

## Assessment of chemical dispersant effectiveness in a wave tank under regular non-breaking and breaking wave conditions

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### Abstract

Current chemical dispersant effectiveness tests for product selection are commonly performed with bench-scale testing apparatus. However, for the assessment of oil dispersant effectiveness under real sea state conditions, test protocols are required to have hydrodynamic conditions closer to the natural environment, including transport and dilution effects. To achieve this goal, Fisheries and Oceans Canada and the US Environmental Protection Agency (EPA) designed and constructed a wave tank system to study chemical dispersant effectiveness under controlled mixing energy conditions (regular non-breaking, spilling breaking, and plunging breaking waves). Quantification of oil dispersant effectiveness was based on observed changes in dispersed oil concentrations and oil-droplet size distribution. The study results quantitatively demonstrated that total dispersed oil concentration and breakup kinetics of oil droplets in the water column were strongly dependent on the presence of chemical dispersants and the influence of breaking waves. These data on the effectiveness of dispersants as a function of sea state will have significant implications in the drafting of future operational guidelines for dispersant use at sea. © 2008 Elsevier Ltd. All rights reserved.

**Keywords:** Oil spill; Droplet size distribution; Energy dissipation rate; Breaking waves; Dispersants

### 1. Introduction

Oil spills in the open ocean are subjected to natural dispersion processes where wave action results in the formation of oil-in-water emulsions of small oil droplets that are eventually diluted to concentrations below toxic threshold limits (Lee, 2002; Li and Garrett, 1998; Shaw, 2003; Tkalic and Chan, 2002). Breaking waves, in particular, play a crucial role in the dispersion of an oil slick by generating velocity shear to break up and transport oil in their turbulent flows (Li and Garrett, 1998; Shaw, 2003; Tkalic and Chan, 2002). The dispersion of oil slicks is significantly enhanced in the presence of chemical dispersants, which reduce the interfacial tension between oil and water (Lesard and Demarco, 2000). With the development of new

formulations that are less toxic and more effective for the treatment of viscous oils, the application of chemical dispersants has recently gained popularity as one of the primary oil spill countermeasures for reducing the overall adverse impact of marine oil spills on the environment (NRC, 1989, 2005). In addition to operational convenience, the application of dispersants to oil slicks on the sea surface minimizes the harmful effects of floating oil on aquatic wildlife such as birds and marine mammals that frequent the water surface, and potentially mitigates the risk of oil slicks contaminating coastal and shoreline environments (NRC, 2005).

Oil dispersion effectiveness depends on the chemical properties of both dispersant and oil and on various environmental factors (Fingas, 2000; NRC, 2005). Standardized bench-scale tests are frequently conducted to evaluate the effectiveness of particular chemical oil dispersants (References in NRC, 2005) to provide data for product selection. However, in the context of actual at sea

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operations, the utility of these tests is limited due primarily to failure to account for the transport and dilution effect in the water column (NRC, 2005). During the physical and chemical dispersion of oil spills, the initial break-up and submergence of a surface oil slick (as well as the secondary break-up of the oil into smaller droplets) depends on the turbulent structures, which also play an important role in the vertical transport of oil droplets in the water column. To overcome the restrictions inherent in bench-scale tests, larger facilities are required to enable a more comprehensive evaluation of chemical dispersant effectiveness under a more realistic setting. In this context, DFO's Center for Offshore Oil and Gas Environmental Research (COOGER) and US EPA's National Risk Management Research Laboratory designed and constructed a wave tank facility (NRC, 2005) to conduct research on the effects of wave-energy on the efficacy of chemical dispersants on crude oils under a range of controlled regular wave and breaking wave hydrodynamic regimes. To achieve this goal, it is important to characterize the hydrodynamics of different wave conditions. Friction associated with velocity shear causes the dissipation of kinetic energy of the fluid, resulting in a temporal and spatial variation of the energy dissipation rate per unit mass of water ( $\epsilon$ , in watts/kg or  $\text{m}^2/\text{s}^3$ ). The operational hypothesis is that  $\epsilon$  plays a major role in the effectiveness of a dispersant, and hence it may serve as an important scalable parameter to characterize chemical dispersant effectiveness under different wave-energy conditions in the field.

To evaluate dispersant effectiveness as a function of  $\epsilon$  in our experimental wave tank, experiments were conducted over three different energy dissipation rates (a regular non-breaking wave and two breaking waves) similar to those found in the open sea (Delvigne and Sweeney, 1988).

## 2. Materials and methods

### 2.1. Wave tank facility

Fig. 1 is a schematic representation of the first version of the wave tank facility located at the Bedford Institute of Oceanography (Dartmouth, NS) with geometric dimensions of 16 m long, 0.6 m wide, and 2 m high (it has subsequently been doubled in length to enable more energetic waves and to reduce wave interference from the end of

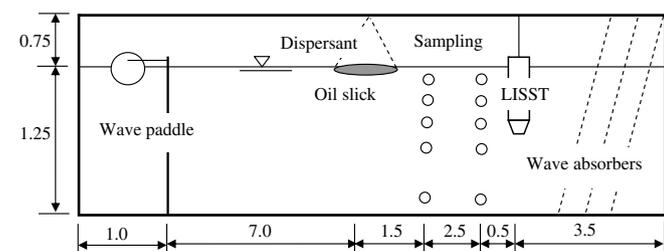


Fig. 1. Schematic representation (all dimensions in m) of the wave tank facility. Note the sampling sites were 1.5 m and 4.0 m downstream from oil, respectively.

the tank). The water depth during the experiments was maintained at 1.25 m. Different waves are generated by a computer-controlled flap-type wave maker situated at one end of the tank linked to an adjustable cam that controlled its stroke length to alter wave-height characteristics. This type of wave generator produces “deep water” waves, which occur when the ratio of water depth to wave length is greater than 0.5 (Dean and Dalrymple, 1984). The wave frequency (and thus the wavelength) is controlled by the rotational speed of the cam. The computer-controlled wave-generator can produce both regular non-breaking waves and breaking waves with designated length, height, and frequency. The system is useful for dispersion studies because recurrent breaking of waves can be generated reproducibly at the same location. This is accomplished using the frequency sweep technique, wherein a wave of one frequency is superimposed on another wave of a different frequency, causing the wave to increase in height until it eventually breaks.

The energy dissipation rate per unit mass ( $\epsilon$ ) was used to characterize the intensity of the breaker. It was evaluated by the correlation function method (Kaku et al., 2006b) using a time series of velocity measurements at select locations in the tank. These measurements were obtained by an Acoustic Doppler Velocimeter (SonTec/YSI, Inc. San Diego, CA).

### 2.2. Experimental procedures

The effects of mixing energy and the presence of a dispersant on dispersion of crude oil were investigated using a representative crude oil and a reference dispersant under three different mixing energy conditions. The experimental design was a two-factor mixed-level full factorial design. The test oil was MESA crude oil (Petro-Canada, Montreal, QC) with an API (American Petroleum Institute) gravity of 29.7°; the oil was artificially weathered by aeration to 86.2% of original weight. Corexit EC9500A (Nalco Energy Service, L.P. Sugar Land, TX), a commercially available product frequently stockpiled for use by oil spill response agencies in Canada and the United States, was used as the reference oil dispersant. For each run, 150 ml of weathered MESA crude oil was first released onto the seawater surface in the middle of the tank within a rigid square frame (30 cm × 40 cm and 30 cm high) constructed of oleophobic material. Dispersant (or seawater for the control) was immediately sprayed onto the oil slick at a dispersant-to-oil ratio (DOR) of 1:25 through a 0.635-mm nozzle. The frame was promptly removed from the water immediately (within less than one second) prior to the incoming breaking wave (or regular wave). Samples were taken from the tank at two horizontal locations ( $L = 1.5$  and 4 m downstream from oil application), five depths (5, 20, 40, 60, and 110 cm from the surface), and four time points (1, 10, 30, and 60 min). Dispersant effectiveness was determined by comparing control (water alone) to experimental (dispersant) runs. Evidence for enhanced oil dispersion

included deeper penetration of dispersed oil into the water column and the formation of smaller oil droplets.

### 2.3. Analytical methods for measuring dispersed oil concentration

Dispersed oil in aqueous samples was extracted with dichloromethane (DCM) according to EPA Method 3510 C (liquid–liquid partitioning) and measured with a Genesys 20 ultraviolet–visible spectrophotometer (Thermo Fisher Scientific; Calgary, Canada) following an established protocol (Chandrasekar et al., 2005; Venosa et al., 2002). Standard solutions of oil for calibration were prepared with the oil and dispersant (or oil alone for the control) for each particular set of experimental runs. A stock solution of dispersant–oil mixture (or oil alone for the control) was prepared by adding 800  $\mu\text{l}$  of the dispersant to 2 ml of oil and then brought up to a final volume of 20 ml with DCM. An eight-point calibration curve was prepared from serial volumetric dilutions of the stock solution, generating the following working standards: 15, 25, 50, 100, 250, 500, 1000, and 2500  $\text{mg l}^{-1}$ . The samples collected from the wave tank were transferred to a 125 ml separatory funnel and extracted three times with 40 ml fresh DCM. Sample volumes were measured using a graduated cylinder that was pre-calibrated by mass. The extracts were then adjusted to a final volume of 10 ml and transferred to a graduated 15-ml glass tube with a Teflon-lined screw cap. The vials were stored at 4 °C prior to analysis. Extracts were analyzed for absorbance at three different wavelengths: 340, 370, and 400 nm. The area was determined by applying the trapezoidal rule according to the equation

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

The concentration of oil in the extract was determined by

$$C_{\text{DCM}} \text{ (mg/l)} = \left( \frac{\text{Area}}{\text{Slope of Calibration Curve}} \right) \quad (2)$$

The concentration of the sample that was collected from the wave tank was calculated by

$$C_{\text{sample}} \text{ (mg/l)} = \frac{C_{\text{DCM}} \times V_{\text{DCM}}}{V_{\text{sample}}} \quad (3)$$

Oil-droplet size distribution in the wave tank was determined with a Type C LISST-100X particle counter (Sequoia Sci. Inc., Seattle, WA). This instrument is frequently used by geologists to measure the particle size distribution of suspended particulates (Gartner et al., 2001; Serra et al., 2002; Traykovski et al., 1999) and has been applied to determine the droplet size distribution of dispersed oil (Sterling et al., 2004, 2003). There are 32 particle size intervals logarithmically placed from 2.5–500  $\mu\text{m}$  in diameter, with the upper size in each bin 1.18 times the lower. Particle size distribution is expressed as the average volumetric concentration of oil droplets within each interval of the size range.

In this study, the LISST-100X was situated in the wave tank 4.5 m downstream from the center of the oil application area with the detection windows 0.6 m from the surface of the water. It was operated in real time mode so that the dynamic oil-droplet size distribution as a function of time was acquired every 3 s. To compare the effects of  $\varepsilon$  and the presence of dispersant on the droplet size distribution, a mass mean diameters (MMD) of the measured droplet size distribution was calculated as a function of time. The MMD is a weighted average droplet size by mass or volumetric fraction

$$\text{MMD} = \frac{\sum m_i \cdot d_i}{M}, \quad (4)$$

where  $M$  is total mass or volume concentration, and  $m_i$  is mass or volume concentration of oil droplets in a size interval of average size  $d_i$ .

### 2.4. Oil droplet breakup kinetic model

The droplet size distribution and its rate of evolution are determined by the process of breakage and coalescence (Baldyga and Podgorska, 1998). In our system, we deal with a diluted dispersed phase (crude oil), and hence it is legitimate to neglect the re-coalescence of the dispersed oil droplets. The kinetics of oil dispersion in regard to oil droplet breakup can be described by a modified semi-empirical model based on the assumption that oil droplet breakage rate is proportional to the generalized Weber number defined by Hinze (1955). The droplet breakage rate is inversely proportional to dispersion time (Polat et al., 1999)

$$\frac{dD}{dt} = -k' \left( \frac{\tau D}{\gamma} \right) \cdot \frac{1}{t}, \quad (5)$$

where  $D$  is the mass mean diameter of droplet size (instead of mass median diameter that was used by Polat et al. (1999)) at time  $t$ ;  $\tau$  is the external stress (force per unit area) at time  $t$ ;  $\gamma$  is the oil and water interfacial tension; and  $k'$  is the rate constant. Assuming that  $\tau$  can be replaced with a time-averaged stress per unit mass (Tatterson, 1991),  $k'$ ,  $\tau$ , and  $\gamma$  can be collected as a new dimensionless rate constant  $k$  and Eq. (5) can be integrated to give:

$$\text{Ln}(D_t) = \text{Ln}(D_1) - k \text{Ln}(t) \quad (6)$$

where  $D_1$  is the mass mean diameter of droplet size distribution at 1 min. Parameter estimation was conducted by forcing an equal value of  $D_1$  for all treatment conditions and performing a linear least-squares regression of the sum of residuals. Forcing an equal  $D_1$  for each treatment is a reasonable assumption considering that oil dispersion starts with a floating oil slick, and the measured initial size distribution has a similar MMD at the initial readings. Eq. (6) was fit to observed data from  $t = 1.0$  to  $t = 60$  min. MMD at  $t = 60$  min ( $D_{60}$ ) were computed to compare the treatment effects on the extent of oil dispersion into droplets.

## 2.5. Statistical data analysis

The effects of the presence/absence of chemical dispersant and  $\varepsilon$  under regular waves, spilling breakers, and plunging breakers on the effectiveness of oil dispersion (as measured by the integrated dispersed oil concentration in the water column) were investigated using a two-factor analysis of variance (ANOVA). A two-way ANOVA was also used to determine the effects of presence/absence of chemical dispersant and mixing turbulence under the three wave conditions on the dispersed oil-droplet size distribution and dispersion kinetics. When significant differences were identified, the least-significant difference (LSD) test was conducted to determine which treatments significantly affected the oil dispersion effectiveness as determined by the criteria of dispersed oil concentration and droplet size distribution.

## 3. Results

### 3.1. Characterization of energy levels

The average energy dissipation rate ( $\varepsilon$ ) of the regular non-breaking wave with a constant frequency of 0.4 Hz and a wave height of about 6 cm was computed to be  $0.0005 \text{ watts kg}^{-1}$  within a depth of 10–40 cm from the sur-

face. The spilling breakers were created by generating alternating trains of high frequency waves (1.0 Hz, wave height 8 cm, duration 20 s) and low frequency waves (0.4 Hz, wave height 4 cm, duration 20 s). The plunging breaking waves were produced similarly, where the high frequency waves had a wave height of 12 cm and the low frequency waves 6 cm. The average energy dissipation rates at the surface were approximately 0.02 and 0.05 watts/kg for the spillers and the plungers, respectively. The  $\varepsilon$  of the two breaking wave types decayed almost exponentially as a function of depth to approximately 0.001 watts/kg at the 40 cm depth. Details of the wave tank hydrodynamic characterization have been reported elsewhere (Wickley-Olsen et al., 2007).

### 3.2. Dispersed oil concentration as a function of energy dissipation rate

The dispersed oil concentrations at two locations downstream from the oil addition in the presence and absence of chemical dispersant were plotted as a function of depth and time. The results are shown in Figs. 2–4.

Under the regular non-breaking wave conditions, the oil was transported as a non-dispersed surface slick to the end of the tank within 5 min, and the surface slick was persistent for the remainder of the experiment. The oil concen-

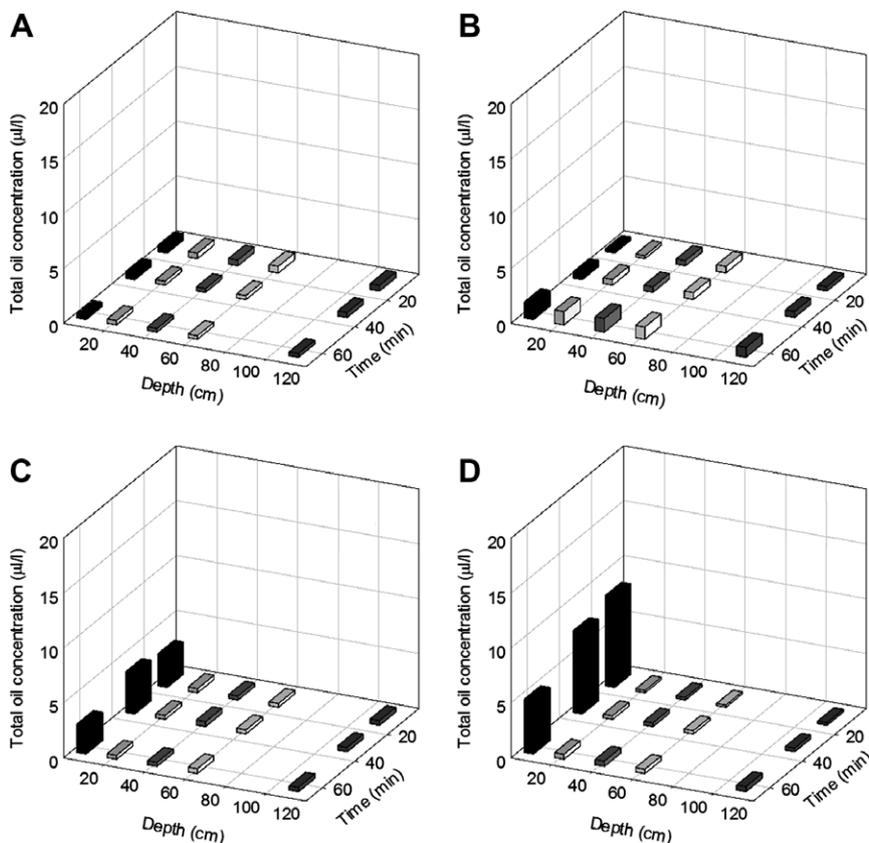


Fig. 2. Dispersed oil concentration as a function of time and space in the presence and absence of dispersant under regular non-breaking waves: (A) 1.5-m downstream, no dispersant; (B) 1.5-m downstream, with dispersant; (C) 4.0-m downstream, no dispersant; and (D) 4.0-m downstream, with dispersant.

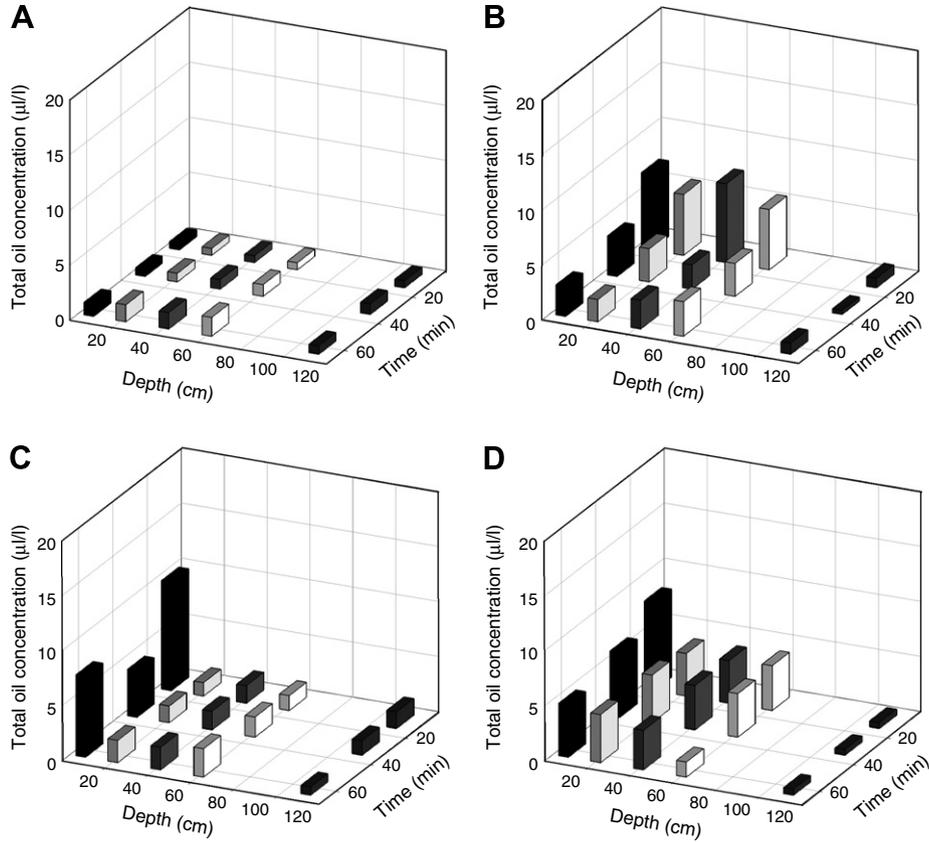


Fig. 3. Dispersed oil concentration as a function of time and space under spilling breaking waves: (A) 1.5-m downstream, no dispersant; (B) 1.5-m downstream, with dispersant; (C) 4.0-m downstream, no dispersant; and (D) 4.0-m downstream, with dispersant.

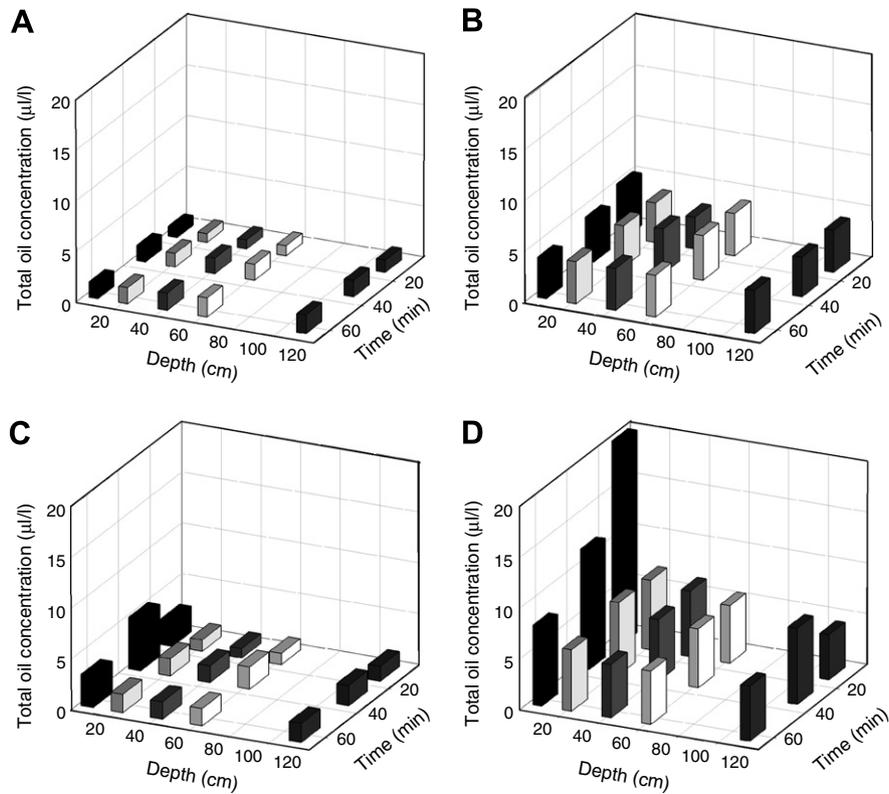


Fig. 4. Dispersed oil concentration as a function of time and space under plunging breaking waves: (A) 1.5-m downstream, no dispersant; (B) 1.5-m downstream, with dispersant; (C) 4.0-m downstream, no dispersant; and (D) 4.0-m downstream, with dispersant.

trations in the water column were consistently less than 1 mg/l at the 1.5-m (Fig. 2A) and 4-m (Fig. 2C) sampling locations downstream, except that the near-surface oil concentration was more than 2.5 mg/l at the 4-m sampling site (Fig. 2C). This indicates that natural oil dispersion was limited under non-breaking wave conditions. The presence of chemical dispersant increased oil concentrations in the water column at 1.5 m downstream (Fig. 2B) and at the surface at 4 m downstream (Fig. 2D). The surface spreading of oil was enhanced by the effect of chemical dispersant. However, the concentrations of oil in the bulk aqueous phase were always less than 1 mg/l. These results indicate that at an  $\varepsilon$  of 0.0005 watts/kg, very little dispersion occurs at any depth below the surface, and application of dispersants under calm seas is likely to be ineffective at these low mixing energies.

The spilling breakers increased the surface  $\varepsilon$  by an order of magnitude and thereby increased the dispersed oil concentrations in the water column (Fig. 3). In the absence of dispersant, the concentrations of the dispersed oil increased gradually over time in the upper portion (in samples taken from depths equal to 20, 40, and 60 cm of the water column), but were still small (Figs. 3A and C). Similar to the regular wave condition, the near-surface oil concentrations at 4 m downstream were much higher in the absence of dispersant, suggesting weak dispersion. The dispersion of oil into the water column was enhanced by the presence of dispersant at this wave condition (Figs. 3B and D): the initial oil concentration was the highest at the surface and decreased to a constant level after 30 min at 1.5 m downstream. The oil concentrations at 4 m downstream were evenly distributed over time and approached approximately 5 mg/l, equivalent to approximately 50% of the nominal oil concentration that would occur if one assumed all the oil was dispersed uniformly throughout the tank. Regardless of the increased oil concentration at the upper portion of the water column, the oil concentrations near the bottom were still low due to the insufficient penetration depth of the dispersed oil.

The plunging breakers increased the energy dissipation rate by half-an-order of magnitude in comparison to the spilling breaking waves, resulting in an increased penetration depth of oil (Fig. 4). Natural dispersion under the plunging breakers slightly increased the dispersed oil concentrations in the bulk aqueous phase (Figs. 4A and C). The presence of dispersant dramatically increased the effectiveness of oil dispersion as illustrated by higher concentrations of oil over the entire depth at both the 1.5-m and 4-m downstream locations (Figs. 4B and D).

The effects of energy dissipation rate and the presence of dispersant on oil dispersion effectiveness are summarized in Table 1 by the intrusion depths and bulk oil concentrations in the water column. A two-way analysis of variance (ANOVA) indicated no significant interaction between wave condition and dispersant on penetration depth ( $p = 0.43$ ). Waves significantly affected intrusion depth of dispersed oil ( $p = 1.34 \times 10^{-10}$ ), and the dispersant did

Table 1  
Summary of intrusion depth and bulk water column oil concentration<sup>a</sup>

Wave	Dispersant <sup>b</sup>	Intrusion (cm) <sup>c</sup>	Oil concentration (mg/l) <sup>d</sup>
Regular non-breaking	-D	3 ± 3 (A)	0.64 ± 0.30 (A)
	+D	14 ± 18 (A)	0.67 ± 0.32 (A)
Spilling breaking	-D	82 ± 32 (B)	2.14 ± 0.68 (B)
	+D	60 ± 0 (B)	3.06 ± 1.46 (B)
Plunging breaking	-D	110 ± 0 (C)	2.60 ± 0.82 (B)
	+D	110 ± 0 (C)	4.71 ± 0.46 (C)

<sup>a</sup> Data reported as the average ± one standard deviation of independent duplicate runs; letters in parentheses indicate whether the differences between each pair of treatments are statistically significant.

<sup>b</sup> Dispersant conditions: “-D”, absence of dispersant; “+D”, presence of dispersant.

<sup>c</sup> The intrusion depth was determined by the average depth from the surface of water at which the measured oil concentration was  $\geq 1$  mg/l (approximately 10% of the nominal oil concentration for a uniform distribution of oil in the water).

<sup>d</sup> The average concentrations at a depth of 60 cm from the surface of the water samples collected from both 1.5 m and 4.0 m downstream of the duplicate runs.

not have a significant effect on intrusion depth ( $p = 0.83$ ) compared to no dispersant. A further least-significant difference test (LSD) revealed that the intrusion depth of oil was strongly correlated to the energy dissipation rate. The two-way ANOVA was also used to analyze wave and dispersant effects on the bulk water column oil concentrations on the average depth of the tank (60 cm). Similar to the oil intrusion depth, there was no significant interaction between wave and dispersant ( $p = 0.09$ ), but both wave condition ( $p = 4.3 \times 10^{-7}$ ) and the presence of dispersant ( $p = 0.0044$ ) significantly increased bulk oil concentrations in the water column. The LSD test indicated that breaking waves significantly increased dispersed oil concentration (with and without chemical dispersants), and plunging breaking waves plus dispersant resulted in the highest oil concentration in the water column (Table 1).

### 3.3. Dispersed oil-droplet size distribution as a function of energy dissipation rate

The particle size distributions from the LISST generally fit a lognormal distribution. The dispersed oil-droplet size distributions expressed as mass mean diameter (MMD) under three different wave conditions in the presence and absence of chemical dispersant were plotted as a function of time. The results are shown in Figs. 5–7; also shown are the best-fits of data using the kinetic expression of Eq. (6).

Under the regular non-breaking waves, the dispersed oil-droplet sizes were always greater than 200  $\mu\text{m}$  (MMD) in the absence of chemical dispersant (Fig. 5A), and the presence of dispersant dramatically reduced the droplet size especially after 30 min dispersion (Fig. 5B). The relatively high variability of MMD under regular non-breaking wave conditions was likely due to droplet entrainment and resurfacing of the oil. Because of the relatively large droplet size,

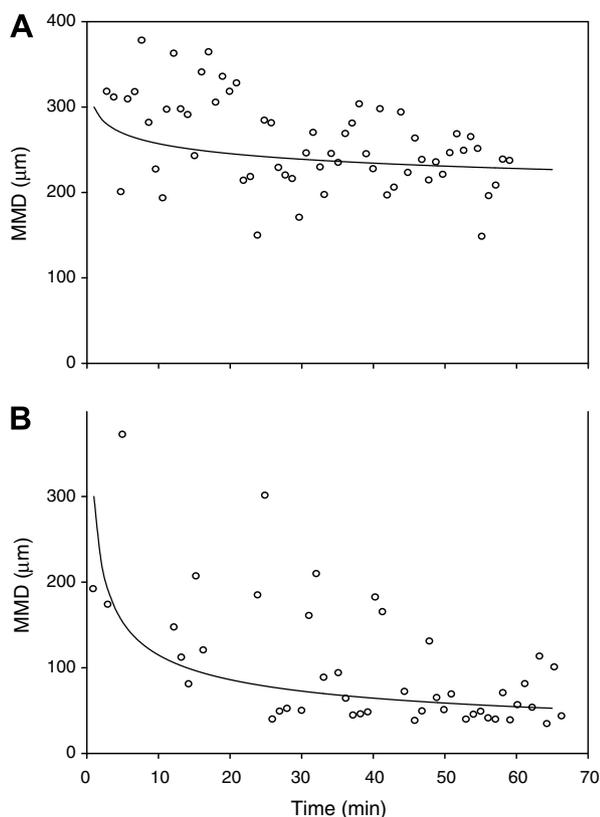


Fig. 5. Dispersed oil-droplet size as a function of time in the absence (A) and presence (B) of dispersant under regular non-breaking waves. The symbols are experimental data and the lines are modeling regression of Eq. (6).

especially in the absence of chemical dispersants, buoyant oil particles tend to resurface, and hence overall dispersion effectiveness is relatively low.

The spilling breaking waves dispersed the oil slick into smaller droplets. Although MMDs lower than  $50\ \mu\text{m}$  were occasionally measured within the first 10 min, relatively stable droplet size distributions were detected after 30 min. The droplet MMD after 60 min was lower than  $100\ \mu\text{m}$  in the absence of dispersant (Fig. 6A) and lower than  $50\ \mu\text{m}$  in the presence of dispersant (Fig. 6B).

The plunging breakers dispersed the oil into smaller droplet sizes similar to the spilling breaking waves, but variability was much lower (Fig. 7).

The presence of an effective chemical dispersant reduced the average dispersed oil-droplet size, especially at lower mixing energies. The average oil-droplet sizes observed in this study under non-breaking waves were within a range of  $200\text{--}300\ \mu\text{m}$ ; the presence of chemical dispersant reduced the oil-droplet size distribution by a factor of 5 to about  $50\ \mu\text{m}$ . Under breaking waves, however, the difference in oil-droplet size distribution in the presence and absence of dispersant was less pronounced, where the terminal oil-droplet sizes were considerably reduced compared to regular wave conditions without dispersant.

A two-way ANOVA was conducted to analyze the factorial effects on the terminal dispersed droplet size distribu-

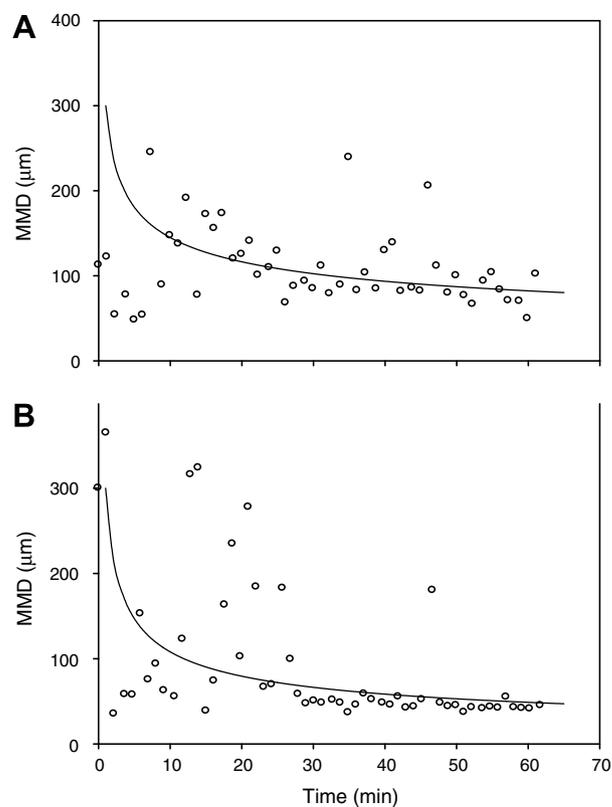


Fig. 6. Dispersed oil-droplet size as a function of time in the absence (A) and presence (B) of dispersant under spilling breaking waves. The symbols are experimental data and the lines are modeling regression of Eq. (6).

tion and oil dispersion kinetics. The results reported in Table 2 indicate a significant ( $p = 0.002$ ) interaction between wave conditions and chemical dispersants on droplet size distribution; the presence of chemical dispersant main effect ( $p = 0.0002$ ) and the wave-energy main effect ( $p = 0.002$ ) also significantly affected the dispersed droplet size distribution. The ANOVA of the factorial effects on the kinetic rate constant of the dispersion process indicates significant interactions between wave and dispersant ( $p = 0.008$ ) and that the presence of chemical dispersant significantly increased the kinetic rate constant ( $p = 0.01$ ). Variations of  $\varepsilon$  also significantly affected the rate constant ( $p = 0.0003$ ), indicating that wave conditions were critical in the oil breakup kinetics. The LSD test indicated no significant differences between the two breaking wave conditions on kinetic rate coefficients or terminal dispersed oil-droplet size (Table 2). However, due to deeper penetration of oil in the water column, plunging waves were still more effective in oil dispersion.

#### 4. Discussion

Mixing energy at the ocean surface, in particular, the energy of the breaking waves, plays an important role in the dispersion of oil slicks (Delvigne and Sweeney, 1988; Hinze, 1955; Li and Garrett, 1998; Shaw, 2003). The energy dissipation rate per unit mass of water is related to the

energy of micro-turbulence eddies and has been proposed as a parameter that can be scaled from laboratory to the field, based on the conservation of energy in studies of chemical dispersant effectiveness (Kaku et al., 2006a,b; Venosa et al., 2005). The energy levels of the different waves that were studied in our wave tank system covered the range of energy conditions typically observed in the field. Terray et al. (1996) reported  $\varepsilon$  to vary between  $10^{-5}$  and  $10^{-2}$  watts/kg at a wave height of about 0.25 m in Lake Ontario. Drennan et al. (1996) conducted similar measurements in the Atlantic Ocean off the Maryland coast and found  $\varepsilon$  to vary between  $1 \times 10^{-4}$  and  $5 \times 10^{-4}$  watts/kg at wave heights of 1 m. The highest energy dissipation rate of the plunging breaking waves generated in our system was near the lower end of the breaking wave-energy dissipation level reported in the field (Delvigne and Sweeney, 1988; Drennan et al., 1996; Terray et al., 1996), whereas the values for regular waves were similar to those found on the sea surface layer (Delvigne and Sweeney, 1988).

The results from the oil dispersion experiments support our hypothesis that the dispersed oil concentration is strongly dependent on  $\varepsilon$  (Table 1). A nonlinear regression of the bulk water column oil concentration ( $C$ ) with  $\varepsilon$  reveals a strong correlation following the empirical expression

$$C_{-D} = 7.61 * \varepsilon^{0.32} \quad (R^2 = 0.95) \quad (7)$$

in the absence of chemical dispersant, and

$$C_{+D} = 19.21 * \varepsilon^{0.43} \quad (R^2 = 0.98) \quad (8)$$

in the presence of dispersant. These expressions are consistent with the empirical relationship between oil entrainment ( $Q$ ) and wave-energy per unit surface area  $D_{ba}$  ( $J/m^2$ ) as  $Q-D_{ba}^{0.57}$  as reported by Delvigne and Sweeney (1988). The observed significant effect of chemical dispersant and mixing energy on the increased oil concentration in the water column was consistent with the chemical dispersant effectiveness tests that were conducted in bench-scale flask tests (Chandrasekar et al., 2005; Sorial et al., 2004). The effect of mixing energy on total dispersed oil concentration was also in agreement with the observation of field trials under low and high energy regime caused by various wind effects (Lunel et al., 1995). The field hydrodynamic parameters such as wave height and wave frequency as well as velocity gradients are readily measurable to obtain energy dissipation rates. Based on this quantitative hydrodynamic information, together with readily measurable oil physical and chemical characteristics (e.g. viscosity and interfacial tension), it is possible to predict the oil dispersability and the chemical dispersant effectiveness under given wave conditions.

The observed dependence of oil-droplet size distributions on energy dissipation rates and chemical dispersants in this study is consistent with other reports (Byford et al., 1984; Jasper et al., 1978; Lunel, 1995). Different kinetic mechanisms for droplet formation have been pro-

posed by a number of authors (Delvigne and Sweeney, 1988; Li and Garrett, 1998; Lunel, 1993, 1995). Lunel (1995), in particular, proposed that droplets are initially generated in several areas of different microscale turbulence, but eventually all the droplets pass through the area of smallest microscale turbulence so that droplet size becomes much smaller over time. Our observation agreed with Lunel's (1995) mechanism that more than 50% of the final dispersed concentration was transferred from the surface oil slick to the bulk aqueous phase within 10 min (Figs. 2–4), whereas further dispersion of oil into smaller droplets continued after an hour (Figs. 5–7).

In this study, the kinetics of oil droplet formation have been described reasonably well by the semi-empirical rate expression that was developed in a baffled agitated vessel (Polat et al., 1999), and the effects of mixing energy and chemical dispersant on the rate and extent of breakup of oil are clearly identified (Table 2). The small rate constant ( $k$ ) under regular waves in the absence of dispersants indicates that microscale turbulence is limited so that oil dispersion is ineffective and slow, but the rate coefficients were significantly increased under spilling and plunging breaking wave conditions, suggesting that the elevated energy dissipation rates accelerated the breakup of oil droplets (Figs. 5–7; Table 2). The effects of chemical dispersant on oil dispersion kinetics are also evident in the dispersion kinetic rate coefficients and the terminal particle size distributions (Table 2). It is expected that large  $\varepsilon$  affects the breakup of oil droplets through its impact on the Kolmogorov scale,  $\eta$  (Kolmogorov, 1949), which is an estimate of the smallest eddy that exists prior to dissipation by viscous friction. Under regular non-breaking wave conditions, the  $\eta$  is approximately 200  $\mu\text{m}$ , which is the same level as the observed terminal mass mean diameter of the oil droplets in the absence of dispersants. Under the spilling and breaking waves the  $\eta$  was reduced to about 100 and 70  $\mu\text{m}$ , respectively, consistent with the observed level of oil-droplet sizes. Clearly, the chemical dispersant changed the surface properties of oil, and hence the droplets were much smaller. Indeed, a large number of dispersed oil droplets of size ranging from 1.0 to 2.5  $\mu\text{m}$  were observed with an epifluorescence microscopic system equipped with motorized stage and image processing software. Since the lower detection limit of the type C LISST-100X particle counter used in this research was 2.5  $\mu\text{m}$ , the exact size of the smallest droplets that were generated in the wave tank systems cannot be determined.

## 5. Conclusions

This research has demonstrated the feasibility of conducting chemical dispersant effectiveness tests in a meso-scale wave tank facility under a range of controlled wave conditions. The hydrodynamic experiments have shown that the regular waves and breaking waves generated in the wave tank have similar energy dissipation rates reported in open seas. This quantitative oil dispersant

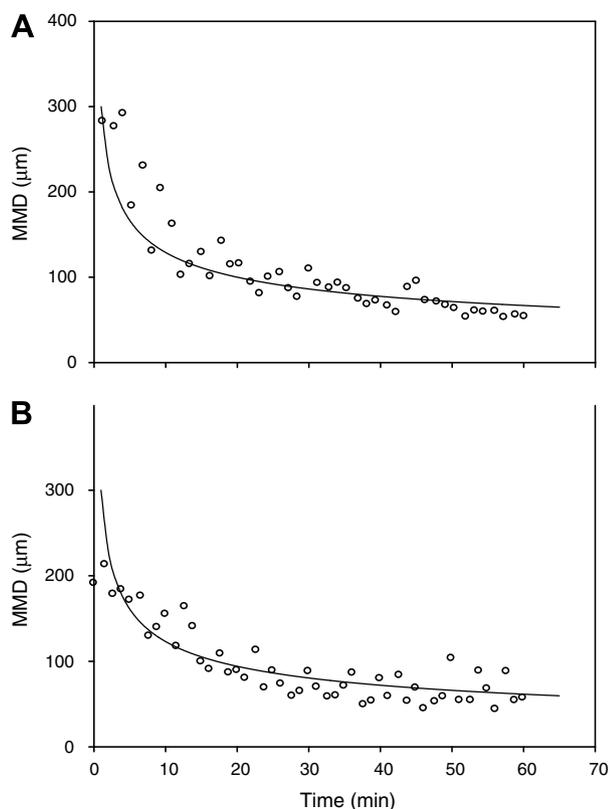


Fig. 7. Dispersed oil-droplet size as a function of time in the absence (A) and presence (B) of dispersant under plunging breaking waves. The symbols are experimental data and the lines are modeling regression of Eq. (6).

Table 2  
Best-fit parameters for oil-droplet size as a function of time [Eq. (6)]. Data shown in Figs. 5–7

Wave	Dispersant <sup>a</sup>	$k^b$	$D_{60}$ ( $\mu\text{m}$ ) <sup>b</sup>
Regular non-breaking	–D	$0.049 \pm 0.026$ (A)	$246 \pm 26$ (A)
	+D	$0.427 \pm 0.015$ (C)	$52 \pm 3$ (C)
Spilling breaking	–D	$0.310 \pm 0.009$ (B)	$85 \pm 3$ (B)
	+D	$0.450 \pm 0.010$ (C)	$47 \pm 2$ (C)
Plunging breaking	–D	$0.293 \pm 0.104$ (B)	$95 \pm 39$ (B)
	+D	$0.374 \pm 0.018$ (C)	$65 \pm 5$ (C)

<sup>a</sup> Dispersant conditions: “–D”, absence of dispersant; “+D”, presence of dispersant.

<sup>b</sup> Model parameters (rate constant  $k$  and average dispersed drop size  $D_{60}$ ) reported as the average  $\pm$  one standard deviation of independent duplicate runs; letters in parentheses indicate whether the differences between each pair of treatment conditions are statistically significant.

effectiveness study has provided a comprehensive data set describing dispersed oil concentrations and dispersed oil-droplet size distributions under different wave conditions. Our findings suggest that dispersant effectiveness is directly related to energy dissipation rates of waves. Breaking waves provide orders-of-magnitude higher energy dissipation rates than regular non-breaking waves. Thus, better effectiveness of oil dispersion can be achieved under conditions that increase  $\epsilon$ , namely breaking waves. Enhancement

of total dispersed oil concentrations by chemical oil dispersants is dependent on the mixing energy state at sea; applying chemical dispersant under regular non-breaking wave conditions or quiescent sea states will not be nearly as effective as under breaking wave conditions. In almost all circumstances, the application of the chemical dispersant significantly stimulated the oil breakup kinetics, which in turn, enhanced overall dispersant effectiveness, particularly in breaking wave conditions.

The data presented here are useful in predicting chemical dispersant effectiveness in different sea mixing conditions. Correlation between total dispersed oil and oil-droplet size distribution with waves at sea may also have significance in assessing the potential biodegradation kinetics and toxicological impact of physically and chemically dispersed oil at sea. Although this research presents a typical range of mixing energies and their effect on the dispersion of oil, more studies are warranted to investigate the influence of various crude oils and dispersant formulations on dispersant effectiveness as a function of energy dissipation rates. Recently, our wave tank facility has been upgraded by extending the length from 16 m to 32 m to simulate more energetic breakers and create higher energy dissipation rates, and incorporating a flow-through system in addition to batch mode to simulate commonly encountered wave- and current- driven oceanographic conditions. Additional experimental studies are being conducted in the upgraded system. In addition, modeling of oil drop breakage in wave- and current-induced intermittent turbulence with computational fluid mechanics approach is currently being pursued to account for the effect of scale of the system on the break-up process including determining the stable and transient size of drops and the break-up rates.

With favorable results from net-benefit analysis during recent spill response operations, chemical oil dispersant use is expected to rise. The application of chemical oil dispersants must now be considered a component within future integrated ecosystem management plans. To fulfill this need, it is required to have additional knowledge on the effects of mixing energy and chemical dispersants on the transport (dispersion), fate (persistence) and effects (acute and chronic toxicity) of dispersed oil in the water column.

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