Laboratory-Scale Testing of Dispersant Effectiveness of 20 Oils Using the Baffled Flask Test

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BACKGROUND AND INTRODUCTION

Bench-scale dispersant effectiveness tests are routinely used around the world to evaluate the potential effectiveness of a dispersant product on standard oils or to study the effect of oil and dispersant type and environmental variables on dispersant effectiveness. In the United States, dispersant products must achieve a measured effectiveness of 45% or greater using the Swirling Flask Test (SFT) in order to be placed on the U.S. Environmental Protection Agency's (EPA's) National Contingency Plan (NCP) Product Schedule (NCPPS) for possible use in an oil spill. However, the effectiveness values recorded in these laboratory tests do not necessarily relate closely to the expected effectiveness in the field. Attempts have been made to correlate the results of bench-scale tests to one another, but these attempts have met with limited success because each test is performed with different variables (mixing speed, oil type, temperature, etc.) that might affect performance.

Limited field data are available comparing bench-scale test results to field success. In 2010, the Bureau of Ocean Energy Management, Regulation, and Enforcement (BOEMRE, formerly the Minerals Management Service) conducted a research project at Ohmsett, which is BOEMRE's national oil spill response test facility located in Leonardo, NJ. Its objective was to develop large-scale test tank dispersant effectiveness (DE) data on 20 crude and fuel oils using Corexit 9500 dispersant[1]. The physical properties of those oils are summarized in Table 1. More recently, BOEMRE initiated other testing to be conducted in round robin-like fashion by various independent laboratories to compare the various types of dispersant effectiveness tests that exist and to see if any or all of the tests are predictive of larger scale performance. The other laboratory tests performed included the Swirling Flask Test (SFT), the EXDET test, and the French IFP test. This report summarizes the data from the BFT. BOEMRE will take the data from all investigators and conduct a comparison among the lab tests. The BFT was originally developed by EPA's National Risk Management Research Laboratory (NRMRL)[2,3,4] to replace the SFT, which they found provided inferior and poorly reproducible results. It is planned to be adopted as the official EPA test later in 2011.

No.	Crude Oil	at 15 °C	(g/cm³ at ~15 °C)	Viscosity, cSt
1	Anadarko	10 @100s	0.906	11
2	ANS (20%)	52 @100s	0.89	58
3	ANS Fresh	35 @100s	0.884	40
4	Billiton	388 @100s	0.924	420
5	Doba	1,955 @100s	0.918	2,130
6	Elly	9700 @20s	0.958	10,125
7	Endicott (18%)	516 @100s	0.922	560
8	Endicott Fresh	120 @100s	0.896	134
9	Harmony	3588 @100s	0.942	3,809
10	IFO 120	1440 @100s	0.948	1,519
11	IFO 380	10,490 @30s	0.966	10,859
12	North Star	8 @100s	0.848	9
13	PER038	2,977 @100s	0.956	3,114
14	PER040	18,500 @10s	0.968	19,112
15	PXP01	9,400 @10s	0.951	9,884
16	PXP02	31,195 @10s	0.965	32,326
17	Rock	3,290 @100s	0.957	3,438
18	Terra Nova	380 @100s	0.867	438
19	Venoco E	11,906 @10s	0.961	12,389
20	Venoco E	64 @100s	0.892	72

Table 1. List of Oils and Physical Properties from the Ohmsett Final Report, Mar 2010

*Kinematic viscosity is absolute viscosity/density.

A dispersant consists of three types of chemicals: surfactants, solvents, and additives. For an effective dispersant, the most important component in the dispersant mixture is the surfactant. Surfactants contain both oil-compatible and water-compatible groups. Because of their opposing solubility tendencies, both classes of compounds will reside at the oil-water interface and will reduce the oil-water interfacial surface tension, which will eventually promote dispersion of oil droplets into the water column. Smaller droplet size enhances biodegradation. However, due to the chemical and physical interactions between spilled oils and the sea, an understanding of the behavior of released oil must be based upon empirical data. The impacts of dispersants on oil slicks are best characterized empirically.

MATERIALS AND METHODS

Sampling Design and General Approach. The protocol uses a 150-mL screw-cap trypsinizing flask (essentially an Erlenmeyer flask with baffles) that has been modified by the placement of a glass stopcock near its bottom so that a subsurface water sample can be removed without disturbing the surface oil layer (Figure 1). After synthetic seawater and oil are added to the flask, a dispersant is added directly to the floating oil slick, and the flask is placed on an orbital shaker to receive moderate turbulent mixing at 200 rpm for 10 ± 0.5 min. The shaker table having a speed control unit with variable speed (40-400 rpm) and an orbital diameter of approximately 0.75 inches (2 cm) is used to impart turbulence to solutions in the test flasks. The mixing is equivalent to an energy dissipation rate of 0.163 W/kg water[5], which is approximately 2 orders of magnitude greater than that obtainable in the Swirling Flask Test. The rotational speed accuracy should be within ± 10%. The contents are allowed to settle for 10 ± 0.25 minutes to allow non-dispersed oil to return to the water surface before removing the subsurface water sample. Each replicate is run individually by the same analyst so that identical test conditions can be maintained for each replicate. The subsurface water sample is then processed by liquid-liquid extraction in dichloromethane (DCM). The oil concentration in the DCM is measured by UV-visible absorption spectrophotometry.

Figure 1. Photograph of the baffled trypsinizing flask.

Synthetic Seawater. "Instant Ocean," manufactured by Aquarium Systems of Mentor OH, was used as the exposure matrix for the study. The synthetic sea water was prepared by dissolving 34 g of the salt mixture in 1 L of Milli-Q water (final salinity of 34 ppt). Table 2 provides a list of the ion composition of the sea salt mixture. Following the preparation, the saltwater solution was allowed to equilibrate to the ambient temperature of the constant temperature room. The temperature in the constant temperature room was 15 ± 0.5 °C.

Table 2. Major Ion Composition of Instant Ocean™ Synthetic Sea Salts		
Major Ion	**Salt Composition, % total weight**	**Salt Composition at 34 ppt Salinity, mg/L**
Chloride (Cl^-)	47.470	18,740
Sodium (Na^+)	26.280	10,454
Sulfate (SO_4^{-2})	6.600	2,631
Magnesium (Mg^{+2})	3.230	1,256
Calcium (Ca^{+2})	1.013	400
Potassium (K^+)	1.015	401
Bicarbonate (HCO^{-3})	0.491	194
Boron (B^{3+})	0.015	6
Strontium (Sr^{2+})	0.001	7.5
Solids Total	86.11%	34,090
Water	13.88	--
Total	99.99%	--

Oil Extraction and Analysis. The solvent dichloromethane (DCM, pesticide quality) was used for extractions of oil-water samples from the baffled trypsinizing flasks and all experimental water samples. A Brinkmann Eppendorf repeater pipettor capable of dispensing 2 □L to 5 mL, depending on the tip selected, was used for dispensing the required amounts of the oil and the dispersant. Dispersed oil was measured with a Shimadzu Recording UV-VIS Spectrophotometer (Model UV-1800) capable of measuring absorbance at

340, 370, and 400 nm (these were the same wavelengths used in the original SFT protocol[6]). Standard transmission-matched quartz 10-mm path length rectangular cells with PTFE cover were used having a transmittance of > 80% over the wavelength range of not > 190 nm at the low end of the spectrum to at least 1,100 nm at the high end of the spectrum.

Oil Standards Procedure. A stock solution of dispersant-oil mixture in DCM was prepared by adding 80 □L of the dispersant to 2 ml of the oil, and then 18 mL of DCM was added. Determinations of stock solution concentrations were based on the mass measurements after each addition. For generating a six-point calibration curve, a specific volume of the stock standard solution was added to 30 mL synthetic seawater in a 125 mL separatory funnel. The volumes of the stock solution used were adjusted to give absorbance readings that fell within the linear dynamic range (LDR) of the spectrophotometer. Liquid/liquid extractions of samples were then performed three times by using 5 mL of DCM for each extraction and adjusting the final extract to 20 or 25 mL (adjusted to maintain the LDR). The final extract was then transferred to 25 mL serum bottles with crimp-style aluminum/Teflon seals and stored at 5 °C until the time of analysis.

Baffled Flask Test Procedure. A volume of 120 mL of synthetic seawater was added to the baffled flask, followed sequentially by addition of the oil and finally by the dispersant. A volume of 100 □L of oil was carefully dispensed directly onto the surface of the synthetic seawater 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-□L syringe tip attachment set to dispense 4 □L, giving a volumetric ratio of dispersant-to-oil of 1:25 (DOR). This was similar to the average DOR reported in the BOEMRE Ohmsett report (~1:30) for 12 test oils. The DOR was not reported for the other 8 oils. Care was taken to make certain the dispersant contacted the oil without first touching the water. The flask was then placed on an orbital shaker (New Brunswick G24 shaker incubator) and mixed for 10 minutes at a rotation speed of 200 rpm. At the end of the mixing period, the flask was removed from the shaker and allowed to remain stationary on the bench top for 10 minutes. At the conclusion of the quiescent period, the first 2 mL of sample was drained from the stopcock and discarded, and then 30 mL of sample was collected in a 50 mL graduated cylinder. The 30 mL sample was transferred to a 125 mL separatory funnel and extracted 3 times with 5 mL fresh DCM. The extract was adjusted to a final volume of 20 or 25 mL and transferred to a 50 mL crimp style glass vial with an aluminum/Teflon seal. The vials were stored at 5 °C until the time of analysis. Dilutions were made in volumetric flasks for some of the oils to achieve the LDR of the spectrophotometer. Each of the four replicates was done separately so that shaking and settling times were exactly the same for all. In addition to the 4 replicate dispersant / oil / seawater mixtures, 4 replicate oil / seawater mixtures with no dispersant, and an overall total of 4 replicate method blanks (seawater alone) were also run for quality control purposes.

Analysis of Extracts. Although we used a recording spectrophotometer for all absorbance measurements, which is capable of measuring absorbance at multiple wavelengths, we recorded the absorbance at three discreet wavelengths of 340, 370, and 400 nm and calculated the area under the absorbance vs. wavelength curve by applying the trapezoidal rule according to the following equation:

$$Area = \frac{(Abs_{340} + Abs_{370}) \times 30}{2} + \frac{(Abs_{370} + Abs_{400}) \times 30}{2} \tag{1}$$

The dispersion effectiveness value that is reported is the lower 95% confidence level of the 4 independent replicates. Equation 2 summarizes the calculation of the LCL_{95}:

This area count is used to calculate the Total Oil Dispersed and then the percentage of oil dispersed (%OD) based on the ratio of oil dispersed in the test system to the total oil added to the system, as follows:

$$TotalOilDispersed (g) = \frac{Area}{CalibrationCurveSlope} \times V_{DCM} \times \frac{V_{tw}}{V_{ew}} \tag{2}$$

where:
V_{DCM} = volume of DCM extract,
V_{tw} = total volume of seawater in flask,

4

Vew = total volume of seawater extracted, and

$$\%OD = \frac{TotalOilDispersed}{\rho_{oil} \times V_{oil}}$$ (3)

where:
ρ_{oil} = density of the specific test oil, g/L, and
V_{oil} = volume (L) of oil added to test flask (100 μL = 10^{-4} L) (4)

The dispersion effectiveness value that is reported is the lower 95% confidence level of the 4 independent replicates. Equation 5 summarizes the calculation of the LCL_{95}:

$$LCL_{95} = \bar{x} - t_{n-1,1-\alpha}\left(\frac{s}{\sqrt{n}}\right)$$ (5)

where $\bar{x}$ = mean dispersion effectiveness of the n = 4 replicates,
  s = standard deviation, and
  $t_{n-1,1-\alpha}$ = 100 x (1 – α)th percentile from the t-distribution with n-1 degrees of freedom.
For four replicates, $t_{n-1,1-\alpha}$ = 2.35, where α = 0.05.

Since a certain amount of physical dispersion occurs when no dispersant is used, that fraction should be accounted for (i.e., subtracted) in the final reporting of chemical dispersion. The statistical equations governing the proper way to accomplish this are summarized below.

The average nominal percent oil dispersed due to dispersant alone is calculated using Equation 6 for coupled experiments with and without dispersant ($\overline{DE_d}$ and $\overline{DE_c}$, respectively):

$$DE_{nom} = \overline{DE_d} - \overline{DE_c}$$ (6)

where DE_{nom} = nominal percent oil dispersed due to dispersant alone,
  $\overline{DE_d}$ = average percent oil dispersed in presence of dispersant (total dispersed oil), and
  $\overline{DE_c}$ = average percent oil dispersed in absence of dispersant (natural dispersion).

The same comparison for reporting the LCL_{95} is made for the coupled experiments with and without dispersant (LCL_{95d} and LCL_{95c}, respectively). The LCL_{95DE} of a chemical dispersant is calculated after correcting for natural dispersion using the following equations:

$$LCL_{95DE} = \overline{DE_d} - \overline{DE_c} - \left(t_{n_d+n_c-2,0.95} * SE_{\overline{DE_d}-\overline{DE_c}}\right)$$ (7)

where: LCL_{95DE} = lower confidence limit for dispersed oil due to dispersant only,
  $t_{n_d+n_c-2,0.95}$ = 1.94, the 95% critical value for a t-distribution with (n_d + n_c - 2) degrees of freedom.
  $SE_{\overline{DE_d}-\overline{DE_c}}$ = standard error, defined in Equation 8:

$$SE_{\bar{d}-\bar{c}} = \sqrt{\frac{s_d^2}{n_d} + \frac{s_c^2}{n_c}}$$ (8)

The data shown in this report (Figure 1) used Equation 7 for reporting the LCL$_{95DE}$ after accounting for physical dispersion. Also reported are $\overline{DE_d}$ and $\overline{DE_c}$ (Figure 2) for comparison purposes.

RESULTS AND DISCUSSION

The results for all the oils are tabulated in Table 3. The table summarizes the $\overline{DE_d}$, the $\overline{DE_c}$, the DE$_{nom}$, and the LCL$_{95DE}$ for all 20 oils provided by BOEMRE in this study.

Figure 1 summarizes the lower 95% confidence level of Corexit 9500 dispersion effectiveness on the 20 different oils. The oils are sorted in descending order by LCL$_{95DE}$. The LCL$_{95DE}$ automatically accounts for variability, so no error bars are necessary. Since the $\overline{DE_c}$, which is the natural dispersion of the oil in the absence of added dispersant, has been subtracted and therefore accounted for in each of the data bars, the LCL$_{95DE}$ reports chemical dispersion due to Corexit 9500 addition. Figure 2 shows both the $\overline{DE_d}$ (total oil dispersed in the presence of dispersant without subtracting natural dispersion) and the $\overline{DE_c}$ of the oil alone in the absence of dispersant. The data order is the same as in Figure 1.

Table 3: Results sorted in descending order by Dispersant Effectiveness LCL$_{95DE}$)

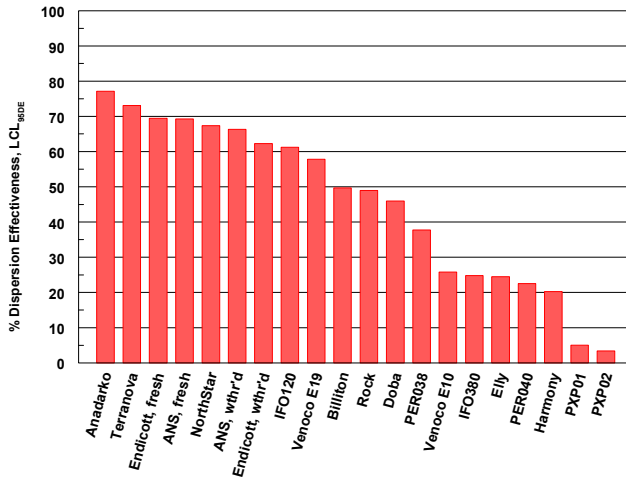| Test Oil	Kinematic Viscosity, cSt	Avg % oil dispersed, $\overline{DE_d}$	LCL$_{95d}$	Avg % oil dispersed in controls, $\overline{DE_c}$	LCL$_{95c}$	Nominal Dispersant Effectiveness, DE_{nom}	Final Dispersant Effectiveness, LCL$_{95DE}$
Anadarko	11	112.33	88.00	14.81	10.66	97.52	77.14
Terra Nova	438	81.00	75.91	3.57	2.20	77.43	73.08
Endicott Fresh	134	80.01	72.47	4.15	2.32	75.86	69.45
ANS Fresh	40	76.33	74.00	5.08	4.59	71.25	69.29
North Star	9	87.84	82.37	10.87	0.60	76.96	67.36
ANS, weathered	58	81.98	67.86	4.00	3.31	77.98	66.31
Endicott, weathered	560	71.97	68.24	5.32	1.51	66.64	62.24
IFO 120	1519	73.11	65.88	5.58	3.31	67.53	61.28
Venoco E-19	72	70.88	57.86	2.28	1.87	68.60	57.85
Billiton	420	58.14	54.95	5.51	3.93	52.63	49.69
Rock	3438	56.84	50.40	2.50	1.72	54.35	48.98
Doba	2130	55.09	51.03	5.64	4.52	49.44	45.97
PER038	3114	53.89	37.97	2.97	1.63	50.92	37.73
Venoco E-10	12389	31.52	26.42	1.50	1.31	30.02	25.81
IFO 380	10859	40.44	26.93	4.34	2.02	36.10	24.78
Elly	10125	31.34	24.14d	0.95	0.74	30.39	24.44
PER040	19112	31.56	21.34	0.61	0.24	30.96	22.51
Harmony	3809	32.28	19.78	1.69	0.83	30.59	20.24
PXP01	9884	11.12	4.67	0.72	0.56	10.40	5.07
PXP02	32326	7.04	3.88	0.99	0.46	6.05	3.41

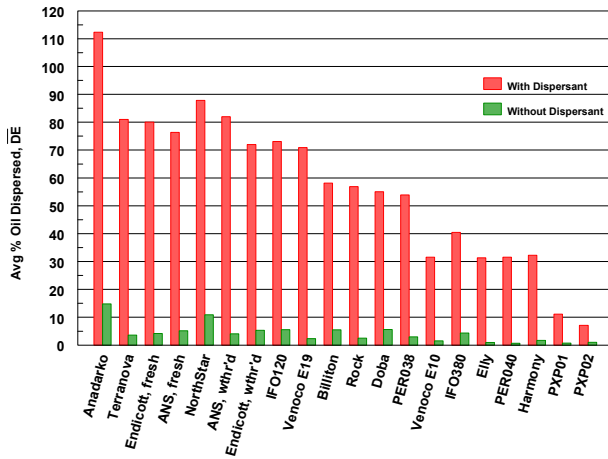Figure 1. LCL$_{95DE}$ for the 20 oils in the study.

Figure 2. Avg. %DE of the oils with and without Corexit 9500.

When it became apparent that dispersion effectiveness was moderately dependent on oil viscosity (the less viscous oils appear at the left end of Figures 1 and 2) (see Table 1 for kinematic viscosities in cSt), we plotted in Figure 3 the LCL$_{95DE}$ as a function of kinematic viscosity (KV). It is apparent that the data conform to a 1st order relationship between DE and kinematic viscosity, with relatively high r^2 values. The higher the viscosity, the lower is the dispersibility. This result is not surprising since viscosity should affect dispersion effectiveness due to the resistance to interfacial tension change in the presence of a surfactant.
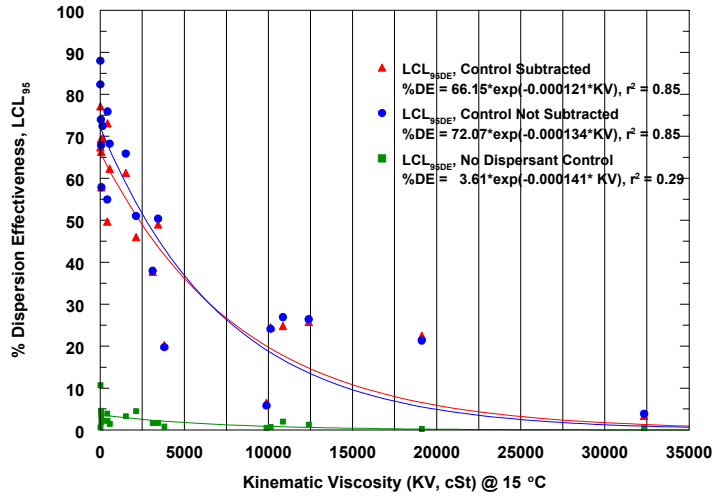
Figure 3. LCL$_{95DE}$ as a function of kinematic viscosity (cSt) at 15 °C.

In the SL Ross report of the Ohmsett experiment[1], the authors presented the results from the testing both at Ohmsett (large scale test) and the Warren Springs Laboratory (WSL) (laboratory test). Figure 4 compares our BFT results to those reported both for Ohmsett and WSL. The correlation among the three different methods of measuring DE appears to be low. Again, the data are sorted in descending order according to the BFT results.
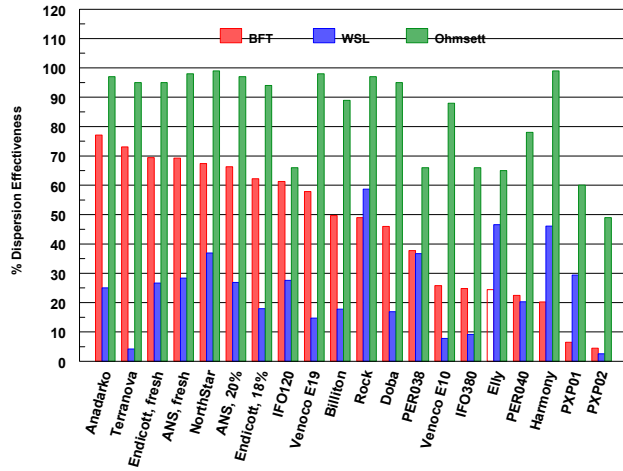

Figure 4. Comparison of DE (LCL$_{95DE}$ for the BFT) results from the BFT to WSL and Ohmsett.

Figure 5 shows a linear correlation between the BFT vs. WSL and Ohmsett. Although the scatter is moderate, the correlation of the BFT results with Ohmsett's is much higher (r^2 = 0.49) than with WSL's (r^2 = 0.0008).
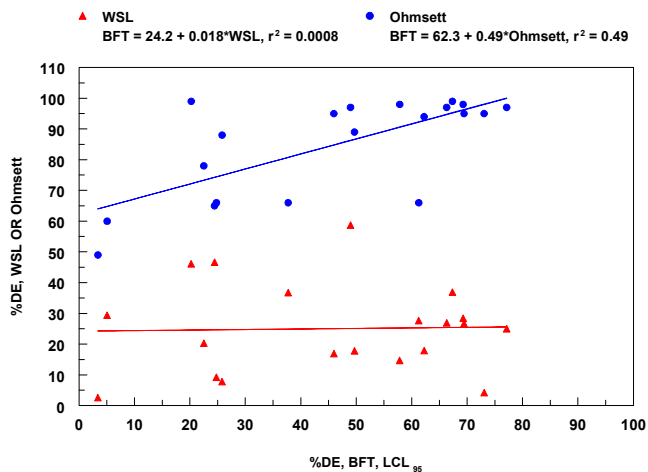

Figure 5. Correlation between the BFT vs. WSL and vs. Ohmsett.

ACKNOWLEDGMENT

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