

GRACE grant no 679266



# Report on natural removal of stranded oil in Arctic climatic regimes

D 4.9

# WP4 Combat of oil spill in coastal arctic water



Foto: Titles treated with heavy fuel oil (IFO 180) on ramps fasten to the rock in low tide level in Narsarsuaq

Prepared under contract from the European Commission Contract n° 679266 Research and Innovation Action Innovation and Networks Executive Agency Horizon 2020 BG-2014-2015/BG2015-2

Project acronym:	GRACE
Project full title:	Integrated oil spill response actions and environmental effects
Start of the project:	01 March 2016
Duration:	42 months
Project coordinator:	Finnish Environment Institute (SYKE)
Project website	http://www.grace-oil-project.eu
Deliverable title:	Report on natural removal of stranded oil in Arctic climatic regimes
Deliverable n°:	4.9
Nature of the deliverable:	Report on studies
Dissemination level:	Public
WP responsible:	WP4

Lead beneficiary:	AU
Due date of deliverable:	31.8.2018
Actual submission date:	31.8.2018

Deliverable status:

Version	Status	Date	Author	Approved by
1	Draft	August 24	Kim Gustavson, Susse Wegeberg, AU	WP 4 August 30, 2018
2	Revised version	August 30	Kim Gustavson, Susse Wegeberg, AU	Steering group August 31, 2018

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# **Executive Summary**

The present report includes summary of results from studies on natural removal of stranded oil on the coast in Arctic climatic regimes and covers studies of Task 4.3.1. The aim of the studies was to increase the knowledge base on the rate of natural removal of oil on rocky surface in low arctic, middle arctic and high arctic climatic regimes. Wind, ocean currents and waves can result in oil spill from ships and offshore activities reaching the coastline. Rocky surfaces are a widespread coastal type in Greenland and other arctic areas. The self-cleaning potential is an essential factor in considering the shoreline clean-up strategy together with the potential adverse environmental impact of shore cleaning. Results of the study will support shoreline clean-up strategies in arctic waters.

In the experiments, removal of oil from oil-treated tiles placed on the rocky coast was studied in a period over 95 days. Tiles were placed on ramps at levels of low tide and high tide as well as above high tide level. On tiles above high tide level the possible influence of sunlight (photooxidation) and precipitation was examined by monitoring removal/degradation of oil from tiles facing upward and downward.

The results from the UV fluorescence analyses and the GC-FID profiles are consistent with regard to highest removal rate of crude oil compared to heavy fuel oil, and that seawater wash as well as exposure to sunlight and precipitation increase removal rate of the crude oil. The results indicate that the removal of heavy fuel oil is significantly slower and less than the removal of crude oil.

Data and result from the experiment will further be processed for publishing in a scientific journal. Removals of the oil from the tiles will be correlated with collected data for temperature, sun radiation and water cover of the titles. Characterization of the bacterial biofilm on the tiles developing within the period of the experiment may be included in the publication.

# 1. Introduction

Wind, ocean currents and waves can result in oil spill from ships and offshore activities reaching the coastline. In addition, risk for oiling the shoreline is high when fjords and bays are used as a safe haven for ships in distress. Rocky surfaces are a widespread coastal type in Greenland and other arctic areas. The self-cleaning potential is an essential factor in considering the shoreline clean-up strategy together with the potential adverse environmental impact of shore cleaning.

The aim of the study is to increase the knowledge base on the rate of natural removal and degradation of stranded oil on rocky surface in low arctic, middle arctic and high arctic climatic regimes. Results of the study will support shoreline clean-up strategies in arctic waters.

# 2. Study design and methods

Approval for field test was given by the Greenland authorities (Department of Nature, Environment and Energy) in permit dated September 30 2016. Claims in the approval were mainly administrative and the implementation of the planned activities was and could be performed within the limits set out in the approval.

In the experiment, removal of oil from crude oil and heavy fuel oil (HFO)-treated tiles placed on ramps on the rocky coast was studied in a period over 95 days. The experimental setup is described in detail in deliverable D 4.8 Protocols for studies on natural removal of stranded oil on the coast in Arctic climatic regimes. Tiles were placed at levels of low tide (A), high tide (B) and above high tide (C+D). On the tiles above high tide level the possible influence of sunlight (photooxidation) and precipitation was examined by monitoring removal/degradation of oil from tiles facing upwards (C) and downwards (D). (Crude oil (A-D); HFO: (E-H)). The D and H samples were used as controls for calculating the disappearance of oil in exposed tiles.

At the three selected locations for the study, tiles of slate (5 \* 5 cm) were treated with a homogenous layer of oil and the tiles were placed on ramps attached to the rock.

The experiments were conducted at three localities: the northernmost location in Northwest Greenland near the town Ilulissat (approx. 71° N), the mid location (approx. 64°N) was placed outside of Nuuk, the Capital of Greenland, and the southern location was placed near the airport town Narsarsuaq (approx. 60°N). See locations on the map below (Figure 1).

At each location and site, study design was accommodated as much uniformity as possible with respect to coastal morphology to exclude local spatial variation. Therefore, the coastal slope, direction and substrate was as comparable as possible for the three locations.

Physical parameters were obtained by local logging (temperature), from other sources such as the Danish Meteorological Institute (tidal amplitude, precipitation, visible light and UV radiation) and wind data will be used for calculation of the relative exposure index (REI). Based on these data water (seawater and rain) and light exposure of the tiles at the different height levels on the coast will be estimated.



**Figure 1.** Map of Greenland. The experimental studies took place in vicinity of Narsaq, the nearest town to the airport town Narsarsuaq, Nuuk and Ilulissat.

Two different oil types were studied; a North Sea type crude oil and a heavy bunker fuel oil. Approximately 0.5 - 1 mm thickness oil film was applied on the tiles at initiation of the experiment, respectively corresponding to 200  $\mu$ l crude oil and 400  $\mu$ l bunker oil. The crude oil is a naphthenic oil with a low pour point and hence representing oil spill in connection with oil exploration. The heavy bunker fuel oil studied, IFO180, is used as fuel in tankers and thereby representing an actual risk of spill from shipping in Greenland.

The deployment and sampling was performed between June 2 and September 5 2017. The replicate number of deployed tiles on each location was 160 tiles including 28 references titles not added oil.

Two sets of duplicates tiles (= four tiles) were sampled after 1, 3, 7, 21, 35, 65, 95 days exposure in the environment. At sampling, the tiles were placed in Rilsan-bags, placed facing each other and stored at -20°C until shipping at the end of the experimental period. Processing and analyses of the tiles was perform in Denmark. Oil on tiles from the one set of duplicates was extracted in laboratory using dichloromethane (DCM), and the amount of oil extracted was measured using UV fluorescence analysis and selected samples was characterized using GC-FID analysis. In addition, the other set of duplicate sampled tiles were used for characterization of bacterial biofilm on the surface of tiles in WP2 by University of Tartu. Amount of oil on title are measured using UV fluorescence. The amounts of oil are in present report expressed as fluorescence units (FU) emission read at 405 nm with excitation at 380 nm.

Unfortunately, tiles shipped from Ilulissat did never reach the analysis laboratory in Denmark. The lost goods are still missing and being searched for.

# 3. Results

Selected and preliminary results are shown below. All data and results will be further processed for publishing in scientific journal. Removal rates of the oil from the tiles will be correlated with collected data for tidal wash and wave exposure, temperature, sun radiation, precipitation, and bacterial biofilm on the titles. All fluorescence units will be converted to amounts as in grams in the publication, as well as physical-chemical properties (viscosity, density, pour and flash point, S content) of the oil types, that were used in the experiment, will be included.

## 3.1 Initial removal of oil

#### 3.1.1 Crude oil

Initial removal of the naphthenic crude oil during the first day and the first tidal periods was relatively pronounced with a reduction of up to 90 % from the initial (control (D)) amount applied to the tiles (Table 1). Please note that some loss may be due to run off of the oil when placing the ramps in their respective locations.

**Table 1**. Remaining amounts of naphthenic crude oil after 1 day on tiles on locations near Narsarsuaq (NAQ) and Nuuk. A: Low tide level, B: High tide level, C: Above high tide level exposed for sunlight and precipitation and D: Above high tide level facing down and shielded against exposure from sunlight and precipitation. The amount of oil on the titles was analysed using UV fluorescence analysis from the extracts.

Location	Oil amount (Fluorescence Units, FU)			
	Α	В	С	D
NAQ	3798	3222	8037	30000
Nuuk	2480	2500	24900	43500

The relative large initial removal of the crude oil from tiles at low and high tide levels (A and B) can be explained by high solubility of the light fraction of the crude oil in sea water. The difference between C and D (exposed and not exposed to light and precipitation) can be explained by an increased evaporation of the light fraction from the oil on the tile exposed for sun radiation following heating up of tiles. There was no precipitation in the first day of the experiment.

#### 3.1.2 Heavy fuel oil (HFO)

Compare to crude oil the removal of heavy fuel oil was relative smaller and possibly correlated with the lower contain of light oil component (Table 2). The reduction was up to 50 % from the initial amount applied to the tiles.

**Table 2.** Remaining amounts of heavy fuel oil (IFO 180) after 1 day on locations near Narsarsuaq (NAQ) and Nuuk measured by UV-fluorescence analysis from the extracts. E: Low tide level, F: High tide level, G: Above high tide level exposed for sunlight and precipitation and H: Above high tide level facing down and shielded against exposure from sunlight and precipitation.

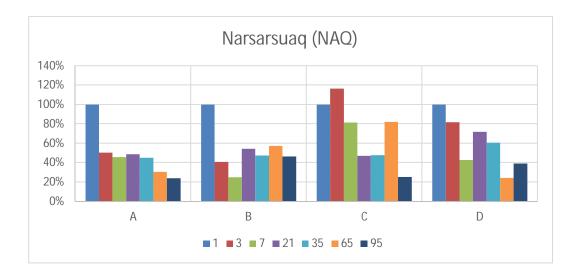
Location	Oil amount (Fluorescence Units, FU)			
	E	F	G	Н
NAQ	103400	213500	202250	269200
Nuuk	145000	153750	382000	448000

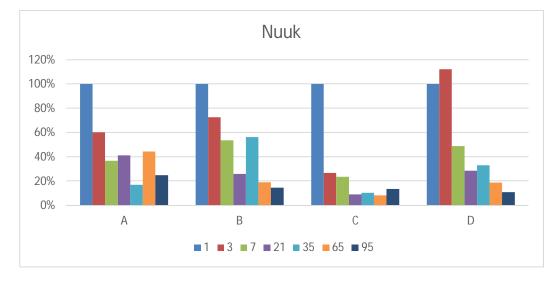
The difference between G and H can be explained by an increased evaporation of the light fraction from the oil on the tile exposed for sun radiation following heating up of tiles. There was no precipitation in the first day of the experiment.

# 3.2 Long-term removal of oil

#### 3.2.1 Crude oil

Removal of the naphthenic crude oil over a period of 95 days are shown in Figure 2. Values are given as percent of Day 1. The amount of oil on the tiles was analysed using UV fluorescence analysis on dichloromethane extracts of oil from the tiles. UV fluorescence analysis on dichloromethane extracts of oil on the tiles.





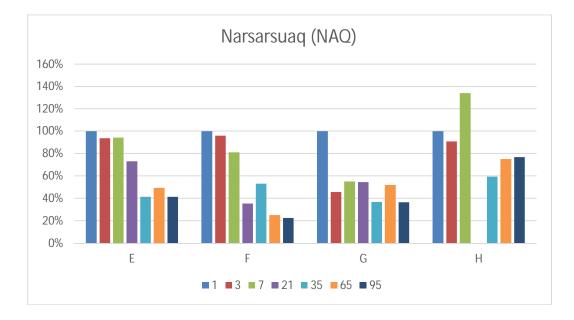
**Figure 2.** Removal of naphthenic crude oil on locations near Narsarsuaq (NAQ) and Nuuk over a period of 95 days. A: tiles at low tide level, B: tiles at high tide level, C: tiles above high tide level exposed for sunlight and precipitation and D: tiles above high tide level facing down and shielded against exposure from sunlight and precipitation. The amount of oil on the tiles was analysed using UV fluorescence analysis on dichloromethane extracts of oil from the tiles and is presented as percent of day 1.

The results indicate that the initial removal of naphthenic crude oil is greatest and fastest at tiles at low tide level and tiles at high tide level (A and B). However, after Day 95 the removal of the crude oil are relative equal for tiles in the tidal zone as well as for tiles above high tide level but exposed to sunlight and precipitation. The results indicate that water wash, due to a relative high degree of water solubility, as well as evaporation may remove film of light crude oil from rocky surfaces. The residual amount of crude oil at Day 95 is approximately between 10-40 % of the oil at Day 1. The removal is relative largest at the Nuuk location for the tiles placed above the high tidal level, but

exposed to sunlight and precipitation. Weather data may explain this difference between Narsarsuaq and Nuuk.

#### 3.2.2 Heavy fuel oil

Removal of the heavy fuel oil (IFO 180) over a period of 95 days is shown in Figure 3. Values are given as percent of Day 1. Removal of the naphthenic crude oil over a period of 95 days is shown in Figure 2. Values are given as percent of Day 1. The amount of oil on the tiles was analysed using UV fluorescence analysis on dichloromethane extracts of oil on the tiles. UV fluorescence analysis on dichloromethane extracts of oil from the tiles.



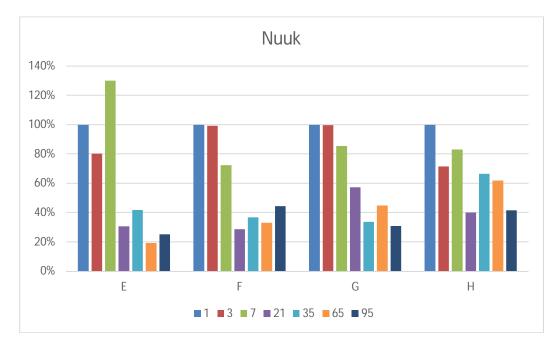


Figure 3. Removal of heavy fuel oil (IFO 180) on locations near Narsarsuaq (NAQ) and Nuuk over a period of 95 days. E: tiles at low tide level, F: tiles at high tide level, G: tiles above high tide level exposed for sunlight and precipitation and H: tiles above high tide level facing down and shielded against exposure from sunlight and precipitation. The amount of oil on the titles was analysed using UV fluorescence analysis on the extracts and is presented as percent of day 1.

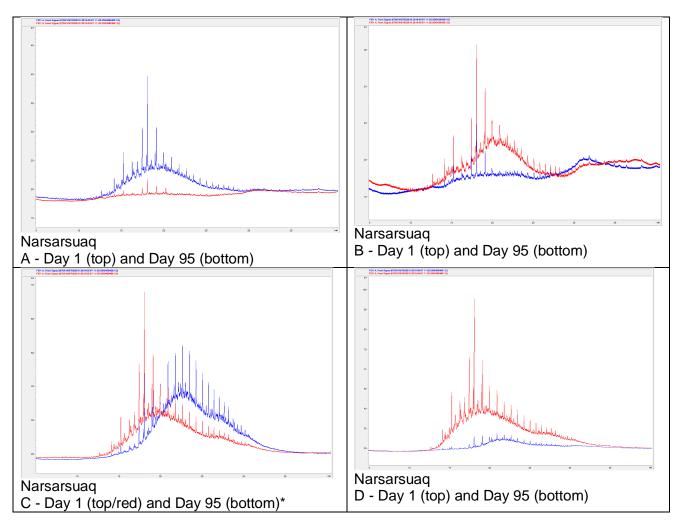
The results indicate that the initial removal and the succeeding removal of heavy Fuel oil (IFO180) over time is significantly slower and less than the removal of crude oil in the experimental period. The removal of IFO 180 is lowest for tiles shielded against exposure from sunlight and precipitation. The results indicate that the heavy fuel oil is more persistent than crude oil. The residual amount of heavy fuel oil at Day 95 is between 25-80 % of the oil at Day 1.

### 3.3 GC-FID analysis

#### 3.3.1 Crude oil

Crude oil on tiles Day 1 and Day 95 is characterized using GC-FID analysis. GC-FID profiles for the locations are shown in figure 4 and figure 5. Note the values on the y-axis are different between the different charts.

The GC-FID profiles in figures 4 and 5 indicate that both the light, medium and heavy fractions of the crude oil are almost removed from the tiles at low tide level (A) and high tide level (B). The GC-FID profiles for tiles above high tide level exposed to sunlight and precipitation (C) and tiles above high tide level shielded against sunlight and precipitation indicate that residues of the heavy fractions of the crude oil are persistent at Day 95.



**Figure 4.** GC-FID chromatograms of crude oil on tiles Day 1 and Day 95 at the location near Narsarsuaq. \* Probably because of an error in the preparation of the sample, the levels are too high, and must be discarded).

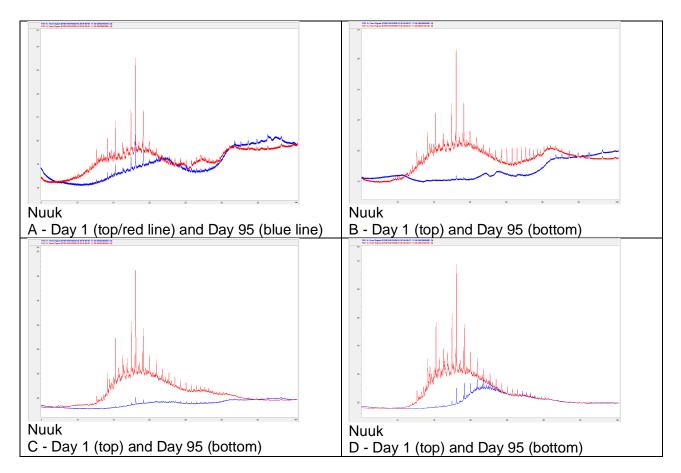


Figure 5. Show GC-FID chromatograms of crude oil on tiles Day 1 and Day 95 at the location near Nuuk.

#### 3.3.2 Heavy fuel oil

Heavy fuel oil (IFO180) on tiles Day 1 and Day 95 is characterized using GC-FID analysis. GC-FID profiles for the locations are shown in figure 6 and figure 7. Note the values on the y-axis are different between the different charts.

The GC-FID profiles in figures 6 and 7 indicate that both medium and heavy fractions of the IFO 180 oil are left at Day 95. Profiles indicate that the removal is least on tiles above high tide level shielded against sunlight and precipitation.

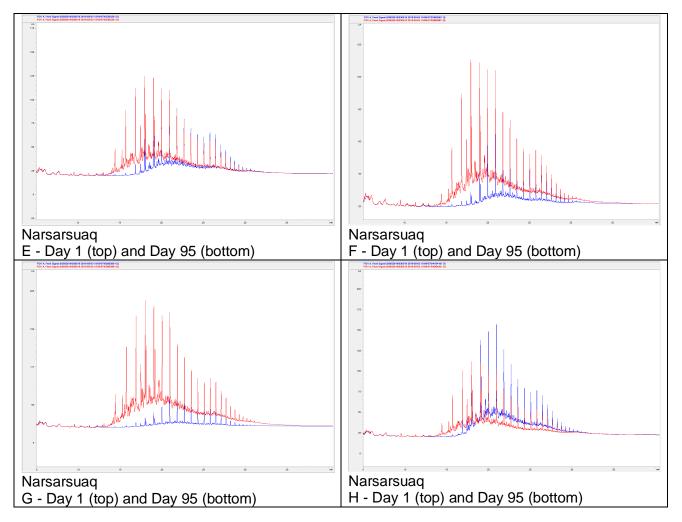
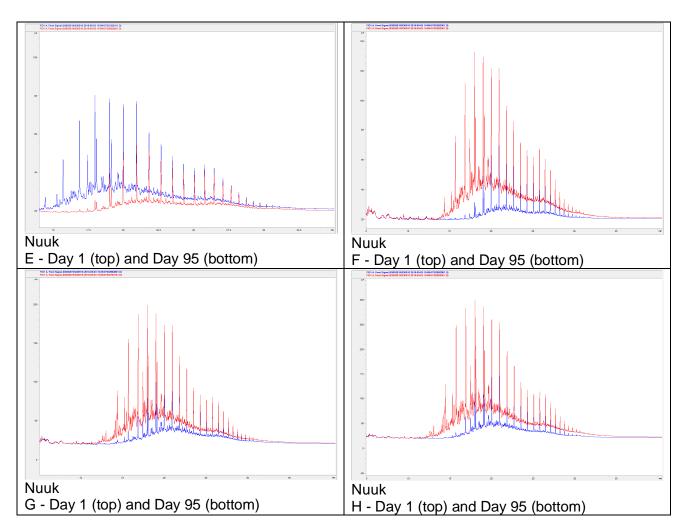


Figure 6. GC-FID chromatograms of heavy fuel oil on tiles Day 1 and Day 95 at the location near Narsarsuaq.



**Figure 7**. Show GC-FID chromatograms of heavy fuel oil on tiles Day 1 and Day 95 at the location near Nuuk.

The results from the UV fluorescence analyses and the GC-FID profiles in the chromatograms are consistent with regard to highest removal rate of crude oil compared to HFO, and that seawater wash (A, B) as well as exposure to sunlight and precipitation (C) increase removal rate compared to no exposure (D).