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Ongoing Research on Herding Agents for *In Situ* Burning in Arctic Waters: Studies on Fate and Effects

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ABSTRACT

Research on the fate and effects of herding agents used to contain and thicken oil slicks for *in situ* burning in Arctic waters continues under the auspices of the International Association of Oil and Gas Producers Arctic Oil Spill Response Technology – Joint Industry Program (JIP). In 2014/2015 laboratory studies were conducted on the fate and effects of herders. The purpose of the studies was to improve the knowledge base used to evaluate the environmental risk of using herders in connection with *in situ* burning for oil spill response in Arctic seas. Two herding agents were studied (OP 40 and ThickSlick 6535).

Laboratory-scale herding and burning experiments were carried out for investigating the physical fate of the two herders during combustion of Alaska North Slope and Grane crude oils (fresh and emulsified). The results showed that after burning, the herder was mainly found on the water surface, and only small concentrations of herders were found in the water column (0.2-22.8 mg/L).

The inherent properties of herders in relation to toxicity and bioaccumulation on the high Arctic copepods (*Calanus hyperboreus*), as well as the biodegradability of herders were studied under arctic conditions. The results indicated that a distinct mortality was seen at the highest test

concentrations of the herders. However, the concentration of herders required to produce acute toxicity in the laboratory was approximately three orders of magnitude higher than the concentrations measured in the water column when herders were used to conduct an *in situ* burn in the laboratory. OP-40 might bio-accumulate whereas TS6535 might not. TS6535 was mostly degraded within 7 days, whereas the degradation of OP-40 was insignificant over 28 days.

Since herders are mainly considered as a surface active chemical compound, the potential impacts of herders on Arctic seabird feathers (from legally hunted Thick-Billed Murre and Common Eider) were investigated. Different dosages of herders were tested; high dosages that might be present just after the application of the herder and low dosages (approximately monolayers) likely to occur for a significant time and distance from the operations. Low dosages corresponding to approximately monolayers of OP-40 and TS6535 did not cause feathers to sink; however they did absorb more water than the controls. The high dosages caused measured damages to the feather microstructure.

Finally, laboratory burning experiments were carried out to determine if there was a difference in the composition of smoke plumes from mechanically contained burns versus herded oil burns. Herder was not measured in the smoke plumes, and there were no other noticeable differences in combustion between the two methods of containment (herder vs. metal ring).

INTRODUCTION

This paper gives an overview and summarizes the findings from one part of a research program designed to increase the knowledge of herding agents: their fate; their environmental effects; and, the windows-of-opportunity to expand the operational utility of *in situ* burning (ISB) in cold open water and loose drift ice conditions. Here we focus on the fate and environmental effects research. The results of the windows-of-opportunity are presented in a separate paper in these

proceedings (Buist et al. 2017). More details on the complete study results can be found in a technical report (Buist et al. in prep.).

ISB of accidentally spilled oil is a method with great potential, particularly in ice covered waters. One of the key parameters to effective ISB is the thickness of the oil slicks: a thick oil slick is required for ignition and efficient burning (Buist et al. 2013). Several ways exist to keep the oil film at the required thickness for burning, e.g. fire resistant booms and ice floes that cover > 60 % of the water surface. In loose drift ice conditions (approximately 10-60 % ice coverage) oil spills can rapidly spread to become too thin to ignite, however the ice concentration is too high for fire resistant booms to be deployed and operated efficiently. Research over the last 12 years has shown that herding agents can contract and thicken oil slicks to allow effective ISB in loose drift ice and open water (Buist et al. 2011; SL Ross and DCE 2015). Herders have the ability to spread rapidly over a water surface into a monomolecular layer as a result of their high spreading coefficients or spreading pressure and the best herding agents have spreading pressures in the mid-40 mN/m range, whereas most crude oils have spreading pressures in the 10-20 mN/m range (SL Ross and DCE 2015). This monomolecular layer of surfactants reduces the surface tension of water from about 70 mN/m to 20-30 mN/m (SL Ross and DCE 2015). When the herders contract the oil slick edge it changes the balance of the interfacial forces acting on the slick edge thereby allowing the interfacial tensions to contract the oil (SL Ross and DCE 2015). Only small quantities of herder are needed, e.g. 150 $\mu l/m^2$ of water surface, is the recommended amount to clear thin films of oil from large areas of water surface, contracting the oil into thicker slicks (SL Ross and DCE 2015). Recent research (in 2013 and 2015) has tested the application of herders from helicopters, thus, herders could potentially allow containment and ignition of the oil from air only.

The two herders included in this project have been placed on the U.S. EPA National Contingency Plan (NCP) Product Schedule list and are commercially available and best available

based on prior testing. ThickSlick 6535 (TS6535) is a blend of 65 % (by volume) of the surfactant sodium monolaurate (Span 20) (the active ingredient), and 35 % 2-ethyl butanol, the solvent. The active ingredient of TS6535 is used as a food additive, in household cleaners as well as in cosmetics, fine fragrances and other toiletries. Siltech OP-40 (OP-40) is a proprietary polydimethylsiloxane copolymer (the surfactant, the active ingredient). Surfactants of the type used in OP-40 are used in household and automotive care products as well as in hair conditioners and skin care products. Selected properties of the herders used in the experiments are given in Table 1

Table 1 – Selected herder properties

TEST	**TS6535**	**OP-40**
Flash Point	>82°C	82°C
Pour Point	-1.7°C	-59°C
Viscosity	24.7 cSt (mm^2/s)	8.27 cSt (mm^2/s)
Specific Gravity at **15°C**	0.974	0.988
Freezes at	-24°C	-71°C
Solubility	Partial Miscibility	Partial Miscibility

Experimental research approach

The research presented here involved several separate studies:

- Evaluation of the physical fate of herders during burning, i.e. analysis to determine herder concentrations in the water column, on the water surface, and in the oil after herder application to test slicks. Laboratory studies conducted at Technical University of Denmark and Danish Centre for Environment and Energy, Aarhus University (DCE).
- Studies on environmental effect of herders including: toxicity and bioaccumulation with Arctic copepods; biodegradation in Arctic conditions; and, the impacts on Arctic seabird feathers conducted at DCE, and in Greenland.
- Analysis of the smoke generated during ISB of oil slicks confined with herders at the SL Ross laboratory in Canada.

PHYSICAL FATE OF THE CHEMICAL HERDER DURING BURNING

The purpose of these experiments was to investigate the physical fate of the herders during burning. The experiments were done as a two-step procedure with samples of water and oil collected from small-scale laboratory burning experiments (170-250 g oil on 390 L of artificial 32 ‰ saltwater at 2 °C in a 1 m^2 basin) with herders (150 µL), followed by chemical analyses with GC-MS to measure the herder content in the samples (for details see Buist et al. in prep.). The experiments involved Alaska North Slope (ANS) and Grane crude oils (fresh and 25 % water-in-oil emulsion) and the two herders (TS6535 and OP-40). The laboratory set-up and sampling was based on the expectation that the herders would quickly form a monolayer on the water surface, but could degrade, evaporate, dissolve, disperse, spread or simply remain on the surface with time, see Figure 1. Further, the burning of the oil slick could also impact the fate of the herder and thereby change its normal behaviour. The following samples were analysed: I) surface water before (but after herding) and after burning, II) water column samples after burning, III) water column samples from below the oil slick after burning and IV) oil samples from the oil slick before (but after herding) and after burning. For more details see Buist et al. (in prep.).

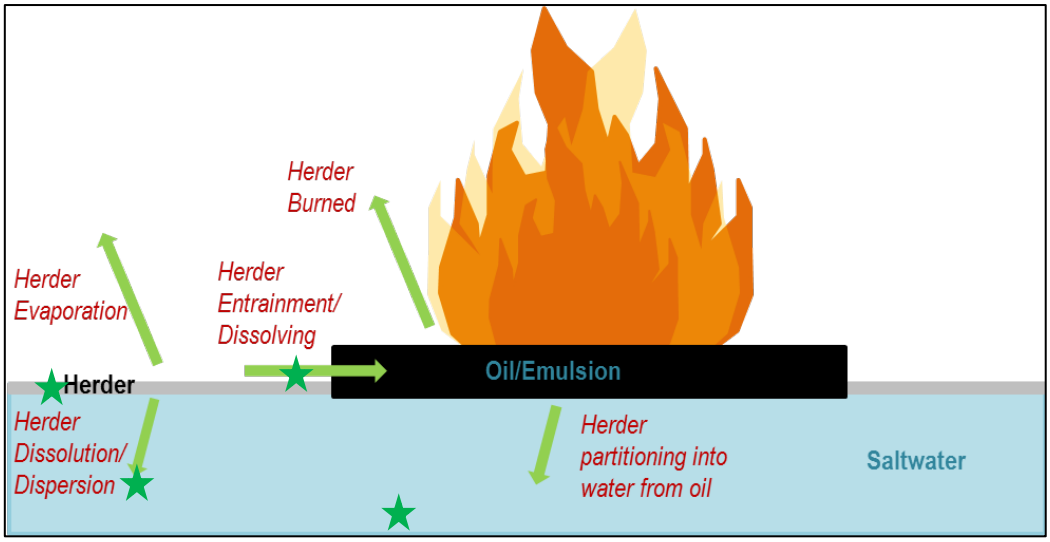


Figure 1: Conceptual outline of the potential herder fate processes during/after burning. Stars indicate where the samples were taken, both pre and post burning.

Results and discussion summary

Measured concentrations of herder in the water column and on the water surface are shown in Figure 2 and Figure 3 respectively.

Small concentrations of herders were found in the water column samples taken at the end of the experiment (< 1 ppb to a maximum of 22.7 pbb). This was the case for both OP-40 as well as TS6535. Samples taken directly under the oil slick had overall higher concentrations, particularly for OP-40 than samples taken in the water column outside the oil slick. This indicates that during burning oil droplets are released to the water causing herder (particular OP-40) entrained or dissolved into the oil droplets to partition into the water column. The GC analyses support this as traces of oil components were found in the water samples.

In the post burn samples the concentrations of herders on the surface and in the water column below the oil slick were higher for emulsions than for fresh crude oils. An explanation could be related to the nature of the herder and the emulsions, as the herder is expected to follow the oil/water interface and thus follow the oil/water interface in the emulsions. To burn emulsions, the water must be removed by e.g. breaking of the emulsions which could lead to release of herder with the water from the emulsions, thus resulting in increased herder concentrations.

Generally, the surface sample results indicate that after burning the herder was mainly found on the water surface. The amount of herder applied in the experiments (150 µl/m^2) generates an excess of herder on the water surface, seen as small droplets. Thus, the herder was not uniformly distributed on the surface in the test tank and this explains the large variations in the concentration in the surface water samples. In spite of these variations there was a tendency for the post burn water surface samples to have slightly lower concentrations of herder compared to the samples taken before burning.

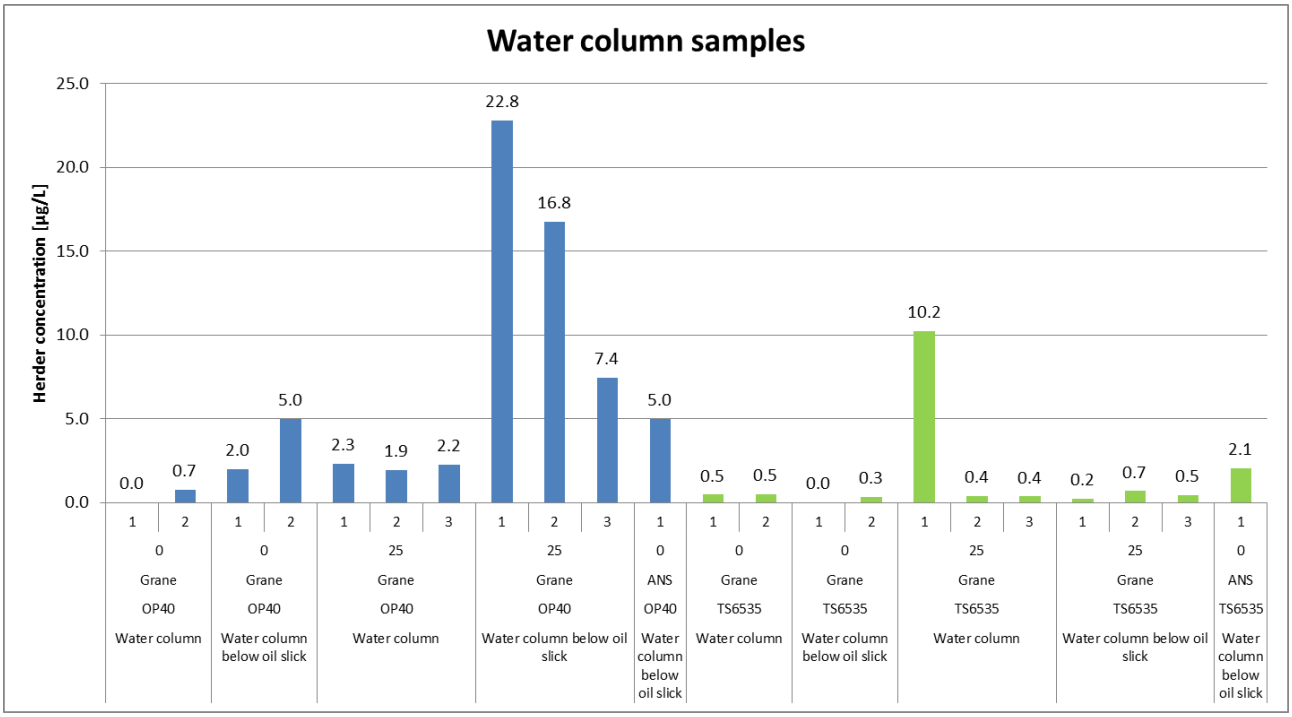


Figure 2: Concentrations of herder in water column samples after burning. OP-40 (blue bars) and TS6535 (green bars) for 0 and 25 % w/o-emulsions. The numbers 1, 2 or 3 indicate replicates. The single high values for TS6535 in 25% w/o-emulsions should be considered as an outlier, due to potential sampling errors.

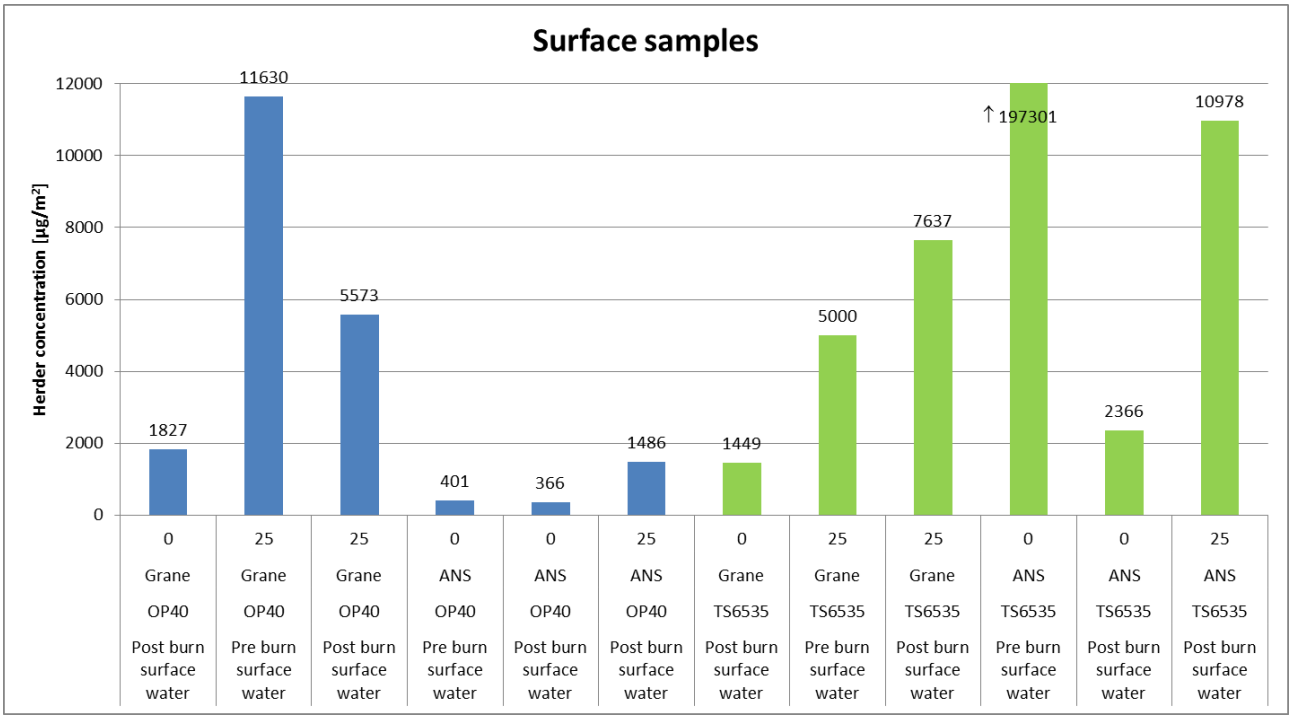


Figure 3: Concentrations of herders in surface water samples. OP-40 (blue bars) and TS6535 (green bars) for 0 and 25 % w/o-emulsions. Note that ANS 0%, TS6535 is much higher than illustrated on the graph.

TOXICITY, BIOACCUMULATION AND BIODEGRADABILITY OF HERDERS IN ARCTIC CONDITION

The basic inherent properties of herders in relation to biodegradability, bio-accumulation and toxicity in Arctic conditions and with Arctic organisms were investigated in this study. Prior to this study, standard U.S. EPA toxicity tests at 24 °C (toxicity and biodegradation) were conducted (SL Ross and DCE 2015). However, these tests were not designed to represent the Arctic conditions and organisms. The Arctic environment is characterized by low temperatures, large seasonal solar radiation variations, a unique animal and plant life adapted to the cold climate and to life associated to the sea ice, generally slow biological processes, short food chains and a high content of lipids in the organisms. This relative high content of lipids / fats serves partly as an energy reserve to withstand long periods without food and partly as insulation against the cold environment.

Toxicity and bioaccumulation of herders in high Arctic copepod (*Calanus hyperboreus*)

The purpose of this investigation was to measure the inherent acute toxicity and bioaccumulation of the two herders (TS6535 and OP-40) on high Arctic copepods (*Calanus hyperboreus*). This copepod is a key species in the Arctic due to its high abundance and important role in the Arctic food web (Hirche & Mumm 1992, Swalethorp et al. 2011), thus it is a representative test organism for the Arctic environment.

Copepods and water were collected in Disko Bay, Arctic Station, Greenland (N69° 13.386 W53° 25.218) (see Figure 4). Incubation was done in the dark using 1 L bottles at 2 °C. Testing was performed on10 adult copepods added to each bottle. The samples (water, copepods) were analysed by GC-MS in SIM mode and quantified against external calibration standards. For details about the method Buist et al (prep.) should be consulted.

Figure 4: Sampling copepods and water from a hole in the sea ice (A) and the copepods (B).

Results and discussion summary

The inherent effect of herders on behaviour and mortality on the copepods was observed over a period of 25 days and the results are given in Table 2. A distinct mortality was seen at the highest test concentrations of the herders and OP-40 appears more toxic than TS6535. The concentrations at which effects were observed for *Calanus hyperboreus* are in the same order of magnitude as the values reported earlier for two other organisms (*Mysidopsis bahia* and *Menidia beryllina)* in standard U.S. EPA toxicity tests at 24 °C (SL Ross and DCE, 2015). These effects concentrations are however three orders of magnitude higher than the concentrations that were found in the water column under slicks (0.2-22.8 µg/L) presented in Figure 2. Hence, to gain knowledge in addition to the basic inherent properties of the herder, about the effect from such operational herder concentrations, additional experiments should be conducted.

Table 2: LC and EC for TS6535 and OP-40 on *Calanus hyperboreus* after 24 and 48 hours, and 25 days (end of the experiment) and based on the nominal concentrations.

	24h - LC	48h - EC	25d - LC
TS6535	<600 mg/L	<12.5 mg/L	<60 mg/L
OP-40	< 12.5 mg/L	<2.4 mg/L	<2.4 mg/L

Exposure and accumulation of lipophilic substances can be critical especially for high Arctic organisms like *Calanus hyperboreus* with a high fat content and where internal exposure may be large in starving periods after exposure. Measured concentrations of herders in test water and copepods (body residue), recovery rates (ratio of measured to nominal concentrations) and estimated bio-concentrations are shown in Table 3. It should be noted that recovery rates are low, in particular for TS6535. The Bio-Concentrations Factors (BCF) estimates indicate that OP-40 *might* bio-accumulate and TS6535 *might not* bio-accumulate in the lipid rich high Arctic copepods. The bioaccumulation may potentially lead to delayed effects either on the animal itself or its off spring when lipid stores are used, e.g. during starvation or reproduction.

Table 3: Measured concentrations of herders in water and *Calanus hyperboreus*, recovery rates and estimated bio-concentrations factor (BCF).

	Day	Nominal concentration (mg/l)	Measured concentration in water (mg/L)	Recovery rates (%)	Body residue (mg/kg ww)	BCF*
OP-40	1	12.5	5.078	40.6	600	48
OP-40	1	60	45.090	75.2	4444	74
OP-40	4	0.096	0.012	12.5	n.m.	-
OP-40	4	0.48	0.114	23.8	n.m.	-
OP-40	4	2.4	0.422	17.6	n.m.	-
OP-40	25	0.096	0.024	25.0	1	10
OP-40	25	0.48	0.129	26.9	2.5	5
TS6535	1	600	305.017	50.8	1036	2
TS6535	4	0.096	0.004	4.3	n.m.	-
TS6535	4	0.48	0.004	0.8	n.m.	-
TS6535	4	2.4	0.001	0.0	n.m.	-
TS6535	4	12.5	0.019	0.2	n.m.	-
TS6535	4	60	3.723	6.2	n.m.	2
TS6535	25	0.096	0.000	0.0	3.2	34
TS6535	25	0.48	0.000	0.0	2.4	5
TS6535	25	2.4	0.000	0.0	3.5	1
TS6535	25	12.5	0.000	0.0	2.5	0
TS6535	25	60	0.158	0.3	106	2

*BCF factor are based on the nominal test concentrations of the herders. (n.m.: not measured)

Biodegradation of TS6535 and OP-40 in Arctic surface waters

The purpose of these experiments was to study the biodegradation of the two herders in high Arctic waters at low temperatures. The water for the biodegradation test was collected at 50 meters depth from a hole cut in the sea ice (N69° 13.386 W53° 25.218) (see Figure 4) and screened through a 100 µm mesh size net. Incubation was done in 1 litre redcap glass bottles at 2°C in the dark and the biodegradation by the natural bacteria was followed over 28 days. The studies followed the OECD 309 guideline (OECD 2004). Studies were performed at low concentrations of the herders (20 µg/L and 100 µg/L) to minimize the risk of inhibition of bacterial activity by the herders. Biodegradation of the herders was measured by chemical analysis of water samples taken day 7, 14, 23 and 28. More details about the methods can be found in Buist et al. (in prep).

Results and discussion summary

The measured concentrations of TS6535 and OP-40 are shown in Table 4 and Table 5. TS6535 could after day 7 only be detected in the "Sterile control" sample where formalin was added for elimination of the microbial degradation activity. A very fast biodegradation is most likely the explanation. The constant concentration of TS6535 in "Sterile control" indicates that the physical / chemical degradation of TS6535 is insignificant. The OP-40 test results indicate that the degradation of OP-40 was insignificant. Results from earlier preliminary standard biodegradation tests have a similar characterization of the biodegradability of the herders (SL Ross and DCE 2015).

Table 4: Concentration of TS6535 in test bottles at day 7, 14, 23 and 28 (µg/L).

Test concentration - TS6535	Replicate	Day 7	Day 14	Day 23	Day 28
20 µg/L	1	0.00	0.00	0.00	0.00
20 µg/L	2	0.00	0.00	0.00	0.00
20 µg/L	3	0.00	0.00	0.00	0.00
20 µg/L	**Mean**	**0.00**	**0.00**	**0.00**	**0.00**

100 µg/L		1	0.00	0.01	0.00	0.00
100 µg/L		2	0.00	0.00	0.00	0.00
100 µg/L		3	0.00	0.00	0.00	0.00
100 µg/L	**Mean**		**0.00**	**0.00**	**0.00**	**0.00**
Formalin - 100 µg/L		1	24.39	27.54	24.62	15.83
Formalin - 100 µg/L		2	14.65	27.79	20.54	26.44
Formalin - 100 µg/L		3	28.13	35.42	22.37	16.82
Formalin - 100 µg/L	**Mean**		**22.39**	**30.25**	**22.51**	**19.69**

Table 5: Concentration of OP-40 in test bottles at day 7, 14, 23 and 28 (µg/L).

Test concentration - OP-40	Replicate		Day 7	Day 14	Day 23	Day 28
20 µg/L		1	5.89	7.70	6.86	5.90
20 µg/L		2	8.52	7.90	9.75	4.33
20 µg/L		3	7.75	7.15	7.91	3.14
20 µg/L	**Mean**		**7.38**	**7.58**	**8.18**	**4.46**
100 µg/L		1	47.49	47.64	49.73	50.98
100 µg/L		2	56.04	54.89	62.76	59.20
100 µg/L		3	46.03	50.61	55.12	56.86
100 µg/L	**Mean**		**49.85**	**51.05**	**55.87**	**55.68**
Formalin - 100 µg/L		1	61.38	56.64	66.10	63.93
Formalin - 100 µg/L		2	65.19	60.83	58.80	63.85
Formalin - 100 µg/L		3	64.11	60.27	55.26	64.20
Formalin - 100 µg/L	**Mean**		**63.56**	**59.25**	**60.05**	**64.00**

IMPACTS OF CHEMICAL HERDERS ON FEATHERS FROM ARCTIC SEA BIRDS

Since herders are mainly considered as a surface active chemical, potential impact is also related to the herder effects on the seabird feathers and potentially fouling by the herder. Most pelagic seabirds spend many months at sea and are dependent on their feathers to keep warm (avoid hypothermia), to fly and to stay afloat. Hence, the purpose was to investigate the effects of herder layers on seawater on Arctic seabird feathers. The laboratory experiments include exposure of seabird feathers in different operational sheens of herders followed by measurements of the feather microstructure and changes in weight by absorbing water and/or herders. The feathers came from the Arctic sea birds, Thick-Billed Murre (*Uria lomvia*) and Common Eider (*Somateria mollissima*), bought in Nuuk, Greenland from legally hunted seabirds. The herders

were applied in the different dosages I) approximate operational dose rate of the herders of 150 $\mu L/m^2$ water surface. A surplus of herder remained as thick droplets (typically one or two) on the water surface, II) a dose rate of 20 $\mu L/m^2$ water surface, corresponding to the approximately minimum effective herder dosage necessary to contract an oil slick, and III) estimated monolayer thickness dose rates of 1 $\mu L/m^2$ and 3 $\mu L/m^2$ for OP-40 and TS6535 respectively. The three dosages are representative of different real-world exposure risks. The two higher dosages represent those that might occur just immediately after herder application. The herder will however, rapidly spread to form a monolayer (the low dosage), likely to occur in open water and drift ice and could extent a significant distance from the ISB operation and could persist for a significant time. Thus, it is assumed that birds would have to land on water near the ISB operations to experience the highest concentrations. A more likely exposure scenario is the monolayer dose rates as this dosage could extend a significant distance from ISB operations and could persist for a significant time.

After exposure the feather was photographed four places with a magnification of 1x11.25 (see Figure 5). The effects on feather microstructure were assessed by measures of weight changes and by use of the ‘barbule amalgamation index (AI)’. AI, developed by O’Hara and Moradin (2010), to quantify the damage on the feathers as the clumping of the barbules. For more details about the experimental methods as well as more results Buist et al (in prep.) should be consulted.

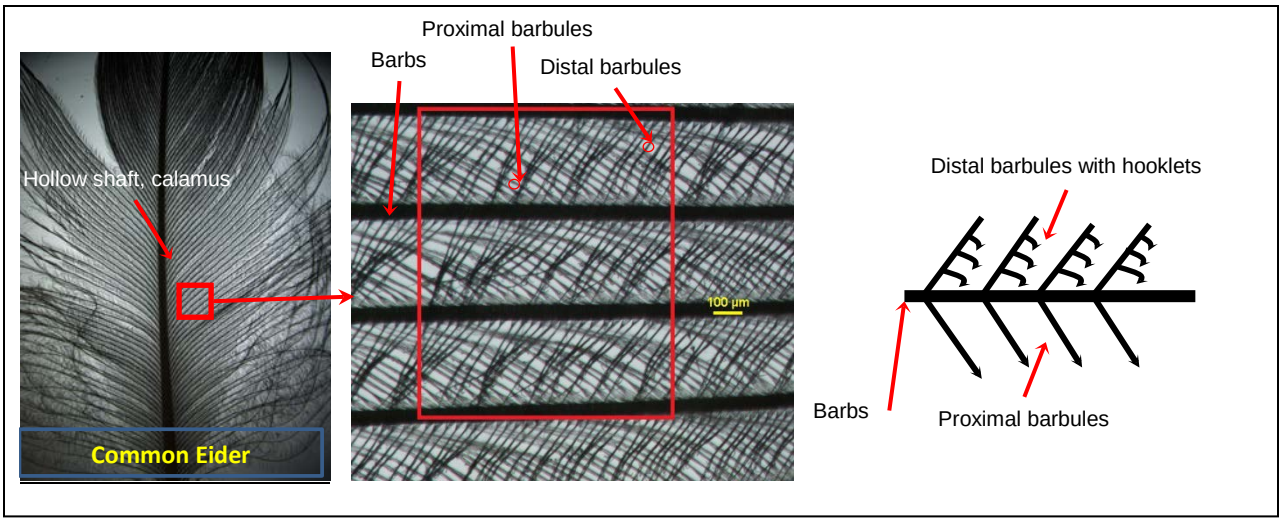
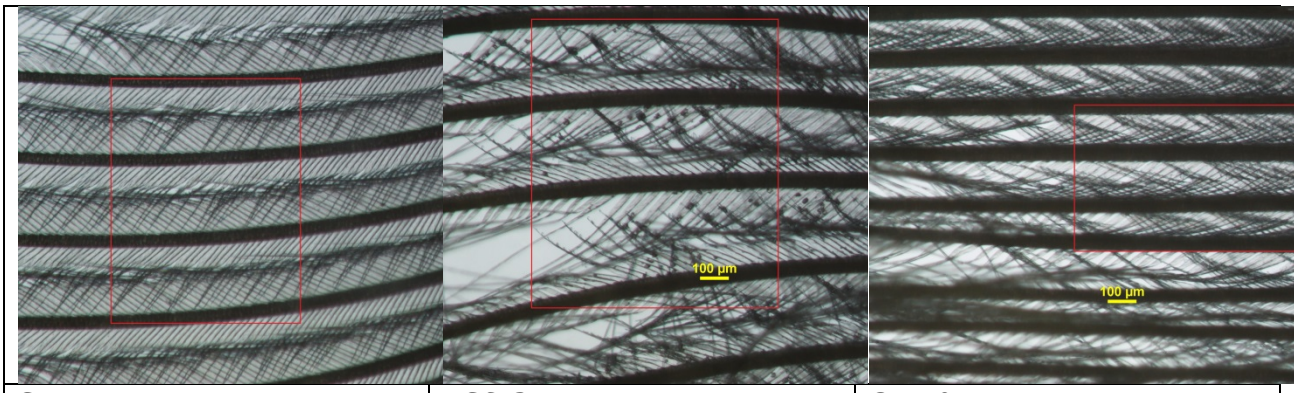


Figure 5: Bird feather terminology (From Fritt-Rasmussen et al. (2016)).

Results and discussion summery

Examples of images are shown in Figure 6: Thick-Billed Murre exposed to seawater, TS6535 and OP-40.



Seawater	TS6535	OP-40

Figure 6: Images of Thick-Billed Murre feathers at 11.25x magnification showing barbs (thick) and barbules (thinner lines) after exposure to herders, and controls (seawater).

Monolayer experiments of OP-40 (1 µL/m^2) and TS6535 (3 µL/m^2) showed that the feathers absorbed water but did not sink. This was the same for both bird species. The feathers exposed to high concentrations of OP-40 (150 µL/m^2 and 20 µL/m^2) sank within seconds after they came in contact with herder. This was not observed for exposure to TS6535 (both 150

μL/m^2 and 20 μL/m^2) but these feathers were slowly (>minutes) saturated with water. The loadings of 150 μL/m^2 and 20 μL/m^2 however, as mentioned, are assumed to be transient in a real incident, as the herders are expected to spread out into a monolayer relatively fast, thus limits the potential for birds to encounter them.

Surface tension is the force that resists infiltration of water into the plumage and the critical surface tension for feather wetting is estimated to be 38-50 mN/m (Stephenson 1997). According to SL Ross and DCE (2015) herders will reduce the surface tension of the surrounding water from approximately 70 mN/m to 20-30 mN/m, which is well below the critical surface tension for feather wetting given by Stephenson (1997), thus supporting the laboratory findings.

CHEMICAL ANALYSIS OF THE SMOKE GENERATED DURING *IN SITU* BURNING OF OIL SLICKS CONFINED WITH HERDERS

During ISB operations large plumes of combustion gases and particulate soot emitted to the atmosphere could impact the nearby wildlife and personnel. Hence, the smoke plume generated during test burns with herders were analysed to determine if the herder or herder combustion products are being emitted or whether the herder changes the emissions in some way.

Hence, the goal of these experiments was to determine whether the two herders would end up in the smoke generated by burning the herded oil. The smoke plume was sampled and analysed to determine if the herder could be detected in the combustion products. The experiments involved two fresh crude oils, ANS and Grane, and one quantitatively evaporated (ANS). The small burn experiments were conducted in the SL Ross laboratory in Ottawa, ON (Figure 7).

Figure 7 Herded slick burning under fume hood suspended over wind/wave tank

For the ISB experiments, metal heat shields were installed along the sides of the tank and the metal fume hood was swung over the burn area. The smoke from the burns was removed with a 200-m^3/min fan, through a 60-cm metal duct that is connected to the fume hood suspended approximately 1 m above the water surface.

Multiple 4 litre air sampling canisters were used to sample smoke plumes. Sampling was initiated approximately 45 seconds after ignition of the oil, while sampling times ranged between 20 to 30 seconds. The chemical analysis, by GC-FID with cryogenic preconcentration, focused on VOCs (Volatile Organic Compounds) and is tailored to identifying multiple compounds that are not typically of interest – but have been identified here for completeness. A full description of the experimental methods may be found in the project report (Buist et al. in press).

Results and discussion summary

A total of eight burn experiments were sampled. Six burn experiments with the two herders (OP-40 and TS6535) and two parent oils (ANS and Grane) were performed, along with two baseline tests which used a 40-cm diameter floating metal ring to contain the oil during the burns. A matrix of the burns can be found in Table 6.

Table 6 - Experimental matrix

Burn Run	Herder / Containment	Oil Sample
#0	none	None
#1	TS6535	ANS fresh oil
#2	OP-40	ANS fresh oil
#3	OP-40	ANS 2 day weathered
#4	OP-40	ANS 14 day weathered
#5	OP-40	GRANE fresh oil
#6	TS6535	GRANE fresh oil
#7	mechanical ring	GRANE fresh oil
#8	mechanical ring	ANS fresh oil

The results showed that neither of the herders had a negative impact on the primary BTEX compounds in the smoke. In fact, when comparing the mechanical containment results with the herded slick results, the BTEX concentrations were generally lower with the herded burns. In addition, the herder was not measured in the smoke samples by GC-FID.

Supplementary testing was performed to provide additional baseline data for the analyses. A sample of each of the herders was placed in a Pyrex® container and subjected to flame impingement from a propane torch for an initial period of approximately 30 seconds, then air sampling was conducted for an additional 20 to 30 seconds while the propane torch continued impinging on the liquid. Both herders ignited. The first test was an empty container as a control, with TS6535 and OP-40 being used in the next two tests.

The results of the flame impingement tests show low VOCs. The first test in this series, the control, showed very low concentrations of most compounds with the exception of propane (which was the fuel source for the flame). As with the analysis of the oil slick smoke plume, no obvious signs of the herders showed up in the chromatograms from samples for the test with TS6535 or OP-40.

CONCLUSIONS

Generally, after burning, the herder was mainly found on the water surface, though reduced in amount compared to pre-burning. Small concentrations of herders were found in the water column samples taken at the end of the experiment. Samples taken directly under the oil slick had overall higher concentrations of herders, in particular for OP-40. These concentrations are several orders of magnitude lower than the acute toxicity levels determined for the herders.

A distinct mortality of the copepod *Calanus hyperboreus* was only seen at the highest test concentrations of the herders. OP-40 was more acute toxic than TS6535. The concentrations at which effect are observed for *Calanus hyperboreus* are in the same order of magnitude as the values reported earlier for two other organisms in standard U.S. EPA toxicity tests at 24 °C however, are as mentioned several orders of magnitude higher than the concentration levels found in the water column measured in laboratory tests. The Bio-Concentrations Factors (BCF) estimates indicate that OP-40 might bio-accumulate and TS6535 might not bio-accumulate in the high Arctic copepods. TS6535 is most likely degraded within 7 days. Degradation of OP-40 was insignificant. The results have a similar characterization of the biodegradability of the herders as previously reported.

The OP-40 monolayer experiments showed that the feathers absorbed water. Feathers exposed to high dosages of OP-40 sank immediately after contact with herder. Feathers exposed to TS6535 did not sink, but slowly absorbed water. As herders rapidly spread to form a monolayer, the monolayer experiments are considered as the most likely exposure scenario.

The overall conclusion from the testing of the smoke is that the data showed no apparent incidences of herder in the smoke plumes. No other noticeable differences on the impacts of combustion were noted between the two methods of containment (herder vs. metal ring).

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