In-situ Remediation of Oil Spills in Ice-Infested Waters: Oil Dispersion by Enhancing Formation of Oil-Mineral Aggregates

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ABSTRACT: A novel remediation technique for oil spills under Arctic conditions, including ice-infested waters based on the application of clay mineral particles and the provision of mixing energy from propeller-wash to promote the formation of oil-mineral aggregates (OMA) has been proposed. Results from previous work in the laboratory and field have shown that the formation of OMA is associated with enhanced oil dispersion and degradation. To evaluate the feasibility of this *in situ* dispersion/bioremediation strategy in ice-covered waters, a field study was conducted with a Canadian Coast Guard ice-breaker in the St. Lawrence River Estuary (offshore of Matane, Quebec, Canada) in the winter of 2007-2008. The effectiveness of the proposed treatment strategy was evaluated by monitoring the temporal and spatial dynamic changes of petroleum hydrocarbon concentrations and investigating the rate/extent of biodegradation of the petroleum hydrocarbons. Results from laboratory microcosm studies of samples recovered from the field using Gas Chromatography/Flame Ionization Detection (GC/FID) and Gas Chromatography/Mass Spectrometry (GC/MS) showed that with hopane normalization, almost 60% of the TPH had been degraded after 56 days incubation at low temperature (0.5^{o}C). These results on the fate and effects of the petroleum hydrocarbons entrained in OMA in the aquatic environment support further research towards the application of technique as operational oil spill countermeasure.

INTRODUCTION

Marine traffic in the Arctic is predicted to increase due to the effects of climate change that has extended the open water season within the Northwest Passage and the potential growth of offshore oil and gas and eco-tourism industries. In response to recent oil spill incidents and the expansion of frontier oil and gas exploration and production activities associated with tanker traffic and construction of pipelines in ice-covered waters, the public, industry and regulatory resource managers are demanding improvements in oil spill countermeasures for use in the Arctic regions.

Existing technologies for oil spill cleanup in the ice-packed open ocean are based on physical recovery and *in-situ* burning that are limited by logistical constraints (e.g., ease of access, availability of equipment, and the aerial coverage possible within a given time frame) and environmental factors (e.g., integrity of booms vs. sea-state). Dispersion of oil through wave- and current-induced mixing energy proves to be one of the most cost-effective responses in open water. However, natural dispersion requires tremendous mixing energy to break up an oil slick into small droplets that do not coalesce and resurface. Chemical dispersants have been developed to enhance the oil-in-water emulsification efficiency, but the application of these dispersants in sensitive ecosystems

1

has been approached cautiously for the protection of human health and the integrity of the environment.

Suspended particulate matter (SPM) has long been recognized as an important factor in the transport of oil from one environmental compartment to another following an oil spill. This interaction includes both the adsorption of hydrocarbons and the associaton of dispersed oil droplets with organic and inorganic SPM (Bassin and Ichiye 1977; Boehm 1987; Karickhoff 1981; Payne et al. 1989). The active generation of oil-mineral-aggregates (OMA) in the field was first employed as "surf-washing," which exposes stranded oil to mineral fines and wave-energy when contaminated sediments are transported into the surf-zone (Lee et al. 1999; Owens 1999). The operational efficacy of this sediment relocation and surf mixing to promote OMA induced oil dispersion has been demonstrated during a major spill of opportunity of 1996 Sea Empress spill in Wales (Lee et al. 1997), and at a large-scale field experiment conducted in 1997 under Arctic conditions in Svalbard (Lee et al. 2003).

Spill response operations in ice covered versus open waters are fundamentally different. These differences must be acknowledged when determining the fate and effects of spilled oil and the most appropriate remedial strategy under various ice conditions. In arctic regions, ice conditions dampen the ambient wave energy for significant periods. However, the natural movement of ice to the edge of ice zones or strong storms can produce mixing conditions needed for dispersion even in high concentrations of ice. It has been recently proposed that sufficient mixing energy could be provided by the use of a mechanical device (such as an azimuth drive icebreaker).

The potential use of OMA as a spill countermeasure in ice-packed waters was illustrated in the late 1990's following an accidental release of oil onto ice from the tanker *Saraband* in the Saguenay Fjord, Canada. To minimize concerns that the oil trapped on or within the ice cover would become stranded on the shoreline following spring ice break-up, a decision was made to apply mineral fines to the oil stranded on or within the ice during a scheduled ice-breaking operation to open a shipping channel. The crew on the ice-breaker observed that the oil was rapidly dispersed into the water column along with the mineral fines. There was no report of any oil ever reaching the shore, but the transport and persistence of the oil in OMA was not systematically documented for that operation.

To test the feasibility of OMA enhanced oil dispersion and biodegradation, a field study was conducted with a Canadian Coast Guard ice-breaker in the St. Lawrence River Estuary (offshore of Matane, Quebec, Canada) in the winter of 2007-2008. The goal of the field trial was to assess the efficacy of the marine oil spill countermeasure strategy based on the formation of oil-mineral aggregates (OMA). The technique of promoting OMA formation as an oil spill countermeasure in ice-packed waters is based on the dispersion of oil from the surface into the water column, on the premise that concentrations are reduced to below the threshold limits that cause detrimental biological effects. In addition, in terms of removal from the environment, the biodegradation rates are higher for oil disassociated from a surface slick in the form of micron-sized droplets or in association with mineral fines that enhances its surface area. This paper reports the results of oil dispersion efficiency based on the field observation, hydrocarbon analysis of the collected samples from the field, and the follow-up laboratory microcosm study on the biodegradation of oil and/or OMA samples that have been retrieved from the field.

MATERIALS AND METHODS

Field Experiments. The tests were carried out from the Canadian Coast Guard Ship CCGS *Martha L. Black* in estuarine waters of the St. Lawrence River off the coast of Matane, Quebec (48° 51.56'N; 067° 47.39'W). The study was designed to simulate the discharge of an oil spill in the presence of ice. Three field experiments were conducted between January 30 and February 1, 2008. During each experiment, the ship was positioned with its stern directly against a section of undisturbed ice while 200L of Heidrun crude oil was poured onto the surface of the ice. Following the release of the oil, the ships' twin propellers were used at alternating speeds to break up the ice sheet while maintaining its approximate relative position. The characterization of the chemical composition of the test Heidrun crude oil is listed in Table 1. During Tests 1 and 2 (conducted on Jan 30 and 31), a slurry of 133g/L calcite mineral fines was sprayed onto the oil using a series of pressurized fire-hoses to enhance OMA formation. Four applications of mineral fines were made along with propeller wash mixing as outlined in Table 2. During Test 3 (Feb 1), no slurry or mineral fines were used during the first stage of mixing and sampling process to serve as an experimental control. After 10 minutes of mixing by the prop wash, water samples were collected using a surface sampling device and transferred into solvent rinsed 4L amber glass bottles. Transects were then conducted by the ship to monitor the extent of physical dispersion and recoalescence of the oil. At the end of the test, mineral fines were also applied along with the application of propeller wash to clean-up the field site. Field samples collected for biodegradation studies in the laboratory were stored at 2°C for transport. The samples collected for monitoring the oil concentration in the water column was sterilized by using 6N hydrochloride, and stored at 2°C until further analysis. The samples for direct microscopic analysis of OMA were stored on ice and analyzed on the same day.

Table 1: Characterization of hydrocarbon compounds in Heidrun Crude Oil

Compound	Concentration ($\mu g\ g^{-1}$)	Compound	Concentration ($\mu g\ g^{-1}$)
n-decane	418.21	dimethylfluorene	36.66
undecane	442.56	trimethylfluorene	6.21
dodecane	433.92	dibenzothiophene	47.38
tridecane	487.16	methyldibenzothiophene	136.20
tetradecane	513.58	dimethyldibenzothiophene	191.19
pentadecane	528.94	trimethyldibenzothiophene	159.95
hexadecane	433.35	tetramethyldibenzothiophene	101.46
heptadecane	451.57	phenanthrene	142.77
2,6,10,14-TMPdecane (pristane)	303.43	anthracene	7.59
octadecane	369.42	methylphenanthrene	266.51
2,6,10,14-TMHdecane (phytane)	248.58	2-methylphenanthrene	88.23
nonadecane	343.77	dimethylphenanthrene	335.27
eicosane	272.36	3,6-dimethylphenanthrene	22.75
heneicosane	260.90	trimethylphenanthrene	243.06
docosane	242.10	tetramethylphenanthrene	114.39
tricosane	209.11	fluoranthene	11.18
tetracosane	193.50	pyrene	12.27
pentacosane	166.97	methylpyrene	71.12
hexacosane	159.66	trimethylpyrene	47.39
heptacosane	154.45	tetramethylpyrene	52.71
octacosane	114.17	dimethylpyrene	83.44
n-nonacosane	116.90	naphthobenzothiophene	21.57
tricontane	90.43	methylnaphthobenzothiophene	72.12
n-heneicontane	82.00	dimethylnaphthobenzothiophene	289.36
dotriacontane	81.12	tetramethylnaphthobenzothiophene	11.73
tritriacontane	69.33	trimethylnaphthobenzothiophene	11.33
tetratriacontane	68.87	benz[a]anthracene	14.18
n-pentatriacontane	76.05	chrysene	26.80
17β(H), 21α(H)-hopane	10.47	methylchrysene	56.42
naphthalene	307.93	dimethylchrysene	60.92
1-methylnaphthalene	270.80	trimethylchrysene	39.67
methylnaphthalene	684.67	tetramethylchrysene	29.65
2,6-dimethlynaphthalene	312.84	benzo[b]fluoranthene	12.25
dimethylnaphthalene	1255.60	benzo[k]fluoranthene	6.81
2,3,5-trimethylnaphthalene	176.35	benzo[e]pyrene	11.96
trimethylnaphthalene	1119.49	benzo[a]pyrene	10.90
tetramethylnaphthalene	483.06	perylene	7.37
acenaphene	13.29	indeno[1,2,3-cd]pyrene	10.30
acenaphthalene	8.03	dibenz[a,h]anthracene	8.59
fluorene	100.26	benzo[ghi]perylene	8.67
methylfluorene	167.03		

Table 2: Field trial data log for the amount of mineral fines (calcite) used at each stage for every test

Test	Stage 1			Stage 2			Stage 3			Stage 4		
	Calcite (kg)	MT [a] (min)	ST [b] (min)	Calcite (kg)	MT (min)	ST (min)	Calcite (kg)	MT (min)	ST (min)	Calcite (kg)	MT (min)	ST (min)
1	40.0	18	8	26.7	12	12	13.3	12	11	80	75	10
2	26.7	12	14	26.6	12	14	26.7	14	11	60	80	11
3	0	10	11	29.3	12	12	20.9	12	12	310	250	NA [c]

[a] MT, mixing time;
[b] ST, sampling time;
[c] NA, samples were not collected.

Construction of Microcosms. In order to monitor the biodegradation of petroleum hydrocarbons in the samples, a series of microcosms were set up in the lab. Duran Bottle (250 ml) microcosms were filled with 100 ml of homogenized samples taken from each treatment. To overcome nutrient limitation within the closed system (nutrient regeneration occurs within the open ocean), the microcosms were amended with nitrogen and phosphorous (0.33 g B-H medium and 0.05 g NH_4Cl). The microcosms were then incubated at 0.5ºC for 56 days.

Micro-Oxymax Respirometry. The production of carbon dioxide from oil mineralization was measured by Micro-Oxymax Respirometer (Columbus Instruments, Columbus, OH). The system is designed to detect low levels oxygen consumption and carbon dioxide production. It monitors the concentration of gas contained within an enclosed head space into which the material being monitored is respiring. Periodic sensing of the gas concentration, along with an equally accurate measurement of the volume of the head space, allows calculations of incremental and accumulated values for consumption and production. The sensitivity of the system is $2x10^{-7}$ litre per hour. Temperature was controlled by a Lindberg/Blue M refrigerated water bath (Fisher Scientific, Ottawa. Ontario, Canada). Oxygen and carbon dioxide sensors were calibrated and the chamber's restriction, volume and leakage were checked up and logged before experiment. The system automatically compensates for the pressure and temperature changes. The headspace of each chamber was refreshed periodically when the gas concentration deviated from pre-set threshold.

Extraction of Petroleum Hydrocarbons. At the end of the incubation period the microcosms were removed from the respirometer for the extraction of total oil. Prior to extraction, each sample was spiked with a surrogate standard containing a series of deuterated PAH and alkanes. Each microcosm was then extracted by adding 15 mL of dichloromethane, shaken vigorously for 30 sec and then placed on an extraction roller (Wheaton R2P) at 60 rpm for 18 h. After extraction, the solvent was removed from the flask with a pipette and concentrated under a gentle stream of nitrogen to 2.0 mL hexane. At this point, the extract was divided in two, with one sample for TPH analysis by GC/FID, and one sample for aliphatic and aromatic hydrocarbon analysis by GC/MS. For GC/MS, samples were purified by passing through a column containing 2 g of 5% deactivated silica gel and 0.5 g of sodium sulphate. The column was rinsed with 10 mL hexane, loaded with the sampled extract, and then eluted with 10 mL of 20:80 dichloromethane:hexane. The solvent was collected and evaporated to 1.0 mL of isooctane and internal standards were added to each sample.

GC-MS Analysis. Samples were analyzed using an Agilent 6890 Gas Chromatograph (GC) coupled to a 5973N Mass Spectrometer (MS). The column was a Supelco MDN-5s 30m x 250µm x 0.25µm (length x i.d. x film thickness) with a 1 m retention gap of deactivated fused silica. The sample was injected using the cool-on-column mode with a sample injection volume of 1 µL. Helium was used as a carrier gas with a flow rate of 1.0 mL/min. The oven temperature program was set to hold 85ºC for 2 minutes, followed by a ramp to 280ºC at 4ºC/min which was held for 20 minutes for a total run time of 70.75 minutes. The mass spectrometer was operated in the selected ion monitoring (SIM) mode

with specific ions and retention windows applied for each compound. Samples were calibrated against a 7 point calibration curve containing a mixture of aliphatic hydrocarbons as well as parent and alkyl PAH. For some of the alkyl PAH where standards were not available, the response of the parent PAH was used for quantification.

GC-FID Analysis. The GC-FID system consisted of an Agilent 6890 Gas Chromatograph with flame ionization detector. The column and injection settings were the same as GC-MS. The initial oven temperature of 50ºC was held for 2 min, followed by an increase to 300ºC at 30ºC/min with a hold time of 10 min for a total run time of 22.33 min. The FID detector was operated at 320ºC with the hydrogen flow set at 40 mL/min and the air flow set at 450 mL/min.

Oil Dispersion and OMA Formation by UVF. The ultraviolet fluorescence spectroscopy technique of Kepkay et al. (2002) was applied to measure the dissolved/dispersed oil in aqueous phase and the oil aggregated into OMAs. Samples collected from the field were vigorously shaken and 3 ml of the suspension were rapidly transferred to an ultraviolet-grade methacrylate disposable cuvette (VWR International Inc., Mississauga, ON). The suspension was then immediately scanned in the dissolved/dispersed fraction and aggregated fraction using a QM-1 spectrofluorometer running FeliX software (PTI, Inc., Birmingham, NJ). The optimal excitation wavelength that produced the highest emission peaks was 320 nm; this wavelength with a slit width of ± 2 nm was used in all subsequent emission scans from 340 to 500 nm.

Epifluorescence Microscopy of Dispersed Oil and OMA. Samples were collected for observation of dispersed oil droplets under transmitted light and ultraviolet-epifluoresence illumination (excitation filter 340-380 nm; reflection short pass filter 400 nm; suppression long pass filter 430 nm) using a Leitz Orthplan microscope (Lee et al. 1985). The microscope is fitted with an Olympus DP70 digital camera, an HBO 50 mercury lamp, and an OptiScan computer-controlled motorized stage (Prior Scientific Inc., Rockland, MA). Photomicrographs of the physically- and chemically-dispersed oil droplets and OMAs were recorded at magnifications of 160× or 400× and quantified using image analysis software Image-Pro5.0 (Media Cybernetics Inc. Silver Spring, MD).

RESULTS AND DISCUSSION

Crude Oil Dispersion Efficacy in the Field. The field trials have been conducted to evaluate the efficacy of oil dispersion through promoting formation of OMA. Visual observations over the trials have shown remarkable difference between the OMA treatment (tests 1 and 2) and the control run (test 3).

Figure 1: Visual evidence of the effectiveness of oil dispersion via OMA formation in Test 1 after two stages of cleaning operation with the combined mineral fines and mixing energy of prop wash.

Figure 2: Visual observation of the resurfaced oil after two stages of oil dispersion in Test 3, where the first stage of cleaning effort was made by providing mixing energy only without mineral fines.

When mineral fines were applied (tests 1 and 2), the oil spiked on ice was quickly dispersed by the concerted clean-up operation of spraying mineral fines and mixing with the icebreaker's propeller wash (Fig. 1). The OMA was dispersed in the water column, and the recoalescene and resurfacing of the dispersed oil was insignificant. On the control operation (test 3), the oil was spilled onto the ice followed by mixing of oil and ice-packed waters using the propeller of the ice breaker in the same manner as the other two tests, except without adding mineral fines during the first stage of operation. The oil dispersion was very ineffective for the control trial, with patches of oil slicks lingering on the surface or frozen into the ice. Furthermore, following physical dispersion by the propeller-wash of the ice-breaker, the dispersed oil was observed to resurface (Fig. 2). Even though a larger amount of mineral fine slurry was applied from the second stage on, clean-up of oil became very difficult due to ineffective interaction among applied mineral fines and the oil trapped in ice. Formation of OMA was ascertained by the observation of samples collected in the field trials with mineral fines using an on-site microscope equipped with a combination of transmitted light and ultraviolet fluorescence illumination. While mineral fines could be distinguished under bright-field (transmitted light) illumination, dispersed oil droplets alone or within OMA were clearly defined under UV-illumination as the ultraviolet fluorescent objects (Fig. 3). The oil droplets and mineral fines were aggregated to form OMA that tend to suspend in the water column to enhance dispersion and dilution without re-coalescence and resurfacing onto the surface.

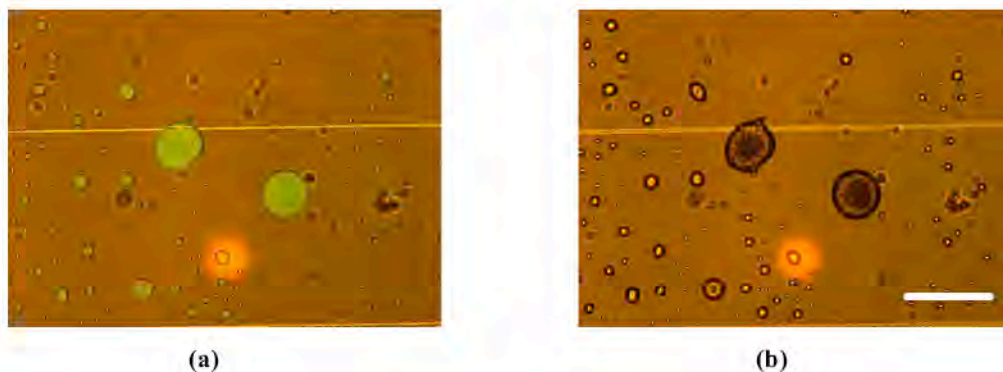(a)   (b)

Figure 3 : Microphotographs as observed in simultaneous ultraviolet epi-fluorescence and transmitted light illumination (a) and transmitted light only (b) for the same frame of slide. Bars shown are 100 μm.

The time-series oil distributions in the water column analyzed by using GC/FID and ultraviolet fluoremetry (data not shown) support the observation that most of the oil was dispersed in the water column for the two tests treated with mineral fines (Fig. 4a). But in the control test in which mineral fines were not used until after an hour, there was significantly less oil in the water column (Fig 4b).
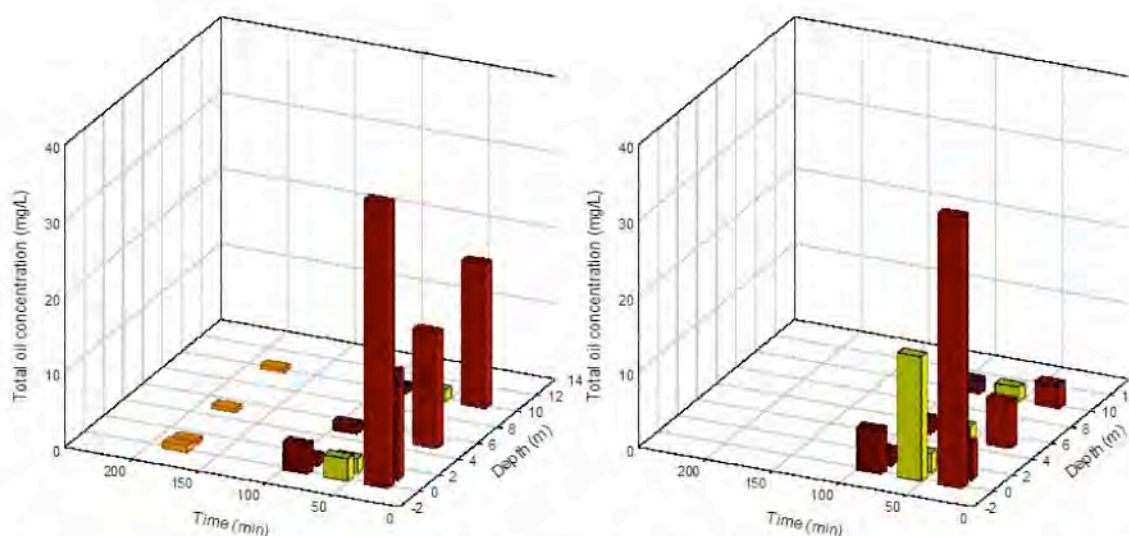
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Figure 4: The measured dispersed total oil concentration as a function of depth and time from the field collected samples of Test 1 (left) and Test 3 (right)

Persistence of the Crude Oil in the Microcosms. Biodegradation of the field samples was investigated through a laboratory microcosm study. Mineralization of oil from the field samples amended with nutrients was measured with a Micro-Oxymax respirometer (Fig. 5). The extent of oil degradation was enhanced by the addition of fine minerals that facilitated OMA formation.
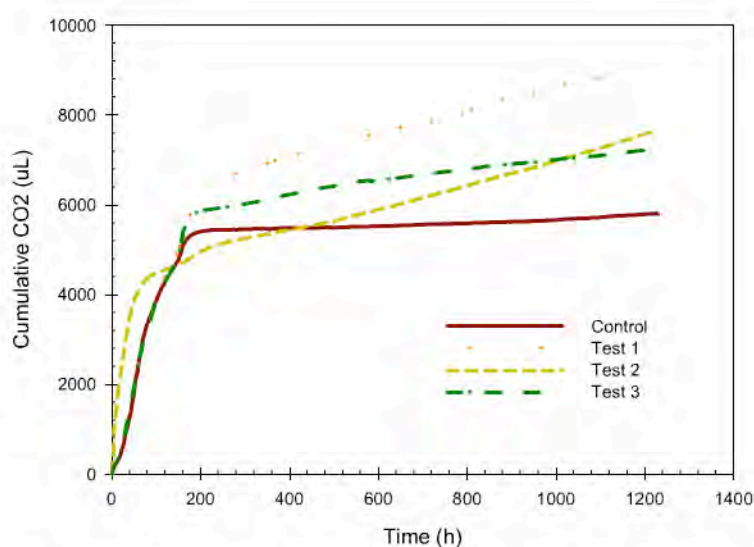
Figure 5: Cumulative carbon dioxide production from oil mineralization in microcosms.

Figures 6 and 7 shows the representative GC-MS chromatograms of the biodegradation samples at T=0 and T=56 days, respectively. The chromatograms show that a large amount of the petroleum hydrocarbons were degraded over the course of the experiment.
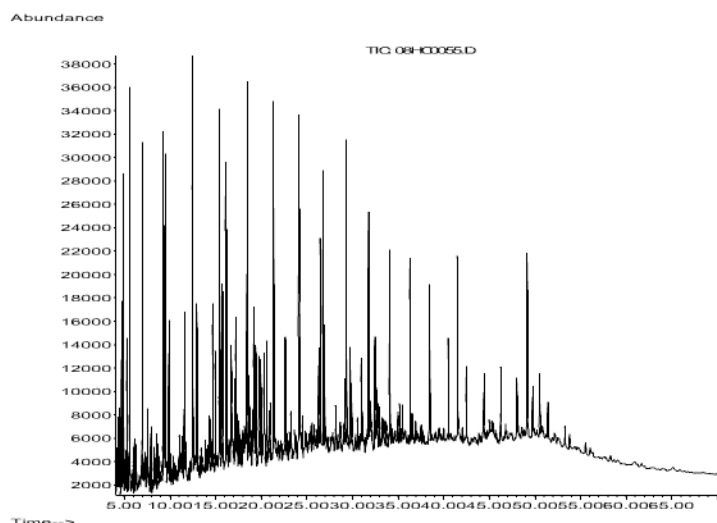
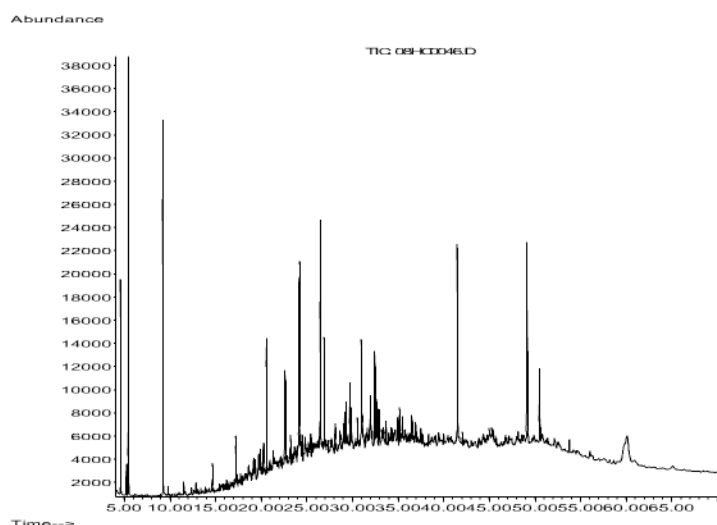**Figure 6: Representative GC-MS chromatograms of Heidrun crude oil before biodegradation.**

Figure 7: Representative GC-MS chromatograms of Heidrun crude oil after biodegradation with incubation at 0.5°C for 56 days

To quantify the amount of amount of oil that was degraded, GC-MS results were normalized to the concentration of the conservative biomarker 17β(H), 21α(H)-hopane (Venosa et al. 1997). The hopane-normalized alkanes (Figure 8) and PAHs (Figure 9) are presented for Test 1 (when oil was treated with mineral fines). The data have been subdivided into resolved aliphatic and aromatic hydrocarbon concentrations before the onset of biodegradation, after biodegradation in the absence of nutrients, and after biodegradation in the presence of added nutrients. Biodegradation of alkanes ranging from n-decane to tritriacontane was observed, and the addition of nutrients stimulated

biodegradation of alkanes at nearly zero degree temperature. Within the time-frame of the experimental study, significant degradation of PAHs was also observed for two- and three-ring compounds (e.g., naphthalene, phenanthrene), although the high molecular weight PAH were less degraded, due to the recalcitrance of these compounds. The degradation of total oil and different fractions of petroleum hydrocarbons are estimated by the loss of the mass normalized by the hopane biomarker.
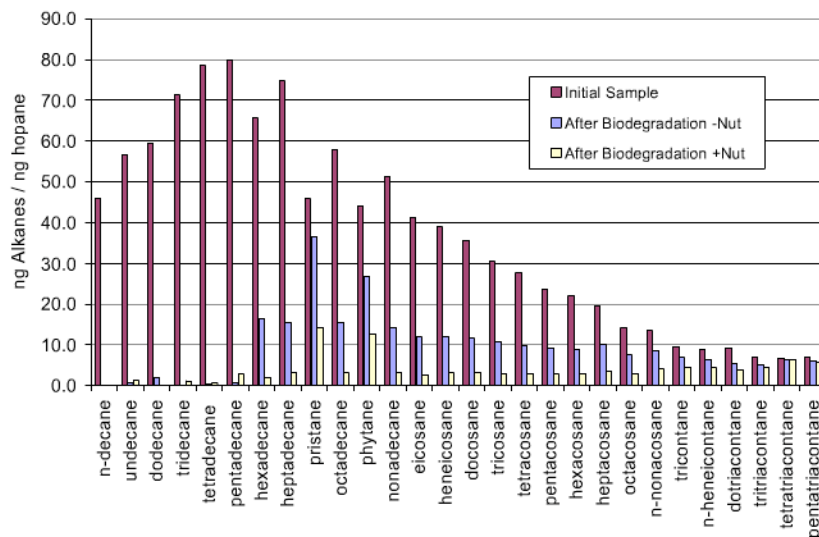
Figure 8: Comparison of Alkanes before and after biodegradation for test#1
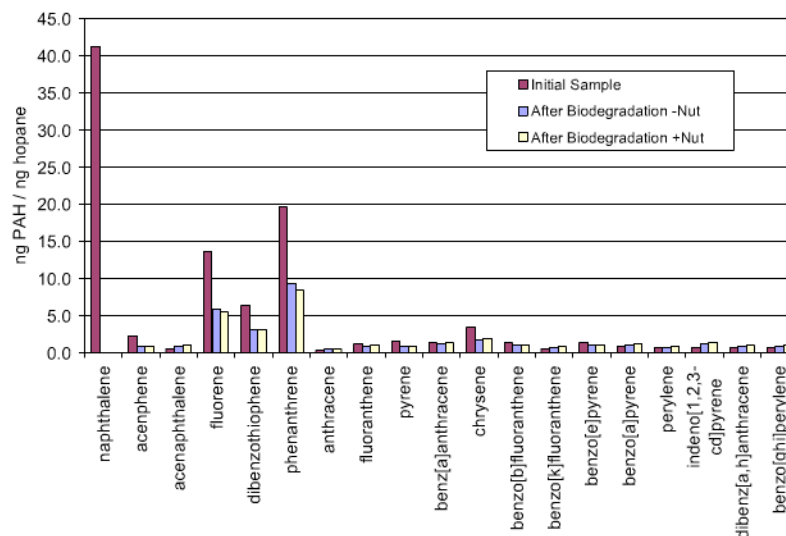
Figure 9: Comparison of PAHs before and after biodegradation for test#1

The treatment effects as a result of different operational conditions during the three independent trials on the degradation rate of hydrocarbons are summarized in Figures 10-

12

12. More than 55% of the total mass of oil was degraded after 56 days at 0.5 ºC. Among the major fractions of oil, the alkanes were most effectively degraded, and nutrients stimulated their degradation (10). The degradation of PAHs (11) and alkylated PAHs (12) was also observed in all three trials, but the addition of nutrients did not stimulate the degradation of aromatic compounds.
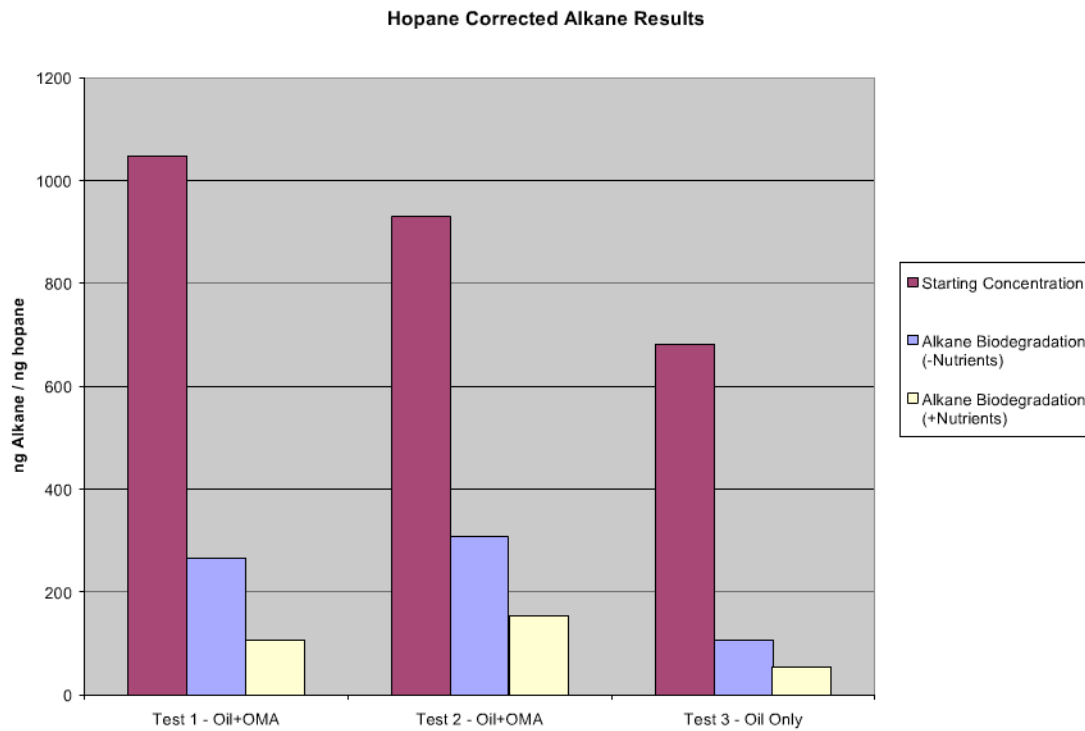

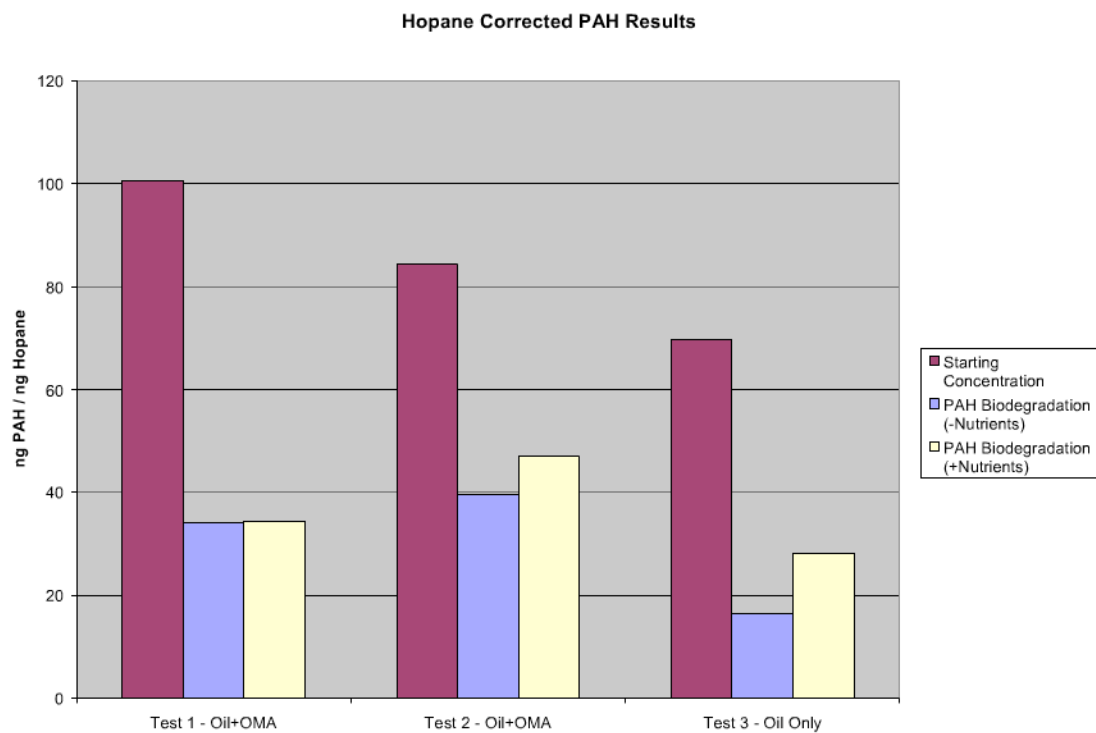Figure 10: Effect of treatment conditions on biodegradation of alkanes.

Hopane Corrected PAH Results

Figure 11: Effect of treatment conditions on biodegradation of PAHs

Hopane Corrected Methyl-PAH Results

Legend:
- Starting Concentration
- Methyl-PAH Biodegradation (-Nutrients)
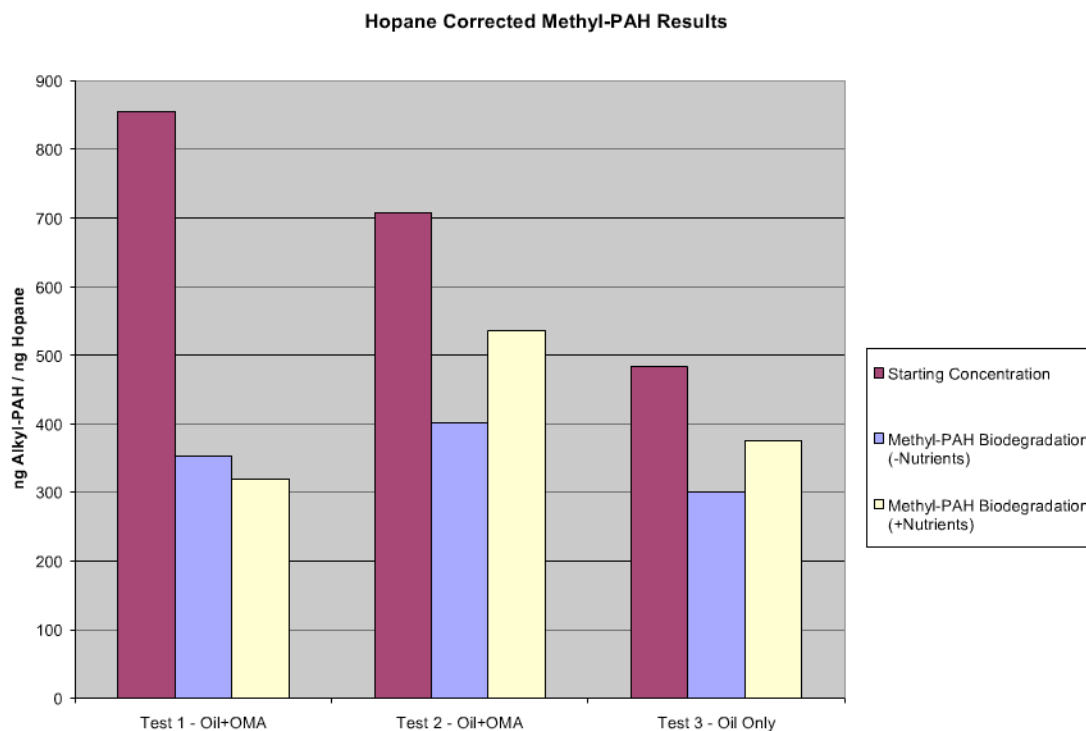- Methyl-PAH Biodegradation (+Nutrients)

Figure 12: Effect of treatment conditions on biodegradation of Alkyl-PAHs

CONCLUSIONS

A unique field trial on the remediation of oil spilled on ice-covered waters has been conducted. Oil spilled within a field of broken ice was effectively dispersed into the water column by the combined action of mineral fine additions and mixing by propeller-wash. The dispersed oil with OMA in the water column was effectively dispersed over large area by natural currents and tides. The premise of enhanced OMA formation as a spill response strategy is contingent upon dilution to concentrations below toxicity threshold limits and the eventual removal of oil by natural biodegradation processes. Enhanced dispersion of the oil was verified during field operations and the results of a 2-month laboratory microcosm study demonstrated that more than 56% of the spilled oil was degraded despite the low temperature of ice-infested waters. Mineral fine additions promoted habitat recovery by enhancing the extent of oil biodegradation.

ACKNOWLEDGEMENTS

15

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