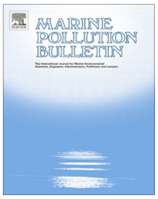
Marine Pollution Bulletin 78 (2014) 146–152

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul



Oil droplet interaction with suspended sediment in the seawater column: Influence of physical parameters and chemical dispersants

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ARTICLE INFO

Keywords:
Crude oil
Suspended particulate material
Adsorption
Chemical dispersant
Temperature

ABSTRACT

The interaction of dispersed oil droplets with large diameter suspended particulate materials (SPM) has been little studied. In the current study, particle size, oil characteristics and chemical dispersant significantly influence the adsorption of oil droplets to SPM in seawater. Sediments with a smaller particulate size (clay) approaching that of the oil droplets (2–20 μm) adsorbed more oil per gram than sediments with large particle size (sand). Heavier, more polar oils with a high asphaltene content adsorbed more efficiently to SPM than lighter, less polar oils. A decrease in the smaller, more water soluble oil components in the sediment adsorbed oil was observed for all oil types. Addition of chemical dispersant decreased the adsorption of oil droplets to suspended carbonate sand in an exponential-like manner. No change in the relative distribution of compounds adsorbed to the sediment was observed, indicating dispersants do not alter the dissolution of compounds from oil droplets.

1. Introduction

Oil spilled at sea may reach a variety of environmental compartments depending on environmental and climatic conditions, location and response strategies employed. Stranding of spilled oil on beaches is typically considered a worst case scenario owing to the potential impacts on wildlife and human installations. Oil spills often occur in coastal regions and coincide with poor weather conditions, where turbulent conditions at the sea surface (wave action) can lead to the breaking up of oil slicks into small droplets (<100 μm) through mechanical dispersion. These droplets become dispersed into the water column where the surface area of the oil in contact with seawater increases resulting in corresponding increases in the rate of other weathering and transport processes such as dissolution, biodegradation, adsorption to suspended particulate matter (SPM) Muschenheim and Lee, 2002; Venosa and Holder, 2007; Fiocco and Lewis, 1999; Chapman et al., 2007. Sedimentation to seafloor also increases which may cause severe damage to marine benthic ecosystems (Carls et al., 2008; Ho et al., 1999; Neff et al., 1976). Response strategies to prevent stranding of oil on shorelines have traditionally included use of adsorbent or protective booms to collect or trap surface oil. However, this technology is not very efficient and becomes unsuitable in turbulent weather and sea conditions. As a result, chemical dispersants are increasingly used as they enhance the formation of oil droplets and mixing of surface oil into the water column, thus increasing the rate of natural weathering and transport processes. Currently, chemical dispersants are only used in open waters due to the uncertainty of how chemically dispersed oil will behave in shallow waters. However, as oil exploration has moved closer to coastal areas in recent years the debate and research activity regarding near-shore dispersant strategies has increased correspondingly (Page et al., 2000).

It is generally accepted that oil-SPM aggregates form when oil droplets collide and adhere to SPM in aqueous environments (Ajijolaiya et al., 2006; Payne et al., 2003). Guyomarch et al. (2002) suggest that formation of oil-SPM aggregates is driven by interactions between polar oil compounds and negatively charged particles. There are, however, conflicting reports regarding the relative importance of SPM adsorption on the removal of oil from the water column. Using a numerical model, Bandara et al. (2011) showed that more than 80% of a spilled oil can interact with suspended particulate materials (SPM), and that up to 65% of released oil may be removed from the water column as oil-particle aggregates. In contrast, Muschenheim and Lee (2002) have reviewed field and enclosure studies and noted that the general opinion is that a maximum of 20–30% of the spilled oil can be adsorbed and subsequently sedimented. From empirical studies, Kirstein (in Payne et al. (1989)) derived a description for the rate of loss of free oil droplets from the water column, as they collide and adhere to SPM. Their study demonstrates that oil droplet concentration, SPM-concentration and SPM-characteristics will be of importance to the adhesion of oil droplets to sediment. In reality,

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0025-326X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.marpolbul.2013.10.049

it is most likely that the amount adsorbed to SPM will be influenced by environmental parameters and the properties of the spilled oil. However, many studies have focused on the adsorption of oil droplets with small-sized suspended particulates (typically clay particles). In contrast, the interaction of oil droplets with large-sized particulate material which may become suspended in the water column in near-shore high energy coastal areas has been little studied. Owing to their large size, such particles may offer a rapid transport route for oil droplets to the sediment.

The application of chemical dispersants to an oil slick increases the formation of oil droplets and droplets of reduced size, when compared to naturally/mechanically dispersed oil (Khelifa et al., 2008; Li et al., 2007; Li and Garrett, 1998; Li et al., 2009). The chemical dispersant reduces the interfacial tension between the oil and seawater, and hence stabilize the formation of oil droplets, normally sized 10–15 μm (Fiocco and Lewis, 1999; Lessard and DeMarco, 2000). Lessard and DeMarco (2000) present one of the advantages of dispersant application as the reduction of "stickiness" of the oil, indicating that chemically dispersed oil droplets are less likely to adhere to SPM and other solids. This is supported in studies by Mackay and Hossain (1982); Page et al. (2000) who observed that chemically dispersed oil associated less with mineral matter than naturally dispersed oil. However, a number of other studies show conflicting results, reporting that oil and SPM will form aggregates efficiently despite dispersant being added (Guyomarch et al., 2002; Khelifa et al., 2008; Khelifa et al., 2005; Sun et al., 2010).

Khelifa et al. (2008) report that oil-SPM aggregate formation was the same, regardless of dispersant application, concluding that chemical dispersants did not form a barrier to oil-SPM aggregation. The authors suggest the reduction in size and increase in concentration of oil droplets in the water column, the alteration of surface properties of the oil droplets and that the smaller, chemically dispersed droplets will require less solid material (fines, clay) in order to sink all contributed to the observed results. Model simulations have also shown that the presence of smaller droplets (<100 μm) increased the predicted amount of oil-SPM aggregates formed (Bandara et al., 2011). It was suggested that droplet residence time in the water phase is prolonged due to the decreased buoyant velocity of smaller particles, allowing for more interaction with SPM.

At present, there are still significant knowledge gap concerning the fate and transport of dispersed oil in the marine environment. Adsorption onto SPM and subsequent sedimentation is one potentially important route for such dispersed oil droplets, but the process is poorly understood, especially in the presence of chemical dispersants. This study investigates how parameters such as oil type, size and type of suspended particulate matter (sediment characteristics) and temperature, which are relevant parameters in near shore high energy coastal areas impacted by oil spills, govern oil-SPM interactions. In addition, the role of chemical dispersants on the adsorption of oil droplets to SPM is also investigated in this study. The current study wishes to answer some of the questions regarding the behaviour of chemically dispersed oil and its interaction with mineral particles. This is highly relevant for shallow waters where high energy wave action may suspend particles of larger sizes and greater quantities than you could expect in coastal waters.

2. Materials and methods

Dichloromethane (DCM, 99% HPLC grade) was supplied by Merck, *n*-hexane (99% HPLC grade) was supplied by Fluka. Surrogate internal standards (SIS); naphthalene-d8, phenanthrene-d10, chrysene-d12 for GC–MS analysis and *o*-terphenyl for GC–FID, and recovery internal standards (RIS); fluorene-d10 for GC–MS analysis, 5-α-androstane for GC–FID, were supplied by Chiron AS (Trondheim, Norway) and dissolved in DCM prior to use.

Four different oil types were selected for the study, comprising two crude oils, one condensate and one heavy fuel oil. A summary of their physico-chemical properties is given in Table 1. Prior to use in the study, all oils except the fuel oil were distilled to 250 °C to simulate natural weathering processes. The chemical dispersant used in the experiments was Dasic Slickgone NS. Oil and dispersant were mixed in two different ratios (1%, 5% v/v) and applied in the same way as pure oil in the experiments. The authors acknowledge that applying a pre-mix of dispersant and oil to seawater is different from a real application scenario where the dispersant is sprayed on top the oil slick. The effectiveness of the dispersant is likely to be reduced when it is applied directly to oil already present in seawater.

Seawater (salinity (33.5 ± 0.2) ‰) was pumped from a depth of 90 m in Trondheim fjord (63°26′N, 10°26′E) and filtered by a sand filter (50 μm). The three natural sediments used in this study were collected at different locations around Trondheim, Norway. *Carbonate sand* was collected from Grandefjæra (+63°40′N, +9°32′E), *quartz sand* from Hansbakkfjæra (+63°25′N, +10°32′E) and *clay* from Buvika (+63°18′N, +10°10′E). The sediments were flushed with clean seawater, dried at 100 °C and passed through a 2 mm sieve before use in experiments. The grain size distribution of the carbonate sand was concentrated between 90 and 500 μm with a maximum in the range 180–250 μm. The grain size distribution of the quartz sand was between 90 and 2000 μm with a maximum in the range 250–355 μm (S1; Supplementary Information). The average grain size of the Buvika clay was <63 μm.

To simulate mechanically dispersed oil droplets, an oil droplet generator consisting of two inlets and four capillary chambers was used. Seawater was supplied to the generator by a CeramPump® QG Valve pump at a rate of 160 mL/min. Oil was supplied by an Aladdin AL-2000 syringe pump at a rate providing an oil concentration of 20 mg/L in the water. The system generates oil droplets in the size range of 2–20 μm (data not shown). Sediment (15 g) was added to a glass beaker (2 L) and seawater (1.5 L) with dispersed oil (20 mg/L) was added by the oil-droplet generator. This is high sediment to oil ratio has been used in order to represent an oil spill in a high energy near-shore environment. The system was mixed by an overhead stirrer (VWR VOS 16, equipped with a PTFE rod and blade, 65 mm width, 25 mm height) for 55 min at ~250 rpm, followed by 5 min at ~50 rpm. The sample was then allowed to settle for 24 h. Residual oil on the water surface and glass wall was removed. The sample was filtered using a GF/C filter paper (Whatman, pore size 1.2 μm) on a Buchner funnel. The sediment was flushed three times on the filter paper with 30 mL of clean seawater and dried at room temperature. The water phase was collected in bottles and acidified (pH < 2).

In the adsorption experiments, oil type, sediment type, use of chemical dispersant and temperature were varied systematically as summarised in Table 2. An experimental system using Troll crude oil mechanically dispersed in seawater containing suspended carbonate sand at 20 °C was used as the basis for systematic variation of the selected parameters.

Sediment samples were Soxhlet extracted for 6 h in cellulose thimbles (Whatman, type 603) using DCM (50 mL). Surrogate internal standards were added to the sediment prior to extraction. The extract was filtered through cotton wool, dried with anhydrous sodium sulphate (Na_2SO_4) and the solvent volume reduced to approximately 0.5 mL using a gentle stream of N_2. Prior to analysis, sediment extracts were subject to clean-up by elution through Supelco® Bond-Elut silica SPE columns (500 mg). Surrogate internal standards were added to the water phase samples, followed by liquid–liquid extraction using DCM (1 × 120 mL and 2