Proceedings of the Annual International Conference on Soils, Sediments, Water and Energy

Volume 12 | Article 23

January 2010

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Ramona Boodoosingh
Tufts University

Christopher Swan
Tufts University

Anne Marie Desmarais
Tufts University

Denise M. Beckles
Tufts University

Chapter 22

THE EFFECT OF BULKING AGENT AND INITIAL CONTAMINANT CONCENTRATION ON THE BIODEGRADATION OF TOTAL PETROLEUM HYDROCARBONS

Ramona Boodoosingh, Christopher Swan, Anne Marie Desmarais, Denise M. Beckles
Department of Civil and Environmental Engineering, Tufts University, Medford, MA 02155; Department of Chemistry, The University of the West Indies, St. Augustine, Trinidad, W.I.

Abstract: Bioremediation is one of the most cost-effective and environmentally friendly methods to remediate many different types of waste materials widely used by many private and public entities. Although the parameters that affect the rate of bioremediation differ for each project, some parameters can be more easily controlled in the field than others. For example, effective microbial action is crucial to the success of bioremediation. However, microbes can be detrimentally affected by an initial contaminant concentration that is too high. In addition, the type of bulking agent or aggregate used affects the ability of the mixture to retain moisture, the amount of drainage, aeration and ultimately the length of time for biodegradation. A two-month field study was conducted in Trinidad and Tobago on crude oil contaminated waste. This paper will look at the effect of two parameters, initial concentration and type of bulking agent, on the rate of biodegradation of Total Petroleum Hydrocarbons (TPH) in the oily waste being treated in this tropical environment. A nutrient-supplying bioremediation agent was used to enhance the bioremediation process. The results of this study can assist in the design of effective bioremediation projects in tropical environments.

Key words: bioremediation; total petroleum hydrocarbons; initial contaminant concentration; aggregate type; bioaugmentation.

1. INTRODUCTION

For many companies that produce toxic, and/or hazardous waste by-products from operations and production, remediation technologies play a vital role in enabling compliance with environmental laws and guidelines. Bioremediation technologies use naturally-occurring microbes to transform waste into (normally) less toxic materials (Cerniglia and Heitkamp, 1989, Sutherland, et al., 1995). Bioremediation has been used extensively for many years as a successful method of treatment for hydrocarbon-contaminated waste (Anderson, 1995).

The oil and gas extraction industry such as that found in Trinidad and Tobago, produces large amounts of hydrocarbon-contaminated waste. With the advent of the Environmental Management Act in 1995, the local oil and gas sector has become more active in investigating and utilizing biological treatment schemes, the most popular of which involve some sort of landfarming (Glasgow, et al., 2003).

As practiced in Trinidad and Tobago, landfarming involves aeration and mixing of contaminated soil by tilling, adding nutrients (and in some cases microorganisms), and controlling moisture content by periodic addition of water. Companies generally excavate the contaminated soils and treat it on biopads with leaching barriers (compacted clay, cement or plastic) constructed to control contaminant infiltration into the ground. The nature of the waste material determines whether any additional treatment or augmentation is used in the landfarming process.

In this study, the waste material was the residual material remaining after de-oiling of tank bottom and settling pond sludge at British Petroleum Trinidad and Tobago. This material consisted of a mixture of oily wax, bottom sediments and possibly saline water. The heavier components of oil tend to flocculate out of solution and settle at the bottom of storage vessels. These components can include asphaltenes, resins, paraffin/wax, diamonoids, and formation solids. However, the settled material has been shown to consist primarily of paraffin/wax, asphaltenes and inorganic mineral material. Also, the settled sediment may contain some oil trapped within the solids (Anonymous, 2003).

This waste material is very dense, and presents a clay-like exterior. In the landfarming process in this study, bulking agents are used to open up the material's structure, allowing air and water to enter. Without this, biodegradation processes would be very limited, as the physical factors most critical for bioremediation are the bioavailability of contaminants to microorganisms, presence of water, and a supply of suitable electron acceptors (oxygen in this case) (Eweis, et al., 1998). Currently, fill sand is used as the bulking agent. In addition, the bioremediation agent Oil Gator (Gator International, Penticton, British Columbia) is added to assist the bioremediation process. Oil Gator is made from the fibers of the cotton seed plant; Oil Gator had been modified to provide necessary nutrients for the growth of the microbes included in the bioremediation agent and also to prevent the easy runoff of waste materials it is being used to treat (Oil Gator International, 2005). It is not often clear whether these commercial bioremediation products developed in temperate countries have any positive effect on treatment systems in the tropics.

In this study, the system currently in place for the treatment of residual material was evaluated. In addition, the effect of changing the type of bulking agent and the ratio of bulking agent to residual material was determined.

2. MATERIALS AND METHODS

2.1 Site Description

The pilot field study was located at Galeota Point, in the extreme south-east of the island of Trinidad. Historically, this area has been the site of significant oil and gas exploration and production. The study began on October 27, 2002, during the island's wet season, with daily temperatures ranging from 27.4 to 32.4 ºC and daily rainfall ranging from 0 to 44 mm. The small remediation units were set up to simulate a landfarming process, and were exposed to the natural environment for the entire duration of the study.

2.2 Experimental Design

Small remediation units were designed to simulate landfarming processes, while allowing easy sampling of soil and leachate. Plastic buckets (10 L) were equipped with overflow holes 15 cm from the bottom, and filled with approximately 15 cm of gravel to facilitate easy drainage. A sampling port at the bottom of the container allowed collection of any leachate. To further parallel the treatment of the site landfarming units, the study units were treated with the same commercial bioremediation agent Oil Gator (Gator International, Penticton, British Columbia). Oil Gator is produced from cotton fibers treated with nutrients (nitrogen, sulphur and phosphorus). It works by encapsulating liquid oil and by stimulating the biodegradation of indigenous bacteria (Oil Gator International, 2005).

Aggregate test units each received a mixture of Oil Gator (350 g), oily sand and one of three bulking agents, gravel, sharp sand or sawdust (1:2 v:v). For each type of bulking agent, there were three units and one control, which consisted of oily sand only. Initial concentration test units each received a mixture of Oil Gator (350 g), oily sand and fill sand at 33%, 50%, 66% and 100% oily sand (by volume, in triplicate). The units were then placed out in the same area as the ongoing landfarming process. Each unit was thoroughly mixed twice a week to allow good aeration. After loading, each unit was sampled at day 0, 28 and 62, and analyzed for total petroleum hydrocarbons and oil and grease – cite the Methodology used for the analyses, particularly for TPH. Was it a colorimetric or spectrophotometric method?

The aggregates chosen in this study were the most inexpensive and readily available in the area. Cost constraints prevented the determination of porosity, density and particle size in the aggregates. However, in Figure 1, it is possible to obtain an idea of the comparative sizes of the materials used in the study.

Figure 1. Appearance and relative size of the different bulking agents used in this study. From left to right: fill sand, gravel, sharp sand and sawdust. The length of each picture corresponds to a length of 7.7 cm.

2.3 Analytical Methods

Soil samples were taken from each bucket at time 0, 28 and 62 days. Leachate samples were taken at time 28 days. At 62 days, there was no leachate in the collection containers. All samples were analysed for total petroleum hydrocarbons (TPH) using Method XXXX and oil and grease (O&G). For this study, it was not important to know what compounds were present, so a total TPH methodology was used (NOTE: TPH methodologies focus on compounds in specific ranges, so it is important to note the method used. The participants at this conference will be well aware of TPH methods and of more sophisticated methods, so it is important to specify what methods were used).

All samples were analyzed by an external laboratory (Analytical Services Unit, University of the West Indies, St. Augustine, Trinidad) using US EPA Method 9071B (US EPA, 1998) okay – include this info above for solid samples and US EPA Method 1664 (US EPA, 1999) for leachate samples. These methods detect petroleum hydrocarbon compounds in the C12 – C 22 range, and may detect compounds with more than 22 carbons if they dissolve in the hexane extractant. In summary, for soil samples, this involved the removal of any foreign objects such as sticks, leaves and rocks and mixing the sample (10 g) thoroughly with sodium sulphate in an extraction thimble. The dried soil sample was then extracted in a Soxhlet apparatus with dichloromethane as the solvent. The solvent was removed, and the oily residue weighed to give the total mass of oil and grease. To measure the TPH of the sample, the oil and grease component was redissolved in dichloromethane followed by the addition of silica gel. After the silica gel was removed, the solvent was removed and the oily residue weighed to give the total mass of total petroleum hydrocarbons. For the soil samples, the values for O&G and TPH were given in terms of percentage by mass.

For leachate samples, the samples were extracted with n-hexane using liquid-liquid extraction. The solvent was dried with sodium sulphate and filtered. The solvent was removed and the oily residue weighed to give the total mass of oil and grease. The TPH measurement was similar to that described for soil samples. For leachate samples, the values for O&G and TPH were given in terms of parts per million.

3. RESULTS AND DISCUSSION

This short field study indicated that the company's current oily sand bioremediation system may not be operating optimally. Oil and grease (O&G) as well as total petroleum hydrocarbon (TPH) were used as indicators of contaminant removal in this study for two reasons: cost effectiveness and ease of analysis. Figure 2 illustrates the effect of varying the bulking agent on contaminant removal

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efficiency. Using O&G, both gravel and sawdust appeared to produce better contaminant removal than fill sand (p = 0.05), the current bulking agent.

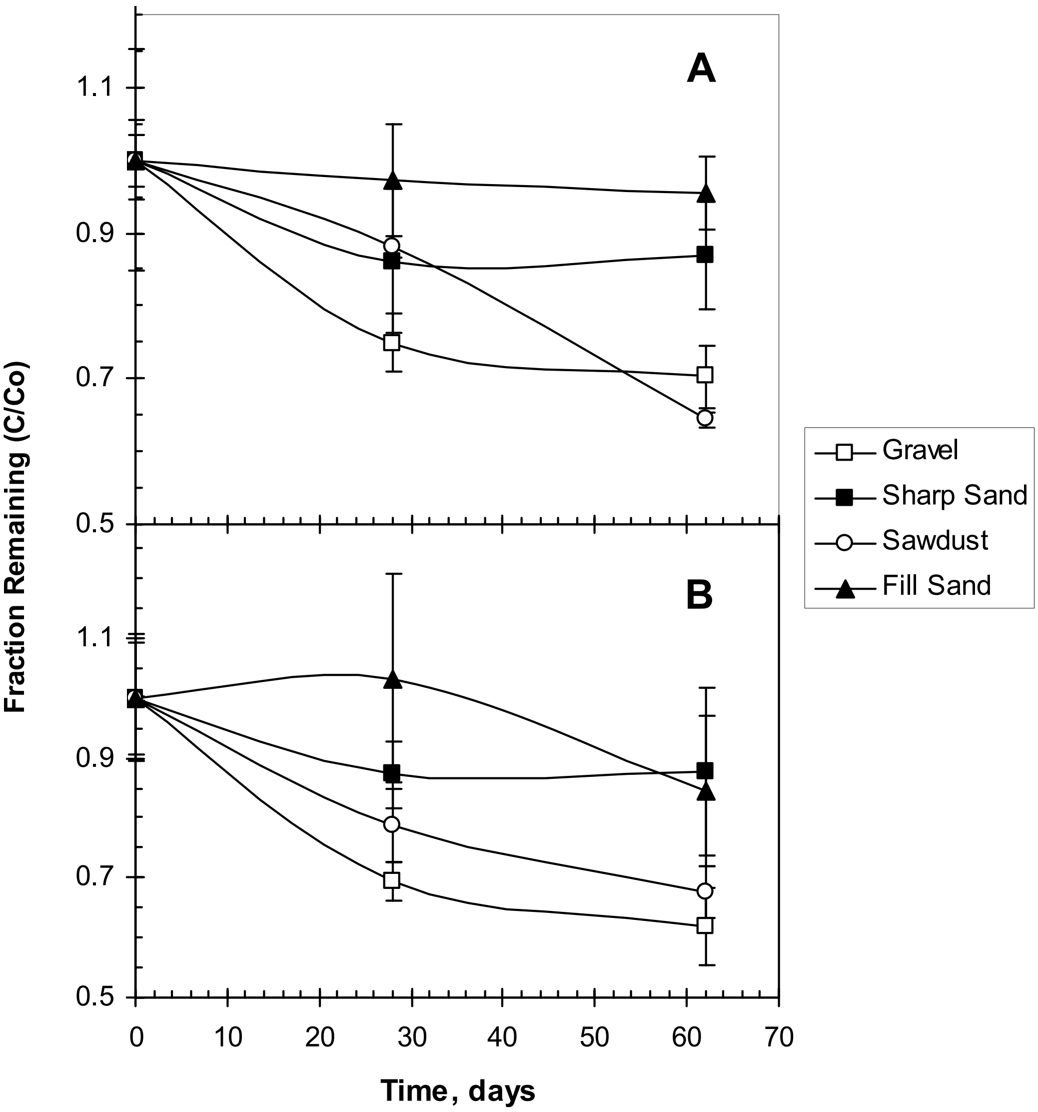

Figure 2. The effect of different bulking agents on the bioremediation of oily sand. **A**: oil and grease; **B**: total petroleum hydrocarbons. The bulking agent currently used in the remediation project (fill sand) is used as the control. Error bars represent one standard deviation, n = 3.

This pattern holds for the TPH analysis as well (p = 0.10), though there is more uncertainty in the TPH results. Of the two bulking agents that resulted in increased contaminant removal, it is interesting to note the consistent removal found in the sawdust units. The removal of contaminants in the gravel units appears to decline with time, resulting in a leveling out of the graphs in Figure 2. In contrast, the sawdust units appear to be exhibiting consistent removal, with what looks like the likelihood for additional removal after Day 62. This observation suggests that in fact the addition of an organic bulking agent may assist in the bioremediation process. There are a number of other studies that indicate that the presence of alternative carbon sources can assist in the removal of petroleum compounds (Felsot and Dzantor, 1997). In most of these studies, the increase in removal is attributed to the ability of the alternate carbon source to sustain higher biomass than the oil material alone. As a result of the greater number of organisms present, there is greater biodegradation (Rosenbrock, et al., 1997, Sarkar, et al., 2005). Other studies have found a variety of processes that can improve biodegradation performance, ranging from cometabolism (Stringfellow and Aitken, 1995, Walter, et al., 1991) to augmentation (Bouchez, et al., 1995, Juhasz, et al., 1996). In addition, the ability of organic bulking agents to absorb oil has been reported as an advantage to bioremediation, and is one of the characteristics of the Oil Gator material, as noted in their promotional material (Oil Gator International, 2005). The results of this study are inconclusive in this area, as the leachate results from Day 28 indicate highly variable levels of TPH in the leachate from the sawdust units. Therefore, it is not possible to determine whether or not the sawdust aided leachate reduction. However, the results of Figure 2 do suggest that an organic bulking agent such as sawdust or bagasse, both readily available locally, would be a better prospect than a mineral bulking agent like sand or gravel.

The effect of changing the ratio of oily sand to bulking agent on contaminant removal is shown in Figure 3. Using O&G, the 33% and 50% oily sand reactors produced better contaminant removal than 66% oily sand ($p = 0.05$), the system currently in place. The pattern is slightly different for the TPH analysis, with only the 50% oily sand reactors producing better contaminant removal ($p = 0.10$). This result would appear to suggest that a smaller fraction of oily material would result in improved performance. The poor performance of bioremediation in treating higher levels of contamination in soils can be traced to a number of factors. Toxicity effects can occur, resulting in the death of degrading microorganisms and reduced bioremediation performance. Normal alkanes in the $C_5 - C_{10}$ range are inhibitory to many hydrocarbon degraders at high concentrations, because as solvents they disrupt lipid membranes, but compounds in this range were not anticipated in the oily residual material used in this investigation.(Eweis, et al., 1998).

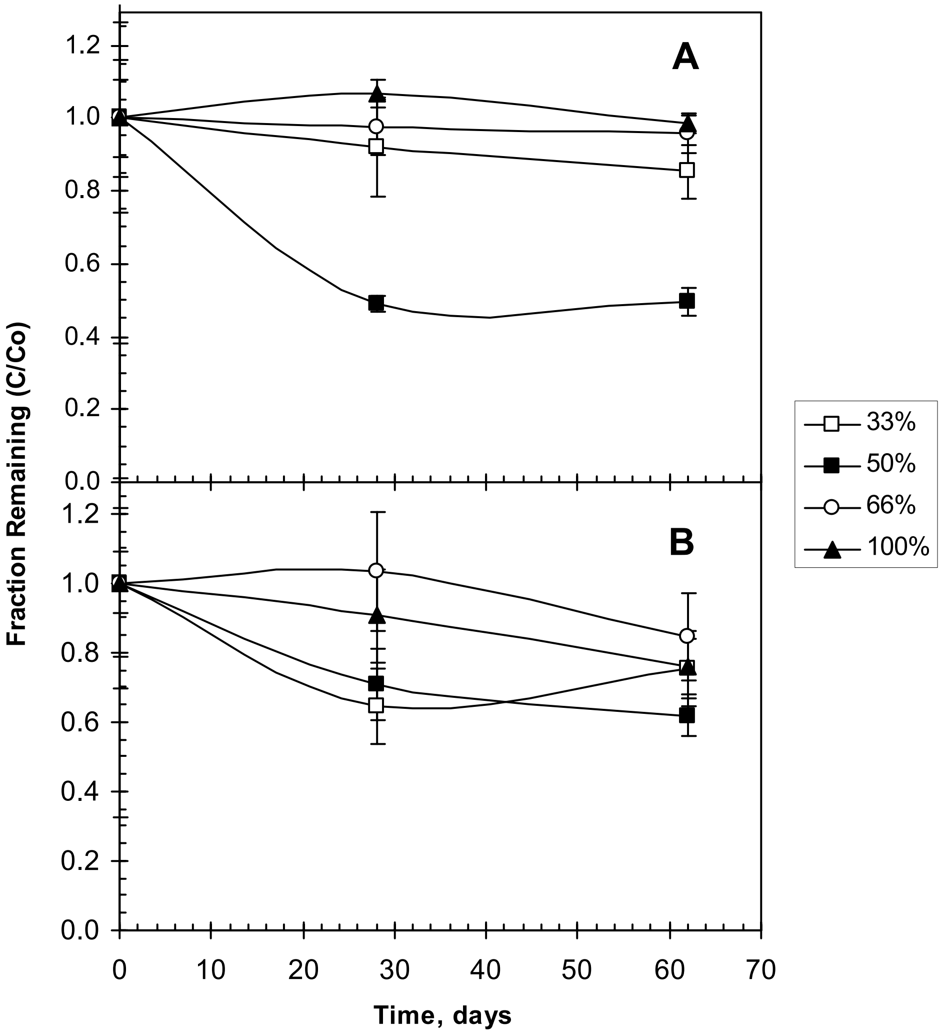

Figure 3. The effect of different oily sand:bulking agent ratios on the bioremediation of oily sand. **A**: oil and grease; **B**: total petroleum hydrocarbons. The bulking agent currently used in the bioremediation process (fill sand) was used in all cases. 100% oily sand was used as the control. Error bars represent one standard deviation, n = 3.

While some comment can be made about the effect of changing the concentration and composition of the bioremediation matrix, there is some uncertainty about the cause of these differences. There are two avenues for loss of petroleum compounds in the field units – biological removal and physicochemical removal. Ideally, all removal should be biological – with the contaminant material being degraded by microorganisms to less harmful compounds. In addition, removal by abiotic chemical reactions like photooxidation, volatilisation and leaching are also possible (Park, et al., 1990, Payne and Phillips, 1985, Wild and Jones, 1993). The results of this study are inconclusive concerning the actual method of contaminant removal. Leachate samples were only available on Day 28, as there was no leachate to be collected at the second sampling event on Day 62. In addition, the leachate results were quite variable, as can be seen in Table 1. Not only were concentrations variable, not all of the reactors units contained leachate. However, some information may still be gleaned from this data.

Table 1. Total petroleum hydrcarbon levels in leachate collected on Day 28 from the different types of field unit. All TPH values in ppm.

Bulking Agents	Gravel	Sharp sand	Sawdust	Fill sand
Unit 1	27.9	24.2	ND	7.4
Unit 2	11.5	ND*	5.36	16.7
Unit 3	31.3	47.4	46.7	1.96
Oily Sand:Bulking Agent Ratio	33%	50%	60%	100%
Unit 1	ND	43.9	7.4	ND
Unit 2	ND	18.7	16.7	1.35
Unit 3	36.1	36.1	1.96	ND

ND: No leachate was present on Day 28.

An examination of the leachate results presented in Table 1 indicates that the leachate from all of the test reactors on Day 28 had a higher concentration of TPH than the fill sand control reactor. It is possible, then, that at least some of the additional removal observed in both the gravel and sawdust units was due to removal in leachate, and not by bacterial degradation. This is also seen in the results comparing the different ratios of oily sand to bulking agent. Table 1 shows that on Day 28, the level of TPH in the leachate decreases as the oily sand ratio increases. The oily sand material was extremely dense, clay-like in texture, with limited porosity. The addition of the sand is necessary to allow air and moisture into the contaminated material to assist biodegradation processes (Dibble and Bartha, 1979, Eweis, et al., 1998). However, this increase in porosity would also increase the possibility of contaminant loss through leaching. It is interesting to note that leachate TPH levels were lowest in the 100% oily sand reactors.

This study determined that the system currently in place for the treatment of residual material could be improved. Bioremediation could be improved by changing the bulking agent to an organic material, such as sawdust or bagasse, instead of mineral material (fill sand) as is used now. In addition, a lower residual material to bulking agent ratio may result in better contaminant removal. There was some uncertainty surrounding the cause of contaminant removal in the field units. As such, any changes in the company's bioremediation setup would have to be accompanied by more stringent mechanisms to contain runoff and leachate, allowing for the collection and treatment of any contaminated liquids produced in the bioremediation process.

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