

***Enhancement of Oil-Mineral-Aggregate Formation to
Mitigate Oil Spills in Offshore Oil and Gas Activities***

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Debra M. Bridge
Contracting Officer
Department of the Interior, Minerals Management Service
Procurement Operations Branch, MS 2101
381 Elden Street
Herndon VA 20170

Submitted by:

Kenneth Lee, PhD, Zhengkai Li, DSc, PE, Haibo Niu, PhD, and Paul Kepkay, PhD
Center for Offshore Oil and Gas Environmental Research; Fisheries and Oceans Canada
1 Challenger Drive, Dartmouth, NS, Canada, B2Y 4A2
Phone: (902) 426-7344, Fax: (902) 426-1440
Email: leek@dfo-mpo.gc.ca

Ying Zheng, Ph.D.
Department of Chemical Engineering, University of New Brunswick,
Fredericton, NB, Canada, E3B 5A3

Michel C. Boufadel, PhD, PE
Department of Civil and Environmental Engineering, Temple University
1947 N. 12th Street, Philadelphia, PA, USA, 19122

Zhi Chen, PhD, PE
Department of Building, Civil, and Environmental Engineering, Concordia University,
1455 de Maisonneuve Blvd. W., Montreal, QC, Canada, H3G 1M8

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Executive summary

The risk of accidental releases of crude oil into the sea is expected to increase with anticipated growth of coastal marine traffic and offshore oil and gas activities. To address this issue, the U.S. Department of the Interior Minerals Management Service (MMS) has identified a need for improved alternative technologies for marine oil spill response operations under their Technology Assessment and Research (TA&R) Program.

The Centre for Offshore Oil, Gas and Energy Research (COOGER) in Canada's Department of Fisheries and Oceans is developing and evaluating the efficacy of a new oil spill countermeasure technique that is based on the enhanced formation and dispersion of oil-mineral aggregates (OMA) in marine oil spill incidents. The advantages of this technology include: 1) enhanced dispersion of oil slicks and stabilization of dispersed oil droplets in the water column; 2) reduction of oil concentrations below toxic threshold limits; 3) reduced re-coalescence of droplets and adhesion properties of oil, and; 4) enhanced oil biodegradation rates.

A comprehensive laboratory experimental program was conducted to elucidate effects of several important factors on the formation of oil-mineral aggregates. Three important factors, namely mineral type, mixing energy and dispersant use, were studied for dispersion of three crude oils with varying physicochemical properties. The physicochemical characteristics of the mineral fines including particle size distributions, surface area, and particularly hydrophobicity, were found to play important roles in oil-mineral interaction and OMA formation. Initially increased hydrophobicity promotes the affinity of mineral fines to oil and formation of OMAs, whereas an optimal range of mineral hydrophobicity exists beyond which repelling forces between mineral fines and oil droplets are predominant. The laboratory experiments also revealed that chemically-dispersed oil droplets are more stable than those that are physically dispersed, suggesting that application of mineral fines in conjunction with chemical dispersant may further enhance OMA formation and oil dispersion in the water column.

A large-scale wave tank study was also conducted to evaluate the feasibility of promoting OMA formation as an oil spill countermeasure in more realistic hydrodynamic conditions. As the most effective mineral type identified in the laboratory study, kaolin was selected as the mineral fines, and weathered MESA crude oil was used in the suite of wave tank experiments. Several factors including the mineral-to-oil ratio (MOR), the presence and absence of dispersant, and the wave conditions, were investigated in the wave tank experiment for their influences on the formation of OMA and subsequent transport and dilution effects. In addition to the hydrodynamic conditions of the regular non-breaking waves or breaking wave conditions, a current flow was introduced to the system by operating the wave tank in the flow-through mode. The dispersion effectiveness of the initially spilled oil at the surface of the wave tank approximately 10 m from the wave maker was continuously monitored by sampling the water column near the end of the wave tank from five different depths at eight time points over the course of the one-hour experiment. The water samples were analyzed using chemical analysis of

total oil concentrations by extracting oil with dichloromethane and reading the ultraviolet absorbance at three different wave lengths with an ultraviolet spectrophotometer. The dispersed oil and OMA particle concentrations and particle size distributions were also monitored by deploying an LISST-100X laser particle counter.

Findings from the wave tank experiment are consistent with those from the laboratory experiment. Higher mixing energy levels associated with breaking waves provided more favorable conditions for oil dispersion, oil and mineral interaction, and OMA formation and dispersion. The use of chemical dispersant, together with mineral fines or on its own, significantly increased the oil concentrations and reduced the average dispersed oil droplet size distributions in the water column. The wave tank experiment also revealed that the larger fraction of OMA remained near the surface under regular wave conditions, suspended in the water column to be carried out by current flow under breaking wave conditions. Within the time-frame of the experiments, very little oil was detected near the bottom of the wave tank especially under regular wave conditions. This suggests that under the hydrodynamic conditions typically found at sea, there is a high probability that OMA formed during operational oil spill countermeasure applications would have little impact on organisms living within the water column and on the bottom due to physical dispersion processes (e.g. current flow) that would rapidly reduce the concentration of oil below toxicity threshold limits.

A random walk particle tracking model was used to simulate the transport of OMA under hydrodynamic conditions involving three dimensional velocity distributions associated with wave action, turbulent diffusion and gravity. Stokes' theory was used to describe the wave-induced velocities. The settling velocities of OMA were calculated using empirical equations derived from experimental data. Simulations were performed to evaluate the effects of wave characteristics, the particle size distributions and effective density of OMA, as well as sediment type on the transport of OMA.

The experimental studies and the model simulations conducted under this research program addressed both fundamental mechanisms and practical applications for the proposed new oil spill response technology. The proposed oil spill response technology based on the promotion of OMA formation will enhance the rates of oil dispersion and biodegradation. A net benefit analysis suggests that the proposed procedure may fill the gap in existing oil spill response operations where conventional mechanical response technologies are constrained due to logistical challenges.

1. Introduction

Oil spilled into the open sea is extremely difficult and expensive to remediate. Existing technologies based on physical recovery are limited by logistical constraints (e.g., availability of equipment, and the aerial coverage possible within a given time frame) and environmental factors (e.g., integrity of booms vs. sea-state). A new oil spill countermeasure procedure is proposed for the treatment of oil slicks on the sea surface and/or naturally occurring oil droplets within the water column generated by physical wave activity.

Studies on oil-mineral aggregate (OMA) formation have demonstrated that both mineral fines and organic particles can stabilize oil droplets within the water column. Various types of aggregates can be formed depending on the physicochemical properties of the particles, the type of oil and environmental conditions (Lee et al. 1998; Muschenheim and Lee 2002; Stoffyn-Egli and Lee 2002). Both controlled laboratory experiments (Cloutier et al. 2002; Khelifa et al. 2005c; Lee et al. 1997; Omotoso et al. 2002; Stoffyn-Egli and Lee 2002) and shoreline field trials (Lee et al. 1997; Lunel et al. 1997; Owens et al. 1995; Owens and Lee 2003) have demonstrated that OMA enhances the natural dispersion of oil spilled in the environment and reduces its environmental persistence. However, no specific studies have been focused on the potential application of mineral fines to facilitate OMA production as an operational marine oil spill countermeasure for use at sea.

OMA formation has been observed in numerous field sites that have ranged from the rivers of Bolivia (Lee et al. 2001; Lee et al. 2002) to the shores of Svalbard Island in the high Arctic (Owens et al. 2003). The OMA occurrence covers the range of natural variance for temperature, salinity, oil types and mineral composition. Numerical models support the hypothesis that OMA can form rapidly (Hill et al. 2002; Khelifa et al. 2003), as long as sufficient mixing-energy is available. Detailed chemical analysis of samples recovered from coastal waters following surf-washing operations after the Sea Empress spill in the United Kingdom conclusively demonstrated that OMA formation enhanced the biodegradation rates of the residual oil (Colcomb et al. 1997; Lee et al. 1997) as the stabilization of oil droplets by mineral fines increased the oil-water interface where microbial activity primarily occurs. Thus, this remediation process not only dilutes oil spilled into the environment, it may effectively eliminate many components of environmental concern. In terms of protection of the fisheries and fisheries habitat, OMA formation and its dispersion will minimize environmental impacts. For example, field studies in Svalbard, Norway demonstrated that OMA within the immediate vicinity of the spill site was dispersed to levels below regulatory toxicity threshold limits (Owens et al. 2003).

To promote OMA formation, mineral fines may be sprayed onto surface slicks as a powder or aerosol mixture. The delivery of mineral fines and the application of additional mixing energy (using prop-wash from ice-breakers) is currently under study in a research program between the Centre for Offshore Oil and Gas Environmental Research

(Fisheries and Oceans Canada) and the Canadian Coast Guard (contact – Martin Blouin) to evaluate the feasibility of an OMA based countermeasure for oil spills in dynamic pack-ice.

Furthermore, OMA formation may augment the effectiveness of existing oil spill response strategies such as chemical oil dispersants. There is renewed interest in these products since they can be rapidly applied by aircraft over a large impacted area. However, their effectiveness has been questioned due to concerns over the potential for recoalescence of chemically dispersed oil droplets. Preliminary wave tank studies at the Bedford Institute of Oceanography have shown that the addition of mineral fines may suppress this process.

The objective of this research is to assess the feasibility of a marine oil spill countermeasure strategy based on the stimulation of OMA formation. Evaluations will be conducted on both laboratory and wave tank systems under controlled conditions to assess its potential effectiveness for the treatment of oil spills from shipboard and rig operations. Conceptual-mathematical models have been developed to identify the key factors affecting transport of OMA as a means to provide guidance for field operations and evaluation of the efficacy and risk assessment of the strategy.

2. Laboratory experiments

2.1. Material and methods

2.1.1. Crude oils and mineral fines

Properties of crude oils

Three different crude oils were studied: MESA, Alaska North Slope (ANS) and Heidrun. The physical properties are summarized in Table 1. Density was measured by portable density meter (DMA 35N, Anton Paar GmbH, Graz, Austria) at 22°C. Viscosity was determined at 40°C following ASTM D445-06 and the measurements were taken by X-CELL Analytical at St. Francis Xavier University in Antigonish, Nova Scotia.

Table 1: Physical properties of the tested crude oils

Oil type	Specific gravity	Kinematic viscosity(cS)
MESA	0.8764	13.06
Alaska North Slope	0.8746	10.82
Heidrun	0.9058	21.09

Minerals

In this study, different types of minerals were tested to study their effectiveness in trapping and spreading oil droplets. Natural minerals, including kaolin (Fisher Scientific), diatomite, fly ash, graphite, and commercial sorbent ‘Miracle Sorb’ (ABASCO, Houston,

Texas) were chosen. Kaolinite, mined as kaolin in numerous parts of the world, is a layered silicate mineral with the chemical composition $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. For this study, two types of modified kaolin with different levels of hydrophobic properties (Kaolin #1 having a lower hydrophobicity level than Kaolin #2) were prepared using a methodology described in the literature (Molphy et al. 1994). Modified Size distribution of the minerals was measured by a laser particle size analyzer (Analysette 22 compact, Fritsch GmbH, Idar-Oberstein, Germany) and surface area was determined by BET nitrogen adsorption (Belsorp-max, Bel, Japan). The hydrophobic property was determined based on the static contact angle that was measured using a JC200A instrument (PowerEach, China) with a digital photo analyzer, imaging at 3s after the water contacted the sample pellet. The coatings of alkyl groups on modified kaolin were identified on the infrared spectra (IRS), generated by a Nicolet 6700, Thermo Scientific, USA.

2.1.2 OMA experimental procedures and conditions

Procedure

Experiments were conducted with a modified experimental procedure for partitioning of oil in three fractions (Lee et al. 2008; Weise et al. 1999). Artificial seawater with 30 ppt salinity was prepared by dissolving an appropriate amount of sodium chloride into distilled water. 120ml of water was placed in a baffled flask (Fisher Scientific) along with 40mg of minerals, and the solution was shaken on an orbital shaker (VWR Scientific) at 150 or 250 rpm for 10min. 100 μl of crude oil was then added to the sediment/saline water suspension and 4 μl dispersant (Corexit 9500, Nalco Energy Service, L.P. Sugar Land, TX) was carefully dispensed onto the oil. The baffled flask, designed to enhance mixing energy (Venosa et al. 2002), was then shaken for another 60min at 150 or 250 rpm to generate OMA. Following this the entire contents of the flask were transferred to a separatory funnel and left static for 60mins to allow for separation into three phases: the bottom fraction – settled OMA (5ml); the middle part – dispersed oil and suspended OMA (110ml), and; the top portion – floating non-dispersed oil (5ml). 5ml of the middle part was extracted for oil droplet and OMA size measurements using a fluorescence microscope and confocal laser scanning microscope. The oil in the middle and bottom parts were extracted with dichloromethane (DCM), and oil in the flask and funnel were rinsed with DCM and mixed with the oil phase from the top part. The total petroleum hydrocarbon dissolved in DCM was measured with a UV spectrophotometer (UV-1800PC). Four replicates were conducted for each condition.

Experimental setup

MESA crude was investigated using the experimental conditions as shown in Table 2. One factor was changed in each set of the experiment. The tests for the ANS and Heidrun oils were performed using factorial experimental design and the results are summarized in Table 3. All the experiments were conducted following the above mentioned procedure.

Table 2: Laboratory experimental conditions of OMA with MESA oil

	Experiment
Reaction vessel	Baffled flask(250ml)
Water volume(ml)	120
Oil	MESA oil (100 µl)
Salinity (ppt)	30
Orbital shaker speed (rpm)	150, 250
Minerals	Kaolin, Diatomite, Fly ash, Graphite, Modified kaolin #1, Modified kaolin #2
Dispersant-to-oil ratio (DOR)	0, 0.5:25, 1:25

Table 3: Laboratory experimental design for the study of OMA with ANS and Heidrun oil

Treatment number	Factors		
	Mixing speed (rpm)	Mineral	Dispersant
1	150	kaolin	0
2	250	kaolin	1:25
3	150	diatomite	1:25
4	250	diatomite	0

2.1.3 Analytical method

Analysis of total oil concentration

The samples of oil–water mixture obtained in the above experiments were extracted using dichloromethane, and then analyzed for ultraviolet absorbance at three different wavelength 340nm, 370nm and 400nm (Venosa et al. 2002) using a UV spectrophotometer. The area between these wavelengths was used according to the following equation:

$$Area = \frac{(Abs_{340} + Abs_{370})}{2} \times 30 + \frac{(Abs_{370} + Abs_{400})}{2} \times 30 \quad (1)$$

Microscopy

5ml samples taken from the middle part of the separatory funnel were collected for observation of OMA and dispersed oil droplets by LEICA transmitted light and UV epifluorescence microscopy (excitation filter 340-380nm, long emission filter 425 nm). The analytical procedure used in this research was described in previous literature (Stoffyn-Egli and Lee 2002). 20X and 100X objectives were employed to image OMAs and dispersed oil globules with 20-40 sequential fields of view for each counting chamber. The recorded photomicrographs were analyzed by image analysis software to acquire the size distribution of OMAs and dispersed oil droplets.

LEICA TCS-SP2 confocal scanning laser microscopy was used to study OMA structure. Simultaneous excitation wavelengths of 488nm and 633nm were used. The signal emitted in the range of 515-540nm was recorded in the green channel and represents fluorescent oil. The signal emitted in the range of 630-642nm was collected in the red channel and the most intense signal represents the reflectance from mineral particles. A second method with a single excitation wavelength of 488nm was also employed to verify the reflection signal. The 484nm-490nm signal was collected in the red channel as the reflectance from minerals, while the same range of wavelength (484nm-490nm) was used for fluorescent oil.

2.2. Results and discussion

2.2.1. Effect of dispersant

Dispersant can be an effective reagent to combat oil spills. Dispersant reduces the oil-water interfacial tension, stimulates break-up of an oil slick into fine droplets, and promotes dispersion of oil from the surface into the water column (Venosa et al., 2002). As an example, Figure 1 shows that the application of dispersant significantly increased the concentration of MESA oil in the middle of the saline water column in test conditions, where approximately 80% of the feed oil was dispersed at dispersant-to-oil ratio (DOR) of 1:25. In the presence of mineral fines, the amount of oil trapped in the middle portion varied with DOR and mixing energy. As shown in Figure 1a, given adequate mixing energy (250 rpm), most oil droplets were stabilized at small sizes and well dispersed in the middle part of the water column. Increasing DOR from 1:50 to 1:25 slightly increased the fraction of Total Petroleum Hydrocarbon (TPH) in the middle portion. In the absence of dispersant, the oil trapped in suspension by OMA was less than 20% for both minerals. At a lower mixing energy (150 rpm), a high percentage of feed oil was retained in the middle portion due to the presence of dispersant, as shown in Figure 1b.

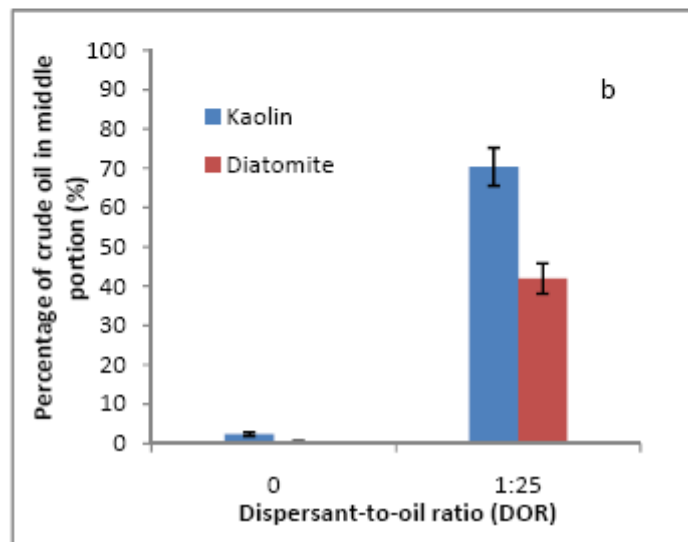
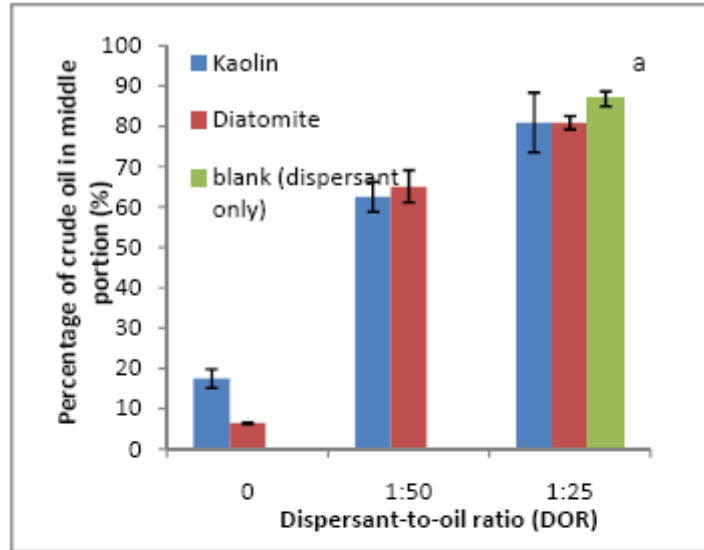


Figure 1: The effect of dispersant on MESA oil at two mixing energies: (a) 250 rpm (top), and (b) 150 rpm (bottom)

Figure 1 also suggests that minerals are less effective than dispersant in keeping oil suspended in the middle portion of the saline water column. Addition of dispersant suspended approximately 80% of feed oil in the middle portion while less than 20% of feed oil was retained in the middle portion by minerals without dispersant. OMA formation was caused by introducing minerals to the oil-water-dispersant mixture. Due to the relatively high density of minerals, some large OMA sank to the bottom of the funnel, as indicated by the percentage of fines observed at the bottom part (e.g. 5.92% for kaolin at 250 rpm). The effectiveness of dispersant was verified using the other two crude oils: ANS and Heidrun. Figure 2 shows the results obtained by using an Orthogonal Array Testing Strategy (OATS) analysis. From this, it was observed that the trends for

dispersant effects at different DOR on ANS and Heidrun oils were consistent with those on MESA oil.

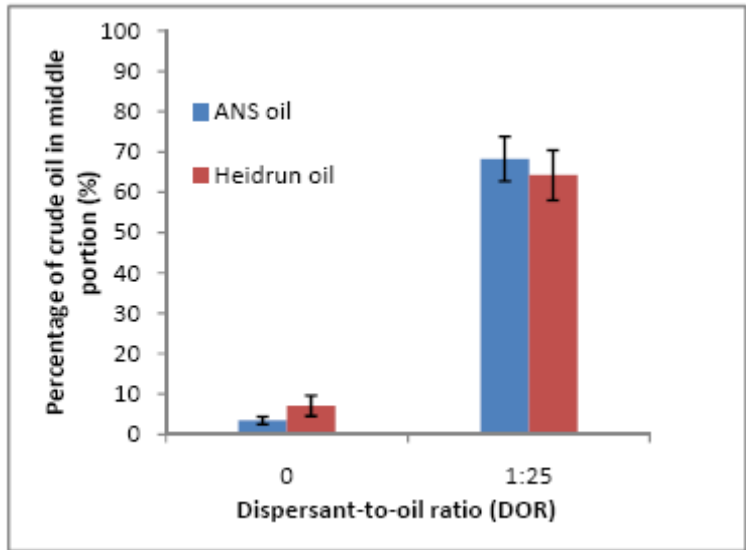


Figure 2: The effect of dispersant on ANS oil and Heidrun oil

2.2.2. Effect of mixing energy

Mixing energy is also an important factor influencing oil distribution. The mixing energy effect was examined by mixing the oil-mineral-water solutions at two different speeds (150 and 250 rpm) in the baffling flasks.

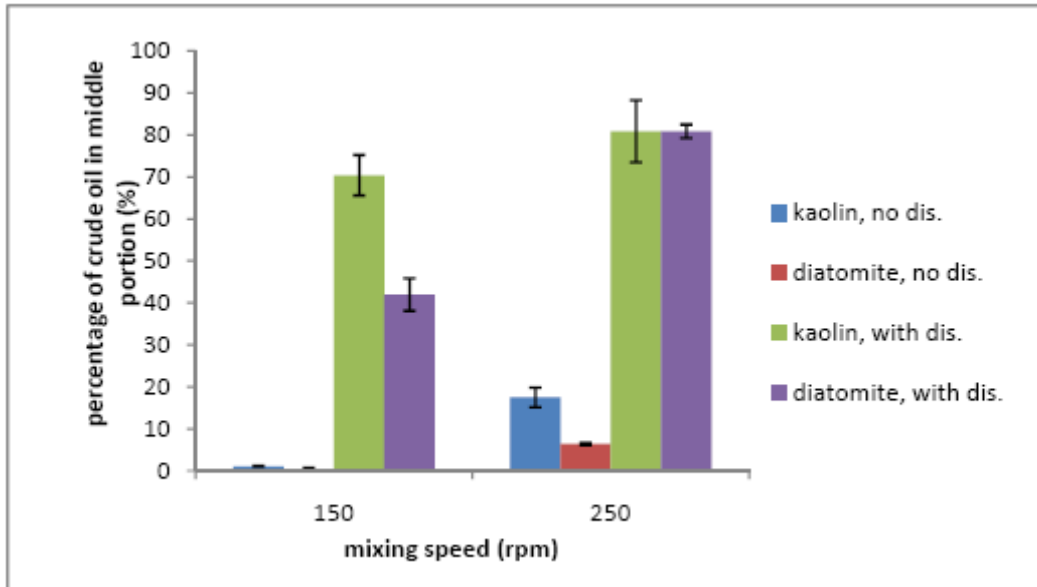


Figure 3: The effect of mixing energy on MESA dispersion

As shown in Figure 3, when the flasks were rotated on an orbital shaker at 150 rpm, in the absence of a dispersant most mineral particles were not agitated due to insufficient mixing energy. This indicates that without a dispersant the mixing energy at this speed is not large enough to take the mineral particles into the middle water column, which significantly limits the interaction between oil and minerals. In the absence of chemical dispersant, the oil trapped in suspended OMA in the middle portion at 250 rpm is approximately 15 times higher than the oil trapped at 150 rpm, indicating that lower mixing energy results in formation of fewer OMAs and therefore a lower amount of trapped feed oil.

In the presence of dispersant, the effect of mixing energy on oil suspension in the water column becomes less significant. For example, at 150 rpm approximately 70% of oil was suspended in the middle water column using kaolin, and nearly 50% using diatomite (Figure 3). However when mixing motion ceased, it was noticed that at 150 rpm the oil tended to resurface from the bulk water column, whereas the same phenomenon was not observed for the oil mixed at 250 rpm. Therefore, higher mixing energy encourages the formation and stability of oil-in-water emulsions.

Similar trends were observed for the other two crude oils. As shown in Figure 4, higher mixing energy increased the amount of oil dispersed in the middle portion of the water column.

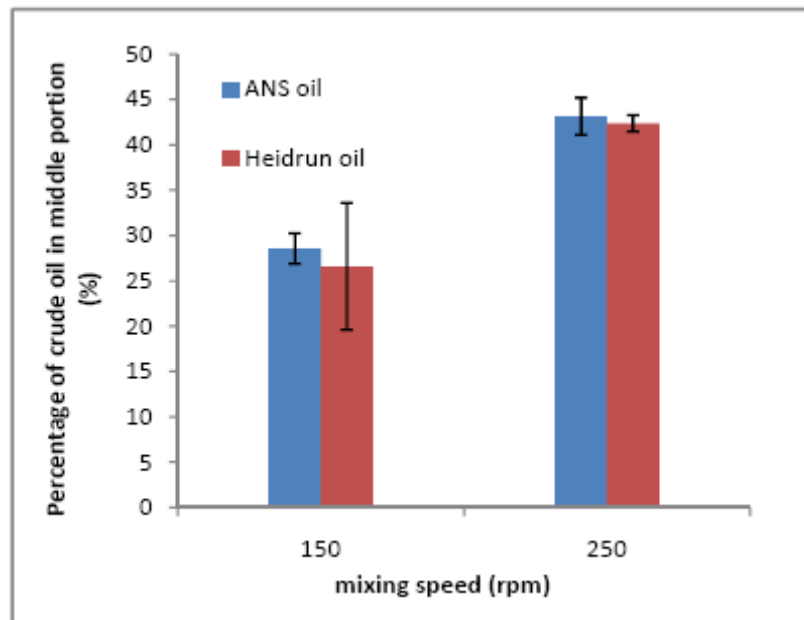


Figure 4: The effect of mixing energy on ANS oil and Heidrun oil

2.2.3. Effect of mineral type

Mineral types

To evaluate the effect that mineral type has on the formation of OMAs, four natural minerals (kaolin, diatomite, graphite, and fly ash), two chemically modified kaolin fines

and one commercial sorbent ('Miracle Sorb') were studied by measuring the suspension of oil droplets in the middle part of the funnel test apparatus in the absence of dispersant. As some OMAs settled to the bottom during static time, the amount of oil trapped in the settled OMAs was added to the suspended concentrations to provide a full-scale evaluation of oil-binding capacity of the tested mineral fines. The properties of selected minerals are shown in Table 4 and Figure 5. For the three hydrophilic minerals (kaolin, diatomite and fly ash), particle size decreases in the order of fly ash, diatomite, and kaolin, while the surface area increases in the same order (Table 4). Average pore sizes of the minerals are similar. Pore size distribution is shown in Figure 5.

Table 4: Properties of the tested mineral fines

Minerals	Average particle size (μm)	Surface area (m^2/g)	Contact angle ($^\circ\text{C}$)
Kaolin	5.0	9.98	11.0
Diatomite	8.4	5.66	0
Fly ash	9.3	1.25	0
Graphite	6.8	9.80	33.7
Modified kaolin 1	5.4	9.81	37.2
Modified kaolin 2	5.1	10.5	68.8

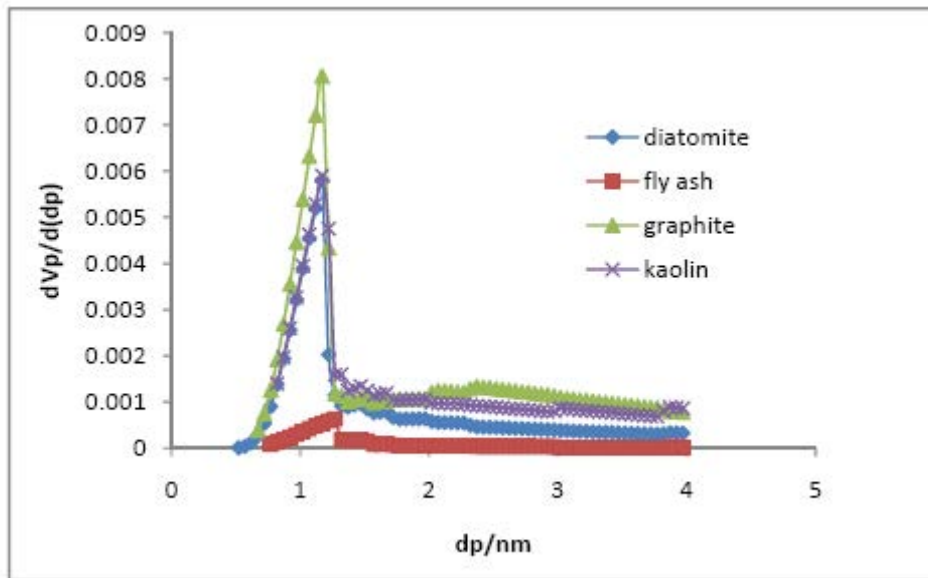


Figure 5: Pore size distribution of the tested mineral fine particles

Figure 6 shows that of the selected hydrophilic minerals, kaolin was the most effective in suspending oil in the middle and lower portions of the test apparatus, followed by diatomite and fly ash. The quantity of oil trapped in OMA decreased as the particle size increased and the surface area decreased. Compared with other minerals tested, kaolin

(which has previously been observed by (Poirier and Thiel 1941) to have a high affinity for oil), with relatively smaller particle size and larger surface area, is more likely to interact with oil and thus has a greater probability of forming OMAs. Diatomite was less efficient than kaolin in binding MESA oil for all treatments (Figure 6) because of its smaller surface area and relatively large particle size, in addition to a hydrophilic surface. Diatomite also did not perform as well as kaolin when tested with the other two crude oils (Figure 7). Except for surface area, diatomite and fly ash have similar physical properties (Table 4). The fact that diatomite performed better than fly ash, as shown in Figure 6, indicates that surface area plays an important role in the formation of OMAs.

With a hydrophobic surface (Table 4), graphite is an effective absorbent for oil, and its exfoliated structure has been reported to have a great oil absorption capacity (Adebajo et al. 2003; Toyoda et al. 2000). However, in our experiments, probably due to its high affinity to oil and non-charged surface, this material had a greater tendency to form large “oil-graphite aggregates” instead of stabilizing the oil in small droplets. Little graphite or free oil was observed in suspension in the bulk water column. The majority of graphite particles were seen to form large graphite/oil droplets (3-5 mm), either sticking to the flask wall or settling to the bottom. Most of the oil added to the flask was absorbed by graphite, with over 70% found sticking to the flask wall. Under intense agitation, the large droplets strongly attached to the glassware. The attached droplets may continue to bind free oil in the water phase. Thus, despite its great adsorption capacity, graphite is not capable of stabilizing oil and forming OMAs, leading to a smaller percentage of suspended oil in the middle part of the test flask (Figure 6).

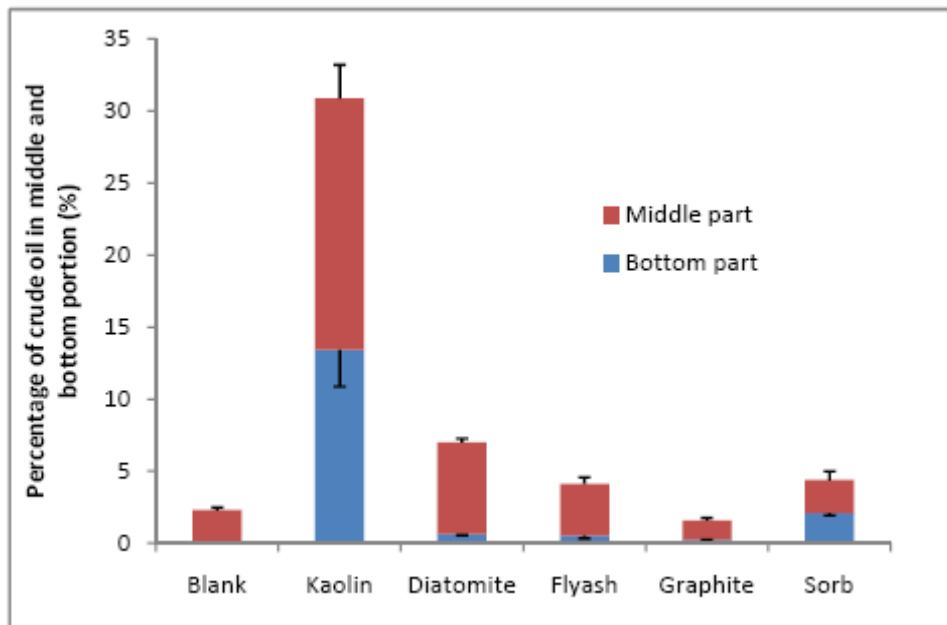


Figure 6: The effect of mineral type on MESA oil

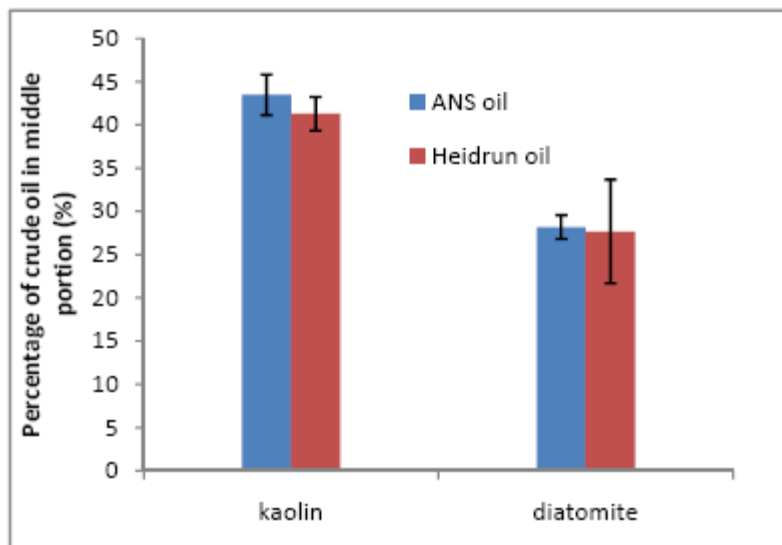


Figure 7: The effect of mineral type on ANS oil and Heidrun oil

The commercial product ‘Miracle Sorb’, a biodegradable hydrocarbon sorbent provided by ABASCO, did not perform well in this test (Figure 6). The particulate size of this material was too large to be suited to the experiments, even after being further ground down in the laboratory. ‘Sorb’ tended to jam in the neck of the funnel or attach to glassware, resulting in a small fraction remaining in the middle portion of the funnel. Additionally, the smaller concentration of oil added and the high buoyancy of the adsorbent may have accounted for a much lower sorption capacity observed in this study compared to previous reports (Bayat et al. 2005).

Modified kaolin

Bayat et al (2005) reported that hydrophobicity (or oleophilicity) is the most important properties of a sorbent related to oil spill cleanup. Many natural minerals have the ability to bind organic compounds; however their ability to stabilize oil is much lower than dispersants, alone or dispersants with minerals. In the current study, natural kaolin was modified with organic compounds to increase its hydrophobic properties and thus enhance its oil-binding capacity. Using different amounts of alcohol, two types of modified kaolin with different levels of hydrophobic properties were prepared and which are referred to in this study as modified kaolin #1 (lower hydrophobicity) and modified kaolin #2 (higher hydrophobicity). Both modified kaolins maintained their ability to form OMAs and high densities that resulted in oil stabilization in the lower portion of the test apparatus, instead of on the water surface like other hydrophobic absorbents. The success of modification was confirmed by Fourier Transform Infrared (FTIR) Spectroscopy results (Figure 8).

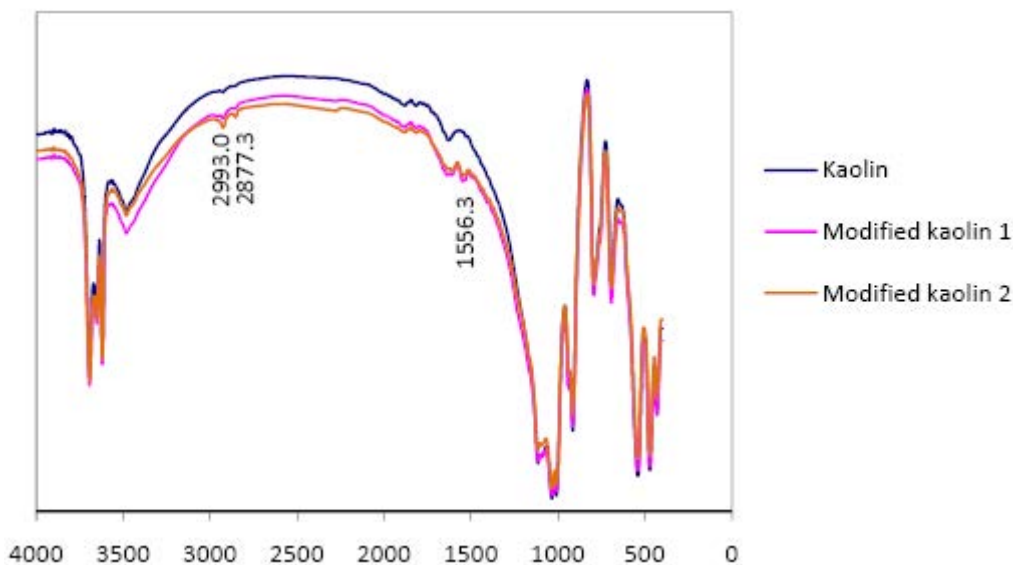


Figure 8: FTIR spectra of original and modified kaolin

The absorption band at 1556.3 cm^{-1} is the characteristic vibrations of NH group, which indicated that kaolin was successfully covalent with (toluene 2, 4-diisocyanate) TDI. The peaks at 2993.0 and 2877.3 cm^{-1} proved the existence of CH_2 , which is derived from the same functional group in aliphatic alcohol (Molphy et al., 1994). Further confirmation of covalent attachment was shown by the increase of the contact angle (Table 4). Particle size and surface area of modified kaolin remained the same.

Modified kaolin #1 absorbed more oil compared to natural kaolin (Figure 9a, b). Provided adequate agitation, almost all the oil was trapped by the modified kaolin. Dark particles (OMAs) were abundant in the flask, while no free oil was observed. After a short static time (10 min), the majority of OMAs remained in the middle part of the test apparatus (Figure 9a), twice the volume compared to natural kaolin. When the static time was extended to 60 min (Figure 9b), the OMAs were observed to settle at the bottom of the test flask due to large number of mineral particles sticking to the oil droplets, thus forming much larger OMAs ($100\text{ }\mu\text{m}$) compared to natural kaolin ($10\text{ }\mu\text{m}$). Although OMA suspension by modified kaolin #1 at 60 min static time was not improved compared with natural kaolin, oil-binding capacity of the modified mineral at both static times was largely enhanced, with twice as much total oil being removed from the surface (Figure 9a, b). This suggests that the hydrophobic property of minerals plays an important role in the formation of OMAs. When agitated, the settled OMAs were readily re-suspended in the bulk water column. Experiments with dispersant showed that the total percentage of oil removed from the surface was similar for the different minerals. In the presence of dispersant, 80-90% of the feed oil was trapped in the middle and bottom sections, with or without minerals (Figure 9c). Oil droplets became very small and uniformly mixed with water due to the hydrophilic heads of the dispersant.

The oil-binding capacity of modified kaolin #2 (higher hydrophobic level) was less than the natural kaolin (Figure 9b). Some bare mineral particles (not attached to oil droplets)

suspended in the water. This may be attributed to their strong hydrophobic property causing mineral particles to attract to each other rather than oil droplets. As hydrophobicity increased, the capability of mineral particles to disperse oil in water dramatically decreases, limiting the interaction with oil droplets. There seems to be an optimal range of mineral hydrophobicity, within which the interaction of oil-mineral interaction is enhanced. Minerals with an extremely high hydrophobicity were tested to validate the negative impact on OMA formation. When the contact angle of the mineral was over 90° , the particles had a large tendency to float on the water surface or to aggregate into larger particles that quickly settle on the bottom, hence dramatically reducing the capacity for the formation of OMAs.

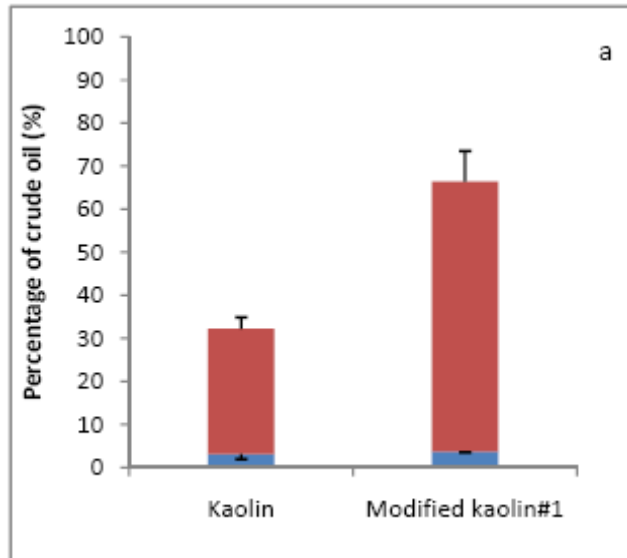


Figure 9a

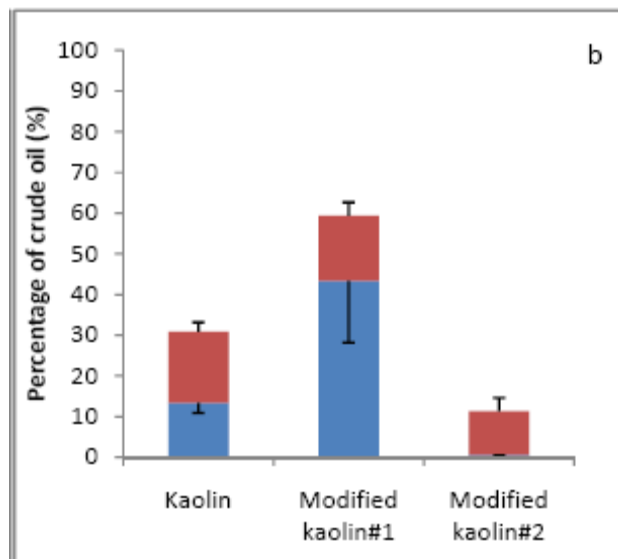


Figure 9b

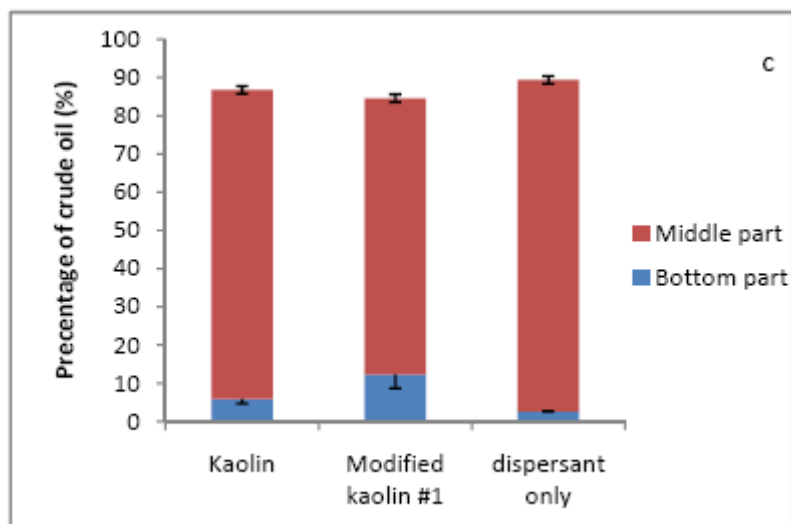


Figure 9c

Figure 9: Oil distribution for modified kaolin and unmodified kaolin, (a) static for 10 min, without dispersant; (b) static for 60 min, without dispersant; and (c) static for 60 min, with dispersant

Observations of OMAs by confocal microscope are presented in Figure 10. All images were collected using two sets of wavelengths, which ensured that the images accurately reflect the position of oil droplets and minerals. Figure 10 (a-c) demonstrate that spherical OMAs were formed with hydrophilic minerals (kaolin and diatomite), with mineral particles staying at the outer layer of the OMA. This finding is consistent with observations in previous literature (Stoffyn-Egli and Lee, 2002). With hydrophobic minerals, the shape of OMAs becomes irregular (Figure 10 d-f). There is also a difference in the size of OMAs formed by hydrophilic and hydrophobic minerals, a few μm (less than 20 μm in general) with the former to tens of μm (up to 100 μm) with the latter. The size range of the modified kaolin-oil aggregates are in agreement with the irregular shapes and the sizes of the droplet OMAs and solid OMAs as reported by Stoffyn-Egli and Lee (2002). Modified mineral particles penetrated into the oil phase, probably due to their hydrophobic characteristics.

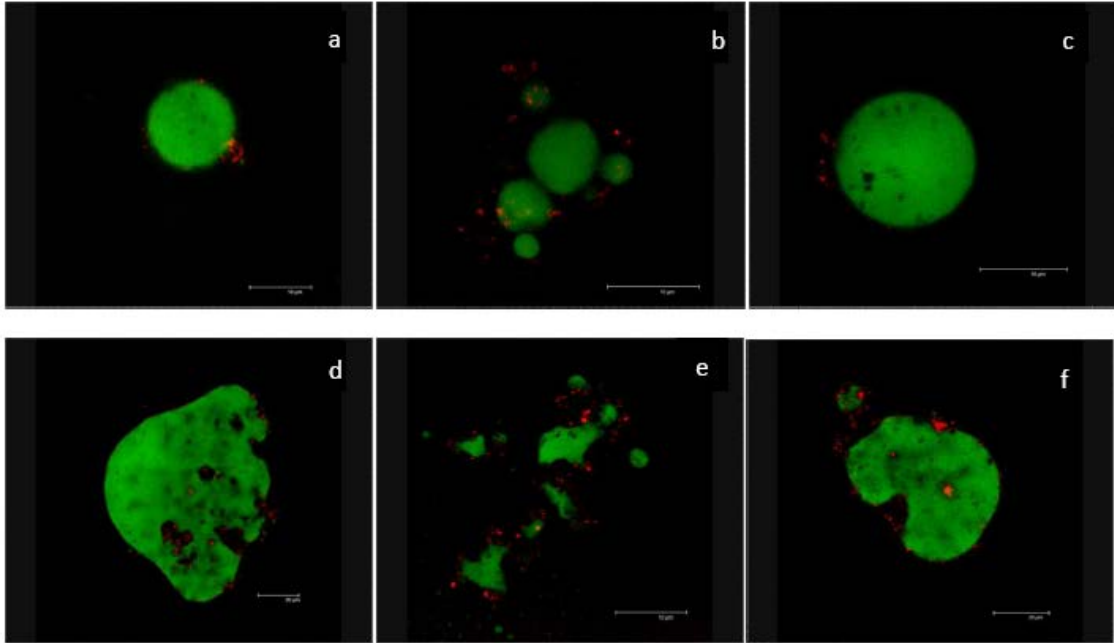


Figure 10: Droplet OMAs with (a) kaolin; (b) multiple droplet OMA with kaolin; (c) droplet OMA with diatomite; (d) single OMA with modified kaolin #1; (e) multiple OMA with modified kaolin #1; (f) OMA with modified kaolin #2

2.2.4. Particle size distribution

The size distributions of the dispersed oil droplets/OMAs were measured to estimate the size range. In order to obtain accurate results, objective lenses of different magnification levels were used. An objective lens having a magnification of 1000 with a theoretical detection limitation of 0.2 μm was selected to image the small-size oil droplet.

The presence of dispersant dramatically enhanced the stability of dispersed oil droplets and OMAs. As shown in Figure 11, small oil droplets and uniform size distribution of oil droplets can be observed in the presence of dispersant). Almost all the oil droplets were smaller than 4 μm in the middle portion. Dispersant can reduce the surface tension of oil, break it into smaller droplets and prevent oil droplets from re-coalescing in the water column. Small OMAs are formed and are more stable as dispersed phase. Without dispersant, oil droplets and OMAs are observed in a wide size range. During a 60 min static time, the larger suspended oil droplets were seen to re-coalesce, with some floating to the surface and more settling to the bottom. This is indicated by the high oil concentration in the top portion (especially for diatomite). Only particles smaller than 5 μm were left suspended in the water. This results in similar particle in the middle water column as found with the presence of dispersant (Figure 11d-e). The unstable suspension is also shown by the low oil fraction in the middle portion after 60 min static time (as shown in Figure 11). Some OMAs slightly attached to the wall of glassware.

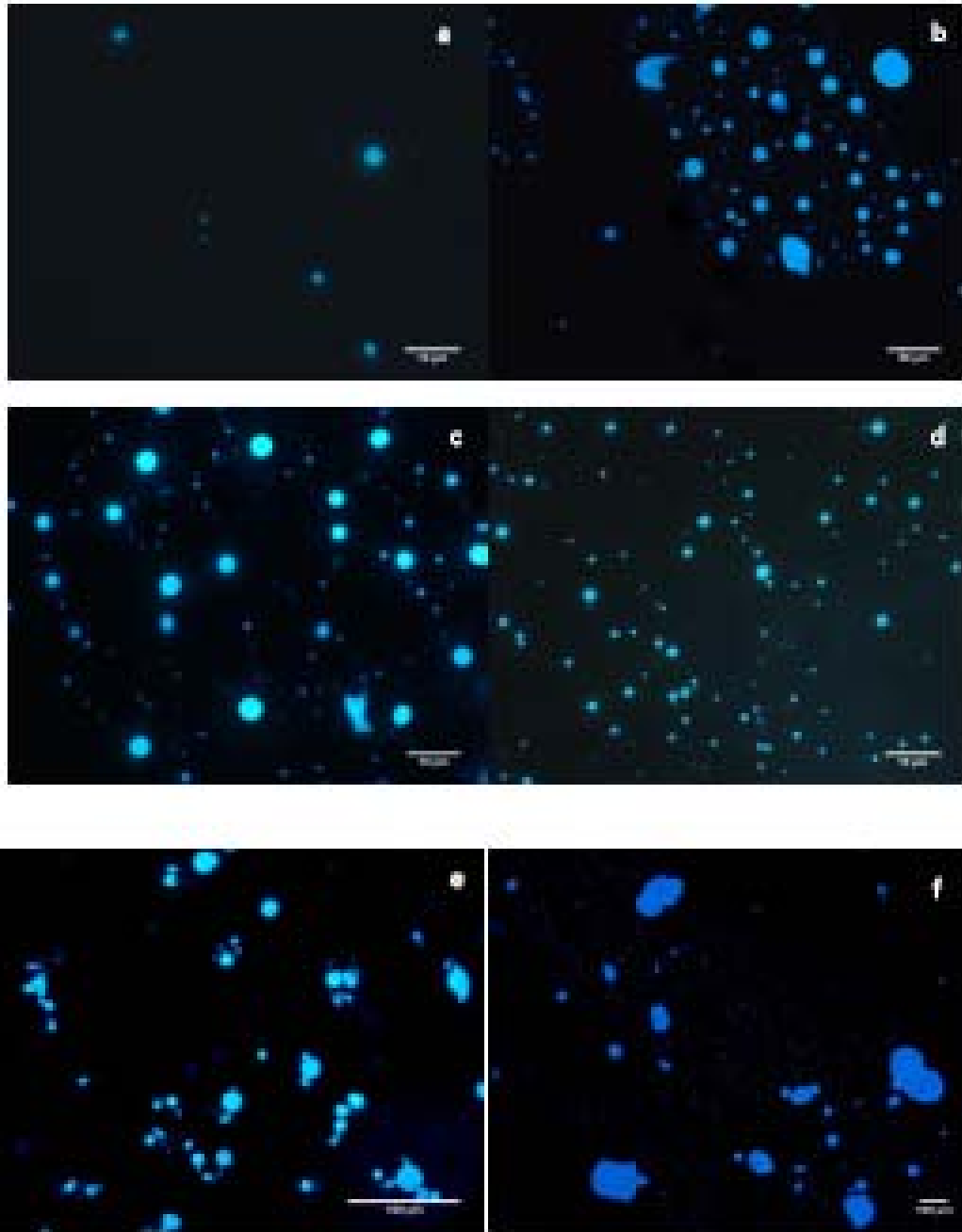


Figure 11: Images of oil droplet and OMAs in middle part by UV epi-fluorescence microscope: a) kaolin, no dispersant, 150 rpm; b) kaolin, with dispersant, 150 rpm; c) kaolin, no dispersant, 250 rpm; d) kaolin, dispersant, 250 rpm; e) kaolin, 250 rpm, after 60 min static time; f) modified kaolin #1 after 60 min static time.

2.3. Summary of mineral fines experiments

The following conclusions can be drawn for the lab experimental study;

- For the effect of mineral type, mineral particle size and surface area were important factors influencing OMA formation.
- Hydrophobicity of minerals plays an important role in mineral-oil interaction. Increased hydrophobicity of mineral fines can promote their affinity to oil and hence enhance the formation of OMAs, within an optimal hydrophobicity range.
- The experimental results showed that the oil trapped in OMAs was increased by two-fold when the water-mineral contact angle increased from 0-10° to approximately 40°. However, repelling forces become dominant between minerals and oil droplets when mineral particles are highly hydrophobic. The contact angle of such minerals reaches about 70° in this study. The OMA sizes increased from a few μm (less than 20 μm) for natural kaolin to tens of μm (up to 100 μm) for modified kaolin #1.
- Chemically-dispersed oil droplets are more stable than physically-dispersed oil droplets, indicating that application of chemical dispersant with mineral fines may be more effective in promoting formation of OMA and dispersion of oil in the water.

3. Wave tank experiments

3.1. Material and methods

3.1.1 Wave tank description

Wave tank experiments were conducted at the Bedford Institute of Oceanography (BIO) in Dartmouth, Nova Scotia, to evaluate the feasibility of forming and utilizing OMA as a means of remediating oil spills in a more realistic hydrodynamic setting. The BIO wave tank (pictured in Figure 12) is situated beside Bedford Basin in Halifax Harbour. The tank measures 32 m long, 0.6 m wide and 2 m high, and under normal test conditions has an average water depth of 1.50 m. Different wave types are generated by a computer-controlled flap-type wave-maker situated at one end of the tank. The wave-maker is linked to an adjustable cam. Wave-heights are altered by controlling the strokes of the cam, and wave frequency is controlled by the rotational speed of the cam. The wave generator can produce both regular non-breaking waves and breaking waves. Breaking waves are generated using the frequency sweep technique (Funke and Mansard 1979), wherein a wave of one frequency is superimposed on another wave of a different frequency, causing the wave to increase in height until it breaks. The energy dissipation rate per unit mass (ϵ) was evaluated by the autocorrelation function method (Kresta and Wood 1993) using a time-series of velocity measurements obtained by an Acoustic Doppler Velocimeter (SonTec/YSI, Inc. San Diego, CA) at select locations in the tank.



Figure 12: The flow-through wave tank facility at the Bedford Institute of Oceanography

3.1.2. Wave conditions and current flows

For this study, two wave conditions, namely regular non-breaking waves and plunging breaking waves, were generated and their hydrodynamics characterized. The regular non-breaking waves were generated with a 12 cm stroke, 0.80 Hz frequency, 2.44 m wave length, and 23 cm wave height. The plunging breaking waves were produced with a 12 cm stroke and alternating trains of high-frequency waves (0.85 Hz, 2.16 m wave length, 26 cm wave height, and 20 s duration) and low-frequency waves (0.5 Hz, 6.24 m wave length, 9 cm wave height, and 5 s duration).

A uniform current was introduced to the wave tank at a flow rate of 60 ± 2 gallons per min. This rate was selected to counteract the surface Stoke's drift velocity of the high frequency (0.85Hz) regular wave conditions. The component influent system includes uptake of seawater from the Bedford Basin, holding tank, electric pump, sediment trap and water filtration, flow meter, distribution pipes, control valves, and a water bypass for flow adjustment. The effluent system consists of outlets and valves, flow meter, electric pump, and wastewater treatment facility.

3.1.3. Experimental design and procedure

Formation and transport of OMAs were investigated in a wave- and current-induced hydrodynamic environment under different wave conditions. Specifically, tests were conducted to evaluate dispersion effectiveness on crude oil through application of mineral fines at mineral-fines to oil ratios (MOR) of 1:12 and 1:3. The oil used in this study was weathered MESA crude and the mineral fines used were kaolin (Sigma-Aldrich, St. Louis, MO). The wave conditions included regular non-breaking waves (RW) and plunging breaking waves (BW), and the wave tank was operated in flow-through mode to simulate the dilution effect from currents. The effect of the application of chemical dispersant (at a dispersant to oil ratio [DOR] of 1:25) on dispersion efficacy was also investigated in the wave tank experiments. The experimental design is shown in Table 5.

Table 5: Experimental Design for OMA Wave Tank Study

Treatment	MOR	DOR	Wave
1	0	0	RW
2	0	1:25	RW
3	0	0	BW
4	0	1:25	BW
5	1	0	RW
6	1	1:25	RW
7	1	0	BW
8	1	1:25	BW
9	2	0	RW
10	2	1:25	RW
11	2	0	BW
12	2	1:25	BW

Prior to each experiment the temperature, salinity and background particle size distribution of the bulk water were recorded. As each experiment began, 300 ml of crude oil was gently poured onto the water surface within a 40 cm (inner diameter) ring (constructed of NSF-51 reinforced clear PVC tube) located 10 m downstream from the wave-maker. If dispersant was included in the treatment, 12 ml of dispersant was sprayed onto the surface of the oil slick through a pressurized nozzle (60 psi; 0.635 mm i.d.) resulting in a DOR of 1:25. The ring was then lifted prior to the upcoming of the first wave. In the meantime, 25 g or 100 g mineral fines, corresponding to MOR of 1:12 or 1:3 respectively, were evenly sprayed on top of the oil slick with a stainless steel sieve to ensure even distribution and minimal aggregation of fines prior to contact with the oil slick. The design wave conditions were operated continually during the next hour of the experiment.

3.1.4. Dispersed oil concentration

Water column samples were collected from five different depths ($d = 5, 35, 75, 105,$ and 145 cm below the average water surface) near the end of the wave tank ($L = 24$ m from the wave generator) at eight time points ($t = 2, 5, 10, 15, 20, 30, 45,$ and 60 min). The water column oil concentrations were determined by extracting water samples using dichloromethane and analyzing total petroleum hydrocarbon concentrations using gas chromatography coupled with a flame ionized detector (GC/FID).

3.1.5. Particle size distribution

The suspended oil droplets or OMA particle size distribution was determined by an *in-situ* laser scattering and transmission particle counter (LISST-100X, Type C, Sequoia Scientific, Seattle, WA), with a particle-size detection range from 2.5 μm to 500 μm . The LISST was suspended vertically in the water column with the detection window submerged around 60 cm below the average water surface and approximately 8 m downstream from the center of the initial oil slick. The *in-situ* dispersed oil droplet size distribution was measured continuously by the LISST over the entire experimental duration of one hour. The resultant measured particle size distribution is expressed as the volume mean diameter of oil droplets

with each interval of the size range.

3.2. Results and discussion

3.2.1. Dispersed oil concentration

Oil concentrations measured from the samples collected from the water column at three different depths (5 cm, 75 cm, and 145 cm from the average water level) are shown in Figure 13-15. The data from the other two depths (35 cm and 105 cm from the average water level) are not shown. Figure 13 presents the dispersed oil concentration at the surface of the wave tank as a function of time. All treatments under regular wave conditions produced higher surface oil concentrations than the treatments under breaking wave conditions, indicating that oil was dispersed more efficiently by the elevated mixing energy of the breaking waves. Under regular waves, higher dosages of mineral fines transferred more oil from the surface to the water column in the absence of dispersant, but had less effect in the presence of dispersant. Under breaking waves, however, lower dosages of mineral fines were always associated with lower surface oil concentrations regardless of whether dispersant was applied.

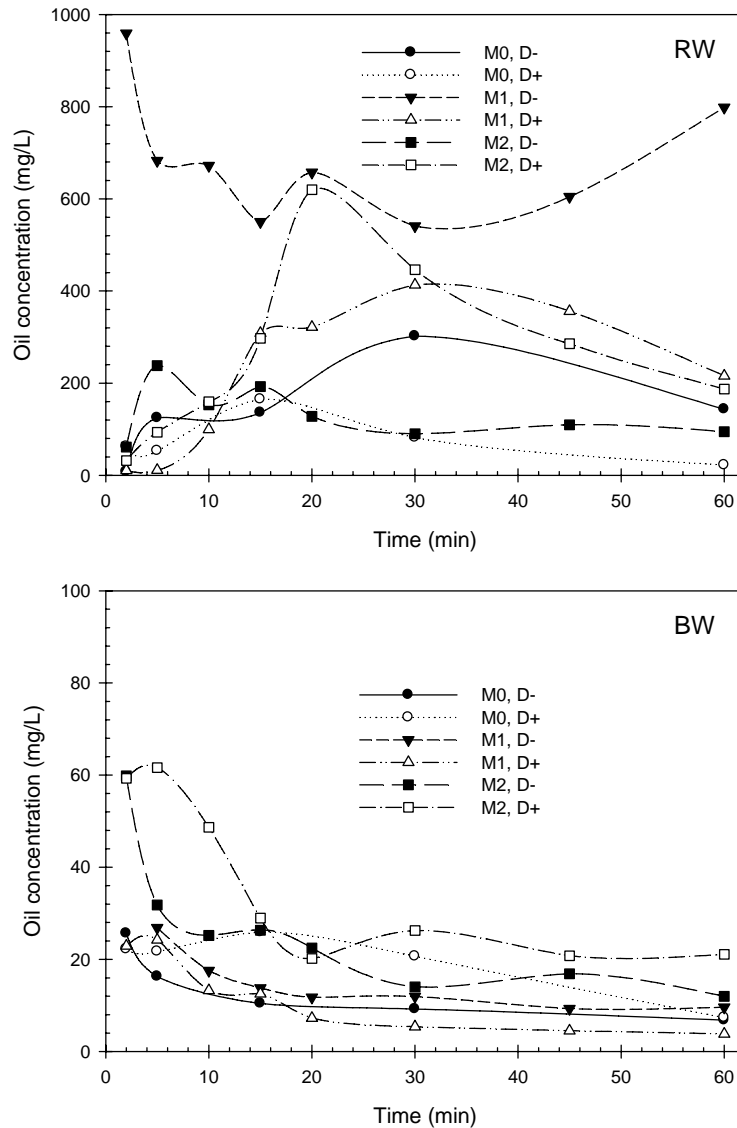


Figure 13: Dispersed oil concentration at the surface of the wave tank under regular non-breaking wave (RW) and breaking wave (BW) conditions

Figure 14 shows the dispersed oil concentration in the middle of the wave tank as a function of time. Contrary to the surface, the oil concentrations in the middle of the wave tank were much higher under breaking wave conditions than under regular wave conditions, indicating that oil was effectively dispersed to the water column due to the breaking wave action. In addition, the effect of chemical dispersant was clearly shown – the dispersed oil concentration increased in the presence of dispersant under breaking wave conditions for all dosages of mineral fines. Similar results were observed from the other two depths (35 cm and 105 cm) in the water column. The presence of mineral fines appears to have reduced the retention time of the dispersed oil in the water column.

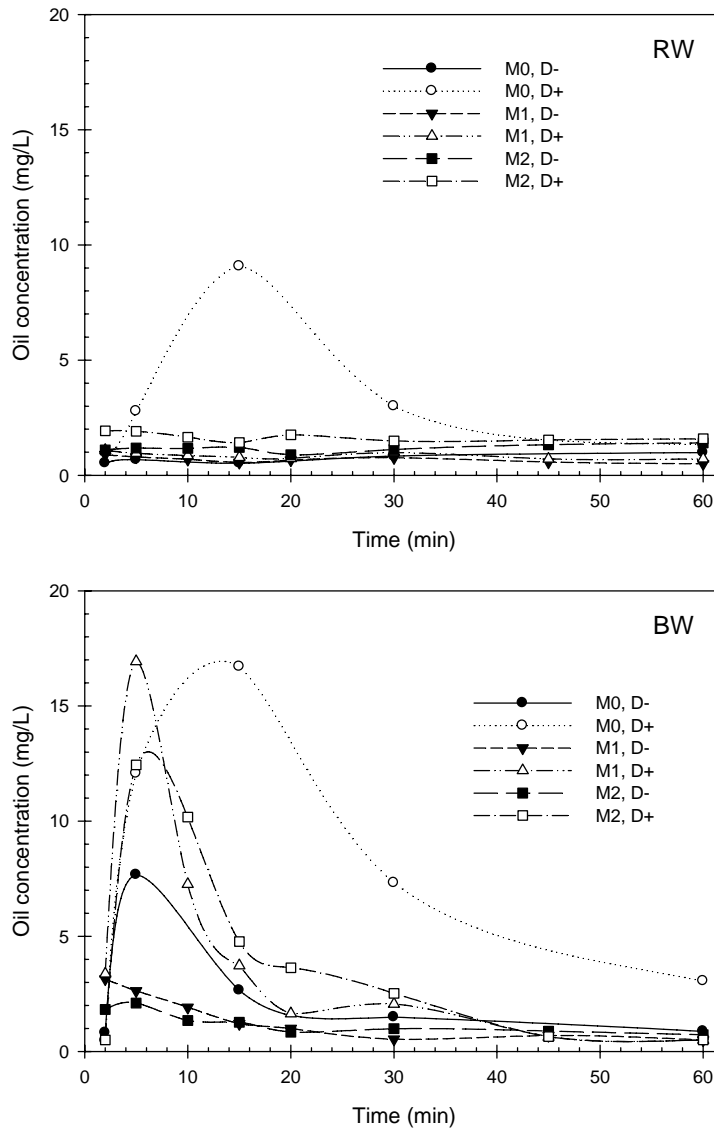


Figure 14: Dispersed oil concentration in the middle of the wave tank under regular non-breaking wave (RW) and breaking wave (BW) conditions

Figure 15 illustrates the dispersed oil concentration near the bottom of the wave tank, where the oil concentrations under dynamic conditions (including regular waves and breaking waves) were consistently lower than those at the surface and in the middle of the wave tank. This indicates that the amount of oil transferred to the bottom of the wave tank under hydrodynamic conditions was restricted, and the vast majority of the oil was either suspended in the water column or remained at the surface.

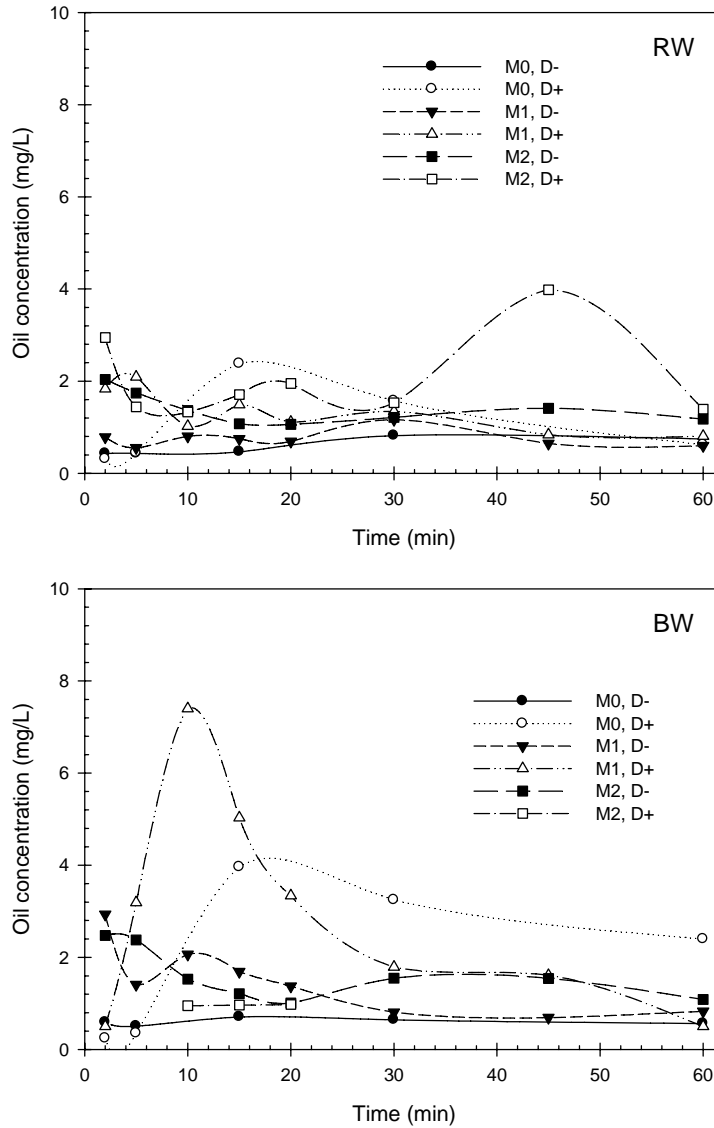


Figure 15: Dispersed oil concentration near the bottom of the wave tank under regular non-breaking wave (RW) and breaking wave (BW) conditions

3.2.2. Particle size distribution

Representative total particle concentrations and volume mean diameter of the particle size distributions, as recorded by the LISST, are shown in Figure 16 and 17. In general, the total particle concentrations were lower under regular wave conditions than under breaking wave conditions. The volume mean diameters, however, were controlled by two factors: they were smaller under breaking wave conditions than under regular wave conditions, and they were smaller in the presence of chemical dispersant than in its absence.

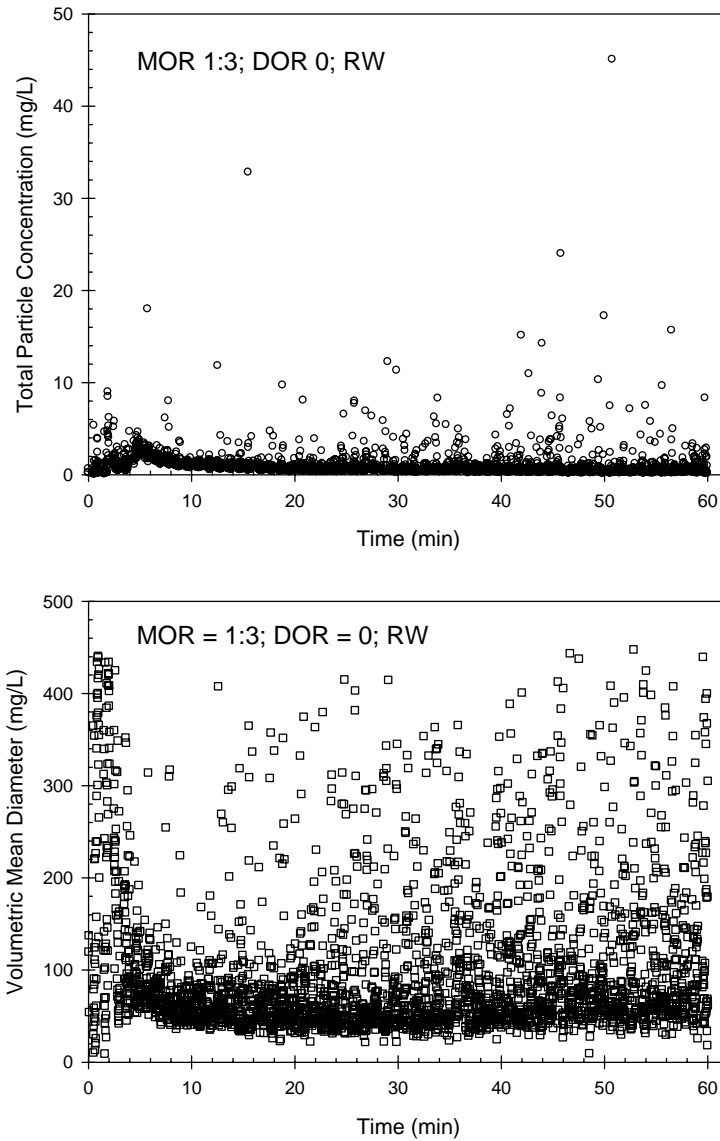


Figure 16: LISST record of the total particle concentration (upper) and volume mean diameter (lower panel) of the OMA in the absence of dispersant under regular wave conditions.

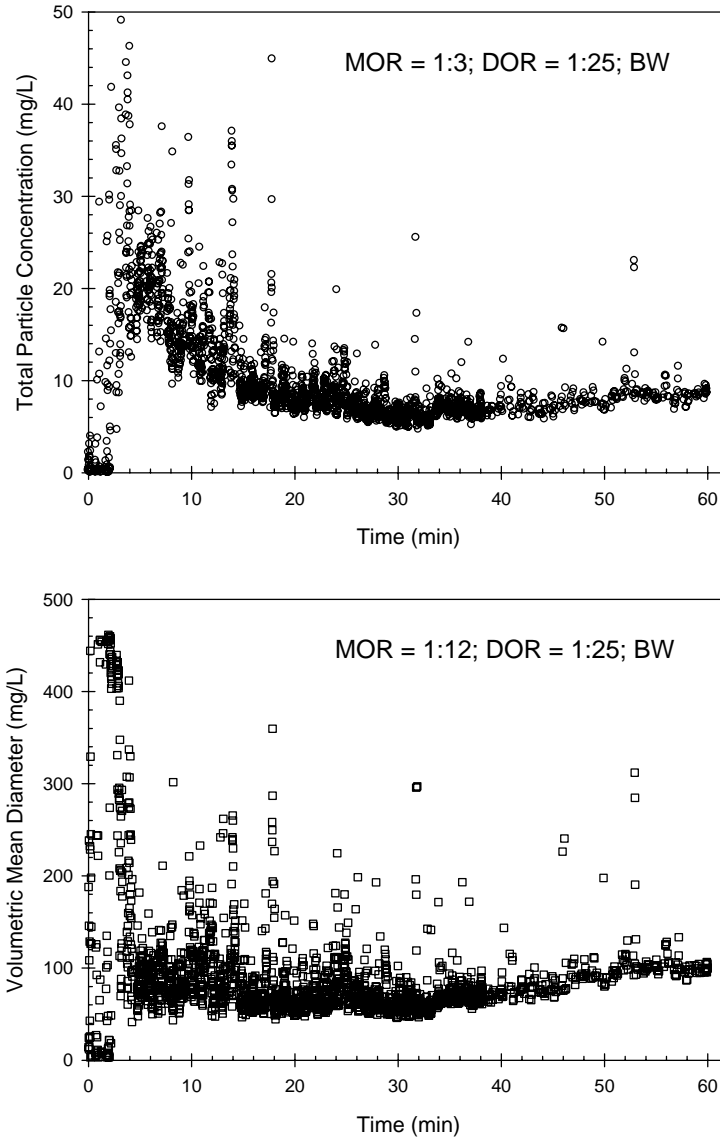


Figure 17: LISST record of the total particle concentration (upper) and volume mean diameter (lower panel) of the OMA in the presence of dispersant under breaking wave conditions

3.3. Summary of wave tank experiments

Wave tank experiments have been conducted to assess the oil dispersion effectiveness of promoting OMA formation in the water column through application of mineral fines. The results of the study support the following conclusions:

- Mineral fines can enhance the dispersion of oil slicks into the water column;
- Mixing energy of breaking waves is important for successful dispersion of oil and transport of oil from the surface to the water column;
- Mineral fines and chemical dispersant may have complementary enhancement effects on oil dispersion in the water column and dilution with the current flows.

- Total particle concentrations and particle size distributions measured with the LISST particle counter indicate that breaking waves and dispersant application enhance dispersion of oil by generating small droplets that can suspend in the water column.

4. Modeling

4.1. Concept

When oil is spilled in the ocean it typically breaks into droplets that are dispersed in the water column. The tendency for oil droplets to resurface is influenced by the droplet size and sea state. When modeling spills, oil droplet formation, size distribution and dynamics are key factors that must be considered. The physical dispersion of oil near the surface can be affected by a number of natural forces, of which breaking waves has the most significant effect (Tkalich and Chan 2002). The mechanism of droplet formation has been studied theoretically (Hinze 1955; Li and Garrett 1998; Raj 1977) and experimentally (Delvigne and Sweeney 1988), and researchers, using different assumptions on dominant forces during the droplet break-up, have derived relationships for the maximal possible droplet radius as a function of oil parameters and energy of breaking waves. Starnatoudis and Tavlarides (1985) and Tkalich and Chan (2002) provided additional means to estimate the size distribution of oil droplets, and (Darling et al. 1990) provided a first order equation to describe the kinetics of oil droplet resurfacing based on the balance of downward directed mixing and upward oil buoyancy. A vertical transport model using the random walk model approach has also been described by Korotenko et al. (2000) as a means to determine the resurfacing time and the maximum size of droplets maintained in suspension in the water column.

When high suspended particle loads are present in the water column, the particles will interact with oil droplets and form OMAs. This process stabilizes the oil droplets in the water column, enhances the breakup of oil slicks, and accelerates the removal of spilled oil from the water surface (Bragg and Owen, 1995; Le Floch et al., 2002; Owens and Lee, 2003; Owens et al., 2003; Page et al., 2000).

It is evident that OMA formation occurs in oil-water environments and can expedite dispersal and degradation of oil (Chaerun et al. 2005; Khelifa et al. 2002; Lee et al. 1999), and a number of studies have identified the potential significance of OMA formation in mediating the transport and removal of oil spilled in aquatic environments (Chaerun et al. 2005; Owens and Lee 2003; Stoffyn-Egli and Lee 2002). With the promotion of OMA formation as a potential oil spill countermeasure, understanding the factors controlling the kinetics of formation has gained interest (Aguilera-Mercado et al. 2006; Hill et al. 2002; Sterling et al. 2004a; Sterling et al. 2005; Sterling et al. 2004b). Laboratory and numerical simulation studies have demonstrated that there is a critical sediment concentration range where formation of OMAs with naturally-dispersed oil increases rapidly (Ajijolaiya et al. in press; Khelifa et al. 2003; Khelifa et al. 2005a; Khelifa et al. 2005b).

While some previous experimental work has been conducted to study the breakup of oil into small droplets and the interactions of oil with minerals fines, limited work has been performed to investigate factors controlling the transport (horizontal spreading and vertical

settling/floating) of OMAs in marine environments under realistic oceanographic conditions. The objective of the modeling work conducted in this study is to evaluate the influence of several factors on, and to identify the most significant factors that control, the transport of OMAs in the aquatic environment. The results of the numerical simulation are anticipated to provide guidelines on controlling the critical steps for applying mineral fines as a potential alternative oil spill countermeasure technology in the offshore oil and gas activities.

The modeling study has two major components: (1) the transport/fate of OMAs using the Dose Related Effects Assessment Model (DREAM) model (which has the advantage of being able to simulate various physical-chemical processes such as dispersion, dissolution, evaporation, degradation and re-suspension), focusing on large-scale transport, and; (2) the physical dispersion and vertical transport (settling or floating) of OMAs using a small-scale particle trajectory-tracking model, allowing the study of the movement of OMAs under different wave conditions through the addition of wave-induced velocity fields. The current work is focused on the second component, identifying significant factors controlling the spreading and settling of OMAs under regular wave conditions using a Lagrangian model. The particle tracking model has been developed and programmed in FORTRAN and modified following the formulation of Boufadel et al. (2006), with the addition of the effects of tidal currents. The three-dimensional positions of an OMA were determined by considering the effects of tidal currents, wave-induced velocities, turbulent velocities and the settling velocities of OMAs due to gravity. Model simulations were conducted to study the effects of wave characteristics, particle size distributions, settling velocity, OMA effective density and currents on the transport of OMAs.

4.2. Model Description

4.2.1. General

To assess the environmental risk associated with the formation and transport of OMAs, this study is focused on the potential impact of the residual oil associated with OMAs on benthic organisms. As with oil dispersed by physical processes alone, oil associated with OMAs undergoes various processes, such as evaporation, dissolution, bio-degradation, advection and diffusion. In the proposed study, with the exception of evaporation (estimated from the NOAA's ADIOS 2 model [NOAA, 2009]), these degradation processes are not considered to be more conservative than when these processes occur.

4.2.2. Random walk scheme

The model used in this study is a three-dimensional random walk model (Webb, 1982; Murray-Smith et al., 1996; Riddle, 1998, 2001; (Boufadel et al. 2006); Boufadel et al., 2007). The OMAs are represented by placing a fixed number of particles in the spill site at the beginning of simulation, and the particles move on each subsequent timestep according to Lagrangian motion:

$$\begin{aligned}x_{t+1} &= x_t + U\Delta t \\y_{t+1} &= y_t + V\Delta t \\z_{t+1} &= z_t + W\Delta t\end{aligned}\tag{2}$$

where x , y , z are the coordinates of an OMA particle, the subscripts $t+1$ and t represent the model timestep, Δt is the timestep length, U , V , and W are the horizontal and vertical velocity components given by:

$$\begin{aligned} U &= u_{tidal} + u_{wave} + u_t \\ V &= v_{tidal} + v_{wave} + v_t \\ W &= w_b + w_{wave} + w_t \end{aligned} \quad (3)$$

where u_{tidal} and v_{tidal} are the u-component (eastward) and v-component (northward) of the tidal currents, u_{wave} , v_{wave} , and w_{wave} are the velocities due to wave action, w_b is a buoyancy or settling velocity depending on the particle density, u_t , v_t , and w_t are the velocities due to turbulence.

The Stokes' theory was used in the model to describe the horizontal and vertical components of the wave-induced velocities. In this work it is assumed that currents do not influence wave velocities and waves propagate eastward, thus v_{wave} becomes zero. The horizontal and vertical velocities due to waves are:

$$\begin{aligned} u_{wave} &= \frac{Hgk}{2\sigma} e^{kz} \cos(kx - \sigma t) + \frac{3H^2\sigma k}{16} e^{2kz} \cos 2(kx - \sigma t) \\ w_{wave} &= \frac{Hgk}{2\sigma} e^{kz} \sin(kx - \sigma t) + \frac{3H^2\sigma k}{16} e^{2kz} \sin 2(kx - \sigma t) \end{aligned} \quad (4)$$

where H is the wave height, g is the acceleration due to gravity, k is the wave number and σ is the wave frequency. The terms u_t , v_t , and w_t can be described by:

$$\begin{aligned} u_t &= R\sqrt{2K_H\Delta t} / \Delta t \\ v_t &= R\sqrt{2K_H\Delta t} / \Delta t \\ w_t &= R\sqrt{2K_V\Delta t} / \Delta t \end{aligned} \quad (5)$$

where R is a normal random number with zero mean and a variance of 1, and K_H and K_V are the horizontal and vertical turbulent diffusion coefficients (m^2s^{-1}), respectively. The initial location of a particle is randomly generated by the model based on the user-specified surface slick size. As a particle moves within the model domain, its location is tested at each timestep. If the particle passes through the surface, it is placed back into the domain at a distance equal to the distance that it exceeds the boundary (i.e., it is reflected vertically). If the particle passes through the bottom, it is placed back on the bottom and stops moving (i.e., it is settled).

4.2.3 Calculation of oil concentrations in sediment

The concentrations of the settled oil ($mass/m^2$), $C_{settled}$, are calculated by counting the number of OMA particles in the user-specified concentration cell:

$$C_{settled} = \sum_{i=1}^k \frac{N_i \times PM_i}{A_{cell}} \quad (6)$$

where k is the number of particle classes, N_i is the number of the i_{th} -class particles in the user-specified cell, A_{cell} is the area of the cell (m^2) and PM_i is the amount of oil per particle for the i_{th} -class particles:

$$PM_i = \frac{M_{Spilled} \times P_{settled} \times p_i}{n_i} \quad (7)$$

where $M_{spilled}$ is the total mass of spilled oil, $P_{settled}$ is the percentage of spilled oil that may be transferred to sediment, n_i is the number of particles used in the simulation for the class i , and p_i is the fraction of settled oil (in percentage) that is carried by the particle class i :

$$p_i = \frac{[V_{oil} \rho_{oil}]_i PSD_i}{\sum_{i=1}^k \{[V_{oil} \rho_{oil}]_i PSD_i\}} \quad (8)$$

where V_{oil} is the volume of oil in an OMA particle of class i , ρ_{oil} is the density of oil and PSD_i is the number distribution of OMA particles of class i .

It is difficult to determine V_{oil} either experimentally or analytically due to the fractal nature of OMAs. V_{oil} is estimated in the model by assuming that the OMAs are spherical and non-porous. Therefore, V_{oil} becomes:

$$V_{oil} = \frac{\rho_{sediment} - \rho_{OMA}}{\rho_{sediment} - \rho_{oil}} V_{OMA} \quad (9)$$

where $\rho_{sediment}$ is the density of sediment, ρ_{OMA} is the density of OMAs determined by the modified Stokes' law based on the experimentally measured settling velocity and V_{OMA} is the volume of an OMA particle. $P_{settled}$ can be determined by laboratory experiments. Khelifa et al. (2008) has concluded that 0.3 to 51 % of the spilled oil may be transferred to sediment depending on the oil type, sediment type and sediment concentration without the addition of chemical dispersant.

4.3. Description of the input parameters

4.3.1 Transport behaviour

Tidal currents were predicted using the DFO Webtide model (DFO, 2009) for a randomly selected location in the Gulf of St. Lawrence. The eastward and northward components of the tidal current are plotted in Figure 18. The minimum, maximum, and mean current speeds are 0.01 m/s, 0.45 m/s, and 0.18 m/s, respectively. The dominant directions are northeast and southwest. Water depth was assumed to be 80 m according to the field conditions to satisfy the deep water wave criterion.

The first set of simulations was a study of the effects of waves and currents on the transport of OMAs. A wave with a period of 10 s and height of 1.0 m (Scenario-W1) was used. The second series of simulations was a study of the effects of different wave characteristics on the transport of OMAs. Two wave periods ($T=6, 10$ s) and two wave heights ($H=0.75, 1.5$ m) were used.

For the studies on the wave and current effects, a single size class was used. OMAs were assumed to have a mean diameter of $100 \mu\text{m}$ and the settling velocity for this size class was based on the experimental data from Khelifa et al. (2008).

As the settling velocity in equation (2) is size-dependent, it is expected that the particle size distribution (PSD) will affect the extent of deposition. Thus, a third set of simulations was then conducted to study the effects of PSD. The PSD data used are from experiments performed by Khelifa et al. (2008) on two sediments: Cook Inlet (CI), and Columbia River Delta (CRD). The simulation here only used the minimum and maximum particle sizes to outline the differences in transport behaviours.

Finally, two more realistic simulations were conducted utilizing the full PSD data (i.e. five size classes ranging from 121.39 to $448.93 \mu\text{m}$ for the CI case, and eight size classes ranging from 56.12 to $625.7 \mu\text{m}$ for the CRD case). The wave used in this set of simulation has a period of 10 s and a height of 0.75 m.

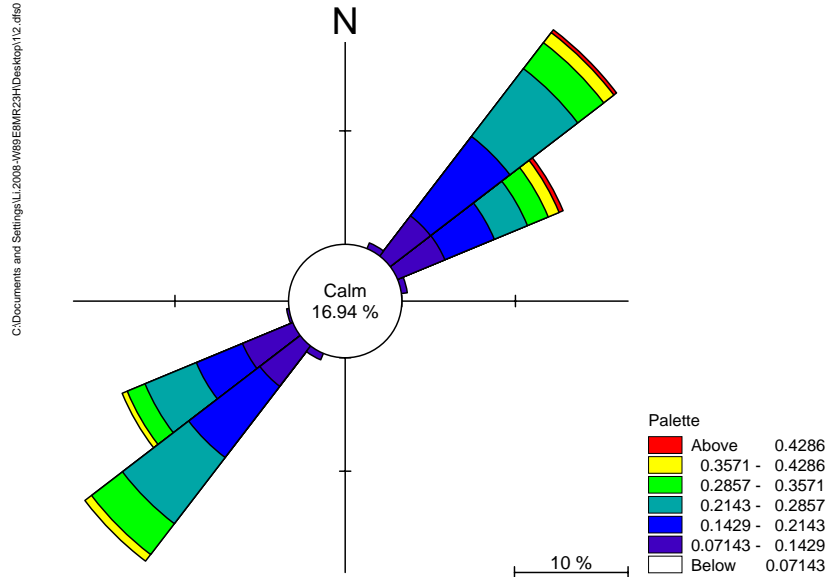


Figure 18: Directions and Magnitude of Tidal Currents (m/s)

4.4. Results and discussion

4.4.1 The effects of waves

Results of the effects of waves and currents are plotted in Figure 19 and listed in Table 6. The transport of OMAs by the wave-induced velocity is only of secondary importance when compared with the effects of currents. The center of mass for the W1 scenario is located at (153, 36) with a range of 7.3 km in the x direction (East-West) and 6.2 km in the y (North-South) direction. With the effects of currents, the C and W1&C scenarios show similar extent and location of deposition.

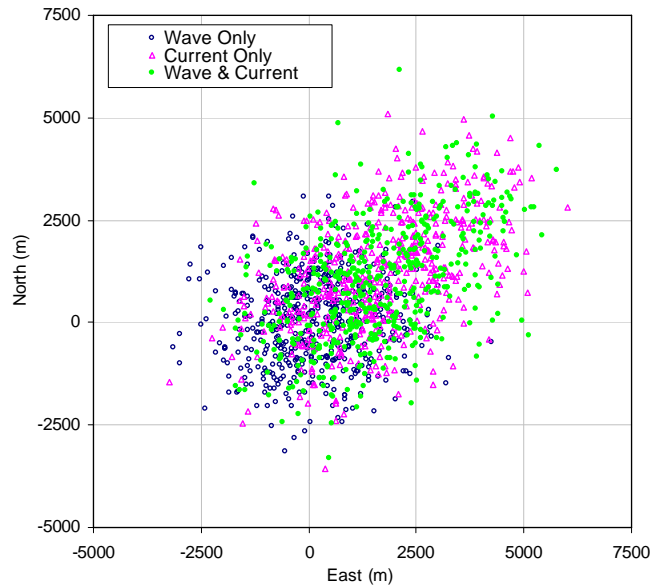


Figure 19: Effects of wave and currents on OMA deposition

To further study the effects of waves, the results from simulations under four different wave conditions were compared. It can be seen in Figure 20 and Table 6 that changing the wave parameters had only slight effects on the extent and location of OMA deposition. The x -coordinate of the centre of mass has changed from 81 m to 319 m east while the y -coordinate remained almost unchanged when the wave propagation direction was set to eastward in the simulation.

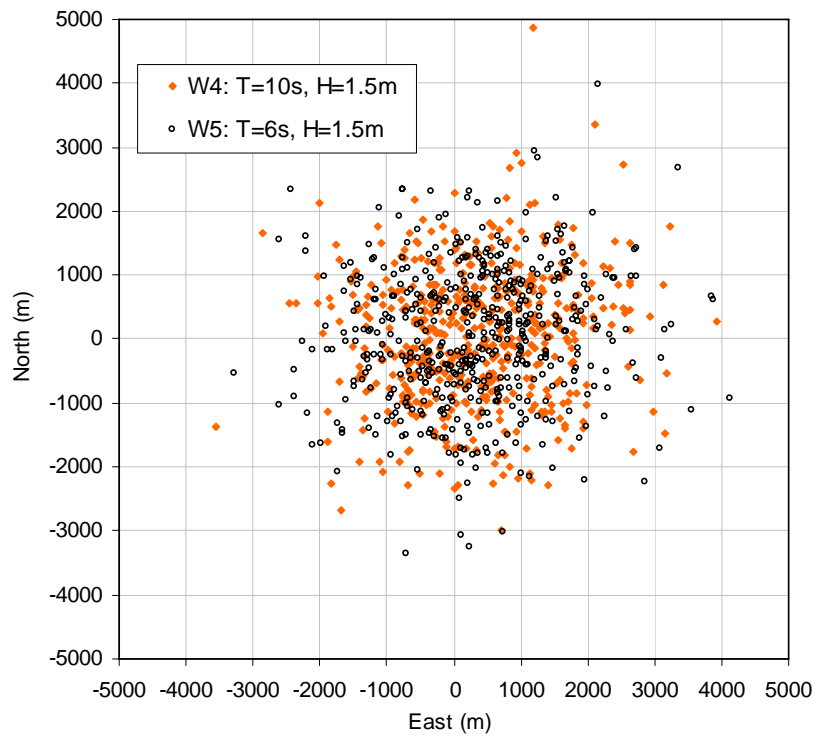
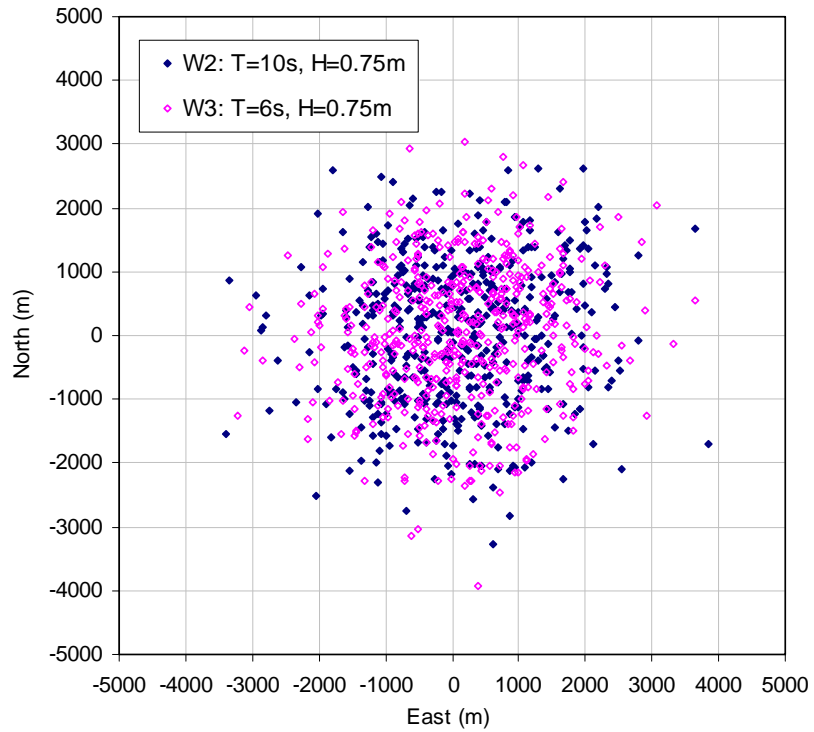


Figure 20 Effects of Waves on OMA Deposition

Given that tidal currents are not included in this case, and only wave- and turbulence-induced velocities are considered, the results suggest that wave-induced velocity is of secondary

importance compared to turbulence-induced velocity. The effects of the turbulent mixing coefficient on transport are not included here and will be discussed in detail in future work.

Table 6: Statistics of the Locations of Deposited OMA Particles

	Scenario	T (s)	H(m)	Mean	Min	Max	Range
East	W1	10	1	153	-3132	4244	7376
	C	-	-	1642	-3230	6012	9242
	W1&C	10	1	1645	-2290	5770	8060
North	W1	10	1	36	-3138	3074	6212
	C	-	-	1227	-3566	5101	8667
	W1&C	10	1	1017	-3292	6169	9461
East	W2	10	0.75	81	-3387	3836	7223
	W3	6	0.75	116	-3209	3651	6860
	W4	10	1.5	303	-3558	3939	7498
	W5	6	1.5	319	-3282	4123	7405
North	W2	10	0.75	35	-3260	2615	5875
	W3	6	0.75	40	-3930	3031	6962
	W4	10	1.5	40	-2978	4870	7848
	W5	6	1.5	43	-3354	3975	7330

*W-Wave, C-Currents, W&C-Wave and Currents

4.4.2 The Effects of Sediment Type/PSD/Settling Velocities

In the case of the two particle sizes used for CRD, the mean time for settling of 56.12 μm particles is 150 h. The deposition started at 109 h and finished at 217 h. For the 625.70 μm particles, the deposition started at 5.43 h and finished at 5.82 h, with a mean settling time of 5.11 h. The effects of the PSD on the deposition of OMA are plotted in Figure 21 and it can be seen that the diameter of the area of deposition for the 625.70 μm particles is approximately 2.5 km. In contrast, the diameter increases to about 13 km for the 56.12 μm particles. If we assume the OMA particles are evenly distributed within the deposition area, the sediment concentration in the former (625.70 μm) case is about 29 times that of the latter (56.12 μm) case.

Similarly, the mean time for settling of 121.39 μm CI particles is 87 h. The deposition started at 66 h and finished at 111 h. The diameter for the area of impact is about 9.5 km. For the coarse (448.93 μm) particle class, the mean deposition time is roughly 11.5 h, which started at 10.42 h and finished at 12.98 h. The diameter of the impact area is approximately 3.25 km and the concentration in the latter (448.93 μm) case is about 8.5 times that of the former (121.39 μm) case.

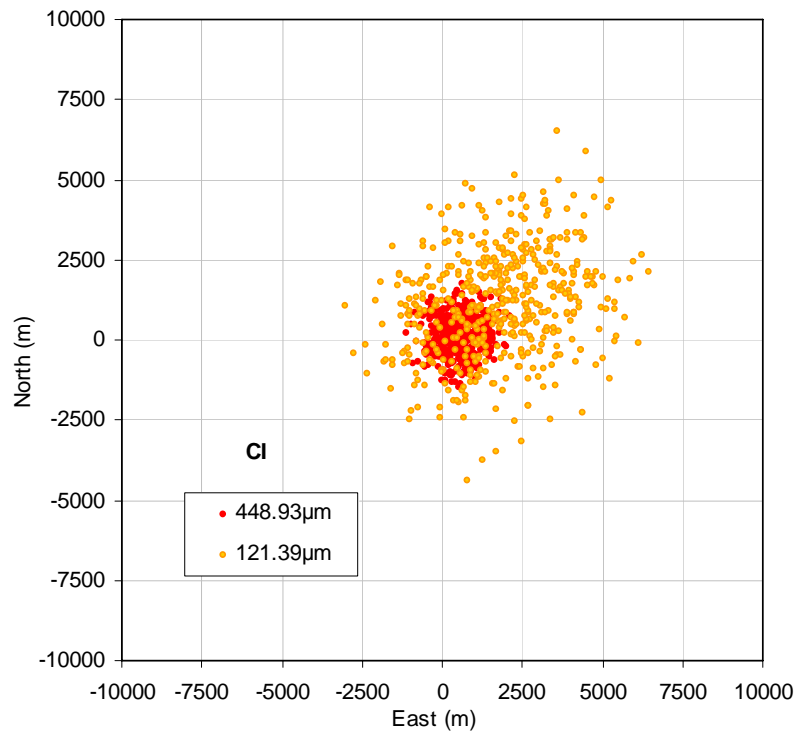
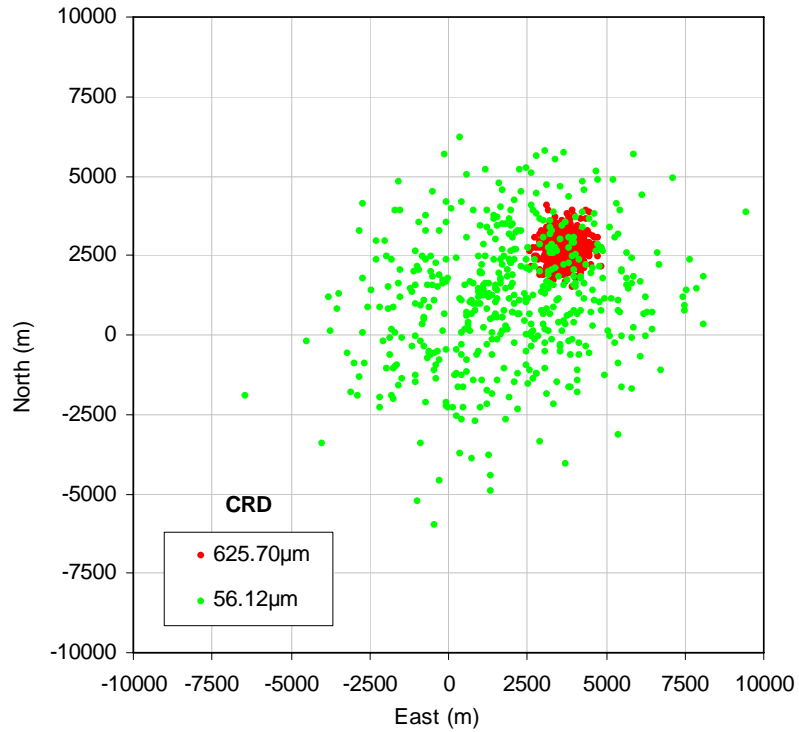
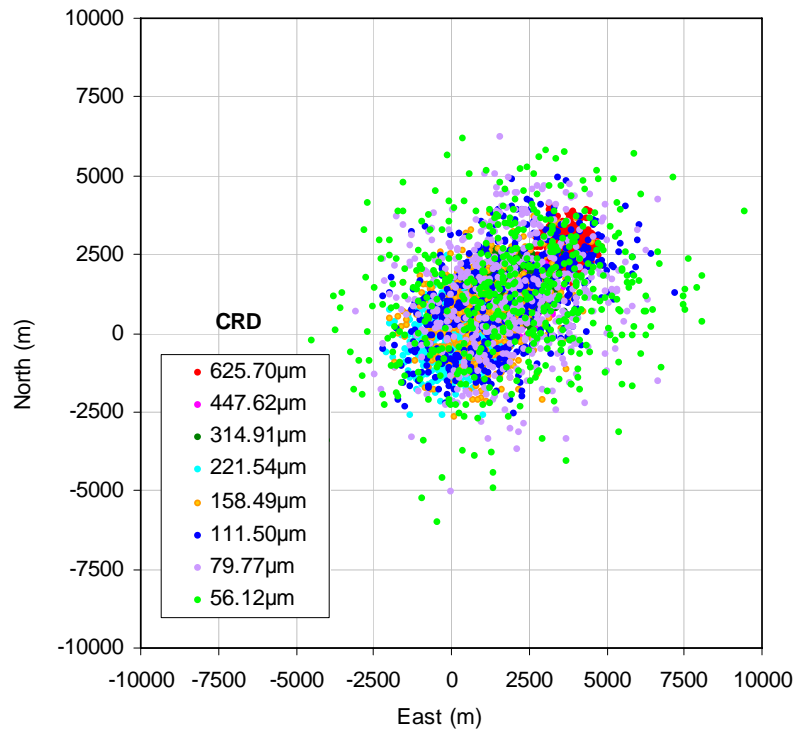


Figure 21: Effects of PSD on OMA deposition; CRD (top), CI (bottom)

Simulation results using two full PSD are plotted in **Figure 22**. The different deposition patterns are due to the difference in PSD and the settling velocity. The two sediments have

different particle size distributions, with minimum sizes of 56.12 μm and 121.39 μm , and maximum sizes of 448.93 μm and 625.70 μm for CRD and CI respectively. Eight size classes were reported for CRD and five classes were reported for CI by Khelifa et al. (2008). Even with the same diameter, OMAs formed with the two sediments have different settling velocities due to the difference in OMA structure. While **Figure 22** shows the extent of deposition, the concentration pattern of settled oil cannot be discerned.



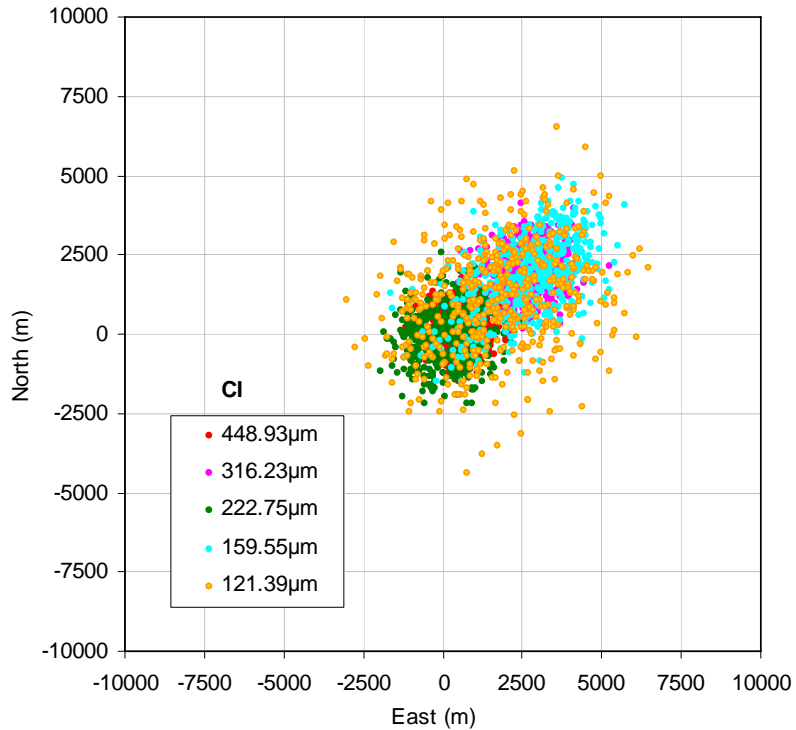


Figure 22: Positions of deposited OMA; CRD (previous page), and CI (above)

To determine the amount of oil settled on the seabed, normalized TPH concentration (as a percent of the total spilled oil per square meter) is plotted in Figure 23. The maximum concentration for CI (9.27×10^{-7} % total mass/m²) in Figure 23 is about 1.44 times that of the CRD (6.42×10^{-7} % total mass/m²). If the amount of oil spilled is 1000 tonnes, there will be a maximum concentration of 359 and 246 mg oil/kg sediment (by assuming that the sediment layer is 1 cm) for CI and CRD, respectively. Over the entire domain, the concentrations for the CI case are generally higher than for CRD. This is because the same amount of oil was distributed in 112 concentration cells of 1 km² in the CRD case and in 56 concentration cells in the CI case. The statistics of the concentration for non-zero value cells are listed in Table 7.

Table 7: Statistics of the normalized oil concentrations in sediments

Parameters	Concentration (% total mass/m ²)	
	CI	CRD
Mean	1.92E-07	2.68E-08
Median	6.22E-08	3.91E-11
Minimum	6.34E-10	7.80E-13
Maximum	9.27E-07	6.46E-07

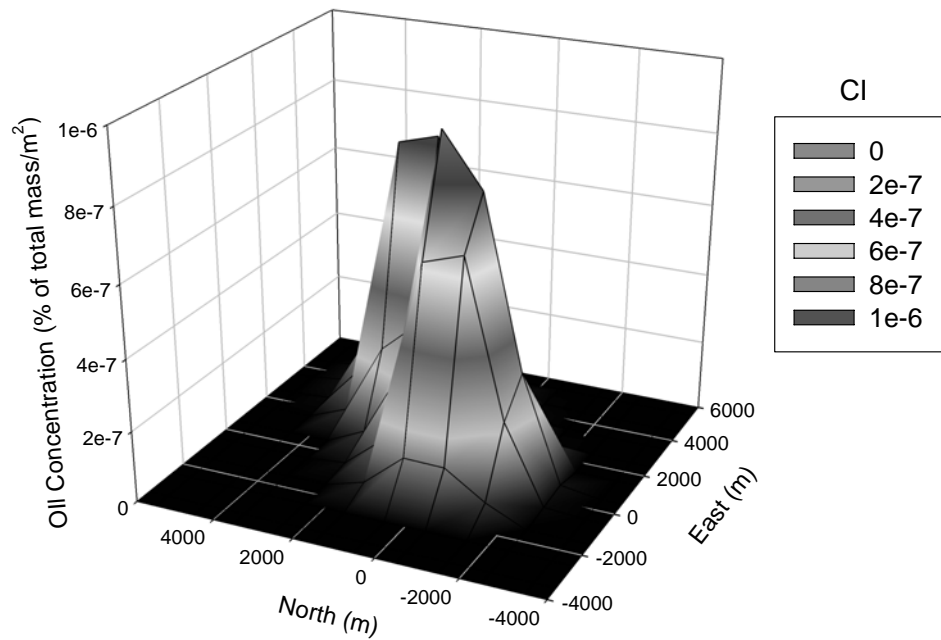
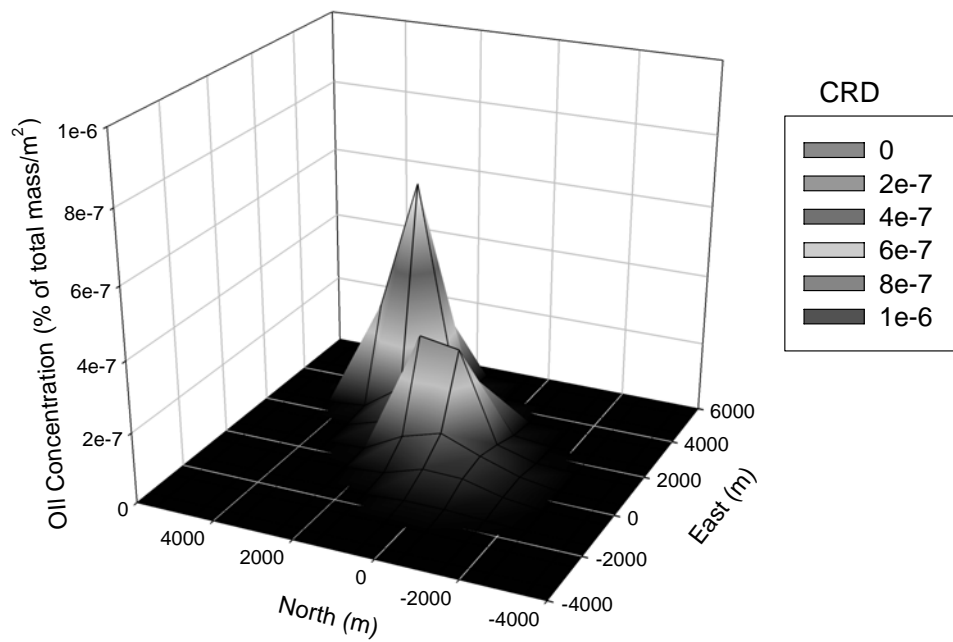


Figure 23: Concentration of deposited oil (percentage of total oil mass/m²); CRD (top), CI (bottom)

4.5. Summary of OMA transport model studies

In this study we investigated a number of factors that affect the transport of OMA particles. The following conclusions can be drawn from the model simulation study;

- Although waves are important in breaking up oil slicks and forming oil droplets, the effect of waves on transport, including advection, diffusion and sedimentation, was found to be smaller than the effects of currents and turbulence.
- The net transport due to “Stokes’ Drift” was relatively small, as the penetration of OMAs from the surface to the water column dramatically reduced the drift of particles associated with the surface movement of oil.
- Particle size distribution is important as it affects the settling velocity and consequently settling time. Smaller OMAs settle more slowly and tend to deposit over a larger area, resulting in reduced oil concentrations in the sediments.

5.0 Project Summary

This project has demonstrated the feasibility of using mineral fine additions to promote the formation of oil mineral aggregates (OMA), as a means to enhance the dispersion of oil slicks into the water column. Natural mixing energy, provided by breaking waves, was sufficient to facilitate the effective transport of oil in the form of OMAs from the surface to the water column. This countermeasure process is further enhanced by the addition of chemical oil dispersants which generate smaller oil droplets that are presumably more biodegradable.

Based on the results of preliminary transport models, with the exception of cases where caution should be taken to avoid application in areas with weak currents or high concentrations of coarse suspended sediment particles, the proposed procedure holds promise as an alternative method for oil spill response. Since OMA formation as well as microbial degradation of oil is known to occur under low temperature conditions, consideration should be given to its application under arctic conditions (including oil spills in ice). Research on using mineral fines to promote the formation of OMA's as a means of enhancing dispersion into the water column in Arctic environments should be further examined. This should include a program of large scale OMA testing in cold water/broken ice conditions at Ohmsett - The National Oil Spill Response Test Facility. To be fully accepted as an operational oil spill countermeasure technology additional studies are warranted to optimize the rates of natural OMA formation, to understand the influence of dispersant applications, and to assess its performance under net environment benefit analysis (NEBA) criteria. Scientific results from this study and those proposed above will support the development of sanctioned operational guidelines for a new oil spill countermeasure for the protection of our marine environment and its living resources.

Deliverables

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Appendix A

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Effects of Chemical Dispersants and Mineral Fines on Partitioning of Petroleum Hydrocarbons in Natural Seawater

Kenneth Lee*, Zhengkai Li, Thomas King, Paul Kepkay
Center for Offshore Oil and Gas Environmental Research, Bedford Institute of Oceanography, Fisheries and
Oceans Canada, P.O. Box 1006, Dartmouth, NS B2Y 4A2, Canada

Michel C Boufadel
Civil and Environmental Engineering Department, Temple University, Philadelphia, PA 19122, USA

Albert D Venosa
National Risk Management Research Laboratory, US EPA, Cincinnati, OH 45268, USA

Joseph V Mullin
Minerals Management Service, US Department of Interior, Herndon, VA 22070, USA

* Corresponding author; phone: (902) 426 7344; fax: (902) 426-1440; email: leek@mar.dfo-mpo.gc.ca

Abstract

The interaction of chemical dispersants and suspended sediments with crude oil influences the fate and transport of oil spills in coastal waters. Recent wave tank studies have shown that dispersants facilitate the dissipation of oil droplets into the water column and reduces the particle size distribution of oil-mineral aggregates (OMAs). In this work, baffled flasks were used to carry out a controlled laboratory experimental study to define the effects of chemical dispersants and mineral fines on the partitioning of crude oil, major fractions of oil, and petroleum hydrocarbons from the surface to the bulk water column and the sediment phases. The dissolved and dispersed oil in the aqueous phase and OMA was characterized using an Ultraviolet Fluorescence Spectroscopy (UVFS). The distribution of major fractions of crude oil (the alkanes, aromatics, resins, and asphaltenes) was analyzed by thin layer chromatography coupled to flame ionized detection (TLC/FID); aliphatic and aromatic hydrocarbons were analyzed by gas chromatography and mass spectrometry (GC/MS). The results suggest that chemical dispersants enhanced the transfer of oil from the surface to the water column as dispersed oil, and promoted the formation of oil-mineral aggregates in the water column. Interaction of chemically dispersed oil with suspended particular materials needs to be considered in order to accurately assess the environmental risk associated with chemical oil dispersant use in particle-rich nearshore and estuarine waters. The results from this study indicate that there is not necessarily an increase in sedimentation of oil in particle rich water when dispersants are applied.

Keywords: crude oil, dispersants, mineral fines, oil droplets, OMAs, breaking waves

Introduction

In nearshore or estuarine waters, oil droplets are likely to be incorporated into oil-mineral-aggregates (OMAs) as a result of their interaction with suspended particulates that are typical of coastal regions (Bragg and Owen 1995; Le Floch et al. 2002; Owens and Lee 2003; Owens et al. 2003; Page et al. 2000). Detailed studies of OMA formation have revealed that both mineral fines and organic particles can stabilize oil droplets within the water column (Bragg and Yang 1995; Delvigne et al. 1987; Lee 2002; Lee and Stoffyn-Egli 2001; Lee et al. 2003; Lee et al. 1996; Muschenheim and Lee 2002; Omotoso et al. 2002). The results of laboratory experiments (Cloutier et al. 2002; Lee et al. 1997; Omotoso et al. 2002; Stoffyn-Egli and Lee 2002) and shoreline field trials (Lee et al. 1997; Lunel et al. 1997; Owens et al. 1995; Owens and Lee 2003) have demonstrated that the production of OMAs enhances the natural dispersion of oil spills and reduces their environmental persistence by enhancing bioremediation.

The application of dispersants alters the rate and extent of oil-mineral aggregate formation and could, hypothetically, reduce droplet size and lead to the formation of smaller and denser OMAs compared to aggregates formed in the absence of the dispersants. At the same time, chemical dispersants could also change the surface physicochemical properties of oil droplets to impair the binding of oil to mineral fines. To distinguish between these two possibilities, a wave tank experiment was recently carried out to investigate the aggregation of mineral fines with physically or chemically dispersed oil and to determine the dynamic particle-size distributions of the OMAs (Li et al. 2007). The study results showed that the formation of oil-mineral-aggregates was associated with both physically and chemically dispersed oil; dispersants reduced oil and OMA droplet size distribution; mineral fines increased the suspended particle concentration in the water column and droplet stability; and that there was a synergistic effect between dispersants and mineral fines that further enhanced the transfer of oil from the surface into the water column. In addition, the small particles generated in the presence of chemical dispersants and mineral fines tended to remain suspended in the water column.

Partitioning of the polycyclic aromatic hydrocarbon (PAH) compounds of crude oil in aquatic environments is of great interest during assessments of the effects of oil spill dispersion (Couillard et al. 2005; Sterling et al. 2003) and other discharges containing hydrocarbons (Faksness et al. 2004). This partitioning of the different fractions of crude oil will impact both the biodegradation rate of the oil (Venosa and Holder in press) and ultimately affect their toxicity to aquatic and benthic species (Kiparissis et al. 2003; Oikari et al. 2001).

In response to these important environmental considerations, we have designed experiments to investigate the effect of chemical dispersants and mineral fines on the partitioning of major fractions of crude oil between surface, water column, and sediment phases. In particular, particularly the distribution of primary toxic components, such as alkanes and polycyclic aromatic hydrocarbons, has been tracked. The data generated from our experiments will be useful in modeling the fate and transport of dispersed oil

and conducting risk assessment related to the application of chemical dispersants in nearshore waters rich in suspended particulates.

Material and Methods

2.1. Materials

In this study, the reference test oil was MESA crude oil (Petro-Canada, Montreal, QC) with an initial API (American Petroleum Institute) gravity of 29.7°; the oil was artificially weathered by aeration to 86.2% of original weight, with Corexit 9500 (Nalco Energy Service, L.P. Sugar Land, TX) as the chemical dispersant. The mineral fines were American Petroleum Institute (API No. 9) kaolin (Mesa Alta, New Mexico), with a cation exchange capacity of 6.8 meq/100 g, a median particle size of 0.6 μm , and a density of 2.60 g/cm^3 .

2.2. Experimental procedure

The experimental design used to determine the effect of chemical dispersants on crude oil in seawater consisted of 4 treatments: C (control: no dispersant or mineral fines), D (with dispersant, without mineral fines), M (without dispersant, with mineral fines), and DM (in the presence of both dispersant and mineral fines). Each treatment was applied as triplicate runs of oil dispersion in baffled flasks following procedure of adding 120 ml filtered seawater to each individual test flask followed by 33 mg mineral fines to Treatments M and DM flasks. This gives an oil-to-sediment ratio of 2.6:1, which was reported being the optimum dose of mineral fines to maximum OMA formation (Stoffyn-Egli and Lee 2002). Flasks were then shaken at 200 rpm for 10 min with an orbital shaker and 100 μL of MESA added to each flask at the surface. After 4 μL of dispersant was added with a 10 μL gas tight syringe in treatments D and DM, all of the baffled flasks were shaken at 200 rpm on an orbital shaker for another 60 min. The entire contents of each flask were then transferred to a corresponding separatory funnel and the baffled flask rinsed with dichloromethane (DCM) to be mixed with the DCM-extracted surface oil fraction. Each funnel was left under static conditions for 30 min to allow the dispersed oil droplets and oil-mineral aggregates to re-surface or settle and separate into three phases. The bottom (5ml) phase of sediments was drained into a pre-cleaned 100ml amber sampling bottle to conduct extraction of crude oil from suspended sediments using roller apparatus (Wheaton R₂P, VWR Scientific Canada). The middle (110ml) phase of material suspended in the water column was drained into a second pre-cleaned separatory funnel for liquid-liquid extraction of crude oil dispersed in seawater. Prior to this extraction step 5 ml of the middle phase from each flask was drained into a clean scintillation vial for ultraviolet fluorescence spectroscopy (UVFS) of dispersed oil and oil-mineral aggregates. The top phase of floating non-dispersed oil was drained into a pre-cleaned 100 ml amber bottle to perform liquid-liquid extraction of non-dispersed oil using roller extraction (Cole et al. 2007). The same experiments were repeated in triplicate to separate and collect samples for thin layer chromatography coupled to flame ionized detection (TLC/FID) analysis of the partitioning of the four fractions of crude oil.

2.3. Oil dispersion and OMA formation by Ultraviolet Fluorescence Spectroscopy (UVFS)

A UVFS technique (Bugden et al. In press) was used to characterize the dissolved/dispersed oil in the aqueous phase and the oil aggregated into OMAs. Samples were vigorously shaken and 3 ml of each suspension were rapidly transferred to an ultraviolet-grade methacrylate disposable cuvette (VWR International Inc., Mississauga, ON). The suspension was then scanned in the dissolved/dispersed fraction and aggregated fraction using a Shimadzu RFS301 spectrofluorometer running Panorana 1.1 software. The optimal excitation wavelength that produced the highest emission peaks was 280 nm; this wavelength with a slit width of ± 2 nm was used in all subsequent emission scans from 300 to 500 nm.

2.4. Partitioning of major oil fractions by TLC/FID

The extracts were used to conduct thin layer chromatography (TLC or Iatroscan) analysis of the three portions to determine the total petroleum hydrocarbon, and alkane, PAH, resins and asphaltenes. The duplicate set of experiments at each time point labelled for "Iatroscan" were extracted with dichloromethane (3x 30ml). The TLC-FID instrument used for this research was an Iatroscan MK-6, (Shell-USA, VA, USA). All extracts were concentrated to a final volume of 1.00ml prior to analysis by Iatroscan. The flame ionized detector was operated with hydrogen flow at 160 ml/min and air flow at 2 l/min. The procedure for developing the chromarods is described briefly as follows: pass the chromarods through the FID hydrogen flame twice (known as blanking the rods) at a slower scan rate (40sec) to deactivate the rods. Once deactivated the rods were scanned to ensure purification. The rods are spotted, allowed to air dry, and placed in a humidity chamber (70:30 v/v sulphuric acid in deionized water) for 10 min. An aliquot (1 μ l) of the concentration-adjusted extract was applied to the origin point of each chromarod. A rack of ten chromarods were placed in the first (hexane) solvent chamber (18 min) to fractionate the aliphatics. Then place the chromarods in the second (toluene) solvent chamber (8 min) to elute the aromatic fraction. Finally the rack was placed in a (95:5 dichloromethane:methanol) third solvent chamber (2 min) to separate the resins from the asphaltenes. After each developing chamber the chromatographic peaks were preserved by air dry for 2 min, followed by 10 min in a humidity chamber. Once the chromarods have all been developed, a rack of 10 chromarods are placed in the Iatroscan MK-6 automated flame ionized detection scanning system for analysis. Set the scan speed to 30 seconds per chromarod; maintain the hydrogen flow rate at 160 ml/min and the airflow rate at 2000 ml/min. The Iatroscan produces chromatograms containing four major peaks present in crude oil extracts, which represent the chemical classes of aliphatics, aromatics, resins, and asphaltenes.

2.5. Partitioning of petroleum hydrocarbons by GC/MS

The contents of the flasks were transferred to a separatory funnel. Prior to extraction surrogate recovery standards were added to each sample. The flasks were rinsed with DCM and the rinsing added to the separatory funnel. Each sample was extracted 3x30ml

with DCM. The DCM extracts were then exchanged into hexane under a stream of dry nitrogen. The hexane extracts were prepared for Silica Gel purification prior to GC/MS analysis. The purified extracts were concentrated to a final volume of 1.00ml followed by addition of an internal standard mixture of deuterated alkane and aromatic hydrocarbons to yield a final concentration of each standard of 10 ng/μl. Concentrations of hydrocarbons in the extracts were quantified using an Agilent 6890 Series GC with a 5973N MSD operated in the selected ion monitoring (SIM) mode. The analytes include 28 alkanes ranging in carbon number from n-C₁₀ to n-C₃₅ plus pristane, phytane, hopane, and 32 aromatics, consisting of the 2-, 3-, and 4-ring aromatics (naphthalenes, phenanthrenes, dibenzothiophenes, fluorenes, naphthobenzothiophenes, pyrenes, and chrysenes), including their alkylated homologs. The column was a 30 m × 0.25 mm ID with 0.2 μm film thickness MS-5 or equivalent column (Supelco, Supelco Park, Bellefonte, PA). Aliphatic and aromatic concentrations were summed to obtain total concentrations for each chemical class in the sample extracts.

2.6. Data analysis

Analysis of variance (ANOVA) was performed to compare treatment effects on the partitioning of the total petroleum hydrocarbon (alkanes and aromatic fractions) and polar fractions (resins and asphaltenes) as well as each individual petroleum hydrocarbon (alkane and aromatic) compound.

3. Results

3.1 Distribution of oil and oil-mineral aggregates in the water column

The effect of chemical dispersants and mineral fines on the distribution of crude oil dispersed in the water column was illustrated by the ultraviolet (UV) emission spectra of dispersed and/or aggregated oil (Figure 1). The UVF spectra from the water column samples were similar to those obtained from results of previous flask and wave tank experiments, where the aggregation of oil with mineral fines results in distinct shifts in the spectra compared to oil dispersed in seawater (Kepkay et al. 2002; Li et al. 2007). The emission peaks at 340nm are characteristic of lower and medium molecular weight aromatics, such as naphthalene whereas higher molecular weight multi-ring compounds are responsible for broader emission peak at 445 nm (Bugden et al. In press). Figure 1 shows that the treatment effects on the dispersion of oil were clear: the natural dispersion of oil was characterized by only one emission peak at 340nm, presumably corresponding to more soluble low molecular weight aromatics. The action of dispersant increased the intensity of 445nm emission peak and the action of mineral fines (regardless of dispersant) suppressed the first peak at 340 nm but propagated the second peak at 445 nm. These results are consistent with previous wave tank work and the results from chemical analysis as described below, indicating that chemical dispersants, mineral fines, and the two in combination stimulated primarily the dispersion of multiple-ring less-soluble aromatic fractions of the oil into the bulk aqueous phase. In addition, the effects of dispersants on shifting the dispersed droplet size distribution to the smaller scale may also contribute to the enlarged emission intensity peaking at 445 nm (Figure 1)

3.2 Distribution of major fractions of crude oil

Figure 2a delineates the distribution of the four major oil fractions in the original MESA oil and those that have been recovered from the partitioning experiments; the two data sets are in good agreement. Figure 2b shows the partitioning of total oil between three different phases — the surface, the water column, and the bottom — and Figure 3 presents the distribution of four different fractions of the oil among the three phases. Several general trends exist: first, the distributions of classes of chemicals and TPH among three different phases are similar to each other; second, the presence of chemical dispersant transfers all four classes of chemicals in crude oil from the surface into the water column; third, the presence of mineral fines results in an increase on the bottom for each component. These results are expected and consistent with the results obtained from previous wave tank studies (Li et al. 2007).

The effect of chemical dispersant on oil-mineral aggregation can be determined by comparing the oil distribution between phases in treatments M and DM. No chemical dispersant was applied in treatment M, so the data are the result of physical dispersion and oil-mineral aggregation with mineral fines transferring oil into the bulk water column and near bottom sediment phases; the majority of total and different oil fractions, however, remained at the surface phase, presumably due to the lack of sufficient amount of mineral fines to bind the physically dispersed oil droplets to form oil-mineral aggregates that overcomes the buoyancy of larger oil droplets. In treatment DM, chemical dispersants were applied in addition to mineral fines and the majority of the oil ended up in suspension in the water column. Much smaller amounts of oil and oil fractions were present at the surface compared to mineral fines in the absence of chemical dispersant (treatment M); interestingly, the near bottom portion of oil and oil fractions was also significantly ($P < 0.05$) reduced by the presence of dispersants.

3.3 Distribution of polycyclic aromatic hydrocarbons

The effect of chemical dispersant on oil-mineral aggregates was further explored by GC/MS analysis of the distribution of the major components of the aliphatic and aromatic fractions of crude oil among three different phases: at the surface, in the water column, and at the bottom. Figures 4 shows the distribution of the methylated PAHs and PAHs. The effect of chemical dispersant on the distribution of the primary components of crude oil among the different phases is in line with the TLC/FID analysis of the distribution of major oil fractions. The presence of chemical dispersants dramatically increased the amount of PAHs in the water column (treatment D) compared to physically dispersed oil (treatment C). The amount of PAHs that are suspended in the water column was also much greater in chemically dispersed OMAs (treatment DM) compared to physically formed OMAs (treatment M). Although dispersant increased PAHs at the bottom in the absence of mineral fines (Treatments C and D), it actually reduced the amount of bottom PAHs in the presence of mineral fines (Treatments M and DM).

Discussion

The stabilization of oil droplets in the water column by the formation of oil-mineral aggregates with suspended sediment have been well described in the literature (Bragg and Yang 1995; Delvigne et al. 1987; Lee 2002; Lee and Stoffyn-Egli 2001; Lee et al. 2003; Lee et al. 1996; Muschenheim and Lee 2002; Omotoso et al. 2002). However, in the context of oil spill response operations, there is little information on the influence of chemical oil dispersants on the formation and fate of OMAs. Given that both chemical and physical dispersion lead to the generation of micron-sized droplets (Darling et al. 1990; Delvigne and Sweeney 1988; Lunel 1995), and that chemical dispersants alter the surface physicochemical properties of the dispersed oil droplets (Al-Sabagh and Atta 1999; Dalmazzone et al. 2005; Oebius 1999), the interactions of chemically dispersed oil with suspended sediment also need to be considered in order to accurately assess the risks involved during the application of dispersants in particle-rich nearshore and estuarine waters.

The results obtained from earlier wave tank studies (Li et al. 2007) indicate that dispersants and mineral fines can have enhanced and cumulative effects on the formation and distribution of oil droplets and OMAs. The interaction of chemical dispersant with oil and mineral fines increases the dissolved and aggregated oil concentration in the bulk aqueous phase and reduces the size of oil droplets and OMAs. The results obtained from this study indicate that the application of dispersant can increase the dispersed concentration of total oil, various chemical classes of oil, and individual compounds in both the absence and presence of mineral fines. These results also suggest that sinking of small OMAs by the compound action of chemical dispersant and suspended particulate material is not increased. Instead, the application of chemical dispersant reduces the oil fractions that were aggregated into the OMAs that may sink to the sediment phase. The effect of chemical dispersant on the formation and sedimentation of OMA, particularly the tendency toward increasing the bulk aqueous phase concentrations of petroleum hydrocarbons has two important and contrary implications. On one hand, of the increased suspension of chemically dispersed OMA in the water column may stimulate the biodegradation of the dispersed oil due to increased surface area. On the other hand, an increase in chemically dispersed OMA may also increase the bioavailability of toxic components, particularly PAHs and alkylated PAHs, to pelagic species susceptible to elevated exposure.

Conclusion

Until recently, the use of chemical oil dispersants has been focused on offshore spills due to concerns over toxic effects of dispersants and chemically dispersed oil on the biota, especially in light of the fact that the extent of dispersion may be limited by the depth of waters in coastal regions. With increased public pressure to remove oil from the sea surface to protect seabirds following spills, the development of “low toxicity” dispersant formulations, the high prevalence of spills in coastal regions, and case studies demonstrating their efficacy and net environmental benefit (Lunel et al. 1997), the application of chemical dispersants in nearshore environments is now being considered.

Our experiments using the baffled flasks support earlier wave tank results highlighting the synergistic effects of chemical dispersants and mineral fines on the dispersion of crude oils. The effect of chemical dispersants contributes to the transfer of surface oil to the bulk water column most significantly. While the action of mineral fines results in the sinking of a certain amount of oil to a bottom sediment phase, the effect of chemical dispersants overcomes the sinking of oil-mineral aggregates by dispersing oil into smaller droplets and promoting suspensions of the dispersed oil drops in the water column. The cumulative effect of this dispersant/sediment interaction on the overall fate and toxicity expressed in terms of biodegradation rate and the potential impact on pelagic and benthic organisms needs to be evaluated further.

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Figure 1

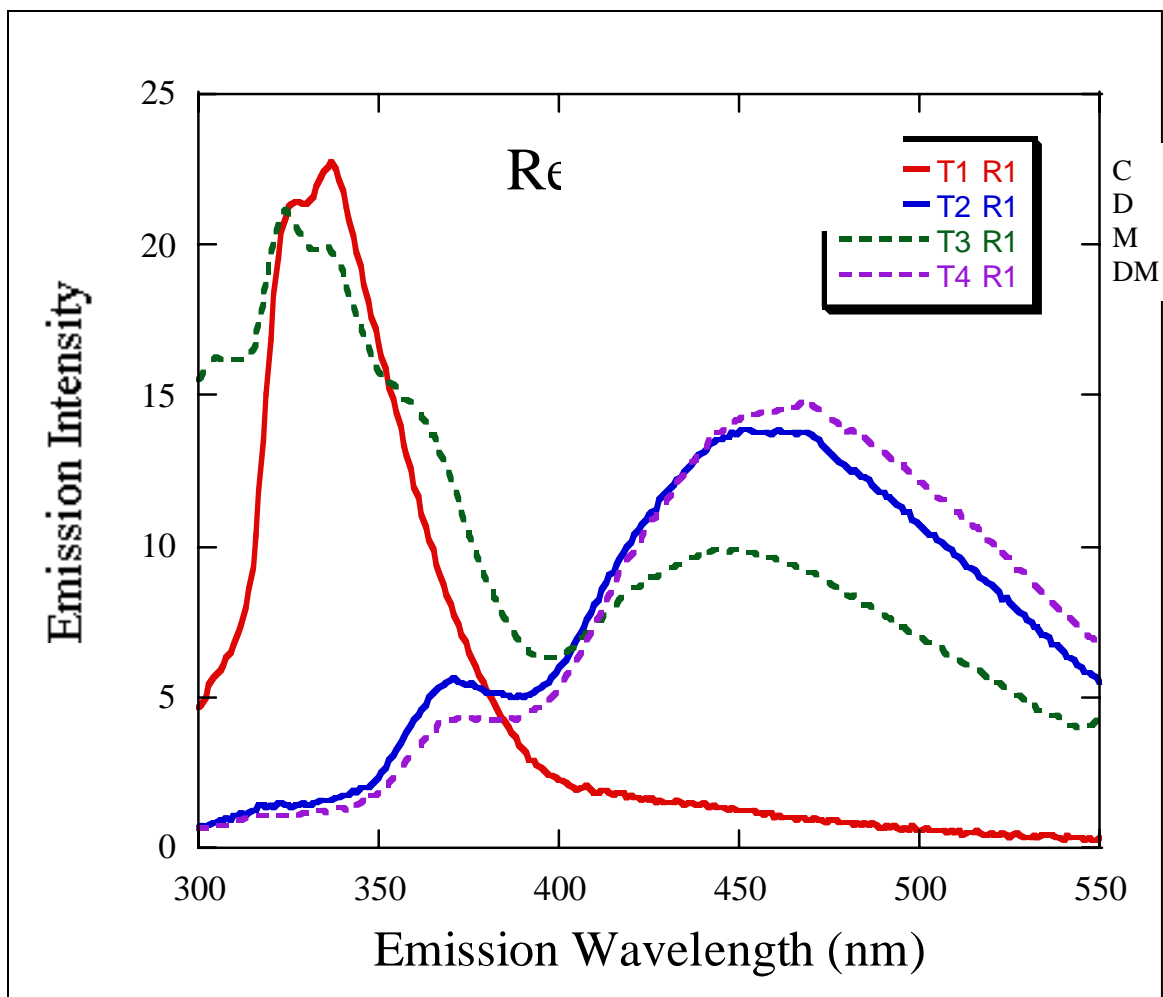


FIGURE 1: Ultraviolet Emission spectra of MESA dispersed in the water column. The UVF spectra have been corrected for natural fluorescence and light scattering by blanks of seawater used in the experiment.

Figure 2

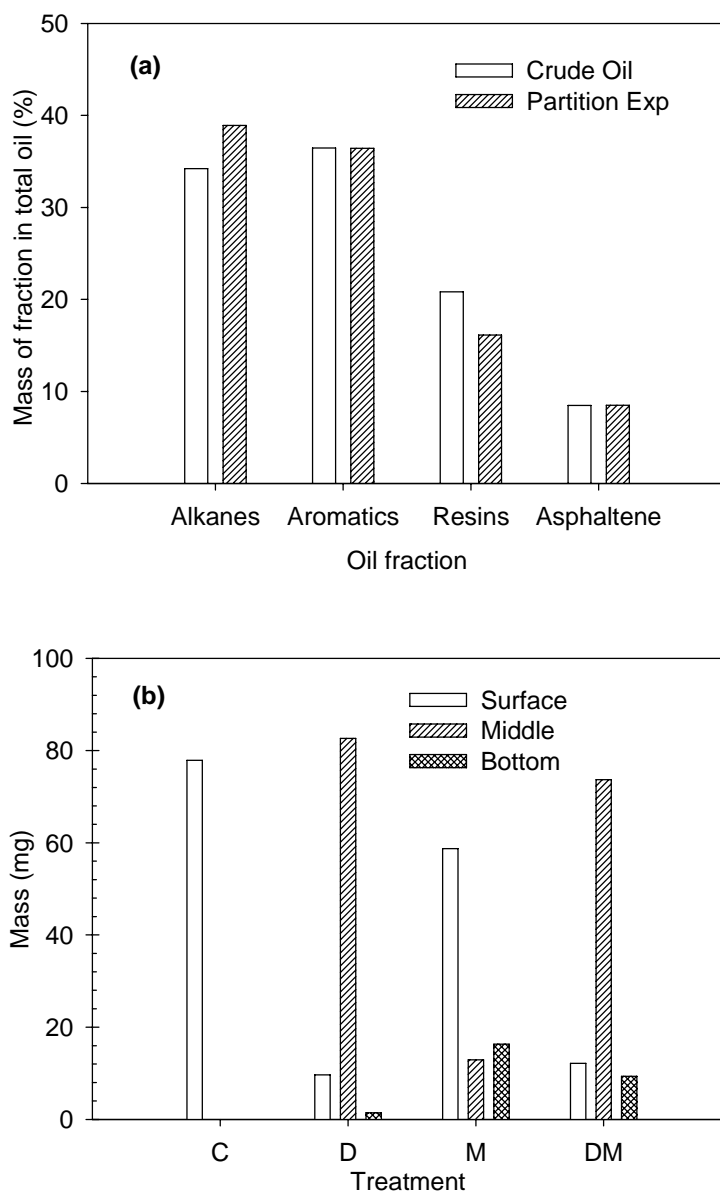


FIGURE 2: TLC-FID measurement of: (a) oil fractions of whole oil and the sum of dispersed oil and (b) distribution of total oil mass in three phases of 4 treatments. The surface, middle, and bottom phase in separatory funnels was 5 ml, 110 ml, and 5 ml, respectively.

Figure 3

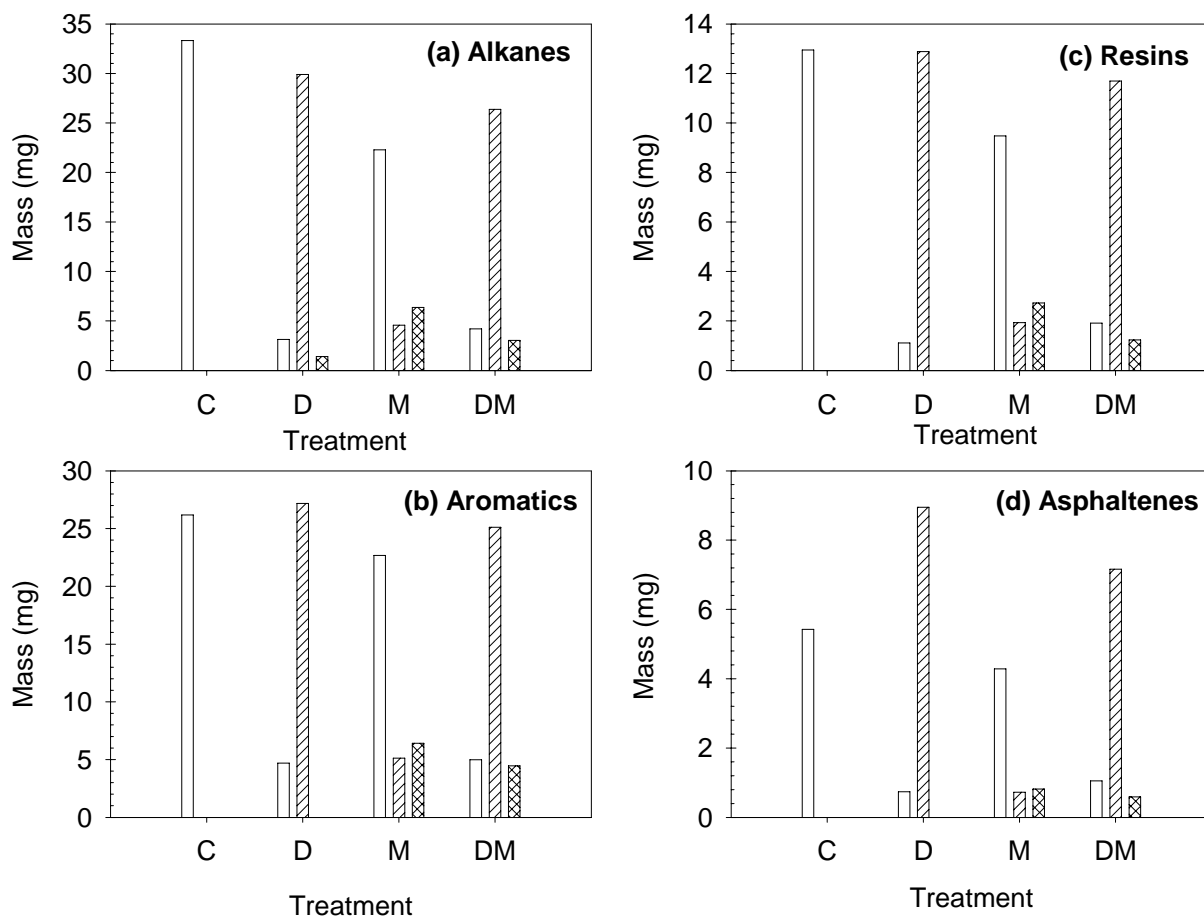


FIGURE 3: TLC-FID analysis treatment effects on (a) alkanes, (b) aromatics, (c) resins, and (d) asphaltenes distribution in three phases. The surface, middle, and bottom phase in separatory funnels was 5 ml, 110 ml, and 5 ml, respectively.

Figure 4

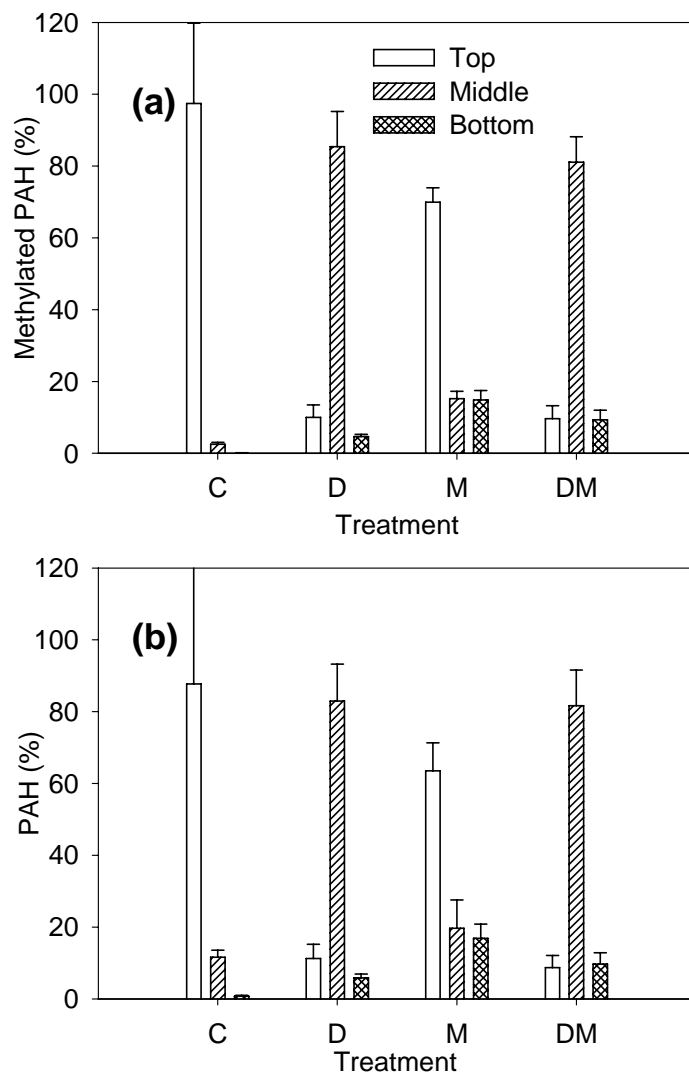


FIGURE 4: GC/MS analysis of treatment effects on the distribution of (a) methylated PAHs and (b) PAHs in the separatory funnels. The surface, middle, and bottom phase in separatory funnels was 5 ml, 110 ml, and 5 ml, respectively.

Appendix B

The 32nd Arctic and Marine Oilspill Program (AMOP) Technical Seminar on
Environmental Contamination and Response. June 9-11, Vancouver, BC, Canada

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Modeling the Transport of Oil-Mineral-Aggregates (OMAs) in the Marine Environment and Assessment of their Potential Risks

Haibo Niu*, Zhengkai Li, Kenneth Lee, and Paul Kepkay

Centre for Offshore Oil, Gas and Energy Research (COOGER), Bedford Institute of Oceanography, Fisheries and Oceans Canada, Dartmouth, NS, Canada, B2Y 4A2

Joseph V Mullin

Minerals Management Service, US Department of Interior, Herndon, VA 22070, USA

*email: NiuH@mar.dfo-mpo.gc.ca

Abstract

A random walk particle tracking model was used to simulate the motions of oil-mineral-aggregates (OMAs) under hydrodynamic conditions involving wave-induced velocities, random velocities due to turbulence, and the settling velocity due to gravity. Wave-induced and settling velocities for OMAs determined from the application of Stokes's theory and empirical equations derived from experimental data were used in a series of simulations to evaluate the effects of wave characteristics, particle size distribution, and settling/floating velocity on the transport of OMAs formed from two different types of minerals. The study found that the wave effect on advection/diffusion is of secondary importance when compared to tidal currents and turbulence induced velocity. To assess the risk of OMAs to benthic organisms, Predicted Environmental Concentrations (PEC) was compared to the Benchmark Concentration (BC) derived for eight different hydrocarbon groups. The simulation results indicate that no risk from both aliphatic and aromatic hydrocarbons can be found for the two cases described in this paper with a 1000 tonnes spill. The study also showed that aromatic hydrocarbons posed more risk than aliphatic hydrocarbons. For both aliphatic and aromatic hydrocarbons, the C₉-C₁₂ group posed greater risk than other groups.

1 Introduction

Following marine oil spills, wave motion may breakup surface oil slicks into micron-sized oil droplets. If the water column has high loads of suspended particles, including mineral particles, they may interact with oil droplets to form oil-mineral-aggregates (OMAs). This natural process stabilizes dispersed oil droplets in the water column and enhances their biodegradation rates (Bragg and Owen, 1995; Le Floch et al., 2002; Owens and Lee, 2003; Owens et al., 2003; Page et al., 2000). Thus, impacts on sea birds and the probability of oil reaching shoreline environments are diminished.

The suspended mineral particles within OMAs may have densities heavier than both crude oil and the seawater. For example, Khelifa et al. (2008) has reported a lowest effective density of 25 kg/m^3 for OMAs formed under laboratory conditions with several types of crude oil and natural sediments at different concentration levels. Therefore, there is a high probability that OMAs will transport residual oil to the seabed that may subsequently cause adverse effect to benthic organisms.

To evaluate the potential impacts of OMAs, it is important to study both their physical characteristics and transport behaviours. The breakup of oil slicks into small droplets and their interactions with mineral fines have been studied experimentally by a number of authors, including Lee and Stoffyn-Egli (2001), Lee (2002), Omotoso et al. (2002), Stoffyn-Egli and Lee (2002), Li et al. (2007), Khelifa et al. (2008). Factors that may affect the formation of OMAs have also been reported by Le Floch et al. (2002) and Khelifa et al. (2005). However, studies on the transport behaviour of OMAs are limited and the risks of oil in OMAs to benthic organisms has not been quantitatively assessed.

Models can be used to study the transport behaviours of OMAs and assess their risks. There are a number of oil spill models available, such as the OilMap (ASA, 2009), OSCAR (SINTEF, 2009) and others (reviewed by Reed et al., 1999). However, these existing models cannot be used to predict the behaviour of OMAs without modification. This manuscript describes the development of a model to simulate the transport behaviour of OMAs and to assess their potential risk to benthic organisms.

2 Description of Model

2.1 General

Although studies on the effective density of OMAs are still limited, recent laboratory experiments have shown the existence of OMAs with densities heavier than seawater which would promote their physical transport to the seabed (Khelifa et al., 2008). To assess the environmental risk associated with this process, this study is focused on the potential impact residual oil associated with OMA on benthic organisms.

As with oil dispersed by physical processes alone, oil associated with OMAs undergoes various processes, such as evaporation, dissolution, bio-degradation, as well as advection and diffusion processes. In the proposed model, with the exception of

evaporation - estimated from the NOAA's ADIOS 2 model (NOAA, 2009), these decay factors are not considered to be more conservative.

2.2 Random Walk Scheme

The model used in this study is a three-dimensional random walk model (Webb, 1982; Murray-Smith et al., 1996; Riddle, 1998, 2001; Bouffadel et al., 2007). The OMAs are represented by placing a fixed number of particles at the spill site at the beginning of simulation, and the particles moves on each subsequent timestep according to Lagrangian motion:

$$\begin{aligned}x_{t+1} &= x_t + U\Delta t \\y_{t+1} &= y_t + V\Delta t \\z_{t+1} &= z_t + W\Delta t\end{aligned}\tag{5}$$

where x , y , z are the coordinates of an OMA particle, the subscripts $t+1$ and t represent the model timestep, Δt is the timestep length, and U , V , and W are the horizontal and vertical velocity components given by:

$$\begin{aligned}U &= u_{tidal} + u_{wave} + u_t \\V &= v_{tidal} + v_{wave} + v_t \\W &= w_b + w_{wave} + w_t\end{aligned}\tag{6}$$

where u_{tidal} and v_{tidal} are the u-component (eastward) and v-component (northward) of tidal currents, u_{wave} , v_{wave} , and w_{wave} are the velocities due to wave motion, w_b is a buoyancy or settling velocity depend on the particle density, u_t , v_t , and w_t are the velocities due to turbulence.

The Stokes's theory was used in the model to describe the horizontal and vertical components of the wave induced velocities. In this work, it is assumed that there is no modification of waves due to currents and the waves are assumed to propagate towards the east. Therefore, v_{wave} becomes zero, and the horizontal/vertical velocities due to wave are:

$$\begin{aligned}u_{wave} &= \frac{Hgk}{2\sigma} e^{kz} \cos(kx - \sigma) + \frac{3H^2\sigma k}{16} e^{2kz} \cos 2(kx - \sigma) \\w_{wave} &= \frac{Hgk}{2\sigma} e^{kz} \sin(kx - \sigma) + \frac{3H^2\sigma k}{16} e^{2kz} \sin 2(kx - \sigma)\end{aligned}\tag{7}$$

where H is the wave height, g is the acceleration due to gravity, k is the wave number, and σ is the wave frequency.

The terms u_t , v_t , and w_t can be described by:

$$\begin{aligned}
u_i &= R\sqrt{2K_H\Delta t} / \Delta t \\
v_i &= R\sqrt{2K_H\Delta t} / \Delta t \\
w_i &= R\sqrt{2K_V\Delta t} / \Delta t
\end{aligned}
\tag{8}$$

where R is a normal random number with zero mean and a variance of 1, and K_H and K_V are the horizontal and vertical mixing coefficient (m^2s^{-1}).

The initial location of a particle is randomly generated by the model based on a user specified surface slick size. As a particle moves within the model domain, its location is tested at each timestep. If the particle passes through the surface, it is placed back into the domain at a distance that is equal to the distance that the particle exceeds the boundary (i.e., it is reflected vertically). If the particle passes the bottom, it is placed back on the bottom and stops moving (i.e., it is settled).

2.3 Calculation of Oil in Sediment Concentration

The concentrations of settled oil (mass/m^2), $C_{settled}$, are calculated by counting the number of OMA particles in the user specified concentration cell:

$$C_{settled} = \sum_{i=1}^k \frac{N_i \times PM_i}{A_{cell}}
\tag{9}$$

where k is the number of particle classes, N_i is the number of the i_{th} -class particles in the user specified cell, A_{cell} is the area of the cell (m^2), and PM_i is the amount of oil per particle for the i_{th} -class particles:

$$PM_i = \frac{M_{spilled} \times P_{settled} \times p_i}{n_i}
\tag{10}$$

where $M_{spilled}$ is the total mass of spilled oil, $P_{settled}$ is the percentage of spilled oil that may be transferred to sediment, n_i is the number of particles used in the simulation for the class i , p_i is the fraction of settled oil (in percentage) carried by the particle class i :

$$p_i = \frac{[V_{oil} \rho_{oil}]_i PSD_i}{\sum_{i=1}^k \{ [V_{oil} \rho_{oil}]_i PSD_i \}}
\tag{11}$$

where V_{oil} is the volume of oil in a OMA particle of class i , ρ_{oil} is the density of oil, and PSD_i is the number distribution of OMA particles of class i .

It is difficult to determine V_{oil} either experimentally or analytically due to the fractal nature of OMAs. The V_{oil} is estimated in the model by assuming that the OMAs are spherical and non-porous. Therefore V_{oil} becomes:

$$V_{oil} = \frac{\rho_{sediment} - \rho_{OMA}}{\rho_{sediment} - \rho_{oil}} V_{OMA} \quad (12)$$

where $\rho_{sediment}$ is the density of sediment, ρ_{OMA} is the density of OMA determined by the modified Stokes's law based on the experimentally measured settling velocity, and V_{OMA} is the volume of a OMA particle.

$P_{settled}$ can be determined by laboratory experiments. Khelifa et al. (2008) has concluded that the 0.3 to 51 percent of the spilled oil may be transferred to sediment depending on the type of oil, sediment type and sediment concentration in the absence of chemical dispersant.

2.3 Assessment of Risk

To evaluate the potential risk of settled oil on benthic organisms, a benchmark concentration must be determined. The model adopted the benchmark concentration developed by Battelle (2007). Because the estimation of ecological risk of petroleum product in sediment based on a single Total Petroleum Hydrocarbon (TPH) value is an over-simplification, and the estimation using tens and possible thousands of individual hydrocarbons is overly complex and impractical, Battelle (2007) divided the individual hydrocarbons with similar chemical and toxicological properties from petroleum into eight groups and developed benchmarks for these groups (Table 8).

Table 8. Sediment Benchmark for Recommended Petroleum Fractions (Battelle, 2007)

Hydrocarbon Fraction		K_{oc}	Final Chronic Value (FCV) ($\mu\text{g/L}$)	Sediment Benchmark (mg/kg oc)	f_{oc} (CI/CRD)
Aliphatic	C ₅ -C ₈	7.24×10^3	218	1591	0.033/0.085**
	C ₉ -C ₁₂	4.37×10^5	6.3	2722	
	C ₁₃ -C ₁₈	1.10×10^8	0.05*	5543	
	C ₁₉ -C ₃₆	8.32×10^{10}	0.0001*	9883	
Aromatic	C ₆ -C ₈	4.47×10^2	1191	531	
	C ₉ -C ₁₂	4.90×10^3	46.2	228	
	C ₁₃ -C ₁₅	2.40×10^4	5.2	125	
	C ₁₆ -C ₂₄	3.39×10^5	0.12*	40	

* The fraction is not likely toxic because mean LC50 exceeds mean aqueous solubility;

**Values used in the case study (source: Khelifa et al., 2008)

The theory is based on that the toxicity of hydrocarbons in sediments to benthic organisms is caused by the hydrocarbon fraction of sediment particles into porewater and from porewater into the tissues of sediment-dwelling organisms. The sediment benchmark concentration can be estimated by:

$$\text{Benchmark Concentration (mg/kg)} = K_{oc} \times FCV \times f_{oc} \quad (13)$$

where K_{oc} is the carbon-to-water partitioning coefficient, FCV is the final chronic value for each hydrocarbon fraction, and f_{oc} is the fraction of organic matter in sediments.

The potential risks of OMAs are calculated by assessing the ratio of Predicted Environmental Concentration to the Benchmark Concentration (PEC/BC). The flowchart of the modeling system is shown in Figure 24.

3 Description of Case Study

3.1 Transport Behaviours

Tidal currents were predicted using the DFO Webtide model (DFO, 2009) for a randomly selected location in the Gulf of St. Lawrence. The eastward and northward components of the tidal current are plotted in Figure 25. The mean current speed is 0.18 m/s. The minimum speed is 0.01 m/s and maximum is 0.45m/s. The dominant direction is northeast and southwest. The water depth was assumed to be 80m to satisfy the deep water wave assumption.

The first set of simulations was a study of the effects of waves and currents on the transport of OMAs. A wave with period of 10s and height of 1.0m (Scenario-W1) was used. The second series of simulations was a study of the effects of different wave characteristics on the transport of OMAs. Two wave periods ($T=6, 10s$) and two wave heights ($H=0.75, 1.5m$) were used.

For the studies on the wave and current effects, a single size class was used. OMAs are assumed to have a mean diameter of 100 μ m. The settling velocity for this size class is based on the experimental data from Khelifa et al. (2008).

As the settling velocity in equation (2) is size dependent, it is expected that the particle size distribution (PSD) will affect the extent of deposition. Thus, the third set of simulations was then conducted to study the effects of PSD. The PSD data used is from the experiments of Khelifa et al. (2008) on two sediments: Cook Inlet (CI), and Columbia River Delta (CRD). The simulation only used the minimum and maximum particle sizes to outline the differences in transport behaviours.

Finally, two more realistic simulations were conducted utilizing the full PSD data, i.e. 5 size classes range from 121.39 to 448.93 μ m for the CI case, and 8 size classes range from 56.12 to 625.7 μ m for the CRD case. The wave used in this set of simulation has a period of 10s and a height of 0.75m.

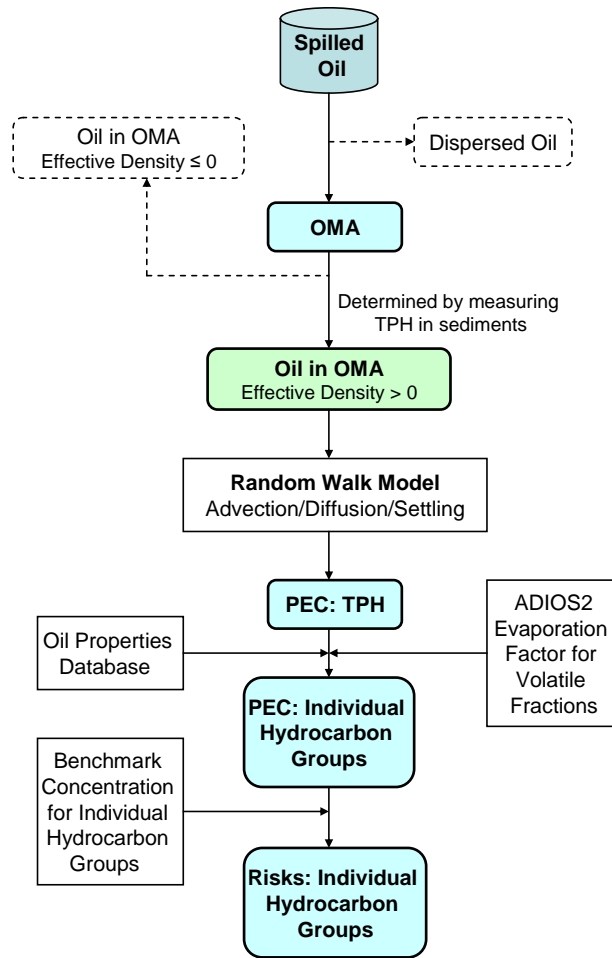


Figure 24. Flowchart of the Modeling System.

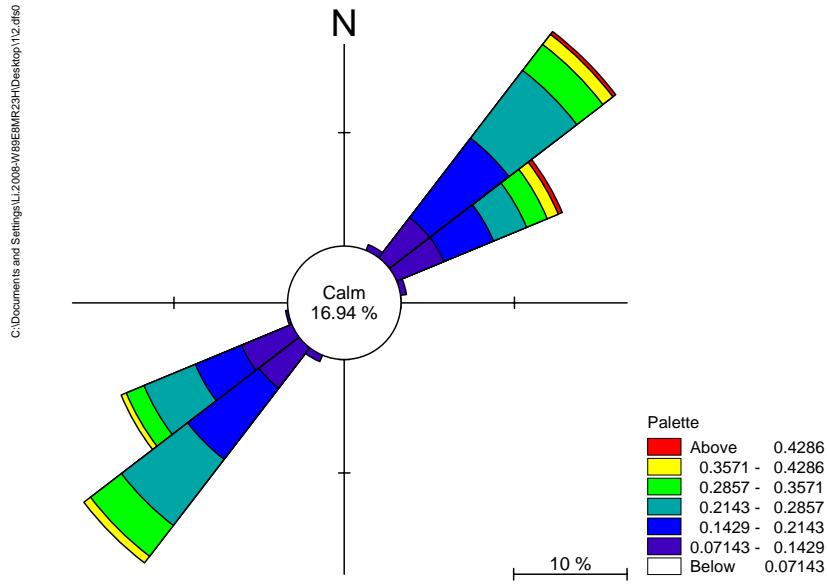


Figure 25. Directions and Magnitude of Tidal Currents (m/s).

3.2 Risk Assessment

For the last set of simulations (using the full PSD for CI and CRD), concentration fields were also calculated. To compute the concentration field, it was assumed that 1000 tonnes of South Louisiana crude oil were spilled. The oil characteristics were obtained from EC (2009) and were used to calculate the concentration of individual hydrocarbon groups.

It was also assumed that the deposited OMA will be evenly mixed with bottom sediments and the depth of the sediment layer was assumed to be 1 cm. This is a relative conservative estimation. The values of the organic matter content in the sediment were obtained from Khelifa et al. (2008).

The benchmark concentrations for individual hydrocarbon groups used in the simulation are from Battelle (2007). Figure 26 shows a comparison of the current benchmark concentrations for four aromatic hydrocarbons with other sediment quality criteria. It can be seen that the current method is more conservative than others in most cases due to the higher ACR values used. The only exception is that the NOAA ERM has a much lower benchmark concentration (strict criteria) for Acenaphthene.

4 Results and Discussions

4.1 The Effects of Waves

The results on the effects of wave and currents are plotted in Figure 27 and listed in Table 9. It can be seen from the figure that while wave induced velocity can advect and diffuse the OMAs, it is only of secondary importance when compared with the effects of currents. The center of mass for the W1 scenario is located at (153, 36) with a range of

7.3 km in the x direction (East-West) and 6.2 km in the y (North-South) direction. With the effects of currents, the C and W1&C scenarios show similar extent and location of deposition.

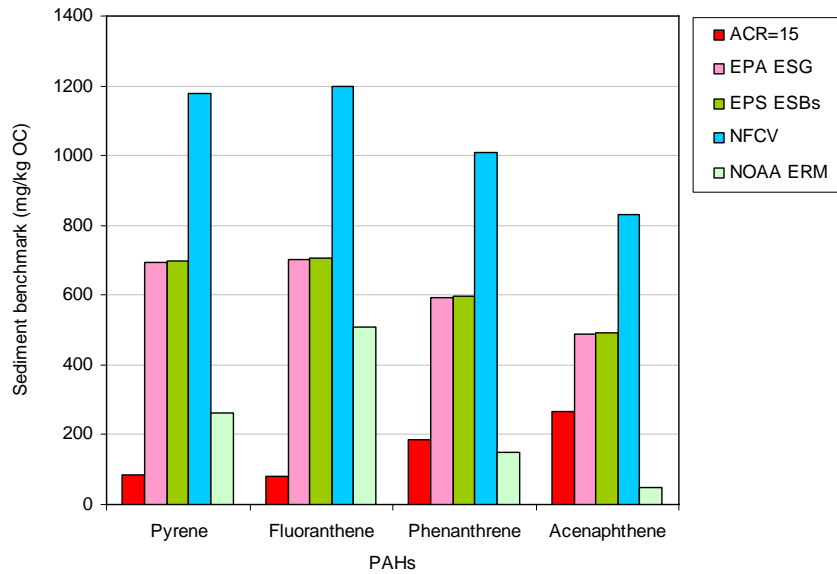


Figure 26. Comparison of Benchmark Concentration, EPA ESG = EPA Equilibrium partitioning Sediment Guidelines (U.S. EPA, 2002) , EPA ESBs= EPA Equilibrium partitioning Sediment Benchmarks (U.S. EPA, 2003), NFCV= (Di Toro, 2000), NOAA ERM= National Oceanic and Atmospheric Administration Effects Range Median (Long and McGrath, 1991).

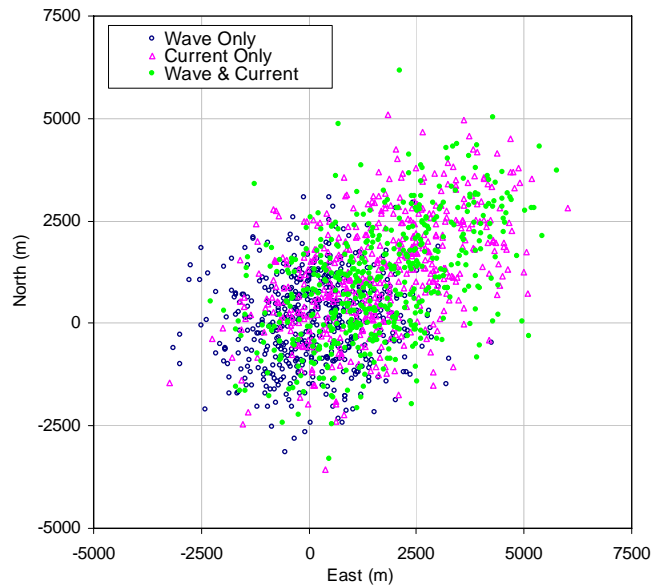


Figure 27 Effects of Wave and Currents on OMA Deposition.

To further study the effects of waves, the results from simulations under four different wave conditions were compared. It can be seen in Figure 28 and Table 9 that changing wave parameters had only slight effects on the extent and location of OMA deposition. The x -coordinate of the centre of mass has changed from 81 m to 319 m east while the y -coordinate keeps almost unchanged due to the wave propagation direction was set to eastward in the simulation.

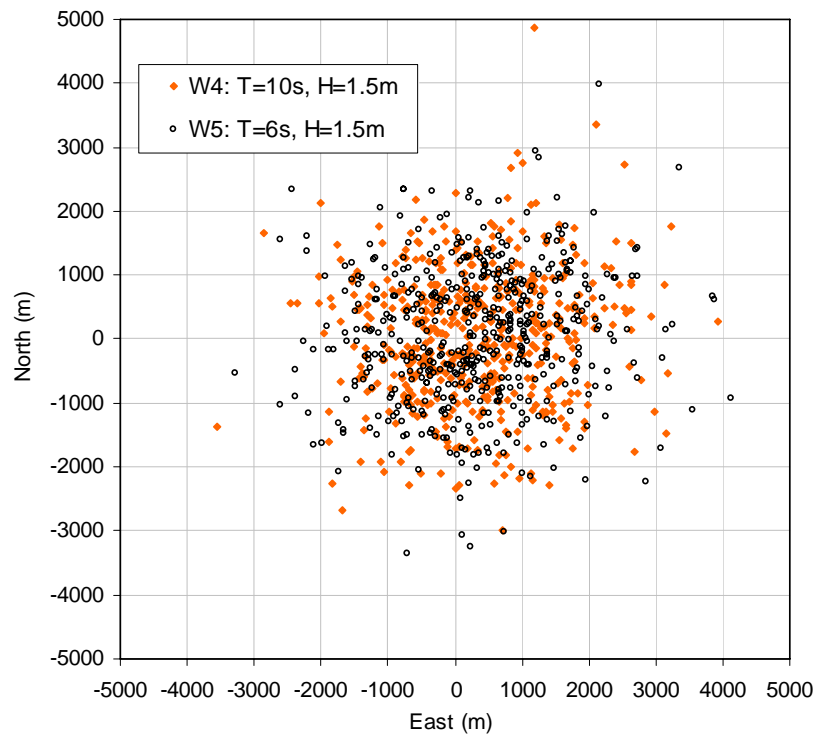
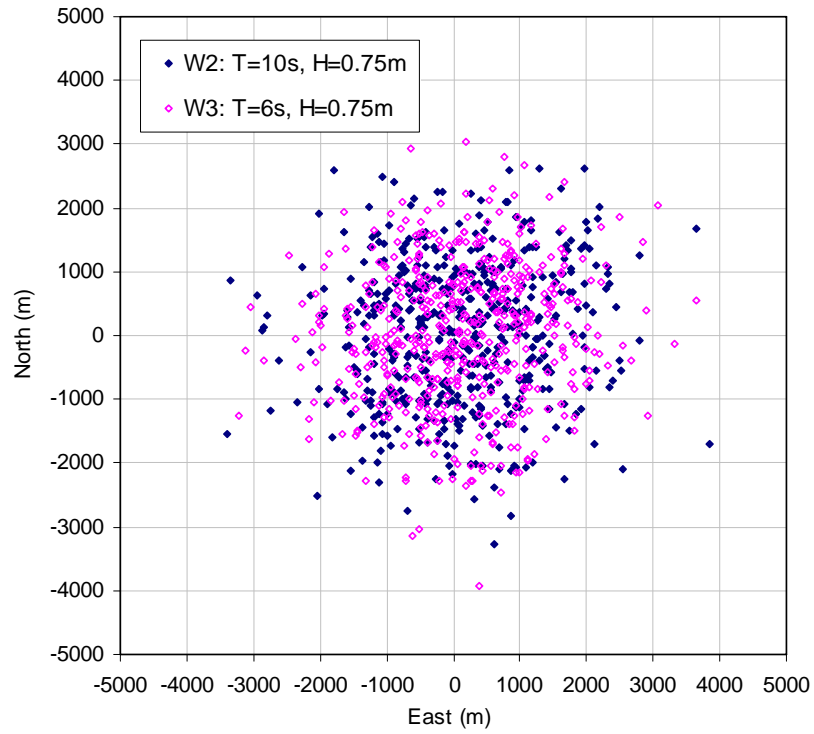


Figure 28 Effects of Waves on OMA Deposition.

Table 9. Statistics of the Locations of Deposited OMA Particles.

	Scenario	T (s)	H(m)	Mean	Min	Max	Range
East	W1	10	1	153	-3132	4244	7376
	C	-	-	1642	-3230	6012	9242
	W1&C	10	1	1645	-2290	5770	8060
North	W1	10	1	36	-3138	3074	6212
	C	-	-	1227	-3566	5101	8667
	W1&C	10	1	1017	-3292	6169	9461
East	W2	10	0.75	81	-3387	3836	7223
	W3	6	0.75	116	-3209	3651	6860
	W4	10	1.5	303	-3558	3939	7498
	W5	6	1.5	319	-3282	4123	7405
North	W2	10	0.75	35	-3260	2615	5875
	W3	6	0.75	40	-3930	3031	6962
	W4	10	1.5	40	-2978	4870	7848
	W5	6	1.5	43	-3354	3975	7330

*W-Wave, C-Currents, W&C-Wave and Currents

Given that tidal currents are not included in this case, and only the wave and turbulence induced velocities are considered, the results suggest that the wave induced velocity is of secondary importance when compared to the turbulence induced velocity used in the study. The effects of turbulent mixing coefficient on transport are not included here and will be discussed in detail in a separate paper.

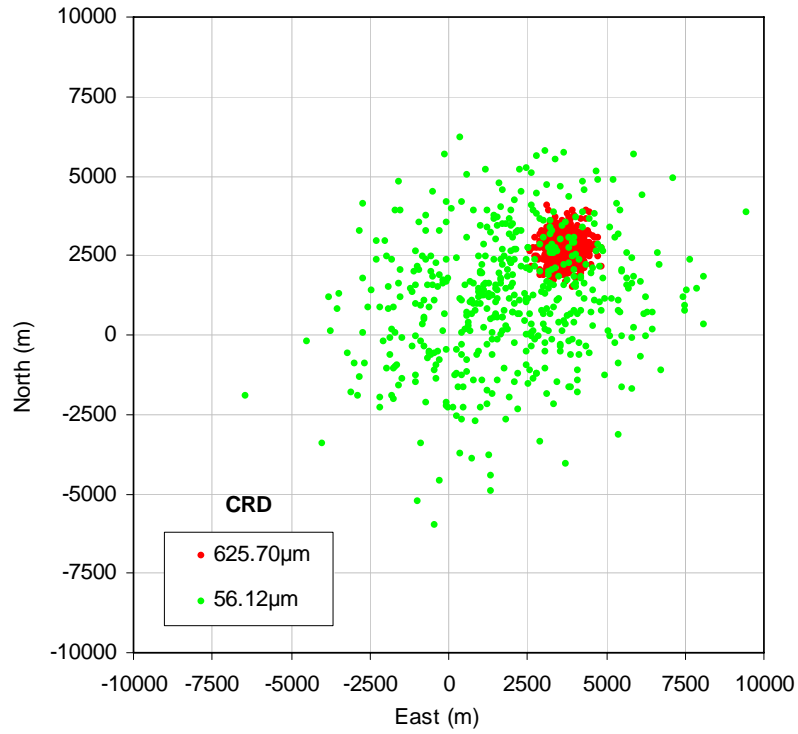
4.2 The Effects of Sediment Type/PSD/Settling Velocities

For the case of the two particle sizes used for CRD, the mean time for the settling of 56.12 μm particles is 150 h. The deposition started at 109 h and finished at 217 h. For the 625.70 μm particles, the deposition started at 5.43 h and finished at 5.82 h, with a mean settling time of 5.11 h. The effects of the PSD on the deposition of OMA are plotted in Figure 29 and it can be seen that the diameter of the area of deposition for the 625.70 μm particles is about 2.5 km. In contrast, the diameter increases to about 13 km for the 56.12 μm particles. If we assume the OMA particles are evenly distributed within the deposition area, the sediment concentration in the former (625.70 μm) case is about 29 times that of the latter (56.12 μm) case.

Similarly, the mean time for the settling of 121.39 μm CI particles is 87 h. The deposition started at 66 h and finished at 111 h. The diameter for the area of impact is about 9.5 km. For the coarse (448.93 μm) particle class, the mean deposition time is about 11.5 h, which started at 10.42 h and finished at 12.98 h. The diameter of the impact area is about 3.25 km and the concentration in the later (448.93 μm) case is about 8.5 times that of the former (121.39 μm) case.

Simulation results using two full PSD are plotted in Figure 30. The difference in deposition pattern is due to the difference in PSD, and the settling velocity. The two sediments have different particle size distributions, with minimum sizes of 56.12 μm and 121.39 μm , and maximum sizes of 448.93 μm and 625.70 μm for CRD and CI respectively. Eight size classes were reported for CRD and five classes were reported for

CI by Khelifa et al. (2008). Even with the same diameter, OMAs formed with the two sediments have different settling velocities due to the difference in OMA structure. While Figure 30 shows the extent of deposition, the concentration pattern of settled oil cannot be discerned.



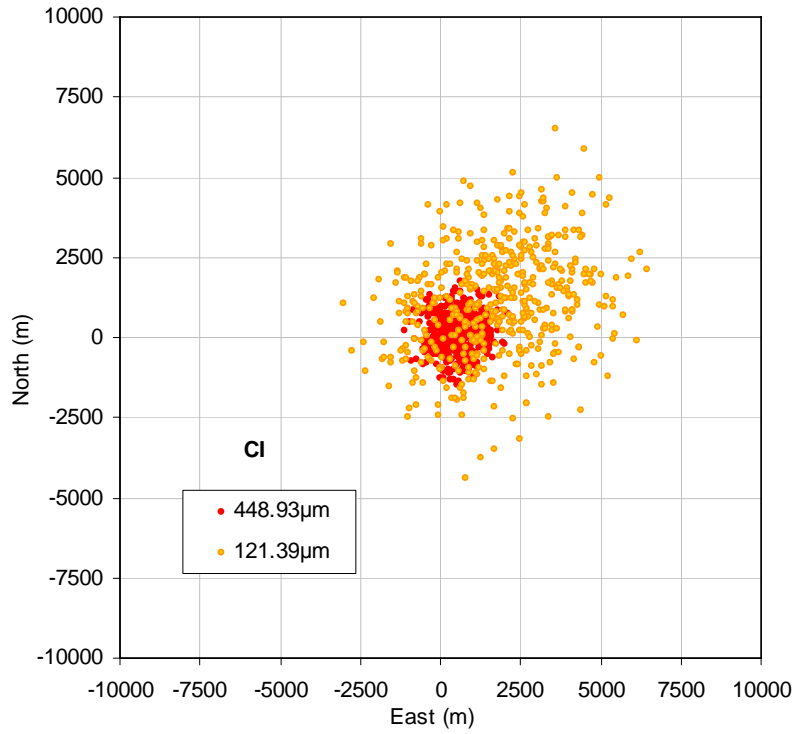
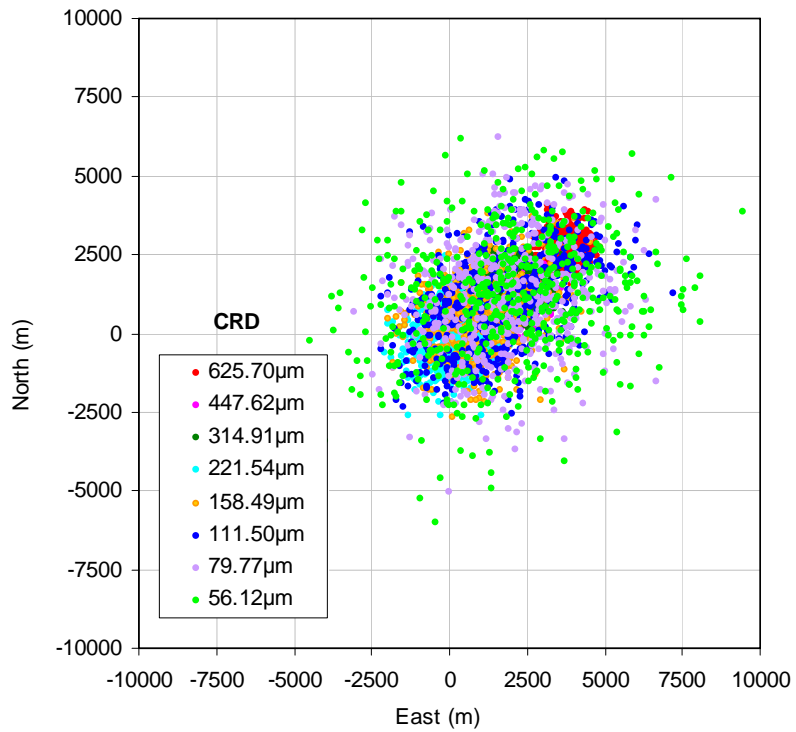


Figure 29. Effects of PSD on OMA Deposition: CRD (top), CI (bottom).



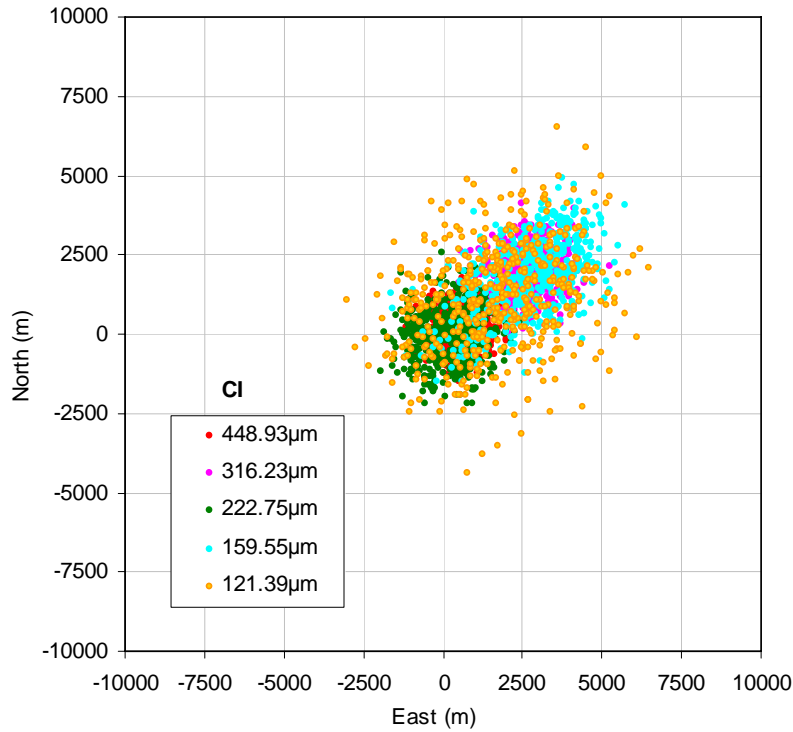


Figure 30. Positions of deposited OMA: CRD (top), and CI (bottom).

To determine the amount of oil settled to the seabed, normalized TPH concentration (as percent of the total spilled oil per square meter) is plotted in Figure 31. The maximum concentration for CI (9.27×10^{-7} % total mass/m²) in Figure 31 is about 1.44 times that of the CRD (6.42×10^{-7} % total mass/m²). If amount of oil spilled is 1000 tonnes, this will give a maximum concentration of 359 and 246 mg oil/kg sediment (by assuming that the sediment layer is 1 cm) for CI and CRD, respectively. Over the entire domain, the concentrations for CI case are generally higher than CRD values. This is because that the same amount of oil was distributed in 112 concentration cells of 1 km² for the CRD case and in 56 concentration cells for the CI case. The statistics of the concentration for non-zero value cells are listed in Table 10.

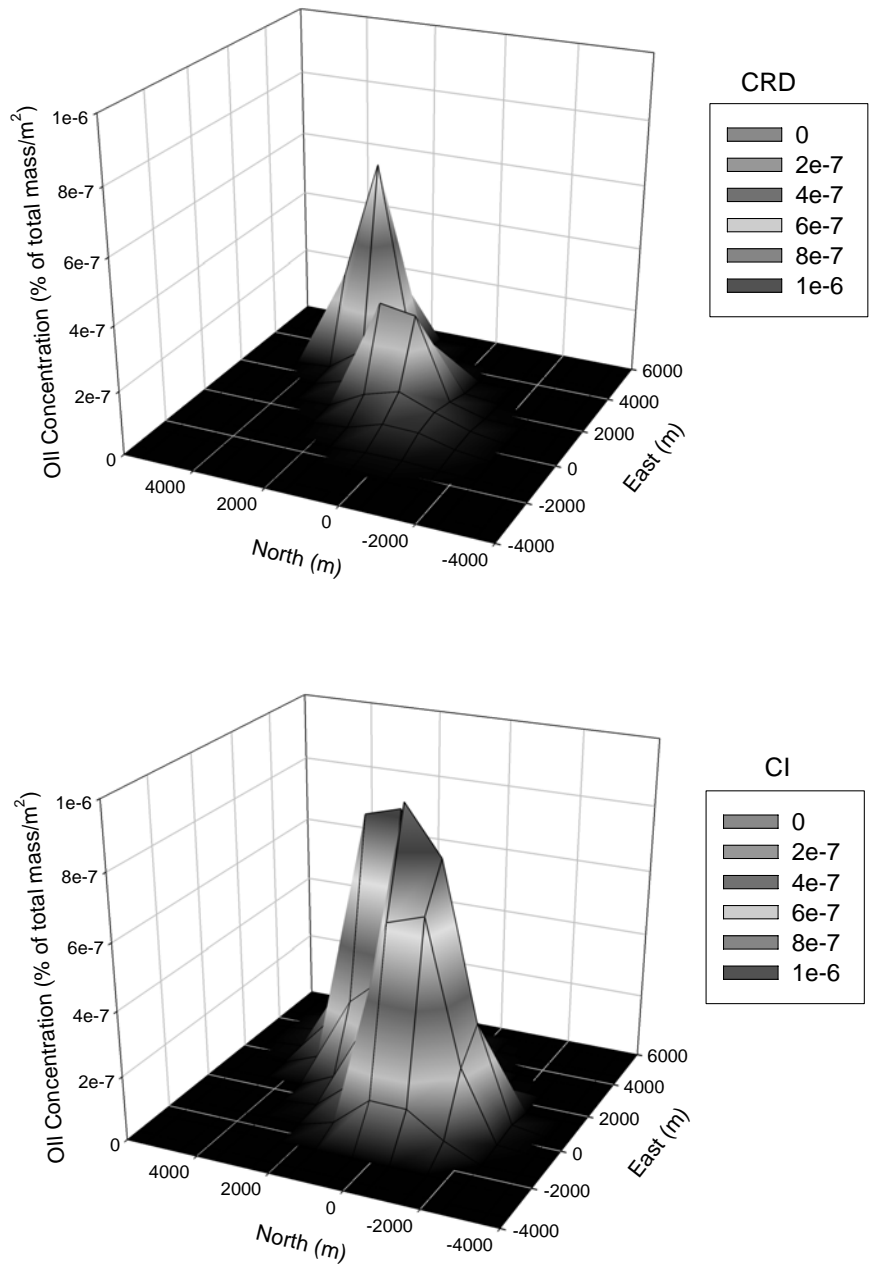


Figure 31. Concentration of Deposited Oil (percentage of total oil mass/m²): CRD (top), CI (bottom).

Table 10 Statistics of the Normalized Concentration.

Parameters	Concentration (% total mass/m ²)	
	CI	CRD
Mean	1.92E-07	2.68E-08
Median	6.22E-08	3.91E-11

Minimum	6.34E-10	7.80E-13
Maximum	9.27E-07	6.46E-07

4.3 Risks to Benthic Organisms

Although the values in Table 10 are small, the background TPH concentration in sediments can be easily exceeded even with a minor oil spill. To quantify the potential risks of petroleum hydrocarbons to benthic organisms, simulation results on the risks using the sediment benchmark concentration established by Battelle (2007) are presented in Figure 32 to Figure 35.

The risks from aliphatic hydrocarbons for the CI case are shown in Figure 32. The results indicate that no risk from aliphatic hydrocarbons at the selected benchmark. The maximum risk is from C₉-C₁₂ group. Even for this group, the maximum PEC/BC value is only 0.081. The risks from aromatic hydrocarbons for the CI case are shown in Figure 33 and it can be seen that the risks from aromatic groups are much higher than those from the aliphatic group. A maximum PEC/BC value of 0.510 was estimated for the C₉-C₁₂ group where C₆-C₈ group poses the smallest risk and a maximum PEC/BC value of 0.16.

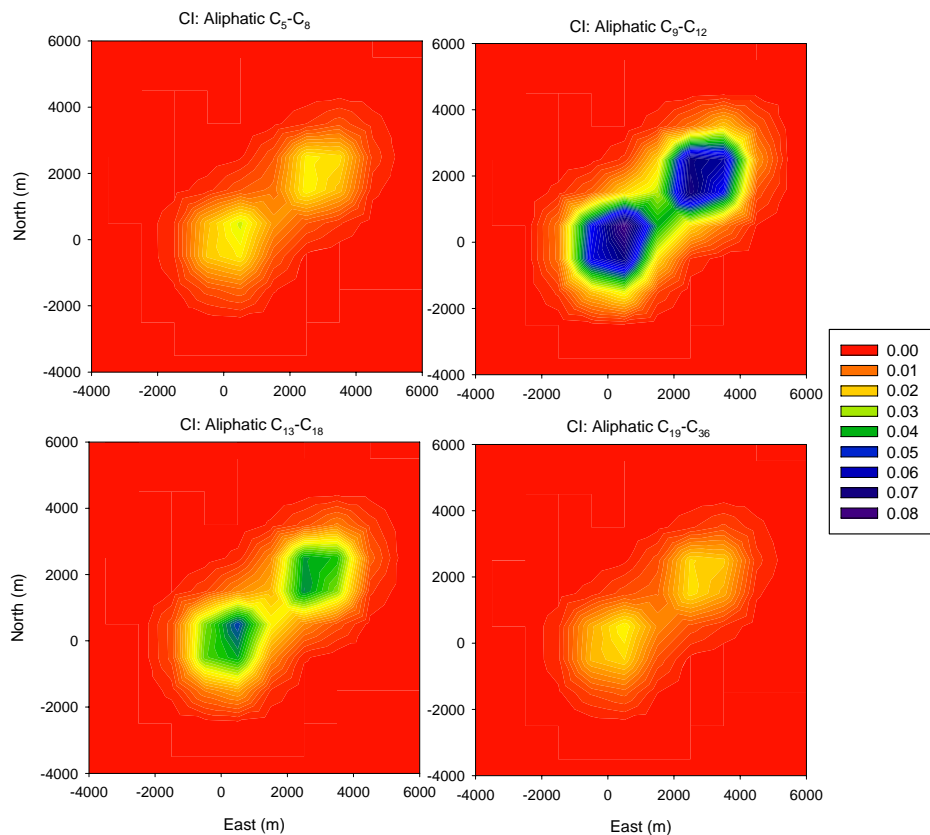


Figure 32. Risk Map of Aliphatic Hydrocarbons (CI).

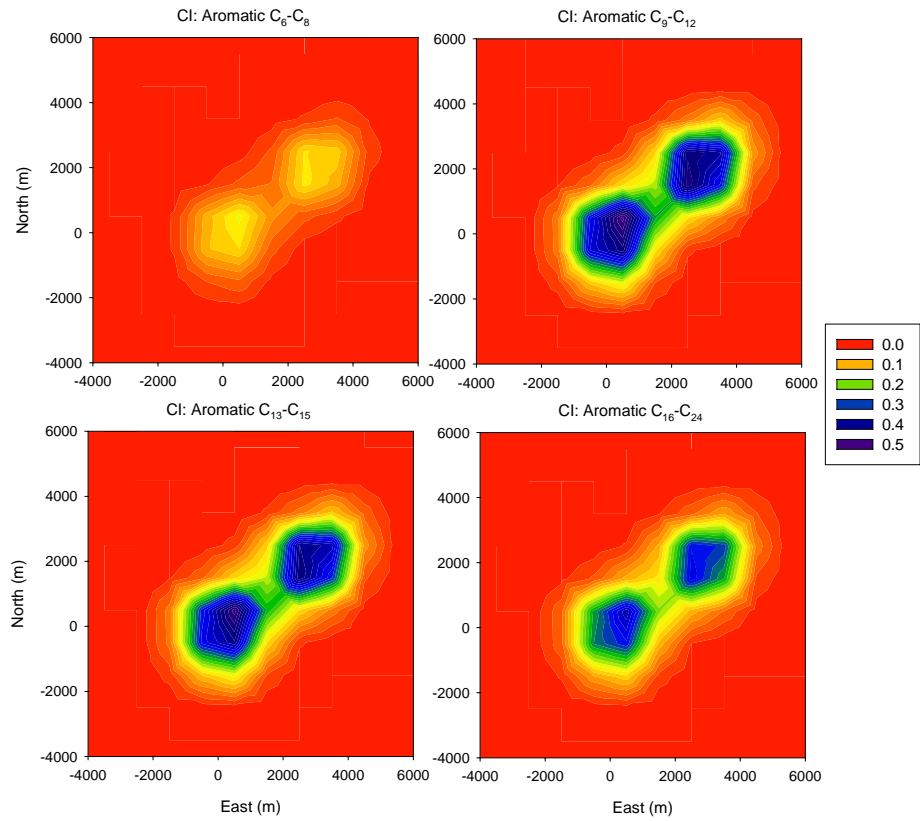


Figure 33. Risk Map of Aromatic Hydrocarbons (CI).

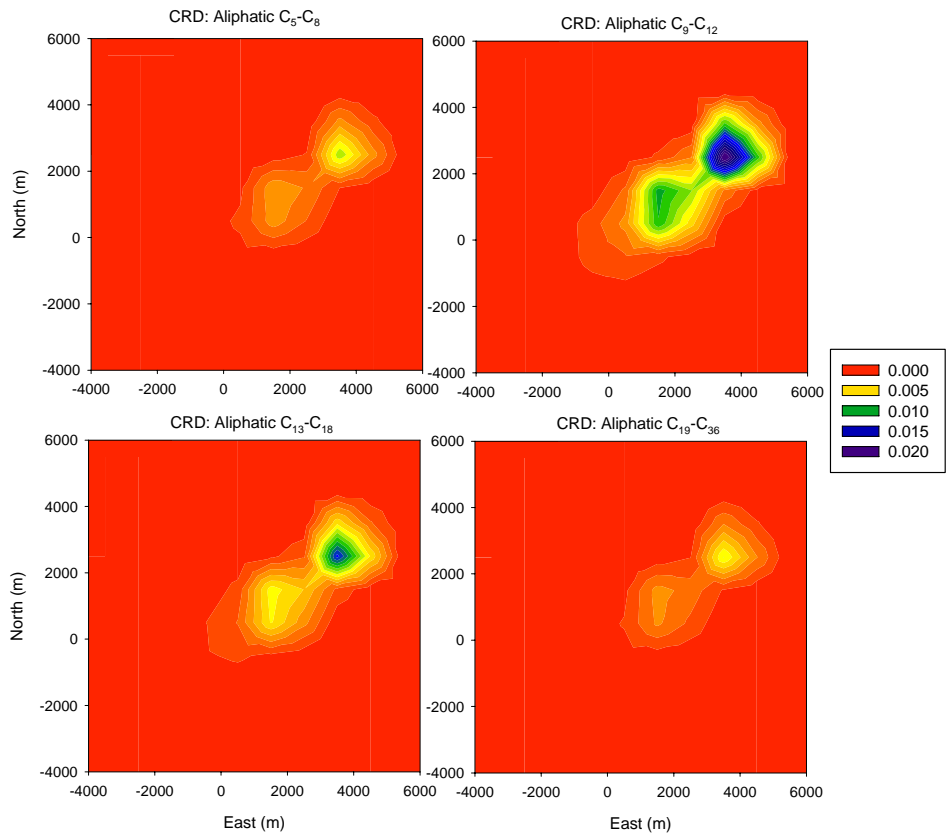


Figure 34 Risk Map of Aliphatic Hydrocarbons (CRD).

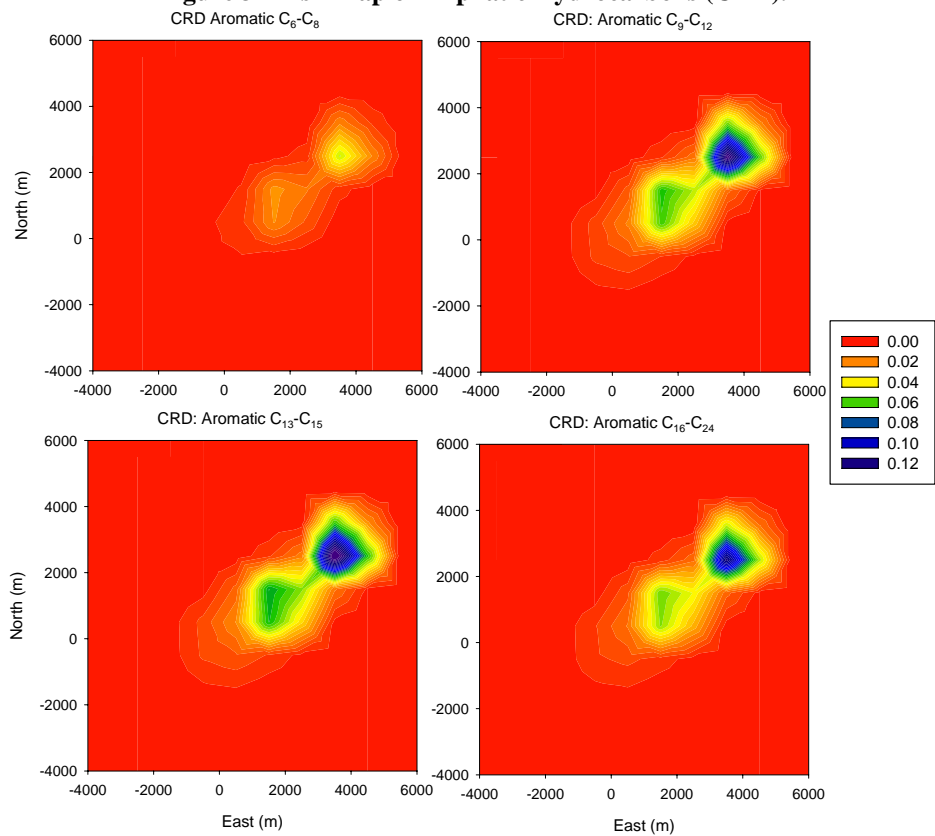


Figure 35 Risk Map of Aromatic Hydrocarbons (CRD).

Similar trends are apparent in the CRD case (Figure 34 and Figure 35). A maximum PEC/BC value of 0.022 was estimated for the aliphatic C₉-C₁₂ group and a maximum value of 0.138 was calculated for the aromatic C₉-C₁₂ group. The overall risks from CRD case are smaller than that of the CI case. The statistics of the maximum risk are listed in Table 11.

Table 11 Potential Risks to benthic organisms.

Hydrocarbon		Maximum Risk	
		CI	CRD
Aliphatic	C ₅ -C ₈	0.029	0.008
	C ₉ -C ₁₂	0.081	0.022
	C ₁₃ -C ₁₈	0.050	0.013
	C ₁₉ -C ₃₆	0.026	0.007
Aromatic	C ₆ -C ₈	0.165	0.045
	C ₉ -C ₁₂	0.510	0.138
	C ₁₃ -C ₁₅	0.492	0.133
	C ₁₆ -C ₂₄	0.396	0.107

5 Conclusion and Recommendations

A number of factors affect the transport of OMA particles. First, although waves are important in breaking the oil slick to form oil droplets, their overall effect on advection/diffusion/settling behaviour is small compared to the effect of currents and turbulence induced velocity. In other words, the level of net transport due to Stokes drift is relatively small. However, particle size distribution is important as it affects the settling velocities and therefore affects the duration of settling. OMAs with smaller diameters settle slower and therefore will deposit over a larger area that will result in lower oil concentrations within the sediments.

In terms of potential environmental effects associated with OMA that settles to the ocean bottom, our simulation showed that aromatic hydrocarbons posed more risk than aliphatic hydrocarbons. For both aliphatic and aromatic hydrocarbons, the C₉-C₁₂ group posed greater risk than other groups. An acceptable level of risk was determined for both test cases following a 1000 tonne spill. However, risk from the aromatic C₉-C₁₂ group became apparent for the CI case when the spill volume is increased to 2000 tonnes. The maximum risk for the aromatic C₉-C₁₂ group will increase from 0.51 to 1.02 which is larger than unity. Under identical simulation settings, the maximum spill volume that posed no risk to benthic organisms for the CRD case is 7240 tonnes.

The current work did not consider the influence of chemical dispersants which are expected to change the amount of oil associated with OMAs (Khelifa et al., 2008; Li et al., 2007) and therefore altering the potential level of risk to benthic organisms. According to the data of Khelifa et al. (2008), the use of chemical dispersant did not affect the amount of oil settled for the CI case with South Louisiana crude oil and 100g/L sediment. However, the settled oil decreased from 3% to 2% when chemical dispersants

were used in the CRD case. Based on literature data, if a different sediment or crude oil was used, the amount of settleable oil may increase 7-fold. As a result, the maximum amount of spill that can be spilled without posing risk to benthic organisms will also decrease by 7-fold.

Another factor that needs to be considered is the concentration of suspended particles. If the concentration of suspended particles is very high, for example 300mg/L, Khelifa et al. (2008) have found that up to 60% of the spilled oil may settle following treatment with chemical dispersants.

Scientists have recently proposed the concept of an oil spill countermeasure based on the the addition of mineral fines that would promote OMA formation (Lee, 2002). Research are being conducted to optimize the characteristics of OMA for the purpose of minimizing environmental effects. The method described in this study may be used as a screening tool for the selection and application of this technology and others, on a case by case basis. This is because many factors will affect the risks. For example, caution should be taken if this method is applied in area with weak currents, or in an area with high concentrations of coarse natural sediment particles. The application of such a technology in shallow water should also be carefully examined due to the limited transport time for OMAs.

Future research is recommended to evaluate the model under different current speeds, oil type, sediment type, particle size distribution, and suspended material loads to determine the maximum amount of oil that can be spilled with the various countermeasure technologies. The accuracy of predictive models will also benefit from data produced from future studies focused on the improvement of our understanding of the various factors influencing the formation of OMAs.

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