

1    **Oil droplet interaction with suspended sediment**

2    **in the seawater column: Influence of physical**

3    **parameters and chemical dispersants**

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10    KEYWORDS

11    crude oil; suspended particulate material; adsorption; chemical dispersant; temperature;

12

## 1 ABSTRACT

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

13

1    INTRODUCTION

2    Oil spilled at sea may reach a variety of environmental compartments depending on  
3    environmental and climatic conditions, location and response strategies employed. Stranding  
4    of spilled oil on beaches is typically considered a worst case scenario owing to the potential  
5    impacts on wildlife and human installations. Oil spills often occur in coastal regions and  
6    coincide with poor weather conditions, where turbulent conditions at the sea surface (wave  
7    action) can lead to the breaking up of oil slicks into small droplets (<100 µm) through  
8    mechanical dispersion. These droplets become dispersed into the water column where the  
9    surface area of the oil in contact with seawater increases resulting in corresponding increases  
10   in the rate of other weathering and transport processes such as dissolution, biodegradation,  
11   adsorption to suspended particulate matter (SPM)<sup>1-4</sup>. Sedimentation to seafloor also increases  
12   which may cause severe damage to marine benthic ecosystems<sup>5-7</sup>. Response strategies to  
13   prevent stranding of oil on shorelines have traditionally included use of adsorbent or  
14   protective booms to collect or trap surface oil. However, this technology is not very efficient  
15   and becomes unsuitable in turbulent weather and sea conditions. As a result, chemical  
16   dispersants are increasingly used as they enhance the formation of oil droplets and mixing of  
17   surface oil into the water column, thus increasing the rate of natural weathering and transport  
18   processes. Currently, chemical dispersants are only used in open waters due to the uncertainty  
19   of how chemically dispersed oil will behave in shallow waters. However, as oil exploration  
20   has moved closer to coastal areas in recent years the debate and research activity regarding  
21   near-shore dispersant strategies has increased correspondingly<sup>8</sup>.

22

23   It is generally accepted that oil-SPM aggregates form when oil droplets collide and adhere to  
24   SPM in aqueous environments<sup>9, 10</sup>. Guyomarch et al.<sup>11</sup> suggest that formation of oil-SPM

1 aggregates is driven by interactions between polar oil compounds and negatively charged  
2 particles. There are, however, conflicting reports regarding the relative importance of SPM  
3 adsorption on the removal of oil from the water column. Using a numerical model, Bandara et  
4 al.<sup>12</sup> showed that more than 80 % of a spilled oil can interact with suspended particulate  
5 materials (SPM), and that up to 65 % of released oil may be removed from the water column  
6 as oil-particle aggregates. In contrast, Muschenheim and Lee<sup>1</sup> have reviewed field and  
7 enclosure studies and noted that the general opinion is that a maximum of 20-30 % of the  
8 spilled oil can be adsorbed and subsequently sedimented. From empirical studies, Kirstein (in  
9 Payne et al.<sup>13</sup>) derived a description for the rate of loss of free oil droplets from the water  
10 column, as they collide and adhere to SPM. Their study demonstrates that oil droplet  
11 concentration, SPM-concentration and SPM-characteristics will be of importance to the  
12 adhesion of oil droplets to sediment. In reality, it is most likely that the amount adsorbed to  
13 SPM will be influenced by environmental parameters and the properties of the spilled oil.  
14 However, many studies have focused on the adsorption of oil droplets with small-sized  
15 suspended particulates (typically clay particles). In contrast, the interaction of oil droplets  
16 with large-sized particulate material which may become suspended in the water column in  
17 near-shore high energy coastal areas has been little studied. Owing to their large size, such  
18 particles may offer a rapid transport route for oil droplets to the sediment.

19

20 The application of chemical dispersants to an oil slick increases the formation of oil droplets  
21 and droplets of reduced size, when compared to naturally/mechanically dispersed oil<sup>14-17</sup>.  
22 The chemical dispersant reduces the interfacial tension between the oil and seawater, and  
23 hence stabilize the formation of oil droplets, normally sized 10-15 µm<sup>3, 18</sup>. Lessard and  
24 DeMarco<sup>18</sup> present one of the advantages of dispersant application as the reduction of  
25 “stickiness” of the oil, indicating that chemically dispersed oil droplets are less likely to

1 adhere to SPM and other solids. This is supported in studies by Mackay and Hossain <sup>19</sup> and  
2 Page et al. <sup>8</sup> who observed that chemically dispersed oil associated less with mineral matter  
3 than naturally dispersed oil. However, a number of other studies show conflicting results,  
4 reporting that oil and SPM will form aggregates efficiently despite dispersant being added <sup>11</sup>,  
5 <sup>14, 20, 21</sup>.

6

7 Khelifa et al. <sup>14</sup> report that oil-SPM aggregate formation was the same, regardless of  
8 dispersant application, concluding that chemical dispersants did not form a barrier to oil-SPM  
9 aggregation. The authors suggest the reduction in size and increase in concentration of oil  
10 droplets in the water column, the alteration of surface properties of the oil droplets and that  
11 the smaller, chemically dispersed droplets will require less solid material (fines, clay) in order  
12 to sink all contributed to the observed results. Model simulations have also shown that the  
13 presence of smaller droplets (< 100 µm) increased the predicted amount of oil-SPM  
14 aggregates formed<sup>12</sup>. It was suggested that droplet residence time in the water phase is  
15 prolonged due to the decreased buoyant velocity of smaller particles, allowing for more  
16 interaction with SPM.

17

18 At present, there are still significant knowledge gap concerning the fate and transport of  
19 dispersed oil in the marine environment. Adsorption onto SPM and subsequent sedimentation  
20 is one potentially important route for such dispersed oil droplets, but the process is poorly  
21 understood, especially in the presence of chemical dispersants. This study investigates how  
22 parameters such as oil type, size and type of suspended particulate matter (sediment  
23 characteristics) and temperature, which are relevant parameters in near shore high energy  
24 coastal areas impacted by oil spills, govern oil-SPM interactions. In addition, the role of

1 chemical dispersants on the adsorption of oil droplets to SPM is also investigated in this  
2 study. The current study wishes to answer some of the questions regarding the behaviour of  
3 chemically dispersed oil and its interaction with mineral particles. This is highly relevant for  
4 shallow waters where high energy wave action may suspend particles of larger sizes and  
5 greater quantities than you could expect in coastal waters.

6 **MATERIALS AND METHODS**

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

12

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

22

1 Seawater (salinity ( $33,5 \pm 0,2$  ‰)) was pumped from a depth of 90 meters in Trondheim fjord  
2 ( $63^{\circ}26'N$ ,  $10^{\circ}26'E$ ) and filtered by a sand filter (50  $\mu m$ ). The three natural sediments used in  
3 this study were collected at different locations around Trondheim, Norway. *Carbonate sand*  
4 was collected from Grandefjæra ( $+63^{\circ}40'N$ ,  $+9^{\circ}32'E$ ), *quartz sand* from Hansbakkfjæra  
5 ( $+63^{\circ}25'N$ ,  $+10^{\circ}32'E$ ) and *clay* from Buvika ( $+63^{\circ}18'N$ ,  $+10^{\circ}10'E$ ). The sediments were  
6 flushed with clean seawater, dried at 100 °C and passed through a 2 mm sieve before use in  
7 experiments. The grain size distribution of the carbonate sand was concentrated between 90-  
8 500  $\mu m$  with a maximum in the range 180-250  $\mu m$ . The grain size distribution of the quartz  
9 sand was between 90-2000  $\mu m$  with a maximum in the range 250-355  $\mu m$  (S1;  
10 Supplementary Information). The average grain size of the Buvika clay was  $< 63 \mu m$ .

11

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

1

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

6

7 Sediment samples were Soxhlet extracted for 6 hours in cellulose thimbles (Whatman, type  
8 603) using DCM (50 mL). Surrogate internal standards were added to the sediment prior to  
9 extraction. The extract was filtered through cotton wool, dried with anhydrous sodium  
10 sulphate ( $\text{Na}_2\text{SO}_4$ ) and the solvent volume reduced to approximately 0.5 mL using a gentle  
11 stream of  $\text{N}_2$ . Prior to analysis, sediment extracts were subject to clean-up by elution through  
12 Supelco® Bond-Elut silica SPE columns (500 mg). Surrogate internal standards were added  
13 to the water phase samples, followed by liquid-liquid extraction using DCM (1 x 120 mL and  
14 2 x 60 mL). The organic extracts were combined and dried with  $\text{Na}_2\text{SO}_4$ . Recovery internal  
15 standards were added to all samples, and final volume adjusted to 1 mL prior to analysis.

16

17 All water and sediment extracts were analysed by GC-FID to determine the total extractable  
18 organic matter (TEOM). The GC-FID system comprised an Agilent 7890A GC fitted with an  
19 Agilent J&W HP-5 fused silica capillary column (30 m length, 0.25 mm id and film thickness  
20 0.25  $\mu\text{m}$ . The carrier gas was helium (grade 4.6), at a constant flow of 1.5 mL/min. 1  $\mu\text{L}$  of  
21 sample was injected using pulsed splitless injection. The temperature was held at 40 °C for 1  
22 min ramped by 6 °C/min until 315 °C and held at 315 °C for 15 min. A selection of samples  
23 were analysed by GC-MS to determine the content of semi-volatile organic compounds

1 (SVOCs), including PAHs. The GC-MS system comprised an Agilent 6890N GC equipped  
2 with an Agilent 5975B quadrupole mass-selective detector (MSD) and EI ion source. The GC  
3 was fitted with an Agilent J&W HP-5MS fused silica capillary column (60 m length, 0.25 mm  
4 id and film thickness 0.25 µm). The carrier gas was helium (grade 6.0) at a constant flow of  
5 1.2 mL/min. 1 µL of sample was injected at 310 °C using pulsed splitless injection. The  
6 temperature was held at 40 °C for 1 minute, then increased at 6 °C/min to 315 °C and held for  
7 15 minutes.

8

## 9 RESULTS AND DISCUSSION

10 The effect of oil type on oil-SPM adsorption was studied at 20 °C using the carbonate sand to  
11 represent large particulate material which may be suspended in the water column from the  
12 sediment in high energy coastal environments. When compared to the pure oils, GC-FID  
13 analysis of the sediment extracts from the four test oils (Table 1) shows a loss of the earliest  
14 eluting components (< C<sub>15</sub>) and an increase in the heavier oil compounds in the sediment  
15 adsorbed samples (Figure 1). This indicates that the lighter compounds are preferentially  
16 retained in the water column leading to a relative enrichment of the heavier compounds in the  
17 oil adsorbed to the sediment adsorbed. The change in relative distribution of the oil  
18 components is consistent with the higher aqueous solubilities of lower molecular weight  
19 compounds and indicates that these compound types preferentially dissolve from the oil  
20 droplets into the water column.

21

22

1    *Effect of oil type*

2    Although the four oil types exhibited similar changes in the distribution of oil components

3    following adsorption, significant differences in the total amount of oil adsorbed to the

4    carbonate sand were observed (Figure 2). Adsorption of the oils was in the following order:

5    IF 380 (heavy fuel oil) (~15 mg) > Avaldsnes crude (~11 mg) > Troll crude (~6 mg) >

6    Kvitebjørn condensate (~4 mg). In contrast, the amount of oil in the water soluble fraction

7    (WSF) was similar (0.5-1 mg) for all oil types. In a study of oil-mineral aggregates,

8    Guyomarch et al.<sup>11</sup> report that the oil/clay ratio of four different crude oils increased with

9    increasing asphaltene content of the oils. It is suggested that the formation of oil-mineral

10   aggregates is caused by the interactions of polar oil compounds and the negatively charged

11   clay particles<sup>11</sup>. As asphaltenes contain high amounts of oxygen, nitrogen and sulphur (NSO)

12   atoms, the asphaltene content can be viewed as a measure of an oil type's polarity. As a result,

13   the high polarity of the asphaltenes could be responsible for preferential adsorption of

14   asphaltene-rich oils to SPM. The extraction of asphaltene-rich oils from reservoirs is well

15   known to be problematic due to asphaltenes adsorbing on to mineral components of reservoir

16   rock and leading to issues with clogging<sup>22-25</sup>. The resin fraction of crude oil also contains

17   NSO atoms and this polar fraction is therefore also likely to play a role in oil-SPM

18   interactions. Resins are strongly adsorbed to asphaltenes when water is present, and it is very

19   difficult to quantitatively separate them from asphaltenes<sup>26</sup>. The complex interactions

20   between asphaltenes and resins make understanding their influence on oil-SPM interactions

21   very difficult. As a result, this has not been studied in any detail. That the asphaltenes have a

22   special property in relation to the oil-SPM interactions is well documented, but that this

23   unilaterally relates to polarity is unclear.

1 In the current study, the asphaltene content (Table 1) of Avaldsnes crude is >10 times higher  
2 than that of the Troll crude and Kvitebjørn condensate. This indicates that asphaltene content  
3 significantly influences the quantity of oil which partitions to large carbonate sand SPM, and  
4 is consistent with previous studies looking at small clay SPM<sup>11</sup>. Although the asphaltene  
5 content of the heavy fuel oil (IF 380) used in this study is not known, standard heavy fuel oil  
6 contains up to 14% asphaltenes and a high quality fuel oil up to 8% asphaltenes. The  
7 asphaltene content of IF 380 will therefore be significantly higher than that of the crude oils  
8 used in this study (max 2.2 % asphaltenes) and would therefore be expected to adsorb to SPM  
9 in the highest amount (Figure 2).

10

11 In the study by Guyomarch et al.<sup>11</sup>, the viscosities of the test oils increased with increasing  
12 asphaltene content, indicating that viscosity could also be an important parameter in  
13 controlling oil-SPM interaction. However, the same relationship between asphaltene content  
14 and viscosity was not observed in the present study (Table 1 and Figure 2). This indicates that  
15 asphaltene content is of greater importance than viscosity to the adsorption properties of an oil  
16 type. In the hours immediately following the release of a fresh crude oil, significant amounts  
17 of the lighter compounds will be lost due to evaporation and dissolution (especially in high  
18 energy environments) thus enriching the relative concentration of the asphaltene fraction. The  
19 remaining oil will therefore have a propensity to adsorb to both small (clay<sup>11</sup>) and large  
20 (carbonate sand; this study) SPM. In the present study, the IF 380 fuel oil adsorbs in greater  
21 quantities to SPM than the artificially weathered crude oils. This indicates that removal  
22 process from the water column via adsorption to SPM and transport to the sediment will be  
23 more significant for fuel oils than for weathered crude oils.

24

1 When compared to the pure oils, GC-MS analysis of the sediment extracts from the  
2 experiments using IF 380 Fresh and Troll 250 °C+ oil types show that the PAHs (3-6 rings,  
3 including alkylated homologues) are preferentially enriched in the carbonate sand SPM,  
4 whilst the decalins and naphthalenes are clearly reduced (Figure 3). In the corresponding  
5 WSF extracts, the naphthalenes are enriched, but are almost free of decalins and 4-6 ring  
6 PAHs. This is consistent with the knowledge that the solubility of individual PAHs in water  
7 will decrease exponentially with increasing number of aromatic rings<sup>27</sup> and log  $K_{ow}$ <sup>28, 29</sup>.  
8 WSFs generated from nine different Norwegian crude oils<sup>30</sup> and ten different Kuwaiti crude  
9 oils were all dominated by naphthalenes and phenols<sup>31</sup>. These two studies show excellent  
10 agreement with the current study, indicating that the naphthalenes will be the dominant  
11 hydrocarbon species in the water column near an oil spill (dispersed droplets or slick).

12

13 The findings of the current study with a large particle diameter carbonate sand are consistent  
14 with results from previous studies<sup>10, 32, 33</sup>, which demonstrate that higher-molecular weight  
15 aliphatics and PAH components prefer to partition to small diameter SPM (e.g. clay) in a  
16 water-oil-SPM system. Payne et al.<sup>10, 32</sup> have specifically shown that C<sub>10</sub>-C<sub>40+</sub> aliphatics and  
17 alkyl-substituted 3-5 ring PAH compounds (log  $K_{ow}$  values > 4) prefer to associate with  
18 particles rather than dissolve in the water column. The same studies showed that monocyclic  
19 aromatics with log  $K_{ow}$  values between 2,1 and 3,7, the more volatile C<sub>1</sub>-C<sub>10</sub> aliphatics and  
20 some lower molecular weight 2-3 ring PAH's with log  $K_{ow}$  values between 3,7 and 4,8 would  
21 preferentially partition to the water column<sup>10</sup>.

22

23

1    *Effect of sediment type*

2    The influence of sediment (SPM) type on oil droplet adsorption was investigated using Troll  
3    crude oil at 20 °C. Figure 4 shows that the adsorption of oil varies with the type of SPM. Per  
4    gram of SPM, the clay adsorbs 2-3 times more oil (present as dispersed oil droplets at 20  
5    mg/L) from the water column with, than the two sand types used in this study. There is no  
6    significant difference in adsorption between the carbonate sand and the quartz sand, which is  
7    consistent with their similar grain size distributions. This also indicates grain size is a  
8    dominant factor in controlling adsorption of oil to SPM, and that mineral particle chemistry  
9    may play less of a role, at least for particles of a similar grain size distribution. For equivalent  
10   masses of SPM (as used in this study) clay contains more but smaller individual particles, and  
11   will therefore have a significantly larger surface area for oil to adsorb. However, the  
12   relationship between surface area and amount of oil associated with the particles does not  
13   appear linear. The amount of oil associated with the clay SPM is 2-3 times higher than for the  
14   sand SPMs. In contrast, the available surface area of the clay is much greater than 2-3 times  
15   that of the sand SPM indicating other processes become controlling factors in adsorption. It is  
16   important to consider that the water column also contains biological SPM such as algae and  
17   plankton which will influence the amount of oil removed from the water column.

18

19   The interaction of clay particles (or small mineral fines) and crude oil has been studied  
20   previously in some detail, and a number of parameters appear to influence the process. The  
21   concentration of oil-mineral aggregated droplets has been shown to be determined mostly by  
22   oil type, but that the droplet size was influenced by clay type and water salinity<sup>34</sup>. Although  
23   different clay types have been observed to promote aggregates of different shapes (droplet,  
24   flake, solid)<sup>35</sup>. Clay concentration also appears to influence the size of oil-mineral aggregates

1 formed, with the largest aggregates formed at a specific clay load. Lower or higher loads led  
2 to significantly smaller aggregates<sup>11</sup>. In many cases, the aggregates appear as oil droplets  
3 coated with fine particulates<sup>9, 11, 20, 34-37</sup>. It is therefore questionable whether the results of  
4 studies using clay can be directly extrapolated and compared to the current study which  
5 investigates the influence of larger particles present in the water column in high energy near-  
6 shore environments. It is most likely that the larger sand particulates will be coated with oil  
7 droplets indicating a very different method of SPM-oil droplet interaction than that observed  
8 for clay. As a result, the formation of aggregates and the amount of oil associated with SPM  
9 appears to be directly linked to the ratio between SPM diameter and oil droplet diameter. In  
10 simulations of oil-SPM aggregation using a numerical model, Bandara et al.<sup>12</sup> showed that  
11 SPM sizes > 500 µm led to less aggregate formation than smaller sizes (< 63 µm), and  
12 explained this by a reduction in SPM number density in the water column. Under normal  
13 environmental conditions, natural waters are dominated by SPM < 2 µm<sup>38</sup>. Under high  
14 energy conditions, it could reasonably be expected that particles of greater size (e.g. sand) will  
15 suspend in the water column and contribute to an increased partitioning of oil to the SPM  
16 load.

17

18 *Effect of sea water temperature*

19 The effect of varying seawater temperature (5, 10, 15, 20 °C) on the adsorption of Troll crude  
20 oil to the carbonate sediment (15 g) was also studied (S2; Supplementary information). The  
21 results demonstrate that the oil adsorbs in the highest quantities (~11 mg) at low temperatures  
22 (5 °C), whilst the amounts adsorbed at 10, 15 and 20 °C are approximately the same (~6-7  
23 mg). These data support similar observations reported in other studies investigating the  
24 influence of temperature on the adsorption of hydrocarbons to SPM<sup>39 40</sup>. The decrease in

1 adsorption with increasing temperature was attributed to the corresponding increase in  
2 solubility of hydrocarbons. Interestingly, one previous study describes a reduction in the oil  
3 content of oil-mineral aggregates at 0 °C when compared to 20 °C which was attributed to the  
4 increased viscosity of oil at low temperature <sup>35</sup>. However, in the study, the authors employed  
5 a low mineral to oil ratio which at low temperature would reduce oil dispersibility and lead to  
6 low interaction of oil and SPM. Under the conditions employed in the current study, a  
7 significant increase in adsorption due to decreased seawater temperature is only observed at 5  
8 °C. This is consistent with observations in previous studies and indicates that increased  
9 viscosity of oil due to decreased temperature (and hence increased "stickiness") results in  
10 higher sorption to particulates. However, the process appears to be more significant at lower  
11 temperatures.

12

13 *Effect of chemical dispersant*

14 The influence of Dasic Slickgone NS chemical dispersant on adsorption of Troll crude oil to  
15 carbonate sand was investigated at a seawater temperature of 20 °C. Increasing the dispersant  
16 to oil ratio (DOR) from 0-5 % decreased the amount of oil adsorbed to SPM (Figure 5).  
17 Addition of 1 % dispersant leads to ~50 % reduction in the amount of oil adsorbed to  
18 carbonate sand SPM whilst 5% dispersant leads to 75 % reduction. The relationship therefore  
19 appears to be exponential ( $R^2= 0.9587$ ), and indicates that addition of chemical dispersant  
20 above the highest DOR tested in this study (5%) would not significantly reduce the adsorption  
21 of oil to sediment further. Importantly, the removal of dispersed oil from the water column  
22 through adsorption to SPM and subsequent sedimentation appears to continue, albeit in a  
23 lower amount, when chemical dispersants are used. Figure 5 also shows that the amount of oil  
24 dissolved in the water column does not change when dispersant is added.

1  
2 The chemical composition of the semi-volatile oil components (SVOC) adsorbed to the  
3 carbonate sand and dissolved in the water column was investigated (Figure 6). An overall  
4 reduction in the amount of SVOC compounds being adsorbed to SPMs was observed in the  
5 case where dispersant (DOR = 1 %) was added to the oil. However, no significant differences  
6 in the relative distribution of SVOC compounds adsorbed were observed in either the SPM or  
7 WSF samples with and without addition of dispersant. This indicates that the chemical  
8 composition of oil droplets is unchanged in the presence of the chemical dispersant,  
9 suggesting no significant effect on dissolution of compounds from the oil droplets. Similar  
10 observations for naphthalene have been made in a previous study <sup>41</sup>. Whilst the dispersant  
11 does not directly affect the partitioning of individual components (or groups of components)  
12 to the water phase, it does reduce the affinity of the oil droplets for the large carbonate sand  
13 SPM. This reduction in adsorption of oil to SPM may be due to the surfactants in the  
14 dispersant stabilizing the smaller oil droplets in the water column (and thus counteracting  
15 adsorption to particulates). The stabilizing effect of dispersants on oil droplets has been  
16 previously described <sup>18 3</sup>.

17  
18 Mackay and Hossain <sup>19</sup> also observed that chemical dispersants inhibited the adsorption of oil  
19 to sediments, while Lessard and DeMarco <sup>18</sup> suggest it is less likely that a chemically  
20 dispersed oil will adhere to SPMs, as it is “less sticky” than a naturally dispersed oil. In  
21 contrast, other studies have found that chemical dispersants did not inhibit the formation of  
22 oil-SPM aggregates <sup>14 12</sup>. At low loads of clay particles (< 25 mg/L), Khelifa et al. <sup>14</sup> observed  
23 that chemical dispersant increased oil sedimentation by a factor of 3-5. For higher mineral  
24 loads, adsorption was equal for experiments with and without chemical dispersant. A

1 reduction in oil droplet size, increase in concentration of oil droplets in the water column and  
2 the alteration of surface properties of the oil droplets are reasons suggested for the increased  
3 adsorption. Numerical model simulations have shown that the presence of smaller oil droplets  
4 increases the predicted amount of oil-SPM aggregates<sup>12</sup>. The authors suggested that droplet  
5 residence time in the water column is prolonged due to the decreased buoyant velocity of  
6 smaller particles, allowing for more interactions with SPM.

7

8 Studies showing increased oil adsorption in the presence of chemical dispersant used fine clay  
9 particles, where the current study used carbonate sand. The interaction mechanism of small  
10 (clay) particles and larger particles (e.g. sand) with oil droplets appears different due to the  
11 SPM:droplet size ratio (this study). The smaller diameter and increased surface area of the  
12 chemically dispersed oil droplets might increase the adsorption of fine mineral particles on  
13 their surface. This would not be observed with the larger sand particles where droplets would  
14 be expected to adsorb to the surface of the particle. The reduction in adsorption to sand  
15 particles might therefore be explained by “less stickiness” of the oil<sup>18</sup>. Alternatively, smaller  
16 grains may reside for longer in the water column, therefore having the opportunity to interact  
17 more with dispersed oil<sup>19</sup>. Irrespective of the process occurring, there is currently no clear  
18 explanation as to why some studies have observed more association of oil-SPMs with  
19 dispersant added than without.

20

## 21 CONCLUSIONS

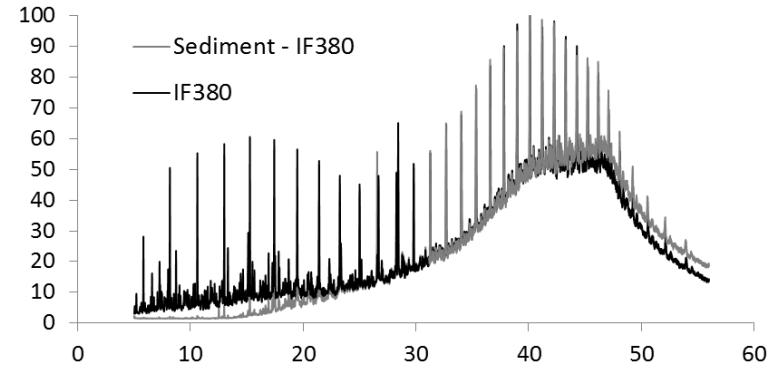
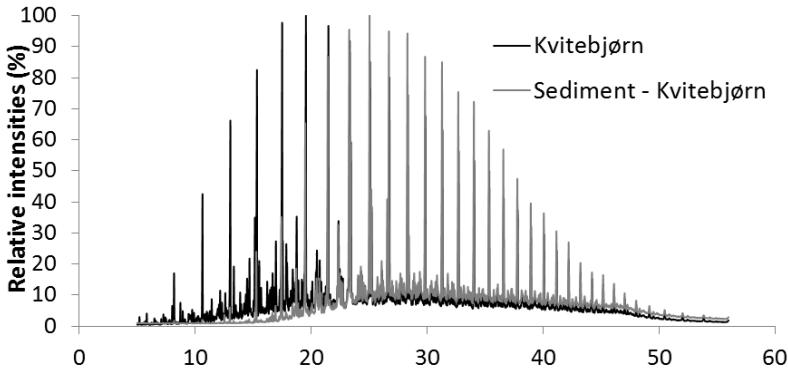
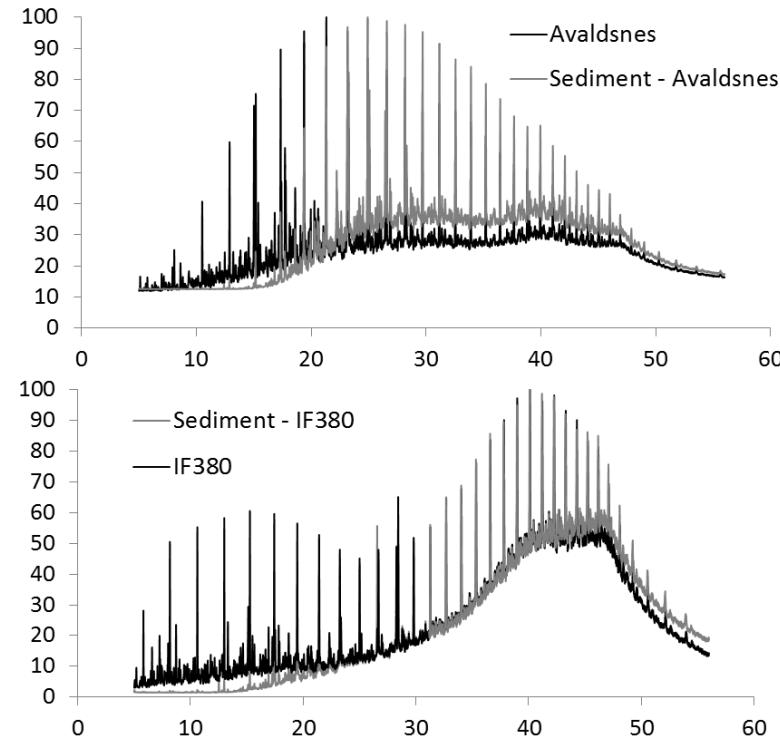
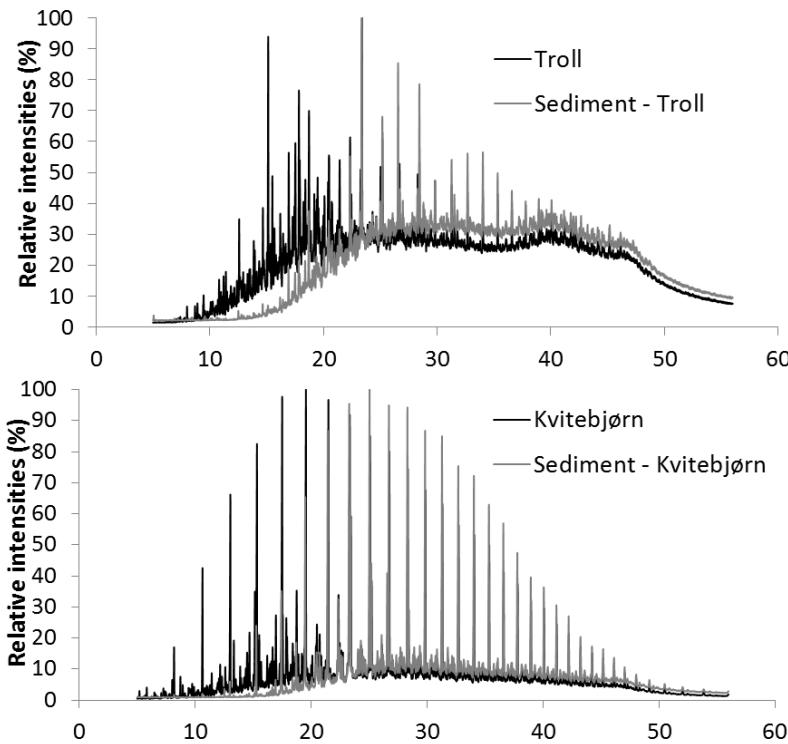
22 The current study shows that oil type and SPM type (grain size and ratio to oil droplet size)  
23 significantly influence the degree spilled oil in the marine environment will adsorb to SPM.

1 Seawater temperature may also play an important role, especially at low temperatures ( $\leq 5^{\circ}\text{C}$ )  
2 relevant to northern or southern ocean environments. However, the combined influence of  
3 these parameters on each other is complex and still represents a significant knowledge gap in  
4 our understanding of SPM adsorption and sedimentation of oil droplets in the marine  
5 environment. In addition, location specific parameters related to climate and seawater  
6 conditions (e.g. energy of the marine system, storm conditions) will also exert some influence  
7 on adsorption of oil to SPM. In a high energy coastal marine environment the water column is  
8 likely to contain relatively high SPM-loads (both large and small grain sizes) which will offer  
9 an increased potential for oil droplet adsorption. Adsorption of chemically dispersed oil  
10 droplets to SPM will also increase or decrease depending on the type (clay or sand SPM) and  
11 composition (ratio of clay to sand SPM) of SPM present in the water column. The use of  
12 chemical dispersant on spilled oil in near-shore environments should therefore be considered  
13 carefully based on parameters such as local SPM size and type, oil type released, temperature  
14 and other environmental conditions such as high vs. low energy systems.

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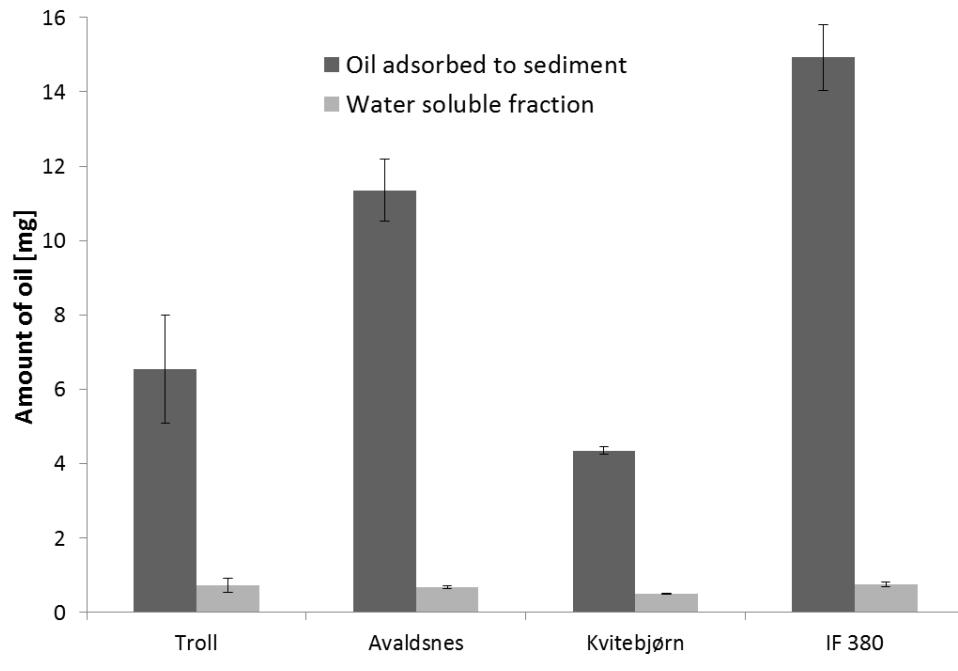
## 16 ACKNOWLEDGEMENTS

17 The work was funded mainly by the Norwegian Research Council. The authors wish to  
18 acknowledge Anders Olsen and Trond Nordtug for constructing the oil-droplet generator. We  
19 also thank the technical staff at SINTEF Environmental Technology for their assistance with  
20 the experimental work and chemical analysis.



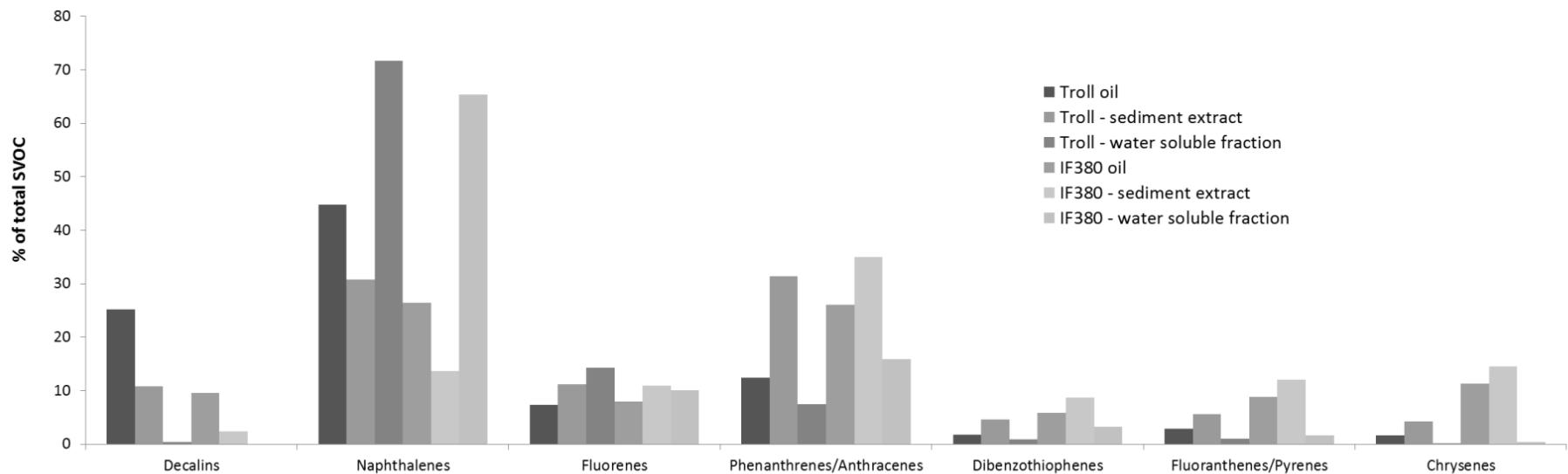
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2 Figure 1. Comparison of chromatograms for all four oils and sediment extracts of experiments where the oils have been applied.



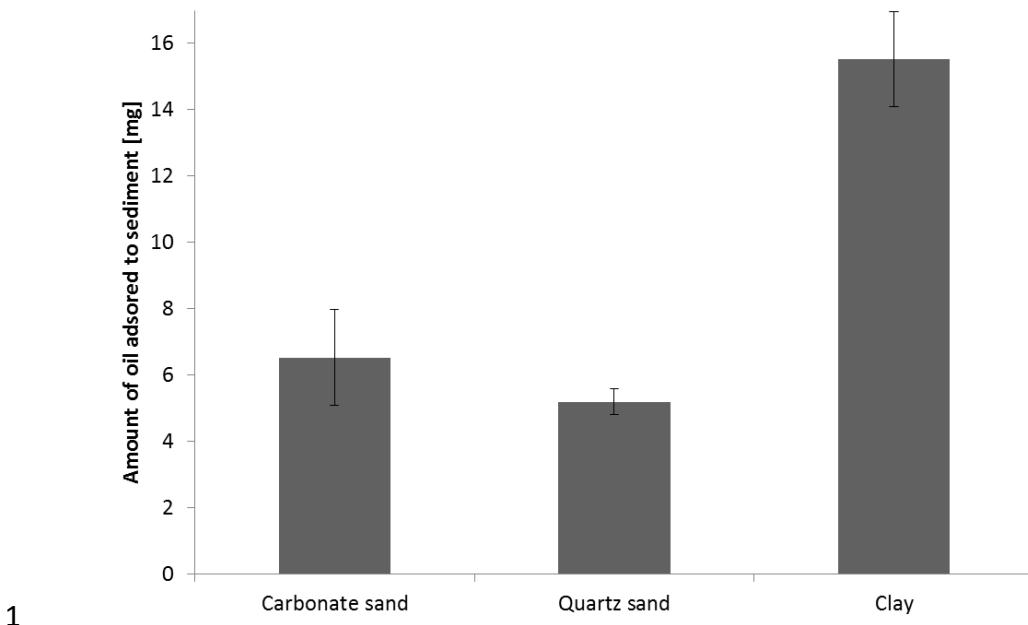
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2 Figure 2. Variation in oil adsorbed to sediment and dissolved in water (mg)  
3 as a function of  
oil type (Error bars represent standard deviation, n= 7; 3; 3; 3).

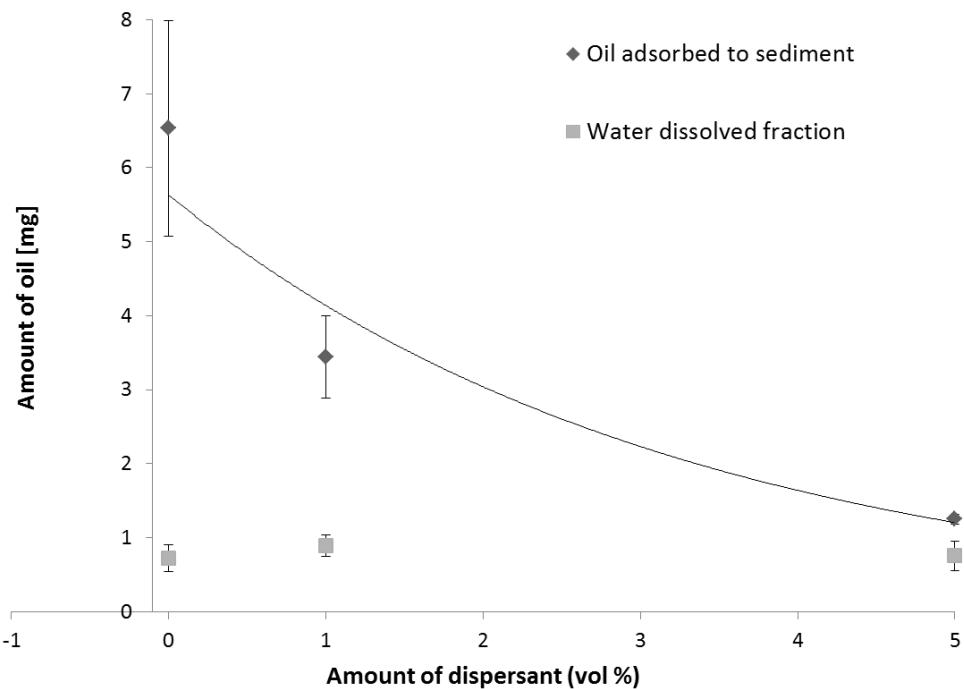


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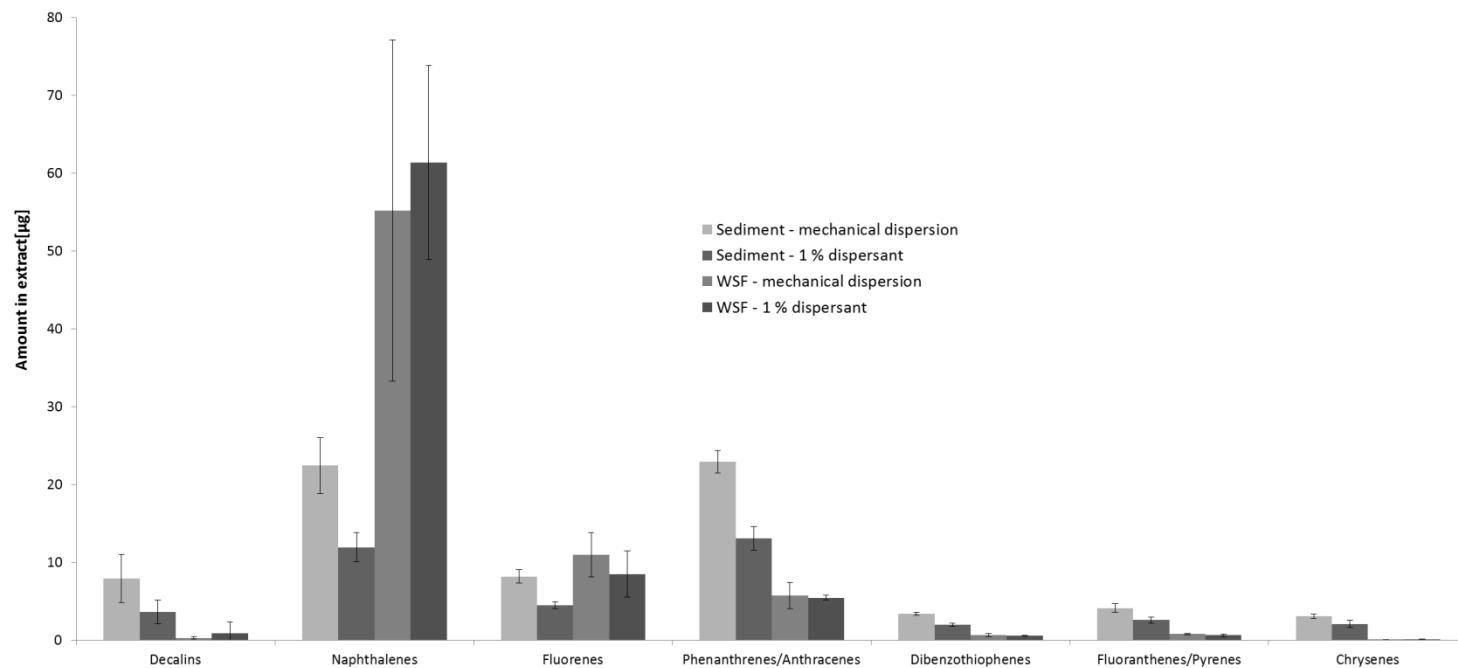
2     Figure 3. Comparison of SVOC profiles of Troll 250 °C+ and IF380 Fresh oils together with the corresponding sediment adsorbed fraction and  
3     WSF of these oils.



2 Figure 4. Variation in oil uptake (mg) in sediment as a function of sediment type (Error bars  
3 represent standard deviation, n=7; 4; 3).



6 Figure 5. Variation in oil adsorbed to sediment and dissolved in water (mg) as a function of  
7 amount dispersant added (Error bars represent standard deviation, n= 7; 5; 3).



1

2     Figure 6. Profile of semi-volatile organic compounds in WSF and sediment extracts from experiments with (1 %) and without chemical  
3     dispersant.

1 Table 1. Physico-chemical properties of the four test oils used in the study.

<b>Name</b>	<b>Type of oil</b>	<b>Density [g/cm<sup>3</sup>]</b>	<b>Viscosity at 13 °C [cP]</b>	<b>Asphaltene content [wt%]</b>	<b>Wax content [wt%]</b>
Troll	Crude oil, topped 250+	0.9296	247	0.08	1.93
Avaldsnes	Crude oil, topped 250+	0.9353	2044	2.2	3.7
Kvitebjørn	Condensate, topped 250+	0.8534	4090	0.15	9.18
IF 380	Heavy fuel oil	0.9631	N/A	N/A	N/A

2

3

4

5 Table 2. Summary of the experimental parameters studied. Italic text indicates the standard  
6 experimental parameters used as basis for variation.

<b>Oil type</b>	<b>Temperature (°C)</b>	<b>Dispersion method</b>	<b>Sediment type</b>
<i>Troll crude</i>	20 °C	<i>Mechanical</i>	<i>Carbonate sand</i>
Avaldsnes crude	15 °C	Mechanical and	Quartz sand
Kvitebjørn condensate	10 °C	chemical; 1 and 5 % dispersant	Clay
IF380 heavy fuel oil	5 °C		

7

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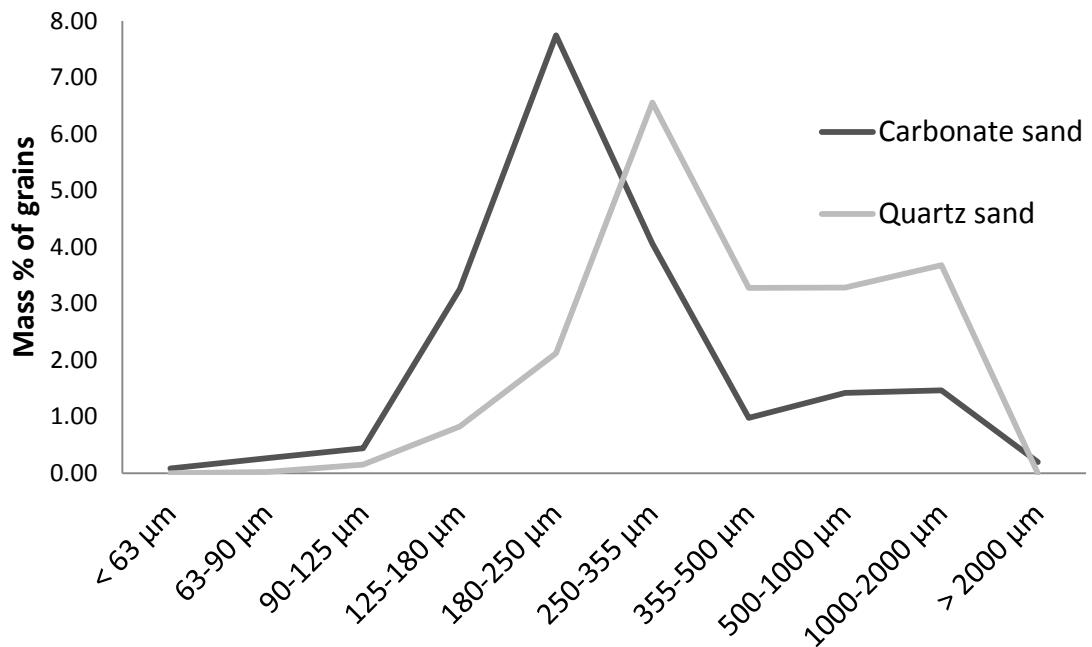
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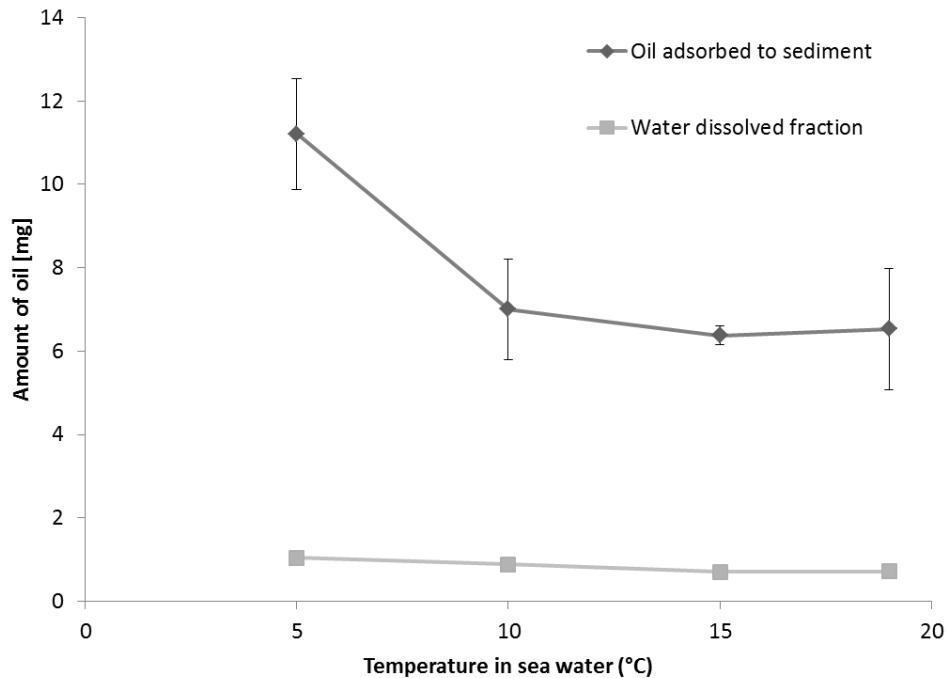
## 1 SUPPLEMENTARY INFORMATION



2

3 S 1. Grain size distribution of carbonate sand and quartz sand used in the experiments.

4



1

2 S 2. Effect of temperature on the adsorption of oil to sediment and dissolution of oil  
3 components to the seawater column.