

Evaluating Chemical Dispersant Efficacy in an Experimental Wave Tank: 2—Significant Factors Determining *In Situ* Oil Droplet Size Distribution

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Received: December 18, 2008

Accepted in revised form: June 15, 2009

Abstract

Chemical dispersion is one of the most cost-effective options to remediate oil spill at open sea. Identifying significant factors that determine *in situ* droplet size distributions facilitates mechanistic understanding of dispersant effectiveness. In this work, *in situ* dispersed oil droplet size distributions were characterized during testing of chemical dispersant effectiveness of two dispersants (Corexit 9500 and SPC 1000) on two oils [Medium South American (MESA) and Alaska North Slope (ANS)] under three wave conditions (regular nonbreaking, spilling breaking, and plunging breaking waves) in an experimental wave tank. Results showed that physical dispersion generated monomodal lognormal oil droplet size distributions of larger median diameters, whereas chemical dispersion produced bi- or trimodal lognormal oil droplet size distributions of smaller median diameters over a wider range. Factorial analysis of variance (ANOVA) followed by Tukey's paired comparison statistical data analysis indicated that the volume mean diameters of dispersed oil droplets were reduced by 36 μm (from 122 to 86 μm) by plunging breaking conditions. Volume mean diameters were decreased by 92 μm (from 153 to 61 μm) and 37 μm (from 153 to 116 μm), respectively, by Corexit 9500 and SPC 1000. These results are useful in optimizing operational guidelines for dispersant use, and providing input for modeling transport, fate, and biological effects of dispersed oil.

Key words: oil spill; chemical dispersant; droplet size distribution; breaking waves; wave energy

Introduction

CHEMICAL DISPERSANTS ARE USED to reduce interfacial tension between oil and water, so as to enhance the natural process of dispersion by generating larger numbers of small droplets of oil that are entrained into the water column by wave energy (Lessard and Demarco, 2000; NRC, 2005; Chapman *et al.*, 2007; Kirby and Law, 2008). The premise for the use of dispersants as a cost-effective oil spill countermeasure is the presence of large volumes of seawater that can render rapid dilution of dispersed oil to concentrations lower than the toxicity threshold of biota. Presently, dispersant-use policies vary from region to region, but the general consensus is that sufficient dilution capacity is essential. In Europe, minimum permitted depths for dispersant spraying range

from 10 m in France to 60 m in Malta (Chapman *et al.*, 2007). In the United States, many states have defined preapproval zones for dispersant use outside three nautical miles from shore and/or in depths greater than 10 m (NRC, 2005).

In dispersant effectiveness testing, it is important for the testing system to have hydrodynamics and dilution [commonly expressed as oil-to-water ratio (OWR)] approach field conditions (Fingas *et al.*, 1989; NRC, 2005). Fingas *et al.* (1989) showed that the dispersant effectiveness values were relatively constant over the OWR ranging from 1:1,000 to 1:120,000, but had a large variation when the ratio was 1:500 or smaller. In that study, however, the effect of OWR, in the range from 1:4,000 to 1:120,000, was evaluated in a recirculation-flow cylinder, which had no control over resurfacing and/or settling of the dispersed oil. NRC (2005) reiterated the importance of OWR in the dispersant effectiveness testing. For example, when OWR is low, anionic and nonionic surfactants with a high hydrophilic-lipophilic balance tend to partition into the aqueous phase, where they cannot effectively promote formation of small oil droplets. When the OWR is high, however, more of the surfactant can be associated

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with the oil phase where it can facilitate droplet formation. Conversely, high OWR could reduce the observed dispersion efficiency by increasing the rate of droplet coalescence, which is proportional to the number concentration of oil droplets (NRC, 1989). Droplet coalescence will produce larger oil droplets that can resurface more quickly and reduce the mass of oil entrained in the aqueous phase.

Due to the constraints of volume, laboratory tests have limited capacity to accommodate transport and dilution effects. For a typical bench-scale laboratory dispersant effectiveness test (such as Fingas *et al.*, 1995; U.S. EPA, 1996; ASTM, 2002), 120 mL of seawater in a testing flask is spiked with 0.1 mL testing oil, resulting an OWR of 1:1,200. Further reducing the dosage of oil can jeopardize the accuracy of the amount of oil that can be measured. As a result, dispersant effectiveness measured as a percentage oil dispersed into the water column in a bench-scale test is sensitive to the settling time that precedes collection of samples, largely due to coalescence and resurfacing of oil droplets promoted by high OWR (Fingas *et al.*, 2002; Fingas, 2005). Conversely, expensive and logistically challenging sea trials often lead to results that are inconclusive due to limitations in the level of replication and control of experimental variables.

Wave tank testing allows for evaluating dispersant effectiveness under more realistic (i.e., field) conditions, including the mixing energy generated by various wave types, and the dilution effect (OWR) that is similar to what is observed in the field. The misleading role of coalescence in small systems may be significantly reduced in large wave tanks where dilution more closely approximates natural conditions. In response to an identified need for testing the performance of chemical dispersants under more realistic oceanographic and environmental conditions including wave-induced mixing energies (NRC, 2005), a wave tank facility has been constructed at the Bedford Institute of Oceanography (BIO, Dartmouth, NS, Canada) for reproducible, quantitative evaluation of chemical dispersant effectiveness under a variety of wave conditions.

To understand the intrinsic mechanisms of dispersant effectiveness obtained in a testing system, it is important to measure the dispersed oil droplet size distributions and compare the data with those observed at sea (Lunel, 1995). *In situ* dispersed oil droplet size distributions are controlled by a variety of hydrodynamic and environmental variables. For example, the intensity of the turbulent mixing energy dictates the breakup of large oil droplets into smaller droplets and the depth of submergence of the droplets. Breaking waves, in particular, have been documented to play a crucial role in dispersion of oil slicks by generating velocity shear to break up and transport oil in turbulent flow (Li and Garrett, 1998; Tkalic and Chan, 2002; Shaw, 2003). The effects of mixing energy on dispersed oil droplet size distributions, and consequently dispersant effectiveness, have been reported in laboratory tests (Byford *et al.*, 1984; Lewis *et al.*, 1985; Sorial *et al.*, 2004; Chandrasekar *et al.*, 2005; Ma *et al.*, 2008) and in field trials under low- and high-energy regimes caused by various wind effects (Lunel, 1993, 1995). The droplet size distributions are also affected by the collision frequency, which has been considered a function of system hydrodynamics, and collision efficiency, which is generally believed to represent the chemistry involved in the coalescence reactions. The influence of chemical dispersants in increasing the number of

small droplets in the water column was reported in laboratory tests (Jasper *et al.*, 1978; Byford *et al.*, 1984; Lewis *et al.*, 1985) and field trials (Lunel, 1993, 1995). Jasper *et al.* (1978) observed that the volume mean diameter of dispersed oil was reduced by 30–40% by the presence of a chemical dispersant. Lunel (1995) reported that dispersants increased the number of small droplets (<50 μm) by 5- to 30-fold in a sea trial, but the number of larger droplets (>50 μm) between the dispersant-treated and untreated oil were the same.

The NRC (2005) report emphasized that existing databases for the droplet-size distributions of physically and chemically dispersed oil must be expanded to determine whether and how factors such as energy dissipation rate, oil type, dispersant characteristics, and dispersant use influence the droplet size distribution and formation kinetics under hydrodynamic conditions approaching those existing in the field. To this end, the BIO wave tank was used to characterize and compare *in situ* droplet size distributions of physically and chemically dispersed oil under a variety of nonbreaking and breaking wave conditions. The data generated in this study will be useful in optimizing operational guidelines, modeling transport and fate, and potentially evaluating biological effects of chemically dispersed oil. This is the second of a series of two articles; the first article focuses on elucidating dispersant effectiveness as a function of energy dissipation rate (Li *et al.*, accepted).

Materials and Methods

Experimental procedures

Figure 1 shows the top and side view schematic representations of the wave tank facility with sampling locations at BIO. The tank measures 32 m long, 0.6 m wide, and 2 m high, with an average water depth of 1.5 m. Three different wave conditions were generated by a computer-controlled flap-type wave maker situated at one end of the tank. Table 1 summarizes the conditions that were used to create the various wave types. The energy dissipation rate per unit mass of water (ϵ) was evaluated by the autocorrelation function method (Kresta and Wood, 1993) using time-series velocity measurements obtained by an Acoustic Doppler Velocimeter (SonTec/YSI, Inc. San Diego, CA) at select locations in the tank. Details of the wave generation and the hydrodynamic characterization of the wave tank have been reported elsewhere (Wickley-Olsen *et al.*, 2008; Li *et al.*, accepted). The dispersant effectiveness of two dispersants (Corexit 9500 and SPC 1000) on two oils [Medium South American (MESA) and Alaska North Slope (ANS)] under the above three wave conditions was assessed using a three-factor, mixed-level factorial experiment with three replications. The design was a noise-reducing randomized block design (Mendenhall *et al.*, 1981) to minimize the impacts of confounding factors such as temperature, salinity, and wind variation. For each experiment, seawater was pumped from the Bedford Basin (NS, Canada) through a double layer sock-filter (Atlantic Purification Ltd, Dartmouth, NS, Canada) with pore sizes of 25 and 5 μm for the coarse and fine filters, respectively. The background temperature, salinity, and particle size distributions were recorded before each experiment. The seawater temperature and salinity were recorded as $16.3 \pm 1.8^\circ\text{C}$, and 26.7 ± 3.2 ppt, respectively, during the experimental period.

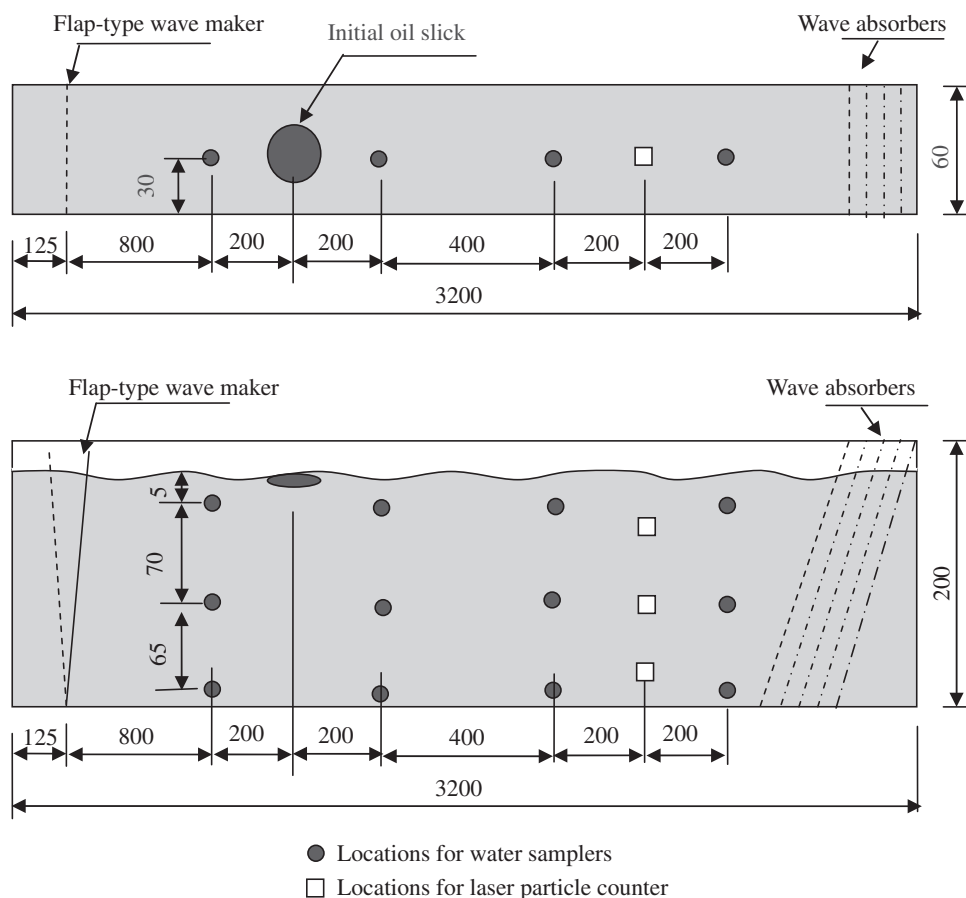


FIG. 1. Top (upper) and side view (lower) of the schematic representation (all dimensions in centimeters, not to scale) of the Bedford Institute of Oceanography (BIO) wave tank facility.

To start an experiment, 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, flexible PVC tube) located 10 m from the wave-maker. The volume of oil in each experiment was intended to achieve an OWR (1:100,000) and a nominal oil concentration (10 mg/L) close to the field (ITOPF, 2005). Subsequently, 12 mL of dispersant (or water for the control) was sprayed onto the oil slick through a pressurized nozzle (60 psi; 0.635 mm i.d.), resulting in a dispersant-to-oil ratio (DOR) of 1:25, a typical dosage as recommended for field application (NRC, 2005). The ring was then lifted immediately prior to the approaching first wave. The specific wave condition selected for each experimental run was maintained continuously during the 2-h experiment. To measure the total dispersed oil concentration, water samples were collected through a set of three 100-mL syringes connected to each of four stainless steel manifolds located at

8, 12, 16, and 20 m downstream from the wave maker. The three syringes at each station collected water samples at three depths (5, 75, and 140 cm below the average water surface) in the water column of the wave tank at four time points (5, 30, 60, and 120 min after the initial mixing). The total oil concentrations of these samples were determined by extracting the total petroleum hydrocarbons (TPH) from the water samples with dichloromethane and then analyzing the TPH concentrations in a UV-Visible spectrophotometer as described elsewhere (Venosa *et al.*, 2002; Li *et al.*, 2008).

In situ droplet size distribution

The dispersed oil droplet size distribution was measured using an *in situ* laser light scattering and transmissometer (LISST-100X, Type C; Sequoia Scientific, Seattle, WA). The LISST-100X records 32 particle size intervals logarithmically

TABLE 1. CONDITIONS USED TO GENERATE VARIOUS WAVE TYPES IN THE WAVE TANK

Wave type	Stroke (cm)	Frequency (Hz)	Wavelength (m)	Height (cm)	Duration (s)
Regular	12	0.80	2.44	23	—
Spiller	8.4	0.85	2.16	18	20
	8.4	0.48	6.77	6	5
Plunger	12	0.85	2.16	26	20
	12	0.50	6.24	9	5

placed from 2.5–500 μm in diameter, with the upper size in each bin 1.18 times the lower. The measured particle size distribution is expressed as the average volumetric concentration of oil within each size interval. The droplet size distributions were measured at three different depths (45, 80, and 125 cm from the average water surface) at one horizontal location (18 m downstream from the wave-maker) over four half-hour time periods (0–30, 30–60, 60–90, 90–120 min). For each depth at each time period, four 10-min continuous records of droplet size distribution data were obtained every 3 s.

To compare the effects of dispersant application, wave conditions, and other factors on dispersed oil droplet size, the volume mean diameters (VMD) of the measured droplet size distribution was calculated as a weighted mean according to its individual volume contribution to the total volume of the droplets:

$$\text{VMD} = \frac{\sum(C_i \cdot d_i)}{\sum C_i} \quad (1)$$

where C_i ($i = 1-32$) is the volume concentration of oil droplets in a size interval with average size d_i , which is the geometric mean of the lower and upper limit of every size range within the range 2.5–500 μm .

Data analysis

A five-way factorial analysis of variance (ANOVA) was performed to test the effects of factors, including dispersants, wave conditions, oil type, dispersion time, and sampling depths, on the average VMD of the dispersed oil droplets. When significant effects were identified, the Tukey's paired comparison was conducted to isolate the factorial effects at each treatment level. Data analyses were conducted using a statistical data analysis package S-PLUS 7.0 (Insightful Inc., Seattle, WA). A significance alpha level of 0.05 was adopted for statistical tests. A Bonferroni adjustment was performed on the alpha level to control for the family-wise alpha rate to reach an adjusted and more strict alpha level at 0.0016.

Results

Physically and chemically dispersed oil droplet size distributions

Figures 2 to 4 display representative dispersed MESA crude oil droplet size distributions measured near the surface of the wave tank for physical and chemical dispersion of oil under three different wave conditions. Similar droplet size distributions were obtained in the middle and near the bottom of the wave tank (data not shown). The dispersed oil droplet size

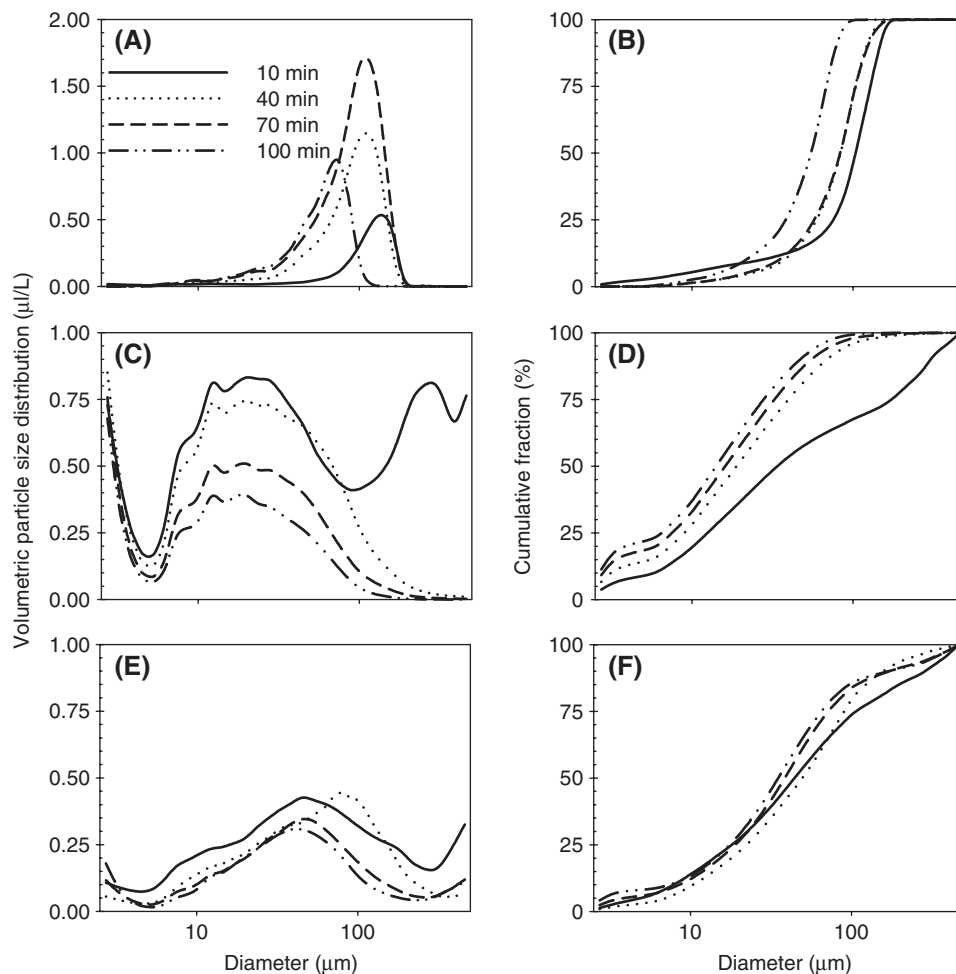


FIG. 2. Volumetric (left) and cumulative (right) Medium South American (MESA) oil droplet size distributions dispersed by water (A, B), Corexit 9500 (C, D), and SPC 1000 (E, F) under regular wave conditions.

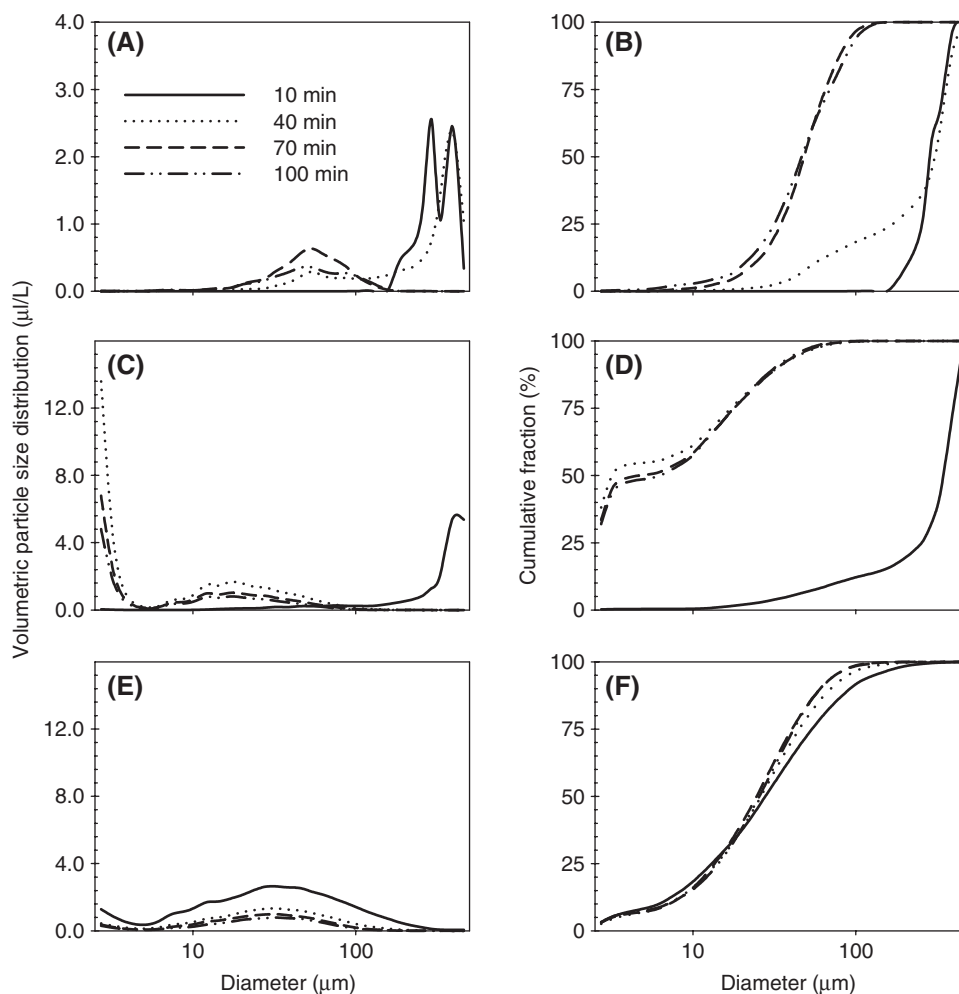


FIG. 3. Volumetric (left) and cumulative (right) MESA oil droplet size distributions dispersed by water (A, B), Corexit 9500 (C, D), and SPC 1000 (E, F) under spilling breaking wave conditions.

distribution data were also recorded for ANS crude from all three depths under different experimental conditions (data not shown). These data were similar to those for MESA. Tables 2 and 3 summarize the droplet size distribution statistics for MESA and ANS oil, respectively, at the surface. Physical dispersion (i.e., dispersion in absence of a chemical dispersant) of MESA oil created monomodal lognormal droplet size distributions under regular wave conditions throughout the entire experiment (Fig. 2A and B). Bi- or trimodal lognormal distributions were generated initially (first 10 min), which were further dispersed to monomodal distributions, under spilling and plunging breakers (Fig. 3A and B and 4A and B). In the presence of chemical dispersants, however, multimodal lognormal size distributions were produced under all three wave conditions throughout the entire duration of the dispersion experiment (Fig. 2C and E–4C and E). A large number of oil droplets with less than $10\ \mu\text{m}$ in size were created in the presence of chemical dispersants, especially by Corexit 9500. Application of dispersants expanded the range of size distributions as indicated by larger geometric standard deviations (GSD) associated with chemical dispersants (Tables 2 and 3). Chemical dispersants also caused much higher dispersed phase volume concentrations (areas under the droplet size distributions) than physical dispersion (Figs.

2–4). However, the droplet size distribution patterns of the chemically dispersed oil droplets were essentially the same after 30 min under all three wave conditions, as indicated by the percentage cumulative droplet size distributions (Fig. 2D and F, 3D and F, and 4D and F).

Significant factors determining the average dispersed oil droplet sizes

The full spectrum of particle size distribution at each sampling time was converted to VMD to compare the influence of different treatment conditions, including wave conditions, dispersant type, and oil type, on the average droplet size. The VMD from physical dispersion (absence of dispersants) under all wave conditions started with wide fluctuations but generally decreased over time. The time-series VMD were in good agreement at all three depths under regular waves and plunging breaking waves, but were smaller at the bottom than in the middle and near the surface under spilling breaking wave conditions, probably caused by less penetration depth of the spilling breaking waves. The VMD from the chemical dispersants were larger near the bottom than near the surface and in the middle of the wave tank under regular waves, but had wider fluctuations in the middle of the wave

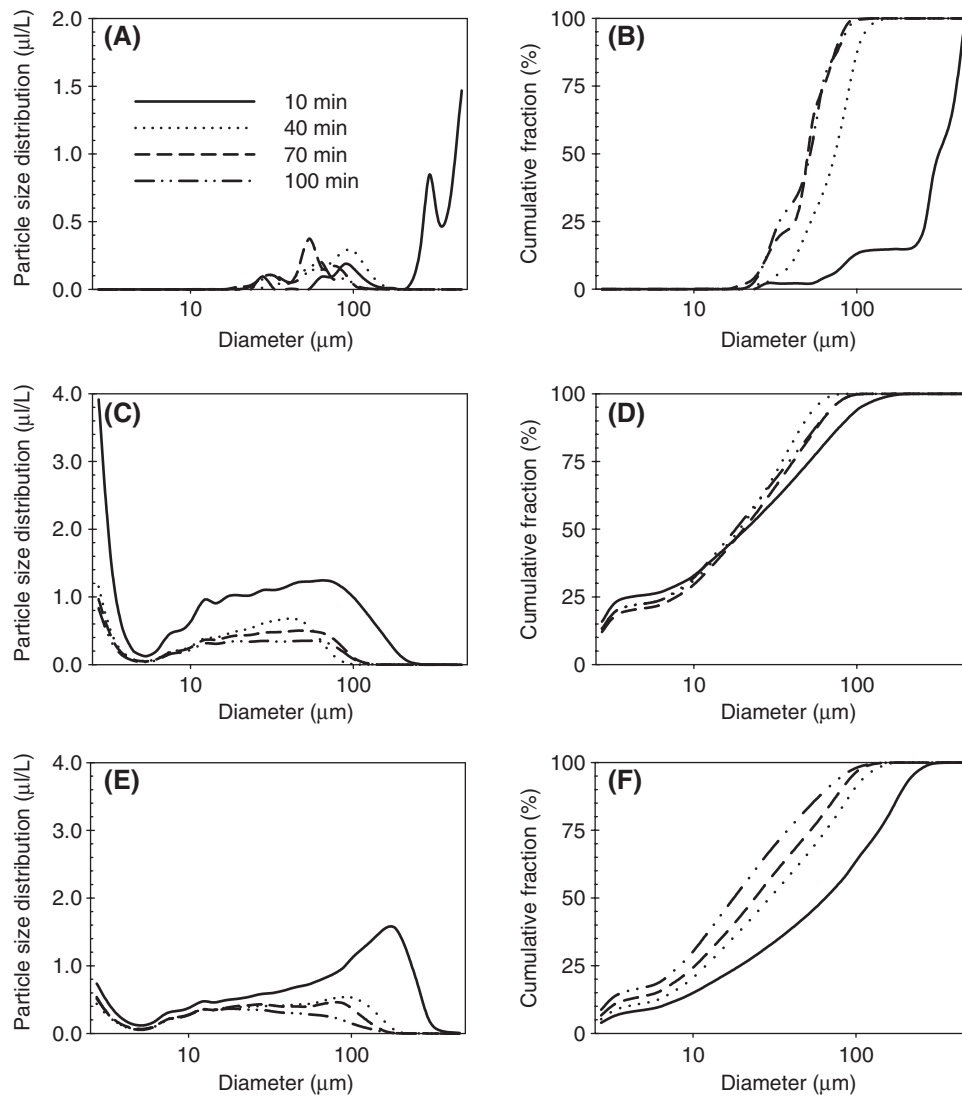


FIG. 4. Volumetric (left) and cumulative (right) MESA oil droplet size distributions dispersed by water (A, B), Corexit 9500 (C, D), and SPC 1000 (E, F) under plunging breaking wave conditions.

tank than near the surface and the bottom of the wave tank under spilling and plunging breaking waves conditions.

In Figures 5 and 6 the average dispersed oil droplet VMD at the surface of the wave tank are illustrated as a function of time at the end of each measurement period for MESA and ANS crude, respectively. Similar trends of the time-series average VMD under different dispersant and wave conditions were observed at the other two depths (in the middle and near the bottom) of the wave tank (data not shown). After 10 min, physically dispersed oil droplets were large ($VMD > 160 \mu\text{m}$) under all three wave conditions (Figs. 5 and 6). In contrast, chemical dispersants (both Corexit 9500 and SPC 1000) created the largest oil droplets ($VMD_{\text{MESA}} > 140 \mu\text{m}$, $VMD_{\text{ANS}} > 200 \mu\text{m}$) under regular nonbreaking waves and the smallest droplets ($VMD_{\text{MESA}} < 80 \mu\text{m}$, $VMD_{\text{ANS}} < 120 \mu\text{m}$) under plunging breaking waves, with the average VMD more dependent on dispersant and oil type under spilling breaking wave conditions. As oil dispersion progressed, the average VMD declined at a rate dependent on

dispersant type and wave conditions. Physical dispersion of both crude oils appears to have required the longest time (100 min) to reach the ultimate stable VMD under regular nonbreaking wave conditions and the shortest time (40 min) under plunging breaking wave conditions. As expected, chemical dispersants facilitated better dispersion at lower energy dissipation rates under regular nonbreaking and spilling breaking wave conditions. Corexit 9500 reduced the average VMD for both MESA and ANS under all three wave conditions at all four time points (Fig. 5A–C). SPC1000, however, decreased the average VMD markedly under spilling and plunging breaking waves for MESA, but reduced the average VMD even more dramatically under regular wave and spilling breaking waves for ANS. The effect of dispersant was clearly illustrated by the ultimate VMD for each combination of dispersant, wave, and oil. Physically dispersed MESA and ANS oil droplets had $VMD > 100 \mu\text{m}$ under all three wave conditions. SPC 1000 dispersed MESA to $150 \mu\text{m}$ under regular nonbreaking waves and less than $70 \mu\text{m}$ under

TABLE 2. DROPLET SIZE DISTRIBUTION STATISTICS FOR MEDIUM SOUTH AMERICAN AT THE SURFACE

Wave	Dispersant	Time (min)	$d_{16\%}^a$ (μm)	$d_{50\%}^a$ (μm)	$d_{84\%}^a$ (μm)	GSD	Modes	% < 70 (μm)	
Regular	Water	10	53	104	143	1.64	1	22%	
		40	46	80	116	1.59	1	34%	
		70	45	80	114	1.59	1	35%	
	Corexit	100	28	55	74	1.63	1	75%	
		10	8	33	250	5.59	4	62%	
		40	6	19	55	3.03	2	90%	
	SPC	70	3.5	16	45	3.59	2	94%	
		100	3	14	38	3.56	2	96%	
		10	11	45	186	4.11	3	65%	
	Spilling	Water	40	15	50	120	2.83	3	65%
			70	13	39	100	2.77	3	72%
			100	12	35	90	2.74	3	77%
Corexit		10	230	280	360	1.25	2	0%	
		40	85	310	380	2.11	2	13%	
		70	29	50	75	1.61	1	78%	
SPC		100	25	48	80	1.79	1	75%	
		10	160	350	430	1.64	1	95%	
		40	2.5	3	25	3.16	2	99%	
Plunging		Water	70	2.5	5	25	3.16	2	99%
			100	2.5	7	25	3.16	2	99%
			10	9	28	74	2.87	2	82%
	Corexit	40	10	27	58	2.41	2	90%	
		70	10	25	50	2.24	2	93%	
		100	10.5	24	50	2.18	2	93%	
	SPC	10	225	330	430	1.38	4	5%	
		40	45	70	96	1.46	2	45%	
		70	31	50	70	1.50	2	82%	
	Corexit	100	29	48	68	1.53	2	92%	
		10	2.8	22	70	5.00	2	88%	
		40	3	19	43	3.79	2	100%	
70		3	20	52	4.16	2	98%		
100		3	18	53	4.20	2	98%		
SPC		10	11	64	170	3.93	2	50%	
		40	8	30	80	3.16	2	77%	
		70	7	24	70	3.16	2	84%	
100		4	18	52	3.61	2	92%		

^a $d_{16\%}$, $d_{50\%}$, $d_{84\%}$ represent the 16, 50, or 84% of total mass of the droplets that are smaller than this diameter (μm); $d_{50\%}$ is the mass median diameter.

GSD, geometric standard deviation.

spilling and plunging breaking wave conditions, but it dispersed ANS crude to around $100\mu\text{m}$ under all three wave conditions. Corexit 9500, however, dispersed both MESA and ANS to small sizes ($<70\mu\text{m}$) under all three wave conditions.

A five-way ANOVA was performed to test the factorial effects on the average VMD by: (1) wave condition, (2) dispersant type, (3) oil type, (4) dispersion time, and (5) measuring depth. Among these factors, testing of dispersion time allows for the identification of a minimum duration that is required for dispersion of oil into relatively stable average droplet sizes. The effect of water depth was tested to evaluate the spatial variation in the dispersed droplet sizes. The ANOVA results are presented in Table 4. As expected, the high-order interactions (all four- and five-factor and all but one three-factor interactions) are insignificant ($p > 0.25$). There was one significant three-factor interaction (dispersant \times oil \times wave, $p < 0.0001$), two significant two-factor interactions at Bonferroni-adjusted level (dispersant \times wave, $p = 0.0003$; and dispersant \times oil, $p = 0.0001$), and two additional significant two-factor interactions at a less strict significant level (depth \times time, $p = 0.041$; and oil \times wave,

$p = 0.027$), indicating that average dispersed oil droplet size was affected nonuniformly by changes in the interacting variables. Besides the significant multifactor interactions, three of the five main factors (wave type, dispersant type, and dispersion time, $p < 0.0001$) were identified to have strong, statistically significant effects on the average dispersed oil droplet sizes. Two other tested main factors did not affect average droplet sizes significantly: oil ($p = 0.917$) and sampling depth ($p = 0.865$). The significant effects of various factors were further compared at each treatment level with the Tukey's paired comparison test, and the results are summarized in Table 5. The two dispersants significantly reduced the dispersed oil droplet size, with the average VMD being reduced by $91.5\mu\text{m}$ by Corexit 9500 and $36.6\mu\text{m}$ by SPC 1000. The plunging wave conditions significantly reduced the average dispersed droplet size by $35.7\mu\text{m}$. The average dispersed oil droplet sizes declined significantly by $42\mu\text{m}$ between the first and second dispersion period. The differences in the average dispersed oil droplet sizes after 30 min were statistically insignificant ($p > 0.05$).

TABLE 3. DROPLET SIZE DISTRIBUTION STATISTICS FOR ALASKA NORTH SLOPE AT THE SURFACE

Wave	Dispersant	Time (min)	$d_{16\%}^a$ (μm)	$d_{50\%}^a$ (μm)	$d_{84\%}^a$ (μm)	GSD	Modes	% < 70 (μm)
Regular	Water	10	219	390	420	1.38	2	7%
		40	70	250	400	2.39	1	15%
		70	46	150	340	2.72	1	25%
		100	46	140	300	2.55	1	27%
	Corexit	10	2.5	27	400	12.65	3	55%
		40	2.5	3	19	2.76	2	99%
		70	2.5	8	36	3.79	2	99%
		100	2.5	4	8	1.79	2	99%
	SPC	10	10	36	85	2.92	2	78%
		40	14	42	80	2.39	2	75%
		70	12	36	70	2.42	2	85%
		100	13	50	74	2.39	2	80%
Spilling	Water	10	280	310	370	1.15	1	0%
		40	200	210	220	1.05	2	0%
		70	110	295	300	1.65	2	4%
		100	35	38	43	1.11	1	98%
	Corexit	10	2.5	19	125	7.07	3	5%
		40	2.5	11	38	3.90	2	95%
		70	2.5	11	38	3.90	2	96%
		100	2.5	10	25	3.16	2	99%
	SPC	10	11	36	74	2.59	2	80%
		40	13	36	60	2.15	2	95%
		70	10	40	45	2.12	2	99%
		100	9	22	36	2.00	2	100%
Plunging	Water	10	60	120	170	1.68	4	20%
		40	50	85	120	1.55	2	35%
		70	40	70	100	1.58	2	45%
		100	36	65	96	1.63	2	62%
	Corexit	10	3	33	190	7.96	2	66%
		40	2.5	12	25	3.16	2	100%
		70	2.5	15	32	3.58	2	100%
		100	2.5	11	22	2.97	2	100%
	SPC	10	10	25	400	6.32	2	81%
		40	7	20	35	2.24	2	98%
		70	4	18	35	2.96	2	99%
		100	3	16	34	3.37	2	100%

^a $d_{16\%}$, $d_{50\%}$, $d_{84\%}$ represent the 16, 50, or 84% of total mass of the droplets that are smaller than this diameter (μm); $d_{50\%}$ is the mass median diameter.

Discussion

The effect of wave-generated mixing energy on the dispersed oil droplet size distribution was examined under three wave conditions with different energy dissipation rates. The average energy dissipation rates were estimated to be approximately 0.005 , 0.1 , and $1 \text{ W} \cdot \text{kg}^{-1}$ near the surface at the mixing zone for regular nonbreaking waves, spilling breaking waves, and plunging breaking waves, respectively. The energy dissipation rates declined exponentially to approximately $0.001 \text{ W} \cdot \text{kg}^{-1}$ for the two breaking wave conditions at a depth of 30 cm and decreased linearly under regular nonbreaking wave conditions (Wickley-Olsen *et al.*, 2008). The energy dissipation rate of plunging breaking waves was similar to those measured for breaking waves in the field (Drennan *et al.*, 1996; Terray *et al.*, 1996; Delvigne and Sweeney, 1988). Regular nonbreaking wave energy was also similar to that reported on the sea surface by Delvigne and Sweeney (1988), and energy level of spilling breakers was in between. These wave conditions had significant effects on the droplet size distributions (Figs. 2–4 and Table 1) and average

droplet size (Figs. 5 and 6 and Tables 2 and 3). High-energy dissipation rates associated with plunging breaking waves reduced the droplet size distributions and increased the percentage fraction of oil dispersed in the water column (Li *et al.*, accepted). In a closed system with little dilution potential, however, coalescence could be promoted by providing mixing energy over a prolonged period of time (NRC, 2005). Sterling *et al.* (2004) has clearly demonstrated that increased mixing energy in an enclosed vessel promoted coalescence and resurfacing of dispersed oil droplets over time at a nominal OWR of 1:6,000, resulting in an incrementally reduced dispersed oil fraction in the aqueous phase.

Application of chemical dispersants substantially altered the dispersed oil droplet size distributions in the wave tank by creating wider range multimodal size distributions including large number of small droplets ($<10 \mu\text{m}$ in diameter) (Figs. 2–4 and Tables 2 and 3) and significantly reduced the average VMD (Figs. 5 and 6). A significant difference in the average dispersed droplet sizes was identified between the two tested chemical dispersants. The apparent superiority of the oil-based dispersant (Corexit 9500) is probably due to its stronger

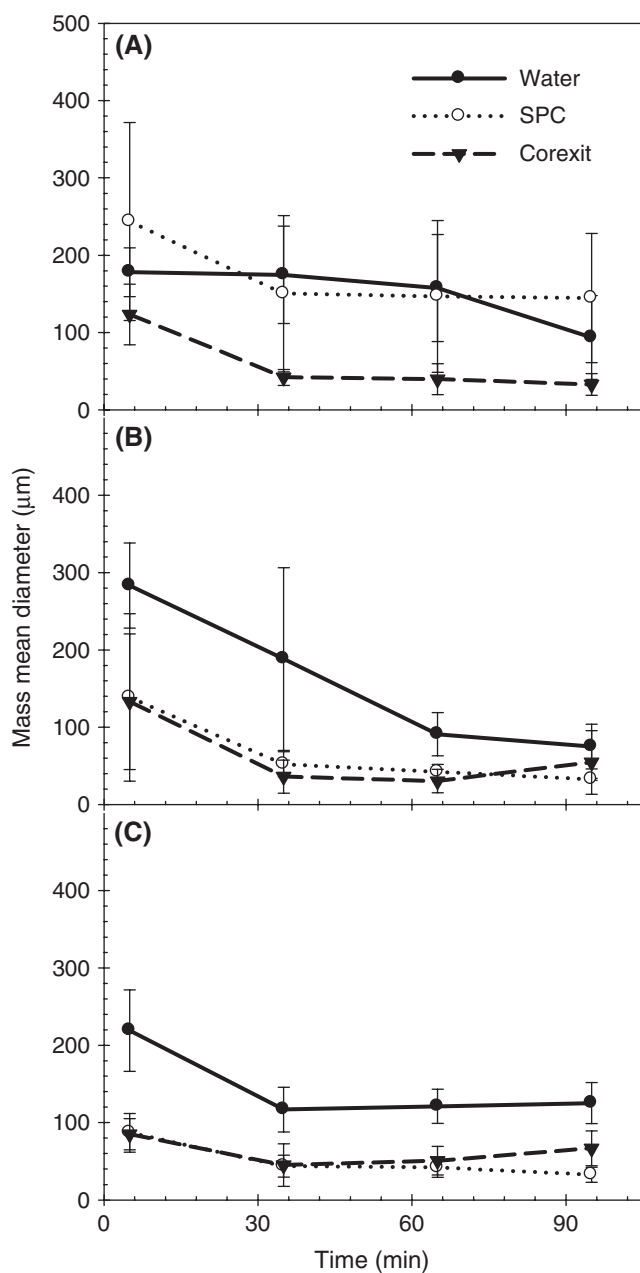


FIG. 5. Dispersed MESA oil droplet size (volume mean diameter) as a function of time under: (A) regular non-breaking, (B) spilling breaking, and (C) plunging breaking wave conditions.

affiliation with oil in the course of oil dispersion, whereas the water-based dispersant (SPC 1000) tends to be washed away from the surface of oil droplets and partitioned into the aqueous phase over a longer period of time, resulting in re-coalescence and resurfacing of the dispersed oil droplets in less vigorously mixed areas. The rearrangement of surfactant-stabilized oil-in-water emulsions has been reported and was explained as a result of the development of a surfactant depletion–floculation process (Sanchez *et al.*, 2001).

Not surprisingly, time is a significant factor in dispersion of crude oils in the wave tank. In these experiments chemical dispersion broke up oil into relatively stable droplet size

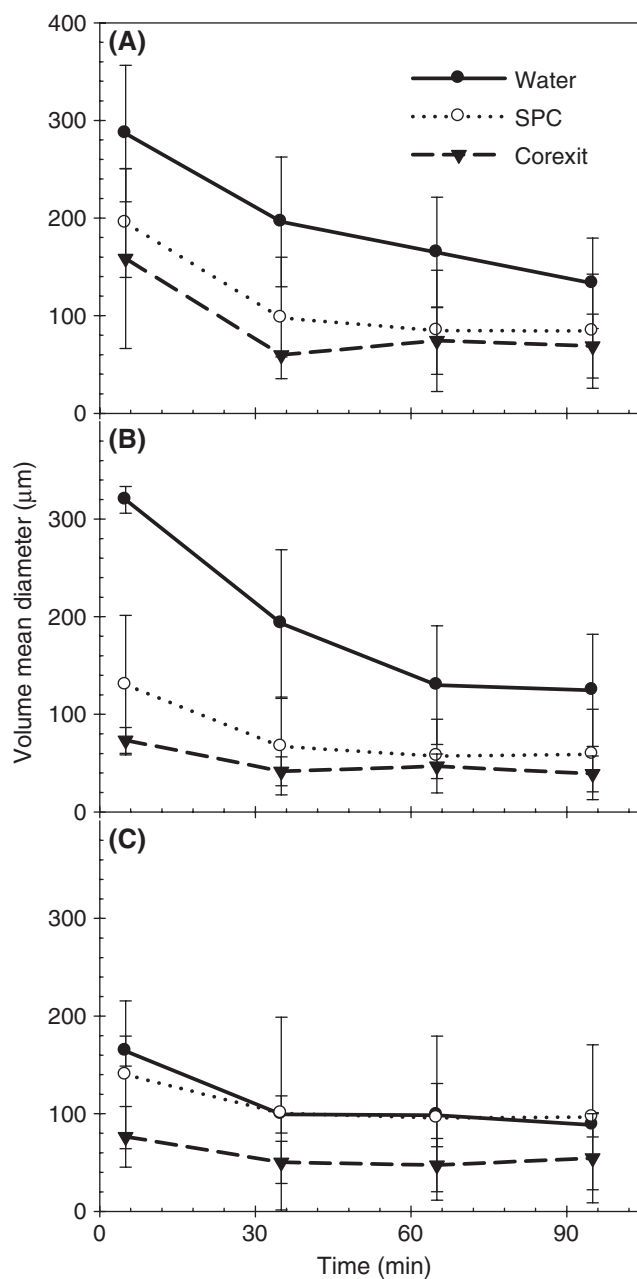


FIG. 6. Dispersed Alaska North Slope (ANS) oil droplet size (volume mean diameter) as a function of time under: (A) regular non-breaking, (B) spilling breaking, and (C) plunging breaking wave conditions.

distributions within a short period (~ 30 min), whereas physical dispersion took much longer to reach the ultimate droplet size distributions (Figs. 2–6 and Tables 2 and 3). Indeed, the oil dispersion kinetic rate coefficients of chemical dispersion are several-fold higher than physical dispersion (data not shown). In addition, the length of time required to disperse oil into relatively stable droplet size distributions, either in the presence or absence of chemical dispersants, is dependent on the system hydrodynamics, especially the intensity and frequency of occurrence of breaking waves. This is also related to the droplet population dynamics of the dispersed oil as a balance of breakup and coalescence kinetics.

TABLE 4. FACTORIAL ANALYSIS OF VARIANCE OF THE EFFECTS ON THE AVERAGE WATER COLUMN DISPERSED OIL DROPLET SIZES

	<i>Df</i>	<i>Sum of Sq</i>	<i>Mean Sq</i>	<i>F Value</i>	<i>Pr (F)</i>
Dispersant	2	915,915	45,7957.5	118.6329	<0.0001***
Oil	1	42	42.0	0.0109	0.9169
Wave	2	185,989	92,994.7	24.0901	<0.0001***
Depth	2	1,124	561.8	0.1455	0.8650
Time	3	338,033	112,677.7	29.1889	<0.0001***
Dispersant : Oil	2	75,480	37,740.2	9.7765	0.0001***
Dispersant : Wave	4	84,215	21,053.8	5.4539	0.0003***
Oil : Wave	2	28,265	14,132.4	3.6610	0.0265*
Dispersant : Depth	4	12,944	3,235.9	0.8383	0.5014
Oil : Depth	2	5,011	2,505.5	0.6491	0.5231
Wave : Depth	4	18,572	4,643.0	1.2028	0.3089
Dispersant : Time	6	47,433	7,905.6	2.0479	0.0582
Oil : Time	3	1,777	592.5	0.1535	0.9274
Wave : Time	6	47,863	7,977.1	2.0665	0.0560
Depth : Time	6	51,246	8,541.0	2.2125	0.0409*
Dispersant : Oil : Wave	4	306,795	76,698.9	19.8687	<0.0001***
Dispersant : Oil : Depth	4	20,321	5,080.3	1.3160	0.2631
Dispersant : Wave : Depth	8	25,722	3,215.3	0.8329	0.5739
Oil : Wave : Depth	4	10,791	2,697.8	0.6989	0.5931
Dispersant : Oil : Time	6	10,436	1,739.3	0.4506	0.8446
Dispersant : Wave : Time	12	29,459	2,455.0	0.6359	0.8117
Oil : Wave : Time	6	1,642	273.7	0.0709	0.9986
Dispersant : Depth : Time	12	15,634	1,302.8	0.3375	0.9820
Oil : Depth : Time	6	3,360	559.9	0.1450	0.9900
Wave : Depth : Time	12	9,548	795.7	0.2061	0.9982
Dispersant : Oil : Wave : Depth	8	11,042	1,380.3	0.3576	0.9422
Dispersant : Oil : Wave : Time	12	19,691	1,640.9	0.4251	0.9535
Dispersant : Oil : Depth : Time	12	6,975	581.3	0.1506	0.9996
Dispersant : Wave : Depth : Time	24	45,060	1,877.5	0.4864	0.9820
Oil : Wave : Depth : Time	12	17,553	1,462.8	0.3789	0.9707
Dispersant : Oil : Wave : Depth : Time	24	20,595	858.1	0.2223	1.0000
Residuals	432	1,667,645	3,860.3		

Statistically significant factors determined by more rigorous Bonferroni-adjusted level, $p < 0.0016$ are flagged with ***. Significant factors determined by less strict level, $p < 0.05$, are labeled with *.

TABLE 5. TUKEY'S PAIRED COMPARISON OF THE DIFFERENT EFFECTS BETWEEN TREATMENT LEVELS ON THE AVERAGE DISPERSED OIL DROPLET SIZE IN THE WATER COLUMN

<i>Factor</i>	<i>Level mean (µm)</i>	<i>Difference estimates</i>	<i>Standard error</i>	<i>Lower limit</i>	<i>Upper limit</i>
Dispersant	Water 152.9	Corexit – SPC = –54.9*	5.98	–69.0	–40.9
	Corexit 61.4	Corexit – Water = –91.5*	5.98	–106.0	–77.4
	SPC 116.3	SPC – Water = –36.6*	5.98	–50.6	–22.5
Wave	Regular 121.9	Plunger – Regular = –35.7*	5.98	–49.7	–21.6
	Spiller 122.4	Plunger – Spiller = –36.2*	5.98	–50.3	–22.2
	Plunger 86.2	Spiller – Regular = 0.566	5.98	–14.6	13.5
Time ^a	P1 148.5	P2 – P1 = –41.9*	6.9	–59.7	–24.1
	P2 106.6	P3 – P1 = –53.5*	6.9	–71.3	–35.7
	P3 94.9	P4 – P1 = –57.7*	6.9	–75.5	–39.9
	P4 90.8	P3 – P2 = –11.7	6.9	–29.5	6.2
		P4 – P2 = –15.8	6.9	–33.6	2.0
Depth	Surface 112.0	Middle – Surface = –3.00	5.98	–17.1	11.1
	Middle 109.0	Bottom – Surface = –2.53	5.98	–16.6	11.5
	Bottom 109.5	Bottom – Middle = 0.47	5.98	–13.6	14.5
Oil	MESA 109.9	ANS – MESA = 0.51	4.88	–9.1	10.1
	ANS 110.4				

^aTime factor is expressed as P1, P2, P3, or P4 to denote the first, second, third, and fourth half-an-hour of measurement period. Within the same time period, the measurements in the middle and the bottom of the tank are 10 and 20 min later than those at the surface, respectively. Significant differences are flagged by * based on 95% simultaneous confidence intervals for specified linear combinations.

A previous wave tank study conducted with less frequently occurring plunging breaking waves with lower wave energies (Li *et al.*, 2008) showed that active breakup of oil into smaller droplets continued beyond 1 h.

The significant factors affecting the average VMD are in good agreement with those having significant effects on dispersant effectiveness that has been evaluated by measurement of the dispersed oil concentration in the water column (Li *et al.*, accepted). For instance, the effects of Corexit 9500 and SPC 1000 on reducing the average VMD from 153 to 61 (or by 92) and 116 (or by 37) μm , respectively, were correspondingly correlated with their significant effects on increasing the dispersant effectiveness by 48 and 26%, respectively. The significant effect of the plunging breaking wave conditions on reducing the average VMD from 122 to 86 (or by 36) μm matched the significant effect of increasing the dispersant effectiveness by 25%. In addition, dispersion time was found to significantly decrease the average VMD from 148 to 106 (or by 42) μm and increase the dispersant effectiveness by 18% during the first 30 min of dispersion. Such good correlation can be explained by the enhanced dispersant effectiveness by dispersants and breaking waves through increasing the fraction of droplets that are more "permanently" dispersed (e.g., $<70 \mu\text{m}$) in the water column (Tables 2 and 3). Although reduction of oil-water interfacial tension by chemical dispersants allows for turbulent shears to form droplets on the order of 10 μm , the plunging breaking waves are associated with elevated energy dissipation rates and a lower Kolmogorov scale that reduces the droplet sizes.

Conclusions

Understanding *in situ* dispersed oil droplet size distribution has significant implications in optimizing dispersant effectiveness testing protocols in systems ranging from small-scale laboratory testing apparatuses to large-scale field trials. This research has identified several significant factors that determine the *in situ* dispersed oil droplet size distributions during dispersant effectiveness testing in an experimental wave tank. The type of chemical dispersant used is the most important factor in controlling the dispersed oil droplet size distributions. Application of dispersant generates a large number of small droplets and reduces the average droplet size. The tested oil-based dispersant Corexit 9500 was apparently more efficient in reducing oil droplet size than the tested water-based dispersant SPC 1000 for the two tested oil types in the batch wave tank testing system. Wave conditions also significantly influence the dispersed oil droplet size distributions, with the experimental plunging breaking waves generating the smallest oil droplets. The data linking dispersant effectiveness and droplet size distributions with the wave mixing energy conditions can provide valuable information to support the formulation of the operational guidelines for dispersant use. These results are also useful for modeling transport, persistence and potentially biological effects of dispersed oil in the aquatic environment.

Acknowledgments

This research was funded by the Program of Energy Research and Development (PERD), U.S. EPA (contract No. 68-C-00-159), and NOAA/UNH Coastal Response Research Center (NOAA Grant Number: NA04NOS4190063 UNH

Agreement No. 06-085). The authors thank Susan Cobanli, Rod Doane, Paul Kepkay, Xiaowei Ma, Brian Robinson, Peter Thamer, and William Yeung for their contributions and logistical support. The findings and opinions expressed in this report are those of the authors and do not necessarily reflect those of the funding agencies.

Author Disclosure Statement

The authors declare that no conflicting financial interests exist.

References

- ASTM. (2002). *American Society for Testing and Materials. F2059-00 Standard Test Method for Laboratory Oil Spill Dispersant Effectiveness Using the Swirling Flask*. ASTM 11.04. West Conshohocken, PA: ASTM, p. 1536.
- Byford, D.C., Laskey, P.R., and Lewis, A. (1984). Effect of low temperature and varying energy input on the droplet size distribution of oils treated with dispersants. *The 7th Annual Arctic and Marine Oilspill Program (AMOP) Technical Seminar*, Ottawa, ON, Canada, p. 208.
- Chandrasekar, S., Sorial, G.A., and Weaver, J.W. (2005). Dispersant effectiveness on three oils under various simulated environmental conditions. *Environ. Eng. Sci.* 22, 324.
- Chapman, H., Purnell, K., Law, R.J., and Kirby, M.F. (2007). The use of chemical dispersants to combat oil spills at sea: A review of practice and research needs in Europe. *Marine Pollut. Bull.* 54, 827.
- Delvigne, G.A.L., and Sweeney, C.E. (1988). Natural dispersion of oil. *Oil Chem. Pollut.* 4, 281.
- Drennan, W.M., Donelan, M.A., Terray, E.A., and Katsaros, K.B. (1996). Oceanic turbulence dissipation measurements in SWADE. *J. Phys. Oceanogr.* 26, 808.
- Fingas, M. (2005). *Stability and Resurfacing of Dispersed Oil*. Prepared for Prince William Sound Regional Citizens' Advisory Council (PWSRCAC). Fredericton, Canada: Environmental Technology Center, Environment Canada.
- Fingas, M.F., Debra, L.M., White, B., Stoodley, R.G., and Crerar, I.D. (1989). Laboratory testing of dispersant effectiveness: The importance of oil-to-water ratio and settling time. *1989 Oil Spill Conference*, San Antonio, TX, p. 365.
- Fingas, M.F., Kyle, D., and Tennyson, E. (1995). Dispersant effectiveness: studies into the causes of effectiveness variations. In P. Lane, Ed., *The Use of Chemicals in Oil Spill Response, ASTM STP 1252*. Philadelphia, PA: American Society for Testing and Materials, p. 92.
- Fingas, M.F., Sigouin, L., Wang, Z., and Thouin, G. (2002). Resurfacing of oil with time in the swirling flask. *The 25th Arctic and Marine Oil Spill Program (AMOP) Technical Seminar*, p. 773.
- ITOPF. (2005). *The Use of Chemical Dispersants to Treat Oil Spills*. London: The International Tanker Owners Pollution Federation Limited, Technical information paper. No. 4, p. 1.
- Jasper, W.L., Kim, T.L., and Wilson, M.P. (1978). Droplet size distributions in a treated oil-water system. In: L.T.J. McCarthy, G.P. Lindblom, and H.F. Walter, Eds., *Chemical Dispersants for the Control of Oil Spills, ASTM STP 659*. Philadelphia, PA: American Society for Testing and Materials, p. 203.
- Kirby, M.F., and Law, R.J. (2008). Oil spill treatment products approval: The UK approach and potential application to the Gulf region. *Marine Pollut. Bull.* 56, 1243.

- Kresta, S.M., and Wood, P.E. (1993). The flow field produced by a pitched blade turbine: Characterization of the turbulence and estimation of the dissipation. *Chem Eng Sci* 48, 1761.
- Lessard, R.R., and Demarco, G. (2000). The significance of oil spill dispersants. *Spill Sci. Technol. Bull.* 6, 59.
- Lewis, A., Byford, D.C., and Laskey, P.R. (1985). The significance of dispersed oil droplet size in determining dispersant effectiveness under various conditions. *International Oil Spill Conference*.
- Li, M., and Garrett, C. (1998). The relationship between oil droplet size and upper ocean turbulence. *Marine Pollut. Bull.* 36, 961.
- Li, Z., Lee, K., King, T., Boufadel, M.C., and Venosa, A.D. (2008). Assessment of chemical dispersant effectiveness in a wave tank under regular non-breaking and breaking wave conditions. *Marine Pollut. Bull.* 56, 903.
- Li, Z., Lee, K., King, T., Kepkay, P., Boufadel, M.C., and Venosa, A.D. (2009). Evaluating chemical dispersant efficacy in an experimental wave tank: 1, dispersant effectiveness as a function of energy dissipation rate. *Environ. Eng. Sci.* 26, 1139.
- Lunel, T. (1993). Dispersion: Oil droplet size measurement at sea. In: *Proceedings of the Sixteenth Arctic and Marine Oil Spill Program (AMOP) Technical Seminar*, Calgary, Alberta, Canada. Ottawa: Environment Canada, p. 1023.
- Lunel, T. (1995). Understanding the mechanism of dispersion through oil droplet size measurements at sea. In P. Lane, Ed., *The Use of Chemicals in Oil Spill Response, ASTM STP 1252*. Philadelphia, PA: American Society for Testing and Materials, p. 240.
- Ma, X., Cogswell, A., Li, Z., and Lee, K. (2008). Particle size analysis of dispersed oil and oil-mineral aggregates with an automated ultraviolet epi-fluorescence microscopy system. *Environ. Technol.* 29, 739.
- Mendenhall, W., Scheaffer, R.L., and Wackerly, D.D. (1981). *Mathematical Statistics with Applications*. Boston, MA: Duxbury Press.
- NRC. (1989). *National Research Council: Using Oil Spill Dispersant on the Sea*. Washington, DC: National Academies Press.
- NRC. (2005). *National Research Council: Understanding Oil Spill Dispersants: Efficacy and Effects*. Washington, DC: National Academies Press.
- Sanchez, M.C., Berjano, M., Guerrero, A., and Gallegos, C. (2001). Emulsification rheokinetics of nonionic surfactant-stabilized oil-in-water emulsions. *Langmuir* 17, 5410.
- Shaw, J.M. (2003). A microscopic view of oil slick break-up and emulsion formation in breaking waves. *Spill Sci. Technol. Bull.* 8, 491.
- Sorial, G.A., Venosa, A.D., Koran, K.M., Holder, E., and King, D.W. (2004). Oil spill dispersant effectiveness protocol. I: Impact of operational variables. *J. Environ. Eng. ASCE*, 130, 1073.
- Sterling, M.C., Bonner, J.S., Ernest, A.N.S., Page, C.A., and Autenrieth, R.L. (2004). Chemical dispersant effectiveness testing: influence of droplet coalescence. *Marine Pollut. Bull.* 48, 969.
- Terray, E.A., Donelan, M.A., Agrawal, Y.C., Drennan, W.M., Kahma, K.K., Williams, A.J., Hwang, P.A., and Kitaigorodskii, S.A. (1996). Estimates of kinetic energy dissipation under breaking waves. *J. Phys. Oceanogr.* 26, 792.
- Tkalich, P., and Chan, E.S. (2002). Vertical mixing of oil droplets by breaking waves. *Marine Pollut. Bull.* 44, 1219.
- U.S. EPA. (1996). *Swirling Flask Dispersant Effectiveness Test. Title 40 code of federal regulations, part 300, Appendix C*. Naragansett, RI: U.S. EPA, p. 245.
- Venosa, A.D., King, D.W., and Sorial, G.A. (2002). The baffled flask test for dispersant effectiveness: A round robin evaluation of reproducibility and repeatability. *Spill Sci. Technol. Bull.* 7, 299.
- Wickley-Olsen, E., Boufadel, M.C., King, T., Li, Z., Lee, K., and Venosa, A.D. (2008). Regular and breaking waves in wave tank for dispersion effectiveness testing. *2008 International Oil Spill Conference*, Savannah, GA, p. 499.