

Biotreatability Studies Lead to Landfarming Innovations *Application of In Situ Bioremediation at Watervliet Arsenal*

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Abstract

Soils at the Siberia Area of the Watervliet Arsenal in Watervliet, New York are contaminated with petroleum hydrocarbons (TPH), including polycyclic aromatic hydrocarbons (PAHs). Malcolm Pirnie, Inc. proposed *in situ* bioremediation as a corrective measure for contaminated soils in the Siberia Area. To demonstrate that in-situ bioremediation is a viable option, a series of laboratory biological treatability studies was performed. Initial studies documented the existence of indigenous microorganisms capable of degrading TPH and PAHs. Pan studies were then conducted for six months to simulate *in situ* landfarming techniques. Data collected from the laboratory studies were used to design a 16,000-square foot landfarming pilot plot to treat 3,200 cubic yards of soil. This pilot plot was constructed in August 2000 and is currently being operated by Malcolm Pirnie, Inc. Unlike most landfarming plots that are designed for treatment zone depths of 1-2 feet, the Watervliet plot achieves a treatment zone depth of 6-7 feet by using a trencher to mix the soil. Preliminary results from the pilot plot show significant reductions in total TPH and PAH concentrations.

Introduction

Watervliet Arsenal, located in Watervliet, New York, five miles north of the City of Albany, is the oldest continuously operating cannon manufacturing facility in the United States. Waste oil and heavy metals, presumably from handling of waste metal chips saturated with cutting oils, have been identified as the primary contaminants in the soil at the Siberia Area of the Arsenal.

Laboratory Biotreatability Studies

A ¹⁴C-phenanthrene evaluation confirmed the existence of indigenous microorganisms capable of degrading TPH and PAHs. A bioslurry evaluation assessed bioremediation under conditions that minimized mass transfer limitations. Fourteen weeks of aerobic slurry conditions resulted in a 90 percent and 85 percent reduction in PAH and TPH concentrations, respectively. Next, a 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.

Pan studies were conducted for six months to simulate *in situ* landfarming techniques to provide a realistic assessment of contaminant degradation during bioremediation efforts. Glass tanks (38-liter capacity) were used as treatment vessels ("pans") in the study. After one month of incubation, PAH levels in aerobic, nutrient-amended samples showed greater than 40% decline, while levels in aerobic samples without nutrients fell approximately 22%. PAH concentrations in flooded (anoxic) samples and killed controls showed a marginal increase during this time compared to initial analysis. After four months of incubation, PAHs and TPH in aerobic tanks with nutrients and the tank receiving only water had both declined approximately 70%. PAH

and TPH concentrations in anoxic samples also declined during this time, but losses were less than aerobic samples. Microbial plate counts showed high levels of PAH and hydrocarbon-degrading bacteria in aerobic soil samples. Data suggests that biodegradation caused marked declines in PAH levels in aerobic samples but not in soil incubated under anoxic, denitrifying conditions. Data indicates that mixing and aeration of soils are more important than nutrient addition in stimulating hydrocarbon biodegradation in the Siberia Area.

Landfarming Pilot Study

Pilot Study Design

Based upon the results of the initial laboratory studies and the pan studies, a pilot-scale landfarming pilot study was designed and is currently being implemented at the Siberia Area. The pilot study consists of two adjacent test plots. Test Plot A, measuring 72 feet by 220 feet in area, encompasses approximately 3,200 cubic yards of soil, including 1,600 cubic yards excavated from a former burn-pit adjacent to the pilot study plot area. The excavated burn-pit soil was spread in a layer approximately 3 feet deep, and was combined with an additional 1,600 cubic yards of soil by mixing it with the 3 feet of soil directly below-grade of the excavated soil layer. This resulted in a combination in-situ and ex-situ land treatment cell with a 6-foot treatment depth. Plot B consists of a 30 feet by 60 feet area with an in-situ depth of 3 feet. The pilot study includes two active treatment periods. The first treatment period, initiated in August 2000, involves 16 weeks of active treatment, and the second treatment period will involve 8 weeks of active treatment. The two landfarming periods are separated by 36 weeks of monitored natural attenuation (MNA).

Pilot Study Implementation

The first mixing event was completed in August 2000, with five hundred cubic yards of wood chips added as a bulking agent. Fertilizer was added to both plots in October 2000. A total of five mixing events have been completed to date. Soil samples are collected from each plot four weeks following each mixing event. Seven composite samples from Test Plot A and three composite samples from Test Plot B are collected and analyzed for concentrations of TPH and individual PAH compounds. Parameters relating to microorganism growth conditions, including pH, moisture content, total organic carbon, and nutrient concentrations are also monitored monthly. In addition, biomass in soil samples has been assessed using a phospholipid fatty acid (PLFA) analysis to determine the general health, concentration, and type of the microbial populations. Sample locations are selected randomly from a sample grid of the plots. Each composite sample is made up of five soil cores that span the depth of the test soil (6-7 feet at Plot A, and 3 feet at Plot B).

Pilot Study Results

Figures 1 and 2 below show the average concentrations (i.e., average of composite soil samples) of individual PAHs versus time at Plots A and B, respectively. PAH concentrations at Plot A show a rapid initial decrease in concentration, consistent with first-order biological degradation kinetics. It is likely that degradation rates slowed during the months of November 2000 to January 2001 because of extreme cold conditions in upstate New York. Also, during these months, the plots have been covered in snow; saturated conditions have likely reduced oxygen levels available to the aerobic bacteria. Degradation rates of lower molecular weight PAHs (e.g.,

naphthalene, fluorene, etc.), are faster than for the higher molecular weight compounds (e.g., benzo[a]anthracene and benzo[a]pyrene). The 95% confidence intervals decrease with time, indicating that the mixing protocol is successfully achieving contaminant distribution homogeneity. The average TPH concentration at Plot A for the 9/15/2000 sampling event was 2621 mg/kg. Results of the 01/30/2001 sampling event yielded an average TPH concentration of 814 mg/kg. This is approaching the 500 mg/kg clean-up standard used by several states.

Concentrations of PAHs at Plot B are approximately one order of magnitude lower than those in Plot A. PAH concentrations increased initially but have decreased during the most recent month of sampling. The increase in PAH concentrations in Plot B may be due to increased physical availability of contaminants to chemical extraction as mixing of the soils breaks soil clumps into smaller particles, exposing more surface area. TPH concentrations for Plot B are insignificant.

The pilot study is currently in the MNA phase. Active landfarming will resume in May 2001. Results to date indicate that landfarm mixing can be achieved effectively to a depth of six feet.

