BIOPILES FOR REMEDIATION OF PETROLEUM-CONTAMINATED SOILS: A POLISH CASE STUDY

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ABSTRACT

The US Department of Energy and the Institute for Ecology of Industrial Areas of Poland demonstrated bioremediation techniques for the clean up of acidic petroleum sludge impacted soils at an oil refinery in southern Poland. The waste was composed of high molecular weight paraffinic and polynuclear aromatic hydrocarbons. Benzo(a)pyrene and BTEX compounds were identified as the contaminants of concern. Approximately 3,300 m^3 of contaminated soil (TPH ~ 30,000 ppm) was targeted for treatment. A biopile design which employed a combination of passive and active aeration in conjunction with nutrient and surfactant application was used to increase the biodegradation of the contaminants of concern. Over the 20 month project, more than 81% (120 metric tons) of petroleum hydrocarbons were biodegraded. Despite the fact the material treated was highly weathered and very acidic, biodegradation rates of 121 mg/kg soil/day in the actively aerated side (82 mg/kg soil/day in the passive side) were achieved in this biopile. Microbial counts and dehydrogenase measurements gave the best correlation with the biodegradation rates. Costs were competitive or significantly lower when compared with other ex situ treatment processes.

Key words: soil, contamination by petroleum, remediation, biopiles

INTRODUCTION

Biodegradation of petroleum hydrocarbons in soil (petroleum land farming) has been used by the oil industry for more than 30 years as an efficient way to destroy oil sludges [6]. By

applying oil to the soil surface, adding fertilizer (P & N), water, and then tilling to aerate (oxygenate), the soil microbes have been shown to completely degrade large quantities of oil. Until recently, the state-of-the-art approach to soil remediation was excavation and disposal at a secure landfill. Changes in liability concerns, increasing costs, and regulatory constraints have decreased the popularity of excavation and landfill disposal as a soil cleanup alternative. Landfill disposal of contaminated soil does not remove the future liability of its generator, who will be held jointly liable with the landfill operator for any future associated contamination. Thus, on site permanent solutions are the preferred method of treatment, especially those that involve the complete destruction of the contaminant using biological (natural) techniques, ie. bioremediation.

This bioremediation demonstration project focused on the clean-up technique known as "biopiles". The biopile process is very similar to active bioventing, where air, as an oxygen source, and other amendments are forced through the vadose zone sediments either by vacuum extraction or by injection to stimulate the microbial oxidation of the hydrocarbons (for a complete set of definitions see Hazen [9]. As the name implies, biopiling is an ex situ process. The contaminated material is excavated and recombined or amended with other materials e.g., nutrients, sand, sawdust, wood chips, compost or other similar bulking agents, as needed, to improve permeability and moisture retention, and then placed in an engineered structure (configuration), to support and stimulate the biological reactions necessary to oxidize the hydrocarbons. Typically, this is a composting process which utilizes forced air via injection or vacuum extraction, moisture control, nutrient addition and environmental monitoring. Using commercially available vacuum pumps, or blowers, leachate pumps, moisture probes, thermocouple temperature probes, and real time soil gas monitoring equipment provides a mature and effective technology base for the operation and monitoring of the biopile.

The US Department of Energy and the Institute for Ecology of Industrial Areas (IETU), Katowice, Poland have been cooperating in the development and implementation of innovative environmental remediation technologies since 1995 (URL: www.iicer.fsu.edu/publications.cfm). A major focus of this program has been the demonstration of bioremediation techniques to clean up the soil and sediment associated with a waste lagoon at the Czechowice Oil Refinery (CZOR) in southern Poland. After an expedited site characterization (ESC), treatability study, and risk assessment study, a remediation system was designed that took advantage of local materials to minimize cost and maximize treatment efficiency. U.S. scientists and engineers worked in tandem with counterparts from the IETU and CZOR throughout this project to characterize, assess and subsequently, design, implement and monitor a bioremediation system. The CZOR was named by PIOS (State Environmental Protection Inspectorate of Poland) as one of the top 80 biggest polluters in Poland. The history of the CZOR dates back more than 100 years to its establishment by the Vacuum Oil Company (a U.S. company and forerunner of Standard Oil). More than a century of continuous use of a sulfuric acid-based oil refining method by the CZOR has produced an estimated 120,000 tons of acidic, highly weathered, petroleum sludge. This waste has been deposited into three open, unlined process waste lagoons, 3 meters deep, now covering 3.8 hectares (Figure 1). Initial analysis indicated that the sludge was composed mainly of high molecular weight paraffinic and polynuclear aromatic hydrocarbons (PAHs). The overall objective of this full-scale demonstration project was to characterize, assess and remediate one of these lagoons. The remediation tested and evaluated a combination of U.S. and Polish-developed biological remediation technologies. Specifically, the goal of the demonstration was to reduce the environmental risk from PAH

compounds in soil and to provide a green zone (grassy area) adjacent to the site boundary. The site was characterized using the DOE-developed Expedited Site Characterization (ESC) methodology. Based on the results of the ESC, a risk assessment was conducted using established U.S. procedures. Based on the results of the ESC and risk assessment, a 0.3-hectare site, the smallest of the waste lagoons, was selected for a modified aerobic biopile demonstration.

Bioremediation is generally attempted by employing biostimulation, a process in which the conditions for microbial growth are optimized by supplying adequate amounts of electron acceptor(s), water, nutrients, in the form of nitrogen, phosphorus and trace elements, to the contaminated material [9]. Because biodegradation rates for petroleum hydrocarbons are fastest under aerobic conditions, maintaining adequate oxygen levels and moisture control are two of the main objectives associated with this project.

The material selected for the technology demonstration contains petroleum sludges, soils contaminated with crude and processed oil and other petroleum by-products and process waste from the refining of crude oil. The predominant contaminants of concern (COCs) are polycyclic aromatic hydrocarbons (PAHs) including benzo(a)pyrene, a known carcinogen. Also benzene, toluene, ethylbenzene and xylene known as BTEX and very recalcitrant high molecular weight molecules, the remnants and residue from tank bottoms of acid refining of crude oil. Although the high molecular weight molecules represent a portion of the total petroleum hydrocarbons (TPH) present in the waste material, it is of less concern to human health and the environment from a risk assessment stand point, due to their highly insoluble state and lack of mobility within a soil matrix. The bioremediation processes will however, reduce even the highly recalcitrant substances found in the waste material over time. The contaminated material presented several unique challenges to the remediation effort. The refinery and its associated lagoons are over one hundred years old, creating highly weathered conditions and material that would require special handling and preparation for the remediation process to be effective. The integrated bioremediation system (biopile), as designed, provided the stimulation needed to support the biological processes required to break down the recalcitrant hydrocarbon complexes to a more innocuous and stable material.

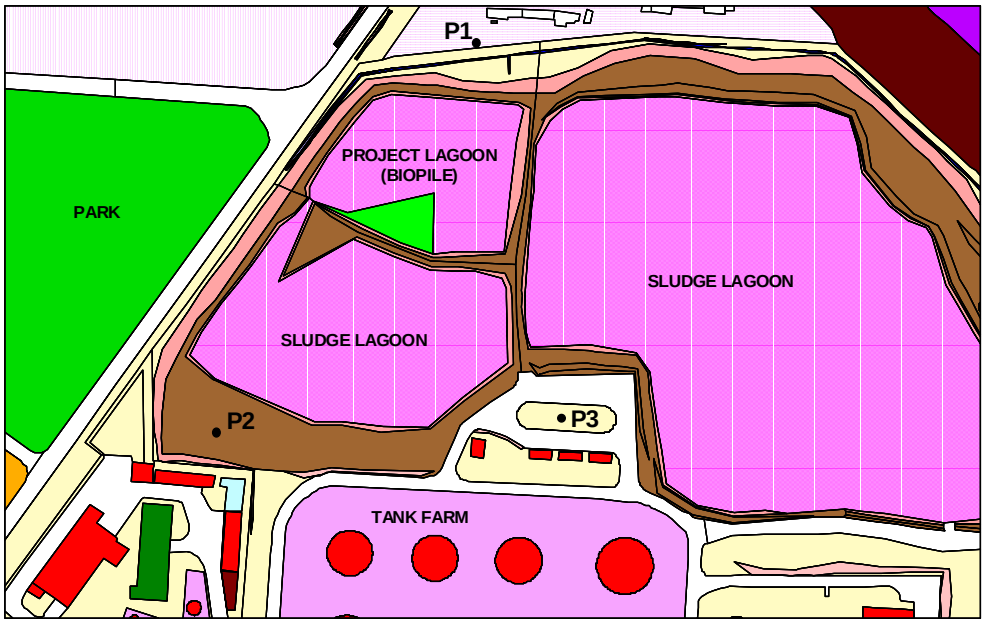
Wood chips (weathered) were selected as a bulking agent for the biopile because they provide the necessary porosity increase while utilizing an inexpensive waste product from a local lumber mill which otherwise would have to be disposed of. [Wood chips are normally sold as feed stock for pressed wood manufacturing. However, weathered (i.e. old and dirty) chips are not usable and must be disposed of separately.] During the construction of the biopile, the refinery took the initiative in utilizing grass clippings, leaf litter, and chipped waste lumber or wood originating from the refinery property. Thus eliminating the need and associated costs for transporting wood chips from Kobior, located approximately 25 km from the refinery in Czechowice.

Dolomite was selected over other materials e.g., gravel, as the leachate collection layer based on several factors including its ease of handling, relative low cost and availability, pH amelioration, and a direct and inexpensive transportation route via train from the quarry to the refinery. Dolomite was also available in a variety of screen sizes which was incorporated into the process design to ensure effective air distribution throughout the system.

The final site use, proposed by the refinery, for the lagoons is a “green zone” to serve as a buffer and visual barrier between the refinery installations and the city of Czechowice-Dziedzice. The green zone will have limited access by trained refinery and IETU personnel for scientific and research purposes and for continued monitoring of the biopile processes.

The area is not intended for recreational use by the general population or the refinery staff. No other regularly scheduled activities associated with the operations of the facility are planned for the site. The removal of the lagoon and the creation of the green zone has great public relations significance and greatly reduces the overall risk of the refinery to the city.

Figure 1. Refinery Lagoons



BIOPILE DESIGN AND CONSTRUCTION

The biopile was constructed utilizing contaminated soil amended with wood chips and other vegetative materials. The pile was constructed in the existing excavated lagoon as seen in Figure 1. The empty lagoon bottom was sloped toward a sump pump, which was connected to the leachate system. A leachate collection system consisting of perforated leachate collection piping was placed at the bottom of a dolomite base, approximately 1 ft (30.48 cm) deep. A cell divider (constructed of clay) was placed within the dolomite to create a separate active and passive section of the biopile. Figure 2 provides a cross sectional perspecitive.

The sump and its associated pump (Figure 2 and 3), is used to recirculate any collected leachate to the top of the biopile. In addition, use of make-up water from the existing wastewater treatment facility at the refinery, ensured that an adequate supply of moisture was available.

Figure 2. Cross Section Design Drawing

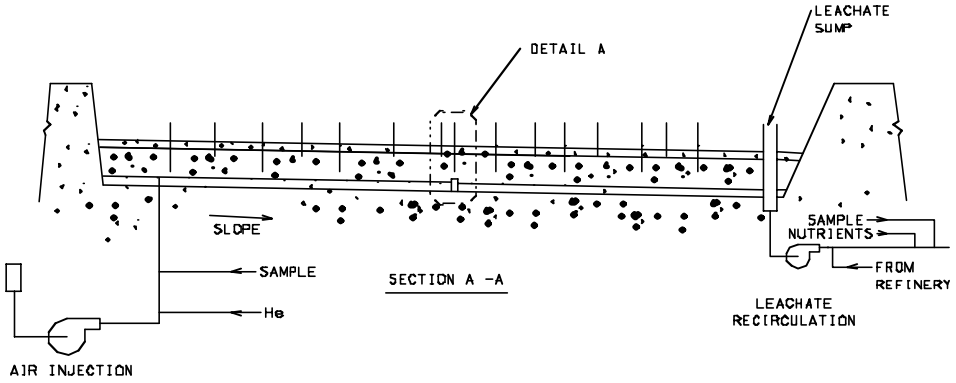
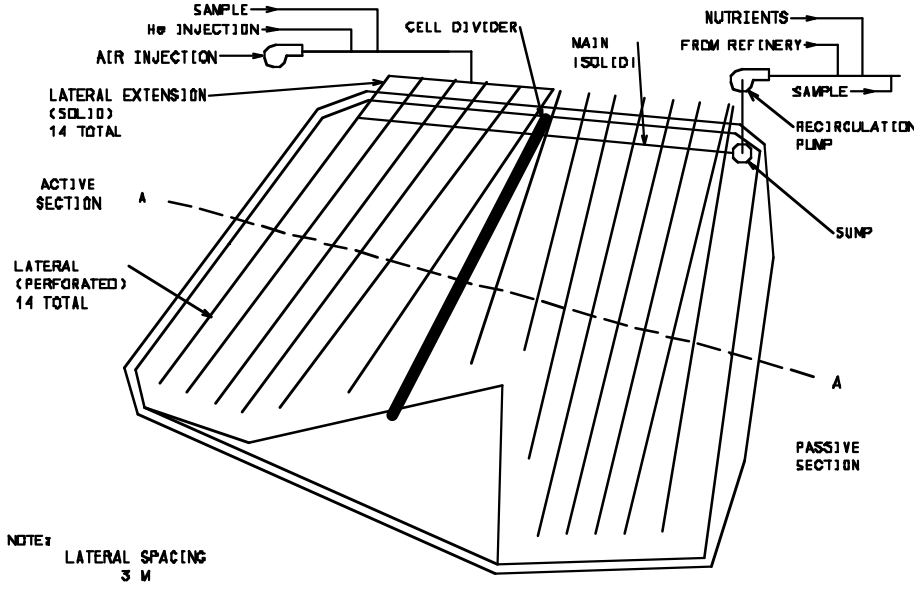


Figure 3. Plan View



As described by the USEPA (EPA/540/R-95/534a), one driving force behind the development of bioventing was the difficulty of delivering oxygen in situ [21]. Many contaminants, especially petroleum hydrocarbons, are biodegradable in the presence of oxygen. Enhanced bioreclamation processes use water to carry oxygen or an alternative electron acceptor to the contaminated zone. This process was common, whether the contamination was present in the ground water or in the unsaturated zone. Media for adding oxygen to contaminated areas have included pure-oxygen-sparged water, air-sparged water, hydrogen peroxide, and air. In all cases where water is used, the solubility

of oxygen is the limiting factor effecting mass transfer. At standard conditions, a maximum of 8 mg/L to 10 mg/L of oxygen can be obtained in water when aerated. The stoichiometric equation 1 shown below is an example that can be used to calculate the quantity of water that must be delivered to provide sufficient oxygen for biodegradation.

Eq. 1 $C_6H_{14} + 9.5\ O_2 \_ 6CO_2 + 7H_2O$

An example of the mass of water that must be delivered for hydrocarbon degradation to occur is shown below. Based on Equation 5.2.2.1, the stoichiometric molar ratio of hydrocarbon to oxygen is 1:9.5 or, to degrade 1 mole of hydrocarbon, 9.5 moles of oxygen must be consumed. On a mass basis:

$$\frac{1\ \text{mole}\ C_6H_{14}}{9.5\ \text{moles}\ O_2} \times \frac{1\ \text{mole}\ O_2}{32\ \text{g}\ O_2} \times \frac{86\ \text{g}\ C_6H_{14}}{1\ \text{mole}\ C_6H_{14}} = \frac{86\ \text{g}\ C_6H_{14}}{304\ \text{g}\ O_2} = \frac{1\ \text{g}\ C_6H_{14}}{3.5\ \text{g}\ O_2}$$

Given an average concentration of 9 mg/L of oxygen dissolved in water, the amount of air-saturated water that must be delivered to degrade 1 g of hydrocarbon is calculated as follows:

$$\frac{3.5\ \text{g}\ O_2\ \text{required}}{\frac{9\ \text{mg}\ O_2}{1\ \text{L}\ H_2O} \times \frac{1\ \text{g}}{1{,}000\ \text{mg}}} = \frac{390\ \text{L}\ H_2O}{1\ \text{g}\ C_6H_{14}}$$

or, to degrade 1 lb:

$$\frac{390\ \text{L}\ H_2O}{1\ \text{g}\ C_6H_{14}} \times \frac{1{,}000\ \text{g}}{2.2\ \text{lb}} = 178{,}600\ \text{L}\ H_2O \Big/ 1\ \text{lb}\ C_6H_{14}$$

Table 1. Oxygen Requirements Based on Source

Oxygen Form	Oxygen Concentration in H_2O	Volume to Degrade 1 lb Hydrocarbon
Air-saturated H2O	8 mg/L to 10 mg/L	180,000 L
Oxygen-saturated H2O	40 mg/L to 50 mg/L	42,000 L
Hydrogen peroxide	Up to 500 mg/L	6,100 L
Air	NA (21% vol./vol. in air)	4,800 L

NA = not applicable.

Based on the findings from the IETU treatability study, and an understanding of the mass transfer limitations of air-saturated water as an oxygen delivery system and the costs and safety concerns associated with pure oxygen generation, air injection was selected for the biopile electron acceptor delivery system.

Previous field demonstrations at SRS have shown that direct air injection is an acceptable method of delivering oxygen to the subsurface microbiota. Additionally, a recent demonstration at a local municipal landfill (Columbia County, GA), has shown that air can be delivered via the leachate collection piping without adversely impacting the collection of leachate. This dual use of the leachate collection system was also applied to the construction of the biopile. A regenerative blower was obtained to provide the necessary airflow for the biopile. The Columbia County Landfill demonstration has shown that air injected into the perforated leachate collection piping is distributed to the entire cell via the leachate drainage layer (i.e. dolomite) (Figure 2).

Approximately 1 meter of amended biopile material was placed above the leachate collection system. The composition of the mixture was approximately 80% to 90% contaminated material, and 10% to 20% wood chips as a bulking agent. Result from the column study for permeability conducted by IETU indicated that 10% wood chips (V/V) to be adequate.

Immediately above the amended biopile material a 20 to 30 cm of cover of silty top soil was used. The cover was planted with grass seed which provided protection from erosion, support of a green zone and provided a biofilter for any VOCs which may reach the surface of the biopile. The refinery additionly planted a mixture of deciduous conifer and beech trees and also some evergreen pines for landscaping purposes.

Atop of the biopile, a trickle system for water application was installed to maintain soil moisture between 20-80% of the biopile's field capacity. The target range is 30-40%. The water supply came from the leachate collection sump with make-up water coming from the refinery's process water sources including treated wastewater.

EXPERIMENTAL PLAN

Criteria for Success

There are three primary criterion by which the overall success of this demonstration was evaluated:

1. Demonstrate the application of bioventing/biosparging as a viable cost-effective process to remediate contaminated sites to reduce risk to man and environment and resulting in a green zone. The ability of the remediation process to degrade high molecular weight compounds (PAHs) will be evidenced by utilizing state-of-the-art monitoring equipment, analytical techniques and treatability studies to determine the rate and volume reduction in the starting concentrations of the contaminants.

2. Evidence of biological destruction (biodegradation) of petroleum (PAH, TPH and BTEX) from the contaminated material. Since a major advantage of bioremediation is destruction, it is important and significant to demonstrate that biodegradation is occurring. The evidence is expected to come primarily from comparison of the biopile material and soils analysis taken before, during and after the material is subjected to the treatment process (nutrient addition, aeration, pH adjustment and moisture control) to stimulate microbial activity and thus biodegradation of the contaminants.

3. Relatively simple and trouble-free operation. A critical assumption for the successful demonstration of the technology is that the system, as designed, will

function with little or no down time and provide operating conditions that minimize fugitive air emissions and maximize biodegradation rates. The proposed project has no precedence in Poland and as such represents new technology for the country. However, since several other nations have demonstrated similar technologies, it represents a relative low risk and should have high public acceptance. The simplistic design contributes direct benefits associated with the ease of management and operation. A minimal staff will be required to operate the equipment, again adding to the low risk factor by limiting exposure to operations personnel.

Process Monitoring

Monitoring of the system was accomplished in a variety of ways. Soil gas piezometers (Figure 4) were installed in the biopile to monitor carbon dioxide (CO_2), oxygen (O_2), methane (CH_4), volatile organic hydrocarbons (VOCs) and semi-volatile organic hydrocarbons (sVOCs). Water and soil samples were analyzed for polycyclic aromatic hydrocarbons (PAHs), nutrients, metals, and microbiological activity. Water quality of the leachate was tested for pH, dissolved oxygen (DO), specific conductance, temperature and other chemical and physical parameters like BOD and COD. The data gained from the monitoring program was used to calculate the biodegradation rates for PAH and total petroleum hydrocarbons (TPH). Respiration testing was conducted to monitor O_2 utilization during the remediation and helium tracer tests were performed to monitor the air flow, distribution and hydraulic conductivity with respect to the permeability of the contaminant mixture within the biopile during air injection. Moisture and temperature were measured by in situ moisture probes and thermocouples set next to each of the vadose zone piezometers.

Monitoring Equipment

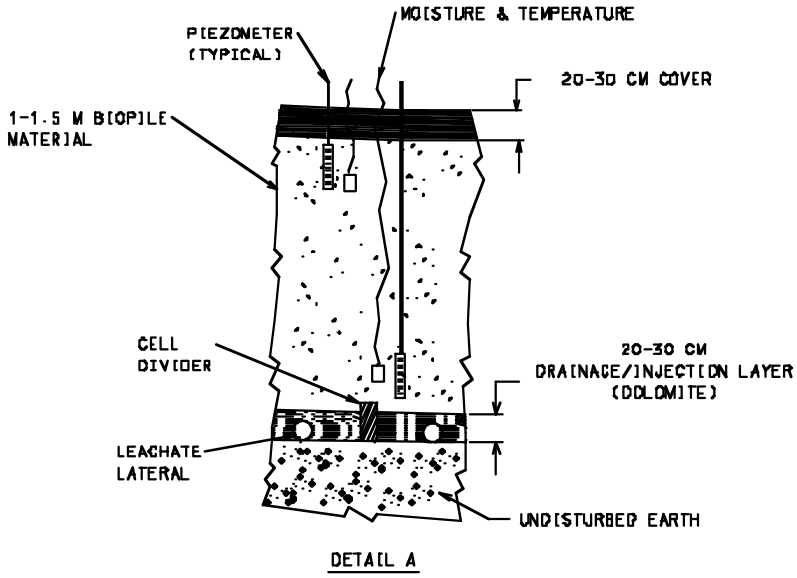
The Brüel & Kjær (B&K) Multi-gas Monitor, Type 1302, photoacoustic infrared spectrophotometer was used to monitor VOCs in the soil gas by direct analysis from the vadose zone piezometers in the field. A Landtec GEM-500 Gas Extraction Monitor was used to measure CH_4, CO_2 and O_2 concentrations in soil gas. Soil moisture was monitored with multiple gypsum moisture blocks installed throughout the biopile at approximately the same locations as the soil piezometers (Figure 4). The soil moisture blocks consist of two concentric electrodes cast into gypsum blocks. When the blocks are placed within the biopile, the moisture content of the gypsum approaches equilibrium with the moisture content of the biopile material. The moisture blocks and moisture meter (Model KS-D1) utilized in this project were manufactured by Delmhorst Instrument Company, Towaco NJ. Soil temperature was monitored using J Type or K Type thermocouples placed within the biopile at approximately the same locations as the piezometers and moisture blocks. The readout device being used on this project was a Fluke Model 52 K/J Thermometer manufactured by the John Fluke Manufacturing Co. Inc., Everett, WA.

SAMPLING AND ANALYSIS

Soils were collected during the Expedited Site Characterization (ESC), the initial phase of the remediation demonstration and again for post demonstration characterization for analysis of VOCs, microbial counts, physical parameters, and miscellaneous parameters. Since the biopile contaminated soil was mixed with wood chips, the soil matrix should be

much more homogeneous than the native soil, thus random soil sampling of the passive and active zones should provide a reasonable estimate of soil parameter changes during interim sampling intervals. With biopile systems, in situ respiration testing can also indicate when the site is clean and, therefore, when to collect final soil samples.

Figure 4. Monitoring Point Design



Soils for organic and inorganic analysis were collected using a hand auger, and placed in a Whirl-Pak bag or other clean container. Samples were placed in a cooler on ice and managed according to the hold times as seen in the Test Plan. Prior to sample analysis, samples were weighed to determine the mass of the sample. Core specimens for microbial analysis were obtained directly from the soil sampler. Cores were sectioned with sterile spatulas and the outermost layer scraped off using a sterile scoopula. The sample was then placed in a sterile Whirl-Pak bag and transported to the laboratory on ice for immediate analysis according to the test plan. Laboratory analyses were performed by personnel at the IETU laboratory.

Helium tracer tests and vadose zone respiration measurements were done using a Mark 4 Helium Detector Model 9821 helium detector using the Bioventing Respiration Test protocols of EPA (EPA/540/R-95/534a) [21].

A sampling port, pump or bailer was used to collect leachate samples from the leachate recirculation system. Water was filtered in the field, if required, with 0.45 µm pore size filters. Field water parameters including dissolved oxygen, oxidation-reduction potential (ORP), pH, specific conductivity, and temperature, were monitored using a Hydrolab Surveyor.

Hydrocarbons were analyzed as follows: EPA Method 8010: 1,2-dichloroethane; EPA Method 8020: benzene, toluene, ethylbenzene, total xylenes total VOCs, n-propylbenzene; EPA Method 5030 and GC-FID California: aromatics; EPA Method 9071: TCLP. Soluble reactive phosphate concentrations were measured by the ascorbic acid colorimetric

determination method (EPA 365.2). Total Phosphorus were determined by the persulfate digestion and ascorbic acid colorimetric determination (EPA 365.2). Total Nitrogen was determined using a thermal conductivity detector (TCD which includes free-ammonia plus organic nitrogen was determined colorimetrically following digestion, distillation and Nesslerization method (EPA 351.3). Ammonia as distilled ammonia nitrogen was determined colorimetrically following distillation and Nesslerization method (EPA 350.2). Nitrate, Nitrite, and Sulfate was determined by the ion chromatography method (EPA 300.0). BOD and COD was determined by 5-day BOD test 5210 B APHA [3] and the 5220B Open Reflux COD method APHA [4]. For EPA methods see [21-25].

DAPI (4, 6 Diamindino 2 phenylindole) was used to provide a direct estimate of the total number of bacteria in the environment, regardless of ability to grow on any media that might be used [11]. A comparison of acridine orange (AODC) stained samples and DAPI stained samples of soil obtained earlier from the refinery site showed the DAPI gave superior results [20]. Calcofluor White (CFW) was used to provide a direct estimate of the total number of fungi in the environment. Naphthalene and crude oil enrichment was done with minimal salts media (MSM) [8]. The plates for naphthalene were incubated in an enclosed environment with naphthalene vapors available to the bacteria as a source of carbon for metabolism. For crude oil degraders MSM was placed in 96 well microtiter plates. Samples were diluted 10 fold across 8 wells in triplicate and a drop of crude oil placed in each well. After incubation, each well was scored for turbidity and oil emulsification to obtain a most probable number (MPN) density per gram dry wt or per ml. Since the actively aerated parts of the biopile could reach high temperatures due to high rates of biodegradation (composting type conditions). Enrichments from the active aeration side were incubated both at 25°C and at 45°C. Oxidation of petroleum by microbes like other types of organic oxidation under aerobic conditions is linked to the electron transport system (ETS) of the cell. The enzymes of the ETS include a number of dehydrogenases, thus dehydrogenase activity can be used as an overall measure of activity in the soil. Triphenyltetrazolium chloride (TTC) is used as an artificial electron acceptor to estimate dehydrogenase activity since the reduction of TTC to triphenyl formazan (TTF) causes a color change that can be quantified using a spectrophotometer. Soil samples were incubated with TTC (1.5 g/100 ml) for 24 h. The samples are then extracted with acetone and the extract measured at 546 nm using a spectrophotometer [1]. Values are presented as TPF µg/gdw.

For a complete description of all techniques and methods see Altman et al. [2]; and URL: www.iicer.fsu.edu/publications.cfm

RESULTS

The project was divided into 5 operating campaigns: OC1. Mobilization and air injection startup (9/25/97-1/27/98), OC2. Air injection (2/1/98-4/15/98), OC3. Air injection + fertilizer (4/16/98-6/30/98), OC4. Air injection + fertilizer + leachate recirculation (7/1/98-9/29/98), and OC5. Air injection + fertilizer + leachate recirculation + surfactants (7/4/99-9/29/99). The surfactant used in OC5 was a Triton N-101 analogue (Rokafenol N-8).

The estimated removal of BTEX for the 20 month project was between 90-99.9% with a reduction in TPH of 65-90% and PAH removal between 50-75%. These results are similar and comparable to a number of other sites reporting bioremediation of petroleum contaminated sediments. Sims [16] reported 50-100% reduction of fossil fuels in soil after only 22 days. St. John and Sikes [18] reported that a prepared bed system, complete with

fugitive air emissions control, at a Texas oil field was able to reduce volatile organic carbon by >99% after 94 days, with semivolatiles being reduced by more than 89%. In California, Ross et al. [15] reported that four acres of soil 15 in (38 cm) deep, contaminated with diesel and waste motor oils were decreased from 2,800 ppm TPH to less than 380 ppm in only four weeks. He also reported that at another site owned by a heavy equipment manufacturer, 7,500 m^3 were reduced to <100 ppm TPH after nine weeks and an additional 9,000 m^3 with 180 ppm TPH were reduced to <10 ppm after only five weeks. Another site in California had 600 m^3 reduced from 1000 ppm TPH to <200 ppm in 35 days. Molnaa and Grubbs [13] report other sites in California where similar results were obtained, e.g., 2000 m^3 with 2800 ppm TPH were reduced to less than 38 ppm in 74 days, a truck stop where 15,000 m^3 were reduced from 3000 ppm TPH to less than 30 ppm TPH in 62 days, and a site contaminated with lubricating oils where 25,000 m3 were reduced from 4800 ppm down to 125 ppm in 58 days. Based on the initial concentrations in the biopile (>200,000 mg/kg TPH in litter) reported by Ulfig, et al. [19], the rates of removal were predicted to be between 10 to 80 mg/kg of soil per day for TPH and could exceed 120 mg/kg of soil per day, based on similar work by Reisinger, et al. [14]. Reisinger experienced a 41% removal of TPH over the first two quarters (180 days) of biopile operations, based on respiration test data. The overall removal rates were as high as 121 mg TPH/kg soil/day, with a total removal of 120 metric tons in 20 months or 81% of the TPH inventory in the biopile (Table 2 and 3).

Table 2. TPH Biodegradation Rate by Operating Campaign and Treatment

Campaign	Average	Passive	Active
OC-1	80	44	119
OC-2	88	82	94
OC-3	<33	33	0
OC-4	<37	0	37
OC-5	91	60	121

All values in mg/kg soil/day

Table 3. TPH Inventory by Operating Campaign

	Baseline	OC1	OC2	OC3	OC4	OC5
Metric Tons	148	100	68.6	68.6	66.8	28.1
% Remaining	100	68	46	46	45	19

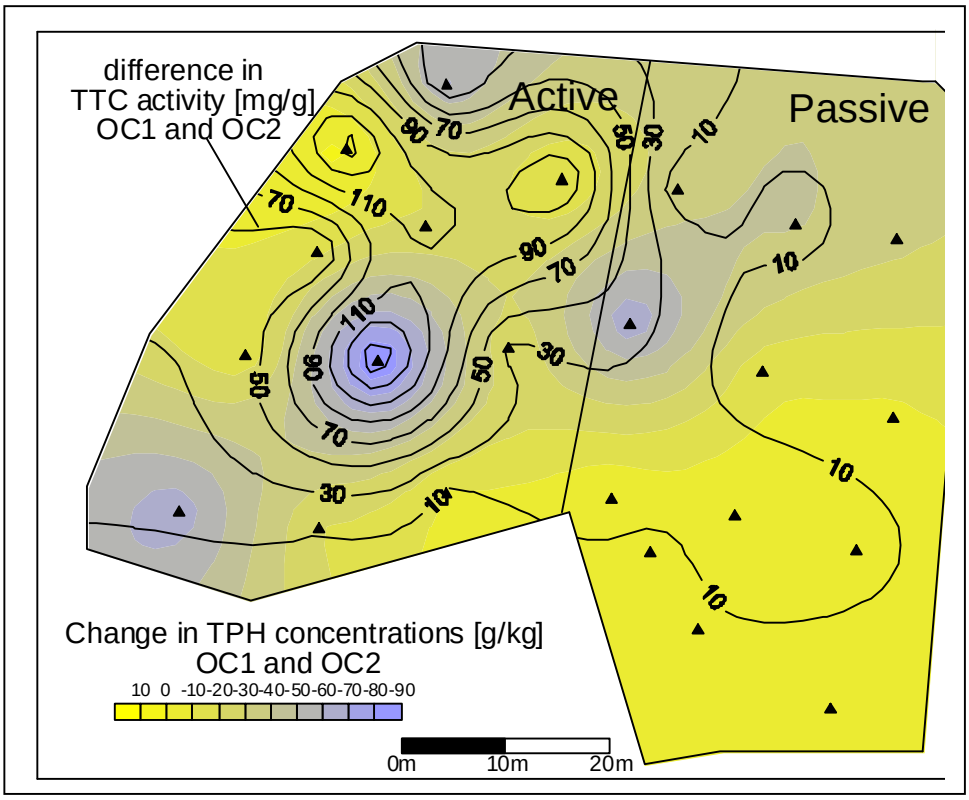
The spatial distribution of contaminants was different between the passive and active sides of the biopile. The active side of the biopile had higher contaminant concentrations initially then the passive side, but the differences between the shallow and deep areas of each side of the biopile were not significant. By the end of the demonstration there was only trace concentrations of TPH and PAHs left in either the passive or active parts of the biopile.

The carbon dioxide concentrations were higher in the passive parts of the biopile and the deep parts of the biopile (data not shown). Where air penetration was the poorest carbon dioxide concentration was the highest, eg. passive and deep areas of the biopile. This coincides with more anaerobic conditions that would generate more carbon dioxide.

By plotting changes in TPH concentrations together changes in microbial activity (TTC), the relationship between reduction in contaminant and microbial activity becomes more

obvious (Figure 5). The highest microbial activity areas for the end of OC2 both shallow and deep coincide nicely with the areas in the biopile that showed the greatest reduction in TPH concentration.

Figure 5. Change in TPH concentration vs. change in TTC activity in the soil of the biopile for OC1 and OC2.



The overall correlations for the soil parameters showed that the direct bacteria counts (DAPI) were significantly inversely correlated with total petroleum hydrocarbons (TPHTOT), polar total petroleum hydrocarbons (TPHPOL), and fluoranthene (FLORAN) (Table 4). This shows that over the entire demonstration as the bacterial numbers increased the contaminant concentrations decreased, suggesting a direct relationship. Further inspection of the matrix also shows that as DAPI numbers increases the fungal numbers (CFW) decreased, this suggests that the microbial community shifted due to an inability of fungi to compete with the smaller and more metabolically active bacteria. The fungi also apparently played little if any role in the reduction in contaminants numbers since CFW was not significantly correlated with any of the contaminant parameters (TPHTOT, TPHPOL, FLORAN, BBFLUORA, BKFLUORA, BAPYRE, BOPERY, and I123CDY). DAPI numbers were also significantly correlated with enzymatic activity (TTC), so that as the bacterial numbers increased the total dehydrogenase enzyme activity in the soil also

increased. The dependence of bacterial densities on adequate sources of phosphate was also indicated by the significant positive correlation between DAPI and PO4. The petroleum degrader enrichments at 20 and 37°C and the naphthalene degrader enrichments at 20 and 37°C appeared to be indicating the density of contaminant-tolerant microbial populations in the soil rather then degraders. This is suggested by the significant direct correlations between these parameters and the contaminants parameters (TPHTOT and TPHPOL), thus the higher the concentration of the contaminant the higher the density of these types of microbes. Both enrichments at 37°C had very few correlations to any of the other soil parameters, in part due to few measurements. The enrichment assays seem to be a poor index of biodegradation activity during the demonstration. Soil pH was also significantly inversely correlated with nearly all the contaminant parameters. This suggests that either the biostimulation process was increasing the pH as the contaminants were being degraded and/or that the biodegradation of the contaminants was causing the soil pH to increase. It is likely to some extent both processes were occurring since it is well known that oxidation processes tend to increase pH when anaerobic acidic environments are driven aerobic. The validity of the soil data matrix is supported by highly significant direct correlations between all the contaminant parameters and between the contaminants and total Kjeldahl nitrogen (TKN), a normal expectation since the contaminants are normal components of petroleum and that petroleum is high in organic nitrogen.

Table 4. Correlation matrix of soil analysis parameters

	Temp	DAPI	CFW	NA20	NA37	PE20	PE37	TTC	
Temp	1								
DAPI	**-0.652**	1							
CFW	-0.2025	**-0.1249**	1						
NA20	**-0.3153**	**-0.3254**	**0.3995**	1					
NA37	-0.001	-0.0344	-0.0322	-0.0692	1				
PE20	**-0.3462**	**-0.3222**	**0.398**	**0.9971**	-0.0597	1			
PE37	**-0.2939**	0.1105	-0.0282	-0.0638	0.0157	-0.0551	1		
TTC	**-0.4051**	**0.227**	**-0.1388**	**-0.2665**	0.0037	**-0.1306**	-0.057	1	
pH	**0.3368**	0.0605	0.0159	-0.0961	0.0961	-0.0143	-0.0255	0.1017	
MOIS	**-0.2185**	0.0941	-0.1241	**-0.1513**	**0.1592**	-0.1087	0.0078	**0.1801**	
NO3	**0.2302**	-0.0361	0.0168	-0.0536	-0.0158	-0.0398	-0.0219	-0.0513	
NO2	0.0728	**0.2026**	-0.1031	**-0.2451**	0.0286	**-0.2313**	-0.0496	0.0176	
PO4	**-0.5656**	**0.1594**	0.0306	0.0289	-0.0426	0.085	**0.3533**	0.0272	
NH4	**-0.3177**	-0.014	**-0.1214**	0.0918	-0.0583	-0.0937	-0.0403	0.0122	
PTOT	**-0.775**	-0.0733	0.1182	-0.018	-0.1356	-0.0169	-0.066	-0.0633	
TKN	**0.2623**	0.0943	-0.0921	**-0.1252**	**0.147**	**-0.1224**	0.055	0.0376	
FLORAN	0.1409	**-0.1904**	-0.0431	**0.2171**	0.0254	**0.2172**	0.0011	0.013	
BBFLUORA	**0.2162**	-0.1067	-0.0703	0.048	0.0472	0.0409	-0.0092	**0.1619**	
BKFLUORA	0.1372	-0.0279	-0.0831	-0.0606	0.0654	-0.0589	0.1105	**0.1596**	
BAPYRE	0.0854	-0.0425	-0.0744	0.0019	0.0361	0.0026	**-0.1535**	**0.1382**	
BOPERY	**0.2512**	**-0.3095**	-0.0636	**0.1776**	**0.1451**	0.0277	-0.0025	0.0855	
I123CDY	0.1632	**-0.141**	-0.0905	0.0814	0.1098	0.0848	0.1046	**0.2188**	
TPHTOT	**-0.1943**	**-0.3574**	-0.0304	**0.2532**	-0.1079	**0.2267**	**-0.2095**	**0.1627**	
TPHPOL	-0.1124	**-0.3187**	-0.053	**0.1932**	-0.0971	**0.1723**	**-0.2012**	**0.1816**	

Temp=temperature, DAPI= direct counts, CFW= fugal element count, NA20 = naphathalene degraders at 20°C, NA37 = naphathalene degraders at 37°C, PE20 = petroleum degraders at 20°C, PE37 = petroleum degraders at 37°C, TTC = dehydrogenase activity, MOIS = moisture content, NO3= nitrate, NO2 = nitrite, PO4= phosphate, NH4 = ammonia, PTOT = total phosphorus, TKN = total kjeldahl nitrogen, FLORAN = flouranthene, BBFLUORA = benzo(b)flouranthene, BKFLUORA = benzo(k)flouranthene, BAPYRE = benzo(a)pyrene, BOPERY = benzo(g,h,i)perylene, I123CDY = indeno(1,2,3-cd)pyrene, TPHTOT = total petroleum hydrocarbons, TPHPOL = total polar petroleum hydrodarbons. All bold values are significant at $P < 0.01$

A simple model that was dependent of non aqueous phase liquid (NAPL) partitioning was found to describe the bioremediation process in the biopile. The mass of contaminants removed during time (t) is given by the following equation:

$$\textbf{Eq. 2.} \quad m(t) = M/R^3(R^2\text{-}2Da\Delta ct/\gamma)^{3/2}$$

Where:

m (t) – mass of NAPL removed in time t
M – mass of NAPL at t=0
R - average radius of NAPL particles at t=0
Da - diffusivity of NAPL in water
c - saturation concentration of NAPL in water
γ - density of NAPL

It is assumed that the all of the TPH in the bioremediated soil inventory can be divided into three categories:

A. NAPL dispersed in form of small droplets or aggregates throughout the whole biopile,
B. a fraction of TPH contained in macropores and/or weakly sorbed to soil structure and by the same readily available to microorganisms attack, and
C. C. a fraction of TPH which is strongly sorbed to soil structures and prior to being degraded has to desorb and diffuse to the place where it is available to a microbial community.

Values of parameters which characterize each individual fraction were assumed based on our own observations and literature data. The following parameters were assumed as characteristic for the contaminated soil bioremediated in the biopile:

NAPL (fraction A) content	~ 40% of total TPH inventory in soil
Readily available fraction content	~ 45% of total TPH inventory in soil
Sorbed fraction content	~ 15% of total TPH inventory in soil
Soil porosity:	= ~ 0.3

Characteristics of NAPL fraction (Fraction A):

Average radius of aggregates (droplets)	R= 1.0 cm
Solubility in water	c= 10 mg/l before the surfactant was added
	c= 100 mg/l after the surfactant was added

Characteristics of readily available fraction (Fraction B):

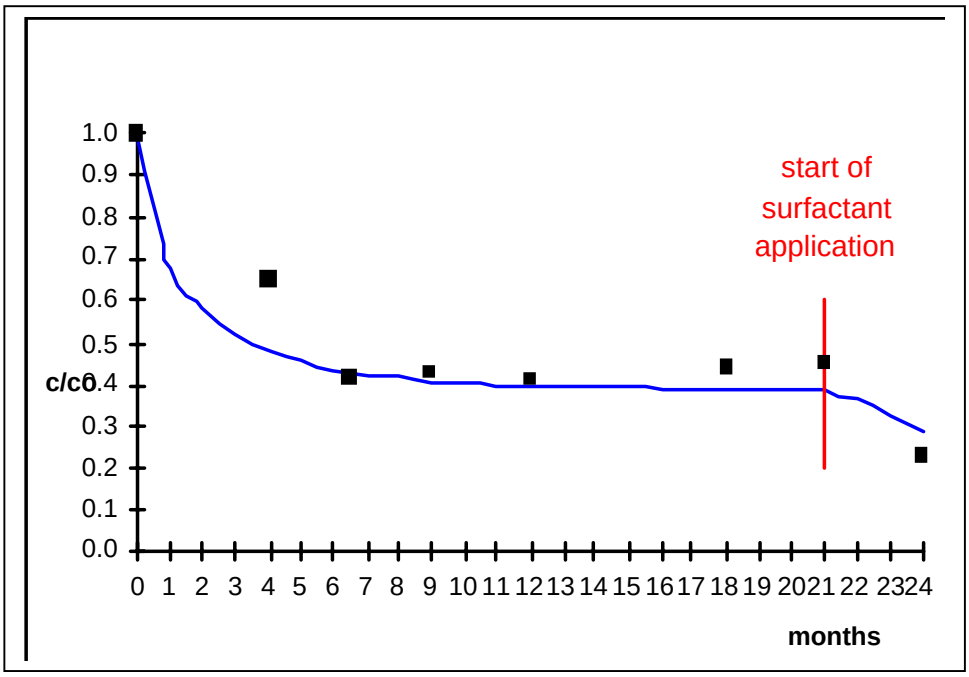
Average radius of soil aggregates:	r0 =	1.0 cm
Desorption coefficient	Kd =	100
Pore diffusivity of contaminant	Deff =	5x10-11 cm2/s
Liquid mass transfer coefficient	kl =	1x10-5 cm/s

Characteristics of sorbed fraction (Fraction C):

Average radius of soil aggregates:	r0 =	30m
Desorption coefficient	Kd =	1x105
Pore diffusivity of contaminant	Deff =	5x10-13 cm2/s
Liquid mass transfer coefficient	kl =	1x10-5 cm/s

As can be seen from Figure 6., the model results are in quite good agreement with experimental data form the biopoile.

Figure 6. Comparison of model with actual TPH concentrations over time in the biopile



COST ANALYSIS

The cost of using this technology to remediate the acidic and highly recalcitrant petroleum contaminated soil at the CZOR is estimated and compared to the actual costs for remediation of petroleum contaminated soil reported in the open literature. A conservative approach was taken in this comparison by using the actual costs of this demonstration. Since this was a demonstration, the analytical costs, and the specialized equipment costs were much higher than they would be in an actual deployment. The calculations use the average hourly rate for a Polish worker and a US worker (DOE site contractor, fully loaded). Equipment and materials costs were converted from $US to Polish Z (4.00 Z/$1.00). All equipment costs are actual purchase prices. The demonstration remediated 120 metric tons of TPH in 5000 metric tons of soil. Thus 4167 cubic yards of contaminated soil were remediated to cleanup standards. The cost per cubic yard was $96.33/Z142.76 (Table 5). If the specialized equipment was removed, the cost was $86.98/Z105.37. If the fully optimized system had been used from the beginning the remediation time would have been cut in half and the cost per cubic yard would have been reduced to $62.21/Z91.69. If we compare these results to published costs for conventional treatment technologies, we see that even in the worst case scenario, this bioremediation application is better than all costs except the soil washing costs reported by Davis et al. [7]. Thus the biopile remediation costs are lower than incineration, landfilling, stabilization, and asphalting. Considering the reduced time scenario this application even beats the cost of soil washing (Table 5). If we

compare this demonstration to other biopile and bioremediation techniques we can see that it falls within the same range but is higher than the prepared bed bioreactor and biopile deployments reported by Kastner et al. [10]. Given that the material being remediated was extremely acidic, more than 100 years old and had heavy metal contamination also it compares well. The costs reported by Kastner et al. [10] were for fresh diesel-contaminated soil, and inherently biodegradable PCS. This demonstration showed that biopile type bioremediation for TPH and PAH contaminated soil can be a highly effective and cost effective solution for waste lagoon cleanup.

Table 5. Cost analysis of the biopile project

			Polish Z	US $
*Total Cost*s			$594,882.	$401,405.
Cost/cy remediated 5000 metric tons or 4167 cy			$142.76	$96.33
Cost/cy less special equipment			$105.37	$86.98
Bioremediation Treatment Costs		Cost/CY	Reference	
Biopile costs at ISL	<100 ppm	$30.75	Kastner et al. [10]	
Prepared Bed bioreactor	<100 ppm	$46.07	Kastner et al. [10]	
Land treatment		$10-$100	EPRI [1988]	
Biotreatment		$40-$100	Levin and Gealt[1993]	
Bioremediation		$39-$111	Molnaa and Grubbs [13]	
Conventional Treatment Costs				
Incinerate (Tennessee)	3 units	$309.00	Davis et al [7]	
Incineration		>$100	EPRI [1988]	
Incineration		$250-$800	Levin and Gealt 1993]	
Incineration (mobile)		$195-$520	Molnaa and Grubbs [13]	
Soil Wash (Tennessee)	2 units	$70.00	Davis et al [7]	
Landfill		$150-$250	Levin and Gealt [1993]	
Landfill		>$100	EPRI [1988]	
Landfill		$176-$202	Molnaa and Grubbs [13]	
Asphalt		$10-$100	EPRI [988]	
Stabilization/fixation		$130-$260	Molnaa and Grubbs [13]	

DISCUSSION

The Polish petroleum refinery biopile field demonstration had a number of significant findings. The first criteria for success was to demonstrate the application of bioventing/biosparging as a viable cost-effective process to remediate contaminated sites to reduce risk to man and environment and resulting in a green zone. Over the entire field demonstration more than 120 metric tons or 81% of the total petroleum hydrocarbons that were present were destroyed (Table 3). By the end of the 20 month biopile demonstration, concentrations of TPH and all PAHs were below the Polish and US risk guidelines for even shallow soils (0.3-15 m) for sites with multiple-uses (including residential). This full scale demonstration simultaneously remediated the contaminants present in the soil to acceptable risk levels and created a permanent green zone with a park like atmosphere in less than 20

months. The comparison of passive with active aeration demonstrated that the Baroballs, for passive aeration, could be used effectively to provide aeration of the biopile via barometric pumping. This comparison showed that passive air injection required 3-5 months longer to reach the same end point as blower injection of air. Passive injection could thus provide significant cost savings whenever there is no urgency for remediation due to immediate risk to human health or the environment. New field instruments that were used to monitor physical and chemical parameters in the field had variable success. The landfill gas analyzer proved extremely robust for measuring changes in carbon dioxide, oxygen, and methane in the soil gas. These measurements helped verify the respiration rates, the degree of injected air penetration into the biopile and a measure of aerobic conditions in the biopile. The installed temperature and moisture blocks were not sensitive enough to indicate significant changes in either parameter, thus were of minimal value. However, the moisture blocks did provide evidence that the biopile was drying out in the later part of operating campaign 5. The photoacoustic infrared spectrophotometer proved difficult to operate and did not provide reliable data on soil gas concentrations in the later part of the demonstration. This was primarily due to humidity interference from water vapor becoming entrained in the instrument. The five operating campaigns showed that initially air injection alone (OC1 & OC2) stimulated dramatic reductions of contaminants (>50%) in the biopile in less than 7 months (Table 3). Subsequent operating campaigns using the addition of fertilizer with the air (OC3) and leachate recirculation (OC4) removed only an additional 1% of the contaminant inventory in a similar period of time. However, the final operating campaign (OC5), which added surfactants, decreased the contaminant inventory an additional 30% and caused a significant reduction of all of the metals in the soil. These findings are verified by the biodegradation rates observed during the different operating campaigns (Table 2). The first two operating campaigns had high rates of biodegradation in the active injection areas and these fell off during OC3 and OC4, but were increased to their highest levels in any area during OC5. This suggests that surfactants make more of the strongly sorbed contaminants bioavailable. The passive section of the biopile responded in a similar manner but with about a 3-5 month lag and did not achieve the rates seen in the active aeration sections. The rates observed are similar for bioremediation of other petroleum contaminated soils, and quite good for similar biopile studies, {e.g., prepared beds (52-641 mg/kg soil/day), biopiles (20-60 mg TPH/kg soil/day), bioventing (2.5-10 mg TPH/kg soil/day)} [4, 10,12]. This demonstration suggests the combination of active aeration, fertilizer, and surfactants with leachate recirculation will provide the fastest site remediation and substituting passive aeration will reduce the cost but increase the time to reach endpoint.

The second criteria for success was to demonstrate evidence of biological destruction (biodegradation) of petroleum (PAH, TPH and BTEX) from the contaminated material. Since a major advantage of bioremediation is destruction, it is important and significant to demonstrate that biodegradation is occurring. Multiple lines of evidence show that biodegradation of PAH and TPH occurred during the demonstration. BTEX compounds were undetectable in the soil after the first samples. First, the contaminant inventory changes showed that large concentrations of non-volatile petroleum contaminants were being removed at rates that could only have been attributed to rapid biodegradation (Table 2). Second, respiration studies showed that the oxygen demand in the active area corresponded to the rates of contaminant reduction observed. Third, over the entire demonstration there was a highly significant inverse correlation between bacterial density and contaminant concentration. Fourth, limiting nutrients like phosphate concentrations

were directly correlated to bacterial density, as were enzymatic activity measurements of soil (TTC). This suggests that bacteria were being biostimulated by the nutrient amendments being applied during the operating campaigns. The treatability and column simulation studies also verified in a like manner that biodegradation was responsible for reduction of contaminants and that the nutrient and surfactant amendments being applied in the field caused similar responses in the laboratory. Fifth, the aeration of the biopile soil created an aerobic environment conducive to aerobic biodegradation of petroleum contaminants. Sixth, all PAHs measured were also being degraded. Seventh, very active, low pH tolerant petroleum and PAH degraders could be isolated from the biopile that used petroleum and PAHs as their sole carbon and energy source. And eighth, the modeling studies of the field data showed that the biodegradation of the contaminants observed during the demonstration could be simulated by a kinetic model of contaminant biodegradation.

The third criteria of success was to demonstrate a relatively simple and trouble-free operation. A critical assumption for the successful demonstration of the technology is that the system, as designed, will function with little or no down time and provide operating conditions that minimize fugitive air emissions and maximize biodegradation rates. The equipment and operation went through a number of delays during the initial 3 months of operation, due to differences in voltage, planning, weather and manpower delays from a variety of sectors in this multi-institutional and multi-national demonstration. However once the initial problems were solved, operation was relatively simple and maintenance free. The simplistic design served the project well and helped make the project the success it was.

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