use of the Randolph pump. This consisted of approximately 10 gallons of water, which was then mixed and sampled for percent solids. Samples weighing approximately 30 grams were also collected from each of the buckets and analyzed for percent solids.

For the final mixing, 12 designated (reactor) buckets were labeled A1 through F1 and A2 through F2. After mixing the contents of Bucket 1a with a shovel and trowel, approximately 1 liter of the material was placed into each of the 12 reactor buckets.

This was repeated until all of the material from Bucket 1a was distributed into all 12 reactor buckets. The same procedure was repeated for the remaining 11 buckets (1 through 6 and 2a through 6a). The contents of the 12 reactor buckets were thoroughly mixed, weighed, and sampled for percent moisture.

Water decanted from the slurry (after the third milling) and placed in the 55-gallon drum was mixed, divided evenly into six buckets, and weighed. This water was used for the initial charging of the reactors.

At this point, the work in the containment area was complete. Calculations were made to determine the weight (volume) of water and slurry needed to charge the reactors to 66 liters at 30 percent solids.

The entire process of screening, milling, and mixing took 1½ days and approximately 35 man-hours to complete. Milling the slurry three times was time-consuming and inefficient. Using a screen or series of screens with smaller openings and a mill that could pulverize the gravel might eliminate multiple passes through the mill. For either a pilot-scale or full-scale project, however, this is not likely to be cost-effective. Milling the slurry also results in considerable spillage during the charging of the slurry into the mill. Having to process the slurry three times added to this unavoidable problem. The general conclusion was that the soil processed at the EPA facility was quite different from the material tested at the ECOVA Technology Development Center, which only had to be milled twice and did not plug the Randolph pump.

3.3.3 Reactor Charging

As a result of the screening, mixing, and milling process, twelve 5-gallon buckets of milled slurry were generated. The buckets were labeled 1 through 6 to correspond to the reactor designations. More slurry was generated than could be accommodated by six buckets alone; therefore, an additional set of six buckets was used to collect the remainder of the slurry from the milling process. The bucket designations then became 1a through 6a for the first set and 1b through 6b for the second set (Figure 3-3). Because 12 buckets of slurry were collected during the milling process, ECOVA's lead technical person expressed concern over the potential inhomogeneities

that might exist among the buckets and the need for each reactor to be charged with material that was statistically similar with respect to contaminant loading and percent solids. Toward this end, ECOVA, in consultation with IT Corporation and S-Cubed, proposed and executed the following Standard Operating Procedure (SOP) for charging the slurry bioreactors:

1) The 12 buckets of slurry were subjected to a 14- to 16-hour settling period under quiescent conditions. After the specified settling interval, the aqueous supernate solutions were pumped to a single 55-gallon drum for interim storage and mixing.

2) Six clean feed buckets were labeled with the designations A through F (one for each of the slurry bioreactors) and weighed to determine the mass of each empty bucket.

3) Settled soil from each bucket was stirred with a hand-held grain-feed scoop to mix and homogenize. An aliquot was removed from each of the 12 buckets with the hand-held scoop and weighed into feed bucket A until a total 32 kg (70.11 lb) wet weight of soil had been dispensed. This process was repeated for each of the remaining buckets (B, C, D, E, and F). Soil mass was calculated on the basis of the following assumptions:

Soil density	=	1.3 kg/L
Specific gravity of slurry	=	1.074 (30% slurry)
Moisture of feed soil	=	24.83 ± 0.31%
Total slurry volume	=	66 liters
Total slurry mass	=	70.88 kg
Dry soil mass required	=	21.27 kg
Water mass required	=	49.61 kg

4) Samples from each of Buckets A through F were collected and analyzed for dry weight to determine the total dry mass of soil added to each reactor. (See Appendix F for raw data table.)

5) After the water content of the wet makeup soil was factored (6.30 kg or 13.85 lb water), it was determined that a total of 97.35 lb of additional makeup water was required to achieve the specified slurry composition. Included in this makeup water volume was the supernate water collected after the initial settling step described under Item 1. This represented 14 lb of the 97.35 lb required for each reactor.

6) Each of the EIMCO airlift reactors was charged with 76 lb of water. The remaining 21.35 lb of makeup water was reserved for preparation of the required inorganic nutrient supplements.

7) The airlift, impellers, and rake controllers for the bioreactors were engaged with the rake speed set at 4 rpm, the impeller speed set at 7 rpm, and the airlift set at approximately 50 scfm. Diffusers were run at a flow rate of 30 scfm.

8) The contents of each of the soil feed buckets (A through F) were dispensed into the respectively designated bioreactors by using a funnel and a hand-held scoop. After most of the soil had been dispensed, the bucket was rinsed with the remaining volume of nutrient-amended make-up water and the contents were added to the reactor. This procedure was repeated for each of the remaining reactors until all reactors were charged to specification.

3.3.4 Inoculation

A concentrated inoculum was prepared at the ECOVA Research and Development Facility in Redmond, Washington. The inoculum consisted of three bacterial isolates (*Pseudomonas stutzeri*, *Pseudomonas fluorescens*, *and Pseudomonas stutzeri* strain FLN-1) obtained from the Burlington Northern site soil samples shipped to ECOVA for bench-scale testing. A total of 60 liters of culture was prepared and concentrated to a final volume of 4.0 liters. The total number of bacteria in the concentrate was 1.2×10^{13}. During bench-scale testing, a desired inoculum level was determined to be approximately 1.0×10^{8} bacteria per gram dry weight of soil. Therefore, each reactor would require supplementation with a targeted number of 2.13×10^{12} bacteria.

After each of the slurry bioreactors had been charged with slurry, the inoculum (cold slurry concentrate) was added at a volume of 666 mL per reactor. Based on the titer of bacteria in the available inoculum, this translated to an actual inoculum titer of 1.98×10^{12} per reactor, or 9.3×10^{7} per gram of soil. At the time of inoculation, the inoculum was 48 hours past its recommended holding time for optimal viability.

3.3.5 Nutrient Amendment

The results of the inorganic analyses performed on the soil samples during the bench-scale study (see Appendix D) suggest that the soil was depleted in available phosphorous measured as o-phosphate. The ratio of total organic carbon (TOC) to

total Kjeldahl nitrogen (TKN) was approximately 40:1, which suggests that a supply of nitrogen would be available for microbial activity. The amount of free nitrogen as measured by ammonia nitrogen, however, was quite low (TOC:N = 950:1); this suggests that ammonia supplementation would be necessary to enhance optimal microbial activity. Elemental analysis for calcium, magnesium, potassium, and sodium was performed to obtain data that could be used to estimate potential effects on the hardness of the aqueous phase of the slurry and, therefore, the impact on surfactant behavior. Based on the levels of these elements, no appreciable effect on water hardness was expected. Therefore, foaming of ionic surfactants could present some materials handling problems.

The postmilled material was analyzed for total volatile solids prior to loading the reactors to ensure a carbon level close to that previously reported. These samples indicated a carbon concentration of 38,888 ppm (see Appendix F). Because this value was higher than that previously reported, it was used for all nutrient calculations.

Nutrient amendments added to the reactor included ammonia and phosphate, along with trace amendments of magnesium, calcium, iron, and ammonium molybdate. Concentration calculations were based on a 66-liter volume of 30 percent soil slurry. Nutrients were added to the reactors by dissolving them in a subsample of preweighed reactor water.

3.3.6 Reinoculation of Bioreactors

After the 9 weeks of treatment testing, Bioreactors 2, 4, 5, and 6 were reinoculated with 125 mL of inoculum. In addition to the inoculum, 5.93 mL of Tween 80 surfactant was added into Reactors 5 and 6. No inoculum or surfactant was added into Reactor 1. Inoculum and surfactant amendments are presented in Table 3-1.

TABLE 3-1. INOCULUM AND SURFACTANT AMENDMENTS

Reactor No.	Amendment	Amount, mL
1	None	-
2	Inoculum	125
4	Inoculum	125
5	Inoculum/Tween 80	125/5.93
6	Inoculum/Tween 80	125/5.93

SECTION 4

SAMPLING AND ANALYSIS ACTIVITIES

Sampling of the bioslurry reactors during the pilot-scale testing was conducted in accordance with the "Sampling and Analysis Plan (SAP) for the Treatment Testing of Slurry-Phase Biological Reactor on Contaminated Soils" (see Appendix A). In addition to the sampling from the bioreactors, air sampling was also incorporated into the sampling and analysis effort to characterize the vapors coming off the bioslurry reactors.

Sampling and analysis activities performed during the pilot-scale test are presented in Subsections 4.1 and 4.2, respectively, and deviations from the SAP are presented in Subsection 4.3. Subsection 4.4 contains information about safety considerations observed during the sampling activities.

4.1 Sampling Methods

Composite samples were collected from each reactor for pre- and posttreatment analysis and throughout the study to monitor system operation. Composite sampling ensured that analyses were performed with a representative sample of the entire slurry column. Some analyses (e.g., particle size distribution, plate counts) were performed on samples collected from individual sampling ports to determine potential differences among the three slurry zones.

All parameters in this study were monitored in accordance with the sampling schedule presented in Table 4-1. Week T_0 corresponds to May 8, 1991, and Week T_{12} corresponds to July 31, 1991. The values in Table 4-1 refer to the volumes of slurry, soil, or water taken for each analysis at each point in time. Table 4-2 presents the sampling constituents and sampling frequency during the run for each of the five

TABLE 4-1. REACTOR MONITORING SCHEDULE

Analysis	Sample Volume Per Reactor, Slurry-Phase Pilot Test Week 0	1	2	3	4	5	6	7	8	9	10	11	12
Semivolatile organics (mL)	2000									2000			2000
PAH/HPLC-Water/Soil (mL)	60	60	60	60	60		60			60	60	240	60
O&G/TPH (mL)	100		100	100	100		100			100	100	100	100
TOC (mL)	100		100		100		100			100	100		100
Nutrients (mL)	40		40		40		40			40	40		40
Ammonia (mL)	10		10		10		10			10	10		10
Total heterotrophs (mL)	10	10	10	10	10		20			10	10		10
PAH degraders (mL)	10		10		10		20			10	10	10	10
Microtox (mL)	20		20		20					20	20		20
TS (mL)	60	60	60	60	60		60			60	60	60	60
TSS & TVSS (mL)	250		150	70	100		100			100	100	100	100
Dissolved oxygen	DR[a]	DR	DR	DR	DR	DR	DR	DR	DR	DR	DR	DR	DR
Temperature	DR	DR	DR	DR	DR	DR	DR	DR	DR	DR	DR	DR	DR
pH	DR	DR	DR	DR	DR	DR	DR	DR	DR	DR	DR	DR	DR
Particle size	NA[b]	NA	NA	NA	NA		NA		NA	NA	NA	NA	NA
Total volume (mL)	2660	130	560	300	510	0	510	0	0	2510	510	510	2510
IT vol. per week (mL)	2160		100	100	100		100			2100	100	100	2100
Ecova vol. per week (mL)	250	70	250	70	250		250			250	250	250	250
Ecova (T&E facility) (mL)	250	60	210	130	160		160			160	160	160	160
Total volume (L)	64	64	64	64	64	64	64	64	64	64	64	64	64
Sample % solids	30	30	30	30	30	30	30	30	30	30	30	30	30.0
Slurry wt. removed (mL)	296	51	218	78	199	0	199	0	0	199	199	199	199
Soil wt. removed (g)	228	39	168	60	153	0	153	0	0	153	153	153	153
Slurry % solids remaining	29.73	29.68	29.48	29.41	29.22	29.22	29.04	29.04	29.04	28.85	28.67	28.49	28.30

[a]DR = Measured using a direct-reading instrument.
[b]NA = Not applicable.

TABLE 4-2. TOTAL NUMBER OF SAMPLES COLLECTED FROM 5 REACTORS AND ANALYSES FOR BIOSLURRY PILOT DEMONSTRATION

Analysis	Week													
	0	1	2	3	4	5	6	7	8	9	10	11	12	Total
CS&D constituents (raw soil)	2													2
Semivolatile organics (critical contaminant list)	5									5			5	15
PAH - Slurry		5	5	5			5			5	5	5	5	40
PAH - Soil	5				5					5			5	20
PAH - Water	5				5					5			5	20
O&G/TPH	5		5		5		5			5		5	5	35
TOC	5		5		5		5			5	5	5	5	40
Nutrients	5		5		5					5	5	5	5	35
Ammonia	5		5		5					5	5	5	5	35
Total heterotrophs	10	5	10	5	10		5			10	5	5	10	75
PAH degraders	10	5	10	5	10		5			10	5	5	10	75
Microtox	5				5					5	5	5	5	30
TS	10	5	10	5	10		5			10	10		10	75
TSS & TVSS	10	5	10	5	10		5			10	10		10	75
Dissolved oxygen	35	35	35	35	35	35	35	35	35	35	35	35	35	455
Temperature	35	35	35	35	35	35	35	35	35	35	35	35	35	455
pH	35	35	35	35	35	35	35	35	35	35	35	35	35	455
Particle size	15	15	15	15	15		15			15				105
Semivolatile organics - air (critical contaminant list)		10	4	4	4	4	2	2	2	2				34
Volatile organics - air		10	4	4	4	4	2	2	2	2				34

reactors. These analyses include the critical constituents, the design and operating parameters, and volatile organics from air emissions.

Figure 4-1 shows the points at which samples were collected during the pilot-scale test. The purpose for collecting each sample, the sampling location, the method and frequency of sampling, and the constituents to be analyzed are presented for each sampling point in Subsections 4.1.1 through 4.1.5, respectively. Details regarding sample containers and sample preparation techniques are presented in Subsection 4.1.6.

4.1.1 Sampling Point 1 - Premilling Sample

Purpose

A premilling sample was collected to characterize the contaminated soil.

Description of Sampling Point

A grab sample was scooped from the homogenized pile of soil at the end of the screening process.

Sample Collection Method

A grab sample of soil was collected from the pile of homogenized screened material in eleven 8-oz wide-mouth glass jars.

Frequency of Sampling

One soil sample was collected from the homogenized soil prior to milling.

Constituents Analyzed

The premilling sample was analyzed for the complete CS&D list presented in Table 4-3.

4.1.2 Sampling Point 2 - Postmilling Sample

Purpose

A postmilling sample was collected to characterize the milled soil and to determine the effect of milling on the contaminants.

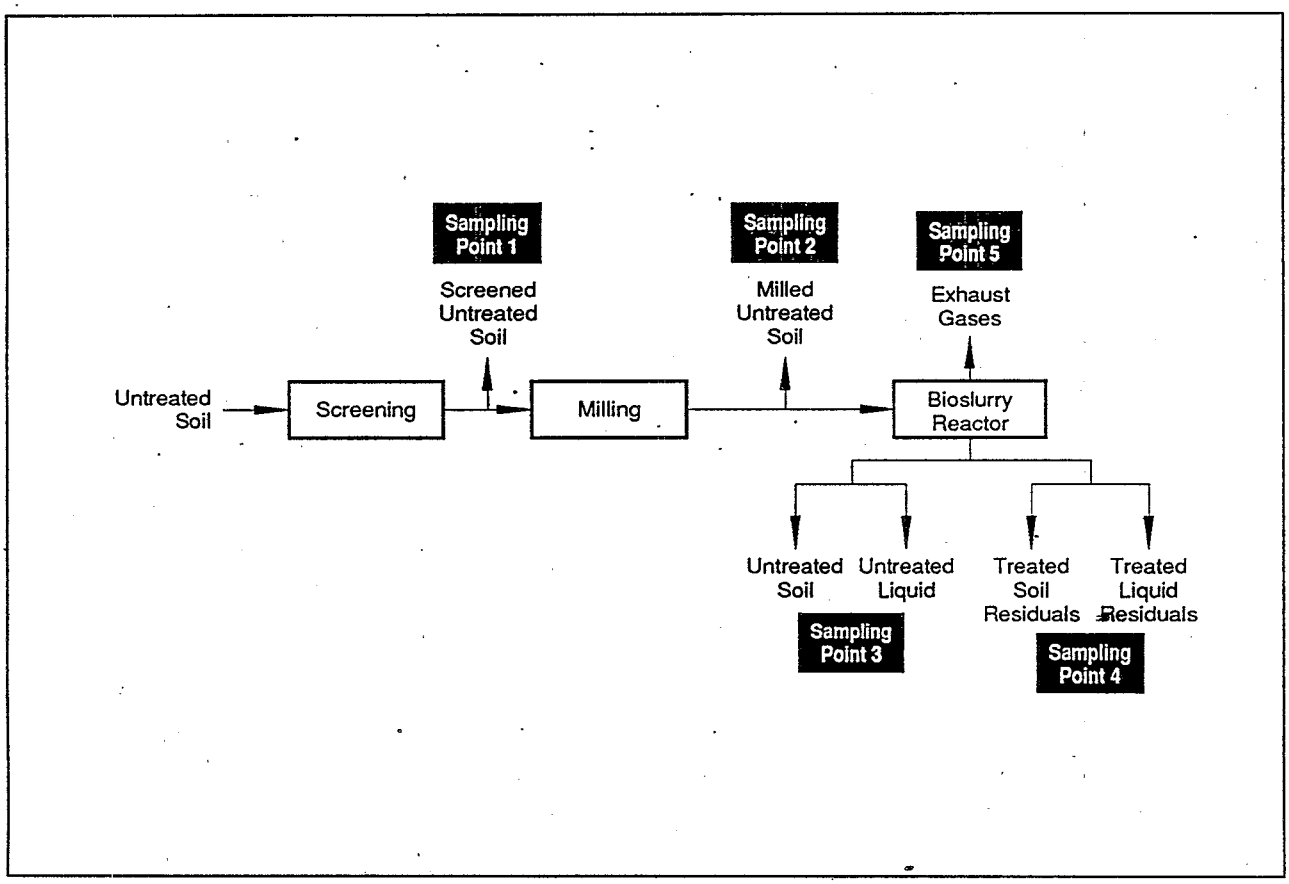

Figure 4-1. Pilot-scale bioslurry treatment sampling locations.

TABLE 4-3. CS&D LIST BY CONSTITUENT TYPE

Constituent	CAS No.[a]	BDAT Reference No.[a]
Volatile organics		
Acetone	67-64-1	222
Acetonitrile	75-05-8	1
Acrolein	107-02-8	2
Acrylonitrile	107-13-1	3
Benzene	71-43-2	4
Bromodichloromethane	75-27-4	5
Bromomethane	74-83-9	6
Carbon tetrachloride	56-23-5	7
Carbon disulfide	75-15-0	8
Chlorobenzene	108-90-7	9
2-Chloro-1,3-butadiene	126-99-8	10
Chlorodibromomethane	124-48-1	11
Chloroethane	75-00-3	12
2-Chloroethyl vinyl ether	110-75-8	13
Chloroform	67-66-3	14
Chloromethane	74-87-3	15
1,2-Dibromo-3-chloropropane	96-12-8	17
1,2-Dibromoethane	106-93-4	18
Dibromomethane	74-95-3	19
cis-1,4-Dichloro-2-butene	1476-11-5	234
trans-1,4-Dichloro-2-butene	110-57-6	20
Dichlorodifluoromethane	75-71-8	21
1,1-Dichloroethane	75-34-3	22
1,2-Dichloroethane	107-06-2	23
1,1-Dichloroethylene	75-35-4	24

(continued)

TABLE 4-3 (continued)

Constituent	CAS No.[a]	BDAT Reference No.[a]
Volatile organics (continued)		
trans-1-2-Dichloroethene	156-60-5	25
1,2-Dichloropropane	78-87-5	26
trans-1,3-Dichloropropene	10061-02-6	27
cis-1,3-Dichloropropene	10061-01-5	28
1,4-Dioxane	123-91-1	29
Ethyl acetate	141-78-6	225
Ethyl benzene	100-41-4	226
Ethyl cyanide	107-12-0	30
Ethyl ether	60-29-7	227
Ethyl methacrylate	97-63-2	31
Ethylene oxide	75-21-8	214
2-Hexanone	591-78-6	-
Iodomethane	74-88-4	32
Methyl ethyl ketone	78-93-3	34
4-Methyl-2-pentanone	108-10-1	-
Methyl methacrylate	80-62-6	35
Methacrylonitrile	126-98-7	37
Methylene chloride	75-09-2	38
Styrene	100-42-5	-
1,1,1,2-Tetrachloroethane	630-20-6	40
1,1,2,2-Tetrachloroethane	79-34-6	41
Tetrachloroethene	127-18-4	42
Toluene	108-88-3	43
Tribromomethane	75-25-2	44
1,1,1-Trichloroethane	71-55-6	45
1,1,2-Trichloroethane	79-00-5	46
Trichloroethene	79-01-6	47

(continued)

TABLE 4-3 (continued)

Constituent	CAS No.[a]	BDAT Reference No.[a]
Volatile organics (continued)		
Trichloromonofluoromethane	75-69-4	48
1,2,3-Trichloropropane	96-18-4	49
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	231
Vinyl acetate	108-05-4	-
Vinyl chloride	75-01-4	50
1,2-Xylene	97-47-6	215
1,3-Xylene	108-38-3	216
1,4-Xylene	106-44-5	217
Semivolatile organics		
Acenaphthylene	208-96-8	51
Acenaphthene	83-32-9	52
Acetophenone	96-86-2	53
2-Acetylaminofluorene	53-96-3	54
Acrylamide	79-06-1	233
4-Aminobiphenyl	92-67-1	55
Aniline	62-53-3	56
Anthracene	120-12-7	57
Aramite	140-57-8	58
Benzo(a)anthracene	56-55-3	59
Benzal chloride	98-87-3	218
Benzenethiol	108-98-5	60
Benzo(a)pyrene	50-32-8	62
Benzo(b)fluoranthene	205-99-2	63
Benzo(g,h,i)perylene	191-24-2	64
Benzo(k)fluoranthene	207-08-9	65
Benzoic acid	65-85-0	-
p-Benzoquinone	106-51-4	66
Benzyl alcohol	100-51-6	-

(continued)

TABLE 4-3 (continued)

Constituent	CAS No.[a]	BDAT Reference No.[a]
Semivolatile organics (continued)		
Bis(2-chloroethoxy)methane	111-91-1	67
Bis(2-chloroethyl)ether	111-44-4	68
Bis(2-chloroisopropyl)ether	39638-32-9	69
Bis(2-ethylhexyl)phthalate	117-81-7	70
4-Bromophenyl phenyl ether	101-55-3	71
Butyl benzyl phthalate	85-68-7	72
2-sec-Butyl-4,6-dinitrophenol	88-85-7	73
p-Chloroaniline	106-47-8	74
Chlorobenzilate	510-15-6	75
p-Chloro-m-cresol	59-50-7	76
2-Chloronaphthalene	91-58-7	77
2-Chlorophenol	95-57-8	78
4-Chlorophenyl phenyl ether	7005-72-3	-
Chrysene	218-01-9	80
2-Methylphenol	95-48-7	81
4-Methylphenol	106-44-5	82
Cyclohexanone	108-94-1	232
Dibenzo(a,h)anthracene	53-70-3	83
Dibenzofuran	132-64-9	-
m-Dichlorobenzene	541-73-1	86
o-Dichlorobenzene	95-50-1	87
p-Dichlorobenzene	106-46-7	88
3,3'-Dichlorobenzidine	91-94-1	89
2,4-Dichlorophenol	120-83-2	90
2,6-Dichlorophenol	87-65-0	91
Diethyl phthalate	84-66-2	92

(continued)

TABLE 4-3 (continued)

Constituent	CAS No.[a]	BDAT Reference No.[a]
Semivolatile organics (continued)		
3,3'-Dimethoxybenzidine	119-90-4	93
p-Dimethylaminoazobenzene	60-11-7	94
3,3'-Dimethylbenzidine	119-93-7	95
2,4-Dimethylphenol	105-67-9	96
Dimethyl phthalate	131-11-3	97
Di-n-butyl phthalate	84-74-2	98
1,4-Dinitrobenzene	100-25-4	99
4,6-Dinitro-o-cresol	534-52-1	100
2,4-Dinitrophenol	51-28-5	101
2,4-Dinitrotoluene	121-14-2	102
2,6-Dinitrotoluene	606-20-2	103
Di-n-octyl phthalate	117-84-0	104
Di-n-propylnitrosamine	621-64-7	105
Diphenylamine	122-39-4	106
Diphenylnitrosamine	86-30-6	219
1,2-Diphenylhydrazine	122-66-7	107
Fluoranthene	206-44-0	108
Fluorene	86-73-7	109
Hexachlorobenzene	118-74-1	110
Hexachlorobutadiene	87-68-3	111
Hexachlorocyclopentadiene	77-47-4	112
Hexachloroethane	67-72-1	113
Hexachlorophene	70-30-4	114
Hexachloropropene	1888-71-7	115
Indeno(1,2,3-cd)pyrene	193-39-5	116
Isophorone	78-59-1	-
Isosafrole	120-58-1	117

(continued)

TABLE 4-3 (continued)

Constituent	CAS No.[a]	BDAT Reference No.[a]
Semivolatile organics (continued)		
Methapyrilene	91-80-5	118
3-Methylcholanthrene	56-49-5	119
4,4'-Methylenebis(2-chloroaniline)	101-14-4	120
Methyl methanesulfonate	66-27-3	36
2-Methyl naphthalene	91-57-6	-
Naphthalene	91-20-3	121
1,4-Naphthoquinone	130-15-4	122
1-Naphthylamine	134-32-7	123
2-Naphthylamine	91-59-8	124
m-Nitroaniline	99-09-2	-
o-Nitroaniline	88-74-4	-
p-Nitroaniline	100-01-6	125
Nitrobenzene	98-95-3	126
2-Nitrophenol	88-75-5	-
4-Nitrophenol	100-02-7	127
N-Nitrosodi-n-butylamine	924-16-3	128
N-Nitrosodiethylamine	55-18-5	129
N-Nitrosodimethylamine	62-75-9	130
N-Nitrosomethylethylamine	10595-95-6	131
N-Nitrosomorpholine	59-89-2	132
N-Nitrosopiperidine	100-75-4	133
N-Nitrosopyrrolidine	930-55-2	134
5-Nitro-o-toluidine	99-55-8	135
Pentachlorobenzene	608-93-5	136
Pentachloroethane	76-01-7	137
Pentachloronitrobenzene	82-68-8	138
Pentachlorophenol	87-86-5	139

(continued)

TABLE 4-3 (continued)

Constituent	CAS No.[a]	BDAT Reference No.[a]
Semivolatile organics (continued)		
Phenacetin	62-44-2	140
Phenanthrene	85-01-8	141
Phenol	108-95-2	142
Phthalic anhydride	85-44-9	220
Pronamide	23950-58-5	144
Pyrene	129-00-0	145
Pyridine	110-86-1	39
Resorcinol	108-46-3	146
Safrole	94-59-7	147
1,2,4,5-Tetrachlorobenzene	95-94-3	148
2,3,4,6-Tetrachlorophenol	58-90-2	149
1,2,4-Trichlorobenzene	120-82-1	150
2,4,5-Trichlorophenol	95-95-4	151
2,4,6-Trichlorophenol	88-06-2	152
Metals (Total and TCLP)		
Aluminum	7429-90-5	-
Antimony	7440-36-0	154
Arsenic	7440-38-2	155
Barium	7440-39-3	156
Beryllium	7440-41-7	157
Calcium	7440-70-1	-
Cadmium	7440-43-9	158
Chromium (total)	7440-47-3	159
Chromium (hexavalent)	-	221
Cobalt	7440-48-4	-
Copper	7440-50-8	160
Iron	7439-89-6	-

(continued)

TABLE 4-3 (continued)

Constituent	CAS No.[a]	BDAT Reference No.[a]
Metals (continued)		
Lead	7439-92-1	161
Magnesium	7439-95-4	-
Manganese	7439-96-5	-
Mercury	7439-97-6	162
Nickel	7440-02-0	163
Potassium	7440-09-7	-
Selenium	7782-49-2	164
Silver	7440-22-4	165
Sodium	7440-23-5	-
Thallium	7440-28-0	166
Vanadium	7440-62-2	167
Zinc	7440-66-6	168
Inorganics other than metals		
Cyanide	57-12-5	169
Fluoride	16964-48-8	170
Sulfide	8496-25-8	171
Organochlorine pesticides		
Aldrin	309-00-2	172
alpha-BHC	319-84-6	173
beta-BHC	319-85-7	174
delta-BHC	319-86-8	175
gamma-BHC	58-89-9	176
Chlordane	57-74-9	177
p,p'-DDD	72-54-8	178
o,p'-DDD	53-19-0	235
p,p'-DDE	72-55-9	179
o,p'-DDE	3424-82-6	236

(continued)

TABLE 4-3 (continued)

Constituent	CAS No.[a]	BDAT Reference No.[a]
Organochlorine pesticides (continued)		
p,p'-DDT	50-29-3	180
o,p'-DDT	789-02-6	237
Dieldrin	60-57-1	181
Endosulfan I	939-98-8	182
Endosulfan II	33213-6-5	183
Endosulfan sulfate	1031-07-8	238
Endrin	72-20-8	184
Endrin aldehyde	7421-93-4	185
Endrin ketone	53494-70-5	-
Heptachlor	76-44-8	186
Heptachlor epoxide	1024-57-3	187
Isodrin	465-73-6	188
Kepone	143-50-0	189
Methoxyclor	72-43-5	190
Toxaphene	8001-35-2	191
Phenoxyacetic acid herbicides		
2,4-Dichlorophenoxyacetic acid (2,4-D)	94-75-7	192
Silvex (2,4,5-TP)	93-72-1	193
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	93-76-5	194
Organophosphorus insecticides		
Disulfoton	298-04-4	195
Famphur	52-85-7	196
Methyl parathion	298-00-0	197
Parathion	56-38-2	198
Phorate	298-02-2	199
PCBs		
Aroclor 1016	12674-11-2	200
Aroclor 1221	11104-28-2	201

(continued)

TABLE 4-3 (continued)

Constituent	CAS No.[a]	BDAT Reference No.[a]
PCBs (continued)		
Aroclor 1232	11141-16-5	202
Aroclor 1242	53469-21-9	203
Aroclor 1248	12672-29-6	204
Aroclor 1254	11097-69-1	205
Aroclor 1260	11096-82-5	206
Dioxins and furans		
Hexachlorodibenzo-p-dioxins	-	207
Hexachlorodibenzofurans	-	208
Pentachlorodibenzo-p-dioxins	-	209
Pentachlorodibenzofurans	-	210
Tetrachlorodibenzo-p-dioxins	-	211
Tetrachlorodibenzofurans	-	212
2,3,7,8-Tetrachlorodibenzo-p-dioxin	1746-01-6	213

[a] Reference numbers taken from Table 3.2 from "Quality Assurance Project Plan for Characterization Sampling and Treatment Tests Conducted for the Contaminated Soil and Debris (CS&D) Program" prepared by the U.S. EPA Office of Solid Waste.

Description of Sampling Point

Samples were collected at the outlet of the mill as the soil was being milled.

Sample Collection Method

A composite sample was obtained by taking a grab sample from each bucket used to collect the effluent from the outlet of the mill. A portion of the composite sample was placed into eleven 8-oz wide-mouth glass jars.

Frequency of Sampling

One composite postmilling soil sample was collected.

Constituents Analyzed

The postmilling sample was analyzed for the complete CS&D list presented in Table 4-3.

4.1.3 Sampling Point 3 - Pretreatment Samples (Week T_0)

Purpose

The pretreatment samples were collected to determine the levels of the critical PAH constituents in the soil prior to bioslurry treatment. These samples served as the baseline for evaluating the technology's performance.

Description of Sampling Points

Composite samples were collected from the three sampling ports located along the side of the reactor at three different vertical locations (Figure 3-1). Samples from these three ports represented the three potentially distinct zones of the slurry. The bottom sampling port provided sample material from within the rake mixing zone, where the heaviest particles were likely to be present. The middle sampling port provided sample material from within the most well-mixed zone. Finally, the top sampling port provided a sample of the finest material.

Sample Collection Method

A 10- to 20-gram sample was taken from each port prior to reactor sampling. Samples were then dried at 98°C for 2 hours. The percent total solids was calculated for each port. Based on the percent total solids and the soil specific gravity, the specific gravity for the slurry at each port was obtained from Denver tables of specific gravity.

The percent total solids and specific gravity for each port were entered into a spreadsheet program that calculates the percent solids of a composite sample when different volumes are sampled from each port. The total sample volume desired was entered, and port volumes were adjusted proportionately until a 30 percent total solids was obtained for the composite sample.

At a given volume, the spreadsheet program also calculated (for each port) the percentage of the total sample being taken, the sample weight from that port, and the weight of dry soil from each port.

Sample volumes from each port were marked on the sampling jars prior to sampling. Samples were collected from each port--the bottom port was sampled first, followed by the middle and top ports. After collection of the sample, the container was shaken to allow for homogenization of the sample. The contents of the container were centrifuged to separate the liquid and sludge layers. The liquid was decanted into 1-liter amber glass bottles and the sludge was collected into 8-oz. glass jars.

Frequency of Sampling

One pretreatment sample from each of the five reactors was collected immediately after the reactors were initially charged (T_0).

Constituents Analyzed

All five pretreatment samples (one from each reactor) were analyzed for the critical contaminants listed in Table 4-4.

TABLE 4-4. CRITICAL CONTAMINANTS OF INTEREST FOR THE BURLINGTON NORTHERN SUPERFUND SITE

Semivolatiles Organics - Total Analysis
Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Chrysene
Dibenzofuran
Fluoranthene
Fluorene
2-Methylnaphthalene
Naphthalene
Phenanthrene
Pyrene

4.1.4 Sampling Point 4 - Posttreatment Samples (Weeks T_9 and T_{12})

Purpose

The posttreatment samples were collected 9 and 12 weeks after the start of testing to determine the levels of the critical PAH constituents remaining in the soil after treatment. These samples were used to evaluate the technology's performance.

Description of Sampling Point

Composite samples were collected from the three sampling ports located along the side of the reactor, as discussed in Subsection 4.1.3.

Sample Collection Method

The procedure used to collect the posttreatment samples was similar to that discussed in Subsection 4.1.3.

Frequency of Sampling

One posttreatment sample from each of the five reactors was collected at Week T_9 and Week T_{12}.

Constituents Analyzed

All five posttreatment samples from Weeks T_9 and T_{12} were analyzed for the critical contaminants listed in Table 4-4.

4.1.5 Sampling Point 5 - Off-Gas Samples

Purpose

Air sampling was conducted to characterize the off-gases emitted from the bioreactors during the operations and to determine organic constituent loss through volatilization. These samples were collected for information only and were not used to evaluate the technology's performance.

Description of Sampling Point

All five reactors were vented through stainless steel piping into a manifold system before carbon filtration and eventual exhausting to the outside air. The air

monitoring was conducted at a point prior to the collective manifold to obtain emissions from two individual reactors.

Sample Collection Method

Two sampling trains were constructed to collect samples for volatile and semivolatile organics. Volatile organics were collected in a SUMMA passivated canister, and semivolatiles were collected in XAD-2 resin tubes. The XAD-2 resin tubes and canisters were installed in the venting systems for the tested reactors.

Frequency of Sampling

Four consecutive sets of samples were collected from each of the two tested reactors during the first week of operation. Two sets of samples were collected during Weeks 2 through 5, and one set of samples was collected during Weeks 6, 7, and 9.

Constituents Analyzed

The XAD-2 resin tubes were analyzed for semivolatile organic compounds, and the SUMMA passivated canisters were analyzed for volatile organic compounds from the Target Compound List (TCL).

4.1.6 Sample Containers and Sample Preservation

For analyses requiring discrete zone samples, slurry samples were collected in individual sample containers in the manner described previously (Subsections 4.1.3 and 4.1.4). The remaining samples were collected as composite samples in clean 4-oz, 8-oz, or 1-liter amber glass bottles with Teflon-lined screw caps. Samples submitted to ITAS-Cincinnati laboratory for TPH and semivolatile analyses were preserved with hydrochloric acid to inhibit biological activity. In addition, samples were centrifuged into discrete solid and liquid phases prior to analyses.

All samples were packed in coolers with ice to 4°C and were either shipped to ECOVA laboratory by an overnight carrier or transported to ITAS-Cincinnati laboratory, depending on the analyses to be performed. Proper shipping papers, chain-of-custody forms, and request-for-analysis forms also accompanied the samples. Table

4-5 summarizes sample containers, preservation methods, and maximum holding times for the various parameter classes, as well as specific analytes for some samples.

4.2 Analytical Procedures

Table 4-6 lists the analytical parameters and the appropriate preparation and analytical methods. A brief description of the methods used to analyze the soil and liquid matrices for the critical parameters is presented in Subsections 4.2.1 and 4.2.2, respectively.

4.2.1 Semivolatile Organics Analysis (Soil Matrix)

The contaminants of most critical concern for this pilot-scale study were the PAHs. Soil samples were prepared in accordance with Method 3550 in SW-846. This method uses ultrasonic sound waves to penetrate and disrupt the soil matrix to allow more efficient extraction of the target analytes. Because of the heavy loading of PAHs expected in the untreated soil, the samples were prepared as medium-level soils. A 1-g soil sample was mixed with anhydrous sodium sulfate and solvent-extracted by ultrasonic pulses three times. The solvent layer was collected by vacuum filtration, concentrated down to a 1-mL aliquot, and stored at 4°C until ready for analysis. Prior to extraction, 1 mL of surrogate standard solution was spiked into the sample to check the extraction efficiency.

The sample was spiked with 20 μL of internal standard solution before analysis to enable the quantitation of the target compounds identified in the sample. The sample was then analyzed in accordance with Method 8270 in SW-846. This is a direct-injection method for semivolatile compound analysis by use of a capillary column and a full-scan mass spectrometer. The mass spectrometer allows qualitative identification as well as quantitative analysis of the target analytes detected in the samples.

4.2.2 Semivolatile Organics Analysis (Liquid Matrix)

The liquid sample for semivolatile organics analysis was extracted by continuous liquid-liquid extraction as outlined in Method 3520 in SW-846. An aliquot of liquid

TABLE 4-5. SAMPLE CONTAINERS, PRESERVATIVES, AND MAXIMUM HOLDING TIMES[a]

Measurement Parameter	Container	Preservatives[b]	Maximum Holding Time[c]
Premilling & Postmilling Soil Samples			
Volatile organics (total)	Widemouth glass	≤4°C	14 days
Semivolatile organics (total)	Widemouth glass	≤4°C[d]	14 days for extraction, analyze within 40 days
Total metals (except mercury)	Widemouth glass	≤4°C	6 months for extraction, 6 months for analysis
Total mercury	Widemouth glass	≤4°C	28 days for extraction, 28 days for analysis
Cyanide	Widemouth glass	≤4°C	14 days
Fluoride	Widemouth glass	≤4°C	28 days
Sulfide	Widemouth glass	≤4°C	7 days
Organochlorine pesticides (total)	Widemouth glass	≤4°C	14 days for extraction, analyze within 40 days
Phenoxyacetic acid herbicides (total)	Widemouth glass	≤4°C	14 days for extraction, analyze within 40 days
Organophosphorus insecticides	Widemouth glass	≤4°C	14 days for extraction, analyze within 40 days
PCBs	Widemouth glass	≤4°C	14 days for extraction, analyze within 40 days
Volatile organics (TCLP)	Widemouth glass	≤4°C	14 days for TCLP, 14 days for analysis
Semivolatile organics (TCLP)	Widemouth glass	≤4°C	14 days for TCLP, 7 days for extraction, 40 days for analysis
Pesticides (TCLP)	Widemouth glass	≤4°C	14 days for TCLP, 7 days for extraction, 40 days for analysis
TCLP metals (except mercury)	Widemouth glass	≤4°C	6 months for extraction, 6 months for analysis
TCLP mercury	Widemouth glass	≤4°C	28 days for extraction, 28 days for analysis
Sulfate	Widemouth glass	≤4°C	28 days
Chloride	Widemouth glass	≤4°C	28 days
TOC	Widemouth glass	≤4°C	28 days
Grain size distribution	Widemouth glass	NA[e]	NA
Oil and grease	Widemouth glass	≤4°C[d]	28 days
TOX	Widemouth glass	≤4°C	18 days
TPH	Widemouth glass	≤4°C[d]	28 days
Surfactants	Widemouth glass	≤4°C	48 hours
Phosphorus	Widemouth glass	≤4°C	28 days
Ammonia	Widemouth glass	≤4°C	
Nutrients	Widemouth glass	≤4°C	
pH	—	—	ASAP
Inorganic materials	Widemouth glass	≤4°C	28 days

TABLE 4-5. (continued)

Measurement Parameter	Container	Preservatives[b]	Maximum Holding Time[c]
Bioreactor Sludge Samples			
Semivolatile organics	Widemouth glass	≤4°C, HCl to pH<2	14 days for extraction, 40 days for analysis
TPH	Widemouth glass	≤4°C, HCl to pH<2	28 days
Phosphorus	Widemouth glass	≤4°C	28 days
Ammonia	Widemouth glass	≤4°C	
Nutrients	Widemouth glass	≤4°C	
TSS/TVSS	Widemouth glass	≤4°C	7 days
Total heterotrophs/PAH degraders	Widemouth glass	≤4°C	2 days
Bioreactor Liquid Samples			
Semivolatile organics	1-liter amber glass	≤4°C, HCl to pH<2	7 days for extraction, 40 days for analysis
TPH	Widemouth glass	≤4°C, HCl to pH<2	28 days

[a] U.S. EPA Test Methods for Evaluating Solid Waste. 1986. Volume 1B. Laboratory Manual Physical/Chemical Methods. SW-846, Third Edition. Office of Solid Waste, Washington, D.C.

[b] Samples were preserved immediately upon sample collection.

[c] Samples were analyzed as soon as possible after collection. The times listed are the maximum times that samples should be held before analysis and still be considered valid. All data obtained beyond the maximum holding times will be flagged.

[d] Slurry samples were preserved with HCl prior to being centrifuged to inhibit biological activity.

[e] NA = Not applicable.

TABLE 4-6. SOIL SAMPLE PREPARATION AND ANALYTICAL METHODS

Parameter class	Preparation method[a]	Analytical method[a]
Volatile organics[b]	NA[c]	8240
Semivolatiles, Solids	3550	8270
Liquid	3520	8270
Metals (total)		
Antimony	3050	6010
Arsenic	3050	7060
Barium	3050	6010
Beryllium	3050	6010
Cadmium	3050	6010
Chromium (T)	3050	6010
Chromium (VI)	7196	7196
Copper	3050	6010
Lead	3050	6010
Mercury	7471	7471
Nickel	3050	6010
Selenium	3050	7740
Silver	3050	6010
Thallium	3050	7841
Vanadium	3050	6010
Zinc	3050	6010
Aluminum	3050	6010
Calcium	3050	6010
Cobalt	3050	6010
Iron	3050	6010
Magnesium	3050	6010
Manganese	3050	6010
Potassium	3050	6010
Sodium	3050	6010
Metals (TCLP)[d]		
Arsenic	3010	7060
Barium	3010	6010
Cadmium	3010	6010
Chromium (T)	3010	6010
Lead	3010	6010
Mercury	7470	7470
Selenium	3010	7740
Silver	3010	6010
PAHs	See Appendix G of SAP	8310
Inorganics (other than metals)		
Cyanide(T)	9012	9012
Fluoride	13B[e]	340.2[f]
Sulfide	Water extraction	9030
Organochlorine pesticides	3550	8080

(continued)

TABLE 4-6 (continued)

Parameter class	Preparation method[a]	Analytical method[a]
Phenoxyacetic acid herbicides	8150	8150
Organophosphorus insecticides	3550	8140
WCAPs and other soil/technology parameters		
pH	NA	9045
Water content	NA	ASTM D2216
Grain size distribution	NA	ASTM D421-85[g]
Oil and grease	NA	413.1[f]
Sulfate	Water extraction	9038
Chloride	Water extraction	9252
TOC	Slurry with water	9060
TOX	9020	9020
Phosphorus content	NA	365.2[f]
Surfactants	NA	425.1[f]
Total petroleum hydrocarbons	NA	418.1[f]
Total suspended solids	SM 209[h]	SM 209[h]
Inorganic materials	NA	300.0
Ammonia	NA	Indophenol Blue (Appendix G of SAP)
Total heterotrophs and PAH degraders	NA	Method SM 907[h]
Microtox	NA	See Appendix G of SAP
Volatile air emissions	TO-14[i]	TO-14
Semivolatile air emissions	See Appendix I of SAP	8270

[a] U.S. EPA - Test Methods for Evaluating Solid Waste. 1986. Volume 1B. Laboratory Manual Physical/Chemical Methods. SW-846, Third Edition. Office of Solid Waste, Washington, D.C.

[b] Alcohols listed in the volatile parameter class will be prepared/analyzed by Methods 5040/8015 and the option of direct aqueous injection in Method 5040 will be used.

[c] NA = Not applicable.

[d] 40 CFR Part 268.50, Subpart E, Appendix I, March 29, 1990.

[e] 40 CFR Part 60, Appendix A, Method 13B, September 14, 1987.

[f] Methods for the Chemical Analysis of Water and Wastes (U.S. EPA 1983).

[g] American Society for Testing and Materials.

[h] Standard Methods for the Examination of Water and Wastewater (SM 1985).

[i] Determination of volatile organic compounds (VOCs) in ambient air.

sample was placed in an extraction vessel, and the pH of the sample was adjusted to pH 2 for extraction of acid-type compounds. One milliliter of surrogate spiking solution was added, and the sample was extracted for 18 hours with a continuous flow of methylene chloride. The pH of the sample was then adjusted to pH 11 for extraction of base-neutral compounds. The sample was extracted for another 18 hours with a continuous flow of fresh methylene chloride. The solvent layers from both extracts were combined in a concentrator tube, and the sample was blown down to a 1-mL volume and stored at 4°C until ready for analysis.

The sample was spiked with 20 μL of internal standard solution before analysis to enable the quantitation of the target compounds identified in the sample. The sample was then analyzed in accordance with Method 8270 in SW-846. This is a direct-injection method for semivolatile compound analysis by use of a capillary column and a full-scan mass spectrometer. The mass spectrometer allows for a qualitative identification as well as quantitative analysis of the target analytes detected in the samples.

4.3 Deviations From the Sampling and Analysis Plan

During the course of the study, several deviations from the SAP were made. Because of the laboratory's difficulty in analyzing samples for TPH by ECOVA's methodology, it was decided that EPA Method 418.1 would be used for TPH analysis. The concentrations of contaminants increased during Weeks 4 through 6 of the study; therefore, a decision was made to reinoculate the bioreactors. As a result, samples were not collected during Week 8 of the study as scheduled. In addition, the final sampling event was changed to Week 9 instead of Week 10. The reactors were reinoculated after the Week 9 sampling event. Additional sampling was performed during Weeks 10, 11, and 12 to monitor the effectiveness of the reinoculation.

4.4 Safety

Activities involved with the bioslurry treatment testing were in accordance with all health and safety guidelines described in the Project Health and Safety Plan (Appendix E).

All personnel involved with the handling of the waste followed the directions of the T&E Health and Safety Officer; no deviations from this plan took place without the approval of the T&E Health and Safety Officer.

SECTION 5

DESIGN AND OPERATING DATA COLLECTED

Prior to the startup of the pilot-scale study at the T&E facility, ECOVA performed a material characterization that involved the physical, chemical, and microbial characterization of site soils. This information was necessary to develop an appropriate design for pilot study. During the pilot-scale bioslurry testing, ECOVA collected and analyzed a series of operating data (particle size, total heterotrophs, nutrient levels, etc.) to monitor and evaluate the performance of bioreactor operations.

5.1 Material Characterization

The information on material characterization generated during the bench-scale testing was also utilized for the pilot-scale testing. Physical characterization was performed by using a standard sieve analysis to determine the particle size distribution of the soil. This information was used to determine appropriate slurry concentrations and to estimate nutrient requirements for the slurries. Chemical and microbial characterizations were performed to determine the levels of target contaminants, to determine the inorganic nutrients required to enhance microbial growth, and to ensure that specific microbial degrader populations were present.

5.1.1 Physical Characterization

The particle size distribution of the soil was determined by wet sieve analysis in accordance with ASTM D 2217. Premilling and postmilling samples were collected for particle size analysis and the results indicated that the milling process was beneficial in reducing particle size. A detailed explanation of particle size analysis is given in Subsection 5.2.2.

5.1.2 *Chemical Characterization*

Baseline chemical analyses were performed on composited soil samples to determine contaminant levels. Analysis for semivolatile contaminant levels was performed in accordance with U.S. EPA Method 8270 (SW 846) and ECOVA's Method SOP SSC-4. In addition, soil was analyzed for oil and grease, TPH, TOC, and inorganic nutrient ions (NO_3, NH_4, PO_4, and SO_4). The inorganic nutrient data were used to determine whether, based on TOC levels, the ratio of nitrogen (N), phosphorus (P), and sulfur (S) was sufficient to support optimal microbial activity. Soil pH was measured at ECOVA's laboratories by shaking 10 g of soil in 10 mL of distilled water for 5 minutes and then analyzing it with a pH meter and probe. A soil toxicity test was also performed by Microtox procedures. Table 5-1 presents a summary of the baseline analyses performed.

TABLE 5-1. CHEMICAL ANALYSES

Compound	Method
Semivolatiles (BNAs)	EPA 8270 ECOVA SSC-4
Oil and grease (O&G)	EPA 413.1
Inorganic nutrients (NO_3, PO_4, SO_4, NH_4)	EPA 300.0
NH_3	EPA 350.2
TOC	EPA 9060
TPH	EPA 418.1
Composited soil sample	Microtox

5.1.3 *Microbial Characterization*

A baseline microbiological evaluation was performed to determine the microbial populations in the soil. Standard agar plate enumeration methods were used to determine total heterotrophic bacteria as well as specific PAH degraders. Total heterotrophic bacterial enumerations were accomplished on a plate count agar (PCA) after the serial dilution plating of samples in accordance with Standard Method 907. Plates

were incubated at 27°C and evaluated daily for growth. Results indicated the existence of a substantial population of heterotrophic bacteria consisting of 6.3×10^7 colony-forming units per gram of soil.

The PAH-degrading organisms were identified and enumerated by serial dilution plating onto PAH mineral salts (PMS) plates and PMS plates with 0.05 percent salicylate (PMSS) [500 ppm]. Controls for bacterial enumeration included uninoculated plates of the three media (PCA, PMS and PMSS plates). Quality control of the PMS plates included plates inoculated but not sprayed with substrate. The PMS plates with salicylate were incubated at 27°C in a humidity-controlled incubator. The PAH mineral salts plates were sprayed with the appropriate substrate solution and incubated at room temperature.

Substrate solutions were composed of 1 percent solutions of phenanthrene, pyrene, fluoranthene, and fluorene dissolved in an appropriate solution. These solutions were sprayed lightly over the surface of the PMS plates, which resulted in a thin film of PAH coating on the agar surface. Crystals of naphthalene were added to the lid of PMS plates and incubated separately because of the higher volatility of naphthalene.

Plates were checked daily for growth. After 1 or 2 days, a significant amount of growth was apparent on PMSS plates, and they were sprayed with substrate. Plates were examined hourly during the first day and daily thereafter.

Baseline microbiological characterizations for total platable heterotrophic populations indicated that these soils contained a robust population of bacteria [on the order of 6.3×10^7 colony-forming units (CFU) per gram of soil]. The more than 20 distinct colonial morphologies that plated out on the PCA reflect the bacterial population diversity. Under the conditions of this assay, several of these were slow-growing isolates (i.e., requiring more than 1 but no more than 3 weeks for colonies to appear). Tables 5-2 and 5-3 summarize the results of substrate-specific enumerations performed on these soils for certain PAH substrates. The data suggest that approximately 10 percent of the total heterotrophic population (platable isolates) is capable of utilizing various PAHs as sole sources of carbon for growth. This subset of the population totals approximately 10^6 CFU/gram of soil (Table 5-2).

TABLE 5-2. ENUMERATION OF BACTERIA CAPABLE OF UTILIZING PAH AS SOLE CARBON SOURCE

Substrate	CFU/gram of soil	Reaction
Naphthalene	1×10^6	Colonies turned dark brown.
Fluorene	3×10^6	Yellowing around colonies. Zones of clearing present.
Phenanthrene	2.5×10^6	Some yellowing around colonies. Zones of clearing present.
Fluoranthene	1×10^6	Various shades of browning.
Pyrene	3.0×10^6	Various shades of browning.

TABLE 5-3. SALICYLATE-UTILIZING BACTERIA WITH PAH COOXIDATION CAPABILITY

Compound	CFU/gram	Reaction
Naphthalene	1.1×10^6	Yellowing around colonies.
Fluorene	1.1×10^6	Dark yellow clearing zones.
Phenanthrene	1.8×10^5	Dark yellow clearing zones.
Fluoranthene	9.0×10^5	No reaction.
Pyrene	9.6×10^5	No reaction.

Another subset of the total bacterial population enumerated consisted of those isolates capable of growth with salicylate as the sole carbon source while also retaining the capability of cooxidizing various PAH compounds.

The salicylate-utilizing population also averaged approximately 10^6 CFU per gram of soil (Table 5-3). This population appeared to lack the capacity to cooxidize PAHs greater than 3 rings in size. This was evident by the lack of reaction when fluoranthene and pyrene were used as the screening substrates.

5.2 Operating Data Collected During Treatment Test

The pilot-scale reactor startup was completed on May 8, 1991. At this time, reactors were capped and samples taken for the initial Week T_0. It should be noted here that only five of the originally scheduled six bioreactors were brought on line.

5.2.1 Evaluation of Biological Conditions Within the Reactor

Evaluation of the environmental conditions created within the reactor was confined to the daily monitoring of water level, pH, dissolved oxygen, temperature, and foaming. Appendix G presents the raw data gathered. Figures H-1 through H-5 in Appendix H present data gathered on each reactor.

Water measurements were taken by measuring the distance from the top of the slurry surface to the top opening in the reactor. Fresh demineralized water was added to the reactor to maintain a level of 14 inches from the top of the reactor. During the first week, water loss in each reactor was 0.5 to 1 liter per day. Early in the pilot-scale operations, the water loss was found to have a major impact on reactor performance. Part of the material blockage problems in the airlift arms could be attributed to falling slurry levels. If the slurry level dropped too far below the airlift arms, it became difficult for the airlifts to push the slurry above the water column.

A hand-held OMEGA pH/Conductivity Meter (Model PHH-60/80) was used to monitor pH and temperature. The pH meter was calibrated daily with pH 7.0 and pH 10 standard solutions. Reactor pH was determined by taking a 100- to-200 mL sample from the top port of the reactor and monitoring its pH for 5 minutes. Adjustments to pH were made with NaOH or phosphoric acid. Daily monitoring of the pH in the reactors revealed that it fluctuated drastically during the initial stages of PAH degradation, particularly during the first two weeks of this study.

Dissolved oxygen (D.O.) readings were taken by using a hand-held YST Dissolved Oxygen Meter. Data indicate that the air delivery system on the EIMCO reactors efficiently maintained the D.O. above the baseline 2-ppm concentration needed for optimal aerobic bioactivity.

Temperature readings were taken by using a hand-held YST Dissolved Oxygen Meter with a temperature probe. Readings from the temperature control panels located on the reactors were also taken, but were not tabulated because of the associated instrument error. The Chromalox 3910 Temperature controllers on the EIMCO Biolift™ Reactors were not calibrated correctly for temperature before startup of the system. The slurry temperature was also affected by the heat produced by the air compressors.

Foaming within the reactor was monitored by rating the foam level within the reactor on a scale of 0 to 4. If no foam was present, a rating of zero was given, and foam filling the reactor was rated as 4. Foaming was monitored to evaluate air delivery, mechanical problems, and biosurfactant production. Foaming affected the reactors by interfering with the air manifold systems. This problem was alleviated by the addition of food-grade antifoam.

5.2.2 Particle Size

A major factor of concern from the initiation of the pilot-scale phase was the particle size of the slurried soil. It was important that at least 30 percent of the soil be smaller than the 100-mesh fine fraction to produce the necessary viscosity for maintaining a manageable slurry suspension. Bioavailability of the soil-bound PAH residues as a function of the path length from particle surface to innermost recesses was crucial for maintaining a timely and efficient biodegradation rate. The soil was therefore wet-milled by passing it through a ball mill three times before using it to charge the reactors. Particle-sizing samples were taken before and after milling and at Week T_8. These samples were analyzed in accordance with ASTM D422-62. The resulting comminution of the soil particles is shown in Table 5-4 and Figure 5-1.

As a percentage of the total solids, soil directly from the site (premilled) has a relatively high concentration of large-size particles (≥ 50 mesh). After milling (postmilling), the fraction of this soil particle size is negligible. The fraction of soil captured on the 100-mesh sieve represented an appreciably greater portion of the total soil (42% vs. 26%). The milling process did increase the proportion of soil

TABLE 5-4. PARTICLE SIZE FRACTIONS

Sieve No.	Inches	mm	Percent of Total Weight		
			Premilling	Postmilling	8 Weeks
10	0.0787	2	9.21	0.39	0.03
18	0.0334	1	2.81	0.37	0.27
30	0.0234	0.6	2.62	0.42	0.38
50	0.11	0.3	17.00	6.99	5.83
70	0.0083	0.212	16.13	18.01	13.17
100	0.0059	0.15	26.07	41.20	35.76
140	0.0041	0.106	7.46	7.20	18.06
200	0.0029	0.075	4.09	6.07	NA[a]
325	0.0017	0.045	3.21	2.86	13.96
Filtrate		<0.045	11.40	16.49	12.54
			100.00	100.00	100.00

[a] NA = Not analyzed.

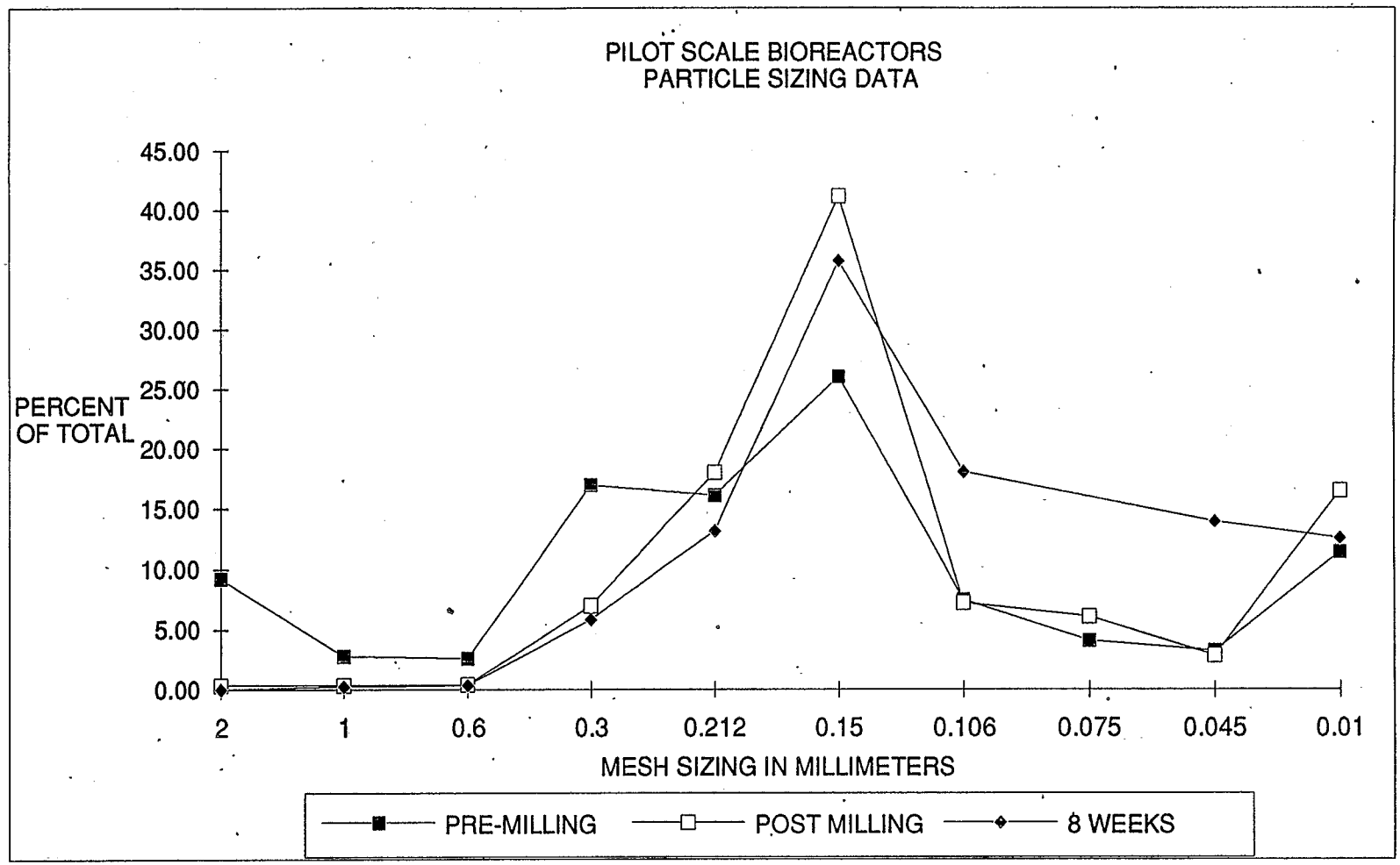

Figure 5-1. Particle sizing.

retained on the 325-mesh. This increase in fines was important in establishing sufficient slurry viscosity to maintain reactor operation. An appreciable breakdown of the larger sand particles to much finer sand particles occurred during this milling. This downward shift in particle size distribution after milling was the intent of the milling process.

Examination of the particle size data (Figure 5-1, Table 5-4) for Week T_8 soil reveals a further phenomenon that must have occurred within the reactors themselves. The percentage of the soil with particle size ≤ 140-mesh at Week T_8 is appreciably greater than that for the pre- or postmilled soil. This indicates a further comminution of the soil particles to a greater fraction of silt particles within the reactors over time. Comminution increases the viscosity of the slurry (as the number of particles increases), decreases the path length that the PAHs within the soil particles must diffuse to the surface (which decreases the mass transfer limitations), creates greater surface area to which bacteria can attach and adsorb PAHs for metabolism, and probably increases the extraction efficiency of soil-bound PAHs.

5.2.3 Total Volatile Solids (TVS)

The data for total volatile solids (which, *theoretically*, are indicative of organic matter in the form of bacteria, PAHs, other hydrocarbons, etc.) pertain to the particle-sizing fractions determined at three of the sampling times (postmilling, premilling, and Week T_8). These data are presented in Tables I-1a, b, and c; I-2a, b, and c; and I-3a, b, and c in Appendix I. Because the data were collected on individual sieve fractions, interpretations should apply *only* to the performance of the EIMCO Airlift™ Reactors and *not* to PAH degradative rates observed in the reactor slurries. The viscosity of the slurry itself increased rapidly in the early part of the study as the fraction of silt particles increased. Data on total volatile solids in various particle-size fractions are shown in Figure 5-2. As shown in the figure the percent TVS within each fraction changes substantially in the milling step, with the volatile fraction being shifted to the lower-sized particles. The Week T_8 sample also shows this trend.

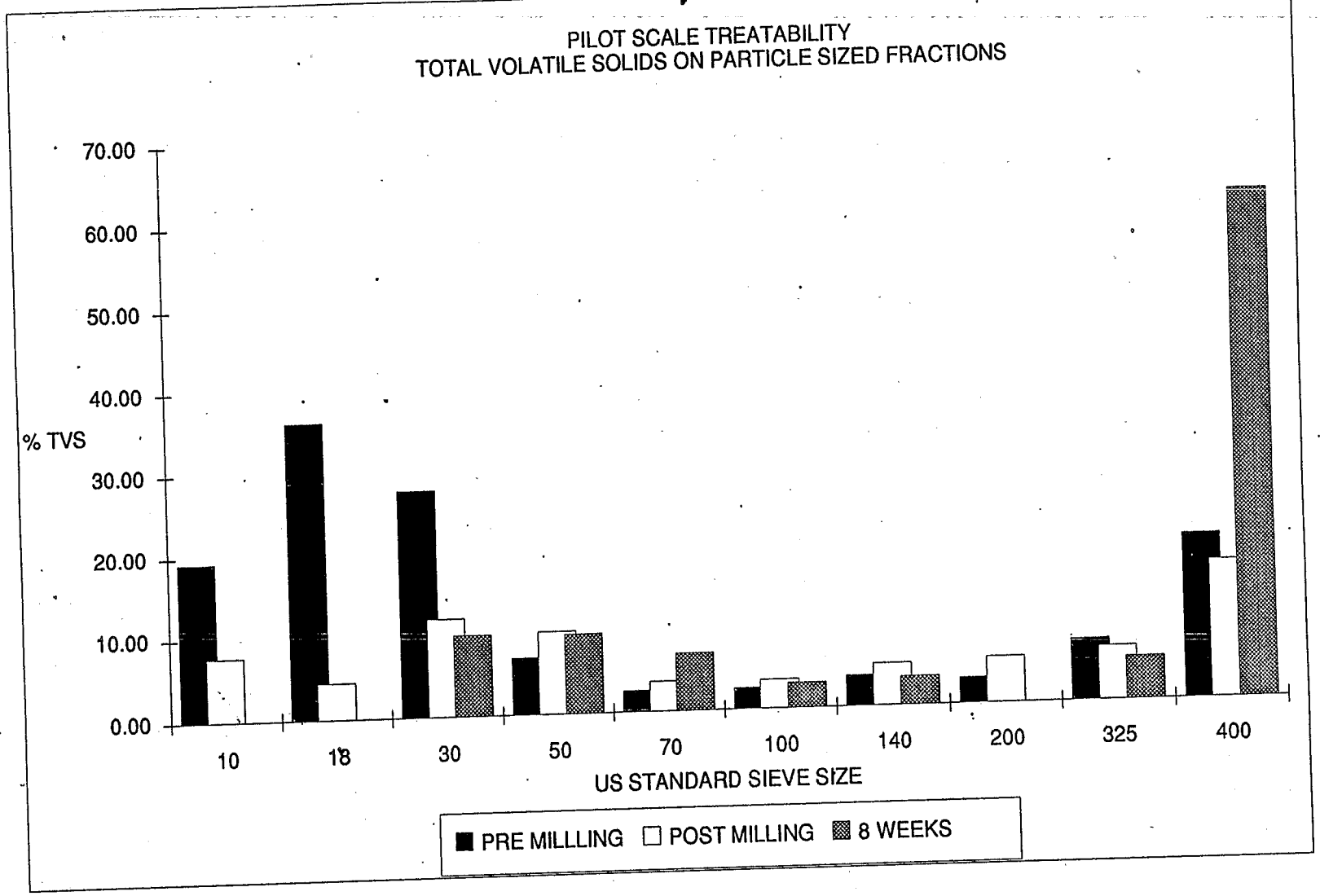

Figure 5-2. Pilot-scale data on total volatile solids on various particle-size fractions.

The total weight of each sieve fraction of soil and the fraction of total volatile solids in each fraction were calculated at post-milled and Week T_8. At post-milled, although most of the soil was retained in the 70- and 100-mesh sizes, most of the total volatile solids were in the small volume of very large soil particles as well as the fine sand and silt particles (<140-mesh size). At Week T_8, the fraction of soil retained by 200- and 325-mesh sizes had increased and the 100-mesh size fraction had dramatically declined (Figure 5-3). Also, the large fraction of TVS that had been in the >70-mesh fraction of soil at post-milled had moved to the 140-mesh fraction by Week T_8. This phenomenon could reflect the bacterial degradation of the TVS in the >70-mesh fraction of soil and the greater abundance of bacteria in the 140-mesh sieve. This apparent translocation is further supporting evidence of the comminution of the soil within the reactors over the course of the study.

5.2.4 Total Solids

Total solids were measured at each of the three reactor ports (top, middle, and bottom) at every time point through Week T_{10}. These measurements determined the proportion of slurry to be taken from each port to achieve a 30 percent slurry sample each time from each reactor. This analysis was necessary because, with this particular soil in a CSTR, the slurry in the reactor varied in solids content at different levels. As indicated in the data presented in Table 5-5, fines tended to remain suspended, whereas progressively heavier particles settled lower in the reactor. The solids content at each port averaged for all five reactors is shown in Figure 5-4. The graphic representations of Table 5-5 data are presented in Figures J-1 through J-5 in Appendix J.

Whenever the solids content at the bottom port dropped, more slurry was removed from that port to compensate and to maintain a 30 percent slurry content in the sample. Tables K-1 through K-8 in Appendix K present the raw data for the percent dry weight removed from each port on each reactor at each time point. So the same distribution of soil grain size would be maintained in each sample, the pro

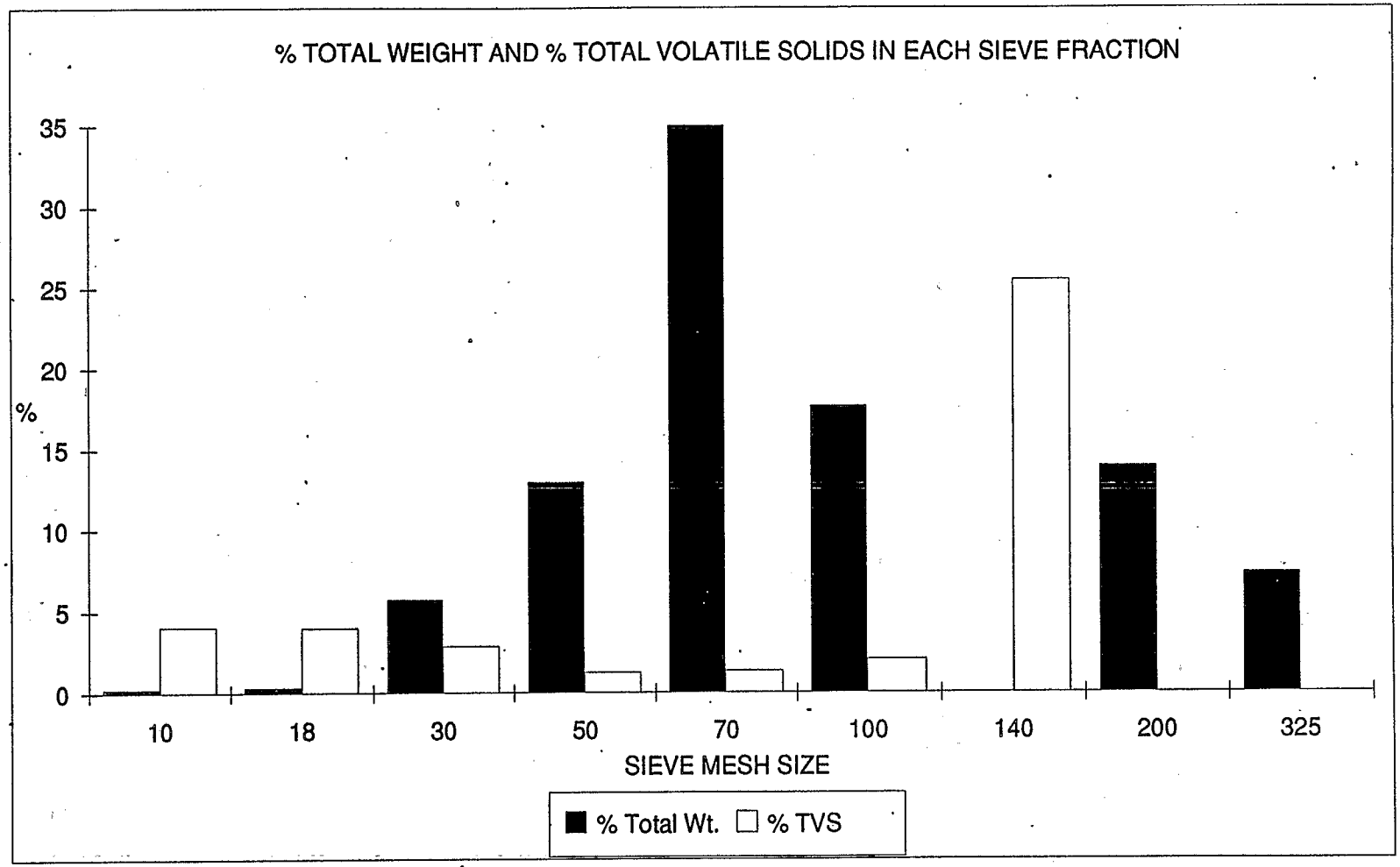

Figure 5-3. Percent total weight and percent TVS in each sieve fraction – T_8.

TABLE 5-5. PERCENT TOTAL SOLIDS DATA

Bioreactor	Port	Week 0	Week 1	Week 2	Week 3	Week 4	Week 6	Week 9	Week 10
1	Top	20.3000	12.8400	13.9100	11.5200	12.9100	9.8000	11.2400	1.5600
	Mid	26.0500	11.7300	12.1500	11.5900	12.9800	8.0000	8.3800	
	Bottom	71.4700	68.3200	69.7600	67.5400	70.1200	67.1000	70.2900	48.8400
2	Top	21.4900	14.3400	12.0900	11.9200	9.5600	11.3000	9.4800	8.8000
	Mid	21.0800	13.5700	13.3600	12.5000	12.8000	13.2000	10.0100	9.3600
	Bottom	69.6800	69.8000	69.6500	62.2900	67.3500	62.9000	15.7200	65.2700
4	Top	14.4200	15.2700	10.7100	9.8200	10.6000	10.4000	8.7100	6.0400
	Mid	14.5600	14.8800	13.1000	12.2700	13.6400	10.4000	8.8000	9.1200
	Bottom	69.4200	70.5600	68.2000	65.5300	52.7100	74.1000	70.7400	59.0500
5	Top	15.1100	13.6400	12.4500	10.8300	10.3300	11.7000	10.3100	8.0100
	Mid	11.3600	15.4300	12.4600	13.3600	14.4800	14.8000	9.3600	7.6200
	Bottom	71.1900	67.3400	69.5400	65.4800	68.0800	73.8000	38.5700	57.0800
6	Top	11.9500	12.6500	12.7500	10.4300	11.2600	9.4000	7.9200	6.6800
	Mid	11.7900	13.6900	11.6200	13.2000	13.4700	9.2000	8.5300	8.8800
	Bottom	69.6000	70.2300	67.2200	66.7300	81.4700	68.7000	26.1800	58.4400
MEAN	Top	16.65	13.75	12.38	10.90	10.93	10.52	9.53	6.22
	Mid	16.97	13.86	12.54	12.58	13.47	11.12	9.02	8.75
	Bottom	70.27	69.25	68.87	65.51	67.95	69.32	44.30	57.74
SD	Top	4.0676	1.0850	1.1571	0.8392	1.2624	0.9731	1.3038	2.8205
	Mid	6.3924	1.4279	0.7055	0.7203	0.6592	2.8199	0.6696	0.7752
	Bottom	0.9754	1.3686	1.1203	1.9987	10.2486	4.7288	25.2613	5.8854

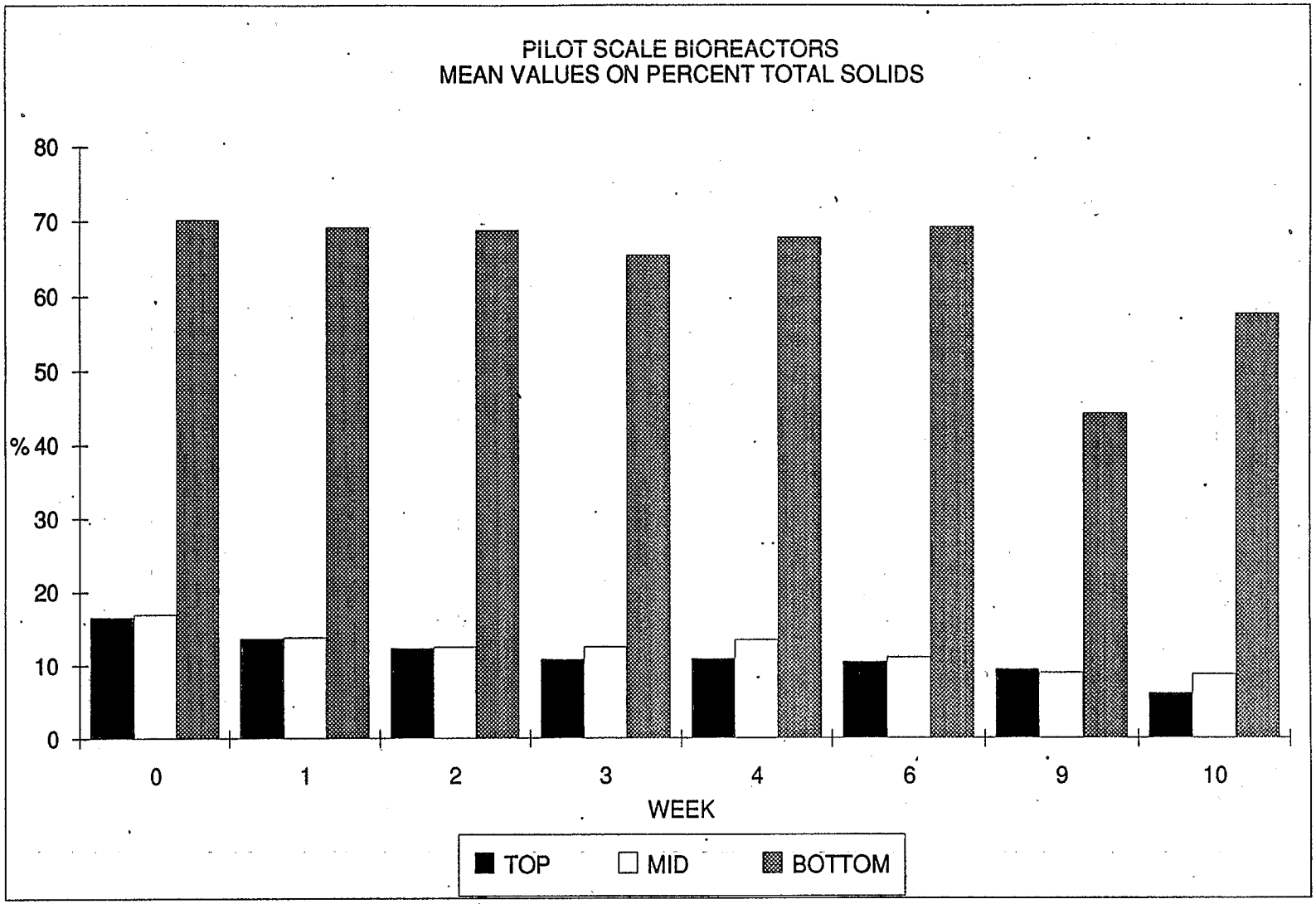

Figure 5-4. Total solids data for all pilot-scale reactors.

portional volumes taken from each port had to be adjusted accordingly for each sampling event. As an example of how the volumes from any given port changed over time, Table 5-6 shows that fraction of total sample removed from the bottom reactor port.

TABLE 5-6. FRACTION OF TOTAL SAMPLE REMOVED FROM THE BOTTOM REACTOR PORT

Week	% Total sample volume
T_0	21.7 ± 7.1
T_1	26.0 ± 1.6
T_2	28.2 ± 1.2
T_3	30.9 ± 1.3
T_4	30.9 ± 6.5
T_6	30.2 ± 3.4
T_9	41.8 ± 5.1
T_{10}	30.4 ± 0.8

In Figure 5-4 (which shows the solids content at each port averaged for all five reactors), at Week T_9 a sharp dip in the apparent solids value occurred in the bottom port. The technician was forced to ignore this reading and assume that the solids content had not changed in the bottom port. Whereas it is possible that the solids content at the bottom ports of all reactors did indeed drop at Week T_9 (the airlift pressure or the rake speed increased through all the reactors), the reactor monitoring check-off sheets do not support this possibility. An analytical error is more likely to have been the cause, inasmuch as the percent of bottom port slurry collected later at Week T_{10} declined to normal levels.

5.2.5 Inorganic Nutrient Levels

The levels of orthophosphate, ammonia, and nitrate were monitored in accordance with the sampling schedule in Table 4-1. The resulting data are presented in

Table 5-7. Initially, the nutrient analyses were performed by a CLP laboratory (Pacific Northwest Environmental Laboratory, Seattle, WA). By Week T_6, however, this protocol proved to have far too long a turnaround time; therefore, ECOVA performed the nutrient analyses for Weeks T_6, T_9, and T_{12} in-house.

Nutrient levels declined in all reactors over the entire course of the study according the data presented in Table 5-8, which is a summary of Table 5-7 in which all reactor values are averaged.

Ammonia nitrogen is typically the nitrogen source of choice for aerobic chemoheterotrophic bacteria; during active metabolism, the levels of available ammonia should decline. Nitrate nitrogen is typically an oxidized end product of bacterial metabolism, assuming the ammonia levels are adequate; however, nitrate nitrogen can be a secondary source of nitrogen. As shown in Table 5-7, nitrate levels peaked at Week T_9 and then declined at Week T_{12}, which indicates that between those two time points ammonia nitrogen levels did indeed become limiting and the bacteria used the available nitrate nitrogen. Ideally, when Reactors 2, 4, 5, and 6 were amended at Week T_{10}, the slurries should have been supplemented with additional ammonia and phosphorous. As indicated later in the data for total heterotrophic plate counts, however, a stable population of heterotrophic bacteria had been established by Week T_3 and provided a stable, sufficient pool of nitrogen (total Kjeldahl nitrogen or TKN) through nitrogen cycling for the duration of the study.

5.2.6 Total Heterotrophs and Specific PAH Degraders

Levels of total heterotrophic bacteria were determined for the slurries of each reactor in accordance with the sampling schedule in Table 4-1. Table 5-9 presents the data in triplicate for each time point, including the means and standard deviations. The graphic representation of these summarized data (means of triplicates) is shown in Figure 5-5 on log-scale. Total heterotrophic bacteria counts initially rose from Week T_0 to Week T_1, and then gradually declined over the first three weeks of the study from

TABLE 5-7. INORGANIC NUTRIENT LEVELS (mg/L)

	Week 0[a]	Week 2	Week 4	Week 6[a]	Week 9[a]	Week 12[a]
Ammonia (NH_3-N) Concentrations						
Reactor 1	172.5	47.8	54.5	54.4	3.1	2.3
Reactor 2	175.3	22.5	58.1	57.6	3.1	2.4
Reactor 4	169.8	10.4	58.9	34.4	2.7	1.7
Reactor 5	186.8	12.2	65	58.5	3.1	2.4
Reactor 6	184	6.85	66.7	65.1	3.4	2.8
Nitrate (NO_3-N) Concentrations						
Reactor 1	10 U[b]	10 U	10 U	0.4	113.9	68.6
Reactor 2	10 U	10 U	10 U	2.9	109.7	70.9
Reactor 4	10 U	10 U	10 U	53.8	93.8	75.1
Reactor 5	10 U	10 U	10 U	2.2	179	81.3
Reactor 6	10 U	10 U	10 U	0.9	156.9	73
Ortho-Phosphate (PO_4-P) Concentrations						
Reactor 1	25.5	10 U[b]	19.1	17.7	8.8	9.9
Reactor 2	27.6	10 U	10 U	8.8	5.9	7
Reactor 4	29.7	10 U	13.9	10.5	7	10.2
Reactor 5	24.1	10 U	19.9	18.2	10	7.7
Reactor 6	28.3	10 U	18.9	22.2	13.1	10.7

[a]Analyses performed in-house.
[b]U = Not detected. Level of detection is 10.

1.21×10^9 (T_1) to 1.08×10^8 (T_3). Populations of heterotrophic bacteria remained stable from Week T_6 through Week T_{10}. At Week T_{12}, three weeks after reinoculation of Reactors 2, 4, 5, and 6, total heterotrophic counts had increased, whereas counts in unamended Reactor 1 continued to decline. The initial low values for total heterotrophs were a result of cell shock from the toxic, highly volatile fraction of phenols and PAHs in the slurry, and perhaps some cell die-off during the period between the development of the inoculum and the charging of the reactors. Declines in total heterotroph counts after Week T_1 can be simplistically attributed to the decline in levels of their carbon energy sources.

TABLE 5-8. BEGINNING AND ENDING NUTRIENT LEVELS (mg/L)

Nutrient	Week T_0	Week T_{12}
Ammonia	177.7 ± 7.4	2.3 ± 0.4
Nitrate	< 10	73.8 ± 4.8
Orthophosphate	27.0 ± 2.2	9.1 ± 1.6

During the pilot-scale phase of this project, the diverse bacterial types within the slurries were characterized and the data were assembled by sampling time point and by reactor (Appendix L). At Week T_0, eight morphologically distinct bacteria types were present, with considerable diversity in the proportions of types among different reactors. By Week T_2, the number of types had increased to 14, and again the different reactor slurries displayed a striking diversity in colony morphology. Finally, by Week T_{12}, as many as 16 distinct morphological types of bacteria colonies were evident in the slurries. This increase in microorganism diversity reflects an increase in the variety of carbon sources for energy and a decline in the dominance of PAH metabolizing and co-oxidizing microorganisms. These additional carbon sources are both metabolic by- and end-products of the metabolism of PAHs in the slurry, as well as organic matter from microorganisms.

Specific bacterial PAH degrader populations were also monitored in accordance with the sampling schedule of Table 4-1. Table 5-10 and Figure 5-6 present a quick

TABLE 5-9. TOTAL HETEROTROPHS (CFU)

	Week								
	0	1	2	3	4	6	9	10	12
Reactor 1	3.84E+07	1.17E+09	3.85E+08	2.50E+08	1.99E+08	1.31E+08	4.40E+07	4.30E+07	1.81E+07
	2.80E+07	2.50E+09	3.31E+08	1.40E+08	1.87E+08	1.06E+08	4.60E+07	4.60E+07	1.96E+07
		1.29E+09	1.22E+08	1.94E+08	2.29E+08	1.10E+08	5.00E+07	3.70E+07	2.31E+07
Mean	3.32E+07	1.65E+09	2.79E+08	1.95E+08	2.05E+08	1.16E+08	4.70E+07	4.20E+07	2.00E+07
Std. Dev.	7.40E+06	7.40E+08	1.39E+08	5.50E+07	2.20E+07	1.30E+07	3.00E+06	5.00E+06	2.60E+06
Reactor 2	3.20E+06	1.25E+09	2.49E+08	2.30E+07	1.43E+08	1.29E+08	4.90E+07	3.60E+07	5.00E+07
	6.80E+06	9.20E+08	1.24E+08	1.21E+08	2.06E+08	8.00E+07	4.10E+07	4.80E+07	4.90E+07
		1.48E+09	1.53E+08	9.90E+07	1.75E+08	1.01E+08	4.10E+07	8.50E+07	5.40E+07
Mean	5.00E+06	1.22E+09	1.75E+08	8.10E+07	1.75E+08	1.03E+08	4.40E+07	5.60E+07	5.10E+07
Std. Dev.	2.50E+06	2.80E+08	6.50E+07	5.10E+07	3.20E+07	2.40E+07	5.00E+06	2.60E+07	3.00E+06
Reactor 4	4.40E+07	1.01E+09	3.40E+08	7.60E+07	3.60E+07	1.93E+07	6.30E+07	5.90E+07	5.10E+07
	3.90E+07	1.18E+09	5.80E+08	3.90E+07	1.40E+07	3.80E+06	8.00E+07	7.30E+07	8.20E+07
	7.10E+07	1.65E+09	4.50E+08	8.60E+07	1.70E+07	1.19E+07	1.57E+08	7.50E+07	8.30E+07
Mean	5.10E+07	1.28E+09	4.60E+08	6.70E+07	2.20E+07	1.17E+07	1.00E+08	6.90E+07	7.20E+07
Std. Dev.	1.70E+07	3.30E+08	1.20E+08	2.50E+07	1.20E+07	7.80E+06	5.00E+07	9.00E+06	1.80E+07
Reactor 5	1.02E+07	1.20E+09	2.30E+08	8.20E+07	5.30E+08	3.30E+06	3.50E+07	2.60E+07	7.60E+07
	9.30E+06	9.90E+08	1.60E+08	2.90E+07	5.30E+08	3.10E+06	4.70E+07	6.00E+07	7.10E+07
	1.20E+07		4.50E+08	2.60E+07	4.40E+08	2.89E+07	3.80E+07	3.50E+07	9.40E+07
Mean	1.05E+07	1.10E+09	2.80E+08	4.60E+07	5.00E+08	1.18E+07	4.00E+07	4.00E+07	8.00E+07
Std. Dev.	1.40E+06	1.50E+08	1.50E+08	3.20E+07	5.00E+07	1.48E+07	6.00E+06	1.80E+07	1.20E+07
Reactor 6	1.33E+07	6.60E+08	5.20E+07	1.28E+08	1.10E+07	5.90E+07	3.70E+07	6.00E+07	6.70E+07
	1.41E+07	8.50E+08	6.70E+07	9.70E+07	7.00E+06	2.80E+07	4.10E+07	7.80E+07	9.10E+07
	1.17E+07	9.10E+08	1.18E+08	2.21E+08	8.00E+06	1.00E+06	6.50E+07	4.70E+07	8.40E+07
Mean	1.30E+07	8.10E+08	7.90E+07	1.49E+08	9.00E+06	2.90E+07	4.80E+07	6.20E+07	8.10E+07
Std. Dev.	1.20E+06	1.30E+08	3.40E+07	6.40E+07	2.00E+06	2.90E+07	1.50E+07	1.60E+07	1.20E+07

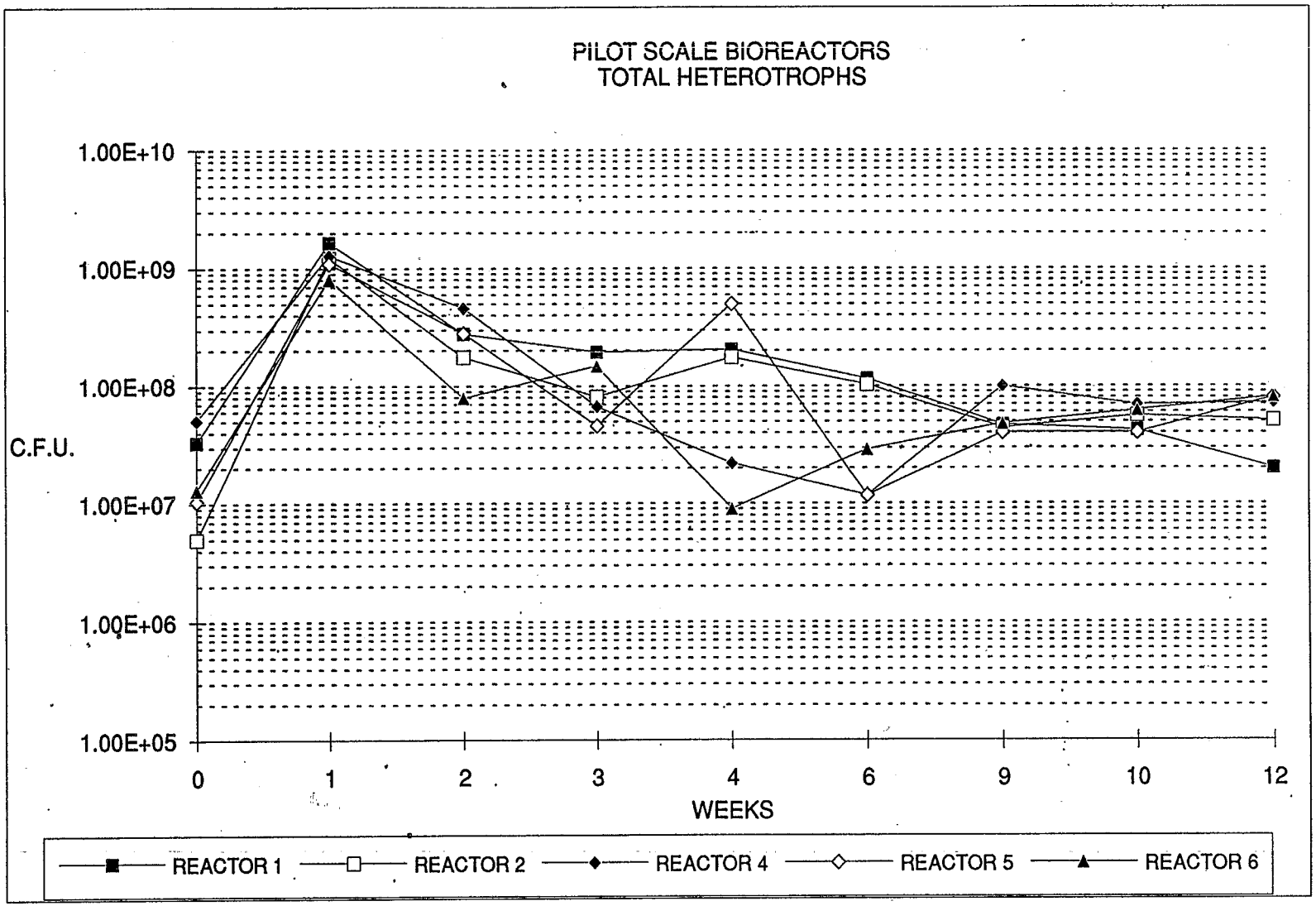

Figure 5-5. Total heterotrophs.

TABLE 5-10. SUMMARY OF TOTAL HETEROTROPHS AND SPECIFIC PAH DEGRADERS (CFU)[a]

	Week								
	0	1	2	3	4	6	9	10	12
Total Heterotrophs	2.25E+07	1.21E+09	2.55E+08	1.08E+08	1.82E+08	5.43E+07	5.58E+07	5.38E+07	6.08E+07
Phenanthrene Degraders	2.45E+06	2.30E+08	1.17E+08	5.58E+07	2.86E+07	3.52E+05	2.79E+05	5.42E+05	1.82E+05
Pyrene Degraders	4.12E+06	1.66E+08	3.52E+07	2.89E+06	1.04E+07	3.64E+05	1.65E+05	7.30E+04	1.44E+05
PMSS - PHEN	2.45E+06	2.30E+08	1.17E+08	5.58E+07	2.86E+07	3.52E+05	2.79E+05	5.42E+05	1.82E+05
PMSS - PYR	4.12E+06	1.66E+08	3.52E+07	2.89E+06	1.04E+07	3.64E+05	1.65E+05	7.30E+04	1.44E+05
PMS - PHEN	6.30E+06	1.20E+08	2.80E+07	3.55E+08	1.02E+08	6.85E+07	2.28E+07	8.43E+07	2.60E+07
PMS - PYR	2.11E+07	2.49E+07	1.20E+08	1.55E+08	2.57E+07	1.37E+07	N/A[b]	1.37E+07	1.77E+06
PCA	2.25E+07	1.21E+09	2.55E+08	1.08E+08	1.82E+08	5.43E+07	5.58E+07	5.38E+07	6.08E+07
PMSS - PHEN	2.45E+06	2.30E+08	1.17E+08	5.58E+07	2.86E+07	3.52E+05	2.79E+05	5.42E+05	1.82E+05
PMSS - PYR	4.12E+06	1.66E+08	3.52E+07	2.89E+06	1.04E+07	3.64E+05	1.65E+05	7.30E+04	1.44E+05
PMS - PHEN	6.30E+06	1.20E+08	2.80E+07	3.55E+08	1.02E+08	6.85E+07	2.28E+07	8.43E+07	2.60E+07
PMS - PYR	2.11E+07	2.49E+07	1.20E+08	1.55E+08	2.57E+07	1.37E+07	N/A	1.37E+07	1.77E+06

[a]Microbial enumerations, mean values.
[b]N/A = Not available.

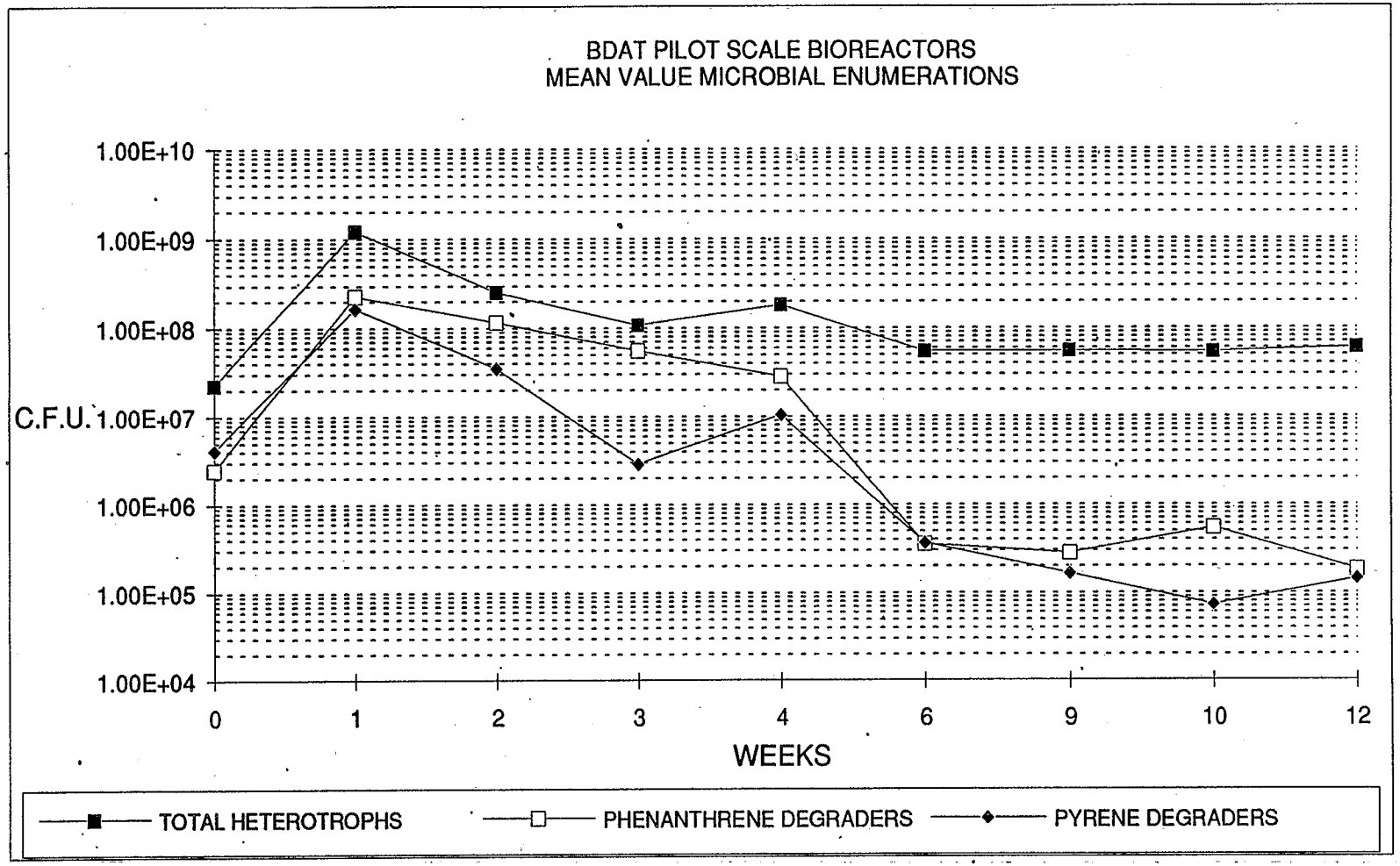

Figure 5-6. Total heterotrophs, phenanthrene degraders, and pyrene degraders.

summary of the total heterotrophic count data and the specific PAH degrader data. As might be expected, the decline of these specific bacterial populations, which primarily use PAHs for their carbon energy source, was more severe than that of the heterotrophic population as a whole.

Aliquots of each reactor at each time point were plated in triplicate at three different dilutions on both PAH mineral salts supplemented with salicylate (PMSS) and PAH mineral salts alone (PMS). Tables 5-11 and 5-12 present the PMS data for phenanthrene and pyrene degraders respectively. The PMSS data for phenanthrene and pyrene are summarized in Tables 5-13 and 5-14. All of the PAH degraders in PMSS appeared to rebound at Week T_1 from very nearly zero activity at Week T_0. Initial inactivity results from the travel of the bacteria at 4°C from Redmond to Cincinnati and, probably, the toxicity of the slurries. Both phenanthrene and pyrene degraders done on PMS peaked in colony-forming units (CFUs) at Week T_3. Phenanthrene, more easily metabolized than pyrene, again caused a more severe decline in CFUs that specifically metabolize phenanthrene. There appeared to be a substantial reduction in co-oxidizing bacteria (evidenced by decreased numbers of microorganisms on the PMSS plates) over time. This implies a shift in population type and diversity, again reflecting a growing change and diversity in the carbon sources for microorganic metabolism. As the concentration of PAHs declined in the slurry, non-PAH degrading microorganisms gained eminence and metabolic importance. The PMS and PMSS data for phenanthene and pyrene degraders are also presented graphically on a log scale in Figures M-1 through M-5 in Appendix M.

5.2.7 Microtox

The Microtox analysis is designed to reveal toxic conditions that might inhibit or suppress microbial activity. ECOVA used this analysis to monitor toxicity levels over the course of the study. These data are presented in Table 5-15 and Figure 5-7. In this analysis, gasoline, organics, and solvents give immediate toxic responses. Metals give a somewhat slower toxic response. It is important to note that individual data

TABLE 5-11. PMS DATA FOR PHENANTHRENE DEGRADERS (CFU)[a]

	Week								
	0	1	2	3	4	6	9	10	12
Reactor 1	7.70E+07	4.10E+07	7.90E+06	6.00E+07	N/A[b]	2.04E+07	N/A	5.00E+06	1.62E+06
Reactor 2	1.00E+04	4.16E+07	4.50E+06	2.24E+08	1.00E+07	5.80E+06	N/A	2.59E+07	2.33E+06
Reactor 4	1.91E+07	1.27E+07	1.02E+07	9.00E+06	7.30E+06	2.73E+07	N/A	1.80E+07	1.19E+06
Reactor 5	8.30E+06	2.08E+07	3.77E+08	2.29E+08	7.20E+07	1.00E+04	N/A	1.86E+07	1.53E+06
Reactor 6	1.00E+06	8.20E+06	1.99E+08	2.52E+08	1.35E+07	1.52E+07	N/A	8.00E+05	2.20E+06
Mean	2.11E+07	2.49E+07	1.20E+08	1.55E+08	2.57E+07	1.37E+07	N/A	1.37E+07	1.77E+06
Std. Dev.	3.22E+07	1.57E+07	1.66E+08	1.12E+08	N/A	1.10E+07	N/A	1.04E+07	4.78E+05

[a]PAH degrader enumerations, PMS platings.
[b]N/A = Not available.

TABLE 5-12. PMS DATA FOR PYRENE DEGRADERS (CFU)[a]

	Week								
	0	1	2	3	4	6	9	10	12
Reactor 1	1.00E+05	5.10E+07	5.50E+07	N/A[b]	1.90E+08	7.30E+07	1.20E+07	2.70E+07	2.29E+07
Reactor 2	2.40E+06	6.20E+07	2.60E+07	4.10E+08	4.90E+07	6.40E+07	2.50E+07	N/A	1.15E+07
Reactor 4	1.00E+05	2.47E+08	N/A	N/A	6.80E+07	N/A	4.90E+07	N/A	2.86E+07
Reactor 5	2.20E+07	1.22E+08	3.00E+06	N/A	1.00E+08	N/A	8.00E+06	4.60E+07	2.58E+07
Reactor 6	6.90E+06	1.19E+08	N/A	3.00E+08	N/A	N/A	2.00E+07	3.40E+07	4.15E+07
Mean	6.30E+06	1.20E+08	N/A	N/A	2.57E+07	N/A	2.28E+07	N/A	2.60E+07
Std. Dev.	9.21E+06	7.79E+07	N/A	N/A	N/A	N/A	1.61E+07	N/A	1.08E+07

[a]PAH degrader enumerations, PMS platings.
[b]N/A = Not available.

TABLE 5-13. PMSS DATA FOR PHENANTHRENE DEGRADERS (CFU)[a]

	Week								
	0	1	2	3	4	6	9	10	12
Reactor 1	7.80E+05	1.89E+08	2.20E+07	2.70E+08	1.00E+05	8.07E+05	4.20E+05	1.05E+05	3.00E+04
Reactor 2	7.00E+05	1.18E+08	7.20E+07	5.30E+06	1.00E+08	3.80E+05	1.35E+05	1.85E+05	1.00E+04
Reactor 4	1.01E+07	2.30E+08	1.74E+08	9.50E+05	1.00E+07	9.67E+04	4.20E+05	1.46E+06	4.30E+05
Reactor 5	1.60E+05	3.75E+08	2.96E+08	1.00E+05	2.20E+07	2.07E+05	3.20E+05	8.20E+05	5.00E+04
Reactor 6	4.90E+05	2.36E+08	1.90E+07	2.60E+06	1.10E+07	2.70E+05	1.00E+05	1.00E+05	3.90E+05
Mean	2.45E+06	2.30E+08	1.17E+08	5.58E+07	2.57E+07	3.52E+05	2.79E+05	5.35E+05	1.82E+05
Std. Dev.	4.29E+06	9.39E+07	1.18E+08	1.20E+08	4.06E+07	2.74E+05	1.53E+05	6.00E+05	2.09E+05

[a]PAH degrader enumerations, PMS/salicylate platings.

TABLE 5-14. PMSS DATA FOR PYRENE DEGRADERS (CFU)[a]

	Week								
	0	1	2	3	4	6	9	10	12
Reactor 1	7.70E+05	1.85E+08	5.20E+06	8.33E+05	1.00E+05	3.57E+05	1.20E+05	5.00E+04	4.50E+04
Reactor 2	1.00E+05	1.96E+08	4.50E+07	6.00E+05	3.20E+07	5.07E+05	8.67E+04	5.50E+04	5.00E+04
Reactor 4	1.91E+07	1.82E+08	2.28E+07	2.30E+06	8.00E+06	1.24E+05	2.80E+05	1.35E+05	4.10E+05
Reactor 5	2.20E+05	1.63E+08	1.02E+08	1.00E+05	1.20E+07	4.43E+05	3.20E+05	7.30E+04	4.70E+04
Reactor 6	4.10E+05	1.06E+08	8.00E+05	1.06E+07	1.00E+05	3.90E+05	2.00E+04	5.70E+04	1.70E+05
Mean	4.12E+06	1.66E+08	3.52E+07	2.89E+06	2.57E+07	3.64E+05	1.65E+05	7.40E+04	1.44E+05
Std. Dev.	8.38E+06	3.58E+07	4.12E+07	4.39E+06	1.31E+07	1.46E+05	1.29E+05	3.52E+04	1.58E+05

[a]PAH degrader enumerations, PMS/salicylate platings.

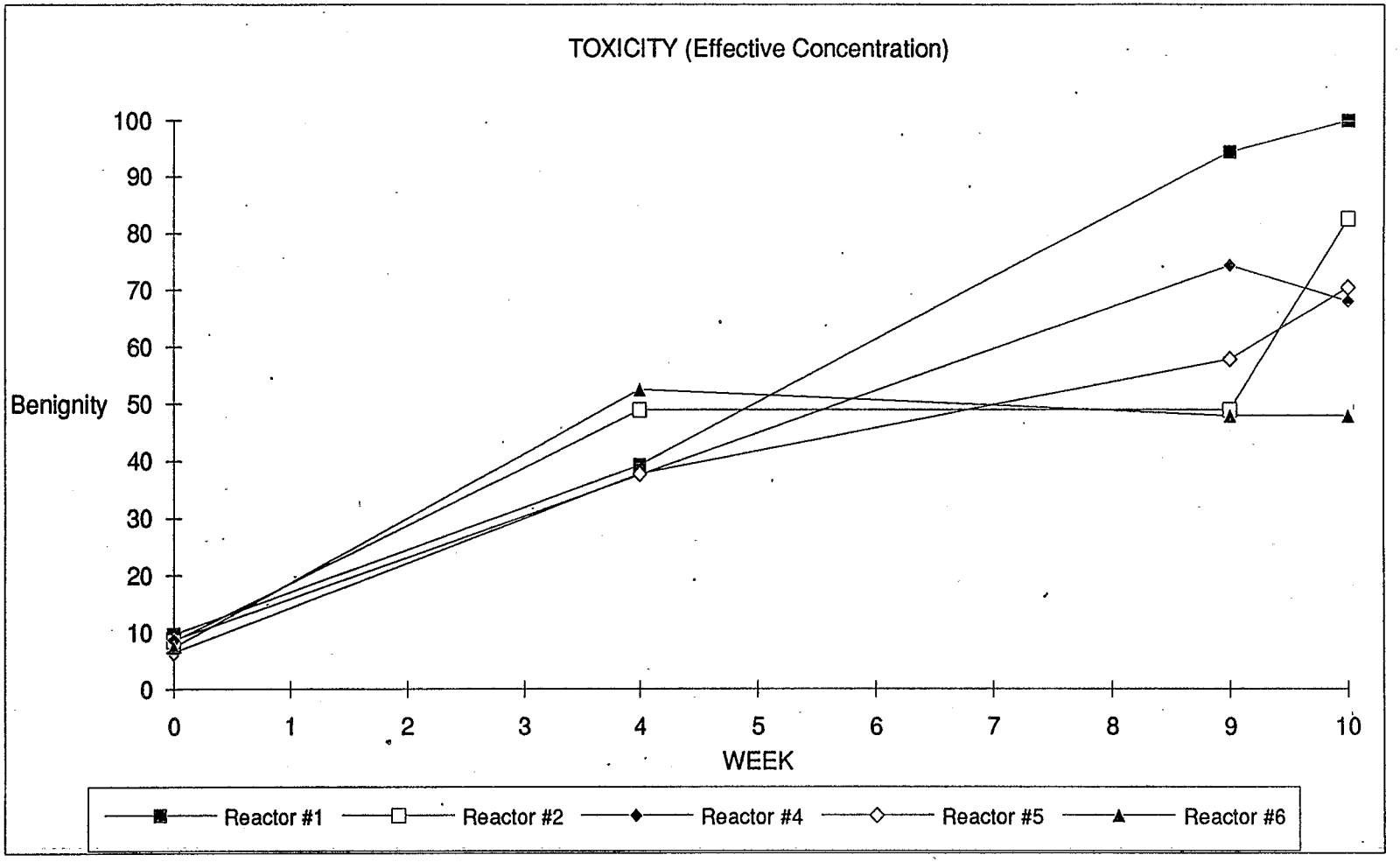

Figure 5-7. Relative effective concentration shows decreasing toxicity and increasing benignity.

points may express appreciable variation, and only trends in a succession of data points should be considered for interpretation.

The general trend in toxicity revealed by these analyses is a decline over the 12 weeks. At Week T_4, some toxicity was still present in all the reactor slurries; and by Week T_9, Reactors 5 and 6 still appeared to have some residual toxicity. By Week T_{10}, either marginal or no toxicity was associated with the slurries.

TABLE 5-15. RELATIVE EFFECTIVE CONCENTRATION OF MICROTOX ANALYSIS[a]

	Week			
	0	4	9	10
Reactor 1	9.69	39.3	94.4	100
Reactor 2	8.57	48.9	N/A[a]	82.6
Reactor 4	8.72	37.6	74.4	68
Reactor 5	6.51	37.8	57.8	70.4
Reactor 6	7.38	52.5	47.9	N/A[b]

[a] Decreasing toxicity indicates increasing benignity.

[b] N/A = not analyzed.

5.3 Evaluation of Pilot-Scale Operations

5.3.1 Problems Encountered During Startup

Immediate difficulties were encountered in the startup of Reactor 3. After the reactor had been completely charged, the cap was tightened. An immediate back pressure occurred within the reactor, slurry was forced up through its center shaft, and a large amount of slurry was spilled on the area around the reactor. The reactor was immediately shut down and the cap loosened. Because of the time restraints in loading the other reactors, the cause of the back pressure was not investigated. An attempt was made to restart the reactor later, but this could not be done without emptying the slurry. After consultation with IT Corporation and U.S. EPA officials, the decision was made to leave this reactor off line because of time constraints and a concern that any analytical data gathered from this reactor would be compromised as

a result of the loss of slurry material as well as the loss of the volatile constituents during the drainage of the reactor.

Later discussions revealed possible reasons for the failure of Reactor 3. The air outlet manifold may not have been large enough to vent the reactors efficiently, which could create back pressure. A clog in this manifold also could have caused the back-pressure buildup. A third possibility is that the air pressure coming into the reactor could have been too great for the manifold system. It should be noted that Reactor 3 was somewhat different from the other reactors; i.e, it was an older reactor with four side ports, and it was of a slightly different design.

5.3.2 Mechanical Evaluation of Problems

Table 5-16 presents a listing of the problems encountered during the pilot-scale operation of the EIMCO Biolift™ Reactors, most of which were encountered and corrected within the first 2 weeks of operation. None of these mechanical problems had any significant impact on the test results. These problems generally fall into four categories--electrical, air-compressor-related, air-manifold-related, and material blockage of the airlifts.

For the most part, the electrical problems encountered during the operation of the pilot-scale reactors were minimal. Twice during reactor operations, fuses were blown on the controller box of the Dayton Gearmotors that rotate the rake and impeller drives. The first fuse was blown on the rake arm control of Reactor 5 prior to startup. A second fuse was blown on the impeller arm control of Reactor 1 on the second day of pilot-scale operations.

Another concern was the backup power supply in the event of a power outage. This power supply was assured by use of a backup generator, as specified in the original design. A power outage was encountered once during startup, at which time the emergency generator came on within 7 seconds and operated as expected. Throughout the pilot-scale operations, this generator was maintained and tested weekly to ensure its performance in an emergency.

TABLE 5-16. CHRONOLOGY OF MECHANICAL PROBLEMS

Date (1991)	Mechanical observation
May 8	Reactor setup complete.
	Reactor 3 experienced back-pressure buildup and clogged airlifts. The decision was made to take it off line.
	Back pressure on the air compressors caused the influent air to heat. Overheating may be a problem within the reactors.
	Back pressure was experienced in Reactor 4.
	Air compressor on Reactor 4 was changed out.
May 9	Airlift arms stopped on Reactor 2.
	Airlift arms plugged on Reactor 2.
May 10	Impeller fuse in Reactor 1 was replaced.
	Air manifold on Reactor 1 clogged as a result of foaming. Slurry was sent up the center shaft. Air monitoring system was disconnected by uncapping reactors.
May 11	Substantial foaming was experienced in all reactors.
	Air lines on Reactors 2, 5, and 6 tore because of overheating. Air lines were later replaced on these reactors.
	Airlifts on Reactor 2 plugged because of a soil blockage of the air lines coming into the reactor.
May 12	Airlift pressure was increased on Reactors 2 and 6 to enhance output from the airlifts.
May 13	Thermal overload on Reactor 1 was caused by the air compressor.
	Air manifold was changed to 3/4-in. polyvinyl chloride (PVC) to stop the clogging problem caused by reactor foaming.
May 16	Bleed valves were placed on air lines to relieve back pressure on the air compressors.
June 19	Air compressor 5 was changed out because of mechanical difficulties.
July 11	Reactors 2 and 4 were reinoculated with fresh inoculum. Reactors 5 and 6 were reinoculated and 340 ppm Tween 80 was added. Reactor 1 was left as a control reactor.

A third electrical problem was encountered on May 14 when the air compressor on Reactor 1 caused a thermal overload on the circuit. Immediate response by IT operations personnel, who changed the bad air compressor and reinitialized the circuit, prevented the failure of Reactor 1. The design of the entire system placed each reactor on a different circuit, which allowed for the failure and startup of a single reactor without affecting the others.

Air compressor problems centered largely around the fact that the air compressors originally designed for the EIMCO Biolift™ Reactors were too small in case extra air was needed to remove blockages in the airlift lines. For this reason, larger air compressors were installed in the bioreactor setup; these air compressors proved to be too large for the reactor air demand. The resulting continual back pressure existed on the air compressors and caused constant overheating. Overheating in the air compressors caused a continual flow of heated air to the reactor, which resulted in overheating and tearing of the air delivery line to the reactors and increased the temperature of the reactor slurry.

A May 13 discussion between IT Corporation and EPA officials resulted in an investigation into alternative air delivery systems. As a result, the bleed air pressure valves were installed on the lines coming off the compressors. Pressure gauges were installed in conjunction with these valves to ensure the pressure going to the reactor was adequate for each reactor.

Other air compressor problems included the May 14 failure of one air compressor on Reactor 1 and an occasional tear in the compressor diaphragm.

The third problem encountered in the pilot operation was back-pressure buildup in Reactors 1, 3, and 4. This buildup can be attributed primarily to a blockage in the air manifold lines, which can occur in one of two ways. Soil foam from the reactor may block the 1/4-in. air manifold, or moisture from the reactor may condense in the central manifold or drain back down through the 1/4-in. manifold toward the reactor and prevent the flow of air out of the reactor. The buildup of back pressure in the reactor forces the slurry up through the center shaft of the reactor and out the top.

On May 13, a meeting was held with IT Corporation and EPA representatives to find solutions to these problems. Subsequently, 3/4-in. polyvinyl chloride manifolds were installed coming off the reactors to the central manifold system. This design correction prevented further problems with back-pressure buildup.

The final (and perhaps most difficult) problem encountered in the operation of the reactor system was the mechanical blockage of the airlift arms by settled material. This occurred once in Reactor 4 and multiple times in Reactor 2. Clearing the airlift arms entailed manually removing the obstruction by partially draining the reactor slurry material and opening the side port of the reactor to gain entrance to the airlift arms. The removal of the obstruction involved pumping recirculated slurry material down through the opening of the airlift and forcing the settled material out. As the settled material is loosened, the airflow coming up through the airlift arms further frees the compacted material. Because the airlift arms must be turned off during this process, a Randolph pump was used to recirculate material between the middle and lower ports and thereby ensured that the majority of the slurry material would not settle and prevent the rake from functioning.

Preventive measures for dealing with material blockage of the airlift arms included increasing the speed of the airlift arms and the air pressure to them, as well as maintaining a constant liquid level in the reactors.

SECTION 6

ANALYTICAL RESULTS

This section presents the results of the analyses of pre- and posttreatment soil and liquid samples for CS&D List and critical contaminants (PAHs) to evaluate the performance of the bioslurry treatment system. Also presented are results of the analyses of air characterization samples collected during the pilot-scale study. All of these samples were collected by ITEP, and the analyses were performed by ITAS-Cincinnati. In addition to ITEP's sampling and analyses, ECOVA performed PAH analyses to evaluate the design and operation of the system. All of these analyses were performed by the ECOVA laboratory in Redmond, Washington.

The pretreatment samples were collected at the start of testing (Week T_0) to determine the baseline concentration of the critical contaminants in the soil prior to treatment. The posttreatment samples were collected 9 weeks (T_9) and 12 weeks (T_{12}) after the start of testing to determine the levels of the critical contaminants remaining in the soil after treatment. The data obtained from Week T_9 should be used for evaluating the technology's performance and for BDAT rulemaking. The data from Week T_{12}, air sampling, and bioreactor monitoring (e.g., TPH) should be used only for information purposes.

The methods for analyzing for critical parameters were described in Subsection 4.2; the other analytical methods used were listed in Table 4-6. Table 6-1 presents the ITEP field sample coding, the ITAS-Cincinnati laboratory sample coding, and the dates samples were received, extracted, and analyzed in the laboratory.

TABLE 6-1. SAMPLE TRACKING INFORMATION

ITEP ID No.	ITAS ID No.	Analysis[a]	Date received	Date extracted	Date analyzed
Semivolatile organics (Total)					
Postmilling	X1-05-057-01	3550/8270	5/7/91	6/4/91	6/11-6/13/91
Premilling	X1-05-057-02	3550/8270	5/7/91	6/4/91	6/11-6/13/91
Trip blank	X1-05-057-04	3520/8270	5/7/91	5/14/91	6/13/91
Postmilling equip. blank	X1-05-057-05	3520/8270	5/7/91	5/14/91	6/13/91
Premilling equip. blank	X1-05-057-06	3520/8270	5/7/91	5/14/91	6/13/91
Bioreactor-001-sludge	X1-05-094-01	3550/8270	5/13/91	6/4/91	6/11/91
Bireactor-001-liquid	X1-05-094-02	3520/8270	5/13/91	5/14/91	6/12/91
Bioreactor-002-sludge	X1-05-094-03	3550/8270	5/13/91	6/8/91	6/11/91
Bioreactor-002-liquid	X1-05-094-04	3520/8270	5/13/91	5/14/91	6/12/91
Bioreactor-004-sludge	X1-05-098-01	3550/8270	5/13/91	6/4/91	6/11/91
Bioreactor-004-liquid	X1-05-098-02	3520/8270	5/13/91	5/14/91	6/13/91
Bioreactor-005-sludge	X1-05-094-07	3550/8270	5/13/91	6/4/91	6/12/91
Bioreactor-005-liquid	X1-05-094-08	3520/8270	5/13/91	5/14/91	6/12/91
Bioreactor-006-sludge	X1-05-094-09	3550/8270	5/13/91	6/4/91	6/12/91
Bioreactor-006-liquid	X1-05-094-10	3520/8270	5/13/91	5/14/91	6/12/91
Equipment blank	X1-05-094-11	3520/8270	5/13/91	5/14/91	6/12/91
Equipment blank	X1-05-098-03	3520/8270	5/13/91	5/14/91	6/13/91
T9-R1-S	X1-07-077-01	3550/8270	7/12/91	7/23/91	8/20/91
T9-R1-W	X1-07-077-06	3520/8270	7/12/91	7/17/91	8/22/91
T9-R2-S	X1-07-077-02	3550/8270	7/12/91	7/23/91	8/21/91
T9-R2-W	X1-07-077-07	3520/8270	7/12/91	7/17/91	8/23/91
T9-R4-S	X1-07-077-03	3550/8270	7/12/91	7/23/91	8/21/91

(continued)

TABLE 6-1 (cont.)

ITEP ID No.	ITAS ID No.	Analysis[a]	Date received	Date extracted	Date analyzed
T9-R4-W	X1-07-077-08	3520/8270	7/12/91	7/17/91	8/23/91
T9-R5-S	X1-07-077-04	3550/8270	7/12/91	7/23/91	8/22/91
T9-R5-W	X1-07-077-09	3520/8270	7/12/91	7/17/91	8/23/91
T9-R6-S	X1-07-077-05	3550/8270	7/12/91	7/23/91	8/22/91
T9-R6-W	X1-07-077-10	3520/8270	7/12/91	7/17/91	8/23/91
Equipment blank 1	X1-07-077-11	3520/8270	7/12/91	7/17/91	8/23/91
Equipment blank 2	X1-07-077-12	3520/8270	7/12/91	7/17/91	8/26/91
Trip blank	X1-07-077-13	3520/8270	7/12/91	7/17/91	8/26/91
TRPH and Oil & Grease					
Postmilling	X1-05-057-01	418.1[b]	5/7/91	5/28/91	6/4/91
Premilling	X1-05-057-02	418.1	5/7/91	5/28/91	6/4/91
Bioreactor-001-sludge	X1-05-094-01	418.1	5/13/91	5/29/91	6/4/91
Bioreactor-001-liquid	X1-05-094-02	418.1	5/13/91	5/29/91	6/4/91
Bioreactor-002-sludge	X1-05-094-03	418.1	5/13/91	5/29/91	6/4/91
Bioreactor-002-liquid	X1-05-094-04	418.1	5/13/91	5/29/91	6/4/91
Bioreactor-004-sludge	X1-05-094-05	418.1	5/13/91	5/29/91	6/4/91
Bioreactor-004-liquid	X1-05-094-06	418.1	5/13/91	5/29/91	6/4/91
Bioreactor-005-sludge	X1-05-094-07	418.1	5/13/91	5/29/91	6/4/91
Bioreactor-005-liquid	X1-05-094-08	418.1	5/13/91	5/29/91	6/4/91
Bioreactor-006-sludge	X1-05-094-09	418.1	5/13/91	5/29/91	6/4/91
Bioreactor-006-liquid	X1-05-094-10	418.1	5/13/91	5/29/91	6/4/91
T2-R1-S-TPH	X1-05-167-01	418.1	5/22/91	6/11/91	6/13/91
T2-R2-S-TPH	X1-05-167-02	418.1	5/22/91	6/11/91	6/13/91
T2-R4-S-TPH	X1-05-167-03	418.1	5/22/91	6/11/91	6/13/91

(continued)

TABLE 6-1 (cont.)

ITEP ID No.	ITAS ID No.	Analysis[a]	Date received	Date extracted	Date analyzed
T2-R5-S-TPH	X1-05-167-04	418.1	5/22/91	6/11/91	6/13/91
T2-R6-S-TPH	X1-05-167-05	418.1	5/22/91	6/11/91	6/13/91
T4-R1-S-TPH	X1-06-021-01	418.1	6/5/91	6/11/91	6/13/91
T4-R2-S-TPH	X1-06-021-02	418.1	6/5/91	6/11/91	6/13/91
T4-R4-S-TPH	X1-06-021-03	418.1	6/5/91	6/11/91	6/13/91
T4-R5-S-TPH	X1-06-021-04	418.1	6/5/91	6/11/91	6/13/91
T4-R6-S-TPH	X1-06-021-05	418.1	6/5/91	6/11/91	6/13/91
T6-R1-S-TPH	X1-06-138-01	418.1	6/19/91	6/26/91	6/28/91
T6-R2-S-TPH	X1-06-138-02	418.1	6/19/91	6/26/91	6/28/91
T6-R4-S-TPH	X1-06-138-03	418.1	6/19/91	6/26/91	6/28/91
T6-R5-S-TPH	X1-06-138-04	418.1	6/19/91	6/26/91	6/28/91
T6-R6-S-TPH	X1-06-138-05	418.1	6/19/91	6/26/91	6/28/91
T9-R1-S	X1-07-077-01	418.1 & 413.1[b]	7/12/91	7/31/91	8/12/91
T9-R1-W	X1-07-077-06	418.1 & 413.1	7/12/91	7/31/91	8/12/91
T9-R2-S	X1-07-077-02	418.1 & 413.1	7/12/91	7/31/91	8/12/91
T9-R2-W	X1-07-077-07	418.1 & 413.1	7/12/91	7/31/91	8/12/91
T9-R4-S	X1-07-077-03	418.1 & 413.1	7/12/91	7/31/91	8/12/91
T9-R4-W	X1-07-077-08	418.1 & 413.1	7/12/91	7/31/91	8/12/91
T9-R5-S	X1-07-077-04	418.1 & 413.1	7/12/91	7/31/91	8/12/91
T9-R5-W	X1-07-077-09	418.1 & 413.1	7/12/91	7/31/91	8/12/91
T9-R6-S	X1-07-077-05	418.1 & 413.1	7/12/91	7/31/91	8/12/91
T9-R6-W	X1-07-077-10	418.1 & 413.1	7/12/91	7/31/91	8/12/91
Volatile Organics (Total)					
Postmilling	X1-05-057-01	8240	5/7/91	NA[c]	5/21/91

(continued)

TABLE 6-1 (cont.)

ITEP ID No.	ITAS ID No.	Analysis[a]	Date received	Date extracted	Date analyzed
Premilling	X1-05-057-02	8240	5/7/91	NA	5/21/91
Field blank	X1-05-057-03	8240	5/7/91	NA	5/21/91
Alcohols					
Postmilling	X1-05-057-01	8015	5/7/91	NA	5/21/91
Premilling	X1-05-057-02	8015	5/7/91	NA	5/21/91
Organochlorine Pest. (Total)					
Postmilling	X1-05-057-01	3550/8080	5/7/91	6/4/91	6/11/91
Premilling	X1-05-057-02	3550/8080	5/7/91	6/4/91	6/11/91
Phenoxyacetic acid herb. (Total)					
Postmilling	X1-05-057-01	3550/8150	5/7/91	6/4/91	6/17/91
Premilling	X1-05-057-02	3550/8150	5/7/91	6/4/91	6/17/91
Organophosphorus insect. (Total)					
Postmilling	X1-05-057-01	3550/8140	5/7/91	6/4/91	6/13-6/18/91
Premilling	X1-05-057-02	3550/8140	5/7/91	6/4/91	6/13-6/18/91
Metals (Total)					
Postmilling	X1-05-057-01	3050/6010	5/7/91	5/14/91	5/19-5/21/91
		3050/7060	5/7/91	5/14/91	5/20/91
		7471	5/7/91	6/3/91	6/3/91
		3050/7740	5/7/91	5/14/91	5/15/91
		7196	5/7/91	5/23/91	5/24/91
Premilling	X1-05-057-02	3050/6010	5/7/91	5/14/91	5/19-5/21/91
		3050/7060	5/7/91	5/14/91	5/20/91
		7471	5/7/91	6/3/91	6/3/91

(continued)

TABLE 6-1 (cont.)

ITEP ID No.	ITAS ID No.	Analysis[a]	Date received	Date extracted	Date analyzed
Premilling	X1-05-057-02	3050/7740	5/7/91	5/14/91	5/15/91
		7196	5/7/91	5/23/91	5/24/91
Chloride					
Postmilling	X1-05-057-01	9252	5/7/91	5/22/91	5/22/91
Premilling	X1-05-057-02	9252	5/7/91	5/22/91	5/22/91
Cyanide					
Postmilling	X1-05-057-01	9012	5/7/91	NA	5/16/91
Premilling	X1-05-057-02	9012	5/7/91	NA	5/16/91
Fluoride					
Postmilling	X1-05-057-01	340.2[b]	5/7/91	5/17/91	5/17/91
Premilling	X1-05-057-02	340.2	5/7/91	5/17/91	5/17/91
Total Phosphorus					
Postmilling	X1-05-057-01	365.2[b]	5/7/91	5/20/91	5/20/91
Premilling	X1-05-057-02	365.2	5/7/91	5/20/91	5/20/91
Sulfate					
Postmilling	X1-05-057-01	9038	5/7/91	5/30/91	5/30/91
Premilling	X1-05-057-02	9038	5/7/91	5/30/91	5/30/91
Sulfide					
Postmilling	X1-05-057-01	9030	5/7/91	5/10/91	5/10/91
Premilling	X1-05-057-02	9030	5/7/91	5/10/91	5/10/91
Total Organic Carbon					
Postmilling	X1-05-057-01	9060	5/7/91	5/29/91	5/29/91
Premilling	X1-05-057-02	9060	5/7/91	5/29/91	5/29/91

(continued)

TABLE 6-1 (cont.)

ITEP ID No.	ITAS ID No.	Analysis[a]	Date received	Date extracted	Date analyzed
Total Organic Halogens					
Postmilling	X1-05-057-01	9020	5/7/91	5/15/91	5/15/91
Premilling	X1-05-057-02	9020	5/7/91	5/15/91	5/15/91
MBAS					
Postmilling	X1-05-057-01	425.1[b]	5/7/91	5/9/91	5/9/91
Premilling	X1-05-057-02	425.1	5/7/91	5/9/91	5/9/91

ITEP ID No.	ITAS ID No.	Analysis[a]	Date received	Date leached	Date extracted	Date analyzed
Semivolatile organics (TCLP)						
Postmilling	X1-05-057-01	3520/8270	5/7/91	5/13/91	5/22 & 6/19/91	7/17/91
Premilling	X1-05-057-02	3520/8270	5/7/91	5/13/91	5/22 & 6/19/91	7/17/91
Volatile organics (TCLP)						
Postmilling	X1-05-057-01	8240	5/7/91	5/13/91	NA[c]	5/24/91
Premilling	X1-05-057-02	8240	5/7/91	5/13/91	NA	5/24/91
Organochlorine pest. (TLCP)						
Postmilling	X1-05-057-01	3520/8080	5/7/91	5/13/91	5/21/91	6/11/91
Premilling	X1-05-057-02	3520/8080	5/7/91	5/13/91	5/21/91	6/11/91
Phenoxyacetic acid herb. (TCLP)						
Postmilling	X1-05-057-01	3520/8150	5/7/91	5/13/91	5/21/91	6/3/91
Premilling	X1-05-057-02	3520/8150	5/7/91	5/13/91	5/21/91	6/3/91
Metals (TCLP)						
Postmilling	X1-05-057-01	3010/6010	5/7/91	5/13/91	5/19/91	5/21/91
		3010/7060	5/7/91	5/13/91	5/17/91	5/20/91
		7470	5/7/91	5/13/91	5/17/91	5/30/91
		7740	5/7/91	5/13/91	5/17/91	5/20/91

(continued)

TABLE 6-1 (cont.)

ITEP ID No.	ITAS ID No.	Analysis[a]	Date received	Date leached	Date extracted	Date analyzed
Premilling	X1-05-057-02	3010/6010	5/7/91	5/13/91	5/19/91	5/21/91
		3010/7060	5/7/91	5/13/91	5/17/91	5/20/91
		7470	5/7/91	5/13/91	5/17/91	5/30/91
		7740	5/7/91	5/13/91	5/17/91	5/20/91

[a] SW-846 Methods for Evaluating Solid Waste.

[b] Methods for Chemical Analysis of Water and Wastes.

[c] NA = Not applicable.

6.1 Premilling and Postmilling Soil Samples

6.1.1 CS&D List

The samples collected from premilling and postmilling processes were analyzed for the CS&D List of volatile organics, semivolatile organics, pesticides, PCBs, dioxins, furans, metals, and inorganics. Table 6-2 presents the CS&D constituents detected in the characterization analysis of premilling and postmilling samples.

6.1.2 Critical Semivolatile Organic Contaminants

The premilling and postmilling samples were also analyzed for the critical semivolatile organic contaminants. Table 6-3 presents the concentrations of critical semivolatile organic contaminants. As shown in Table 6-3, concentrations of the individual PAHs varied before and after milling; some concentrations actually increased after the milling process. Analyses showed an overall 13.8 percent drop in PAHs after milling. This drop is not as statistically significant as it would appear because of the considerable variation in analytical results that occurred throughout testing.

Copies of the analytical data provided by the ITAS laboratory for the CS&D constituents and critical contaminants in the premilling and postmilling samples are included in Appendix N.

6.2 Results of Pretreatment and Posttreatment Soil Samples

Table 6-4 presents a summary of the results of analysis for critical semivolatile organic contaminants in the pretreatment soil samples (Week T_0) for the five reactors. Tables 6-5 and 6-6 present the results for the posttreatment soil samples for the five reactors for Weeks T_9 and T_{12}, respectively.

In addition to the analytical results, Tables 6-5 and 6-6 list the Method Detection Limit (MDLs) for the contaminants in the soil matrix. The MDLs are based on laboratory results from instrument detection limits for semivolatile compounds injected in the GC/MS and the matrix spike/matrix spike duplicate results from the posttreatment soil samples. Section 7 contains a complete discussion on determining MDLs. When

TABLE 6-2. CS&D CONSTITUENTS DETECTED IN THE CHARACTERIZATION ANALYSIS OF PREMILLING AND POSTMILLING SOIL SAMPLES

Constituents	Premilling	Postmillling
Volatile Organic (total, mg/kg)		
Methylene chloride	12.0 B[a]	12.0 B
2-Butanone	1.1 J[b]B	0.86 JB
Benzene	0.24 J	0.52 J
Toluene	2.8 B	2.9 B
Ethylbenzene	1.4	1.4
Styrene	1.7	1.6
Total Xylenes	8.8	7.2
Volatile Organic (TCLP, mg/L)		
Benzene	0.014 J	0.018 J
Pesticides (total, mg/kg)		
Methyl Parathion	0.12	ND[c]
Famphur	ND	0.15
Metals (total, mg/kg)		
Aluminum	4100.0	3600.0
Arsenic	1.4	2.6
Barium	200.0	280.0
Cadmium	0.78	0.58
Chromium	7.7	12.0
Cobalt	2.2	1.9
Copper	13.0	13.0
Iron	9300.0	7000.0
Lead	16.0	24.0
Magnesium	1700.0	1600.0
Manganese	140.0	120.0
Mercury	0.19	0.25
Nickel	6.4	8.1
Potassium	260.0	260.0
Sodium	88.0	92.0
Vanadium	8.9	6.5
Zinc	52.0	33.0
Metals (TCLP, mg/L)		
Barium	1.6	2.0
Mercury	0.052	0.035
Inorganic (mg/kg)		
Fluoride	40.0	48.0
Cyanide	1.0	1.0
Sulfate	71.0	ND
Sulfide	330.0	200.0
Chloride	27.0	21.0
TOC (mg/kg)	18000.0	28000.0
MBAS (mg/kg)	3.3	4.8
TRPH (mg/kg)	38000.0	31000.0

[a]B = Analyte is found in the blank as well as in the sample.

[b]J = Estimated value of compound detected below specified detection limit.

[c]ND = Not detected above the reported detection limit.

TABLE 6-3. CONCENTRATIONS OF CRITICAL SEMIVOLATILE ORGANIC CONTAMINANTS IN PREMILLING AND POSTMILLING SOIL SAMPLES (mg/kg)

Contaminant	Premilling	Postmilling
Naphthalene	370	460
2-Methylnaphthalene	210	200
Acenaphthylene	39	30
Acenaphthene	240	190
Dibenzofuran	190	160
Fluorene	290	250
Phenanthrene	770	590
Anthracene	280	290
Fluoranthene	490	430
Pyrene	330	280
Benzo(a)anthracene	120	110
Chrysene	100	110
Benzo(b)fluoranthene	140	59
Benzo(k)fluoranthene	140	47
Benzo(a)pyrene	69	55
Indeno(1,2,3-cd)pyrene	30	23
Dibenzo(a,h)anthracene	<40	<40
Benzo(g,h,i)perylene	19	14
Total	3827	3298

TABLE 6-4. CONCENTRATIONS OF CRITICAL SEMIVOLATILE ORGANIC CONTAMINANTS IN PRETREATMENT SOIL SAMPLES[a] (Week T_0)
(mg/kg)

Contaminant	R1	R2	R4	R5	R6
Naphthalene	600	360	40	540	64
2-Methylnaphthalene	220	130	16	210	28
Acenaphthylene	39	18	5.5	44	9.6
Acenaphthene	240	130	46	320	95
Dibenzofuran	190	100	34	230	67
Fluorene	330	150	57	380	110
Phenanthrene	680	460	150	840	300
Anthracene	410	300	92	520	140
Fluoranthene	570	330	130	660	180
Pyrene	360	210	68	500	150
Benzo(a)anthracene	140	80	24	180	47
Chrysene	140	85	27	210	54
Benzo(b)fluoranthene	130	37	28	190	49
Benzo(a)pyrene	70	33	11	96	22
Indeno(1,2,3-cd)pyrene	<40	<40	<40	<40	<40
Dibenzo(a,h)anthracene	<40	<40	<40	<40	<40
Benzo(g,h,i)perylene	<40	<40	<40	<40	<40
Total	4119	2423	728.5	4920	1315.6

[a]Data generated by IT Corporation using GC/MS

TABLE 6-5. CONCENTRATIONS OF CRITICAL SEMIVOLATILE ORGANIC CONTAMINANTS IN POSTTREATMENT SOIL SAMPLES (Week T_9)
(mg/kg)

Contaminant	R1	R2	R4	R5	R6	MDLs[a]
Naphthalene	7.1	1.1J	6.8	6.0	3.6	1.4
2-Methylnaphthalene	1.5J[b]	0.23J	<14.0	<14.0	0.94J	14.0
Acenaphthylene	4.1	0.72	5.8	5.3	3.4	0.71
Acenaphthene	2.1J	0.37J	2.0J	2.4J	1.3J	19.0
Dibenzofuran	2.2J	0.39J	2.1J	2.1J	1.3J	6.4
Fluorene	<1.8	0.35J	1.7J	2.1	1.2J	1.8
Phenanthrene	10.0	1.9J	8.4	9.5	4.8	3.0
Anthracene	6.3J	1.1J	<7.6	6.2J	3.7J	7.6
Fluoranthene	13.0	2.6	12.0	13.0	7.4	1.1
Pyrene	10.0	2.3J	7.9	9.4	6.1	4.1
Benzo(a)anthracene	5.9	1.6J	5.5	5.4	4.0	2.0
Chrysene	9.2	3.2J	9.9	8.5J	5.8J	9.0
Benzo(b)fluoranthene	130.0	19.0	180.0	150.0	72.0	5.9
Benzo(a)pyrene	78.0	9.9	120.0	100.0	41.0	8.9
Indeno(1,2,3-cd)pyrene	<2.1	4.1	<2.1	<2.1	17.0	2.1
Dibenzo(a,h)anthracene	6.5	3.5	<1.5	<1.5	13.0	1.5
Benzo(g,h,i)perylene	<19	<19.0	<19.0	<19.0	16.0	19.0
Total	<308.8	<71.4	<406.3	<356.5	<202.5	

[a]MDLs = Method Detection Limits.
[b]J = Estimated value of compound detected below specified detection limit.

TABLE 6-6. CONCENTRATIONS OF CRITICAL SEMIVOLATILE ORGANIC CONTAMINANTS IN POSTTREATMENT SOIL SAMPLES (Week T_{12})
(mg/kg)

Contaminant	R1	R2	R4	R5	R6	MDLs[a]
Naphthalene	8.2	6.6	1.6	7.1	6.0	1.5
2-Methylnaphthalene	<17	1.3J	.41J	<17	1.4J	17
Acenaphthylene	5.1	<.59	1.5	6.9	4.5	.59
Acenaphthene	<17	1.7J	.56J	<17	<17	17
Dibenzofuran	2.5J	2.2J	.58J	1.9J	2.1J	6
Fluorene	<1.6	<1.6	.53J	<1.6	1.6J	1.6
Phenanthrene	11	8.5	2.3J	7.8	8.9	2.5
Anthracene	6.6	4.8J	1.6J	5.9	6.7	5.4
Fluoranthene	14	9.8	3.2	13	13	.88
Pyrene	8.0	9.0	2.9J	8.5	8.8	3.8
Benzo(a)anthracene	5.9	4.6	1.5J	5.5	5.5	1.6
Chrysene	8.5J	10	1.9J	8.6J	8.4J	9.2
Benzo(b)fluoranthene	130	130	33	180	140	6.3
Benzo(a)pyrene	87	84	22	120	96	8.4
Indeno(1,2,3-cd)pyrene	16	<1.9	8.2	15	<1.9	1.9
Dibenzo(a,h)anthracene	13	<1.2	1.6	16	<1.2	1.2
Benzo(g,h,i)perylene	34	<17	<17	38	<17	17
Total	<385.4	<294.79	<100.38	<469.8	<340	

[a]MDLs = Method Detection Limits.
[b]J = Estimated value of compound detected below specified detection limit.

compounds were not detected, the results are reported as being less than the detection limit.

The concentrations of the PAH contaminants in the pretreatment soil samples ranged from 5.5 to 840 mg/kg. The concentrations of the PAHs in posttreatment samples indicated a significant reduction of PAHs in the soil matrix. Results from the posttreatment samples indicate the more complex PAHs, such as benzo(b)fluoranthene and benzo(a)pyrene were more recalcitrant to the biological activity than the less complex PAHs, such as naphthalene and acenaphthene. Results from Week 12 indicate that additional spiking during Week 9 did not assist in further degradation of the complex PAHs. On the contrary, the level of contamination due to the presence of the more complex PAHs was greater in Week 12 than in Week 9. The lower level of PAHs contamination in Week 9 soil samples may have resulted due to inconsistent laboratory procedures. These nonhomogeneous soil samples may not have been thoroughly remixed before the sample aliquot was obtained for extraction.

Table 6-7 presents the percentage reduction of PAHs in the soil matrix based on the data in Tables 6-4 through 6-6. The total percent reduction of PAHs for Week T_9 samples for the five reactors ranged from >44.2 to >97.1 percent. The total percent reduction of PAHs for Week T_{12} samples for the five reactors ranged from >74.2 to >90.6 percent.

Copies of the analytical data provided by the ITAS laboratory for the critical contaminants in the pre- and posttreatment soil samples are included in Appendix N.

6.3 Pretreatment and Posttreatment Liquid Samples

Table 6-8 presents a summary of analytical results for critical semivolatile organic contaminants in the pretreatment liquid samples (Week T_0) for the five reactors. Tables 6-9 and 6-10 present the results for the posttreatment liquid samples for the five reactors for Weeks T_9 and T_{12}, respectively. The MDLs for the contaminants in the liquid matrix are also listed in Tables 6-9 and 6-10.

TABLE 6-7. PERCENT REDUCTION OF CRITICAL SEMIVOLATILE ORGANIC CONTAMINANTS IN SOIL BY TREATMENT WITH BIOSLURRY REACTORS.

Contaminant	Week T_9					Week T_{12}				
	R1	R2	R4	R5	R6	R1	R2	R4	R5	R6
Naphthalene	98.8	99.7	83.0	98.9	94.4	98.6	98.2	96.0	98.7	97.7
2-Methylnaphthalene	99.3	99.8	>12.5	>93.3	96.6	>92.3	99.0	97.4	>91.9	95.0
Acenaphthylene	89.5	96.0	-5.5	88.0	64.6	86.9	>96.7	72.7	84.3	53.1
Acenaphthene	99.1	99.7	95.7	99.3	98.6	>92.9	98.7	98.8	>94.7	>82.1
Dibenzofuran	98.8	99.6	93.8	99.1	98.1	98.7	97.8	98.3	99.2	96.9
Fluorene	>99.5	99.8	97.0	99.4	98.9	>99.5	>98.9	99.1	>99.6	98.5
Phenanthrene	98.5	99.6	93.7	98.9	98.4	98.3	98.2	98.5	99.1	97.0
Anthracene	98.5	99.6	>91.7	98.8	97.4	98.4	98.4	98.3	98.9	95.2
Fluoranthene	97.7	99.2	90.8	98.0	95.9	97.5	97.0	97.5	98.0	92.8
Pyrene	97.2	98.9	88.4	98.1	95.9	97.8	95.7	95.7	98.3	94.1
Benzo(a)anthracene	95.8	98.0	77.1	97.0	91.5	95.8	94.3	93.8	96.9	88.3
Chrysene	93.4	96.2	63.3	96.0	89.3	94.0	88.2	93.0	95.9	84.4
Benzo(b)fluoranthene	100.0	48.6	-364.3	21.1	-46.9	100.0	-251.4	-17.9	5.3	-185.7
Benzo(a)pyrene	-11.4	70.0	-990.9	-4.2	-86.4	-24.3	-154.5	-100.0	-87.5	-336.4
Indeno(1,2,3-cd)pyrene	NA[a]	89.8	NA	NA	57.5	60.0	NA	79.5	62.5	NA
Dibenzo(a,h)anthracene	83.8	91.3	NA	NA	67.5	67.5	NA	96.0	60.0	NA
Benzo(g,h,i)perylene	NA	NA	NA	NA	60.0	15.0	NA	NA	5.0	NA
Total	>92.5	>97.1	>44.2	>92.8	>84.6	>90.6	>87.8	>86.2	>90.5	>74.2

[a]NA = Not Applicable.

TABLE 6-8. CONCENTRATIONS OF CRITICAL SEMIVOLATILE ORGANIC CONTAMINANTS IN PRETREATMENT LIQUID SAMPLES (Week T_0)
(mg/L)

Contaminant	R1	R2	R4	R5	R6
Naphthalene	1.2 E[a]	<0.04	18.0	0.008 J[b]	0.45
2-Methylnaphthalene	0.37	<0.04	3.2	0.006 J	0.26
Acenaphthylene	0.064	0.031 J	0.83	0.036 J	0.069
Acenaphthene	0.23	0.22	2.9	0.22	0.32
Dibenzofuran	0.18	0.13	2.2	0.16	0.25
Fluorene	0.19	0.19	2.8	0.18	0.29
Phenanthrene	0.24	0.24	7.2	0.25	0.44
Anthracene	0.055	0.058	2.8	0.053	0.098
Fluoranthene	0.078	0.092	3.5	0.091	0.17
Pyrene	0.056	0.066	2.9	0.057	0.14
Benzo(a)anthracene	0.012J	0.014 J	1.4	0.012 J	0.033 J
Chrysene	0.016J	0.017 J	1.3	0.014 J	0.037 J
Benzo(b)fluoranthene	0.012 J	0.013 J	1.47	0.007 J	0.037 J
Benzo(a)pyrene	<0.04	<0.04	0.72	<0.04	0.012 J
Indeno(1,2,3-cd)pyrene	<0.04	<0.04	0.25	<0.04	<0.04
Dibenzo(a,h)anthracene	<0.04	<0.04	<0.04	<0.04	<0.04
Benzo(g,h,i)perylene	<0.04	<0.04	0.2	<0.04	<0.04
Phenol	0.12	0.12	0.14 J	0.12	0.17
2-Methylphenol	0.73 E	0.76 E	1.0	0.76 E	1.0 E
4-Methylphenol	0.82 E	0.49	0.76	0.52	1.0 E
2,4-Dimethylphenol	1.1 E	1.2 E	1.9	1.1 E	1.3 E

[a]E = Estimated value of compound detected above linear range of the instrument.
[b]J = Estimated value of compound detected below specified detection limit.

TABLE 6-9. CONCENTRATIONS OF CRITICAL SEMIVOLATILE ORGANIC CONTAMINANTS IN POSTTREATMENT LIQUID SAMPLES (Week T_9)
(mg/L)

Contaminant	R1	R2	R4	R5	R6	MDLs[a]
Naphthalene	<0.0041	<0.0041	<0.0041	0.013	<0.0041	0.0041
2-Methylnaphthalene	<0.043	<0.043	<0.043	<0.043	<0.043	0.043
Acenaphthylene	<0.0017	<0.0017	<0.0017	<0.0017	<0.0017	0.0017
Acenaphthene	<0.047	<0.047	<0.047	<0.047	<0.047	0.047
Dibenzofuran	<0.016	<0.016	<0.016	<0.016	<0.016	0.016
Fluorene	<0.0045	<0.0045	<0.0045	<0.0045	<0.0045	0.0045
Phenanthrene	<0.0072	<0.0072	<0.0072	0.01	<0.0072	0.0072
Anthracene	<0.017	<0.017	<0.017	0.017 J	<0.017	0.017
Fluoranthene	<0.0028	<0.0028	<0.0028	0.012	<0.0028	0.0028
Pyrene	<0.013	<0.013	<0.013	0.011 J	<0.013	0.013
Benzo(a)anthracene	<0.0047	<0.0047	<0.0047	<0.0047	<0.0047	0.0047
Chrysene	<0.025	<0.017J	<0.025	<0.025	<0.025	0.025
Benzo(b)fluoranthene	0.042	0.114	0.041	0.14	0.041	0.015
Benzo(a)pyrene	0.013 J[b]	0.047	0.021	0.075	0.021 J	0.024
Indeno(1,2,3-cd)pyrene	<0.006	0.015	<0.006	0.027	<0.006	0.006
Dibenzo(a,h)anthracene	<0.0035	<0.0035	<0.0035	0.0035	<0.0035	0.0035
Benzo(g,h,i)perylene	<0.055	<0.055	<0.055	0.023	<0.055	0.055
Phenol	<0.04	<0.04	<0.04	<0.04	<0.04	0.04
2-Methylphenol	<0.04	<0.04	<0.04	<0.04	<0.04	0.04
4-Methylphenol	<0.04	<0.04	<0.04	<0.04	<0.04	0.04
2,4-Dimethylphenol	<0.04	<0.04	<0.04	<0.04	<0.04	0.04

[a]MDLs = Method Detection Limits.
[b]J = Estimated value of compound detected below specified detection limit.

TABLE 6-10. CONCENTRATIONS OF CRITICAL SEMIVOLATILE ORGANIC CONTAMINANTS IN POSTTREATMENT LIQUID SAMPLES (Week T_{12})
(mg/L)

Contaminant	R1	R2	R4	R5	R6	MDLs[a]
Naphthalene	<0.0024	<0.0024	<0.0024	<0.0024	<0.0024	0.0024
2-Methylnaphthalene	<0.023	<0.023	<0.023	<0.023	<0.023	0.023
Acenaphthylene	<0.001	<0.001	<0.001	<0.001	<0.001	0.001
Acenaphthene	<0.029	<0.029	<0.029	<0.029	<0.029	0.029
Dibenzofuran	<0.011	<0.011	<0.011	<0.011	<0.011	0.011
Fluorene	<0.003	<0.003	<0.003	<0.003	<0.003	0.003
Phenanthrene	<0.0041	<0.0041	<0.0041	<0.0041	<0.0041	0.0041
Anthracene	<0.0091	0.003 J[b]	<0.0091	<0.0091	<0.0091	0.0091
Fluoranthene	<0.0018	<0.0018	<0.0018	<0.0018	<0.0018	0.0018
Pyrene	<0.008	0.002 J	<0.008	<0.008	<0.008	0.008
Benzo(a)anthracene	<0.003	<0.003	<0.003	<0.003	<0.003	0.003
Chrysene	<0.016	<0.016	<0.016	<0.016	<0.016	0.016
Benzo(b)fluoranthene	0.013	<0.0072	0.014	0.02	0.019	0.0072
Benzo(a)pyrene	<0.016	<0.016	<0.016	0.012 J	<0.016	0.016
Indeno(1,2,3-cd)pyrene	<0.0046	<0.0046	<0.0046	<0.0046	<0.0046	0.0046
Dibenzo(a,h)anthracene	<0.0029	<0.0029	<0.0029	<0.0029	<0.0029	0.0029
Benzo(g,h,i)perylene	<0.048	<0.048	<0.048	<0.048	<0.048	0.048
Phenol	<0.04	<0.04	<0.04	<0.04	<0.04	0.04
2-Methylphenol	<0.04	<0.04	<0.04	<0.04	<0.04	0.04
4-Methylphenol	<0.04	<0.04	<0.04	<0.04	<0.04	0.04
2,4-Dimethylphenol	<0.04	<0.04	<0.04	<0.04	<0.04	0.04

[a]MDLs = Method Detection Limits.
[b]J = Estimated value of compound detected below specified detection limit.

The concentrations of the PAH contaminants in the pretreatment samples ranged from 0.006 to 18 mg/L. The concentrations for the majority of PAHs in the posttreatment samples were below the established MDLs for the instrument. After 9 weeks of treatment, only the more recalcitrant complex PAHs remained in the liquid matrix. These contaminants ranged in concentration from 0.013 to 0.14 mg/L. Results from Week 12 indicated a further reduction in contamination of the treatment matrix as the levels of complex PAHs in the soil were diminished and the MDLs for the contaminants from Week 12 were lower than MDLs for the contaminants from Week 9. The lower MDLs from Week 12 may have been due to less interferences and less contamination as a result of a cleaner matrix as discussed in Subsection 6.2.

Copies of the analytical data provided by the ITAS Laboratory for the critical contaminants in the pre- and posttreatment liquid samples are included in Appendix N.

6.4 Bioreactor Monitoring Samples

6.4.1 Polycyclic Aromatic Hydrocarbons (PAH)

Table 6-11 summarizes the results of the baseline (Week T_0) characterization of the soil used in the pilot-scale phase of this study. These samples were analyzed by ECOVA by HPLC Method which was developed by ECOVA. Naphthalene, acenaphthene, and fluoranthene appear to be the constituents present at the highest levels (range of 2170
± 250 ppm), followed by fluorene and benzo(a)anthracene (range of 960 ± 8 ppm). Total PAH levels in these soils are 10,970 ppm. The 2- and 3-ring PAHs constitute 5890 ppm of the total, and the 4+ ring PAHs account for 5080 ppm.

Total PAHs were degraded 93.4 ± 3.2 percent over all five operating reactors during the 12-week study (Tables 6-12 and 6-13). After only 2 weeks of slurry-phase treatment, 89.3 ± 3.9 percent of the total PAHs were degraded. Degradation rates (mg/kg/wk) for 2- and 3-ring PAHs were appreciably higher at two weeks (95.9 ± 1.8%) than they were for 4+ ring PAHs (89.3 ± 3.9%). The more rapid degradation of the lower-molecular-weight PAHs reflects the preference of the bacterial populations for these PAHs over the higher-molecular-weight PAHs. The final levels at Week T_{12}

TABLE 6-11. BASELINE SOIL PAH CONCENTRATIONS (Week T_0)[a]

PAH	Mean (5),[b] ppm	Std. Dev., ppm
Naphthalene	2143.3	710
Acenaphthylene	17.4	7.6
Acenaphthene	1937.1	1016.8
Fluorene	967.8	288.4
Phenanthrene	518.9	12.1
Anthracene	307.0	34.7
Fluoranthene	2428.7	732.6
Pyrene	161.1	51.2
Benzo(a)anthracene	957.2	284.8
Chrysene	468.1	129.6
Benzo(b)fluoranthene	389.4	112.7
Benzo(k)fluoranthene	279.6	83.1
Benzo(a)pyrene	260.2	75.4
DiBenzo(a,h)anthracene	119.9	94.1
Indeno(1,2,3-cd)pyrene	17.2	4.8

[a] Data generated by ECOVA Corporation using HPLC.

[b] Average of the five reactors.

TABLE 6-12. TOTAL, 2- AND 3-RING, AND 4- AND 6-RING PAH LEVELS (SOLID PHASES)

BDAT Pilot-Scale Polyaromatic Hydrocarbon Levels										
	Week									
	0	1	2	3	4	6	9	10	11	12
	2- and 3-Ring PAHs									
Reactor 1	4380.59	64.26	312.25	37.55	682.82	31.66	63.09	56.66	600.95	78.42
Reactor 2	6158.29	970.17	160.72	55.66	247.76	212.93	116.37	72.96	492.38	95.29
Reactor 4	6699.04	2904.45	189.59	41.48	150.26	333.88	124.09	307.52	551.41	104.97
Reactor 5	3758.81	683.53	168.53	85.05	359.75	69.2	85.04	317.95	80.12	249.72
Reactor 6	8460.94	948.59	304.9	144.92	241.23	51.62	183.71	66.04	42.44	232.32
	4- and 6-Ring PAHs									
Reactor 1	3526.33	2273.11	1043.28	445.29	1734.92	417.93	238.82	470.94	524.9	488.13
Reactor 2	5696.53	3754.18	942.26	480.62	1278.03	1132.16	463.94	552.36	503.44	432.39
Reactor 4	6603.17	11827.17	840.23	409.88	645.52	1830.56	449.57	503.68	481	375.2
Reactor 5	3360.94	2397.9	644.33	559.17	1318.67	1178.01	549.64	449.14	654.13	593.56
Reactor 6	6220.41	3259.33	877.3	1035.39	1035.92	402.25	274.42	498.19	715.29	617.6
	Total PAHs									
Reactor 1	7906.92	3015.94	1355.53	482.84	2417.74	449.59	301.91	527.6	1125.85	566.55
Reactor 2	11854.82	4724.35	1102.98	536.28	1525.79	1345.09	580.31	625.32	995.82	527.68
Reactor 4	13302.21	14731.62	1029.82	451.36	795.78	2164.44	573.66	811.2	1032.41	480.17
Reactor 5	7119.75	3081.43	812.86	644.22	1678.42	1247.21	634.68	767.09	734.25	843.28
Reactor 6	14681.35	4207.92	1182.2	1180.31	1277.15	453.87	458.13	564.23	757.73	849.92

TABLE 6-13. TOTAL, 2- AND 3-RING, AND 4- AND 6-RING PAH DEGRADATION RATES (SOLID PHASES)

BDAT Pilot-Scale Polyaromatic Hydrocarbon Levels									
	Week								
	1	2	3	4	6	9	10	11	12
	2- and 3-Ring PAH Degradation Rate, % Degradation								
Reactor 1	98.53	92.87	99.14	84.41	99.28	98.56	98.71	86.28	98.21
Reactor 2	84.25	97.39	99.10	95.98	96.54	98.11	98.82	92.00	98.45
Reactor 4	56.64	97.17	99.38	97.76	95.02	98.15	95.41	91.77	98.43
Reactor 5	81.82	95.52	97.74	90.43	98.16	97.74	91.54	97.87	93.36
Reactor 6	88.79	96.40	98.29	97.15	99.39	97.83	99.22	99.50	97.25
	4- and 6-Ring PAH Degradation Rate, % Degradation								
Reactor 1	35.54	70.41	87.37	50.80	88.15	93.23	86.65	85.11	86.16
Reactor 2	34.10	83.46	91.56	77.56	80.13	91.86	90.30	91.16	92.41
Reactor 4	-79.11	87.28	93.79	90.22	72.28	93.19	92.37	92.72	94.32
Reactor 5	28.65	80.83	83.36	60.76	64.95	83.65	86.64	80.54	82.34
Reactor 6	47.60	85.90	83.35	83.35	93.53	95.59	91.99	88.50	90.07
	Total PAH Degradation Rate, % Degradation								
Reactor 1	61.86	82.86	93.89	69.42	94.31	96.18	93.33	85.76	92.83
Reactor 2	60.15	90.70	95.48	87.13	88.65	95.10	94.73	91.60	95.55
Reactor 4	-10.75	92.26	96.61	94.02	83.73	95.69	93.90	92.24	96.39
Reactor 5	56.72	88.58	90.95	76.43	82.48	91.09	89.23	89.69	88.16
Reactor 6	71.34	91.95	91.96	91.30	96.91	96.88	96.16	94.84	94.21

were 653.5 ± 178.9 ppm for total PAHs, 152.1 ± 81.9 ppm for 2- and 3-ring PAHs, and 501.4 ± 103.5 ppm for 4+ ring PAHs.

As shown in Figures 6-1, 6-2, and 6-3, the degradation rates of the different PAHs varied appreciably during the course of the study to reflect changes in the reactor environments. Clearly, a very large amount of the total PAH residue was degraded after only 2 weeks; however, the apparent level of soil-bound PAH residues began to rise slightly for all PAHs through Week T_6, to decrease through Week T_9, to rise again through Week T_{11}, and finally, to decrease through Week T_{12}. It is important to note that these data necessarily reflect not only the nominal concentrations of soil-bound PAHs, but also the extraction efficiency of the analytical method. Apparent increases in the levels of soil-bound PAHs probably reflect an increased PAH extraction efficiency rather than the unlikely production of soil-bound PAHs during the study. The phenomenon of increasing PAH residue levels shown in these figures has been seen elsewhere (personal communication from Dr. Ron Lewis, U.S. EPA Cincinnati, 7/29/91) and clearly reflects a widespread, intractable, methodological problem. The variations in concentrations of soil-bound individual PAHs mirror the results for classes of PAHs, as shown in Table 6-14 and Figures 6-4 through 6-7.

Immediately after sampling at Week T_9, Reactors 2 and 4 were reinoculated with fresh bacterial populations, and Reactors 5 and 6 were both reinoculated and amended with the surfactant Tween 80. Reactor 1 was not amended in any way. At Week T_{11}, levels of total PAHs in unamended Reactor 1 and reinoculated Reactors 2 and 4 increased dramatically; whereas total levels in reinoculated and surfactant-amended Reactors 5 and 6 essentially did not change (Table 6-13, Figures 6-1, 6-2, and 6-3). By Week T_{12}, the total levels in Reactors 1, 2, and 4 had again declined, but total levels in Reactors 5 and 6 increased.

Anomalies in the PAH degradation rates occurred in Reactor 4 for 4+ ring PAHs at Weeks T_1 and T_6 (Figure 6-3). At both points in time, the total PAH level was appreciably higher than for all other reactor levels. Among the individual PAHs, levels

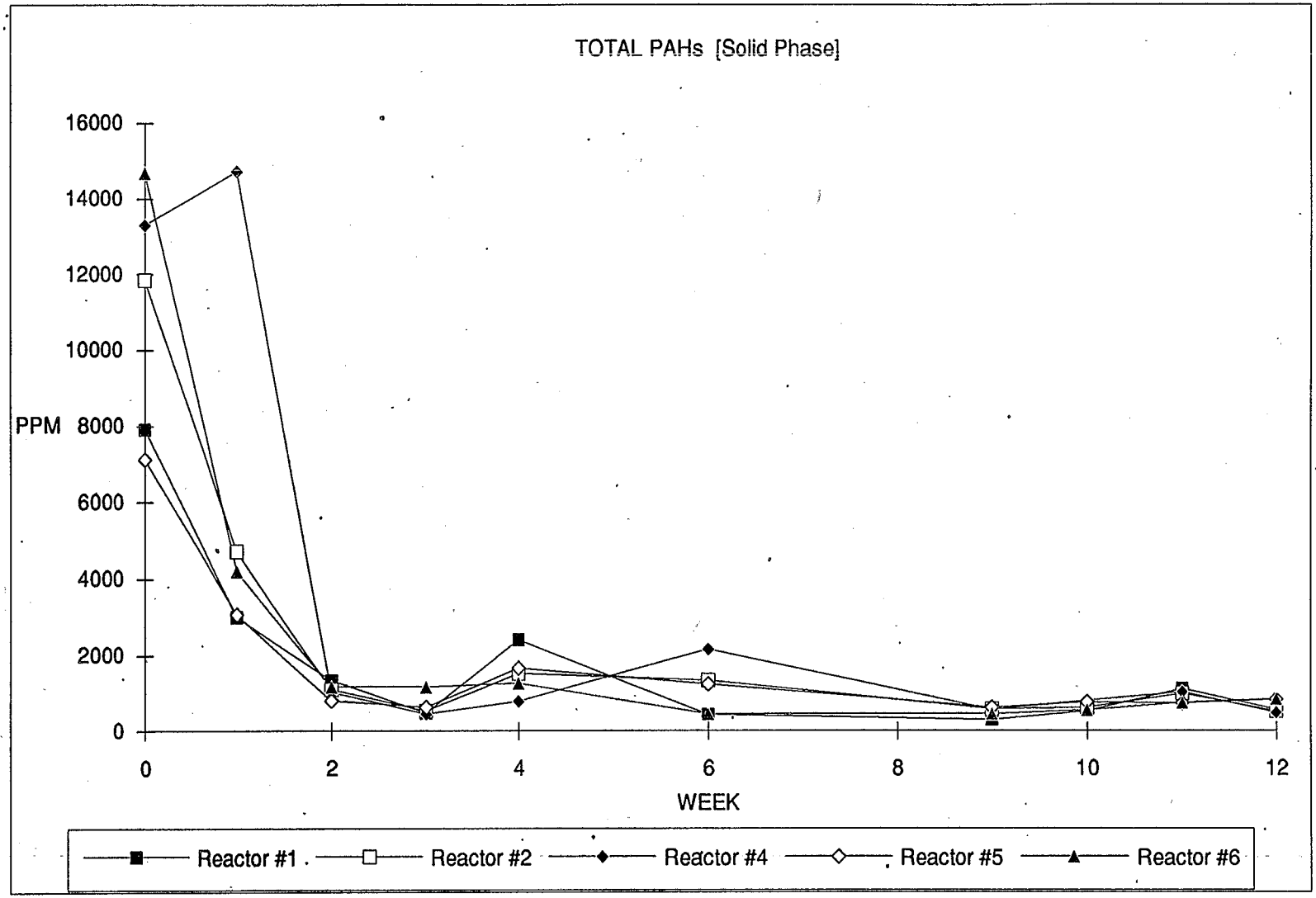

Figure 6-1. Total PAH soil residue levels.

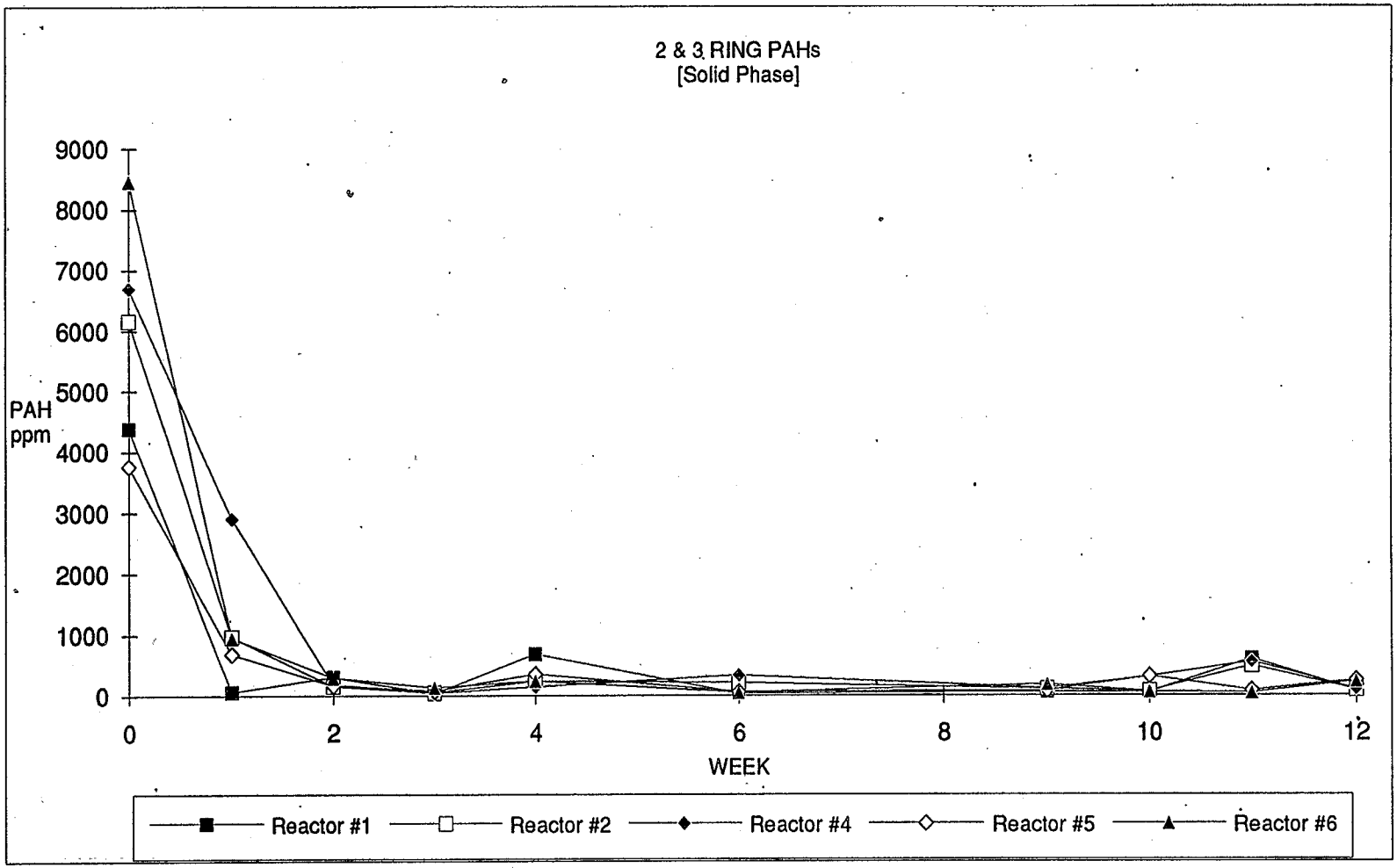

Figure 6-2. Two- and three-ring PAH soil residue levels.

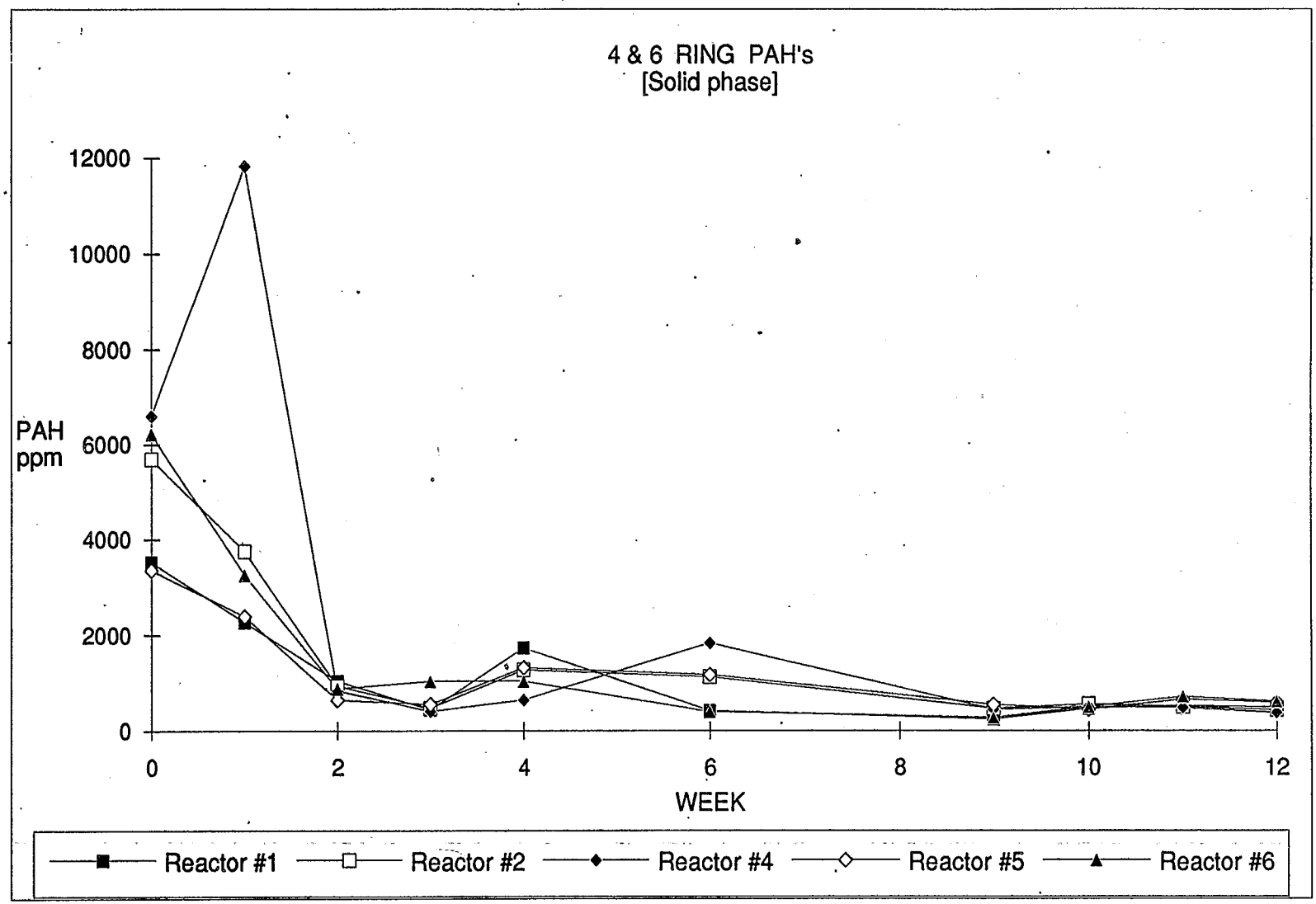

Figure 6-3. Four- and six-ring PAH soil residue levels.

TABLE 6-14. SPECIFIC PAH CONCENTRATIONS (MEANS AND STD. DEV.)

	Mean PAH Concentration by Specific PAH (Solids), ppm									
	Weeks									
PAHs	0.0	1.0	2.0	3.0	4.0	6.0	9.0	10.0	11.0	12.0
Naphthalene	2143.3	293.5	0.0	0.0	0.0	81.1	27.2	42.0	48.5	29.3
Acenaphthylene	17.4	1.1	0.0	0.1	1.8	0.6	2.4	0.1	0.1	1.6
Acenaphthene	1937.1	634.4	127.6	38.5	251.4	0.0	62.3	101.2	288.4	96.2
Fluorene	967.8	57.6	15.3	3.8	37.9	9.2	5.8	4.5	3.6	8.3
Phenanthrene	518.9	116.9	39.6	16.3	23.8	31.3	12.9	12.4	11.0	12.9
Anthracene	307.0	146.4	44.7	14.2	21.4	17.6	4.0	3.9	2.0	3.9
Fluoranthene	2428.7	1559.1	139.1	76.1	164.4	121.5	47.7	49.5	63.8	56.0
Pyrene	161.1	610.8	46.4	8.1	17.4	46.4	16.7	25.2	27.9	21.9
Benzo(a)anthracene	957.2	767.3	81.0	40.5	84.1	63.8	21.7	25.6	25.1	28.4
Chrysene	468.1	461.1	50.3	32.1	81.0	34.8	12.5	18.9	28.0	7.8
Benzo(b)fluoranthene	389.4	456.9	197.1	124.3	270.4	229.1	103.9	108.2	128.2	116.9
Benzo(k)fluoranthene	279.6	334.1	123.3	73.2	116.5	115.6	47.7	62.3	73.0	60.1
Benzo(a)pyrene	260.2	301.6	92.7	102.0	217.9	177.5	72.5	88.8	102.2	88.7
Dibenzo(a,h)anthracene	119.9	128.0	115.5	102.2	188.3	146.4	45.3	86.3	93.3	89.7
Indeno(1,2,3-cd)pyrene	17.2	83.5	24.0	27.6	62.6	57.0	27.2	29.9	34.3	31.9
	Standard Deviation of Mean PAH Concentration by Specific PAH (Solids), ppm									
Naphthalene	710.0	226.2	23.7	0.0	0.0	112.1	4.0	6.2	15.7	8.8
Acenaphthylene	7.6	2.5	23.7	0.2	4.1	1.0	1.1	0.2	0.1	1.5
Acenaphthene	1016.8	524.1	61.7	22.6	210.5	0.0	44.0	138.6	267.3	74.9
Fluorene	288.4	18.4	17.0	4.7	13.0	6.4	2.4	0.9	2.2	3.3
Phenanthrene	12.1	76.5	8.9	10.1	19.1	20.5	1.5	4.7	7.4	2.2
Anthracene	34.7	87.8	11.9	11.9	12.6	9.6	0.6	1.1	2.7	0.9
Fluoranthene	732.6	1424.6	46.1	25.9	54.4	88.7	14.3	8.0	17.3	10.8
Pyrene	51.2	517.2	47.3	4.3	5.1	32.6	6.6	6.0	5.7	5.8
Benzo(a)anthracene	284.8	721.7	16.9	25.2	20.2	40.5	10.0	4.0	5.9	8.1
Chrysene	129.6	413.3	8.2	14.6	48.3	38.2	10.4	11.3	12.7	2.6
Benzo(b)fluoranthene	112.7	366.1	75.8	56.6	95.8	103.7	18.2	9.1	22.9	25.6
Benzo(k)fluoranthene	83.1	247.0	36.4	28.1	33.8	85.7	26.6	7.0	11.1	11.9
Benzo(a)pyrene	75.4	216.1	71.6	48.9	78.3	91.5	16.7	8.3	20.2	23.0
Dibenzo(a,h)anthracene	94.1	81.6	51.6	45.6	55.6	115.1	41.6	7.1	13.8	16.7
Indeno(1,2,3-cd)pyrene	4.8	60.0	23.3	18.9	20.8	34.8	3.0	2.4	5.1	6.5

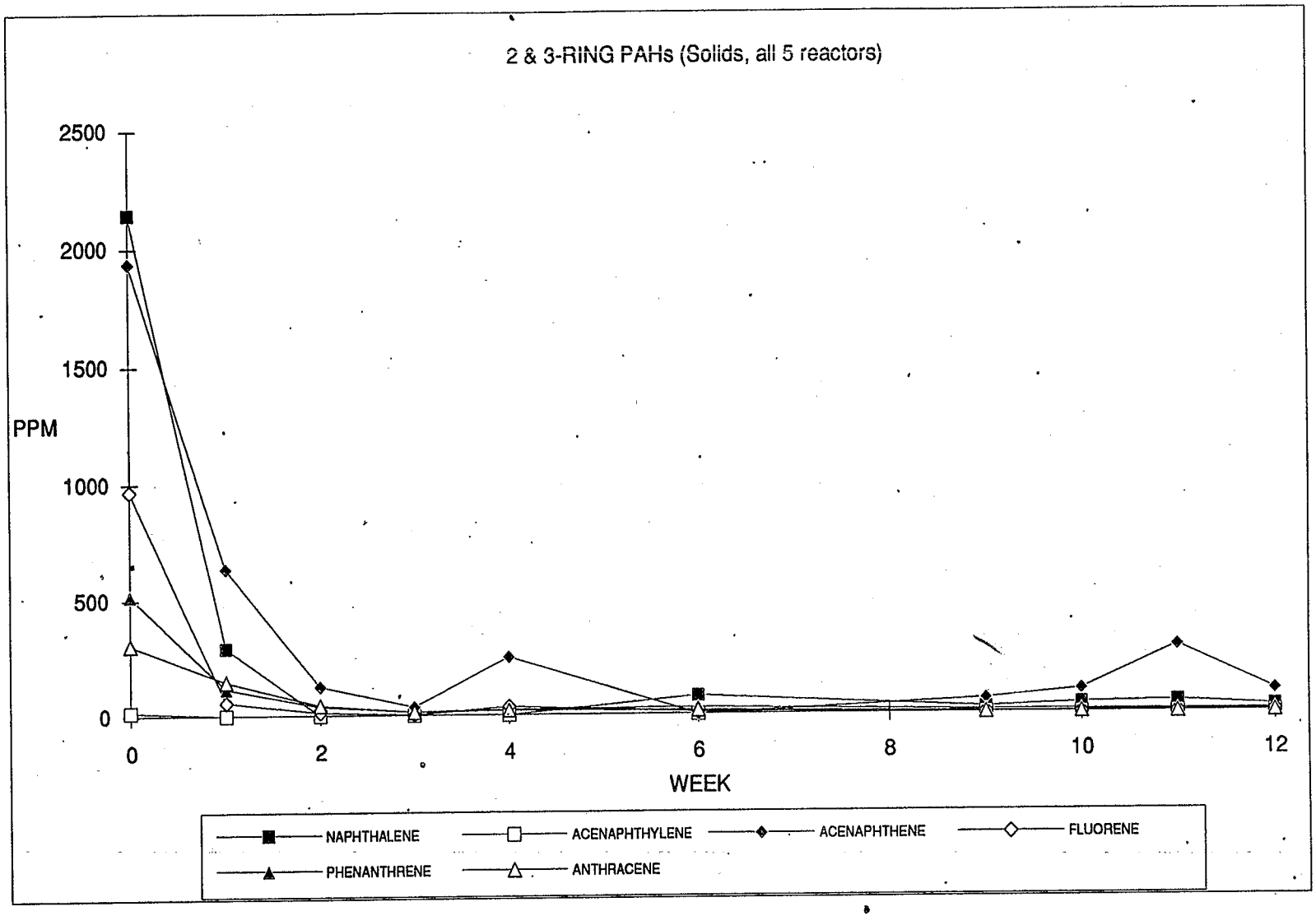

Figure 6-4. Two- and three-ring individual mean PAH levels.

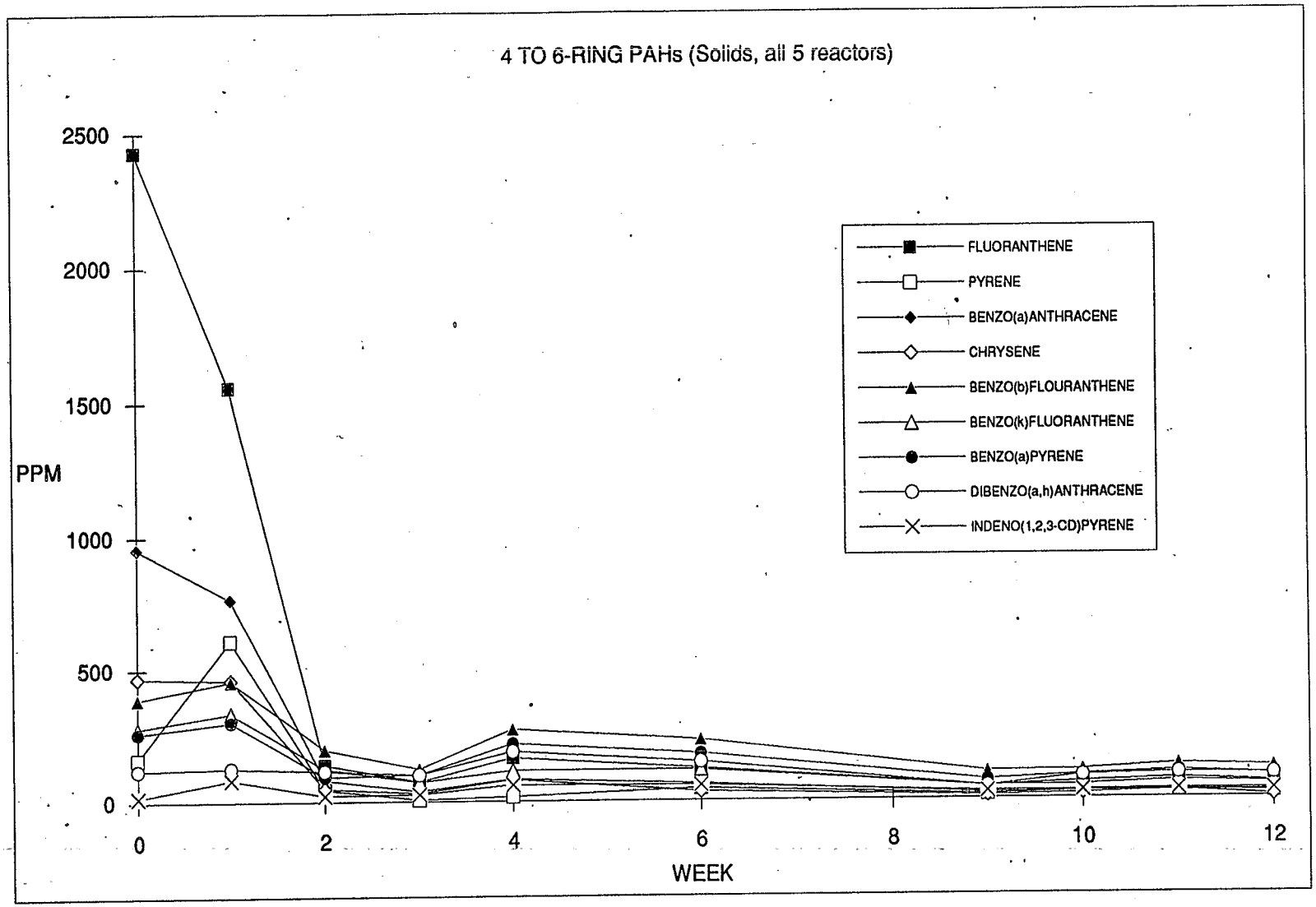

Figure 6-5. Four- to six-ring individual mean PAH levels.

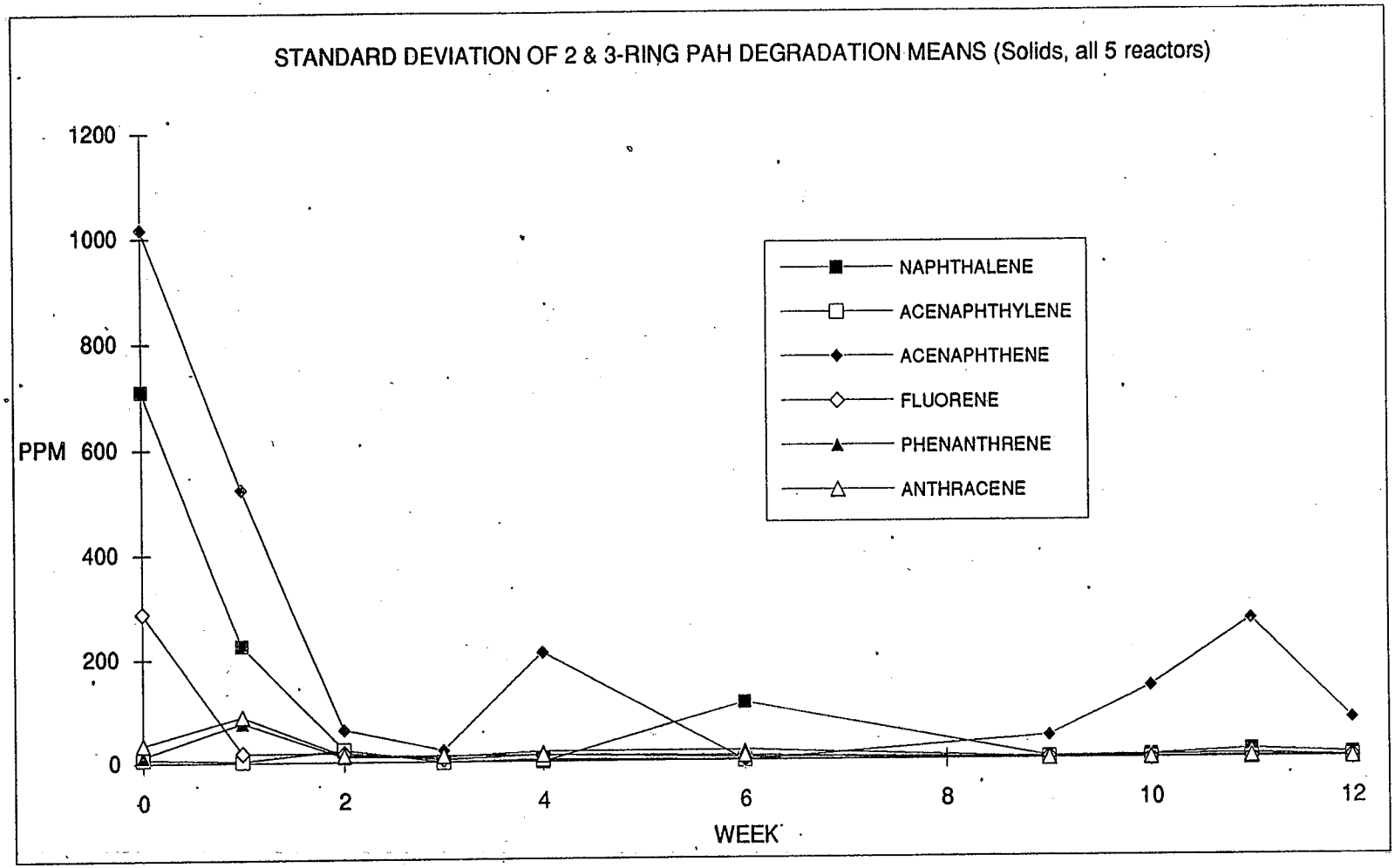

Figure 6-6. Standard deviation of the mean concentration for 2- and 3-ring PAH at each sample interval during slurry-phase treatment.

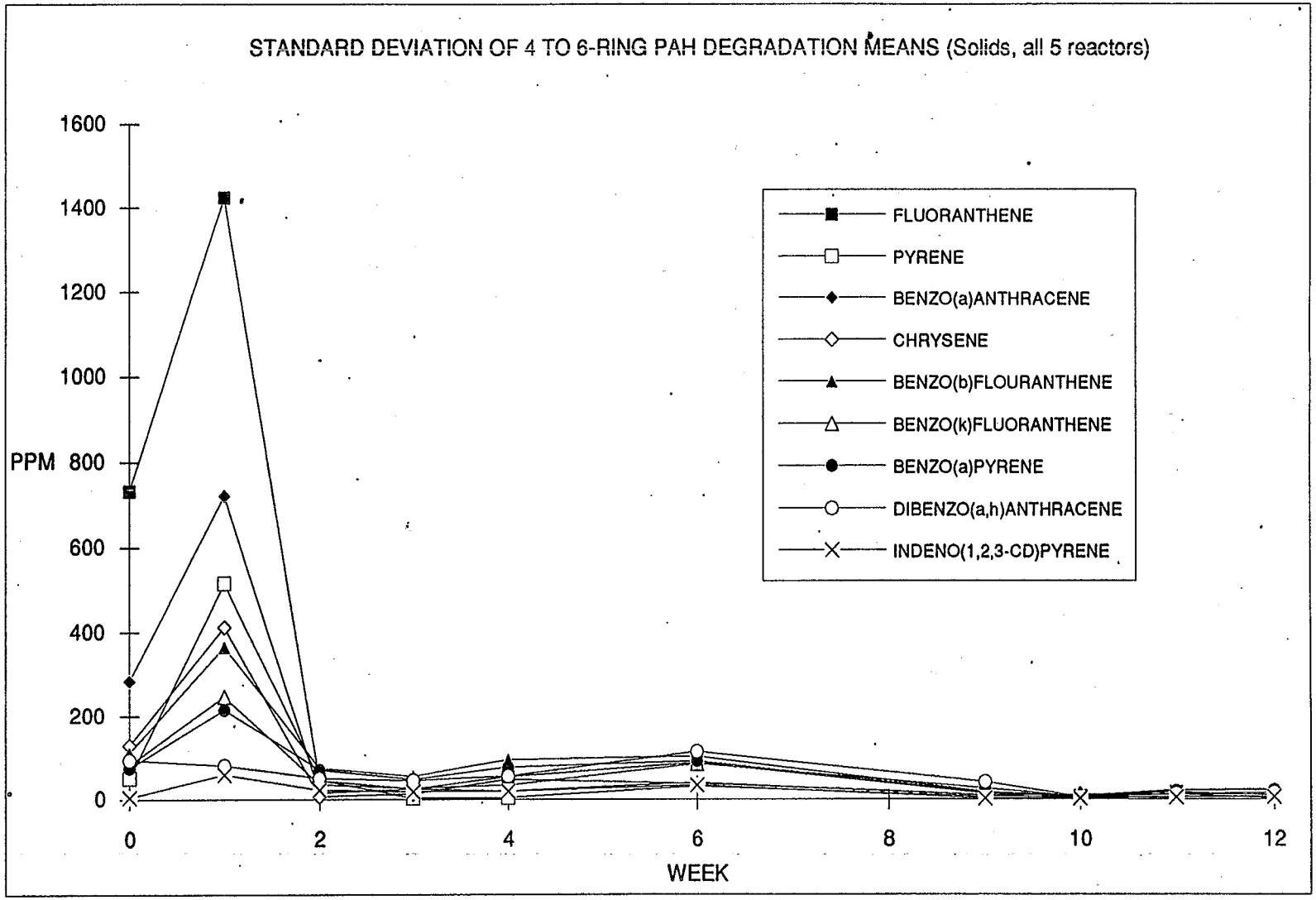

Figure 6-7. Standard deviation of the mean for 4- to 6-ring PAHs at each sampling interval.

of acenaphthene were clearly higher than those of other 2- and 3-ring PAHs at Weeks T_4 and T_{11} (Figure 6-2). This anomaly may be related to widely varying levels of acenaphthene among the five reactors (see standard deviation data for acenaphthene in Figure 6-6 or Table 6-14). A final anomaly was the surge in both the mean levels and standard deviations for the 4+ ring PAHs at Week T_1. This was not exhibited by the 2- and 3-ring PAHs for that time point, and the standard deviations were appreciably higher than those for all other time points for all PAH types (Figure 6-7).

These anomalies are indicative of several problems and events. Clearly, further comminution of the soil particles accounted for a portion of the rise in soil-bound PAH residues by reducing the resistance to mass transfer. This, in turn, allowed a higher extraction efficiency in the analytical method and therefore higher apparent concentrations. Although acenaphthene is an identifiable compound in an analytical method, it is difficult to quantitate accurately. It has the lowest molar extinction coefficient of all the PAHs in ECOVA's analytical method and is therefore the PAH most subject to errors in quantitation. After Week T_2, PAH residue levels were low enough that a small error in the area assessed for acenaphthene could have an enormous effect on the total levels of PAH residues.

6.4.2 Total Petroleum Hydrocarbons (TPH)

ITEP monitored TPH by gas chromatographic analysis over the course of the study. The data for soil-bound TPH are presented in Table 6-15. These data indicate that, as with the PAH data, variations occurred in TPH levels in the slurry. As with the PAHs, the greatest decline in TPH occurred in the first 2 weeks of the study. A rise in the levels of TPH occurred at Week T_6, however, which is 2 weeks after Total PAHs rose in the slurries. This delay could reflect the actual production of TPH compounds as metabolic products of the biodegradation of the PAHs. It could also reflect a simple rise in extraction efficiency due to soil particle comminution.

6.5 Air Samples

The air sampling program measured semivolatile, volatile, and total organics during the first 9 weeks of treatment. Total organics as methane was determined

according to procedures in U.S. EPA Method 25A.[a] This sampling was conducted continuously at the main exhaust line for the first 5 days of operation. Sampling for volatiles (by Modified Method TO14)[b] and semivolatiles (for Modified Method TO13)[b] was conducted periodically during the first 9 weeks of operation.

TABLE 6-15. CONCENTRATIONS OF TPH IN SOIL (mg/kg)

	Week						
Reactor	0	2	4	6	9	11	12
1	35000	7200	1800	3100	1800	1900	1700
2	17500	2600	1800	2300	3200	1700	1800
4	13000	2700	1600	2100	1800	1700	1900
5	16000	3600	2300	2900	1700	3700	2700
6	19500	2400	2400	3600	2200	4900	2700

6.5.1 Total Hydrocarbons (THC)

Table 6-16 presents the THC emission results of the exhaust-line sampling. These exhaust line data encompass data from all five operating reactors. The background/ambient air shows THC concentrations averaging 3 ppm on a dry basis. THC emissions gradually increase during charging of the reactors, with peak concentrations averaging 390 ppm from 1751 to 1800 on May 8, 1991. Table 6-16 presents concentrations, emission rates, and flow rates used to calculate emissions. All data are reported as methane because it was the calibration gas used during sampling.

Figure 6-8 is a graph of the THC data during the 5 days of continuous monitor operation. The THC data compare well with the other organic data, showing extremely high emissions the first 2 days of process operation, followed by a steady decline and eventually baseline recordings by the fifth day of operation.

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[a] 40 CFR 60, Appendix A.

[b] Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Compounds in Ambient Air. EPA-600/4-84-041. April 1984.

TABLE 6-16. THC RESULTS - EXHAUST LINE

Date (1991)	Time (24-h)	THC concentration, ppm		Moisture, %	Flow rate, dscfm[c]	THC emissions, lb/h[d]	Notes
		Wet[a]	Dry[b]				
5/7	1353-1456	3.1	3.1	1.0	-	-	Background
5/8	1134-1155	3.0	3.0	1.0	-	-	Ambient air
	1155-1245	5.5	5.6	1.0	-	-	Exhaust pipe - no flow
	1245-1255	12.0	42.2	2.0	<15	0.00046	Reactor 1 charging H_2O
	1255-1310	46.5	47.5	2.0	<15	0.00178	Reactor 2 charging H_2O
	1310-1320	58.2	59.4	2.0	<15	0.00222	Reactor 3 charging H_2O
	1320-1325	74.0	75.5	2.0	<15	0.00282	-
	1325-1335	87.5	89.3	2.0	<15	0.00334	-
	1335-1340	102.7	104.8	2.0	<15	0.00392	Range to 500 ppm scale
	1345-1426	23.1	23.7	2.4	<15	0.00089	-
	1454-1517	115.5	118.3	2.4	<15	0.00442	No waste in reactors
	1517-1533	158.5	162.4	2.4	<15	0.00607	Reactor 1 waste
	1533-1536	303.7	311.2	2.4	<15	0.01163	Reactor 1 capped off
	1536-1556	325.2	333.2	2.4	<15	0.01245	Reactor 2 waste
	1556-1603	379.0	388.3	2.4	<15	0.01451	Reactor 3 waste
	1603-1612	366.0	375.0	2.4	<15	0.01402	Reactor 3 capped
	1612-1633	357.4	366.2	2.4	<15	0.01369	Reactor 3 down
	1633-1706	357.4	366.2	2.4	<15	0.01369	Reactor 4 waste
	1706-1722	373.5	382.7	2.4	<15	0.01430	Reactor 5 waste
	1722-1739	376.8	386.1	2.4	<15	0.01443	Reactor 6 waste
	1739-1746	379.0	388.3	2.4	<15	0.01451	Calibration check
	1751-1800	380.5	389.9	2.4	<15	0.01457	-
	1800-1900	369.8	378.9	2.4	<15	0.01416	-
	1900-2100	348.3	356.9	2.4	<15	0.01334	-
	2100-2300	370.2	379.3	2.4	<15	0.01418	-
5/9	2300-0100	351.2	359.8	2.4	<7.5	0.00672	-
	0100-0200	332.2	340.4	2.4	<7.5	0.00636	-
	0200-0250	321.4	329.3	2.4	<7.5	0.00615	-
	0250-0800	-	-	-	<7.5	-	CEM flame out
	0900-1000	224.9	230.4	2.4	<7.5	0.00431	Reactor caps "vented"
	1000-1200	205.6	210.7	2.4	<7.5	0.00394	-
	1200-1345	168.0	172.1	2.4	<7.5	0.00322	-
	1345-1400	-	-	2.4	<7.5	-	Velocity
	1400-1500	138.9	142.3	2.4	<7.5	0.00266	-
	1500-1600	119.6	122.5	2.4	<7.5	0.00229	-
	1600-1700	108.8	111.5	2.4	<7.5	0.00208	-
	1700-1900	91.6	93.9	2.4	<7.5	0.00176	-
	1900-2100	80.3	82.3	2.4	<7.5	0.00154	-
	2100-2300	72.8	74.6	2.4	<7.5	0.00139	-
	2300-0000	68.0	69.7	2.4	<7.5	0.00130	-

(continued)

TABLE 6-16 (continued)

Date (1991)	Time (24-h)	THC concentration, ppm		Moisture, %	Flow rate, dscfm[c]	THC emissions, lb/h[d]	Notes
		Wet[a]	Dry[b]				
5/10	0000-0100	72.5	74.3	2.4	8.0	0.00148	-
	0100-0400	67.1	68.8	2.4	8.0	0.00137	-
	0400-0900	63.9	65.5	2.4	8.0	0.00131	-
	0900-1000	59.6	61.1	2.4	8.0	0.00122	-
	1010-1200	56.3	57.7	2.4	8.0	0.00115	-
	1200-1500	59.6	61.1	2.4	8.0	0.00122	-
	1500-1900	67.1	68.8	2.4	8.0	0.00137	-
	1900-0000	67.1	68.8	2.4	8.0	0.00137	-
5/11	0000-0500	64.9	66.5	2.4	2.1	0.00035	Overflow of reactors
	0500-1025	54.2	55.5	2.4	2.1	0.00029	Caps off
	1030-1200	51.0	52.3	2.4	2.1	0.00027	-
	1200-1500	51.0	52.3	2.4	2.1	0.00027	-
	1500-2000	48.8	50.0	2.4	2.1	0.00026	-
	2000-0000	51.0	52.3	2.4	2.1	0.00027	-
5/12	0000-0500	45.6	46.7	2.4	2.1	0.00024	-
	0500-1000	42.4	43.4	2.4	2.1	0.00023	-
	1000-1800	34.8	35.7	2.4	2.1	0.00019	-
	1800-0000	34.8	35.7	2.4	2.1	0.00019	-
5/13	0000-0600	30.5	31.3	2.4	2.1	0.00016	-
	0600-1300	27.3	28.0	2.4	2.1	0.00015	-
	1300-1900	24.1	24.7	2.4	2.1	0.00013	-
	1900-0000	20.9	21.5	2.4	2.1	0.00011	-
5/14	0000-0300	17.6	18.0	2.4	4.1	0.00018	Caps "loose"
	0300-0600	16.6	17.0	2.4	4.1	0.00017	-
	0600-0650	16.6	17.0	2.4	4.1	0.00017	Monitor off

[a] Wet concentration (ppm) reported directly from instrument.

[b] Dry concentration (ppm) = $ppm_{(wet)}\left(\frac{1}{1\text{-moisture}}\right)$.

[c] dscfm = Dry standard cubic feet per minute; flow rate from hot-wire anemometer or reactor cumulative flows.

[d] THC emission rate, pounds per hour (lb/h) as methane (CH_4), THC lb/h = $\frac{ppm\ (16)}{385.3 \times 10^6} \times 60\ min/h \times flow\ (dscfm)$.

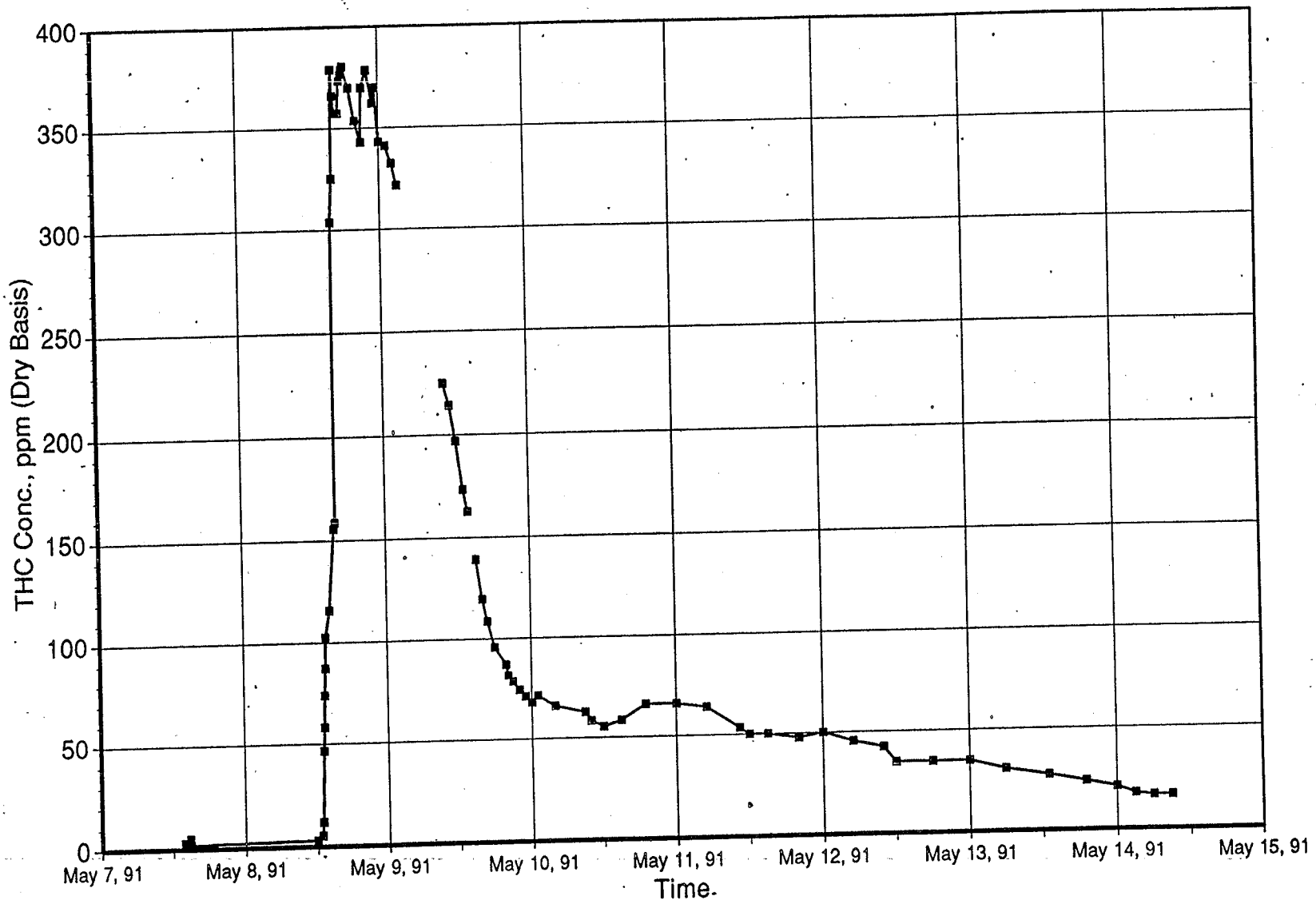

Figure 6-8. THC emission data during the first 5 days of operation.

6.5.2 Semivolatile Organics

Table 6-17 presents the sampling schedule, volume of air sampled, duration of sampling, and sampling location for semivolatile organic emissions. Sampling was conducted on Reactors 1 and 2 for the first 4 days of operation. The main exhaust line was sampled for the remainder of the program. Table 6-18 lists the semivolatile organic analytes and their detection limits. Table 6-19 lists only the results of semivolatile organic emissions that were detected during the study. Once again, semivolatile organic emissions (naphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, dibenzofuran, fluorene, phenanthrene, and anthracene) were detectable during the first 4 days of sampling. Beginning the sixth day of operation, very small quantities (at or below detection) of semivolatiles were found.

6.5.3 Volatile Organics

Table 6-20 presents the sampling schedule, duration of sampling, and sampling location for volatile organic emissions. The sampling was conducted simultaneously with the semivolatile organic sampling on Reactors 1 and 2 for the first 4 days of operation. The main exhaust line was sampled for the remainder of the program. Table 6-21 lists the volatile organic analytes and their approximate detection limits. Detection limits will vary with dilution requirements of each sample. Table 6-22 lists the sampling runs during which volatile organics were detected and the corresponding detection limits. Samples again show that ~~the majority of~~ most emissions occurred during the first few days of reactor operation. Samples analyzed by Air Toxics Lab (CAN 1-15, 2-16, 1-17, and 2-17) show four compounds that were not detected previously. These detections are believed to be laboratory contaminants and not a result of reactor emissions.

Copies of the analytical data for THC, semivolatile organic, and volatile organic analyses provided by ITAS laboratory are included in Appendix N.

TABLE 6-17. SEMIVOLATILE ORGANIC SAMPLE ID AND LOCATION

Run No.	Date (1991)	Sample volume[a] Liters	Sample volume[a] ft³	Air flow, dscfm[b]	Approximate sampling time, h[c]	Sampling location[d]
XAD-1-1	5/8	348.006	12.288	3	24	Reactor 1
XAD-2-1		283.105	10.0	3	24	Reactor 2
XAD-1-2	5/9	363.189	12.82	1.5	24	Reactor 1
XAD-2-2		271.200	9.576	1.5	24	Reactor 2
XAD-1-3	5/10	289.075	10.207	1.33	24	Reactor 1
XAD-2-3		319.469	11.281	1.33	24	Reactor 2
XAD-1-4[e,f]	5/11	67.236	2.37	<1.33	24	Reactor 1
XAD-2-4		386.053	13.632	<1.33	24	Reactor 2
XAD-1-5[f]	5/14	330.513	11.671	4.10	24	Main exhaust
XAD-2-5[f]		434.332	15.337	4.10	24	Main exhaust
XAD-1-6	5/15	885.466	31.265	6.92	48	Main exhaust
XAD-2-6		793.649	28.024	6.92	48	Main exhaust
XAD-1-7	5/21	624.172	22.040	6.42	24	Main exhaust
XAD-2-7		529.768	18.707	6.42	24	Main exhaust
XAD-1-8	5/22	764.299	26.988	6.17	48	Main exhaust
XAD-2-8		898.858	31.739	6.17	48	Main exhaust
XAD-1-9	5/28	424.013	14.972	6.26	24	Main exhaust
XAD-2-9		347.095	12.256	6.26	24	Main exhaust
XAD-1-10	5/29	403.739	14.256	6.20	24	Main exhaust
XAD-2-10		362.716	12.808	6.20	24	Main exhaust
XAD-1-11	6/3	823.058	29.063	6.17	24	Main exhaust
XAD-2-11		398.504	14.071	6.17	24	Main exhaust
XAD-1-12	6/6	860.102	30.371	6.17	24	Main exhaust
XAD-2-12		433.528	15.308	6.17	24	Main exhaust
XAD-1-13	6/10	1419.919	50.138	6.13	48	Main exhaust
XAD-2-13		1008.73	35.619	6.13	48	Main exhaust
XAD-1-14	6/12	1257.265	44.395	6.03	48	Main exhaust
XAD-2-14		883.041	31.181	6.03	48	Main exhaust
XAD-1-15	6/17	1314.93	46.431	6.23	48	Main exhaust
XAD-2-15		989.644	34.945	6.23	48	Main exhaust
XAD-1-16	6/26	1665.992	58.827	6.83	24	Main exhaust
XAD-2-16		397.293	14.029	6.83	24	Main exhaust
XAD-1-17	7/10	719.544	25.408	5.5	48	Main exhaust
XAD-2-17		801.689	28.308	5.5	48	Main exhaust

[a] Sample volume corrected to standard conditions.

[b] Biolift reactor exhaust air flow, dry standard cubic feet per minute.

[c] Sampling time either 1 day (24 h) or 2 days (48 h), usually depending on canister size.

[d] Sampling for Runs 1 through 4 was conducted on Reactors 1 and 2. Runs 5 through 17 were conducted in the main exhaust serving all five reactors.

[e] XAD-1-4 was void because the reactor overflowed.

[f] Runs 4 and 5 were sampled with the reactors venting directly to ambient air.

TABLE 6-18. HAZARDOUS SUBSTANCE LIST OF SEMIVOLATILE ORGANICS AND THEIR DETECTION LIMITS

CAS No.	Description	µg/tube	CAS No.	Description	µg/tube
108-95-2	Phenol	10	51-28-5	2,4-Dinitrophenol	50
111-44-4	bis(2-chloroethyl)ether	10	100-02-7	4-Nitrophenol	50
95-57-8	2-Chlorophenol	10	132-64-9	Dibenzofuran	10
541-73-1	1,3-Dichlorobenzene	10	121-14-2	2,4-Dinitrotoluene	10
106-47-7	1,4-Dichlorobenzene	10	606-20-2	2,6-Dinitrotoluene	10
100-51-6	Benzyl alcohol	10	84-66-2	Diethyl phthalate	10
95-50-1	1,2-Dichlorobenzene	10	7005-72-34	Chlorophenyl phenyl ether	10
95-48-7	2-Methylphenol	10			
39638-32-9	bis(2-Chloroisopropyl) ether	10	86-73-7	Fluorene	10
			100-01-6	4-Nitroaniline	50
106-44-5	4-Methylphenol	10	534-52-1	4,6-Dinitro-2-methyl-phenol	50
621-64-7	N-nitrosodi-n-propylamine	10			
67-72-1	Hexachloroethane	10	534-52-1	N-nitrosodiphenylamine	10
98-95-3	Nitrobenzene	10	101-55-3	4-Bromophenyl phenyl ether	10
78-59-1	Isophorone	10			
88-75-5	2-Nitrophenol	10	118-74-1	Hexachlorobenzene	10
105-67-9	2,4-Dimethylphenol	10	87-86-5	Pentachlorophenol	50
65-85-0	Benzoic acid	50	85-01-8	Phenanthrene	10
111-91-1	bis(2-Chlorethoxy) methane	10	120-12-7	Anthracene	10
120-83-2	2,4-Dichlorophenol	10	84-74-2	Di-n-butyl phthalate	10
120-82-1	1,2,4-Trichlorobenzene	10	206-44-0	Fluoranthene	10
91-20-3	Naphthalene	10	129-00-0	Pyrene	10
106-47-8	4-Chloroaniline	10	85-68-7	Butylbenzyl phthalate	10
87-68-3	Hexachlorobutadiene	10	91-94-1	3,3'-Dichlorobenzidine	20
59-50-7	4-Chloro-3-methylphenol	10	56-55-3	Benzo(a)anthracene	10
91-57-6	2-Methylnaphthalene	10	117-81-7	bis(2-ethylhexyl) phthalate	10
77-47-4	Hexachlorocyclopentadiene	10			
88-06-2	2,4,6-Trichlorophenol	10	218-01-9	Chrysene	10
95-95-4	2,4,5-Trichlorophenol	50	117-84-0	Di-n-octyl phthalate	10
91-58-7	2-Chloronaphthalene	10	205-99-2	Benzo(b)fluoranthene	10
88-74-4	2-Nitroanaline	50	205-08-9	Benzo(k)fluoranthene	10
131-11-3	Dimethyl phthalate	10	50-32-8	Benzo(a)pyrene	10
208-96-8	Acenaphthylene	10	193-39-5	Indeno(1,2,3-cd)pyrene	10
99-09-2	3-Nitroaniline	50	53-70-3	Dibenzo(a,h)anthracene	10
83-32-9	Acenaphthene	10	191-24-2	Benzo(g,h,i)perylene	10

TABLE 6-19. SEMIVOLATILE ORGANIC EMISSIONS DATA, mg/m^3

Measured parameter	Run No.										
	XAD1-1	XAD2-1	XAD1-2	XAD2-2	XAD1-3	XAD2-3	XAD2-4	XAD1-5	XAD2-5	XAD1-6	XAD2-6
Naphthalene	24.9	30.4	0.27	0.91	0.04	0.06	0.02	0.03	0.02	0.01	0.01
2-methylnaphthalene	4.3	5.5	0.55	1.39	0.04	0.03	0.03	0.03	0.02	0.01	0.01
Acenaphthylene	0.22	0.25	0.15	0.25	0.12	0.20	0.16	0.03	0.02	0.01	0.01
Acenaphthene	0.95	1.38	0.99	1.55	1.35	1.57	1.82	0.05	0.05	0.01	0.02
Dibenzofuran	0.49	0.64	0.44	0.59	0.48	0.63	0.60	0.03	0.02	0.01	0.01
Fluorene	0.34	0.39	0.30	0.44	0.48	0.53	0.57	0.03	0.01	0.01	0.01
Phenanthrene	0.09	0.12	0.11	0.20	0.14	0.22	0.18	0.03	0.02	0.01	0.01
Anthracene	0.02	0.25	0.02	0.04	0.03	0.04	0.06	0.03	0.02	0.01	0.01

TABLE 6-20. VOLATILE ORGANIC SAMPLE ID AND LOCATION

Run No.	Start Time (24-h)	Start Date (1991)	Stop Time (24-h)	Stop Date (1991)	Airflow,[a] dscfm	Approximate sampling time, h[b]	Sampling location[c]
CAN-1-1	1535	5/8	1417	5/9	3	24	Reactor 1
CAN-2-1	1556	5/8	1436	5/9	3	24	Reactor 2
CAN-1-2	1433	5/9	1354	5/10	1.5	24	Reactor 1
CAN-2-2	1520	5/9	1403	5/10	1.5	24	Reactor 2
CAN-1-3	1402	5/10	1106	5/11	1.33	24	Reactor 1
CAN-2-3	1430	5/10	1135	5/11	1.33	24	Reactor 2
CAN-1-4[d]	1121	5/11	1035	5/12	<1.33	24	Reactor 1
CAN-2-4	1156	5/11	1117	5/12	<1.33	24	Reactor 2
CAN-1-5	1418	5/14	1340	5/15	4.1	24	Main exhaust
CAN-2-5	1424	5/14	1255	5/15	4.1	24	Main exhaust
CAN-1-6[d]	1253	5/15	1130	5/17	6.92	48	Main exhaust
CAN-2-6	1306	5/15	1130	5/17	6.92	48	Main exhaust
CAN-1-7[d]	1027	5/21	1345	5/22	6.42	24	Main exhaust
CAN-2-7	1033	5/21	1348	5/22	6.42	24	Main exhaust
CAN-1-8[e]	1400	5/22	1420	5/24	6.17	48	Main exhaust
CAN-2-8	None	-	-	-	6.17	-	Main exhaust
CAN-1-9[d]	1210	5/28	1050	5/29	6.26	24	Main exhaust
CAN-2-9	1210	5/28	1050	5/29	6.26	24	Main exhaust
CAN-1-10	1125	5/29	1055	5/30	6.20	24	Main exhaust
CAN-2-10	1125	5/29	1055	5/30	6.20	24	Main exhaust
CAN-1-11	1504	6/3	1243	6/4	6.17	24	Main exhaust
CAN-2-11	1509	6/3	1244	6/4	6.17	24	Main exhaust
CAN-1-12[e]	None	-	-	-	6.17	-	Main exhaust
CAN-2-12	None	-	-	-	6.17	-	Main exhaust
CAN-1-13[f]	1300	6/10	1342	6/12	6.13	48	Main exhaust
CAN-2-13	1310	6/10	1343	6/12	6.13	48	Main exhaust
CAN-1-14[f]	1422	6/12	1452	6/14	6.03	48	Main exhaust
CAN-2-14	1422	6/12	1251	6/14	6.03	48	Main exhaust
CAN-1-15[f]	1405	6/18	1339	6/19	6.23	24	Main exhaust
CAN-2-15	1405	6/18	1339	6/19	6.23	24	Main exhaust
CAN-1-16[f]	1023	6/26	0948	6/27	6.83	24	Main exhaust
CAN-2-16	1023	6/26	0948	6/27	6.83	24	Main exhaust
CAN-1-17	1452	7/10	1422	7/12	5.5	48	Main exhaust
CAN-2-17	1455	7/10	1422	7/12	5.5	48	Main exhaust

[a] Biolift reactor exhaust airflow, dry standard cubic feet per minute.

[b] Sampling time either 1 day (24 h) or 2 days (48 h), usually depending on canister size.

[c] Sampling for Runs 1 through 4 was conducted on Reactors 1 and 2. Runs 5 through 7 were sampled in the main exhaust line serving all five reactors.

[d] Canisters did not fill because of slurry in the flow regulator. Condition was not discovered until analysis showed no sample volume. Flow regulator was replaced and sample flow was rechecked.

[e] No canisters available for sampling.

[f] Canisters inadequately emptied and cleaned by laboratory prior to analysis.

TABLE 6-21. VOLATILE ORGANIC LIST AND APPROXIMATE DETECTION LIMITS

Volatile organic	Detection limit, ppb
Chloromethane	0.5
Vinyl chloride	0.3
Bromomethane	0.3
Chloroethane	0.5
1,1-Dichloroethene	0.3
Carbon disulfide	0.2
Methylene chloride	0.2
t-1,2-Dichloroethene	0.3
1,1-Dichloroethene	0.3
c-1,2-Dichloroethene	0.3
Chloroform	0.3
1,1,1-Trichloroethane	0.3
Carbon tetrachloride	0.2
Benzene	0.2
1,2-Dichloroethane	0.3
Trichloroethene	0.2
1,2-Dichloropropane	0.3
Bromodichloromethane	0.2
c-1,3-Dichloropropene	0.4
Toluene	0.2
t-1,3-Dichloropropene	0.4
1,1,2-Trichloroethane	0.3
Tetrachloroethene	0.2
Dibromochloromethane	0.2
Chlorobenzene	0.2
Ethylbenzene	0.2
m- and/or p-Xylene	0.2
o-Xylene	0.2
Styrene	0.2
Bromoform	0.2
1,1,2,2-Tetrachloroethane	0.2

TABLE 6-22. VOLATILE ORGANIC EMISSIONS DATA

Compound	1-1 ppb	1-1 DL[a]	2-1 ppb	2-1 DL	1-2 ppb	1-2 DL	2-2 ppb	2-2 DL	1-3 ppb	1-3 DL	2-3 ppb	2-3 DL	2-4 ppb	2-4 DL	1-5 ppb	1-5 DL
Carbon disulfide	6.9	0.4	67[c]	0.4	4.7	0.4	17	0.4	5	0.4	5.7	0.4	20	0.4	1.2	0.4
Methylene chloride	4.8	0.4	-	0.4	-	0.4	0.78	0.4	4.8	0.4	9.2	0.4	1.1	0.4	2.2	0.4
Chloroform	-	0.5	-	0.6	-	0.5	-	0.6	0.8	0.7	1.3	0.6	0.77	0.6	-	0.6
1,1,1-Trichloroethane	-	0.5	-	0.6	1.0	0.5	1.6	0.6	1.5	0.7	2.8	0.6	1.6	0.6	0.93	0.6
Benzene	55	0.4	45	0.4	1.5	0.4	2.3	0.4	1.8	0.4	2.4	0.4	1.2	0.4	0.79	0.4
Toluene	240	0.4	230	0.4	3.2	0.4	4.6	0.4	5.6	0.4	8.0	0.4	3.2	0.4	2.6	0.4
Tetrachloroethene	-	0.4	-	0.4	-	0.4	-	0.4	1.2	0.4	1.6	0.4	-	0.4	-	0.4
Chlorobenzene	-	0.4	-	0.4	-	0.4	-	0.4	0.48	0.4	0.88	0.4	-	0.4	-	0.4
Ethylbenzene	150	0.4	160	0.4	2.2	0.4	3.4	0.4	0.86	0.4	1.5	0.4	0.91	0.4	0.63	0.4
m- and/or p-Xylene	720	0.4	800	0.4	12	0.4	17	0.4	0.32	0.4	7.3	0.4	3.0	0.4	1.9	0.4
o-Xylene	300	0.4	320	0.4	7.7	0.4	14	0.4	1.4	0.4	3.5	0.4	1.4	0.4	0.7	0.4
Styrene	44	0.4	81	0.4	1.8	0.4	3.6	0.4	-	0.4	0.85	0.4	0.45	0.4	0.42	0.4

Compound	2-5 ppb	2-5 DL	1-6 ppb	1-6 DL	1-7 ppb	1-7 DL	1-8 ppb	1-8 DL	2-9 ppb	2-9 DL	1-10 ppb	1-10 DL	2-10 ppb	2-10 DL	1-11 ppb	1-11 DL
Carbon disulfide	1.2	0.4	0.86	0.3	6.5	0.5	0.79	0.4	1.2	0.6	0.99	0.6	1.0	0.6	1.1	0.6
Methylene chloride	1.8	0.4	2.7	0.3	9.0	0.5	2.8	0.4	4.8	0.6	2.2	0.6	7.2	0.6	2.0	0.6
Chloroform	-	0.6	-	0.5	-	0.8	0.44	0.6	-	0.9	-	0.9	-	0.9	-	0.9
1,1,1-Trichloroethane	1.0	0.6	1.7	0.5	2.5	0.8	1.2	0.6	1.4	0.9	1.0	0.9	1.5	0.9	1.2	0.9
Benzene	0.82	0.4	0.62	0.3	0.66	0.5	0.99	0.4	1.1	0.6	0.87	0.6	0.83	0.6	0.71	0.6
Toluene	2.2	0.4	2.2	0.3	2.8	0.5	3.6	0.4	4.5	0.6	1.9	0.6	4.2	0.6	2.6	0.6
Tetrachloroethene	-	0.4	0.46	0.3	0.7	0.5	0.66	0.4	-	0.6	-	0.6	-	0.6	-	0.6
Chlorobenzene	-	0.4	0.47	0.3	-	0.5	-	0.4	2.6	0.6	-	0.6	-	0.6	-	0.6
Ethylbenzene	0.5	0.4	0.49	0.3	-	0.5	0.64	0.4	-	0.6	-	0.6	-	0.6	-	0.6
m- and/or p-Xylene	1.4	0.4	1.2	0.3	1.2	0.5	1.7	0.4	0.98	0.6	0.78	0.6	1.5	0.6	0.63	0.6
o-Xylene	0.53	0.4	0.37	0.3	-	0.5	0.58	0.4	-	0.6	-	0.6	0.49	0.6	-	0.6
Styrene	-	0.4	-	0.3	-	0.5	-	0.4	-	0.6	-	0.6	-	0.6	-	0.6

(continued)

TABLE 6-22 (continued)

Compound	2-11		1-15[b]		2-16[b]		1-17[b]		2-17[b]	
	ppb	DL	ppb	DL	ppb	DL	ppb	DL	ppb	DL
Carbon disulfide	-	0.6	-	2.0	-	2.0	-	2.0	-	2.0
Methylene chloride	1.7	0.6	-	2.0	-	2.0	-	2.0	-	2.0
Chloroform	-	0.9	-	2.0	-	2.0	0.92	2.0	1.1	2.0
1,1,1-Trichloroethane	1.0	0.9	-	2.0	-	2.0	1.1	2.0	1.1	2.0
Benzene	0.69	0.6	1.4	2.0	0.77	2	0.76	2.0	1.2	2.0
Toluene	2.3	0.6	6.5	2.0	5.4	2	3.6	2.0	3.8	2.0
Tetrachloroethene	-	0.6	-	2.0	-	2.0	-	2.0	-	2.0
Chlorobenzene	-	0.6	-	2.0	-	2.0	-	2.0	-	2.0
Ethylbenzene	-	0.6	-	2.0	-	2.0	-	2.0	-	2.0
m- and/or p-Xylene	-	0.6	NA[c]	NA	NA	NA	NA	NA	NA	NA
o-Xylene	-	0.6	NA	NA	NA	NA	NA	NA	NA	NA
Styrene	-	0.6	-	2.0	-	2.0	-	2.0	-	2.0
Acetone			56	9.0	47	8.0	14	9.0	15	9.0
2-Butanone			24	9.0	18	8.0	-	9.0	-	9.0
4-Methyl-2-pentanone			13	9.0	8.4	8.0	-	9.0	-	9.0
Total xylenes			1.4	2.0	-	2.0	0.97	2.0	0.94	2.0

[a] DL = Detection Limit.

[b] Samples analyzed by Air Toxics Laboratory.

[c] NA = Not analyzed.

SECTION 7

QUALITY ASSURANCE/QUALITY CONTROL MEASURES

This section describes the quality assurance/quality control (QA/QC) measures associated with the sampling and analysis activities. Sample tracking information was provided in Table 6-1. Analytical methods were listed in Table 4-6 and references for these were footnoted at the bottom of this table. Subsection 7.1 describes the QA/QC performed on pre- and posttreatment samples to ensure the quality of the data produced by the pilot-scale testing. Subsection 7.1.1 describes the process for determining the detection limits used in the study. Accuracy and precision data are presented in Subsections 7.1.2 and 7.1.3, respectively. Results of analyses of blanks associated with the treatment samples and surrogate recoveries are presented in Subsections 7.1.4 and 7.1.5. Problems encountered during the analysis of the treatment samples and modifications to established analytical methods are discussed in Subsection 7.1.6. Subsection 7.1.7 presents the results of the systems audit and laboratory audit performed during the course of the study. Subsection 7.2 describes the laboratory QC results for air sampling. Subsection 7.3 describes the QA/QC procedures used by the ECOVA laboratory.

7.1 Pretreatment and Posttreatment Samples

7.1.1 Detection Limits

The following subsections describe how method detection limits and practical quantitation limits were determined and the effect they have on the data.

Method Detection Limits for Semivolatile Organics

Method detection limits (MDLs) represent the minimum concentration of a substance that can be measured and reported (with 99 percent confidence) at a value above zero. These limits were calculated by using the Instrument Detection Limits (IDLs), matrix spike and matrix spike duplicate recoveries from the posttreatment soil matrix, and dilution factors from extraction procedures and sample preparation.

The IDLs for the semivolatile organics were determined by injecting seven replicate samples spiked with 5 μg/L of each critical contaminant. The standard deviation for each compound's recovery was calculated and multiplied by 3 to give the compound a specific IDL. Table 7-1 presents the results of the IDL study performed on the Extrel 400 GC/MS.

The MDLs were calculated by the following equation:

$$MDL = [(IDL/AR) * DF] * 100$$

where MDL = method detection limit for the contaminant
IDL = instrument detection limit for the contaminant
AR = average percent recovery calculated from MS/MSD samples
DF = dilution factor of samples calculated from extraction process and sample preparation

The MDLs are based on individual analytical methods; therefore, the extraction process and efficiency are important in determining the detection limits. For this study, the extraction efficiency of the soil was determined by the percent recovery values for the critical contaminants, which were spiked at predetermined values into the posttreatment test soil matrix, extracted, and analyzed by GC/MS. The extraction process affects the detection limits by the amount of sample that is used during the extraction procedure. Typically, 30 g of soil is used in the extraction process. This results in a dilution factor of approximately 34, as the results are converted to the concentration of contaminants per kilogram. Because of the nature of the matrix involved, only 1 g of pretreatment soil was extracted. The treatment soil samples also underwent a Gel Permeation Chromatography (GPC) cleanup procedure to make them more amenable

TABLE 7-1. RESULTS FROM THE INSTRUMENT DETECTION LIMIT (IDL) STUDY FOR SEMIVOLATILE ORGANICS ON THE EXTREL 400 (µg/L)

Critical contaminant	Spike amt.	Conc. Run 1	Conc. Run 2	Conc. Run 3	Conc. Run 4	Conc. Run 5	Conc. Run 6	Conc. Run 7	IDL
Naphthalene	5	4.4	4.4	4.4	4.4	4.5	4.1	4.3	0.38
2-Methylnaphthalene	5	4.2	3.9	3.6	4.2	0.4	4.7	4.0	4.32
Acenaphthylene	5	4.0	4.0	4.1	4.0	4.0	4.0	3.9	0.17
Acenaphthene	5	4.4	4.3	4.6	4.4	4.1	4.6	0	5.02
Dibenzofuran	5	4.2	4.2	4.4	4.3	4.3	4.4	2.7	1.83
Fluorene	5	3.8	3.8	3.9	3.6	3.7	3.6	3.4	0.5
Phenanthrene	5	4.2	4.2	4.0	4.2	4.3	4.2	3.5	0.82
Anthracene	5	3.8	3.7	3.3	3.6	3.7	2.8	2.2	1.78
Fluoranthene	5	2.8	2.7	2.8	3.0	2.9	2.8	2.9	0.29
Pyrene	5	3.1	3.0	2.9	3.1	3.0	2.9	1.0	1.38
Benzo(a)anthracene	5	3.7	3.8	3.6	3.6	3.6	3.4	4.0	0.57
Chrysene	5	4.1	3.9	4.0	4.0	3.2	3.7	1.3	2.99
Benzo(b)fluoranthene	5	2.5	1.0	2.1	2.1	2.3	2.2	2.1	0.64
Benzo(k)fluoranthene	5	2.3	2.5	2.4	2.1	2.2	2.2	1.8	0.68
Benzo(a)pyrene	5	2.6	2.6	2.3	2.1	2.0	2.1	0.1	2.58

to analysis. This resulted in a dilution factor of 2 because the sample volume was split. Another dilution factor of 2 resulted from performing a pesticide split on the sample, which entailed dividing the sample into two equal portions so a pesticide extraction could be performed. Although no pesticides were analyzed for in the posttreatment samples, pesticide splits were performed in an attempt to clean up the matrix to make it more amenable to analysis. The final dilution factor for the treatment soil was 4000, based on the extraction aliquot and the GPC cleanup procedure.

Posttreatment samples were originally analyzed as medium-level soils with a dilution factor of 4000. Since the MDLs for the samples were above 1 ppm (the QA/QC criteria for the CS&D program), the samples were reextracted and reanalyzed as low-level soils to lower the MDLs. For the reextracts, 30 grams of soil were extracted (as opposed to 1 gram for medium level). The resulting extract underwent GPC to clean up the extract and make it more amenable for analysis. Serial dilutions were performed on the samples to bring the analytes within the instrument's curve range resulting in a dilution factor of 2664. However, MDLs for the majority of the compounds were still above 1 ppm. This could be due to the presence of high concentrations of petroleum hydrocarbons in the soil which may have resulted in poor extraction efficiencies and matrix interferences for the target analytes. The analytical data for the low-level soil analyses was used to evaluate the treatment technology.

The low-level analyses allowed for detection of compounds present in the soil in small concentrations but diluted out during the medium-level extraction. Table 6-5 and 6-6 present the analytical data for the low-level extractions, while Appendix N presents the analytical data for all analyses provided by the ITAS laboratory on the soil, including medium-level extraction data and low-level extraction data. For liquids, 1 liter of sample is generally extracted. The volume of sample that could be obtained from the reactors was limited; therefore adjustments had to be made in the volume of sample extracted. For the samples from Week T_9, 300 mL of liquid was extracted from the samples; whereas 500 mL of liquid were extracted from the samples from Week T_{12}. This resulted in dilution factors of 3.3 and 2 for Weeks T_9 and T_{12} respectively. Because liquid extractions are divided into acid fractions and base-neutral fractions,

another dilution factor of 2 results when the two fractions are combined to form the analytical sample. The final dilution factor for the treatment liquid was 6.7 and 4 for Weeks T_9 and T_{12} respectively. The MDLs calculated for treatment soil and liquid samples are presented in Table 7-2 and 7-3 respectively.

Practical Quantitation Limits for Semivolatile Organics

Practical Quantitation Limits (PQLs) are limits at which the concentration of a substance can be quantitated accurately (with 99 percent confidence). The PQLs were determined from the values listed in Table 2 of Method 8270 in SW-846. The PQLs in this table are based on an IDL of 10 ppb, a 30-g extraction aliquot, and a GPC cleanup procedure for soil samples; and on an IDL of 10 ppb, a 1-L extraction aliquot, and the combination of base-neutral and acid fractions for liquid samples. The treatment soil samples used a 1-g extraction aliquot and underwent a pesticide split; therefore, the PQLs for the treatment soil matrix are raised by a factor of 60. The treatment liquid samples used 300 mL and 500 mL of sample for the extraction process during Weeks T_9 and T_{12} respectively; therefore, the PQLs for the treatment liquid matrix are raised by a factor of 3.3 and 2 for Weeks T_9 and T_{12} respectively. Table 7-4 presents the PQLs reported by the ITAS laboratory for this study.

Data Interpretation

The calculations used to determine MDLs and PQLs are similar in nature. The main difference is the laboratory and instrument specificity of the MDLs compared with the PQLs, which were compiled and averaged from studies performed in many different labs. Therefore, the PQLs reported in the Certificate of Analysis for semivolatile organic data should not be used for this study. Instead, the method- and soil-specific MDLs calculated for this study should be used in evaluating the data. Where critical constituents are not detected, the concentrations are reported as being below the detection limit specific to the constituent and the sample.

TABLE 7-2. METHOD DETECTION LIMITS (MDLs) FOR CRITICAL SEMIVOLATILE ORGANIC CONTAMINANTS BY METHOD 3550/8270 (TREATED SOIL)

Critical Contaminant	Week T_9				Week T_{12}			
	IDL(ppb)[a]	Avg. Recovery	Dilution Factor	MDL, ppm	IDL (ppb)	Avg. Recovery	Dilution Factor	MDL, ppm
Naphthalene	0.38	74.2	2664	1.4	0.38	67.0	2664	1.5
2-Methylnaphthalene	4.32	83.2	2664	14.0	4.32	69.0	2664	17.0
Acenaphthylene	0.17	63.9	2664	0.71	0.17	76.3	2664	0.59
Acenaphthene	5.02	72.0	2664	19.0	5.02	79.5	2664	17.0
Dibenzofuran	1.83	76.6	2664	6.4	1.83	80.9	2664	6.0
Fluorene	0.50	73.6	2664	1.8	0.50	80.9	2664	1.6
Phenanthrene	0.82	73.3	2664	3.0	0.82	85.9	2664	2.5
Anthracene	1.78	62.4	2664	7.6	1.78	88.1	2664	5.4
Fluoranthene	0.29	72.7	2664	1.1	0.29	87.7	2664	0.88
Pyrene	1.38	88.8	2664	4.1	1.38	96.3	2664	3.8
Benzo(a)anthracene	0.57	76.8	2664	2.0	0.57	96.3	2664	1.6
Chrysene	2.99	88.6	2664	9.0	2.99	87.0	2664	9.2
Benzo(b)fluoranthene	1.32	59.9	2664	5.9	1.32	56.0	2664	6.3
Benzo(a)pyrene	2.58	77.5	2664	8.9	2.58	81.8	2664	8.4

[a]IDL = Instrument detection limit.

TABLE 7-3. METHOD DETECTION LIMITS (MDLs) FOR CRITICAL SEMIVOLATILE ORGANIC CONTAMINANTS BY METHOD 3520/8270 (TREATED LIQUID)

Critical Contaminant	Week T_9				Week T_{12}			
	IDL (ppb)[a]	Avg. Recovery	Dilution Factor	MDL, ppb	IDL (ppb)	Avg. Recovery	Dilution Factor	MDL, ppb
Naphthalene	0.38	62.4	6.7	4.1	0.38	64.2	4	2.4
2-Methylnaphthalene	4.32	67.7	6.7	43.0	4.32	76.5	4	23.0
Acenaphthylene	0.17	68.5	6.7	1.7	0.17	67.2	4	1.0
Acenaphthene	5.02	71.0	6.7	47.0	5.02	69.4	4	29.0
Dibenzofuran	1.83	74.5	6.7	16.0	1.83	66.2	4	11.0
Fluorene	0.50	74.3	6.7	4.5	0.50	66.8	4	3.0
Phenanthrene	0.82	75.8	6.7	7.2	0.82	80.5	4	4.1
Anthracene	1.78	70.5	6.7	17.0	1.78	78.0	4	9.1
Fluoranthene	0.29	68.5	6.7	2.8	0.29	65.2	4	1.8
Pyrene	1.38	72.8	6.7	13.0	1.38	69.3	4	8.0
Benzo(a)anthracene	0.57	80.6	6.7	4.7	0.57	77.0	4	3.0
Chrysene	2.99	80.1	6.7	25.0	2.99	73.5	4	16.0
Benzo(b)fluoranthene	1.32	58.8	6.7	15.0	1.32	73.8	4	7.2
Benzo(a)pyrene	2.58	71.5	6.7	24.0	2.58	66.5	4	16.0

[a]IDL = Instrument detection limit.

TABLE 7-4. PRACTICAL QUANTITATION LIMITS (PQLs) FOR CRITICAL SEMIVOLATILE ORGANIC CONTAMINANTS BY METHOD 3550/8270 FOR SOIL MATRIX AND 3520/8270 FOR LIQUID MATRIX

	Pretreatment soil matrix (Week T_0)				Posttreatment soil matrix (Weeks T_9 and T_{12})				Posttreatment liquid matrix (Week T_9)				Pre- and posttreatment liquid matrix (Week T_0 and T_{12})			
Critical contaminant	IDL[a], mg/L	Sample aliquot, g	Dilution factor	PQL, mg/kg	IDL[a], mg/L	Sample aliquot, g	Dilution factor	PQL, mg/kg	IDL, mg/L	Sample aliquot, mL	Dilution factor	PQL, mg/L	IDL mg/L	Sample aliquot, mL	Dilution factor	PQL mg/L
Naphthalene	10	1	4000	40	10	30	2700	27	10	300	6.7	67	10	500	4	40
2-Methylnaphthalene	10	1	4000	40	10	30	2700	27	10	300	6.7	67	10	500	4	40
Acenaphthylene	10	1	4000	40	10	30	2700	27	10	300	6.7	67	10	500	4	40
Acenaphthene	10	1	4000	40	10	30	2700	27	10	300	6.7	67	10	500	4	40
Dibenzofuran	10	1	4000	40	10	30	2700	27	10	300	6.7	67	10	500	4	40
Fluorene	10	1	4000	40	10	30	2700	27	10	300	6.7	67	10	500	4	40
Phenanthrene	10	1	4000	40	10	30	2700	27	10	300	6.7	67	10	500	4	40
Anthracene	10	1	4000	40	10	30	2700	27	10	300	6.7	67	10	500	4	40
Fluoranthene	10	1	4000	40	10	30	2700	27	10	300	6.7	67	10	500	4	40
Pyrene	10	1	4000	40	10	30	2700	27	10	300	6.7	67	10	500	4	40
Benzo(a)anthracene	10	1	4000	40	10	30	2700	27	10	300	6.7	67	10	500	4	40
Chrysene	10	1	4000	40	10	30	2700	27	10	300	6.7	67	10	500	4	40
Benzo(b)fluoranthene	10	1	4000	40	10	30	2700	27	10	300	6.7	67	10	500	4	40
Benzo(k)fluoranthene	10	1	4000	40	10	30	2700	27	10	300	6.7	67	10	500	4	40
Benzo(a)pyrene	10	1	4000	40	10	30	2700	27	10	300	6.7	67	10	500	4	40

[a] IDL = Instrument detection limit.

Critical Constituents With Detection Limits Greater Than 1 mg/kg

The treatment soil sample had to be extracted as a medium-level soil because of the high levels of PAHs that were present. The medium-level extraction resulted in detection limits greater than 1 mg/kg and ranging as high as 29 mg/kg.

No phenolic compounds were detected. They may have been diluted out as a result of the medium-level extraction; however, data interpretation would not have been possible with a low-level extraction of a pretreatment sample because of the PAH levels. Overlapping of isomer peaks as well as peaks of different compounds would have compromised the data because the contaminants could not be accurately quantified.

7.1.2 Accuracy Data

Accuracy data were calculated from the analysis of matrix spike/matrix spike duplicate samples. Accuracy is expressed as the percent recovery of the constituents spiked into the sample in known amounts. The equation for calculating percent recovery is as follows:

$$\textit{Percent Recovery} = 100\ \frac{(C_i - C_o)}{C_t}$$

where C_o = value of unspiked aliquot
C_i = value of spiked aliquot
C_t = value for spike added

As stated in the SAP, the QA objective for accuracy (percent recovery) is in the range of 20 to 200 percent. Tables 7-5, 7-6, and 7-7 present the percent recoveries calculated from matrix spike/matrix spike duplicate samples for the pretreatment soil matrix, the soil matrix after 9 weeks of treatment, and the soil matrix after 12 weeks of treatment, respectively. Tables 7-5, 7-8, and 7-9 present the percent recoveries calculated from matrix spike/matrix spike duplicate samples for the pretreatment liquid

TABLE 7-5. MATRIX SPIKE DATA FOR CRITICAL SEMIVOLATILE CONTAMINANTS, UNTREATED MATRIX
(percent recovery)

	Bioreactor-001 sludge		Bioreactor-001 liquid	
Constituent	MS[a]	MSD[b]	MS	MSD
Naphthalene	32.9	46.9	28.5	26.1
2-Methylnaphthalene	39.8	44.4	22.9	21.3
Acenaphthylene	52.4	44.2	31.9	32.5
Acenaphthene	-2.9	-91.4	28.7	29.1
Dibenzofuran	11.4	-41.7	29.5	29.6
Fluorene	-12.4	-110	30	30.5
Phenanthrene	-93.8	-318	30.2	34.1
Anthracene	-20.8	-153	27.6	29.2
Fluoranthene	-74.2	-243	25.4	26.3
Pyrene	-7.2	-111	28.9	28.4
Benzo(a)anthracene	38.4	-29	27.5	26.3
Chrysene	34.6	-33.1	26.5	25.6
Benzo(b)fluoranthene[c]	35.6	16.5	22.3	22.2
Benzo(a)pyrene	24.4	2.2	19.9	16.7

[a] MS = Matrix spike sample.

[b] MSD = Matrix spike duplicate sample.

[c] Benzo(b) and benzo(k)fluoranthene were found to co-elute; therefore, a total amount was given under benzo(b)fluoranthene.

TABLE 7-6. MATRIX SPIKE DATA FOR CRITICAL SEMIVOLATILE CONTAMINANTS, TREATED SOIL (WEEK T_9)
(percent recovery)

Constituent	Bioreactor 1		Bioreactor 2		Bioreactor 4		Bioreactor 5		Bioreactor 6	
	MS[a]	MSD[b]	MS	MSD	MS	MSD	MS	MSD	MS	MSD
Naphthalene	0	78.3	80	83.7	91	74.6	86.2	79.2	82.8	86.2
2-Methylnaphthalene	100	75.4	77.4	88.2	86.8	71.9	86	76.3	81.6	88.1
Acenaphthylene	0	64.4	71.7	72	75.7	66.7	75.8	66.6	72.5	73.4
Acenaphthene	0	74.4	79.9	81.7	83.3	74.1	86.9	74.6	81.6	83.3
Dibenzofuran	0	80.1	82.6	85.9	90.6	78.9	92.8	78.5	88.6	88.4
Fluorene	0	77.5	80.2	81.4	87.1	75	86.7	76.8	85.1	85.8
Phenanthrene	0	76.7	84.3	84.9	85.4	86.2	89.3	72.6	75.2	78.4
Anthracene	91.1	56.5	64.8	60.7	62.5	59.3	61	51.7	55.6	60.6
Fluoranthene	0	78.6	86.3	80.8	90.1	84.4	81.6	68.5	75.2	81.8
Pyrene	86.9	83.6	94.5	88	100	88.7	95.8	78.5	83.3	89
Benzo(a)anthracene	0	85.4	84.9	82.3	90.4	84	90.7	75.9	80.4	93.9
Chrysene	72.5	82.8	99.3	87.4	96.5	90.8	90.9	80.9	89.7	95
Benzo(b)fluoranthene[c]	0	92.2	118.2	52.6	51.1	101.1	65	56.6	18.2	43.6
Benzo(a)pyrene	57.9	73.3	130.2	56.2	72.6	112.6	69.4	57.7	58.7	85.9

[a] MS = Matrix spike.
[b] MSD = Matrix spike duplicate.
[c] Benzo(b) and benzo(k)fluoranthene were found to co-elute; therefore, a total amount was given under benzo(b)fluoranthene.

TABLE 7-7. MATRIX SPIKE DATA FOR CRITICAL SEMIVOLATILE CONTAMINANTS, TREATED SOIL (WEEK T_{12})
(percent recovery)

Critical Contaminant	Bioreactor 1		Bioreactor 2		Bioreactor 4		Bioreactor 5		Bioreactor 6	
	MS[a]	MSD[b]	MS	MSD	MS	MSD	MS	MSD	MS	MSD
Naphthalene	70.4	76.3	79.0	69.5	69.8	97.5	17.0	59.4	58.0	73.1
2-Methylnaphthalene	76.9	79.0	80.9	66.1	72.1	98.1	17.2	64.6	59.4	76.1
Acenaphthylene	87.1	82.4	80.1	71.8	75.0	110.0	14.0	87.4	75.7	79.6
Acenaphthene	90.9	86.7	86.1	75.7	75.8	110.0	15.9	91.6	79.9	82.8
Dibenzofuran	91.7	88.7	84.5	76.4	76.3	110.0	16.2	96.8	85.7	82.6
Fluorene	90.1	86.4	80.2	76.8	79.2	110.0	14.9	100.0	89.4	81.5
Phenanthrene	94.3	88.7	82.9	79.9	82.3	117.0	14.0	113.4	100.0	86.6
Anthracene	95.6	95.6	91.6	82.8	87.3	120.0	13.6	115.8	96.3	82.6
Fluoranthene	98.9	88.2	86.5	90.2	81.0	115.1	10.4	108.5	110.0	88.6
Pyrene	91.5	101.5	93.0	87.5	87.0	130.0	22.3	130.0	110.0	110.0
Benzo(a)anthracene	110.0	100.0	88.9	88.8	90.3	130.0	21.2	130.0	110.0	93.4
Chrysene	91.0	101.0	86.6	81.5	87.0	120.0	11.7	102.6	99.9	88.8
Benzo(b)fluoranthene[c]	50.0	0.0	78.4	88.4	77.6	88.2	-84.3	80.0	53.8	43.8
Benzo(a)pyrene	104.8	64.8	92.7	92.7	91.7	110.5	-48.3	111.9	79.3	69.3

[a]MS = Matrix spike sample.

[b]MSD = Matrix spike duplicate sample.

[c] Benzo(b) and benzo(k)fluoranthene were found to co-elute; therefore, a total amount was given under benzo(b)fluoranthene.

TABLE 7-8. MATRIX SPIKE DATA FOR CRITICAL SEMIVOLATILE CONTAMINANTS, TREATED LIQUID (WEEK T_9)
(percent recovery)

Constituent	Bioreactor 1		Bioreactor 2		Bioreactor 4		Bioreactor 5		Bioreactor 6	
	MS[a]	MSD[b]	MS	MSD	MS	MSD	MS	MSD	MS	MSD
Naphthalene	62.9	64.9	76	64.7	70.4	42.5	75.5	72.2	40.7	54.6
2-Methylnaphthalene	63.2	67.7	78.8	72	77	47.4	79.3	81.9	45.4	64.1
Acenaphthylene	66.8	68	79.6	67.4	78.5	50.8	79.4	75	47.1	72.2
Acenaphthene	69	69.6	81.4	70.2	82.9	53.4	81.4	78.5	48.8	74.3
Dibenzofuran	74.3	77.2	84.4	72.8	84.9	55.7	86.4	79.6	51.1	78.4
Fluorene	77.3	81.1	84.7	69.2	82.6	57.1	83.8	81	51.5	75
Phenanthrene	79.7	83.3	82.2	73.4	83.6	64.4	79.2	82.2	53.2	77
Anthracene	73.4	77.6	80.7	73.7	84	42.6	75.5	73.5	52.6	71.5
Fluoranthene	69.2	75.7	76.4	66.9	87.1	57.4	73.6	66.3	49	63
Pyrene	74.5	83.2	83.3	64.9	88.9	58.8	74.1	77.6	51.9	70.6
Benzo(a)anthracene	81.7	88.9	92.2	76.7	95.8	63.1	82	87.8	61.4	76.4
Chrysene	84.9	91.9	90.8	72.6	92	63.5	84.3	88.2	55.4	77
Benzo(b)fluoranthene[c]	73.4	78.1	60.5	47.8	71.8	50	48.8	43.3	47.1	67.6
Benzo(a)pyrene	76.9	80	81	74	81	57	69.1	67.7	54.9	73.2

[a] MS = Matrix spike sample.

[b] MSD = Matrix spike duplicate sample.

[c] Benzo(b) and benzo(k)fluoranthene were found to co-elute; therefore, a total amount was given under benzo(b)fluoranthene.

TABLE 7-9. MATRIX SPIKE DATA FOR CRITICAL SEMIVOLATILE CONTAMINANTS, TREATED LIQUID (WEEK T_{12})
(percent recovery)

Critical Contaminant	Bioreactor 1		Bioreactor 2		Bioreactor 4		Bioreactor 5		Bioreactor 6	
	MS[a]	MSD[b]	MS	MSD	MS	MSD	MS	MSD	MS	MSD
Naphthalene	60.4	62.3	76.2	70.4	61.3	61.5	62.6	68.2	58.4	60.3
2-Methylnaphthalene	66.5	76.9	80.0	72.9	64.4	66.4	79.4	91.7	81.8	84.8
Acenaphthylene	65.5	64.7	77.9	71.7	68.0	67.8	66.4	65.4	62.0	62.2
Acenaphthene	68.0	67.6	78.5	72.3	67.2	68.7	69.1	70.3	66.7	65.8
Dibenzofuran	65.7	67.4	78.9	46.6	66.9	68.5	68.2	68.6	66.6	65.0
Fluorene	65.5	65.2	81.4	50.2	70.5	72.7	66.5	64.5	67.3	64.5
Phenanthrene	89.7	88.4	83.7	57.1	70.3	69.9	77.6	81.3	87.7	99.5
Anthracene	90.8	89.2	75.0	55.1	72.8	62.7	82.1	81.2	83.1	88.0
Fluoranthene	64.0	64.9	80.0	72.9	69.6	67.3	55.9	57.2	61.1	59.4
Pyrene	66.5	76.2	73.6	66.7	70.1	69.2	66.4	65.2	69.8	69.7
Benzo(a)anthracene	79.4	85.3	80.6	70.0	70.3	67.4	82.9	77.0	80.1	77.1
Chrysene	78.4	78.8	76.4	69.2	67.5	65.6	74.4	72.7	76.8	75.6
Benzo(b)fluoranthene[c]	72.8	76.0	90.8	76.6	74.0	74.5	62.7	72.2	72.8	65.9
Benzo(a)pyrene	67.1	65.8	75.5	63.5	63.0	72.0	61.6	63.9	68.9	63.5

[a]MS = Matrix spike sample.

[b]MSD = Matrix spike duplicate sample.

[c] Benzo(b) and benzo(k)fluoranthene were found to co-elute; therefore, a total amount was given under benzo(b)fluoranthene.

matrix, the liquid matrix after 9 weeks of treatment, and the liquid matrix after 12 weeks of treatment, respectively.

Recoveries in the pretreatment samples were generally low. In addition, the soil matrix showed the phenomenon of having negative recoveries for critical constituents. This means that critical constituents were being detected at lower concentrations in the MS/MSD samples than in the unspiked sample. There are two possible reasons for this phenomenon. The poor recoveries may have been caused by matrix interferences resulting from overloading the soil and analytical system with PAHs. The original levels of PAHs in the soil may have been close to saturating the extraction fluid with contaminants, and the additional spiking of each contaminant into the soil may have oversaturated the extraction fluid and resulted in the poor extraction efficiency. The other possible explanation for the poor recoveries may be layering of PAHs in the soil due to the centrifuging process. Because centrifuging partitions mixtures out by weight, the PAHs may have been layered out in the soil, which would result in a nonhomogeneous sample. A thorough remixing of the soil sample may not have been done in the laboratory. Thus, analytical results would present data of varying concentrations depending on where the sample aliquot was obtained. The recoveries for the liquid sample, although low, were still within the acceptable limits established in the SAP except for benzo(a)pyrene.

Although recoveries in the posttreatment samples were better, problems still existed in some samples. The MS sample from Bioreactor 1 during Week T_9 showed 0 percent recovery for many of the compounds. This may have been due to an error in spiking the sample during the extraction process. The recovery for benzo(b)fluoranthene was below 20 percent in the MS sample from Bioreactor 6 for Week T_9. The MS/MSD set from Bioreactor 5 showed the most inconsistency; the MS sample showed very poor recoveries, and the MSD sample showed very good recoveries. Again, the inconsistencies may be due to possible layering of the PAH compounds during the centrifuge process.

Recoveries of the critical constituents in the treated liquid matrices from Weeks T_9 and T_{12} were good. Recoveries ranged from a low of 40.7 percent to 99.5 percent. All recoveries were within the acceptable limits established in the SAP.

7.1.3 Precision Data

Precision data were calculated from the analysis of matrix spike/matrix spike duplicate samples. Precision is expressed as the relative percent difference (RPD) between the matrix spike and the matrix spike duplicate concentration values. The equation for calculating relative percent difference is as follows:

$$RPD = \frac{(D_1 - D_2)\ 100}{(D_1 + D_2)\ /2}$$

where RPD = relative percent difference
D_1 = larger of the two observed values
D_2 = smaller of the two observed values

As stated in the SAP, the QA objectives for precision (RPD) were ±20 percent for concentrations greater than 200 µg/kg and ±100 percent for concentrations less than or equal to 200 µg/kg. Tables 7-10 and 7-11 present the precision data calculated from the matrix spike and matrix spike duplicate samples for the soil fraction and liquid fraction respectively.

The RPD values for the pretreatment soil fraction were generally outside the acceptable limits of ± 20 percent established for concentrations greater than 200 µg/kg. Because of the poor recovery in the Week T_9 MS sample for Bioreactor 1, the RPD values for many of the compounds were outside the acceptable limits of ± 100 percent for concentrations less than 200 µg/kg. The Week T_{12} MS/MSD samples from Bioreactor 5 also showed RPDs greater than 100 percent. The RPDs for the other MS/MSD sets were generally good; most values were less than 20 percent. The RPDs for Bioreactor 4 from Week T_{12} showed values of 30 percent.

The RPDs for the MS/MSD samples in the liquid fraction were all within the acceptable limits established in the SAP. The RPD values in the liquid fraction were

TABLE 7-10. PRECISION DATA FOR CRITICAL SEMIVOLATILE ORGANIC CONTAMINANTS (SOIL, WEEK T_0, WEEK T_9 and WEEK T_{12}) (relative percent difference)

	Week T_0	Week T_9					Week T_{12}				
Critical Contaminant	Reactor 1	Reactor 1	Reactor 2	Reactor 4	Reactor 5	Reactor 6	Reactor 1	Reactor 2	Reactor 4	Reactor 5	Reactor 6
Naphthalene	17.5	200.0	4.4	19.9	8.5	4.0	7.4	12.8	32.3	111.0	21.9
2-Methylnaphthalene	6.7	28.1	12.9	18.9	12.1	7.7	2.7	20.2	30.5	116.0	24.6
Acenaphthylene	11.1	200.0	0.4	12.6	12.9	1.2	5.6	10.9	37.9	144.7	4.9
Acenaphthene	43.2	200.0	2.1	11.6	15.3	2.0	4.7	12.9	36.8	140.8	3.5
Dibenzofuran	32.7	200.0	4.0	13.9	16.7	0.2	3.4	10.2	36.1	142.8	3.7
Fluorene	42.0	200.0	1.5	14.9	12.1	0.9	4.3	4.4	32.6	148.1	9.2
Phenanthrene	46.7	200.0	0.6	0.9	20.6	4.0	5.8	3.6	33.8	141.5	14.4
Anthracene	45.8	47.0	6.5	5.2	16.6	8.6	0.0	10.1	31.6	148.3	14.8
Fluoranthene	47.8	200.0	6.7	6.5	17.3	7.7	10.3	4.0	33.2	138.2	21.6
Pyrene	41.1	3.9	7.2	12.0	19.9	6.2	9.5	6.1	39.7	141.5	0.0
Benzo(a)anthracene	46.5	200.0	3.0	7.3	17.8	15.5	9.5	0.1	36.0	144.0	16.3
Chrysene	45.5	13.2	12.8	6.1	11.6	5.8	9.5	6.1	31.9	141.0	11.7
Benzo(b)fluoranthene	22.0	200.0	61.1	34.5	11.0	23.7	25.6	8.7	7.3	139.4	7.4
Benzo(a)pyrene	27.6	23.5	71.9	28.6	18.4	28.2	22.2	0.0	13.4	145.7	7.4

TABLE 7-11. PRECISION DATA FOR CRITICAL SEMIVOLATILE ORGANIC CONTAMINANTS (LIQUID, WEEK T_0, WEEK T_9 and WEEK T_{12}) (relative percent difference)

	Week T_0	Week T_9					Week T_{12}				
Critical Contaminant	Reactor 1	Reactor 1	Reactor 2	Reactor 4	Reactor 5	Reactor 6	Reactor 1	Reactor 2	Reactor 4	Reactor 5	Reactor 6
Naphthalene	8.9	3.2	16.0	49.4	4.3	29.1	3.1	7.9	0.4	8.6	3.1
2-Methylnaphthalene	5.8	6.8	9.0	47.6	3.2	34.1	14.5	9.3	3.1	14.3	3.6
Acenaphthylene	1.5	1.7	16.6	42.8	5.7	42.2	1.3	8.2	0.4	1.5	0.4
Acenaphthene	0.8	0.9	14.9	43.4	3.7	41.5	0.6	8.2	2.2	1.7	1.3
Dibenzofuran	0.3	3.9	14.8	41.6	8.2	42.1	2.5	51.5	2.4	0.5	2.4
Fluorene	1.6	4.8	20.1	36.5	3.4	37.1	0.5	47.4	3.0	3.0	4.2
Phenanthrene	11.5	4.4	11.2	25.9	3.6	36.6	1.5	37.8	0.6	4.6	12.6
Anthracene	5.1	5.4	9.0	65.5	2.4	30.4	1.8	29.9	14.9	1.1	5.7
Fluoranthene	2.6	9.0	13.2	41.0	9.8	25.1	1.4	9.3	3.3	2.4	2.7
Pyrene	1.5	11.0	24.4	40.7	4.4	30.5	13.5	9.8	1.3	1.8	0.1
Benzo(a)anthracene	4.6	8.5	18.4	41.2	6.8	21.7	7.2	14.1	4.3	7.3	3.9
Chrysene	3.5	7.9	20.9	36.6	4.5	32.6	0.4	9.9	2.8	2.4	1.6
Benzo(b)fluoranthene	0.2	5.4	14.4	29.8	6.3	29.4	4.0	15.5	0.6	12.3	8.8
Benzo(a)pyrene	17.7	3.7	7.6	31.9	1.5	26.0	1.9	17.3	13.3	3.3	7.9

generally less than 20 percent. The MS/MSD set for Bioreactor 4 during Week T_9 of sampling showed the worst precision; the RPD values ranged from 25.9 percent for phenanthrene to 65.5 percent for anthracene.

7.1.4 Blank Data for Soil Analyses

Equipment blanks were collected during the premilling, postmilling, and centrifuging operations. Trip blanks were also collected for each major sampling event in Weeks T_0, T_9, and T_{12} in the study. These blanks were analyzed for possible semivolatile organic contamination. The analyses of these samples showed no sign of contamination in the sampling procedures. In addition, method blanks were extracted for each set of samples submitted to the lab. These samples were also analyzed for semivolatile organic contamination, and results were negative.

During the premilling and postmilling sampling operations, field blanks were collected to determine possible volatile organic contamination. Daily blanks were also analyzed prior to sample analysis to ensure that the instrumentation was free of any major volatile organic contamination. Volatile organic compounds detected in the analysis of these blanks are presented in Table 7-12. All compounds detected were less than the maximum control limits established for blanks in SW-846 Method 8240.

7.1.5 Surrogate Recoveries Data

In addition to the preceding quality assurance procedures, all samples analyzed for volatile and semivolatile organics were spiked with surrogates as a means of checking recovery efficiency. The results for surrogate recoveries during semivolatile and volatile organic analyses are presented in Tables 7-13 and 7-14 respectively. Of particular importance are the recoveries of terphenyl-d14 in the semivolatile organic analyses and toluene-d8 in the volatile organic analyses. Terphenyl-d14 is the surrogate most representative of the complex PAHs present in the treatment soil. Recoveries for this surrogate ranged from a low of 38 in the pretreatment soil to a high of 130 percent in the posttreatment soil samples. Poor recoveries of this surrogate

TABLE 7-12. BLANK DATA FROM ANALYSIS OF BIOSLURRY SAMPLES

	Field blank, mg/L	VBLKJ3, mg/L	VBLKJ4, mg/kg	VBLKJ6, mg/L
Methylene chloride	0.014 B[a]	0.005	0.018	
Acetone	0.020 B	0.024	0.013	
Carbon disulfide			0.003 J[b]	
Chloroform				0.001 J
2-Butanone		0.01	0.007 J	
1,1,1-Trichloroethane			0.002 J	
Trichloroethene	0.002 JB	0.002 J	0.002 J	
Toluene			0.001 J	
1,2,3-Trichloropropane		0.002 J		

[a] B = Target analyte detected in method blank as well as the sample.

[b] J = Estimated value for analyte detected below established detection limit.

TABLE 7-13. SURROGATE RECOVERIES IN SEMIVOLATILE ORGANIC SAMPLES
(percent recovery)

	Nitrobenzene-d5	2-Fluorobiphenyl	Terphenyl-d14	Phenol-d6	2-Fluorophenol	2,4,6-Tribromophenol
Premilling soil	29	33	38	37	41	53
Postmilling soil	29	36	40	35	44	46
Trip blank	67	69	83	57	60	57
Premilling equip blank	71	68	85	52	58	73
Postmilling equip blank	59	62	84	62	73	81
Soil blank SBLK396	25	32	46	34	41	38
Water blank SBLK304	59	72	77	64	68	92
Premilling soil TCLP	60	57	56	38	33	37
Postmilling soil TCLP	49	54	57	34	23	23
TCLP method blank	41	43	47	66	69	79
Bioreactor 001 sludge	58	76	87	69	86	115
Bioreactor 001 liquid	68	70	22[a]	59	60	68
Bioreactor 002 sludge	56	60	78	58	67	84
Bioreactor 002 liquid	73	70	27[a]	59	62	73
Bioreactor 004 sludge	38	36	47	40	45	60
Bioreactor 004 liquid	43	6[a]	5[a]	47	30	12
Bioreactor 005 sludge	60	71	87	77	82	101
Bioreactor 005 liquid	64	70	21[a]	59	65	85
Bioreactor 006 sludge	53	76	80	70	80	90
Bioreactor 006 liquid	66	69	29[a]	74	83	90
Equipment blank	41	51	76	62	70	89
Soil blank SBLK396	51	64	93	68	82	76

(continued)

TABLE 7-13 (cont.)

	Nitrobenzene-d5	2-Fluorobiphenyl	Terphenyl-d14	Phenol-d6	2-Fluorophenol	2,4,6-Tribromophenol
Water blank SBLK304	59	72	77	64	68	92
Equipment blank	36	44	83	36	48	75
T9-R1-S-BNA	82	89	97	55	75	65
T9-R1-W-BNA	67	69	80	0[a]	2[a]	49
T9-R2-S-BNA	78	79	86	65	70	70
T9-R2-W-BNA	72	71	81	0[a]	6[a]	26
T9-R4-S-BNA	75	80	91	60	70	70
T9-R4-W-BNA	65	69	82	0[a]	6[a]	67
T9-R5-S-BNA	81	79	83	70	75	70
T9-R5-W-BNA	76	77	78	0[a]	0[a]	11
T9-R6-S-BNA	86	91	93	75	75	85
T9-R6-W-BNA	69	75	69	0[a]	1[a]	36
T12-R1-S-BNA	73	79	93	65	70	85
T12-R1-W-BNA	56	63	32[a]	58	63	77
T12-R2-S-BNA	65	79	85	37	65	70
T12-R2-W-BNA	59	60	27[a]	57	57	67
T12-R4-S-BNA	80	93	120	75	80	105
T12-R4-W-BNA	52	54	28[a]	40	47	71
T12-R5-S-BNA	65	73	130	60	65	100
T12-R5-W-BNA	126[a]	132[a]	75	118[a]	123[a]	135[a]
T12-R6-S-BNA	86	94	120	75	85	100
T12-R6-W-BNA	51	57	27[a]	53	56	63

a Surrogate recovery outside acceptable limits.

TABLE 7-14. SURROGATE RECOVERIES IN VOLATILE ORGANIC SAMPLES (percent recovery)

	1,2-Dichloroethane-d4	Toluene-d8	Bromofluorobenzene
Premilling soil	100	113	115
Postmilling soil	91	93	90
Field blank	104	104	102
Method blank VBLKJ3	98	103	104
Method blank VBLKJ4	92	109	110
Premilling soil TCLP	94	104	109
Postmilling soil TCLP	93	104	101
Method blank VBLKJ6	94	103	103
Method blank VBLKJ9	92	102	100
TCLP blank VBLK294	96	105	103

were obtained in the liquid fractions. All of the pretreatment liquid samples and four of the five posttreatment samples showed recoveries below the acceptable limits established in SW-846. Reextraction and reanalysis of these samples verified a matrix interference problem in the analysis of these samples.

Recoveries for toluene-d8, the surrogate most representative of the volatile organic contaminants possibly present in the soil, were all within the acceptable limits established in SW-846.

Standard reference solutions were analyzed for metals and inorganics to evaluate the efficiency of the analytical method. The results of the analyses of the standard reference solutions are presented in Table 7-15.

7.1.6 Analytical Problems

Because of the complex nature of the matrix under evaluation, several analytical problems occurred during their analyses that may have an effect on the data.

The holding times for extraction of the premilling, postmilling, and Week T_0 samples were exceeded. The samples were originally extracted as low-level soils, which resulted in a thick oily extract that was not amenable to analysis. The samples had to be reextracted as medium-level soils, which resulted in missed holding times. In addition, the liquid fractions from Week T_0 and the sludge from Bioreactor 1 from Week T_0 were extracted a third time so a matrix interference could be proven for the liquids and the proper MS/MSD spiking solution could be used on Bioreactor 1 sludge. It is believed that the missed holding times should not affect the data because the samples were preserved with concentrated hydrochloric acid in the hope of inhibiting further biological activity. In addition, the samples were stored at 4°C, which also would impair biological activity and help to ensure sample integrity.

The detection limits for many of the critical constituents were greater than 1 mg/kg as a result of the medium-level extractions being performed on the soil fractions. Medium-level extractions were performed on the soil because of the high level of total petroleum hydrocarbons detected in the soil matrix. The posttreatment samples from Weeks T_9 and T_{12} produced data with many nondetections of critical

TABLE 7-15. STANDARD REFERENCE SOLUTION RESULTS FROM ANALYSIS FOR METALS AND INORGANICS (percent recovery)

Metals and inorganics	Total analysis	TCLP analysis
Aluminum	109	
Antimony	97	
Arsenic	80.7	94.5
Barium	111	108
Beryllium	104	
Cadmium	96.6	95.7
Calcium	103	
Chromium	106	97.5
Chromium VI	100	
Cobalt	98.9	
Copper	100	
Iron	98.6	
Lead	110	94.6
Magnesium	101	
Manganese	108	
Mercury	102, 100, 99, 100	102
Nickel	102	
Potassium	97.6	
Selenium	91.9	85.2
Silver	112	104
Sodium	99.1	
Thallium	104	
Vanadium	101	
Zinc	99.1	
Chloride	105	
Cyanide	102	
Fluoride	88.8	
Total phosphorus	98.6	
Sulfate	94.7	

(continued)

TABLE 7-15 (continued)

Metals and inorganics	Total analysis	TCLP analysis
Sulfide	123	
TOC	99.4	
TOX	91.8	

contaminants. The contaminants present in low concentrations may have been diluted out in the medium-level extraction process. As a result, the soil fractions from Weeks T_9 and T_{12} were reextracted and reanalyzed as low-level soils. The holding times for the reextractions were exceeded; however, the integrity of the data should not be affected because the samples were preserved with concentrated hydrochloric acid. The reextraction data are important because of the effect they may have on the evaluation of the treatment efficiency of the bioslurry system. The low-level extracts use a larger sample aliquot which allows for a more representative sample of the soil being studied and allow for detection of contaminants at lower concentrations that were not available in the medium-level extracts due to dilution effects, thereby enabling a better evaluation of the treatment technology.

The data for this treatment study should be used with caution, based on the analysis of the MS/MSD samples and the surrogate recovery results. Although recoveries of the spike compounds were better in the treated samples than in the untreated samples (which indicates a cleaner matrix free of interferences), the inconsistencies in recoveries shown by the RPD values indicate that the samples may not have been homogeneous. As stated previously, the centrifuge process may have caused layering of the soil samples, with the heavier PAH-contaminated fraction settling at the bottom and the less contaminated fraction settling at the top. As a result, the final analytical data may be affected by the place where the extraction aliquot was obtained.

The surrogate recoveries for terphenyl-d14 in the liquid fraction indicate a matrix interference that may have affected the ability to extract PAHs out of the matrix.

In addition to the problems concerning the critical contaminants, a few minor analytical problems were also observed in the analysis of the remaining CS&D constituents. For example, the holding time for cyanide was exceeded during the study. Because cyanide was not a critical contaminant, however, the integrity of the soil data was not affected. The holding time for the extraction of pesticides was also exceeded during the study. Again, because pesticides were not critical contaminants, the integrity of the soil data was not affected.

7.1.7 Audits

Audits were performed by S-Cubed, a subcontractor of the U.S. EPA, on the treatment system sampling procedures and on the laboratory's analytical procedures. Conditional ratings for QA/QC procedures were given to both the sampling and analytical methods IT followed during the study. Copies of the Corrective Action Recommendation Forms and the final report for both audits are presented in Appendix O.

7.2 Air Samples

Routine Standard Reference Method QC procedures were followed throughout this test series. These included, but were not limited to, the following:

- Calibration of field sampling equipment.
- Sampling train configuration and calculation checks.
- Onsite quality assurance checks, such as sampling train leak checks.
- Use of designated analytical equipment and sampling reagents.
- Laboratory analytical procedures.

The field sampling equipment, reagents, and analytical procedures used during this test series met all the necessary guidelines set forth for accurate test results. The laboratory quality control samples included blanks, matrix spikes, and duplicate analyses. Laboratory QC results are discussed by analysis type in the following subsections.

7.2.1 *Analyses of Total Hydrocarbon (THC) Emission Monitoring*

Method 25A was used for continuous monitoring of THC concentrations, and all calibrations and system checks were well within the guidelines for this method. Table 7-16 presents example calibration data from this test program. All other calibration data are contained in Appendix N.

TABLE 7-16. EXAMPLE METHOD 25A THC CALIBRATION DATA

Date	Contaminant monitored	Drift, % of span[a]	Linearity, % of span[b]	Correlation coefficient
5/7	THC	1.6[c]	-0.2[c]	0.9999
5/8	THC	-1.4	-0.2	0.9999
5/9	THC	-0.8	0.2	0.9999

[a] Drift % of span

$$= \frac{\text{(Posttest calib. response - initial calib. response)}}{\text{Span value, ppm}} \times 100$$

[b] Based on predicted concentrations from linear regression equation and the span value as follows:

$$\text{Linearity} = \frac{\text{(Gas concentration - predicted concentration)}}{\text{Span value, ppm}} \times 100$$

[c] Drift and linearity present maximum errors based on four calibration standards.

7.2.2 *Analyses for Hazardous Substance List (HSL) Semivolatile Organics*

All analyses for semivolatile organics were conducted by gas chromatography/mass spectrometry (GC/MS) in accordance with SW 846 Method 8270.

Table 7-17 is an example of surrogate recoveries on sample tubes and field blank tubes. Table 7-18 presents the acceptable recovery limits for surrogates in Method 8270. All other blank data and surrogate recoveries data are included in Appendix N. All semivolatile laboratory data met Method 8270 requirements.

TABLE 7-17. SEMIVOLATILE SURROGATE RECOVERIES ON SAMPLE AND FIELD BLANK TUBES

Client sample ID	Lab No.	d5-Nitrobenzene	2-Fluorobiphenyl	d14-Terphenyl	d6-Phenol	2-Fluorophenol	2,4,6-Tribromophenol
XAD-1-1 Front	01	69	66	83	69	90	69
	01 DL	78	67	66	66	66	60
	01 DL2	49	74	55	54	62	60
XAD-1-1 Back	01	61	60	79	77	102	74
	01 DL	68	71	64	77	82	65
XAD-2-1 Front	02	54	60	87	75	89	66
	02 DL	65	75	68	63	66	63
	02 DL2	54	65	48	49	61	45
XAD-2-1 Back	02	63	62	81	79	96	77
	02 DL	56	72	66	66	69	66
XAD - Field Blank Front	03	62	58	86	67	90	60
XAD - Field Blank Back	03	60	59	86	67	84	67
Method Blank	XADBLK	58	62	86	75	94	70

TABLE 7-18. ACCEPTABLE SURROGATE RECOVERY LIMITS

	QC recovery limits, percent	
Surrogate compound	Solids	Waters
Nitrobenzene-D_5	23-120	35-114
2-Fluorobiphenyl	30-115	43-116
p-Terphenyl-D_{14}	18-137	33-141
Phenol-D_6	24-113	10-94
2-Fluorophenol	25-121	21-100
2,4,6-Tribromophenol	19-122	10-123

7.2.3 Volatile Organic Analyses

All of the canister samples were analyzed for volatile organics by concentrating aliquots cryogenically and analyzing by gas chromatography/mass spectrometry. Table 7-19 lists the volatile organics which is an example canister blank and their corresponding detection limits. Table 7-20 is an example of surrogative recoveries in canisters and method blanks. All other blank data and surrogate recoveries are included in Appendix N.

7.3 Bioreactor Monitoring Samples

As samples were collected by an ECOVA Research Associate at the T&E Facility in Cincinnati, each group of samples was given a number corresponding to the central sample log book at ECOVA's laboratories in Redmond, Washington. This number was assigned when the Research Associate called ECOVA's labs. Upon their receipt at ECOVA's lab, the samples were checked, the Chain of Custody was signed, and a Sample Group Worksheet was begun that followed each sample group through its testing protocol at ECOVA. The sample group numbers for all 12 weeks of analysis are presented in Table 7-21.

7.3.1 Analytical Methods

Table 7-22 lists the methods used in monitoring the reactors in the pilot-scale phase of this project.

TABLE 7-19. VOLATILE CANISTER BLANK RESULTS

Compound	Blank	Detection limit
Chloromethane	ND[a]	0.5
Vinyl chloride	ND	0.3
Bromomethane	ND	0.3
Chloroethane	ND	0.5
1,1-Dichloroethene	ND	0.3
Carbon disulfide	ND	0.2
Methylene chloride	ND	0.2
t-1,2-Dichloroethene	ND	0.3
1,1-Dichloroethene	ND	0.3
c-1,2-Dichloroethene	ND	0.3
Chloroform	ND	0.3
1,1,1-Trichloroethane	ND	0.3
Carbon tetrachloride	ND	0.2
Benzene	ND	0.2
1,2-Dichloroethane	ND	0.3
Trichloroethene	ND	0.2
1,2-Dichloropropane	ND	0.3
Bromodichloromethane	ND	0.2
c-1,3-Dichloropropene	ND	0.4
Toluene	ND	0.2
t-1,3-Dichloropropene	ND	0.4
1,1,2-Trichloroethane	ND	0.3
Tetrachloroethene	ND	0.2
Dibromochloromethane	ND	0.2
Chlorobenzene	ND	0.2
Ethylbenzene	ND	0.2
m +/or p xylene	ND	0.2
o- xylene	ND	0.2
Styrene	ND	0.2
Bromoform	ND	0.2
1,1,2,2-Tetrachloroethane	ND	0.2

[a] ND = None detected.

TABLE 7-20. EXAMPLE SURROGATE VOLATILE ORGANIC RECOVERIES

Sample ID	Lab No.	Surrogate organic volatile recoveries, percent		
		d4-1,2-Dichloro-ethane	d8-Toluene	p-Bromo-fluoro-benzene
Can 1-1	04	99	101	107
	04 DL	99	99	102
Can 2-1	05	105	95	106
	05 DL	119	115	88
Method blank	VBLKQ4	106	99	97
Method blank	VBLKQ5	106	94	106
Method blank	VBLKQ6	97	102	98

TABLE 7-21. SAMPLE GROUP NUMBERS ASSIGNED BY ECOVA LABS

Test Week	Date	Sample Group
0	May 8	277-122
1	May 15	277-127
2	May 22	277-133
3	May 29	277-142
4	June 5	277-146
6	June 19	277-162
9	July 10	277-184
10	July 17	214-1
11	July 24	214-11
12	July 31	214-30

TABLE 7-22. METHOD USED TO MONITOR REACTORS DURING PILOT-SCALE PHASE

Compound	Method
Semivolatiles (BNAs)	EPA 8270 & ECOVA SSC-4
Oil and grease (O&G)	EPA 413.1
Inorganic nutrients	EPA 300.0
NH_3	EPA 350.2
TPH	EPA 418.1
Nitrate	ECOVA SSC-9
Ortho-phosphate P	ECOVA SSC-14
Composited soil sample	Microtox

The following is a synopsis of the methods used by ECOVA in this study:

Polynuclear Aromatic Hydrocarbons (PAHs) - The PAH analysis by HPLC (EPA 8310 Mod) was conducted at the ECOVA laboratory in Redmond, Washington. This analysis generated the primary process monitoring data used to track the degradation progress and to provide the necessary information for process modifications, if required. The analytical results provided individual quantitation of specific PAH compounds, including those considered to be critical contaminants.

Oil and Grease (O&G)/Total Petroleum Hydrocarbon (TPH) - The O&G (EPA 413.1) and TPH by IR (EPA 418.1) analyses were performed by IT Corp. The results are nonspecific, but they provided good monitoring data for the general organic content of the slurry.

Nutrients and Ammonia - The nutrient analysis (by EPA Method 300) and the ammonia analysis (by the modified Nessler Method) were conducted at ECOVA's laboratory. These analyses were used to track nutrient levels during the pilot test and provided data necessary to insure optimal nutrient levels.

Total Heterotrophs and PAH Degraders - The total heterotroph analysis (by SM 907) and PAH degrader analysis (by SM 907 Mod) were conducted at the ECOVA laboratory in Redmond. These analyses were used to track the activity of the heterotrophic and specific PAH degrading populations of microorganisms during the pilot test.

Microtox - Microtox analyses were conducted at ECOVA's laboratories to monitor the change in toxicity over the course of the study.

Field Measurements - Four field measurements were made at the T&E Facility--dissolved oxygen (DO), temperature, pH, and particle size distribution. The DO, temperature, and pH measurements were made by lowering probes into the reactor. The particle size distribution was assessed by wet screening techniques.

7.3.2 Analytical Problems and Deviations

A major problem with the analyses for polycylic aromatic hydrocarbons was the efficient extraction of the PAHs from the soil matrix. During both the bench-scale and the pilot-scale phases of the project, despite exhaustive attempts to mill, sonicate, and extract PAHs from virgin soil, concentrations of soil-bound PAHs increased after several weeks in a bioreactor. The most reasonable explanation, based on empirical evidence and total suspended solids data, is that the shear forces within the reactors comminuted the larger soil particles to finer ones. This, in turn, diminished their resistance to mass transfer effect (e.g., smaller particles exhibited a shorter surface-to-center path length) and allowed a higher PAH extraction efficiency because PAH residues could more easily diffuse to the particle surface.

Although this phenomenon was noted in the bench-scale phase and resulted in having to subject the soil to ball milling three times during the pilot-scale test, the comminution effect was still readily apparent.

No other major deviations from standard procedures were noted.

7.3.3 Detection Limits

Table 7-23 reflects the current limits of detection (LOD) of individual PAHs at the ECOVA laboratories. These limits were derived by serially diluting standards until the HPLC could no longer quantitate the results. This lowest standard concentration was then run 10 times to develop a statistical universe. The values from the next-to-the-last standard dilution were used to calculate an LOD by the following equation:

$$\text{LOD} = \text{Standard amount} + 3 \text{ standard deviations}$$

TABLE 7-23. CURRENT LIMITS OF DETECTION (LOD) OF INDIVIDUAL PAHs AT THE ECOVA LABORATORIES[a]

PAH	Lowest standard, ppm	LOD, ppm
Naphthalene	0.3908 ± 0.0528	0.5492
Acenaphthylene	0.7894 ± 0.1347	1.1935
Acenaphthene	0.2691 ± 0.0717	0.4842
Fluorene	0.0870 ± 0.0053	0.1029
Phenanthrene	0.0401 ± 0.0029	0.0488
Anthracene	0.0378 ± 0.0025	0.0453
Fluoranthene	0.0594 ± 0.0151	0.1047
Pyrene	0.2280 ± 0.0846	0.4818
Benzo[a]anthracene	0.0411 ± 0.0038	0.0525
Chrysene	0.0379 ± 0.0026	0.0457
Benzo[b]fluoranthene	0.0769 ± 0.0059	0.0946
Benzo[k]fluoranthene	0.0355 ± 0.0061	0.0538
Benzo[a]pyrene	0.0395 ± 0.0117	0.0746
Dibenz[a,h]anthracene/ Benzo[g,h,i]perylene	0.0374 ± 0.0094	0.0656
Indeno[1,2,3-cd]pyrene	0.0338 ± 0.0079	0.0575

[a] All other methods have detection limits <1 ppm.

SECTION 8

CORRESPONDENCE

Table 8-1 presents the activities and correspondence that were critical to the outcome of this study.

TABLE 8-1. CRITICAL ACTIVITIES AND CORRESPONDENCE

Date and Type of Activity or Correspondence	Contact	Subject/Action
11/7/89 Site Visit	Jim Brown ReTec	ITEP sent sampling team to characterize BN soil.
11/20/89 Site Visit	Jim Brown ReTec	ITEP sent sampling team to drum up potential soil for treatment studies; drums stored at site.
7/90 Meeting	Richard Lauch U.S. EPA	BN soil chosen as test soil for Bioslurry study.
10/1/90 Telephone	Richard Trax ReTec	Discussed ITEP's plan to collect more soil. R. Trax relayed that BN would not allow ITEP to reopen their soil liner. ITEP will sample from drums stored at site.
10/5/90 Telephone	Jim Brown ReTec	Verified ITEP's plan to travel to BN site on 10/15/90, dump and repackage soil from 3 drums, and transport drums to Cincinnati.
10/15/90 Site Visit	Jim Brown ReTec	ITEP sent team to dump and repackage soil from 3 drums for treatment studies.
11/90 Telephone	ECOVA	Bench-scale work began on BN soil.
12/14/90 Meeting	R. Lauch R. Lewis U.S. EPA ECOVA	Visited ECOVA to observe bench-scale work, discussed pilot-scale study.
2/91 Reporting	G. Simes U.S. EPA	Pilot-scale SAP submitted to EPA for review.
2/22/91 Transport	ECOVA	Additional drum of soil shipped to ECOVA for further studies.

(continued)

TABLE 8-1 (continued)

Date and Type of Activity or Correspondence	Contact	Subject/Action
2/25/91 Transport	U.S. EPA T&E Facility	Additional drums of soil shipped to Cincinnati for pilot-scale test.
4/17/91 Reporting	G. Simes U.S. EPA	Letter submitted to EPA responding to QA comments on SAP.
4/26/91 Reporting	G. Simes U.S. EPA	Letter submitted to EPA responding to further QA comments on SAP.
5/8/91 Treatment Test	ECOVA IT U.S. EPA	Pilot-scale work began on BN soil with screening and milling processes.
5/10/91 Treatment Test	ECOVA IT U.S. EPA	Reactors charged with slurry and spike with inoculum.
6/91 Analytical	B. Blackburn S-Cubed R. Lauch U.S. EPA	B. Blackburn performed audit on analytical laboratory. Conditional pass given on basis of holding time for critical contaminants being exceeded.
7/1/91 Meeting	J. Herrmann R. Lauch E. Grossman U.S. EPA A. Jones B. Mahaffey C. Krauskopf ECOVA	Discussed bioslurry results through Week 6. ITEP to collect T_9 samples on 7/10/91 (Week 9): ECOVA to amend slurries and ITEP to collect T_{12} samples on 7/31/91 (Week 12).
7/10/91 Treatment Test	C. Krauskopf ECOVA	T_9 samples collected from reactors.
7/11/91 Treatment Test	C. Krauskopf ECOVA	Reactors 2, 4, 5, and 6 were respiked with inoculum. Reactors 5 and 6 had surfactant added to them.
7/31/91 Treatment Test	Mike Smith ITEP	T_{12} samples collected from reactors. Reactors shut down.
9/91 Reporting	L. Tomassoni ITAS-Cincinnati	All data pertaining to bioslurry study reported to ITEP.
9/91 Reporting	L. Jones U.S. EPA	Data summary form for bioslurry study submitted to U.S. EPA.
10/91 Reporting	R. Lauch U.S. EPA	OER for bioslurry study submitted to U.S. EPA.