EFFECTS OF CHEMICAL DISPERSANTS AND MINERAL FINES ON PARTITIONING OF PETROLEUM HYDROCARBONS IN NATURAL SEAWATER

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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.

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

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associated with both physically and chemically dispersed oil; disper- 
sants 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 ef-
fect between dispersants and mineral fines that further enhanced 
the transfer of oil from the surface into the water column. In ad-
dition, 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 dif-
ferent 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 com-
ponents, 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

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/cm³.

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, with-
out 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 (5 ml) phase of 
sediments was drained into a pre-cleaned 100 ml amber sampling 
bottle to conduct extraction of crude oil from suspended sediments 
using roller apparatus (Wheaton R-P. VWR Scientific Canada). 
The middle (110 ml) phase of material suspended in the water col-
umn 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 extrac-
tion 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.

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

A UVFS technique (Bugden et al. in press) was used to character-
ize 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., Missis-
sauga, ON). The suspension was then scanned in the dissolved/dis-
persed fraction and aggregated fraction using a Shimadzu RF501 
spectrofluorometer running Panorama 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.

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 asphalt-
tenes. The duplicate set of experiments at each time point labelled 
for "Iatroscan" were extracted with dichloromethane (3x 30 ml). 
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 1.00 ml 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 
chromatograms is described briefly as follows: pass the chromatograms 
through the FID hydrogen flame twice (known as blanking the 
rods) at a slower scan rate (40/sec) 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 ali-
quot (1 μl) of the concentration-adjusted extract was applied to the 
origin point of each chromatom. A rack of ten chromatom were 
placed in the first (hexane) solvent chamber (18 min) to fractionate 
the aliphatics. Then place the chromatom 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 sol-
vent chamber (2 min) to separate the resins from the asphaltenes. 
After each developing chamber the chromato or graphic peaks were 
performed by air dry for 2 min, followed by 10 min in a humidity 
chamber. Once the chromatom have all been developed, a rack of 
10 chromatom are placed in the Iatroscan MK-6 automated flame 
ionized detection scanning system for analysis. Set the scan speed 
30 seconds per chromatom; 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 alphi-
atics, aromatics, resins, and asphaltenes.

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 stan-
dard 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 an-
alytes 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 chrysene), including their alkylated homologs. The column
was a 30 m x 0.25 mm ID with 0.2 μm film thickness MS-5 or
equivalent column (Supelco, Supelco Park, Bellefonte, PA). Al-
phatic and aromatic concentrations were summed to obtain total
concentrations for each chemical class in the sample extracts.

**Data analysis**

Analysis of variance (ANOVA) was performed to compare treat-
ment 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.

**RESULTS**

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

The effect of chemical dispersants and mineral fines on the distri-
bution of crude oil dispersed in the water column was illustrated
by the ultraviolet (UV) emission spectra of dispersed and/or ag-
gregated oil (Figure 1). The UVF spectra from the water column
samples were similar to those obtained from results of previous
flush 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 me-
dium 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 distri-
bution to the smaller scale may also contribute to the enlarged
emission intensity peaking at 445 nm (Figure 1)

**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 agree-
ment. 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
different phases are similar to each other; second, the pres-
ence of chemical dispersant transfers all four classes of chemicals
in crude oil from the surface into the water column; third, the pres-
ence 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 ap-
plied in treatment M, so the data are the result of physical disper-
sion 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 signifi-
cantly (P<0.05) reduced by the presence of dispersants.

**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 col-
umn, 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 forma-
tion 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 disper-
sants on the formation and fate of OMAs. Given that both chemi-
cal 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 physico-
chemical 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
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 en-
hanced 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, 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 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: 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.