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Biotreatment of Synthetic Drill-Cutting Waste in Soil

Laleh Rastegarzadeh (lrastega@calpoly.edu) and Yarrow Nelson
(California Polytechnic State University, San Luis Obispo, CA. USA)
G. Todd Ririe (Unocal Corp., USA)

ABSTRACT: Oil and gas drilling operations create drill cutting wastes around the world. Drill cutting waste includes synthetic drilling fluids typically consisting of petroleum-based compounds mixed with clay-type materials and water. Biological treatment is an effective means of disposing of drill cutting wastes, but proper biodegradation conditions are critical. In this study biological treatment of drill cutting wastes containing Saraline® (synthetic paraffin mineral oil) was examined using a variety of amendments to study the effect of different conditions on the biodegradability of synthetic drill cutting wastes. Soil was collected from a drilling site in Southeast Asia and soil microcosms were incubated in a sealed and controlled environment to mimic the dry season of the field site. Amendments evaluated included native soil as a bulking agent and as a source of inoculum, rice hulls as a bulking agent to improve aeration and moisture retention, and urea as a source of nitrogen fertilizer. All microcosms were maintained with 15 – 20 % moisture and kept at 30^{o} C. Hydrocarbon biodegradation was evaluated using gas chromatographic (GC) analysis of total petroleum hydrocarbon (TPH) concentration of each microcosm. Microcosms were sampled every 30 days for a period of 4 months.

Maximum biodegradation was observed with a 1:1 mixture of soil and drill cuttings containing 1% urea and 10% rice hulls. Biodegradation proceeded with a half-life of about 30 days under these optimal conditions. After 4 months, 91% of the TPH was biodegraded under optimum conditions. Little or no biodegradation was observed for drill cuttings without amendments suggesting addition of soil bulking agent and fertilizer is essential. No decrease in TPH concentration was observed for a control with 1% sodium azide, indicating observed decreases in TPH were due to biodegradation alone. No volatilization was observed in the sealed soil microcosms. A separate volatilization experiment in open containers showed evaporation could contribute significantly to TPH loss in the field.

INTRODUCTION

Petroleum production facilities generate large quantities of oily wastes from drilling, processing or accidental contamination. Drill cuttings are produced during the drilling of wells for petroleum extraction. Drill cuttings are composed of the excavated mineral matrix mixed with the drilling fluid containing a fuel oil used in the cutting. When not managed properly, the oily drill cuttings are potential long-term contaminants (Breuer et al., 2004). Unocal developed synthetic paraffin oil called Saraline that is used for their drilling operations. The purpose of this research is to determine the suitability and optimum conditions of biotreatment for disposing of drill cutting wastes containing Saraline®.

The oily sludge and drill cutting wastes are often expensive to store or destroy and contaminated areas have required expensive remediation processes to minimize

contaminant dispersion. Previous methods designed to deal with waste by-products included storage, landfill, relocation, and incineration. An alternative to these methods involves biodegradation of hydrocarbons by populations of microorganisms present in soil. Bioremediation is an attractive approach of bioremediation petroleum hydrocarbons because it is simple to maintain, applicable over large areas, cost-effective and leads to the complete destruction of the contaminant (Frankenberger,1992). Bioremediation technology can accelerate naturally occurring biodegradation under optimized conditions [oxygen supply, pH, the presence or addition of suitable microbial population (bioaugmentaion), nutrients (biostimulation), water content, and mixing] (Trindade et al., 2005).

Biodegrading microorganisms are widely distributed and can be found in all natural areas, so the limiting factor in biodegradation of hydrocarbons is rarely the lack of appropriate microorganisms. The major limitation for the biodegradation of hydrocarbons on land and water is often an available source of nitrogen and phosphorus (Prince, 1993). Biostimulation is the process of introducing additional nutrients in the form of organic and/or inorganic fertilizers into a contaminated system, thereby increasing the population of the indigenous microorganisms. These requirements can generally be satisfied by addition of nitrate, phosphate and sulfate containing salts (Rosenberg et al., 1996). Oxygen and moisture are other important factor for contaminated soil biodegradation. Bulking agents are materials of low density when added to soils, lower the soil bulk density, increase porosity, may increase oxygen diffusion, and may help form water stable aggregates. These changes to a soil increase aeration and microbial activity (Hillel, 1980).

In this study, the optimized conditions for biotreatment of Saraline® drill cutting wastes were studied for conditions in a tropical climate. Rice hulls and native soil were used as bulking agents to facilitate the oxygen diffusion into the system. Native soil was applied to drill cutting wastes in two different ratios. Temperature was controlled to mimic the actual biotreatment site temperature in Bangladesh. Urea was used as a fertilizer to biostimulate bacterial activity. The duration of the experiment was four months. Biodegradation and volatilization were examined separately through controlled experiments.

MATERIAL AND METHODS

Saraline based drill cutting soil and native soil were collected from an oil drilling site in Srimongal, Bangladesh. The drill cuttings were mixed with variety of amendments and incubated in microcosms to determine the optimum conditions for biodegradation.

Soil Moisture. The moisture content of soil was measured by heating 1 g of soil for 2 hours at 105ºC and measuring the change of soil weight. Native soil and drill cutting waste had moisture of 15.6 % and 13.5%, respectively. Soil moisture content was adjusted to 20% by adding distilled water as needed. Earlier studies indicated that 20% moisture content is optimum for this kind of treatment (Chokshi et al., 2003).

Amendments. Urea was added at a rate of 1% of the TPH concentration in the soil to supply nitrogen for biodegradation. Ten percent rice hulls (w/w) were added to each microcosm as a bulking agent to facilitate aeration and to hold moisture. Rice hulls were

not composted prior to use. Native soil was added in two different ratios (10% and 50%) to provide an inoculum of active soil bacteria.

Microcosms. Seven microcosms were prepared with drill cuttings and varieties of amendments. The total weight of solids and amendments in each microcosm was 500 g. One gallon wide-mouth jars with Teflon®-lined lids were used to contain the soils and amendments. The detailed composition in each jar is presented in Table 1. Jar number 1 contained 500 g of non-amended drill cutting waste. A second jar had a mixture of 500 g drill cutting and 0.81 g of urea. The third jar contained drill cutting plus 10% rice hulls, and 1% urea. The fourth jar had a mixture of 9:1 drill cutting to native soil, and 1 % urea. Jar number five contained 9:1 drill cutting to native soil, plus 10% of rice hulls, and 1% urea. The sixth jar contained 1:1 drill cutting wastes to native soil, 10 % rice hulls and 1% urea. A killed- control was prepared with similar composition as the sixth microcosm with additional of 1% (5 g) sodium azide to inhibit the microbial activity. All the microcosms were incubated at 30ºC in a controlled incubator to mimic dry-season average temperature in Srimongal, Bangladesh. The duration of the experiment was 4 months and initial and monthly samplings were taken from each jar to analyze the total petroleum hydrocarbon (TPH) in the mixture. Once a week, the lids of jars were opened to provide oxygen for microorganisms. During the incubation time the lids were tightly closed to prevent any evaporation.

TABLE 1. Weights of components added to each microcosm jar.

Jar#	Description	Total (g)	Drill Cutting (g)	Soil (g)	Rice Hulls (g)	Urea (g)	Water (g)	Sodium azide (g)
1	Unamended Drill cutting	500	500	0	0	0.00	32.3	0
2	Drill cutting+Urea	500	500	0	0	0.81	32.3	0
3	Drill cutting+Rice Hulls+Urea	500	450	0	50	0.73	29.1	0
4	Drill cutting+Soil+Urea	500	450	50	0	0.73	31.3	0
5	Drill cutting+Soil+Rice Hulls+Urea	500	400	50	50	0.65	28.0	0
6	Drill cutting+Soil+Rice Hulls+Urea	500	225	225	50	0.37	24.4	0
7	Control (1% sodium azide)	500	225	225	50	0.37	24.4	5

Volatilization Experiment. To examine the volatilization of hydrocarbon, two open 1-gallon jars were prepared, one with the same composition as in the fifth jar (Table 1) and one control killed jar (like Jar 7). These containers were stored for 2 months at 30ºC in a temperature controlled incubator with ventilation. Initial sampling was conducted at the time of preparing the jars followed by monthly sampling.

Hydrocarbon Extraction and Analysis. Prior to samplings, the soil mixtures were well mixed. Duplicate soil samples were removed from each jar. A modified standard EPA soil extraction method (EPA method number 3510) was used to extract hydrocarbons

from the soil samples. A 25 g soil sample was added to 100 mL of methylene chloride and sonicated for 3 minutes (sonicator cycles 3 second on with 1 second off cycle). An additional 100 mL methylene chloride was added and the sonication was repeated. The extract mixture was filtered with filter paper. Gas chromatography (EPA method number 8015) using an HP 6890 GC with a flame ionization detector was used to measure the TPH concentration. TPH concentrations were calculated using a standard curve prepared based on hydrocarbon diluent from an oil field in California. Native soil was extracted to determine if any initial TPH existed in the native soil.

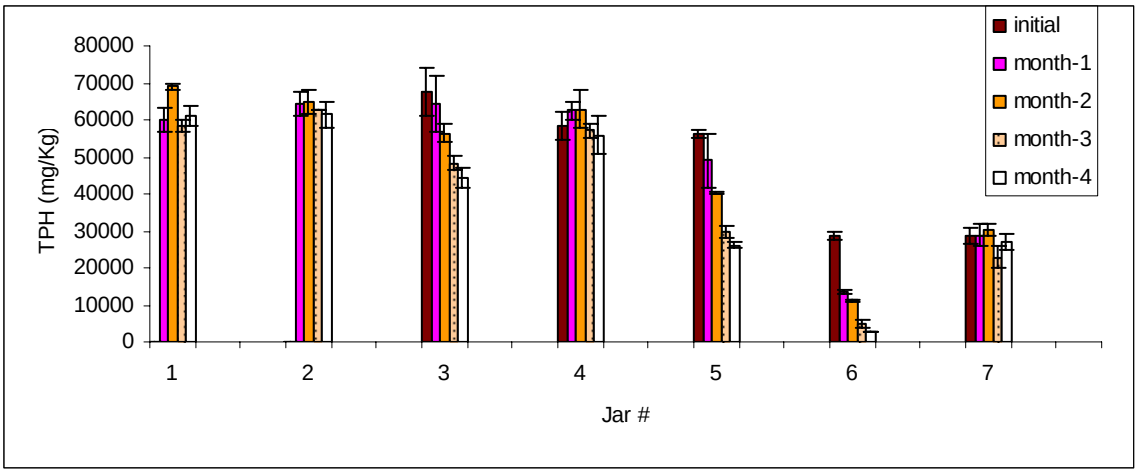
RESULTS

Hydrocarbon Biodegradation. Significant hydrocarbon biodegradation was observed with proper amendments during the microcosm experiments in sealed jars (Figure 1). The TPH concentration in the killed control (Jar 7) remained almost constant (less than 5% change) for the entire 4-month experiment, indicating no TPH loss due to evaporation or adsorption (Table 2 and Figure 1). The drill cuttings without amendments also exhibited no change in TPH. Drill cuttings with added urea (Jar 2) had about 5 % TPH removal; however the same mixture with 10 % rice hulls (Jar 3) had 34 % TPH removal. The mixture of 9:1, drill cutting:native soil and 1 % urea (Jar 4) removed only 4 % of TPH concentration. The microcosm with 9:1 drill cutting:native soil with 10 % rice hulls (Jar 5) removed a much higher TPH concentration (about 54 %). The difference of TPH removal in Jar 4 and 5 indicates the importance of rice hulls as an aid in aeration. The highest TPH removal (about 91 %) was observed in 1:1 drill cutting: native soil mixture and 10 % rice hulls (Jar 6). The high TPH removal in Jar 6 (compared with Jar 5) suggests the 1:1 mixture with soil created a much better biodegradation condition than did the 9:1 soil mixture.

Hydrocarbon Volatilization. The killed control in the volatilization experiment exhibited only a small decrease in TPH in the first month of incubation (4%). The total TPH removal after 2 months increased to 46% in the killed control open jar (see Table 3 and Figure 2). In comparison, the biologically active soil in the open jar had 63 % TPH loss after two months. The volatilization observed in this experiment suggests that additional TPH removal could be expected in the actual land-treatment operation in addition to expected TPH removal based on biodegradation described above.

CONCLUSIONS

The optimum condition for biotreatment of the synthetic drill cutting waste was achieved using the 1:1 ratio of drill cutting to native soil with 10% rice hulls, 1 % urea, and 20% moisture. TPH removal for this optimum condition was 91% after 4 months. Little or no biodegradation was observed for the non-amended drill cutting. The volatilization experiment showed an additional TPH removal could be observed in the field, and some VOC (volatile organic compound) release could be expected due to volatilization.



Jar#	Description
1	Unamended drill cutting
2	Drill cutting+Urea
3	Drill cutting+Rice Hulls+Urea
4	1:9, Drill cutting : Soil+Urea
5	1:9, Drill cutting : Soil+Rice Hulls+Urea
6	1:1 Drill cutting : Soil+Rice Hulls+Urea
7	Control (1% sodium azide)

FIGURE 1. TPH concentrations in sealed microcosms.
(Treatment descriptions at left.)

TABLE 2. Soil TPH concentrations (mg/kg) in 4-month biotreatment study.

		Initial	Month 1	Month 2	Month 3	Month 4	
Jar #	**Description**	**TPH (Ave)**	**TPH (Ave)**	**TPH (Ave)**	**TPH (Ave)**	**TPH (Ave)**	**Total %TPH Change**
1	Unamended drill cutting	NA*	59966	69047	58484	61199	-
2	Drill cutting and Urea	NA*	64476	64807	62714	61364	5
3	Drill cutting, rice halls and urea	67482	64259	56478	48177	44337	34
4	9:1 Drill cutting:soil, and urea	58385	62483	62790	57185	55831	4
5	9:1 Drill cutting:soil, rice hulls, and urea	56196	49072	40253	29805	26067	54
6	1:1 Drill cutting:soil, rice hulls, and urea	28636	13671	11190	4973	2486	91
7	Killed Control (1:1 Drill cutting:soil, rice hulls, and urea)	28513	28901	30401	22941	26949	5

*No initial data were available for the non-amended control and Jar 2 because of an analytical problem.

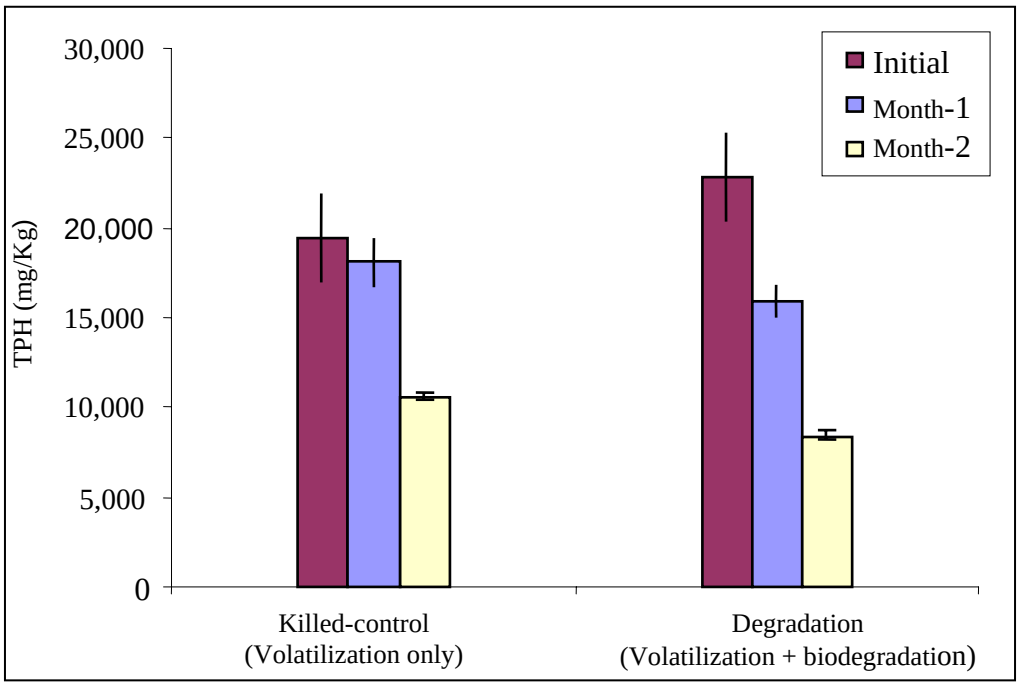


FIGURE 2. Volatilization results over 2 months with TPH concentrations in the open microcosms.

TABLE 3. Volatilization results in open microcosms. Both jars contained 1:1, drill cutting:native soil, 10 % rice hulls and urea.

Jar	Sampling	Ave. TPH	Total % Change
Killed-control	Control Initial	19,472	46
	Control mo.1	18,619	
	Control mo.2	10,570	
Biologically active	Degradation Initial	22,883	63
	Degradation mo. 1	15,920	
	Degradation mo. 2	8,375	

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