Remediation of Diesel and Fuel Oil Hydrocarbons in High Clay Content Soils: A Field Comparison of Amendment Performance Conducted at the Mare Island Naval Shipyard

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ABSTRACT

Past practices at the now closed Mare Island Naval Shipyard in Vallejo, CA caused diesel and fuel oil range organic (DFRO) contamination of the soil. The high clay content of the soils makes any remediation effort especially challenging. Chromatography of methylene chloride extracts of Mare Island soil confirmed that little weathering or degradation of petroleum hydrocarbons had occurred and very few hydrocarbon degrading bacteria were present in contaminated soil samples. A treatability study demonstrated that the addition of nitrogen, phosphorus, and rice hulls to contaminated soil stimulated the outgrowth of an active population of hydrocarbon degrading bacteria.

To test these findings, excavated soil (concentration of DFRO 560-1,670 ppm) amended with nitrogen and phosphorus was used to construct biopiles with and without rice hulls. The performance of these piles was compared to soil amended with rice hulls, nitrogen, and phosphorus that was mechanically mixed at regular intervals, a static pile with rice hulls but no nutrients, and a static unamended control pile. Contaminated soil was also treated with a microbial humic polymer nutrient mix and a time release oxygen compound supplemented with nitrogen and phosphorus.

Unexpectedly, the concentration of hydrocarbons increased in some of the soils after the initial sampling. It was determined that rice hulls and other non-petroleum organic compounds in the soil, artificially inflated the concentration of residual hydrocarbons. This problem was solved in the final sampling round by changing the extraction procedure.

After six months, the concentration of DFROs in soil treated with the humic polymer and the time release oxygen compound were less than 100 ppm which was the local water board limit for soil reuse. The concentration of DFROs in the static pile with no rice hulls was slightly above the water board limit. The concentration of DFROs in the rice hull amended soil was < 300 ppm. These results demonstrate that high clay content soils can be remediated to acceptable levels within a reasonable time.

INTRODUCTION

Remediating high clay content soils characteristic of Mare Island is a challenge (Conklin, 1995). High clay content soils retard the passage of water and air and may be anaerobic. For example,

aerobic hydrocarbon degrading bacteria in highly impermeable clay soils contaminated with petroleum hydrocarbons could easily deplete the oxygen. When soils become anaerobic the rate of hydrocarbon degradation is markedly decreased and some compounds are not degraded (Fox, 1992).

At the Navy's Mare Island facility, past fuel leaks from underground storage tanks (USTs) and pipelines resulted in the localized contamination of subsurface soil. Most of the excavated soil was mixed with nutrients and amendments and/or shredded prior to transport to Mare Island's Soil Treatment Facility (STF), previously an ammunition warehouse, for a 6 month treatability study.

Five ex-situ remediation methods were evaluated: fully aerated (using a blower and perforated piping) with and without rice hulls, lift/turning to aerate the soil and two commercial products, a humic material, and a time release oxygen compound. The results were compared to a control pile that was not aerated, turned, or amended. Evaluation criteria were overall cost, time to reach treatment levels, and/or reduction of total petroleum hydrocarbons (TPH) achieved in 6 months.

The primary objectives of the treatability study were:

- Evaluate the potential of aerobic ex-situ bioremediation to remediate TPH contaminated soil. This evaluation was conducted using the quantities of soil expected with full-scale production and remediation.

- Determine the best method based on overall cost, time to reach target TPH levels and/or reduction in TPH achieved in 6 months.

Soil cleanup requirements. Clean-up levels and methods (Table 1) were established by the California Regional Water Quality Control Board San Francisco Bay Region (CRWQCBSFBR, 1997).

Table 1. Treatment requirements.

Parameter	EPA Method	Limit
TPH	8015 M	100 mg/kg
BTEX	8020	0.005 mg/kg (each)
PAHs	8310	none

Soil Analysis and Classification. TPH contamination was primarily from fuel oil tanks that may have been taken out of service over 50 years ago. Five of six samples had a Unified Soil Classification System (USCS) Classification of CL (lean clay) and ML (silt) with a mean silt and clay content of 73.05% by grain volume. The sixth sample had an USCS Classification of ML - gravelly silt with sand. This sample which represents 5% of the total soil used in the treatability study was engineered base and backfill from trenches and drainage ditches and it is not representative of the soil at Mare Island.

Biopiles and Biocells: Preparation and Design. Four biopiles were constructed: control (CBP), fully aerated (FAB), non-rice hull (NRB) aerated, and lift/turn (LTB). Biopiles were 5 feet high, which was the load bearing limit for the STF concrete floor, and a maximum 38 feet wide.

Five 4-inch diameter PVC well screen aeration pipes were used to aerate the fully aerated and non-rice hull biopiles. A positive displacement blower was used to pull air through each biopile. All air exhausted from the blower went through two granulated activated carbon canisters (GACs) connected in series prior to venting to the atmosphere.

In the lift/turn biopile physical mixing of the soil was used to increase the oxygen level. This was accomplished by lifting the soil and slowly dropping it while spraying it with water for moisture and dust control. Lift/turning also promoted the exchange of accumulated carbon dioxide with fresh oxygen from the air. The biopile was lift/turned when low levels of oxygen were detected. The design and operation of the biopiles is summarized in Table 2.

Table 2. Summary of biopile properties.

TYPE	VOLUME yd^3	SHREDDING/ SCREENING	AERATION PIPING	RICE HULLS	NUTRIENTS
Control	50	X	--	X	--
Fully Aerated	500	X	X	X	X
Non-Rice Hull	200	X	X	--	X
Lift/Turn	150	X	--	X	X

'--' Indicates category not utilized.

Biocells. Biocells were constructed using 10 cubic yards of soil which was placed in 40 cubic yard dumpsters. They consisted of a control biocell (CBC), and two cells amended with a humic material or a time release oxygen compound. Before adding soil, the inside of each biocell was sealed with plastic sheeting. Each soil pile measured 7 feet (the width of the dumpster) and 2 to 4 feet high. Table 3, summarizes the properties of the biocells.

Table 3. Summary of biocell properties.

TYPE	VOLUME yd^3	HUMIC MATERIAL	MIXING WITH FRONT END LOADER	TIME RELEASE OXYGEN	RICE HULLS	NUTRIENTS
Control	10	--	--	--	--	--
Humic Material	10	X	X	--	--	X (manufacturer provided)
Time Release Oxygen	10	--	--	X	--	X

'--' Indicates category not utilized.

Shredding/Screening. Shredding was used to improve the aeration and distribution of moisture, and nutrients if added. Soil was initially laid out in a pile 1 to 2 feet high and allowed to air dry

so that it would break up when dropped using a front end loader. The dried soil was shredded and screened with a shredder-mixer. Soil was sprayed with a hand-held garden hose during loading into the grizzly. Fixed nozzels were used to add water and nutrients to the soil on the conveyor belt and as the soil exited the shredder.

Moisture. Water was added to all biopiles, except the control, and to all biocells during the first 6 months. The target moisture level for the biopiles was 15-20% dry weight. Over 6 months, the average moisture levels were: 12.0% CBP, 17.5% FAB, 14.2% NRB, 15.9% LTB, 20.5% time release oxygen biocell, 24.2% humic material biocell, and 14.3% CBC.

Rice Hulls. Rice hulls were added to all biopiles, except the non-rice hull biopile to increase the permeability of the high clay content soils (rice hulls were not used in the biocells). Rice hulls were used because they work well in modifying the soil structure, they are not a food source for the bacteria (NFESC, 1998), and they are cost effective. The cost effectiveness is due to a low purchase cost per ton, a high volume to weight ratio and a relatively low transportation cost due to the close proximity of the rice processing plants that produce rice hulls as a by-product.

Nutrients/Humic Material. Nutrients in the form of nitrogen and phosphorous are required for bacterial growth. For bioremediation, carbon is provided by the petroleum contaminants. The NFESC study (NFESC, 1998) determined that nitrogen and phosphorous amendments were required and were added in concentrations of 400 mg/kg and 50 mg/kg, respectively. For the humic material, the manufacture's representative supplied and applied nutrients. The humic material was added to the contaminated soil at a ratio of 25% (v/v).

Time Release Oxygen Compound. The compound is a time release form of magnesium peroxide which produces oxygen when it comes in contact with water. The compound was added to the soil prior to placement in the biocell. The oxygen compound was mixed with water and sprayed on at a concentration of 0.25% per cubic yard of soil (7 pounds of compound per cubic yard of soil). The company recommends that the compound be added at 1% for most applications. However, the company's laboratory studies suggest that concentrations of 0.50% and 0.25% also work, although the degradation rate is slightly reduced. The cost of the compound was $70 per cubic yard for the 0.25% mixture. This amount was high for an ex-situ treatment, but the cost of the 1% solution ($280 per cubic yard) was prohibitive. The company recommends that the soil be wet to capacity and works best in groundwater.

Soil Placement, Monitoring and Instrumentation for the Treatability Study. Soil was prepared and moved to the STF between 6 June and 15 July 1997. All biocells and biopiles were monitored for soil gases (oxygen, carbon dioxide, and volatile hydrocarbons), temperature, and moisture on a weekly schedule, and more frequently during the first month. The biodegradation rate in the FAB and NRB (blower aerated) biopiles was calculated using shutdown respiration tests.

RESULTS AND DISCUSSION

Initial TPH Analyses. After 6 months, the residual concentration of TPH in the biopiles and biocells exceeded the target of 100 mg/kg (Figure 1). However, the increase in hydrocarbon concentrations suggests that nonhydrocarbon organics interfere with the analyses.

Nonhydrocarbon Organics. These results are similar to Azevedo et al (1994). They describe the misidentification of naturally occurring compounds as petroleum hydrocarbons when analyzed using EPA 8015M. However, fingerprint analysis demonstrated that wood by-products and degradation products artificially inflated the concentration of TPH.

Extracts of pure rice hulls showed TPH readings of non-detect to 2,000 mg/kg for high molecular weight hydrocarbons ($> C_{24}$). In the rice hull biopiles, chromatograms appear to be enriched for fuel oil range hydrocarbons. Pure humic material also showed TPH readings between 750 and 2,750 mg/kg.

The use of hexane as an extraction solvent was investigated as a method for reducing the effects of organics in the rice hulls, humic material, and wood waste present in the soil (Bruya, 1998). Hexane being less polar than methylene chloride extracts fewer of the polar natural products that may inflate the TPH values. If the methylene chloride extract is analyzed directly, then non-petroleum hydrocarbons are also reported as petroleum hydrocarbons (Bruya, 1995). In addition, the methylene chloride or hexane extract can be put through a silica gel column or columns prior to analysis.

Final TPH Analyses. To investigate the potential contribution of nonhydrocarbon organics, the biopiles and biocells were sampled in January 1999. Analyses were conducted using methylene chloride and hexane. The TPH concentrations in the methylene chloride extracts of the samples taken in January 1999 were similar to concentrations in the samples taken in December 1997 (Figure 1). Since, the biopiles and biocells were not aerated, turned, or watered, it is not unexpected that there was no additional degradation.

The hexane extracts show a significant reduction in the TPH concentration and some samples are near or below the clean-up requirement of 100 mg/kg, (Figure 1). Furthermore, the lower concentrations in the hexane extracts suggest that the presence of nonhydrocarbon organics did artificially inflate the hydrocarbon concentrations. These results suggest that six months of bioremediation is adequate to meet the clean-up requirements.

CONCLUSIONS AND RECOMMENDATIONS

- Ex-situ treatment of Mare Island contaminated soils for reuse in a 6 month period is a viable remediation option.
- Both the humic material and time release oxygen biocells met the Water Board's Total TPH acceptance limit. The humic material is more cost effective than the time release oxygen compound.

- For biopiles, the NRB biopile provided the best bioremediation. However, the residual TPH was above the Water Board's TPH limit.
- TPH reduction was greatest in the soils with the highest moisture levels; the humic material and time release oxygen biocells.
- Rice hulls and the humic material artificially inflated TPH values, however, they did appear to improve the distribution of moisture and air.
- Hexane is the recommended solvent for future EPA 8015M analyses when nonhydrocarbon organics are present.
- Additional studies of the time release compound at reduced concentrations are recommended. The cost of the oxygen compound is prohibitive for ex-situ treatments at the concentration used. The compound may be a viable alternative for ex-situ remediation if it proves to meet acceptance limits at reduced concentrations.

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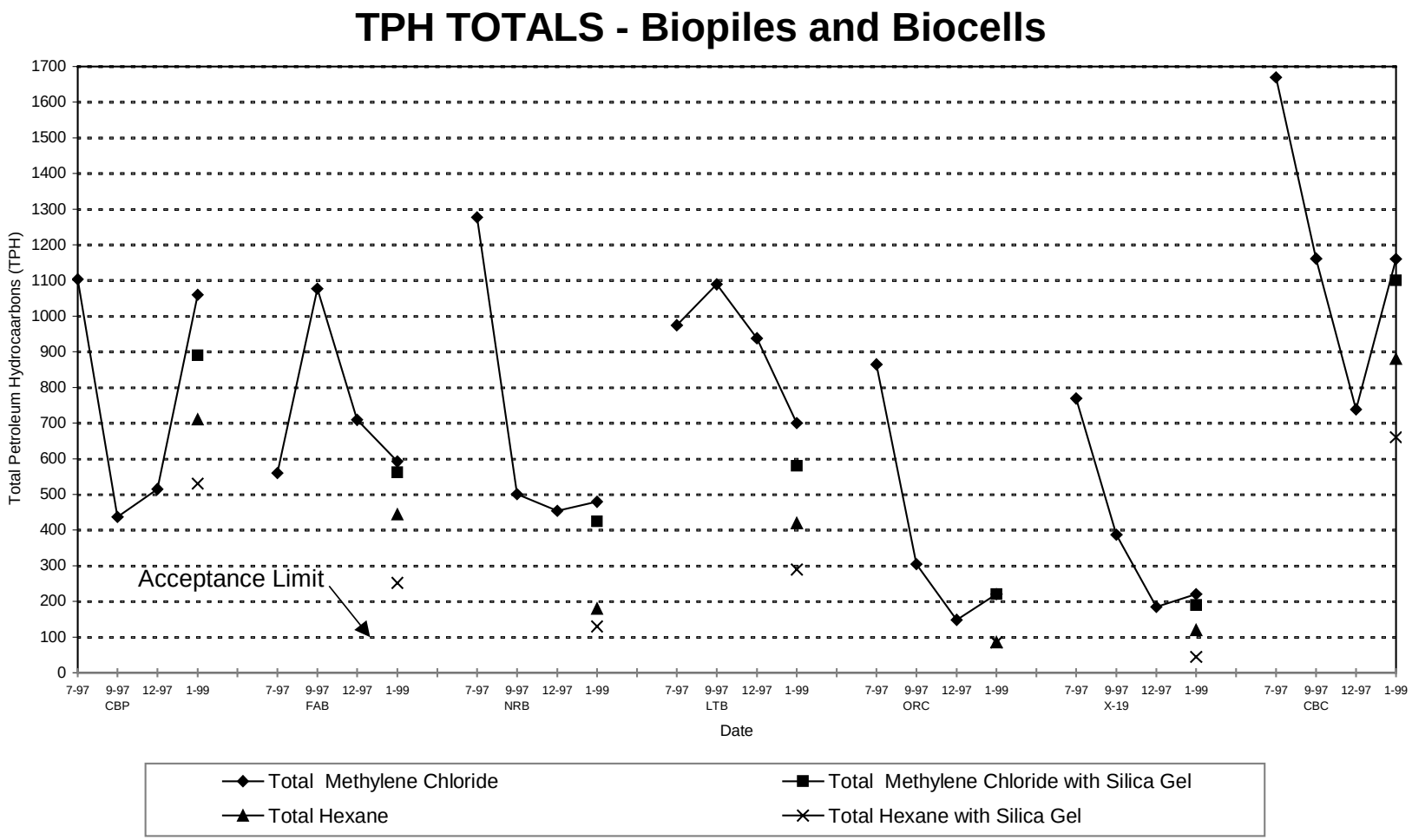

Figure 1. TPH concentrations in biopiles and biocells. For comparison, some samples were extracted with methylene chloride or hexane followed by silica gel cleanup.