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BIOREMEDIATION OF OIL-CONTAMINATED SITES

Case Studies Involving Light and Heavy Petroleum Hydrocarbons

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1.0 INTRODUCTION

Petroleum or crude oil is a natural product, resulting from the anaerobic conversion of biomass under high temperature and pressure. It has always entered the biosphere by natural seepage, but at rates much slower than the forced recovery by drilling. Currently estimated at about two billion metric tons produced per year, petroleum hydrocarbons are the most commonly used chemicals in the industrial world. Manufactured from crude oil, petroleum hydrocarbons are found in gasoline, kerosene, fuel oil, asphalt, and even in some chemicals used at home or at work. They are transported to places all over the world by ship, rail, truck, and pipelines. Unfortunately, because of the large volumes of petroleum hydrocarbons produced and subsequent releases during transport, use and storage, such as in underground pipelines or storage tanks, petroleum hydrocarbons have become one of the most prevalent contaminants in the subsurface soil and groundwater. The production, transportation, refining, and ultimate disposal of petroleum are introducing, by conservative estimate, 3.2 million metric tons annually into the oceans alone (National Research Council, 1985). There are also many incidents in which significant quantities of oil were accidentally released into the environment, causing environmental disasters. Exxon Valdez (1989) and the Gulf War (1990) oil spills are possibly the most publicized and studied environmental tragedies in history.

When petroleum hydrocarbons are released through a spill or leak into the environment, they migrate down through soils, becoming adsorbed to the soil particles until they reach groundwater, where they will dissolve in water, float on the water surface or sink to the bottom of a water aquifer. Any petroleum hydrocarbons that dissolve in the water will then travel with the flowing groundwater to some extent. Light-end petroleum products, such as gasoline, are more volatile, and will tend to float on water, whereas the heavy-end petroleum hydrocarbons, such as heavy heating fuel oil, will tend to sink.

Initial attempts in cleanup focussed on free product removal. As our knowledge of the fate and transport of petroleum hydrocarbons in the subsurface grew, treatment technologies evolved to address the dissolved phases present in the groundwater, and the phases sorbed to soil particles. A variety of techniques have been successfully used to cleanup soil and groundwater contaminated with petroleum hydrocarbons, including pump and treat of groundwater, excavation of shallow contaminated soils, and vapor extraction. However, many of these technologies are either costly or do not result in the complete destruction of the contaminants. Biological treatment, on the other hand, has developed as one of the most promising treatment technologies for petroleum hydrocarbons.

2.0 OIL COMPOSITION AND FRACTIONS

Petroleum hydrocarbons refers to a mixture of compounds in petroleum products that are all made mainly from hydrogen and carbon, hence "hydrocarbon." These compounds can be categorized into four simple fractions:

- saturates (or alkanes);
- aromatics, including such compounds as benzene, toluene, ethylbenzene and xylenes (BTEX) and polyaromatic hydrocarbons (PAHs);
- resins, consisting of compounds containing nitrogen, sulphur, and oxygen, that are dissolved in oil; and
- asphaltenes, which are large and complex molecules that are colloidally dispersed in oil.

The relative proportions of these fractions are dependent on many factors, including source, age, migration, etc. Of these fractions, the shorter alkane chain compounds and the lighter aromatics (such as BTEX) tend to be more readily biodegradable.

3.0 BIOREMEDIATION OF PETROLEUM HYDROCARBONS

Bioremediation is a treatment process whereby contaminants are metabolized into less toxic or nontoxic compounds by naturally occurring microorganisms. The microorganisms can utilize many of the petroleum hydrocarbon constituents as a source of carbon and energy. The by-products are mainly carbon dioxide and water. Strategies used by microorganisms for the degradation of petroleum hydrocarbon contaminants include:

- Use of constitutive enzymes;
- Enzyme induction;
- Co-metabolism;
- Transfer of plasmids coding for certain metabolic pathways; and
- Production of biosurfactants to enhance bioavailability of hydrophobic compounds.

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 such as BTEX and gasoline.

There are two basic ways to treat petroleum hydrocarbon-impacted sites by bioremediation: in situ treatment and treatment of the impacted soil after excavation.

In situ bioremediation has the advantage that the in situ nature of the process reduces the requirement for surface treatment and disposal, and minimizes contaminant exposure. Contaminants are treated in place and converted to innocuous products, such as water and carbon dioxide. Ex situ treatment involves the excavation of the impacted soil and treating it by a suitable technique such as landfarming, windrow composting piles, bioventing, or phytoremediation.

There are several techniques that can be applied to enhance the biological degradation of petroleum hydrocarbon contaminants and speed up the restoration of soil and groundwater:

i) supplementation with suitable sources of nitrogen and phosphorus to enhance biodegradation of Site contaminants by indigenous microbial population;
ii) enhancing the oxygen concentration by injection or infusion of air, oxygen, or slow oxygen release compounds (ORCs) to optimize aerobic biodegradation of petroleum hydrocarbon contaminants;
iii) applying surfactants to enhance the bioavailability of the hydrocarbon contamination; and
iv) bioaugmentation. If the indigenous microbial population is low or inadequate (for example, due to toxicity), key microorganisms can be isolated from the site, grown up in large volumes, and used for inoculation. However, this is rarely required for the treatment of petroleum hydrocarbons.

The supplementation of these reagents for in situ treatment would be made via frequent injection possibly through some of the existing monitoring wells and additional monitoring points installed in and around the areas of known contamination.

Oxygen is typically 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 rate. Oxygen can be provided into the subsurface by injecting air into the subsurface soil above the water table. An air blower may be used to push or pull air into the soil through the injection wells. As the air flows through the soil, the oxygen in it is used to enhance the growth and activities of microorganisms. The airflow would be maintained at low flowrates to avoid volatilization and release of volatiles into the atmosphere. This technique is known as bioventing. Oxygen gas could also be injected into the subsurface via the trenches. Compared to air injection, injection of oxygen gas into the subsurface would involve higher capital costs.

ORC releases oxygen slowly when it contacts water. It 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. It can be applied using retrievable filter socks placed in monitoring wells, or as a slurry mixture pumped into the subsurface through trenches. However, multiple applications of ORC are typically needed, which makes it more expensive than direct injection of air or oxygen. ORC can only be effective if there is no nutrient limitation. Laboratory treatability studies involving microcosm tests are recommended to assess the feasibility of in situ bioremediation and to identify key nutrient parameters limiting biodegradation. The treatability studies are required also to optimize the treatment performance.

Biosparging involves the injection of a flow of air or oxygen into the groundwater at low flowrates to enhance biodegradation. The air or oxygen flow is controlled such that VOCs are not generated and released into the atmosphere but instead are biodegraded in the groundwater or in the vadose zone. Additionally, suitable sources of nitrogen and phosphorus may be required. This technique would be applied through a series of sparge points/horizontal wells advanced through the vadose zone into the groundwater.

Most of the conventional methods for injecting oxygen into groundwater are, however, not very efficient, since most of the oxygen is not captured or utilized by bacteria. The majority of the injected oxygen forms bubbles, which rise to the top of groundwater table and escape before they have a chance to dissolve or to be utilized by hydrocarbon-degrading microorganisms. This can result in limited biodegradation response, particularly in an aquifer with high ferrous iron, moderate biological oxygen demand (BOD), and/or high concentration of hydrocarbon constituents. In order to overcome this problem, more efficient oxygen delivery methods are being developed. For instance, supersaturated oxygen can be applied in the form of microbubbles or by infusion under pressure through microporous filters. These methods can result in increasing oxygen concentration in the treated groundwater to levels significantly higher than oxygen saturation levels depending on the depth of the contaminated zone. These techniques can potentially be used to create a treatment zone or reactive barrier at the leading edge of contaminant plumes to reduce/minimize migration of contaminants.

4.0 CASE STUDIES

Following are three examples of sites where bioremediation technology has been successfully applied to treat a range of petroleum hydrocarbon contamination varying from crude oil spills and heavy engine hydraulic oil to light refined petroleum hydrocarbons.

4.1 Bioremediation of Heavy Oils in Soil

Soils at a locomotive maintenance yard in California were contaminated with extremely elevated concentrations of heavy petroleum oils as a result of refueling, operation, and general locomotive servicing activities. The soil was contaminated with mostly long chain alkanes in the C_{22} plus range, which are harder to biodegrade at extremely high concentrations. In some cases, the levels present in the soil were reaching the saturation level of the soil.

A cost-effective biological treatment was developed and field-demonstrated at the site. The program consisted of a multi-step laboratory treatability study followed by a field demonstration. Laboratory study results showed up to 94 percent removal of TPH in less than 16 weeks.

The field demonstration consisted of 120 m^3 demonstration plots. The soils used in the demonstration contained over 100,000 mg/Kg dry soil of TPH. The soils were bioaugmented with a mixture of microbial inocula and organic and inorganic fertilizers. More than 85 percent degradation was achieved in less than 28 weeks (see Figure 1 below).

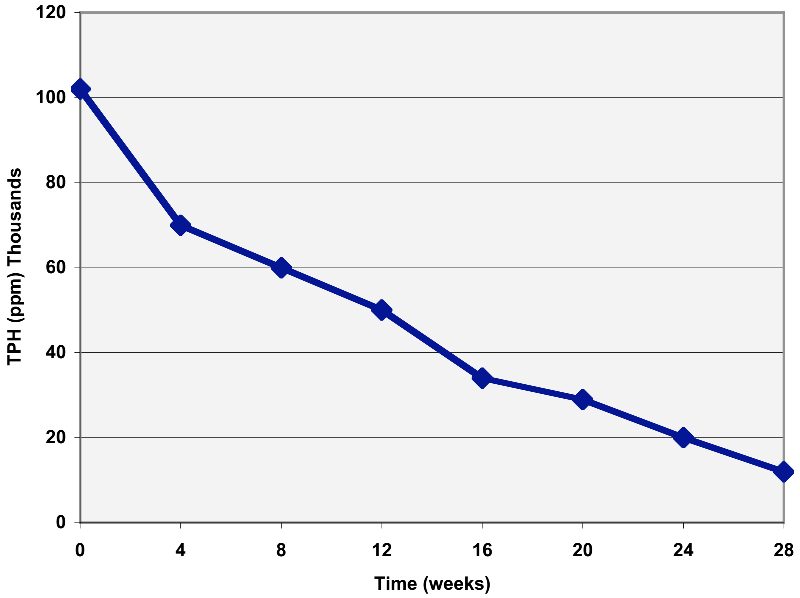

Figure 1. Bioremediation of heavy petroleum oil in soil (Results represent means of 13 samples)

4.2 Bioremediation of Light Oils in Soil

The subsurface soils (up to 20 feet below ground surface) and groundwater were impacted by naphthene at an oil refinery in Germany. A dual treatment process was designed and field demonstrated at the site. Approximately 200 m^3 of the more highly contaminated shallow soils (with concentrations as high as 12,800 mg/Kg) were excavated and treated by landfarming, while the remaining 1,600 m^3 less contaminated soils (highest concentrations of 180 mg/Kg) were treated in situ. Both treatments were conducted aerobically and involved application of a surface-active agent along with nutrients and microbes. Oil hydrocarbon concentrations in the ex situ treatment were reduced to less than 2,000 mg/Kg within 24 weeks (an 84 percent reduction). Similar results were seen for the in situ treatment (86 percent reduction to 26 mg/Kg within 15 weeks, see Figure 2 below).

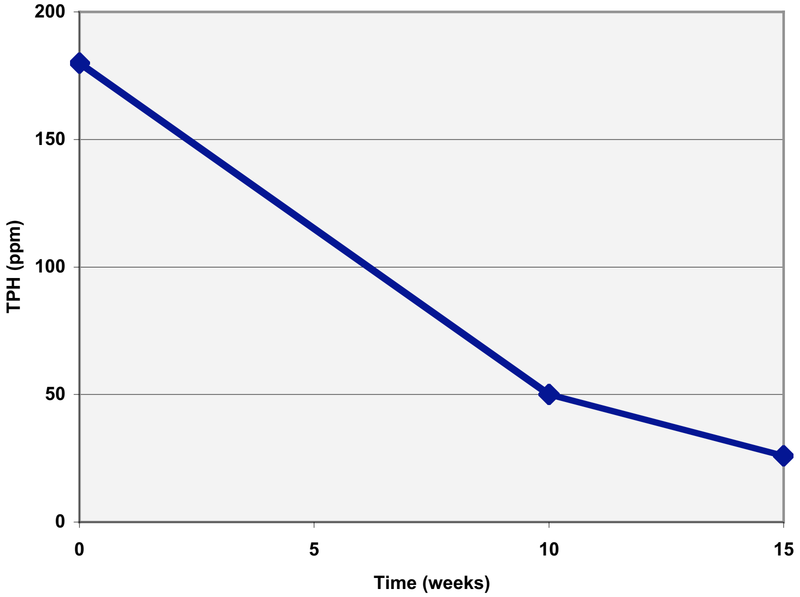

Figure 2. Reduction in TPH Levels over Time
(Results indicate mean concentrations
of oil hydrocarbons at various depths;
20 samples per depth)

4.3 *Bioremediation of Oil-Contaminated Desert Soil*

Over 49 Km^2 of Kuwait's desert soil were contaminated as a result of exploding oil wells during the Iraqi invasion and occupation of 1990. Intensive studies were conducted jointly by the Kuwaiti government, Kuwait Oil Company, and the Petroleum Energy Center of Japan to field demonstrate bioremediation as an alternative option for remediation of the oil-contaminated soil. Three bioremediation methods were field demonstrated at a large scale; these included landfarming, composting piles, and bioventing soil piles (with irrigation and bioventing).

The results of hydrocarbon degradation in the field was assessed based on the TPH analyses and confirmed by following the progressive changes in the ratio of selected straight chain alkanes and their branched alkane isomers, such as C_{17}:pristane and C_{18}:phytane. Hydrocarbon-degrading microorganisms usually degrade branched alkanes such as pristane and phytane at much slower rates than their straight chain isomers. Therefore, the ratio of straight–chain alkanes to these branched biomarker compounds can reflect the extent to which microorganisms have degraded the hydrocarbon in a petroleum mixture (Wang et al, 1994; Prichard and Costa, 1991; Kennicutt, 1988). Table 1 below presents the results of C_{18}:phytane ratio for the different bioremediation methods.

Table 1. Correlation of C_{18}:phytane ratio with TPH degradation

	C_{18}:phytane ratio			***TPH concentration (mg/Kg)***			***TPH reduction***
Treatment	***T_0***	***T_6***	***T_{12}***	***T_0***	***T_6***	***T_{12}***	***%***
Landfarming	2.4	0.3	ND (0.3)	39400	14000	7200	81.7
Control test	2.4	2.3	2.2	39400	35500	31700	19.5
Windrow piles	2.4	0.4	ND (0.3)	34700	19400	9500	72.6
Control test	2.4	2.4	2.2	35900	39800	30600	14.8
Static piles	1.7	0.5	ND (0.3)	14400	8500	4600	68.1
Control test	1.7	1.6	1.4	14100	13600	12200	13.5

The results showed that the ratio progressively decreased over the course of bioremediation. Hydrocarbon degradation in the treated soil was accompanied by significant reduction in the ratio compared to little or no changes in the control tests.

TPH analyses confirmed TPH degradation and showed that landfarming treatment reduced lightly contaminated soils by 80 percent within 6 months and heavily contaminated soils by 80 percent within 12 months. These results confirm that the reduction in TPH concentration is caused primarily by microbial biodegradation and not volatilization.

The bioremediated soils appeared to have significantly improved the fertility characteristics and water retention capacity of the bioremediated soils compared to the native non-contaminated desert soil.

Phytoremediation was also used as a polishing method to further reduce the residual level of TPH in the treated soil and to assess phytotoxicity of residual TPH on the growth and performance of a wide range of domestic and ornamental plant species. Enhanced removal of TPH was demonstrated by the use of plants and their rhizospheric microorganisms. The plants stimulated oil degradation, and the plant roots enhanced microbial population and activity in the contaminated soil. Alfalfa vegetation resulted in much cleaner soil as evident from the analysis of TPH, total extractable matter (TEM), and PAHs (see Figure 3 below).

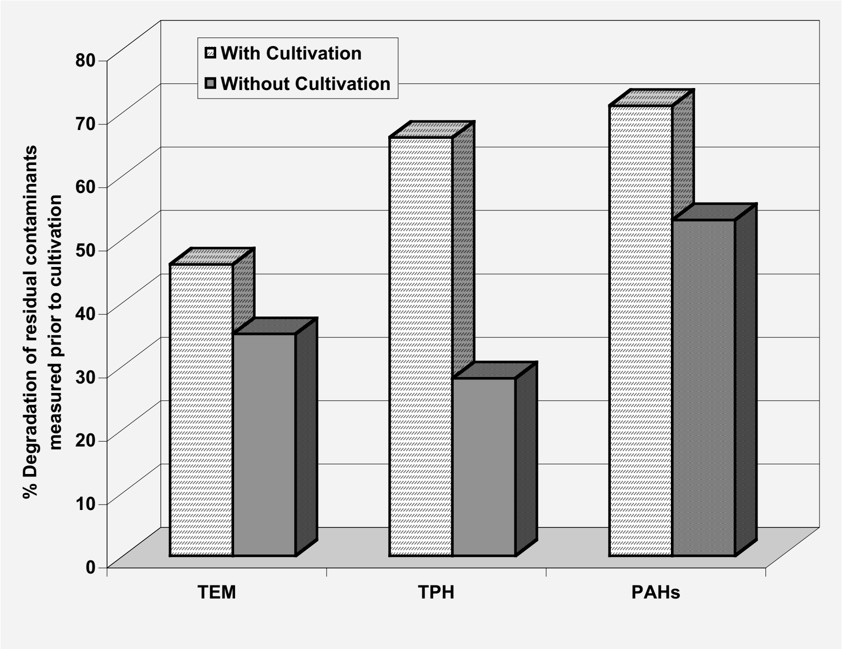

Figure 3. Effect of plant cultivation after 12 months bioremediation on degradation of TEM, TPH, and PAHs

The results of the phytoremediation/phytotoxicity tests also showed that the majority of plants tolerated up to 1% TPH.

5.0 CONCLUSION

Bioremediation is a promising technology for the treatment of a wide range of contaminants in soil and groundwater. The method is cost-effective, particularly for dealing with petroleum hydrocarbon contamination, and can be easily integrated with other remedial technologies. However, bioremediation is site-specific, and treatability studies are therefore highly recommended before full-scale remediation is considered. The degradation rate of hydrocarbons by these methods is dependent on the type of contaminants, metabolic capabilities of the indigenous microbial population, type of plant species used in phytoremediation, and also on predominant environmental factors. Therefore, the effectiveness of the bioremediation process depends to a great extent on the success in identifying the biodegradation rate–limiting factors and optimizing them during the feasibility studies. During these studies, both the microbiological and engineering aspects of the treatment can be developed and optimized. It is also important to define the limitations to the process; both with respect to the range of contaminants that can be treated and the residual concentrations that can be achieved within an appropriate time frame.

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