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Simulating the influence of physicochemical parameters on subsurface oil on beaches: Preliminary results

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ABSTRACT

Monitoring of sandy beaches after the Prestige oil spill revealed thick subsurface layers (up to 1 m thick) of grey-coloured sand. These horizons were sometimes found under more than 3 m of clean sand. Examination of the sand by electron microscopy confirmed that the colouring was due to oil-coated sand grains, and revealed a sequence of degradation of buried oil. Further analysis of the sand revealed high concentrations of hydrocarbon in the oil-coated sand and that the main biomarkers were indicative of biodegradation, even though the oil was buried.

A set of experiments was designed to analyze the evolution of oil from tar balls to coatings. The results revealed that biodegradation is a secondary process in the changes that take place in the buried oil, and that water flow slows down the appearance of grey sand and that low salinity may hinder the oil degradation process.

1. Introduction

In November 2002, the Prestige tanker spilled 64,000 tons of heavy fuel-oil, affecting 786 of the 1064 beaches along the North Atlantic coast of Spain. The rapid mass response following the accident helped to clean up the surface oil from most of the affected beaches. Subsequent monitoring and assessment of the beaches revealed thick subsurface horizons (of up to 1 m) of grey-coloured sand, at various depths (Fig. 1). Some of these grey-coloured horizons were overlaid by more than 3 m of clean sand. Examination of the sand by electron microscopy revealed that the colouring was due to oil-coated sand grains (Bernabeu et al., 2006). This type of coating was restricted to beaches where the seasonal cycle of erosion/accretion did not affect the deepest buried oiled horizons. In such cases, the buried oil remained embedded for longer periods, and the initially buried tar balls degraded to the final stage of grey oil-coated sand.

Detailed geochemical analysis of the sediment column revealed that the highest concentrations of hydrocarbon occurred in the deeply buried grey layers of sand (Bernabeu et al., 2009). The concentrations of sterane and triterpane biomarkers, commonly used for oil fingerprinting and assessment of weathering (Daling et al., 2002; Wang and Fingas, 2003), were interpreted as indicative of biodegradation, facilitated by the supply of oxygen, degrading microorganisms and nutrients from the water flowing through the sand column. The PAH-based indices trends also were consistent with those observed in previous studies (Jiménez et al., 2006; Díez et al., 2007), and indicate appreciable weathering, although the oil was deeply buried, and were indicative of relative degradation of oil in the deeply buried grey sand. These observations contrasted with previous findings of slow degradation of buried oil (Teal et al., 1978; Hayes et al., 1993; Burns et al., 1994) as a result of the absence of mechanical energy from waves, tides and currents (which minimizes oil abrasion and dispersion), as well as by the scarcity of oxygen and nutrients (limiting factors for oil biodegradation) and by the absence of light (which inhibits photo-oxidation of oil).

Here we report the results of a set of experiments designed to simulate and quantify the time scale of degradation of deeply buried oil, from tar balls into coatings, in which the different physicochemical factors representative of the major natural factors that may affect oil degradation were controlled.

2. Methods

The experimental design consisted of six columns representing sand microcosms. Each column consisted of PVC tubing (0.5 m length and 15.5 cm diameter) cut in half along its length and sealed with a transparent methacrylate plate. The columns were filled with 19–20 cm of sand, with oil buried at 10–12 cm depth from the sand surface. Seawater filtered to 1 μ was periodically introduced through the top part of the PVC tubing. A flow control device was inserted at the base of the containers, allowing seawater to be drained from the system (Fig. 2). The tar balls were placed against

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Fig. 1. Photograph showing grey sand on a Spanish beach after the Prestige oil spill.

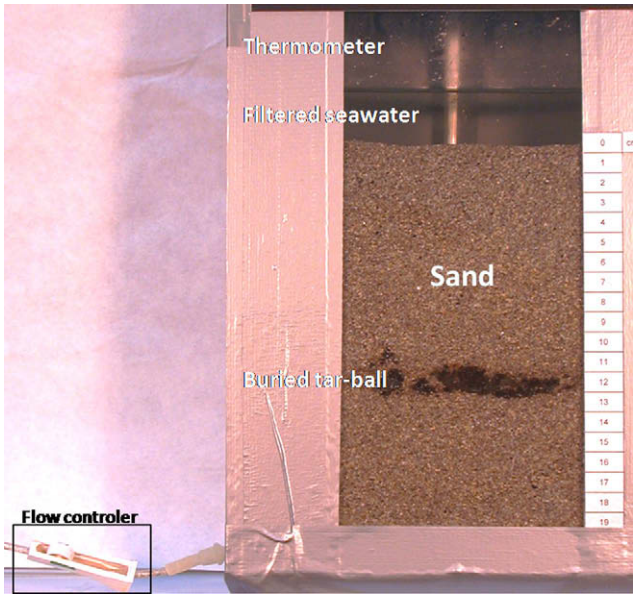

Fig. 2. Diagram of the microcosm design.

Table 1
Summary of the different experimental conditions in the microcosms.

Microcosm	Factors			
	Flow (m^3/s)	Organic matter content	Recycling seawater	Salinity
Reference microcosms				
SC1	–	Treated	No	Seawater
SC2	–	Natural	No	Seawater
SC3	1.23×10^{-10}	Treated	No	Seawater
SC4	5.7×10^{-10}	Natural	No	Seawater
SC5	9.9×10^{-10}	Natural	Yes	Seawater
SC6	6.2×10^{-10}	Natural	No	Seawater/ freshwater (1:1)

the transparent plate so that they could be easily observed. All columns were covered with a black cloth to prevent photooxidation.

The sand and tar balls were collected from the intertidal zone of Nemiña beach (Galicia, NW Spain), one of the beaches most affected by the POS. The sediment consisted of a mixture of bioclastic–silicilastic sediments, medium sized sand grains ($X = 0.394$ mm), moderately well sorted and slightly coarse skewed. According to Bear (1972), the hydraulic conductivity of sand varies between 1 and 10^{-2} cm/s, defining the permeable sediment. The average content of TOC was 0.51%.

Four different environmental conditions were evaluated in the microcosms (Table 1): (a) seawater flow: in columns SC1 and SC2, the seawater was maintained static, and the remaining columns were each subjected to a different constant flow of seawater; (b) organic matter content: in columns SC1 (static seawater) and SC3 (flowing seawater) the organic matter was eliminated by treatment of the sand with hydrogen peroxide, (H_2O_2), and the seawater disinfected by exposure to UV light; (c) recycled seawater: the seawater in SC5 was continuously recirculated throughout the sand column; (d) salinity: in column SC6 the salinity of the water was modified by adding freshwater at a ratio of 1:1 freshwater:seawater.

The experimental set up was monitored over a period of 130 days. The temperature was measured daily in the sand beside the tar balls. Photographic reporting and spectrophotometric colour determination (Konica Minolta CM-2600d) were carried out weekly. The colour measurement strategy consisted of three vertical sets of measurements: one on the tar ball and the others 5 cm

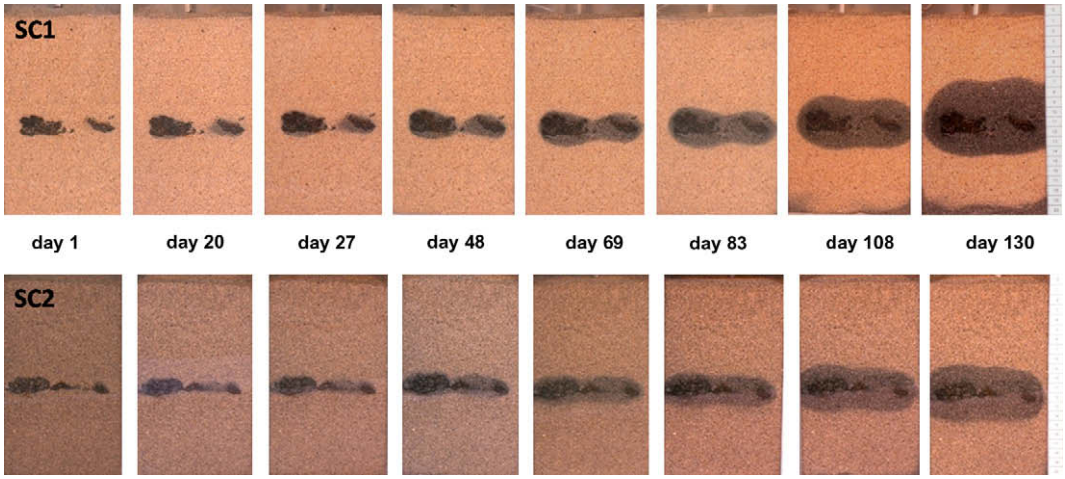

Fig. 3. Photograph of microcosms evolution during the experiment: column SC1: static, natural; SC2: static, disinfected.

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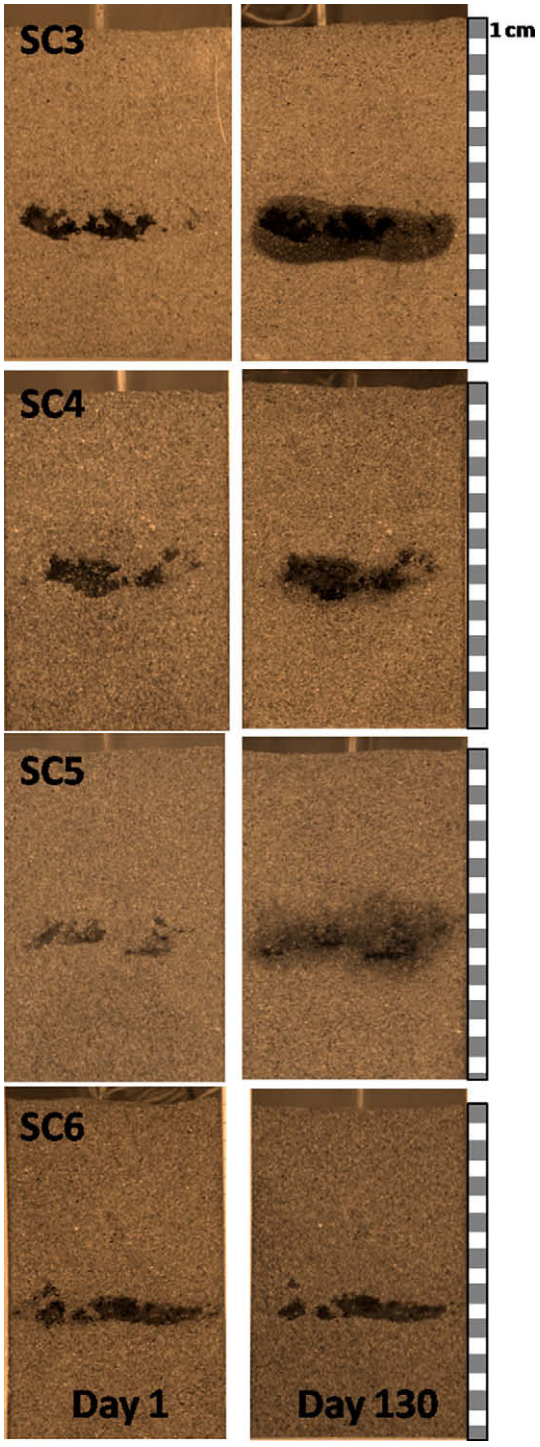

Fig. 4. Photographs of the columns on the first and last day of the experiment: SC3: lowest flow, disinfected; SC4: fast flow, natural; SC5: fastest flow, natural water recycled throughout the experiment; SC6: fast flow, natural, reduced salinity.

to the right and left of the tar ball. Vertical data were collected in 1-cm steps from top to bottom.

Samples of outflowing seawater (500 ml) were collected midway through the experiment and filtered to detect any oil present in the water. Residues were collected on filter paper (Whatman, pore size 0.45 μ) and subsequently photographed under a magnifying glass.

At the end of the experiment, columns SC3, SC5 and SC6 were opened up and systematically cut into 1 cm sections. Each section of columns SC3 and SC5 was photographed and the grey "halos" that formed around the tar balls was measured. Finally, the tar ball was removed and the remaining sand was placed in hydrogen peroxide. The resulting supernatant was collected and examined by means of a binocular magnifier for the presence of oil.

3. Results

The mean temperature of the sand beside the buried tar ball during the 130-day period of the experiment was approximately 14 °C. Two notable increases in temperature occurred, one of 18 °C (between day 87 and 94) and another of 21 °C (between day 118 and the end of the experiment).

In the reference columns (SC1 and SC2), the halos around the tar ball began to be faintly visible to the naked eye by day 20 (Fig. 3). By day 34, the halos were completely defined, and increased steadily in thickness throughout the experiment.

In the remaining columns (Fig. 4), characterized by a constant water flow, the halo was not visible until day 46 in column SC5, day 83 in column SC3 and day 126 in column SC4. No halos appeared in column SC6. A proportional relationship between the flow rate and the appearance of the halo was established. Thus the greater the flow rate, the later the halo appeared, except in column SC5; the flow rate was greatest in this column (9.9×10^{-10} m^3/s), and the halo appeared earlier than in the other columns.

Expansion of the halos differed in the static columns and the columns with flowing water (Fig. 5). In columns SC1 and SC2 (static), the expansion followed a similar pattern, with an estimated (by linear regression) mean increase of 6.45 cm per year. In column SC5 (fastest flow) the halo expanded at a similar speed, whilst in columns SC3 and SC4, the halos expanded faster, at rates of between 8.4 and 14.1 cm/year.

Analysis of the filtered water collected at the output of the microcosms revealed the presence of microparticles of oil (Fig. 6). The maximum size of these oil particles would be controlled by the effective porosity of the sand columns in the experiment.

The horizontal movement of the grey-coloured sand was similar to the vertical expansion described. It is however worth noting that in column SC3 (lowest flow), the halo was limited to two small areas 2.5 cm long by 0.5 cm wide, adjacent to the tar ball. Consistently with this, in column SC5 (fastest flow) there was a continuous halo of 0.3–0.5 cm surrounding the tar ball, supporting the general trend of increasing width of halo with greater flow velocity.

Finally, the filtered supernatant from the sand treated with hydrogen peroxide revealed the presence of tiny oil balls, stained sand and micas with oil-stained rim holes.

4. Discussion

This set of experiments enabled estimation of the effects of different physicochemical factors on the process of degradation of buried oil.

The end results from the two static microcosm columns SC1 (natural) and SC2 (disinfected) were identical, indicating that the degradation of buried fuel is not driven by the presence of microorganisms. Although biodegradation occurs in buried oil (Bernabeu et al., 2009), it is not the determining process in the breakdown of tar balls to oil particles.

The results of the other experiments demonstrate that oil degradation progresses steadily during burial, after activation of processes other than biodegradation and bioremediation. Assessment of the importance and nature of these processes in natural conditions has been somewhat constrained as the evolution of

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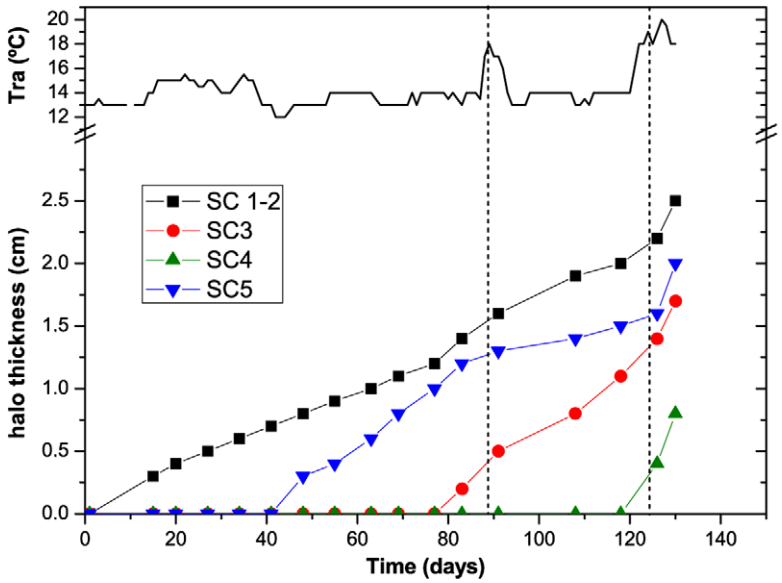

Fig. 5. Initial appearance and development of halos in the different columns throughout the experiment.

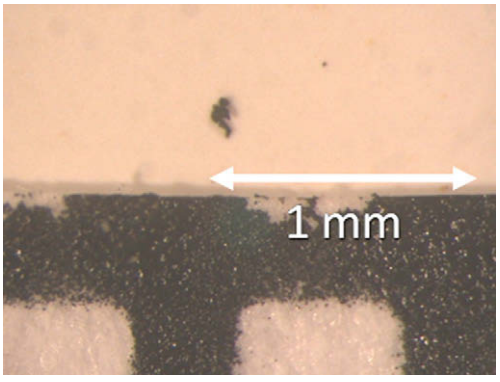

Fig. 6. Magnified view of an oil grain recovered from the outflow water of SC3.

deeply buried fuel has only been reported relatively recently (Bernabeu et al., 2006).

The results obtained in columns SC3 (slow flow) and SC4 (fast flow) established an inverse relation between water flow velocity and appearance of the halo: the faster the water flow the slower the development of the halo. However, this trend was disrupted by recycling of the water, as the halo developed fastest in microcosm SC5 (fastest flow). The oil particles segregated from the tar ball are quickly transported back into the sand column by the recirculating water, and thus increase in concentration in the water. The higher concentration of tiny oil particles (millimetre scale) in the water appears to be the main responsible for the initial appearance of the grey sand associated with buried oil. Finally, no halo developed in column SC6 (fast flow, low salinity), indicating that low salinity may hinder degradation of the buried oil.

The initial Prestige oil contained asphaltens and resins at concentrations of up to 28% (Albaigés and Bayona, 2003), well above the 3% established (Berridge et al., 1968; Bobra, 1990, 1991, 1992; Fingas et al., 1993) for stable emulsions. The direct contact between seawater and oil on the surface of the tar ball activates the release of oil particles mainly by emulsion, even under low energetic conditions (Daling and Brandvik, 1988; Brandvik and Daling, 1991). Furthermore, the confinement of oil in sand prevents changes in volume of the tar ball, leading to the onset of oil-in-water emulsification whereby the oil particles are released and incorporated into the water at the oil–water interface. Both the results of this laboratory experiment and our own field observations (Bernabeu et al., 2006, 2009) indicate that the first stages of oil-in-water emulsification are completed relatively quickly, within days or weeks. The presence of inorganic salts in the seawater hinders coalescence of the oil particles (Nesterova et al., 1983; Mao and Marsden, 1977; Zaki, 1997). A reduction in salinity affects emulsions formation to the point of preventing development of the halo. This is an important factor on beaches where there are large inputs of fresh water.

Insofar as the concentration of oil particles remains high close to the tar ball surface, the diffusion process favours movement of the oil particles from the tar ball surface (Atkins, 2002). The flow of seawater into the sand column results in some of the oil particles being swept out with the flux, whilst the others adhere to the sand grains as coatings. The latter gives rise to the development of thick grey-coloured oil-coated sand particles, generating a halo around the tar ball, which gradually expands outwards. In the present study, the mobility of oil particles through the sand column and the movement of oil by the seawater flow were possible because the oil particles were smaller than the intergranular porosity of the sand medium. The oil particle mobility pattern is similar to that of the fluorescent tracer dyes used in field experiments of groundwater movement (i.e. Carls et al., 2003). These interrelated processes would progress in time until the buried tar balls disappear.

5. Conclusions

The final stage of degradation of the buried oil (formation of oil-coated sand particles) was reproduced in a set of controlled laboratory experiments, with seawater, sand and tar balls collected from an oiled beach after the POS.

One of the main findings of the microcosm study was that degradation of the buried oil follows a series of processes other than previously described mechanisms such as photooxidation and bioremediation. The sequence of processes involves: an oil-in-water emulsification process that acts on the tar ball surface, diffusion of the oil particles, and finally, advection of oil particles by water flow, resulting in partial elimination of oil from the microcosm,

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and adsorption on the sediment grains as an oil retaining mechanism, giving rise to the oil coatings that are observed in the field. The equilibrium between advection and adsorption probably depends on the concentration of oil particles. These processes occur within a short time scale, in the order of weeks or months.

These findings have direct environmental implications. As previously proposed (Bernabeu et al., 2006), the evaluated time scale of degradation of buried oil indicates that on beaches with high seasonal sand mobility, formation of oil coatings will not occur. Natural morphodynamic processes would lead to exhumation of the buried oil before the degradative processes would be activated.

The oscillation of groundwater associated with tidal variations generates internal sand flows, which, in light of the present results, may be considered as a natural clean-up mechanism, whereby the microparticles that are shed from the tar ball are mobilized to the seawater and finally removed from the sand.

Salinity was found to be a determining factor in the formation of the microparticles by emulsification. In this sense, oil would remain without being degraded for longer on beaches in brackish environments or with a high freshwater discharge than on other beaches.

Acknowledgements

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