ARCTIC RESPONSE TECHNOLOGY
OIL SPILL PREPAREDNESS

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CEDRE

715, rue Alain Colas, CS 41836

29218 BREST CEDEX 2 - FRANCE

ANALYSIS OF DISPERSIBILITY OF OIL FROZEN INTO ICE WITH AND WITHOUT DISPERSANT

EXECUTIVE SUMMARY

The work described in this report is an exploratory work carried out in the framework of the Project 2B "Unique Arctic Communities and Oil Spill response Consequences, Oil Biodegradation & Persistence".

In 2015 the Arctic Oil Spill Response Technology – Joint Industry Programme (IP) 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. Eight mesocosms were installed in the sea ice of the Van Mijenfjorden in Svea, Svalbard, Norway in January 2015 and remained in place until July 2015. Oil was introduced into two mesocosms and allowed to freeze in without any treatment (natural attenuation). 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 (labeled as T1, T2 and T3). 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 fresh reference oil, oil melted from ice untreated with dispersant prior to encapsulation, untreated oil treated with dispersants after the melt and oil pre-mixed with dispersant prior to being frozen into ice.

The main findings of these tests are:

- Fresh dispersant applied to oil melted from the ice cores after 3 months of being frozen in achieved good efficiency.
- Dispersant mixed with the oil prior to being frozen in was still efficient even after 3 months trapped in at the upper surface of the ice sheet, although with reduced efficiency compared to fresh samples.

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1. INTRODUCTION

The work described in this report is an additional task of the Project 2B "Unique Arctic Communities and Oil Spill response Consequences, Oil Biodegradation & Persistence". The project 2B concerns the investigation of oil biodegradation and persistence in the Arctic environment, more specifically after the use of response techniques such as the chemical dispersion and in situ burning.

In 2015 the Arctic Oil Spill 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.

Eight mesocosms with a diameter of 1.6 m were successfully installed in the sea ice of the Van Mijenfjorden in Svea, Svalbard, Norway in January 2015 and remained in place until July 2015. The use of these semi-open systems to study effects of contaminants in marine systems is well established, but this technique had never been used in Arctic ice environments. Right after installation of the mesocosm through the ice, the exposure medium was introduced onto the water inside the mesocosms to examine the impact of untreated and treated oil on biodegradation and sea ice communities.

Two mesocosms served as control with no oil. Two others contained only oil to follow natural attenuation. In the other two, an unsuccessful dispersant application was simulated by adding dispersant mixed with oil (1:20) without any additional mixing energy. The final two mesocosms contained residues from an in-situ burn response.

In all exposure mesocosms the amount of oil was kept constant (20 litres oil or burn residue resulting from burning 20 litres of oil). In the mesocosm simulating natural attenuation this resulted in a slick of 1 cm thickness. In all cases, the oil with or without dispersant, and burn residue were added to the cold freezing water (at the surface) and frozen into the very surface layer of the ice and, then, naturally covered with snow. In some of the mesocosms, the oil was covered with a thin layer of ice due to the natural wind effects on the sea surface while freezing.

Ice cores were collected from all mesocosms at periods of 1, 2, and 3 months (labelled as T1, T2 and T3) by using a 9-cm diameter corer. Samples of oil were collected from these ice cores and sent to Cedre laboratory. Effectiveness of dispersion was tested with fresh reference oil, oil melted from the ice cores (no dispersant added prior to being frozen in), oil with dispersants added after the melt and oil pre-mixed with dispersant prior to being frozen into the ice.

2. MATERIAL AND METHOD

2.1 Oil samples

All samples come from the field work performed under the Project 2B "Unique Arctic Communities and Oil Spill response Consequences, Oil Biodegradation & Persistence"

At each time point during the ice period (T1, T2 and T3), three cores were collected from each mesocosm (random distribution of sampling points in each mesocosm) using a 9 cm diameter corer, which was cleaned after drilling in each mesocosm.

Once a core was obtained, length measurements and photographs were taken (Figure 1). Then, ice cores were cut in 3 or 4 sections, depending upon length: packed Snow of variable thickness –when present; Top ice section which contained the main oil layer – oil slick; Middle ice section; and Bottom ice section which was the ice - water interface.

2.2 Sea ice sample preparation

Immediately after sampling, ice sections were 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 amber bottles and shipped to the Cedre laboratory in Brest, France, where they were stored for 6 months at minus 80 °C. It was decided to study the remaining efficiency of the dispersant contained in these samples (Figure 1).

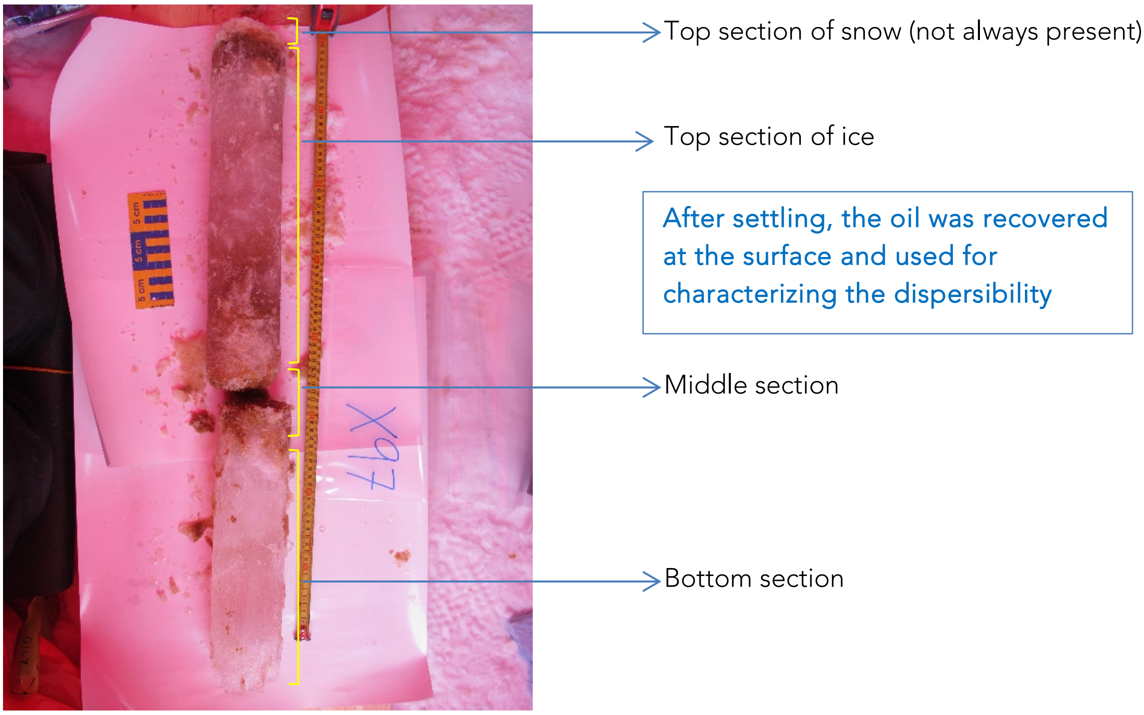


Figure 1 : Example of a core and the cutting applied.

Samples from the Natural Attenuation treatment (mesocosms A or B) and from the Chemical Dispersion treatment (mesocosms C or D) were studied at T1, T2 and T3. Prior analyzing, each sample from an amber bottle (a sampling time) was divided into 3 in order to carry out 3 tests per sample (triplicate) to validate the homogeneity of the sample (Table 1).

Table 1 : List of samples studied.

		T0	T1	T2	T3
Original oil (KOBBE)	Without dispersant	1 FT test			
	With fresh dispersant	1 FT test			
Untreated oil (Natural attenuation, Mesocosme A or B)	Without dispersant		A – M75 (1 FT test)	A – A92 (1 FT test)	B – X106 (1 FT test)
	With fresh dispersant added		A – M75 (3 FT tests)	A – A92 (3 FT tests)	B – X106 (3 FT tests)
Oil pre-treated with dispersant (Mesocosme D or C)	Without fresh dispersant		D – M63 (3 FT tests)	C – A65 (3 FT tests)	C – X90 (3 FT tests)

Note: for the labelling, the following technique is used

A – M75

This letter corresponds to the mesocosm (mesocosm A or B = untreated oil, Natural attenuation; mesocosm C or D = Chemical Dispersion treatment)

Name of the ice core (same name than in the project 2B)

The fresh dispersant used is the FINASOL OSR 62, provided by TOTAL Fluids. For samples coming from the Natural Attenuation Treatment (mesocosms A or B), no fresh dispersant was added. This decision was taken in agreement with the IOGP.

2.3 Method

The measurement of the remaining efficiency of dispersant was made by using the Field Test protocol delivered by IOGP. This FT protocol was adapted taking into account i) the storage of the samples and ii) the use of brackish water as requested by IOGP.

The following steps were implemented at Cedre:

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 litres of brackish water (salinity of 20 ppt) was prepared and, also, placed in the thermoregulated room at 10°C for one night;
3. The testing procedure was:
    a. A 100 mL volumetric cylinder was filled with 80 mL of brackish water;

b. 1,5 mL of oil (or oil dispersant mixture) was added gently on the water surface by using a glass syringe;

c. The glass cylinder was gently turned upside down (corresponding to approx. 30 rpm) in 1 min;

d. The FT criteria were used to assess the oil dispersibility (visual estimation). 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:

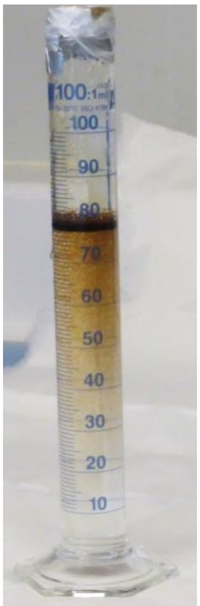
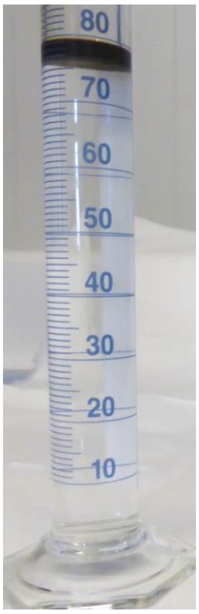
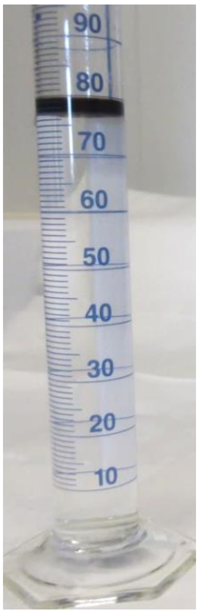
Good dispersibility:	Formation of brown dispersion (oil droplets). The oil droplets will slowly rise to the surface at a standstill.
Reduced dispersibility:	Formation of dark/black, large oil droplets. Fast rise of droplets to the surface.
Bad dispersibility:	Little/ no difference from reference oil (untreated) cylinder. Fast rise of large oil droplets (at a standstill).

3. RESULTS

3.1 Original oil

The methodology was applied on the original oil (KOBBE CRUDE OIL, the same used in the field work) in order to estimate the dispersibility of this oil and, also, to validate the protocol. Results with and without dispersant are presented in Table 2.

Table 2 : Measurement of the Kobbe Crude Oil dispersibility by the FT protocol.

		T0	T+1 min	T+5 min	T+15 min
KOBBE	Mechanical dispersion (without dispersant)				
	Chemical dispersion (with dispersant)				

The KOBBE crude oil is not mechanically dispersible: less than 1 min of settling is needed for the oil to rise the surface without adding any dispersant.

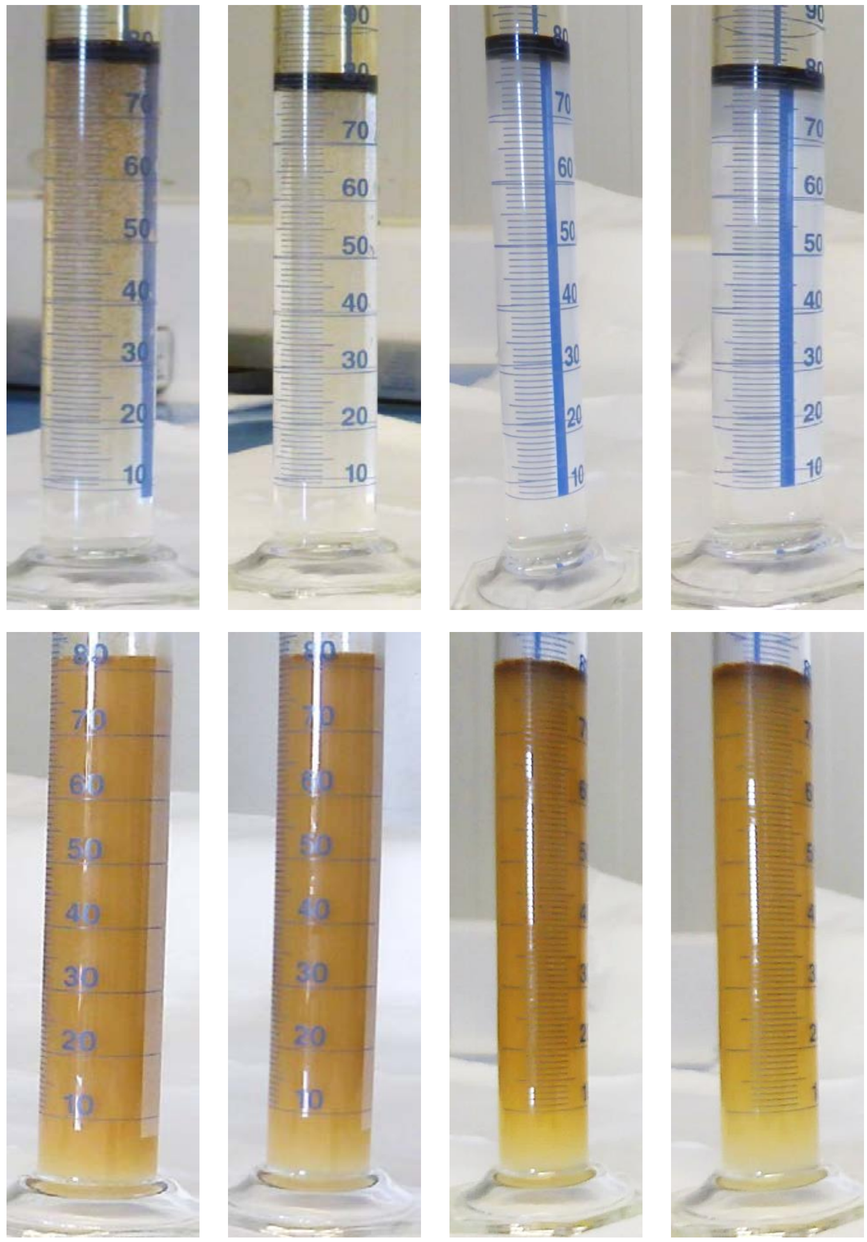
Nevertheless, the dispersion is very stable when dispersant is added: only a little oil is observed at the water surface after 15 min of settling.

In conclusion, the FT protocol allows monitoring the dispersant effectiveness on the KOBBE crude oil.

3.2 Comparison between Natural Attenuation and Chemical dispersion treatments

3.2.1 *Samples collected at T1*

During the experiment, the first ice cores sampling was carried out in March 2016, about 1 month after the start of the experiment.

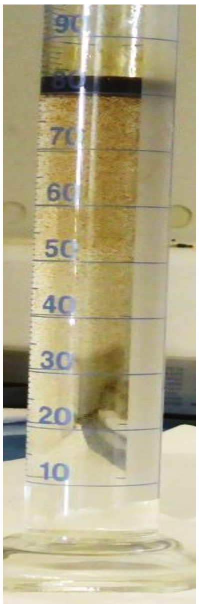
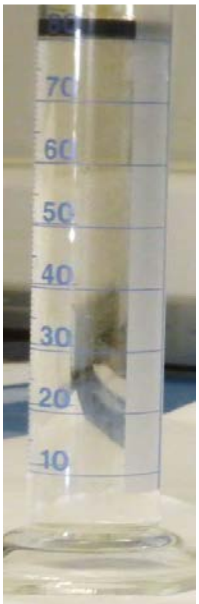
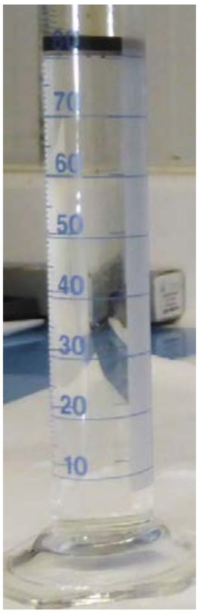
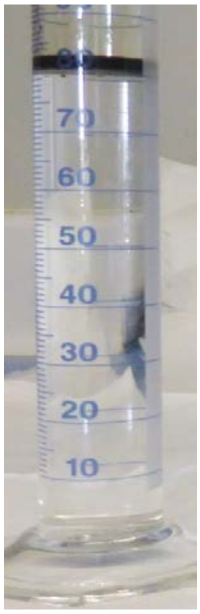


For the mesocosm allocated to Natural Attenuation (Mesocosm A), the oil is not dispersible: less than 1 min of settling is needed for the oil to rise the surface when no dispersant is added. This result agrees with findings above in 3.1 with the original oil.

For the mesocosm allocated to Chemical Dispersion (Mesocosm D), the oil + dispersant mixture that was frozen in is still dispersible. This result demonstrates that the dispersant remains efficient for at least one month after the start of the experiment.

3.2.2 Samples collected at T2

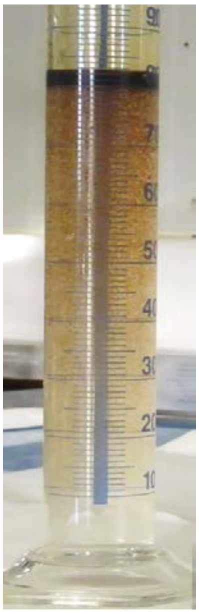
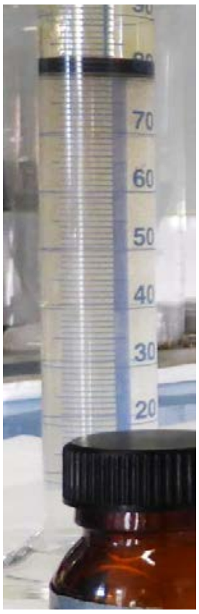
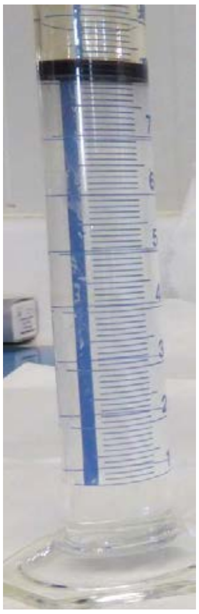
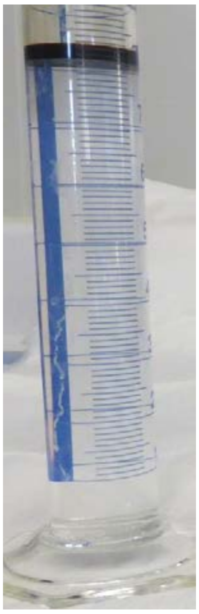
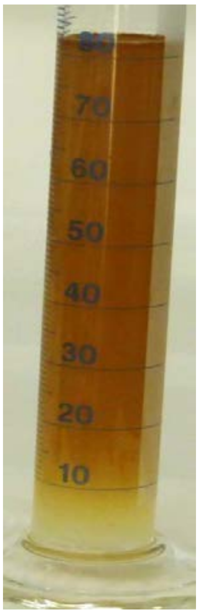
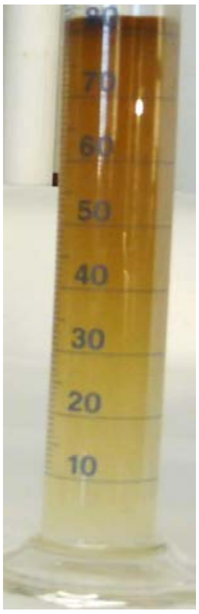
The second sampling was performed in April 2016, about 2 month after the start of the experiment.

Treatment	Mesocosm	Sample	T0	T+1 min	T+5 min	T+15 min
Natural Attenuation treatment	A	A92				
Chemical Dispersion treatment	C	A65				

As noted before no mechanical dispersibility is observed for the Natural Attenuation treatment. For the Chemical Dispersion treatment, the mixture of oil + dispersant is still dispersible: after 1 min of settling, a brown suspension can be observed, indicating a good dispersion. Nevertheless after 15 min of settling, the dark coloration indicates a decrease in the dispersion stability, which is correlated to a decrease in the droplet density.

3.2.3 Samples collected at T3

The third sampling was performed in May 2016, about 3 months after the start of the experiment.

Treatment	Mesocosm	Sample	T0	T+1 min	T+5 min	T+15 min
Natural Attenuation treatment	A	X106				
Chemical Dispersion treatment	C	X90				

Again, no dispersibility is observed for the Natural Attenuation treatment. For the Chemical Dispersion treatment, the dispersion is still efficient: after 1 min of settling, oil droplets are suspended in the water column (brown dispersion). As observed for T2 (3.2.2 above), the stability of the dispersion decreases with time and oil droplets coalesce at the surface after 15 min of settling.

All results are summarized in the Table 3.

Table 3 : Dispersibility of the free oil collected in the mesocosms during the field work (Oil = Natural Attenuation Treatment, Oil+Disp = Chemical Dispersion Treatment).

Sampling date	Treatment	T0	T+1 min	T+5 min	T+15 min
T1	Oil	B	B	B	B
	Oil+Disp	G	G	G	G
T2	Oil	B	B	B	B
	Oil+Disp	G	G	R	R
T3	Oil	B	B	B	B
	Oil+Disp	G	G	R	R

Note: G = Good dispersibility, R = Reduced dispersibility and B = Bad dispersibility.

3.3 Dispersibility of the Natural Attenuation treatment

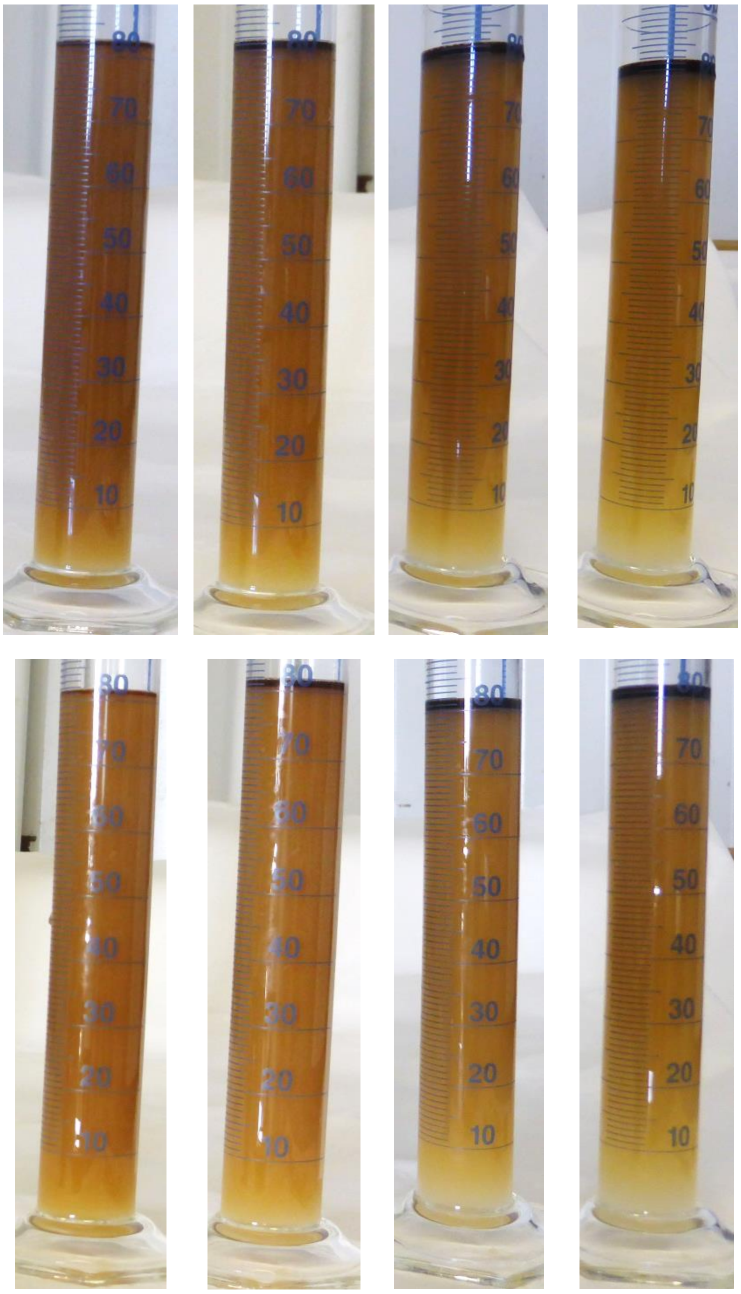
Additional Field Tests were carried out to evaluate the potential of dispersing the oil coming from the Natural Attenuation Treatment. The same free oil samples were used as in the previous work: before the testing, each sample was divided into 4 volumes (1 to test the dispersibility without any fresh dispersant –previous result, 3 to test the dispersibility with fresh dispersant - Table 4).

Table 4 : Matrix followed to monitor the dispersion option response.

Natural Attenuation Treatment	T1	T2	T3
Without Dispersant	Mesocosm A (M75)	Mesocosm A (A92)	Mesocosm B (X106)
With fresh dispersant	Mesocosm A (M75)	Mesocosm A (A92)	Mesocosm B (X106)
	Mesocosm A (M75)	Mesocosm A (A92)	Mesocosm B (X106)
	Mesocosm A (M75)	Mesocosm A (A92)	Mesocosm B (X106)

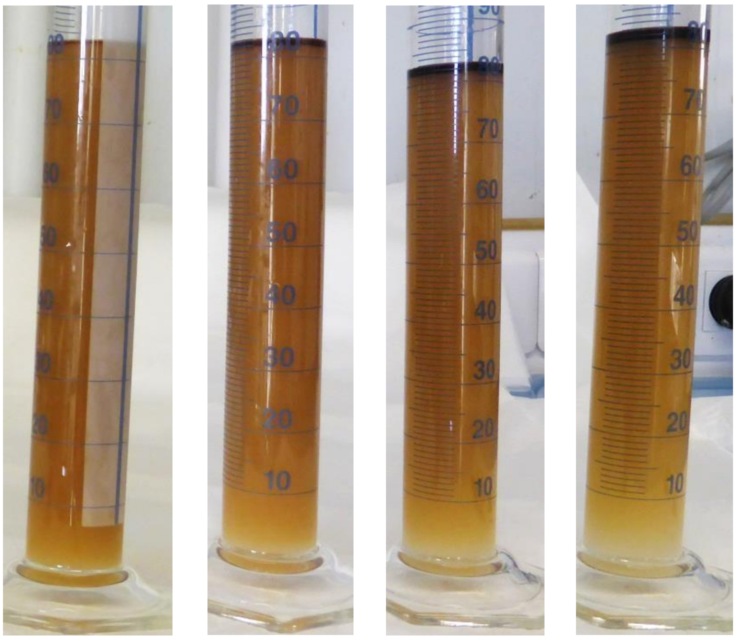
Note: results obtained without dispersant are presented previously.

		T0	T+1 min	T+5 min	T+15 min
Mesocosm A (M75)	T1				
Mesocosm A (A92)	T2				



Mesocosm B (X106)

T3



In all cases, the free oil is still dispersible even after 3 months of weathering while frozen into the ice sheet.

4. CONCLUSION

This report describes exploratory work carried out in the framework of the Project 2B "Unique Arctic Communities and Oil Spill response Consequences, Oil Biodegradation & Persistence".

The main findings of these tests are:

- Fresh dispersant applied to oil melted from the ice cores after 3 months of being frozen in achieved good efficiency.
- Dispersant mixed with the oil prior to being frozen in was still efficient even after 3 months trapped in at the upper surface of the ice sheet, although with reduced efficiency compared to fresh samples.

APPENDIX

Appendix 1: Field test – Check of the oils dispersibility

1.Field test – check of the oils dispersibility

This plastic box contains a simple field test used to determine wheth or not the oil /emulsion sampled are dispersible or not.

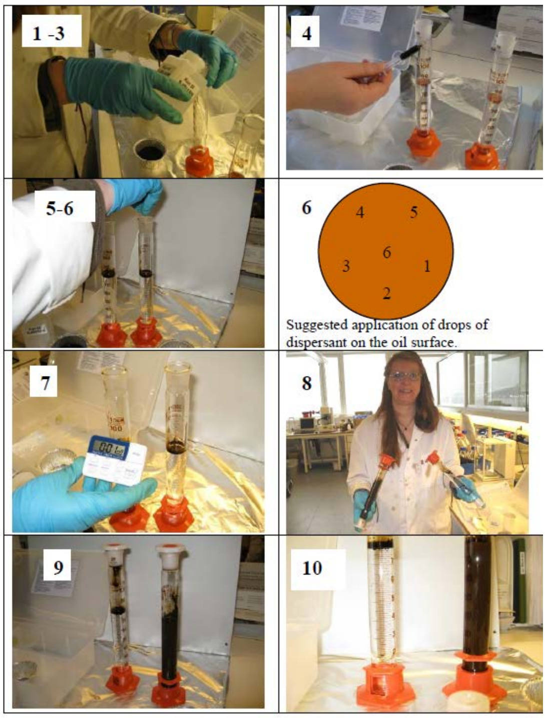
Field testing of oil / emulsion dispersibility	Quantity in box
Aluminum cylinders (100 ml. round)	5
Glass cylinders (100 ml glass) with foot and plastic top	2
Plastic bottle (250 ml labeled: "Seawater only")	1
Plastic bottle (30 ml) with dispersant (Type: Dasic NS)	1
Plastic syringe (2 ml) for application of oil/emulsion on the sea water in the glass cylinders	5
Plastic pipettes (1 ml) for application of dispersants on the oil	5

Step by step approach:

1. A few milliliters of the oil /emulsion sample taken at sea are transferred to one of the round aluminum cups.
2. Clean seawater is brought up with sampling bucket. The water is drained into 250 ml plastic bottle labeled "Reserved for seawater".
3. The two 100 ml volumetric cylinder is filled with 80 ml of sea wa (NB! Tap water must NOT be used).
4. Fill one of the plastic syringes with approx. 1.5 ml oil / emulsion which is then added gently on the water surface in each of the two glass cylinders.
   NB! Try to prevent the oil from sticking to the glass wall.
   NB! If the emulsion is so viscous that it is difficult to soak into the syringe, cut off the tip / bottom of the syringe.
5. Soak up some of the dispersant in a plastic pipette.
6. **Add 6 drops** of dispersant (approx. 60µl) and evenly distribute around the entire oil surface in **one** of the glass cylinders (see fig. 6). This provides a dosage of dispersant / emulsion (DER) = 1:25. In the second glass cylinder no dispersant is added, and the sampl will be used as a **reference** on natural dispersion.
7. Let the glass cylinders remain untouched in 1 min (contact time between oil and dispersant).
8. The glass cylinders are then gently turned upside down (corresponding to approx. 30 rpm) in 1 min.

Criteria for dispersibility:
Good dispersible: Formation of brown **dispersion** (oil droplets). The oil droplets will slowly settling to the surface at a standstill.
Reduced dispersibility: Formation of dark/black, large oil droplets. Fast settling.
Bad dispersible: Little/ no difference from reference oil (untreated) cylinder. Fast settling of large oil droplets (at a standstill).

Photo series at the next page shows the testing of "good -dispersible" (figure 9 and 10).



Suggested application of drops of dispersant on the oil surface.

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