DETERMINING DISPERSANT EFEFCTIVENESS DATA FOR A SUITE OF ENVIRONMENTAL CONDITIONS

Subhashini Chandrasekar and George Sorial
Department of Civil and Environmental Engineering
University of Cincinnati
Cincinnati, Ohio 45221

James W. Weaver
Ecosystems Research Division
National Exposure Research Laboratory
Office of Research and Development
United States Environmental Protection Agency
Athens, Georgia 30605

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^{3}S) *model (http://www.epa.gov/athens/research/projects/eros/). Due to the complexity of chemical and physical interactions between spilled oils, dispersants and the sea, an empirical approach to the interaction between the dispersant and oil slick may provide a useful or practical approach for including dispersants in a model. The main objective of this research was 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^{3}S *model. These data are intended to give an indication of the amount of dispersal of these oils under certain environmental conditions. Recently, the US EPA developed an improved dispersant testing protocol, called the baffled flask test (BFT) which was a refinement of the swirling flask test. 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 that were tested were South Louisiana Crude Oil, Alaska North Slope Crude, and Number 2 fuel oil. Two dispersants that scored effectiveness above 85% by the BFT 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 were studied at three levels except for the dispersant factor where only two dispersants were considered. Statistical analysis of the experimental data were performed separately for the three oils. Analysis of variance was conducted to determine which factors, or set of factors, were related to the percent effectiveness. Empirical relationships between the amount of oil dispersed and the variables studied were developed.*

Materials

The two dispersants used in the study, namely, Corexit 9500 and Dispersit-SPC 1000, were obtained from Exxon Chemical U.S.A. and Polychem U.S.A., respectively. In this manuscript these dispersant are designated by letters "A" and "B". South Louisiana Crude Oil (SLC), Prudhoe Bay Crude Oil (PBC), and Number 2 Fuel Oil (2FO) were used as the test oils. A modified 150-mL trypsinizing flask with a glass stopcock (2 mm plug bore) placed near the bottom of the flask (baffled flask) was used as the test flask. An orbital shaker (Lab-line Instruments Inc, Melrose Park, Illinois) with variable speeds up to 400 rpm and an orbital diameter of 2 cm was used to mix the oil/water/dispersant combinations. A Brinkmann Eppendorf repeater pipetter capable of dispensing 1µL to 5 mL was used for dispensing the required amounts of the oil and the dispersant. Dispersed oil was measured with a UV-VIS spectrophotometer (UV mini 1240, Shimadzu, Chicago, IL) capable of measuring absorbance at 340, 370, and 400 nm.

Methods

The oils standard procedure and the test procedures were conducted according to the procedures given by Sorial *et al.* (2001).

Weathering of oils. The three oils: PBC, SLC, and 2FO were used in the study at three levels of volatilization (weathering). The weathering of the oil was performed by bubbling air up through 1-L graduated cylinder filled with oil. The volume of the oil remaining in the measuring cylinder was recorded with time. The evaporative loss was then expressed as a volume percent.

$$\%\,Oil\,volatilized = \frac{Inital\,volume - Final\,volume}{Initial\,volume} * 100 \qquad (1)$$

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

Factorial experimental design. The main aim was to determine what factors are related to the effectiveness of a dispersant used in oil remediation. The response variable for the experiment was 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), dispersant ("A" and "B"), temperature (4 ^{0}C, 22 ^{0}C and 35 ^{0}C), and flask speeds (150, 200, and 250 rpm). With these levels for each of the factors, a factorial experiment consisting of 54 runs was conducted. The factorial experiment was also performed for each of the three crude oils separately, i.e., no dispersant added. Statistical analysis of the experimental data was performed separately for the three oils. Analysis of variance was conducted to determine which factors, or sets of factors, are related to percent effectiveness.

Results and discussion

There are various factors that affect dispersant effectiveness like temperature, salinity, mixing energy, oil properties like viscosity etc. Of these, mixing energy, weathering and temperature were studied in the current research.

Mixing energy. After dispersants have been added to the oil at sea and after small oil droplets are formed, mixing energy is further required to disperse these oil droplets in the water column. In the experiments conducted in the laboratory, this mixing energy was imparted in the form of revolutions per minute (rpm) of the orbital shaker. As reported by Clayton *et al.* (1993), the applications of dispersants reduces the interfacial tension between oil and water, which results in the formation of oil droplets. Actual dispersion of oil in the water column depends on mixing energy. 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) conducted experiments that indicated dispersion reduces the size of the oil droplets. Smaller oil droplets are less likely to coalesce and are more likely to biodegrade.

Table 1 shows the results obtained for dispersant "A" at 35±1 °C. From table 1, it is seen that for a given oil at a specified weathering condition, as the speed of the orbital shaker increases, the percent effectiveness also increases. This was true for oil control experiments too (data not shown).

Weathering. 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 Kristiansen *et al.* (1997). Weathering increases the viscosity of the oil due to evaporation of the lighter components. Oil viscosity has been perceived as a major factor affecting the dispersibility of oil. As the oil weathers and the viscosity increases, it has been demonstrated that the effectiveness of the chemical dispersant declines (Daling 1988). Highly viscous oils resist the breakup of the oil into dispersed droplets and hence the efficiency of dispersion decreases. This is also evident from table 1.

Temperature. Now, it is interesting to note the effect of temperature on dispersion efficiency. Lower water temperatures increase the viscosity 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). Higher water temperatures usually increase the solubility of dispersants in water. Higher

Table 1. Oil + Dispersant 'A'(Temperature = 35 ±1 ^{0}C).

Oil	Weathering Condition	%Effectiveness at 150 rpm	%Effectiveness at 200 rpm	%Effectiveness at 250 rpm
SLC	0 %	81.6	96.3	98.2
SLC	10%	74.1	94.2	97.4
SLC	20%	73.8	87.6	90.7
PBC	0%	33.6	72.2	75.9
PBC	10%	33.1	71.5	72.8
PBC	20%	31.9	68.5	71.7
2FO	0%	34.6	47.9	89.8
2FO	3.8%	34.2	46.6	76.9
2FO	7.6%	32.2	45.1	75.6

Table 2. Dispersant "A" effectiveness at different temperatures.

Oil (Weathering)	%Effectiveness at 5 ^{0}C	%Effectiveness at 22 ^{0}C	%Effectiveness at 35 ^{0}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

water temperatures will also affect the spilled oil temperature. So, an increase in temperature will reduce oil viscosity and hence improve dispersion. Mackay *et al* (1981), Byford *et al* (1983), Fingas *et al.* (1991) and Lentinen *et al.* (1984) conducted studies on the impact of water temperature on the effectiveness of dispersants on spilled oil. Studies conducted indicate an increase in dispersion efficiency with an increase in temperature. However, there have been conflicting results in the trend of dispersant effectiveness with either increasing or decreasing water temperature. For example, studies performed by Byford *et al.* (1983) varied from those conducted by Fingas *et al.* (1991). Table 2 shows the results obtained for oil + dispersant 'A' experiments conducted for a flask speed of 250 rpm. From the table, we see that dispersant efficiency increases with increase in temperature from 6 to 22 ^{0}C, but decreases at 35 ^{0}C for PBC and 2FO and increases for SLC.

Statistical analysis of the results. The results of the factorial experiments were analyzed using an analysis of variance (ANOVA) with α=.05. The highest order interaction in all cases was assumed to be non_significant and its degrees of freedom used for error. A significant interaction means that the effect of one input parameter varies at differing levels of another input parameter. Whenever a hypothesis test showed an effect to be significant, least squares means were examined to determine the exact nature of the difference. Based on the statistical results, it was decided to consider the two-way interactions that contain the dispersant factor and were significant (i.e., $p<0.05$). Table 3 gives the various two way interactions that were significant, experimental conditions considered and total number of runs. The experimental runs conducted revealed that the relative percent difference (RPD) given by

$$RPD = \frac{Avg.\ Effectiveness\ of\ current\ results - Effectiveness\ of\ previous\ results}{Avg.\ Effectiveness\ of\ current\ results} x\ 100 \quad (2)$$

was less than15%.

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

$$y_i = \beta_0 + \beta_v x_{v(i)} + \beta_t x_{t(i)} + \beta_s x_{s(i)} + \beta_{vt} x_{v(i)} x_{t(i)} + \beta_{vs} x_{v(i)} x_{s(i)} + \beta_{ts} x_{t(i)} x_{s(i)} + \beta_{vts} x_{v(i)} x_{t(i)} x_{s(i)} \quad (3)$$

for i=1,....n

Where y_i is the effectiveness value at the corresponding levels of the factors, β_0 is the intercept, β_v is the volatilization effect, β_t is the temperature effect, β_s is the speed effect, β_{vt} is the effect of the volatilization by temperature interaction, β_{vs} is the effect of the volatilization by speed interaction, β_{ts} is the effect of temperature by speed interaction, and β_{vts} is the effect of the three way interaction between all of the factors.

Table 4 shows a comparison between the predicted effectiveness values (equation 3) and the experimental values. It is seen that a very good prediction is obtained for SLC. The predictions were relatively poor for PBC at 150 rpm and 2FO at 150 and 200 rpm.

Table 3. Two way interactions.

OIL	INTERACTION	CONDITIONS	NO: OF 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 ^{0}C * 4 replicates	24
PBC	Temperature * Dispersant	0% volatilization * 2 dispersants * 3 temperatures *250 rpm * 2 replicates	12
PBC	Volatilization * Dispersant	22 ^{0}C * 250 rpm * 3 volatilization * 2 dispersants * 2 replicates	12
PBC	Speed * Dispersant	0% volatilization * 2 dispersants * 3 speeds * 22 ^{0}C * 4 replicates	24

Table 4. Empirical prediction of Dispersant "A" effectiveness (Temperature = 35 ±1 ^{0}C).

Oil (Weathering)	Speed (rpm)	Empirical Predictions (eq. 3)	Experimental Values	RPD %
SLC (10%)	150	74.8	74.1	0.9
SLC (10%)	200	87.2	94.2	7.4
SCL (10%)	250	99.6	97.4	2.2
PBC (10%)	150	45	33.1	36.1
PBC (10%)	200	64.2	71.5	10.1
PBC (10%)	250	83.4	72.8	14.5
2FO (3.8%)	150	43.5	34.2	27.2
2FO (3.8%)	200	64.6	46.6	38.8
2FO (3.8%)	250	85.8	76.9	11.6

Summary and conclusions

The experimental results obtained in this study reveal the following: 1) dispersant effectiveness increases with increase in mixing energy; 2) dispersant effectiveness decreases with increase of weathering or volatilization; and 3) no particular trend is seen with respect to the effect of temperature.

The empirical correlation for the collected experimental data predicted within a good accuracy the effectiveness of the dispersant. These correlations have the potential to serve as an input parameter to the ERO^{3}S model.

Biography

George Sorial is an associate professor in the Civil and Environmental Engineering Department, University of Cincinnati, Ohio. His research interests are developing protocols for oil spill cleanup, electrochemical processes, activated carbon adsorption, and soil remediation.

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