



# Dispersibility and biotransformation of oils with different properties in seawater



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## HIGHLIGHTS

- Commercial dispersants efficiently dispersed crude oils with different properties.
- IFT testing showed different surfactant leaching properties for oils and dispersants tested.
- Biodegradation of alkanes and PAH did not differ significantly between the different oils.
- Biodegradation of saturate and aromatic oil compound groups were provided for an oil spill model.
- Oil biodegradation stimulated growth of heterotrophic and oil-degrading prokaryotes in all oils.

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## ABSTRACT

Dispersants are used to remove oils slicks from sea surfaces and to generate small oil-droplet dispersions, which may result in enhanced biodegradation of the oil. In this study, dispersibility and biodegradation of chemically dispersed oils with different physical-chemical properties (paraffinic, naphthenic and asphaltenic oils) were compared in natural temperate SW at 13 °C. All selected oils were chemically dispersible when well-known commercial dispersants were used. However, interfacial tension (IFT) studies of the dispersed oils showed different IFT properties of the oils at 13 °C, and also different leaching of the dispersants from oil droplet surfaces. Biodegradation studies of the chemically dispersed oils were performed in a carousel system, with initial median droplet sizes <30 μm and oil concentrations of 2.5–2.8 mg/L. During biodegradation, oil droplet concentrations were rapidly reduced, in association with the emergence of macroscopic 'flocs'. Biotransformation results showed that half-lives of semivolatile total extractable organic carbon (TEOC), single target 2- to 4-ring PAH, and 22 oil compound groups used as input data in the oil spill contingency model OSCAR, did not differ significantly between the oils ( $P > 0.05$ ), while *n*-alkanes half-lives differed significantly ( $P < 0.05$ ). Biotransformation was associated with rapid microbial growth in all oil dispersions, in association with *n*-alkane and PAH biotransformation. These results have implications for the predictions of biodegradation of oil slicks treated with dispersants in temperate SW.

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## 1. Introduction

The use of chemical dispersants is an important operational tool for treatment of surface or subsurface oil discharges in the marine environment. Dispersants have been used in several oil spill operations (Prince, 2015). Dispersants were also injected subsurface during the *Deepwater Horizon* (DWH) blowout in 2010, to reduce oil

surfacing (Atlas and Hazen, 2011; Kujawinski et al., 2011), and subsequent stranding of the oil.

Chemical dispersants are mixtures of surfactants and solvents, creating more hydrophilic oil surfaces, and generating small oil droplets with low rising velocities in the seawater (SW) column (Lessard and DeMarco, 2000; Prince, 2015). Several laboratory studies under different environmental conditions have shown that the use of chemical dispersants promote oil biodegradation (Brakstad et al., 2014; McFarlin et al., 2014; Prince et al., 2013; Siron et al., 1995; Venosa and Holder, 2007; Zahed et al., 2011). However, other studies have suggested no or uncertain effects of dispersants

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on oil biodegradation after dispersant treatment (Lindstrom and Braddock, 2002; Macnaughton et al., 2003), and even inhibitory effects of dispersant components on oil biodegradation rates have been suggested (Kleindienst et al., 2015; Rahsepar et al., 2016). Several biodegradation studies of chemically dispersed oil have been performed with unrealistically high concentrations of oil or dispersant, which may limit biodegradation due to nutrient depletion (Lee et al., 2013), or cause prolonged lag-periods due to toxic effects. It was also observed that low oil concentrations resulted in more efficient biodegradation of chemically dispersed oil than high concentrations (Zahed et al., 2010). The surfactant dioctyl sulfosuccinate (DOSS) and the hydrocarbon fraction of the dispersant Corexit 9500, used during the DWH spill, have also been shown to be biodegradable with enrichment cultures from Gulf of Mexico (GoM) SW at 25 °C or 5 °C (Bælum et al., 2012; Campo et al., 2013).

It is important that the oil is dispersed to small-oil droplet dispersions for efficient biodegradation. It was recently shown that hydrocarbons in oil dispersions with median droplet diameters of 10–30 µm are rapidly biodegraded in Norwegian or GoM SW, using a fresh paraffinic oil (Brakstad et al., 2014, 2015a; Hu et al., 2017; Wang et al., 2016). However, non-dispersed oil emulsions are poorly biodegradable, with the exceptions of oil compounds dissolving to the SW (Brakstad et al., 2014). Slightly weathered emulsions may be dispersible under breaking wave conditions, but the generated droplets are large (>100 µm) (Daling et al., 2014). Biodegradation of compounds in these large droplets is therefore expected to be poor (Brakstad et al., 2014). Dispersant treatment will result in breaking of the emulsions at various degrees, resulting in generations of dispersions (Strøm-Kristiansen et al., 1997), and the conditions for biodegradation will be improved.

The ability of an oil to disperse is important for the ability of the oil to biodegrade. The dispersibility of the oil may depend on its physical-chemical properties at different weather and temperature conditions. For instance wax-rich oils have shown poorer dispersibility properties than paraffinic, naphthenic, and asphaltenic oil in SW, especially in cold SW if the wax solidifies (Strøm-Kristiansen et al., 1997). Data on the dispersibility of an oil are therefore important both for decision of using dispersants after an oil spill, and as a background for predicting its biodegradability after an oil spill.

Dynamic models are used to predict the fate of the oil after a spill, and for the estimation of the efficiency of oil spill operations. One of these models is the three-dimensional oil spill OSCAR model (Reed et al., 1995). In this model, experimental biotransformation rates of oil compound groups have been included as part of the fate predictions (Brakstad and Faksness, 2000; Reed et al., 2001). These compound groups represent a boiling point range of  $\pm 160$  to  $>500$  °C, covering more than 80% of most light oils, according to the true boiling point curve (Pasquini and Bueno, 2007). The biodegradation rates used in the OSCAR model were originally derived from paraffinic oils with similar physical properties, using mechanically prepared dispersions (Brakstad and Faksness, 2000). Biodegradation data are therefore required for chemically dispersed oils with different properties, as part of the fate predictions after dispersant oil spill treatment.

The main objective of this study was to compare the dispersibility and biodegradation of North Sea crude oils with different properties, when treated with common commercial chemical dispersants. The selected oils included both paraffinic, naphthenic and asphaltenic oils, and biodegradation was performed in natural SW at a temperature relevant for North Sea summer conditions (13 °C). The results from this project would also address if generic rather than oil-specific biodegradation data were needed for oil spill models like OSCAR, when predicting the fate of an oil spill treated

with dispersants at conditions relevant for this study.

## 2. Materials and methods

### 2.1. Crude oils, dispersants and seawater

Norwegian crude oils, representing paraffinic (Statfjord C), naphthenic (Troll C) and asphaltenic (Grane) oils were used in this study (Table S1, Supplementary Information). In addition, an expected asphaltenic oil (Balder) proved to be a blend of asphaltenic (40%) and paraffinic (Ringhorne, 60%) oils (Table S1). All oils were heated prior to use (50 °C, 1 h) to melt wax generated during storage. Water-in-oil (w/o) emulsions (50 or 75% SW) of evaporated (250 °C) or photo-oxidized (xenon high pressure lamp, IR and UV filters [sunlight conditions]; 20 h) Statfjord C or Troll C oils were prepared in rotating centrifuge funnels as previously described (Daling et al., 1990). Properties of fresh and evaporated/photo-oxidized oils are described in Table S1.

Three commonly used commercial dispersants, Slickgone NS (Dasic International Ltd., Romsey, Hampshire, UK), Corexit 9500A (Nalco Environmental Solutions LLC, Sugar Land, Tx, USA), and Finasol OSR-52 (Total Special Fluids, Paris, France), were included in this study. Slickgone NS is an approved dispersant in several European countries, including use as a secondary tool in oil spill operations on the Norwegian Continental Shelf. Corexit 9500A was injected at the wellhead during the Deepwater Horizon spill in 2010, but also on surfaced oil during the spill (Atlas and Hazen, 2011; Kujawinski et al., 2011). Finasol OSR-52 is a common dispersant approved for use in several countries worldwide.

Natural SW was collected from a depth of 80 m (below thermocline) in a Norwegian fjord (Trondheimsfjord; 63°26'N, 10°23'E), outside the harbour area of Trondheim. The SW is supplied via a pipeline system to our laboratories, and the water source is considered to be non-polluted and not influenced by seasonal variations, with a salinity of 34‰. Inorganic nutrient analyses of the SW showed 130 µg/L nitrite/nitrate, 3 µg/L ammonium and 16 µg/L ortho-phosphate (Brakstad et al., 2015a).

### 2.2. Dispersibility testing

Oil dispersibility was tested with the three dispersants by high energy, according to the Mackay-Nadeau-Steelman (MNS) method (Mackay and Szeto, 1981), generating breaking waves during dispersion. The test system and method has recently been described (Daling et al., 2014). Both fresh oils and w/o emulsions of evaporated (250 °C+) or photo-oxidized oils were included (Daling et al., 1990). Fresh oils (0.8 g) or emulsions (8 g emulsion with 50% or 75% (w/w) SW) were applied to 6 L SW, and dispersants applied on the oil surface at dispersant-to-oil ratios (DORs) of 1:100 (fresh oils) or 1:25 (emulsions). The oils and dispersants were allowed to mix for 1–2 min. The experiments were performed with continuous breaking wave conditions (generated by blowing air across the SW surface) at 13 °C for up to 6 h. Samples were then collected from the water column at different times during the experiments (5, 15, 30, 60, 130, 240, and 360 min) for measurements of oil droplet concentrations and size distributions by Coulter Counter (see below).

Standard dispersibility testing of Troll evaporated or photo-oxidized emulsions (see above) with 50% (w/w) SW were tested with Slickgone NS, Corexit 9500A and Finasol OSR-52 (DOR 1:25) in the MNS system for 120 min at 13 °C. Dispersant efficiency was determined by UV spectrophotometry (410 nm), and oil droplet concentrations and size distributions by Coulter Counter (see below).

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