DRAFT FINAL
BIOLOGICAL TREATABILITY STUDIES OF SIBERIA AREA, WATERVLIET ARSENAL, Watervliet, New York

U.S. Army Corps of Engineers
Baltimore, Maryland

US Army Corps
of Engineers
Baltimore District
DRIVEN BY A VISION...to be the BEST

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EXECUTIVE SUMMARY

The goals of the treatability studies are to evaluate specified parameters and demonstrate the viability of bioremediation for treatment of contaminated soils at the Siberia Area. Bioremediation is a preferred remediation alternative because the associated costs are generally much lower than other alternatives, particularly when excavation may be necessary for these alternatives. Bioremediation may not be applicable to all areas of contamination at Siberia, especially areas of highest contamination such as the "hot spot" associated with the main substation in the vicinity of MW-29, where total petroleum hydrocarbons (TPH) concentrations reached 100,000 ppm and total polycyclic aromatic hydrocarbons (PAH) concentrations reached 1,000 ppm.

A series of laboratory bench-scale tests were completed to evaluate specific parameters for cost effective scale-up of enhanced bioremediation of TPH and PAH contaminated soils from the Siberia Area. Successfully completed laboratory bench-scale tests, indicated in Table 1, include radiotracer phenanthrene tests, microbial isolation experiments, bioslurry evaluations, column evaluations, and pan evaluations.

Table 1: Completed Laboratory Evaluations

Evaluation	Objective(s)	Status
^{14}C-Phenanthrene	Validate existence of indigenous PAH and TPH mineralizating organism	Completed Feb. 1999
PAH Degrader Isolation	Determine if site specific bacteria can be isolated and cultured to enhance remediation	Completed Oct 1999
Bioslurry	Assess maximum rate and extent of TPH biodegradation under optimal conditions (minimized mass transfer limitations).	Completed Jul 1999
Column	Mimic conditions found in Siberia Area subsurface and determine optimal parameters for enhanced biodegradation.	Completed Mar 1999
Pan	Compare aerobic and anaerobic biodegradation protocols for in situ bioremediation of Siberia Area soils. Assess and compare before and after treatment toxicity	Completed Oct 1999 Completed Dec 1999

Each completed laboratory test has resulted in significant data optimizing the final protocol for full-scale remediation of TPH and PAH contaminated soils from the Siberia Area. The ^{14}C-phenanthrene evaluation confirmed the existence of indigenous microorganisms capable of biologically degrading PAH and TPH. The results indicated a rapid initial rate of mineralization of the PAHs and TPH under both aerobic and anaerobic conditions, with an overall greater extent of mineralization under aerobic conditions. These positive results indicated that it is clearly appropriate for follow-on evaluation, optimization, and toxicity screening of Siberia Area soils for full-scale bioremediation.

PAH-degrading microorganism isolation experiments were conducted to provide supporting evidence for aerobic and anaerobic PAH biodegradation in contaminated soils from the Siberia Area. These experiments were designed to show that PAH-degrading bacteria are naturally present in contaminated soil from the site. This was done by isolating and growing cultures from Siberia Area soils, which enhanced aerobic and/or anaerobic mineralization of PAHs.

The bioslurry evaluation assessed bioremediation under conditions that minimized the mass transfer limitations. Characterization of soils collected for bioslurry evaluations (t=0) indicated the absence of detectable PAH contamination. Therefore, a second bioslurry evaluation with new soils was conducted. While both aerobic and anaerobic treatements demonstrated significant reduction of both PAH and TPH contamination under slurry conditions, final PAH and TPH concentrations in the aerobic slurries were half those in the anaerobic slurries. Fourteen weeks of aerobic slurry conditions resulted in a 90 percent and 85 percent reduction in PAH and TPH concentrations, respectively. Results from this study demonstrate that bioslurry of soils at the Site is a viable option for remediation.

The column evaluation demonstrated that biological remediation under field-simulated conditions of mixing and nutrient amendment, conducted in duplicate, approached the stated objective of 50 percent reduction in contaminant concentration using exclusively indigenous organisms. The evaluation demonstrated an overall TPH degradation of 75 percent, diesel range organics (DRO) degradation of 23 percent, and PAH degradation of 54 percent.

A pan study was conducted using soils/fill collected from the Siberia Area. This study was designed to simulate in-situ land farming techniques (bioremediation approach) and to provide an assessment of expected degradation of TPH and PAHs under relevant field conditions during a bioremediation effort. Study treatments were designed to represent aerobic and anaerobic land farming treatment options at the site. Results of the pan study indicate that land-farming remediation of contaminated soils from Siberia Area is an appropriate remediation technology.

1.0 INTRODUCTION

The U.S. Army Corps of Engineers (USACE) Baltimore District contracted Malcolm Pirnie, Inc. (Malcolm Pirnie) to perform bench-scale and pilot-scale field treatability tests on soils contaminated with TPH and PAHs from the Siberia Area, Watervliet Arsenal, New York under the Indefinite Delivery Contract DACA31-94-D-0017. Laboratory tests were initiated by Malcolm Pirnie to:

1. assess the existence of indigenous microorganisms,
2. assess the ability of existing microorganisms to degrade the contaminants of concern (COCs),
3. ascertain changes in toxicity associated with biological degradation of the COCs,
4. simulate full-scale remediation alternatives,
5. develop necessary information for field pilot-scale tests and follow on full-scale remediation.

This composite report includes the work and results for five biotreatability tests for contaminated soils including a carbon-14 (^{14}C) study, a bioslurry study, a PAH degrading microorganism isolation experiment, a column study, and a pan study. The biotreatability tests support efforts to evaluate, optimize, and validate in-situ bioremediation as a corrective measure for contaminated soils in the Siberia Area and were conducted under the direction and supervision of Malcolm Pirnie.

1.1 SITE BACKGROUND

Watervliet Arsenal, located in Watervliet, New York, is the oldest continuously operating cannon manufacturing facility in the United States. The City of Watervliet is situated near the eastern boundary of Albany County, New York, on the West Bank of the Hudson River, approximately four miles south-southwest of the confluence of the Mohawk and Hudson Rivers. The Arsenal consists of two contiguous areas that comprise a total land area of 140 acres. The main process area of the Arsenal is a 125-acre tract on

which manufacturing and administration operations occur. The second area is a 15-acre tract known as the Siberia Area. The Siberia Area was purchased by the Arsenal in May of 1942.

The Siberia Area is used as a shipping yard and for the interim storage of raw and hazardous materials, finished goods and supplies. The surrounding properties are residential and industrial, including an abandoned plating facility, steel factories and an auto repair facility. Waste oil and heavy metals (primarily chromium, lead and arsenic) have been identified as the primary contaminants in the soil in the Siberia Area. A major source of the waste oil contamination may have been the handling of waste metal chips, which were saturated with cutting oils (RCRA RFI Report, August 1996). Waste oil was also reportedly used to control dust within the Siberia Area. It is believed that the chromium contamination located in the northeastern section of the Siberia Area, is attributable to the off-post Perfection Plating facility.

2.0 RADIO-LABELED PHENANTHRENE MICROCOSM STUDY

2.1 OVERVIEW

The objective of the microcosm Phenanthrene study was to validate the existence of indigenous PAH and TPH mineralizing organisms in soil at the Siberia Area. To accomplish this, a radiotracer microcosm study was conducted using 14C-phenanthrene as a representative PAH.

Phenanthrene is a three-ring PAH, which is commonly used to assess overall PAH biodegradability at a site due to its relative recalcitrance, low vapor pressure, and ease of commercial acquisition. Although PAHs with a higher molecular weight are likely to behave differently with respect to degradation (e.g., slower or possibly not at all), it is assumed that microorganisms with the ability to degrade phenanathrene will have the capability to degrade PAH s with molecular weights both higher and lower than phenanthrene. This assumption is based on past experience with PAH biological degradation. Due to the costs associated with this work, it is not fiscally reasonable to perform multiple studies with radiolabled compounds of different molecular weights. Use of higher molecular weight compounds with significantly slower degradation rates may provide a false negrative during a relatively short incubation test. Therefore as a compromise, phenanthrene is chosen to represent relatively recalcitrant PAHs.

Soil was collected for the study on 3 June 1998, sieved to remove the rock/debris fraction, and stored in tightly sealed mason jars at $4^{o}C$ until used.

2.2 EXPERIMENTAL DESIGN

A ^{14}C-phenanthrene study was completed to validate the existence of indigenous microorganisms capable of degrading PAH and TPH in contaminated soil from the Siberia Area. To accomplish this task, five experimental treatments were assessed and analyzed in triplicate at four time intervals. The treatments evaluated are listed in Table 2 below.

Table 2: ^{14}C-Experimental Treatments

Treatment	Amendment
Anaerobic + NO_3	620-ppm NO_3^-
Anaerobic + NO_3 + Nutrients	620-ppm NO_3^-, 870-ppm PO_4^{3+}, 270-ppm NH_4^+
Anaerobic (live control)	Water
Anaerobic (sterilized control)	500-ppm $HgCl_2$, 500-ppm NaN_3
Aerobic + Nutrients	870-ppm PO_4^{3+}, 270-ppm NH_4^+

2.3 METHODS AND MATERIALS

Collected soil samples were initially passed through a 6.3-mm (1/4-in) sieve to remove large rocks and debris. Twenty-five (25) gram portions of soil (dry wt) were added to160-mL serum bottles. Microcosm flasks are shown in Figure 1.

Figure 1: Five Microcosm Radiotracer Bottles

The soil samples were amended with 10 uL of radiolabeled phenanthrene (9-^{14}C; Sigma) dissolved in dichloromethane. The solution contained 1.25-ug ^{14}C-phenanthrene/uL and exhibited 30,000 disintegrations per minute (dpm)/uL. Soft beta emissions are measured as dpm. 24,000 dpm are associated with each ug of ^{14}C-phenanthrene. This resulted in a final soil concentration of 500-ug ^{14}C-phenanthrene/kg soil (dry wt), and the total radiolabel added to each bottle was 300,000 dpm.

The nutrient amendments included 1 mL of a solution containing 19.2 mg/mL $(NH_4)_2HPO_4$ and 9.6 mg/mL $(NH_4)H_2PO_4$, which provided approximately 1000-ug PO_4^{3-} and 270-ug NH_4^+/g soil. Killed controls were amended with 0.5 mL of a solution containing 23.6-mg/mL $HgCl_2$ and 0.5 mL of a 25.0-mg/mL solution of NaN_3 and maintained under anoxic conditions. The final soil moisture in all samples was approximately 80 percent of field capacity. After all additions were made, the bottles were sealed using Teflon™ septa and aluminum crimp caps. Microcosms were incubated at room temperature in the dark.

A sparging-train system (Figure 2) was used to collect volatile radiolabeled products from the soil microcosms including volatile organic metabolites and CO_2. Six scintillation vials were connected in series as traps using Teflon™ tubing inserted through the caps of consecutive vials. The first and fourth vials in the series were empty and served as back-flow traps. The second and third vials contained a universal scintillation fluid (Liquiscint™; National Diagnostics) that traps volatile organic compounds, but not CO_2. The fifth and sixth vials contained a phenethylamine-containing scintillation fluid (^{14}C-Oxosol™; National Diagnostics) that specifically traps CO_2. One end of each Teflon™ tube was extended into the headspace volume of the upstream vial, and the other end was extended down into the scintillation fluid of the downstream vial (or into the headspace for the back-flow traps). Two 20-gauge needles were pushed through the septa in each sample bottle prior to sampling. To collect volatile compounds in the headspace, a positive pressure gas line was attached to one of the needles in the septum and the other needle was connected to the sparging train. Air was used to flush the headspace of aerobic bottles, and nitrogen was used to flush the headspace of anaerobic and sterile control bottles. The headspace gas was flushed for 12 minutes. The resultant gas stream pushes gaseous CO_2 and any other radiolabeled volatiles produced in the soil into the scintillation trapping fluids. In the case of the aerobic bottles, the air replenishes the oxygen supply.

The radioactivity in all trapping vials was counted using a Pharmacia LKB 1209 Rackbeta liquid scintillation counter to quantify the radioactivity vented from each sample. Standard deviations were developed from the analysis of scintillation cocktail from three replicate microcosms for each condition investigated.

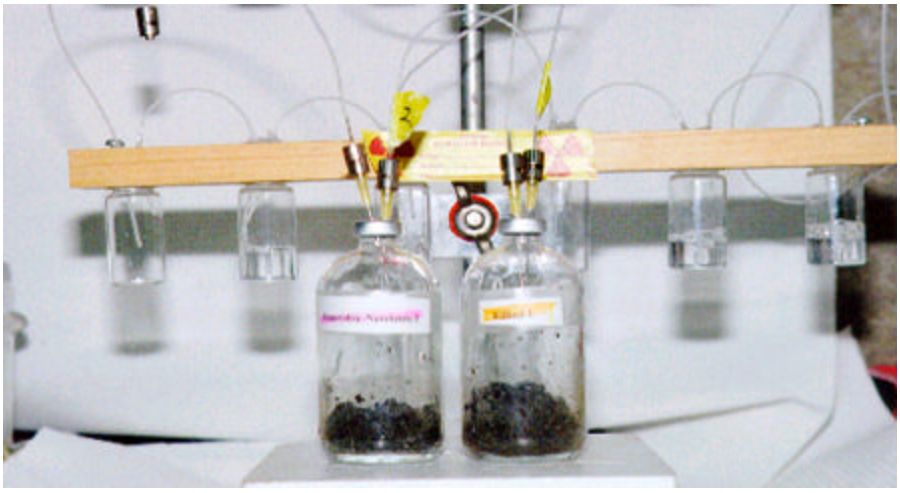
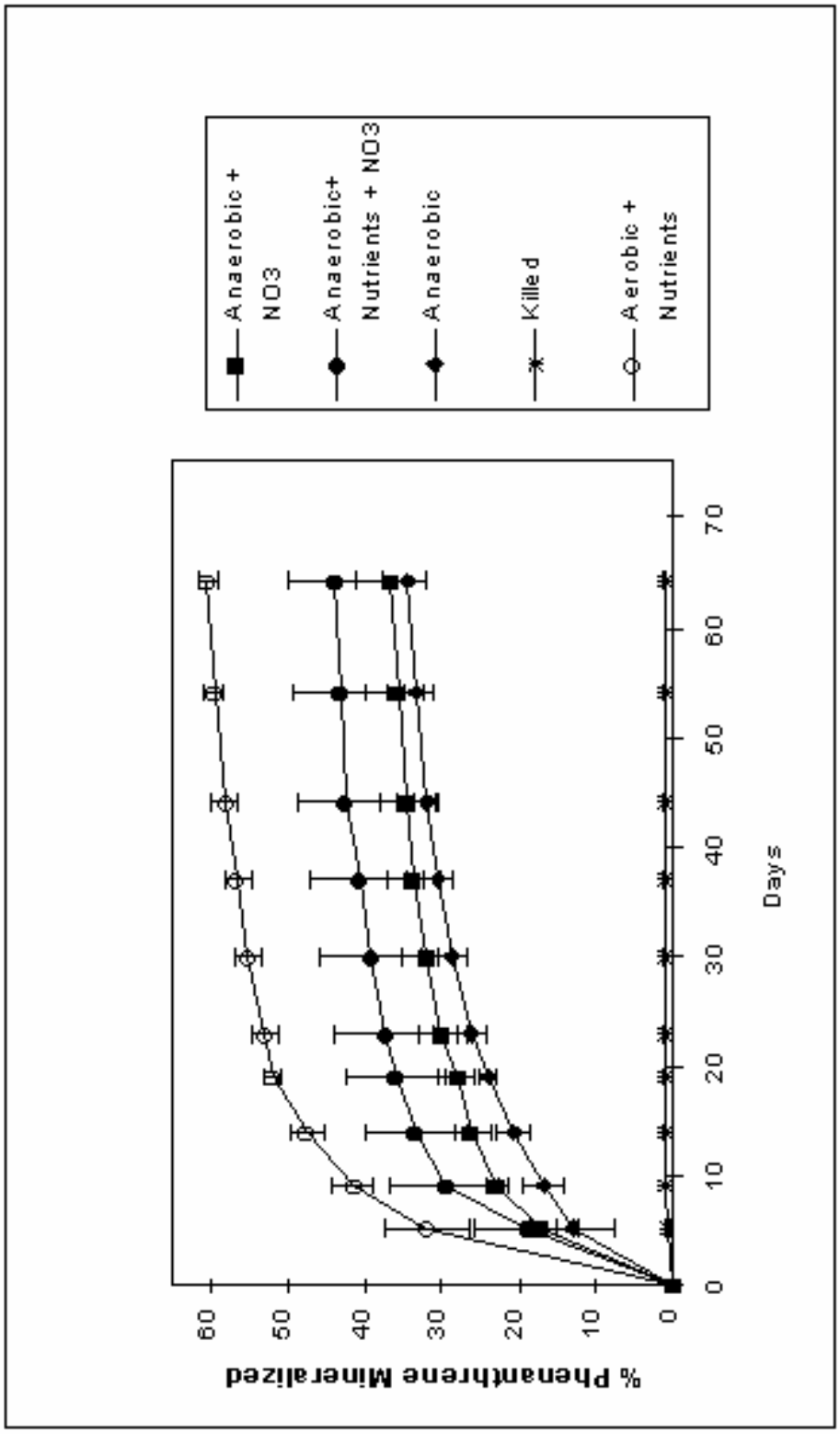


Figure 2: $^{14}CO_2$ Sparging-train System

2.4 RESULTS AND DISCUSSION

The most rapid and extensive mineralization of phenanthrene occurred in aerobic samples + nutrients. More than 30 percent of the added phenanthrene was mineralized within five days and greater than 60 percent was collected as $^{14}CO_2$ by 64 days (Figure 3).



Cumulative % (± standard deviation) of total radioactivity recovered as CO_2.
Standard deviations developed from analysis of three replicate flasks for each condition.

Figure 3: Microcosm Radio-tracer Results

Mineralization of phenanthrene was also observed in all anaerobic samples except for killed controls. More than 13 percent of the added phenanthrene was detected as $^{14}CO_2$ within five days in all anaerobic treatments. After 64 days, 34, 37, and 44 percent of added phenanthrene was collected as $^{14}CO_2$ in anaerobic samples amended with water, nitrate, and nitrate + nutrients, respectively. The addition of nutrients and/or nitrate at day 15 to some samples did not appreciably stimulate mineralization in aerobic or anaerobic samples. Less than one percent of the initial radiolabel was collected as $^{14}CO_2$ in the killed controls. The rapid and extensive mineralization in these initial evaluations suggests that PAH-mineralizing bacteria are present and active in soil samples at this site.

2.5 CONCLUSIONS FROM RADIO-LABELED MICROCOSM EVALUATION

The ^{14}C-Phenanthrene microcosm evaluation results supports the following conclusions:

- aerobic and anaerobic PAH degraders are present at the Site,
- rapid initial biodegradation rates in aerobic and anaerobic samples suggests both processes may be useful for bioremediation,
- and the greater extent of mineralization in aerobic compared to anaerobic samples suggests that the aerobic process is more efficient.

3.0 PAH DEGRADING BACTERIA ISOLATION

3.1 OVERVIEW

An experiment was conducted to isolate bacteria capable of aerobic and/or anaerobic mineralization of PAHs from Watervliet Arsenal soils. This experiment was performed to provide supporting evidence for aerobic and anaerobic PAH biodegradation in contaminated soils from the Arsenal. The study was designed to show that PAH-degrading bacteria are naturally present in contaminated soil from the site.

3.2 EXPERIMENTAL METHODS

3.2.1 Aerobic Enrichments

Aerobic and anaerobic enrichment media was prepared. The media for aerobic enrichments consisted of autoclaved basal salts medium (BSM: Hareland, 1979) amended with 0.025 percent casamino acids (Difco). The media was pipetted in 30-mL volumes to sterile 160-mL serum bottles fitted with foam stoppers and covered with aluminum foil. Each bottle then received solid phenanthrene that had previously been recrystalized from 100 percent ethanol so that excess solid phenanthrene was present. One bottle was initially amended with approximately 1 g of soil from the Siberia Area. The same soil was used for the subsequent pan studies (see Section 7.0). The serum bottle was shaken at 100 rpm at room temperature until growth was observed (approximately two weeks), then a small volume of liquid (50 ? L) was transferred to a fresh bottle containing BSM, casamino acids, and crystalline phenanthrene. This bottle was then incubated for two weeks, and a small volume transferred to fresh media. This “enrichment” procedure, which is designed to select phenanthrene-degrading bacteria from the soil, was repeated several times in succession. After the sixth transfer the enrichment was tested for the presence of phenanthrene-degrading bacteria using ^{14}C-phenanthrene (see Section 3.2.3).

3.2.2 Anaerobic Enrichments

Anaerobic enrichments were prepared to isolate denitrifying and sulfate-reducing bacteria capable of phenanthrene degradation from the Watervliet soil. The anaerobic medium consisted of a modified BSM recipe, which included additional trace metals, 1.0 g/L yeast extract and 1.0 g/L casamino acids. The media was boiled and purged with nitrogen gas for 30 minutes to remove oxygen, then transferred to a Coy Environmental Chamber (anaerobic chamber). Forty–five milliliter volumes of the media were transferred to 50-mL serum bottles within the chamber, then the bottles were sealed with Teflon-lined septa and crimp sealed. All bottles were then autoclaved for 45 minutes. Prior to adding soil, phenanthrene crystals were added to two sample bottles. One bottle was then amended with KNO_3 to provide a final nitrate level of 1 g per L of media, and a second bottle received $NaSO_4$ to yield 2.0 g sulfate per L of media. The samples amended with sulfate also received cysteine to scavenge any residual oxygen and resazurin as an indicator of reduction potential in the sample. Approximately 1 g of soil from the Watervliet site was added to each bottle of enrichment media in the Coy chamber, then the bottles were closed with Teflon-lined septa, crimp-sealed, and placed sideways on a shaker operating at 100 rpm. After one month of incubation, a small volume of liquid from each bottle (sulfate, nitrate) was transferred to fresh media in the Coy Chamber. This procedure was repeated a total of three times, then each enrichment was tested for the presence of phenanthrene-degrading bacteria using ^{14}C-phenanthrene.

3.2.3 ^{14}C-Phenanthrene Assay

Enrichment samples that became turbid during successive transfers (indicating bacterial growth) were tested for the presence of phenanthrene-degrading cultures. To conduct this assay, 15 mL of sterile enrichment medium was pipetted into several 25-mL serum bottles. The medium was amended with ^{14}C-phenanthrene to a final aqueous concentration of 1 ppm. Samples were then inoculated with 0.5 mL of sample from one of the positive enrichments. A sterile Durham tube (small test tube) containing 0.4 mL of 0.5-N NaOH was placed upright within each sample bottle, and the bottles were placed on a rotary shaker operating at 100 rpm. The base solution within the tube was used as a trap for any $^{14}CO_2$ produced by microbial mineralization of ^{14}C-phenanthrene. The aerobic enrichment was prepared with air in the bottle headspace and the anaerobic

enrichments were prepared in the Coy Environmental Chamber with a headspace of N_2. The presence of $^{14}CO_2$ in the samples during incubation was determined by periodically removing the NaOH within each trap and determining the quantity of radioactivity present by liquid scintillation counting.

3.3 RESULTS AND DISCUSSION

The aerobic enrichment was observed to rapidly become turbid during transfers to fresh media. After a short incubation time, free phenanthrene crystals in solution appeared to become coated with a yellow film of bacterial biomass. Microscopic evaluation at 1000 X magnification showed the biomass surrounding the crystals to consist primarily of a Gram-negative, cocci-shaped bacterium which occurred as single cells and in chains. The aerobic enrichment was observed to rapidly mineralize ^{14}C-phenanthrene to CO_2. After only two days of incubation, more than 43 percent of the phenanthrene present in solution was mineralized. After eight days, approximately 47 percent of the initial phenanthrene had been collected as CO_2. By comparison, less than three percent of the phenanthrene present in the uninoculated control sample was collected as CO_2 during the eight-day experiment.

The anaerobic enrichment amended with nitrate to stimulate denitrifying bacteria also became turbid after transfers to fresh media, suggesting that bacterial growth on phenanthrene was occurring. However, the production of CO_2 from ^{14}C-phenanthrene by this enrichment was not observed, even after more than three weeks of incubation (data not shown). Interestingly, the samples amended with nitrate became turbid during the mineralization assay, suggesting bacterial growth, but CO_2 was not detected. It is possible that denitrifying strains were partially degrading phenanthrene, resulting in microbial growth without CO_2 production. Anaerobic samples amended with sulfate became slightly turbid during incubation; however, as with the nitrate-amended samples CO_2 was not detected during the mineralization assay.

3.4 CONCLUSIONS FROM MICROBIAL ISOLATION EVALUATION

An aerobic enrichment capable of the rapid mineralization of phenanthrene was isolated from Watervliet Arsenal soil during this study. This enrichment consists primarily of a Gram-negative bacterium that attaches to phenanthrene during growth on the PAH. The culture was not identified further. The enrichment of this bacterium shows the existence of aerobic PAH-degrading bacteria within contaminated soils at the Watervliet Arsenal Site. These data support results from the pan, bioslurry, and column studies, where appreciable losses of PAHs were observed, presumably due to biodegradation.

Denitrifying or sulfate-reducing cultures capable of mineralizing ^{14}C-phenanthrene were not obtained during this study. This finding may mean that such bacteria do not exist in high numbers in Watervliet soils. However, anaerobic bacteria of this type tend to be difficult to enrich and culture. Therefore, it is possible that these bacteria are present at the Watervliet site, but that the enrichment media and techniques used during this study did not favor their growth.

4.0 BIOSLURRY EVALUATIONS NO.1

4.1 OVERVIEW

Aerobic and anaerobic bioslurry studies (Figure 4) were conducted to assess the rate and extent of TPH, in particular PAHs, degradation in contaminated water and soil from the Siberia Area within the time frame of these tests. However, T = 0 sample analysis revealed that PAH levels were below detection limits in the slurries. Slurry samples resubmitted for analysis using a procedure to reduce detection limits (concentrating extracts to reduce limits about 10-fold) still revealed PAH levels below detection.

Despite the lack of relevant PAH data, the bioslurry tests were continued focusing on degradation of TPH in saturated slurry conditions. However, a second bioslurry evaluation was conducted with a different soil, which did contain PAHs. This test is described in Section 5.0.

4.2 EXPERIMENTAL DESIGN

Sieved soil (15 g dry wt) from the Siberia Area was weighed into 125-mL serum bottles either in an anaerobic chamber (anaerobic treatments) or under aerobic conditions (aerobic treatment). The anaerobic bottles were then amended with 75 mL of one of the following solutions and crimp sealed:

- Reduced Anaerobic Medium (RAM) + nitrate (5 mM) - 6 bottles
- Anaerobic distilled water (no treatment) - 9 bottles
- Anaerobic distilled water + nitrate (5 mM) - 6 bottles
- RAM + nitrate (5 mM) + $HgCl_2$ (killed) - 6 bottles

The aerobic treatments for this study consisted of the addition of 75 mL of the following solutions:

- Basal Salts Medium (BSM) - 6 bottles
- BSM + H_2SO_4 (acid-killed) - 6 bottles

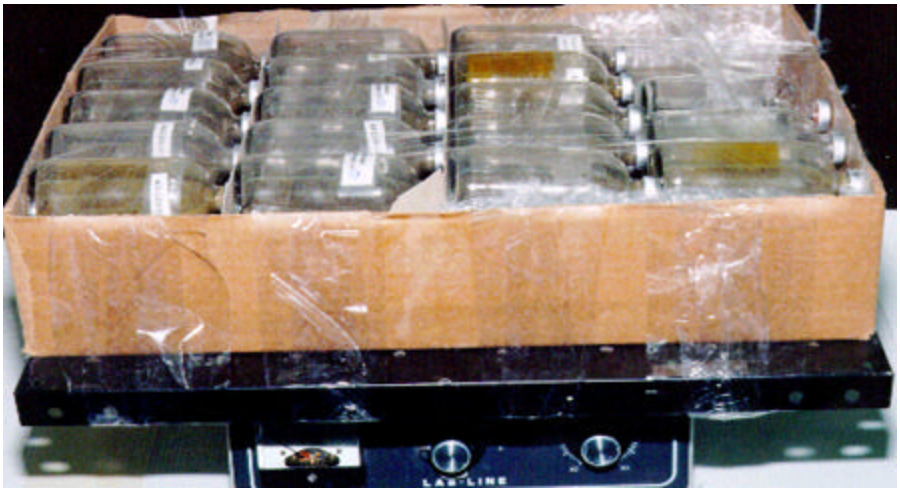


Figure 4: Soil Slurry Mixing

Three replicates, prepared as anaerobic distilled water (no treatment), were sacrificed at the initiation of the study for analysis to estimate the initial concentrations of contaminants in all bottles. Three replicates from each condition were sacrificed after six and 12 weeks of treatment for analysis of contaminants and nitrate where appropriate.

4.3 METHODS AND MATERIALS

All samples were sealed with Teflon stoppers, placed on a shaker operating at 125 rpm, and maintained at 23^{o}C in the dark. The aerobic samples and acid-killed controls were periodically (every two to three weeks) flushed with pure oxygen for one minute to insure that aerobic conditions were maintained. After six and 12 weeks of incubation, samples were killed using both mercuric chloride and sodium azide. The six-week samples were stored at 4^{o}C pending decisions on analysis (PAH and/or TPH). All samples were analyzed for TPH immediately after taking the 12-week samples. In addition, some of the anaerobic samples were submitted for analysis of nitrate.

4.4 RESULTS AND DISCUSSION

The TPH levels in the aerobic and anaerobic samples showed a steady pattern of decline from the original levels (Table 3). However, there was reasonable variability among replicate samples and the "killed" control samples also showed a similar decline

in TPH levels. The TPH loss in the acid and mercuric chloride controls most likely results from residual biological activity. Stopping all biological activity in heavily contaminated samples is difficult, particularly when the samples cannot be autoclaved due to potential loss of contaminants.

Table 3: TPH Results from Bioslurry Evaluation No. 1

Treatment	TPH - 0 Weeks (mg/L)		TPH - 6 Weeks (mg/L)		TPH-12 Weeks (mg/L)	
	Mean	SD	Mean	SD	Mean	SD
Aerobic+ Nutrients	2,250	636	1092	224	862	174
Anaerobic	2,250	636	1513	367	851	110
Anaerobic + NO_3^-	2,250	636	1240	82	1040	64
Anaerobic + NO_3^- + Nutrients	2,250	636	1298	182	814	158
Acid Killed	2,250	636	1537	297	972	171
$HgCl_2$ Killed	2,250	636	1290	112	771	118

Standard deviations were developed from the analysis of separate samples from three replicate bottles.

Nitrate screening in anaerobic flasks indicated there was no significant denitrification (Table 4).

Table 4: NO_3^- Results from Bioslurry Evaluation No. 1

Treatment	NO_3^- at 6 Weeks (mg/L)		NO_3^- at 12 Weeks (mg/L)	
	Mean	SD	Mean	SD
Aerobic+ Nutrients	NA	NA	NA	NA
Anaerobic	NA	NA	NA	NA
Anaerobic + NO_3^-	168	11	101	12
Anaerobic + NO_3^- + Nutrients	513	25	455	51
Acid Killed	NA	NA	NA	NA
$HgCl_2$ Killed	NA	NA	484	0

Standard deviations were developed from the analysis of separate samples from three replicate bottles.

4.5 CONCLUSIONS FROM BIOSLURRY EVALUATION NO. 1

From evaluation of the soil slurries, the following conclusions can be drawn:

- TPH concentrations declined in all treatments,
- average TPH reduction for all treatment was approximately 60 percent from the initial value of 2,250 mg/L,
- TPH loss due to volatilization was unlikely from the sealed system,
- sterile controls likely were not "killed",
- aerobic treatment may have been hindered by poor diffusion of oxygen,
- degradation rates slower than those in the study should be expected at temperatures below the test temperature of 23°C.

5.0 BIOSLURRY EVALUATIONS NO. 2

5.1 OVERVIEW

Because no PAHs were found in soils used for the initial bioslurry evaluation, a second set of aerobic and anaerobic bioslurry studies were conducted to assess the rate and extent of TPH, in particular PAHs, degradation in contaminated soil from the Siberia Area within the time frame of these tests. The soil from a second sampling event was used in this experiment. This soil was was collected from a location (see Section 7.2.1) at which soils with higher initial PAH levels were found. The objective of this bioslurry test was to evaluate PAH and TPH biodegradation under aerobic and anaerobic conditions.

5.2 EXPERIMENTAL DESIGN

Sieved soil (15-g dry wt) from the Siberia Area (drum PS-02) was weighed into sterile 160-mL serum bottles either in an anaerobic chamber (anaerobic treatments) or under aerobic conditions (aerobic treatment). The anaerobic bottles were then amended with 60 mL of one of the following solutions and crimp sealed with Teflon-lined septa:

- Anaerobic water (no treatment) - 9 bottles
- Anaerobic water + nitrate (50 mM) + inorganic nutrients (N + P) (denitrifying conditions) - 6 bottles
- Anaerobic water + sulfate (350 mM) + sodium sulfide (2 mM) + inorganic nutrients (N + P) (sulfate-reducing conditions) - 6 bottles
- Anaerobic water + NaN_3 (1000 ppm)+ $HgCl_2$ (1000 ppm) (killed control) – 6 bottles

The anaerobic treatments were designed to evaluate PAH and TPH degradation with: (1) no addition of nutrients or electron acceptors, (2) under denitrifying conditions (nitrate added for stimulation of PAH and TPH degraders capable of using nitrate as an electron acceptor), and (3) under sulfate-reducing conditions (sulfate added for

stimulation of PAH and TPH degraders capable of using sulfate as an electron acceptor). Sodium sulfide was added to the sulfate-reducing samples to lower the redox value to conditions favored by this class of bacteria. In addition, resazurin (a colorimetric redox indicator) was added to all anaerobic samples to ensure that anaerobic conditions were maintained. Controls were prepared with the microbial inhibitors mercuric chloride and sodium azide.

The aerobic treatments for this study consisted of the addition of 60 mL of the following solutions:

- Aerobic water + nutrients (N + P) - 6 bottles
- Aerobic water + NaN3 (1000 ppm)+ HgCl2 (1000 ppm) (killed control) – 6 bottles

The aerobic treatment was designed to evaluate the aerobic degradation of PAHs and TPH with the addition of inorganic nutrients.

Three replicates, prepared as anaerobic distilled water (no treatment), were sacrificed at the initiation of the study for analysis to estimate the initial concentrations of contaminants in all bottles. Three replicates from each condition were sacrificed after six and 12 weeks of treatment for analysis of contaminants.

5.3 METHODS AND MATERIALS

All samples were sealed with Teflon stoppers, placed on a shaker operating at 150 rpm, and maintained at 23^{o}C in the dark. The aerobic samples and killed controls were flushed with pure oxygen for 30 seconds every seven days to insure that aerobic conditions were maintained. Three bottles from the anaerobic (*no treatment*) group were submitted for PAH and TPH analysis immediately after preparation (T = 0). After six and 14 weeks of incubation, triplicate samples from each treatment were treated with both mercuric chloride and sodium azide as microbial inhibitors. These samples were then submitted for PAH and TPH analysis.

5.4 RESULTS AND DISUCSSION

The initial PAH levels in the slurries were 10,200 ± 2,200 ug/L (Table 5) and the TPH levels were 1900 ± 120 mg/L (Table 6). Both the PAH and TPH levels in the aerobic slurries + nutrients showed a marked decline during 14 weeks of incubation. The total PAHs declined by more than 90 percent and TPH levels fell by more than 85 percent. The PAH levels in the various anaerobic treatments also declined significantly, by 75 percent or more in the various treatments. In the best anaerobic treatment (anaerobic + sulfate), however, approximately twice the amount of total PAHs remained as observed in the aerobic samples. The TPH levels also declined by 65 percent or more in the various anaerobic samples. As observed for the PAHs, declines in TPH were greater in the aerobic than the anaerobic samples. A decline in the PAH and TPH values occurred in the "killed" control samples, as was observed in the initial bioslurry evaluation. Although these samples were treated with both mercuric chloride and sodium azide as microbial inhibitors, losses of the target contaminants in these samples were most likely again due to biological activity.

Table 5: PAH Results from Second Bioslurry Evaluation No.2

Treatment	**PAH - 0 Weeks (ug/L)**		**PAH - 6 Weeks (ug/L)**		**PAH-14 Weeks (ug/L)**	
	Mean	SD	Mean	SD	Mean	SD
Aerobic + Nutrients	10,200	2200	2100	750	830	430
Anaerobic (No Treatment)	10,200	2200	6100	580	1900	350
Anaerobic + NO_3^- + Nutrients	10,200	2200	4600	1500	2200	760
Anaerobic + SO_4^- + Nutrients	10,200	2200	2100	1000	1600	680
Anaerobic Killed	10,200	2200	3900	1000	2700	1600
Aerobic Killed	10,200	2200	2800	1300	1600	415

Standard deviations were developed from the analysis of separate samples from three replicate bottles.

Table 6: TPH Results from Second Bioslurry Evaluation No.2

Treatment	TPH - 0 Weeks (mg/L)		TPH - 6 Weeks (mg/L)		TPH-14 Weeks (mg/L)	
	Mean	SD	Mean	SD	Mean	SD
Aerobic + Nutrients	1,900	120	610	170	270	100
Anaerobic (No Treatment)	1,900	120	1300	170	480	80
Anaerobic + NO_3^- + Nutrients	1,900	120	980	200	510	170
Anaerobic + SO_4^- + Nutrients	1,900	120	480	210	630	150
Anaerobic Killed	1,900	120	1700	1400	600	170
Aerobic Killed	1,900	120	840	250	430	130

Standard deviations were developed from the analysis of separate samples from three replicate bottles.

5.5 CONCLUSIONS FROM BIOSLURRY EVALUATION NO. 2

From evaluation of the second soil slurries, the following conclusions can be drawn:

- PAH and TPH concentrations declined appreciably in all treatments, but the greatest losses were observed in aerobic samples amended with nutrients;
- PAH levels were reduced >90percent in the aerobic slurry with nutrients from an initial level of 10.2 mg/L during the 14-week incubation;
- TPH levels were reduced 85percent in the aerobic slurry with nutrients from an initial level of 1,900 mg/L during the 14-week incubation;
- TPH or PAH losses due to volatilization is unlikely from the sealed system;
- sterile controls likely were not completely "killed" by the inhibitors added; biological activity resulted in losses of target contaminants in controls,
- degradation rates slower than those in the study should be expected at temperatures below the test temperature of 23°C.

6.0 SOIL-COLUMN EVALUATION

6.1 OVERVIEW

Malcolm Pirnie performed a bench-scale biotreatability study on soils contaminated with total petroleum hydrocarbons (TPH) and polynuclear aromatic hydrocarbons (PAHs) from the Siberia Area. These biotreatability tests support efforts to evaluate in-situ bioremediation as a corrective measure for contaminated soils in the Siberia Area and serve as a basis for the follow-on larger pan-scale evaluations.

Soil-column studies provide the necessary basis for a successful field demonstration and enable evaluators to determine the optimal parameters that enhance biodegradation. Column studies are usually preceded by microcosm bench studies (conducted earlier by Malcolm Pirnie). In many cases, larger-scale pan studies follow column evaluation to provide for appropriate modeling of full-scale mixing parameters and provide sufficient treated material for toxicity and bioaccumulation analysis.

The aerobic soil-column experiments were conducted at Malcolm Pirnie's Environmental Technology Laboratory in Monsey, New York in accordance with the Corrective Measures Study (CMS) Work Plan For Bench-Scale Treatability Tests Siberia Area, Watervliet Arsenal, New York, June 1997. The purpose of this work was to assess the ability of indigenous microorganisms to degrade petroleum hydrocarbons and PAHs in soil through the addition of nutrients and aeration in a soil column designed to mimic the conditions found in the subsurface at the Siberia Area. The specific objectives of the treatability study were as follows:

- determine if the indigenous microorganisms can biodegrade 50 percent of the TPH present in the soil used for the study,
- determine if the indigenous microorganisms can biodegrade the PAHs present in the soil used for the study,
- determine the rates of biodegradation for PAHs and TPH.

6.2 EXPERIMENTAL DESIGN

To accomplish these objectives, four columns were evaluated to determine the effects of mixing, nutrients, and moisture on simulated field remediation. Table 7 shows the experimental design.

Table 7: Column Evaluation Parameters

Columns	Parameters
Control A	Mixing, No Nutrients, Moisture
Control B	No Mixing, No Nutrients, Moisture
Treatment A	Mixing, Nutrients, Moisture
Treatment B	Mixing, Nutrients, Moisture

Treatment A and Treatment B were conducted as duplicates of the same treatment. Their overall performance was compared against two different controls, which represented alternative degrees of passive remediation.

6.3 METHODS AND MATERIALS

6.3.1 Soil Collection, Transport

Soil samples were collected in the vicinity of MW-32. These soils were considered to be representative of the typical PAH and TPH concentration at the site as outlined in Section 3.2 of the Corrective Measures Study (CMS) Work Plan for Bench-Scale Treatability Tests Siberia Area (June 1997). Site characterization data from the RFI and the site investigations (ESE, 1991) indicate the average total PAH for shallow soil (0 to 2 feet) is approximately 31 ppm. The average TPH in the shallow soil (0 to 3 feet) is approximately 2,000 ppm.

A clean backhoe was used to break the surface and expose contaminated soil down to three feet. Hand operated sampling tools were used to immediately collect the samples. The samples were placed in plastic sampling containers and completely filled to minimize headspace. Samples were maintained at 4°C and shipped within 24 hours to Malcolm Pirnie's Environmental Technology Laboratory in Monsey, New York. During transport and storage, samples were protected from sunlight and temperature extremes.

6.3.2 Initial Characterization and Storage

Once soil samples were received in the laboratory, they were homogenized by mixing the contents of the sample containers into a plastic cooler with stainless steel scoops. Both the cooler and utensils were cleaned with acetone, rinsed with deionized (DI) water, cleaned with 10 percent HCl, then rinsed again with DI water before use. Soil was mixed for approximately 10 minutes. Sieving through a 2-mm screen proved impractical, as clumping occurred when attempts were made to pass soil through the sieve. Soil was homogenized manually; noticeable rocks and roots were removed during this process. Soil weight (minus cooler) was 29.6 kg. Figure 5 shows an example of the debris that was separated from the soil.

Figure 5: Soil Sample from Vicinity MW-32

Although mixing may have resulted in some volitalization of TPH, the major focus of the treatability study was recalcitrant PAHs. TPHs were demonstrated to biodegrade quite readily in the previous soil slurry and column evaluations; therefore, their presence as a cometabolite is of particular significance. If PAHs biodegrade at acceptable rates and to agreeable clean-up levels, much of the TPHs present will likely be consumed as the initial energy source for microbial activity. Recalcitrant PAHs will not volatilize at any appreciable level. Mixing was considered complete when visual homogeneity had been attained. The soil was stored at 4°C until subsampled for the initial analysis or used in the biodegradation studies. The homogenized soil samples

were analyzed as described in Table 8 below. A single analysis was conducted for each parameter.

Table 8: Parameters and Methods for Initial Analyses

Parameters	Extraction Method	Analysis Method
PAH	SW 3540C	SW8270C
TPH	SW 3540C	SW 8015B
TOC (total organic carbon)	Water	EPA 415.1
Ammonia-Nitrogen	Water	EPA 350.1 modified
Nitrate-Nitrogen	Water	EPA 353.1 modified
Ortho-Phosphate	Water	EPA 365.3 modified

Table 9 summarizes the initial chemical analysis (8 Sept 97) for TPH and PAHs for the collected soil samples (vicinity MW-32) and compares it with current TAGM clean-up levels. Initial values for TPH (1930 ppm) are comparable to the site average of 2,000 ppm. However, total PAHs (8 ppm) are considerably lower than site average of 31 ppm. This initial difference in total PAH concentrations could be attributed to a number of different factors. Soil at the Siberia Area has been shown (ESI, 1991) to possess significant heterogeneity both in contaminant concentrations and geotechnical make-up (debris). Limiting the initial characterization to single analysis could have reflected such heterogeneity. This in fact is the case, as additional soils obtained for PAH studies had significantly higher PAH concentrations. These additional samples were obtained from similar areas at the Siberia Area

In addition, natural attenuation could have contributed to lower values since the site characterization data is over seven years old. Natural physical, chemical, and biological processes could easily result in a loss of naphthalene and other less-recalcitrant PAHs. These two factors may account for the lower value for total PAHs. Comparison between the initial characterization values and TAGM levels reveals that most PAHs are already below clean-up standards. Although samples from a later PAH study showed higher PAH levels, most of the listed compounds were still well below the TAGM levels. Therefore, PAHs of concern were limited to benzo(a)anthracene, chrysene, benzo(a)pyrene, and dibenz(a,h)anthracene. These four specific PAHs were

present at low levels, but benzo(a)pyrene and dibenz(a,h)anthracene were still approximately an order of magnitude above TAGMs.

Table 9: Initial Analyses of Soil Used in Column Study

Parameters	Clean-up TAGM Levels (ppm)	InitialAnalysis (ppm)
Naphthalene	13	0.084
Acenaphthylene	41	0.13
Acenaphthene	50	0.083
Fluorene	50	0.1
Phenanthrene	50	0.55
Anthracene	50	0.28
Fluoranthrene	50	1
Pyrene	50	1.1
Benzo(a)anthracene	0.224	0.51
Chrysene	0.4	0.52
Benzo(b)fluoranthrene	1.1	1
Benzo(k)fluoranthene	1.1	0.39
Benzo(a)pyrene	0.061	0.71
Indeno(1,2,3-cd)pyrene	3.2	0.58
Dibenz(a,h)anthacene	0.014	0.14
Benzo(g,h,i)perylene	50	0.82
Total PAHs	N/A	8.00
TPH	N/A	1930

6.3.3 Soil Column Operation

The evaluation was run at room temperature (approximately 25°C) for almost nine months. Approximately 7.4 kg of homogenized soil was placed into each of four soil columns. The columns (designated as Control A, Control B, Treatment A, and Treatment B) were approximately 30 inches in height and 4 inches in diameter. Soil-gas sampling ports constructed of copper tubing were located at 6, 12 and 18 inches from the bottom of the columns. Soil gas was analyzed for O_2, CO_2, and VOCs. Soil was added to each column to an initial height of 24 inches. The columns were loosely covered during the test to minimize loss of vapor and gas. An overall mass balance was not performed on the columns; however, the data from soil and gas sampling were used to

determine general trends with respect to biodegradation. Figure 6 shows the soil columns after loading.

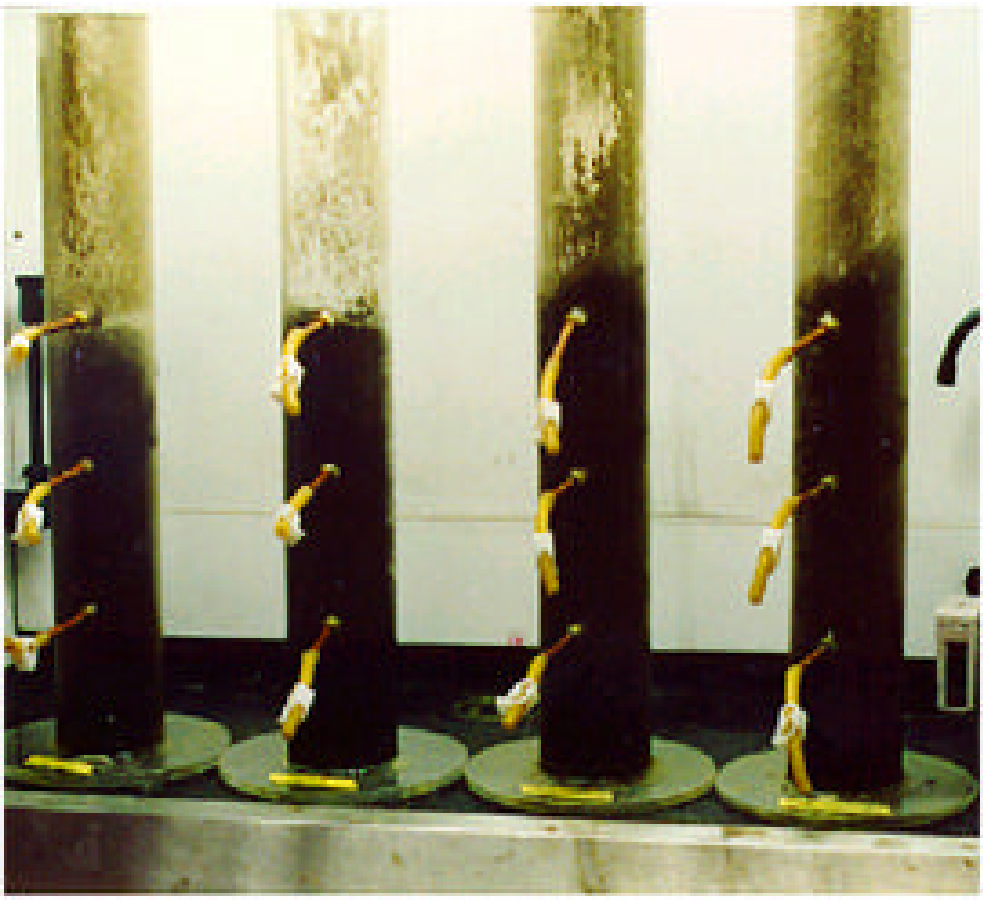


Figure 6: Loaded Soil Columns

The soil in Control A was mixed three times a week. In mixing, the column was inverted, emptying its contents into a plastic cooler; the sample was then manually mixed with stainless steel scoops. Control A received a moisture addition but no nutrient addition. Soil in Control B was not mixed, and received a moisture addition, but no nutrient addition.

Treatment A and Treatment B were duplicate treatments. Each was mixed three times a week and had nutrient and moisture supplements added. The specific amount of nutrients added was based on a sample, collected on 8 September 1997, which was analyzed for total organic carbon (TOC) by Envirotech Research, Inc. of Edison, NJ. The result indicated a TOC concentration of 19,600 mg/kg (dry weight). Based on this result, a nutrient and moisture supplement was calculated and added to Treatments A and B

resulting in a carbon to nitrogen to phosphorus ratio of 100:10:1. This ratio has generally been found to be a good starting point for enhancing biotreatment.

Amendments were added to the soil columns following the project work plan. Labile carbon was added in the form of $C_6H_{12}0_6$ (1.000 mg/kg soil = 14.8g). Nitrogen was added in the form of NH_4NO_3 (114.28 mg/kg soil = 1.69g). Phosphorus was added in the form of KH_2PO_4 (316.88 mg/kg soil = 4.69g) and K_2HPO_4 (158.34 mg/kg soil = 2.34g). All four columns were placed under a laboratory hood and kept at room temperature.

Soil gas measurements were made at 6, 12, and 18 inches from the bottom of the column. Eighteen inches was near the top of the soil in the columns. O_2 and CO_2 levels did not exhibit significant variation with depth in the soil columns. Initially, readings were taken every Monday before mixing. O_2 levels in Controls A and B were typically above 11 ppm. O_2 concentrations in Treatments A and B were initially lower (5 - 6 ppm), but after a few days had risen to levels typically above 10 ppm. To ensure aerobic conditions and good availability of O_2 as an electron acceptor, the soil was mixed any time O_2 levels fell below 10 ppm. CO_2 readings were discontinued after an initial period of time. CO_2 readings were typically in the 2-3 ppm range.

On 17 September 1997, when additional analytical results of the 8 September sample became available, a second nutrient supplement was added to both Treatments A and B while the soil in each was being mixed. 4.20 g of NH_4NO_3, 0.46g of KH_2PO_4 and 0.23g of K_2HPO_3 were dissolved in 307 mL of ASTM Type I water and added to Treatment A. 4.38g of NH_4NO_3, 0.48g of KH_2PO_4 and 0.24g of K_2HPO_4 were dissolved in 320 mL of ASTM Type I water and added to Treatment B.

Nutrient soil analyses were performed approximately every 10 days using a Hach NPK-1 soil analysis kit. Results of analysis with this kit (which is based on a colorimetric method) proved to have a relatively wide variance from observer to observer yet seemed consistent when used by one individual; accordingly this analysis was performed, when possible by the same person. The work schedule called for additional nutrient supplements if nitrogen and phosphorus analyses results indicated that levels of these substances had fallen below 25 percent of the prior added amount. Based on the colorimetric analyses and these criteria, additional nutrient supplements were not added.

Moisture levels were measured approximately every ten days. When levels were detected below 10 percent, additional ASTM Type I water was added to bring moisture content back up to above 10 percent. On 1 December 1997, it was decided to increase the optimum moisture level from 15 percent to 20 percent, and the action level from 10 percent to 15 percent; subsequent decisions on moisture additions were based on these criteria. These moisture levels are lower than those reported in the literature. Side experiments on the bench revealed that any moisture content above 20 percent resulted in a soup or "slurry-type" mix. Although these conditions would most likely have improved biodegradation, they were considered unrepresentative of typical land farming operations in the field.

6.3.4 Soil Column Sampling

Six sampling and analysis events were conducted for each column. The first three sampling events occurred approximately every month. The final three sampling events generally occurred every two months. PAHs were analyzed during every event. TPH was analyzed only during the last three sampling events. A summary of sampling events is shown in Table 10.

Table 10: Sample Event Schedule

Sampling Events	Date of Sampling Event	Parameters
1	9/8/97	PAHs/TPH/DRO
2	10/6/97	PAHs
3	11/20/97	PAHs
4	12/22/97	PAHs
5	2/23/98	PAHs/TPH/DRO
6	4/6/98	PAHs/TPH/DRO
7	6/3/98	PAHs/TPH/DRO

6.4 RESULTS AND DISCUSSION OF CONTAMINANT ANALYSIS

Hydrophobic (water-repelling) organic compounds (HOCs) such as PAHs have a high affinity for sorption onto soil particles and into soil aggregates. This characteristic limits the chemical, physical, and biological availability of the contaminant. Aggressive

mixing can help to reduce this mass transfer limitation by breaking down the soil aggregates and increasing the physical availability of the HOC. Therefore, the initial baseline concentrations may not represent the true concentration of HOCs present, but rather only a partial concentration, depending on how rigorous an extraction technique for analysis is used. In some cases, experiments have shown that the commonly used Soxlet extraction is effective in removing only 55 percent of the aged contaminant present in the sample (Sawhney et al., 1988). This is especially true when analyzing HOCs. It is not uncommon to see an initial increase in HOC concentrations in systems that have aggressive mixing (ALCOA, 1995, Talley et al., 1998). This initial increase in concentrations can occur over many months. Of course, as the availability of the HOC increases, so may its bioavailability. Increased contact between the water present in the soil and the HOC generally results in increased solubilization, resulting in increased bioavailability. Therefore, an initial increase in PAHs was expected for Treatments A and B and Control A.

Mixing also serves to enhance the transfer of oxygen (electron acceptors) within the soil while homogenizing the soil with respect to other contaminants (TPH) and amendments. Although TPHs are not highly hydrophobic like PAHs, they too can show increases in availability. The overall effect of mixing generally results in increased bioavailability and enhanced biodegradation. Observing biodegradation trends associated with the controls and treatments can provide critical information about assessing the potential success for engineered biotreatment.

Treatments A and B represent the level of engineered biotreatment associated with in-situ landfarming. In both columns, nutrients and moisture levels were maintained at conditions considered optimal. Aggressive mixing was also maintained (three times per week). Despite the potential for quantitative differences due to heterogeneity, the general mixing trends for Treatments A and B should be similar. Control A maintained mixing with appropriate moisture levels, but no nutrients were added. This column provided information as to whether nutrients were limiting the biodegradation activity. Control B provided no mixing or addition of amendments. In essence, Control B represents the effects of natural attenuation or intrinsic bioremediation. Since natural attenuation of TPH is well documented, biodegradation of TPH in Control B was expected.

The results from each sampling event were compared to the initial chemical analyses (8 September 1997) to assess general trends in biodegradation. Many concentrations for PAHs were at or below the analytical quantification limits. For values below the quantification limits (QL), the analytical laboratory extrapolated the calibration and estimated the actual analytical result. For values well below the QL, the value was determined to be non-detect (ND). In our estimation of biodegradation trends, QL/2 was used to represent ND. The results are summarized inFigure 7, Figure 8, and Figure 9.

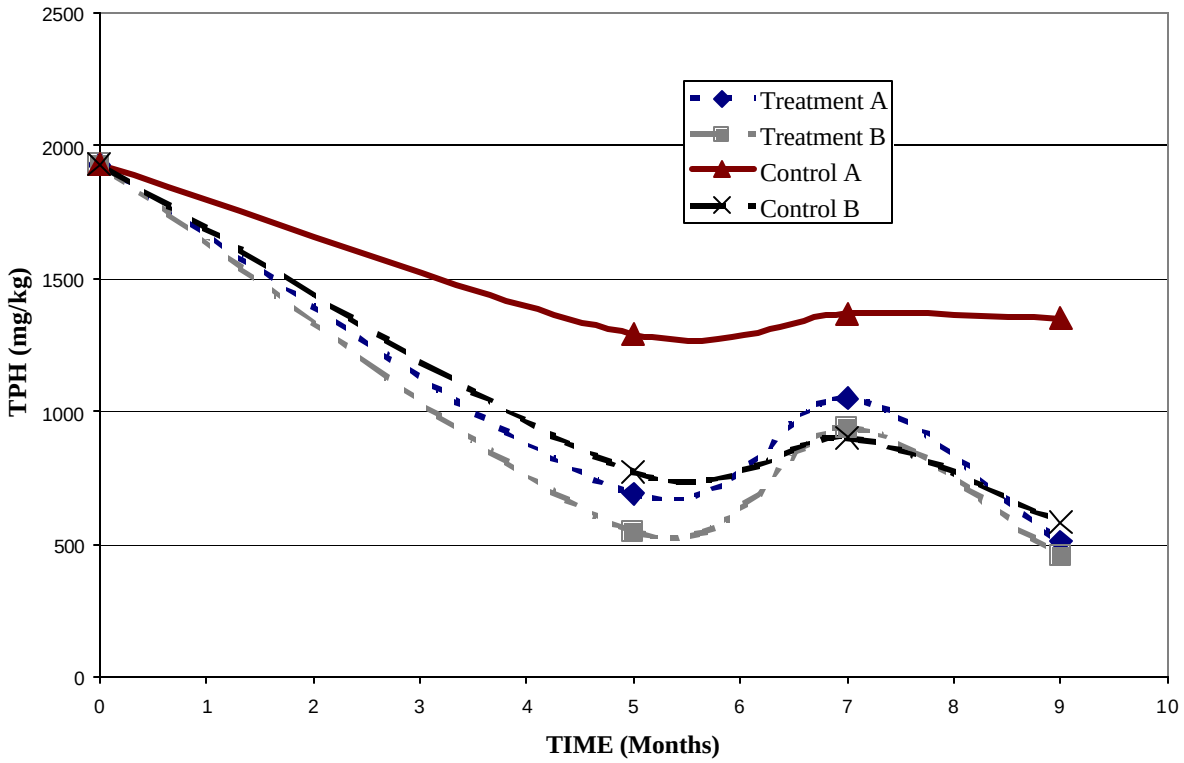


Figure7: TPH Results from Soil-column Evaluation

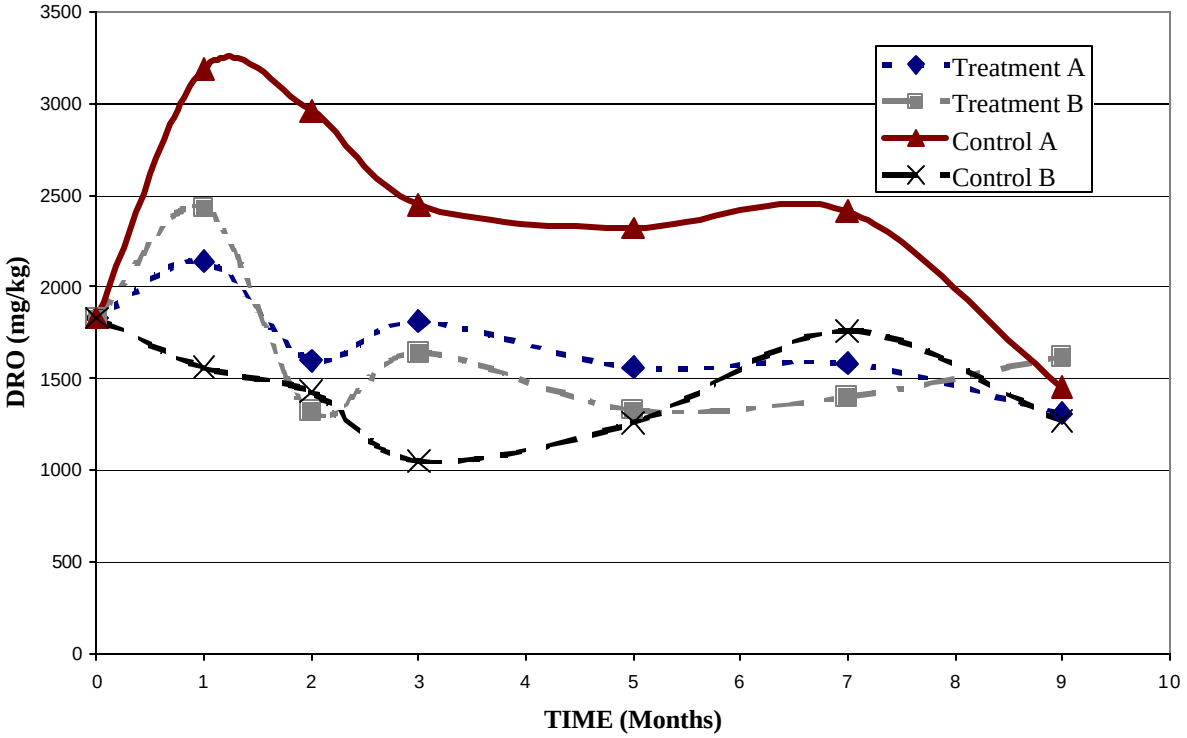


Figure 8: DRO Results from Soil-column Evaluation

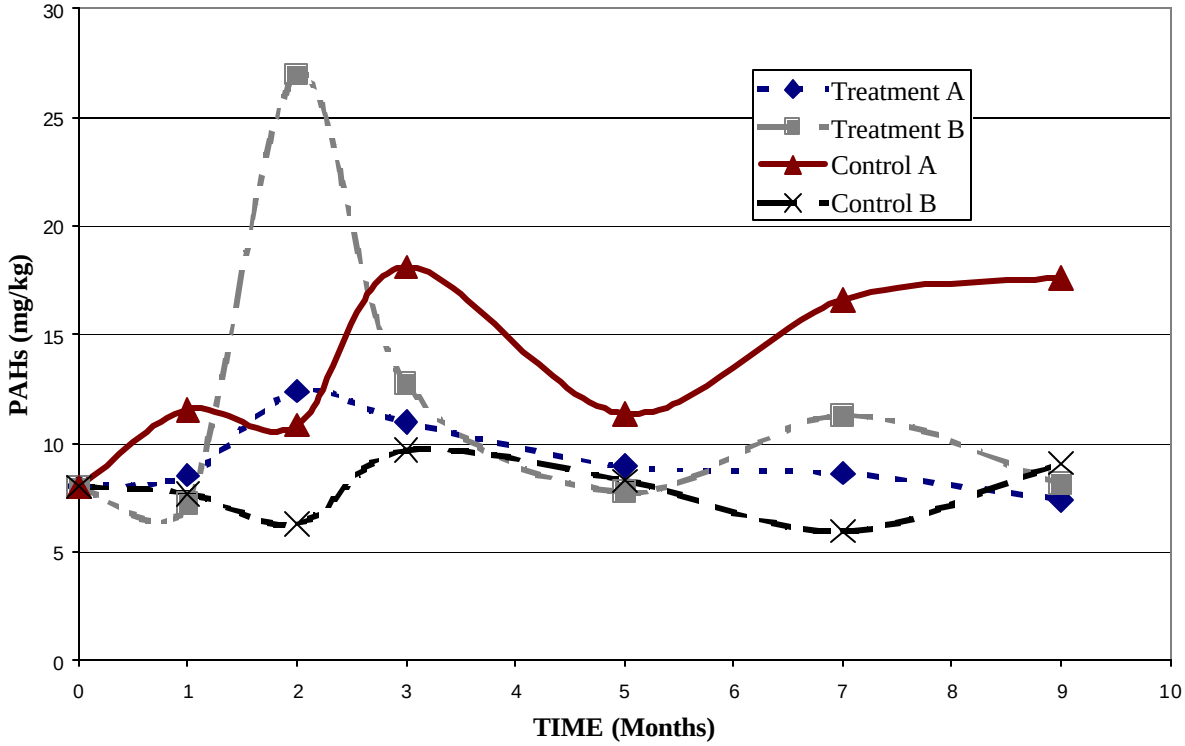


Figure 9: PAH Results from Soil-column Evaluation

It is important to understand that biological systems can respond differently from one analysis to another. This, coupled with the specific heterogeneity of HOCs in the Siberia Area, can result in significant variances in chemical data. One method of minimizing these effects is to perform triplicate analysis of samples and then average the results. This typically provides sufficient data to develop statistical significance and a truer representation of actual site conditions, which is necessary to interpret experimental results for their implications on full-scale remediation. This work was limited to single analysis. Therefore, it is very important to *focus on the general trends associated with the data and not the specific values themselves*. Trends in data can be used to make generalized statements of interpreted significance. However, because data replication was not developed, specific values can have neither significant nor technically accurate interpretation.

As expected, concentrations of PAHs and DROs did increase above the initial baseline concentrations during the early months of the study. Generally, DROs peaked within the first month, while PAHs (in some cases) required up to three months to reach their highest availability. Although TPHs did show significant variations in concentrations for some soil columns, they never exceeded the initial levels determined from the 8 September 1997 sample. Comparing the highest concentrations observed for each contaminant group and soil column with the final values, a general decreasing trend was observed in Treatments A and B for TPH, DRO and Total PAHs.

Using the initial and final values, an average TPH reduction of 75 percent was observed for Treatment A and Treatment B combined. Control A showed only a 30 percent reduction in TPH, suggesting that nutrients may have become limiting as aerobic bioactivity increased in the column. Control B showed a TPH reduction of 70 percent, which suggests that anaerobic or anoxic natural attenuation of TPH was occurring. However, it is important to realize that since Control B wasn't mixed, the PAHs remained less available than in the other soil columns; therefore, in Control B, it is likely that the microbial communities were not able to readily access the PAHs, and therefore, nutrients may not have become limiting, as in the case of Control A. This is one possible explanation for the high degradation rate for TPH. This supports the premise that mass transfer limitations do not generally control the availability of TPHs. Another possible explanation is that anaerobic biological processes taking place in

Control B did not have the same nutrient requirements as the aerobic biological processes in the Column A, and therefore were not limited by nutrient requirements.

DROs represent a composite of heavy oils. These heavy oils are less desirable for microbial consumption than TPHs and biodegrade at slower rates. A comparison of the initial and final values of DRO concentration shows no significant difference in DRO reduction between the columns. Overall average DRO reduction for the four columns was approximately 23 percent of the initial value. Control B, no mixing or nutrient addition, showed the same reduction in DRO as the other columns indicating that natural attenuation of DRO does occur in this soil. It is possible that if TPH, which is easier for microorganisms to degrade, were reduced further in this soil, the intrinsic bioremediation activity for DRO would eventually increase.

The total PAH concentration remained approximately the same for all columns except Control A, which showed a general increasing trend of PAH concentration. Based on this information alone, the conclusion would be that no reduction of PAH occurred in the soils. However, as discussed at the beginning of this section, mixing of the soil has been shown to increase the availability of HOCs to both chemical extraction and biological activity. This point is demonstrated by general trend of increasing total PAH concentration seen in Control A. Assuming Treatment A and Treatment B, which were also mixed, experienced a similar increase in total PAH availability as Control A, the lack of total PAH concentration increase in these columns may then be interpreted as a reduction of total PAH in the soil. This can be explained by biological degradation of PAHs, as they were made increasingly available due to mixing of the soil. From this interpretation, the total PAH removal from the soil is the difference between the final samples from Control A and the average of Treatment A and Treatment B. The calculated removal of total PAH is approximately 54 percent due to mixing and nutrient amendments. This calculation is conservative due to the likely hood that some degradation of PAHs occurred in Control A. Without a sterile control for comparison, it can only be assumed that there was no PAH degradation in Control A. Because Control B was not mixed, it is assumed that there was no increase in the availability of PAHs in the soil. Based on this assumption, the lack of an increase in total PAHs in Control B is interpreted as no degradation of PAHs in the soil column.

The sample from month 2 for Treatment B showed a dramatic increase in total PAH concentration, greater than 300 percent, from the initial concentration. This data point also does not fit with the general trend of data for this or any other column. For this reason it is assumed that there was a problem in the analysis of this sample.

Several factors combine to confound the results from chemical analysis of PAHs in soil: the nature of PAHs to bind strongly with the soil, the lack of an efficient extraction technique for these compounds, changes in their bioavailability and extractable fraction due to mixing, and the spatial heterogeneity of contamination in the soils. These challenges are addressed by the interpretation of the data compared to controls columns maintained in the study. Although there are other possible interpretations of the data from this study, it is felt that the interpretation given in the preceding paragraphs is the most appropriate.

6.5 CONCLUSIONS FROM SOIL-COLUMN EVALUATION

The interpreted results for this study are summarized in Tale 11. These results indicate a decrease in TPH, DRO, and PAH concentrations in Treatments A and B. In all cases, the observed contaminant reduction approached or exceeded the stated objective. Despite the tremendous heterogeneity of the Siberia Area soil and the lack of statistical validation due to single analysis, these observations do support the specific objectives of the study. This indicates that in-situ bioremediation (in-situ land farming) is a feasible remediation option provided scale-up parameters can be clearly identified and demonstrated, and further that appropriate whole organism toxicity analysis confirm reduction in toxicity after treatment.

Table 11: Summary of Soil-Column Results

Column	Conditions	TPH	DRO	PAH
Treatment A & B	mixing, nutrients	75%	23%	54%
Control A	mixing	30%	23%	0%
Control B		70%	23%	0%

The following conclusions can be drawn from the column study results:

- mixing and nutrient amendments will decrease the concentrations of TPH, DRO, and PAHs significantly,
- mixing of this soil will initially increase the availability of PAHs to both chemical extraction and biological degradation,
- natural attenuation can produce significant removal of TPH and DRO in the short term,
- natural attenuation will not remove significant PAHs in the short term,
- a nutrient deficiency exists in the soil and is limiting the degradation of PAHs,
- tremendous heterogeneity exists in Siberia Area soil demanding that all future studies include duplicate or triplicate analysis for statistical relevance.

7.0 PAN STUDY EVALUATIONS

7.1 OVERVIEW

A pan study was conducted using soils/fill collected from the Siberia Area. This study was designed to simulate in-situ landfarming techniques (bioremediation approach) and to provide an assessment of expected degradation of TPH and PAHs under relevant field conditions during a bioremediation effort. This technique uses soil-blending equipment, slow release nutrients, and soil bulking factors to a depth of six to eight feet. This in-situ bioremediation approach could result in significant cost savings in comparison to other applicable remediation technologies. Successful biotreatment in the laboratory evaluation is a necessary precursor to field-scale pilot application. Study treatments were designed to represent and compare aerobic and anaerobic landfarming treatment options at the site.

Anaerobic landfarming is performed the same as aerobic landfarming except mixing operations are performed much less often. Mixing is performed primarily to redistribute contaminants, nutrients, and biological mass. It is assumed that heavily contaminated soils with vigorous biological activity will become anoxic/anaerobic without frequent mixing of the soil for aeration. Due to the shallow soil depth in the study pans, anaerobic test pans were flooded to ensure anaerobic conditions were achieved in the study. However, it is not recommended that flooding of soils on site be performed due to the possibility of leaching contaminants to the groundwater.

7.2 EXPERIMENTAL PROTOCOL

7.2.1 Soil Collection and Preparation

Malcolm Pirnie collected soil samples from three contaminated zones in the Siberia Area in December 1998. The samples were taken from the following areas: PS-01 in the vicinity of the chip handling area west of MW-36/MW-37, PS-02 in the vicinity of the chip handling area east of MW-36/MW-37, and PS-03 adjacent to the substation in the vicinity of MW-29. The soils were placed in three 55-gallon drums and

shipped to Envirogen, Inc on January 11, 1999. The drums were stored at 15°C prior to the initiation of bench studies. Soil from drum PS-02 was chosen for use in the Pan Study due to high initial PAH levels.

Soil from drum PS-02 (55 gallon) was transferred to a large, sterilized Nalgene tank (approximately 100-gallon capacity) as shown in Figur 10. The soil was thoroughly mixed for one hour to homogenize the sample, but was not sieved prior to the study (i.e., the rock fraction was included).

Figure 10: Initial mixing of soil

7.2.2 Experimental Treatments

Glass tanks (38-liter capacity) were used as treatment vessels ("pans") in the study (Figure 11). The dimensions of these pans were 50 cm (length) x 25 cm (width) x 30 cm (height). The pans were washed and then sterilized using a concentrated bleach solution prior to the addition of soil. The homogenized soil was added to six pans to a

depth of 24 cm. Approximately 37 kg of soil at field moisture (32.5-kg dry wt) was added to each pan. The treatments evaluated are listed in Table 12, and a detailed description of each evaluation follows.

Figure 11: Pans

Table 12: Experimental Design

Pan	Treatment
1	Aerobic Incubation with Nutrient Amendments (Aerobic - Nutrient I)
2	Aerobic/Anaerobic Incubation with Nutrient Addition (Aerobic – Nutrient II)
3	Anaerobic Incubation under Denitrifying Condition (Anaerobic – Nitrate)
4	Anaerobic Control (Anaerobic – Killed)
5	Aerobic Control (Aerobic – Killed)
6	Aerobic Incubation (Aerobic)

Pan 1: Aerobic Incubation with Nutrient Amendments (Aerobic - Nutrient I)

Pan 1 was designed to evaluate aerobic biodegradation of TPH and PAHs with nutrient amendment. Pan 1 was amended with 1.46 L of water-soluble fertilizer (K-GRO). This fertilizer is readily available in a commercial mixture (K-Mart), applicable in water, and has been found by Envirogen to promote microbial growth as a nutrient

source in bioreactor systems. The fertilizer was made to a 50-g/L stock. K-GRO contains 15-g N (ammoniacal nitrogen), 30-g phosphorus (available phosphate, P_2O_5), and 15-g K (soluble potash, K_2O) per 100-g solid. The quantity of K-GRO added to the soil provides 21.9 g of phosphorus (P) and 11 g of nitrogen (N) to the treatment vessels. This corresponds to approximately 700 mg P/kg soil and approximately 350 mg N/kg soil in the treatment vessel. The volume of water added brought the soil moisture to 75 percent of field water-holding capacity based on initial soil measurements.

Pan 2: Aerobic/Anaerobic Incubation (Aerobic - Nutrient II)

Pan 2 was originally designed to evaluate aerobic biodegradation of PAHs and TPH for three months, then anaerobic biodegradation of these contaminants for three months. Initially, Pan 2 was amended with 1.46 L of 50-g/L water-soluble fertilizer (K-GRO) as described for Pan 1. The Pan was scheduled to be flooded with nitrate solution after three months of incubation to promote denitrifying conditions (see Pan 3). However, due to poor biodegradation results in the anaerobic pan (Pan 3), Pan 2 was not flooded after three months.

Pan 3: Anaerobic incubation under denitrifying conditions (Anaerobic – Nitrate)

Pan 3 was designed to evaluate anaerobic biodegradation of TPH and PAHs with nitrate added as an electron acceptor (denitrifying conditions). Pan 3 was treated with 4.0 L of 50-g/L water-soluble fertilizer (K-GRO) amended with potassium nitrate (10 g/L). This pan then received an additional 4.5 L of distilled water (8.5 L total addition). This amendment flooded the soil, leaving approximately 3 cm of standing water.

Pan 4: Killed Anaerobic Control (Anaerobic – Killed)

Pan 4 was designed to evaluate nonbiological losses of TPH and PAHs during anaerobic incubation (flooded conditions). This pan served as a killed control for Pan 3. Pan 4 was treated with 2.85 L mercuric chloride stock (50-g/L $HgCl_2$), 2.85-L sodium azide stock (50-g/L NaN_3), then amended with an additional 2.8 L of distilled water (8.5 L total addition). The mercuric chloride and sodium azide were added as inhibitors

of microbial activity. The total amendment flooded the soil, leaving approximately 3 cm standing water.

Pan 5: Killed Aerobic Control (Aerobic – Killed)

Pan 5 was designed to evaluate nonbiological losses of TPH and PAHs during aerobic incubation. This pan served as a killed control for Pans 1, 2, and 6. Pan 5 was treated with 0.73-L mercuric chloride stock ($HgCl_2$:50 g/L) and 0.73-L sodium azide stock (NaN_3:50 g/L). The mercuric chloride and sodium azide were added as inhibitors of microbial activity. This treatment provided approximately 1,000 ppm of each inhibitory compound in the soil (i.e., 1 g/kg).

Pan 6: Aerobic Incubation (Aerobic)

Pan 6 was designed to evaluate aerobic biodegradation of TPH and PAHs by aeration only, without addition of fertilizer nutrients. Pan 6 was amended with 1.46 L of distilled water only. This pan was incubated aerobically for the duration of the study.

7.2.3 Incubation Conditions

The pan study was initiated on 11 February 11 1999. The pans were incubated inside a walk-in hood in Envirogen's Pilot Plant at ambient temperature. The release of volatile hydrocarbons from the soil necessitated incubation in a hooded area. The incubation temperature ranged from 18.5 to 35.5°C during the study. The mean temperature was lower at the beginning of the study, then increased gradually during the summer months with ambient temperature. Temperature readings were typically not taken on weekends. The temperature profile is illustrated in Figure 12 and is broken down into ranges in Table 13. All pans were covered with glass plates to preserve moisture levels in the soil (Figure 13). The plate glass covers on the anaerobic (flooded) pans (Pans 3 and 4) were sealed to the tanks with silicone grease to reduce oxygen transfer into the headspace of the pans from the outside atmosphere. The anaerobic treatment was designed to approximate conditions during flooding of a field site.

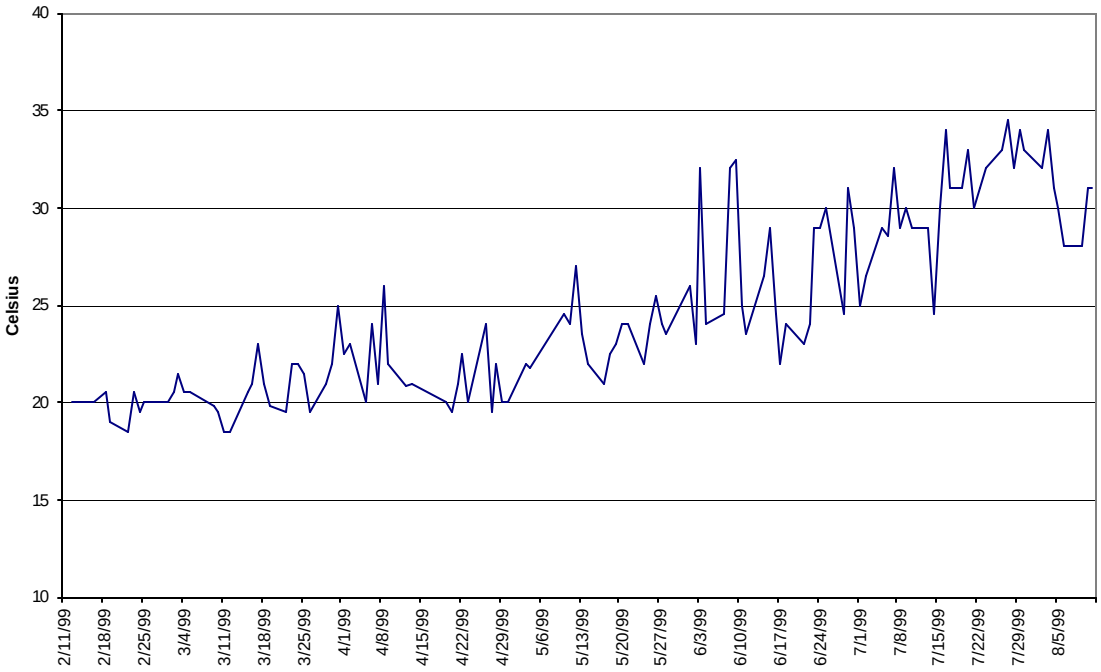


Figure 12: Temperature profile during pan study

Table 13: Pan study temperature profile

Range (°C)	Days	% of Measured
T < 20	12	10
20 ≤ T ≤ 25	65	54
25 < T ≤ 30	23	19
> 30	21	17
Not Measured	61	
Total	182	
Minimum	18.5	
Maximum	35.5	

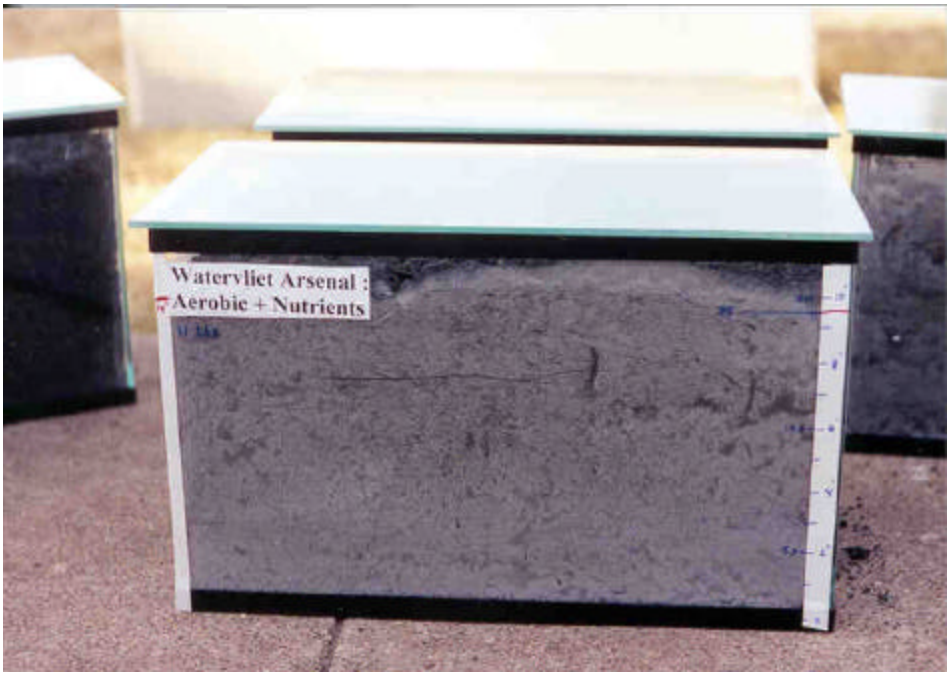


Figure 13: Moisture retaining covers

The soil in the aerobic pans (Pans 1, 2, 5, 6) was initially brought to approximately 75 percent of field capacity by the addition of 1.46 L of solution (nutrient solution, water, or mercuric chloride/sodium azide). The moisture level in the aerobic samples was periodically checked to ensure that water levels remained between 60 to 80 percent field capacity. The aerobic pans were amended with additional solution approximately every five weeks during the incubation period. At weeks 5, 11, 16, and 21, solution was added to the pans at the respective volumes of 0.6, 0.75, 0.75, and 1-liter. Pans 1 and 2 were amended with K-GRO (50 g/L) plus 15-g/L KH_2PO_4 as an additional source of phosphorus. Pan 5 received water amended with 25-g/L NaN_3, and Pan 6 received only water.

The aerobic soil samples were removed from each pan to a larger vessel and thoroughly mixed by hand every seven days to allow thorough aeration of the soil. This treatment is equivalent to mixing or tilling a field soil during land farming. In addition, the glass plates were removed from the aerobic pans two additional times per week to allow exchange of gases with the atmosphere and aeration of the soil. The anaerobic pans remained sealed and were not mixed.

Figure 14: Intermediate mixing of aerobic pans

7.3 SAMPLE COLLECTION AND ANALYSIS

Duplicate samples were collected from each of the six pans for analysis on a monthly basis. Soil samples were collected in 250-mL glass bottles fitted with Teflon-lined caps. Subsamples of lesser volumes were taken from 12 to 15 different locations in a pan and consolidated in the 250-mL glass bottles. To collect samples from flooded pans, the glass top was removed, and a sterile spatula was used to collect subsamples from the top, middle, and bottom of the pans at numerous locations. Samples from the aerobic pans were taken after the soil had been moved to the mixing tank. After soils were mixed for 10 minutes, subsamples were taken from 12 to 15 different locations in the tank. After sampling, the soil in each 250-mL jar was thoroughly mixed using a sterile spatula. Two small samples were then removed from each jar: a 10-g sample for moisture analysis and a 5-g sample for plate counts of total and hydrocarbon-degrading bacteria (see Section 7.3.3). The remainder of the soil samples were then preserved with sodium azide and submitted for the analyses described in Sections 7.3.1 and 7.3.2.

7.3.1 Hydrocarbons

Polycyclic Aromatic Hydrocarbons (PAHs)

Soil samples were submitted to Severn Trent Laboratories (Whippany, NJ) for analysis of 16 individual PAH analogs. The soils were extracted according to EPA Method 3550B (Ultrasonic Extraction: Manual SW-846), then analyzed for semivolatile compounds by EPA Standard Method 8270C (Semivolatile Organics by GC/MS: Manual SW-846).

Total Petroleum Hydrocarbons (TPH).

Soil samples were submitted to Severn Trent Laboratories for analysis of TPH. This analysis was performed according to State of New Jersey Department of Environmental Protection (NJDEP) Method QAM-025. This method utilizes a gas chromatograph fitted with a flame ionization detector (GC/FID) for total semi-volatile petroleum products (C6 –C40). This method is derived from EPA Method 8015B, but surrogates and QA/QC procedures are more stringently defined than in Method 8015B.

7.3.2 Soil Chemistry

Anions/Cations

Soil samples were submitted to the Envirogen Analytical and Treatability Laboratory for analysis of nitrate, ammonia, sulfate, and phosphate. EPA Series 300 Methods were used for these analyses.

TKN/Total P

Soil samples were submitted to the Envirogen Analytical and Treatability Laboratory for analysis of Total Kjeldahl Nitrogen (TKN) and total phosphorus. EPA Method 350.1 was used to determine TKN, and EPA Method 365.2 was used to determine total phosphorus.

Soil pH

Soil samples were submitted to the Envirogen Analytical and Treatability Laboratory for analysis of pH. This analysis was performed according to EPA Method 150.1.

Soil Moisture

Soil moisture was determined according to standard protocol (drying at 105°C).

7.3.3 Microbiology

Bacterial plate counts were performed to evaluate microbial numbers in live soil samples and killed controls. Plate counts were performed on soil samples from day one after the initiation of the experiment and after each month of operation for a total of seven samples. The soils used for the monthly plate counts were taken from the samples collected for chemical analyses. Both total bacteria (total aerobic heterotrophs) and bacteria capable of degrading petroleum hydrocarbons (fuel oil degraders) were enumerated. The plate counts were performed to ensure that the "killed" controls did not contain high numbers of viable bacteria and to monitor total and hydrocarbon-specific bacterial populations in the soil throughout the six-month incubation. This work was performed in addition to the defined scope of work for the project.

Total Heterotrophs

Total Heterotrophic Bacteria were determined by plate counts using R2A Agar (Becton Dickinson, Cockeysville, MD). The basic method for total heterotrophs is as described in SM-9215C (Heterotrophic Plate Count/Spread Plate Method; *Standard Methods for the Examination of Water and Wastewater, 18th ed.).* A 5.0-g soil sample from each sample bottle (250-mL bottle collected for all analyses) was added to 25 mL of sterile basal salts medium (BSM). The soil and diluent were mixed together for one minute using a vortex mixer. The resulting soil slurry was serially diluted in sterile BSM, and a 0.10-mL volume from each dilution tube was spread on a plate of R2A agar. The agar plates were incubated for 10 days at ambient temperature, and the bacterial colonies on each plate were counted. Plates containing 30 – 300 colonies were used whenever

possible to determine final cell numbers in the soil. The moisture in each soil sample was determined, and cell numbers were reported per gram of soil (dry weight).

Hydrocarbon-Degrading Bacteria

Total Hydrocarbon-Degrading Bacteria were determined by plate counts using BSM Agar with #2 fuel oil (0.06 mL/L agar) as a sole source of carbon. An accepted standard EPA method for this procedure is not available. However, this counting technique is frequently used by Envirogen Analytical and Treatability Laboratory (ATL) to determine numbers of specific heterotrophs, and the general method is detailed in the Envirogen ATL Standard Operating Procedures. Overall, the plating and counting procedure was as described for total heterotrophs except that plates were incubated for 21 days prior to counting colonies.

7.3.4 Soil Toxicity and Biological Accumulation

Bioremediation is defined by the U.S. Environmental Protection Agency (EPA) as a managed or spontaneous process in which microbiological processes are used to degrade or transform contaminants to less toxic or nontoxic forms, thereby, remedying or eliminating environmental contamination (EPA, 1994). These microbiological processes may reduce hydrocarbon concentrations in various types of soils to levels that no longer pose an unacceptable risk to the environment or human health (Nakles and Linz, 1997). However, hydrocarbons that remain in treated soils still might not meet stringent regulatory levels, even if they represent site specific, environmentally acceptable endpoints (NRC, 1997). Therefore, this unresolved issue of the availability of residual hydrocarbon contaminants was the focus of these toxicological bioassays.

Earthworm toxicity and bioaccumulation tests were conducted in conjunction with this pan study. Earthworm tests were performed by AquaSurvey, Inc. The toxicity of soil samples both before and after the 6-months of biotreatment in the pan study were assessed. These studies consisted of acute 14-day toxicity screening tests on *E. foetida* (three replicates) and 28-day bioaccumulation testing. These tests represent the standard for demonstrating toxicity associated with contaminated soils and will serve as validation of the effectiveness of the biotreatment studies.

Fourteen-day acute earthworm toxicity tests were performed with test soils mixed with a reference soil at the following concentrations of test soils: 0, 6.25, 12.5, 25, 50, and 100 percent. Tests were performed in replicates of three for each concentration. Ten organisms were used for each replicate concentration. Replicate concentrations were pooled for endpoint calculations.

Test concentrations used for the 28-day bioaccumulation test were 0, 25, and 100 percent as test soil. Tests were performed in replicates of three for each concentration. Sixty organisms per replicate were used per replicate concentration with the exception of the 100 percent test concentration in April when 120 organisms were utilized per replicate concentration. After 28 days replicate concentration tissue was submitted to Environmental Testing Laboratories, Inc. for chemical analysis. Replicate concentrations were pooled for survivability statistics.

7.4 RESULTS AND DISCUSSION

7.4.1 Hydrocarbons

Polycyclic Aromatic Hydrocarbons (PAHs)

The results from the soil PAH analyses are presented in Figure 15. Initial Total PAHs in all pans was 58.7 $\pm$ 9.6 mg/kg. This value is the average from nine soil samples. Three soil samples were collected after homogenization of the barrel of soil, and one soil sample was collected from each of the six pans after addition of soil to the pan at the beginning of the study.

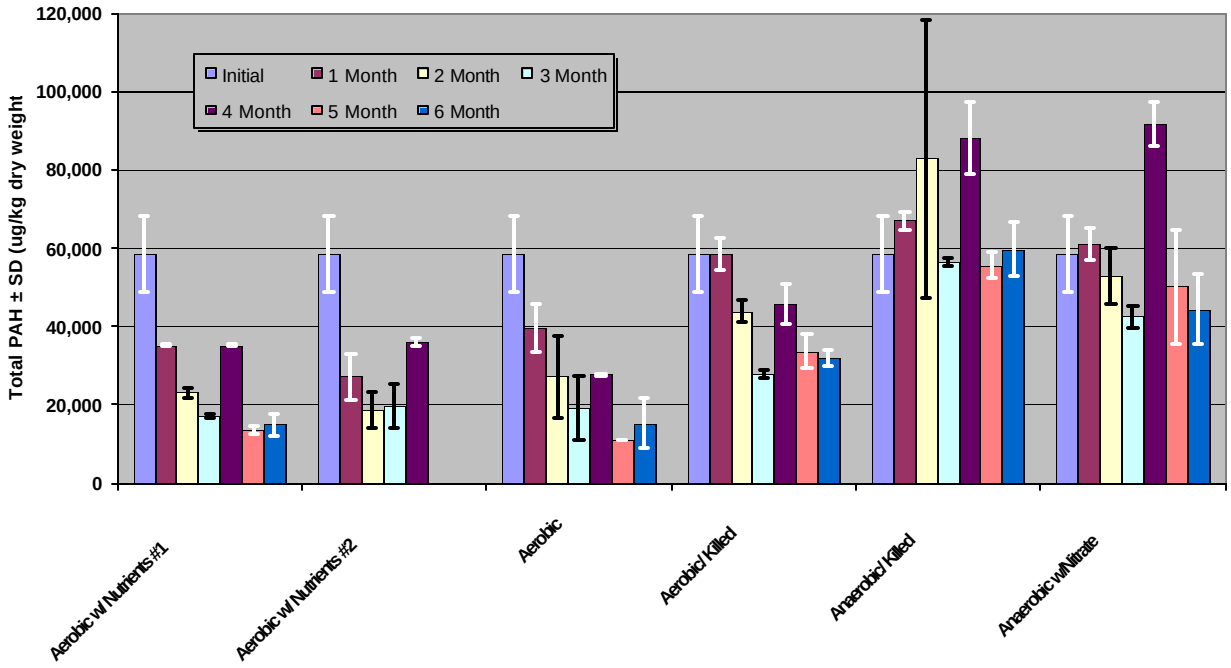


Figure 15: PAH results

An estimate of PAH degradation/removal in the soil is better represented by fitting a line or curve through the data points than simply using the initial and final concentrations. This is especially true for systems with non-linear degradation rates or heterogeneous distribution of contaminants. For most systems, either a zero-order or a first-order degradation rate is assumed. A zero-order system assumes that the rate of contaminant degradation is constant over time and nothing in the system becomes limiting. However, this is typically not the case in most systems. A first-order system assumes that the rate of contaminant degradation is proportional to some rate-limiting variable in the system. Since engineered systems strive to remove all limitations to contaminant degradation other than the concentration of the contaminant in the system, it is generally assumed that the concentration of the contaminant is the rate-limiting variable. Visual inspection of the data from the biologically active aerobic pans seems to support this theory. The rate of PAH degradation in these pans appears to slow as PAH concentrations decrease. This trend is not as evident in the killed and anaerobic pans where the decrease of total PAHs was not as significant. However, the assumption is

being made that removal of total PAHs in all the pans will follow a first-order degradation curve with respect to the concentration of total PAHs in the soil.

Both zero-order and first-order rate constants were calculated for comparison. These rate constants were estimated from the total PAH results and are shown in Table 14 and Table 15. Zero-order rate constants were derived by fitting a straight line through the data points by the method of least squares. First-order rate constants were derived by fitting a straight line through the natural logs of the total PAH concentrations by the method of least squares.

Table 14: Estimated zero-order degradation rates of total PAH

	Aerobic w/ Nutrients #1	Aerobic w/ Nutrients #2	Aerobic	Aerobic/ Killed	Anaerobic/ Killed	Anaerobic w/Nitrate
k_0	5804	5277	6687	4560	514	888
C_0	45722	42672	48531	56607	68545	60073
r^2	0.604	0.260	0.783	0.625	0.007	0.013
Reduction	76%	74%	83%	48%	4%	9%
	6 months	6 months	6 months	6 months	6 months	6 months

Estimated reduction levels for Aerobic w/Nutrients #2 were extrapolated to 6 months from the 4 months of data.

k_0: Zero-order kinetic rate constant ($ug \cdot kg^{-1} \cdot month^{-1}$)

C_0: estimated concentration at t=0 ($ug \cdot kg^{-1}$)

r^2: square of the Pearson product moment correlation coefficient

Table 15: Estimated first-order degradation rates of total PAH

Treatment	Aerobic w/ Nutrients #1	Aerobic w/ Nutrients #2	Aerobic	Aerobic/ Killed	Anaerobic/ Killed	Anaerobic w/Nitrate
k_1	0.200	0.130	0.235	0.103	0.009	0.024
lnC_0	10.7	10.5	10.8	10.9	11.1	11.0
r^2	0.641	0.192	0.805	0.568	0.011	0.039
Reduction	70%	54%	76%	46%	5%	13%
	6 months	6 months	6 months	6 months	6 months	6 months

Estimated reduction levels for Aerobic w/Nutrients #2 were extrapolated to 6 months from the 4 months of data.

k_1: 1st-order kinetic rate constant

lnC_0: estimated concentration at t=0

r^2: square of the Pearson product moment correlation coefficient

The "r^2" values given in the tables are a measure of how well the data is fit by the curve. An r^2 value of one (1) is a perfect fit. The percent reduction in the contamination estimated by a zero-order system can be determined by using the equation of the line fit through the data as described in Equation 1 below. The percent reduction in the contamination estimated by a first-order system can be determined by using the equation of the line fit through the natural log of the contaminant concentrations as shown in Equation 2.

Equation 1: Use of zero-order degradation rates

$$C_t = C_i - kt$$

t is the time in months

C_t is the contaminant concentration at time t

C_i is the initial contaminant concentration (constant)

(contaminant concentrations are ppm for TPH and ppb for PAHs)

$$\%\text{Reduction} = \frac{C_i - C_t}{C_i} \cdot 100$$

Equation 2: Use of first-order degradation rates

$$\ln C_t = \ln C_i - kt$$

or $$C_t = C_i \cdot e^{-kt}$$

t is in months

C_t is the contaminant concentration at time t

C_i is the initial contaminant concentration (constant)

(contaminant concentrations used only need to be consistent)

$$\%\text{Reduction} = \frac{C_i - C_t}{C_i} \cdot 100$$

Because the extraction of PAHs from soils is difficult and often results in significant variability, results from this study were checked for significant variations in the concentration of a high molecular weight PAH, Indeno(1,2,3-cd)pyrene (Indenopyrene). Because of Indenopyrene's high molecular weight and general recalcitrant nature, it was assumed that Indenopyrene was not degraded significantly during the course of this six-month study. Based on this assumption, a significant deviation of the Indenopyrene concentration in a particular sample from the mean of all

samples from a given pan was used as an indicator of problems with the PAH analysis or sampling procedures for that sample. The levels of Indenopyrene in sample results from Month 4 were approximately two standard deviations from the mean in all pans as shown in Table 16. A bar graph of the Indenopyrene data, Figure 16, visually illustrates the data divergence of Month 4 from other data points of the same pans. This degree of divergence from the mean is representative of a statistical outlier.

Table 16: Variation of Indenopyrene

Treatment / Time	Aerobic w/ Nutrients #1 (ug/kg)	Aerobic w/ Nutrients #2 (ug/kg)	Aerobic (ug/kg)	Aerobic/ Killed (ug/kg)	Anaerobic/ Killed (ug/kg)	Anaerobic w/Nitrate (ug/kg)
Initial	1521	1521	1521	1521	1521	1521
1 Month	1550	1250	1350	1300	1500	1400
2 Month	1450	1250	1350	1400	2450	1400
3 Month	1150	1300	1065	990	2000	1400
4 Month	2800	2900	2250	2100	3650	4050
5 Month	930		875	1450	2600	2300
6 Month	1200		1040	1450	1500	1100
Mean	1514	1644	1350	1459	2174	1882
SD	610	711	455	333	796	1026
Time	**(Value-Mean)/SD**					
Initial	0.0	-0.2	0.4	0.2	-0.8	-0.4
1 Month	0.1	-0.6	0.0	-0.5	-0.8	-0.5
2 Month	-0.1	-0.6	0.0	-0.2	0.3	-0.5
3 Month	-0.6	-0.5	-0.6	-1.4	-0.2	-0.5
4 Month	2.1	1.8	2.0	1.9	1.9	2.1
5 Month	-1.0		-1.0	0.0	0.5	0.4
6 Month	-0.5		-0.7	0.0	-0.8	-0.8

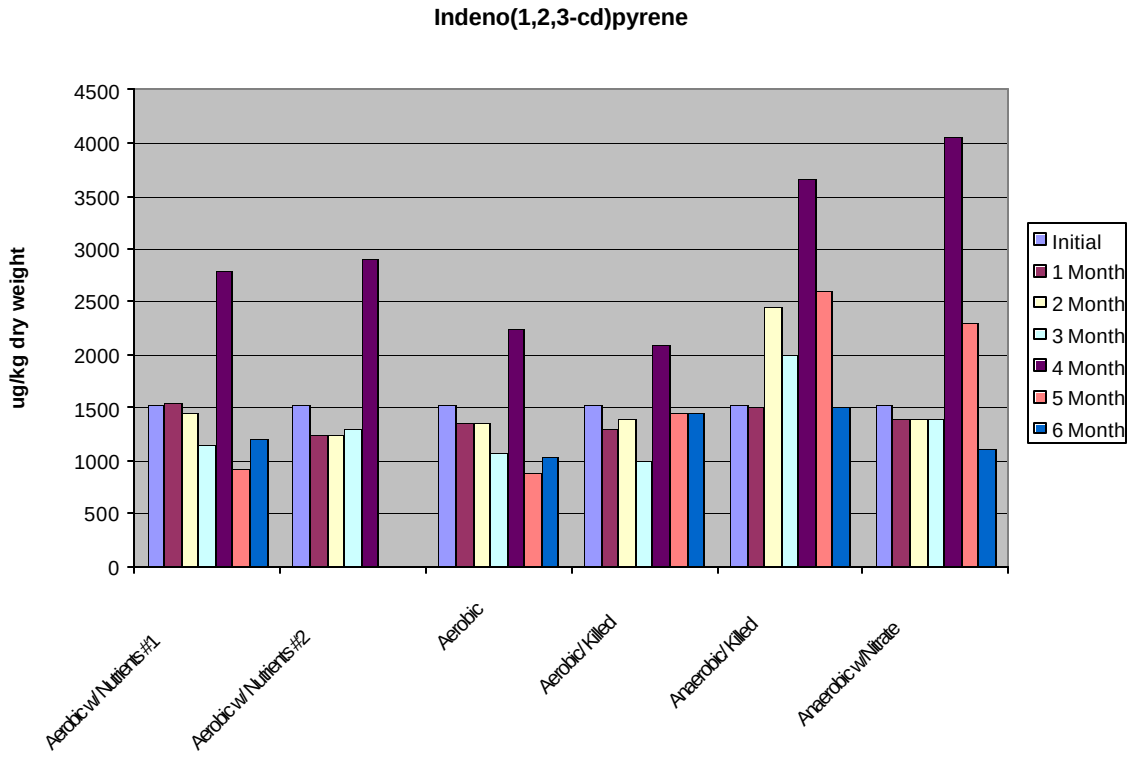


Figure 16: Indenopyrene graph

While the data from Month 4 cannot be completely ignored solely based on it being a statistical outlier, the data from this month is certainly suspect. Review of sample analysis reports and interviews with the analytical laboratory did not reveal any additional evidence of analytical errors, however it is highly unlikely that a relatively consistent increase in all pans would be seen at the same time. For this reason both zero-order and first-order rate constants were also estimated from the total PAH results while excluding data from Month 4, as shown in Table 17 and Table 18, respectively. Estimations of zero and first-order rate constants were performed in the same manner as discussed earlier.

Table 17: Estimated zero-order degradation rates of total PAH (excluding Month 4)

	Aerobic w/ Nutrients #1	Aerobic w/ Nutrients #2	Aerobic	Aerobic/ Killed	Anaerobic/ Killed	Anaerobic w/Nitrate
k_0	6357	12501	6944	4884	1457	2426
C_0	45169	49897	48273	56282	67602	58535
r^2	0.720	0.743	0.810	0.694	0.106	0.579
Reduction	84%	150%	86%	52%	13%	25%
	6 months	6 months	6 months	6 months	6 months	6 months

Estimated reduction levels for Aerobic w/Nutrients #2 were extrapolated to 6 months from the 3 months of data.

k_0: Zero-order kinetic rate constant ($ug \cdot kg^{-1} \cdot month^{-1}$)

C_0: estimated concentration at t=0 ($ug \cdot kg^{-1}$)

r^2: square of the Pearson product moment correlation coefficient

Table 18: Estimated first-order degradation rates of total PAH (excluding Month 4)

Treatment	Aerobic w/ Nutrients #1	Aerobic w/ Nutrients #2	Aerobic	Aerobic/ Killed	Anaerobic/ Killed	Anaerobic w/Nitrate
k_1	0.223	0.363	0.250	0.112	0.022	0.046
lnC_0	10.7	10.8	10.8	10.9	11.1	11.0
r^2	0.836	0.800	0.879	0.658	0.116	0.557
Reduction	74%	89%	78%	49%	12%	24%
	6 months	6 months	6 months	6 months	6 months	6 months

Estimated reduction levels for Aerobic w/Nutrients #2 were extrapolated to 6 months from the 3 months of data.

k_1: 1st-order kinetic rate constant ($month^{-1}$)

lnC_0: estimated concentration at t=0

r^2: square of the Pearson product moment correlation coefficient

When the PAH results are analyzed with the Month 4 data included (Table 14 and Table 15 above), relatively good fits are only seen for the Aerobic w/Nutrients, Aerobic, and Aerobic/Killed pans. The r^2 values for all other pans were extremely low indicating that the fit of the data using zero or first-order kinetics is very poor. The average reduction of total PAHs in the Aerobic w/Nutrients #1 and Aerobic pans is 73 percent when estimated by first-order kinetics from an initial estimated level of 46.7 mg/kg.

PAH results analyzed with the exclusion of data from Month 4 provided significantly better fits of the data (Table 17 and Table 18 above). Zero and first order analyses provided relatively good fits of the data for all aerobic pans. Analysis of the results from the anaerobic pans did not provide a satisfactory fit of the data. First-order analysis of the biologically active aerobic pans provided good fits of the data with r^2 values above 0.8. The average reduction of total PAHs in the Aerobic w/Nutrients #1

and Aerobic pans is 76 percent when estimated by first-order kinetics from an initial estimated level of 46.7 mg/kg.

Volatilization is a possible pathway for loss of contaminants from soil. However, only a small amount, one to two percent, of PAH losses in the pans could be accounted for by volatilization of naphthalene, which is a two-ring semivolatile compound. Given the weight of the PAHs with three rings and above, any significant volatilization of these compounds is unlikely. In a bioslurry study of PAHs with air sparging, it was found that only 0.08 percent of the two-ring and three-ring PAHs were lost by volatilization during four months of operation (Cornelissen et al. 1998). Most of these losses were from Naphthalene. For these reasons, volatilization is not considered significant in the analysis of this data.

Although the analysis of the anaerobic pans did not provide good fits of the data, the estimated final concentrations of total PAHs in the biologically active aerobic pans were approximately one-quarter the final concentration observed in the biologically active anaerobic pan. As expected, these results indicate that aerobic landfarming (regular mixing) results in much higher rates of PAH degradation than anaerobic treatment.

Table 19 below is a comparison of aerobic landfarming treatment times required to degrade individual PAH compounds to the lowest proposed clean-up goals. The lowest proposed treatment goals are excerpted from the Draft Corrective Measures Study (CMS) Preliminary Screening Report Watervliet Arsenal, Siberia Area (Malcolm Pirnie, 1999). Time estimates were calculated using the average first-order degradation rates from Aerobic w/Nutrient #1 and Aerobic pans. The calculation of these rates included the questionable data acquired during month 4, which results in lower degradation rates than calculations omitting this data. Analysis of individual PAH compounds in initial soil samples revealed that only four PAH compounds (benzo(a)anthracene, chrysene, benzo(a)pyrene, benzo(b)flouranthene) were above their respective lowest proposed clean-up levels. Of these compounds, benzo(a)pyrene appears to require a significantly longer period of aerobic landfarming, 24 months, to reach the clean-up goal. The remaining three compounds required less than 10 months of treatment to reach their respective clean-up goals.

Table 19: Estimated treatment time for individual PAHs to reach SSTL or TAGM levels

	No. of Rings	NYSDEC TAGM 4046 Value (mg/kg)	RFI-Adjusted TAGM Value[1] (mg/kg)	On-Site Surface Soil SSTL (mg/kg)	All On-Site Soil SSTL (mg/kg)	Avg. Initial Conc. (mg/kg)	Avg. k_1	Time to Reach SSTL or TAGM (months)
Naphthalene	2	13	104	N/C	N/C	0.316	N/A[4]	N/A[4]
Acenapthene	3	50	400	>SSC	>SSC	0.85	0.144	N/A[3]
Acenapthylene	3	41	328	N/C	N/C	0.308	N/A[4]	N/A[4]
Anthracene	3	50	400	>SSC	>SSC	2.076	0.297	N/A[3]
Fluorene	3	50	400	>SSC	>SSC	1.071	0.162	N/A[3]
Phenanthrene	3	50	400	N/C	N/C	9.156	0.332	N/A[3]
Benzo(a)anthracene	4	0.224 or MDL	N/A	3.15	46.27	5.389	0.327	9.7
Chrysene	4	0.4	3.2	>SSC	>SSC	5.178	0.212	2.3
Fluoranthene	4	50	400	>SSC	>SSC	9.856	0.294	N/A[3]
Pyrene	4	50	400	>SSC	>SSC	8.089	0.244	N/A[3]
Benzo(a)pyrene	5	0.061 or MDL	N/A	0.31	4.63	4.578	0.177	24.4
Benzo(b) fluoranthene	5	1.1	8.8	3.15	46.27	6.5	0.229	3.2
Benzo(k) fluoranthene	5	1.1	8.8	31.49	>SSC	1.956	0.158	N/A[3]
Dibenz(a,h)anthracene	5	0.014 or MDL	N/A	0.31	4.63	0.308	N/A[4]	N/A[4]
Benzo(g,h,i,)perylene	6	50	400	N/C	N/C	1.526	0.028	N/A[3]
Indeno(1,2,3-cd)pyrene	6	3.2	25.6	>SSC	>SSC	1.521	0.046	N/A[3]

Note 1 = Adjusted TAGM values based on soil organic carbon content of 8%, as presented in the *RCRA Facility Investigation Report, Siberia Watervliet Arsenal, Watervliet, NY*. Malcolm Pirnie, Inc. December 1997
Note 2 = Average of first-order rate constants for 'Aerobic w/Nutrients #1' pan and 'Aerobic' pan.
Note 3 - Initial soil concentration is lower than Adjusted TAGM and SSTL values
Note 4 - Compound was non-detect for the majority of analyses, so kinetic calculations are inappropriate
N/A = Not Applicable
N/C = Not Calculated
>SSC = SSTL is greater than the soil saturation concentration
Lowest proposed clean-up goal. This value was used to compute required treatment time

Total Petroleum Hydrocarbons

The results from the soil TPH analyses are presented in Figure 17. The average initial level of TPH in all pans was 9,600 ± 2,700 mg/kg dry soil. The initial value of TPH for the pans was calculated in the same manner described for the calculation of the initial value for total PAHs.

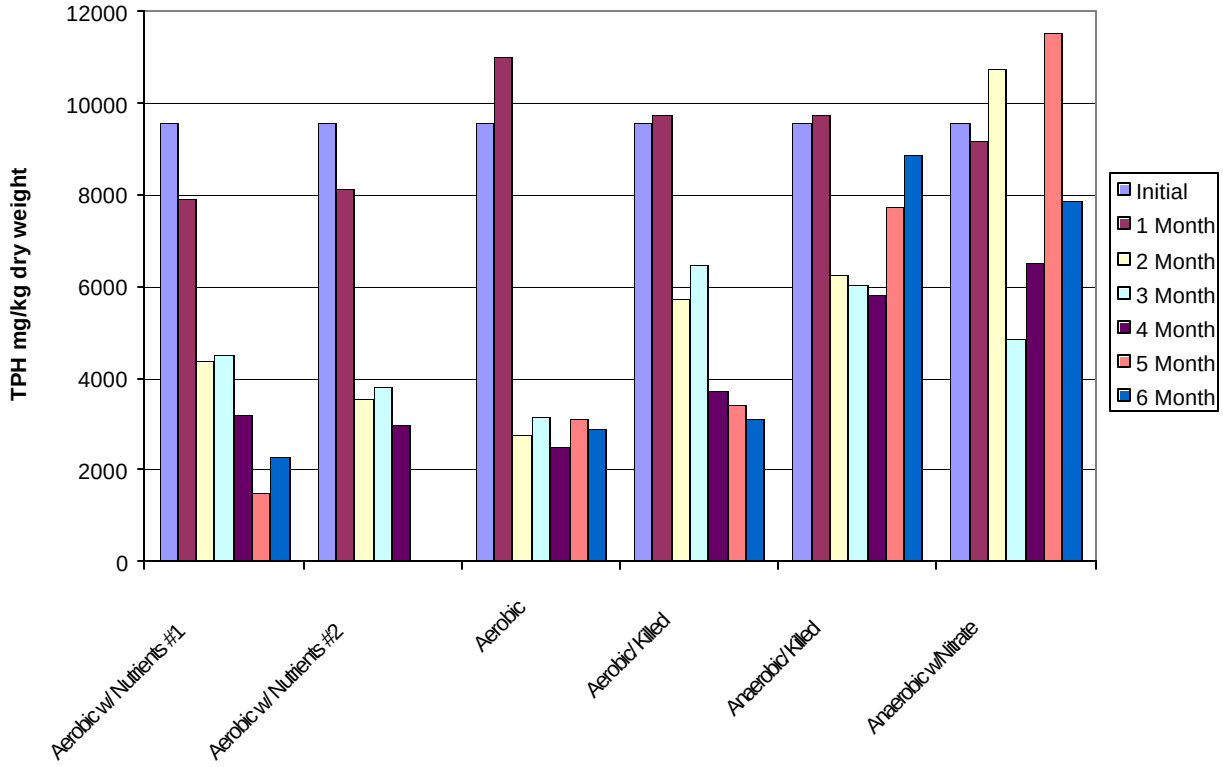


Figure 17: TPH results

As with total PAH, it is assumed that the degradation of TPH in soil will follow first-order degradation with respect to TPH concentration in the soil. Both zero-order and first-order TPH degradation rate constants were estimated for comparison. The estimated rates are given in Table 20 and Table 21. Calculations of the percent reduction of TPH were conducted the same as described for the total PAHs in Equation 1 and Equation 2.

Table 20: Estimated zero-order degradation rates of TPH

Treatment	Aerobic w/ Nutrients #1	Aerobic w/ Nutrients #2	Aerobic	Aerobic/ Killed	Anaerobic/ Killed	Anaerobic w/Nitrate
k_0	1279	1746	1289	1219	237	169
C_0	8596	9097	8863	9611	8429	9104
r^2	0.872	0.840	0.583	0.874	0.090	0.024
Reduction	89%	58%	87%	76%	17%	11%
	6 months	3 months	6 months	6 months	6 months	6 months

k_0: Zero-order kinetic rate constant ($mg_{*}kg^{-1}{}_{*}month^{-1}$)

C_0: estimated concentration at t=0 (mg/kg)

r^2: square of the Pearson product moment correlation coefficient

Table 21: Estimated first-order degradation rates of TPH

Treatment	Aerobic w/ Nutrients #1	Aerobic w/ Nutrients #2	Aerobic	Aerobic/ Killed	Anaerobic/ Killed	Anaerobic w/Nitrate
k_1	0.283	0.308	0.222	0.212	0.028	0.023
lnC_0	9.1	9.1	9.0	9.2	9.0	9.1
r^2	0.870	0.855	0.583	0.910	0.070	0.027
Reduction	82%	60%	74%	72%	15%	13%
	6 months	3 months	6 months	6 months	6 months	6 months

k_1: 1st-order kinetic rate constant

lnC_0: natural log of estimated concentration at t=0

r^2: square of the Pearson product moment correlation coefficient

The aerobic pans demonstrated very high reductions in the TPH concentration. Biologically active aerobic pans had an average removal of 78 percent of the TPH in the six-month study. This number does not include the Aerobic w/Nutrient II pan that was only monitored for four months. TPH removal in the killed aerobic was almost as high as the biologically active pans. In contrast to PAHs, a significant fraction of the removal from the killed pan is possibly due to volatilization as many of the compounds in the TPH range measured (C_b to C_{40}) are volatile. It is impossible in an open system such as this to determine the actual fate of the TPH. However, the anaerobic pans, which were sealed for the majority of the study, showed very little removal of TPH. Because an aerobic pans were sealed, volatilization of TPH from the soil would have been limited. This is one possible explanation for much of the difference in TPH removal between the aerobic and anaerobic pans.

These results suggest that TPH will be removed rapidly in aerobic systems, but that much of this removal may be by volatilization. The issue of TPH volatilization may need to be addressed before implementation of any remediation plan which involves mixing or significant disturbance of soil with high levels of TPH contamination. Any further studies conducted on TPHs should attempt to directly measure the levels of TPH volatilization from the soil.

7.4.2 Soil Chemistry

Ammonia and TKN

Soil ammonia and total Kjeldahl nitrogen (TKN) were monitored throughout the study, primarily to ensure that sufficient nitrogen was present in the live samples to allow microbial degradation of organic contaminants. The ammonia level in the original soil

used for the pan study was 32 mg/kg soil (Table 22). This value did not change appreciably in the pans receiving no fertilizer treatment (no addition) during the study, suggesting that nitrogen was not limiting microbial degradation of TPH or PAHs in this pan even though fertilizer was not applied as a nitrogen source. The declines in TPH and PAHs in this pan during the study are consistent with this observation. In the aerobic pans that received fertilizer, ammonia levels were maintained at greater than 100 mg/kg throughout the study. These two pans received additional fertilizer approximately every five weeks after the initial amendment at day 0. The ammonia level in the anaerobic pan amended with nitrate was always greater than 200 mg/kg soil and as high as 485 mg/kg during the study. Fertilizer was only added to this pan at day 0, but levels remained high for the following six months. Levels of ammonia in the aerobic and anaerobic killed pans varied from 33 to 90 mg/kg during the study. The data suggest that insufficient nitrogen did not limit biodegradation of TPH or PAHs in any live treatment.

Table 22: Ammonia in soil during study

	Soil Ammonia as NH_3-N (mg/kg)[a]						
Treatment (Pan)	**Day 1**	**1 Month**	**2 Months**	**3 Months**	**4 Months**	**5 Months**	**6 Months**
Aerobic-Nutrients 1	320	125 ± 21	165 ± 21	170 ± 14	230 ± 84	200 ± 14	230 ± 28
Aerobic-Nutrients 2	240	120 ± 28	145 ± 35	155 ± 7	185 ± 21	NA	NA
Aerobic	NA[c]	50 ± 0	51 ± 3	47 ± 5	125 ± 21	44 ± 13	U[b]
Aerobic-Killed	NA	90 ± 3	73 ± 18	33 ± 1	48 ± 6	42 ± 17	54 ± 5
Anaerobic-Nitrate	230	225 ± 106	330 ± 141	485 ± 106	415 ± 21	435 ± 7	320 ± 141
Anaerobic-Killed	NA	36 ± 18	71 ± 6	61 ± 2	77 ± 32	73 ± 6	55 ± 19
Original Soil	32 ± 2	NA	NA	NA	NA	NA	NA

[a] Values are the mean ± standard deviations from duplicate soil samples. Individual values without standard deviations are from single soil samples.
[b] U; Undetected. Value below the minimum detection limit for the assay
[c] NA; Not Analyzed. Sample was not analyzed for compound.

The TKN measurement quantifies not only ammonia but also other forms of organic nitrogen that are present in organic matter and bacterial biomass. Bacteria are capable of using some of these other forms of nitrogen (besides ammonia) for growth, although ammonia nitrogen is generally preferred. Levels of TKN in the Watervliet soil ranged from 430 and 1440 mg/kg (0.043 – 0.144 percent) in all live pans throughout the six-month study (Table 23). These values are in the range of TKN in many agricultural soils throughout the United States, which generally range from 0.05 – 0.30 percent total nitrogen.

Table 23: Total Kjeldahl nitrogen in soil during study

	TKN as N (mg/kg)[a]					
Treatment (Pan)	**1 Month**	**2 Months**	**3 Months**	**4 Months**	**5 Months**	**6 Months**
Aerobic-Nutrients 1	790 ± 156	975 ± 318	945 ± 78	1150 ± 71	430 ± 42	620 ± 85
Aerobic-Nutrients 2	705 ± 64	1440 ± 658	730 ± 311	1150 ± 71	NA[b]	NA
Aerobic	595 ± 78	475 ± 7	455 ± 49	505 ± 460	765 ± 64	660 ± 14
Aerobic-Killed	550 ± 42	525 ± 148	480 ± 128	565 ± 120	640 ± 410	525 ± 219
Anaerobic-Nitrate	535 ± 64	825 ± 35	680 ± 170	920 ± 113	510 ± 71	700 ± 127
Anaerobic-Killed	405 ± 35	290 ± 85	360 ± 0	365 ± 92	535 ± 106	390 ± 127

[a] Values are the mean ± standard deviations from duplicate soil samples.
[b] NA; Not Analyzed. Sample was not analyzed for compound.

Nitrate

The levels of nitrate in the soil were measured monthly during the study. This measurement was most important for the anaerobic treatment that was amended with nitrate and then flooded to promote PAH and TPH degradation by denitrifying strains. The nitrate levels in this pan were consistently greater than 35 mg NO_3–N/kg soil (Table 24). At all but two sample times (one day, five months), values exceeding 48 mg NO_3-N/kg soil were recorded. The levels of nitrate present in the flooded soil remained reasonably consistent during the study, indicating that denitrification did not occur to a significant extent in this treatment. Had denitrification occurred, nitrate would have been converted to nitrogen gas, resulting in declining levels of the anion. PAH and TPH levels in this pan also did not decline during the study. Thus, the data suggest that denitrifying bacteria capable of metabolizing PAHs or TPH were not active in this pan during the study.

Table 24: Nitrate in soil during study

	Soil Nitrate as NO_3-N (mg/kg)[a]						
Treatment (Pan)	**Day 1**	**1 Month**	**2 Months**	**3 Months**	**4 Months**	**5 Months**	**6 Months**
Aerobic-Nutrients 1	U[b]	U	NA	42 ± 1	95 ± 7	NA[c]	NA
Aerobic-Nutrients 2	U	U	NA	74 ± 11	175 ± 21	NA	NA
Aerobic	NA	U	NA	U	U	NA	NA
Aerobic-Killed	NA	U	NA	U	U	NA	NA
Anaerobic-Nitrate	36	54 ± 18	60 ± 4	54 ± 16	59 ± 4	35 ± 6	48 ± 11
Anaerobic-Killed	NA	U	NA	U	U	NA	NA
Original Soil	U	NA	NA	NA	NA	NA	NA

[a] Values are the mean ± standard deviations from duplicate soil samples. Individual values without standard deviations are from single soil samples.
[b] U Undetected. Value below the minimum detection limit for the assay
[c] NA; Not Analyzed or Not Available. Interference with azide (used to fix samples) did not allow detection of nitrate in some samples.

Nitrate levels in the other pans were generally below detection or not quantifiable due to interference with azide. Because azide and nitrate elute at nearly the same time in ion chromatography, low levels of nitrate could often not be quantified due to interference with the azide, which was used to inhibit microbial activity in all samples after collection. However, nitrate could easily be distinguished from azide in samples where nitrate levels were high. Nitrate was detected at reasonably high levels in nutrient-amended pans during months 3 and 4. The appearance of nitrate in these samples may reflect nitrification in the soil. Nitrification is the bacterial conversion of ammonia to nitrate, which occurs under aerobic conditions in many soils. This process is unlikely to have influenced PAH or TPH degradation in these samples.

Phosphate/Total Phosphorus

Insufficient phosphorus often limits biodegradation of organic pollutants in contaminated environments. In this study, phosphorus was added to the soil in the two nutrient pans both as orthophosphate (PO_4) and pyrophosphate (P_2O_5), the latter being the form present in many commercial fertilizers, including the one used in this study (K-GRO). Phosphate levels in the aerobic nutrient-amended pans ranged from 1.6 to 75 mg/kg during the study (Table 25). At each collection time, phosphate was detected in soil from these pans, suggesting that insufficient phosphorus (P) did not limit PAH or TPH biodegradation. Phosphate levels above 4.9 ppm were also detected in the anaerobic, nitrate-amended pan throughout the study; thus, inadequate phosphorus also was unlikely to limit biodegradation in this treatment.

Table 25: Phosphate in soil during study

	Soil Phosphate as PO_4-P (mg/kg)[a]						
Treatment (Pan)	**Day 1**	**1 Month**	**2 Months**	**3 Months**	**4 Months**	**5 Months**	**6 Months**
Aerobic-Nutrients 1	6.5	1.6 ± 1.1	9.5 ± 2.1	75 ± 1	24 ± 1	8.8 ± 0.5	15 ± 4
Aerobic-Nutrients 2	6.2	2.2 ± 0.5	6.2 ± 0.1	54 ± 16	13 ± 2	NA	NA
Aerobic	U[b]	U	U	1.3 ± 1.8	U	U	U
Aerobic-Killed	NA[c]	U	U	1.8 ± 2.5	U	U	U
Anaerobic-Nitrate	10	4.9 ± 1.6	6.3 ± 0.7	7.5 ± 2.2	5.5 ± 1.1	6.7 ± 0.7	8.4 ± 1.6
Anaerobic-Killed	NA	0.7 ± 0.1	U	U	U	U	U
Original Soil	1.1 ± 0.5	NA	NA	NA	NA	NA	NA

[a] Values are the mean ± standard deviations from duplicate soil samples. Individual values without standard deviations are from single soil samples.
[b] U; Undetected. Value below the minimum detection limit for the assay
[c] NA; Not Analyzed. Sample was not analyzed for compound.

Phosphate was not detected in the aerobic pan that received no fertilizer amendment (aerobic, no addition). Despite the lack of measurable phosphate, however, appreciable losses of both PAHs and TPH occurred in this pan. In this case, it is likely that the bacteria degrading these organic contaminants were utilizing a complex form of phosphorus for growth, other than orthophosphate. This complex form of phosphate was most likely phosphorus present with microbial biomass and/or organic matter (i.e., organic phosphorus compounds). Levels of total phosphorus in the soil were measured during the study (Table 26). This method detects not only simple inorganic P, such as orthophosphate, but also complexed forms of the element. Although data from this analytical procedure tend to be inherently variable, levels of total phosphorus in the aerobic pan without fertilizer were always greater than 5.9 mg/kg, and an average value as high as 37 mg/kg was detected at month 3. Thus, a reasonable quantity of phosphorus was found to be present in the soil, probably in a complex organic form. This complex phosphorus, rather than orthophosphate, was probably used by bacteria for growth during degradation of PAHs and TPH in this pan during the six-month study.

Table 26: Total phosphorus in soil during study

	Soil Phosphorus as P (mg/kg)[a]					
Treatment (Pan)	**1 Month**	**2 Months**	**3 Months**	**4 Months**	**5 Months**	**6 Months**
Aerobic-Nutrients 1	76 ± 13	35 ± 10	230 ± 71	46 ± 36	52 ± 7	NA
Aerobic-Nutrients 2	24 ± 29	52 ± 2	135 ± 7	NA[c]	NA	NA
Aerobic	5.9 ± 5.4	14 ± 4	37 ± 22	6.8 ± 7.4	6.0 ± 1.3	NA
Aerobic-Killed	49 ± 42	5.6 ± 1.2	12 ± 0	36 ± 15	2.8 ± 0.3	NA
Anaerobic-Nitrate	46 ± 52	76 ± 7	20 ± 4	41 ± 39	44 ± 9	NA
Anaerobic-Killed	61 ± 84	U[b]	12 ± 1	53 ± 16	24 ± 1	NA

[a] Values are the mean ± standard deviations from duplicate soil samples.
[b] U; Undetected. Value below the minimum detection limit for the assay
[c] NA; Not Analyzed. Sample was not analyzed for compound.

Sulfate

Soil sulfate levels were measured for all pans during the study (Table 27). A sulfide odor (rotten eggs) would indicate that dramatic sulfate reductions were occurring in the soil. This process, which is carried out by sulfate-reducing bacteria, indicates that anaerobic conditions are prevalent in a sample. More vigorous and more frequent mixing of all aerobic pans would have been conducted if sulfate reduction was indicated. However, sulfate levels in all live pans and the aerobic killed control either remained constant, or increased somewhat (nutrient-amended pans) during the study.

Table 27: Sulfate in soil during study

	Soil Sulfate as SO_4 (mg/kg)[a]					
Treatment (Pan)	**1 Month**	**2 Months**	**3 Months**	**4 Months**	**5 Months**	**6 Months**
Aerobic-Nutrients 1	36 ± 0	45 ± 6	95 ± 35	82 ± 10	75 ± 18	101 ± 13
Aerobic-Nutrients 2	28 ± 0	39 ± 1	80 ± 27	84 ± 7	NA[b]	NA
Aerobic	89 ± 3	98 ± 2	125 ± 35	92 ± 3	120 ± 14	110 ± 14
Aerobic-Killed	87 ± 11	88 ± 6	80 ± 11	79 ± 7	89 ± 0	88 ± 13
Anaerobic-Nitrate	43 ± 7	50 ± 6	71 ± 13	79 ± 7	55 ± 9	75 ± 6
Anaerobic-Killed	255 ± 7	240 ± 42	225 ± 35	190 ± 0	160 ± 42	142 ± 68

[a] Values are the mean ± standard deviations from duplicate soil samples.
[b] NA; Not Analyzed. Sample was not analyzed for compound.

Sulfate levels in the anaerobic killed control were appreciably higher than in any other samples throughout the study. The reason for elevated sulfate levels in this treatment is unclear. The sulfate levels in this pan also declined from 255 to 142 mg/kg during the study. This decline, which appears as a trend throughout the study, may indicate that sulfate-reducing bacteria were active in this treatment during the course of the study.

Soil pH

The pH of soil samples from each pan was checked throughout the six-month study. Although there were some differences among pans, the pH of all live soil samples remained in a range that is suitable for biodegradation. The pH of the original soil used for the pan study was 7.58 ± 0.44 (Table 28), which would be typical of a slightly to moderately alkaline mineral soil. In the nutrient-amended pans, the soil pH gradually declined during the study to 6.95 after six months of incubation (see Aerobic-Nutrients-1). This gradual reduction in pH was most likely caused by the periodic addition of the soluble fertilizer solution, the pH of which was approximately 6.0. Conversely, the pH of the soil in the aerobic pan without nutrient addition as well as the aerobic killed control increased somewhat from the starting soil, particularly during the first half of the study. The reason for this increase is not readily apparent and may reflect changes in several chemical factors controlling pH during the study (e.g., loss of CO_2 during mixing, changes in redox state of minerals during aeration). A neutral or slightly elevated pH may actually be beneficial for PAH and TPH degradation at the Watervliet site due to the reduced solubility of many toxic heavy metals at higher pH values.

Table 28: Soil pH during study

	Soil pH[a]						
Treatment (Pan)	**Day 1**	**1 Month**	**2 Months**	**3 Months**	**4 Months**	**5 Months**	**6 Months**
Aerobic-Nutrients 1	7.63	7.43 ± 0.09	7.45 ± 0.16	7.32 ± 0.04	7.04 ± 0.06	6.81 ± 0.01	6.95 ± 0.01
Aerobic-Nutrients 2	7.61	7.40 ± 0.04	7.58 ± 0.16	7.05 ± 0.01	6.94 ± 0.13	NA[b]	NA
Aerobic	7.92	7.88 ± 0.01	8.21 ± 0.01	8.41 ± 0.03	8.43 ± 0.03	8.36 ± 0.05	8.36 ± 0.04
Aerobic-Killed	7.57	7.80 ± 0.06	8.04 ± 0.03	8.40 ± 0.02	7.74 ± 0.42	8.48 ± 0.03	8.62 ± 0.05
Anaerobic-Nitrate	7.81	8.19 ± 0.13	8.11 ± 0.01	8.24 ± 0.06	8.02 ± 0.59	8.25 ± 0.01	8.34 ± 0.06
Anaerobic-Killed	6.95	7.43 ± 0.01	7.18 ± 0.01	7.47 ± 0.08	7.71 ± 0.21	7.69 ± 0.04	8.01 ± 0.11
Original Soil	7.58 ± 0.44	NA	NA	NA	NA	NA	NA

[a] Values are the mean ± standard deviations from duplicate soil samples. Individual values without standard deviations are from single soil samples.

[b] NA; Not Analyzed. Sample was not analyzed for pH.

7.4.3 Microbiology

Total Heterotrophs

Most uncontaminated field soils contain approximately 1 – 20 x 10^7 heterotrophic bacteria per gram according to standard plate counts (Alexander, 1977). The number of heterotrophic bacteria in the Watervliet soil used for the pan study was 11.3 x 10^7 cells/g soil dry wt (Table 29). This value indicates that the soil used in this study does not contain concentrations of petroleum hydrocarbons or other contaminants (e.g., heavy metals) that are overwhelmingly toxic to bacteria, or numbers would be expected to be much lower. In the aerobic, nutrient-amended pans, the numbers of total heterotrophs increased to greater than 800 x 10^7 cells/g by two months, then declined gradually for then next four months. Bacterial numbers in the aerobic pan without nutrients added increased more slowly and to a lesser extent than in the nutrient-amended pans. Numbers reached a high of 216 x 10^7 cells/g at three months, then declined marginally, thereafter. Cell numbers in the anaerobic pan flooded with nutrients and nitrate were consistently lower than in the aerobic pans: total heterotrophs increased to 14 - 20 x 10^7 cells/g during months 1 to 3, but then declined below 4 x 10^7 cells/g during the remainder of the study. The increase of cells during the first couple of months coincided with the rapid reduction of contaminant concentrations. The reduction of cells indicates that something in the system was limiting the growth and sustainment of the microbial population. This was probably due to lack of an available carbon source, which would be the contaminants in this study.

Table 29: Total aerobic heterotrophic bacteria present in soil during the study (plate counts on R2A Agar)

	Total Heterotrophs per Gram Dry Soil (CFU x 10^7 / g)[a]							
Treatment (Pan)	**Day 1**	**2 Weeks**	**1 Month**	**2 Months**	**3 Months**	**4 Months**	**5 Months**	**6 Months**
Aerobic-Nutrients 1	8.51	213 ± 3	396 ± 11	1710	587	88.6 ± 8.7	36.7 ± 8.5	9.12 ± 0.92
Aerobic-Nutrients 2	8.00	236 ± 23	469 ± 98	888 ± 117	485 ± 158	234 ± 15	NA	NA
Aerobic	21.9	110 ± 26	106 ± 4	176 ± 34	216 ± 22	103	109 ± 9	168 ± 27
Aerobic-Killed	0.028	0.026 ± 0.021	< 0.0001	0.0008 ± 0.0005	0.0001 ± 0.0001	< 0.0001	< 0.0001	< 0.0001
Anaerobic-Nitrate	1.64	ND[b]	21.4 ± 3.1	20.4 ± 6.4	14.1 ± 4.0	3.85 ± 1.00	3.39 ± 0.01	1.87 ± 0.27
Anaerobic-Killed	< 0.0001	ND	< 0.0001	0.0001 ± 0.0000	< 0.0001	< 0.0001	< 0.0001	< 0.0001
Original Soil	11.3 ± 4.0	ND	ND	ND	ND	ND	ND	ND

[a] Values are the mean ± standard deviations from duplicate soil samples. Individual values without standard deviations are from single soil samples.
[b] ND; Value not determined.
[b] NA; Not Analyzed. Sample was not analyzed for compound.

Total heterotrophs in the aerobic and anaerobic pans that were treated with mercuric chloride and sodium azide to inhibit microbial activity were below detection (approximately 0.0001 x 10^7 cells/g) at most sampling times. Cell numbers in the aerobic killed pan declined to 0.028 x 10^7cells/g one day after treatment and remained at this level at two weeks. Additional sodium azide and mercuric chloride were added to the soil in powdered form to increase concentrations of both in the soil. After this addition, total heterotrophs were below detection or very near the lower detection limit of the plating assay for the remainder of the study. Additional sodium azide was added to the soil in this pan each time water was added to increase soil moisture. In the anaerobic killed pan, levels of total heterotrophs were below detection by day 1 and remained at or below detection for the duration of the study.

The levels of TPH and PAHs in the aerobic killed control (Pan 5) declined appreciably even though this pan was treated with high concentrations of both mercuric chloride and sodium azide as microbial inhibitors. A small percentage of this loss may reflect volatilization of the lower molecular weight compounds in each class during mixing of the soil. However, a large percentage of this decline is probably due to biological degradation by bacteria and/or fungi that survived in the presence of the microbial toxins and/or developed resistance to these compounds. Soils are composed of physical aggregates of sand, silts, and clays that are bound together by organic materials including humic and fulvic acids, microbial polysaccharides, and various lipids. As a consequence of particle aggregation, as much as 60 percent of the total volume of a soil may occur as air and water filled pores, many of which are in the micrometer size range

or below (Brady, 1984, Pignatello, 1989). These micropores provide remote sites where bacteria may be protected from microbial inhibitors due to poor diffusion of the compounds into these zones. The survival of bacteria within protected regions that were not influenced by microbial inhibitors, and their subsequent slow biodegradation of PAHs and TPH may account for the losses of these compounds in Pan 5. This hypothesis is also consistent with the observation that only small losses of the target compounds occurred in the flooded killed control (Pan 4). Flooding the soil will both break down soil aggregates and vastly improve the overall distribution of water-soluble microbial inhibitors, such as the two used in this study. Thus, the numbers of bacteria not contacted by the microbial toxins is likely to be much smaller in the flooded compared to the non-flooded soil.

The microbial plate counts performed throughout the study showed low levels (generally less than 10^3 per gram) of total heterotrophs and hydrocarbon-degrading bacteria in both Pan 4 and Pan 5. The plate count assays performed serve as a general indicator of the effectiveness of the microbial inhibitors used, and if appreciable bacterial counts were detected at any time in Pans 4 or 5, additional measures would have been taken to better inhibit microbial activity. However, one inherent difficulty with plate counts is that it is not possible to culture many of the bacteria that reside in natural environments, including soils. Microscopic examinations of soils frequently show 10 to 100 times more bacteria than detected by plate counts, even when a variety of different culture conditions and media are used (Alexander, 1977; Winding et al., 1994). Thus, it is possible that there were one or several PAH and/or TPH-degrading microorganisms surviving in the soil in Pan 5 that were not detected by plate counts either because these organisms were not culturable by standard techniques or because they did not grow on the specific agar media selected. Metabolic assays, including respirometry, reduction of tetrazolium salts, and addition of ^{14}C-substrates (and subsequent measurement of $^{14}CO_2$), could have been used to test for the presence of active but nonculturable bacteria in the killed control soils. However, such assays were beyond the scope of this project. Thus, the losses of PAHs and TPH in Pan 5 may have resulted from biological degradation even though the plate count assay used to measure microbial inhibition showed low bacterial numbers.

Data from the aerobic plate counts show: (1) the soil collected for this study from the Siberia Area is not appreciably toxic to aerobic bacteria, (2) total heterotrophs can be stimulated approximately 20-fold with aeration alone and more than 150-fold with nutrient addition and aeration combined, and (3) mercuric chloride and sodium azide were added at levels sufficient to greatly diminish bacterial plate counts throughout the study.

Petroleum Hydrocarbon-Degrading Bacteria

The bacteria specifically able to grow on petroleum hydrocarbons were determined by plating dilutions from the soils on agar plates containing fuel oil as the only carbon source available for bacterial growth. Approximately 3.55 x 10^7 cells/g soil capable of growth on fuel oil were detected in the original soil from Watervliet. Bacterial numbers on the fuel oil plates increased by more than an order of magnitude in nutrient-amended pans during the first month of incubation and remained at this level through Month 3 (Table 30). These bacteria then declined gradually in density (in nutrient pan 1) such that levels at months 5 and 6 were very near that present in the original soil. In the aerobic samples without nutrient addition, numbers of hydrocarbon degraders also increased by more than an order of magnitude, reaching 54 x 10^7 cells/g soil by month 3. The numbers then declined somewhat to 15.1 x 10^7 cells/g by month 6. The density of hydrocarbon degraders increased slightly in the anaerobic pan amended with nitrate from month 1 to month 3, reaching a high of 6.64 x 107 cells/g at month 3. The density of these cells then declined appreciably, falling to 0.14 x 10^7 cells/g at 6 months. The numbers of hydrocarbon degraders in the aerobic killed and anaerobic killed pans were consistently below detection during the study.

Table 30: Petroleum hydrocarbon degrading bacteria present in soil during the pan study (determined by plate counts using #2 fuel oil as a carbon source)

	Hydrocarbon-Degrading Bacteria per Gram Dry Soil (CFU x 10^7 / g)[a]					
Treatment (Pan)	**Day 1**	**1 Month**	**3 Months**	**4 Months**	**5 Months**	**6 Months**
Aerobic-Nutrients 1	6.63	50.1 ± 5.5	42.5 ± 20.0	27.8 ± 4.47	4.49 ± 0.17	2.19 ± 0.62
Aerobic-Nutrients 2	5.08	36.1 ± 7.3	78.6 ± 1.9	116 ± 62	ND	ND
Aerobic	ND[b]	7.73 ± 1.82	53.9 ± 11.0	36.7 ± 6.7	20.1 ± 8.9	15.1 ± 9.1
Aerobic-Killed	0.001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001
Anaerobic-Nitrate	ND	1.95 ± 0.17	6.64 ± 1.27	0.25 ± 0.24	0.026 ± 0.000	0.14 ± 0.16
Anaerobic-Killed	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001
Original Soil	3.55 ± 1.25	ND	ND	ND	ND	ND

[a] Values are the mean ± standard deviations from duplicate soil samples. Individual values without standard deviations are from single soil samples.
[b] ND; Value not determined.

These results from the contaminant-specific plate counts conducted during the study suggest the following: (1) aerobic bacteria capable of degrading petroleum hydrocarbons reside in the soil at the Watervliet site; (2) these bacteria can be stimulated to increase in density by mixing and aerating the soil; (3) nutrient amendment combined with aeration causes a more rapid stimulation of the hydrocarbon-degrading community than aeration alone, but the maximum density observed in the two treatments is similar; (4) sodium azide and mercuric chloride limited the growth of aerobic hydrocarbon degrading bacteria for the length of the study, but it is likely that low numbers of these microorganisms were still active during the study.

7.4.4 Soil Toxicity and Biological Accumulation

Toxicity

Results from the 14-day acute earthworm toxicity tests are shown in Table 31. As shown in the table, survivability was above 50 percent in the initial soil samples, even at a test soil concentration of 100 percent. The same situation is seen in the test soil after six months of treatment by aerobic land farming without nutrient additions. The LC50 in acute toxicity tests is defined as the concentration of the test substance that is lethal to 50 percent of the test organisms. The results for these two test soils do not allow for a calculation of the LC50, therefore, the LC50 is estimated at greater than 100 percent test soils. However, 0 percent survivability (100 percent mortality) was seen in the soils after six months of treatment with aerobic land farming with nutrient additions. The LC50 for this test soil is estimated to be 67.5 percent.

Table 31: 14-day acute earthworm test results

Sample ID Location	LC_{50}	SURVIVAL					
		14-day Acute Earthworm Test					
		Control	6.25	12.5	25	50	100
Watervliet Arsenal (April)	>100%	93%	90%	90%	93%	83%	67%
No additive (October)	>100%	100%	100%	100%	100%	100%	100%
Nutrients (October)	67.5%	100%	100%	100%	95%	100%	0%

The reason for the increase in acute toxicity to earthworms for the soil treated by aerobic landfarming with nutrient additions is unknown. Since this treatment did result in similar reductions of PAH (Figure 15) and TPH (Figure 17) concentrations in the soils as the aerobic land farming without nutrient additions, it is postulated that the cause of the increased mortality is related either directly or indirectly to the nutrient additions. Nutrients may have reached a level where they were directly toxic to the earthworms, or they may have caused contaminants in the soil to become more bioavailable.

The sudden increase in mortality seen between the 50 and 100 percent test soil concentrations is not uncommon when testing soils. "Unlike toxicity tests with single compounds, which usually result in a regular progression in percent mortality or effect with increasing toxicant concentration, toxicity test with elutriates, soils, or complex aqueous mixtures tend to yield all-or-nothing responses" (EPA, 1989).

Although the LC50 for the test soil both before treatment and after treatment with aerobic land farming without nutrient addition is >100 percent, a comparison can be drawn between the survivability of earthworms at 100 percent test soil concentration for the two soils. Earthworms did show a significant increase in survivability in the test soil after six months of treatment. The survivability increased from 67 to 100 percent. This increase in survivability does indicate some level of toxicity reduction of the soil to earthworms.

Bioaccumulation

The results from the 28-day earthworm bioaccumulation test are shown in Table 32 and Figure 18. Table 32 shows the survivability of earthworms in 25 and 100 percent test soil concentrations before and after treatment by six months of aerobic land farming without nutrient additions. These results show that the survivability of the earthworms in the test soil increased from 52 to 88 percent after treatment by aerobic land farming. This increase in survivability is an indication that toxicity of the soil to earthworms was decreased by land farming of the soil. The survivability results of the 28-day test in 100 percent test soil are almost identical to those seen in the 14-day test.

Table 32: 28-day earthworm bioaccumulation test survivability

Sample ID Location	SURVIVAL		
	28-day Earthworm BioaccumulationTest		
	Control	25	100
Watervliet Arsenal (April)	92%	92%	52%
No additive (October)	98.3%	97.2%	88.3%

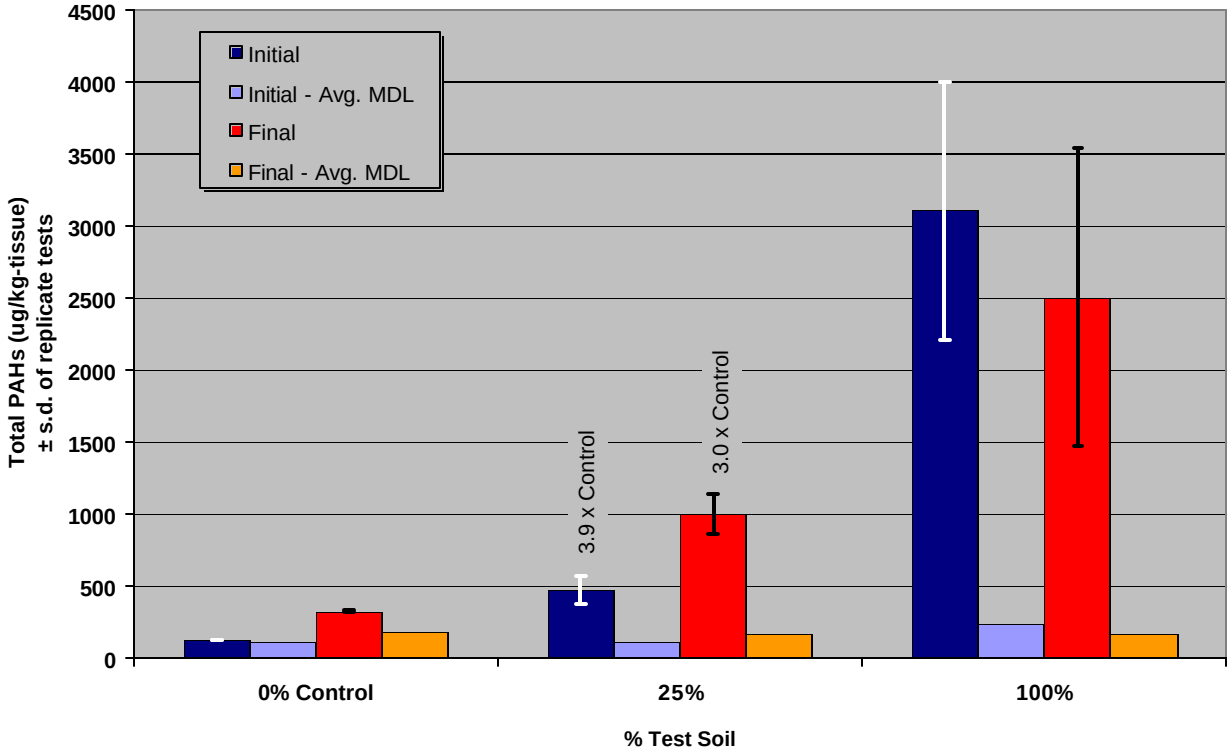


Figure 18: 28-Day Earthworm Bioaccumulation Test Analytical Results

Chemical analyses from the 28-day test (Figure 18) indicate the levels of PAHs accumulated in earthworm tissue. Analyses of the earthworm tissue from tests conducted before and after treatment show that the mean level of PAH concentrations found in the earthworm tissue did decrease in the 100 percent test soil concentration. Although no statistically significant trend can be discerned from this data, a decrease in the mean of the PAH concentrations in the earthworm tissues does indicate a possibility of a decrease in bioavailability of PAHs in the soil to earthworms. This information combined with the increased survivability of the earthworms in 100 percent test soil is a positive indication of toxicity reduction in the soil.

Although results of chemical analysis of the 25 percent test soil dilution show an increase in the mean level of total PAH concentrations found in the earthworm tissues after 28-days of exposure, this increase can be explained by increased levels in the control soils. When the 25percent test soil dilutions are compared to their respective control soils used for the dilutions, it can be seen that the PAH increase in the 25 percent test soil dilutions is approximately the same both before treatment (3.9X) and after six months of landfarming (3.0X). Therefore, the higher levels of PAHs found in the

earthworm tissues in the 25 percent test soil dilution after treatment by landfarming can be attributed to the control soils used for dilution.

7.5 CONCLUSIONS FROM PAN STUDY EVALUATIONS

Data collected suggests that biodegradation caused marked and rapid declines in total PAH levels under aerobic landfarming conditions. Conversely, loss of PAHs observed in the anaerobic treatment amended with nitrate was much slower. As expected, these results suggest that anaerobic biodegradation of PAHs will occur at a much slower rate in this area of the Arsenal. Six months of aerobic landfarming is estimated to result in a 75 percent reduction of total PAHs in the soil from initial levels of approximately 59 mg/kg. Comparison of individual PAH compounds indicates that all PAH compounds, except benzo(a)pyrene, should be below their respective lowest proposed clean-up goals after 10 months of aerobic landfarming. Reduction of benzo(a)pyrene concentrations in the soil to its lowest proposed clean-up goal could require two years of aerobic landfarming.

TPH levels were reduced greater than 70 percent, from an initial concentration of 9,600 mg/kg, in all aerobic pans, including the killed aerobic pan, which appeared to have much lower numbers of bacteria. Removal levels from both the active and killed anaerobic pans, which were sealed, were approximately 10 percent. This information, along with the fact that a significant fraction of the petroleum hydrocarbons measured by the TPH method are volatile, suggests that a significant fraction of TPH removal may be due to volatilization. The actual fraction of TPH removal attributed to biological degradation cannot be stated without direct measurement of volatilized compounds. This issue may need to be addressed if a remediation technique is used which involves mixing or significant disturbance of the soil.

The results also indicated no significant benefit from the addition of nutrients to this soil. Further, results from the acute earthworm toxicity tests indicate that nutrients added at levels similar to those used in this test may cause toxicity to earthworms.

From the data the following general conclusions can be made:

- removal of both PAHs and TPH will occur much more rapidly under mixed aerobic conditions than anaerobic conditions;
- the addition of nutrients does not appear to enhance the rate of total PAH or TPH degradation in the soils tested;
- nutrient levels used in this study may have caused toxicity to earthworms;
- volatilization may be a significant pathway for TPH losses from the soil, particularly during warmer months;
- a reduction of approximately 75 percent in total PAHs (59 mg/kg initial) and TPH (9,600 mg/kg initial) should be achievable in six months with adequate mixing and temperatures similar to those seen in the study (approximately 25°C);
- benzo(a)pyrene levels may require up to two years of aerobic landfarming to reduce the initial levels to the lowest proposed clean-up goal;
- biological degradation rates will be much slower at the colder temperatures seen during the winter months at the Site.

8.0 CONCLUSIONS

Each previous study has provided the data expected from the experimental design and analytical rigor. Positive results have been attained from all aspects of completed biological treatability tests. Initial studies indicated the presence of indigenous aerobic and anaerobic microorganisms capable of degrading the PAHs. Follow-on biological testing demonstrated significant reduction of PAH, TPH, and DRO in controlled experiments approaching simulated land-farming scenarios.

- aerobic and anaerobic PAH and TPH degraders are present at the Site;
- aerobic degradation of PAHs and TPH will be faster than anaerobic;
- the addition of nutrients improved PAH degradation in the soil-columns, therefore the addition of nutrients is recommended for future treatments;
- nutrient levels similar to those used in the pan study may have caused toxicity to earthworms, therefore lower levels are suggested for future treatments;
- a reduction of approximately 75 percent in total PAHs (59 mg/kg initial) and TPH (9,600 mg/kg initial) should be achievable in six months of land farming with weekly mixing and temperatures similar to those seen in the study (approximately 25°C);
- six months of land farming during summer months can reduce the toxicity level of the soils;
- a reduction of approximately 90 percent and 85 percent of total PAHs (10.2 mg/L initial) and TPH (1,900 mg/L initial) respectively is achievable with aerobic bioslurries in 14-weeks at 23°C;
- depending on TPH levels in the soil, volatilization of TPH may be an issue during soil mixing particularly in warmer months.

However, questions remain concerning the full-scale application of in-situ land farming at the Watervliet Arsenal. Of possible concern is the volatilization of TPHs to the atmosphere, especially during mixing of the soils. Estimates of TPH volatilization are needed to determine if the use of land farming will be affected by applicable regulations. Also, the minimum mixing frequency and duration of active treatment

necessary to maintain acceptable degradation rates of COCs is unknown. Specifically, less frequent mixing and a shorter active-remediation phase followed by a monitored passive-attenuation phase may accomplish the same goals in an acceptable time frame.

APPENDIX A

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APPENDIX A
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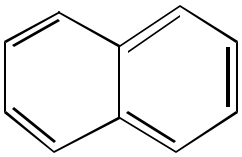
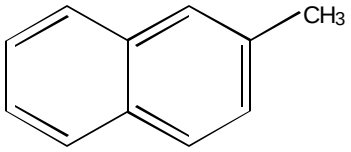
APPENDIX B

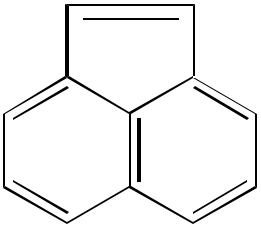
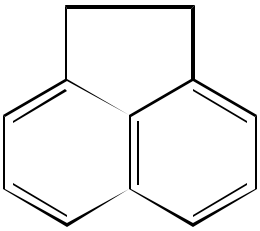
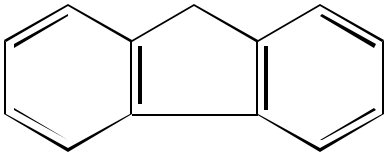
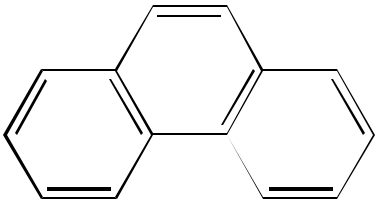
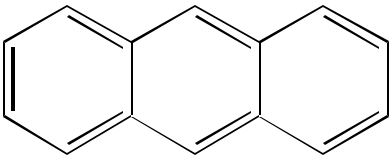
Polycyclic Aromatic Hydrocarbon Structures

APPENDIX B
POLYCYCLIC AROMATIC HYDROCARGON STRUCTURES

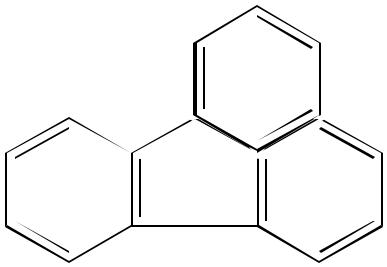
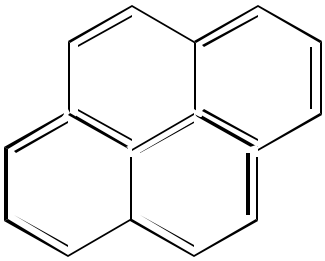
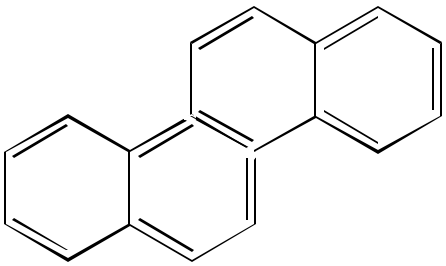
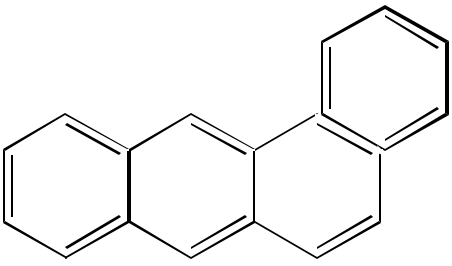
2-Ring Compounds

Name	Abbreviation	Structure
Napthalene	NAPHTH	
2-methylnaphthalene	2-MeNAPH	

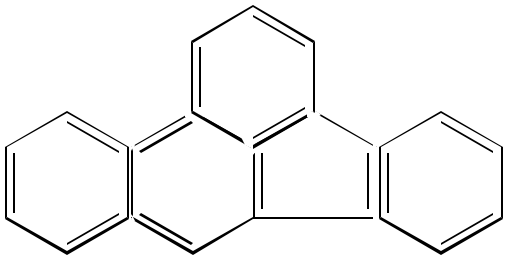
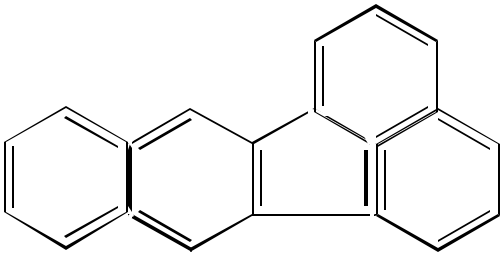
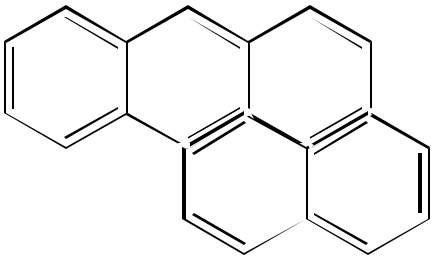
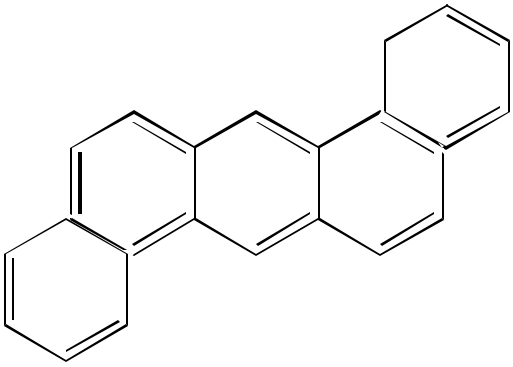
3-Ring Compounds

Acenaphthylene	ACENAY	
Acenaphthene	ACENAP	
Fluorene	FLUORE	
Phenanthrene	PHENAN	
Anthracene	ANTRAC	

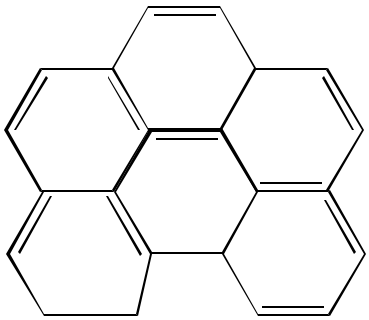
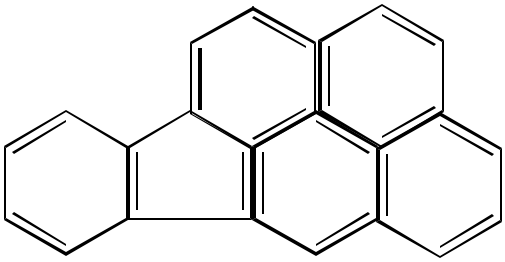
4-Ring Compounds

Name	Abbreviation	Structure
Fluoranthene	FLANTHE	
Pyrene	PYRENE	
Chrysene	CHRYSE	
Benzo(a)anthracene	BAANTHR	

5-Ring Compounds

Name	Abbreviation	Structure
Benzo(b)fluoranthene	BBFLANT	
Benzo(k)fluoranthene	BKFLANT	
Benzo(a)pyrene	BAP	
Dibenzo(a,h,)anthracene	DBAHANT	

6-Ring Compounds

Name	Abbreviation	Structure
Benzo(g,h,i)perylene	B-GHI-PY	
Indeno(1,2,3-c,d)pyrene	I123PYR	

APPENDIX C

Raw Data Pan Tests

APPENDIX C
Raw Data Pan Tests

PAH and TPH in Original Soil Samples and T = 0

Treatment	Original Soil 1	Original Soil 2	Original Soil 3	Aerobic w/ Nutrients #1	Aerobic w/ Nutrients #2	Aerobic	Aerobic/ Killed	Anaerobic/ Killed	Anaerobic w/Nitrate	All Average	All SD	Original 3 Average	Original 3 SD
PAH	(ug/kg)	(ug/kg)	(ug/kg)	(ug/kg)	(ug/kg)	(ug/kg)	(ug/kg)	(ug/kg)	(ug/kg)	(ug/kg)	(ug/kg)	(ug/kg)	(ug/kg)
Acenapthene	890	830	1000	450	890	800	860	1100	830	850	177	907	86
Acenapthylene	290	285	300	310	295	305	370	330	285	308	27	0	0
Anthracene	2200	2000	2600	980	2200	2000	2000	2800	1900	2076	510	2267	306
Benzo(a)anthracene	5100	5700	7000	2300	5600	4400	5000	8200	5200	5389	1637	5933	971
Benzo(b) Fluoranthene	6800	7000	8800	2600	7000	6100	4900	9300	6200	6500	1989	7467	1172
Benzo(k) Fluoranthene	1700	2500	1800	1200	1800	2000	1400	3200	2000	1956	596	2000	436
Benzo(g,h,i,)perylene	1500	1400	1600	930	1300	1200	1800	2300	1700	1526	394	1500	100
Benzo(a)pyrene	4300	4900	5700	1900	4600	4000	4200	7200	4400	4578	1414	4967	702
Chrysene	5100	5400	6000	2600	5200	4700	4900	8000	4700	5178	1409	5500	458
Dibenz[a,h]anthracene	290	285	300	310	295	305	370	330	285	308	27	292	8
Fluoranthene	9900	10000	12000	5300	10000	9200	10000	13000	9300	9856	2123	10633	1185
Fluorene	1300	1300	1500	650	1300	305	1400	1600	285	1071	514	1367	115
Indeno(1,2,3-cd)pyrene	1500	1400	1600	890	1400	1200	1600	2300	1800	1521	392	1500	100
Naphthalene	290	285	350	310	295	305	370	350	285	316	32	308	36
Phenanthrene	9400	9100	12000	4500	9500	8700	9100	12000	8100	9156	2218	10167	1595
Pyrene	8100	8200	9300	4500	8200	7200	8300	11000	8000	8089	1721	8533	666
Total PAHs	58460	60585	71860	29730	59875	52720	56570	83010	55270	58674	14406	53567	7196
TPH Values	6200	12000	11000	11000	13000	8300	8600	11000	5100	9578	2686	8918	3101

Bold values indicate non-detect results
Red italicized values indicate J detections below one-half of the quantitation limit.

Month 1 - Aerobic w/Nutrients #1

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	*300*	350	**325**	**35**	**850**	***62%***
Acenapthylene	**300**	**285**	**293**	**11**	**308**	***5%***
Anthracene	790	1100	**945**	**219**	**2076**	***54%***
Benzo(a)anthracene	2800	3000	**2900**	**141**	**5389**	***46%***
Benzo(b) Fluoranthene	4900	4400	**4650**	**354**	**6500**	***28%***
Benzo(k) Fluoranthene	1500	1400	**1450**	**71**	**1956**	***26%***
Benzo(g,h,I,)perylene	1700	1400	**1550**	**212**	**1526**	***-2%***
Benzo(a)pyrene	4100	4000	**4050**	**71**	**4578**	***12%***
Chrysene	3300	3200	**3250**	**71**	**5178**	***37%***
Dibenz(a,h)anthracene	**300**	**285**	**293**	**0**	**308**	***5%***
Fluoranthene	5300	4900	**5100**	**283**	**9856**	***48%***
Fluorene	*300*	360	**330**	**42**	**1071**	***69%***
Indeno(1,2,3-cd)pyrene	1600	1500	**1550**	**71**	**1521**	***-2%***
Naphthalene	**300**	*285*	**293**	**11**	**316**	***7%***
Phenanthrene	3000	3800	**3400**	**566**	**9156**	***63%***
Pyrene	5000	4800	**4900**	**141**	**8089**	***39%***
Total PAHs	**35490**	**35065**	**35278**	**301**	**58674**	***40%***
TPH Values	**8200**	**7600**	**7900**	**424**	**9578**	***18%***

Bold values in columns a and b indicate non-detect results
Red italicized values indicate J detections below one-half of the quantitation limit.

Month 1 - Aerobic w/Nutrients #2

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	*285*	**285**	**285**	**0**	**850**	***66%***
Acenapthylene	**285**	**285**	**285**	**0**	**308**	***7%***
Anthracene	820	530	**675**	**205**	**2076**	***67%***
Benzo(a)anthracene	2900	1700	**2300**	**849**	**5389**	***57%***
Benzo(b) Fluoranthene	3900	2800	**3350**	**778**	**6500**	***48%***
Benzo(k) Fluoranthene	1400	830	**1115**	**403**	**1956**	***43%***
Benzo(g,h,I,)perylene	1400	1100	**1250**	**212**	**1526**	***18%***
Benzo(a)pyrene	3600	2400	**3000**	**849**	**4578**	***34%***
Chrysene	2700	2400	**2550**	**212**	**5178**	***51%***
Dibenz(a,h)anthracene	**285**	**285**	**285**	**0**	**308**	***7%***
Fluoranthene	4500	3200	**3850**	**919**	**9856**	***61%***
Fluorene	*285*	**285**	**285**	**0**	**1071**	***73%***
Indeno(1,2,3-cd)pyrene	1400	1100	**1250**	**212**	**1521**	***18%***
Naphthalene	**285**	**285**	**285**	**0**	**316**	***10%***
Phenanthrene	3100	2100	**2600**	**707**	**9156**	***72%***
Pyrene	4300	3400	**3850**	**636**	**8089**	***52%***
Total PAHs	**31445**	**22985**	**27215**	**5982**	**58674**	***54%***
TPH Values	**8400**	**7800**	**8100**	**424**	**9578**	***15%***

Bold values in columns a and b indicate non-detect results
Red italicized values indicate J detections below one-half of the quantitation limit.

Month 1 - Aerobic

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	*285*	310	**298**	**18**	**850**	***65%***
Acenapthylene	**285**	**295**	**290**	**7**	**308**	***6%***
Anthracene	800	840	**820**	**28**	**2076**	***60%***
Benzo(a)anthracene	3100	4000	**3550**	**636**	**5389**	***34%***
Benzo(b) Fluoranthene	4600	6500	**5550**	**1344**	**6500**	***15%***
Benzo(k) Fluoranthene	2000	2600	**2300**	**424**	**1956**	***-18%***
Benzo(g,h,I,)perylene	1400	1300	**1350**	**71**	**1526**	***12%***
Benzo(a)pyrene	3600	5100	**4350**	**1061**	**4578**	***5%***
Chrysene	3000	4900	**3950**	**1344**	**5178**	***24%***
Dibenz(a,h)anthracene	**285**	*295*	**290**	**7**	**308**	***6%***
Fluoranthene	5900	6300	**6100**	**283**	**9856**	***38%***
Fluorene	*285*	300	**293**	**11**	**1071**	***73%***
Indeno(1,2,3-cd)pyrene	1400	1300	**1350**	**71**	**1521**	***11%***
Naphthalene	**285**	*295*	**290**	**7**	**316**	***8%***
Phenanthrene	2600	2700	**2650**	**71**	**9156**	***71%***
Pyrene	5600	7100	**6350**	**1061**	**8089**	***21%***
Total PAHs	**35425**	**44135**	**39780**	**6159**	**58674**	***32%***
TPH Values	**11000**	**11000**	**11000**	**0**	**9578**	***-15%***

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Month 1 Samples - Aerobic/Killed

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	900	830	**865**	**49**	**850**	***-2%***
Acenapthylene	*285*	**275**	**280**	**7**	**308**	***9%***
Anthracene	2200	1900	**2050**	**212**	**2076**	***1%***
Benzo(a)anthracene	6000	5100	**5550**	**636**	**5389**	***-3%***
Benzo(b) Fluoranthene	6100	5600	**5850**	**354**	**6500**	***10%***
Benzo(k) Fluoranthene	2700	2500	**2600**	**141**	**1956**	***-33%***
Benzo(g,h,I,)perylene	1400	1200	**1300**	**141**	**1526**	***15%***
Benzo(a)pyrene	5000	4100	**4550**	**636**	**4578**	***1%***
Chrysene	6000	5400	**5700**	**424**	**5178**	***-10%***
Dibenz(a,h)anthracene	**285**	**275**	**280**	**7**	**308**	***9%***
Fluoranthene	10000	9700	**9850**	**212**	**9856**	***0%***
Fluorene	1200	1100	**1150**	**71**	**1071**	***-7%***
Indeno(1,2,3-cd)pyrene	1400	1200	**1300**	**141**	**1521**	***15%***
Naphthalene	*285*	*275*	**280**	**7**	**316**	***11%***
Phenanthrene	9100	8800	**8950**	**212**	**9156**	***2%***
Pyrene	8400	7500	**7950**	**636**	**8089**	***2%***
Total PAHs	**61255**	**55755**	**58505**	**3889**	**58674**	***0%***
TPH Values	**10000**	**9500**	**9750**	**354**	**9578**	***-2%***

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Month 1 - Anaerobic/Killed

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	1000	890	**945**	**78**	**850**	***-11%***
Acenapthylene	**295**	**325**	**310**	**21**	**308**	***-1%***
Anthracene	2500	2300	**2400**	**141**	**2076**	***-16%***
Benzo(a)anthracene	6600	6200	**6400**	**283**	**5389**	***-19%***
Benzo(b) Fluoranthene	6600	7400	**7000**	**566**	**6500**	***-8%***
Benzo(k) Fluoranthene	3500	3100	**3300**	**283**	**1956**	***-69%***
Benzo(g,h,I,)perylene	1400	1500	**1450**	**71**	**1526**	***5%***
Benzo(a)pyrene	5000	4600	**4800**	**283**	**4578**	***-5%***
Chrysene	7200	6300	**6750**	**636**	**5178**	***-30%***
Dibenz(a,h)anthracene	**295**	**325**	**310**	**21**	**308**	***-1%***
Fluoranthene	12000	11000	**11500**	**707**	**9856**	***-17%***
Fluorene	1400	1400	**1400**	**0**	**1071**	***-31%***
Indeno(1,2,3-cd)pyrene	1500	1500	**1500**	**0**	**1521**	***1%***
Naphthalene	*295*	*325*	**310**	**21**	**316**	***2%***
Phenanthrene	10000	10000	**10000**	**0**	**9156**	***-9%***
Pyrene	9200	8400	**8800**	**566**	**8089**	***-9%***
Total PAHs	**68785**	**65565**	**67175**	**2277**	**58674**	***-14%***
TPH Values	**7500**	**12000**	**9750**	**3182**	**9578**	***-2%***

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Month 1 - Anaerobic w/Nitrate

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	800	930	**865**	**92**	**850**	***-2%***
Acenapthylene	**315**	**320**	**318**	**4**	**308**	***-3%***
Anthracene	2200	2200	**2200**	**0**	**2076**	***-6%***
Benzo(a)anthracene	4700	5700	**5200**	**707**	**5389**	***4%***
Benzo(b) Fluoranthene	5800	6100	**5950**	**212**	**6500**	***8%***
Benzo(k) Fluoranthene	2500	3100	**2800**	**424**	**1956**	***-43%***
Benzo(g,h,I,)perylene	1300	1300	**1300**	**0**	**1526**	***15%***
Benzo(a)pyrene	4200	4600	**4400**	**283**	**4578**	***4%***
Chrysene	5900	6700	**6300**	**566**	**5178**	***-22%***
Dibenz(a,h)anthracene	**315**	**320**	**318**	**4**	**308**	***-3%***
Fluoranthene	10000	11000	**10500**	**707**	**9856**	***-7%***
Fluorene	1100	1400	**1250**	**212**	**1071**	***-17%***
Indeno(1,2,3-cd)pyrene	1500	1300	**1400**	**141**	**1521**	***8%***
Naphthalene	*315*	*320*	**318**	**4**	**316**	***-1%***
Phenanthrene	9300	9900	**9600**	**424**	**9156**	***-5%***
Pyrene	7800	8700	**8250**	**636**	**8089**	***-2%***
Total PAHs	**58045**	**63890**	**60968**	**4133**	**58674**	***-4%***
TPH Values	**9800**	**8500**	**9150**	**919**	**9578**	***4%***

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Month 2 - Aerobic w/Nutrients #1

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	*291*	**288**	**290**	**0**	**850**	***66%***
Acenapthylene	**291**	**288**	**290**	**2**	**308**	***6%***
Anthracene	560	480	**520**	**57**	**2076**	***75%***
Benzo(a)anthracene	1500	1600	**1550**	**71**	**5389**	***71%***
Benzo(b) fluoranthene	2500	3500	**3000**	**707**	**6500**	***54%***
Benzo(k) fluoranthene	910	660	**785**	**177**	**1956**	***60%***
Benzo(g,h,I,)perylene	1300	1600	**1450**	**212**	**1526**	***5%***
Benzo(a)pyrene	2200	3000	**2600**	**566**	**4578**	***43%***
Chrysene	2300	2400	**2350**	**71**	**5178**	***55%***
Dibenz(a,h)anthracene	**291**	**288**	**290**	**2**	**308**	***6%***
Fluoranthene	3000	2900	**2950**	**71**	**9856**	***70%***
Fluorene	*291*	**288**	**290**	**2**	**1071**	***73%***
Indeno(1,2,3-cd)pyrene	1300	1600	**1450**	**212**	**1521**	***5%***
Naphthalene	**291**	**288**	**290**	**2**	**316**	***8%***
Phenanthrene	2400	1800	**2100**	**424**	**9156**	***77%***
Pyrene	2900	3100	**3000**	**141**	**8089**	***63%***
Total PAHs	**22325**	**24080**	**23203**	**1241**	**58674**	***60%***
TPH Values	**4800**	**3900**	**4350**	**636**	**9578**	***55%***

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Month 2 - Aerobic w/Nutrients #2

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	**294**	**291**	**293**	**2**	**850**	***66%***
Acenapthylene	**294**	**291**	**293**	**2**	**308**	***5%***
Anthracene	460	*291*	**376**	**120**	**2076**	***82%***
Benzo(a)anthracene	1600	970	**1285**	**445**	**5389**	***76%***
Benzo(b) fluoranthene	2700	1900	**2300**	**566**	**6500**	***65%***
Benzo(k) fluoranthene	1200	600	**900**	**424**	**1956**	***54%***
Benzo(g,h,I,)perylene	1400	1300	**1350**	**71**	**1526**	***12%***
Benzo(a)pyrene	2800	1700	**2250**	**778**	**4578**	***51%***
Chrysene	2100	1500	**1800**	**424**	**5178**	***65%***
Dibenz(a,h)anthracene	**294**	**291**	**293**	**2**	**308**	***5%***
Fluoranthene	2500	1800	**2150**	**495**	**9856**	***78%***
Fluorene	**294**	**291**	**293**	**2**	**1071**	***73%***
Indeno(1,2,3-cd)pyrene	1400	1100	**1250**	**212**	**1521**	***18%***
Naphthalene	**294**	**291**	**293**	**2**	**316**	***7%***
Phenanthrene	1900	1100	**1500**	**566**	**9156**	***84%***
Pyrene	2700	1900	**2300**	**566**	**8089**	***72%***
Total PAHs	**22230**	**15616**	**18923**	**4677**	**58674**	***68%***
TPH Values	**3800**	**3300**	**3550**	**354**	**9578**	***63%***

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Month 2 - Aerobic

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	*294*	**275**	**285**	**13**	**850**	***67%***
Acenapthylene	**294**	**275**	**285**	**13**	**308**	***8%***
Anthracene	620	*275*	**448**	**244**	**2076**	***78%***
Benzo(a)anthracene	2900	1200	**2050**	**1202**	**5389**	***62%***
Benzo(b) fluoranthene	5100	3400	**4250**	**1202**	**6500**	***35%***
Benzo(k) fluoranthene	2100	800	**1450**	**919**	**1956**	***26%***
Benzo(g,h,I,)perylene	1400	1100	**1250**	**212**	**1526**	***18%***
Benzo(a)pyrene	3900	2400	**3150**	**1061**	**4578**	***31%***
Chrysene	3200	1800	**2500**	**990**	**5178**	***52%***
Dibenz(a,h)anthracene	**294**	**275**	**285**	**13**	**308**	***8%***
Fluoranthene	4200	2000	**3100**	**1556**	**9856**	***69%***
Fluorene	*294*	**275**	**285**	**13**	**1071**	***73%***
Indeno(1,2,3-cd)pyrene	1600	1100	**1350**	**354**	**1521**	***11%***
Naphthalene	**294**	**275**	**285**	**13**	**316**	***10%***
Phenanthrene	3100	1200	**2150**	**1344**	**9156**	***77%***
Pyrene	5100	3300	**4200**	**1273**	**8089**	***48%***
Total PAHs	**34690**	**19950**	**27320**	**10423**	**58674**	***53%***
TPH Values	**3000**	**2500**	**2750**	**354**	**9578**	***71%***

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Month 2 Samples - Aerobic/Killed

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	670	600	**635**	**49**	**850**	***25%***
Acenapthylene	**298**	**298**	**298**	**0**	**308**	***3%***
Anthracene	1400	1300	**1350**	**71**	**2076**	***35%***
Benzo(a)anthracene	4100	3600	**3850**	**354**	**5389**	***29%***
Benzo(b) fluoranthene	4400	4000	**4200**	**283**	**6500**	***35%***
Benzo(k) fluoranthene	2100	1000	**1550**	**778**	**1956**	***21%***
Benzo(g,h,I,)perylene	1600	1300	**1450**	**212**	**1526**	***5%***
Benzo(a)pyrene	3500	3000	**3250**	**354**	**4578**	***29%***
Chrysene	4400	4400	**4400**	**0**	**5178**	***15%***
Dibenz(a,h)anthracene	**298**	**298**	**298**	**0**	**308**	***3%***
Fluoranthene	7200	6800	**7000**	**283**	**9856**	***29%***
Fluorene	950	850	**900**	**71**	**1071**	***16%***
Indeno(1,2,3-cd)pyrene	1500	1300	**1400**	**141**	**1521**	***8%***
Naphthalene	*298*	**298**	**298**	**0**	**316**	***6%***
Phenanthrene	6900	6500	**6700**	**283**	**9156**	***27%***
Pyrene	6400	6300	**6350**	**71**	**8089**	***21%***
Total PAHs	**46014**	**41844**	**43929**	**2949**	**58674**	***25%***
TPH Values	**5400**	**6000**	**5700**	**424**	**9578**	***40%***

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Month 2 - Anaerobic/Killed

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	780	1500	**1140**	**509**	**850**	***-34%***
Acenapthylene	**321**	*321*	**321**	**0**	**308**	***-4%***
Anthracene	1600	3500	**2550**	**1344**	**2076**	***-23%***
Benzo(a)anthracene	5100	11000	**8050**	**4172**	**5389**	***-49%***
Benzo(b) fluoranthene	6400	15000	**10700**	**6081**	**6500**	***-65%***
Benzo(k) fluoranthene	2900	5600	**4250**	**1909**	**1956**	***-117%***
Benzo(g,h,I,)perylene	1900	2500	**2200**	**424**	**1526**	***-44%***
Benzo(a)pyrene	4900	10000	**7450**	**3606**	**4578**	***-63%***
Chrysene	5900	12000	**8950**	**4313**	**5178**	***-73%***
Dibenz(a,h)anthracene	**321**	*321*	**321**	**0**	**308**	***-4%***
Fluoranthene	8100	13000	**10550**	**3465**	**9856**	***-7%***
Fluorene	1200	2000	**1600**	**566**	**1071**	***-49%***
Indeno(1,2,3-cd)pyrene	2000	2900	**2450**	**636**	**1521**	***-61%***
Naphthalene	*321*	480	**401**	**112**	**316**	***-27%***
Phenanthrene	8200	15000	**11600**	**4808**	**9156**	***-27%***
Pyrene	7800	13000	**10400**	**3677**	**8089**	***-29%***
Total PAHs	**57743**	**108122**	**82933**	**35623**	**58674**	***-41%***
TPH Values	**5800**	**6700**	**6250**	**636**	**9578**	***35%***

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Red italicized values indicate J detections below one-half of the quantitation limit.

Month 2 - Anaerobic w/Nitrate

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	780	930	**855**	**106**	**850**	***-1%***
Acenapthylene	**309**	**321**	**315**	**8**	**308**	***-2%***
Anthracene	1600	1800	**1700**	**141**	**2076**	***18%***
Benzo(a)anthracene	4400	5400	**4900**	**707**	**5389**	***9%***
Benzo(b) fluoranthene	5300	7600	**6450**	**1626**	**6500**	***1%***
Benzo(k) fluoranthene	1400	1900	**1650**	**354**	**1956**	***16%***
Benzo(g,h,I,)perylene	1400	1500	**1450**	**71**	**1526**	***5%***
Benzo(a)pyrene	3800	4800	**4300**	**707**	**4578**	***6%***
Chrysene	5200	6300	**5750**	**778**	**5178**	***-11%***
Dibenz(a,h)anthracene	**309**	**321**	**315**	**8**	**308**	***-2%***
Fluoranthene	6900	7800	**7350**	**636**	**9856**	***25%***
Fluorene	1000	1300	**1150**	**212**	**1071**	***-7%***
Indeno(1,2,3-cd)pyrene	1300	1500	**1400**	**141**	**1521**	***8%***
Naphthalene	*309*	330	**320**	**15**	**316**	***-1%***
Phenanthrene	7400	8800	**8100**	**990**	**9156**	***12%***
Pyrene	6600	7300	**6950**	**495**	**8089**	***14%***
Total PAHs	**48007**	**57902**	**52955**	**6997**	**58674**	***10%***
TPH Values	**13000**	**8500**	**10750**	**3182**	**9578**	***-12%***

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Red italicized values indicate J detections below one-half of the quantitation limit.

Month 3 - Aerobic w/Nutrients #1

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	**291**	**298**	**295**	**5**	**850**	***65%***
Acenapthylene	**291**	**298**	**295**	**5**	**308**	***4%***
Anthracene	430	*298*	**364**	**93**	**2076**	***82%***
Benzo(a)anthracene	1100	1200	**1150**	**71**	**5389**	***79%***
Benzo(b) fluoranthene	1900	2400	**2150**	**354**	**6500**	***67%***
Benzo(k) fluoranthene	680	510	**595**	**120**	**1956**	***70%***
Benzo(g,h,I,)perylene	1000	1200	**1100**	**141**	**1526**	***28%***
Benzo(a)pyrene	1700	2100	**1900**	**283**	**4578**	***58%***
Chrysene	2000	2400	**2200**	**283**	**5178**	***58%***
Dibenz(a,h)anthracene	**291**	**298**	**295**	**5**	**308**	***4%***
Fluoranthene	1900	1600	**1750**	**212**	**9856**	***82%***
Fluorene	*291*	**298**	**295**	**5**	**1071**	***73%***
Indeno(1,2,3-cd)pyrene	1100	1200	**1150**	**71**	**1521**	***24%***
Naphthalene	**291**	**298**	**295**	**5**	**316**	***7%***
Phenanthrene	1700	1200	**1450**	**354**	**9156**	***84%***
Pyrene	1900	2000	**1950**	**71**	**8089**	***76%***
Total PAHs	**16865**	**17598**	**17232**	**518**	**58674**	***71%***
TPH Values	**4400**	**4600**	**4500**	**141**	**9578**	***53%***

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Month 3 - Aerobic w/Nutrients #2

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	**286**	**298**	**292**	**8**	**850**	***66%***
Acenapthylene	**286**	**298**	**292**	**8**	**308**	***5%***
Anthracene	580	*298*	**439**	**199**	**2076**	***79%***
Benzo(a)anthracene	1600	930	**1265**	**474**	**5389**	***77%***
Benzo(b) fluoranthene	2500	1900	**2200**	**424**	**6500**	***66%***
Benzo(k) fluoranthene	1200	510	**855**	**488**	**1956**	***56%***
Benzo(g,h,I,)perylene	1400	1100	**1250**	**212**	**1526**	***18%***
Benzo(a)pyrene	2600	1900	**2250**	**495**	**4578**	***51%***
Chrysene	3300	2100	**2700**	**849**	**5178**	***48%***
Dibenz(a,h)anthracene	**286**	**298**	**292**	**8**	**308**	***5%***
Fluoranthene	2600	1400	**2000**	**849**	**9856**	***80%***
Fluorene	*286*	**298**	**292**	**8**	**1071**	***73%***
Indeno(1,2,3-cd)pyrene	1400	1200	**1300**	**141**	**1521**	***15%***
Naphthalene	**286**	**298**	**292**	**8**	**316**	***7%***
Phenanthrene	2100	1100	**1600**	**707**	**9156**	***83%***
Pyrene	3000	1900	**2450**	**778**	**8089**	***70%***
Total PAHs	**23710**	**15828**	**19769**	**5573**	**58674**	***66%***
TPH Values	**3800**	**3800**	**3800**	**0**	**9578**	***60%***

Bold values in columns a and b indicate non-detect results

Red italicized values indicate J detections below one-half of the quantitation limit.

Month 3 - Aerobic

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	*% Loss*
Acenapthene	**295**	**305**	**300**	**7**	**850**	***65%***
Acenapthylene	**295**	**305**	**300**	**7**	**308**	***3%***
Anthracene	**295**	330	**313**	**25**	**2076**	***85%***
Benzo(a)anthracene	770	1600	**1185**	**587**	**5389**	***78%***
Benzo(b) fluoranthene	1900	4300	**3100**	**1697**	**6500**	***52%***
Benzo(k) fluoranthene	770	1200	**985**	**304**	**1956**	***50%***
Benzo(g,h,I,)perylene	770	1100	**935**	**233**	**1526**	***39%***
Benzo(a)pyrene	1700	3300	**2500**	**1131**	**4578**	***45%***
Chrysene	1600	3200	**2400**	**1131**	**5178**	***54%***
Dibenz(a,h)anthracene	**295**	**305**	**300**	**7**	**308**	***3%***
Fluoranthene	1000	2200	**1600**	**849**	**9856**	***84%***
Fluorene	**295**	**305**	**300**	**7**	**1071**	***72%***
Indeno(1,2,3-cd)pyrene	830	1300	**1065**	**332**	**1521**	***30%***
Naphthalene	**295**	**305**	**300**	**7**	**316**	***5%***
Phenanthrene	**295**	1400	**848**	**781**	**9156**	***91%***
Pyrene	2200	3800	**3000**	**1131**	**8089**	***63%***
Total PAHs	**13605**	**25255**	**19430**	**8238**	**58674**	***67%***
TPH Values	**3100**	**3200**	**3150**	**71**	**9578**	***67%***

Bold values in columns a and b indicate non-detect results

Red italicized values indicate J detections below one-half of the quantitation limit.

Month 3 Samples - Aerobic/Killed

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	*% Loss*
Acenapthene	420	440	**430**	**14**	**850**	***49%***
Acenapthylene	**284**	**300**	**292**	**11**	**308**	***5%***
Anthracene	720	730	**725**	**7**	**2076**	***65%***
Benzo(a)anthracene	2200	2100	**2150**	**71**	**5389**	***60%***
Benzo(b) fluoranthene	3300	2600	**2950**	**495**	**6500**	***55%***
Benzo(k) fluoranthene	890	890	**890**	**0**	**1956**	***54%***
Benzo(g,h,I,)perylene	920	880	**900**	**28**	**1526**	***41%***
Benzo(a)pyrene	2300	2000	**2150**	**212**	**4578**	***53%***
Chrysene	3700	3700	**3700**	**0**	**5178**	***29%***
Dibenz(a,h)anthracene	**284**	**300**	**292**	**11**	**308**	***5%***
Fluoranthene	3900	3800	**3850**	**71**	**9856**	***61%***
Fluorene	640	600	**620**	**28**	**1071**	***42%***
Indeno(1,2,3-cd)pyrene	1000	980	**990**	**14**	**1521**	***35%***
Naphthalene	**284**	**300**	**292**	**11**	**316**	***7%***
Phenanthrene	4200	3900	**4050**	**212**	**9156**	***56%***
Pyrene	3600	3500	**3550**	**71**	**8089**	***56%***
Total PAHs	**28642**	**27020**	**27831**	**1147**	**58674**	***53%***
TPH Values	**6000**	**6900**	**6450**	**636**	**9578**	***33%***

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Red italicized values indicate J detections below one-half of the quantitation limit.

Month 3 - Anaerobic/Killed

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	1000	760	**880**	**170**	**850**	***-4%***
Acenapthylene	**321**	**295**	**308**	**18**	**308**	***0%***
Anthracene	1800	1500	**1650**	**212**	**2076**	***21%***
Benzo(a)anthracene	5000	5100	**5050**	**71**	**5389**	***6%***
Benzo(b) fluoranthene	5900	7900	**6900**	**1414**	**6500**	***-6%***
Benzo(k) fluoranthene	1900	490	**1195**	**997**	**1956**	***39%***
Benzo(g,h,I,)perylene	1700	1900	**1800**	**141**	**1526**	***-18%***
Benzo(a)pyrene	4600	5300	**4950**	**495**	**4578**	***-8%***
Chrysene	7800	7200	**7500**	**424**	**5178**	***-45%***
Dibenz(a,h)anthracene	*321*	**295**	**308**	**18**	**308**	***0%***
Fluoranthene	7700	7400	**7550**	**212**	**9856**	***23%***
Fluorene	1300	1000	**1150**	**212**	**1071**	***-7%***
Indeno(1,2,3-cd)pyrene	1900	2100	**2000**	**141**	**1521**	***-31%***
Naphthalene	420	*295*	**358**	**88**	**316**	***-13%***
Phenanthrene	8400	7500	**7950**	**636**	**9156**	***13%***
Pyrene	7400	6700	**7050**	**495**	**8089**	***13%***
Total PAHs	**57462**	**55735**	**56599**	**1221**	**58674**	***4%***
TPH Values	**5100**	**7000**	**6050**	**1344**	**9578**	***37%***

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Red italicized values indicate J detections below one-half of the quantitation limit.

Month 3 - Anaerobic w/Nitrate

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	560	640	**600**	**57**	**850**	***29%***
Acenapthylene	**301**	**284**	**293**	**12**	**308**	***5%***
Anthracene	1100	1300	**1200**	**141**	**2076**	***42%***
Benzo(a)anthracene	3400	3900	**3650**	**354**	**5389**	***32%***
Benzo(b) fluoranthene	4100	4400	**4250**	**212**	**6500**	***35%***
Benzo(k) fluoranthene	1200	1500	**1350**	**212**	**1956**	***31%***
Benzo(g,h,I,)perylene	1300	1200	**1250**	**71**	**1526**	***18%***
Benzo(a)pyrene	3000	3400	**3200**	**283**	**4578**	***30%***
Chrysene	5700	6100	**5900**	**283**	**5178**	***-14%***
Dibenz(a,h)anthracene	*301*	*284*	**293**	**12**	**308**	***5%***
Fluoranthene	5600	6400	**6000**	**566**	**9856**	***39%***
Fluorene	890	1000	**945**	**78**	**1071**	***12%***
Indeno(1,2,3-cd)pyrene	1400	1400	**1400**	**0**	**1521**	***8%***
Naphthalene	*301*	**284**	**293**	**12**	**316**	***7%***
Phenanthrene	6000	6300	**6150**	**212**	**9156**	***33%***
Pyrene	5300	6300	**5800**	**707**	**8089**	***28%***
Total PAHs	**40453**	**44692**	**42573**	**2997**	**58674**	***27%***
TPH Values	**3500**	**6200**	**4850**	**1909**	**9578**	***49%***

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Red italicized values indicate J detections below one-half of the quantitation limit.

Month 4 - Aerobic w/Nutrients #1

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	*286*	**313**	**300**	**19**	**850**	***65%***
Acenapthylene	**286**	**313**	**300**	**19**	**308**	***3%***
Anthracene	580	590	**585**	**7**	**2076**	***72%***
Benzo(a)anthracene	2500	2500	**2500**	**0**	**5389**	***54%***
Benzo(b) fluoranthene	3900	3900	**3900**	**0**	**6500**	***40%***
Benzo(k) fluoranthene	1200	1100	**1150**	**71**	**1956**	***41%***
Benzo(g,h,I,)perylene	3000	3100	**3050**	**71**	**1526**	***-100%***
Benzo(a)pyrene	3600	3600	**3600**	**0**	**4578**	***21%***
Chrysene	4000	3900	**3950**	**71**	**5178**	***24%***
Dibenz(a,h)anthracene	410	400	**405**	**7**	**308**	***-32%***
Fluoranthene	4200	4000	**4100**	**141**	**9856**	***58%***
Fluorene	*286*	*313*	**300**	**19**	**1071**	***72%***
Indeno(1,2,3-cd)pyrene	2800	2800	**2800**	**0**	**1521**	***-84%***
Naphthalene	**286**	**313**	**300**	**19**	**316**	***5%***
Phenanthrene	2800	2800	**2800**	**0**	**9156**	***69%***
Pyrene	5300	5100	**5200**	**141**	**8089**	***36%***
Total PAHs	**35434**	**35042**	**35238**	**277**	**58674**	***40%***
TPH Values			**3200**		**9578**	***67%***

Bold values in columns a and b indicate non-detect results

Red italicized values indicate J detections below one-half of the quantitation limit.

Month 4 - Aerobic w/Nutrients #2

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	*298*	*284*	**291**	**10**	**850**	***66%***
Acenapthylene	**298**	**284**	**291**	**10**	**308**	***5%***
Anthracene	630	550	**590**	**57**	**2076**	***72%***
Benzo(a)anthracene	2500	2500	**2500**	**0**	**5389**	***54%***
Benzo(b) fluoranthene	3700	3800	**3750**	**71**	**6500**	***42%***
Benzo(k) fluoranthene	1500	1100	**1300**	**283**	**1956**	***34%***
Benzo(g,h,I,)perylene	3400	3200	**3300**	**141**	**1526**	***-116%***
Benzo(a)pyrene	3800	3700	**3750**	**71**	**4578**	***18%***
Chrysene	4000	4000	**4000**	**0**	**5178**	***23%***
Dibenz(a,h)anthracene	1100	420	**760**	**481**	**308**	***-147%***
Fluoranthene	3900	4000	**3950**	**71**	**9856**	***60%***
Fluorene	*298*	*284*	**291**	**10**	**1071**	***73%***
Indeno(1,2,3-cd)pyrene	2900	2900	**2900**	**0**	**1521**	***-91%***
Naphthalene	**298**	**284**	**291**	**10**	**316**	***8%***
Phenanthrene	2800	2700	**2750**	**71**	**9156**	***70%***
Pyrene	5400	5200	**5300**	**141**	**8089**	***34%***
Total PAHs	**36822**	**35206**	**36014**	**1143**	**58674**	***39%***
TPH Values			**3000**		**9578**	***69%***

Bold values in columns a and b indicate non-detect results

Red italicized values indicate J detections below one-half of the quantitation limit.

Month 4 - Aerobic

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	**296**	**313**	**305**	**12**	**850**	***64%***
Acenapthylene	**296**	**313**	**305**	**12**	**308**	***1%***
Anthracene	350	370	**360**	**14**	**2076**	***83%***
Benzo(a)anthracene	1500	1800	**1650**	**212**	**5389**	***69%***
Benzo(b) fluoranthene	4000	3300	**3650**	**495**	**6500**	***44%***
Benzo(k) fluoranthene	1200	1200	**1200**	**0**	**1956**	***39%***
Benzo(g,h,I,)perylene	2500	2100	**2300**	**283**	**1526**	***-51%***
Benzo(a)pyrene	3300	2800	**3050**	**354**	**4578**	***33%***
Chrysene	2800	3000	**2900**	**141**	**5178**	***44%***
Dibenz(a,h)anthracene	430	**313**	**372**	**83**	**308**	***-21%***
Fluoranthene	2200	3000	**2600**	**566**	**9856**	***74%***
Fluorene	**296**	**313**	**305**	**12**	**1071**	***72%***
Indeno(1,2,3-cd)pyrene	2500	2000	**2250**	**354**	**1521**	***-48%***
Naphthalene	**296**	**313**	**305**	**12**	**316**	***4%***
Phenanthrene	1500	1800	**1650**	**212**	**9156**	***82%***
Pyrene	4400	4600	**4500**	**141**	**8089**	***44%***
Total PAHs	**27864**	**27535**	**27700**	**233**	**58674**	***53%***
TPH Values			**2500**		**9578**	***74%***

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Red italicized values indicate J detections below one-half of the quantitation limit.

Month 4 Samples - Aerobic/Killed

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	510	580	**545**	**49**	**850**	***36%***
Acenapthylene	**297**	**305**	**301**	**6**	**308**	***2%***
Anthracene	840	1100	**970**	**184**	**2076**	***53%***
Benzo(a)anthracene	3400	3900	**3650**	**354**	**5389**	***32%***
Benzo(b) fluoranthene	3800	4200	**4000**	**283**	**6500**	***38%***
Benzo(k) fluoranthene	1000	1600	**1300**	**424**	**1956**	***34%***
Benzo(g,h,I,)perylene	2000	2300	**2150**	**212**	**1526**	***-41%***
Benzo(a)pyrene	2900	3300	**3100**	**283**	**4578**	***32%***
Chrysene	4800	5600	**5200**	**566**	**5178**	***0%***
Dibenz(a,h)anthracene	340	420	**380**	**57**	**308**	***-23%***
Fluoranthene	7000	8000	**7500**	**707**	**9856**	***24%***
Fluorene	720	830	**775**	**78**	**1071**	***28%***
Indeno(1,2,3-cd)pyrene	2000	2200	**2100**	**141**	**1521**	***-38%***
Naphthalene	**297**	**305**	**301**	**6**	**316**	***5%***
Phenanthrene	5200	6300	**5750**	**778**	**9156**	***37%***
Pyrene	7200	8400	**7800**	**849**	**8089**	***4%***
Total PAHs	**42304**	**49340**	**45822**	**4975**	**58674**	***22%***
TPH Values			**3700**		**9578**	***61%***

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Red italicized values indicate J detections below one-half of the quantitation limit.

Month 4 - Anaerobic/Killed

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	1300	1000	**1150**	**212**	**850**	***-35%***
Acenapthylene	**325**	**317**	**321**	**6**	**308**	***-4%***
Anthracene	2100	1900	**2000**	**141**	**2076**	***4%***
Benzo(a)anthracene	7000	6300	**6650**	**495**	**5389**	***-23%***
Benzo(b) fluoranthene	8500	7500	**8000**	**707**	**6500**	***-23%***
Benzo(k) fluoranthene	3300	2200	**2750**	**778**	**1956**	***-41%***
Benzo(g,h,I,)perylene	3800	3700	**3750**	**71**	**1526**	***-146%***
Benzo(a)pyrene	7000	5800	**6400**	**849**	**4578**	***-40%***
Chrysene	11000	9100	**10050**	**1344**	**5178**	***-94%***
Dibenz(a,h)anthracene	560	520	**540**	**28**	**308**	***-75%***
Fluoranthene	15000	13000	**14000**	**1414**	**9856**	***-42%***
Fluorene	1800	1400	**1600**	**283**	**1071**	***-49%***
Indeno(1,2,3-cd)pyrene	3800	3500	**3650**	**212**	**1521**	***-140%***
Naphthalene	*325*	**317**	**321**	**6**	**316**	***-2%***
Phenanthrene	13000	11000	**12000**	**1414**	**9156**	***-31%***
Pyrene	16000	14000	**15000**	**1414**	**8089**	***-85%***
Total PAHs	**94810**	**81554**	**88182**	**9373**	**58674**	***-50%***
TPH Values			**5800**		**9578**	***39%***

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Red italicized values indicate J detections below one-half of the quantitation limit.

Month 4 - Anaerobic w/Nitrate

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	1100	1000	**1050**	**71**	**850**	***-24%***
Acenapthylene	**337**	**325**	**331**	**8**	**308**	***-8%***
Anthracene	1900	2300	**2100**	**283**	**2076**	***-1%***
Benzo(a)anthracene	7300	7800	**7550**	**354**	**5389**	***-40%***
Benzo(b) fluoranthene	8100	9000	**8550**	**636**	**6500**	***-32%***
Benzo(k) fluoranthene	2200	2400	**2300**	**141**	**1956**	***-18%***
Benzo(g,h,I,)perylene	4100	4200	**4150**	**71**	**1526**	***-172%***
Benzo(a)pyrene	6600	7200	**6900**	**424**	**4578**	***-51%***
Chrysene	10000	11000	**10500**	**707**	**5178**	***-103%***
Dibenz(a,h)anthracene	480	530	**505**	**35**	**308**	***-64%***
Fluoranthene	14000	16000	**15000**	**1414**	**9856**	***-52%***
Fluorene	1600	1500	**1550**	**71**	**1071**	***-45%***
Indeno(1,2,3-cd)pyrene	3800	4300	**4050**	**354**	**1521**	***-166%***
Naphthalene	*337*	360	**349**	**16**	**316**	***-10%***
Phenanthrene	11000	12000	**11500**	**707**	**9156**	***-26%***
Pyrene	15000	16000	**15500**	**707**	**8089**	***-92%***
Total PAHs	**87854**	**95915**	**91885**	**5700**	**58674**	***-57%***
TPH Values			**6500**		**9578**	***32%***

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Red italicized values indicate J detections below one-half of the quantitation limit.

Month 5 - Aerobic w/Nutrients #1

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	*225*	*222*	**224**	**2**	**850**	***74%***
Acenapthylene	**225**	**222**	**224**	**2**	**308**	***27%***
Anthracene	440	*222*	**331**	**154**	**2076**	***84%***
Benzo(a)anthracene	980	920	**950**	**42**	**5389**	***82%***
Benzo(b) fluoranthene	1500	1500	**1500**	**0**	**6500**	***77%***
Benzo(k) fluoranthene	680	650	**665**	**21**	**1956**	***66%***
Benzo(g,h,I,)perylene	920	1200	**1060**	**198**	**1526**	***31%***
Benzo(a)pyrene	1400	1500	**1450**	**71**	**4578**	***68%***
Chrysene	1300	1200	**1250**	**71**	**5178**	***76%***
Dibenz(a,h)anthracene	**225**	**222**	**224**	**2**	**308**	***27%***
Fluoranthene	2000	1500	**1750**	**354**	**9856**	***82%***
Fluorene	310	*222*	**266**	**62**	**1071**	***75%***
Indeno(1,2,3-cd)pyrene	880	980	**930**	**71**	**1521**	***39%***
Naphthalene	*225*	*222*	**224**	**2**	**316**	***29%***
Phenanthrene	1500	940	**1220**	**396**	**9156**	***87%***
Pyrene	1500	1200	**1350**	**212**	**8089**	***83%***
Total PAHs	**14310**	**12922**	**13616**	**981**	**58674**	***77%***
TPH Values	**2000**	**980**	**1490**	**721**	**9578**	***84%***

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Red italicized values indicate J detections below one-half of the quantitation limit.

Month 5 - Aerobic

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	**226**	**281**	**254**	**39**	**850**	***70%***
Acenapthylene	**226**	**281**	**254**	**39**	**308**	***18%***
Anthracene	*226*	**281**	**254**	**39**	**2076**	***88%***
Benzo(a)anthracene	580	640	**610**	**42**	**5389**	***89%***
Benzo(b) fluoranthene	1500	1600	**1550**	**71**	**6500**	***76%***
Benzo(k) fluoranthene	610	300	**455**	**219**	**1956**	***77%***
Benzo(g,h,I,)perylene	1100	1000	**1050**	**71**	**1526**	***31%***
Benzo(a)pyrene	1300	1300	**1300**	**0**	**4578**	***72%***
Chrysene	880	820	**850**	**42**	**5178**	***84%***
Dibenz(a,h)anthracene	**226**	*281*	**254**	**39**	**308**	***18%***
Fluoranthene	1200	1000	**1100**	**141**	**9856**	***89%***
Fluorene	**226**	**281**	**254**	**39**	**1071**	***76%***
Indeno(1,2,3-cd)pyrene	860	890	**875**	**21**	**1521**	***42%***
Naphthalene	**226**	**281**	**254**	**39**	**316**	***20%***
Phenanthrene	610	540	**575**	**49**	**9156**	***94%***
Pyrene	1100	1500	**1300**	**283**	**8089**	***84%***
Total PAHs	**11096**	**11276**	**11186**	**127**	**58674**	***81%***
TPH Values	**3300**	**2900**	**3100**	**283**	**9578**	***68%***

Bold values in columns a and b indicate non-detect results
Red italicized values indicate J detections below one-half of the quantitation limit.

Month 5 Samples - Aerobic/Killed

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	400	340	**370**	**42**	**850**	***56%***
Acenapthylene	**277**	**287**	**282**	**7**	**308**	***8%***
Anthracene	870	720	**795**	**106**	**2076**	***62%***
Benzo(a)anthracene	2900	2300	**2600**	**424**	**5389**	***52%***
Benzo(b) fluoranthene	3600	3000	**3300**	**424**	**6500**	***49%***
Benzo(k) fluoranthene	840	720	**780**	**85**	**1956**	***60%***
Benzo(g,h,I,)perylene	1900	1500	**1700**	**283**	**1526**	***-11%***
Benzo(a)pyrene	2600	2200	**2400**	**283**	**4578**	***48%***
Chrysene	3200	2600	**2900**	**424**	**5178**	***44%***
Dibenz(a,h)anthracene	510	410	**460**	**71**	**308**	***-49%***
Fluoranthene	6400	5300	**5850**	**778**	**9856**	***41%***
Fluorene	510	410	**460**	**71**	**1071**	***57%***
Indeno(1,2,3-cd)pyrene	1600	1300	**1450**	**212**	**1521**	***5%***
Naphthalene	**277**	287	**282**	**7**	**316**	***11%***
Phenanthrene	4700	4100	**4400**	**424**	**9156**	***52%***
Pyrene	6200	5200	**5700**	**707**	**8089**	***30%***
Total PAHs	**36784**	**30674**	**33729**	**4320**	**58674**	***43%***
TPH Values	**3200**	**3600**	**3400**	**283**	**9578**	***65%***

Bold values in columns a and b indicate non-detect results

Red italicized values indicate J detections below one-half of the quantitation limit.

Month 5 - Anaerobic/Killed

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	710	720	**715**	**7**	**850**	***16%***
Acenapthylene	**325**	**336**	**331**	**8**	**308**	***-7%***
Anthracene	1200	1400	**1300**	**141**	**2076**	***37%***
Benzo(a)anthracene	4100	4400	**4250**	**212**	**5389**	***21%***
Benzo(b) fluoranthene	5200	5700	**5450**	**354**	**6500**	***16%***
Benzo(k) fluoranthene	1300	1300	**1300**	**0**	**1956**	***34%***
Benzo(g,h,I,)perylene	2700	3000	**2850**	**212**	**1526**	***-87%***
Benzo(a)pyrene	3800	4300	**4050**	**354**	**4578**	***12%***
Chrysene	4100	5100	**4600**	**707**	**5178**	***11%***
Dibenz(a,h)anthracene	780	880	**830**	**71**	**308**	***-170%***
Fluoranthene	9000	9700	**9350**	**495**	**9856**	***5%***
Fluorene	940	960	**950**	**14**	**1071**	***11%***
Indeno(1,2,3-cd)pyrene	2500	2700	**2600**	**141**	**1521**	***-71%***
Naphthalene	**325**	**336**	**331**	**8**	**316**	***-5%***
Phenanthrene	7200	7500	**7350**	**212**	**9156**	***20%***
Pyrene	9100	9700	**9400**	**424**	**8089**	***-16%***
Total PAHs	**53280**	**58032**	**55656**	**3360**	**58674**	***5%***
TPH Values	**8700**	**6800**	**7750**	**1344**	**9578**	***19%***

Bold values in columns a and b indicate non-detect results

Red italicized values indicate J detections below one-half of the quantitation limit.

Month 5 - Anaerobic w/Nitrate

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	810	520	**665**	**205**	**850**	***22%***
Acenapthylene	**352**	**338**	**345**	**10**	**308**	***-12%***
Anthracene	1500	920	**1210**	**410**	**2076**	***42%***
Benzo(a)anthracene	4900	3000	**3950**	**1344**	**5389**	***27%***
Benzo(b) fluoranthene	5900	3600	**4750**	**1626**	**6500**	***27%***
Benzo(k) fluoranthene	1600	1200	**1400**	**283**	**1956**	***28%***
Benzo(g,h,I,)perylene	3000	2000	**2500**	**707**	**1526**	***-64%***
Benzo(a)pyrene	4500	2800	**3650**	**1202**	**4578**	***20%***
Chrysene	4800	3300	**4050**	**1061**	**5178**	***22%***
Dibenz(a,h)anthracene	890	580	**735**	**219**	**308**	***-139%***
Fluoranthene	10000	6800	**8400**	**2263**	**9856**	***15%***
Fluorene	1000	710	**855**	**205**	**1071**	***20%***
Indeno(1,2,3-cd)pyrene	2800	1800	**2300**	**707**	**1521**	***-51%***
Naphthalene	**352**	**338**	**345**	**10**	**316**	***-9%***
Phenanthrene	8100	5300	**6700**	**1980**	**9156**	***27%***
Pyrene	10000	6800	**8400**	**2263**	**8089**	***-4%***
Total PAHs	**60504**	**40006**	**50255**	**14494**	**58674**	***14%***
TPH Values	**14000**	**9000**	**11500**	**3536**	**9578**	***-20%***

Bold values in columns a and b indicate non-detect results

Red italicized values indicate J detections below one-half of the quantitation limit.

Month 6 - Aerobic w/Nutrients #1

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	**250**	**250**	**250**	**0**	**850**	***71%***
Acenapthylene	**250**	**250**	**250**	**0**	**308**	***19%***
Anthracene	**250**	**250**	**250**	**0**	**2076**	***88%***
Benzo(a)anthracene	730	1200	**965**	**332**	**5389**	***82%***
Benzo(b) fluoranthene	1100	1300	**1200**	**141**	**6500**	***82%***
Benzo(k) fluoranthene	660	1300	**980**	**453**	**1956**	***50%***
Benzo(g,h,I,)perylene	1100	1600	**1350**	**354**	**1526**	***12%***
Benzo(a)pyrene	1300	1800	**1550**	**354**	**4578**	***66%***
Chrysene	1200	1700	**1450**	**354**	**5178**	***72%***
Dibenz(a,h)anthracene	300	**250**	**275**	**35**	**308**	***11%***
Fluoranthene	1400	2000	**1700**	**424**	**9856**	***83%***
Fluorene	**250**	**250**	**250**	**0**	**1071**	***77%***
Indeno(1,2,3-cd)pyrene	1000	1400	**1200**	**283**	**1521**	***21%***
Naphthalene	**250**	**250**	**250**	**0**	**316**	***21%***
Phenanthrene	830	1200	**1015**	**262**	**9156**	***89%***
Pyrene	2000	2000	**2000**	**0**	**8089**	***75%***
Total PAHs	**12870**	**17000**	**14935**	**2920**	**58674**	***75%***
TPH Values	**2900**	**1700**	**2300**	**849**	**9578**	***76%***

Bold values in columns a and b indicate non-detect results

Red italicized values indicate J detections below one-half of the quantitation limit.

Month 6 - Aerobic

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	*% Loss*
Acenapthene	**295**	**250**	**273**	**32**	**850**	***68%***
Acenapthylene	**295**	**250**	**273**	**32**	**308**	***11%***
Anthracene	370	**250**	**310**	**85**	**2076**	***85%***
Benzo(a)anthracene	**295**	540	**418**	**173**	**5389**	***92%***
Benzo(b) fluoranthene	3500	1200	**2350**	**1626**	**6500**	***64%***
Benzo(k) fluoranthene	1300	620	**960**	**481**	**1956**	***51%***
Benzo(g,h,I,)perylene	890	1100	**995**	**148**	**1526**	***35%***
Benzo(a)pyrene	2700	1300	**2000**	**990**	**4578**	***56%***
Chrysene	2100	900	**1500**	**849**	**5178**	***71%***
Dibenz(a,h)anthracene	**295**	**250**	**273**	**32**	**308**	***11%***
Fluoranthene	2000	890	**1445**	**785**	**9856**	***85%***
Fluorene	**295**	**250**	**273**	**32**	**1071**	***75%***
Indeno(1,2,3-cd)pyrene	1100	980	**1040**	**85**	**1521**	***32%***
Naphthalene	**295**	**250**	**273**	**32**	**316**	***14%***
Phenanthrene	1300	540	**920**	**537**	**9156**	***90%***
Pyrene	2700	1100	**1900**	**1131**	**8089**	***77%***
Total PAHs	**19730**	**10670**	**15200**	**6406**	**58674**	***74%***
TPH Values	**2700**	**3100**	**2900**	**283**	**9578**	***70%***

Bold values in columns a and b indicate non-detect results

Red italicized values indicate J detections below one-half of the quantitation limit.

Month 6 Samples - Aerobic/Killed

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	*% Loss*
Acenapthene	440	390	**415**	**35**	**850**	***51%***
Acenapthylene	**250**	**250**	**250**	**0**	**308**	***19%***
Anthracene	640	510	**575**	**92**	**2076**	***72%***
Benzo(a)anthracene	2700	2400	**2550**	**212**	**5389**	***53%***
Benzo(b) fluoranthene	1900	1800	**1850**	**71**	**6500**	***72%***
Benzo(k) fluoranthene	2200	2000	**2100**	**141**	**1956**	***-7%***
Benzo(g,h,I,)perylene	1600	1400	**1500**	**141**	**1526**	***2%***
Benzo(a)pyrene	2400	2200	**2300**	**141**	**4578**	***50%***
Chrysene	3400	3100	**3250**	**212**	**5178**	***37%***
Dibenz(a,h)anthracene	**250**	**250**	**250**	**0**	**308**	***19%***
Fluoranthene	5700	5300	**5500**	**283**	**9856**	***44%***
Fluorene	590	540	**565**	**35**	**1071**	***47%***
Indeno(1,2,3-cd)pyrene	1500	1400	**1450**	**71**	**1521**	***5%***
Naphthalene	**250**	**250**	**250**	**0**	**316**	***21%***
Phenanthrene	4700	4200	**4450**	**354**	**9156**	***51%***
Pyrene	5000	4500	**4750**	**354**	**8089**	***41%***
Total PAHs	**33520**	**30490**	**32005**	**2143**	**58674**	***45%***
TPH Values	**2400**	**3800**	**3100**	**990**	**9578**	***68%***

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Red italicized values indicate J detections below one-half of the quantitation limit.

Month 6 - Anaerobic/Killed

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	690	740	**715**	**35**	**850**	***16%***
Acenapthylene	**295**	**305**	**300**	**7**	**308**	***3%***
Anthracene	1900	1600	**1750**	**212**	**2076**	***16%***
Benzo(a)anthracene	5800	4800	**5300**	**707**	**5389**	***2%***
Benzo(b) fluoranthene	8000	6400	**7200**	**1131**	**6500**	***-11%***
Benzo(k) fluoranthene	2600	2100	**2350**	**354**	**1956**	***-20%***
Benzo(g,h,I,)perylene	1400	890	**1145**	**361**	**1526**	***25%***
Benzo(a)pyrene	5300	4200	**4750**	**778**	**4578**	***-4%***
Chrysene	7600	6100	**6850**	**1061**	**5178**	***-32%***
Dibenz(a,h)anthracene	*295*	400	**348**	**74**	**308**	***-13%***
Fluoranthene	9800	8700	**9250**	**778**	**9856**	***6%***
Fluorene	1200	1100	**1150**	**71**	**1071**	***-7%***
Indeno(1,2,3-cd)pyrene	1900	1100	**1500**	**566**	**1521**	***1%***
Naphthalene	*295*	*305*	**300**	**7**	**316**	***5%***
Phenanthrene	7600	7000	**7300**	**424**	**9156**	***20%***
Pyrene	10000	9200	**9600**	**566**	**8089**	***-19%***
Total PAHs	**64675**	**54940**	**59808**	**6884**	**58674**	***-2%***
TPH Values	**11000**	**6700**	**8850**	**3041**	**9578**	***8%***

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Red italicized values indicate J detections below one-half of the quantitation limit.

Month 6 - Anaerobic w/Nitrate

PAH	a (ug/kg)	b (ug/kg)	mean (ug/kg)	SD (ug/kg)	T=0 Mean (ug/kg)	% Loss
Acenapthene	580	490	**535**	**64**	**850**	***37%***
Acenapthylene	**310**	**427**	**369**	**83**	**308**	***-20%***
Anthracene	1400	1000	**1200**	**283**	**2076**	***42%***
Benzo(a)anthracene	4600	**427**	**2514**	**2951**	**5389**	***53%***
Benzo(b) fluoranthene	6400	4300	**5350**	**1485**	**6500**	***18%***
Benzo(k) fluoranthene	1400	1600	**1500**	**141**	**1956**	***23%***
Benzo(g,h,I,)perylene	990	790	**890**	**141**	**1526**	***42%***
Benzo(a)pyrene	4000	3000	**3500**	**707**	**4578**	***24%***
Chrysene	5200	4000	**4600**	**849**	**5178**	***11%***
Dibenz(a,h)anthracene	430	*427*	**429**	**2**	**308**	***-39%***
Fluoranthene	8300	7200	**7750**	**778**	**9856**	***21%***
Fluorene	940	750	**845**	**134**	**1071**	***21%***
Indeno(1,2,3-cd)pyrene	1200	1000	**1100**	**141**	**1521**	***28%***
Naphthalene	**310**	**427**	**369**	**83**	**316**	***-17%***
Phenanthrene	6100	5200	**5650**	**636**	**9156**	***38%***
Pyrene	8700	7200	**7950**	**1061**	**8089**	***2%***
Total PAHs	**50860**	**38238**	**44549**	**8925**	**58674**	***24%***
TPH Values	**5700**	**10000**	**7850**	**3041**	**9578**	***18%***

Bold values in columns a and b indicate non-detect results
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APPENDIX D

Bioaccumulation Data Pan Tests

APPENDIX D
Bioaccumulation Data Pan Tests

Initial Control – 0% Test Soil

		Sample Collected	Control-Composite (90745) 5/15/99 14:00		
CAS #	Analyte	MDL (ug/kg)	Concentration (ug/kg)	Qualifier	Value (ug/kg)
91-20-3	Naphthalene	19.7	9.50	JB	19.7
208-96-8	Acenapthylene	2.68	2.68	U	2.68
83-32-9	Acenapthene	2.31	2.20	J	2.31
86-73-7	Flourene	3.95	5.20	B	5.20
85-01-8	Phenanthrene	6.26	19.5	B	19.5
120-12-7	Anthracene	2.01	2.01	U	2.01
206-44-0	Fluoranthene	4.02	2.90	JB	4.02
129-00-0	Pyrene	12.2	1.70	JB	12.2
56-55-3	Benzo[a]anthracene	5.44	5.44	U	5.44
218-01-9	Chrysene	7.90	7.90	U	7.90
205-99-2	Benzo[a]fluoranthene	4.02	4.02	U	4.02
207-08-9	Benzo[k]fluoranthene	7.08	7.08	U	7.08
50-32-8	Benzo[a]pyrene	13.6	13.6	U	13.6
193-39-5	Indeno[1,2,3-cd]pyrene	7.60	7.60	U	7.60
53-70-3	Dibenz[a,h]anthracene	2.46	2.46	U	2.46
191-24-2	Benzo[g,h,i]perylene	4.77	1.60	J	4.77
106-46-7	1,4-Dichlorobenzene	7.45	3.10	JB	7.45
	Total PAHs	106			**120**

Qualifiers

U - The analytical result is a non-detect.

J - Indicates an estimated value. The concentration reported was below the Method Detection Limit.

B - The analyte was found in the associated method blank as well as the sample. It indicates possible/probable blank contamination and warns the data user to take appropriate action.

E - The concentration of the analyte exceeded the calibration range of the instrument.

D - Identifies compounds identified in an analysis at a secondary dilution.

Initial – 25% Test Soil

Analyte	25% (Tank 8) (90715) 5/15/99 14:00				25% (Tank 5) (90715) 5/15/99 14:00			
	MDL (ug/kg)	Concentration (ug/kg)	Qualifier	Value (ug/kg)	MDL (ug/kg)	Concentration (ug/kg)	Qualifier	Value (ug/kg)
	20.3	4.70	JB	20.3	21.2	5.20	JB	21.2
	2.75	2.75	U	2.75	2.88	2.88	U	2.88
	2.37	2.37	U	2.37	2.48	2.48	U	2.48
	4.05	4.05	U	4.05	4.24	4.24	U	4.24
	6.43	12.2	B	12.2	6.72	9.60	B	9.60
	2.07	2.07	U	2.07	2.16	2.16	U	2.16
	4.13	21.0	B	21.0	4.32	7.50	B	7.50
	12.5	74.9	B	74.9	13.1	66.2	B	66.2
	5.58	29.1		29.1	5.84	16.4		16.4
	8.11	46.3		46.3	8.48	34.4		34.4
	4.13	57.0		57.0	4.32	58.6		58.6
	7.27	59.8		59.8	7.60	34.0		34.0
	13.9	96.7		96.7	14.6	48.2		48.2
	7.80	65.8		65.8	8.16	47.2		47.2
	2.52	41.6		41.6	2.64	32.2		32.2
	4.90	51.1		51.1	5.12	30.6		30.6
	7.65	2.90	JB	7.65	8.00	2.90	JB	8.00
	109			**587**	114			**418**

Initial – 100% Test Soil

Analyte	MDL (ug/kg)	Concentration (ug/kg)	Qualifier	Value (ug/kg)	MDL (ug/kg)	Concentration (ug/kg)	Qualifier	Value (ug/kg)
	21.2	5.60	JB	21.2	20.4	7.20	JB	20.4
	2.88	2.88	U	2.88	2.76	2.10	J	2.76
	2.48	5.50		5.50	2.38	15.7		15.7
	4.24	5.70	B	5.70	4.07	19.4	B	19.4
	6.72	40.5	B	40.5	6.45	92.7	B	92.7
	2.16	10.3		10.3	2.07	23.5		23.5
	4.32	161	B	161	4.15	240	B	240
	52.5	700	B	700	50.3	786	B	786
	5.84	170		170	5.61	209		209
	33.9	298		298	32.5	374		374
	17.3	413		413	16.6	532		532
	7.60	240		240	29.2	396		396
	58.2	459		459	55.9	542		542
	32.6	197		197	31.3	254		254
	2.64	186		186	2.53	222		222
	5.12	274		274	19.6	239		239
	8.00	2.60	JB	8.00	7.68	2.70	JB	7.68
	260			**3184**	286			**3968**

Final Control – 0% Test Soil

	Value (ug/kg)	Control - 92753 11/22/99 0:00 MDL (ug/kg)	Concentration (ug/kg)	Qualifier	Value (ug/kg)	Control - 92754 11/22/99 0:00 MDL (ug/kg)	Concentration (ug/kg)	Qualifier	Value (ug/kg)
	110	11.0	110		110	11.0	120		120
	120	120	120	U	120	120	120	U	120
	16.0	16.0	16.0	U	16.0	16.0	16.0	U	16.0
	5.90	5.90	5.90	U	5.90	5.90	5.90	U	5.90
	6.60	1.00	6.60		6.60	5.90	5.90	U	5.90
	11.0	0.54	11.0		11.0	0.54	12.0		12.0
	28.0	0.78	28.0		28.0	4.60	4.60	U	4.60
	4.00	0.44	4.00		4.00	2.60	2.60	U	2.60
	4.50	4.50	4.50	U	4.50	4.50	4.50	U	4.50
	1.40	1.40	1.40	U	1.40	1.40	1.40	U	1.40
	11.0	0.78	11.0		11.0	0.78	9.60		9.60
	2.60	2.60	2.60	U	2.60	2.60	2.60	U	2.60
	2.40	2.40	2.40	U	2.40	2.40	2.40	U	2.40
	4.70	4.70	4.70	U	4.70	4.70	4.70	U	4.70
	5.40	5.40	5.40	U	5.40	5.40	5.40	U	5.40
	5.40	5.40	5.40	U	5.40	5.40	5.40	U	5.40
5	**339**	183	**339**		**339**	194			**323**

Sample Received			25% - 92756 11/22/99 0:00				25% - 92757 11/22/99 0:00			
CAS #	Analyte	MDL (ug/kg)	Concentration (ug/kg)	Qualifier	Value (ug/kg)	MDL (ug/kg)	Concentration (ug/kg)	Qualifier	Value (ug/kg)
91-20-3	Naphthalene	11.0	250		250	11.0	320		320
208-96-8	Acenaphthylene	130	120	U	120	130	130	U	130
83-32-9	Acenaphthene	16.0	16.0	U	16.0	2.8	30.0		30.0
86-73-7	Fluorene	5.80	5.80	U	5.80	1.00	33.0		33.0
85-01-8	Phenanthrene	1.00	12.0		12.0	1.00	15.0		15.0
120-12-7	Anthracene	0.54	20.0		20.0	0.54	20.0		20.0
206-44-0	Fluoranthene	0.78	33.0		33.0	0.78	36.0		36.0
129-00-0	Pyrene	0.44	100		100	0.44	100		100
56-55-3	Benzo[a]anthracene	4.40	4.40	U	4.40	4.60	4.60	U	4.60
218-01-9	Chrysene	1.40	1.40	U	1.40	0.24	100		100
205-99-2	Benzo[b]fluoranthene	0.78	140		140	0.78	160		160
207-08-9	Benzo[k]fluoranthene	0.44	19.0		19.0	0.44	21.0		21.0
50-32-8	Benzo[a]pyrene	0.41	100		100	0.41	120		120
193-39-5	Indeno[1,2,3-cd]pyrene	0.52	27.0		27.0	5.50	29.0		29.0
53-70-3	Dibenz[a,h]anthracene	5.20	5.20	U	5.20	5.50	5.50	U	5.50
191-24-2	Benzo[g,h,i]perylene	0.92	24.0		24.0	0.92	35.0		35.0
	Total PAHs	170	**878**		**878**	166			**1159**

Qualifiers

U - The analytical result is a non-detect.

J - Indicates an estimated value. The concentration is reported less than the Method Detection Limit.

B - The analyte was detected in the associated method blank as well as the sample. It indicates possible/likely blank contamination and should be taken into consideration when the data user is to take appropriate action.

E - The concentration of the analyte exceeded the calibration range of the instrument.

D - Identifies compounds identified in an analysis at a secondary dilution.

			100% - 92759 11/22/99 0:00			100% - 92760 11/22/99 0:00		
		MDL (ug/kg)	Concentration (ug/kg)	Qualifier	Value (ug/kg)	MDL (ug/kg)	Concentration (ug/kg)	Qualifier	Value (ug/kg)
		11.0	410		410	11.0	430		430
		130	130	U	130	130	130	U	130
		17.0	17.0	U	17.0	17.0	17.0	U	17.0
		1.00	140		140	6.00	6.00	U	6.00
		1.00	11.0		11.0	1.00	11.00		11.0
		0.54	51.0		51.0	0.54	37.0		37.0
		4.70	4.70	U	4.70	4.70	4.70	U	4.70
		0.44	320		320	0.44	220		220
		4.60	4.60	U	4.60	4.60	4.60	U	4.60
		1.40	1.40	U	1.40	1.40	1.40	U	1.40
		0.78	460		460	0.78	320		320
		0.44	34.0		34.0	0.44	22.0		22.0
		0.41	290		290	0.41	210		210
		0.80	160		160	0.80	110		110
		0.91	9.50		9.50	0.91	6.70		6.70
		0.92	180		180	0.92	120		120
		176			**2223**	181			**1650**