Biodegradation and Detoxification of Soil Contaminated with Heavily Weathered Hydrocarbons

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ABSTRACT

One of the principal challenges that the petroleum industry in the Gulf of Mexico region is facing is the remediation of highly contaminated sites resulting from poor historical practices; these sites being contaminated with very weathered hydrocarbons. Studies were carried out to evaluate the potential to treat regional soils contaminated with this kind of hydrocarbon. In the first experiments a mixed culture isolated from contaminated soil, was evaluated with respect to its capacity to biodegrade and mineralize local crude oil. In liquid culture, it was able to mineralize 7 % of the hydrocarbons, with light and medium weight aliphatics being preferentially biodegraded, and total reduction in hydrocarbon concentration was 62 %. In another experiment, the capacity of native microorganisms to biodegrade heavily weathered hydrocarbons was evaluated in contaminated soil, achieving only 14% reduction in three months, most of which occurred in the first month. The final concentration was still ~4.2 % TPH, however the toxicity was reduced at least 35%, and down to a range equivalent to background for regional soils. Bioaugmentation using an undefined mix of native microorganisms produced similar results. These experiments illustrate the difficulty in mineralizing highly weathered hydrocarbons but show how the toxic affect to soil caused by hydrocarbons can be overcome by biodegradation.

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INTRODUCTION

Due to poor historical practices, many petroelum producing areas were contaminated due to untreated discharges or chroinic leaks into the environemnt in the last century. In more developed economies, these areas have largely been remediated, sometimes at a very high cost using stratigies aimed at reducing the concentration of hydrocarbons in the soil to very low leveles which do not harm the soil. However, it can be shown that the heavily weathered hydrocarbons are very difficult to biodegrade (1), and have relatively low toxicity (2), but in high concentrations severely alter the physical and chemical properties of the soil, thereby reducing its fertility (3, 4). In this paper we investigate the possibility of detoxifying soils contaminated with very weathered hydrocarbons using bioremediation as a first step in the their treatment.

METHODOLOGY

In the first set of experiments, sediments were collected from a marshy area in which several grasses and *Cyperus* spp. were present as clusters in a heavily contaminated marshy area behind a refinery which was constructed nearly 100 years ago. The hydrocarbons contamination was due to chronic discharges over several decades (roughly eight) during which the hydrocarbons were weathered in a humid tropical environment. Sediments were collected from the roots of *Cyperus laxus* and extracted with an osmotic buffered solution to obtain an undefined mixed culture by sequential enrichment with crude petroleum. The culture was then challenged with 3 % % Maya Crude oil, and mineralization was measured by respirometry. Total degradation was determined by difference in the hydrocarbon concentration in the growth medium using gas chromatography (EPA 8015 equivalent, 5).

In the second set of experiments, sediments were collected from a beach area in an artificial reservoir prevoiulsy used to contain waste water from a sulfur mine. This area had been contaminated with acid waste water which also contained hydrocarbons derived from the salt domes that were exploited for sulfur (the hydrocarbons were not recovered and were considered waste products by the mine operators). This area had been treated to neutralize the acidity but was still very contaminated with very viscous hydrocarbons which had been co-weathered in the presence of hydrocarbons for 10 – 20 years in a humid tropical environment.. These samples were transported to the UJAT, where they were thoroughly mixed and divided into equal volumes representing the biostimulation treatment and a control. Each of these volumes was further divided into three replicates, each replicate consisting of a treatment cell of 0.4 m x 0.4 m x 0.2 m deep. The treatment method consisted of addition of inorganic nutrients (Grow-Feed 20-30-10 commercial fertilizer) sufficient to provide 100 ppm of nitrogen, daily aeration and periodic moisture addition (to maintain approx. 15 -22 % moisture). Hydrocarbons were determined using EPA method 418.1 (5), and acute toxicity using the Microtox bioassay (6).

RESULTS

The máximum TPH mineralization as determined by respirometry in the undefined mixed culture was achieved within 36 days and represented seven percent of the hydrocarbons added to the mixture. Total hydrocarbon reduction in the growth medium during this period was 62 %, the difference possibly representing the conversion of hydrocarbons into cell biomass or metabolic intermediates. In these experiments, the ratio of hydrocarbon mineralization to total reduction (biodegradation) was roughly 11 %. Interpretation of the gas chromatographs showed that the light and medium weight aliphatics were preferentially biodegraded.

In the second set of experiments, the hydrocaron concentration in the soil matrix dropped from nearly 4.8 % TPH to rougly 4.1 %, the major part of which occured during the first month, representing a total reduction of only 14 % (see figure 1). However, the toxicity was reduced from toxic [15.3 Toxicity Units (TU), background ≈ 10.5 TU (10, 11)] to completely non toxic [all replicates with less than 10 TU(7)]. It is interesting to note that in this much more weathered oil, a considerably lower amount of hydrocarbon was biodegraded, roughly one-fifth the amount in unweathered crude oil.

CONCLUSIONS

The very weathered hydrocarbons investigated in this study were essentially nonbiodegradable or only to a very slight extent. In is interesting to note that the amount of hydrocarbon reduction was very different depending on the weathering process. None-the-less, in the treatment in soil phase, it was demonstrated that biological treatment was sufficient to reduce the toxicity to background levels, even without greatly reducing the overall concentration. It is likely that the hydrocarbons removed in the soil matrix were also principally the lighter aliphatics (as shown in the liquid phase experiments), and that removal of this fraction was the major factor in the toxicity reduction. Lighter weight hydrocarbons are know to be more toxic to mamals that the medium and heavy weight hydrocarbons (8). Likewise, it has been shown that in environmental media, toxicity is strongly correlated to the concentration of light weight hydrocarbons but unrelated to the concentration of heavier weight hydrocarbons (2). Thus for the remediation of sites with heavily weathered hydrocarbons, a short bioremediation treatment (of about one month in tropical or semitropical environments) may be sufficient to reduce accute toxicity to low, possibly background levels. Subsequently, a soil restoration treatment may be used to recover the chemical and physical impacts to the soil caused by high concentrations of heavily weathered hyrocarbons using organic conditioners (4).

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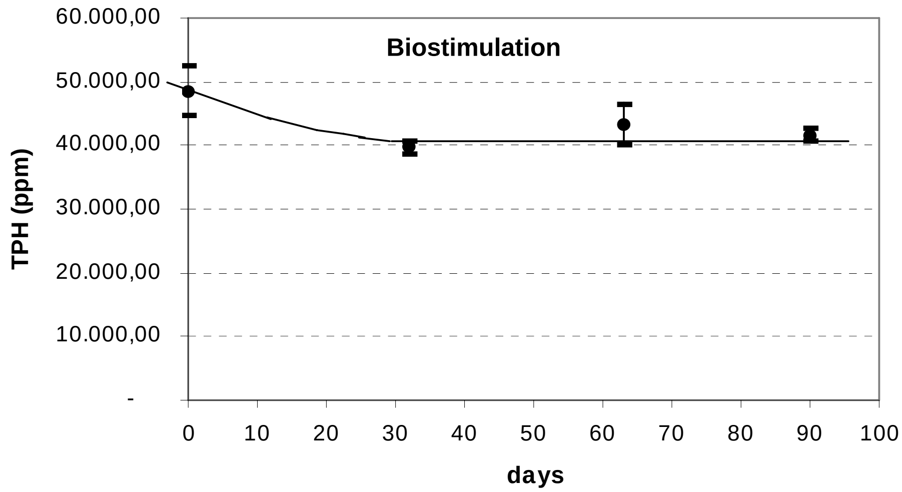

Figure 1. Hydrocarbon reduction in biostimulation treatment for sediments with heavily weathered hydrocarbons.