

EPA/600/R-08/037  
March 2008

# **Dispersion of Crude Oil and Petroleum Products in Freshwater**

Prepared  
By

Brian A. Wrenn  
Department of Energy, Environmental, and Chemical Engineering  
Washington University, Box 1180  
St. Louis, MO 63130

Order No. EP06C000259

## **EPA Project Officer**

Albert D. Venosa  
Land Remediation and Pollution Control Division  
National Risk Management Research Laboratory  
Cincinnati, Ohio 45268

National Risk Management Research Laboratory  
Office of Research and Development  
U.S. Environmental Protection Agency  
Cincinnati, Ohio 45268

## Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threaten human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

Sally Gutierrez, Director  
National Risk Management Research Laboratory

## **Notice**

The U.S. Environmental Protection Agency through its Office of Research and Development funded the research described here under order number EP06C000259 to Brian A. Wrenn at the Washington University Department of Energy, Environmental, and Chemical Engineering. It has been subjected to the Agency's review and has been approved for publication as an EPA document.



## **1. Abstract**

The objective of this research was to investigate the relationship between dispersion effectiveness in freshwater and the surfactant composition for fresh and weathered crude oil. Although limited research on the chemical dispersion of crude oil and petroleum products in freshwater has been conducted, previous studies did not identify the dispersants that were investigated, much less describe the chemistry of the surfactants that were used. The absence of information on surfactant composition is a major impediment to the scientific investigation of dispersant effectiveness because this information is necessary for the development of a more fundamental understanding of dispersant effectiveness. Therefore, the relationship between surfactant chemistry and dispersant effectiveness was systematically evaluated. This report showed that, at least with Mars Blend crude oil in simulated lake water, dispersants can be designed to drive an oil slick into the freshwater column with the same efficiency as in saltwater as long as the hydrophilic-lipophilic balance (HLB) is optimum. Clearly, many more oils would need to be tested under different conditions (temperature, organic content, water composition, etc.) to enable firm conclusions that oil can be dispersed in freshwater as a response tool. The ultimate decision to use dispersants in treating freshwater petroleum oil spills is up to the federal on-scene coordinator, the incident command team, the regional response teams, and EPA Headquarters, since many other factors need to be considered before rendering a decision to disperse oil into the water column. It is beyond the scope of this report to consider such factors. Its purpose was simply to determine if freshwater dispersion is possible and to determine whether effective freshwater dispersants can be designed to produce stable oil droplet distributions in such an environment.

## **2. Introduction**

### **2.1. Question addressed by this report**

This report attempts to answer the question about whether petroleum oils can be dispersed in a freshwater environment. Most dispersants currently on the National Contingency Plan Product Schedule (NCPSP) have been developed for saltwater environments, and the literature is lacking in regards to freshwater dispersion. Research data presented herein will show that effective freshwater dispersants can be developed as a response tool, but the decision to use them is a policy decision that is not addressed by this technical report.

### **2.2. Chemical Properties of Dispersants**

One response alternative for marine crude petroleum oil spills is chemical dispersion. Dispersion is accomplished by addition of chemicals that interact with the floating oil to reduce the oil-water interfacial tension and facilitate the formation of small oil droplets (NRC, 2005). The individual chemicals are formulated into mixtures that are collectively known as dispersants. The composition of most commercially available dispersants is proprietary, but in general they consist of one or more nonionic surfactants dissolved in a solvent carrier (NRC, 1989). Some dispersants also include one or more anionic surfactants and other additives (*e.g.*, phosphoric acid). The purpose of the solvent is to provide the surfactant mixture with an appropriate viscosity, which ensures that it can be pumped through spray nozzles at environmental temperatures. The solvent may be water miscible (*e.g.*, 2-butoxyethanol) or immiscible (normal alkanes) (NRC, 2005).

Surfactants are the active (*i.e.*, interfacial tension reducing) ingredients in dispersants. Surfactants are compounds that have hydrophobic and hydrophilic components within the same molecule. The amphiphilic character of surfactants causes them to accumulate at interfaces because the hydrophilic part of the molecule interacts strongly with water, and the hydrophobic part interferes with more thermodynamically-favorable hydrogen bonding interactions between water molecules. These interactions are thus displaced from the water phase (Porter, 1991). Nonionic surfactants are most common in dispersants because they have much lower aqueous solubility than do anionic surfactants (Porter, 1991), and they are generally less toxic and less affected by electrolyte concentration than are anionic and cationic surfactants (Porter, 1991; Myers, 2006). This is not necessarily true for the alkyl phenol ethoxylates, which have been linked to endocrine disrupting activity. The latter surfactants were not a part of this study. The lower water solubility tends to increase the extent to which the surfactants partition into the oil phase when the aqueous phase is in great excess, as it is for environmental applications. The nonionic surfactants used in past dispersant studies are ethoxylated derivatives of fatty acids, fatty alcohols, and fatty acid esters of sorbitan (NRC, 1989; Fingas *et al.*, 1990; Georges-Ares and Clark, 2000), in which the hydrophilic portion of the molecule consists of polyethylene glycol chains of varying lengths, and the hydrophobic portion is contributed by the fatty acyl chains, usually ranging between about 12 and 18 carbon atoms in length.

A typical measure of the relative importance of the hydrophobic and hydrophilic portions of nonionic surfactants is the hydrophile-lipophile balance (HLB), which ranges from zero for completely lipophilic (hydrophobic) molecules to 20 for completely hydrophilic (uncharged) molecules. Packing arguments suggest that the dominant group, characterized by the ratio of linear cross-sectional areas, will tend to orient into the continuous phase (NRC, 1989; Porter, 1991). So, surfactants with low HLB tend to stabilize water-in-oil emulsions, whereas those with high HLB stabilize the more desirable oil-in-water emulsions (NRC, 1989; Clayton *et al.*, 1993). Commercial dispersants tend to have overall HLBs in the range of 9 to 11, which is often achieved by combining surfactants with higher and lower HLB. Although the industry consensus suggests that combining surfactants with different HLB improves dispersant effectiveness (NRC, 1989; Clayton *et al.*, 1993), others have offered alternative findings (Fingas *et al.*, 1990).

Although the HLB is the parameter that is most commonly used to describe the characteristics of dispersants, the same HLB can be obtained in many different ways. For example, a single surfactant with the desired HLB can be used, or two or more surfactants can be mixed in proportions that give the same desired HLB. The HLB of surfactant mixtures is given by the mass-weighted average of the individual surfactants (Myers, 2006). Furthermore, dispersants with different chemical characteristics may have the same HLB but exert different effects on the system (Bruheim *et al.*, 1999; Van Hamme and Ward, 1999; Bruheim and Eimhjellen, 2000). Therefore, the composition of the dispersant formulations used in this research were varied systematically to produce dispersants with similarly defined HLBs but different chemical compositions.

### **2.3. Effect of Salinity on Dispersion Effectiveness**

The effectiveness of chemical dispersants can be strongly influenced by salinity (*i.e.*, ionic strength), but the relationship between dispersion effectiveness and salinity can vary for different dispersant-oil combinations (Lehtinen and Vesala, 1984; Belk *et al.*, 1989; Fingas *et al.*,

1991; Blondina *et al.*, 1999). Dispersants that were optimized for marine use [*e.g.*, Corexit 9500 (<http://www.epa.gov/emergencies/docs/oil/ncp/schedule.pdf>), Enersperse 700 (no longer on the EPA Product Schedule)] are often ineffective in freshwater (Fingas *et al.*, 1991; Blondina *et al.*, 1999), while those that are optimized for use in freshwater are less sensitive to salinity (Belk *et al.*, 1989). Although most studies vary salinity by diluting natural or artificial seawater, which is dominated by sodium and chloride ions, minor ions such as calcium and magnesium may be more important in determining dispersion effectiveness. One study using the Labofina method of measuring dispersant effectiveness showed very high effectiveness of freshwater and marine dispersants at calcium concentrations that were low relative to seawater concentrations (Belk *et al.*, 1989). The effectiveness of the unidentified marine dispersant increased from 6% in deionized water to 81% in water containing calcium at a concentration of 400 mg/L as CaCO<sub>3</sub>, which is less than half the concentration found in seawater but still high relative to most freshwater. Dispersants optimized for freshwater were less sensitive to the calcium concentration than those optimized for marine use.

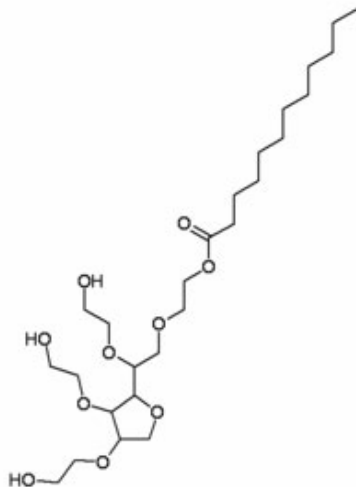
### **3. Objective of Research**

The objective of this research was to investigate the relationship between dispersion effectiveness in freshwater and the surfactant composition for weathered crude oil. Although limited research on the chemical dispersion of crude oil and petroleum products in freshwater has been conducted, previous studies (*e.g.*, Belk *et al.*, 1989) did not identify the dispersants that were investigated, much less describe the chemistry of the surfactants that were used. The absence of information on surfactant composition is a major impediment to the scientific investigation of dispersant effectiveness because this information is necessary for the development of a more fundamental understanding of dispersant effectiveness. Therefore, the relationship between surfactant chemistry and dispersant effectiveness was systematically evaluated.

## **4. Materials and Methods**

### **4.1. Surfactants**

The surfactants that were used in this research are listed in Table 1. The surfactants were selected from three chemical classes: sorbitan esters, fatty acid ethoxy esters, and fatty acyl ethoxy ethers. Because many of the surfactants used in this research are widely distributed and used for a variety of purposes, Table 1 provides the trade names in addition to the chemical names of the surfactants that were used. For brevity, the structure of the hydrophilic groups is given as POE(x), where “POE” means “polyoxyethylene” and “x” is the total number of ethylene oxide units in the POE chains. The size of the hydrophilic groups is also abbreviated as “E<sub>x</sub>” in some abbreviations. The meaning of the variable ‘x’ in E<sub>x</sub> is identical to POE(x). They both refer to the number of ethoxyl groups. (The sorbitan ester surfactants frequently have several POE chains esterified to different hydroxyl groups of the sorbityl group, but the total number of ethylene oxide monomers is as indicated.) Example of polyoxyethylene (20) sorbitan monolaurate is shown below:



The chain length and chemical characteristics of the fatty acyl groups is indicated by  $C_{y:z}$ , where “y” is the number of carbon atoms in the fatty acyl chain and “z” is the number of carbon-carbon double bonds. The number of carbon-carbon double bonds is important because, for a given chain length, the melting point is a function of the degree of unsaturation. Greater unsaturation (*i.e.*, number of double bonds) is correlated with lower melting point for a given chain length and, therefore, greater tendency to exist as a liquid at ambient temperatures. Several of the surfactants include more than one fatty acyl group in the hydrophobic portion. These are indicated by the use of “di-” (*i.e.*, two fatty acyl groups), “tri-” (*i.e.*, three fatty acyl groups), or “hexa-“ (*i.e.*, six fatty acyl groups). The Tergitols (fatty acyl ethers) are composed of mixtures of fatty acyl groups varying from 11 to 15 carbon atoms in chain length.

The HLB of the individual surfactant molecules is determined by the balance between the size of the hydrophilic group (*i.e.*, “x”, the number of ethylene oxide units in the polyoxyethylene chain) and the length (*i.e.*, “y”, the number of carbon atoms) and number (*i.e.*, di-, tri-) of the fatty acyl group that constitutes the hydrophobic portion.



**Table 1:** List of surfactant trade names and chemical names

surfactant class	trade name	chemical name	HLB
sorbitan esters	Span 20	sorbitan monolaurate (S-C <sub>12</sub> )	8.6
	Span 40	sorbitan monopalmitate (S-C <sub>16</sub> )	6.7
	Span 60	sorbitan monostearate (S-C <sub>18</sub> )	4.7
	Span 80	sorbitan monooleate (S-C <sub>18:1</sub> )	4.3
	Tween 60	POE(20) sorbitan monostearate (E <sub>20</sub> -S-C <sub>18</sub> )	14.9
	Tween 65	POE(20) sorbitan tristearate (E <sub>20</sub> -S-triC <sub>18</sub> )	10.5
	Tween 80	POE(20) sorbitan monooleate (E <sub>20</sub> -S-C <sub>18:1</sub> )	15.0
	Tween 85	POE(20) sorbitan trioleate (E <sub>20</sub> -S-triC <sub>18:1</sub> )	11.0
		POE(50) sorbitan hexaoleate (E <sub>50</sub> -S-hexaC <sub>18:1</sub> )	11.6
fatty acid ethoxy esters		POE(2) monolaurate (E <sub>2</sub> -C <sub>12</sub> )	6.5
		POE(4) monolaurate (E <sub>4</sub> -C <sub>12</sub> )	9.8
		POE(12) monolaurate (E <sub>12</sub> -C <sub>12</sub> )	14.9
		POE(12) dilaurate (E <sub>12</sub> -diC <sub>12</sub> )	12.2
		POE(4) monostearate (E <sub>4</sub> -C <sub>18</sub> )	7.9
	Myrj 45	POE(8) monostearate (E <sub>8</sub> -C <sub>18</sub> )	11.2
	Myrj 52	POE(40) monostearate (E <sub>40</sub> -C <sub>18</sub> )	17.3
		POE(4) distearate (E <sub>4</sub> -diC <sub>18</sub> )	5.0
fatty alcohol ethoxy ethers		POE(6) tridecyl ether (E <sub>6</sub> -C <sub>13</sub> )	11.4
	Brij 52	POE(2) hexadecyl ether (E <sub>2</sub> -C <sub>16</sub> )	5.2
	Brij 58	POE (20) hexadecyl ether (E <sub>20</sub> -C <sub>16</sub> )	15.7
	Brij 76	POE(10) stearyl ether (E <sub>10</sub> -C <sub>18</sub> )	12.4
	Brij 98	POE(20) oetyl ether (E <sub>20</sub> -C <sub>18:1</sub> )	15.3
	Tergitol-15-S-3	(E <sub>3</sub> -C <sub>11-15</sub> )	8.0
	Tergitol-15-S-5	(E <sub>5</sub> -C <sub>11-15</sub> )	10.0
	Tergitol-15-S-7	(E <sub>7</sub> -C <sub>11-15</sub> )	12.1

#### 4.2. Composition of Synthetic Lake Water

Experiments were conducted in artificial freshwater that was designed to have a divalent cation composition similar to Lake Michigan water. The artificial Lake Michigan water has the following composition (mg/l): NaHCO<sub>3</sub> (96), CaCl<sub>2</sub>·2H<sub>2</sub>O (128), MgSO<sub>4</sub>·7H<sub>2</sub>O (111). It is not known to what extent this formulation differs from other freshwater sources. After dissolving the components, the artificial lake water was aerated to reduce the pH to approximately 8 and filtered through a 0.2 μm membrane filter. The synthetic lake water and Lake Michigan water are compared in Table 2. The alkalinity of the synthetic lake water is lower than Lake Michigan water, and the sodium and chloride concentrations are higher, but these factors were not expected to have a significant effect on dispersant performance. Natural organic matter might also have an influence on dispersant performance, but such a factor is difficult to simulate in a small laboratory study such as this.

**Table 2:** Composition of synthetic lake water

Component	Concentration, mg/l	
	Lake Michigan	Synthetic Lake Water
calcium	34	35
magnesium	10	11
sodium	5	26
chloride	8	62
sulfate	20	43
alkalinity	108	57

### 4.3. Experimental Design

The dispersant formulations that were tested in this research are shown in Table 3. The dispersants were prepared by dissolving the surfactants in n-dodecane (Sigma-Aldrich, St. Louis, MO). The total concentration of surfactants in all dispersant formulations was 70% by mass, and the concentration of dodecane was 30%. These dispersant formulations were designed to test the effects of three factors on performance: (A) HLB, (B) surfactant chemical characteristics, and (C) dispersant composition. All treatment factors were tested at three levels. The dispersant formulations shown in Table 3 encompass the HLB range of most interest (*i.e.*, between about 8 and 12), and the dispersants were formulated using surfactants with three different chemical characteristics: sorbitan esters, fatty acid ethoxylates, and ethoxylated fatty acyl ethers. Some investigators have suggested that dispersants with lower HLB should be more effective in freshwater, whereas dispersants with higher HLB should be more effective in seawater (Clark, personal communication). The surfactants used to formulate these dispersants are similar in that the hydrophilic part of the molecule is composed primarily of polyethoxy groups, and the hydrophobic part is contributed by long-chain ( $C_{12}$  to  $C_{18}$ ) fatty acyl chains, which may be fatty acids (as in sorbitan ester and fatty ester surfactants) or fatty alcohols (as in fatty ether surfactants). The biggest structural difference between these surfactants is the presence of a sorbitan molecule (*i.e.*, a cyclic anhydride of the sugar alcohol sorbitol), to which the fatty acid and polyethoxy groups are connected, in the sorbitan esters. Also, the Span-type sorbitan esters are not ethoxylated. The third factor that was tested, dispersant composition, evaluated the benefit conferred by using mixtures of two surfactants instead of a single surfactant. Since the superiority of surfactant mixtures over single-surfactant formulations has been rationalized based on packing arguments (Porter, 1991; Myers, 2006), it seems reasonable to speculate that mixtures that are dominated by one surfactant will not be as effective as those that contain equal amounts of all surfactants. Therefore, dispersants with the same HLB were prepared in three different ways for each surfactant chemical class: one dispersant was prepared with a single surfactant with HLB that was sufficiently close to the target HLB, one dispersant was prepared by adding two surfactants in different proportions, and the third was prepared by combining two surfactants in similar proportions (*i.e.*, close to a 1:1 ratio).

The only commercial dispersant whose composition is known is Corexit 9500 with an HLB of 10-11, and its composition is similar to the Span80-Tween80 ratio shown in Table 3 under Sorbitan esters for HLB 10.

**Table 3:** Dispersant formulations for testing in freshwater

HLB <sub>target</sub>		Surfactant Type <sup>†</sup>		
		Sorbitan Esters (B1)	Fatty Acid Ethoxy Esters (B2)	Fatty Alcohol Ethoxy Ethers (B3)
8 (A1)	C1	Span 20	E <sub>4</sub> -C <sub>18</sub>	Tergitol 15-S-3
	C2	65% Span 80 + 35% Tween 80	70% diC <sub>18</sub> -E <sub>4</sub> + 30% E <sub>12</sub> -C <sub>12</sub>	73% Brij 52 + 27% Brij 98
	C3	48% Span 60 + 52% Tween 85	54% E <sub>4</sub> -diC <sub>18</sub> + 46% Myrj 45	56% Brij 52 + 44% E <sub>6</sub> -C <sub>13</sub>
10 (A2)	C1	Tween 65	E <sub>4</sub> -C <sub>12</sub>	Tergitol 15-S-5
	C2	60% Span 40 + 40% Tween 60	31% E <sub>2</sub> -C <sub>12</sub> + 69% Myrj 45	34% Brij 52 + 66% Brij 76
	C3	47% Span 80 + 53% Tween 80	50% E <sub>4</sub> -diC <sub>18</sub> + 50% E <sub>12</sub> -C <sub>12</sub>	53% Brij 52 + 47% Brij 98
12 (A3)	C1	E <sub>50</sub> -S-hexaC <sub>18:1</sub>	E <sub>12</sub> -diC <sub>12</sub>	Tergitol 15-S-7
	C2	28% Span 80 + 72% Tween 80	29% E <sub>4</sub> -diC <sub>18</sub> + 71% E <sub>12</sub> -C <sub>12</sub>	33% Brij 52 + 67% Brij 98
	C3	46% Span 20 + 54% Tween 60	49% E <sub>2</sub> -C <sub>12</sub> + 51% Myrj 52	48% Tergitol 15-S-3 + 52% Brij 58

<sup>†</sup>see Table 1 and Section 3.1 for description of the chemical characteristics of these surfactants and for a definition of the abbreviations

A total of 10 g of each dispersant (7 g of surfactants plus 3 g n-dodecane) was prepared. Each component was weighed to an accuracy of  $\pm 0.01$  g. After the surfactants and solvent were combined, the mixtures were heated (if required to make the surfactants dissolve) and mixed for a minimum of 15 minutes at 200 RPM on an orbital shaker. Although all formulations were evaluated, not all have physical characteristics that would be conducive to practical application in oil-spill response. Two problems were noted with these formulations: (1) some of the dispersants were solids at room temperature, and (2) some of the surfactants were insoluble in the solvent used to make the dispersant (dodecane). The physical characteristics of the dispersants are indicated in Table 4, and the problem formulations are depicted in boldface font.

Dispersant formulations that were solids at room temperature were equilibrated at 50 °C prior to use to facilitate their use in dispersion experiments. All of the dispersant formulations that were tested in this research were liquids at this temperature. To prevent refreezing of the dispersants during transfer, the pipette tips were also equilibrated at 50 °C before use. Dispersants for which one or more of the surfactants was insoluble in the solvent were well mixed prior to use. This procedure appeared to be adequate for use in these dispersion experiments because it produced a cloudy suspension that separated into two phases relatively slowly.

**Table 4:** Physical characteristics of dispersant formulations

HLB <sub>target</sub>		Surfactant Type		
		Sorbitan Esters (B1)	Fatty Acid Ethoxy Esters (B2)	Fatty Alcohol Ethoxy Ethers (B3)
8 (A1)	C1	homogenous liquid	<b>2-phase solid</b>	homogenous liquid
	C2	homogenous liquid	homogenous <b>solid</b>	homogenous solid
	C3	homogenous <b>solid</b>	homogenous <b>solid</b>	<b>2-phase</b> liquid
10 (A2)	C1	<b>2-phase solid</b>	homogenous liquid	homogenous liquid
	C2	homogenous <b>solid</b>	<b>2-phase solid</b>	homogenous <b>solid</b>
	C3	homogenous liquid	homogenous <b>solid</b>	homogenous <b>solid</b>
12 (A3)	C1	homogenous liquid	homogenous liquid	homogenous liquid
	C2	homogenous liquid	<b>2-phase solid</b>	homogenous <b>solid</b>
	C3	homogenous liquid	homogenous <b>solid</b>	homogenous <b>solid</b>

\*the problem formulations are depicted in **boldface** font

Each dispersant formulation was tested using three independently replicated effectiveness tests. The order of testing was randomized except that all dispersants were tested once before any dispersant was tested a second time. Because it took several weeks to test all of the dispersants once, this type of blocking prevented confounding of treatment effects with time effects. That is, in a completely randomized design, it would have been possible for all three replicates of one dispersant to be conducted at almost the same time and all three replicates of another dispersant to be conducted at another time. If slow systematic changes in performance occurred over time, the effect of time could have been identified as a treatment effect. Such temporal grouping of replicates was not possible with the experimental design that was used.

#### 4.4. Oil

Artificially weathered Mars Blend crude oil (from the Gulf of Mexico) was used in these experiments. Approximately 200 ml of this oil, which had an initial API gravity of about 30, was weathered by evaporation under nitrogen for 3 days. Density measurements were not made after weathering. To minimize mass transfer limitations, the oil was mixed by magnetic stirring during the evaporation process. The mass of oil was reduced by 18.5% by this process. This oil is listed in Environment Canada's ETC database.

#### 4.5. Dispersion Effectiveness Experiments

The dispersant formulations listed above in Table 3 were tested using the baffled flask test (BFT), a bench-scale dispersion effectiveness test that was developed for testing of dispersants for listing on the National Contingency Plan Product Schedule (Sorial *et al.*, 2004). Dispersion effectiveness was evaluated by adding 100 µl of weathered Mars Blend crude oil to a 150-ml baffled flask containing 120 ml of synthetic freshwater using a Repeater Plus Pipette (Eppendorf, Westbury, NY) with a 0.5 ml pipette tip. Next, 4 µl of dispersant was added to the floating oil using the same pipette with a 0.1 ml pipette tip. This produced a dispersant-to-oil ratio (DOR) of 1:25. This baffled flask was mixed for 10 minutes at 200 rpm using a Lab-Line Orbit Environ Shaker (Lab-Line Instruments, Inc., Melrose Park, IL). After the mixing period,

the flask was carefully removed from the shaker and the dispersion was allowed to settle for 10 minutes. Figure 1 shows the baffled flask during the settling period.

After the settling period, a 40-ml sample was collected through the stopcock at the bottom of the baffled flask. A 30-ml subsample of the 40-ml sample was extracted with



**Figure 1:** Baffled flask during the settling period

dichloromethane (DCM) to measure the mass of dispersed oil, and a 40- $\mu$ l sample from the remaining volume was diluted with 100 ml of deionized water and analyzed using a model LS-200 Liquilaz Optical Particle Counter (OPC) (Particle Measuring Systems, Inc, Boulder, CO) to determine the size distribution of dispersed oil droplets.

Dispersion effectiveness was estimated from the mass concentration of dispersed oil, which was measured by extraction of the oil into DCM. A 30-ml sample of the dispersed phase was added to a 125-ml separatory funnel containing 5 ml of a 250 g/L sodium chloride solution. The dispersed oil was then extracted by adding 10 ml of DCM to the separatory funnel, and the mixture was shaken for approximately two minutes. This mixture was allowed to settle until it separated into two distinct phases, and the DCM phase was collected by draining from the bottom of the separatory funnel. This procedure was repeated at least three times and until the DCM phase was colorless after extraction. Addition of sodium chloride facilitated separation of the DCM and aqueous phases into two separate phases with a distinct interface.

The solvent recovered from all three extraction steps was combined and filtered through DCM-rinsed anhydrous sodium sulfate to remove water. The resulting solution was transferred to a tared weighing-vial and the solvent was evaporated under a stream of air in a N-Evap Analytical Evaporator (Organomation Associates, Berlin, MA). After evaporation of the DCM, the tared vials were placed in a desiccator for 24 hours to remove any residual moisture. The vials were then weighed a second time to determine the mass of the dispersed oil.

The dispersion effectiveness ( $\eta$ ) was estimated from the mass of the extracted oil as follows:

$$\eta = \frac{(M_f - M_o) \left( \frac{V_{\text{aq,tot}}}{V_{\text{aq,extract}}} \right)}{V_{\text{oil,tot}} \rho_{\text{oil}}} \times 100\% \quad (1)$$

where  $M_o$  is the initial mass of the tared vial,  $M_f$  is the mass of the vial containing the residue remaining after evaporating the solvent,  $V_{\text{aq,tot}}$  is the total aqueous-phase volume used in the dispersion experiments (*i.e.*, 120 ml),  $V_{\text{aq,extract}}$  is the volume of aqueous phase that was extracted (*i.e.*, 30 ml),  $V_{\text{oil,tot}}$  is the volume of oil added at the beginning of the experiment (*i.e.*, 0.1 ml), and  $\rho_{\text{oil}}$  is the density of the weathered Mars Blend crude oil (*i.e.*, 0.9142 g/ml). The oil density was measured by weighing at least 10 aliquots of oil delivered by the Eppendorf Repeater Plus Pipette fitted with the 0.5-ml tip.

The dispersion efficiency and the size distribution of the dispersed oil droplets was also measured using an optical particle counter (OPC). The OPC counts the number of oil droplets within 15 user-defined size ranges between 2 and 120  $\mu\text{m}$ . The droplet-size distribution was used to estimate the total volume of dispersed oil, which was used to calculate the dispersion efficiency, and two particle-size statistics: the number mean diameter (NMD,  $\bar{d}$ ) and the diameter of mean volume (DMV,  $d_{\bar{v}}$ ). Six replicate measurements of the number of oil droplets in each size range ( $n_i$ ) were averaged before calculating size-distribution statistics. (The droplet-size distribution was actually measured nine times for each sample, but the first three measurements were discarded to insure that the detector was completely flushed of previous samples or wash solutions.) The average diameter for each size range was used to represent all droplets within the bin. For example, if the lower limit of the size bin was 2  $\mu\text{m}$  and the upper limit was 3  $\mu\text{m}$ , all droplets within the bin were assumed to have a diameter of 2.5  $\mu\text{m}$ .

The NMD ( $\bar{d}$ ,  $\mu\text{m}$ ) is a simple average of the droplet sizes:

$$\bar{d} = \frac{\sum_{i=1}^{15} \bar{n}_i d_i}{N_{\text{tot}}} \quad (2)$$

where  $d_i$  is the average diameter of size bin “i”,  $\bar{n}_i$  is the average number of droplets in bin “i” from six replicate measurements as described above, and  $N_{\text{tot}}$  is the total number concentration of oil droplets in the sample:

$$N_{\text{tot}} = \sum_{i=1}^{15} n_i \quad (3)$$

The DMV ( $d_{\bar{v}}$ ;  $\mu\text{m}$ ) is the volume-weighted average droplet diameter:

$$d_{\bar{v}} = \sqrt[3]{\frac{\sum_{i=1}^{15} n_i d_i^3}{N_{\text{tot}}}} \quad (4)$$

The DMV is a better measure of the mean of the droplet-size distribution because droplet volume is proportional to the mass, whereas number is not (*i.e.*, a small droplet contains less oil than a large droplet, but both are weighted equally in calculation of the NMD). The NMD is always smaller than the DMV in these size distributions because a large number of small droplets are formed during dispersion, but they represent a relatively small fraction of the total oil mass.

The dispersion efficiency was estimated as follows:

$$\eta = \frac{\left( \frac{\pi d_{\bar{v}}^3}{6} N_{\text{tot}} \right) \left( \frac{V_{\text{dil}}}{V_{\text{sample}}} \right) V_{\text{aq,tot}}}{V_{\text{oil,tot}} (10^{12} \mu\text{m}^3/\text{ml})} \times 100\% \quad (5)$$

where  $V_{\text{dil}}$  is the volume of the diluted sample (typically 100 ml),  $V_{\text{sample}}$  is the volume of the dispersed oil sample collected from the baffled flask after 10 minute settling period (typically 0.04 ml), and  $V_{\text{aq,tot}}$  is the total volume of the aqueous phase used in the dispersion experiments (120 ml).

The results were analyzed using analysis of variance (ANOVA) to evaluate the statistical significance of any main effects or interactions. Where significant differences were identified ( $p < 0.05$ ) by ANOVA, the means were separated using Tukey's method for paired comparisons. ANOVA and Tukey's method were performed using Systat version 10 (SPSS, Inc., Chicago, IL).

## 5. Results

### 5.1. Comparison of Dispersion Effectiveness Measurements

Two methods were used to measure dispersion effectiveness in this research: liquid-liquid extraction of the dispersed oil from the aqueous phase into dichloromethane (DCM) followed by gravimetric analysis of the extracted oil (Eq. 1) and estimation of the total volume of dispersed oil from the droplet-size distribution measured using the optical particle counter (OPC). On average, the OPC gave higher estimates of dispersion effectiveness than did the gravimetric method ( $\eta_{\text{OPC}} = 76.7 \pm 10.0\%$  vs.  $\eta_{\text{grav}} = 68.1 \pm 10.2\%$ ), but the variance of the gravimetric method was smaller (avg.  $s_{\text{OPC}} = 8.8 \pm 3.6\%$  vs. avg.  $s_{\text{grav}} = 5.0 \pm 3.4\%$ ). The average dispersion effectiveness (averaged over the three independent replicate dispersion experiments) as measured by both methods is shown in Table 5. The average difference between the OPC-based effectiveness and the effectiveness estimated by the gravimetric method was  $8.6 \pm 12.7\%$  [degrees of freedom (d.f.) = 26], which was statistically significant ( $p = 0.002$ ). The lower average dispersion effectiveness measured by the gravimetric method was probably due to

evaporation of volatile oil components during evaporation of the solvent. Loss of extracted oil by evaporation was observed to occur despite using evaporatively weathered crude oil in these experiments. Due to the systematic underestimation of dispersion effectiveness by the gravimetric method, the treatment effects associated with dispersant formulation were evaluated using the OPC-based measurement of dispersion effectiveness.

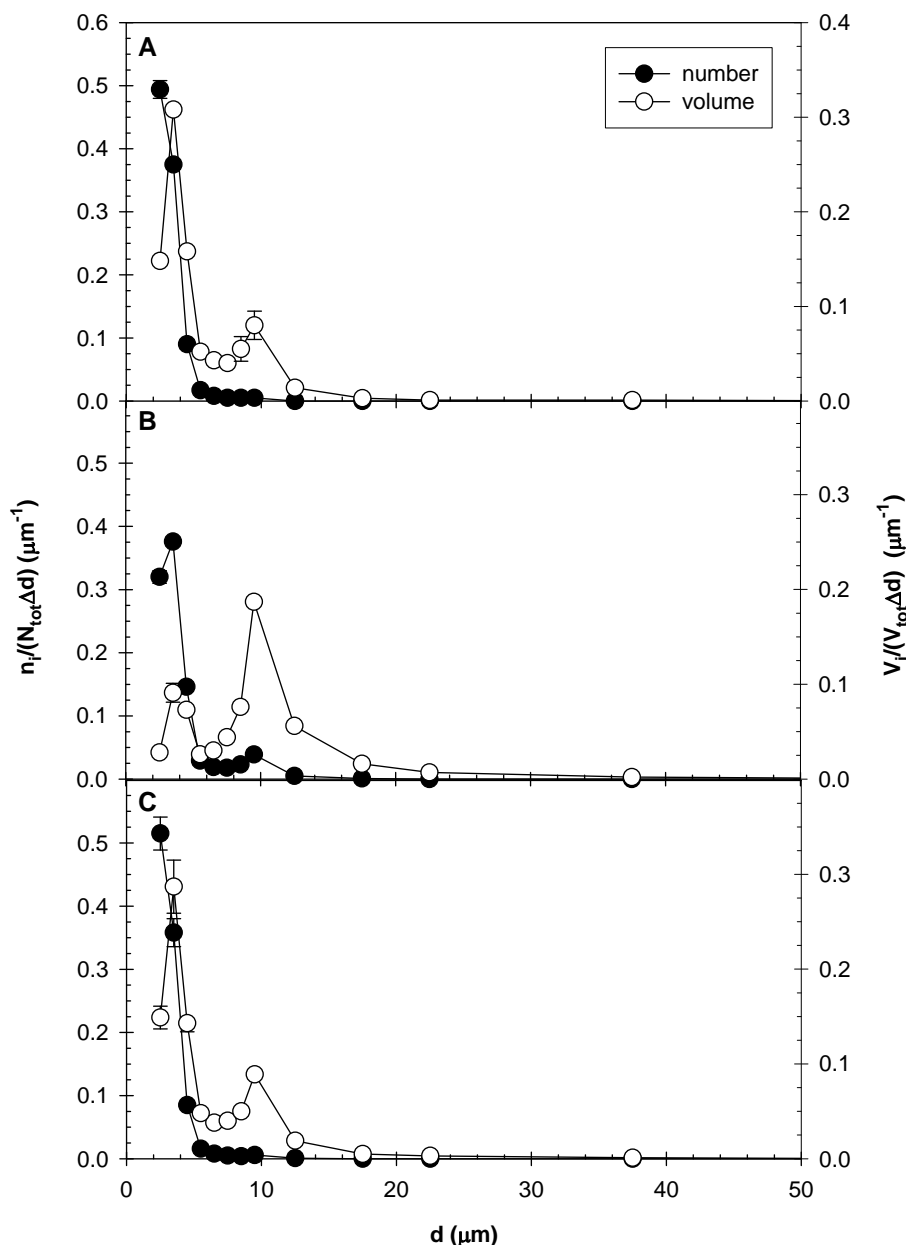
**Table 5:** Comparison of dispersion effectiveness using OPC and gravimetric analysis.

HLB	Chemistry	Composition	dispersion effectiveness (%)	
			OPC	gravimetric
8	sorbitan ester	single	72.7 ± 6.18	79.7 ± 3.40
		two, unequal	86.2 ± 3.03	73.3 ± 0.67
		two, equal	96.2 ± 7.07	68.1 ± 7.74
	fatty acid ester	single	82.2 ± 10.6	68.2 ± 7.74
		two, unequal	80.3 ± 4.04	63.8 ± 2.71
		two, equal	78.6 ± 16.8	60.6 ± 6.53
	fatty alcohol ether	single	74.4 ± 6.60	83.4 ± 2.16
		two, unequal	79.4 ± 8.01	68.5 ± 2.64
		two, equal	71.6 ± 9.28	83.2 ± 6.49
10	sorbitan ester	single	82.8 ± 12.0	60.2 ± 16.9
		two, unequal	93.7 ± 6.32	79.9 ± 1.38
		two, equal	78.4 ± 13.0	68.4 ± 4.38
	fatty acid ester	single	79.0 ± 4.03	83.8 ± 3.54
		two, unequal	72.4 ± 8.48	59.6 ± 8.31
		two, equal	79.3 ± 11.9	58.6 ± 8.31
	fatty alcohol ether	single	71.6 ± 9.28	82.5 ± 4.59
		two, unequal	65.0 ± 13.1	66.8 ± 1.66
		two, equal	69.6 ± 7.09	63.6 ± 7.14
12	sorbitan ester	single	96.2 ± 5.61	65.6 ± 6.47
		two, unequal	61.1 ± 15.4	53.6 ± 5.40
		two, equal	79.3 ± 7.91	75.4 ± 0.25
	fatty acid ester	single	74.7 ± 13.9	61.2 ± 5.30
		two, unequal	75.4 ± 6.03	61.1 ± 3.51
		two, equal	57.4 ± 11.4	44.5 ± 4.40
	fatty alcohol ether	single	58.0 ± 8.04	76.8 ± 3.28
		two, unequal	66.5 ± 4.73	56.0 ± 7.23
		two, equal	82.4 ± 6.28	72.9 ± 2.49

## 5.2. Size Distributions



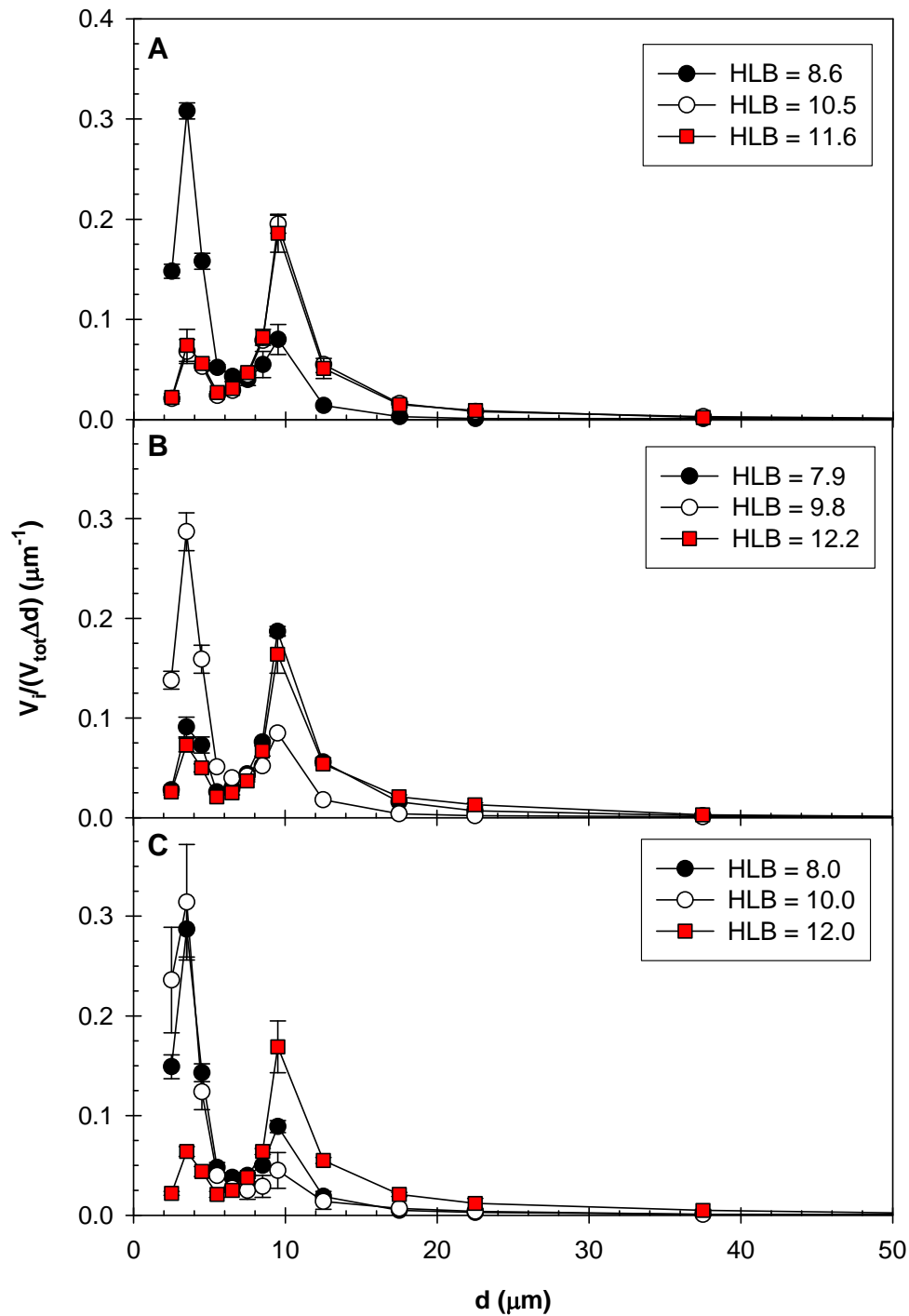
The droplet-size distributions can be based on either number or volume. Figure 2 shows a comparison of the normalized number and volume distributions for three dispersions produced by single-surfactant dispersants with HLB = 8. Normalized size distributions are obtained by dividing the number ( $n_i$ ) or volume ( $V_i$ ) concentration of oil droplets in each size bin by the total number ( $N_{tot}$ ) or volume ( $V_{tot}$ ) concentration of the dispersion and by the size of the bin ( $\Delta d_i$ ). These two operations ensure that the area under the size-distribution curve is equal to 1.0 (*i.e.*, the normalized size distributions have properties similar to histograms). In two of three cases, the number distribution was unimodal, but all of the volume distributions were bimodal. The



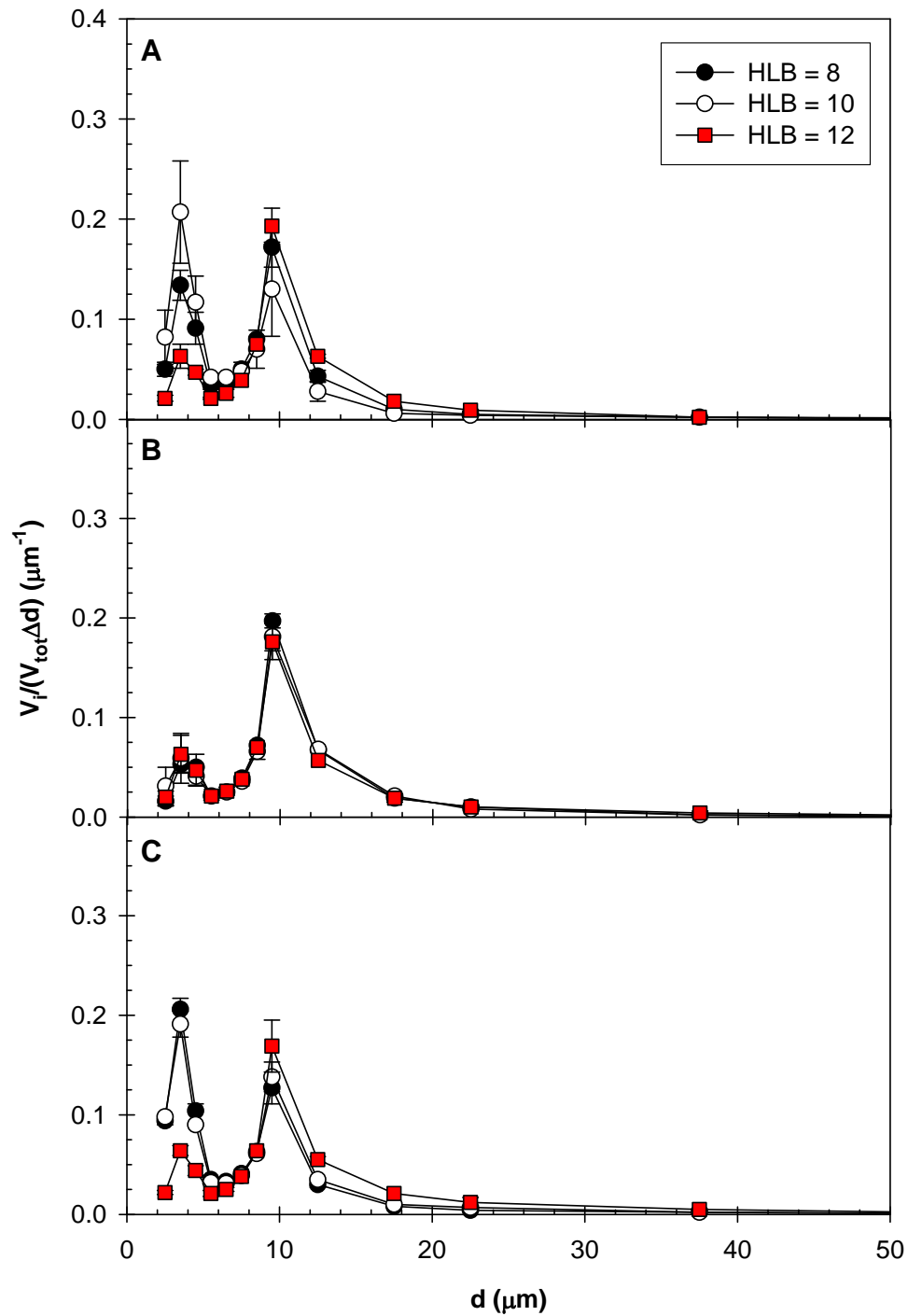
**Figure 2:** Comparison of normalized number (left axis) and volume (right axis) distributions for dispersions produced by single-surfactant dispersants with HLB = 8. The dispersants used included (A) Span 20 (HLB = 8.6), (B) POE(4) monostearate (HLB = 7.9), or (C) Tergitol 15-S-3 (HLB = 8.0) as the sole surfactant.

mean diameter of the largest size mode was about 10  $\mu\text{m}$ , whereas the mean diameter of the smallest size mode was only about 4  $\mu\text{m}$ . The bimodality of the volume distribution reflects the disproportionate influence of large droplets. Whereas oil droplets in the larger size mode constituted less than 2% of the total number of dispersed oil droplets in dispersants prepared with Span 20 and Tergitol 15-S-3, they represented about 20% of the total dispersed oil volume. Similarly, in the dispersion produced by application of the dispersant containing POE(4) monostearate, the large droplet-size mode constituted less than 10% of the total number of dispersed droplets but it represented about 40% of the total dispersed oil volume. Because the volume of dispersed oil is more important than the number of droplets from the perspective of ecological effects and performance in spill response, the dispersant formulations tested in this research will be compared based on the characteristics of the volume distributions. It is recognized, however, that smaller droplet sizes promote emulsion stability, thereby resulting in more rapid biodegradation rates due to the resultant higher surface area of the smaller droplets.

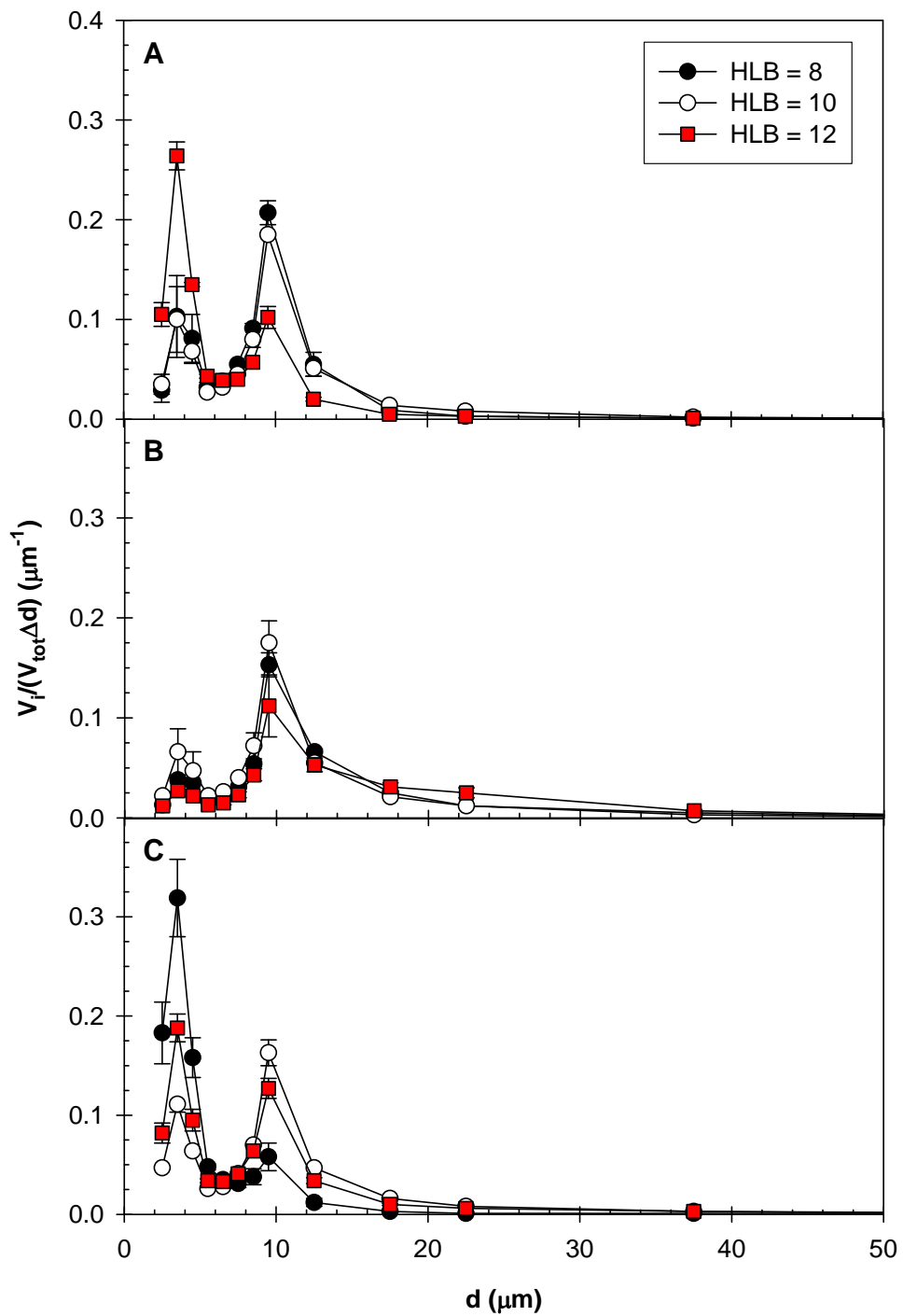
The normalized volume distributions that were produced during this research are shown in Figures 3, 4, and 5. Figure 3 shows the volume distributions that were obtained using single-surfactant dispersants, whereas Figs. 4 and 5 show the droplet-volume distributions for dispersions that were produced with dispersions prepared with two surfactants present in unequal or approximately equal proportions, respectively. All three figures also compare the size distributions obtained with dispersants prepared with sorbitan ester (panel A), fatty acyl ester (panel B), and fatty acyl ether (panel C) surfactants. They also compare the size distributions produced by dispersants with HLB of 8 (filled circles), 10 (open circles), and 12 (filled squares). The error bars represent one standard deviation for three independent replicates (*i.e.*, dispersions prepared in independent experimental units at different times). These figures clearly show that the overall characteristics of the dispersions are similar regardless of the dispersant that was used: all of the dispersions show two main size modes with mean diameters of approximately 4  $\mu\text{m}$  and 10  $\mu\text{m}$ . The distribution of oil between the two modes, however, does depend on the characteristics of the dispersant. The distribution of oil between the two modes can be quantified using the diameter of mean volume (DMV; Eq. 4).



**Figure 3:** Normalized volume distributions for single-surfactant dispersants prepared from (A) sorbitan ester surfactants, (B) fatty acyl ester surfactants, and (C) fatty acyl ether surfactants. The error bars represent one standard deviation of three independent dispersion experiments.



**Figure 4:** Normalized volume distributions for dispersions produced by dispersants prepared with two surfactants that were present in unequal proportions. The surfactants used were (A) sorbitan esters, (B) fatty acyl esters, or (C) fatty acyl ethers.



**Figure 5:** Normalized volume distributions for dispersions produced using dispersants prepared with two surfactants present in equal proportions. The surfactants that were used were (A) sorbitan esters, (B) fatty acyl esters, and (C) fatty acyl ethers.

### 5.3. Evaluation of Effects of Dispersant Characteristics

Treatment effects on dispersion effectiveness were evaluated by performing ANOVA on the data shown in Table 5 (OPC; based on droplet-size distribution). The null hypothesis tested was that none of the main effects or interactions was significant at the  $\alpha = 0.05$  level. The results are shown in Table 6, which shows that surfactant HLB and chemistry exerted significant effects on dispersion effectiveness. In addition, the three-factor interaction (*i.e.*, HLB, dispersant composition, surfactant chemistry) is statistically significant, indicating that the treatment main effects are not strictly additive. A similar analysis was performed to evaluate treatment effects on the droplet-size distribution, as indicated by the DMV. The results of this analysis are shown in Table 7 and demonstrate that all three main effects were highly significant ( $p < 0.001$ ) as were all three two-factor interactions and the three-factor interaction ( $p < 0.001$ ).

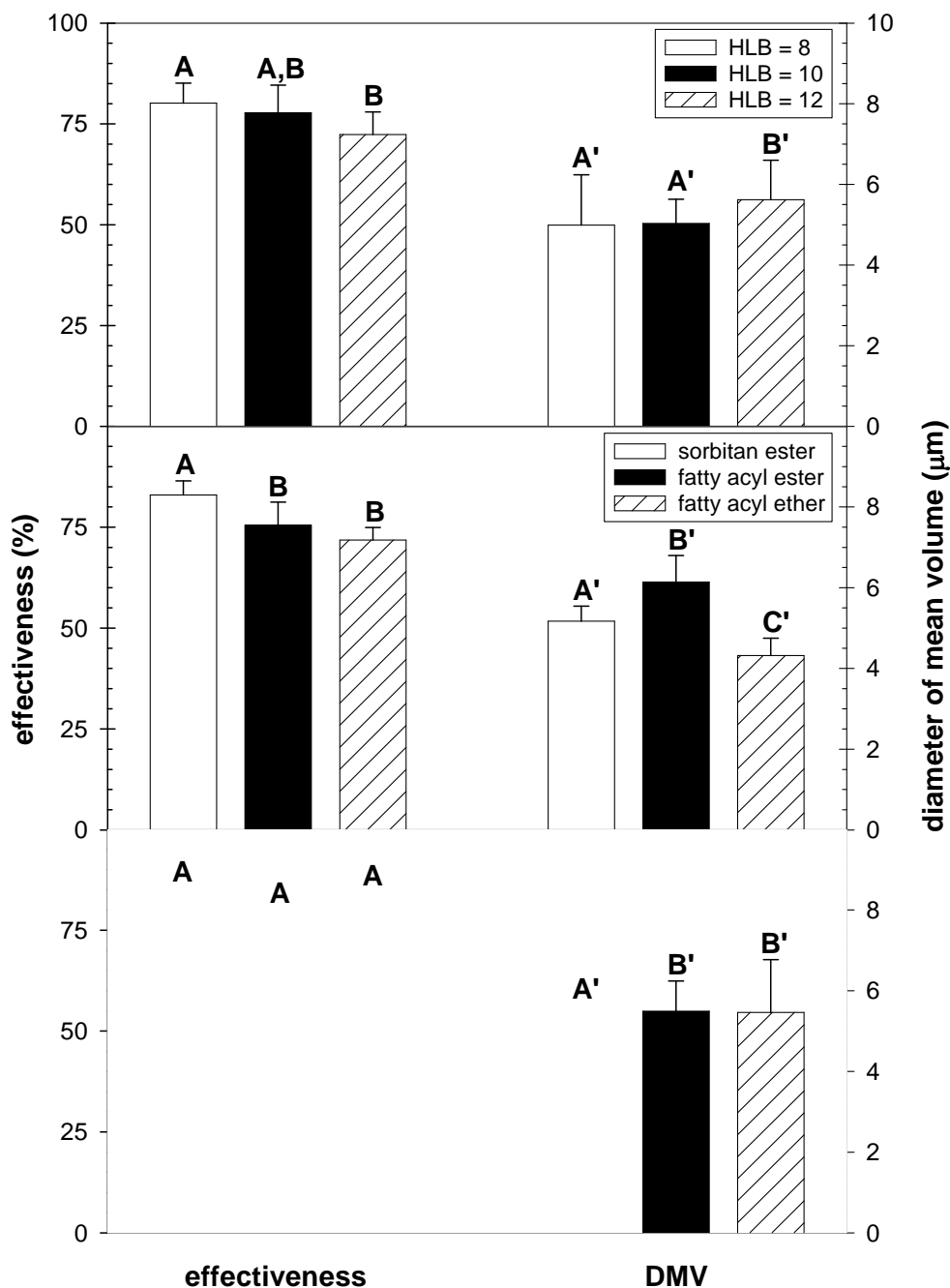
**Table 6:** ANOVA for treatment effects on dispersion effectiveness

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F-ratio	p
HLB	869.0	2	434.5	4.858	0.011
Composition	70.2	2	35.1	0.392	0.677
Chemistry	1743.5	2	871.8	9.746	<0.001
HLB x Composition	524.5	4	131.1	1.466	0.225
HLB x Chemistry	122.6	4	30.6	0.343	0.848
Composition x Chemistry	884.9	4	221.2	2.473	0.055
HLB x Composition x Chemistry	3646.6	8	455.8	5.096	<0.001
Error	4830.4	54	89.5		

**Table 7:** ANOVA for treatment effects on diameter of mean volume (DMV)

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F-ratio	p
HLB	6.68	2	3.34	34.18	<0.001
Composition	11.4	2	5.71	58.46	<0.001
Chemistry	44.7	2	22.4	228.7	<0.001
HLB x Composition	5.58	4	1.40	14.28	<0.001
HLB x Chemistry	7.02	4	1.76	17.95	<0.001
Composition x Chemistry	12.0	4	3.01	30.78	<0.001
HLB x Composition x Chemistry	24.3	8	3.04	31.08	<0.001
Error	5.28	54	0.098		

The treatment main effects on dispersion effectiveness and diameter of mean volume are shown in Figure 6. Significant differences between treatment means were identified using Tukey's method for pairwise comparisons, which allows comparison of all possible pairs of

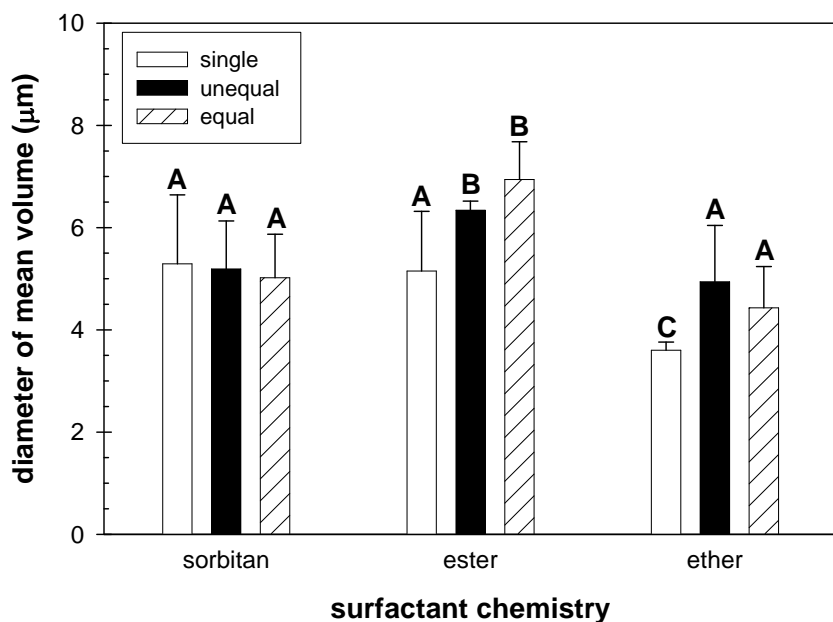


**Figure 6:** Comparison of treatment main effects on dispersion effectiveness (left axis) and droplet DMV (right axis). The top panel shows the effects of dispersant HLB on these performance parameters, the middle panel shows the effects of surfactant chemistry, and the bottom panel shows the effects of dispersant composition. The error bars represent one standard deviation. Bars labeled with the same letter are not significantly different at the 95% confidence level.

means while keeping the global Type I error at 5%. In Figure 6, dispersion effectiveness means are compared only to other effectiveness means, and DMVs are compared only to other DMVs.

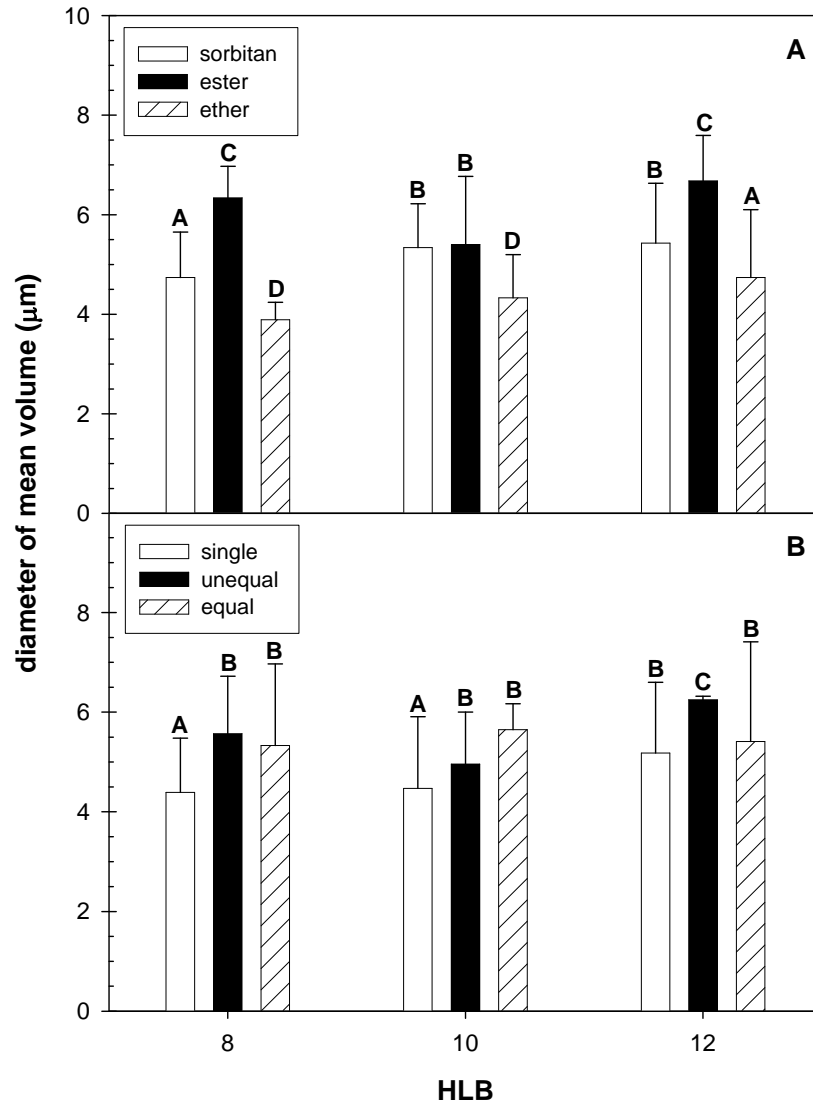
Figure 6 shows that, whereas dispersants with HLB = 12 were less effective than those with HLB = 8, the differences between dispersants with HLB = 8 and 10 and between dispersants with HLB = 10 and 12 were not statistically significant. Dispersants with HLB = 12 also produced dispersions with a larger fraction of the dispersed oil in larger droplets. Also, dispersants that contained sorbitan-ester surfactants (*e.g.*, Tweens and Spans) were significantly more effective than those containing fatty acyl ester and fatty acyl ether surfactants. The fatty acyl ether surfactants, however, produced the smallest oil droplets. Although dispersant composition (*e.g.*, formulation with one or two surfactants) had no effect on dispersion effectiveness, dispersants formulated with a single surfactant resulted in the formation of smaller oil droplets.

Figures 7 and 8 show the effects of two-factor interactions on droplet DMV. In these figures, the significant differences that are indicated are those identified using the Least-Significant Difference (LSD) test because use of Tukey's method for pairwise comparisons produced too many comparisons (and too many differences) to easily show graphically. The differences identified using Tukey's method are shown in Tables 8-10. Figure 7 shows the interactions between surfactant chemistry and dispersant composition. In general, oil droplets formed by dispersants containing a single, fatty acyl ether surfactant were smaller than those produced with other dispersants, and droplets formed by dispersants containing two fatty acyl ester surfactants were larger. Figure 8 shows the interactions between dispersant HLB and (A) surfactant chemistry or (B) dispersant composition. In general, the smallest droplets were formed when dispersants with HLB of 8 or 10 containing fatty acyl ether surfactants were used.



**Figure 7:** Comparison of treatment effects on droplet-size distribution (DMV) due to the surfactant chemistry-dispersant composition interaction. Error bars represent one standard deviation of three independent replicate dispersion experiments. Single, unequal, and equal refer to the fatty acyl chain from either a single surfactant or two surfactants in unequal or equal composition levels.

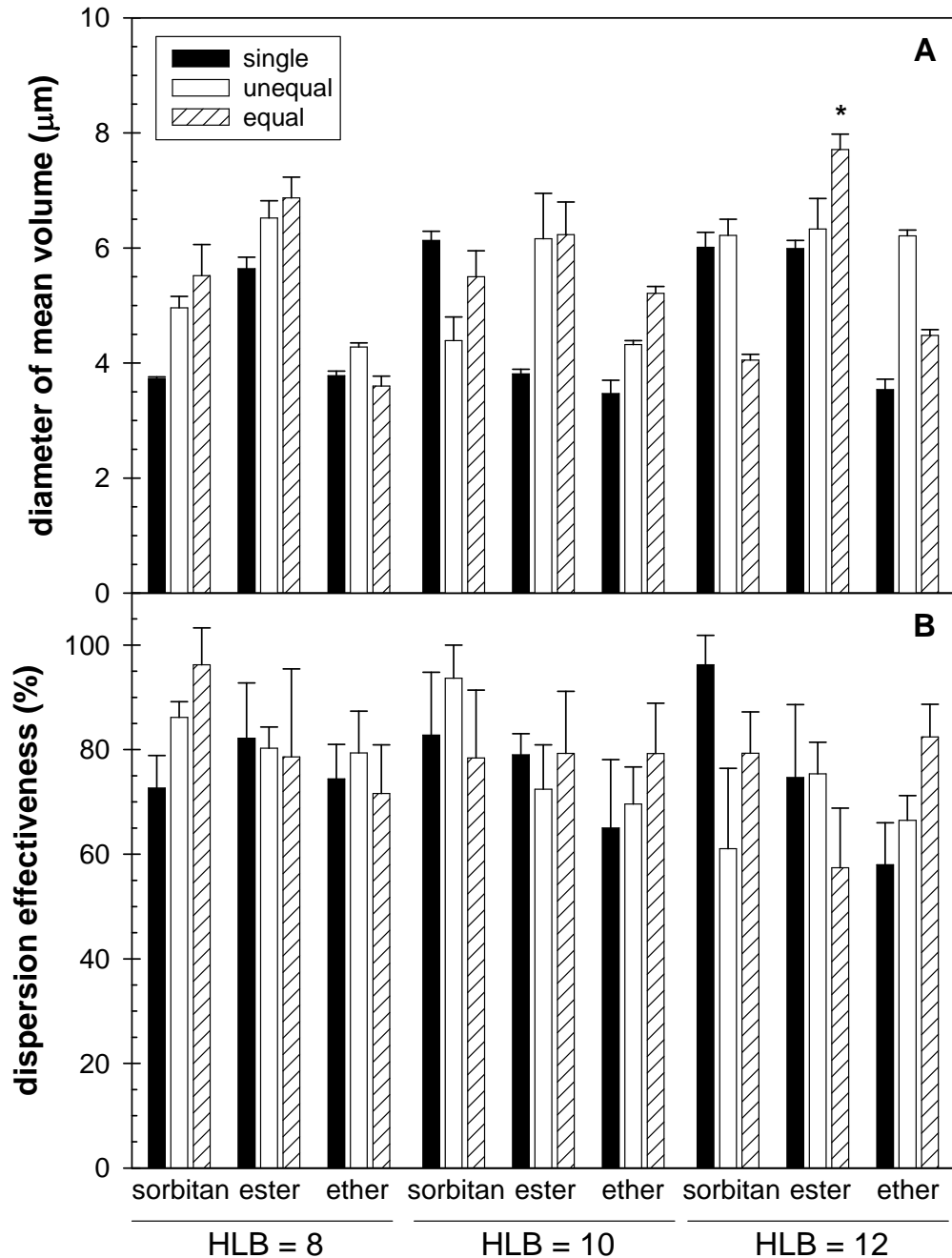




**Figure 8:** Comparison of treatment effects on droplet-size distribution (DMV) due to the interactions between dispersant HLB and (A) surfactant chemistry and (B) dispersant composition. Error bars represent one standard deviation of three independent replicate dispersion experiments. Single, unequal, and equal refer to the fatty acyl chain from either a single surfactant or two surfactants in unequal or equal composition levels.

The largest droplets, however, were produced by dispersants containing fatty acyl ester surfactants with HLB of 8 or 10. Overall, the correlation between dispersant effectiveness and droplet size is relatively weak, but the differences between the largest and smallest diameters of mean volume were relatively small (*i.e.*, 3.2 to 8.0 µm).

The three-factor interactions for DMV and dispersion effectiveness are shown in Figure 9A and B, respectively. Once again, due to the very large number of pairwise comparisons that are possible (351), the differences that are indicated are those identified using the LSD test. The significant differences identified using Tukey's method for pairwise comparisons are shown in



**Figure 9:** Comparison of three-factor interactions for (A) droplet-size distribution (DMV) and (B) dispersant effectiveness. Error bars represent one standard deviation of three independent replicate dispersion experiments. The asterisk denotes a significant difference ( $p < 0.05$ ) as determined by the LST test.

Tables 11 and 12. Tukey’s method identifies many more significant differences than does the LSD. For example, although the ANOVA determined that the three-factor interaction for dispersion effectiveness was highly significant ( $p < 0.001$ ; see Table 6), the LSD test was unable to identify any differences between adjacent pairs of means when they were rank ordered, whereas Tukey’s method identified 104 significant differences when all possible pairwise comparisons were evaluated (Table 12).

**Table 8:** Probabilities that the means of any pair of DMVs are significantly different for the two-factor interaction between dispersant HLB and surfactant chemistry

Interaction	8-sorb	10-sorb	12-sorb	8-ester	10-ester	12-ester	8-ether	10-ether	12-ether
8-sorb	1.000								
10-sorb	0.005	1.000							
12-sorb	0.001	1.000	1.000						
8-ester	0.000	0.000	0.000	1.000					
10-ester	0.001	1.000	1.000	0.000	1.000				
12-ester	0.000	0.000	0.000	0.380	0.000	1.000			
8-ether	0.000	0.000	0.000	0.000	0.000	0.000	1.000		
10-ether	0.158	0.000	0.000	0.000	0.000	0.000	0.081	1.000	
12-ether	1.000	0.005	0.001	0.000	0.001	0.000	0.000	0.148	1.000

**Table 9:** Probabilities that the means of any pair of DMVs are significantly different for the two-factor interaction between dispersant HLB and dispersant composition

Interaction	8-single	8-unequal	8-equal	10-single	10-unequal	10-equal	12-single	12-unequal	12-equal
8-single	1.000								
8-unequal	0.000	1.000							
8-equal	0.000	1.000	1.000						
10-single	1.000	0.000	0.000	1.000					
10-unequal	0.008	0.538	0.238	0.044	1.000				
10-equal	0.000	0.182	0.450	0.000	0.001	1.000			
12-single	0.000	1.000	0.983	0.000	0.837	0.060	1.000		
12-unequal	0.000	0.000	0.000	0.000	0.000	0.004	0.000	1.000	
12-equal	0.000	0.976	1.000	0.000	0.072	0.799	0.822	0.000	1.000

**Table 10:** Probabilities that the means of any pair of DMVs are significantly different for the two-factor interaction between dispersant HLB and surfactant chemistry

Interaction	sorb-single	sorb-uneq	sorb-equal	ester-single	ester-uneq	ester-equal	ether-single	ether-uneq	ether-equal
sorb-single	1.000								
sorb-uneq	0.999	1.000							
sorb-equal	0.673	0.967	1.000						
ester-single	0.988	1.000	0.995	1.000					
ester-uneq	0.000	0.000	0.000	0.000	1.000				
ester-equal	0.000	0.000	0.000	0.000	0.005	1.000			
ether-single	0.000	0.000	0.000	0.000	0.000	0.000	1.000		
ether-uneq	0.308	0.738	1.000	0.881	0.000	0.000	0.000	1.000	
ether-equal	0.000	0.000	0.005	0.000	0.000	0.000	0.000	0.029	1.000

**Table 11: Probabilities that the means of any pair of DMVs are significantly different for the three-factor interaction between dispersant HLB, surfactant chemistry, and dispersant composition**

Interaction	8/S/ sorb	8/U/ sorb	8/E/ sorb	10/S/ sorb	10/U/ sorb	10/E/ sorb	12/S/ sorb	12/U/ sorb	12/E/ sorb	8/S/ ester	8/U/ ester	8/E/ ester	10/S/ ester	10/U/ ester	10/E/ ester	12/S/ ester	12/U/ ester	12/E/ ester	8/S/ ether	8/U/ ether	8/E/ ether	10/S/ ether	10/U/ ether	10/E/ ether	12/S/ ether	12/U/ ether	12/E/ ether	
8/S/sorb	1.000																											
8/U/sorb	0.003	1.000																										
8/E/sorb	0.000	0.886	1.000																									
10/S/sorb	0.000	0.007	0.808	1.000																								
10/U/sorb	0.675	0.874	0.011	0.000	1.000																							
10/E/sorb	0.000	0.921	1.000	0.753	0.014	1.000																						
12/S/sorb	0.000	0.027	0.970	1.000	0.000	0.951	1.000																					
12/U/sorb	0.000	0.002	0.563	1.000	0.000	0.498	1.000	1.000																				
12/E/sorb	1.000	0.115	0.000	0.000	1.000	0.000	0.000	0.000	1.000																			
8/S/ester	0.000	0.601	1.000	0.974	0.002	1.000	0.999	0.862	0.000	1.000																		
8/U/ester	0.000	0.000	0.052	0.998	0.000	0.040	0.960	1.000	0.000	0.165	1.000																	
8/E/ester	0.000	0.000	0.001	0.443	0.000	0.001	0.195	0.701	0.000	0.003	1.000	1.000																
10/S/ester	1.000	0.009	0.000	0.000	0.862	0.000	0.000	0.000	1.000	0.000	0.000	0.000	1.000															
10/U/ester	0.000	0.005	0.728	1.000	0.000	0.665	1.000	1.000	0.000	0.948	1.000	0.535	0.000	1.000														
10/E/ester	0.000	0.002	0.535	1.000	0.000	0.470	1.000	1.000	0.000	0.843	1.000	0.728	0.000	1.000	1.000													
12/S/ester	0.000	0.054	0.973	1.000	0.000	0.958	1.000	1.000	0.000	0.999	0.997	0.506	0.000	1.000	1.000	1.000												
12/U/ester	0.000	0.001	0.283	1.000	0.000	0.236	1.000	1.000	0.000	0.591	1.000	0.925	0.000	1.000	1.000	1.000	1.000											
12/E/ester	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.005	0.212	0.000	0.000	0.000	0.000	0.000	1.000										
8/S/ether	0.820	0.516	0.001	0.000	1.000	0.001	0.000	0.000	1.000	0.000	0.000	0.000	0.952	0.000	0.000	0.000	0.000	0.000	1.000									
8/U/ether	0.907	0.619	0.003	0.000	1.000	0.004	0.000	0.000	1.000	0.001	0.000	0.000	0.981	0.000	0.000	0.000	0.000	0.000	1.000	1.000								
8/E/ether	1.000	0.001	0.000	0.000	0.319	0.000	0.000	0.000	0.990	0.000	0.000	0.000	1.000	0.000	0.000	0.000	0.000	0.000	0.443	0.601	1.000							
10/S/ether	1.000	0.000	0.000	0.000	0.111	0.000	0.000	0.000	0.869	0.000	0.000	0.000	1.000	0.000	0.000	0.000	0.000	0.000	0.161	0.276	1.000	1.000						
10/U/ether	0.850	0.710	0.004	0.000	1.000	0.006	0.000	0.000	1.000	0.001	0.000	0.000	0.960	0.000	0.000	0.000	0.000	0.000	1.000	1.000	0.507	0.212	1.000					
10/E/ether	0.000	1.000	1.000	0.115	0.249	1.000	0.297	0.045	0.007	0.994	0.001	0.000	0.000	0.083	0.040	0.387	0.013	0.000	0.057	0.098	0.000	0.000	0.134	1.000				
12/S/ether	1.000	0.000	0.000	0.000	0.201	0.000	0.000	0.000	0.957	0.000	0.000	0.000	1.000	0.000	0.000	0.000	0.000	0.000	0.287	0.435	1.000	1.000	0.350	0.000	1.000			
12/U/ether	0.000	0.002	0.582	1.000	0.000	0.516	1.000	1.000	0.000	0.874	1.000	0.684	0.000	1.000	1.000	1.000	1.000	0.000	0.000	0.000	0.000	0.000	0.000	0.048	0.000	1.000		
12/E/ether	0.435	0.974	0.029	0.000	1.000	0.037	0.000	0.000	0.994	0.007	0.000	0.000	0.656	0.000	0.000	0.000	0.000	0.000	1.000	1.000	0.160	0.046	1.000	0.452	0.092	0.000	1.000	

Note: All p-values shown as 0.000 signify  $< 0.001$ .

**Table 12:** Probabilities that the means of any pair of dispersant effectivenesses are significantly different for the three-factor interaction between dispersant HLB, surfactant chemistry, and dispersant composition

Interaction	8/S/ sorb	8/U/ sorb	8/E/ sorb	10/S/ sorb	10/U/ sorb	10/E/ sorb	12/S/ sorb	12/U/ sorb	12/E/ sorb	8/S/ ester	8/U/ ester	8/E/ ester	10/S/ ester	10/U/ ester	10/E/ ester	12/S/ ester	12/U/ ester	12/E/ ester	8/S/ ether	8/U/ ether	8/E/ ether	10/S/ ether	10/U/ ether	10/E/ ether	12/S/ ether	12/U/ ether	12/E/ ether
8/S/sorb	1.000																										
8/U/sorb	0.080	1.000																									
8/E/sorb	0.003	0.189	1.000																								
10/S/sorb	0.187	0.658	0.082	1.000																							
10/U/sorb	0.008	0.325	0.738	0.156	1.000																						
10/E/sorb	0.453	0.309	0.022	0.563	0.048	1.000																					
12/S/sorb	0.003	0.189	0.999	0.081	0.737	0.022	1.000																				
12/U/sorb	0.130	0.002	0.000	0.006	0.000	0.026	0.000	1.000																			
12/E/sorb	0.385	0.369	0.030	0.647	0.063	0.905	0.029	0.019	1.000																		
8/S/ester	0.215	0.599	0.069	0.934	0.134	0.621	0.068	0.007	0.707	1.000																	
8/U/ester	0.318	0.442	0.040	0.743	0.083	0.803	0.040	0.014	0.896	0.806	1.000																
8/E/ester	0.437	0.322	0.024	0.582	0.051	0.978	0.024	0.024	0.926	0.640	0.824	1.000															
10/S/ester	0.405	0.350	0.027	0.620	0.058	0.934	0.027	0.021	0.970	0.680	0.867	0.956	1.000														
10/U/ester	0.972	0.075	0.003	0.176	0.007	0.433	0.003	0.139	0.366	0.203	0.302	0.417	0.386	1.000													
10/E/ester	0.387	0.367	0.029	0.644	0.062	0.907	0.029	0.019	0.997	0.705	0.894	0.929	0.973	0.368	1.000												
12/S/ester	0.243	0.680	0.115	0.987	0.198	0.616	0.114	0.013	0.694	0.953	0.781	0.634	0.669	0.231	0.691	1.000											
12/U/ester	0.722	0.160	0.008	0.332	0.019	0.692	0.008	0.063	0.606	0.374	0.519	0.672	0.633	0.696	0.609	0.394	1.000										
12/E/ester	0.048	0.000	0.000	0.001	0.000	0.008	0.000	0.631	0.005	0.002	0.004	0.007	0.006	0.052	0.006	0.004	0.021	1.000									
8/S/ether	0.759	0.031	0.001	0.088	0.002	0.269	0.001	0.188	0.219	0.105	0.172	0.257	0.234	0.787	0.220	0.135	0.493	0.070	1.000								
8/U/ether	0.381	0.372	0.030	0.651	0.064	0.899	0.030	0.019	0.995	0.712	0.902	0.921	0.965	0.363	0.992	0.698	0.602	0.005	0.216	1.000							
8/E/ether	0.889	0.060	0.002	0.145	0.005	0.374	0.002	0.168	0.314	0.169	0.256	0.360	0.332	0.917	0.316	0.197	0.620	0.066	0.875	0.311	1.000						
10/S/ether	0.316	0.007	0.000	0.023	0.000	0.083	0.000	0.601	0.064	0.028	0.049	0.078	0.070	0.333	0.065	0.042	0.177	0.318	0.443	0.064	0.387	1.000					
10/U/ether	0.685	0.033	0.001	0.087	0.002	0.250	0.001	0.264	0.205	0.103	0.163	0.239	0.218	0.711	0.206	0.128	0.448	0.113	0.899	0.203	0.790	0.548	1.000				
10/E/ether	0.389	0.365	0.029	0.641	0.062	0.911	0.029	0.020	0.994	0.702	0.890	0.933	0.977	0.371	0.996	0.688	0.612	0.006	0.222	0.988	0.318	0.066	0.208	1.000			
12/S/ether	0.057	0.000	0.000	0.002	0.000	0.009	0.000	0.687	0.007	0.002	0.005	0.009	0.007	0.062	0.007	0.005	0.025	0.939	0.083	0.007	0.077	0.356	0.131	0.007	1.000		
12/U/ether	0.415	0.012	0.000	0.035	0.001	0.121	0.000	0.477	0.095	0.043	0.073	0.115	0.103	0.435	0.096	0.061	0.244	0.236	0.572	0.094	0.499	0.849	0.681	0.097	0.267	1.000	
12/E/ether	0.204	0.622	0.073	0.959	0.142	0.598	0.073	0.007	0.684	0.974	0.781	0.617	0.656	0.192	0.681	0.977	0.357	0.002	0.098	0.688	0.160	0.025	0.096	0.678	0.002	0.040	1.000

Note: All p-values shown as 0.000 signify  $< 0.001$ .

## 6. Conclusions

In this research, dispersant effectiveness was measured using two methods: measurement of the droplet-size distribution using an optical particle counter (OPC) and extraction of the dispersed oil into dichloromethane followed by gravimetric measurement of the mass of extracted oil. The gravimetric method produced systematically lower estimates of dispersion effectiveness than the size-distribution method, probably due to evaporation of volatile oil components during evaporation of the solvent. Therefore, treatment effects were evaluated based on the size-distribution data.

All dispersants produced bimodal droplet-volume distributions, and the two major modes had similar mean diameters (about 4  $\mu\text{m}$  and 10  $\mu\text{m}$ ). This bimodal size distribution may be due primarily to the characteristics of the baffled flask test, although experiments conducted in salt water using the same dispersants tend to produce trimodal volume distributions (unpublished data). In the latter case, an additional large volume mode (mean diameter of about 25  $\mu\text{m}$ ) is produced. Despite the similar characteristics of all of the dispersed-oil volume distributions, dispersant formulations tended to change the distribution of oil between the two droplet-size modes. The relative amount of oil in the large and small size modes was quantified using the diameter of mean volume (DMV). Although the overall differences among DMV for dispersant formulations was relatively small, the dispersant characteristics exerted highly significant effects on DMV with all three main effects, all three two-factor interactions (*i.e.*, HLB x dispersant composition; HLB x surfactant chemistry; dispersant composition x surfactant chemistry), and the three-factor interaction (*i.e.*, HLB x dispersant composition x surfactant chemistry) being significant at the 95% confidence level. The strong statistical significance (ANOVA results in Tables 6 and 7) of these treatment effects and interactions appears to be due to the high reproducibility of the droplet-size distributions that were produced by each dispersant formulation. Dispersion effectiveness was much more variable than were the size distributions. It is also of interest to note that divalent cations seem to exert a more important influence than monovalent cations in terms of droplet size distribution effects from the use of dispersants (Belk, *et al.*, 1989)

Dispersants formulated with sorbitan ester surfactants and with HLB of between about 8 and 10 exhibited the best performance when the dispersion of a weathered Mars Blend crude oil was tested in the synthetic lake freshwater. At least two of the dispersant formulations that were tested were highly effective with >90% of the added oil transferred to the aqueous phase in the baffled flask test. Dispersants formulated with fatty acyl ester or ether surfactants and higher HLB were relatively ineffective. The least effective dispersants transferred less than 60% of the added oil to the aqueous phase. It is unknown to what extent this observation applies to other types of freshwater formulations.

This report showed that, at least with Mars Blend crude oil in simulated lake water, dispersants can be designed to drive an oil slick into the freshwater column with the same efficiency as in saltwater as long as the HLB is optimum. Clearly, many more oils would need to be tested under different conditions (temperature, organic content, water composition, etc.) to enable firm conclusions that oil can be dispersed in freshwater as a response tool. The ultimate decision to use dispersants in treating freshwater petroleum oil spills is up to the federal on-scene coordinator, the incident command team, the regional response teams, and EPA Headquarters, since many other factors need to be considered before rendering a decision to disperse oil into

the water column. It is beyond the scope of this report to consider such factors. Its purpose was simply to determine if freshwater dispersion is possible and to determine whether effective freshwater dispersants can be designed to produce stable oil droplet distributions in such an environment.

## 7. References

- Belk, J.L., D.J. Elliott and L.M. Flaherty (1989). The comparative effectiveness of dispersants in fresh and low salinity waters. In: *Proceedings, 1989 Oil Spill Conference*, 333-336. American Petroleum Institute. Washington, DC
- Blondina, G.J., M.M. Singer, I. Lee, M.T. Ouano, M. Hodgins, R.S. Tjeerdema and M.L. Sowby (1999). Influence of salinity on petroleum accommodation by dispersants. *Spill Science and Technology Bulletin* 5(2): 127-134.
- Bruheim, P., H. Bredholt and K. Eimhjellen (1999). Effects of surfactant mixtures, including Corexit 9527, on bacterial oxidation of acetate and alkanes in crude oil. *Applied and Environmental Microbiology* 65(4): 1658-1661.
- Bruheim, P. and K. Eimhjellen (2000). Effects of non-ionic surfactants on the uptake and hydrolysis of fluoresceindiacetate by alkane-oxidizing bacteria. *Canadian Journal of Microbiology* 46(4): 387-390.
- Clayton, J.R., J.R. Payne and J.S. Farlow (1993). *Oil Spill Dispersants: Mechanisms of Action and Laboratory Tests*. CRC Press, Inc. Boca Raton, FL
- Clark, J. 2004. Dispersant basics: Mechanism, chemistry, and physics of dispersants in oil-spill response. Presented to the National Research Council Committee on Oil-Spill Dispersants: Efficacy and Effects, March 15, 2004.
- Fingas, M., I. Bier, M. Bobra and S. Callaghan (1991). Studies on the physical and chemical behavior of oil and dispersant mixtures. In: *Proceedings, 1991 Oil Spill Conference*. American Petroleum Institute. Washinton, DC
- Fingas, M.F., B. Kolokowski and E.J. Tennyson (1990). *Study of oil spill dispersants effectiveness and physical studies*. Thirteenth Arctic and Marine Oilspill Program Technical Seminar, Edmonton, Alberta, Canada, Environment Canada.
- Georges-Ares, A. and J.R. Clark (2000). Aquatic toxicity of two Corexit dispersants. *Chemosphere* 40: 897-906.
- Lehtinen, C.M. and A.-M. Vesala (1984). Effectiveness of oil spill dispersants at low salinities and low water temperatures. In: *Oil Spill Chemical Dispersants: Research, Experience, and Recommendations*, 108-121. T. E. Allen. American Society for Testing and Materials. Philadelphia, PA
- Myers, D. (2006). *Surfactant Science and Technology*, Third Edition. John Wiley and Sons, Inc. Hoboken, NJ
- NRC (2005). *Oil Spill Dispersants: Efficacy and Effects*. National Academies Press. Washington, DC
- NRC, N.R.C. (1989). *Using Oil Spill Dispersants on the Sea*. National Academy Press. Washington, DC



- Porter, M.R. (1991). *Handbook of Surfactants*. Blackie and Sons, Ltd. Glasgow, Scotland
- Sorial, G.A., A.D. Venosa, K.M. Koran, E. Holder and D.W. King (2004). Oil spill dispersant effectiveness protocol. II: Performance of revised protocol. *Journal of Environmental Engineering (ASCE)* 130(10): 1085-1093.
- Stoffyn-Egli, P. and K. Lee (2002). Formation and characterization of oil-mineral aggregates. *Spill Science & Technology Bulletin* 8(1): 31-44.
- Van Hamme, J.D. and O.P. Ward (1999). Influence of chemical surfactants on the biodegradation of crude oil by a mixed bacterial culture. *Canadian Journal of Microbiology* 45: 130-137.