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# Application of entropy analysis of *in situ* droplet-size spectra in evaluation of oil chemical dispersion efficacy

Zhengkai Li<sup>a,\*</sup>, Kenneth Lee<sup>a</sup>, Thomas King<sup>a</sup>, Haibo Niu<sup>a</sup>, Michel C. Boufadel<sup>b</sup>, Albert D. Venosa<sup>c</sup>

<sup>a</sup> COOGER, Bedford Institute of Oceanography, Fisheries and Oceans Canada, 1 Challenger Drive, Dartmouth, NS, Canada B2Y 4A2
<sup>b</sup> Department of Civil and Environmental Engineering, Temple University, Philadelphia, PA 19122, USA
<sup>c</sup> National Risk Management Research Laboratory, US EPA, Cincinnati, OH 45268, USA

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#### ABSTRACT

*In situ* droplet-size distributions were measured using a laser *in situ* scattering and transmissiometry (LISST-100X) particle size analyzer during the evaluation of natural and chemical dispersion efficiency of crude oils under different wave and current conditions. An entropy grouping of the *in situ* dispersed oil droplet-size spectra has classified the multi-modal droplet-size distributions into different groups based on similar droplet-size spectra characteristics within groups and distinction between groups. A generalized linear logistic regression model was fitted to analyze the effects of a number of factors and their interactions on the grouping of oil droplet-size spectra. The grouped results corresponded to the oil dispersion efficiency at different levels. This new method for droplet-size distribution data analysis can have significant implication in field evaluation of natural and chemical dispersion efficiency of oil.

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#### 1. Introduction

Evaluation of natural and chemical dispersion efficiency of oil in the field is very important in the overall budget of the oil mass balance during an oil spill emergency response (Lehr et al., 2010; Schrope, 2010). An oil budget calculation estimates oil that may be amenable to response decisions as opposed to oil that has already been removed (such as in dissolution and evaporation), which may subsequently inform decisions in allocating resources in oil spill responses. In such practice, processes such as direct capture and *in situ* burning that are directly measured on scene have the smallest uncertainty, whereas dispersion efficiencies, which often have to be estimated based on laboratory test results and empirical experiences from past incidents, have the greatest uncertainty.

Understanding *in situ* dispersed oil droplet size distributions is very important for evaluating natural and chemical dispersion efficiency of oil. To understand the intrinsic mechanisms of oil dispersion efficiency, it is important to measure the dispersed oil droplet size distributions (Daling et al., 1990; Lewis et al., 1985; Lunel, 1995; NRC, 2005). *In-situ* dispersed oil droplet size distributions result from the interaction of different processes, including droplet formation and destruction by turbulent shear and size fractionation due to differential rise velocities (Baldyga and Podgorska, 1998; Li and Garrett, 1998; Lunel, 1995; Sterling et al., 2004). These processes are controlled by system hydrodynamics, environmental conditions, and the oil and dispersant characteristics. 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.

Dispersed oil droplet-size distributions are often reported as mean or median diameter and standard deviation in characterizing the central tendency of droplet size distributions, based on the assumption of normal or transformed normal distributions (Byford et al., 1984; Daling et al., 1990; Delvigne and Sweeney, 1988; Jasper et al., 1978; Lewis et al., 1985). However, when particles are present in multi-modal size distributions, parameters such as mean and median diameters can be incomplete and sometimes misleading in describing the shape of the size distribution spectrum, which often do not conform to the log-normal distribution mean and standard deviation measurements (Mikkelsen et al., 2007; Okada et al., 2009; Orpin and Kostylev, 2006; Stewart et al., 2009).

Entropy analysis, conversely, is a method for analyzing size distribution spectra that makes no assumptions about the underlying shape of the spectra. This concept originates from information theory (Shannon, 1948), which evaluates the randomness of an event or a signal, and then either assigns that signal to a group that contains similar signals or places it in a new group. The entropy analysis has been applied to sorting samples into self-similar groups by minimizing the amount of within-group variance





<sup>\*</sup> Corresponding author. Tel.: +1 902 426 3442; fax: +1 902 426 1440. *E-mail address:* Zhengkai.Li@dfo-mpo.gc.ca (Z. Li).

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through the testing for all possible groupings of samples. This method has been successfully used to discriminate geological facies (Forrest and Clark, 1989; Woolfe et al., 2000; Woolfe and Michibayashi, 1995), and to describe *in situ* suspended sediment grain size and seabed texture (Mikkelsen et al., 2007; Okada et al., 2009; Orpin and Kostylev, 2006; Stewart et al., 2009).

This paper reports characterization of the *in situ* droplet size distribution in testing of oil dispersion efficiency in an experimental flow-through wave tank. An entropy analysis of *in situ* droplet-size spectra has been applied to evaluate dispersion efficiency of oil. The grouping of size-distribution spectra into different groups has also been analyzed in response to a number of explanatory variables, including wave conditions, currents, oil type, and dispersant type, using a generalized linear logistic regression model to clarify significant factorial effects on *in situ* droplet-size spectra. The new method of information-theory-based droplet size spectra entropy analysis can be a useful operational tool during field evaluation of oil dispersion efficiency.

#### 2. Experimental

#### 2.1. Wave tank testing facility

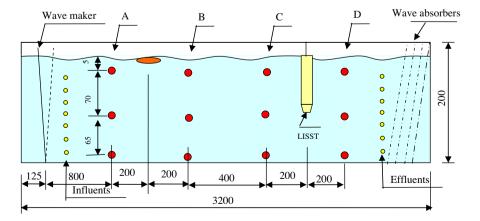
The experimental investigation of natural and chemical dispersion of oil was conducted in an experimental wave tank (Fig. 1). The average water depth was 1.50 m. Different regular and breaking waves were generated by a computer-controlled flap-type wave maker situated at one end of the tank, progressing toward the other end, where the extra energy was absorbed by perforated boards deployed in water. Two wave conditions, regular nonbreaking waves and plunging breaking waves, were used in this study. The breaking waves were generated using the frequency sweep technique (Funke and Mansard, 1979), wherein a wave of one frequency is superimposed on another wave of a different frequency, causing the wave to increase in height until it breaks. A uniform current  $(3.8 \pm 0.2 \text{ L s}^{-1})$  was introduced into the wave tank through a manifold system. This resulted in at an average current speed of 0.43 cm s<sup>-1</sup> inside the wave tank along the direction of wave propagation. The current flow rate was selected to counteract the previously measured surface Stoke's drift velocity of the high frequency (0.85 Hz) regular wave conditions. The presence of current allows for dilution and transport of dispersed oil away from the slick, which simulates prevailing currents in the sea to achieve more realistic field conditions. In this work, during wave breaking, the wave height of the breaking wave was about 26 cm and increased to 33 cm, while the velocity at the surface increased from 0.3 to 0.5 m s<sup>-1</sup>. The energy dissipation rate at the breaking point was at least two orders-of-magnitude higher than that of regular waves. The high energy dissipation rate under plunging breaking waves was similar to the breaking wave energy dissipation rate 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).

#### 2.2. Dispersants and oils

Two commercial chemical dispersants were tested, Corexit 9500 and SPC 1000; both are listed on EPA's National Contingency Plan Product Schedule, and their precise compositions are proprietary. Corexit 9500 is a hydrocarbon-based formulation and is meant to be applicable for higher viscosity oils and emulsions. SPC 1000 is a water-based formulation. Two crude oils were tested: (1) Medium South American (MESA), viscosity 42.3 cP at 21 °C and (2) Alaska North Slope (ANS), viscosity 50.1 cP at 21 °C. MESA oil was weathered by evaporation (sparging with air for 130 h) to simulate the loss (approximately 14%) of volatile components at sea shortly after a spill. ANS oil was fresh and not weathered to test the dispersion efficiency assuming an ideal oil spill response scenario in which dispersant application is immediately available in the incident.

#### 2.3. Oil dispersion efficiency

Natural and chemical dispersion of the crude oils under different wave conditions was tested under either batch mode or flow-through mode using a three-factor, mixed-level factorial experimental design (Li et al., 2009a,b). For each experiment, seawater was pumped from the Bedford Basin (NS, Canada) through a double laver fabric-filter (Atlantic Purification Ltd. Dartmouth, NS. Canada) of pore sizes 25 and 5 µm to remove coarse and fine particles, respectively. In flow-through mode, the seawater from the Basin was first pumped through filter into a holding tank, from which another electric pump drew seawater and fed into the wave tank through the tank influent manifold. The background temperature, salinity, and particle size distributions were recorded before each experiment. To start an experiment, 300 ml of test 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, and 12 ml of dispersant



**Fig. 1.** Schematic representation (all dimensions in cm, not to scale) of the wave tank. Red dots represent four horizontal sampling locations: (A) 2 m upstream, (B) 2 m downstream, (C) 6 m downstream, and (D) 10 m downstream from the center of the spiked oil slick. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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