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## Effects of chemical dispersants and mineral fines on crude oil dispersion in a wave tank under breaking waves

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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. A wave tank study was conducted to investigate the effects of chemical dispersants and mineral fines on the dispersion of oil and the formation of oil–mineral-aggregates (OMAs) in natural seawater. Results of ultraviolet spectrofluorometry and gas chromatography flame ionized detection analysis indicated that dispersants and mineral fines, alone and in combination, enhanced the dispersion of oil into water column. Measurements taken with a laser *in situ* scattering and transmissometer (LISST-100X) showed that the presence of mineral fines increased the total concentration of the suspended particles from 4 to 10  $\mu\text{l l}^{-1}$ , whereas the presence of dispersants decreased the particle size (mass mean diameter) of OMAs from 50 to 10  $\mu\text{m}$ . Observation with an epifluorescence microscope indicated that the presence of dispersants, mineral fines, or both in combination significantly increased the number of particles dispersed into the water.

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**Keywords:** Crude oil; Dispersants; Mineral fines; Oil droplets; OMAs; Breaking waves

### 1. Introduction

Marine oil spills have become more common as offshore oil production and transport increased over the last few decades (Anderson and LaBelle, 2000; NRC, 2003). The detrimental impacts of crude oil spills in the open ocean are largely mitigated by natural dispersion processes where wave action leads to the formation of micron-sized droplets that are eventually diluted to concentrations below toxic threshold limits (Delvigne and Sweeney, 1988; Lee, 2002; Li and Garrett, 1998; Shaw, 2003; Tkalich and Chan, 2002). In nearshore or estuarine waters, oil droplets are likely to be incorporated into oil–mineral-aggregates

(OMAs) as a result of their interaction with the high loads of suspended particulates that are typical in 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., 1996, 2003; 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.

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53 There is a renewed interest to consider the use of chemi- 107  
54 cal oil dispersants to combat oil spills at sea to minimize 108  
55 the impact of oil slicks on seabirds and the transport of 109  
56 oil to coastal and/or shoreline environments. The utiliza- 110  
57 tion of dispersants in coastal regions has been approached 111  
58 with caution due to concerns over the potential exposure of 112  
59 both pelagic and benthic organisms to chemically-dispersed 113  
60 oil. Conflicting results have been reported with regard to 114  
61 the effects of chemical dispersants on formation and fate 115  
62 of OMAs in both laboratory and field studies (Gearing 116  
63 and Gearing, 1983; Guyomarch et al., 1999, 2002; MacKay 117  
64 and Hussain, 1982; Page et al., 2000). For example, Mac- 118  
65 Kay and Hussain (1982) and Gearing and Gearing (1983) 119  
66 found that OMA formation was negligible with chemi- 120  
67 cally-dispersed oil in water column, whereas Guyomarch 121  
68 et al. (1999, 2002) reported that significantly high amount 122  
69 of oil was incorporated into OMAs when oils and chemical 123  
70 dispersants were mixed with mineral fines. 124

71 The application of dispersants may alter the rate and 125  
72 extent of oil–mineral aggregate formation relative to that 126  
73 which occurs between oil and mineral fines alone. On one 127  
74 hand, chemical dispersants could reduce droplet size and 128  
75 lead to the formation of smaller and denser OMAs com- 129  
76 pared to aggregates formed in the absence of the disper- 130  
77 sants. On the other hand, chemical dispersants may 131  
78 change the surface physicochemical properties of oil drop- 132  
79 lets to impair the binding of oil to mineral fines. To distin- 133  
80 guish between these possibilities, we carried out a wave 134  
81 tank experiment to: (1) investigate the aggregation of min- 135  
82 eral fines with physically or chemically-dispersed oil and (2) 136  
83 determine the dynamic particle size distributions of the 137  
84 physically- and chemically-dispersed oil and OMAs. Data 138  
85 generated from this study are useful in modeling fate and 139  
86 transport of the dispersed oil and conducting risk assess- 140  
87 ment related to the application of chemical dispersants in 141  
88 nearshore waters and estuarine environments that are rich 142  
89 in suspended particulates. 143

## 90 2. Methods 144

### 91 2.1. Wave tank facility and the generation of breaking waves 145

92 The oil–mineral aggregation experiment was conducted 146  
93 at a wave tank facility located at the Bedford Institute of 147  
94 Oceanography (Dartmouth, Nova Scotia, Canada) which 148  
95 was designed and constructed under a Joint Project Agree- 149  
96 ment between Fisheries and Oceans Canada and the US 150  
97 Environmental Protection Agency. The wave tank facility 151  
98 measures 16 m long, 0.6 m wide, and 2 m high, with an 152  
99 average water depth of 1.25 m (Fig. 1). Different wave pat- 153  
100 terns are generated by a paddle situated 1 m from the 154  
101 front wall of the tank. The paddle is linked to an adjust- 155  
102 able cam that controls stroke length to alter wave height. 156  
103 The wave frequency (and thus the wavelength) is con- 157  
104 trolled by the rotation speed of the cam. Wave absorbers 158  
105 are made of eight porous stainless-steel screens and were 159  
106 placed opposite the wave maker to minimize wave reflec- 160

tion by dissipation wave energy upon passing of the waves 107  
through them. The pore sizes of the screens ranged from 108  
0.2 to 2.5 cm and the area porosity were approximately 109  
between 40% and 70%. The order of the screens and their 110  
spacing were obtained by trial and error to minimize 111  
reflection. 112

The wave tank simulated the propagation and breaking 113  
of deep water waves based on linear wave theory. Breaking 114  
waves cause velocity shear and hence result in the mixing of 115  
oil and dispersant and the dispersion of oil slick (Nilson 116  
et al., 1985; Shaw, 2003; Tkalic and Chan, 2002). Velocity 117  
shear with its associated friction causes the dissipation of 118  
kinetic energy of the fluid. Of particular interest is the 119  
kinetic energy dissipation rate per unit mass ( $\epsilon$ ), a scalable 120  
parameter in evaluating the extent of mixing and dispersion 121  
of oils at sea (Delvigne and Sweeney, 1988; Kaku et al., 122  
2006) and the interaction kinetics between oil and sus- 123  
pended particulate matters (Payne et al., 2003). 124

For this study, the paddle stroke of the wave tank was 125  
set at 7 cm to generate a train of high frequency waves 126  
(1.0 Hz with a wave height of 0.12 m and wave length of 127  
1.56 m) for 20 s, followed by a cycle of low frequency 128  
waves (0.4 Hz with a wave height of 0.05 m and wave 129  
length of 9.75 m) for 20 s. Because the propagation speed 130  
of a wave is proportional to its period, the train of large 131  
period waves eventually catches up with the train of short 132  
period waves. This design was made to create recurrent 133  
breaking waves approximately 7.5 m downstream of the 134  
paddle. The energy dissipation rate in the mixing zone of 135  
the wave tank was estimated through the water profile 136  
measurements using seven wave gauges and a time-series 137  
of water velocity measurements at various depths and loca- 138  
tions. The energy dissipation rate in the mixing zone was 139  
computed to decrease from 0.5 W/kg (or  $\text{m}^2/\text{s}^3$ ) at the sur- 140  
face to about 0.01 W/kg at the depth of 25 cm. This mixing 141  
energy level corresponded to the lower end of the breaking 142  
waves of the surface layer at sea (Delvigne and Sweeney, 143  
1988). 144

### 2.2. Experimental procedures for oil dispersion study in the 145 wave tank 146

A two-factor, two-level [dispersant (0, 3 ml) and mineral 147  
fines (0, 50 g)] factorial experimental design was used to 148  
investigate the effects of chemical dispersants on the forma- 149  
tion and fate of OMAs. The test oil was 150 ml of weath- 150  
ered Scotia shelf condensate, a light crude oil (with a 151  
density of  $0.8690 \text{ mg l}^{-1}$ , dynamic viscosity of  $6 \text{ mPa s}$  152  
and oil/water interfacial tension of  $18.4 \text{ mN m}^{-1}$ ). The disper- 153  
sant was Corexit 9500 (Nalco Energy Service, L.P. 154  
Sugar Land, TX) at a dispersant-to-oil (DOR) ratio of 155  
1:50. The mineral fines were American Petroleum Institute 156  
(API No. 9) kaolin (Mesa Alta, New Mexico), with a cation 157  
exchange capacity of 6.8 meq/100 g, a median particle 158  
size of  $0.6 \mu\text{m}$ , and a density of  $2.60 \text{ g/cm}^3$ . The wave tank 159  
was filled with filtered ( $5 \mu\text{m}$ ) natural seawater from the 160  
Bedford Basin of Halifax harbor (with average water tem- 161

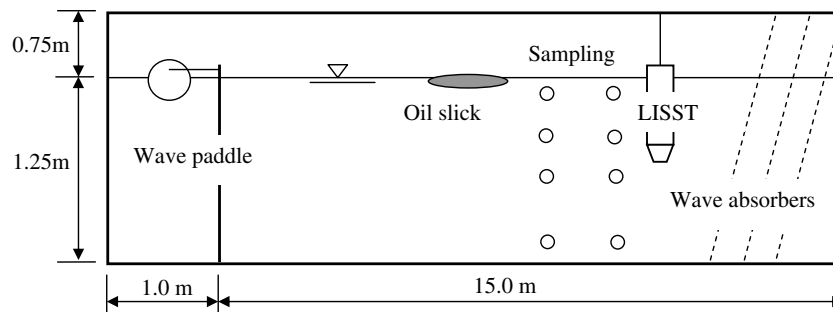


Fig. 1. Schematic representation (all dimensions in mm) of the wave tank: LISST is laser *in situ* scattering and transmission particle counter; sampling ports are stainless-steel tubes connected to a gang of 100 ml syringes.

162 perature of 5 °C and salinity 30 PSU). For each experi- 202  
 163 ment, one liter of seawater containing a combination of 203  
 164 oil, dispersant, and mineral fines (defined by the experi- 204  
 165 mental design matrix) was premixed in a 2-L flask on a reciprocating shaker at 150 cycles per min and 22 mm stroke 205  
 166 length for 2 h; the mixing energy level has been found to 206  
 167 be the minimum rate to disrupt the layer of surface oil  
 168 (Khelifa et al., 2005; Stoffyn-Egli and Lee, 2002). The mix-  
 169 ture was then released on the surface in the middle of the  
 170 tank immediately prior to an incoming breaking wave.  
 171 Samples (100 ml) were collected simultaneously from two  
 172 horizontal locations (1.5 and 4 m downstream of oil appli-  
 173 cation) and four depths (5, 20, 60, and 110 cm under water)  
 174 at five time points (1, 10, 30, 60, and 300 min after oil addi-  
 175 tion). The side and bottom walls and the wave absorbers  
 176 were thoroughly cleaned after each experimental run to  
 177 minimize the residual oil amount that was left in the system  
 178 and to reduce the influence of the oil input for the following  
 179 runs. The distribution of oil in the tank was determined by  
 180 (1) ultraviolet fluorescence (UVF) spectroscopy of samples  
 181 taken directly from the wave tank and (2) gas chromatog-  
 182 raphy with flame ionization detection (GC-FID) analysis  
 183 of total petroleum hydrocarbons (TPH) after solvent  
 184 extraction. The dynamic particle size distribution and total  
 185 suspended particle concentration were measured using a  
 186 laser *in situ* scattering and transmissometer (LISST-  
 187 100X). The morphology of the formed oil droplets and  
 188 OMAs were observed by an epifluorescence microscopy.  
 189 Description of these methods is detailed below.

### 191 2.3. Oil dispersion and OMA formation by UVF

192 The ultraviolet fluorescence spectroscopy technique of  
 193 Kepkay et al. (2002) was applied to measure the dis-  
 194 solved/dispersed oil in aqueous phase and the oil aggre-  
 195 gated into OMAs. Briefly, samples collected from the  
 196 wave tank were vigorously shaken and 3 ml of the suspen-  
 197 sion were rapidly transferred to an ultraviolet-grade meth-  
 198 acrylate disposable cuvette (VWR International Inc.,  
 199 Mississauga, ON). The suspension was then immediately  
 200 scanned in the dissolved/dispersed fraction and aggregated  
 201 fraction using a QM-1 spectrofluorometer running FeliX

software (PTI, Inc., Birmingham, NJ). The optimal excita-  
 202 tion wavelength that produced the highest emission peaks  
 203 was 320 nm; this wavelength with a slit width of  $\pm 2$  nm  
 204 was used in all subsequent emission scans from 340 to  
 205 500 nm. 206

### 207 2.4. Oil dispersion and OMA formation by GC-FID

208 Samples ( $100 \pm 20$  ml) collected from the tank were fil-  
 209 tered through micro-fiber-glass filters ( $1.2 \mu\text{m}$ , Whatman  
 210 GF/C, Fisher Scientific, Canada) to separate the dis-  
 211 solved/colloidal phase from the aggregated phase. The fil-  
 212 trate was transferred to a separatory funnel for extraction  
 213 of hydrocarbon with dichloromethane (DCM) using EPA  
 214 method 3510 C (EPA, 2003). The solid phase was pro-  
 215 cessed using soxhlet extraction with dichloromethane over  
 216 an 18 h cycle with EPA method 3540 C (EPA, 2003). The  
 217 extracts from both phases were concentrated to 1 ml and  
 218 analyzed by GC-FID (NRCC, 1997) to measure total  
 219 petroleum hydrocarbon (TPH) in the filtrate phase (mg  
 220 TPH per liter of tank water) and the particulate phase  
 221 (mg TPH per gram of solids). The GC analysis was per-  
 222 formed using high resolution Agilent 6890 gas chromatog-  
 223 raphy coupled to an Agilent 5973N flame ionization  
 224 detector (Agilent Technologies, Willmington, DE, USA)  
 225 and an MDN-5S column of  $30 \text{ m} \times 0.25 \text{ mm id } 0.25 \mu\text{m}$   
 226 film thickness (Supelco, Canada); the GC conditions are:  
 227 helium carrier gas at 1 ml/min, cool on-column injection  
 228 with oven track mode (track 3 °C higher than the oven  
 229 temperature program), hold at 50 °C for 2 min, ramp at  
 230 30 °C/min to 300 °C and hold 10 min at this temperature;  
 231 the FID conditions are: 320 °C, hydrogen flow 40 ml/  
 232 min, air flow 450 ml/min and helium flow at 45 ml/min.  
 233 These conditions are designed to measure the C10–C35  
 234 hydrocarbons, a range representing the major components  
 235 identified in the sample extracts. A fuel oil standard (Res-  
 236 tek Diesel Fuel #2, 50% weathered; Bellefonte, PA,  
 237 USA), which represents an ideal quantification range from  
 238 C10 to C35, was used to prepare a 5-point calibration curve  
 239 based on the average response factors of the total peak area  
 240 of the standard chromatogram. For quality assurance, a  
 241 method blank was prepared with each batch of ten sam-

242 ples, and the method recoveries ( $89 \pm 13\%$  soxhlet and  
243  $90 \pm 14\%$  dissolve extractions) were monitored to ensure  
244 adequate accuracy and precision. These recoveries are com-  
245 parable to surrogate recoveries using the same extraction  
246 procedure and using gas chromatography mass spectrome-  
247 try (GC-MS).

248 The ratio of the TPH in the two phases ( $l\ g^{-1}$ ) is a mea-  
249 surement of the extent of partitioning of TPH between  
250 liquid and solid phases. Oil distribution as TPH in the bulk  
251 aqueous phase was also calculated as the sum of dissolved/  
252 colloidal or aggregate phases inside the tank.

### 253 2.5. Particle size distribution using LISST-100X

254 Oil droplet size distribution inside the wave tank was  
255 determined by a Type C laser *in situ* scattering and trans-  
256 missometer (LISST-100X; Sequoia, Seattle, WA) situated  
257 4.5 m downstream from oil application in the wave tank  
258 with the detection window at a depth of 0.6 m. This loca-  
259 tion was approximately in the middle of the tank down-  
260 stream from oil addition both horizontally (between oil  
261 addition and the end) and vertically (from the surface to  
262 the bottom) to represent overall particle distribution down-  
263 stream. The particle size distributions were subdivided into  
264 32 particle size intervals located logarithmically from 2.50  
265 to 500  $\mu\text{m}$  in diameter, with the upper size in each bin  
266 1.18 times the lower. Particle size distribution was  
267 expressed as the average volumetric concentration of parti-  
268 cles falling into each interval of the size range. In general,  
269 the particle size distribution from LISST fits a lognormal  
270 distribution, and the mass (or volume) mean diameter of  
271 the dispersed oil droplets is used to quantitatively compare  
272 the average size of the particles. The LISST-100X was  
273 operated in real time mode to acquire dynamic particle size  
274 distribution and total particle concentrations (from 2.5 to  
275 500  $\mu\text{m}$ ) every 3 s.

### 276 2.6. Epifluorescence microscopy of dispersed oil and oil- 277 mineral-aggregates (OMAs)

278 Samples were collected for observation of dispersed oil  
279 droplets under transmitted light and ultraviolet-epifluore-  
280 scence illumination (excitation filter 340–380 nm; reflection  
281 short pass filter 400 nm; suppression long pass filter  
282 430 nm) using a Leitz Orthoplan microscope (Lee et al.,  
283 1985). The microscope is fitted with an Olympus DP70 digi-  
284 tal camera, an HBO 50 mercury lamp, and an OptiScan  
285 computer-controlled motorized stage (Prior Scientific  
286 Inc., Rockland, MA). Photomicrographs of the physically-  
287 and chemically-dispersed oil droplets and OMAs were  
288 recorded at magnifications of 160 $\times$  or 400 $\times$  and quantified  
289 using image analysis software Image-Pro5.0 (Media Cyber-  
290 netics Inc. Silver Spring, MD). Enumeration results were  
291 reported as number of particles per unit volume of water  
292 samples.

## 3. Results

### 3.1. Distribution of oil and oil–mineral aggregates in the wave tank

296 Distribution of crude oil dispersed in the wave tank was  
297 quantified by three indicators: the UVF emission spectra of  
298 dispersed and/or aggregated oil, the GC-FID analysis of  
299 TPH, and the LISST-100X for total oil-containing particle  
300 concentration in the bulk aqueous phase.

301 The UVF spectra from the wave tank samples (Fig. 2)  
302 were similar to those obtained from results of previous  
303 flask experiments, where the aggregation of oil with min-  
304 eral fines results in distinct shifts in the spectra compared  
305 to oil dispersed in seawater (Kepkay et al., 2002). The  
306 UVF spectra emission peaks at various excitation ranges  
307 are correlated to the different dissolved/dispersed fractions  
308 of crude oil (ASTM, 2002): most single ring aromatics,  
309 such as BTEX, phenol, and cresol, produce strong emission  
310 peaks between 290 and 320 nm; lower and medium molec-  
311 ular weight aromatics, such as naphthalene and phenan-  
312 threne, generate peaks at 325–370 nm; and higher  
313 molecular weight multi-ring compounds, such as resins,  
314 form another major broad peak from 400–470 nm. Since  
315 the concentration of single ring aromatics have likely been  
316 reduced from the weathering of the Scotia Shelf Condensate  
317 and the solubility of these compounds are high, the  
318 effects of dispersants and mineral fines on their partitioning  
319 into the bulk water phase are probably insignificant.

320 The treatment effects on the vertical dispersion of oil at  
321 the 1.5 m downstream location were clear: the natural dis-  
322 persion of oil was limited in its effectiveness (Fig. 2a); the  
323 action of dispersant (Fig. 2b) or mineral fines (Fig. 2c)  
324 on their own enhanced oil dispersion; and the action of  
325 mineral fines and dispersant in combination was the most  
326 effective in dispersing the oil into the bulk aqueous phase  
327 (Fig. 2d). Samples taken at 4 m downstream location did  
328 not exhibit strong UVF signals over all depths after 1 min.

329 After 10 min, emission spectra from samples taken at  
330 different depths and horizontal locations became similar  
331 for the same treatment, indicating that breaking waves  
332 resulted in a complete mixing downstream of the breaking  
333 waves. Hence, the fluorescence intensity was presented in  
334 Fig. 3 as an average value from samples taken at the four  
335 different depths and two horizontal locations (8 readings)  
336 for each treatment at each time point (from 10 to  
337 300 min). The average fluorescence intensity of oil over  
338 340–370 nm emission bandwidth followed the general  
339 order: oil < oil + kaolin < oil + dispersant < oil + disper-  
340 sant + kaolin (Fig. 3a). After 300 min of dispersion, the  
341 chemically-dispersed oil and the oil dispersed by mineral  
342 fines exhibited average emissions between 340 and  
343 370 nm that were 2–3.5 times higher than the naturally dis-  
344 persed oil. The dispersant and kaolin in combination  
345 increased the average fluorescence between 340 and  
346 370 nm by 5.6-fold relative to the natural oil. The dispersal  
347 of oil fractions with fluorescence between 400 and 480 nm

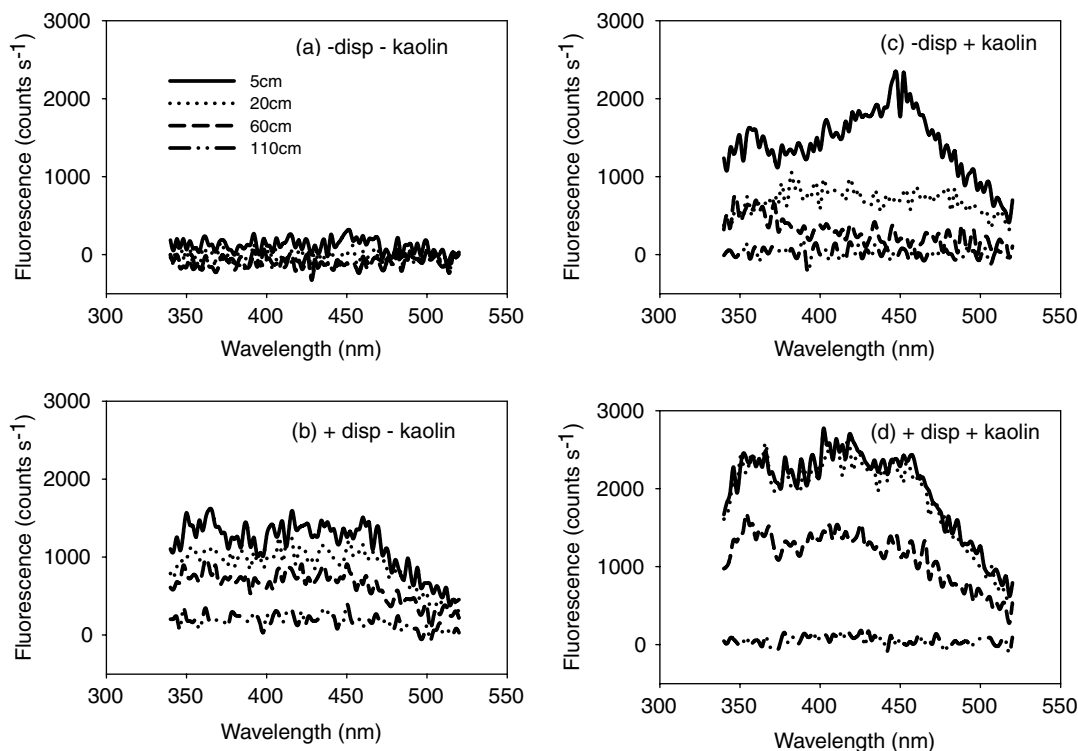


Fig. 2. Ultraviolet Emission spectra of Scotia Light condensate dispersed at 4 depths (5, 20, 60, and 110 cm) 1.5 m downstream 1 min after addition into seawater in combination with low concentrations of kaolin particles and/or oil dispersant under breaking waves. All the UVF spectra have been corrected for natural fluorescence and light scattering by blanks of seawater used in each wave tank treatment.

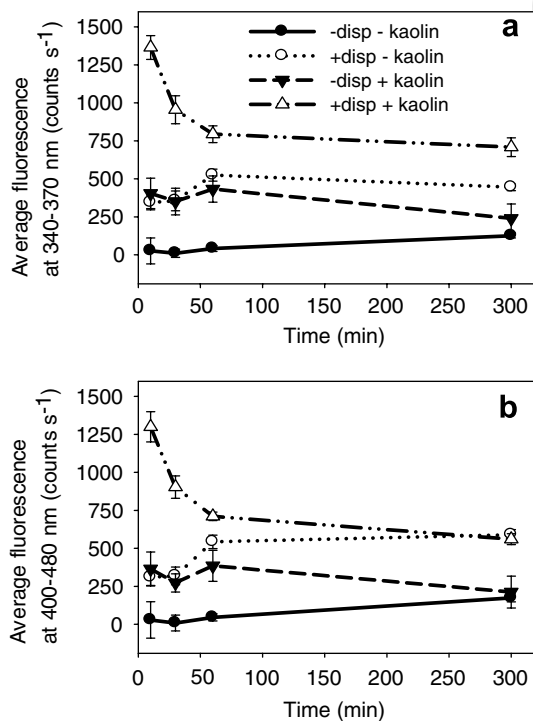


Fig. 3. Ultraviolet fluorescence measurement of (a) dispersed oil fraction with average fluorescence at 340–370 nm and (b) oil fraction with average fluorescence at 400–480 nm over time. Results shown are the tank average value for each time point and error bars represent one standard deviation of eight samples.

followed a similar pattern, except that kaolin on its own 348  
did not increase the final fluorescence at 300 min, whereas 349  
dispersants or kaolin plus dispersants increased average 350  
fluorescence by three times. Together, these results suggest 351  
that chemical dispersants, mineral fines, and the two in 352  
combination stimulated the dispersion of two-ring and 353  
multiple-ring aromatic fractions of oil into the bulk aqueous 354  
phase. 355

The distribution of oil as a result of dispersal by dispersants 356  
and mineral fines in the wave tank was further quantified 357  
with GC-FID analysis of total petroleum hydrocarbons (TPH) 358  
from samples collected at four depths and two locations. 359  
Similar to the UVF results, TPH concentrations from both the 360  
dissolved/colloidal and aggregated phases exhibited no temporal 361  
and spatial difference among samples taken at time points after 362  
10 min due to the mixing effect in the wave tank. Hence the 363  
average concentrations of dissolved/colloidal TPH in the seawater, 364  
in the aggregated solid phase, and the total TPH from two 365  
horizontal locations and four depths (8 readings) were calculated; 366  
the results are presented in Fig. 4. 367  
368

The presence of chemical dispersants significantly 369  
( $P = 0.01$ ) increased the concentration of dissolved/colloidal 370  
oil in the wave tank (Fig. 4a); the presence of mineral 371  
fines appears to have reduced the amount of soluble/colloidal 372  
oil in seawater. Conversely, the presence of chemical 373  
dispersants ( $P = 0.007$ ) and the combination of the two 374  
( $P = 0.00001$ ) significantly increased the concentration of 375

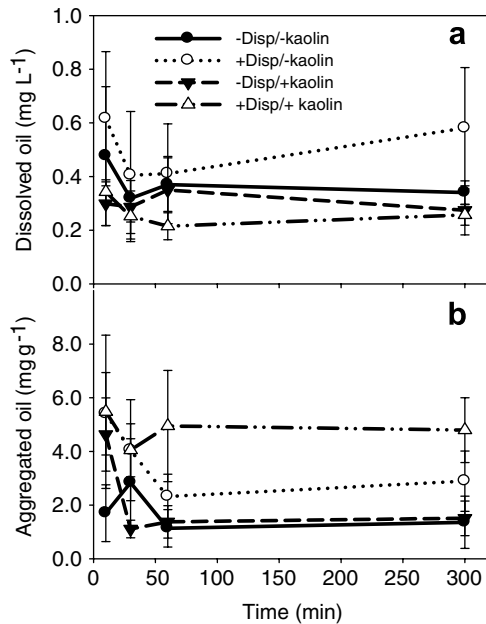


Fig. 4. GC-FID measurement of: (a) dissolved oil (mg per liter of seawater) and (b) aggregated oil (mg per gram of particles). Results shown are the average value for each time point and error bars represent one standard deviation of eight samples.

TPH associated with aggregates within the solid phase (Fig. 4b). The effects of dispersants and mineral fines on oil dispersion in the water column of the wave tank are also revealed by the partitioning ratios of oil between the liquid phase and the solid phase after 300 min dispersion (Fig. 5). Under natural dispersion of oil alone, the liquid to solid ratio was probably due to the ratio of insoluble/aggregated components to the soluble/colloidal fraction of the TPH. The presence of either mineral fines or dispersants alone increased the partitioning ratio, suggesting that either part of the insoluble/aggregated TPH has been dispersed by the presence of chemical dispersants, or part of the TPH was absorbed by mineral fines and hence the overall density was increased to overcome the buoyancy. The presence of both dispersants and mineral fines increased the ratio further, indicating that the combination of the two had syner-

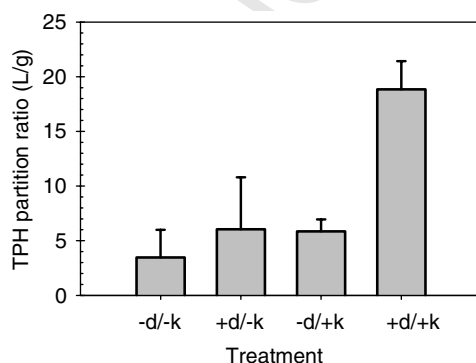


Fig. 5. Treatment effects on the partitioning ratio of oil between dissolved/colloidal phase and solid phase (d: dispersant; k: kaolin).

gistic effects, stimulating the entrainment of oil into the bulk aqueous phase.

### 3.2. Particle size distribution

The dynamic concentrations of suspended particles (oil droplets or OMA) in the bulk aqueous phase were measured by the LISST-100X and the results are shown in Fig. 6. In the absence of mineral fines, the total dispersed oil concentrations first increased to a maximum at 10 min and then decreased gradually to a relatively constant value. In the presence of mineral fines, however, the peak concentrations were detected earlier and gradually decreased with time. The total particle concentrations in the presence of mineral fines were always two times higher than in their absence, with the final total average concentrations being 10 and 4  $\mu\text{l l}^{-1}$ , respectively. Chemical dispersants did not affect total suspended particle concentrations, probably due to the vigorous mixing caused by breaking waves.

Fig. 7 displays the time-series particle size distribution expressed as mass mean diameter (MMD) of the particles measured by using the LISST-100X. The natural (physical) dispersion of oil in the absence of either dispersant or mineral fines first produced large droplets (with MMDs of 150  $\mu\text{m}$ ) that gradually decreased in size to MMDs of approximately 40  $\mu\text{m}$  after continuous dispersion under breaking waves for 200 min. The presence of mineral fines reduced the initial particle size to MMDs of about 70  $\mu\text{m}$ , but the OMA with these sizes appear to become stable and did not break up further. The presence of dispersant dramatically reduced the sizes of both dispersed oil droplets (+disp/-kaolin) and OMA (+disp/+kaolin) to MMDs of 15–25  $\mu\text{m}$  in the beginning, and further reduced the MMDs to nearly 10  $\mu\text{m}$  after 200 min dispersion.

Fig. 8 presents typical distributions of particle size that were recorded by LISST-100X for different treatments over four representative time points; the particle size statistics are listed in Table 1. In the absence of chemical dispersants and mineral fines, naturally dispersed oil has relatively large oil droplets size initially, with the majority of the particles present in a lognormal distribution (Fig. 8a), and

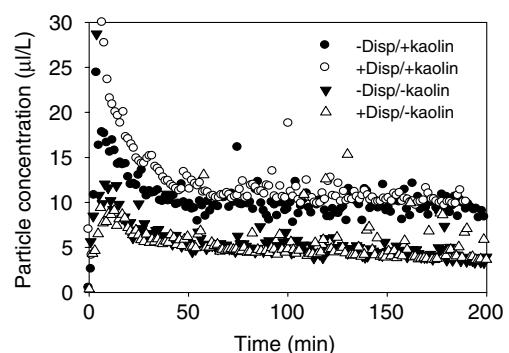


Fig. 6. LISST measurement of total particle concentration of dispersed oil and OMA. Note that the maximum value occurred at time zero for situations where a dispersant was added.

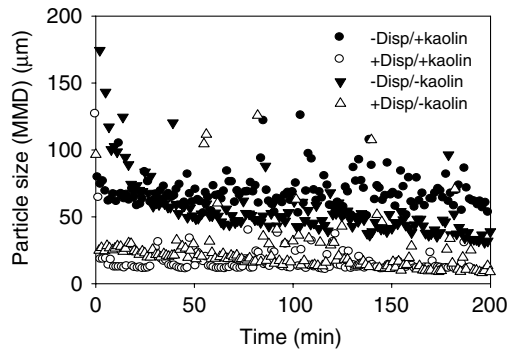


Fig. 7. LISST measurement of mass mean particle diameter of dispersed oil and OMAs.

431 more than 50% of the dispersed oil volume present as drop-  
 432 lets larger than 200  $\mu\text{m}$  (mass medium diameter, or  $d_{50\%}$ )  
 433 and a geometric standard deviation (GSD) of 1.90 (Table  
 434 1). Further dispersion of the oil by breaking waves gradu-  
 435 ally reduced the size of oil droplets over time and resulted  
 436 in a shift of the peak area of lognormal size distribution and  
 437 a decrease of the peak height (Fig. 8a), so that the  
 438  $d_{50\%}$  of the droplet size was almost an order of magnitude  
 439 lower than initial size after 300 min of turbulent mixing by  
 440 breaking waves (Table 1). The presence of chemical disper-  
 441 sants dramatically decreased the initial droplet size  
 442 (Fig. 8b), with a  $d_{50\%}$  of only 22  $\mu\text{m}$ , an order-of-magnitude  
 443 lower than in the absence of dispersants. This is because the  
 444 dispersants dramatically reduced the surface tension of the  
 445 oil, which was broken into small droplets when it was  
 446 homogenized on the reciprocating shaker. Further disper-  
 447 sion of oil in the presence of chemical dispersants in wave  
 448 tank generated large amount of smaller particles so that

Table 1

Statistics of the particle size distribution of the dispersed oil droplets or OMAs

Treatment	Time (min)	$d_{16\%}^a$	$d_{50\%}^a$	$d_{84\%}^a$	GSD <sup>b</sup>
-Disp/-sed	1	75	200	270	1.90
	10	54	128	240	2.11
	60	23	50	77	1.83
	300	3.5	30	57	4.04
+Disp/-sed	1	5	22	39	2.79
	10	7	22	37	2.30
	60	3	20.5	34	3.37
	300	<2.5	2.7	11	NA
-Disp/+sed	1	25	70	112	2.12
	10	4	53	102	5.05
	60	4.5	54	95	4.59
	300	6	54	80	3.65
+Disp/+sed	1	3.5	10.5	23	2.56
	10	3	10	22	2.71
	60	3	10	27	3.00
	300	3	9.5	17	2.38

<sup>a</sup>  $d_{16\%}$ ,  $d_{50\%}$ ,  $d_{84\%}$  represent the 16%, 50%, or 84% of total mass of the droplets that are smaller than this diameter ( $\mu\text{m}$ );  $d_{50\%}$  is the mass medium diameter.

<sup>b</sup> GSD is geometric standard deviation calculated as:  $(d_{84\%}/d_{16\%})^{1/2}$ ; the GSD value reflects the variation of the particle size.

after 300 min 84% of droplets were less than 11  $\mu\text{m}$  in  
 449 diameter and 50% were less than 3  $\mu\text{m}$  (Table 1). The pres-  
 450 ence of mineral fines also decreased the initial particle size  
 451 compared to the natural dispersion of oil (Fig. 8c). How-  
 452 ever, the formed oil–mineral aggregates appear to be more  
 453 stable than their counterparts of the dispersed oil droplets.  
 454 The shift of peak location on the size distribution profiles  
 455 was not observed over time, only the variation of peak area  
 456

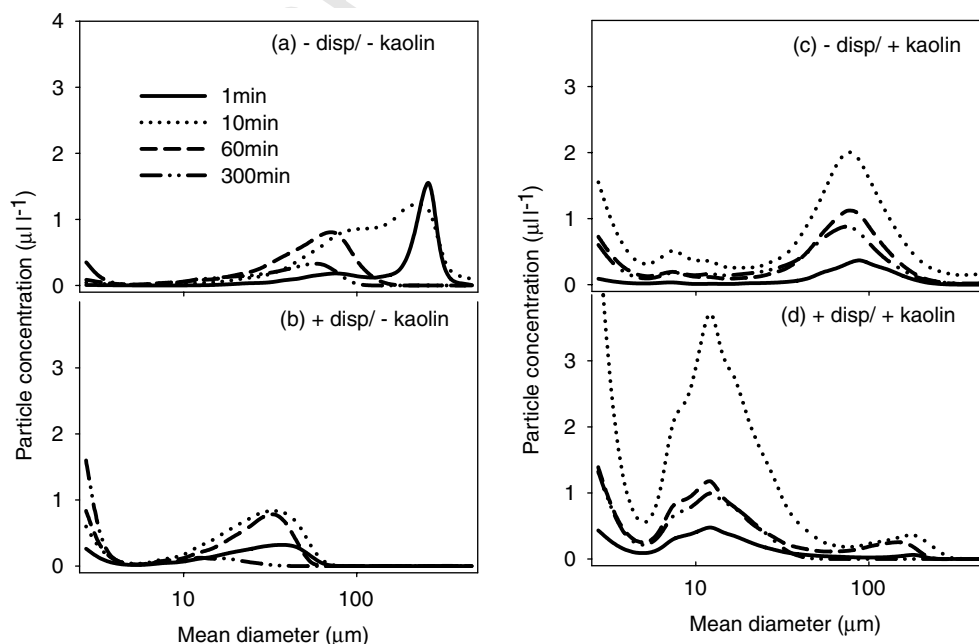


Fig. 8. LISST measurement of time-series particle size distribution in volumetric concentration as a function of particle size interval.

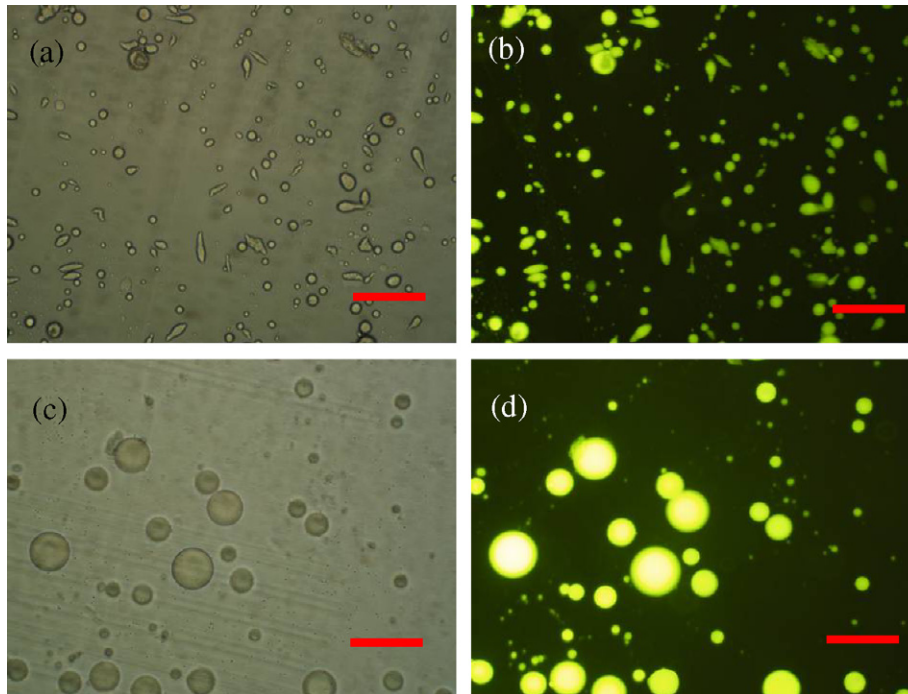


Fig. 9. Images of oil droplet formation under the inspection of epifluorescent microscope: OMAs formed in the presence (a and b) and absence (c and d) of dispersant from the observation under transmitted light (a and c) or epifluorescent (b and d) light illumination. Samples taken for imaging were diluted by a factor of 20 before microscopy. Bars shown are 100  $\mu\text{m}$ .

457 and height due to the transport of the OMAs in the tank  
 458 (Fig. 8c). The presence of both chemical dispersants and  
 459 mineral fines produced the smallest initial particle size  
 460 (Fig. 8d), with the  $d_{50\%}$  of 10.5  $\mu\text{m}$  and remained small  
 461 for the whole duration of the experiment (Table 1). The  
 462 volumetric fraction of OMAs had three peak areas: a small  
 463 peak centered at size of more than 100  $\mu\text{m}$ , a large peak  
 464 located at approximately 10  $\mu\text{m}$ , and a third peak situated  
 465 around 2.5  $\mu\text{m}$ , the optical cutting edge of the LISST-100X  
 466 (Fig. 8d). The peak of the largest size was leveled off with  
 467 dispersion, whereas the fraction of small OMAs remained  
 468 much larger than in the absence of dispersants, suggesting  
 469 that the small chemically-dispersed OMAs were suspended  
 470 in the bulk water column through hydrodynamic mixing.

471 Consistent with the LISST results, the size of the OMAs  
 472 formed by chemically-dispersed oil were much smaller than  
 473 the physically dispersed when observed by transmitted and  
 474 epifluorescent microscopy (Fig. 9). The chemically-dis-  
 475 persed OMAs appeared to have predominantly fractal  
 476 structures in morphology, whereas the physically dispersed  
 477 OMAs were largely spherical. Enumeration of the dis-  
 478 persed oil and OMA particles under the microscope indi-  
 479 cated that either chemical dispersants or mineral fines  
 480 alone dramatically increased the particle number per unit  
 481 volume.

#### 482 4. Discussion

483 Observations on the stabilization of oil droplets in the  
 484 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., 1996,  
 2003; Muschenheim and Lee, 2002; Omotoso et al.,  
 2002). However in the context of oil spill response opera-  
 tions, 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 gen-  
 eration of micron-sized droplets (Darling et al., 1990; Delv-  
 igne 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 need  
 also to be understood to accurately assess the risks  
 involved during the application of dispersants in particle-  
 rich nearshore and estuarine waters.

The results obtained from our wave tank study indicate  
 that dispersants and mineral fines can have strong and  
 cumulative effects on the formation and transport of oil  
 droplets and OMAs. The interaction of chemical dispersant  
 with oil and mineral fines increased the dissolved and  
 aggregated oil concentration in the bulk aqueous phase  
 (Figs. 3, 4 and 6) and reduced the size of oil droplets and  
 OMAs (Figs. 7 and 8). OMAs formed in the absence of dis-  
 persant exhibited stable distributions in suspension, but  
 their particle sizes were generally larger than the naturally  
 dispersed oil droplets subjected to hours of dispersion  
 under breaking waves (Fig. 7; Table 1). The chemical dis-  
 persion of the same oil promoted the entrainment of the



oil into the bulk aqueous phase (Figs. 3, 4 and 6) and decreased the size of dispersed oil droplets within a short period of time (Figs. 7 and 8; Table 1). The effects of chemical dispersant and mineral fines on size distribution and morphology of dispersed oil and OMAs were verified by observation via microscope (Fig. 9).

The oil-droplet size distribution observed in this study is consistent with the range reported by previous investigators. Darling et al. (1990) and Fingas et al. (1995) reported mass mean diameters of 20–45  $\mu\text{m}$  in laboratory dispersant effectiveness tests. Lunel (1993, 1995) reported that more than 80% of the chemically-dispersed oil droplets in the sea were in the range of 1–70  $\mu\text{m}$ , and that the effect of chemical dispersants increased the number of small droplets by 5–30-fold compared to untreated oil while the number of large droplets did not change appreciably. In our system, the mass mean diameter of the untreated oil droplets was progressively reduced from more than 150 to 40  $\mu\text{m}$  after the prolonged action of the breaking waves. In contrast, the chemically dispersed oil was reduced from a MMD of 25 to 15  $\mu\text{m}$  for the same period of mixing time and energy dissipation rate in the wave tank (Fig. 7).

The reported OMA size distribution was also variant from system to system, depending on the types of oil, loading and type of suspended particles, and the mixing energy of the system (Guyomarch et al., 1999, 2002; Khelifa et al., 2002, 2005; Sterling et al., 2004, 2005). Guyomarch et al. (2002) reported an average size of the OMAs in the settled phase in the flask experiment varied from 50 to 1000  $\mu\text{m}$ . Sterling et al. (2004, 2005) reported that the diameters of the suspended oil–mineral aggregates at a sediment-to-oil ratio of 1:3 with were between 10 and 100  $\mu\text{m}$  under a shear rate of 20  $\text{s}^{-1}$ . In our system, the observed mass mean diameter of the OMAs was nearly 50  $\mu\text{m}$  in the absence of chemical dispersants and 10  $\mu\text{m}$  in the presence of dispersants, which are within the observed range of Sterling et al. (2004, 2005). Suspension of dispersed oil or OMAs at the representative hydrodynamic regime may be critical for enhancing oil dispersion because oil that subsequently becomes entrained within bottom sediments may persist for a long time due to the slow biodegradation rates of polycyclic aromatic hydrocarbon under anaerobic conditions (Quantin et al., 2005).

A synergistic effect by chemical dispersants and mineral fines on the transfer of oil to dissolved/dispersed phases was observed in this study (Figs. 3 and 4) and this effect can be due to a number of contributing factors. First, dispersant reduced water–oil interfacial tension and stimulated the breakup of the oil slick (Lessard and Demarco, 2000). Second, mineral fines reduced the time period for the splitting of oil droplets into small and stable drops (Hill et al., 2002), which is otherwise rate-limiting step for oil dispersion by microscale turbulence (Lunel, 1995). Third, the interaction of mineral fines and oil reduced the buoyancy of oil droplets and therefore transferred more oil into bulk aqueous phase (Lee, 2002; Owens and Lee, 2003). In addition, the partition of oil from dissolved phase to solid

phase was remarkably increased when chemical dispersants and mineral fines were present in combination (Fig. 5). Mineral fines are reported to absorb oil at their surface due to the hydrophobic surface properties (Marczewski and Szymula, 2002; Szymula and Marczewski, 2002). Dispersants, while mainly reduce the oil/water interfacial tension, may also stimulate the interaction between oil and mineral fines because of their amphiphilicity (Dantas et al., 2001).

## 5. Summary and 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 the development of “low toxicity” dispersant formulations 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.

Since oil spills most frequently occur in nearshore and estuarine waters (NRC, 2005), where the suspended sediment load is usually high, the interaction of physically and chemically-dispersed oil during oil spill response or other offshore oil and gas activities is inevitable. Our results from a unique wave tank facility demonstrate how physical and chemical dispersion under breaking waves may interact with suspended sediments in the nearshore marine environment. The results from this study support the conclusion that oil–mineral aggregation can occur for both physically and chemically-dispersed oil. The effect of dispersants reduces oil and OMA droplet size distribution. The effect of mineral fines increases the suspended particle concentration in the water column and droplet stability; once formed, OMAs neither readily breakup further nor re-coalesce after dispersion. The synergistic effect of dispersants and mineral fines enhances transferring oil from the surface downward into bulk water column; and a large number of small particles is produced as a result of interaction of dispersants and mineral fines with crude oil. The small particles tend to be suspended in the water column rather than settle down to the bottom because of the hydrodynamic mixing. The impact of this synergistic effect on overall fate and toxicity of the oil, such as biodegradation rate and the potential impact on pelagic and benthic organisms need to be evaluated further.

Although this experimental study on the interaction between chemical dispersants and mineral fines during oil dispersion was conducted under breaking waves that are typical of the coastal waters and the open sea with respect to energy dissipation rate (Delvigne and Sweeney, 1988), various mixing energy conditions should be studied to represent a broader environmental conditions in the field. For example, although mixing energy has proven to be essential for the formation of OMAs as well as their size distribution

627 and buoyancy (Lee and Stoffyn-Egli, 2001), and OMA for-  
 628 mation has been observed in the field with the breaking  
 629 wave heights of less than 30 cm (Owens et al., 1995; Sergy  
 630 et al., 2003), a quantitative association of OMA formation  
 631 and transport with the level of mixing energy at sea does  
 632 not exist yet. Since this study, the wave tank facility has  
 633 been upgraded to extend the length from 16 to 32 m for  
 634 further dispersant effectiveness test under a variety of  
 635 non-breaking regular wave and breaking wave conditions  
 636 (to simulate more violent breakers and create higher energy  
 637 dissipation rate); additional studies are planned to investi-  
 638 gate the interaction of oil, mineral fines and chemical dis-  
 639 persants under a suite of sea mixing energy conditions.  
 640 Many other factors, such as oil types and weathering state,  
 641 surface properties of mineral fines, and the ratio of oil to  
 642 mineral fines, should also be evaluated for their impact  
 643 on oil dispersion effectiveness by chemical dispersants.  
 644 The potential application of chemical oil dispersants to  
 645 “surf washing” operations warrants further study since  
 646 oil droplet formation has been hypothesized to be a cata-  
 647 lyst for the OMA formation on which this shoreline  
 648 clean-up procedure is based (Lee, 2002). Further research  
 649 is warranted to model interactions between crude oil, sus-  
 650 pended sediments and chemical dispersants, and to investi-  
 651 gate the time-scale of chemical oil dispersion and oil-  
 652 mineral aggregation. The knowledge gained from these sys-  
 653 tematic studies in the wave tank that can reproduce a vari-  
 654 ety of natural waves is expected to provide quantitative  
 655 guidance for risk assessment and decision-making during  
 656 the selection of nearshore oil-spill countermeasure  
 657 techniques.

## 658 6. Uncited reference

659 Venosa et al. (2005).

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## 672 References

673 Al-Sabagh, A.M., Atta, A.M., 1999. Water-based non-ionic polymeric  
 674 surfactants as oil spill dispersants. *Journal of Chemical Technology  
 675 and Biotechnology* 74 (11), 1075–1081.  
 676 Anderson, C.M., LaBelle, R.P., 2000. Update of comparative occurrence  
 677 rates for offshore oil spills. *Spill Science & Technology Bulletin* 6 (5–6),  
 678 303–321.

ASTM, 2002. American Society for Testing and Materials. Standard Test  
 Method for Waterborne Petroleum Oils by Fluorescence Analysis.  
 ASTM D3650-90, West Conshohocken, PA.  
 Bragg, J.R., Owen, E.H., 1995. Shoreline Cleansing by Interactions  
 between Oil and Fine Mineral Particles. American Petroleum Institute,  
 Washington, DC, pp. 219–227.  
 Bragg, J.R., Yang, S.H., 1995. Clay-oil flocculation and its effects on the  
 rate of natural cleansing in Prince William Sound following the *Exxon  
 Valdez* oil spill. In: Wells, P.G., Butler, J.N., Hughes, J.S. (Eds.), *Exxon  
 Valdez Oil Spill – Fate and Effects in Alaskan Waters*. American Society  
 for Testing and Materials, Philadelphia, PA, pp. 178–214.  
 Cloutier, D., Amos, C.L., Hill, P.R., Lee, K., 2002. Oil erosion in an  
 annular flume by seawater of varying turbidities: a critical bed shear  
 stress approach. *Spill Science & Technology Bulletin* 8 (1), 83–93.  
 Dalmazzone, C., Noik, C., Komunjer, L., 2005. Mechanism of crude-oil/  
 water interface destabilization by silicone demulsifiers. *SPE Journal* 10  
 (1), 44–53.  
 Dantas, T.N.D., Neto, A.A.D., Moura, E.F., 2001. Microemulsion  
 systems applied to breakdown petroleum emulsions. *Journal of  
 Petroleum Science and Engineering* 32 (2–4), 145–149.  
 Darling, P.S., Mackay, D., Mackay, N., Brandvik, P.J., 1990. Droplet size  
 distributions in chemical dispersion of oil spills: toward a mathemat-  
 ical model. *Oil and Chemical Pollution* 7 (3), 173–198.  
 Delvigne, G.A.L., Sweeney, C.E., 1988. Natural dispersion of oil. *Oil and  
 Chemical Pollution* 4 (4), 281–310.  
 Delvigne, G.A.L., Van del Stel, J.A., Sweeney, C.E., 1987. Measurements  
 of vertical turbulent dispersion and diffusion of oil droplets and oil-  
 particles. Anchorage, Alaska. US Department of the Interior, Minerals  
 Management Service. Report No. MMS 87-111, p. 501.  
 EPA, 2003. US Environmental Protection Agency. Test Methods (2003).  
 EPA Methods 3510C, 3540C and 8100.  
 Gearing, J.N., Gearing, P.J., 1983. Suspended load and solubility effect on  
 sedimentation of petroleum hydrocarbons in controlled estuarine  
 ecosystems. *Canadian Journal of Fisheries and Aquatic Science* 40, 54–  
 62.  
 Guyomarch, J., Le Floch, S., Merlin, F.X., 2002. Effect of suspended  
 mineral load, water salinity and oil type on the size of oil–mineral  
 aggregates in the presence of chemical dispersant. *Spill Science &  
 Technology Bulletin* 8 (1), 95–100.  
 Guyomarch, J., Merlin, F., Bernanose, P., 1999. Oil interaction with  
 mineral fines and chemical dispersion: behaviour of the dispersed oil in  
 coastal or estuarine conditions. Environment Canada’s 22nd Arctic  
 and Marine Oilspill (AMOP) Technical Seminar, Calgary, Alberta,  
 Canada, pp. 137–149.  
 Hill, P.S., Khelifa, A., Lee, K., 2002. Time-scale for oil droplet  
 stabilization by mineral particles in turbulent suspensions. *Spill  
 Science & Technology Bulletin* 8 (1), 73–81.  
 Kaku, V.J., Boufadel, M.C., Venosa, A.D., 2006. Evaluation of mixing  
 energy in laboratory flasks used for dispersant effectiveness testing.  
*Journal of Environmental Engineering-ASCE* 132 (1), 93–101.  
 Kepkey, P.E., Bugden, J.B.C., Lee, K., Stoffyn-Egli, P., 2002. Application  
 of ultraviolet fluorescence spectroscopy to monitor oil–mineral aggre-  
 gate formation. *Spill Science & Technology Bulletin* 8 (1), 101–108.  
 Khelifa, A., Stoffyn-Egli, P., Hill, P.S., Lee, K., 2002. Characteristics of oil  
 droplets stabilized by mineral particles: effects of oil type and  
 temperature. *Spill Science & Technology Bulletin* 8 (1), 19–30.  
 Khelifa, A., Stoffyn-Egli, P., Hill, P.S., Lee, K., 2005. Effects of salinity  
 and clay type on oil–mineral aggregation. *Marine Environmental  
 Research* 59 (3), 235–254.  
 Le Floch, S., Guyomarch, J., Merlin, F.X., Stoffyn-Egli, P., Dixon, J., Lee,  
 K., 2002. The influence of salinity on oil–mineral aggregate formation.  
*Spill Science & Technology Bulletin* 8 (1), 65–71.  
 Lee, K., 2002. Oil-particle interactions in aquatic environments: influence  
 on the transport, fate, effect and remediation of oil spills. *Spill Science  
 & Technology Bulletin* 8 (1), 3–8.  
 Lee, K., Stoffyn-Egli, P., 2001. Characterization of oil–mineral aggregates.  
 In: Proceedings of the 2001 International Oil Spill Conference.  
 American Petroleum Institute, Washington, DC, pp. 991–996.

- 747 Lee, K., Lunel, T., Wood, P., Swannel, R., Stoffyn-Egli, P., 1997. Shoreline cleanup by acceleration of clay-oil flocculation process. American Petroleum Institute, Washington, DC, Publication No. 4651, pp. 235–240.
- 748 Lee, K., Stoffyn-Egli, P., Tremblay, G.H., Owens, E.H., Sergy, G.A., Guenette, C.C., Prince, R.C., 2003. Oil–mineral aggregate formation on oiled beaches: natural attenuation and sediment relocation. *Spill Science & Technology Bulletin* 8 (3), 285–296.
- 749 Lee, K., Weise, A.M., St-Pierre, S., 1996. Enhanced oil biodegradation with mineral fine interaction. *Spill Science & Technology Bulletin* 3 (4), 263–267.
- 750 Lee, K., Wong, C.S., Cretney, W.J., Whitney, F.A., Parson, T.R., Lalli, C.M., Wu, J., 1985. Microbial response to crude oil and Corexit 9527: SEAFLEXES enclosure study. *Microbial Ecology* 11, 337–351.
- 751 Lessard, R.R., Demarco, G., 2000. The significance of oil spill dispersants. *Spill Science & Technology Bulletin* 6 (1), 59–68.
- 752 Li, M., Garrett, C., 1998. The relationship between oil droplet size and upper ocean turbulence. *Marine Pollution Bulletin* 36, 961–970.
- 753 Lunel, T., 1995. Understanding the mechanism of dispersion through oil droplet size measurements at sea. In: Lane, P. (Ed.), *The Use of Chemicals in Oil Spill Response*. ASTM STP 1252. American Society for Testing and Materials, Philadelphia, PA, pp. 240–270.
- 754 Lunel, T., Swannell, R., Rusin, J., 1997. Monitoring the effectiveness of response operations during the Sea Empress incident: a key component of the successful. *Oceanographic Literature Review* 44 (12), 1570–1571.
- 755 MacKay, D., Hussain, K., 1982. An exploratory study of sedimentation of naturally and chemically-dispersed oil. Environment Canada Report, EE-35, Ottawa, Ontario, Canada, 24p.
- 756 Marczewski, A.W., Szymula, M., 2002. Adsorption of asphaltenes from toluene on mineral surface. *Colloids and Surfaces A–Physicochemical and Engineering Aspects* 208 (1–3), 259–266.
- 757 Muschenheim, D.K., Lee, K., 2002. Removal of oil from the sea surface through particulate interactions: review and prospectus. *Spill Science & Technology Bulletin* 8 (1), 9–18.
- 758 Nilson, J., Naess, A., Volent, Z., 1985. Measurements of oil concentrations in the water column under breaking waves. Norwegian Hydro-technical Laboratory, Report STF 60 A 85079, Trondheim, Norway.
- 759 NRC, 2003. National Research Council: Oil in the Sea III: Inputs, Fates and Effects. National Academies Press, Washington, DC.
- 760 NRC, 2005. National Research Council: Understanding Oil Spill Dispersants: Efficacy and Effects. National Academies Press, Washington, DC.
- 761 NRCC, 1997. National Research Council of Canada, Centre D'Expertise en Analyse Environnementale du Québec, Dosage Des Hydrocarbons, MA 410-HYD. 1.0.1997.
- 762 Oebius, H.U., 1999. Physical properties and processes that influence the clean up of oil spills in the marine environment. *Spill Science & Technology Bulletin* 5 (3–4), 177–289.
- 763 Omotoso, O.E., Munoz, V.A., Mikula, R.J., 2002. Mechanisms of crude oil–mineral interactions. *Spill Science & Technology Bulletin* 8 (1), 45–54.
- 764 Owens, E.H., Davis Jr. R.A., Michel, J., Stritzke, K., 1995. Beach cleaning and the role of technical support in the 1993 Tampa Bay spill. American Petroleum Institute, Washington, DC, Publication No. 4620, pp. 627–634.
- 765 Owens, E.H., Lee, K., 2003. Interaction of oil and mineral fines on shorelines: review and assessment. *Marine Pollution Bulletin* 47 (9–12), 397–405.
- 766 Owens, E.H., Sergy, G.A., Guenette, C.C., Prince, R.C., Lee, K., 2003. The reduction of stranded oil by in situ shoreline treatment options. *Spill Science & Technology Bulletin* 8 (3), 257–272.
- 767 Page, C.A., Bonner, J.S., Sumner, P.L., McDonald, T.J., Autenrieth, R.L., Fuller, C.B., 2000. Behavior of a chemically-dispersed oil and a whole oil on a near-shore environment. *Water Research* 34 (9), 2507–2516.
- 768 Payne, J.R., Clayton Jr., J.R., Kirstein, B.E., 2003. Oil/suspended particulate material interactions and sedimentation. *Spill Science & Technology Bulletin* 8 (2), 201–221.
- 769 Quantin, C., Joner, E.J., Portal, J.M., Berthelin, J., 2005. PAH dissipation in a contaminated river sediment under oxic and anoxic conditions. *Environmental Pollution* 134 (2), 315–322.
- 770 Sergy, G.A., Guenette, C.C., Owens, E.H., Prince, R.C., Lee, K., 2003. In situ treatment of oiled sediment shorelines. *Spill Science & Technology Bulletin* 8 (3), 237–244.
- 771 Shaw, J.M., 2003. A microscopic view of oil slick break-up and emulsion formation in breaking waves. *Spill Science & Technology Bulletin* 8 (5–6), 491–501.
- 772 Sterling, M.C., Bonner, J.S., Ernest, A.N.S., Page, C.A., Autenrieth, R.L., 2005. Application of fractal flocculation and vertical transport model to aquatic sol-sediment systems. *Water Research* 39 (9), 1818–1830.
- 773 Sterling, M.C., Bonner, J.S., Page, C.A., Fuller, C.B., Ernest, A.N.S., Autenrieth, R.L., 2004. Modeling crude oil droplet-sediment aggregation in nearshore waters. *Environmental Science & Technology* 38 (17), 4627–4634.
- 774 Stoffyn-Egli, P., Lee, K., 2002. Formation and characterization of oil–mineral aggregates. *Spill Science & Technology Bulletin* 8 (1), 31–44.
- 775 Szymula, M., Marczewski, A.W., 2002. Adsorption of asphaltenes from toluene on typical soils of Lublin region. *Applied Surface Science* 196 (1–4), 301–311.
- 776 Tkalich, P., Chan, E.S., 2002. Vertical mixing of oil droplets by breaking waves. *Marine Pollution Bulletin* 44 (11), 1219–1229.
- 777 Venosa, A.D., Kaku, V.J., Boufadel, M.C., Lee, K., 2005. Measuring energy dissipation rates in a wave tank. In: *Proceedings of 2005 International Oil Spill Conference*, Miami, FL. American Petroleum Institute, Washington, DC.