

# **Characteristics of Spilled Oils, Fuels, and Petroleum Products:**

## **2a. Dispersant Effectiveness Data for a Suite of Environmental Conditions – The Effects of Temperature, Volatilization, and Energy**

by

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## **Notice**

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## Foreword

The National Exposure Research Laboratory's Ecosystems Research Division (ERD) in Athens, Georgia, conducts research on organic and inorganic chemicals, greenhouse gas biogeochemical cycles, and land use perturbations that create direct and indirect, chemical and non-chemical stresses, exposures, and potential risks to humans and ecosystems. ERD develops, tests, applies and provides technical support for exposure and ecosystem response models used for assessing and managing risks to humans and ecosystems, within a watershed / regional context.

The Regulatory Support Branch (RSB) conducts problem-driven and applied research, develops technology tools, and provides technical support to customer Program and Regional Offices, States, Municipalities, and Tribes. Models are distributed and supported via the EPA Center for Exposure Assessment Modeling (CEAM) and through access to Internet tools ([www.epa.gov/athens/onsite](http://www.epa.gov/athens/onsite)).

At the request of the US EPA Oil Program Center, ERD is developing an oil spill model that focuses on fate and transport of oil components under various response scenarios. Since crude oils and petroleum products are composed of many chemicals that have varying physical properties, data are required to characterize these fluids for use in models. The data and regressions presented in this report illustrate the interaction between oils and dispersants under a variety of environmental conditions. EPA expects these data to be useful both for modeling and to provide a resource for the oil spill response community as a whole.

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## Oil Spill Report Series

A series of research reports is planned to present data and models for oil spill planning and response. To date, these include:

### 1. Oil Composition

Zhendi Wang, B.P. Hollebone, M. Fingas, B. Fieldhouse, L. Sigouin, M. Landriault, P. Smith, J. Noonan, and G. Thouin, 2003, Characteristics of Spilled Oils, Fuels, and Petroleum Products: 1. Composition and Properties of Selected Oils, United States Environmental Protection Agency, National Exposure Research Laboratory, EPA/600/R-03/072.

### 2. Dispersants

George Sorial, Subhashini Chandrasekar, James W. Weaver, 2004, Characteristics of Spilled Oils, Fuels, and Petroleum Products: 2a. Dispersant Effectiveness Data for a Suite of Environmental Conditions – The Effects of Temperature, Volatilization, and Energy, United States Environmental Protection Agency, National Exposure Research Laboratory, EPA/600/R-04/119.

### 3. Simulation Models

James W. Weaver, 2004, Characteristics of Spilled Oils, Fuels, and Petroleum Products: 3a. Simulation of Oil Spills and Dispersants Under Conditions of Uncertainty, United States Environmental Protection Agency, National Exposure Research Laboratory, EPA/600/R-04/120.

As more reports are added to the series, they may be found on EPA's web site at:  
<http://www.epa.gov/athens/publications>.

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## **Abbreviations and Acronyms**

2FO - Number Two Fuel Oil

BFT - Baffled Flask Test

DCM - Dichloromethane

DOR - Dispersant-to-oil ratio

ERO<sup>3</sup>S - EPA Research Object-Oriented Oil Spill model

EXDET - Exxon Dispersant Effectiveness Test

NRC - National Research Council

PBC - Prudhoe Bay Crude Oil

QAPP - Quality Assurance Project Plan

RPD - Relative Percent Difference

RSD - Relative Standard Deviation

SFT - Swirling Flask Test

SLC - South Louisiana Crude Oil

SOP - Standard Operating Procedure

U.S.EPA - United States Environmental Protection Agency

## Abstract

Chemical dispersants are used in oil spill response operations to enhance the dispersion of oil slicks at sea as small oil droplets in the water column. To assess the impacts of dispersant usage on oil spills, US EPA is developing a simulation model called the EPA Research Object-Oriented Oil Spill (ERO<sup>3</sup>S) model (<http://www.epa.gov/athens/research/projects/eros/> and (Weaver, 2004). Due to the complexity of chemical and physical interactions between spilled oils, dispersants and the sea, an empirical approach to characterizing the interaction between the dispersant and oil slick may provide a useful or practical approach for including dispersant action in a model. The main objective of this research is to create a set of empirical data on three oils and two dispersants that has the potential for use as an input to the ERO<sup>3</sup>S model. These data are intended to give an indication of the amount of dispersal of these oils under certain conditions.

The US EPA is developing an improved dispersant testing protocol, called the baffled flask test (BFT), which is a refinement of the swirling flask test (Venosa *et al.*, 2002). Use of this protocol was the basis of the experiments conducted in this study. The variations in the effectiveness of dispersants caused by changes in oil composition, dispersant type, and the environmentally related variables of temperature, oil weathering, and rotational speed of the BFT were studied. The three oils tested were South Louisiana Crude Oil (SLC), an Alaska North Slope Crude (Prudhoe Bay Crude Oil, PBC), and Number 2 fuel oil (2FO). The two dispersants with the highest effectiveness scores under certain test conditions reported earlier were selected for this study. A factorial experimental design was conducted for each of the three oils for four factors: volatilization, dispersant type, temperature and flask speed. Each of the four factors was studied at three levels except for the dispersant factor where only two dispersants were considered. Statistical analysis of the experimental data was performed separately for the three oils. Empirical relationships between the amount of oil dispersed and the variables studied were developed. The experiments showed that dispersal increased with mixing energy/flask speed for each experiment performed, although there were cases with overlapping ranges of dispersal for different flask speeds. In these cases, increases in dispersal due to lack of weathering or

increased temperature evidently accounted for the overlap. In about half of the experiments there was no significant relationship between weathering and dispersal. Where weathering was significant, it was inversely related to dispersal. In either case, the weathering affect was small compared to either flask speed or temperature. Dispersal did not show a consistent pattern with temperature increase. For most of the experiments, either the maximum or the minimum amount of dispersal occurred at the middle temperature of 22 °C.

## **Introduction**

Transportation and consumption of petroleum products around the world has created the potential for oil spills into the environment. Offshore drilling and production platforms are another potential source of oil spills at sea. Other important sources of oil spills are facilities that store oil and ships that clean or empty ballast water at sea. Oil spills at sea can affect the water surface, the water column, sediments and shorelines. Oil initially forms a slick at the water surface due to its immiscibility. Oil spills spread under the action of gravitational, viscous and surface tension forces (Hoult, 1972). Wave and wind action disrupts the oil/water interface, resulting in the formation of oil droplets that enter the water column. Usually only a small amount of spilled oil can be dispersed in this fashion—without the addition of a chemical dispersing agent or dispersant (Delvigne, 1987a). Depending upon the characteristics of the oil, entrainment of water can result in an emulsion of varying stability (Wang *et al.*, 2003).

Spilled oil will most likely spread over a large area if a quick response is not initiated. So careful response planning and preparedness are essential for successful response to oil spills at sea. In general, there are three major response operations for cleanup of oil spills at sea: mechanical response, in-situ burning, and the use of chemical dispersants (NRC, 1989). Some of the recovery options for oil on the seabed include manual removal by divers, dip nets, or seines; pump and vacuum systems; nets and trawls; or dredging.

Chemical dispersants are mixtures of surfactants and other substances that are usually sprayed onto oil slicks to remove oil from the surface and disperse it into the water column at very low concentrations (Lessard and Demarco, 2000). Surfactants are surface active agents that are dissolved in one or more solvents. They have a chemical affinity for both oil (lipophilic) and water (hydrophilic) molecules. When applied to an oil film, surfactants diffuse to the oil/water interface and align themselves so that the lipophilic end of the molecule is attached to the oil phase and the hydrophilic end extends into the water phase, thereby allowing some oil to mix into the top of the water column in the form of tiny droplets. It is also believed that chemical dispersants help reduce the droplet size when viscous shear is the dominant breakup mechanism (Ming and Chris, 1998).

Dispersant effectiveness is defined as the amount (quantity) of oil that the dispersant puts into the water column compared to the amount of oil that remains on the surface. Many factors influence dispersant effectiveness, including oil composition, sea energy, state of oil weathering, the type of dispersant used and the amount applied, temperature, and salinity of the water. Certain components of oil, such as resins, asphaltenes, and larger aromatics or waxes, are barely dispersible (Fingas, 2000). Oils that are made primarily of these components will disperse poorly even when dispersants are applied. On the other hand, oils that contain mostly saturates, will disperse both naturally and when dispersants are added. The additional amount of oil dispersed when dispersants are used compared to the amount that would disperse naturally depends strongly on the amount of sea energy present (Mackay *et al.*, 1984). The amount of dispersant applied is very important to effectiveness. It was found that the effectiveness falls to nearly zero for a light oil at a dispersant-to-oil ratio (DOR) between 1:40 and 1:60 (Delvigne, 1987b; Fingas *et al.*, 1993b; Fingas *et al.*, 1997).

## **Background**

Many different types of dispersant test procedures and apparatus have been described in the literature. In general, three approaches have been used for dispersant applications in these tests: (1) premixing of a dispersant with the oil before the test begins (Fingas *et al.*, 1989a; U.S Environmental

Protection Agency, 1996); (2) premixing of the dispersant with water before oil is introduced to the system.(Rewick *et al.*, 1981 ; Rewick *et al.*, 1984) and (3) mixing of the dispersant with the oil at the oil-air interface as part of the testing procedure itself.

Clayton *et al.*(1993) evaluated the performance of the revised standard EPA method (U.S Environmental Protection Agency, 1984), Environment Canada's Swirling Flask Test (SFT) (Fingas *et al.*, 1987; Fingas *et al.*, 1989a; Fingas *et al.*, 1989b; Blondina *et al.*, 1997b) and the IFP-Dilution test (Bardot *et al.*, 1984; Desmarquest *et al.*, 1985; Daling *et al.*, 1990). They also evaluated three versions of the SFT (premixed dispersant and oil, and 1-droplet and 2-droplet dispersant-to-oil-slick addition). Based on their results, the SFT premixed procedure was recommended to EPA for testing dispersants due to its relative simplicity and straightforwardness. Becker et al. (1991) studied the Exxon Dispersant Effectiveness Test (EXDET) and found that the results obtained from this method and the SFT were similar. The SFT was adopted in the final EPA regulation in September 1994. The SFT was reexamined after its first year of use (IT Corporation, 1995). Due to discrepancies in found in practice, a redesign of the test flask was considered by EPA. The design of the new test which is referred to as the Baffled Flask Test (BFT) and the experiments leading to major changes in the protocol reflecting a much more reproducible and stable effectiveness test were described by (Sorial *et al.*, 2001a). The BFT has the promise of being able to overcome limitations of previous test methodologies which included non-reproducibility and non-representativeness of field conditions, as reported by earlier researchers. In this project, the baffled flask test was used to test for variation in the effectiveness of dispersants caused by changes in temperature, oil composition, oil weathering, dispersant type, and rotation speed.

Currently, US EPA is developing a simulation model called the EPA Research Object-Oriented Oil Spill (ERO<sup>3</sup>S) model that is intended to assess the overall impacts (environmental, health, safety) of chemical dispersant usage on oil spills. This model is designed for simulating a portion of the oil slick behavior (Weaver, 2004). However, due to the complexity of chemical and physical interactions between spilled oils and the sea, a portion of the behavior of the oil spill must be based upon empirical data. The impacts of dispersants on oil slicks are best characterized by

empirical data. So the aim of this project is to create a set of empirical data on three oils and two dispersants that has the potential for use as an input to the ERO<sup>3</sup>S model. Depending on the nature of the results, the data might be used to determine the amount of oil that is dispersed in a spill scenario.

The three oils tested were South Louisiana Crude Oil (SLC), Prudhoe Bay Crude Oil (PBC) and Number Two Fuel Oil (2FO). The two dispersants were commercial products denoted “A” and “B” for the purposes of this study. These two dispersants were those with the highest effectiveness scores under certain test conditions reported earlier (Sorial *et al.*, 2001b). Of the three oils under investigation, PBC and SLC are medium weight EPA/API standard reference oils and 2FO is a light refined oil.

### **Factors affecting dispersion**

A number of factors influence the effectiveness of dispersants, including the properties of the oil: viscosity, slick thickness, dispersant-to-oil ratio, surfactant loss at the water surface, surface tension, emulsion formation, temperature, salinity, mixing energy, etc (Sorial *et al.*, 2001). Of these, the effect of temperature, mixing energy and weathering were studied. Of those omitted: viscosity and surface tension changes with weathering and so are included implicitly, and the oils chosen do not form appreciable emulsions (Wang *et al.*, 2003).

After dispersants have been added to the oil at sea and the small oil droplets formed, mixing energy is further required to disperse these oil droplets in the water column. In order for the dispersion process to be successful, oil droplets must stay submerged in the water column and not return to the surface to re-coalesce into an oil slick. As reported by Clayton *et al.* (1993), the application of dispersant reduces the interfacial tension between the oil and water, which results in the formation of oil droplets. The initial droplet size distribution is controlled by mixing energy, as well as the specific dispersant and oil, and dispersant-oil and oil-water ratios.

Experimental studies performed by a number of scientists indicated that the sizes of the oil droplets are inversely related to the amount of mixing energy input into test vessels. (Clayton *et al.*, 1993) and (Fingas *et al.*, 1993a) conducted experiments that indicated dispersants reduce the size of the oil droplets, making re-coalescence unlikely.

The chemical composition and physical properties of a crude oil determine the behavior of the oil and the way its properties will change when the oil is spilled at sea. Weathering increases the viscosity of the oil due to evaporation of the lighter components. Oil viscosity has been implicated as a major factor affecting the dispersibility of oil (Canevari *et al.*, 2001). As oil weathers and the viscosity increases, it has been demonstrated that the effectiveness of the chemical dispersants decline (Daling, 1988). Low water temperatures increase the viscosities of both the oil and the dispersant. As oil gets more viscous due to low water temperature or weathering, the energy requirement for mixing the dispersant and oil also increases (Clayton *et al.*, 1993). High water temperatures usually increase the solubility of dispersants in water and the temperature of the spilled oil itself. So, an increase in temperature is expected to reduce oil viscosity and hence improve dispersion. However, there have been conflicting results in the trend of dispersant effectiveness with either increasing or decreasing water temperature (Mackay and Szeto, 1981; Byford *et al.*, 1983; Lentinen and Vesala, 1984; Fingas, 1991). The general conclusion drawn from this body of work is that the ideal condition for dispersal is be a light oil spilled on warm water with moderate wind and wave action (Paul *et al.*, 1999) that does not impede response activities.

## **Objectives**

The objective of this project was to use the baffled flask test data to generate empirical dispersant effectiveness relationships to explore the behavior of oils under varying conditions and to develop a data set for use in oil spill models. Three oils and two dispersants were tested for a suite of environmental conditions including weathering, temperature and speed of the flask. Sub-

objectives were:

- To conduct a factorial experimental design for three oils, namely, SLC, PBC, and 2FO for determining the significance of the above factors on the effectiveness of two dispersants referred to as Dispersant 'A' and Dispersant 'B' in this study. Of the three oils chosen, PBC and SLC are medium weight reference oils and 2FO is a light refined oil.
- To determine if the baffled flask test has sufficient sensitivity for generating dispersant effectiveness data over the specified range of environmental conditions.
- To develop and evaluate quantitative, empirical relationships that relate dispersant effectiveness to weathering, speed (mixing energy) and temperature for each oil/dispersant pair.

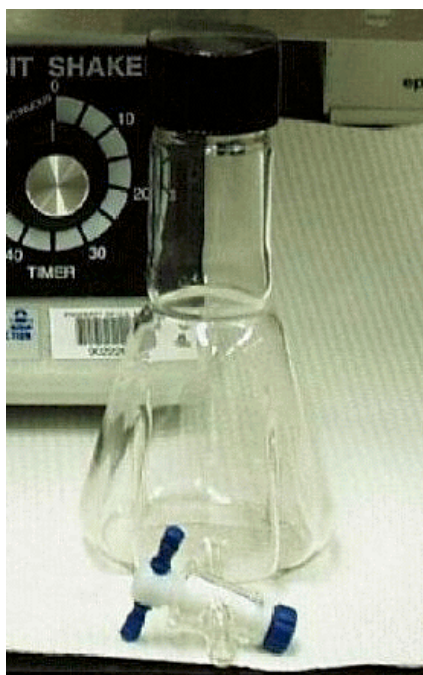
## **Experimental Methods**

The required glassware and analytical equipment that were used are listed below:

- **Modified Trypsinizing Flask:** 150 mL glass Trypsinizing flasks were modified to include a stopcock near the bottom (Figure 1) to provide the BFT apparatus. These are commercially available and can be obtained from Fischer Scientific.
- **Shaker Table:** A shaker table with a variable speed control unit (40-400 rpm) and an orbital diameter of approximately 0.75 inches (2 cm) was used to create turbulence in the test flask liquids.
- **Micropipettor:** A Brinkmann Eppendorf repeater plus pipettor with 100  $\mu$ L and 5mL syringe tip attachments capable of dispensing 4  $\mu$ L of dispersant and 100  $\mu$ L of oil was used, producing a delivery accuracy  $\pm 0.3\%$  and precision  $\pm 0.25\%$ .
- **Glassware:** Glassware consisting of 25, 50, and 100 mL graduated cylinders, 125 mL separatory funnels with Teflon stopcocks, 1,2,5 and 10 mL pipettes, 50 mL crimp-style amber glass vials and other lab glassware were used in the experiments.



- Syringes: 50, 100 and 1000  $\mu$ L gas-tight syringes were used.
- Spectrophotometer: A UV-visible spectrophotometer, capable of measuring absorbance at 340, 370 and 400 nm was used in the experiments.
- Analytical balance: calibrated per standard laboratory procedures was used.
- Synthetic Seawater: The synthetic sea water 'Instant Ocean', manufactured by Aquarium Systems of Mentor OH, was used for the study. The synthetic sea water was prepared by dissolving 68 g of the salt mixture in 2 liter of Milli-Q water to provide a salinity of 34 ppt.
- Test Oils: Three types of oil samples provided by EPA-Prudhoe Bay Crude Oil (Alaska North Slope Crude Oil - PBC), South Louisiana Crude Oil (SLC) and Number 2 Fuel Oil (2FO) were used in the study.
- Dispersants: Two dispersant samples were provided by EPA.
- Methylene Chloride: Dichloromethane (DCM), pesticide quality, was used for extraction of all sample water and oil-standard water samples.



**Figure 1** Baffled flask test apparatus.

## Factorial Experimental Design

The response variable for the experiments conducted is the percent effectiveness of the dispersant. The factors and levels of each of the factors are as follows: volatilization (0, 10, and 20% for SLC and PBC and 0, 3.8 and 7.6% for 2FO); dispersants 'A' and 'B'; temperature (4, 22 and 35 °C); and flask speeds (150, 200 and 250 rpm). With these levels for each of the factors, a complete factorial experiment consisting of 54 runs was conducted for each oil. The total number of samples prepared was 162: 3 oils, 3 temperatures, 3 flask speeds, 2 dispersants, 3 volatilizations. In addition to these experiments, control experiments using the oils with no dispersant were also conducted. For this, the number of flasks prepared were: 3 oils, 3 temperatures, 3 flask speeds, 3 volatilizations for a total of 81. Thus the experimental program consisted of 243 flasks for the unreplicated portion of the experiments.

## Methods

The complete set of standard operating procedures (SOPs) for the experiments appear in Appendix 3. The following sections summarize the main points of each.

### Weathering of Oil

The three oils (PBC, SLC and 2FO) were used in the study at three levels of volatilization (weathering), each. The weathering of the oil was performed by bubbling air up through a one Liter graduated cylinder filled with each oil sample. The volume of the oil remaining in the measuring cylinder was recorded as a function of time. By using the one Liter volume and the volatilization levels selected, the amount of oil that sticks to the cylinder is negligible compared to the amount evaporated. The evaporative loss was then expressed as a volume percent.

$$\% \text{ oil volatilized} = \frac{\text{Initial volume} - \text{Final volume}}{\text{Initial volume}} \times 100 \quad (1)$$

PBC and SLC were volatilized to 10% and 20%, whereas 2FO was volatilized to 3.8% and 7.6% .

## **Oil Standards**

Standard solutions of oil for calibrating the UV-visible spectrophotometer were prepared with each specific reference oil and dispersant combination used for a particular set of experimental test runs. A 6-point calibration curve was generated for each set of experiments (See Appendix 3).

For treatments with no dispersant, i.e, oil control experiments, only oil was used to make the standard solution. First, the Oil Alone Stock Standard was prepared. The density of 2 mL of each oil mixed with 18 mL DCM added was measured by using a 1 mL gas-tight syringe, and the concentration of the oil solution determined. Specific volumes of 11, 20, 50, 100, 125, and 150  $\mu$ L of PBC-DCM stock or 100, 150, 200, 300  $\mu$ L of SLC-DCM stock or 150, 200, 400, 600, 800, 1000  $\mu$ L of 2FO-DCM stock were each added to 30 mL of synthetic sea water in a separatory funnel and extracted thrice with 5 mL of DCM. The final DCM volume for each extract was adjusted to 20 mL with DCM. The extracts were transferred to a 50 mL crimp-style glass vial with a Teflon/aluminium seal. The contents of the sealed vial were mixed by inverting. The vials were stored at  $4 \pm 2$  °C until the time of analysis. Prior to any analysis, the spectrophotometer ultraviolet lamp was turned on and allowed a 30-minute warm-up period.

For treatments with oil plus dispersant, Oil Plus Dispersant Stock Standards were first prepared. The densities of 2 mL of each oil, 80  $\mu$ L of the dispersant and 18 mL DCM was measured using a 1 mL gas-tight syringe and the concentrations determined. These stock solutions were used to prepare standard solutions in a similar way as described previously for the Oil Alone Stock Standards.

## **Dispersant Effectiveness Procedure**

For each test, 120 mL of synthetic sea water, equilibrated to the desired temperature was added to a modified trypsinizing flask (Baffled Flask). 100  $\mu\text{L}$  of oil was dispensed directly onto the surface of the synthetic sea water using an Eppendorf repeater pipettor with a 5 mL syringe tip attachment. The dispersant was then dispensed onto the center of the oil slick by using a 100  $\mu\text{L}$  syringe tip attachment that was set to dispense 4  $\mu\text{L}$ , giving a dispersant-to-oil ratio of 1:25. The flask was placed on an orbital shaker and mixed for 10 minutes at the desired rotation speed, at the end of which it was removed from the shaker and allowed to remain stationary on the bench top for another 10 minutes. At the end of the settling time, 2 mL was drained from the stopcock and discarded. Then a 30 mL sample was collected in a 50 mL measuring cylinder. This 30 mL sample was then transferred to a 125 mL separatory funnel and extracted three times with fresh 5 mL DCM. The extract was then adjusted to a final volume of 20 mL and transferred to a 50 mL crimp-style, glass vial with an aluminum/Teflon seal. These vials were stored at  $4\pm 2$   $^{\circ}\text{C}$  until the time of analysis.

## **Sample analysis**

The experimental sample extracts and the standard solutions were removed from the cold room and allowed to equilibrate to the laboratory temperature. First, a blank solution (DCM) was placed into the UV-visible spectrophotometer. Then the six calibration standards were measured in the order of increasing concentration and the absorbance values recorded for wavelengths of 340, 370 and 400 nm. After this, the experimental samples were measured. Samples that exceeded the highest calibration standard point were diluted. A factor of 10 dilution was needed for the SLC.

## QA/QC Checks

### Precision

Instrument precision objectives for the dispersant effectiveness tests were based on analyzing measurements in replicate. The acceptance criterion was based upon agreement of the replicate sample values within  $\pm 5\%$  of their mean value. The operator precision objectives were determined by using the relative standard deviation (RSD) for percent dispersant effectiveness from four replicate flasks. This acceptance criterion was established as an RSD less than 15% (Venosa, 2002)

$$RSD = \frac{\text{Standard Deviation of Replicates}}{\text{Average Concentration}} \times 100 \quad (2)$$

### Accuracy

The accuracy was determined by using a mid-point standard calibration check after every 4 experimental samples analyzed. The acceptance criterion was based upon percent recovery of 90-110%. The percent recovery was determined by using the following equation:

$$\% R = \frac{C_m}{C_a} \times 100 \quad (3)$$

where  $\% R$  is the percent recovery,  $C_m$  is the measured concentration of the check standard, and  $C_a$  is actual concentration of the check standard.

### Method Detection Limit

The concentration reporting limits (RLs) by UV-Spectrophotometer for PBC, SLC and 2FO were 0.04, 0.05 and 0.09 mg/L respectively. These RLs were at the low end of the calibration curves for the analytes. The analyses for all these oils were measured within the calibration concentration

range. For samples whose measured concentrations were above the range, the samples were diluted and re-analyzed. Conversely, there was no sample whose measured concentration was below detection limits.

### Calculation Procedure

The dispersant performance (i.e, percent of oil dispersed, or Effectiveness) was determined by:

$$Eff\% = \frac{Total\ oil\ dispersed}{\rho_{oil} V_{oil}} \times 100 \quad (4)$$

where  $\rho_{oil}$  is the density of specific test oil, g/L, and  $V_{oil}$  is the Volume (L) of oil added to the test flask. This calculation is a simple ratio of the oil dispersed into the water column to the amount of oil added to the flask. The complete procedures for this calculation are given in Appendix 3.

### Results

#### Experimental Data Summary

The percent dispersal effectiveness for each oil and dispersant combination are given in Tables 11 to 20 of Appendix 1, along with replicate results given in Tables 22 to 26 of Appendix 2. Because the dispersant behavior differs by oil, each of the three oils are discussed separately by using a set of histogram-like tables and plots of the data.

#### Summary of Prudhoe Bay Crude Dispersal Characteristics

Table 1 summarizes the 27 Prudhoe Bay Crude with dispersant “A” experimental data.

Each experiment is represented by a “triple” that indicates its value of weathering, temperature and speed, respectively. To compare relative effects, the values are indicated by H, M, or L indicating that the high, medium or low value of the parameter was used. The data are grouped in columns that represent a 10% increment in dispersal efficiency. Within each column, the dispersal increases bottom to top. The highest dispersal, for example, occurred with the combination M,M,H that appears in the 90 to 100% column in the topmost occupied row.

							L H H		
							L H H		
						H H M	M H H		
		L L L	L H L		L L M	M L H	L H M	H M M	M M H
		M L L	M H L	L M L	M L M	H L H	H H H	M M M	L M H
		H L L	H H L	H M L	H L M	M M L	M H M	L M M	H M H
0 - 10	10 - 20	20 - 30	30 - 40	40 - 50	50 - 60	60 - 70	70 - 80	80-90	90-100

Weathering Temperature Speed\*

\*H = high, M = medium, L = low

Example M H L = medium weathering, high temperature, low flask speed

**Table 1** % Dispersal Efficiency of Prudhoe Bay Crude with Dispersant “A”

Several features of the results are evident from this table. First, all of the experiments produced at least 20% dispersal of the oil. These values are at least 14% higher than the control experiments (Table 3, described below), indicating that dispersal above 20% does not occur in these experiments without the dispersant. Second, dispersal of the oil is normally expected to decrease with weathering and increase with speed and temperature. If this expectation was

completely fulfilled, the least dispersal would occur at H L L and the most dispersal at L H H. The cells containing these values are highlighted in each table, and the combination H L L, indeed had the lowest dispersal. It is worth noting, however, that medium and low weathering produced the next two lowest values of dispersal (2<sup>nd</sup> and 3<sup>rd</sup> entries in the 20 - 30% dispersal column). This result indicates that any amount of weathering occurring with low speed and low temperature results in only 20% to 30% dispersal. The highest dispersal, however, did not occur as expected with lowest weathering, highest temperature and highest speed (L H H). Although dispersal was high for this combination, it was not the highest.

The third point is indicated by the dotted line at 50% dispersal of the oil. All of the flask speeds are low for all levels of dispersal less than 50% (left of the dotted line). These dispersal levels occur with high, medium and low values of temperature and weathering. Thus, speed appears to be the most significant factor that causes dispersal of 50% or less. The fourth observation is that all dispersal greater than 80% occurs with medium (not high) temperatures, but all of the flask speeds are medium or high, again indicating the importance of energy input. Weathering, again, seems to be relatively unimportant as high, medium and low values occur in the 80% plus range of dispersal. In fact, all three values of weathering occur in almost all of the 10% dispersal increments (each column except 40% - 50%).



									L M H
									M M H
				M M L		L H M			H M H
				L L M		H M M			M L H
				M L M	M H L	M H M	L L H		M H H
		M L L		H M L	H H L	H H M	L M M		H L H
		H L L	L L L	H L M	L M L	L H L	M M M	H H H	L H H
0 - 10	10 - 20	20 - 30	30 - 40	40 - 50	50 - 60	60 - 70	70 - 80	80-90	90-100

Weathering Temperature Speed\*

\*H = high, M = medium, L = low

Example M H L = medium weathering, high temperature, low flask speed

**Table 2** % Dispersal Efficiency of Prudhoe Bay Crude with Dispersant “B”

Table 2 displays data for Prudhoe Bay Crude with Dispersant “B.” As for dispersant “A” the dispersal is at least 20% in all cases. The minimum and maximum dispersals occurred at the expected end points (shaded boxes). Dispersal efficiency of greater than 80% occurs only with high flask speed. At lower percent effectiveness, the pattern is less clear, than that for PBC with dispersant “A,” but high, medium or low weathering can occur over the entire range of dispersal efficiencies. Most (two-thirds) of the low temperatures have dispersal efficiencies of less than 50%. Compared with dispersant “A”, dispersant “B” gave fewer results that were less than 40% or above 90%, which implies more assurance of dispersal between 40% and 90% despite the varying conditions.

With no dispersant (Table 3), the maximum percent dispersal effectiveness was less than

7%, with two-thirds of the efficiencies less than 4%. Dispersal above 4% mostly occurred with high speed. These occurred in combination with each condition of weathering and temperature, suggesting that speed was the most important factor.

	L H M									
	H H M									
	M H M									
	L L M		L M L		M M M					
L H L	H L M		L M H		H M M					
H L L	M L M		H L H		H H H					
M L L	H H L		M M L		L L H	H M H				
L L L	M H L	L M M	H M L		M L H	L H H	M M H			
0 - 1	1 - 2	2 - 3	3 - 4		4 - 5	5 - 6	6 - 7	7 - 8	8 - 9	9 - 10

Weathering Temperature Speed\*

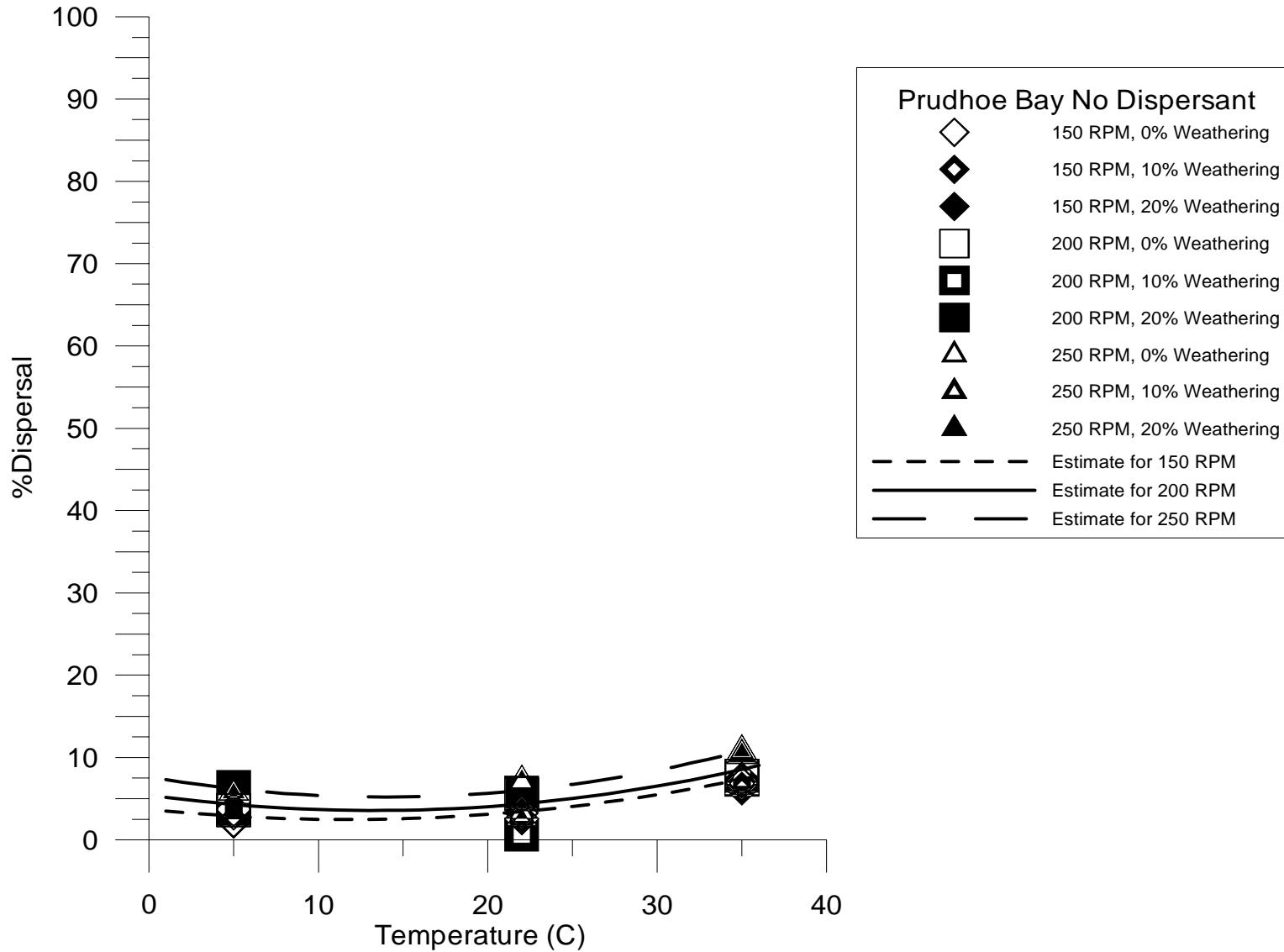
\*H = high, M = medium, L = low

Example M H L = medium weathering, high temperature, low flask speed

**Table 3** % Dispersal Efficiency of Prudhoe Bay Crude with No Dispersant

The responses of the Prudhoe Bay Crude in all experiments are plotted in Figures 2 to 4. These, and subsequent figures for No. 2 Fuel Oil and South Louisiana Crude, oil show the experimental data and regression lines described later. In some cases, there is only one regression line per flask speed. This occurred when there was no statistically significant relationship for weathering within the data set.

The percent dispersal efficiency increased with flask speed in all cases. When weathering was significant (Figures 6 and 7), dispersal increased inversely with weathering. In each case, there was a tendency for the maximum dispersal to occur at the middle temperature. This tendency was strongest for dispersant "A", but occurred for most cases of either dispersant addition.



**Figure 2** Comparison of regression equations (curves) against measured Prudhoe Bay Crude/no dispersant efficiency.

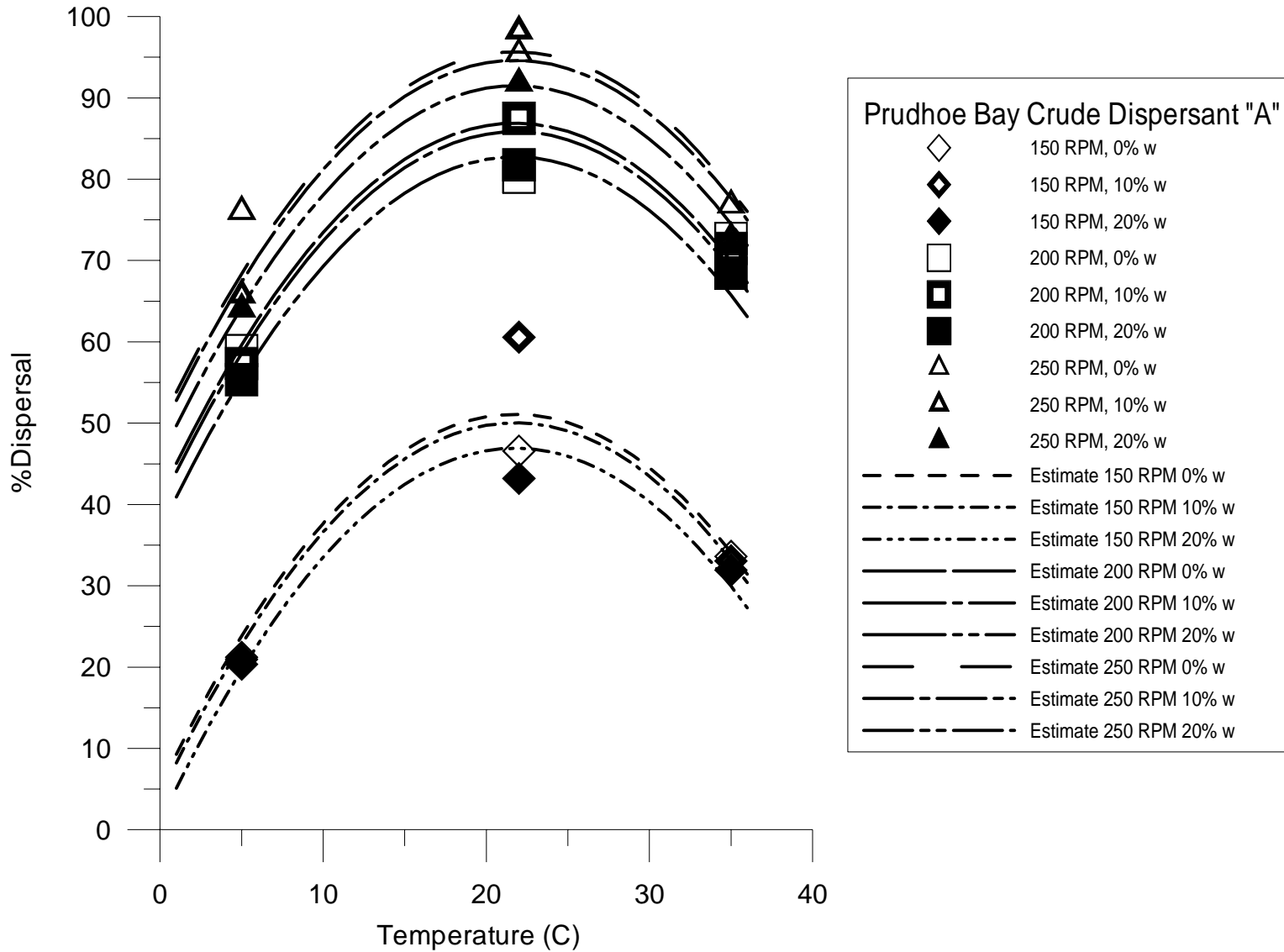
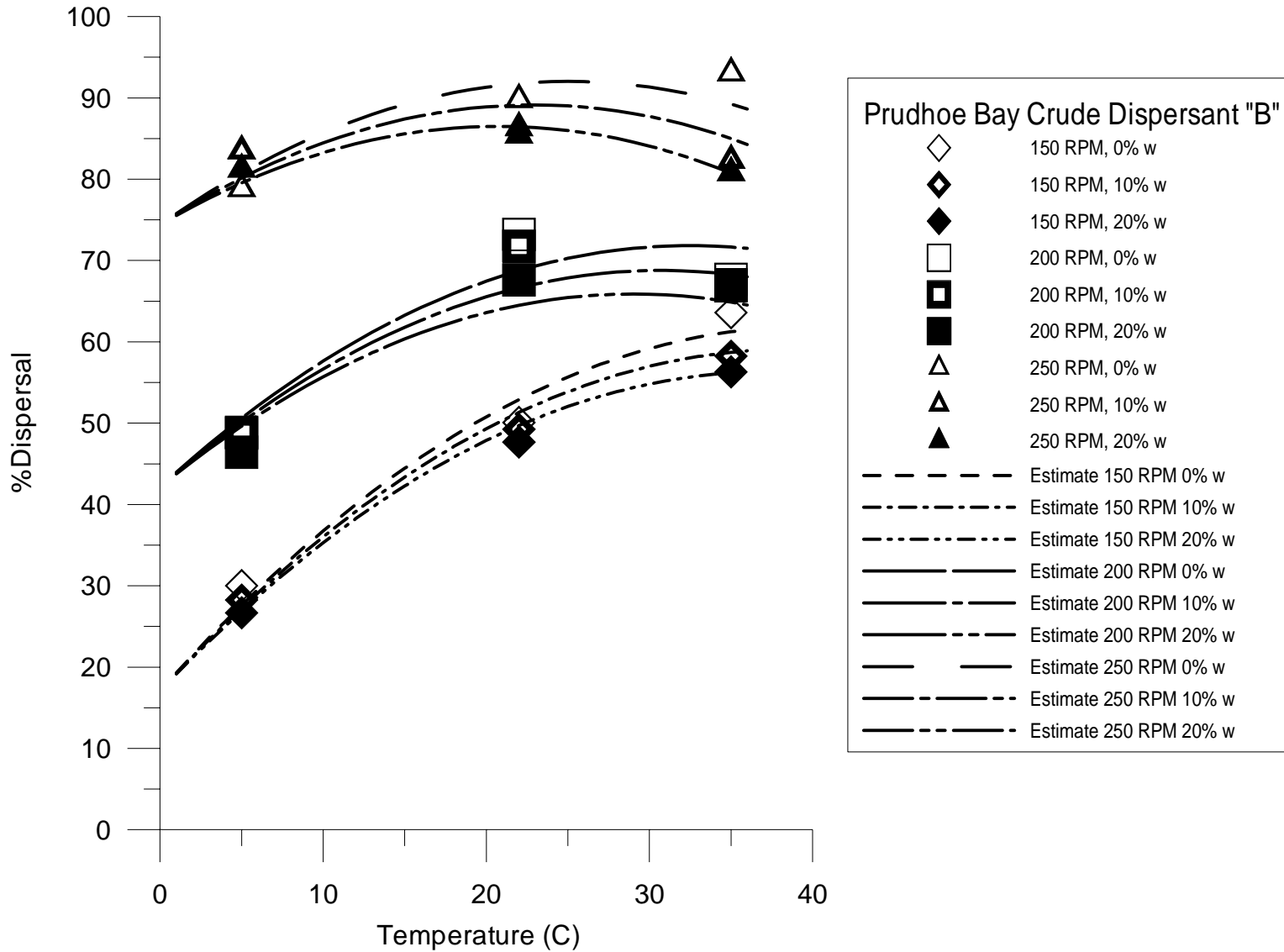


Figure 3 Comparison of regression equations (curves) against measured Prudhoe Bay Crude/dispersant "A" efficiency.



**Figure 4** Comparison of regression equations (curves) against measured Prudhoe Bay Crude/dispersant "B" efficiency.

## **Summary of No. 2 Fuel Oil Dispersal Characteristics**

Dispersal of the No. 2 Fuel Oil with dispersant “A” ranged from about 10% to nearly 100% (Table 4). Most dispersal above 70% occurred at high speed, but even 80% - 90% dispersal was achieved at medium speed. These very high dispersals occurred with low, medium and high values of both weathering and temperature. The lowest dispersals – 10% to 40% – occurred with low speed, but there was also dispersal of 50% to 70% at low speed (Table 4). Dispersal of 40% to 50% occurred with medium speed.

Dispersal of 2FO with dispersant “B” ranged from 20% to nearly 100% (Table 5). Dispersal above 70% occurred with medium and high speeds. All of the highest dispersals (90% - 100%) occurred at the highest speed with medium or high temperatures. Dispersals of 70% - 80% occurred at low to medium temperatures. With four exceptions, dispersal increased with increasing speed, while any of the weathering and temperature levels occurred across the range of dispersals.

With no dispersant the maximum dispersal was nearly 11% (Table 6). Dispersal above this value required use of the dispersant. Low values of dispersal tended to be associated with low temperature and speed. Conversely both temperature and speed tended to be higher where dispersal was high.

				L M L					
				L H M					
				M H M			L L H		
				L L M			M L H	L H H	
			L H L	H H M			M H H	H M M	H M H
	M L L		M H L	M L M			H H H	M M M	M M H
	H L L	L L L	H H L	H L M	M M L	H M L	H L H	L M M	L M H
0 - 10	10 - 20	20 - 30	30 - 40	40 - 50	50 - 60	60 - 70	70 - 80	80-90	90-100

Weathering Temperature Speed\*

\*H = high, M = medium, L = low

Example M H L = medium weathering, high temperature, low flask speed

**Table 4** % Dispersal Efficiency of No. 2 Fuel Oil with Dispersant "A"

				L M L					
				L L M			L M M	L H H	
				M L M			M M M	L M H	
				H L M	H M L		H M M	M H H	
		M L L		L H L	L H M		L L H	H H H	
		H L L		H H L	M H M		M L H	H M H	
		L L L	M M L	M H L	H H M		H L H	M M H	
0 - 10	10 - 20	20 - 30	30 - 40	40 - 50	50 - 60	60 - 70	70 - 80	80-90	90-100

Weathering Temperature Speed\*

\*H = high, M = medium, L = low

Example M H L = medium weathering, high temperature, low flask speed

**Table 5** % Dispersal Efficiency of No. 2 Fuel Oil with Dispersant "B"



							L H M			
		M M H					M H M			
		H M L	L L M		M L H	L H L	H H L			
		H L L	M L M		H L H	M M L	H H M			L H H
		L L L	H L M		L M M	L L H	L M H			M H H
M M M		M L L	L M L		H M M	M H L	H M H			H H H
0 - 1	1 - 2	2 - 3	3 - 4	4 - 5	5 - 6	6 - 7	7 - 8	8 - 9	9 - 10	10 - 11

Weathering Temperature Speed\*

\*H = high, M = medium, L = low

Example M H L = medium weathering, high temperature, low flask speed

**Table 6** % Dispersal Efficiency of No. 2 Fuel Oil with No Dispersant

Figures 5 to 7 show dispersal of No. 2 Fuel Oil over the suite of experimental conditions. With the exception of an anomolous point (no dispersant, 22 °C, 200 rpm and 10% weathering), dispersal increased with flask speed. For the dispersant treatments, weathering did not result in significant patterns, as each flask speed is represented by only one curve. The data show highest dispersal at the highest temperature for the control at all speeds, dispersant “B” at 250 rpm and dispersant “B” at 150 rpm and 10% weathering. Otherwise, the data follow the pattern for Prudhoe Bay Crude, where maximum dispersal occurred at the middle temperature of 22 °C.

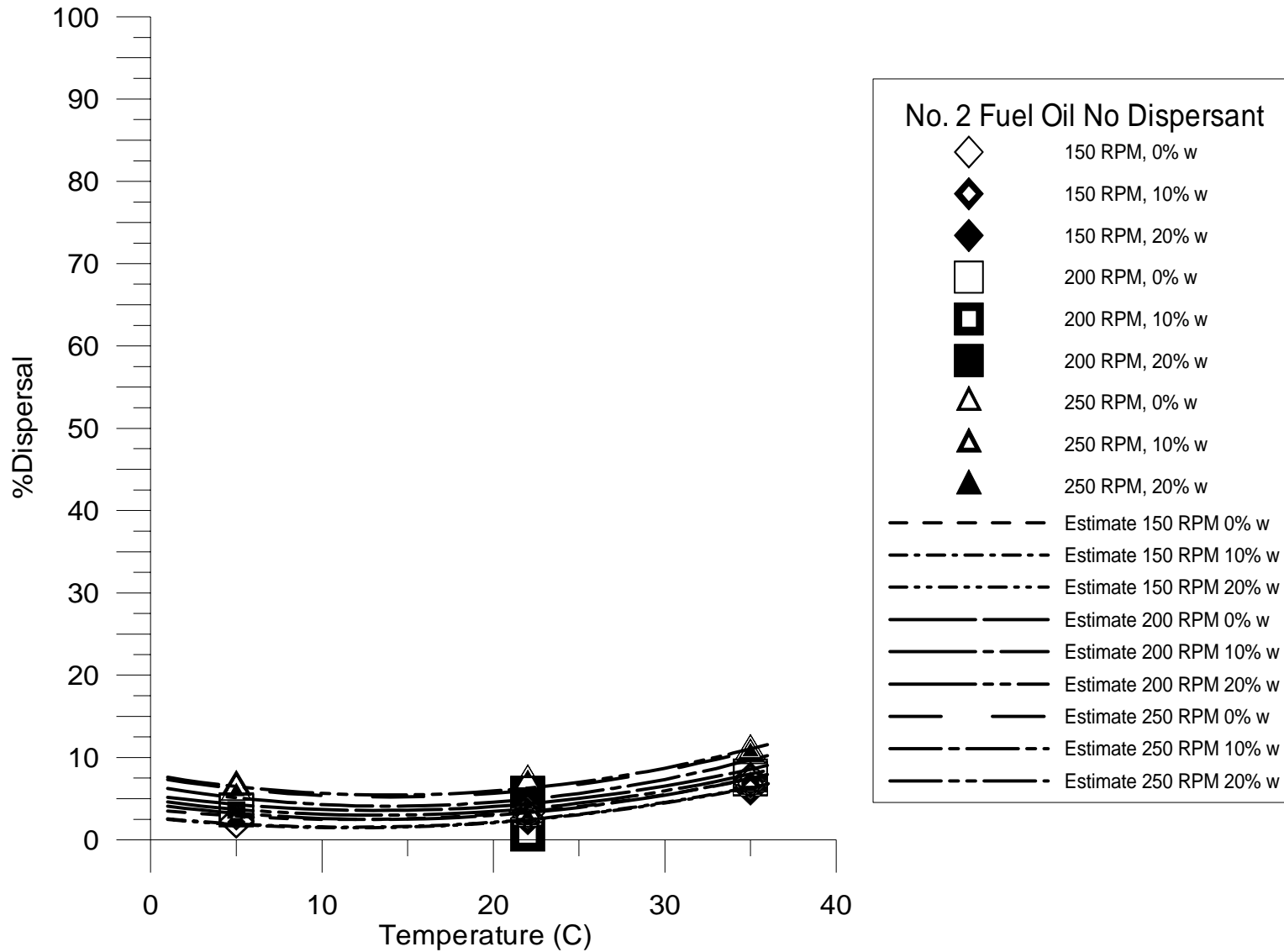
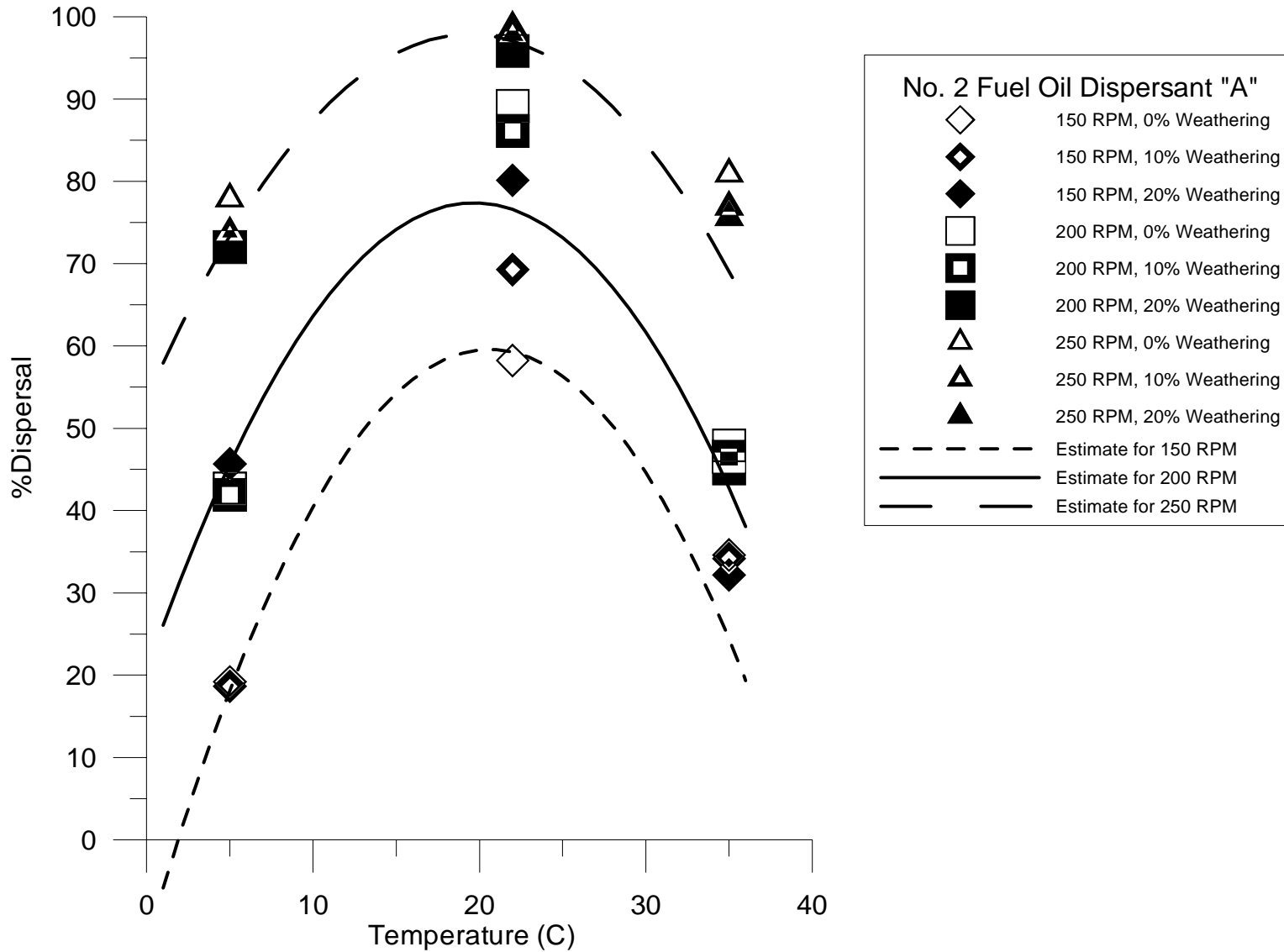


Figure 5 Comparison of regression equations (curves) against measured No. 2 Fuel Oil/No dispersant efficiency.



**Figure 6** Comparison of regression equations (curves) against measured No. 2 Fuel Oil/Dispersant "A" efficiency.

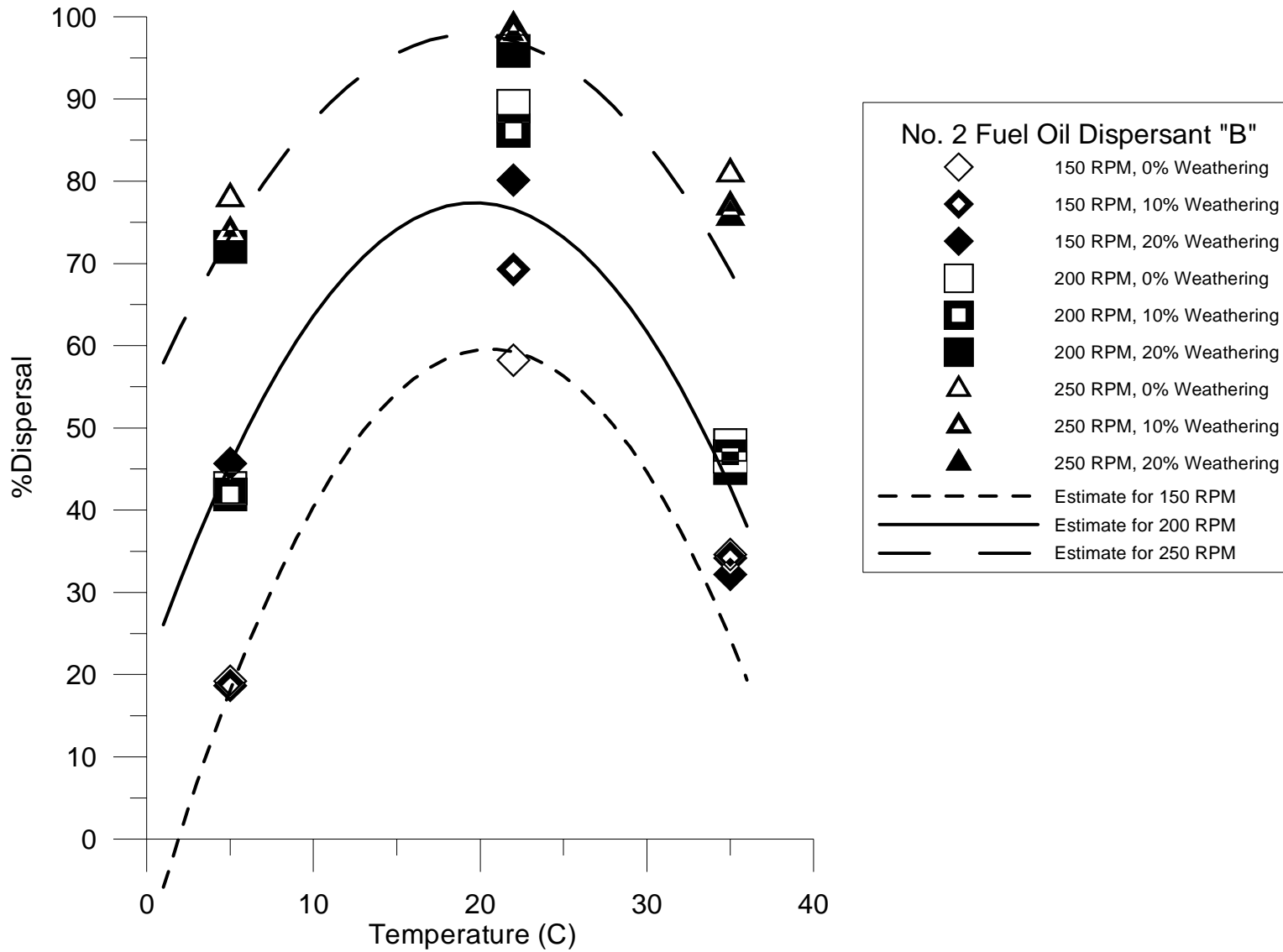


Figure 7 Comparison of regression equations (curves) against measured No. 2 Fuel Oil/Dispersant "B" efficiency.

## Summary of South Louisiana Crude Dispersal Characteristics

The South Louisiana Crude showed generally high dispersal with dispersant “A” as most of the values were above 50% (Table 7). Values above 70% occurred at both medium and high speeds, while those lower than 70% occurred with only medium or low speeds. Various values of weathering occurred throughout the range of dispersal values, indicating a minor influence of weathering on dispersal. Experiments with the highest temperatures had dispersals between 60% and 80%.

								MMH	
							LHH	LLH	
						MMM	LHM	LMH	
				LMM	HLM	HHH	MLH		
				LLL	LHL	LLM	HLH	LML	
			HML	MLL	HHL	HHM	MHH	HMH	
			MML	HLL	MHL	MLM	MHM	HMM	
0 - 10	10 - 20	20 - 30	30 - 40	40 - 50	50 - 60	60 - 70	70 - 80	80-90	90-100

Weathering Temperature Speed\*

\*H = high, M = medium, L = low

Example M H L = medium weathering, high temperature, low flask speed

**Table 7** % Dispersal Efficiency of South Louisiana Crude with Dispersant “A”

Dispersal of SLC with dispersant “B” showed a cluster of values above 70% (Table 8). These high values were associated with medium or high speeds and various combinations of temperature and weathering. Low dispersal occurred mostly with low speeds. The control (Table 9) showed most of the relatively high dispersals (7% and above) occurred with medium or high speeds, and uniformly high temperatures. The lowest dispersal values (<2%) occurred mostly with low speeds and temperatures, but with each weathering condition.

								HLH		
								MHM		
								LHM		
								LMH		
								HHM		
								MMM	HMH	
				HLL				HMM	HHH	
		LMM		LHL				LLM	MMH	LHH
		MML		MHL	LLL			MLM	LLH	MHH
		HML		HHL	MLL			HLM	MLH	LML
0 - 10	10 - 20	20 - 30	30 - 40	40 - 50	50 - 60	60 - 70	70 - 80	80-90	90-100	

Weathering Temperature Speed\*

\*H = high, M = medium, L = low

Example MHL = medium weathering, high temperature, low flask speed

**Table 8** % Dispersal Efficiency of South Louisiana Crude with Dispersant “B”

			MLH	LMH						
			HLH	MMH						
HLL	HML	HLM	LLH	HHL			HMH			
MLL	LMM	MLH	MMM	HMM			LHM	HHM		
LLL	MML	LLM	MHL	LHL	LML		MHM	MHH	LHH	HHH
0 - 1	1 - 2	2 - 3	3 - 4	4 - 5	5 - 6	6 - 7	7 - 8	8 - 9	9 - 10	10 - 11

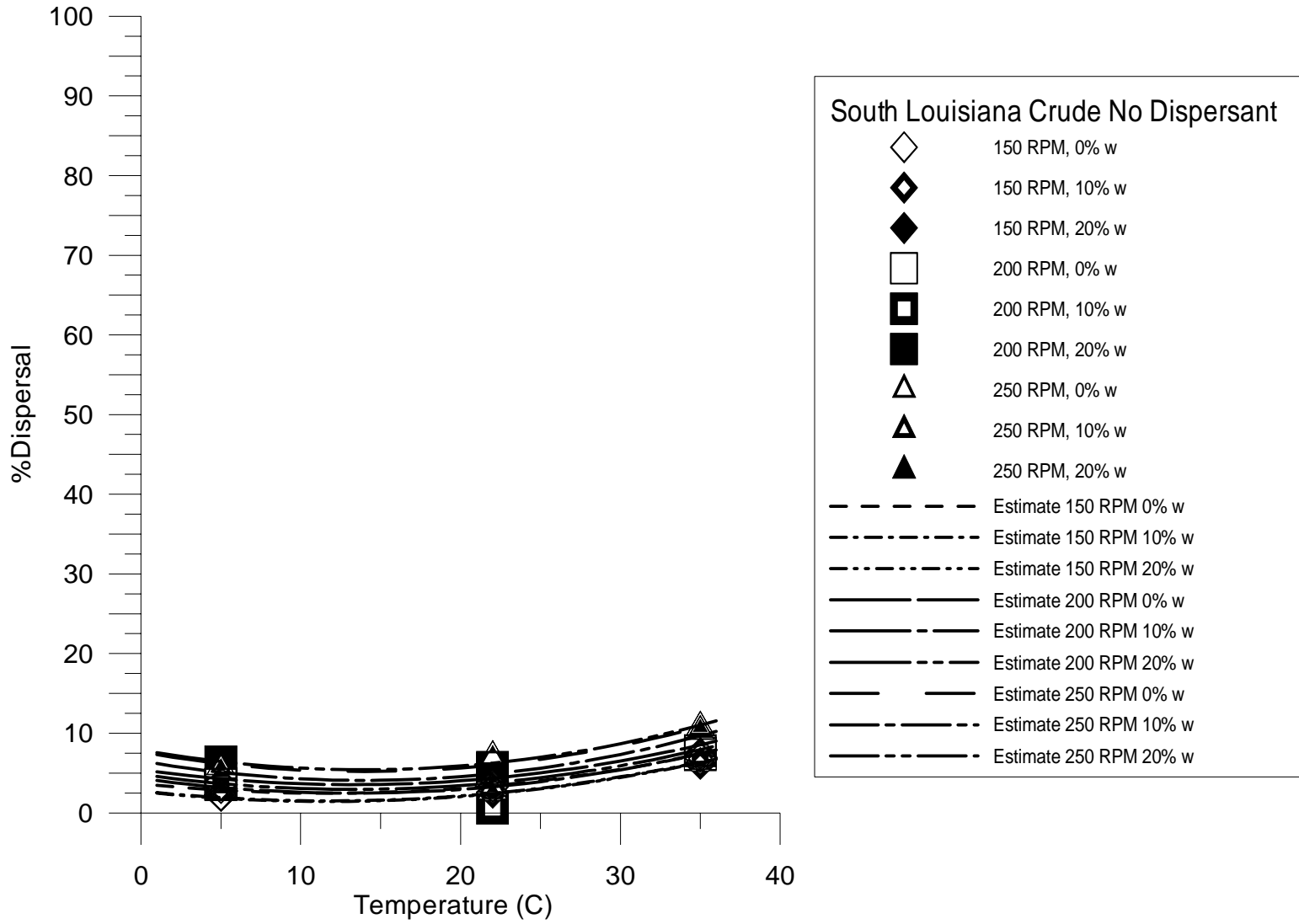
Weathering Temperature Speed\*

\*H = high, M = medium, L = low

Example MHL = medium weathering, high temperature, low flask speed

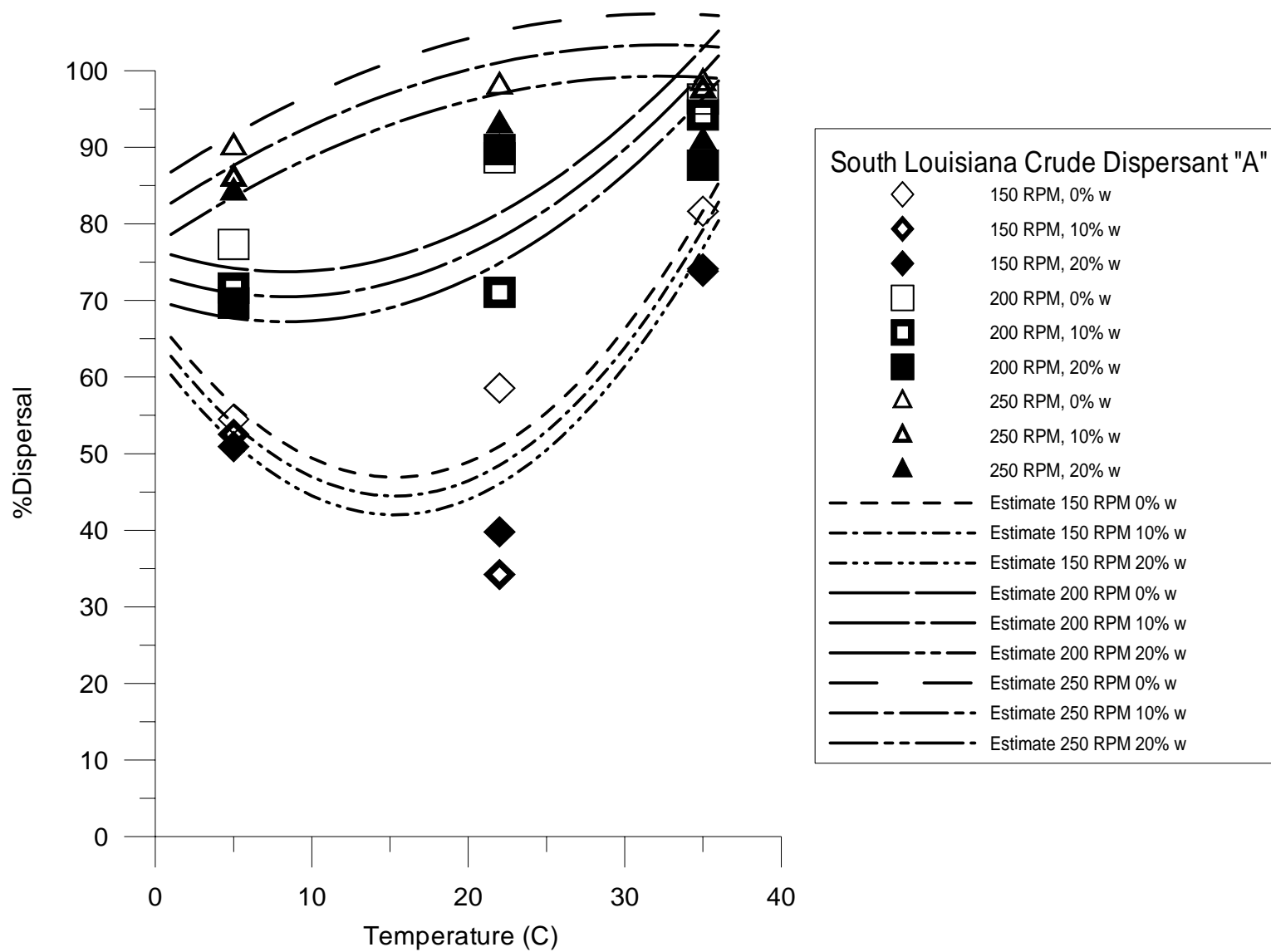
**Table 9** % Dispersal Efficiency of South Louisiana Crude with No Dispersant

Figures 8 to 10 show the data and regression curves for South Louisiana Crude. Dispersal increased with speed for all experimental conditions. Significant effects of weathering were indicated for dispersant “A” and the control experiments. These showed the inverse relationship between weathering and dispersal for dispersant “A” and some of the control. Although the scatter in the data at 150 rpm and 200 rpm makes the relationships less clear for dispersant “A”, results for both dispersants “A” and “B” show minimum dispersal at the middle temperature (22 °C) at 150 and 200 rpm but maximum dispersal at this temperature for 250 rpm. The shapes of the regression lines indicate a relationship that is concave up at lower speeds and transitions into one that is concave down at higher speeds.



**Figure 8** Comparison of regression equations (curves) against measured South Louisiana Crude/No Dispersant efficiency.





**Figure 9** Comparison of regression equations (curves) against measured South Louisiana Crude/Dispersant "A" efficiency.

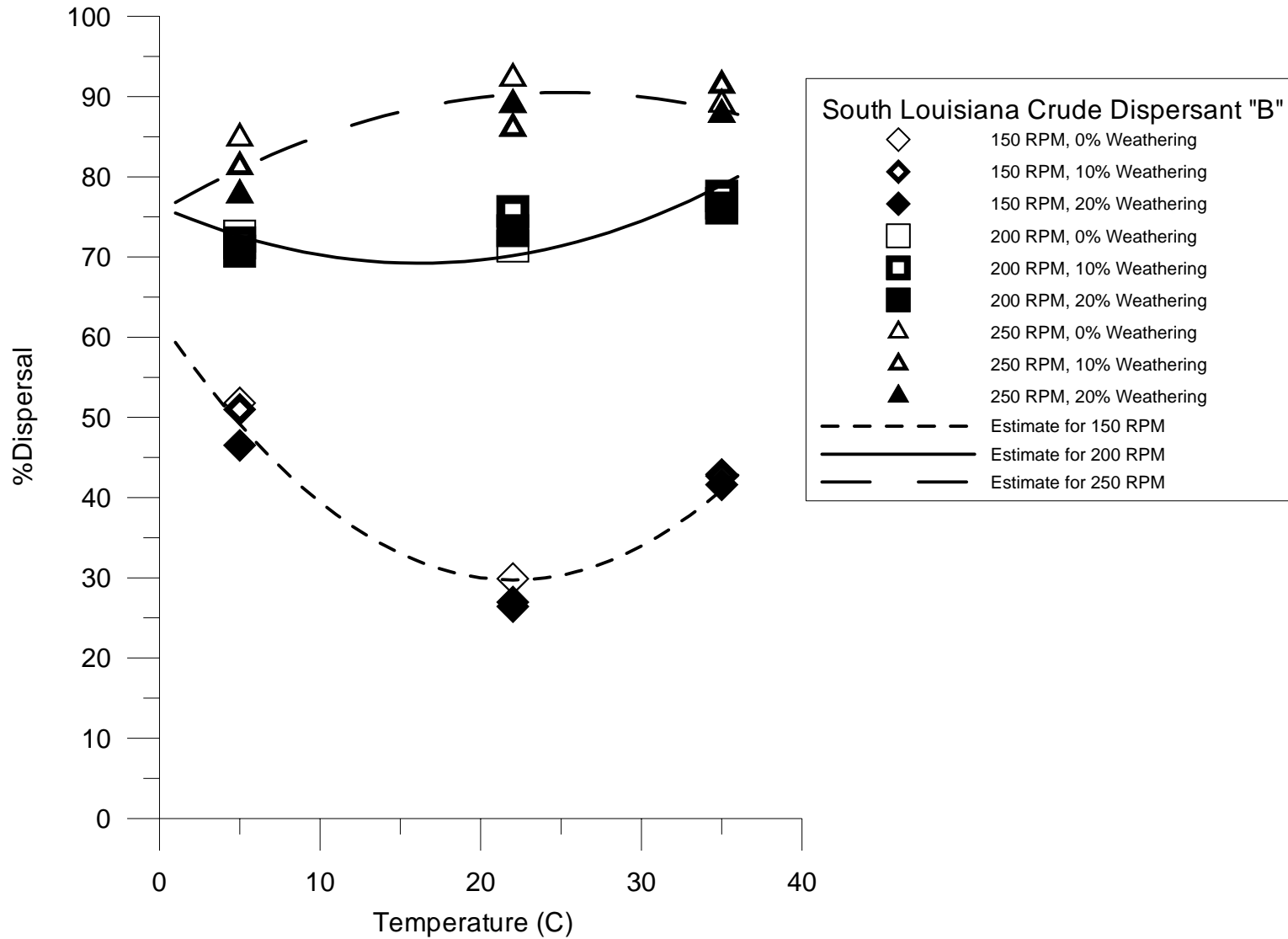


Figure 10 Comparison of regression equations (curves) against measured South Louisiana Crude/Dispersant "B" efficiency.

## Regression Equations

A linear regression empirical model was fit to the experimental data for each of the oil/dispersant combinations. The model takes the following form:

$$\begin{aligned}
 \% \text{ Efficiency}_{oil,dispersant} = & \beta_0 + \beta_w w + \beta_t t + \beta_s s \\
 & + \beta_{wt} w t + \beta_{ws} w s + \beta_{ts} t s + \beta_{wts} w t s \\
 & + \beta_{w^2} w^2 + \beta_{t^2} t^2 + \beta_{s^2} s^2 \\
 & + \beta_{w^2 t^2} w^2 t^2 + \beta_{w^2 s^2} w^2 s^2 + \beta_{t^2 s^2} t^2 s^2 + \beta_{w^2 t^2 s^2} w^2 t^2 s^2
 \end{aligned} \tag{5}$$

where  $w$  represents weathering in %,  $t$  is the temperature (water) in °C, and  $s$  is the flask speed in RPM. The terms were chosen to include linear<sup>1</sup> and parabolic<sup>2</sup> effects of each variable and possible two- and three-factor<sup>3</sup> interactions. If all variables and interactions were statistically significant, the model would include 15 terms. Because for each oil/dispersant combination there are no more than 27 data points, no additional interaction or non-linear terms were included in the model. Data from the replicate study (Appendix 2) were used to enhance the regressions: each replicated point at the speed of 200 rpm and dispersants “A” and “B” was replaced by the average result from the replicate study. As seen in the results (Table 10), only a few terms were significant for a given oil/dispersant combination as determined by step-wise multiple regression with an acceptance/rejectance level of 0.05. Between 4 and 9 terms represented all the data for these experiments on the three oils tested. Notably, the step-wise regression showed that adding more of the 15 possible terms did not improve the fits.

The various parameters of Equation 5 for the various oil - dispersant combinations are

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<sup>1</sup> Coefficients appearing in the first line of Equation 5.

<sup>2</sup> Coefficients appearing in the third line of Equation 5.

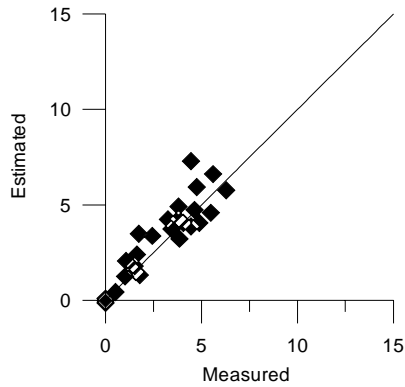
<sup>3</sup> Coefficients appearing in the second and forth lines of Equation 5.

given in Table 10 together with  $R^2$  values, which indicates the linearity of the model. Generally,  $R^2$  values above 90% indicate good linear fits. With the exception of 2FO with no dispersant (86.9%), all the  $R^2$  values were above 90%. Regression equation terms that include weathering as a variable are highlighted in Table 10 with gray shading. Note from the table that none of the regressions include weathering alone as a term. This indicates the secondary nature of weathering as a variable as described previously for each oil. Figures 11 to 19 show comparisons of estimated and measured values of dispersal efficiency. Each of the plots show that the data cluster along the 1:1 line, indicating, obviously, a close match. Prudhoe Bay Crude with either dispersant (Figures 14 and 17) and the South Louisiana Crude with dispersant B (Figure 19) show particularly tight clustering along this line.

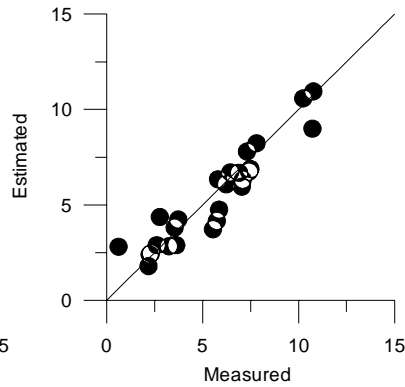
**Table 10** Coefficients of Regression Equations with Terms Determined by Step-Wise Linear Regression

Factor <sup>(1)</sup>	Prudhoe Bay Crude			No. 2 Fuel Oil			South Louisiana Crude		
	No Dispersant	Dispersant A	Dispersant B	No Dispersant	Dispersant A	Dispersant B	No Dispersant	Dispersant A	Dispersant B
constant	-5.9325	-264.6	-15.16	1.490	-112.0	-17.65	-17.25	41.39	-69.24
w									
t	1.2090	4.222	3.506		10.67	3.032	-0.1381	-8.873	-9.149
s		2.609			0.6617		0.1680	0.1762	1.322
w t			-8.386e-3				-6.391e-3		
w s				-2.452e-3				-1.631e-3	
t s	-4.120e-3		-8.386e-3	-1.4089e-3	-2.435e-2		7.656e-4	4.092e-2	4.132e-2
w t s			-4.845e-5						
w <sup>2</sup>		-1.038e-2							
t <sup>2</sup>	-1.979e-2	-9.697e-2	-2.817e-2	6.996e-3	-0.2000	-6.313e-2	4.382e-3	0.1516	0.1178
s <sup>2</sup>	1.468e-4	-5.409e-3	1.433e-3	9.871e-5		1.256e-3	-3.3750e-4		-2.970e-3
w <sup>2</sup> t <sup>2</sup>							9.99e-6		
w <sup>2</sup> s <sup>2</sup>				1.39e-6			5e-8		
t <sup>2</sup> s <sup>2</sup>	2.6e-7			9e-8	1.30e-6			-2.87e-6	-2.26e-6
w <sup>2</sup> t <sup>2</sup> s <sup>2</sup>									
R <sup>2</sup>	91.1%	97.5%	98.2%	86.9%	96.7%	94.8%	98.2%	90.8%	98.6%

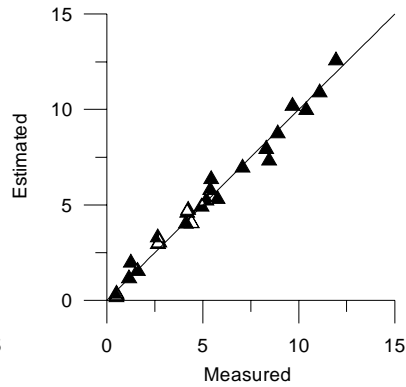
<sup>(1)</sup> w = weathering, t = temperature, s = speed



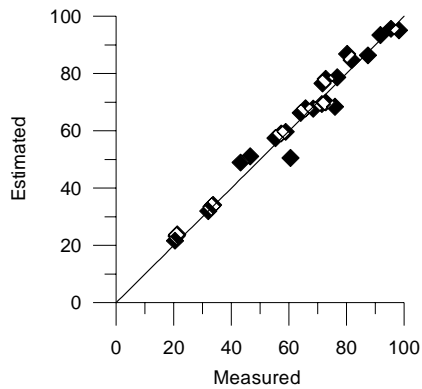
**Figure 11** Estimated vs Measured % Dispersal of PBC with No Dispersant.



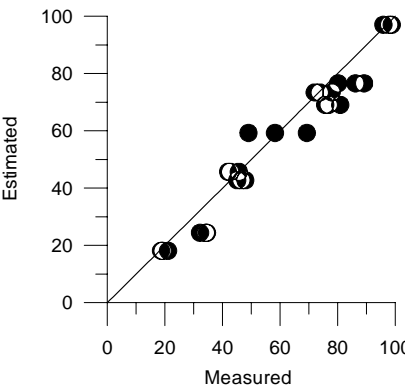
**Figure 12** Estimated vs Measured % Dispersal of 2FO with No Dispersant.



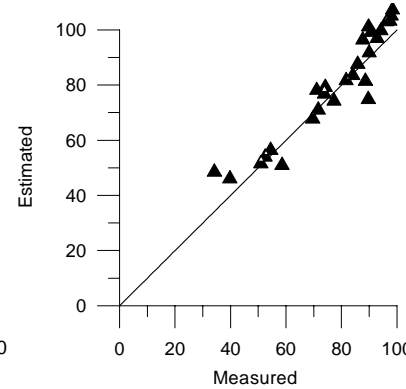
**Figure 13** Estimated vs Measured % Dispersal of SLC with No Dispersant.



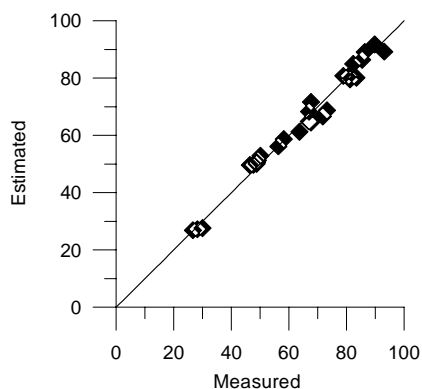
**Figure 14** Estimated vs Measured % Dispersal of PBC with Dispersant "A".



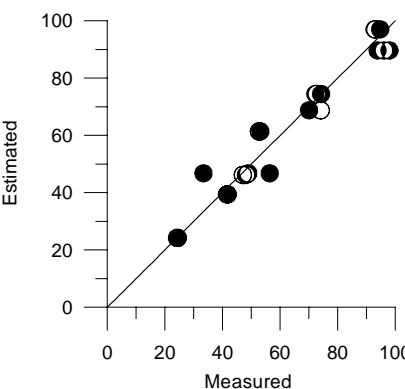
**Figure 15** Estimated vs Measured % Dispersal of 2FO with Dispersant "A".



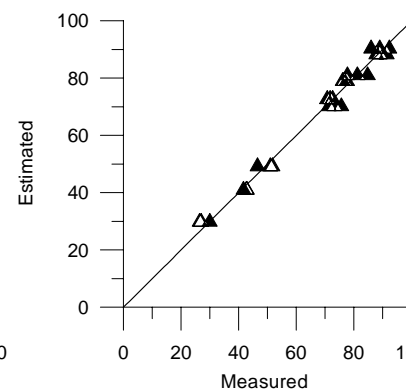
**Figure 16** Estimated vs Measured % Dispersal of SLC with Dispersant "A".



**Figure 17** Estimated vs Measured % Dispersal of PBC with Dispersant "B".



**Figure 18** Estimated vs Measured % Dispersal of 2FO with Dispersant "B".



**Figure 19** Estimated vs Measured % Dispersal of SLC with Dispersant "B".

Figure 2 (described previously) shows a comparison of the regression equations and measured values plotted for the Prudhoe Bay Crude with no dispersant. The squares, for example, should cluster about the 200 rpm dashed line. The measured values, however, span almost the entire range of dispersal for speeds of 150 rpm to 250 rpm. This result indicates that the measured variation in dispersal at 200 rpm is as great as the fitting error in the regression equations. The coefficients for these regressions (Table 10) contain no terms that involve weathering. Thus, the amount of volatilization weathering that occurs does not affect the dispersal efficiency. Therefore, the three curves for the different speeds represent all possibilities for dispersal of the oil.

Similarly, Figure 3 shows a comparison of the regression equations and measured values plotted for the Prudhoe Bay Crude with dispersant A. The regression equations for this pair contain no terms involving weathering (Table 10), so that the regression equations only need to be plotted for speed and temperature. The graph shows the inverted parabolic shape of the curves (i.e., highest dispersal at the mid-temperature), and the experimental data for each speed and percent weathering. That weathering is unimportant for this oil and dispersant is shown by the data points falling generally near each other regardless of the amount of weathering.

## Conclusions

A factorial experimental design for determining the impact of temperature, oil type, oil weathering, and rotation speed on the effectiveness of two dispersants was studied and then implemented. Regression formulas were developed that provide a smoothed representation of the data, using a minimum number of significant parameters.

The experimental results obtained in this study reveal the following:

1) Under each set of experimental conditions dispersal increased with increasing flask speed. This reflects increased mixing energy supplied to the flask for each increase in speed. When the other variables – temperature and weathering – were varied, however, some lower speed experiments yielded relatively high dispersal (e.g., PBC-A, SLC-none, SLC-A), that overlapped the range of dispersals produced at the highest flask speed.

2) Where weathering was significant, increased weathering reduced dispersal (PBC-A, PBC-B, 2FO-none, SLC-none, SLC-A). For other oil/dispersant combinations, the variation of dispersal with weathering did not follow a consistent pattern. The magnitude of this effect was generally small in either case.

3) The changes in dispersal with temperature did not show consistent behavior. In some cases, the peak dispersal occurred at the middle temperature (PBC-none, PBC-A, 2FO-A, 2FO-B, SLC-A-250 rpm, SLC-B-250 rpm), contrary to expectation. Also contrary to expectation, in many of the other experimental combinations, the minimum dispersal also occurred at the middle temperature (2FO-none, SLC-A-150 rpm, SPC-B-150 rpm, SLC-B-200 rpm).

4) The regression equations provided a reasonable fit to the experimental data. The equations reproduced, in a smoothed fashion, the main behavior indicated by the data. As expected, however, the regression curves did not go through every data point. The deviation was



partly due to scatter in the data (see SLC, 150 rpm, 22 °C) and partly the nature of regression. In some cases (e.g., SLC, 250 rpm, 35 °C) the regression curves lay somewhat above all the measured data points. Improved approaches to fitting, and adding more experimental data might overcome these difficulties.

In order to establish further the behavior of dispersants with these oils, additional work could be performed:

- 1) to establish more strongly the temperature effect,
- 2) to determine the effect of salinity variation,
- 3) to determine the amount that viscosity of the test oils increased during weathering,
- 4) to determine the tendency for dispersed oil to refloat, and
- 5) to predict dispersal in the flask experiments using the empirical regression equations.

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## Appendix 1: Experimental Data

The following tables contain the dispersant effectiveness data from the set of 243 experiments described previously in the text.

Oil	Weathering Condition	Percent Effectiveness at 150 rpm	Percent Effectiveness at 200 rpm	Percent Effectiveness at 250 rpm
SLC	0 %	0.51	2.73	4.42
SLC	10%	0.51	2.66	4.40
SLC	20%	0.52	2.65	4.24
PBC	0%	0.00	1.58	4.45
PBC	10%	0.00	1.52	4.06
PBC	20%	0.00	1.52	3.80
2FO	0%	2.24	3.73	6.44
2FO	3.8%	2.18	3.63	5.86
2FO	7.6%	2.31	3.54	5.80

**Table 11** Oil control experiments (Temperature =  $5 \pm 1$  °C)

<b>Oil</b>	<b>Weathering Condition</b>	<b>Percent Effectiveness at 150 rpm</b>	<b>Percent Effectiveness at 200 rpm</b>	<b>Percent Effectiveness at 250 rpm</b>
SLC	0 %	54.50	77.32	89.65
SLC	10 %	52.51	71.60	85.90
SLC	20%	50.91	69.65	84.09
PBC	0%	21.10	58.91	69.71
PBC	10%	20.96	57.31	65.75
PBC	20%	20.36	55.34	64.04
2FO	0%	21.09	45.67	79.29
2FO	3.8%	19.21	42.67	77.90
2FO	7.6%	18.65	41.92	73.77

**Table 12** Oil + Dispersant ‘A’ experiments (Temperature =  $5 \pm 1$  °C)

<b>Oil</b>	<b>Weathering Condition</b>	<b>Percent Effectiveness at 150 rpm</b>	<b>Percent Effectiveness at 200 rpm</b>	<b>Percent Effectiveness at 250 rpm</b>
SLC	0 %	51.80	72.59	83.13
SLC	10%	50.99	71.75	81.25
SLC	20%	46.52	70.71	77.73
PBC	0%	30.02	48.85	84.11
PBC	10%	28.23	48.76	83.48
PBC	20%	26.67	46.44	81.21
2FO	0%	24.18	48.14	73.06
2FO	3.8%	24.42	47.12	72.75
2FO	7.6%	24.41	47.01	72.25

**Table 13** Oil + Dispersant ‘B’ experiments (Temperature =  $5 \pm 1$  °C)



<b>Oil</b>	<b>Weathering Condition</b>	<b>Natural Dispersal 150 rpm</b>	<b>Natural Dispersal at 200 rpm</b>	<b>Natural Dispersal at 250 rpm</b>
SLC	0 %	1.26	5.77	7.07
SLC	10%	1.10	4.19	5.44
SLC	20%	1.61	5.19	8.45
PBC	0%	3.86	2.43	3.81
PBC	10%	3.44	4.89	6.29
PBC	20%	3.25	4.63	5.58
2FO	0%	3.24	5.70	7.12
2FO	3.8%	0.00	0.60	2.78
2FO	7.6%	2.63	5.57	7.02

**Table 14** Oil control experiments (Temperature = 22 +/-1 °C.)

<b>Oil</b>	<b>Weathering Condition</b>	<b>Percent Effectiveness at 150 rpm</b>	<b>Percent Effectiveness at 200 rpm</b>	<b>Percent Effectiveness at 250 rpm</b>
SLC	0 %	57.19	87.64	97.31
SLC	10%	34.21	69.76	89.80
SLC	20%	39.79	91.97	92.88
PBC	0%	40.82	80.12	95.95
PBC	10%	60.55	84.33	97.94
PBC	20%	43.20	86.00	90.61
2FO	0%	48.99	82.93	95.52
2FO	3.8%	58.25	84.07	97.85
2FO	7.6%	69.28	87.38	98.76

**Table 15** Oil + Dispersant ‘A’ experiments ( Temperature = 22±1 °C )

<b>Oil</b>	<b>Weathering Condition</b>	<b>Percent Effectiveness at 150 rpm</b>	<b>Percent Effectiveness at 200 rpm</b>	<b>Percent Effectiveness at 250 rpm</b>
SLC	0 %	28.64	76.67	90.68
SLC	10%	26.99	75.45	86.03
SLC	20%	26.42	73.54	88.99
PBC	0%	52.32	69.18	87.96
PBC	10%	49.24	63.47	85.15
PBC	20%	47.69	62.34	83.53
2FO	0%	48.94	78.00	98.24
2FO	3.8%	33.38	76.49	92.79
2FO	7.6%	56.39	75.89	94.75

**Table 16** Oil + Dispersant 'B' experiments ( Temperature = 22±1 °C )

<b>Oil</b>	<b>Weathering Condition</b>	<b>Natural Dispersal at 150 rpm</b>	<b>Natural Dispersal at 200 rpm</b>	<b>Natural Dispersal at 250 rpm</b>
SLC	0 %	4.92	8.90	11.09
SLC	10%	4.12	8.25	9.68
SLC	20%	5.39	10.39	11.94
PBC	0%	0.53	1.77	5.47
PBC	10%	1.04	1.63	4.76
PBC	20%	1.06	1.74	4.46
2FO	0%	6.89	7.84	10.81
2FO	3.8%	6.23	7.50	10.73
2FO	7.6%	7.44	7.33	10.22

**Table 17** Oil control experiments ( Temperature =  $35 \pm 1$  °C )

<b>Oil</b>	<b>Weathering Condition</b>	<b>Natural Dispersal at 150 rpm</b>	<b>Natural Dispersal at 200 rpm</b>	<b>Natural Dispersal at 250 rpm</b>
SLC	0 %	81.64	96.28	98.17
SLC	10%	74.12	94.20	97.41
SLC	20%	73.81	87.64	90.69
PBC	0%	33.62	72.21	75.92
PBC	10%	33.06	71.47	72.79
PBC	20%	31.93	68.46	71.68
2FO	0%	34.60	47.92	89.79
2FO	3.8%	34.19	46.55	76.87
2FO	7.6%	32.19	45.11	75.62

**Table 18** Oil + Dispersant ‘A’ experiments ( Temperature =  $35 \pm 1$  °C )

<b>Oil</b>	<b>Weathering Condition</b>	<b>Percent Effectiveness at 150 rpm</b>	<b>Percent Effectiveness at 200 rpm</b>	<b>Percent Effectiveness at 250 rpm</b>
SLC	0 %	42.88	76.69	92.06
SLC	10%	42.68	77.57	91.39
SLC	20%	41.60	76.11	87.76
PBC	0%	63.59	67.69	89.23
PBC	10%	58.23	67.02	82.34
PBC	20%	56.29	66.87	80.79
2FO	0%	41.74	53.13	98.92
2FO	3.8%	41.53	52.67	97.98
2FO	7.6%	41.71	52.64	96.06

**Table 19** Oil + Dispersant ‘B’ experiments ( Temperature =  $35 \pm 1$  °C )

Oil	Weathering Condition	%Effectiveness at 5 °C	%Effectiveness at 22 °C	%Effectiveness at 35 °C
SLC	0%	89.7	97.3	98.2
SLC	10%	85.9	89.8	97.4
SLC	20%	84.1	92.9	90.7
PBC	0%	69.7	96.0	75.9
PBC	10%	65.8	97.9	72.8
PBC	20%	64.0	90.6	71.7
2FO	0%	79.3	95.5	89.8
2FO	3.8%	77.9	97.9	76.9
2FO	7.6%	73.8	98.8	75.6

**Table 20** Results of oil-dispersant combinations at different temperatures (Dispersant ‘A’, 250 rpm, 34 ppt)

## Appendix 2: Replicate Study

Based on a statistical analysis (ANOVA) of the factorial experimental design, and assumed linear interactions between factors, significant two-way interactions were identified. Table 21 lists these and the specific conditions selected for replication. Two replicates were included for each two-way interaction and four replicates of two of these experiments were conducted.

The results of the three two-way interactions namely: temperature by dispersant, volatilization by dispersant and speed by dispersant are shown in Tables 22 to 24. Factors that were not involved in the two-way interactions were fixed at certain values: speed-250 rpm, volatilization-0%, and temp-22 °C. These tables show a comparison between the replicate results and the results reported earlier. This comparison was based on determining the Relative Percent Difference (RPD) which is given by:

$$RPD = \frac{\text{Avg. eff of current results} - \text{Eff of previous results}}{\text{Avg. eff of current results}} \times 100 \quad (6)$$

The acceptance criterion was an RPD of less than 15%.

A four-replicate study was also conducted for all the three oils, the three levels of volatilization and the two dispersants at 22 °C and a flask speed of 200 rpm. The total number of experiments conducted was thus: 3 oils \* 3 volatilization \* 2 dispersants \* 4 replicates =72. The precision objectives were determined by using the relative standard deviation (RSD) for percent effectiveness based on four replicate flasks. The results of these experimental runs are shown in Tables 25 and 26. The RSD is given by:



$$RSD = \frac{\text{Standard Deviation}}{\text{Average Effectiveness}} \times 100 \quad (7)$$

The acceptance criterion an RSD of less than 15%. The replicate data were used in developing the regression formulas described in the main body of the report.

OIL	INTERACTION	CONDITIONS	NO: OF EXPERIMENTAL RUNS
2FO	Temperature * Dispersant	0% volatilization * 2 dispersants * 3 temperatures *250 rpm * 2 replicates	12
SLC	Temperature * Dispersant	0% volatilization * 2 dispersants * 3 temperatures *250 rpm * 2 replicates	12
SLC	Speed * Dispersant	0% volatilization * 2 dispersants * 3 speeds * 22 °C * 4 replicates	24
PBC	Temperature * Dispersant	0% volatilization * 2 dispersants * 3 temperatures *250 rpm * 2 replicates	12
PBC	Volatilization * Dispersant	22 °C * 250 rpm * 3 volatilizations * 2 dispersants * 2 replicates	12
PBC	Speed * Dispersant	0% volatilization * 2 dispersants * 3 speeds * 22 °C * 4 replicates	24

**Table 21** Two way interactions.

Oil	Temp( <sup>0</sup> C)	Dispersant	% Effectiveness of replicates		Avg eff.	RSD	%Eff. of previous samples	RPD
			R1	R2				
PBC	22	A	96.20	94.05	95.12	1.59	95.95	0.87
PBC	35	A	80.32	74.20	77.26	5.59	75.92	1.73
PBC	6	A	71.41	87.01	79.21	13.92	69.71	11.99
PBC	22	B	88.66	84.76	86.71	3.18	87.96	1.44
PBC	35	B	95.62	94.38	94.99	0.92	89.23	6.07
PBC	6	B	82.41	70.04	76.22	11.47	84.11	10.34
2FO	22	A	95.97	95.87	95.92	0.07	95.63	0.30
2FO	35	A	74.28	81.60	77.94	6.65	89.79	15.20
2FO	6	A	75.11	64.06	69.58	11.22	79.29	13.95
2FO	22	B	90.64	92.13	91.39	1.15	98.24	7.50
2FO	35	B	90.79	96.84	88.82	3.14	98.92	11.37
2FO	6	B	74.26	75.08	74.66	0.77	73.06	2.15
SLC	22	A	96.25	98.96	97.60	1.96	97.35	0.26
SLC	35	A	98.69	98.33	98.51	0.25	98.17	0.35
SLC	6	A	90.18	90.11	90.15	0.05	89.65	0.55
SLC	22	B	92.82	88.60	90.71	3.28	90.68	0.03
SLC	35	B	91.29	83.73	87.51	6.11	92.06	5.19
SLC	6	B	85.58	85.74	85.66	0.13	83.13	2.96

**Table 22** Dispersant by temperature interaction ( Flask speed =250 rpm, Weathering =0%).

Oil	Weathering	Dispersant	% Effectiveness of replicates		Avg eff.	RSD	%Eff. of previous samples	RPD
			R1	R2				
PBC	0%	A	89.96	93.76	91.86	2.92	95.95	4.45
PBC	10%	A	99.82	96.88	98.35	2.11	97.94	0.42
PBC	20%	A	90.08	94.72	92.40	3.55	90.61	1.93
PBC	0%	B	89.89	86.19	88.04	2.96	87.96	0.09
PBC	10%	B	87.21	86.63	86.92	0.47	85.15	2.03
PBC	20%	B	83.91	88.84	86.37	4.04	83.53	3.29

**Table 23** Dispersant by volatilization interaction (Flask speed =250 rpm, Temperature = 22±1 °C).

Oil	Speed	Disp	% Effectiveness of replicates				Avg eff.	RSD	%Eff. of previous samples	RPD
			R1	R2	R3	R4				
SLC	150	A	54.69	55.7	55.18	69.97	58.88	12.56	57.21	2.87
SLC	200	A	88.70	92.51	87.71	87.88	89.20	2.52	87.45	1.98
SLC	250	A	99.52	98.40	98.05	96.90	98.20	1.09	97.35	0.88
PBC	150	A	51.25	46.37	48.00	46.38	48.00	4.78	40.82	14.96
PBC	200	A	79.38	82.43	81.28	78.99	80.52	2.01	80.12	0.49
PBC	250	A	99.05	95.80	96.05	98.10	97.20	1.60	95.95	1.33
SLC	150	B	30.48	30.18	31.47	28.79	30.23	3.67	28.64	5.40
SLC	200	B	71.38	72.29	71.79	70.98	71.61	0.78	76.67	7.06
SLC	250	B	91.03	93.74	89.38	99.74	93.47	4.86	90.68	3.03
PBC	150	B	49.73	49.87	49.70	48.76	49.51	1.03	52.32	5.51
PBC	200	B	76.09	76.15	72.15	72.21	74.15	3.07	69.18	6.70
PBC	250	B	92.46	88.49	93.77	97.78	93.12	4.11	87.96	5.54

**Table 24** Dispersant by speed interaction ( Weathering = 0%, Temperature = 22 ± 1 °C ).

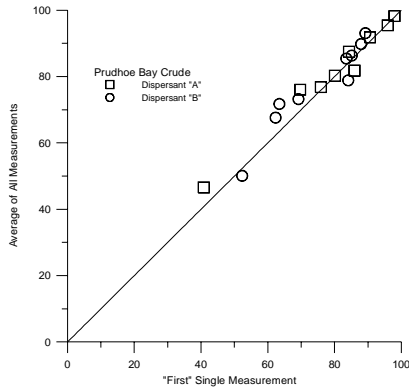
Oil	% Effectiveness of replicate samples				Average effectiveness	RSD	%Eff. of previous samples	RPD
	R1	R2	R3	R4				
SLC 0%	88.99	88.30	88.28	87.79	88.34	0.55	87.45	1.01
SLC 10%	70.54	73.89	67.44	73.48	71.33	4.20	69.94	1.96
SLC 20%	87.80	87.80	89.75	91.13	89.12	1.82	91.97	3.14
PBC 0%	80.11	78.63	82.43	78.92	80.02	2.16	80.12	0.12
PBC 10%	86.24	88.14	88.65	90.09	88.28	1.80	84.33	4.57
PBC 20%	88.43	89.07	83.79	65.78	81.76	13.35	86.00	5.17
2FO 0%	81.26	80.68	76.91	78.87	79.43	2.47	82.97	4.45
2FO 3.8%	92.54	88.66	91.94	88.66	90.45	2.30	84.03	7.09
2FO 7.6%	89.06	84.79	82.89	86.08	85.71	3.02	87.88	2.54

**Table 25** Replicate determination: Oil + Dispersant 'A' experiments ( Temperature = 22±1°C , Speed = 200 rpm).

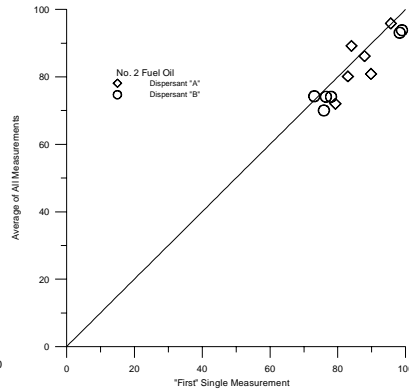
Oil	% Effectiveness of replicate samples				Average effectiveness	RSD	%Eff. of previous samples	RPD
	R1	R2	R3	R4				
SLC 0%	66.16	72.35	70.13	65.29	68.48	4.86	76.67	11.28
SLC 10%	76.38	75.76	75.33	75.40	75.71	0.64	75.45	0.34
SLC 20%	73.96	74.22	71.90	72.75	73.20	1.48	73.54	0.46
PBC 0%	75.18	75.24	71.28	71.34	73.26	3.07	69.18	5.57
PBC 10%	69.18	72.82	79.88	73.34	73.81	6.03	63.47	14.00
PBC 20%	68.32	69.01	69.66	68.77	68.94	0.81	62.34	9.57
2FO 0%	71.70	70.22	74.00	76.59	73.12	3.81	78.00	6.66
2FO 3.8%	73.34	75.70	71.84	73.20	73.52	2.18	76.49	4.03
2FO 7.6%	66.63	63.89	75.05	68.80	68.60	6.92	75.89	10.64

**Table 26** Replicate determination: Oil + Dispersant ‘B’ experiments ( Temperature = 22±1 °C , Speed = 200 rpm ).

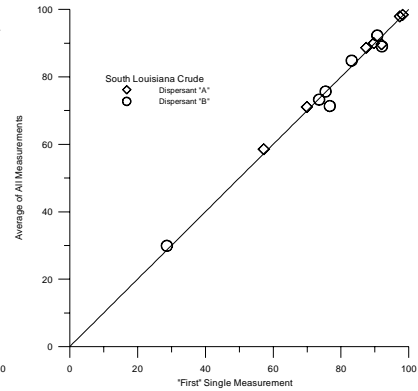
The entire suite of replicates are summarized in Tables 27, 28, and 29 and Figures 20, 21, and 22. Figures 20, 21, and 22 show plots of the average of all measurements versus the first single measured value. The latter are the original data measured before the replicate study. These plots show generally that the averages and the first single values show a one-to-one relationship.



**Figure 20** Average vs “First” single measured dispersal efficiency for PBC.



**Figure 21** Average vs “First” single measured dispersal efficiency for 2FO.



**Figure 22** Average vs “First single measured dispersal efficiency for SLC.

The tables list the values of the experimental conditions (weathering, speed, and temperature), the number of replicates, the average and standard deviation of the replicates and the first single value measured. The last column gives the difference between the original measurement (first single value) and the average of all measurements in units of standard deviation.

$$NSD = \frac{\% \text{ Efficiency}_{\text{original measurement}} - \text{Average } \% \text{ Efficiency}}{\text{Standard Deviation}} \quad (8)$$

This measure indicates how the first measurement made of dispersal for a given set of conditions differed from the average and indicates how well a single measurement predicts the average.

Weathering (%)	Speed (rpm)	Temperature (°C)	Number of Replicates	Average of all Experiments	Standard Deviation	First Single Value	NSD
<i>Prudhoe Bay Crude with Dispersant "A"</i>							
0	150	22	5	46.56	3.778	40.82	-1.519
0	200	22	9	80.25	1.472	80.12	-0.09
0	250	5	3	76.04	9.535	69.71	-0.664
0	250	22	9	95.44	2.651	95.95	0.1924
0	250	35	3	76.81	3.156	75.92	-0.282
10	200	22	5	87.49	2.230	84.33	-1.417
10	250	22	3	98.21	1.489	97.94	-0.181
20	200	22	4	81.77	9.640	88.43	0.6909
20	200	22	3	91.80	2.540	90.61	-0.469
<i>Prudhoe Bay Crude with Dispersant "B"</i>							
0	150	22	5	50.08	1.330	52.32	1.6842
0	200	22	9	73.20	2.513	69.18	-1.6
0	250	5	3	78.85	7.680	84.11	0.6849
0	250	22	10	89.80	3.865	87.96	-0.476
0	250	35	3	93.08	3.389	89.23	-1.136
10	200	22	5	71.74	6.019	63.47	-1.374
10	250	22	3	86.33	1.062	85.15	-1.111
20	200	22	5	67.62	2.991	62.34	-1.765
20	250	22	3	85.43	2.962	83.53	-0.641

**Table 27** Summary of Prudhoe Bay Crude replicates.



Weathering (%)	Speed (rpm)	Temperature (°C)	Number of Replicates	Average of all Experiments	Standard Deviation	First Single Value	NSD
<b><i>No. 2 Fuel Oil with Dispersant "A"</i></b>							
0	200	22	5	80.14	2.324	82.97	1.2177
0	250	5	4	72.01	2.555	79.29	2.8493
0	250	22	4	95.85	0.1506	95.63	-1.461
0	250	35	4	80.90	6.636	89.79	1.3397
3.8	200	22	5	89.17	3.390	84.03	-1.516
7.6	200	22	5	86.14	2.447	87.88	0.7111
<b><i>No. 2 Fuel Oil with Dispersant "B"</i></b>							
0	200	22	5	74.10	3.239	78.00	1.2041
0	250	5	4	74.26	0.8703	73.06	-1.379
0	250	22	4	93.10	3.480	98.24	1.477
0	250	35	4	93.84	4.807	98.92	1.0568
3.8	200	22	5	74.11	1.921	76.49	1.2389
7.6	200	22	5	70.05	5.251	75.89	1.1122

**Table 28** Summary of No. 2 Fuel Oil replicates.

Weathering (%)	Speed (rpm)	Temperature (°C)	Number of Replicates	Average of all Experiments	Standard Deviation	First Single Value	NSD
<i>South Louisiana Crude with Dispersant "A"</i>							
0	150	22	5	58.55	6.454	57.21	-0.208
0	200	22	9	88.62	1.538	87.45	-0.761
0	250	5	3	89.98	0.2879	89.65	-1.146
0	250	22	7	97.92	1.158	97.35	-0.492
0	250	35	3	98.40	1.363	98.17	-0.169
10	200	22	5	71.06	2.669	69.94	-0.42
20	200	22	5	89.69	1.899	91.97	1.2006
<i>South Louisiana Crude with Dispersant "B"</i>							
0	150	22	5	29.91	1.194	28.64	-1.064
0	200	22	8	71.36	3.133	76.67	1.6949
0	250	5	3	84.82	1.463	83.13	-1.155
0	250	22	7	92.28	3.745	90.68	-0.427
0	250	35	3	89.03	4.603	92.06	0.6583
10	200	22	5	75.66	0.4327	75.45	-0.485
20	200	22	5	73.27	0.9485	73.54	0.2847

**Table 29** Summary of South Louisiana Crude replicates.

### Appendix 3: SOPs Appearing in the Quality Assurance Project Plan

These procedures were taken from the Quality Assurance Project Plan (QAPP) developed for this project (Suidan *et al.*, 2001).

#### Quality Assurance Project Plan Appendix 1: SOP for Oil Alone Stock Standard Preparation

- a. Weigh a clean vial with a loose Teflon and aluminum cap (x grams).
- b. Add 2 ml of the specific reference oil to the vial and re-weigh vial with the cap (y grams).
- c. Add 18 ml DCM to the vial and re-weigh the vial with the cap (z grams).
- d. Crimp the aluminum cap and mix the vial contents by hand shaking.
- e. Measure the density of the specific reference oil + DCM by either using a density bottle or a 1 ml gas tight syringe (first weigh the syringe empty and then when full up to the 1 ml mark with the solution) ( $\rho_{\text{oil+DCM}}$ , g/L).
- f. Determine the concentration of the oil solution

$$\text{Concentration, g/L} = \frac{(y - x)}{(z - x) / \rho_{\text{oil+DCM}}} \quad (1)$$

**Quality Assurance Project Plan Appendix 2: SOP for Oil Plus Dispersant Stock Standard Preparation**

- a. Weigh a clean vial with a loose Teflon and aluminum cap ( $x'$  grams).
- b. Add 2 ml of the specific reference oil to the vial followed by 80  $\mu\text{L}$  of the dispersant (to make a ratio of dispersant:oil = 1:25) and re-weigh vial with the cap ( $y'$  grams).
- c. Add 18 ml DCM to the vial and re-weigh the vial with the cap ( $z'$  grams).
- d. Crimp the aluminum cap and mix the vial contents by hand shaking.
- e. Measure the density of the specific reference oil + dispersant + DCM by either using a density bottle or a 1 ml gas tight syringe (first weigh the syringe empty and then when full up to the 1 ml mark with the solution) ( $\rho'_{\text{oil+dispersant+DCM}}$ , g/L).
- f. Determine the concentration of the oil solution

$$\text{Concentration, g / L} = \frac{(y' - x')}{(z' - x') / \rho'_{\text{oil+dispersant+DCM}}} \quad (2)$$

**Quality Assurance Project Plan Appendix 3: SOP for Preparation of Standard Solutions from the Stock Standard Solutions**

- a. Add a specific volume (see Step f for the required volumes) of the stock oil-DCM solution prepared in Quality Assurance Project Plan Appendix 1, or of the stock oil-dispersant-DCM solution prepared in Quality Assurance Project Plan Appendix 2, to 30 ml of synthetic sea water in a separatory funnel.
- b. Extract the oil-water mixture with a 5-ml volume of DCM (15 seconds of vigorous shaking followed by 2-minute stationary period to allow for phase separation). For this first extraction, drain only about 3 ml from the separatory funnel due to a web-like emulsion formation at the solvent/water interface. Collect the extract in a 25-mL graduated cylinder.
- c. Repeat the extraction two more times (3 times total), each time using a 5-ml portion of DCM, and drain the solvent to the solvent water interface (no web like emulsions are formed after the first extraction). Do not allow any water to be drained. Collect the extracts in a 25-mL graduated cylinder. Adjust the final DCM volume for the combined extracts to 20 ml with DCM.
- d. Transfer the DCM extract to a 50-ml crimp style glass vial with an aluminum/Teflon seal. Mix contents of the sealed vial by inverting at least 10 times.
- e. Store the vials at  $4 \pm 2$  °C until the time of analysis.
- f. The quantities of oil (or oil/dispersant) used to achieve the desired six concentrations for developing a 6-point calibration curve are as follows: (a) for Alaska North Slope Crude and Number 2 Fuel Oil, the volumes of the stock oil (or oil/dispersant) standard added to the 30 ml seawater are: 11 $\mu$ L, 20  $\mu$ L, 50  $\mu$ L,

100  $\mu\text{L}$ , 125  $\mu\text{L}$ , and 150  $\mu\text{L}$ ; (b) for South Louisiana Crude the volumes are: 20  $\mu\text{L}$ , 50  $\mu\text{L}$ , 100  $\mu\text{L}$ , 150  $\mu\text{L}$ , 200  $\mu\text{L}$ , and 300  $\mu\text{L}$ . For Alaska North Slope Crude and Number 2 Fuel Oil, the maximum volume that can be added is 150  $\mu\text{L}$  because absorbance saturation in the spectrophotometer occurs above this concentration value. For South Louisiana Crude, volumes below 20  $\mu\text{L}$  are not considered because the absorbance is close to the detection limit of the spectrophotometer.

#### Quality Assurance Project Plan Appendix 4: SOP for Spectrophotometer Calibration

- a. Remove the standard vials from the cold room or the refrigerator and allow to equilibrate at the laboratory temperature.
- b. Scan a pure DCM solvent at the three analytical wavelengths, namely, 340, 370, and 400 nm, and set the calibration at a zero absorbance reading.
- c. Determine the absorbance of the six standards at each of the three analytical wavelengths (i.e., 340, 370, and 400 nm). The calibration standards should be introduced in increasing order of concentration.
- d. Determine the area under the absorbance vs. wavelength curve between wavelengths 340 and 400 nm by using the trapezoidal rule according to the following equation:

$$\text{Area} = \frac{(\text{Abs}_{340} + \text{Abs}_{370}) * 30}{2} + \frac{(\text{Abs}_{370} + \text{Abs}_{400}) * 30}{2} \quad (3)$$

- e. Before DCM-extracts of dispersed oil-water samples can be analyzed for their oil content, the UV-visible spectrophotometer must meet an instrument-stability criterion. This criterion is determined with the six oil standards analyzed in step c and involves determination of response factors (RFs) for the oil at each concentration level. The response factor at each concentration level is determined by using the following equation:

$$RF = \frac{\text{Theoretical Concentration}}{\text{Area}} \quad (4)$$

where: theoretical concentration = oil concentration in g/L of DCM in standard solution; Area = the area under the absorbance vs. wavelength curve between wavelengths 340 and 400 nm determined by equation (3).

- f. Instrument stability for the initial calibration is acceptable when the RFs of the six standard extracts are <10% different from the overall mean value for the six standards.

$$\% \text{ difference} = \frac{|\text{RF} - \text{Av. RF}|}{\text{Av. RF}} \times 100 \quad (5)$$

- g. If one or more of the standard oil extracts does not meet this linear-stability criterion, then the “offending” standard(s) must be prepared a second time (i.e., extraction of the specified amount of oil from 30-ml of seawater for the “offending” standard according to the procedure in Quality Assurance Project Plan Appendix 3). If replacement of the re-analyzed standard solution(s) in the standard curve meets linear stability (i.e., no RF > 10% different from the overall mean), then the analysis of the sample extracts can begin.
- h. If the initial-stability criterion is still not satisfied, analysis of the sample extract cannot begin, and the source problem (e.g., preparation protocol for the oil standards, spectrophotometer stability, etc.) must be determined and corrected.
- i. Determine the slope of the calibration points by using linear regression with zero intercept.

$$y = mx \quad (6)$$

where:



$y$  = area under absorbance curve;  $x$  = concentration of oil, g/L;  $m$  = slope

- j. The initial six-point calibration of the UV-visible spectrophotometer is required at least once per day.

## Quality Assurance Project Plan Appendix 5. *SOP for SAMPLE ANALYSIS*

- a. Remove the experimental water sample extract vials from the cold room or refrigerator and allow to equilibrate at the laboratory temperature.
- b. Once a successful initial calibration curve has been established and verified, introduce the experimental method blank sample (i.e., sea water alone run in the experimental flask and then a 30 ml sample withdrawn and extracted with DCM three times), followed by the experimental samples. Analyze the samples at the three wavelengths (i.e., 340, 370, and 400 nm) and record the values.
- c. If any sample result exceeds the highest calibration standard (which was sometimes the case for Prudhoe Bay Crude Oil), the sample needs to be diluted with DCM and re-analyzed to fall within the calibration range of the instrument. If any sample result is less than the lowest calibration standard, report the result with a footnote indicating that the concentration value was lower than the lowest calibration standard.
- d. Introduce a standard check after the analysis of the four experimental samples.
- e. The sequence of analyses is thus: (1) solvent blank; (2) six calibration standards for the specific test oil plus dispersant; (3) experimental sample method blank; (4) four experimental samples (same test oil and dispersant); (5) solvent blank; (6) mid-point standard calibration check; (7) six calibration standards for the specific test oil alone; and (8) experimental sample of oil control blank (i.e., oil with no dispersant). It is worthwhile to note that for the full test only 4 replicates of oil control blanks of each test oil and 4 replicates of method blanks are conducted. Therefore, the above sequence is applicable only when a method blank and oil control blank are analyzed. Otherwise, skip sequence # 3, 7, and 8 if no blanks

are analyzed.

- f. The acceptance criterion for the four or more experimental sample replicates is based upon the relative standard deviation (RSD) as determined by Equation 7 of Appendix 2 to be less than 15%. If the RSD is greater than 15% for one of the replicates, this replicate should be flagged and one more replicate run for this specific oil/dispersant test. However, if the replicates seemed clustered into two groups and the RSD is greater than 15%, all the replicates for this specific oil/dispersant test need to be rerun and the original data flagged. If a situation occurs where the acceptance criterion is not met for the third trial, report all results, and indicate that the acceptance criterion was never met.
  
- g. At least 5% of all UV-visible spectrophotometric measurements will be performed in duplicate as a QC check on the analytical method. The absorbance values for the duplicates should agree within  $\pm 5\%$  of their mean values.
  
- h. Review QC results as early as possible to determine if all acceptance criteria are met. Notify data user if any QC check falls outside of acceptance limit.

**Quality Assurance Project Plan Appendix 6. Calculation Procedure for Experimental Samples**

- a. The calculation procedure for determining the calibration curve is presented under Quality Assurance Project Plan Appendix 4.
- b. Determine the area for the absorbance values obtained for the experimental samples by using Equation (3) in Quality Assurance Project Plan Appendix 4.
- c. Determine the concentration of oil of the experimental samples by using the following equation:

$$\text{Concentration of oil, g / L} = \left( \frac{\text{Area as determined by Equation (3)}}{\text{Slope of the calibration curve}} \right) \quad (7)$$

- d. Determine the mass of oil dispersed in the 30 ml of extracted experimental sample by using the following equation:

$$\text{Mass of oil, g} = \text{Concentration of oil} * V_{\text{DCM}} \quad (8)$$

where  $V_{\text{DCM}}$  = the final volume of the DCM-extract of the water sample (0.020 L).

- e. Determine the mass of the total oil dispersed by the following equation:

$$\text{Total oil dispersed, g} = \text{Mass of oil} * \left( \frac{V_{\text{tw}}}{V_{\text{ew}}} \right) \quad (9)$$

where:

$V_{\text{tw}}$  = total water volume in the testing flask (120 ml),

$V_{\text{ew}}$  = volume of water extracted for dispersed oil content (30 ml).

- f. Determine the dispersant performance (i.e., percent of oil dispersed, or Eff) based on the ratio of oil dispersed in the test system to the total oil added to the system as follows:

$$\text{Eff \%} = \frac{\text{Total Oil Dispersed}}{\rho_{\text{oil}} * V_{\text{oil}}} \times 100 \quad (10)$$

where:

$\rho_{\text{oil}}$  = density of the specific test oil, g/L

$V_{\text{oil}}$  = Volume (L) of oil added to the test flask ( $100 \mu\text{L} = 10^{-4} \text{L}$ )

- g. Calculate Eff using Equation 10 for coupled experiments with and without dispersant ( $\text{Eff}_d$  and  $\text{Eff}_c$ , respectively).  $\text{Eff}_c$  is the effectiveness of the control and represents natural dispersion of oil in the test apparatus. It is determined by using the average of the four replicates of the specific oil control runs.  $\text{Eff}_d$  is the measured, uncorrected value.
- h. Calculate the final dispersant performance of the chemical dispersant agent after correcting for natural dispersion using the following equation

$$\text{Eff}_D = \text{Eff}_d - \text{Eff}_c \quad (11)$$

where:

$\text{Eff}_D$  = percent dispersed oil due to dispersant only,

$\text{Eff}_d$  = percent oil dispersed with dispersant added,

$\text{Eff}_c$  = percent oil dispersed with no dispersant added (average of the four replicate oil controls).

- i. Report all the calculations in the form of a spread sheet.

- j. Report number of times test acceptance criteria (when the replicates for the experimental samples are conducted) were violated and how the problem was rectified.