

## **A Wave Tank Facility to Assess Chemical Oil Dispersant Effectiveness as a Function of Energy Dissipation Rate**

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### **Abstract**

A wave tank facility was constructed at the Bedford Institute of Oceanography (Dartmouth, NS, Canada), stemming from cooperation between the Center for Offshore Oil and Gas Environmental Research (COOGER) of Fisheries and Oceans Canada and United States Environmental Protection Agency (EPA) Oil Program, to quantify the effects of wave-energy on the efficacy of chemical dispersants on crude oils. A wide variety of energy dissipation rates (0.001 to 0.5  $\text{m}^2 \cdot \text{s}^{-3}$ ) representative of natural sea surface layer and breaking-wave energies were produced in the experimental wave tank through sequential generation of waves of designated length, height and frequency. Effectiveness of chemical dispersant was quantified by the measurement of dispersed oil concentration and oil-droplet size distribution. A correlation was established between the energy dissipation rate and oil dispersion efficacy of chemical dispersant. The effect of dispersant on re-coalescing kinetics of the dispersed oil was also investigated. The results indicated that chemical dispersant significantly reduced the average oil drop size; the elevated energy dissipation rate promoted the penetration of oil into bulk aqueous phase; and the presence of dispersant dramatically influenced the coalescence kinetics of dispersed oil under variant hydrodynamic conditions.

*Keywords:* energy dissipation rate, breaking-wave, dispersant efficacy, crude oil, oil dispersants

### **Introduction**

The application of chemical dispersants is considered to be one of the primary oil spill countermeasure for reducing the overall environmental impact of marine oil spills ( NRC 1989; Lessard and Demarco 2000; NRC 2005). In addition to operational convenience, application of dispersants to treat oil slicks on the sea surface has advantages to minimize the harmful effect of floating oil on animals such as birds and marine mammals that frequent the water surface, and to reduce the risk of oil slicks contaminating coastal and/or shoreline

environments.

Dispersants are chemicals that contain surfactants that reduce the surface tension between oil and water, resulting in the formation of oil droplets (oil-in-water emulsion). The dispersion of oil slicks is significantly enhanced in the presence of waves. Waves provide mixing energy, which breaks the surface oil film and propels oil droplets in the water column. Thus, in the context of oil spill response operations, dispersion is a physical-chemical process, whose effectiveness depends on the chemical properties of both dispersant and the oil and the mixing energy generated by the physical action of waves (Fingas 2000; NRC 2005). The hydrodynamic behavior may dramatically influence natural and chemical dispersion of oil (Delvigne and Sweeney 1988; Shaw 2003). In particular, breaking waves play a crucial role in the mixing of oil and dispersant and hence the dispersion of an oil slick (Shaw 2003). Breaking of waves occurs when the forward horizontal velocity of water in a wave crest is greater than the wave propagation speed. These waves cause velocity shear and hence result in the mixing of oil and dispersant. In turbulent flows, the velocity shear results from both spatial and temporal (turbulent) variation of velocities, but usually the turbulence contribution is dominant. Velocity shear with its associated friction also causes the dissipation of kinetic energy of the fluid. Of interest is the kinetic energy dissipation rate per unit mass,  $\epsilon$ , which varies both in time and space. One may use velocity measurements in a selected water body to compute the shear, and subsequently the energy dissipation rate.

The effectiveness of a particular dispersant is typically evaluated at various scales ranging from the smallest (5 cm, typical of the Baffled Flask Test in the laboratory) to the largest (10's to 100's meters, typical of field scale open water dispersion tests). In terms of product selection for spill response operations, standard laboratory assays for the evaluation of oil dispersant effectiveness such as the swirling flask test and the baffled flask test have limitations due to insufficient mixing energy and/or failure to account for the transport and interaction between oil and dispersant in water column (Sorial et al. 2004a; Sorial et al. 2004b; Venosa et al. 2002). Testing on the sea, however, is expensive and not always reproducible due to uncontrolled environmental variables, and hence unrealistic for routine testing of different dispersants on different oils. To address these concerns, a wave tank facility was constructed for evaluation of chemical oil dispersant effectiveness at intermediate or pilot scales.

The current hypothesis is that the energy dissipation rate per unit mass,  $\epsilon$ , plays a major role in the effectiveness of a dispersant. Conservation of  $\epsilon$  between the wave tank and actual field conditions provides support for the use of our test system to evaluate the operational effectiveness of chemical oil dispersants. Preliminary hydrodynamic tests have demonstrated that the non-breaking waves and breaking waves that were generated in our test tank facility were similar to the reported energy dissipation rates for natural waters (Delvigne and Sweeney 1988; Venosa et al. 2005).

In response to recent spills of heavy and/or waxy crude oils from accidental releases associated with marine transport and activities at offshore oil and gas production facilities, assessment of the effectiveness of new oil dispersant formulations against various types of oil is needed. The objective of this study is to illustrate the utility of a new wave-tank facility to investigate the effectiveness of oil dispersion by physical (natural) dispersion or chemical dispersion under a variety of non-breaking and breaking-wave energy conditions.

## Materials and Methods

### *Wave tank facilities*

Fig. 1 presents the schematic of the wave tank. The tank facility measures 16 meters long, 0.6 meter wide, and 2 meters high. The water depth during the present experiments was 1.25 m. Different waves can be generated by a paddle situated at one end of the tank linked to an adjustable cam that controls its stroke length to alter wave-height characteristics. The wave frequency (and subsequently wave length) is controlled by the rotation speed of the cam. The computer-controlled wave-generator is capable of producing both regular non-breaking waves and breaking waves with designated length, height and frequency. The system is very useful for dispersion studies because recurrent breaking of waves can be generated at the same location. This is done using the dispersive focusing technique in which a wave of one frequency is superimposed onto a wave of another frequency, causing the wave to break under different inertial forces. Calibration of non-breaking and breaking-wave energy was conducted using a scalable parameter, energy dissipation rate. The details of wave energy calibration have been reported elsewhere (Venosa et al. 2005).

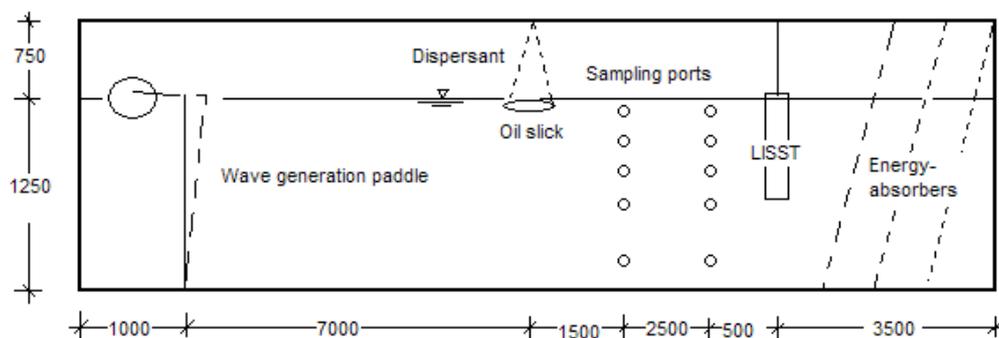


FIGURE 1: Schematic representation (all dimensions in mm) of the wave tank.

### *Experimental procedures*

In this preliminary study the effects of mixing energy and dispersant on dispersion of crude oil was investigated with a full factorial experimental design.

A variety of energy conditions, including a regular non-breaking wave ( $\epsilon = 0.001 \text{ m}^2 \cdot \text{s}^{-3}$ ), a minor breaking-wave ( $\epsilon = 0.05 \text{ m}^2 \cdot \text{s}^{-3}$ ), a medium breaking-wave ( $\epsilon = 0.1 \text{ m}^2 \cdot \text{s}^{-3}$ ), and a major breaking-wave ( $\epsilon = 0.5 \text{ m}^2 \cdot \text{s}^{-3}$ ), were considered. The reference test oil was MESA light crude oil from the Petro-Canada refinery in Montreal with an API gravity of 29.7 and flash point of 4 °C (weathered by aeration to 86.2% of original fresh weight). Corexit EC9500A (Nalco Energy Services, L. P., Sugar Land, TX) was used as the reference dispersant. For each run, 150 ml of weathered MESA oil was first released on the sea surface in the middle of the tank within a rigid square frame constructed of oleophobic material (30 cm long  $\times$  40 cm wide  $\times$  30 cm high). 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 nozzle connected to an electronic-valve. The frame was removed from the water immediately prior to the incoming breaking wave (or regular wave). Samples were taken from the tank at two horizontal locations, 1.5 and 4 m downstream of oil application, at five depths [5, 20, 40, 60, and 110 cm (under water)], and at four time points [1, 10, 30, and 60 min (after oil spike)]. Oil dispersion effectiveness was quantified by recording the intrusion depth of the dispersed and/or dissolved oil and measuring the dispersed oil-droplet size distribution. The intrusion depth of oil was determined by chemical analysis of oil concentration and verified by ultraviolet fluorescence (UVF, see below) measurements of the dispersed oil in bulk aqueous phase. The oil-droplet particle size distribution was measured *in situ* using a laser *in-situ* scattering and transmissometer (LISST Model 100X, see below).

In addition, the effect of chemical dispersant on the coalescence of the dispersed oil droplets was investigated in a separate experiment. For this purpose, high breaking-waves were initially applied for the first 3h, and then the mixing energy was removed from the wave tank to maintain a static hydrodynamics regime for the remainder of each experimental run of 24 hours. Time-series data for total volumetric oil concentrations were generated from *in situ* oil droplet measurements made by the LISST.

#### *Total petroleum hydrocarbons*

The dispersed oil in aqueous samples was extracted with dichloromethane and measured with a DU series 60 ultraviolet-visible spectrophotometer (Beckman Instruments, Inc., Fullerton, CA) capable of measuring absorbance at 340, 370, and 400 nm (Venosa et al. 2002).

The direct ultraviolet fluorescence spectroscopy was also applied to monitor the dispersed/dissolved oil in seawater using a method reported previously (Kepkay et al. 2002). Briefly, samples removed from the wave tank at specified times and locations were vigorously shaken by hand, and 3 ml of the suspension was rapidly transferred to an ultraviolet-grade methyl acrylate disposable cuvette (VWR International Inc., Mississauga, ON). The suspension was immediately scanned in the dissolved/dispersed fraction using a QM-1 spectrofluorometer

running FeliX software (PTI, Inc., Birmingham, NJ). The optimal excitation wavelength that produced the highest emission peaks was 320 nm. This wavelength with a slit width of  $\pm 2$  nm was used in all subsequent emission scans from 340 to 500 nm.

### *Particle size distribution*

Oil droplet size distribution inside the wave tank was determined by a Type C LISST-100X particle counter (Sequoia, Seattle, WA), which has 32 particle size intervals logarithmically spaced 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 falling into each interval of the size range. In general, the particle size distribution measured using LISST fits a lognormal distribution, which has been extensively used for measuring aerosol size distribution in natural environment (Hinds 1999). The LISST particle counter was situated in the wave tank 4.5 m downstream from the oil application area with the detection windows 0.6 meter under water; the LISST was operated in a real time mode for the dynamic oil droplet size distribution and total dispersed oil concentration was acquired about every 3 – 4 seconds.

Water samples were also collected from the 4-m downstream location of the wave tank at all five depths after 30 min for direct observation of dispersed oil droplets under transmitted light and UV-epifluorescence illumination (Lee et al., 1985) using a Leitz Orthoplan microscope equipped with a computer-controlled motorized stage. Photomicrographs of the naturally- and chemically-dispersed oil droplets were recorded at magnifications of 160 $\times$  or 400 $\times$  and quantified using image analysis software (Image-Pro5.0).

## **Results and Discussion**

### *Characterization of energy levels*

The energy dissipation rate per unit mass  $\varepsilon$  was evaluated by the correlation function method (Kaku *et al.*, 2006a, b) using time series of velocity measurements at select locations in the tank. These measurements were obtained by an Acoustic Doppler Velocimeter (ADV). While additional field studies are needed to fully quantify and define  $\varepsilon$ , at a significant wave height of about 0.25 m in Lake Ontario, Terray *et al.* (1996) reported  $\varepsilon$  to vary between  $10^{-5}$  and  $10^{-2} \text{ m}^2/\text{s}^3$ . Drennan *et al.* (1996) conducted similar measurements in the Atlantic Ocean off of the Maryland Coast. They found  $\varepsilon$  varying between  $10^{-4}$  and  $5.0 \times 10^{-4} \text{ m}^2/\text{s}^3$ . These values are smaller than those reported by Terray *et al.* despite the fact that the wave height (1 m) was four times larger. However, as discussed by Drennan *et al.* (1996), the measurements of Terray *et al.* were in strongly-forced fetch-limited waves, whereas those of Drennan *et al.* (1996) represent fully-developed sea with an almost infinite fetch (the Atlantic Ocean). Delvigne and Sweeney (1988) reported that  $\varepsilon$  varies between  $10^{-3}$  and  $10^{-2} \text{ m}^2/\text{s}^3$ .

for the surface layer and between 1 and 10  $\text{m}^2/\text{s}^3$  for breaking waves. However, they did not define the “surface layer” nor did they explain the type of wave breaker.

*The intrusion depth and the concentration of dispersed oil*

Natural rates of oil dispersion were extremely limited under non-breaking wave conditions, and the addition of chemical dispersant did not improve oil dispersion efficiency significantly. Results suggested that a certain level of mixing energy is required for dispersant to be effective and that the application of dispersant under calm sea conditions may not be effective.

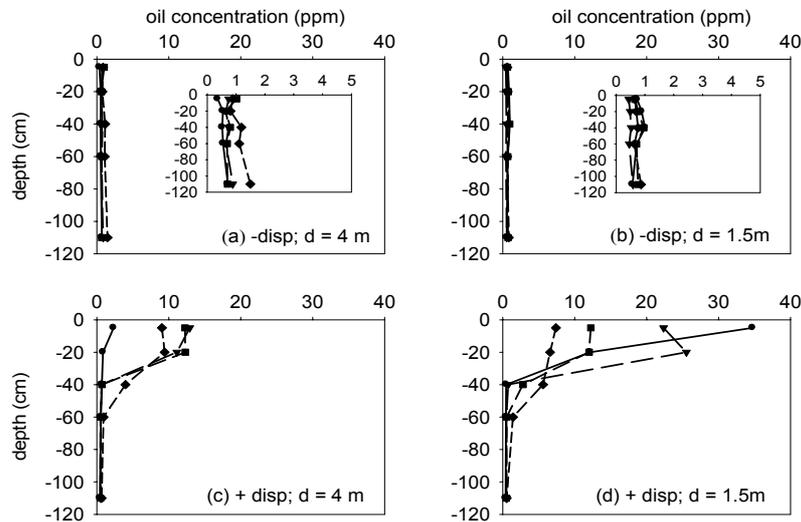


FIGURE 2: Temporal and spatial distribution of total petroleum hydrocarbon in the wave tank at low energy breaking wave (imbeds show same data but in larger scales). Upper panels (a, b) are in the absence of dispersant (- disp); lower panels (c, d) are in the presence of dispersant (+ disp); left panels (a, c) are from the 4 meter downstream location (d = 4 m); and right-panels (b, d) are from the 1.5 meter downstream location (d = 1.5 m). Symbols are: (●) t = 1 min, (▼) t = 10 min, (■) t = 30 min, and (◆) t = 60 min.

At low energy breaking-wave conditions, physical dispersion was still inefficient (Fig. 2 a,b). However, the effects of chemical dispersants were readily observed at the location closer to the mixing-zone (d = 1.5m); the intrusion depth of oil and the oil concentration near surface layer increased significantly (Fig 2: c, d). Due to the limitation of energy dissipation rate, the bulk aqueous phase oil

concentration was still relatively low. These results strongly suggest that effectiveness of oil dispersant is limited by energy condition.

Physical oil dispersion increased with the application of a medium-energy breaking-wave. Furthermore, the application of chemical dispersants increased oil droplet intrusion depth and overall oil concentrations in near surface waters.

Since the horizontal and vertical mixing were relatively strong at high energy breaking-wave, both physical and chemical dispersion became more efficient (Fig 3). Natural oil dispersion processes under high breaking-wave conditions increased dispersed oil concentrations in bulk aqueous phase (Fig 3: a, b). Chemical dispersant dramatically increased the effectiveness of oil dispersion under high energy dissipation rate conditions, as illustrated by the intrusion of higher concentrations of oil to a deeper depth at both horizontal sampling locations (Fig 3: c, d).

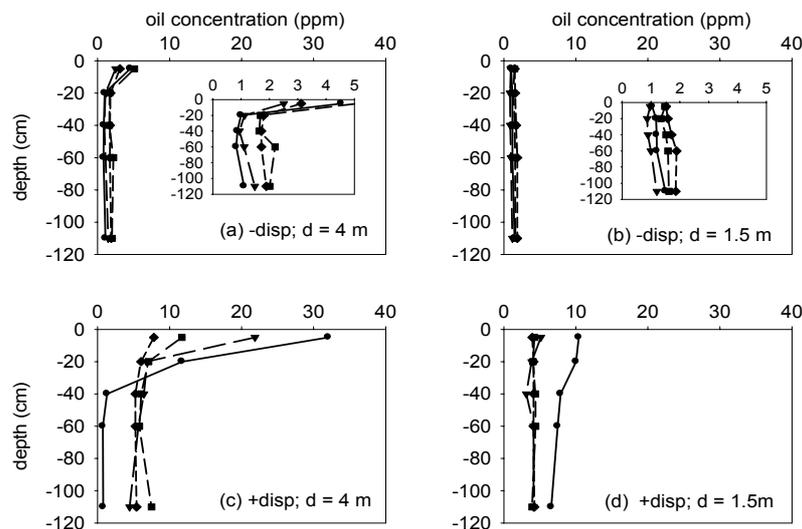


FIGURE 3: Temporal and spatial distribution of total petroleum hydrocarbon in the wave tank at high energy breaking wave (imbeds show same data but in larger scales). Legends are the same as in Fig. 2

Fig. 4 shows the correlation of intrusion depth (Fig. 4a) or bulk aqueous-phase oil concentration (Fig. 4b) as a function of energy dissipation energy after 1 hour physical and chemical dispersion. Clearly, intrusion depth of oil was proportional to mixing energy, and chemical dispersion always had deeper penetration depth than physical dispersion. Similarly, the average oil concentration in the bulk aqueous phase was proportional to the logarithm of energy dissipation rate, and chemical dispersion caused a bulk aqueous phase

concentration approximately 50% higher than that caused by physical dispersion.

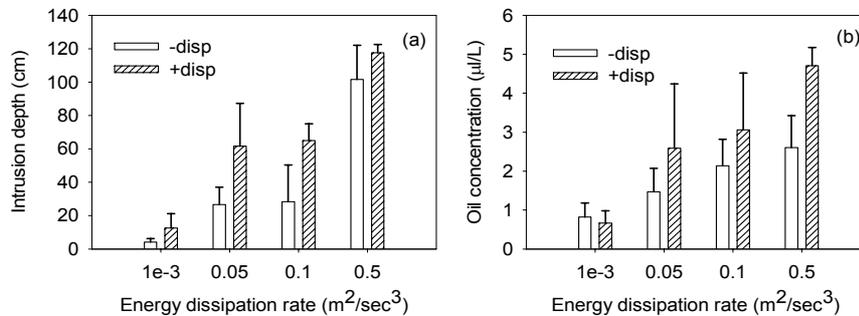


FIGURE 4: (a) Oil intrusion depth and (b) average oil concentration (0.6m underwater; results from chemistry analysis) as a function of energy dissipation rate.

#### *Oil-droplet size distribution of the dispersed oil*

In addition to intrusion depth and oil concentration, another important indicator of oil dispersion effectiveness is the dispersed oil-droplet size distribution. Fig. 5a and 5b shows the mass mean oil-droplet size and total volume concentration as a function of energy dissipation rate, respectively. The data set is the average of mass mean diameter from duplicate runs after one hour of physical or chemical dispersion. In the absence of dispersant, the mass mean diameters of the oil droplets were inversely proportional to the energy dissipation rates; the presence of chemical dispersant dramatically reduced the average droplet size even at the lowest mixing energy level (Fig. 5a). Conversely, the total oil concentrations were directly proportional to energy dissipation rate levels (Fig. 5b). This is consistent with the results obtained with chemical analysis. The presence of dispersant increased the total oil concentration at any given energy level compared to the absence of dispersant. Hence the LISST-100X measurements support the conclusion that dispersant treatment reduced the oil droplet size and energy dissipation rate correlated with concentration of dispersed oil.

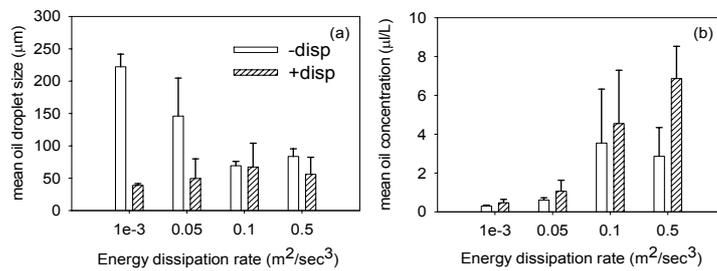


FIGURE 5: (a) Average mass mean diameter of oil-droplets and (b) average oil concentration (4.5 m downstream and 0.6m underwater results from LISST) as a function of energy dissipation rate.

Fig. 6 summarizes the oil droplet size distribution under high wave energy conditions in the absence (Fig. 6a) and presence (Fig. 6b) of chemical dispersant.

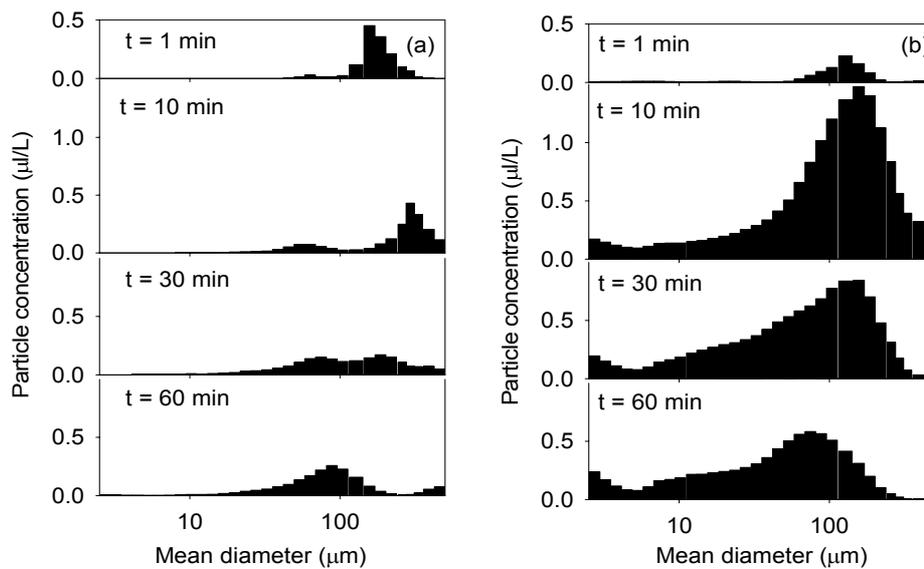


FIGURE 6: Oil droplet size distribution of (a) physically-dispersed oil and (b) chemically dispersed oil

Physical dispersion of oil occurred rapidly under high energy conditions (Fig. 6a). The total oil concentration was nearly 70% of the oil concentration at steady-state within the first minute. However, since the average oil-droplet size was  $>150 \mu\text{m}$ , it appears that dispersion of the oil into small droplets did not occur to any appreciable extent. As time progressed, further physical dispersion resulted in a reduced oil droplet size distribution and temporally uniform oil concentration. The final mean mass diameter of the dispersed oil was  $>100 \mu\text{m}$ , suggesting that natural dispersion of oil at this energy level was limited.

By influencing oil-water interfacial tension, chemical dispersants dramatically reduced the particle size distribution of oil droplets and increased their concentration in the water column (Fig. 6b). For example, after 1 h, the final oil concentration was approximately four-fold higher than that noted in the reference control run without dispersant additions.

### *Coalescence of the dispersed oil*

Oil dispersion is the net result of three separate processes: initial dispersion, subsequent transport into the water column, and coalescence of the oil droplets. Data presented above showed that chemical dispersants enhanced the dispersion process by promoting the intrusion depth of oil, increasing total dispersed oil concentration, and reducing the oil droplet size. The efficiency of the chemically enhanced crude oil dispersion is further dependent on the stability of the dispersed oil droplets in the water column to overcome resurfacing or re-coalescence.

Fig 7 shows the continuous total dispersed oil concentration in the absence (Fig. 7a) and presence (Fig. 7b) of chemical oil dispersants as a function of time. For the first 3 h, because of the continually-applied intermittent breaking-wave, dispersion of oil is a predominant phenomenon regardless of whether or not the dispersant was present. The presence of dispersant, however, increased the steady-state total dispersed oil concentration by nearly 3-fold (Fig. 7b).

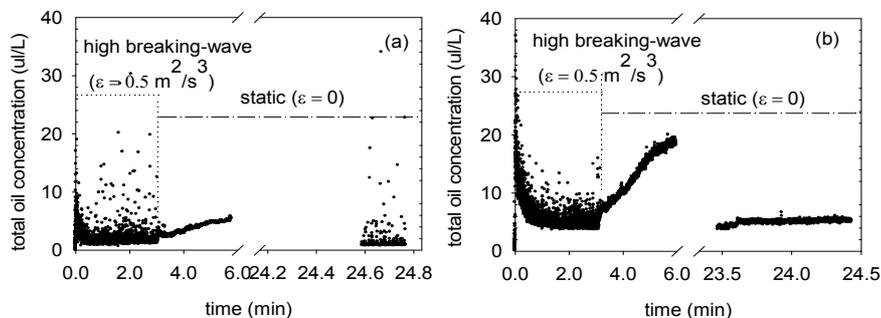


FIGURE 7: Total volume oil concentration from dispersion and coalescence of oil (a) in the absence of dispersant, and (b) in the presence of dispersant

After the wave maker was turned off and a static hydrodynamic regime was maintained for the wave tank, the total oil concentration measured from the LISST increased constantly for the next 3 hours, suggesting that resurfacing of the physically and chemically-dispersed oil was occurring. The oil concentrations in the chemically-dispersed oil were consistently more than three times higher than those in the physically-dispersed oil. After 20 h coalescence of the dispersed oil under static hydrodynamic regime, the final oil concentration for the physically-

dispersed oil declined to nearly 50% of the initial steady-state dispersed oil concentration, whereas the chemically-dispersed oil remained approximately the same as the initially dispersed oil concentration under rapid mixing condition. This suggests that that stability of the chemically-dispersed oil in water column is much higher than the physically-dispersed oil.

## Conclusions

The data reported in this paper support the following conclusions: First, oil dispersion effectiveness was correlated with energy dissipation rate. Elevated dissipation energy promotes the penetration of oil into the bulk aqueous phase. The presence of dispersant increased the dispersed oil concentration at the same energy levels. Second, chemical dispersant significantly reduced the oil droplet sizes, especially at low energy states. Third, re-coalescence prevailed at static conditions; and the stability of dispersed oil is significantly increased in the presence of dispersant.

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## References:

- Delvigne, G. A. L., and Sweeney, C. E. (1988). "Natural dispersion of oil." *Oil and Chemical Pollution*, 4(4), 281-310.
- Drennan, W. M., Donelan, M. A., Terray, E. A., and Katsaros, K. B., 1996, "Oceanic turbulence dissipation measurements in SWADE," *J. Physical Oceanography*, 26, pp. 808-815.
- Fingas, M. F. (2000). "Use of Surfactants for Environmental Applications." *Surfactants: Fundamentals and Applications to the Petroleum Industry*, L. L. Schramm, ed., Cambridge University Press, 461-539.
- Hinds, W. C. (1999). *Aerosol technology: Properties, behavior, and measurement of airborne particles*, John Willey & Sons, Inc, New York, NY.
- Kaku, V. J., M. C. Boufadel, and A. D. Venosa, Evaluation of mixing energy in laboratory flasks used for dispersant effectiveness testing, *J. of Environmental Engineering*, ASCE, 132(1), 93-101, 2006a.
- Kaku, V. J., M. C. Boufadel, A. D. Venosa, and J. Weaver, Hydrodynamics and energy dissipation in rotated flasks, *Environmental Fluid Mechanics*, accepted, 2006b.

- Kepkay, P. E., Bugden, J. B. C., Lee, K., and Stoffyn-Egli, P. (2002). "Application of ultraviolet fluorescence spectroscopy to monitor oil-mineral aggregate formation." *Spill Science & Technology Bulletin*, 8(1), 101-108.
- Lee, K., C.S. Wong, W.J. Cretney, F.A. Whitney, T.R. Parsons, C.M. Lalli and J. Wu (1985) Microbial response to crude oil and Corexit 9527: SEAFLEXES enclosure study. *Microbial Ecology* 11: 337-351.
- Lessard, R. R., and Demarco, G. (2000). "The significance of oil spill dispersants." *Spill Science & Technology Bulletin*, 6(1), 59-68.
- NRC. (1989). "Using oil spill dispersant on the sea. Report of the Committee on Effectiveness of Oil Spill Dispersants." National Research Council, Washington D.C.
- NRC. (2005). *National Research Council: Understanding Oil Spill Dispersants: Efficacy and Effects*, The National Academies Press, Washington, D.C.
- 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.
- Sorial, G. A., Venosa, A. D., Koran, K. M., Holder, E., and King, D. W. (2004a). "Oil spill dispersant effectiveness protocol. I: Impact of operational variables." *Journal of Environmental Engineering-Asce*, 130(10), 1073-1084.
- Sorial, G. A., Venosa, A. D., Koran, K. M., Holder, E., and King, D. W. (2004b). "Oil spill dispersant effectiveness protocol. II: Performance of revised protocol." *Journal of Environmental Engineering-Asce*, 130(10), 1085-1093.
- Terray, E. A., Donelan, M. A., Agrawal, Y. C., Drennan, W. M., Kahma, K. K., Williams III, A. J., Hwang, P. A., and Kitaigorodskii, S. A., 1996, "Estimates of kinetic energy dissipation under breaking waves," *J. Physical Oceanography*, 26, pp. 792-807.
- Venosa, A. D., Kaku, V. J., Boufadel, M. C., and Lee, K. "Measuring energy dissipation rates in a wave tank." *International Oil Spill Conference*, Miami, FL.
- 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 Science & Technology Bulletin*, 7(5-6), 299-308.