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Item Type	conference;article
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Download date	2025-01-17 04:55:25
Link to Item	https://hdl.handle.net/20.500.14394/43544

Chapter 27

BIODEGRADATION OF WEATHERED OIL IN SOILS WITH A LONG HISTORY OF TPH CONTAMINATION

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Abstract: Sites with a long history of exposure to petroleum hydrocarbons contain mainly long chain hydrocarbons or "weathered oil". This is because petroleum is a complex mixture of many organic compounds and these compounds biodegrade at different rates. Under aerobic conditions the shorter hydrocarbon chains biodegrade first and the longer chains are more recalcitrant.

Long chain hydrocarbons are less soluble in water and more like tar in consistency than the shorter chain hydrocarbons, so a major problem with the degradation of these compounds is that bacteria that break down hydrocarbons do not come into contact with them. These compounds are not bioavailable and therefore do not biodegrade.

A petroleum refinery that has been active for many years has a large amount of weathered oil in the surrounding soil and groundwater. A treatability study was performed on samples from the Site to determine whether conditions could be manipulated to stimulate the biodegradation of the weathered oils. Several sets of microcosms containing soil and groundwater were set up. Along with nutrients and an oxygen source, a biodegradable surfactant was added to some of the sets in order to determine whether increasing the bioavailability of the hydrocarbons would enhance their degradation.

After the microcosms were set up, there was an initial increase in hydrocarbons in the aqueous phase and a decrease in hydrocarbons in the soil phase in the microcosms that had received surfactant. This change was due to the surfactant solubilizing hydrocarbons out of the soil and into the water. As the experiment progressed however, a decline in hydrocarbon levels in both soil and groundwater was observed.

It was determined that by manipulating the conditions and solubilizing the hydrocarbons, biodegradation of weathered oils could be stimulated. Hydrocarbons could be removed from soils that had contained these weathered oils for many years without any appreciable degradation.

Key words: biodegradation; TPH; weathered oil; surfactant

1. INTRODUCTION

Several areas at an oil refinery site with a long history of operation have weathered oil floating on the surface of the groundwater and oil-saturated soil. CRA was requested to perform a treatability study to determine the feasibility of biodegradation for treatment of the oil-saturated soil.

Bioremediation is a treatment process whereby contaminants are metabolized into less toxic or nontoxic compounds by naturally occurring microorganisms. The microorganisms utilize the contaminants as a source of carbon and energy. The by-products are mainly carbon dioxide and water. Once the microorganisms have consumed all of the contaminants, the microbial population becomes dormant or dies out.

Bioremediation can take place under aerobic or anaerobic conditions in the presence of other suitable electron acceptors such as nitrate, sulfate, or carbonate. Bioremediation can be applied in situ or ex situ to treat both soil and groundwater. It has been shown to be effective in treating a broad range of chemicals including petroleum hydrocarbons and chlorinated solvents.

Site conditions can be manipulated to enhance bioremediation and speed up the degradation rates of the contaminants. There are several techniques that can be applied to enhance the biological degradation of contaminants:

i. supplementation with suitable sources of nitrogen and phosphorus;
ii. manipulation of redox potential by the injection of air, oxygen, or nitrate to enhance aerobic biodegradation;
iii. injection of co-substrates such as molasses, or lactate to enhance the biodegradation of chlorinated contaminants;
iv. addition of surfactants to make the contaminants bioavailable; and
v. site microbial inoculation.

Oxygen is often the limiting factor in aerobic bioremediation at many sites. The degradation of petroleum hydrocarbons occurs much faster under aerobic conditions compared to anaerobic conditions. Therefore, the addition of oxygen can significantly increase the remediation rates. Oxygen addition is most frequently used to address dissolved phase contamination, such as total petroleum hydrocarbons and BTEX, as well as contamination in the capillary fringe zone. Oxygen can only be effective if the hydrocarbons are bioavailable and there is no nutrient limitation.

Petroleum hydrocarbons are chemicals that occur naturally and have been used by humans as fuels and manufacturing chemicals. Because of this widespread use, environmental contamination by petroleum hydrocarbons is fairly common. Petroleum hydrocarbons are a broad class of compounds that include short chain compounds such as the components found in gasoline, medium chain compounds that comprise such products as fuel oil and heavy long chain compounds that are present in tar. Petroleum hydrocarbons are biodegradable under both aerobic and anaerobic conditions.

The objectives of the laboratory treatability study were to determine whether biodegradation of the oil in the soil is feasible and to identify amendments that would enhance biodegradation of the oil.

2. MATERIALS AND METHODS

A 5-gallon plastic bucket of soil was collected from the Site and homogenized in a cold room and then characterized for key parameters pertinent to biodegradation:

- Total hexane extractable hydrocarbons;
- pH;
- Ammonia nitrogen;
- Orthophosphate phosphorus;
- Total heterotrophic microbial counts; and
- C16 specific microbial counts.

Microcosm tests were then performed on the oil-saturated soil sample to assess the degradation rates of the weathered oil under optimized conditions. The testing included determination of the maximum percentage removal of oil from the soil by biodegradation and by solubilization of oil by Biosolve (a surfactant). The tests were conducted in serum bottles, each containing 20 g of soil and 100 mL of distilled water. The microcosm tests consisted of the following treatments:

I. Soil and water only (biotic control);

II. Soil, water and Biosolve;
III. Soil, water, Biosolve, and nutrients;
IV. Soil, water, Biosolve, nutrients and an oxygen source; and
V. As in treatment (IV), with the addition of sodium azide (abiotic control).

Microcosms were sacrificed at T=0, 3 and 6 weeks and analyzed for hexane extractable hydrocarbons in the soil and water fraction.

3. RESULTS

The results of the initial analyses are shown in Table 1. Total petroleum hydrocarbons (TPH) in the soil were approximately 100,000 mg/kg. The pH of the soil was slightly above neutral and the microbial counts were fairly high. The high C16 specific counts indicated that a microbial population capable of degrading hydrocarbons is present at the Site. Nutrients, particularly ammonia-nitrogen, were low indicating that nutrient limitation may be impeding microbial growth.

Table 1. Initial Analysis of Soil Sample

	Units	**Initial Soil Sample**
Total Petroleum Hydrocarbons	mg/kg	116000/94100
PH	S.U.	7.8
Total Aerobic Microbial Count	CFU/g	2.5×10^6
Total C16 Degrading Microbial Count	CFU/g	5.7×10^6
Ammonia-Nitrogen	mg/kg	2.13
Orthophosphate-Phosphorus	mg/kg	18.1

The results of the analyses performed after 3 weeks are shown in Table 2 and after 6 weeks are shown in Table 3. Overall biodegradation of petroleum hydrocarbons (TPH) did not appear to occur in the soil microcosms within the six week period. The concentrations of TPH in the samples analyzed after six weeks were similar to those found in the T=0 samples.

The addition of biosolve, however, did result in the solubilization of TPH from the soil into the water. In the abiotic controls, after 3 weeks 6220 mg TPH per kg of soil had been solubilized from the soil into the water. After 6 weeks, the level was slightly lower, 4720 mg/kg. This decline may be due to oil re-adhering to the soil or to the sides of the serum bottle after initial solubilization.

Table 2. T=# Weeks Analysis of Microcosm Tests

	Units	**T=0**	**Soil and Water**	**Soil, Water and Biosolve**	**Soil, Water, Biosolve and nutrients**	**Soil, water, biosolve, Nutrients and O_2**	**Nutrients, O_2 and azide**
		Soil Fraction	Soil Fraction	Soil Fraction	Soil Fraction	Soil Fraction	Soil Fraction
Total Petroleum Hydrocarbons	mg/kg	105000/ 101000	121000/ 90900	84200/ 90100	98300/ 87200	83300/ 109000	90800/ 10800
		Water Fraction	Water Fraction	Water Fraction	Water Fraction	Water Fraction	Water Fraction
Total Petroleum Hydrocarbons	mg/L	249/263	70.4/64.3	519/638	186/302	438/311	1660/1340
% TPH Removal from Soil	%		<1	15.3	9.84	6.58	3.58
% TPH Removal from Water	%		73.7	<1	4.63	<1	<1
Overall % TPH Removal	%		<1	13.6	9.78	5.93	<1
TPH solubilized by Biosolve	mg/kg						6220

Table 3. T=6 Weeks Analysis of Microcosm Tests

	Units	T=0	Soil and Water	Soil, Water and Biosolve	Soil, Water, Biosolve and nutrients	Soil, water, biosolve, Nutrients and O2	Soil, water, biosolve, Nutrients, O2 and azide
		Soil Fraction	Soil Fraction	Soil Fraction	Soil Fraction	Soil Fraction	Soil Fraction
Total Petroleum Hydrocarbons	mg/kg	105000/ 101000	110000 /117000	103000/ 101000	105000/ 105000	124000/ 87300	103000/ 125000
		Water Fraction	Water Fraction	Water Fraction	Water Fraction	Water Fraction	Water Fraction
Total Petroleum Hydrocarbons	mg/L	249/263	120/155	225/325	153/202	303/244	1100/1300
% TPH Removal from Soil	%		<1	0.67	<1	<1	<1
% TPH Removal from Water	%		46.2	<1	30.7	<1	<1
Overall % TPH Removal	%		<1	0.57	<1	<1	<1
TPH solubilized by Biosolve	mg/kg						4720

4. DISCUSSION

Although microbial counts in the soil were quite high, microbial degradation of TPH was not observed during the 6 week period. It is likely that six weeks is not a long enough time for measurable removal of the hydrocarbons to occur, since the TPH in the soil consists of the longer chain hydrocarbons, which degrade slowly. The addition of nutrients and biosolve did not appear to speed up biodegradation.

Since biosolve did solubilize a significant amount of TPH from the soil, it is possible that it could be utilized to enhance recovery of TPH during groundwater extraction. The residual TPH in the soil could probably be removed by enhanced biodegradation, however the process would be slow.