The Effectiveness of Dispersants on Oil Encapsulated in Ice for Extended Periods

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Abstract

Oil spill response in ice-prone regions requires access to all response tools because of the multiple challenges that ice produces. Oil spilled in ice can become rapidly encapsulated into the ice during the ice-growth season. This encapsulation minimizes marine organisms contactwith oil, but also restricts / eliminates access to the oil for response. Encapsulation also prevents oil slick evaporation, dispersion and emulsification to any significant degree and allows responders to track the oil through the winter and respond to the released oil during the spring melt.

This paper describes research to determine if oil encapsulated in ice for long periods remains dispersible after ice melt. In 2015 the Arctic Response Technology Joint Industry Programme (JIP) executed a unique, long-term mesocosm experiment to improve the scientific knowledge of the fate and biodegradation of oil and oil spill response residues in ice, as well as the environmental effects to ice associated ecology. Several mesocosms were installed in the sea ice of the Van Mijenfjorden in Svea, Svalbard in February and remained in place until May. Oil was introduced into two mesocosms and allowed to freeze in without any treatment. In two other mesocosms oil pre-mixed with dispersant was introduced and was allowed to freeze in. Ice cores were collected from all mesocosms at periods of 1, 2, and 3 months. These ice cores were subsequently melted in the CEDRE laboratory to simulate spring ice melt and the release of oil into open water. Effectiveness of dispersion was tested with untreated oil, oil treated with dispersants after the melt and oil pre-mixed with dispersant prior to being frozen into ice.

Results of this study provide valuable information for planning dispersant operations for oil spills in ice-covered waters.

1 Introduction

Arctic oil production both onshore and offshore has produced greater than 25 billion barrels of oil (IHS, 2014). Oil production in the Arctic began almost 100 years ago with Norman Wells field in Canada's Northwest Territories. Offshore Arctic exploration began over 40 years ago and has led to the completion of approximately 440 wells (IHS, 2014).

A distinguishing feature of the Arctic is the presence of ice for all or part of the year. The extent, thickness, and duration of ice vary throughout the Arctic and from year to year. During the summer and fall many areas are ice free for significant periods. In the near term, offshore oil exploration will likely occur during these ice-free periods. Therefore, any oil spill response planning for these operations will include developing strategies for these open water periods. However, robust contingency planning will include scenarios where oil could become entrapped in ice.

The dynamic nature of the Arctic (ice cover, low temperatures, remoteness, and extended periods of darkness) causes some unique challenges for Arctic activities including oil spill response. These challenges are well known and often described. However, one benefit of ice cover and subsequent encapsulation of spilled oil is the significant benefit of extending response times (Sørstrøm et al., 2010). Rapid response is often necessary for spills to open water because of the dynamic nature of spilled oil – slicks are rapidly spreading, breaking into smaller slicks,

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moving, emulsifying, and ultimately stranding on shorelines. In fact, depending on where an offshore oil spill occurs, oil spilled in open water could strand on shorelines before significant response activities can even start. Oil spilled in significant ice cover has the potential to contain oil in a much smaller area than in open water as illustrated by two experimental releases of Sture Blend crude oil in 1989 and 1993 (Vefsnmo and Johannessen, 1994). The 1989 experiment released 30 m^3 of oil into open water while the 1993 experiment released 26 m^3 of oil in 70 – 90% concentrations of broken ice. After 10 hours of spreading the thickest portion of the open water slick covered an area of 2 km x 50 m (100,000 m2) with a 13 km sheen “tail.” After 10 hours the spill in broken ice covered only 100 m2. Concentrated ice cover also minimizes wave motion and hence slick dispersion and emulsification rates. Low temperatures, smaller slick areas and greater thickness reduce volatilization rates. As a result, oil remains fresh, burnable and dispersible for a longer period of time than under otherwise similar scenarios in open waters of a temperate region. Further, land-fast ice will prevent oil spilled offshore from reaching shorelines until the spring / summer melt and allow collection of oil concentrated against the ice edge. All of these advantages provide responders additional time to plan for and implement an effective response to at least partly offset challenges caused by Arctic remoteness and conditions.

In 2009, three oil industry trade associations (IPIECA, International Oil and Gas Producers, and American Petroleum Institute) formed a committee to review Arctic oil spill response capabilities and to identify potential technology enhancements and research needs. This resulted in a joint report describing this effort (Potter et al., 2012). In 2012, nine international oil and gas companies began a joint industry project (JIP) to conduct research designed to enhance Arctic oil spill response capabilities based on recommendations from the 2009 study. This effort developed into multiple working groups to further advance various aspects of oil spill response. The Dispersants working group was focused on enhancing industry’s understanding on the use of dispersants in the Arctic and Environmental Effects working group was focused on increasing the understanding of the effects of oil and response techniques in the Arctic.

The JIP Environmental Effects working group coordinated and oversaw placement of several mesocosms in the sea ice of the Van Mijenfjorden in Svea, Svalbard from February to May 2015. These mesocosms were installed to study oil weathering, natural biodegradation, and the sensitivity / resiliency of sea ice communities (IOGP-ART, 2017). One potential scenario that the mesocosms allowed study of is a subsea blowout during the ice growth season where dispersants are applied to the oil at the release point. This oil will be fresh when the dispersant is applied and at least a portion of the oil could rise under the ice where it could become encapsulated until spring melt.

The Dispersants working group used the mesocosm study as an opportunity to collect ice cores containing either crude oil alone or oil crude oil premixed with dispersant to conduct dispersant effectiveness study. The objective of the study was to evaluate the potential for dispersion of encapsulated crude oil released from melting ice. This paper describes the results of dispersion effectiveness testing performed on the oil samples from the ice cores after the cores were melted to release the oil and illustrate 3 scenarios:

- Dispersion of untreated oil released from melted ice without addition of dispersant
- Dispersion of untreated oil released from melted ice treated with new dispersant after the melt
- Dispersion of oil pre-treated with dispersant prior to freeze in. No additional dispersant added after the melt.

2 Materials and Methods

Eight 1.6 m diameter mesocosms were installed in late February 2015 into the sea ice of a fjord near Svea, Svalbard (IOGP-ART, 2017). A conceptual drawing of a mesocosm is shown in Figure 1.

To install a mesocosm, an opening was cut into the ice in January and the 1.6 m mesocosm was placed in the opening. The mesocosms contained buoyancy that allowed them to float with about 25 cm of freeboard. Oil was placed on the surface of the water inside the central area of a mesocosm and allowed to freeze in place. Variable snow accumulation in the mesocosms caused 10 – 20 cm of accumulation that packed to a relatively solid slush. Between 34 – 37 cm of ice grew below the oil. Two of the mesocosms contained oil only; two contained dispersant mixed with oil at a dose rate of 1:20; two contained crude oil burn residue, and two were controls with no oil. In the mesocosms with crude oil, 20 liters of oil was put in place to produce an oil layer approximately 1 cm thick. In the mesocosms with burn residue, the residue from 20 liters of oil was put in place. The controls were used for a separate study that compared differences in microbial communities for the various treatments. For this study, cores were only used from the mesocosms with crude oil and crude oil plus dispersant.

The oil used in the mesocosms was from the Kobbe field in the North Sea offshore of Norway. The Kobbe oil has the properties shown in Table 1.

Table 1 Properties of Kobbe Oil used in the Mesocosm Studies

Density (g/ml; at 20°C)	0.797
Pour Point (°C)	-36
Viscosity (cP at 13°C and 100 s^{-1} shear)	3
Asphaltene (weight %)	0.03
Waxes (weight %)	3.4

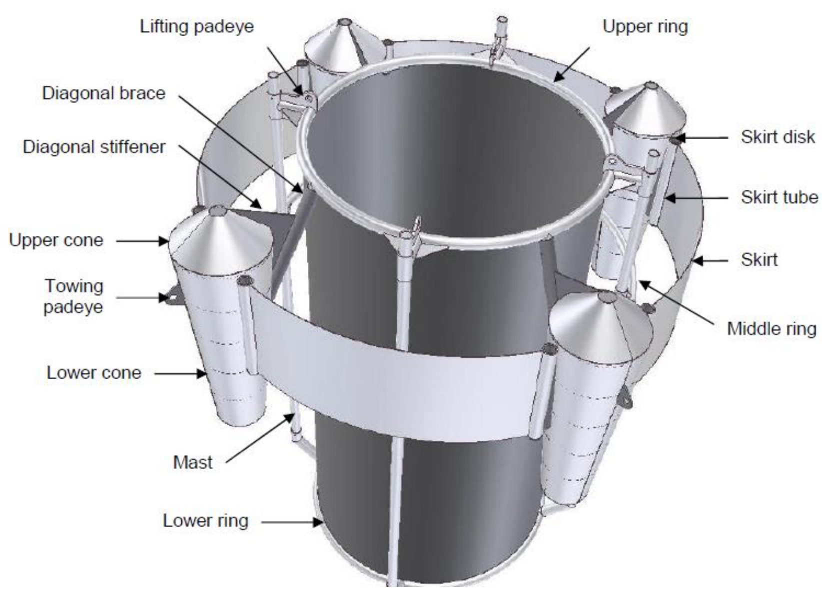

Figure 1 Conceptual drawing of a mesocosm (IOGP-ART, 2017).

Cores for this study were collected using a 9-cm diameter corer from each of the four mesocosms 1 month (T1), 2 months (T2), and 3 months (T3) after beginning of the experiment. The corer was cleaned after taking each core. Then, ice cores were cut in 3 or 4 sections: packed **Snow** of variable thickness; **Top** ice section which contained the main oil layer – oil slick; **Middle** ice section; and **Bottom** ice section which was the ice - water interface. Ice sections were immediately placed in a bag containing 500 mL of 3°C filter-sterilized (0.2 µm filter) seawater and put into a refrigerator at 2-3°C to melt. Once melted, an oil sample from each core was collected from the surface of the melt water, stored in a single amber bottle for each core and shipped to the CEDRE laboratory in Brest, France where they were stored for 6 months at minus 80°C. Figure 2 shows a photograph of a core collected from a crude oil plus dispersant mesocosm at 3 months (T3). These samples were then split into triplicate prior to dispersant effectiveness testing to allow three tests per mesocosm per sampling time.

The mesocosms did provide a wind-protecting freeboard above the water. This ultimately allowed greater snow accumulation than on the surrounding ice. This in turn caused the oil that froze on the water surface to be overlain by a packed layer of snow as shown in Figure 2. This layer had variable thickness depending on the mesocosm. This packed layer reduced the amount of weathering that the oil would have undergone had it been frozen in the ice surface and been more closely connected to the air. Therefore, the mesocosm encapsulation process simulated a field release between a release to water surface followed by rapid freezing of ice beneath the oil and a field release where oil was released under a layer of ice that protected it from release of volatiles to the atmosphere.

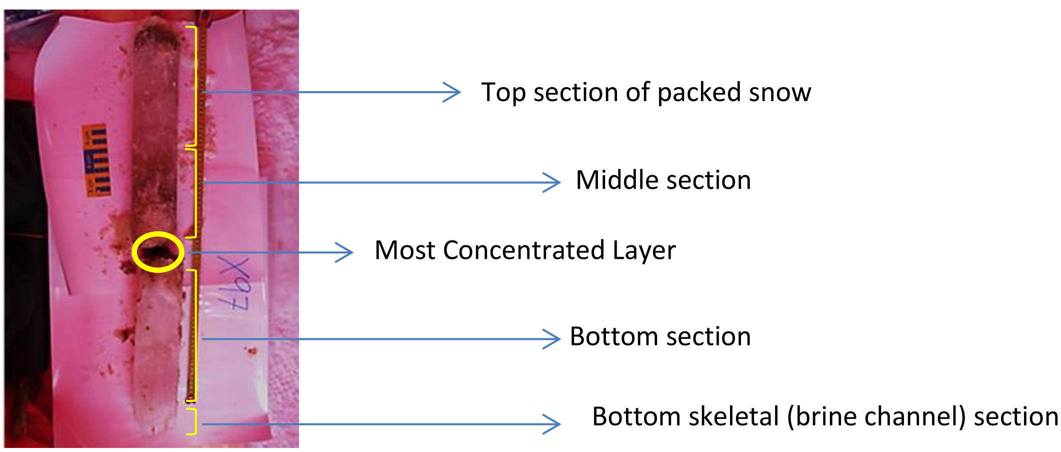

Figure 2 Example of a core collected from a crude oil plus dispersant mesocosm at 3 months (T3).

The triplicate samples from each core at each sampling time underwent dispersant efficiency testing using a Field Test protocol developed previously (Fiocco et al., 1999). This protocol was chosen to control project costs while providing a qualitative differentiation between dispersibility of the various treatments tested. Further, when the oil was still in the cores, the project team was uncertain if each core would contain enough oil for more quantitative tests with triplicates.

The dispersant used for the lab testing and in the mesocoms was FINASOL® OSR 52 dispersant. The protocol was adapted to account for storage of the samples and the use of brackish water as follows:

1. Oil samples were placed in a thermoregulated room at 10°C for one night (from 6 PM to 8 AM);
2. A volume of 5 liters of brackish water (salinity of 20 ppt) was prepared and, also, placed in the thermo-regulated room at 10°C for one night (brackish water was made using filtered, UV-treated natural sea water (~33 ppt) and diluted with freshwater generated by reverse osmosis to produce a final salinity of 20 ppt);
3. The testing procedure was as follows:
    a. A 100 mL volumetric cylinder was filled with 80 mL of brackish water;
    b. 1.5 mL of oil was added gently on the water surface by using a glass syringe;
    c. For the samples requiring addition of new dispersant, 6 drops (~60 μL) of dispersant was evenly distributed around the entire oil surface in the volumetric cylinder. The dispersant-treated oil did not have additional dispersant added.
    d. The oil and the dispersant in the cylinder were allowed to sit undisturbed for 1 min.
    e. The glass cylinder was then gently turned upside down (corresponding to approx. 30 rpm) for 1 min;
    f. The visual estimation criteria provided by the protocol (below) were used to assess the oil dispersibility. Pictures were taken at T0 (immediately after stopping the agitation), T+1min (after 1 min of rest / settling), T+5min (after 5 min of rest) and T+15min (after 15 min of rest).

Criteria for dispersibility estimation:

Good dispersibility: Formation of brown **dispersion** (oil droplets). The oil droplets will slowly rise to the surface at a standstill. This dispersibility was given a rating of 10.

Reduced dispersibility: Formation of dark/black, large oil droplets. Fast rise of droplets to the surface. This dispersibility was given a rating of 5.

Bad dispersibility: Little/ no difference from reference oil (untreated) cylinder. Fast rise of large oil droplets (at a standstill). This dispersibility was given a rating of 1.

Subjectivity was not an issue for this study because the samples tested were readily placed in the three broad categories described above. Table 2 shows the samples that were tested. A control dispersant effectiveness test was performed on the fresh Kobbe oil that had not been placed in a mesocosm.

Table 2 List of Samples that Underwent Dispersant Effectiveness Testing

		T0	T1	T2	T3
Original Kobbe oil	without dispersant	1 test			
	with dispersant	1 test			
Untreated Kobbe Mescosm oil	without dispersant		1 test	1 test	1 test
	with fresh dispersant		3 tests	3 tests	3 tests
Pre-treated Kobbe Mesocosm oil	without fresh dispersant		3 tests	3 tests	3 tests

3 Results and Discussion

The fresh Kobbe crude oil (oil that was not placed in a mesocosm) did not disperse without adding dispersant. It took less than 1 min of settling for the oil to rise the surface without adding any dispersant. The dispersion was stable when dispersants were added with little oil resurfacing after 15 minutes of settling as illustrated in Figure 3. Untreated fresh Kobbe crude oil was classified as having "bad dispersibility" while treated fresh Kobbe crude oil was classified as having "good dispersibility" even after 15 minutes of settling time.

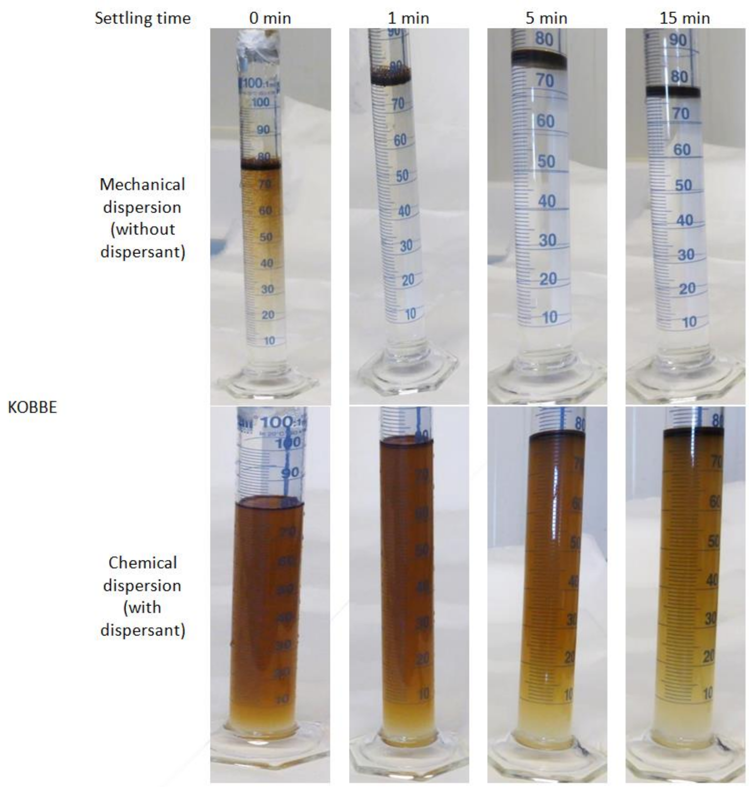

Figure 3 Photographs of the graduated cylinders containing brackish water and fresh Kobbe crude oil taken at 0, 1, 5, and 10 minutes after the 1 minute of mixing time specified for the test.

Table 3 provides the results for the mesocosm samples. The mesocosm oil that was not treated with dispersant before or after the cores were collected was classified as "bad dispersibility” for all three coring periods – 1 month to 3 months. After less than 1 minute of settling time the oil had risen to the surface. The appearance of the cylinders after the mixing time was very similar to those shown for mechanical dispersion in Figure 3.

The oil pretreated with dispersant prior to placement in the mesocosms (pre-treated oil) collected at 1 month was classified as having “good dispersion” for the total 15 minutes of settling time. The same pretreated oil was classified as having “good dispersion” after 1 minute of settling but “reduced dispersion” at 5 and 15 minutes of settling for the cores collected after 2 and 3 months. Figure 4 shows the photos of a cylinder after mixing taken after 0, 1, 5, and 15 minutes of settling for the pre-treated oil from a core collected after 3 months in the mesocosm.

Dispersants are known to leach from oil to water over time with faster leaching rates for lower salinity water (Knudsen et al., 1994). This is because dispersants contain a mix of hydrophilic and oleophilic surfactants. The melting process required to collect the oil from the cores for this testing may have allowed leaching of the hydrophobic surfactants from the oil to the water; however, it is possible that surfactants leached from the oil onto the ice while the mesocosms were in place. This could have caused the reduced dispersion after 1 minute of settling time.

Table 1 Dispersibility of the oil collected from the mesocosms.

	Treatment	No settling	1 min settling	5 min settling	15 min settling	Average Rating
1 month (T1)	Untreated oil	B / 1	B / 1	B /1	B / 1	1
	Pre-treated oil	G /10	G /10	G /10	G /10	10
	Post-treated oil	G /10	G /10	G /10	G /10	10
2 months (T2)	Untreated oil	B / 1	B / 1	B / 1	B / 1	1
	Pre-treated oil	G /10	G /10	R / 5	R / 5	7.5
	Post-treated oil	G /10	G /10	G /10	G /10	10
3 months (T3)	Untreated oil	B / 1	B / 1	B / 1	B / 1	1
	Pre-treated oil	G /10	G /10	R / 5	R / 5	7.5
	Post-treated oil	G /10	G /10	G /10	G /10	10

G = Good dispersibility / rating 10, R = Reduced dispersibility / rating 5, and B = Bad dispersibility / rating 1

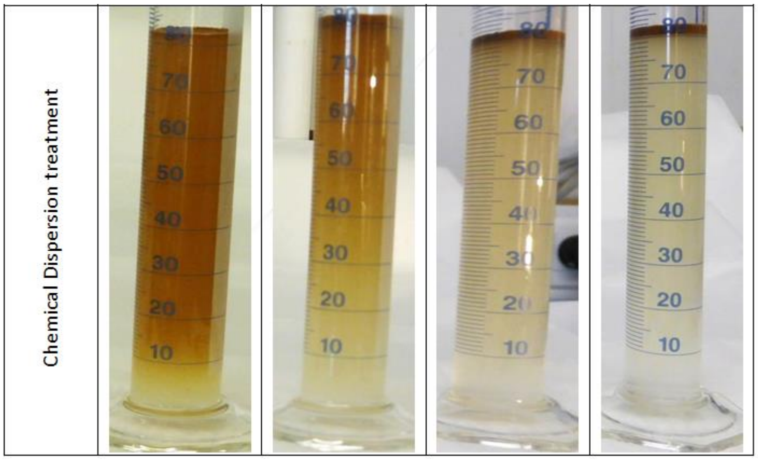

Figure 4 Photographs of the graduated cylinders containing brackish water and Kobbe crude oil pretreated with dispersant prior to placement in the mesocosm and tested without additional dispersant. The core was collected at 3 months. Photos were taken at 0, 1, 5, and 10 minutes after the 1 minute of mixing time specified for the test.

The oil that was treated with dispersants only after the cores were collected and melted (post-treated oil) showed the best dispersant effectiveness. This oil was classified as "good dispersion" for cores collected at 1, 2, and 3 months even after 15 minutes of settling time (Table 3). This oil was as dispersible as the fresh Kobbe oil that had not been placed in a mesocosm. This indicates that the oil frozen into the mesocosms may have remained relatively fresh even after 3 months.

Figure 5 shows that average rating for all the dispersant efficiency testing. The average rating was determined for each sample by averaging the rating at each settling time period as shown in Table 3.

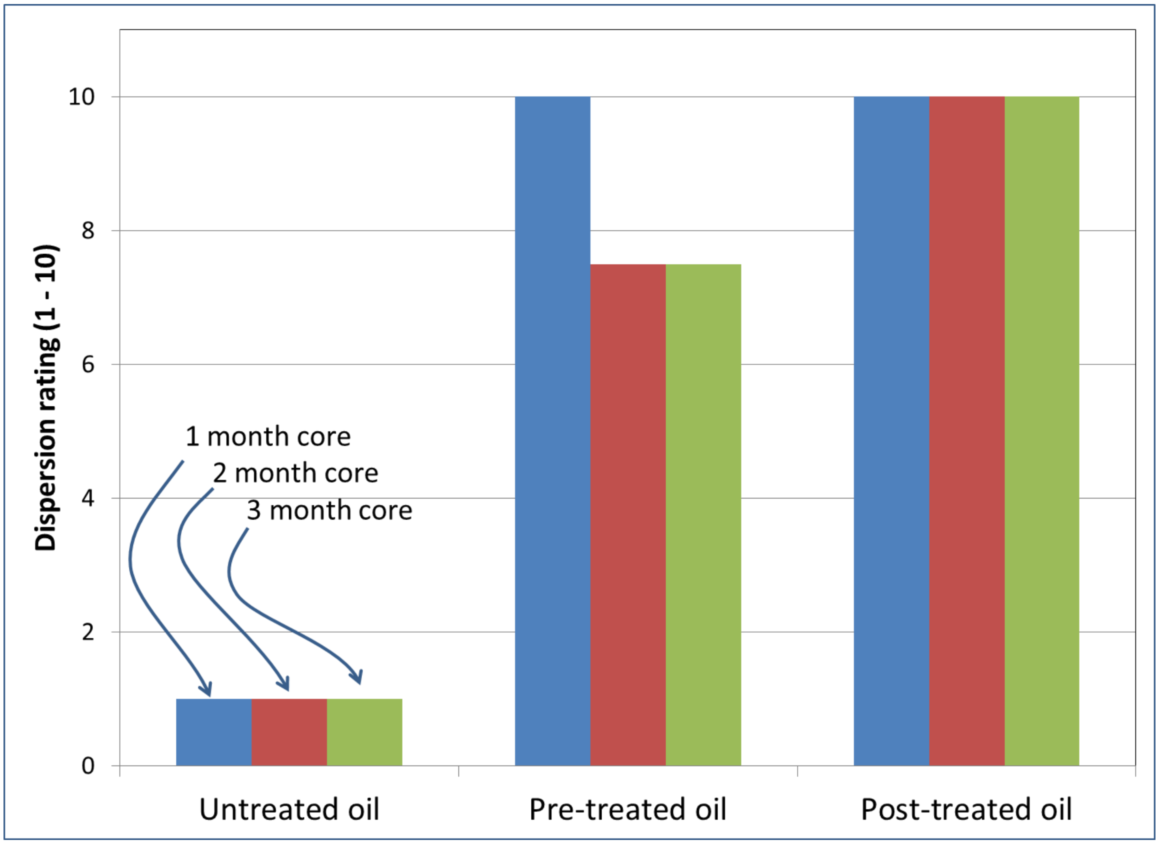

Figure 5 Graph of average dispersion rating for each core collection time and for each treatment.

4 Conclusions

A low density and viscosity crude oil, Kobbe, was frozen into sea ice in a fjord near Svea, Svalbard from February through May 2015. Cores that contained the frozen crude oil were collected at 1 month intervals over this period. The cores were melted to release crude oil samples that were then tested for dispersibility using a field effectiveness test.

The crude oil that was frozen into the ice and treated with dispersant after the core collection and melting maintained "good dispersion" even after 3 months frozen into the ice. In fact, this oil was as dispersible as fresh Kobbe crude oil.

The crude oil that was pre-treated with dispersant prior to freezing into the ice was still dispersible but less so than the oil that was post-treated with dispersant. The melt process used to collect samples and partitioning of surfactants from the oil to ice in the mesocosms may have allowed leaching into the water of some of the surfactants in these oil samples causing the reduced dispersion.

This study indicates that oil trapped in sea ice over the winter could remain dispersible for at least 3 months. Dispersion can happen if the oil is pre-treated with dispersants, but dispersant efficiency may be higher if the oil is treated with dispersants after it is released from the ice after a melt.

Thus, application of dispersants could be a viable option for oil found in ice leads before it has a chance to significantly weather and emulsify either during the ice growth season or during the ice melt. Further, oil found in melt pools on top of ice and freshly released into water could be treated with dispersant and disperse when exposed to wave action after the ice breaks up. One potential scenario is a subsea blowout during the ice growth season where dispersants are applied to the oil at the release point. This oil will be fresh when the dispersant is applied and at least a portion of the oil could rise under the ice where it could become encapsulated until spring melt. The findings of this study indicate that the oil could disperse when this oil is released during the spring melt.

5 References

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