Study on how oil type and weathering of crude oils affect interaction with sea ice and polyethylene skimmer material

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ABSTRACT

Understanding the fate of spilled oil in cold environments is essential for oil spill response in Arctic areas. The potential for oils to adhere to sea ice and mechanical skimmers can significantly impact the success of oil spill response and influence the fate of oil in the marine environment. Therefore, the affinity of oil to sea ice and skimmer material was quantified experimentally for three different types of oils at various degrees of weathering. Contact angle measurements of crude oil droplets were performed on the top of and under sea ice and polyethylene-based skimmer material, being submerged in seawater (−2 °C). In addition, “dip- and refloat” tests were performed to quantify the adhesion and study the re-floating process of oil from sea ice at −2 °C (moist ice) and −20 °C (cold dry ice), and from a skimmer material prior to and subsequently to its submersion in seawater (−2 °C). The results indicated limited interaction of oils with sea ice submerged in seawater, but a strong affinity of oils towards polyethylene-based skimmer material.

1. Introduction

Oil spills in ice-covered water make cleaning and separation of oil and ice, as well as tracking and detection of oil spreading difficult. Oil spills like MT Antonio Gramsci in the Baltic Sea (1987), MT Exxon Valdez in Prince William Sound Alaska (1989) and Godafoss in Hvaler, Norway (2011) have shown that the separation of oil from polluted sea ice is a challenging, time-consuming and extremely costly task, where success is highly dependent on the adhesion of oil to sea ice (The Norwegian Coastal Administration, 2011). These challenges provide motivation for developing better response methods by improving the understanding of oil interaction with sea ice under different temperature conditions.

Crude oils are often characterised into four categories having different chemical and physical properties; asphaltenic, naphthenic, paraffinic and waxy. When spilled at sea, oils will be subjected to several weathering processes such as evaporation (lighter components evaporates), water-in-oil (W/O) emulsification (water droplets are incorporated in the oil phase) and photo-oxidation (changing the physical and chemical properties due to sun exposure). These weathering processes change the physical and chemical properties of the oils, which is of great importance for the weathered oils fate and behaviour at sea (Moldestad et al., 2006). For this reason, a selection of oils representing some of the abovementioned crude oil categories, at different weathering degrees, was evaluated, namely Troll B (naphthenic oil), Grane Blend (asphaltenic oil) and Statfjord C Blend (paraffinic oil).

The objective of this study was to achieve a better understanding of the fate of spilled oil in cold environments in terms of the strength at which fresh and weathered crude oils adhere to sea ice and polyethylene-based mechanical skimmer material. Weathered oils are here defined as oil residues that have lost their lighter components by either natural evaporation or distillation at a given temperature (i.e. 150 °C or 250 °C). Furthermore, some of the oil residues were also emulsified with seawater as described below in Section 2.1. In contrast to residues (weathered oils), “fresh crude oils” are the crude oils that after de-pressurization to ambient pressure, have been stored appropriately to avoid additional evaporation of light components and alterations of the crude oil properties after their production from the given reservoir. In this work, the affinity of oil to sea ice and skimmer material was evaluated by contact angle measurements and quantification of the volume of oil droplet attached to the substrate. Moreover, adhesion was studied by “dip- and refloat” tests, performed by submerging the rods of sea ice and skimmer material in oil, followed by the study of the release of the oil upon submersion into seawater.

To achieve the objectives of this study, different tests aiming at resembling the Arctic scenarios were set-up and used in the laboratory to quantify adhesion and wettability:
• Oil was placed on sea ice and skimmer material submerged in surrounding seawater. Adhesion was studied by estimating the volume of oil and measuring the contact angle of remaining oil attached to the substrate.

• Oil was placed under sea ice and skimmer material submerged in surrounding seawater, the contact angle was used as a measure of the cohesion of oil to the surfaces under given conditions.

• “Dip- and refloat” tests were conducted to study the oil adhesion/cohesion by using moist and dry cold sea ice and skimmer material. Both adhesion and cohesion forces (described below) are represented but not possible to distinguish with the selected method. The re-floating was documented by video.

Adhesion is the term used to describe the strength of intermolecular forces between two media of different types, while cohesion refers to the internal attraction of similar molecules within one media, such as water or oil. Cohesion energy is directly related to the interfacial tension (IFT) or surface tension of liquids and gases (Israelachvili, 2011), e.g. the interfacial tension between oil and seawater, where seawater is the surrounding “gas”, is a measure of the cohesive energy present at an interface arising from the imbalance of forces between the oil molecules. Surface active molecules (surfactants) such as asphaltene, resins and naphthenic acids, present in most crude oils, will reduce the IFT of a freshly formed surface when adsorbed to an oil-water interface. One effect is a reduction in the energy needed to form droplets and in addition they most often stabilize such droplets by hindering coalescence.

Wettability is a quantifiable property and is determined by the force balance between the intermolecular interaction of adhesive type (liquid to solid) and cohesive type (liquid to liquid). Wettability deals with the three phases of materials needed for creating a contact angle. Normally these three materials are a gas phase, a liquid phase and a solid phase, however, two liquid phases (oil and water) and a solid phase also suffice for creating a contact angle (i.e. wetting of a surface). The wettability is most often measured and related to the contact angle of a liquid (or gas) to a solid surface immersed in a third phase (liquid or gas). A common practice is to relate wettability of a surface to the contact angle that a water droplet forms on that specific surface under given pressure and temperature conditions at thermodynamic equilibrium. Furthermore, as indicated in Fig. 1, from left to right, surfaces can be hydrophobic resulting in a contact angle higher than 90°, have intermediate wettability (contact angle is ~ 90°) or be hydrophilic providing contact angles smaller than 90°. For completely wetted surfaces the contact angle cannot be measured and the term “full spreading” is used.

2. Experimental

2.1. Selection and weathering of crude oils

The selected crude oils were evaporated following the procedure described by Stiver and Mackay (1984). Evaporation of the lighter components from the fresh crude oils was carried out in a one-step distillation to vapour temperatures of 150 °C + and 250 °C +, representing an evaporation loss corresponding to approximately 0.5–1 h and 0.5–1 week of oil weathering on the sea surface respectively (depending on environmental conditions).

Some of the oil residues were also emulsified with seawater to prepare 50 wt% Water-in-Oil (50% W/O) emulsions. The emulsification was performed using a rotating cylinder method developed by Mackay and Zagorski (1982), as described in detail by Hokstad et al. (1993). All W/O emulsions were prepared at 5 °C. The methods have been accepted at several oil spills research laboratories to generate residues that simulate the evaporative loss of spilled oils at sea (Daling et al., 2014).

2.2. Physical and chemical analysis

The pour point, asphaltenes and wax contents, density, viscosity and yield stress of the oils were determined according to standard procedure as described by Dalin et al., 2014. These physical and chemical parameters were measured to help the interpretation of the data.

2.3. Interfacial tension measurements by Pendant drop method

A drop shape analysis system (DSA100, KRUSS GmbH) was used to measure the interfacial tension between different oils (fresh and weathered) and seawater. The aqueous phase was kept in a standard cuvette and an oil drop was immersed into the solution by a syringe connected to a needle with an inverted tip (Fig. 2). The syringe was equipped with a valve to close off the sample volume in the needle from the syringe to keep a constant drop volume (normally around 8–12 μL). Measurements were initiated immediately upon expelling the drop, and the drop profiles were recorded at 1 image per second continuously for 2 h. Due to high pour point of some of the oil residues, the measurements were performed at 20 °C (unless explicitly stated), although interfacial tension is slightly lower at the test temperature (20 °C) than at temperatures closer to 0 °C (surface tension decreases upon increasing temperature).

2.4. Surface tension and contact angle measurements

Surface tension is normally measured either by the ring/plate method, or the pendant drop method, the last being the most used and versatile. In this study, the surface tension is measured by the pendant drop method. The pendant drop method captures an image of a liquid drop and analyses the drop shape with the Young-Laplace equation (Eq. (1)) (Sjoblom et al., 2006). The theoretical drop shape is then compared to the measured shape to yield the surface tension. The only necessary input parameters are the densities of the two phases, (Konno and Izumiyama, 2002). The Young-Laplace equation (Eq. (1)) describes the pressure difference (ΔP), where γ is the surface tension of the fluid pair (newtons per meter) and R1 and R2 are the radii of curvature.

\[
\Delta P = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right)
\]

To determine the wetting of a surface by a liquid, Young’s relation equation (Eq. (2)) relates the contact angle (θ) at the three-phase gas-liquid-solid (g, l, and s) point of a droplet to the surface tensions (or energies) of the respective phases. The “gas” is the surrounding fluid and can be the water phase if the contact angle between oil and surface immersed in water is to be determined.

Fig. 1. Illustration of contact angle on a solid surface. The figure illustrates a water droplet on three surfaces with different wettability. From left to right a water droplet is deposited on a hydrophobic surface resulting in a contact angle higher than 90°, a surface with intermediate wettability (contact angle is ~ 90°) and a hydrophilic surface where the contact angle is smaller than 90°.
The adhesion of oil to ice has been reported by a few authors over the last four decades (Mackay et al., 1976; Liukkonen et al., 1997; Konno and Izumiyama, 2002). The literature reports methods involving the displacement of an oil droplet either on the ice or under the ice, submerged in seawater, and visual determination of the contact angle between the ice surface and the droplet. Furthermore, the contact angle has been determined by a combination of gravitational forces, buoyancy (in water), and the interfacial forces (adhesion and cohesion) of three relevant materials (ice/skimmer-material, oil and water). As stated by Mackay et al. (1976), the main differences between an air-ice-oil system and a water-ice-oil system is the lower gravitational force (85–80% lower) on the oil droplet in water under ice compared to oil on ice in air, and the difference in wetting for a dry ice substrate in contrast to a water-wet ice substrate. Mackay et al., 1976 also observed that small (<5 mm diameter) drops were almost spherical in shape and showed almost no adhesion to the ice under water. Their conclusion was that most crude oils had contact angles in the range of 140° and 170° and displayed non-wetting behaviour on ice under water. Liukkonen et al., 1997 also obtained similar contact angles with crude oil and diesel. It was observed that oil droplets <1 cm² behaved as a mobile spherical particle under ice, while larger oil droplets behaved as lenses without significant wetting properties (i.e. contact angles will be much higher than 90°). Liukkonen et al., 1997 also measured the velocity of the droplet and inclination angle when oil droplets started to move. Furthermore, for the oils tested by Liukkonen et al., 1997 the inclination angle was highest for fresh crude oil (6.6° ± 3.3°) and lowest for diesel (3.5° ± 2.2°). These results suggest that different types of crude oils (and distillation fractions) may adhere to ice differently, even when submerged in seawater. Furthermore, spreading coefficients were calculated to be around −94 mJ/m², confirming that oil does not spread to an ice surface in water (underside the solid ice).

Literature indicates that contact angle measurements can be used to characterize the affinity of oil to skimmer material (Broje and Keller, 2005, 2007) and the mass of oil recovered by different skimmers increases with decreasing contact angle and vice versa. It was recommended that for developing the relationship between oil properties and recovery materials, contact angle measurements can be performed along with “dip- and withdraw” tests (Broje and Keller, 2007).

2.5. Preparation of sea ice

To ensure reproducible production of sea ice with similar surface properties (e.g. irregularities and hardness), seawater with a salinity of 3.5 wt% was diluted with freshwater, to reduce the salinity to 0.5 wt%. Low salinity seawater was used to produce a smooth ice surface as high salinity seawater gives more porous ice. Sea ice was prepared at a temperature of −20 °C.

For adhesion and wettability experiments, low salinity seawater was frozen in the form of sheets (Fig. 3), having a dimension of 140 × 31 × 10 mm, which was further cut into pieces of 36 × 31 × 10 mm using a saw. To get a smooth surface for the experiments, the ice-sheets were polished by a metal plate. Sea ice rods used for the “dip- and refloat” test were produced in a metal container divided into 30 × 30 × 150 mm sections representing the dimensions of the rods. To retrieve the ice rods, the container was placed in room temperature for a short time period. Pictures documenting the preparation of the sea ice rods and sheets are shown in Fig. 3.

A previous study reported that a water layer would form on the surface of sea ice as the ice thawed and may affect the adhesion of oil (JIP, 2014). In order to test the adhesion of oil under realistic conditions, two different temperatures of sea ice were included in the “dip- and refloat” test. The lowest temperature at which a liquid layer of water is present on the surface of sea ice without freezing is reported to be −13 °C (Makkonen et al., 1997). We, therefore, tested the interaction of oil to sea ice being frozen at −20 °C and sea ice being thaw at −2 °C.

2.6. Adhesion of oil on sea ice and skimmer material submerged in seawater

Adhesion of oil to submerged sea ice and polyethylene skimmer material was measured using the contact angle method. Sea ice and skimmer material were completely submerged in filtered seawater (salinity of 3.5 wt%). A single drop of oil was applied to the surface of sea ice or skimmer material using a syringe. The optimal droplet

\[
\gamma_d = \gamma_s + \gamma_d \cos(\theta)
\]
and the seawater was −0.5 °C. Therefore, the temperature of the sea ice was held close to the freezing point, which was approximately −0.5 °C for sea ice having a salinity of 0.5 wt%. Both experiments were performed in a temperature-controlled chamber to provide a stable test temperature of −0.5 °C.

2.8. “Dip- and refloat” test

A modification of the “dip and withdraw” technique, developed by Jokuty et al. (1995, 1996) and Liukkonen et al. (1995) was used to study the amount of oil residue and emulsion remaining at the sea ice and skimmer material. This modified technique called the “dip- and refloat” test, included submersion of the test material in seawater after exposure to oil. This method was recently used by Farooq et al. (2018) to study the oil adhesion to oil spill recovery skimmer material.

The “dip- and refloat” tests were performed with skimmer material (−2 °C) and sea ice (−20 °C and −2 °C). At −2 °C, sea ice was covered by a layer of water on its surface due to natural melting. The sea ice and skimmer materials were immersed into a container of oil (−2 °C) for 30 s and subsequently installed vertically with clamps for 30 min to allow excess oil to runoff. Excess oil was collected and weighed in separate aluminum dishes for quantification (Fig. 8). To document the adhesion of oil in the presence of seawater, the oil-covered sea ice and skimmer materials were then immersed into a glass container of seawater (i.e. re-floatation) at −2 °C and the fate of oil was photo documented (Fig. 8).

3. Results and discussion

3.1. The physical and chemical properties of the crude oils and their weathered residues

The physical and chemical properties of the crude oils and their weathered residues are given in Table 1. Evaporation of volatile components increases the relative amount of higher molecular weight components and consequently changes the physical and chemical properties of the residual oils. Density, viscosity, pour point, relative wax and asphaltene contents all increased due to weathering (evaporation) (Table 1). The Grane Blend had an asphaltene content of 1 wt% and wax content of 6.7 wt%, which is much higher than the other crude oils used in this study. The wax and asphaltene contents of different residues of Grane blend were not available, but the values were expected to increase upon distillation. On the contrary, Troll B contained a small percentage of asphaltenes and wax contents, and the 250 °C+ residue had asphaltene and wax contents of 0.11 wt% and 1.61 wt% respectively.

3.2. Interfacial tension between oil and water using the Pendant drop method at 20 °C

The interfacial tension for the fresh and weathered crude oils are given in Table 2 which includes the initial interfacial tensions (IFT<sub>in</sub>) and the equilibrium interfacial tensions (IFT<sub>eq</sub>). Large differences in the IFT<sub>in</sub> values were observed due to the variation in the crude oil properties, while the equilibrium values were almost identical. Statfjord C Blend 250 °C+ residue had a pour point higher than the test temperature of 20 °C which may affect the initial values. The effect of temperature and emulsification on IFT was investigated by measuring the IFT values for the Troll B 150 °C+ residue at −1 °C and 20 °C, and for Troll B 150 °C+ 50% W/O emulsion. Seawater temperature and emulsification were found to have little effect on the IFT for Troll B 150 °C+ residue (Table 2). On the contrary, 50% W/O emulsion prepared from different residues of Troll B had a large effect on the IFT<sub>in</sub> and IFT<sub>eq</sub> values e.g. the IFT<sub>eq</sub> of 50% W/O emulsions prepared from Troll B 250 °C+ and Troll B 150 °C+ residues were 22.5 mN/m and 11.2 mN/m respectively. The nature of the comparatively higher IFT

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Fig. 4. An illustration of the droplet adhesion and contact angle test on an ice surface A) Droplet formed at the tip of needle B) Oil droplet forced into contact with surface C) Removal of a needle, and contact angle and volume of oil droplet remaining were measured.

Fig. 5. Contact angle measurements performed after the adhesion test on skimmer surface.

Contact angle measurements of oils under sea ice and polyethylene skimmer material submerged in seawater

Contact angle measurements of oil under sea ice and polyethylene skimmer material was performed similar to contact angle measurements of oil on top of the test material (Section 2.6), except that the oil droplet was placed beneath the ice using an inverted needle, as shown in Figs. 6 & 7. In the study performed by Liukkonen et al. (1997), a drop volume of 10–500 μL was used, however, to reduce the effect of buoyancy on the droplet shape, a droplet size of 5–50 μL was applied in this study.

For the adhesion and contact angle measurements of oil on the top and under sea ice submerged in seawater, the main challenge was to keep the ice from melting as the temperature of the sea ice was −20 °C

Fig. 6. An illustration of contact angle measurement of oil/emulsion under sea ice. A) Droplet formed at the tip of needle B) Oil droplet forced into contact with surface C) Removal of needle and measurement of contact angle.

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Fig. 4.

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Fig. 5.

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Fig. 6.
values of Troll B 250 °C+ 50% W/O emulsion was not further investigated in this study, but IFT results indicated that even a small change in the concentration of asphaltenes might contribute to a change in the properties of the emulsion.

3.3. Measurements on sea ice in seawater - adhesion and contact angle measurements of non-weathered and weathered oil

Selected fresh oils, residues and emulsified residues were tested by droplet adhesion test (as described in Section 2.6) on the surface of sea ice and skimmer material in the presence of seawater. Fig. 9 illustrated a time lapse of the attempt to attach a droplet of Troll B fresh oil on sea ice. The results given in Table 3 show that neither weathered nor emulsified residues adhered to solid sea ice submerged in seawater, confirming previous studies from the literature (Liukkonen et al., 1997 and Mackay et al., 1976). However, the residues and emulsions showed strong affinity towards skimmer surface, compared to the sea ice. Fig. 10 shows the remaining Troll B 150 °C+ residue after contact with the skimmer material for 2 min. Moreover, the contact angle measurements and the quantification of the oil droplet volume remaining after retracting of the oil filled syringe, showed that the Grane Blend 250 °C+ 50% W/O emulsion interacted stronger (83°) with the skimmer surface compared to Troll B 250 °C+ 50% W/O emulsion (103°). The reason for the stronger interaction of the Grane Blend may be related to its relatively higher asphaltene content. Oils with high asphaltene content have previously indicated stronger adhesive properties (Buckley et al., 1998; Buckley and Liu, 1998; Sayyouh et al., 1991). Furthermore, the Troll B 250 °C+ 50% W/O emulsion showed higher (103°) contact angle compared to non-emulsified 250 °C+ residue (86°), indicating comparatively lower interaction of the emulsion towards the skimmer material (Table 3). This is probably due to the water in the emulsion which has a repelling effect on the liquid layer on top of the skimmer surface. Moreover, the emulsions showed an increase in oil droplet volume remaining on the skimmer surface, depicting the higher cohesive properties of the emulsion droplets due to the increase in the IFT of the emulsion. Fig. 11 summarizes the results from the adhesion tests.

3.4. Measurements under sea ice in seawater - contact angle measurements of non-weathered and weathered oils

For all the tested oil residues and emulsions, the results indicated a limited interaction to sea ice immersed in seawater, resulting the contact angles in the range of 130 to 160° (Table 4). The fact that the measured contact angle is lower than 180°, may be due to a deformation of the oil droplet caused by the buoyancy effect, rather than adhesion to the sea ice (as discussed by both Liukkonen et al., 1997 and Mackay et al., 1976). In contrast to sea ice, the results indicated that the interaction of oil to skimmer material was considerably stronger, with contact angles in the range of 42 to 105° (Table 4). Contact angle measurements on skimmer material indicated a lower degree of affinity for the Troll B 250 °C+ 50% W/O emulsion (105°) than for the non-emulsified residue (42°) having the same evaporative loss (250 °C+). Moreover, the Troll B 250 °C+ 50% W/O emulsion also showed a lower affinity (105°) than the Grane Blend 250 °C+ 50% W/O emulsion (73°). This corresponded well with the results found for the adhesion test performed on top of skimmer material in seawater, see Section 3.3. The results are summarized in Fig. 12.

These results have also confirmed the previously reported studies in the literature; that there is little or no affinity of oil to moist or/wetted ice (Liukkonen et al., 1997 and Mackay et al., 1976). Liukkonen et al. (1997) reported contact angles between oil and ice in seawater ranging from 160° to 165° for crude oil, pre-altered (crude oil where 30% by weight of the light components has been removed) and diesel fuel. For the present work, the aim was to study not only the fresh oils but also investigated the weathered and emulsified oils. From the contact angle measurements performed on the top and under sea ice in seawater, it is confirmed that weathered oils also showed no interaction towards the ice surface (CA ≈ 180°). However, as discussed by Liukkonen et al. (1997), a thin layer of water is present between the moist or/wetted solid ice and the oil droplets, preventing direct contact with oil and ice, so the contact angle may actually represent oil-
water rather than the oil-ice interface.

The results indicate strongly that contact angle measurements can be used as an indication of adhesion strength of oils towards skimmer materials. Moreover, the contact angle can serve as a tool to compare and quantify the adhesion strength of a given oil or oil-continuous emulsion towards solid surfaces.

### 3.5. Inclination test

A simple inclination test was performed for the oil droplets of Statfjord C Blend under sea ice and Troll B 250 °C+ residue under skimmer material by tilting the sheets by hand. For the Statfjord C Blend under sea ice, a tilting of 10° was needed to set the droplet into motion (Fig. 13 A), confirming the weak adhesion between the oil and ice. In comparison, literature (Liukkonen et al., 1997) reports the movement of the oil droplet at a tilting angle of 6.6° ± 3.3°. Moreover, the oil droplets of Troll B 250 °C+ residue in contact with skimmer material did not move and kept its initial shape even with an inclination of 55° (Fig. 13 B) indicating quite strong adhesion to the skimmer material in contrast to sea ice.

### 3.6. “Dip- and refloat” test

The “dip- and refloat” test showed that almost all the tested oils adhered to both sea ice and skimmer material in absence of seawater (Fig. 14), except for those oils which have a pour point above the test temperature (−2 °C), making it difficult to submerge the ice rods into the oil. Grane Blend 250 °C+, Statfjord C Blend 150 °C+ and Statfjord C Blend 250 °C+ have a pour point of 9 °C, 12 °C and 27 °C respectively.

Owens (2004) reported that oil is likely to adhere to the exposed ice surfaces at temperatures below 0 °C. Our results showed that the oils, especially the oil emulsions adhered much stronger to the ice at −20 °C than to ice at −2 °C. This could be explained by a combination of the oil residues solidifying properties and the seawater incorporated in the oil emulsions that may freeze when contacted with the cold ice. These effects will lead to a decrease in the flow properties of the oils, hence decreasing the oil runoff from the sea ice and skimmer materials.

Adhesion is a process working in the boundary layer between the ice and oil, creating the initial contact between the two phases. Due to the high loading of oil to the ice surface during the “dip- and refloat” test, the results indicated that the cohesion properties of the oil dominated the adhesion properties. Cohesion is defined as the property of like molecules of the same substance stick together due to mutual attraction. The amount of oil left on the substrate (sea ice and skimmer material) after runoff phase (in the absence of seawater) was dependent on the yield stress of the oil, which is strongly dependent on the cohesion properties of the oil. The yield stress is defined as the force applied to a medium before the internal structure breaks and the medium starts to flow. Hence, the results showed that Troll B (having low yield stress) had a higher runoff than the more viscous oils Grane Blend and Statfjord C Blend, as less oil was left on the rods after runoff of excess oil.

Depending on the oil properties, different oils exhibited various degrees of adhesion when the oily sea ice and skimmer rods were submerged in seawater after the dipping phase. During the refloat test, no oil was released from the skimmer material, even by shaking the skimmer rods by hand. In contrast, the oil from the moist ice rods (−2 °C) was easily removed, Troll B 150 °C+ residue was completely removed from the ice rods after 2 s and Grane Blend 250 °C+ was refloated after 3 min. For ice at −20 °C, the adhesion between oil and ice was much stronger and it was very difficult to release oil by static refloating. For the most adhered oils, a motion was applied by hand to release the oil from the ice surface. In seawater, the heaviest weathered oils (i.e. Grane Blend 150 °C+ and 250 °C+ and Statfjord C Blend 250 °C+) were released (re-floated) from the ice surface as a banana shape.

### Table 2

<table>
<thead>
<tr>
<th>Oil</th>
<th>IFT&lt;sub&gt;20 °C&lt;/sub&gt; [mN/m]</th>
<th>IFT&lt;sub&gt;−1.8 °C&lt;/sub&gt; [mN/m]</th>
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</thead>
<tbody>
<tr>
<td>Troll B Fresh</td>
<td>13.0</td>
<td>No value</td>
</tr>
<tr>
<td>Troll B 150 °C+</td>
<td>12.5 ± 0.1</td>
<td>8.8</td>
</tr>
<tr>
<td>Troll B 150 °C+ at −1 °C</td>
<td>12.4</td>
<td>8.7</td>
</tr>
<tr>
<td>Troll B 150 °C+ 50% W/O</td>
<td>11.0</td>
<td>11.2</td>
</tr>
<tr>
<td>Troll B 250 °C+</td>
<td>11.5 ± 0.1</td>
<td>7.4 ± 0.1</td>
</tr>
<tr>
<td>Troll B 250 °C+ 50% W/O</td>
<td>35</td>
<td>22.5</td>
</tr>
<tr>
<td>Grane Blend Fresh</td>
<td>10.8</td>
<td>8.1</td>
</tr>
<tr>
<td>Grane Blend 150 °C+</td>
<td>13.0 ± 0.7</td>
<td>10.0 ± 0.5</td>
</tr>
<tr>
<td>Grane Blend 250 °C+</td>
<td>12.6 ± 0.2</td>
<td>10.3 ± 0.3</td>
</tr>
<tr>
<td>Statfjord C Blend Fresh</td>
<td>27.3</td>
<td>10.2</td>
</tr>
<tr>
<td>Statfjord C Blend 150 °C+</td>
<td>26.9</td>
<td>9.8</td>
</tr>
<tr>
<td>Statfjord C Blend 250 °C+</td>
<td>23.2</td>
<td>13.8</td>
</tr>
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* Heptane-insoluble.

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Fig. 9. From left to right, time lapse of adhesion test of Troll B Fresh on sea ice in seawater at −0.5 °C. The drop was in contact with the sea ice but moved upward the needle due to buoyancy. No part of the oil droplet remained at the ice.
peel from the bottom and up, in one continuous piece. Fig. 15 showed the difference in re-floating between oils on cold dry ice (−20 °C) and the re-floating of Statfjord C Blend on cold versus moist ice (−2 °C) after 15 s static re-floating.

While studying the interaction of oil with the cold dry ice, small cracks and structures were observed on the ice surface. Oil migrated to these cracks might function as an “anchor” that help more oil to stick with ice rods. As a result, the oil was released from most of the ice surface, except from sites with irregularities (Fig. 16). For the moist ice (−2 °C), these small cracks would likely be filled with melted seawater and have little or no effect on the re-floating of oil.

4. Conclusions and recommendations

The adhesion and contact angle measurements indicated limited or no interaction of fresh and weathered oils with low salinity (seawater diluted to 0.5 wt% salt concentration) sea ice when the ice surface was submerged in natural seawater (−2 °C). In contrast to the contact angles under sea ice which were in the range of 130°-160°, the contact angle of different oils under the skimmer material submerged in seawater was in the range of 42° to 105° suggesting a considerably stronger interaction than to sea ice. This was further confirmed with an inclination test that suggested a weak adhesion between the oil and ice and the strong adhesion between oil and skimmer material. Both tests also indicated a stronger affinity of non-emulsified oil residues to skimmer material than emulsified residues. These tests further indicated that affinity of the asphaltenic Grane Blend towards the skimmer material was stronger compared to the naphthenic Troll B.

This study also suggests that contact angle measurements can be used as a valuable quantitative parameter and provide as a fast and

Table 3

<table>
<thead>
<tr>
<th>Oil phase</th>
<th>T [°C]</th>
<th>Substrate</th>
<th>Droplet volume remaining [μL]</th>
<th>Contact angle [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Troll B Fresh</td>
<td>−0.7</td>
<td>Sea ice</td>
<td>0</td>
<td>No adhesion −180</td>
</tr>
<tr>
<td>Troll B 250 °C+</td>
<td>−0.6</td>
<td>Sea ice</td>
<td>0</td>
<td>No adhesion −180</td>
</tr>
<tr>
<td>Troll B 250 °C+ 50% W/O</td>
<td>−0.8</td>
<td>Sea ice</td>
<td>0</td>
<td>No adhesion −180</td>
</tr>
<tr>
<td>Grane Blend Fresh</td>
<td>−0.8</td>
<td>Sea ice</td>
<td>0</td>
<td>No adhesion −180</td>
</tr>
<tr>
<td>Grane blend 250 °C+ 50% W/O</td>
<td>−0.8</td>
<td>Sea ice</td>
<td>0</td>
<td>No adhesion −180</td>
</tr>
<tr>
<td>Statfjord Blend Fresh</td>
<td>−0.8</td>
<td>Sea ice</td>
<td>0</td>
<td>No adhesion −180</td>
</tr>
<tr>
<td>Troll B 150 °C+</td>
<td>−0</td>
<td>Skimmer (PE)</td>
<td>0.97</td>
<td>86</td>
</tr>
<tr>
<td>Troll B 250 °C+</td>
<td>−0</td>
<td>Skimmer (PE)</td>
<td>0.71 ± 0.3</td>
<td>86 ± 4</td>
</tr>
<tr>
<td>Troll B 250 °C+ 50% W/O</td>
<td>−0.7</td>
<td>Skimmer (PE)</td>
<td>2.0 ± 0.1</td>
<td>103 ± 1</td>
</tr>
<tr>
<td>Grane blend 250 °C+ 50% W/O</td>
<td>−0.4</td>
<td>Skimmer (PE)</td>
<td>9.0</td>
<td>83</td>
</tr>
</tbody>
</table>

Fig. 10. Image of Troll B 150 °C+ on skimmer material in seawater at −0 °C. The picture shows the remaining oil after 2 min contact time.

Fig. 11. Graphical representation of contact angle and droplet volume of fresh oils, residues and emulsified residues after 2 min contact time on sea ice and skimmer surface immersed in seawater.
reproducible tool for evaluating the interaction of skimmer materials for different oil types under various temperature conditions.

The “dip- and refloat” test also showed a weak adhesion of oil to moist sea ice at −2 °C as the oil was easily released when submerged in seawater. A stronger adhesion of oil was observed with cold dry ice at −20 °C as the oil’s rheological flow properties were reduced due to low temperature. In addition, it was observed that oil migrated into cracks in the cold dry sea ice (−20 °C), which likely anchored oil to the ice surface when immersed in seawater. On the contrary, “dip- and refloat” tests confirmed that the polyethylene skimmer material exhibited a stronger interaction towards the non-emulsified and emulsified oils. The skimmer material did not release any oil when submerged in seawater.

Based on these results, one can expect minor or no adhesion of oil to the skimmer material in seawater.

### Table 4
Contact angle (CA) of fresh oils, residues and emulsified residues under sea ice and skimmer material in seawater. The initial droplet size was 5–50 μL.

<table>
<thead>
<tr>
<th>Oil phase</th>
<th>T [°C]</th>
<th>Substrate</th>
<th>Average CA [°]</th>
<th>Standard deviation</th>
<th>Computation method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Troll B Fresh</td>
<td>−0.5</td>
<td>Sea ice</td>
<td>138</td>
<td>9</td>
<td>DSA</td>
</tr>
<tr>
<td>Troll B 150 °C+</td>
<td>−1.5</td>
<td>Sea ice</td>
<td>129</td>
<td>one data point</td>
<td>Measured manually</td>
</tr>
<tr>
<td>Troll B 250°C+</td>
<td>−1.5</td>
<td>Sea ice</td>
<td>147</td>
<td>4</td>
<td>Measured manually</td>
</tr>
<tr>
<td>Troll B 250°C+ 50% W/O</td>
<td>−1.5</td>
<td>Skimmer (PE)</td>
<td>42</td>
<td>11</td>
<td>1 DSA, 2, 3 and 4 measured manually</td>
</tr>
<tr>
<td>Troll B 250 °C+ 50% W/O</td>
<td>−1.5</td>
<td>Sea ice</td>
<td>157</td>
<td>1</td>
<td>Measured manually</td>
</tr>
<tr>
<td>Troll B 250 °C+ 50% W/O</td>
<td>−1.5</td>
<td>Skimmer (PE)</td>
<td>105</td>
<td>5</td>
<td>1 and 3 DSA, 2, 4 measured manually</td>
</tr>
<tr>
<td>Grane Blend Fresh</td>
<td>−1.5</td>
<td>Sea ice</td>
<td>149</td>
<td>3</td>
<td>1 DSA, 2, 3 measured manually</td>
</tr>
<tr>
<td>Grane Blend 250 °C+ 50% W/O</td>
<td>−1.5</td>
<td>Sea ice</td>
<td>153</td>
<td>3</td>
<td>Measured manually</td>
</tr>
<tr>
<td>Grane Blend 250 °C+ 50% W/O</td>
<td>−1.5</td>
<td>Skimmer (PE)</td>
<td>73</td>
<td>16</td>
<td>1 DSA, 2 measured manually (left side of droplet)</td>
</tr>
<tr>
<td>Statfjord C Blend Fresh</td>
<td>−1.5</td>
<td>Sea ice</td>
<td>161</td>
<td>11</td>
<td>1, 2 measured manually, 3 DSA</td>
</tr>
</tbody>
</table>

* DSA – droplet shape analysis 4 (software).

![Fig. 12](image-url)

Contact angle measurements of fresh and weathered oils/emulsions under sea ice and skimmer material immersed in natural seawater.

![Fig. 13](image-url)

A) Tilting of the sea ice resulted in the oil rolling off at an inclination angle of 10°, indicated by the white line (Statfjord C Fresh) B) Tilting of the skimmer material (polyethylene disc) at an inclination angle of 55°, indicated by the white line, the oil still adhering to the surface (Troll B 250 °C+).
solid sea ice if it is wetted by seawater or being below the melting temperature of sea ice (e.g. in a thawing situation). In case of adhesion to moist sea ice, the oil will most probably be repelled quite easily, either by re-floating or by wave activity. There is no indication in the data that there are differences between the oil types tested or between different weathering degrees (evaporated and emulsified samples). The oil will then be able to migrate along a solid ice edge following the wind and surface current. In the case of oil migrating beneath the ice, one can conclude that the adhesion of oil to the sea ice will be negligible. The spreading of oil under ice will, therefore, be dependent on the velocity of the water current, the direction of the water mass, and the friction between oil and ice, which again will be dependent on the roughness of the ice. A more challenging scenario would be if oil gets trapped in brash or pancake ice, the oil could then be pushed on top of and/or along the edges of the ice floes.

Fig. 14. Weathered oils/emulsions adherence to moist, cold sea ice and skimmer material during “Dip- and refloat” test.

Fig. 15. Immersing oiled ice rods into a container of seawater having a temperature of −0.5 °C. The ice rods are arranged with an increasing weathering degree; 150 °C+, 150 °C+ 50% W/O, 250 °C+, 250 °C+ 50% W/O (from left to right) in each picture. Time: 15 s after submerging.
Acknowledgement

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References


Fig. 16. Illustration of oil filling the cracks and cavities on the cold sea ice.