Removing mineral oil residues from beaches with vegetable oils

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Abstract

Experiments conducted in artificial sand columns with Brent Crude Oil have demonstrated the loss of short-chain volatile *n*-alkanes from the surface and the chromatographic separation of the remaining compounds down core. The weathering index ranged from ~4 in the crude oil to ~0.3 after 14 days. Biodiesel derived from rapeseed oil was able to dissolve the remaining heavy fractions and these were carried into the sediments. Periodic washing with clean seawater was also able to lift more of the crude oil from the sediment than untreated sands. The effectiveness of the biodiesel in increasing the mobility of the residual crude oil fractions was dependent upon the time of addition after a spill; the shorter the delay, the more effective the system. Previous experiments have demonstrated the rapidity in which crude oil residuals can be removed if effectively agitated in relatively small volumes of biodiesel. These results indicate that if biodiesel if left on sediments contaminated with crude oil, there is a continuing effect leading to the removal of surface oil to either the water column through tidal washing or deeper into the sediments. Due to the rapid degradability of biodiesel, leaving biodiesel in the sediments should improve beach remediation.

Introduction

The economic damage from oil spillages is usually temporary and is primarily caused by the physical properties of the oil creating a nuisance,

324   Oil & Hydrocarbon Spills, Modelling, Analysis & Control

although tainting of fish flesh can lead to longer term effects. The economics of several seaside resorts around Europe rely on having clean, uncontaminated sand available for holiday makers and contamination with oil products reduces their attraction and may jeopardise livelihoods for a season. In contrast, the biological effects of oil on marine life can be extremely damaging; a severely impacted rocky shore community may take in excess of 10 years to recover (Southward,[1]).

In contrast to the relatively rapid weathering processes that occur on the water's surface, crude oil incorporated into sediments usually exhibits a slow degradation rate and substantial quantities of oil may persist for many years (Teal et al,[2]; Hayes et al.,[3]; Burns et al.,[4]). These residues are not inert asphalts as they remain similar to crude oils modified by evaporation of the lower boiling point components and by partial microbial degradation (Blumer et al.,[5]).

The technology available for use in the event of an oil spill is well developed although particular mechanisms have different windows-of-opportunity for effective use (Champ et al.,[6]). In many cases, the objective is to keep the oil from reaching the shore. Once on shore, the diversity of methods to assist in clean-up is less and they often use either toxic chemicals or are labour intensive. Shoreline and particularly subsurface contamination is extremely difficult to remove by current beach remediation techniques as a result of both a reduction in the surface area available for the active ingredient to act upon, and in a reduction of mixing by seawater. The application of dispersants on the shore is significantly less effective than when applied to floating oil. It is important that the bulk of the oil is removed mechanically first, since the effectiveness of the dispersant relies on its penetration throughout the oil layer. Once in the sediments, the removal of oil by dispersants is extremely difficult, since the available surface area of the oil for interaction with the dispersant is much reduced. In situ burning is relatively ineffective since it is difficult to ignite and when ignited, combustion is usually incomplete due to the cooling effect of the underlying sediment. Absorbents are unlikely to do more than remove oil from the upper surface thereby being ineffective for subsurface oil. In addition, there are practical problems in the methods of distribution and then of collecting it when it has absorbed the oil. Mechanical mixing of the oil into deep subsurface layers has been carried out, however, this will only compound the problem by increasing the persistence of the oil, which may then be available for re-entry to surface layers and the water column during periods of winter storms.

Recent studies have suggested the use of vegetable oil methyl ester (biodiesel) as a biological solvent for spilt crude oil. In this context its function would be to act two fold. Firstly, the spilled mineral oils would dissolve within the biodiesel, facilitating the processes of dispersion, thereby preventing significant incorporation within the sediments; and secondly by increasing the surface area of the mineral oil, which would facilitate in the processes of microbial degradation. Biodiesel is produced from vegetable oils *via* a simple esterification process and is composed primarily of the 16:0, 18:0, 18:1ω9, 18:2ω6, and 18:3ω3 fatty acid methyl esters (FAMEs). Large quantities can be manufactured at a low cost.

In contrast to mineral oils, fatty acid methyl esters undergo significant modification upon being deposited in sediments and disappear rapidly from sediments (98% in 4 weeks). They produce few or no persistent intermediate compounds, proceed rapidly to CO_2 and have been demonstrated to be significantly less toxic than mineral oils towards a wide-range of algae, macrophytes and animals (Birchall *et al.*,[7]).

Assessments of the effectiveness of biodiesel to remove crude oil from contaminated beaches has been reported elsewhere (Miller & Mudge,[8]), and this paper reports results of laboratory experiments in which the penetration and leachability of biodiesel in oil contaminated sand columns was studied.

Materials & Methods

Opaque plastic containers of 15 litre capacity with clear perspex lids were filled to a depth of 150 mm with clean beach sand (grain size, 94.1% greater than phi size 3; total pore volume: 2124 ± 18.4 cm^3; water saturation, 88.63 ± 0.83 % (mean $\pm$ SEM, n=7)). A length of plastic tubing fitted with a flow control device was inserted through a hole in the base of the containers to allow liquid to be drained through the system and analysed. The containers were placed outside.

Seven such sand columns were prepared, four experimental and three control. To each of the experimental containers, 200 ml of untopped Brent crude was applied to the surface of the sediments floated upon 2 litres of fresh seawater. 100 ml of biodiesel was then applied to four boxes after 0, 3, 7, and 14 days respectively.

A surface sediment sample of approximately 60 grams was obtained 1, 3, 7 and 14 days following the addition of the biodiesel. After the taking of each sediment sample, approximately 1 litre of fresh seawater was flushed through the sediment and collected. Three controls consisting just crude oil,

326   Oil & Hydrocarbon Spills, Modelling, Analysis & Control

just biodiesel and neither crude oil or biodiesel, were sampled as above. The liquid and sediment samples were analysed for crude oil and biodiesel components according to standard Gas Chromatography - Mass Spectrometry procedures.

Water Analysis. The lipids were separated from the seawater using a double liquid/ liquid extraction in 40 ml DCM:hexane (1:1). The samples were reduced until they were close to dryness in a rotary evaporator (Büchi Rotavapor RE120) at 40°C, before being taken to dryness under a stream of pure nitrogen. The lipid weight was recorded and a sub-sample was taken for analysis.

Sediment Analysis. The sediment samples were freeze dried (Edwards Super Modulyo) at -50°C for a minimum of 72 hours. 30 g was Soxhlet extracted for 41 h in DCM:hexane (1:1). Samples were taken to dryness as above.

Crude Oil Analysis. The aliphatic hydrocarbons were quantified after the addition of squalane (2,6,10,15,19,23- hexamethyltetracosane) on a Fisons Instruments MD800 GC-MS system. A (SGE) BPX-5 50m non-polar column (0.32mm I.D., 0.1μm film thickness) was used for the separation and quantification of all hydrocarbon compounds. The chromatographic conditions were as follows: helium carrier gas (1.0 ml/min); 1μl cool on-column; temperature program; isothermal at 50°C for 2 min, 15°C min^{-1} to 300°C, and 5°C min^{-1} to 350°C.

Fatty Acid Methyl Ester (FAME) Analysis. The fatty acid methyl esters were quantified after the addition of tricosanoic acid methyl ester ($C_{24}H_{48}O_2$) on a Fisons Instruments MD800 GC-MS system. The much more polar (SGE) BPX-70, 50m column (0.32mm I.D., 0.1μm film thickness) was used for the separation and quantification of all FAME compounds. The chromatographic conditions for the BPX-70 column (FAME analysis) were as before except for the temperature program; isothermal at 50°C, 40°C min^{-1} to 160°C, 0.5°C min^{-1} to 170°C, and 10°C min^{-1} to 250°C.

Results & Discussion

The crude oil control time series experiment clearly shows the short-term processes that are occurring in the artificially oil contaminated sand columns with respect to time, in the absence of the effects of the biodiesel. The change in abundance with respect to time of *n*-alkanes in oil samples washed from the sediment and in oil samples extracted from surface

sediment samples, suggest that the principal mode of weathering is *via* evaporation. An example plot (Figure 1) is characterised by the progressive decrease in the relative concentrations of the lower boiling point *n*-alkanes relative to the higher boiling point fractions and a progressive increase in the relative concentrations of the higher boiling point *n*-alkanes as a result of volume reduction. The ratios of *n*-alkanes relative to *n*-C17 are calculated; this compound was chosen because it was well resolved, had a high relative abundance and allowed both the decrease in the lower boiling point compounds and the resulting apparent increase in the higher boiling point compounds to be observed.
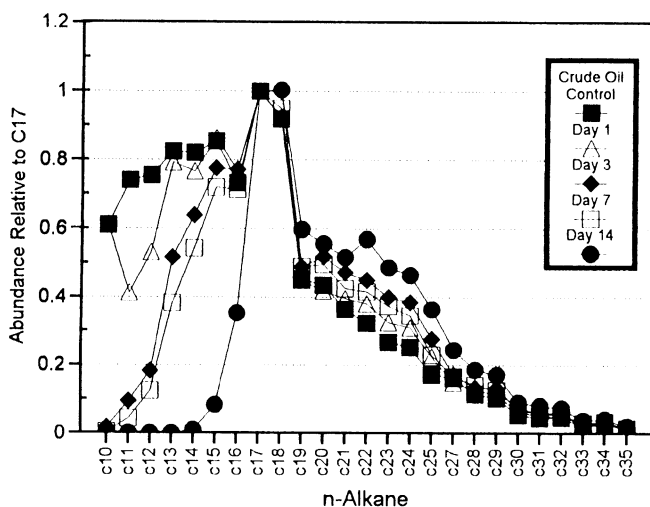

Figure 1. Loss of short-chain *n*-alkanes from crude oil spilled onto the surface of artificial sand columns.

The weathering index (Equation 1, adapted from Wang & Fingas,[9]) was calculated for each sample and can be used to describe the weathering behaviour of oil and to evaluate the degree of evaporation of individual samples.

$$\text{Weathering Index (WI)} = \frac{C_{10} + C_{12} + C_{14} + C_{16}}{C_{22} + C_{24} + C_{28} + C_{30}}, \tag{1}$$

Table 1 shows the weathering indices for the crude oil control samples and demonstrates the preferential loss of the lower boiling point compounds as time proceeds. Gross hydrocarbon concentration data have been shown not to be a particularly sensitive indicator of the weathering processes (Atlas *et al.*,[10]), since one could erroneously conclude, that a high concentration of oil indicates a low degree of degradation. A more likely explanation is that

328   Oil & Hydrocarbon Spills, Modelling, Analysis & Control

the weight data reflects the rate at which the oil permeates the sediment due to the combined function of the porosity of the sediment and the viscosity of the oil. In this context the gross hydrocarbon and biodiesel weights washed from the sediment are likely to indicate the rate at which the oils are removed from the sediments and not their rate of degradation.

Table 1. Weathering Indices for crude oil in artificial sand columns.

	Liquid/ Liquid Extracted Oil	Soxhlet Extracted Oil	Length of Sediment Contamination with Oil (days)			
	t=0	t=0	1	3	7	14
Oil Washed Through Sediment	3.99	-	3.03	1.55	1.42	0.28
Surface Sediment Sample	-	0.47	0.34	0.13	0.12	0.09

The control results suggest that only a relatively small fraction of the total crude oil (1.7%) and biodiesel (15.4%) added to the sediments was washed out within the 14 day sampling period, although considerably more biodiesel was lost compared to the crude oil. This would suggest that biodiesel has a considerably greater mobility within the sediment than the crude oil. It also suggests that the oils are being retained within the sediment, possibly by being adsorbed onto the sediment particle surfaces. In this way, the periodic addition of the seawater does not possess enough mechanical energy to remove significant quantities of the oils from the sediment particle surfaces. Oil stranded in the intertidal zone of high wave-energy environments has been shown to be rapidly dispersed by the hydraulic action of the breaking waves, resulting in a self-cleaning process that can occur in a period of weeks (Owens,[11]). By contrast oil that is stranded in low wave-energy environments (including the artificial environments created in these experiments) can persist in the order of tens of years (Vandermeulen & Gordon,[12]).

When biodiesel was added to the sediment at day 0, the crude oil can be considered to be unweathered and retained initially within the surface sediment layers. It is proposed that initially, the biodiesel rapidly passes

through the oil/sediment layer during which time the more soluble, low boiling point n-alkanes (C_{10} - C_{21}) dissolve within it and are transported to sub-surface sediment layers. It is within these upper sub-surface layers that the biodiesel containing the lower boiling point n-alkanes becomes adsorbed onto the sediment particle surfaces. As progressively more biodiesel mixes with the oil/sediment layer and as the length of time that the oil is in contact with the biodiesel increases, the larger, less soluble n-alkanes dissolve in greater quantities within the biodiesel. It is therefore proposed that the addition of the biodiesel greatly increases the mobility of all crude oil components, although particularly the more soluble, low molecular weight compounds.

The oil-in-biodiesel then rapidly permeates to progressively deeper sediment layers of the sand column. In addition, the preferential retention of the smaller molecular weight n-alkanes within the sediment, may be explained as a result of a greater affinity for the sediment particles. Any further transport of oil through the sediment, would result in the preferential retention of the smaller molecular weight n-alkane fractions within the biodiesel adsorbed onto the sediment particles. This would lead to a depth profile consisting of progressively lower concentrations of the low boiling point n-alkanes and higher concentrations of the higher boiling point compounds with increasing depth. This may help to explain the higher relative abundances of the higher boiling point compounds within the deeper sediment layers compared to the surface and the almost immediate removal of the lower molecular weight n-alkanes from surface sediment layers and from samples flushed through the sediment. However, the analysis of the n-alkanes distribution in samples extracted from sediments on day 14, also showed a virtual absence of n-alkanes between C_{10} and C_{21}. It is possible that during the 14 day period prior to sampling, the n-alkanes C_{10} to C_{21} had been subject to an enhanced rate of microbial degradation although this seems unlikely in these sands. It is also possible that the low molecular weight alkanes were being retained on the sediment grains in a relatively narrow layer immediately below the surface, between the surface and 5 cm sampling depths.

It would appear from analysis of the n-alkane distributions in the other experimental boxes that, as the delay between the addition of the biodiesel to the contaminated sediment increases, the effects are reduced (Table 2). When the biodiesel was added to the sediment 3 days after oil contamination, the relative abundances of C_{10} - C_{17} extracted from both the water flushes and surface sediment samples, were significantly lower than the corresponding abundances from the untreated box. However, the

330   Oil & Hydrocarbon Spills, Modelling, Analysis & Control

relative abundances of C_{13} - C_{17} were similar to those of the higher carbon number n-alkanes. This suggests that they were present at relatively high concentrations, and significantly higher than those from the addition at day 0, which showed that the n-alkanes C_{10} - C_{21} were virtually absent from all samples.

Table 2. Weathering index of the oil extracted from the sand column after the addition of biodiesel.

Sampling time	Untreated Crude Oil	Delay period until Biodiesel added (days)			
(days)		0	3	7	14
0	3.91	-	-	-	-
1	3.03	0.002	0.55	6.55	0.45
3	1.55	0.003	0.46	5.56	0.4
7	1.42	0.001	0.3	3	0.26
14	0.28	0^a	0.14	0.72	0.1

^{a}WI = 0, since C_{10}, C_{12}, C_{14} and C_{16} were absent.

Although the results still suggest that there is preferential retention of the lower carbon number n-alkanes within the sub-surface sediment layers, the magnitude of this effect is considerably lower as the time of the sediment contamination with the oil increases. Presumably this was the result of the increased viscosity and water content of the oil with respect to time, which may act to decrease the solubility of the crude within the biodiesel and also, to a certain degree, prevent the preferential removal of the lower boiling point fractions. In addition, the oil may have become adsorbed onto the sediment particle surfaces and as a result, exhibit a lower solubility within the biodiesel due to increased affinity towards the sediment particles.

In common with the untreated crude oil, the relative abundances of the low boiling point compounds decrease with respect to time and the relative abundances of the high boiling point compounds increase with respect to time. In addition, the surface sediment oil samples were considerably more weathered than those extracted from the sub-surface water and sediment samples. These effects were most probably due to;

1. an increase in evaporative losses, particularly in surface layers,
2. an increased diffusion of the lower boiling point compounds to deeper layers and

3. an increase in the proportion of the lower boiling point fractions relative to the higher boiling point fractions that were transported to deeper depths, dissolved within the biodiesel,

all with respect to time.

Conclusions

Results suggest that the biodiesel was responsible for a considerable increase in the total proportion of the crude oil that could be washed from the sediments and dispersed by the tides even in low energy environments. The almost complete absence of the n-alkanes C_{10} to C_{21} from the sediment samples after 14 days suggests that either these compounds have been rapidly degraded or that they have been dissolved within the biodiesel and tightly associated to sub-surface sediment particles. If these compounds were being retained within sub-surface sediments, they may persist in a low energy beach environment. However, the incorporation of these crude oil fractions into the biodiesel may result in their release in a high energy beach environment, due to an increase in sediment mixing and a greater potential for the biodiesel to be dispersed into the water column. More crude oil was observed floating following the addition of the biodiesel and suggests that once the crude oil has dissolved within the biodiesel, that there is a greater tendency for it to be dispersed within the water column. This would be particularly effective within a high wave energy environment, where it would reduce the oil loading within intertidal sediments.

Experiments are being conducted under a wide variety of environmental conditions and on different oil types at varying stages of weathering to assess the best application methods and long-term fates. This will involve field trials of the biodiesel subject to natural environmental processes. However, it is often not possible to simulate a real spill situation and the most useful information is likely to come from studies made on simulated crude oil spillages.

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332   Oil & Hydrocarbon Spills, Modelling, Analysis & Control

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