Development of Scientifically-Based Planning Standards and Test Methods to Predict Effectiveness and Usage Rates for Surface and Subsea Dispersant Use in Various Types of Environmental Conditions

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DISCLAIMER

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EXECUTIVE SUMMARY

The fundamental goal of oil spill planning is to reduce the ecological and socioeconomic impacts of a spill to a minimum. Since the early 1980s oil spill response planning and operations have focused primarily on identifying qualified personnel, procuring available equipment, and establishing proper lines of communication to combat the effects of oil spill disasters. Much time and work has been focused on resources at risks and evaluating the ecological implications of cleanup methods and the pros and cons associated with these methods. The oil spill community (industry, government agencies, and universities) has developed many guidelines and protocols for the planning and management of oil spill incidents, primarily focusing on spill management, control measures (e.g. skimming, booming, and dispersing) and enhancing the remediation decision-making process. There has been very little scientifically-based planning for standardization of dispersant effectiveness and usage rate guidelines for oil spill incidents. The American Society for Testing and Materials (ASTM) and American Petroleum Institute (API) have organized multiple agency task forces designed to develop methods for site-specific, advance planning for dispersant use. The ASTM and API planning guidelines are useful during oil spills, but primarily focus on habitat prioritization, protection, and cleanup recommendations.

In order to provide a complete analysis of dispersant effectiveness and usage rates testing, LSU's Department of Environmental Sciences conducted a one (1) year study to provide detailed scientific information and data on the development of methodology for testing effectiveness and determining usage rates for surface and subsea dispersant use in various types of environmental conditions. The goals of this project were achieved through a series of laboratory studies conducted at LSU's Department of Environmental Sciences' Response and Chemical Assessment Team (RCAT) laboratory. Subsequently, a 1-day workshop presenting the final results and protocol was held at NOAA's Gulf of Mexico Disaster Response Center in Mobile, Alabama. Attendees included oil spill representatives from BSEE, LSU, NOAA's Emergency Response Division (ERD), and the USCG Gulf Strike Team.

INTRODUCTION

Our coastal shorelines and saltwater marshes accommodate a diverse range of vegetative, aquatic, and mammalian habitats. For this reason, large amounts of resources are devoted to preventing offshore oil spills from impacting near shore environments. In calm and pristine sea conditions, booming and skimming techniques are the preferred cleanup and recovery methodology. In situ burning is another cleanup option, but is limited to condensed spills which produce a more intense and complete burn. In situ burning also produces large plums of harmful smoke and tends to leave residual oil within the water column. Unfortunately, inclement weather is often encountered during oil spills making sea conditions less than optimum for these cleanup techniques. In rough seas, chemical dispersants appear to be the most effective cleanup tool for removing spilled oil from the water surface. Dispersant application is primarily a spill control method designed to remove the oil from the water's surface. Oil spill dispersants are special blends of surfactants in a carrier solvent. The surfactant is the most effective component of the mixture and is composed of a compound that contains both oleophilic (non-polar) and hydrophilic (polar) regions within the same molecule. Surfactants alter the physical and chemical properties of the oil so that the interfacial tension between the oil and the water surface are greatly reduced, promoting the formation of small oil droplets. The dispersant, along with wave energy, breakup the oil slick and force it into the water column as small oil droplets. The reduction in droplet size increases the oil's overall surface area, thus enhancing microbial degradation within the water column and reducing the oil's impact on aquatic species and shoreline ecosystems [1].

Dispersant effectiveness is a broad term used by the oil spill community to describe the non-quantitative indication of the degree to which a dispersant appears to be working, i.e. dispersion of oil in water column. There are multiple dispersant test methods and protocols used throughout the United States and the international community. By design they are all similar in function and output; a specific dispersant is added to oil on seawater in a vessel and the mixture is agitated via a swirling or shaking device. After a specific period of time the device is stopped and an aliquot of water is removed and analyzed for oil content. The various methods can differ greatly; the degree of agitation and the volume of oil and water are two of the most important. Method evaluations have shown that different dispersant test methods produce significantly different results when using the same dispersant and oil combinations under identical conditions. The lack of a standard method for predicting dispersant effectiveness and usage rates has made it difficult for oil spill responders to effectively utilize chemical dispersants during surface and subsurface oil spill operations. The investigators propose to develop a standardized method and protocol to predict the effectiveness of surface and subsurface dispersant use in various types of environmental conditions. The new method will enable oil spill responders to accurately apply the most effective dispersant at the best application rate in order to produce the least amount of environmental impact following an oil spill incident.

Multiple laboratory and field studies have been performed to evaluate the effectiveness of dispersants under various sea conditions. Field studies have proven to be difficult to replicate due to constantly changing meteorological and sea conditions and for economic reasons. For this reason most dispersant effectiveness testing has been conducted as small-scale bench experiments. Approximately 50 different laboratory tests methods have been reported for determining the effectiveness of dispersants on oil. A few of the most popular test methods include the Exxon dispersant effectiveness test method (EXDET), the French IFP test method, the Warren Spring Laboratory test method, the swirling flask test (SFT) method, and the baffled flask test (BFT) method. Until recently the most widely accepted test method throughout the United States was the SFT method. The SFT method was officially adopted by the US Environmental Protection Agency (EPA) in 1994 as its official laboratory screening methodology for determining the effectiveness of dispersants in seawater. Soon after its adoption unexpected discrepancies were discovered between the data submitted by independent laboratories and those generated by EPA contract laboratories for numerous dispersant products on the National Contingency Plan (NCP) schedule list. Within the last decade, a new method has been adopted by the EPA for the determination of dispersant effectiveness on oil spills. The Baffled Flask Test (BFT) was developed at the Andrew W. Breidenbach Environmental Research Center in the National Risk Management Research Laboratory, a division of the U.S. Environmental Protection Agency's Office of Research and Development. The BFT has proven to be substantially more reproducible and repeatable when performed by independent and EPA laboratories [1]. In addition, the BFT is the only available device that has been scientifically calibrated with respect to mixing energy.

PROBLEM STATEMENT

The fundamental goal of oil spill planning is to reduce the ecological and socioeconomic impacts of a spill to a minimum. Since the early 1980s oil spill response planning and operations have focused primarily on identifying qualified personnel, procuring available equipment, and establishing proper lines of communication to combat the effects of oil spill disasters. Much time and work has been focused on resources at risks and evaluating the ecological implications of cleanup methods and the pros and cons associated with these methods. The oil spill community (industry, government agencies, and universities) has developed many guidelines and protocols for the planning and management of oil spill incidents, primarily focusing on spill management, control measures (e.g. skimming, booming, and dispersing) and enhancing the remediation decision-making process. A review of oil spill incidents (i.e. open water) have shown that mechanical containment and recovery is the primary control measure for reducing ecological and socioeconomic impacts from oil spills in the United States [2]. Some countries almost completely rely on chemical dispersants contain oil spills because frequently rough or choppy sea conditions prevent the use mechanical containment and cleanup [3]. However, dispersants have not been used extensively in the United States because of possible long term environmental effects, difficulties with timely and effective application, disagreement among scientists and research data about their environmental effects, effectiveness, and toxicity concerns.

There has been very little scientifically-based planning for standardization of dispersant effectiveness and usage rate guidelines for oil spill incidents. The American Society for Testing and Materials (ASTM) and American Petroleum Institute (API) have organized multiple agency task forces designed to develop methods for site-specific, advance planning for dispersant use. The ASTM and API planning guidelines are useful during oil spills, but primarily focus on habitat prioritization, protection, and cleanup recommendations. The European Maritime Safety Agency (EMSA) [4] has developed an international manual on the applicability of oil spill dispersants. The manual is very detailed and contains data from dispersant effectiveness studies and operational treatment rates for dispersants. Unfortunately, the tests used in the EMSA manual are complicated and have limited value when comparing to dispersant effectiveness measurements at sea. The National Contingency Plan (NCP) [5] is the United States Environmental Protection Agency's (USEPA) blueprint for responding to both oil spills and hazardous substance releases. The NCP is the result of efforts to develop a national response capability and promote coordination among the hierarchy of responders and contingency plans. The plan is quite effective, but is very broad in its guidance and only recommends approved dispersants, not their predicted effectiveness and usage rates for varying environmental conditions. The USEPA is currently employing the BFT to determine the effectiveness of dispersants on oils. The test is effective but does not take into account for variations in application rates, sea state, or temperature. The BFT shares many of the same limitations as the SFT, providing ranks rather than absolute effectiveness numbers. The test is not yet standard in any jurisdiction. Many scientist argue that this test overestimates the effectiveness of dispersants by making unrealistically large amounts of energy available to the mixture and that real ocean waves have much less energy available to force the dispersion. Further, no approved analytical method has yet been chosen for this test. The United States Coast Guard (USCG) and the National Oceanographic and Atmospheric Administration (NOAA) have employed the Special Monitoring of Applied Response Technologies (SMART) [6] to monitor dispersant application during oil spill operations. Again, the current USCG and NOAA protocol does not address effectiveness and usage rates of specific NCP dispersants. During the most recent large-scale dispersant application, the *Deepwater Horizon* spill, an estimated 1.84 million gallons of Corexit EC9500A and Corexit EC9527A had been applied during surface and subsea operations over a four (4) month period. During this time period, no official guidance or standard was followed during dispersant operations. Reports showed that dispersants were applied at usage rates ranging from 1:10 dispersant to oil ratio (DOR) to as low as 1:200 DOR. The Texas City Y is a good example of oil spill responder's limitations when predict dispersant efficacy in the field. On March 22, 2014 a ship and barge collided in the Galveston, TX ship channel, releasing approximately 162,000 gallons of a moderately heavy fuel oil (RMG 380). A team from LSU responded to the spill within 36 hours and were notified the USCG was considering dispersant application. The contractor for the responsible party determined the oil collected from the ship's fuel tank was dispersible and would start dispersant operations the following day. Just prior to making the final decision to disperse the oil, LSU performed a quick "tailgate" test on oil collected from the water surface to determine its dispersibility. A visual test indicated that Corexit 9500A was less than 10% effective in dispersing the oil. RMG 380 is a marine fuel oil produced from a blend of marine gas oil (MGO) and heavy fuel oil (HFO) [7]. The oil is blended to produce a product with a kinematic viscosity of 380 mm^2/s and density of <0.991 g/cm^3. This type of heavy fuel oil typically floats following the initial oil release, but slowly sinks as its low-molecular weight components evaporate over time. Due to the variability of blended oils and weathering conditions, it is imperative that responders evaluate oil dispersibility just prior to beginning chemical dispersant operations.

Because of the unpredictability of oil spills (i.e. time, location, environmental conditions) and lack of guidance data, specific guidelines must be established to direct the selection of the most effective dispersant and its usage rate for varying oil spill scenarios. A review of the current oil spill planning guidelines and protocols used by the United States environmental agencies does not provide adequate guidance or standardized protocol to accurately predict the effectiveness of surface and subsea dispersant use in various types of environmental conditions. Clearly, further research is needed in developing standardized protocols and test methods to predict effectiveness and usage rates for surface and subsea dispersant use in various types of environmental conditions.

PROJECT DESCRIPTION

The use of dispersants on oil spills has been renewed in the United States by recent high – profile oil spills (e.g. *Deepwater Horizon* and Texas City Y) and the increased transport of oil products within our navigable waterways. Much interest has been generated towards predicting effectiveness and usage rates for surface and subsea dispersant use in various types of environmental conditions. The current dispersant effectiveness test, BFT, is effective and its results are widely documented. Unfortunately, most studies employing the BFT are standardized and do not investigate variations in temperatures, dispersant-to-oil ratios (DORs), and mixing energy levels. Recently, Venosa and Holder (2013) conducted a study to determine the dispersibility of South Louisiana crude oil by eight oil dispersants at multiple water temperatures (25°C and 5°C). This was one of the few times that a BFT was used to determine dispersibility of oils at subsea temperatures. Kaku et al. (2006) performed an extensive evaluation of mixing energy in laboratory flasks used for dispersant effectiveness tests. Their research showed that the turbulence generated at 200 revolutions per minute (rpm) using the BFT resembled the turbulence occurring at sea during breaking waves. Again, very few studies have been conducted investigating variations in mixing energy during dispersant effectiveness testing.

In order to provide a complete analysis of dispersant effectiveness and usage rates testing, LSU's Department of Environmental Sciences conducted a one (1) year study to provide detailed scientific information and data on the development of methodology for testing effectiveness and determining usage rates for surface and subsea dispersant use in various types of environmental conditions. The goals of this project were achieved through a series of laboratory studies conducted at LSU's Department of Environmental Sciences' Response and Chemical Assessment Team (RCAT) laboratory. Subsequently, a 1-day workshop presenting the final results and protocol was held at NOAA's Gulf of Mexico Disaster Response Center in Mobile, Alabama. Attendees included oil spill representatives from LSU, NOAA's Emergency Response Division (ERD), and the USCG Gulf Strike Team.

RESEARCH GOAL

Response and analytical reports from the *Deepwater Horizon* and other spill incidents indicate that the use of dispersant, in both surface and subsurface application, significantly reduced the shoreline impact of oil following the spills [8,9,10]. The lack of current scientifically-based planning standards for dispersant effectiveness and usage rates during past oil spill incidents indicates there is a need for further study into development of a standard protocol to employ during surface and subsurface oil spills. In addition, a universal dispersant effectiveness and usage rate method (laboratory and field-based) should to be developed to scientifically validate the standard protocol. In response to the above needs, a joint research team, comprised of researchers from Louisiana State University's Department of Environmental Sciences, USEPA, NOAA, and USCG, propose the development of laboratory and field-based dispersant effectiveness/usage rate methods and a standardized protocol to assist responders in predicting the effectiveness of surface and subsurface dispersant use in various environmental conditions. The goal of this study were accomplished through a series of five (5) research objectives: (1) Evaluation of multiple oils under varying environmental and physical conditions (temperature, rotational energy level, weathering state, and dispersant usage rate) using the standardized BFT, (2) Evaluation of multiple oils under varying environmental and physical conditions (temperature, pressure, and dispersant usage rate) using a 1-liter stainless steel pressure vessel equipped with an integrated paddle stirrer, (3) Development of a 1-L baffled flask test protocol to predict the effectiveness of dispersantson multiple oils using an in situ fluorescence probe and turbidity meter, (4) Organize a 1-day dispersant workshop to discuss project results and determine if a field deployable 1-L BFT methodology can enhance current SMART protocol, and (5) Preparation and completion of a draft and final report using BSEE reporting guidelines.

LSU has determined there will be multiple benefits from this project. Task #1 will allow researchers to evaluate the standardized BFT using fluorescence analysis, which is the same technology used during field operations. Task #2 will allow investigators to evaluate the effects of pressure and various environmental conditions on oil when released in deep sea environments. Task #3 will help to bridge the gap between laboratory methodology and field analysis by incorporating the modified 1-L BFT and fluorescence probe for determining dispersant effectiveness in the field. A portable 1-L BFT method will allow responders to rapidly test unknown oils at multiple weathering states at forward field sites. Task #4 will allow federal responders to review and evaluate the results from this project. In addition, participants in the 1-day dispersant workshop will make recommendations as to whether the new testing protocol is applicable to the SMART protocol.

MATERIALS AND METHODS

Experimental Oil Characterization and Dispersant

The crude oils used in this project were obtained through the Bureau of Environmental Safety and Enforcement (BSEE) and British Petroleum (BP). The South Louisiana crude (SLC) oil used in the laboratory tests was distributed by BP as a surrogate research oil for the MC252 oil released during the DWH incident. The oil was collected from the Marlin Platform of the Dorado field, located approximately 23 miles NE of the Macondo spill site. This oil was chosen because it possesses physical properties and chemical characteristics similar to most South Louisiana Crude oil. The Alaskan North Slope and Hondo crude oils were representative samples obtained from BSEE's Ohmsett research facility in Leonardo, New Jersey. The dispersant Corexit 9500A was used in all tests. The physical characteristics of the experimental oils are shown in Table 1.

Table 1. Physical Properties of the Oils Used in the Experiments

Crude Oil Name	Viscosity (cP) at 15°C	API Gravity	Measured Density (g/ml) at 23°C and 0% Weathering	Measured Density (g/ml) at 23°C and 10% Weathering	% Aromatics at 0% Evaporation
South Louisiana Crude	7.1	37.1	0.886	0.944	16.9
North Slope Crude	18	29.8	0.915	0.957	32.0
Hondo Crude	735	19.6	0.987	1.02	31.0

Synthetic Water Preparation

Instant Ocean (Aquarium Systems, Mentor OH) will be used for the exposure water for all experiments. The synthetic seawater will be prepared by dissolving 34 g of the salt mixture into 1 L of deionized water (final salinity 34 ‰) and allowed to equilibrate to the testing temperature (5±0.5°C and 23±2°C) for approximately 4 hours prior to the start of the test.

Analytical Instrumentation

As part of this project, our research team developed and validated analytical methods and protocols designed for real-time dispersibility determination of crude oils following surface and deep sea spill incidents. The dispersibility of simulated field oil samples were determined using a laboratory-based spectrofluorometer system and field-portable turbidity and fluorescence probe units. The spectrofluorometer system used was a Horiba Aqualog® spectrofluorometer capable of simultaneously measuring fluorescence and absorbance with matching optical bandpass resolution. The turbidity meter used was a Hach® model 2100P Portable Turbidimeter and meets the design criteria specified by the United States Environmental Protection Agency (USEPA) for water quality measurements using method 180.1. The field fluorescence probe used was a Turner Designs Cyclops-7™ Submersible Sensor, the same probe integrated into the Turner Designs C3 submersible probe for use in NOAA’s SMART protocol. The Cyclops-7 probe has a dynamic detection range of 0-25 ppm of dispersed crude oil in water. Analytical instrumentation used during this project are shown in Figure 1.

Preparation of Crude Oil Standards

A stock standard oil solution of each crude oil- Corexit 9500 dispersant in dichloromethane (DCM) was prepared by adding 80 µl of the dispersant to a 2.0 ml aliquot of oil, and then adjusted to a final volume of 20 ml with DCM. A six-point calibration oil calibration curve was constructed by adding a specific volume of the stock standard oil solution to a 125-ml seperatory funnel containing a 30 ml aliquot of artificial seawater. Liquid/liquid extractions of the spiked water samples were then performed three times using a 5 ml aliquot of DCM for each extraction. The extracts were collected in a 25-ml graduated cylinder and the final volume adjusted to 20 ml with DCM. The 20 ml sample extract was transferred to a 40-ml vial with a Teflon-lined enclosure. Approximately 1-2 g of anhydrous sodium sulfate was added to the vial to remove water within the DCM extract. The final extract volume was stored at 5°C until time of analysis.

Oil Extraction and Analysis

Pesticide-grade dichloromethane (DCM) was used to extract oil-water samples from the baffled flask apparatus. A Brinkmann Eppendorf pipettor was used to dispense the required amount of oil and dispersant into the experimental flasks. Dispersed oil was measured with a Horiba Aqualog Spectrofluorometer capable of simultaneously measuring UV-VIS absorbance at 340, 370, and 400 nm and measuring fluorescence excitation-emission matrices. UV-VIS absorbance measurements were originally used with the SFT protocol and later adopted into the BFT protocol. Fluorescence excitation/emission analysis was performed on the select oils to determine their maximum peak excitation/emission wavelengths. Excitation-emission matrix spectroscopy (EEMS) was utilized to characterize the individual crude oils and determine their maximum excitation and emission wavelengths. The maximum excitation and emission wavelength for South Louisiana and North Slope crude oil were 290 nm and 360 nm, respectively. The maximum excitation and emission wavelength for Hondo crude oil was 290 nm and 380 nm, respectively. The fluorescence analysis allowed investigators to compare and correlate BFT results with pressure vessel and field BFT results. Standard transmission-matched quartz 10-mm path length rectangular cells with PFTE covers were used. The excitation-emission matrix spectroscopy contour plots for South Louisiana, North Slope, and Hondo crude oils are displayed in Figure 2.

Figure 1. Photographs of Aqualog spectrofluorometer (top), Turner Designs Cyclops-7 probe (mid), and Hach portable turbidimeter (bottom).

Analysis of Sample Extracts

Following the protocol used by the BFT, investigators recorded the absorbance at three discreet wavelengths of 340, 370, and 400 nm. The area under the absorbance vs. wavelength curve was calculated by applying the trapezoidal rule according to the following equation:

$$\text{Area Count} = \frac{(\text{Abs340} + \text{Abs370}) \text{ x } 30}{2} + \frac{(\text{Abs370} + \text{Abs400}) \text{ x } 30}{2}$$

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 flask, as follows:

$$\text{Total Oil Dispersed (g)} = \frac{\text{Area}}{\text{Calib. Curve Slope}} \times V_{\text{DCM}} \times \frac{V_{\text{tw}}}{V_{\text{ew}}}$$

where V_{DCM} is the volume of DCM extract, V_{tw} the total volume of seawater in the baffled flask, and V_{ew} is the total volume of seawater extracted, and

$$\%\text{OD} = 100 \times \frac{\text{Total Oil Dispersed}}{p_{\text{oil}} \times V_{\text{oil}}}$$

where ρ_{oil} is the density of the specific test oil, g/L and V_{oil} is the volume (L) of oil added to test flask (100 µL). The dispersion effectiveness value that is reported is the lower 95% confidence level of the five (5) independent replicates.

The following equation summarizes the calculation of the DE_{LCL95}:

$$DE_{LCL_{95}} = \text{mean}\ \%OD - t_{n\text{-}1,\ 1\text{-}\alpha}(\ s/n^{-2}\ )$$

where mean %OD is the mean dispersion effectiveness of the $n = 5$ replicates, s the standard deviation, and $t_{n-1,1-\alpha} = 100 \times (1 - \alpha)^{th}$ percentile from the t-distribution with $n - 1$ degrees of freedom.

For five (5) replicates, $t_{n\text{-}1,1\text{-}\alpha}$=2.132, where $\alpha = 0.05$. We performed the same calculations for the physically dispersed oil (absence of added dispersant) for comparison purposes. An additional set of dispersion effectiveness values were generated using fluorescence areas. This data set was used to determine if the fluorescence analysis is more sensitive and accurate when compared to the UV-VIS method and to correlate dispersant effectiveness values with results from the pressure vessel and field BFT.

Statistical Analysis

Prior to conducting the statistical comparisons, the replicates within a given treatment were subjected to the Grubb's Test (or Maximum Normal Residual test) (Grubbs, 1950) for outliers, and if an outlier is detected ($p < 0.05$), an additional replicate was run and analyzed to obtain the required number of replicates. In addition to calculating the DE_{LCL95} for each task, multiple factorial analysis of variance (ANOVA) were performed to determine if there is a mean difference between treatments and identify interactions between the various environmental and physical conditions. Statistical analysis was performed using IBM SPSS Statistical software.

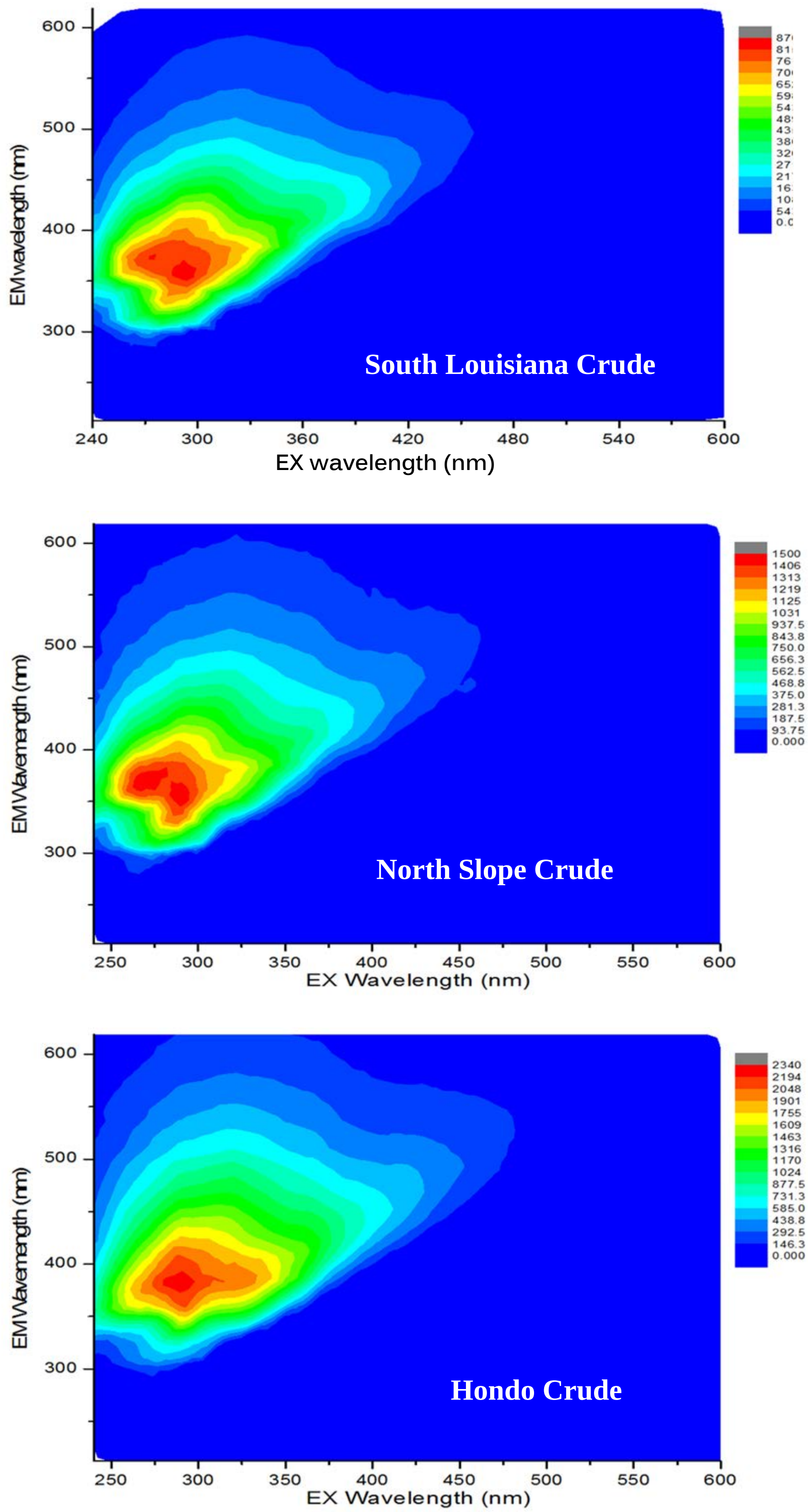

Figure 2. Normalized intensity contour plots of excitation-emission matrix spectra (EEMs) of South Louisiana, North Slope, and Hondo crude oils.

Task #1: 150-ml Baffled Flask Test Study

A series of bench-scale laboratory studies were performed to determine dispersant efficiency and usage rates for various environmental conditions within a baffled-flask microcosm following addition of Corexit 9500 to select crude oils. The objective of this study was to compare analytical methods (Fluorescence vs. UV-Vis) so as to determine which method is best suited for performing oil recovery analyzes for the standardized baffled flask tests. Five (5) individual replicate tests for each oil were used in the protocol (5 replicates × 2 temperatures × 4 DORs × 2 mixing energies × 3 oils × 2 weathering states) for a total of 480 tests. In addition, the instrument calibration curves required a total of 15-18 extractions (5-6 calib. points × 3 oils), plus a continuing calibration standard and method blank were extracted prior to the daily analysis of water samples on the spectrofluorometer. The three oils (SLC, ANC, and HC) were evaluated using the following factors: temperature (5°C and 23°C), DOR (0, 1:20, 1:50, and 1:100), mixing energy (150 rpm and 200 rpm), and weathering state (fresh and 10% weathered). Corexit 9500A was used throughout the BFT procedure and the salinity was maintained at 34 ‰. For the tests performed at 5°C, the shaker unit was housed in a large volume refrigerator and maintained at 5°C±1. All necessary tubing and wiring was plumbed through an insulated port located on the refrigerator side wall. The shaker unit and pressure vessel apparatus was located on top of laboratory bench and maintained at 23°C±1 for tests performed at ambient temperature.

The tests used a 150-ml screw-cap trypsinizing flask that has been modified with the addition of a glass stopcock near the bottom so that a subsurface water sample can be removed without disturbing the surface oil layer. A 120 ml volume of synthetic water was added, followed by a 100 µl volume of oil and an appropriate volume of Corexit 9500A. The flask was placed on an orbital shaker to receive low (non-breaking waves) and moderate (breaking waves) turbulent mixing at 150 and 200 rpm, respectively, for 10 ± 0.25 min. The shaker table has a speed control unit with variable speed (40–400 rpm) and an orbital diameter of approximately 0.75 in. (1.9 cm) and is used to impart turbulence to solutions in the test flasks. The 150 and 200 mixing rates are equivalent to an energy dissipation rates of 0.0155 m^2/s^3 and 0.163 m^2/s^3, respectively. The rotational speed accuracy was maintained within ±10%. The contents of the flasks were allowed to settle for 10 ± 0.25 min to allow non-dispersed oil to return to the water surface before removing the subsurface water sample. Each replicate was run individually by the same analyst so that identical test conditions can be maintained for each replicate. A 30 ml volume of synthetic seawater was collected from each test and placed in a 150-ml seperatory funnel. Liquid/liquid solvent extraction of the sample was performed three (3) times with 5 ml of DCM for each extraction. The extracts were collected in a 25-ml graduated cylinder and the final volume adjusted to 20 ml with DCM. The 20 ml sample extract was transferred to a 40-ml vial with a Teflon-lined enclosure. Approximately 1-2 g of anhydrous sodium sulfate (drying agent) was added to each vial to remove water within the DCM extract. The final extract vials were stored at 5°C until time of analysis. The oil concentration in the DCM was measured by the Aqualog benchtop spectrofluorometer, simultaneously measuring UV-VIS absorbance and fluorescence excitation/emission wavelengths. Absorbance was recorded at 340, 370, and 400 nm for determination of UV-Vis absorbance for all crude oils. Oils concentrations (UV-Vis) were calculated using the trapezoidal rule equation and 5-point UV-Vis standard calibration curve (Figure A2). South Louisiana and North Slope crude oil fluorescence concentrations were determined using an excitation wavelength of 290 nm and an emission wavelength of 360 nm. Hondo crude oil fluorescence concentration was determined using an excitation wavelength of

290 nm and an emission wavelength of 390 nm. Oil concentrations were calculated using the 5-point fluorescence standard calibration curve for the individual oils (Figure A1).

Results & Discussion: 150-ml Baffled Flask Tests

The results for the experimental design are displayed in Figs. 3-8, which show the percent effectiveness from the analytical methods "fluorescence" and "UV-Vis" at various flask speeds, temperatures, weathering state, and DOR for all three oils. To better understand the significance of the analytical results, statistical analyses of the experimental data were performed individually for the three oils. The results of the design experiments were analyzed using a factorial analysis of variance (ANOVA) at α =0.05 to determine which factors affect percent effectiveness. A significant interaction means that the effect of one independent variable varies at differing levels of another independent variable. The condition for significance was determined by statistical analysis was that the *p*–value should be less than 0.05 for a factor to be significant. Although this experiment was designed to determine if a significant difference exist between the two analytical methods, interactions between the other environmental factors (e.g. temperature, weathering, energy, and DOR) were examined.

The results showed that all four factors significantly affected the dispersant effectiveness in SLC ($p < 0.005$). Figs. 3 and 4 clearly illustrate that all four factors (temperature, weathering, energy, and DOR) produced significant change in the percent effectiveness values, thus, all these factors were deemed significant. Results from the statistical analysis indicated there was no significant difference between the two analytical methods ($p = 0.325$). There was no significant two-way interaction between the method factor and the temperature, weathering, energy, and DOR factors ($p > 0.572$). For NSC, all four factors (temperature, weathering, energy, and DOR) were found to significantly affect the dispersant effectiveness ($p < 0.005$). Figs. 5 and 6 show that all four factors (temperature, weathering, energy, and DOR) produced significant change in the percent effectiveness values, thus, all these factors were deemed significant. Results from the statistical analysis indicated there was no significant difference between the two analytical methods ($p = 0.267$). There was no significant two-way interaction between the method factor and the temperature, weathering, energy, and DOR factors ($p > 0.649$). For HC, all four factors (temperature, weathering, energy, and DOR) were found to significantly affect the dispersant effectiveness ($p < 0.005$). Figs. 7 and 8 show that all four factors (temperature, weathering, energy, and DOR) produced significant change in the percent effectiveness values, thus, all these factors were deemed significant. Results from the statistical analysis indicated there was no significant difference between the two analytical methods ($p = 0.411$). There was no significant two-way interaction between the method factor and the temperature, weathering, energy, and DOR factors ($p > 0.420$).

A general statistical comparison of the two analytical methods (fluorescence and UV-Vis) indicated there was no significant difference in the results from either method. There are several pros and cons associated with each method. Fluorescence is (1) sensitive, (2) specific for oil, and (3) ease of operation. Fluorometry instrumentation is more expensive and requires a higher degree of maintenance compared to UV-Vis instrumentation. When conducting standardized BFT, the fluorescence analysis requires a 100-200 fold dilution before reaching the detectors linear range. In contrast, the less sensitive UV-Vis analysis requires no dilutions to reach the instruments linear range. This experiment indicates that either method would be acceptable for the determination of oil dispersibility when performing the standardized baffled flask test.

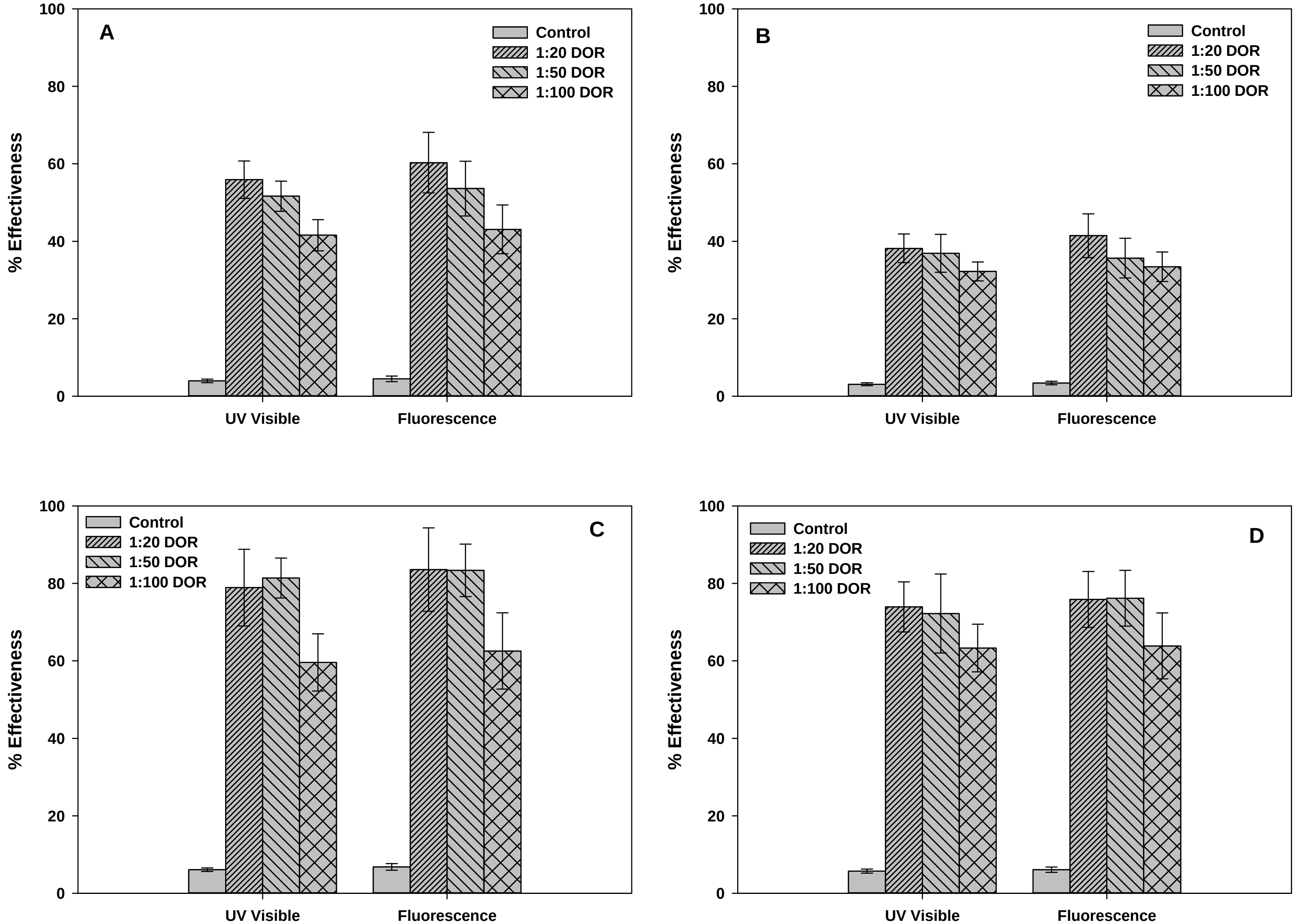

Figure 3. Average percent effectiveness for South Louisiana crude baffled flask study at 5°C with 150 rpm and 0% weathered (A), 150 rpm and 10% weathered (B), 200 rpm and 0% weathered (C), and 200 rpm and 10% weathered (D).

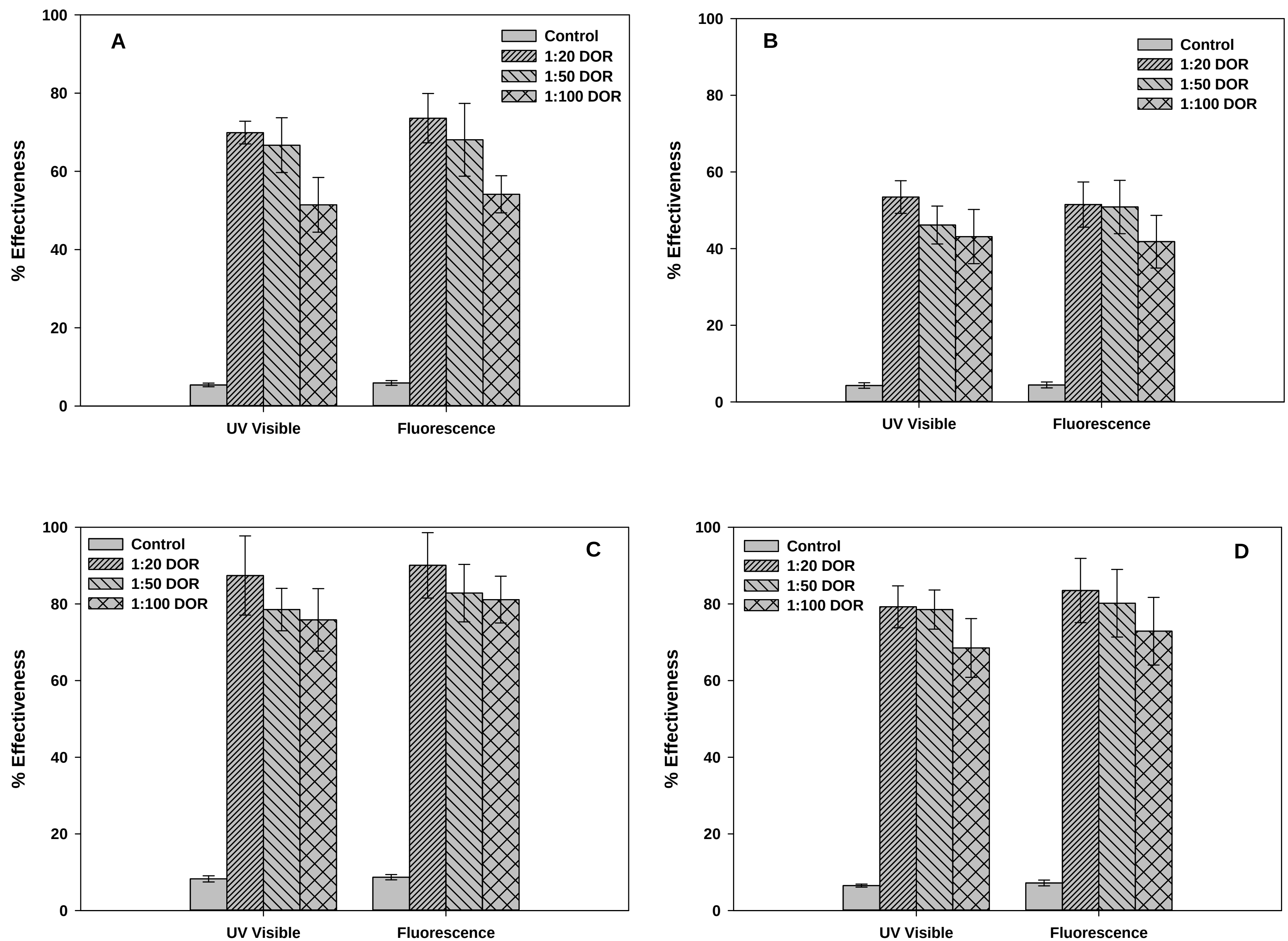

Figure 4. Average percent effectiveness for South Louisiana crude baffled flask study at 23°C with 150 rpm and 0% weathered (A), 150 rpm and 10% weathered (B), 200 rpm and 0% weathered (C), and 200 rpm and 10% weathered (D).

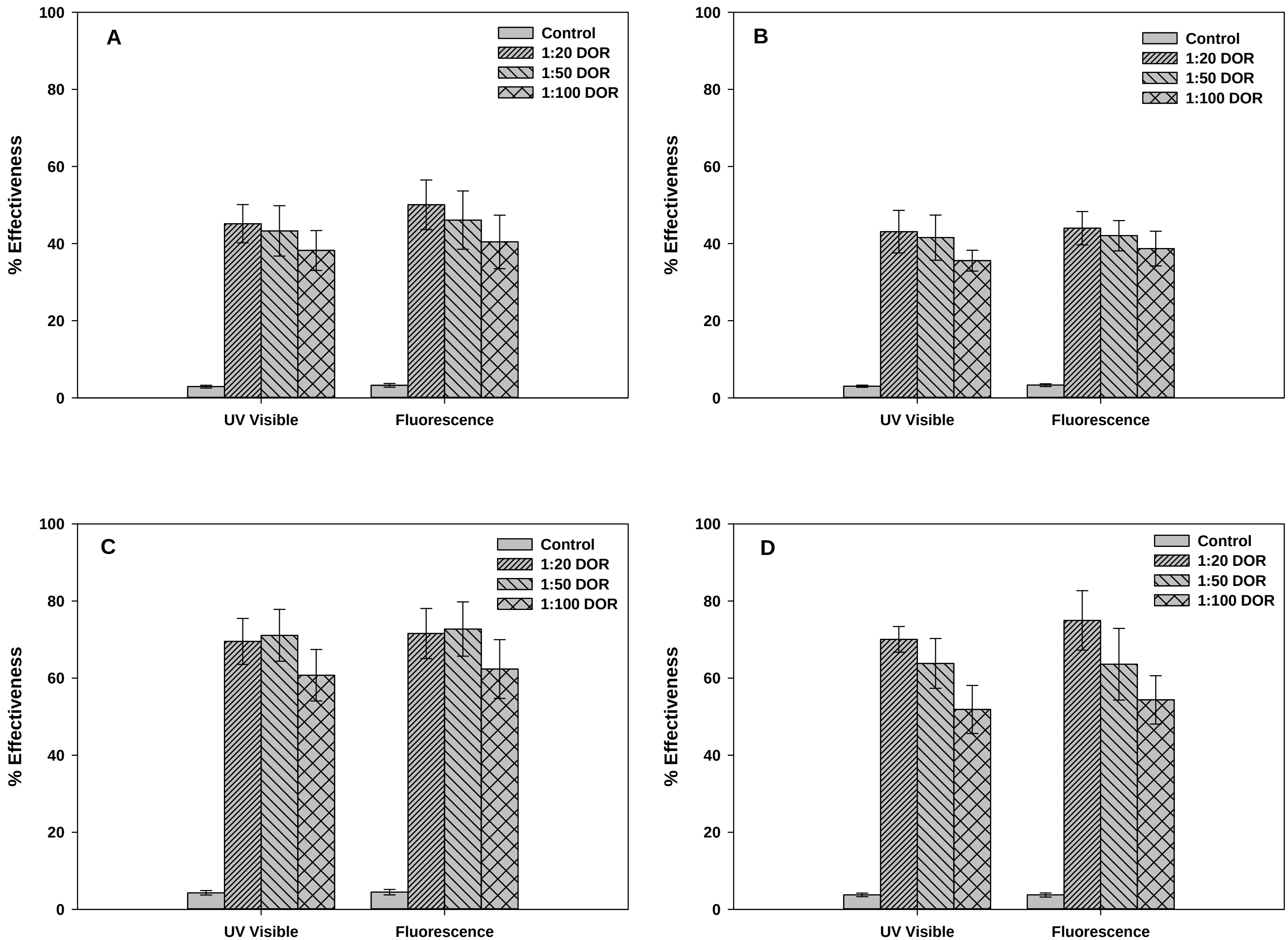

Figure 5. Average percent effectiveness for North Slope crude baffled flask study at 5°C with 150 rpm and 0% weathered (A), 150 rpm and 10% weathered (B), 200 rpm and 0% weathered (C), and 200 rpm and 10% weathered (D) .

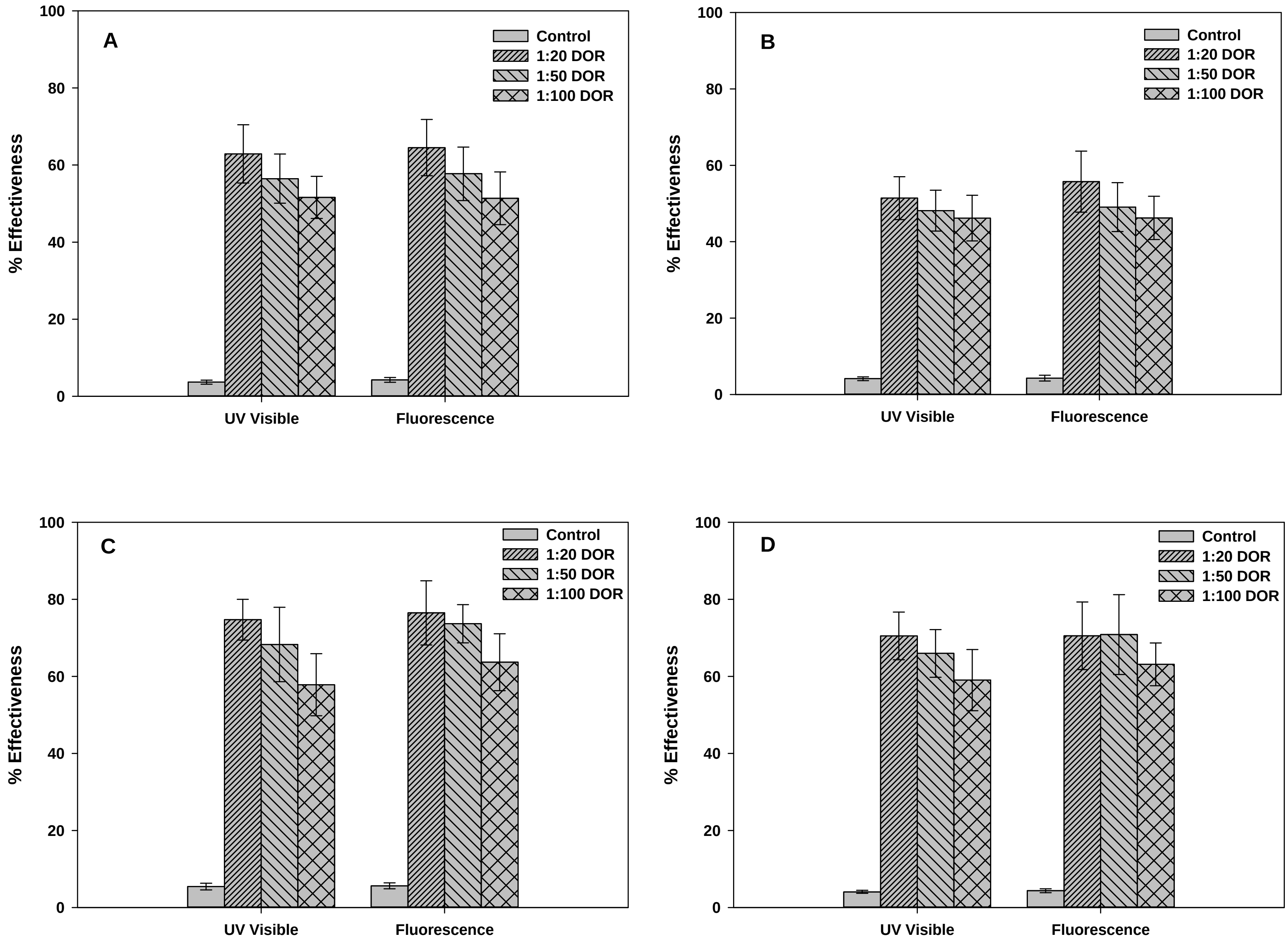

Figure 6. Average percent effectiveness for North Slope crude baffled flask study at 23°C with 150 rpm and 0% weathered (A), 150 rpm and 10% weathered (B), 200 rpm and 0% weathered (C), and 200 rpm and 10% weathered (D).

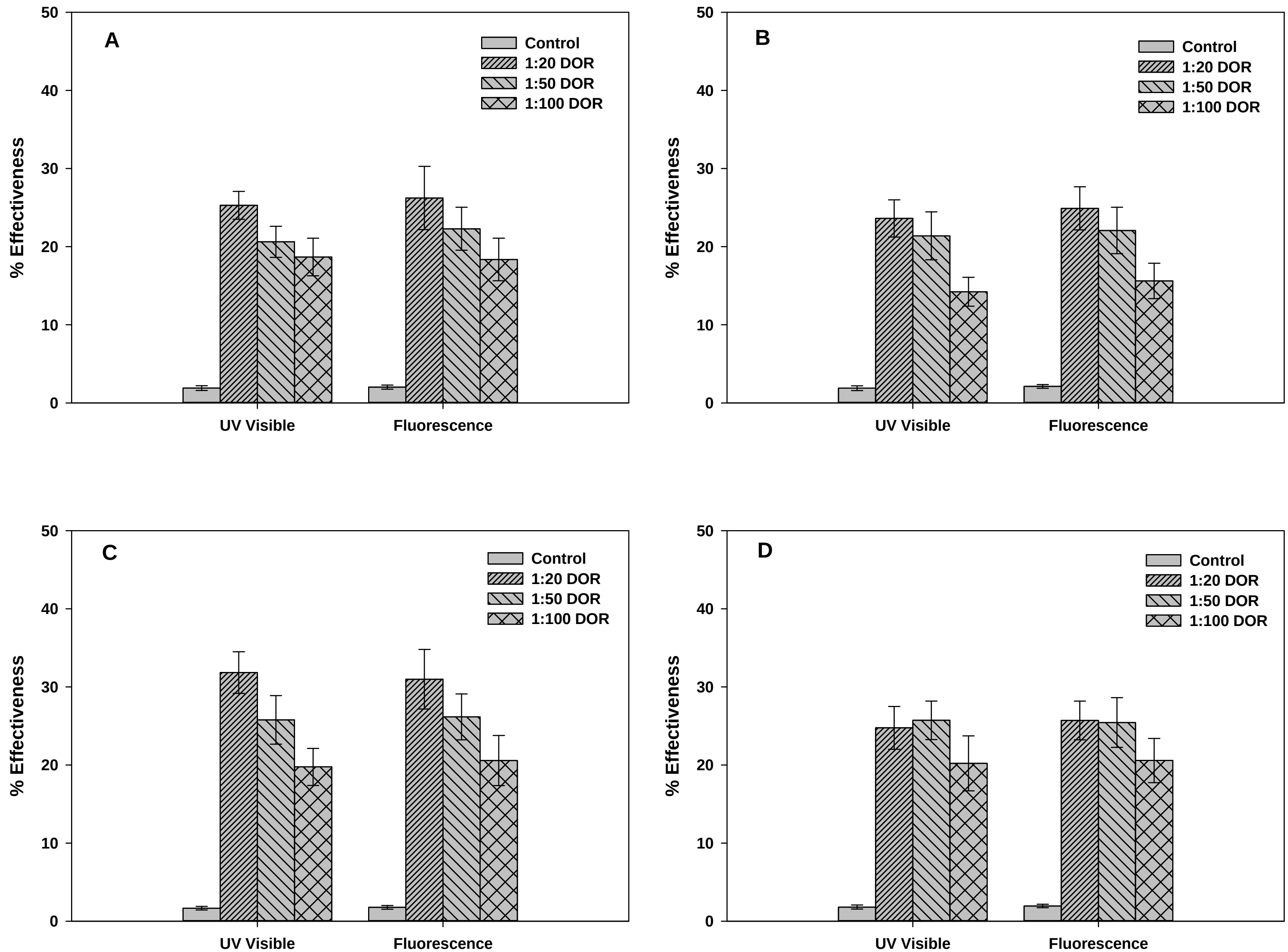

Figure 7. Average percent effectiveness for Hondo crude baffled flask study at 5°C with 150 rpm and 0% weathered (A), 150 rpm and 10% weathered (B), 200 rpm and 0% weathered (C), and 200 rpm and 10% weathered (D).

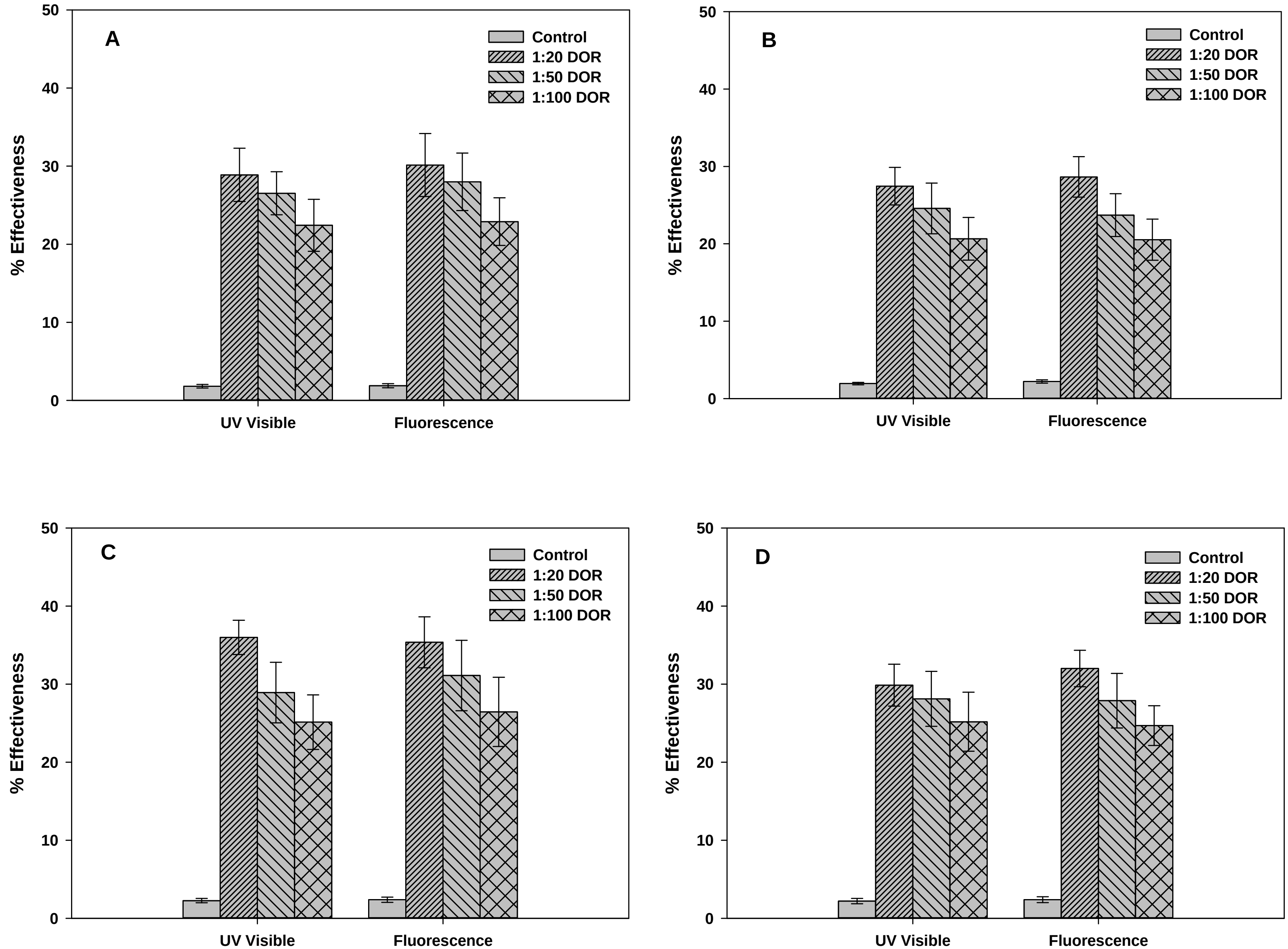

Figure 8. Average percent effectiveness for Hondo crude baffled flask study at 23°C with 150 rpm and 0% weathered (A), 150 rpm and 10% weathered (B), 200 rpm and 0% weathered (C), and 200 rpm and 10% weathered (D).

Task #2: Pressure Vessel Study

A series of high-pressure static vessel laboratory studies were performed to determine dispersant effectiveness and usage rates for subsea dispersant use in various types of environmental conditions within a 1-L stainless steel pressure vessel with the addition of Corexit 9500 to three select crude oils. The study was designed to simulate the release of oil from subsea releases at various depths and pressure. The objective of this research was to develop a set of empirical data on three oils and two pressures, by studying the variation in the dispersant effectiveness caused by changes in temperature, oil weathering, and dispersant to oil ratio. The pressure apparatus was developed and manufactured through a previous grant from BSEE. The main vessel (Figures 9 and 10) is manufactured by Applied Separations, Inc. (Allentown, PA) and designed to withstand pressures up to 10,000 psi. Accessories included with the vessel are a high-pressure liquid pump with an integrated microprocessor logging unit, a temperature and pressure probe, a high-pressure stirrer unit, and multiple sampling ports. The high-pressure stirrer operated at a rotational speed of 400 rpm. The sampling port was connected to a ¼” sampling tube which collected samples from the centerline of the vessel and approximately three (3) inches below the paddle stirrer. The high-pressure liquid pumping system was designed to maintain a constant pressure level throughout the experiments, allowing researchers to sample the vessel contents with no significant drop in pressure.

The three oils (SLC, ANC, and HC) were tested within the pressure vessel at various temperatures (5°C and 23°C) and pressures (200 psi, and 2000 psi) using control crude oils (no dispersant) and chemically-dispersed (DOR=1:20, 1:50, and 1:100) crude oil treatments. Corexit 9500A was used throughout the pressure vessel study and the salinity was maintained at 32 ‰.

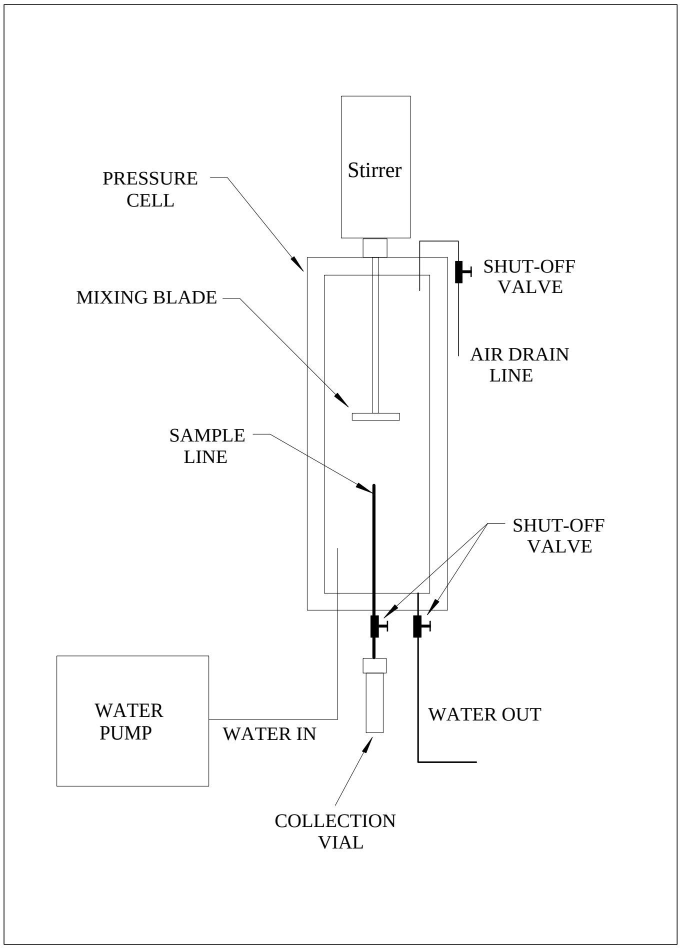

Figure 9. Experimental design for the determination of dispersant effectiveness in water at elevated pressures.

Three (3) individual replicate tests for each oils were used in the protocol (3 replicates × 2 temperatures × 4 DORs × 3 oils × 2 weathering states) for a total of 144 tests. Oil concentration in water was determined using the fluorescence analytical method detailed in the Task #1 study. In addition, a continuing calibration standard and method blank were extracted prior to the daily analysis of water samples on the spectrofluorometer. Each replicate was run individually by the same analyst so identical test conditions can be maintained for each replicate.

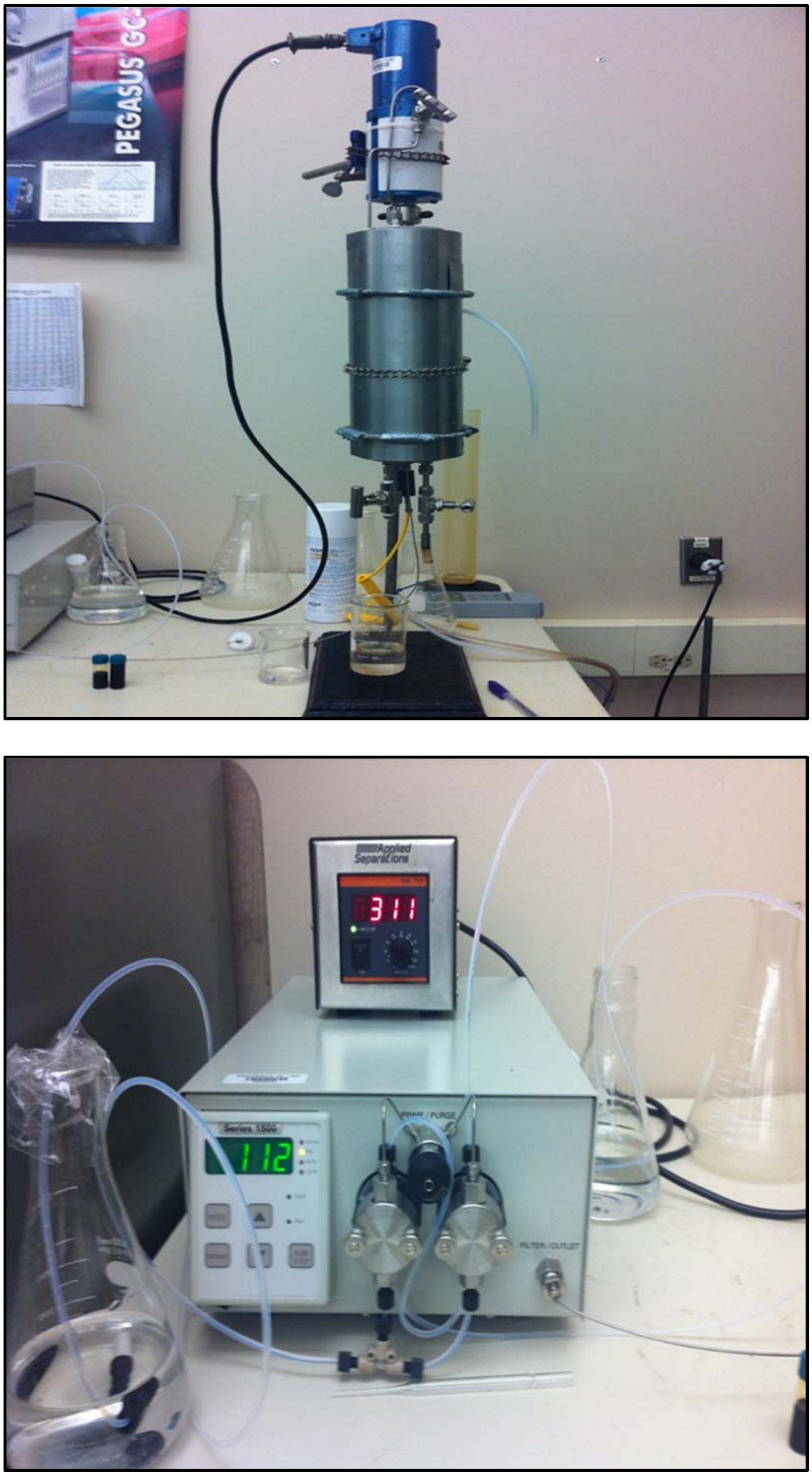

Figure 10. Photographs of high-pressure vessel and pumping system.

A 1 ml volume of oil or oil/dispersant mixture was injected through a 1/8" injection port into the 1-L vessel filled with synthetic seawater and allowed to equilibrate to the designated test temperature. For the tests perform at 5°C, the pressure vessel apparatus was housed in a large volume refrigerator and maintained at 5°C±1. All necessary tubing and wiring was plumbed through an insulated port located on the refrigerator side wall. The stirrer unit and pressure vessel apparatus was located on a laboratory bench and maintained at 23°C±1 for tests performed at ambient temperature. The stirrer unit was activated and the vessel slowly pressurized to the designated test pressure and allowed to equilibrate for approximately 15 minutes. The contents of sampling tube were pre-drained to remove any water trapped within the tube. A 30 ml volume of synthetic seawater was collected from each test and placed in a 150-ml seperatory funnel. Liquid/liquid solvent extraction of the sample was performed three (3) times with 5 ml of DCM for each extraction. The extracts were collected in a 25-ml graduated cylinder and the final volume adjusted to 20 ml with DCM. The 20 ml sample extract was transferred to a 40-ml vial with a Teflon-lined enclosure. Approximately 1-2 g of anhydrous sodium sulfate (drying agent) was added to each vial to remove water within the DCM extract. The final extract vials were stored at 5°C until time of analysis. South Louisiana and North Slope crude oil fluorescence concentrations were determined by the Aqualog benchtop spectrofluorometer using an excitation wavelength of 290 nm and an emission wavelength of 360 nm. Hondo crude oil fluorescence concentration was determined using an excitation wavelength of 290 nm and an emission wavelength of 390 nm. Oil concentrations were calculated using the 5-point fluorescence standard calibration curve for the individual oils (Figure A1).

Results & Discussion: Pressure Vessel Study

The results for the experimental design are displayed in Fig. 11, which show the percent effectiveness at various pressures, temperatures, and DOR for all three oils. The averaged results for the high-pressure vessel experiments are displayed in Tables A9 and A10. To better understand the significance of the analytical results, statistical analyses of the experimental data were performed individually for the three oils. The results of the design experiments were analyzed using a factorial analysis of variance (ANOVA) at $\alpha = 0.05$ to determine which factors affect percent effectiveness. A significant interaction means that the effect of one independent variable varies at differing levels of another independent variable. The condition for significance was determined by statistical analysis was that the *p*–value should be less than 0.05 for a factor to be significant. Although this experiment was designed to determine if a significant difference exist between the two pressures, interactions between the other environmental factors (e.g. temperature, energy, and DOR) were examined.

The results showed that two factors (temperature and DOR) significantly affected the dispersant effectiveness in SLC ($p < 0.005$). Fig. 11 illustrates that two of the three factors (temperature, pressure, and DOR) produced significant change in the percent effectiveness values, thus, temperature and DOR were deemed significant. Results from the statistical analysis indicated there was no significant effect from changes in pressure ($p = 0.235$). The statistical analysis determined there was a significant two-way interaction between temperature and DOR ($p = 0.001$), but no two-way significant interaction with the pressure vs. temperature and pressure vs. DOR interactions ($p = 0.163$ and 0.307, respectively). A Tukey Post Hoc test indicated there was no significant difference between the DOR 1:20 and 1:50 treatments ($p = 0.065$). For NSC, two of the three factors (temperature and DOR) were found to significantly affect the dispersant effectiveness ($p < 0.005$). Fig. 11 shows that two factors (temperature and DOR) produced significant change in the percent effectiveness values, thus, all these factors were deemed significant. Results from the statistical analysis indicated there was no significant effect from changes in pressure ($p = 0.864$). The statistical analysis determined there was a significant two-way interaction between temperature and DOR ($p = 0.007$), but no two-way significant interaction with the pressure vs. temperature and pressure vs. DOR interactions (p = 0.891 and 0.886, respectively). A Tukey Post Hoc test indicated there was no significant difference between the control and three dispersant treatments ($p < 0.018$). For HC, two of the three factors (temperature and DOR) were found to significantly affect the dispersant effectiveness ($p < 0.005$). Fig. 11 shows that two factors (temperature and DOR) produced significant change in the percent effectiveness values, thus, all these factors were deemed significant. Results from the statistical analysis indicated there was no significant effect from changes in pressure ($p = 0.323$). The statistical analysis determined there was no significant two-way interaction between pressure vs. temperature, pressure vs. DOR, and temperature vs. DOR ($p = 0.897$, $p = 0.929$, and $p = 0.430$, respectively). A Tukey Post Hoc test indicated there was no significant difference between the control and three dispersant treatments ($p < 0.004$).

Dispersant effectiveness of oil by chemical dispersants is driven by a range of physical and environmental variables and includes: type of oil, degree of weathering, type of dispersant used, mixing energy, and sea water temperature. One of the most important physical properties of oil is its viscosity, which is a critical parameter influencing the chemical dispersion of oil at various sea temperatures. A number of correlations for the estimation of oil viscosity based on measured fluid properties have been formulated, but all indicate viscosity is inversely proportional to temperature.

Figure 11 shows that as temperature increases from 5°C to 23°C, dispersion efficacy increased 15.8%, 22.0%, and 12.4% for South Louisiana, North Slope, and Hondo crude oils, respectively. This trend in dispersant effectiveness with an increase in the sea water temperature has been observed in previous dispersant studies designed to investigate the effects of temperature on various oil and dispersant properties such as density, viscosity, and surface tension [11]. These studies have shown there is a clear inverse correlation between dispersant effectiveness and temperature at the experiment temperature range (5°C to 23°C).

The effect of DOR on dispersant effectiveness is observed by examining Figure 11. Generally, as the DOR in the oil increases, dispersant effectiveness increases. For example, with unweathered SLC with DOR = 1:20 at 2000 psi and 5°C, the average dispersant effectiveness was 48.9%, whereas the DOR = 1:50 and 1:100 averaged 45.6% and 36.8% at the same conditions, respectively. Similarly, for unweathered NSC with DOR = 1:20 at 2000 psi and 5°C, the average dispersant effectiveness was 44.7%, whereas the DOR = 1:50 and 1:100 averaged 38.5% and 36.2% at the same conditions, respectively. Again, for unweathered HC with DOR = 1:20 at 2000 psi and 5°C, the average dispersant effectiveness was 13.9%, whereas the DOR = 1:50 and 1:100 averaged 12.4% and 8.37% at the same conditions, respectively.

Figure 11 shows the results obtained for oil and oil + dispersant combinations at 32 ppt salinity at various pressures. From this figure, it is seen that for a given oil at a specified temperature or DOR, as the pressure of the system increases, no significant change in dispersant effectiveness was observed. For example, for unweathered SLC (5°C and DOR = 1:20) at 200 psi, the average dispersant effectiveness was 48.3%, whereas at 2000 psi the average effectiveness was 48.9%. In the case of NSC, unweathered oil (5°C and DOR = 1:20) at 200 psi, the average dispersant effectiveness was 45.1%, whereas at 2000 psi the average effectiveness was 44.7%. With HC, the increase in pressure from 200 to 2000 psi did not produce a significant change in dispersant effectiveness (14.5% and 13.9%, respectively). The lack of change in dispersant effectiveness at different pressures can be explained by the mechanisms involved with the chemical dispersion of oil. In order for dispersion to occur, sufficient mixing energy must be provided to deform the oil, deform the water, and create new surface area for the oil. For low viscosity oils most of the mixing energy is consumed generating new surface area for the oil. For higher viscosity oils the majority of the mixing energy will be consumed in deformation of the oil, which means that less energy will be available to stimulate formation of new surface area that results in dispersed oil droplets. Oil viscosity, like many other physical property, is affected by both temperature and pressure. A decrease in pressure causes a decrease in viscosity, provided that the only effect of pressure is to compress the liquid. The reason is that non-Newtonian oils and liquids are almost non-compressible at low or medium pressures. For most liquids, a considerable change in pressure from 0.1 to 30 MPa causes approximately +10% in viscosity, or about the same changes in viscosity as a temperature change of about 1°C.

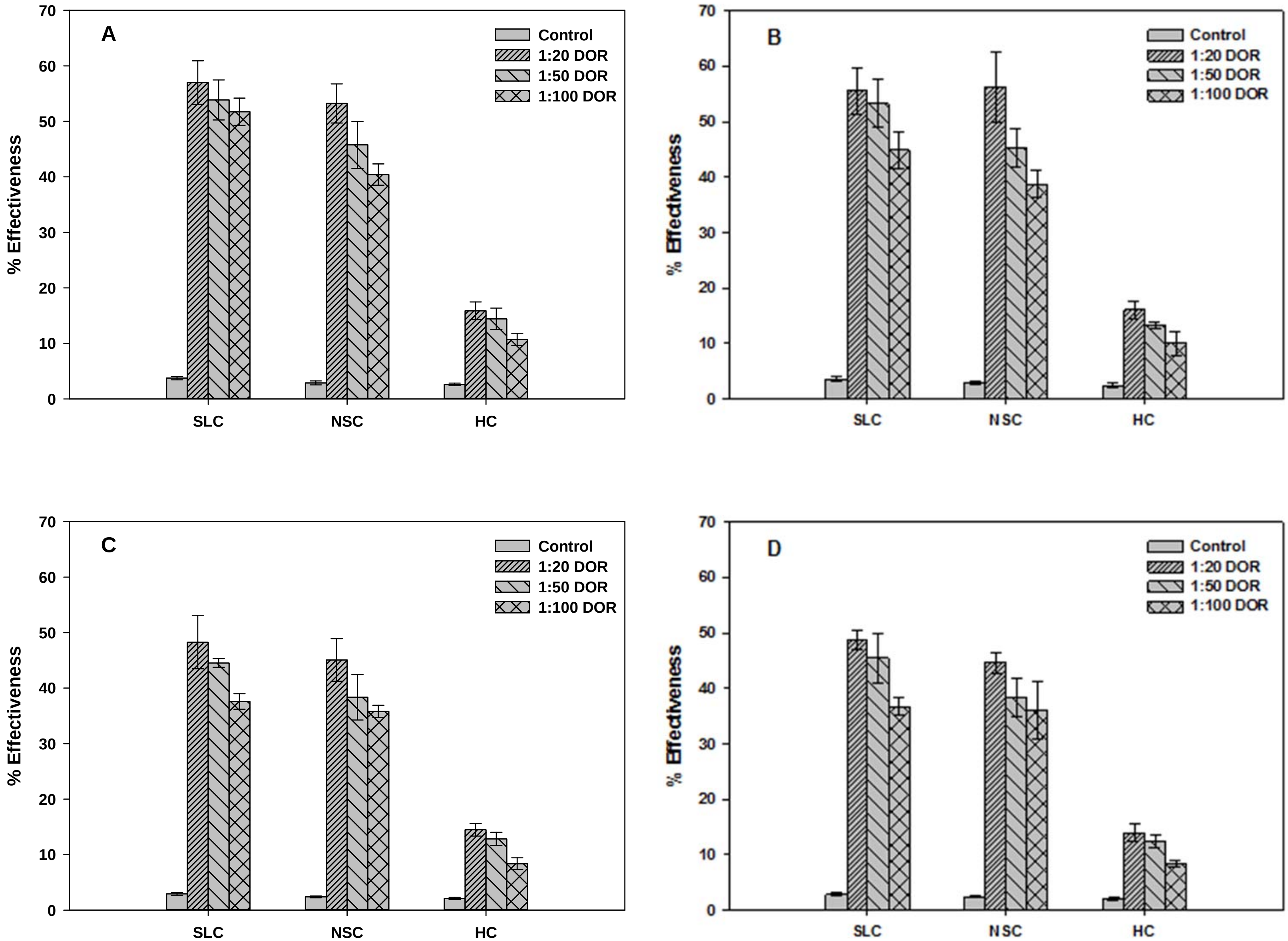

Figure 11. Average percent effectiveness for South Louisiana, North Slope, and Hondo crude baffled flask study at 23°C and 200 psi (A), 23°C and 2000 psi (B), 5°C and 200 psi (C), and 5°C and 2000 psi (D).

Task #3: 1-L Baffled Flask Test Study

A series of large bench-scale laboratory studies were performed to determine dispersant efficiency and usage rates for various environmental conditions using a 1-L baffled-flask to evaluate three specific oils. The objective of this study was to develop a standardized method and protocol to estimate the real-time effectiveness of dispersants using common laboratory glassware and an in-situ fluorescence probe. The field-portable testing "kit" will allow oil spill responders to determine if a specific oil is "dispersable" prior to actual full-scale operations. In addition to testing the fluorescence probe, a portable turbidimeter was utilized for comparison to the laboratory-based and portable fluorescence probe dispersant effectiveness results. Three (3) individual replicate tests for each oil were used in the protocol (3 replicates × 2 temperatures × 4 DORs × 2 mixing energies × 3 oils × 2 weathering states) for a total of 288 tests. In addition, a continuing calibration standard and method blank were extracted prior to the daily analysis of water samples on the spectrofluorometer. The three oils (SLC, ANC, and HC) were evaluated using the following factors: temperature (5°C and 23°C), DOR (0, 1:20, 1:50, and 1:100), mixing energy (150 rpm and 200 rpm), and weathering state (fresh and 15% weathered). Corexit 9500A was used throughout the 1-L BFT procedure and the salinity was maintained at 32 ‰. For the tests performed at 5°C, the shaker unit was housed in a large volume refrigerator and maintained at 5°C±1. All necessary tubing and wiring were plumbed through an insulated port located on the refrigerator side wall. The shaker unit and pressure vessel apparatus were located on a laboratory bench and maintained at 23°C±1 for tests performed at ambient temperature.

The 1-L BFT test utilizes a 1-L open trypsinizing flask that has been modified with the addition of a glass stopcock near the bottom so that a subsurface water sample can be removed without disturbing the surface oil layer. A 600 ml volume of synthetic water is added, followed by the addition of a 500 μl aliquot of oil and an appropriate volume of Corexit 9500A to achieve the desired DOR. The oil to water ratio used in the 1-L BFT is equivalent to the oil to water ratio employed in the 150-ml standardized BFT. The cylindrical stainless steel probe is 6” in length and 1” in diameter. This device is the same fluorescence probe that is currently installed on the larger Turner Designs C3 fluorometer unit used by the USCG for in situ monitor of oil spills during full-scale dispersant operations. The flask is placed on a small digital orbital shaker (11” × 13”) to receive low (non-breaking waves) and moderate (breaking waves) turbulent mixing at 150 and 200 rpm, respectively, for 10 ± 0.25 min. The shaker table has a speed control unit with variable speed (40–400 rpm) and an orbital diameter of approximately 0.75 in. (1.9 cm) is used to impart turbulence to solutions in the test flasks. The rotational speed accuracy should be within ±10%. The contents of the flasks are allowed to settle for 10 ± 0.25 min to allow non-dispersed oil to return to the water surface before removing the subsurface water sample. Prior to collecting sample from the 1-L baffled flask, a 10-15 ml aliquot of water is wasted from the stopcock drain in order to remove any residual oil trapped within the drain stem. Each replicate is run individually by the same analyst so that identical test conditions can be maintained for each replicate.

For the fluorescence probe and turbidity determinations, a 200-ml volume of sample was slowly drained into a calibrated 300 ml glass jar. The Cyclops-7 probe was inserted into the samples and held approximately 2” below the water surface. The probe was swirled slowly to remove any air bubbles trapped beneath the probe tip. The fluorescence probe was activated and fluorescence measurements were recorded for approximately 30-35 seconds at a scan rate of 1 scan per second. The fluorescence response (mv) was averaged and recorded. The linear response range for the Cyclops-7 field probe was determined to be 60-1500 mv, 60-500 mv, and

60-250 mv for SLC, NSC, and HC, respectively. The baseline response for artificial seawater averaged 12 mv throughout the experiment. If the sample response exceeded the linear range for that specific oil, the sample was diluted until the response reached 40-60% of the maximum linear response for that oil. Field probe and turbidimeter calibration curves were constructed for each unweathered oil by performing a 1-L BFT at 23°C, DOR = 1:20, and 150 rpm. This combination of parameters (0% weathering, 23°C, DOR = 1:20, and 150 rpm) was designate as the baseline condition for predicting percent dispersant effectiveness. These parameters were chosen because they represented the conditions that are considered optimal for the safe application of chemical dispersants during field operations. Field probe and turbidimeter responses were measured at seven (7) levels (undiluted and 2x, 4x, 8x, 16x, 32x, and 64x dilution) using serial dilutions and corresponding water samples extracted to determine oil concentration by laboratory-based fluorescence. The percent oil dispersed was determined using the calculations presented in the analysis of sample extracts section of this document. A 5-point calibration curve for each oil was then constructed by plotting the percent effectiveness versus the field probe or turbidimeter response within their respective linear range. The 5-point field probe and turbidimeter calibration curves with 95% confidence levels for each oil is shown in Figures A3 and A4, respectively.

The percent dispersant effectiveness for each oil and treatment was determined by the linear regression equations found in Figure A3. A 10-ml turbidity and 30-ml laboratory fluorescence analysis subsample was immediately taken from the calibrated 300-ml glass jar. The 10 ml turbidity sample was collected in a 15-ml vial and immediately measured using a tungsten white light source and detector spectral peak response between 400nm and 600nm. The linear response range for the turbidimeter was factory calibrated to 0.1-1000 NTU. If the sample response was greater than the upper limit, a dilution was made until response was within the linear range. The percent dispersant effectiveness for each oil and treatment was determined by the linear regression equations found in Figure A4.

For the laboratory-based benchtop fluorescence analysis, a 30 ml volume of synthetic seawater was collected from each test and placed in a 150-ml seperatory funnel. Liquid/liquid solvent extraction of the sample was performed three (3) times with 5 ml of DCM for each extraction. The extracts were collected in a 25-ml graduated cylinder and the final volume adjusted to 20 ml with DCM. The 20 ml sample extract was transferred to a 40-ml vial with a Teflon-lined enclosure. Approximately 1-2 g of anhydrous sodium sulfate (drying agent) was added to each vial to remove water within the DCM extract. The final extract vials were stored at 5°C until time of analysis. The oil concentration in the DCM was measured by the Aqualog benchtop spectrofluorometer, simultaneously measuring UV-VIS absorbance and fluorescence excitation/emission wavelengths. UV-VIS absorbance measurements were not recorded for the 1-L Baffled flask experiment. South Louisiana and North Slope crude oil fluorescence concentrations were determined using an excitation wavelength of 290 nm and an emission wavelength of 360 nm. Hondo crude oil fluorescence concentration was determined using an excitation wavelength of 290 nm and an emission wavelength of 390 nm. Oil concentrations were calculated using the 5-point fluorescence standard calibration curve for the individual oils (Figure A1).

Results & Discussion: 1-L Baffled Flask Tests

The results for the experimental design are displayed in Figs. 12-17 and tables A11-A22, which show the percent effectiveness from the analytical devices “laboratory”, “field probe”, and “turbidimeter” at various flask speeds, temperatures, weathering state, and DOR for all three oils. To better understand the significance of the analytical results, statistical analyses of the experimental data were performed individually for the three oils. The results of the design experiments were analyzed using a factorial analysis of variance (ANOVA) at $\alpha = 0.05$ to determine which factors affect percent effectiveness. A significant interaction means that the effect of one independent variable varies at differing levels of another independent variable. The condition for significance was determined by statistical analysis was that the *p*–value should be less than 0.05 for a factor to be significant. This experiment was designed to determine if a significant difference exist between the three analytical devices, so no interactions between other environmental factors (e.g. temperature, weathering, energy, and DOR) were examined.

A preliminary ANOVA statistical analysis showed there was an overall significant difference when comparing the “laboratory”, “field probe”, and “turbidimeter” percent effectiveness results ($p < 0.0005$) for all three oils. Tukey post hoc tests showed there was no significance interaction between the laboratory-based fluorescence and field probe percent effectiveness results for South Louisiana, North Slope, and Hondo crude oils ($p = 0.368$, $p = 0.743$, and $p = 0.689$, respectively). The Tukey post hoc tests indicated the overall significant interaction between the instrument’s responses occurred between the laboratory-based fluorescence and turbidimeter ($p < 0.02$) and the field probe and turbidimeter ($p < 0.002$). Due to the significant differences between the turbidimeter results and the laboratory-based fluorescence results, the investigators determined turbidity was not a valid parameter for estimating dispersant effectiveness during field operations. A second ANOVA was performed, without the turbidimeter results, to confirm the correlation between the laboratory-based fluorescence analysis and the field probe analysis. Again, the ANOVA tests showed there was no significance mean difference between the laboratory-based fluorescence and field probe percent effectiveness results for South Louisiana, North Slope, and Hondo crude oils ($p = 0.757$, $p = 0.582$, and $p = 0.265$, respectively).

A statistical comparison of the two analytical instruments (laboratory-based fluorescence and field probe fluorescence) indicated there was no significant difference in the results from either instrument. The investigators' objective for this experiment was to develop an in-situ method for predicting the percent effectiveness of chemical dispersants in field conditions and be comparable to laboratory-based fluorescence results. The experiment clearly showed the 1-L BFT was capable of producing percent effectiveness results comparable to laboratory results. In order to use the existing oil calibration curves and estimated percent effectiveness equations in the field, investigators had to formulate a correction factor (CF) to compensate for the different variables (e.g. water temperature, weathering, and sea state) encountered during actual dispersant operations. The correction factor was created by normalizing the average percent effectiveness at the specific oil's baseline condition (0% weathering, 23°C, DOR = 1:20, and 150 rpm). For example, the average percent effectiveness for unweathered SLC at 23°C and 200 rpm (breaking waves) and SLC's baseline condition were 79.2% and 63.2%, respectively. The CF for unweathered SLC at 23°C and 200 rpm was calculated by dividing the field condition percent effectiveness by the baseline condition percent effectiveness (79.2/63.2 = 1.25). The CF for all oils and field conditions are displayed in Table 2.

Table 2. Correction factors for oils and field conditions.

Oil Name	Temperature (°C)	Weathering (%)	Sea State[a]	Correction Factor (CF)
South Louisiana Crude	5	0	non-breaking	0.844
South Louisiana Crude	5	10	non-breaking	0.626
South Louisiana Crude	5	0	breaking	1.13
South Louisiana Crude	5	10	breaking	1.15
South Louisiana Crude[b]	**23**	**0**	**non-breaking**	**1.00**
South Louisiana Crude	23	10	non-breaking	0.719
South Louisiana Crude	23	0	breaking	1.25
South Louisiana Crude	23	10	breaking	1.13
North Slope Crude	5	0	non-breaking	1.09
North Slope Crude	5	10	non-breaking	0.929
North Slope Crude	5	0	breaking	1.42
North Slope Crude	5	10	breaking	1.28
North Slope Crude[b]	**23**	**0**	**non-breaking**	**1.00**
North Slope Crude	23	10	non-breaking	1.14
North Slope Crude	23	0	breaking	1.49
North Slope Crude	23	10	breaking	1.41
Hondo Crude	5	0	non-breaking	0.965
Hondo Crude	5	10	non-breaking	0.907
Hondo Crude	5	0	breaking	1.11
Hondo Crude	5	10	breaking	0.884
Hondo Crude[b]	**23**	**0**	**non-breaking**	**1.00**
Hondo Crude	23	10	non-breaking	0.956
Hondo Crude	23	0	breaking	1.41
Hondo Crude	23	10	breaking	1.19

[a] non-breaking (1-4' seas), breaking (4-8' seas)

[b] Baseline condition for estimating % dispersant effectiveness

In the field, a responder would have to collect an oil sample from a vessel, transport the sample back to a nearby vessel or facility, and perform a 1-L BFT (at baseline conditions) to determine the percent dispersant effectiveness of Corexit 9500 on that specific oil. The field probe response would then be inputted into the baseline condition equation and multiplied with the field CF and dilution factor (DF) to compute the predicted percent effectiveness. The predicted dispersant effectiveness equations formulated in this study were developed exclusively for South Louisiana, North Slope, and Hondo crude oils. In order to predict the dispersant effectiveness of other oils, laboratory and field instrument calibration curves and dispersant effectiveness equations must be determined prior to use. The predicted dispersant effectiveness equations for South Louisiana, North Slope, and Hondo crude oils are displayed in Table 3.

Table 3. Predicted dispersant effectiveness equation for South Louisiana, North Slope, and Hondo crude oils at baseline conditions

Oil Type	1-L BFT condition	Predicted dispersant effectiveness equation
South Louisiana Crude	0% weathering, 23°C, DOR = 1:20, and 150 rpm	% Effectiveness = (DF)(CF)(0.0118)(Probe Response)
North Slope Crude	0% weathering, 23°C, DOR = 1:20, and 150 rpm	% Effectiveness = (DF)(CF)(0.0364)(Probe Response)
Hondo Crude	0% weathering, 23°C, DOR = 1:20, and 150 rpm	% Effectiveness = (DF)(CF)(0.2017)(Probe Response)

For example, a large oil tanker and freighter have collided in the Bering Sea and the tanker has the potential to sink. The tanker is carrying an unknown amount of North Slope crude oil and the water temperature is approximately 5°C. The waves are currently non-breaking at 3-4 feet. A responder would sample the oil and transport it to a nearby response vessel for 1-L baffled flask testing. At baseline conditions (0% weathering, 23°C, DOR = 1:20, and 150 rpm), the field probe's response was 185 mv with an 8-fold dilution. The predicted dispersant effectiveness would be calculated:

$$\% \text{ Effectiveness} = (8)\ (1.09)\ (0.0364)\ (185) = 58.7\%$$

To test the predictability of our method and equation, a random group (n=10) of simulated 1-L BFTs were performed at various environmental conditions (water temperature, mixing energy, and weathering state) for each experimental oil (SLC, NSC, and HC). The observed or predicted percent effectiveness was measured with the field probe and the actual percent effectiveness was measured using the liquid-liquid extraction methods and laboratory-based fluorescence analysis. A linear regression analysis was performed on the results from the laboratory and field measurements and plotted on a graph. The 95% prediction interval for each oil was then determined for each oil. Prediction intervals tell you where you can expect to see the next data point sampled, assuming the data is randomly sampled from a Gaussian distribution. The key point is that the prediction interval tells you about the distribution of values, not the uncertainty in determining the population mean. Prediction intervals are always greater than a confidence interval. The 95% prediction interval for South Louisiana, North Slope, and Hondo crude oil were ±7.59%, ±6.52%, and ±9.48% dispersant effectiveness, respectively. Using Hondo crude oil as an example, we can be 95% confident that this range (±9.48%) includes the predicted percent dispersant effectiveness obtained while using the linear regression equation and percent effectiveness calculation.

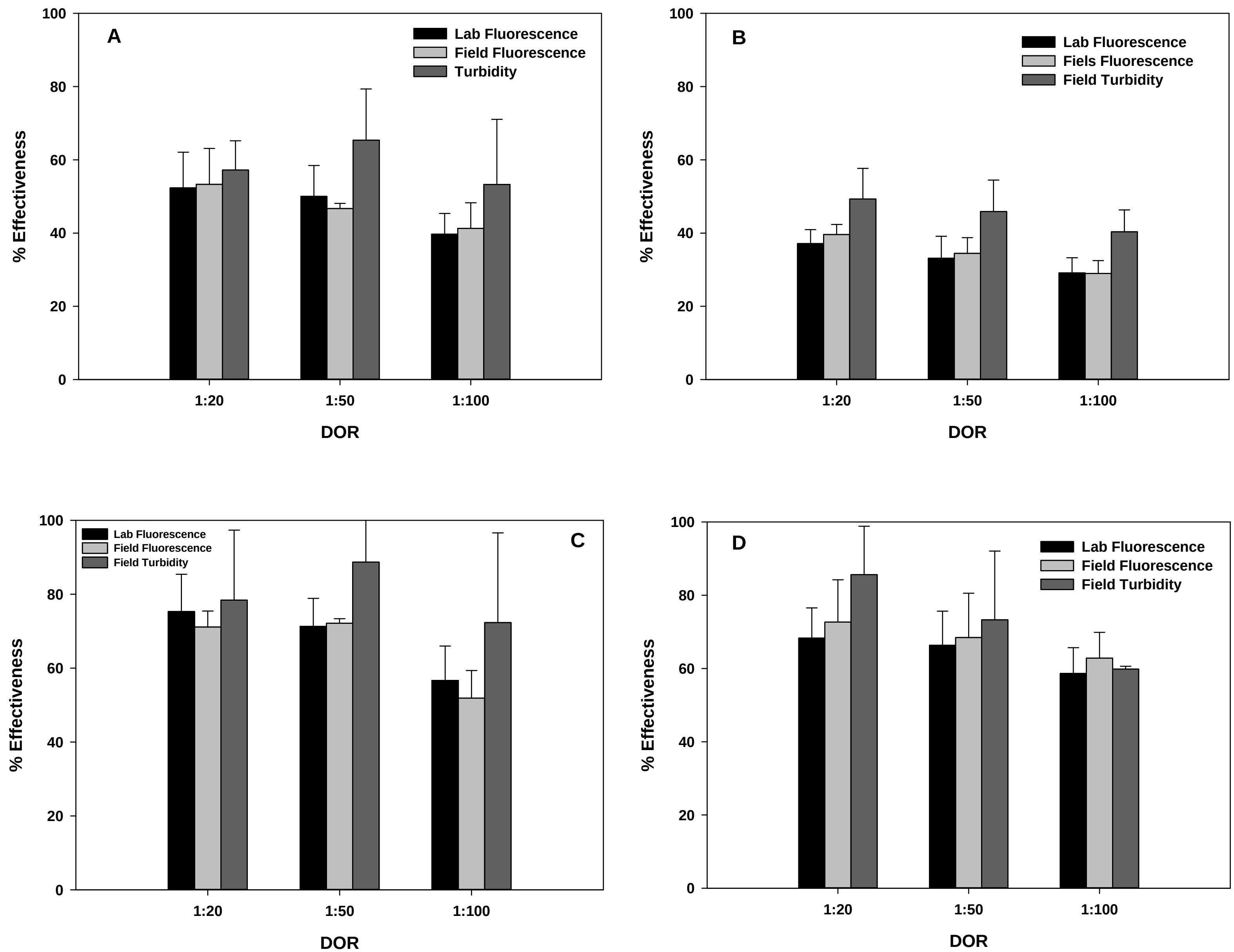

Figure 12. Average percent effectiveness for South Louisiana crude baffled flask study at 5°C with 150 rpm and 0% weathering (A), 150 rpm and 10% weathering (B), 200 rpm and 0% weathering (C), and 200 rpm and 10% weathering (D).

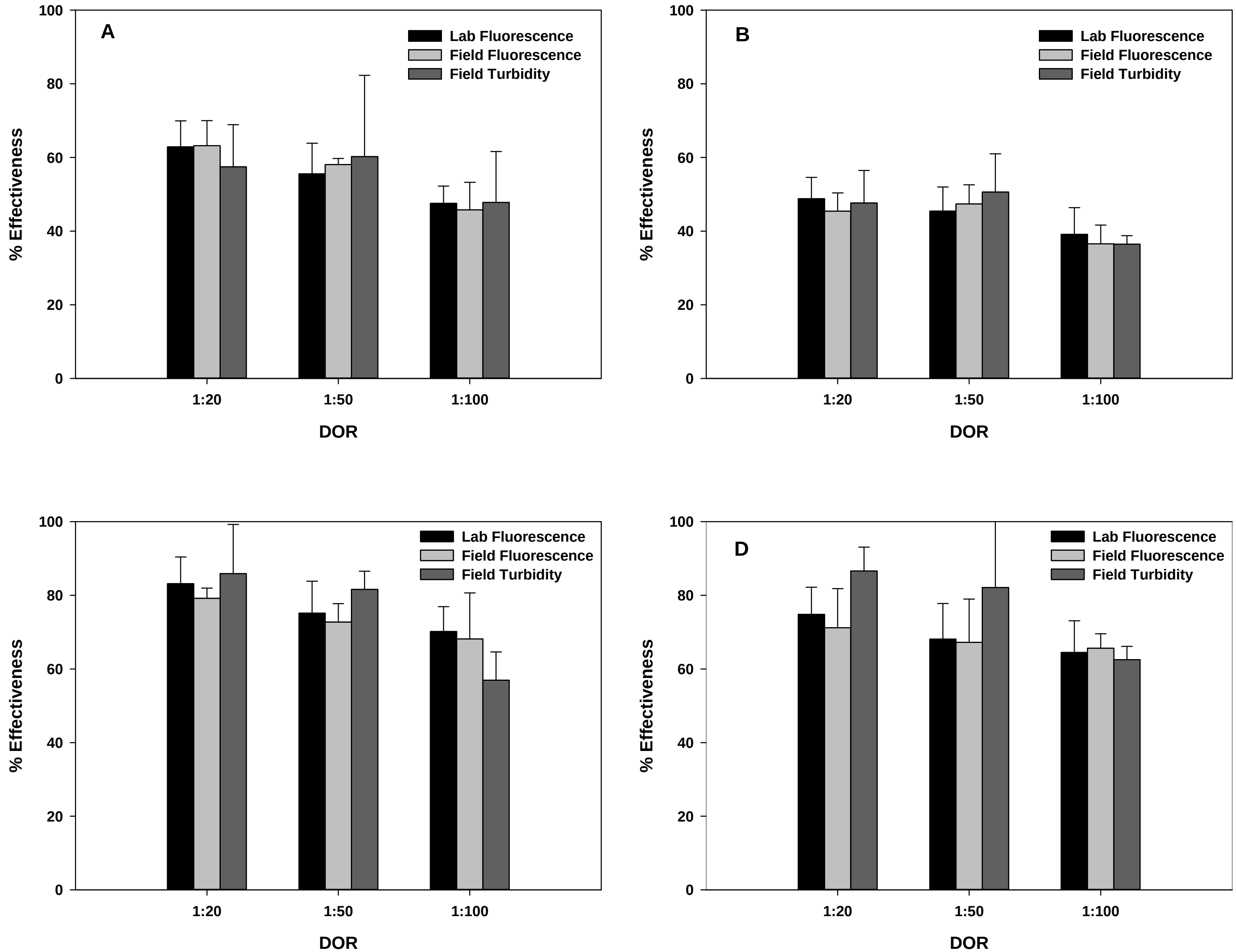

Figure 13. Average percent effectiveness for South Louisiana crude baffled flask study at 23°C with 150 rpm and 0% weathering (A), 150 rpm and 10% weathering (B), 200 rpm and 0% weathering (C), and 200 rpm and 10% weathering (D).

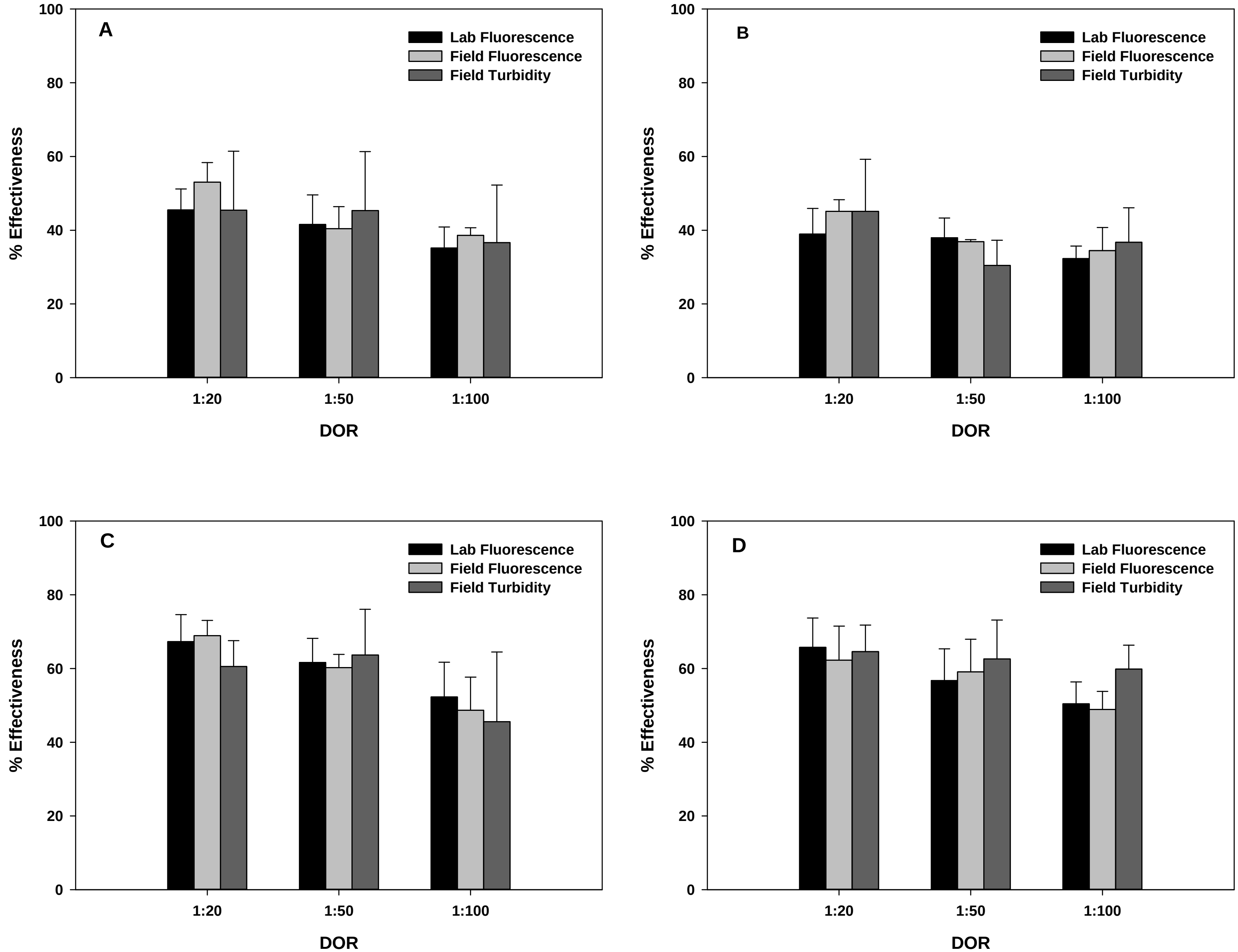

Figure 14. Average percent effectiveness for North Slope crude baffled flask study at 5°C with 150 rpm and 0% weathering (A), 150 rpm and 10% weathering (B), 200 rpm and 0% weathering (C), and 200 rpm and 10% weathering (D).

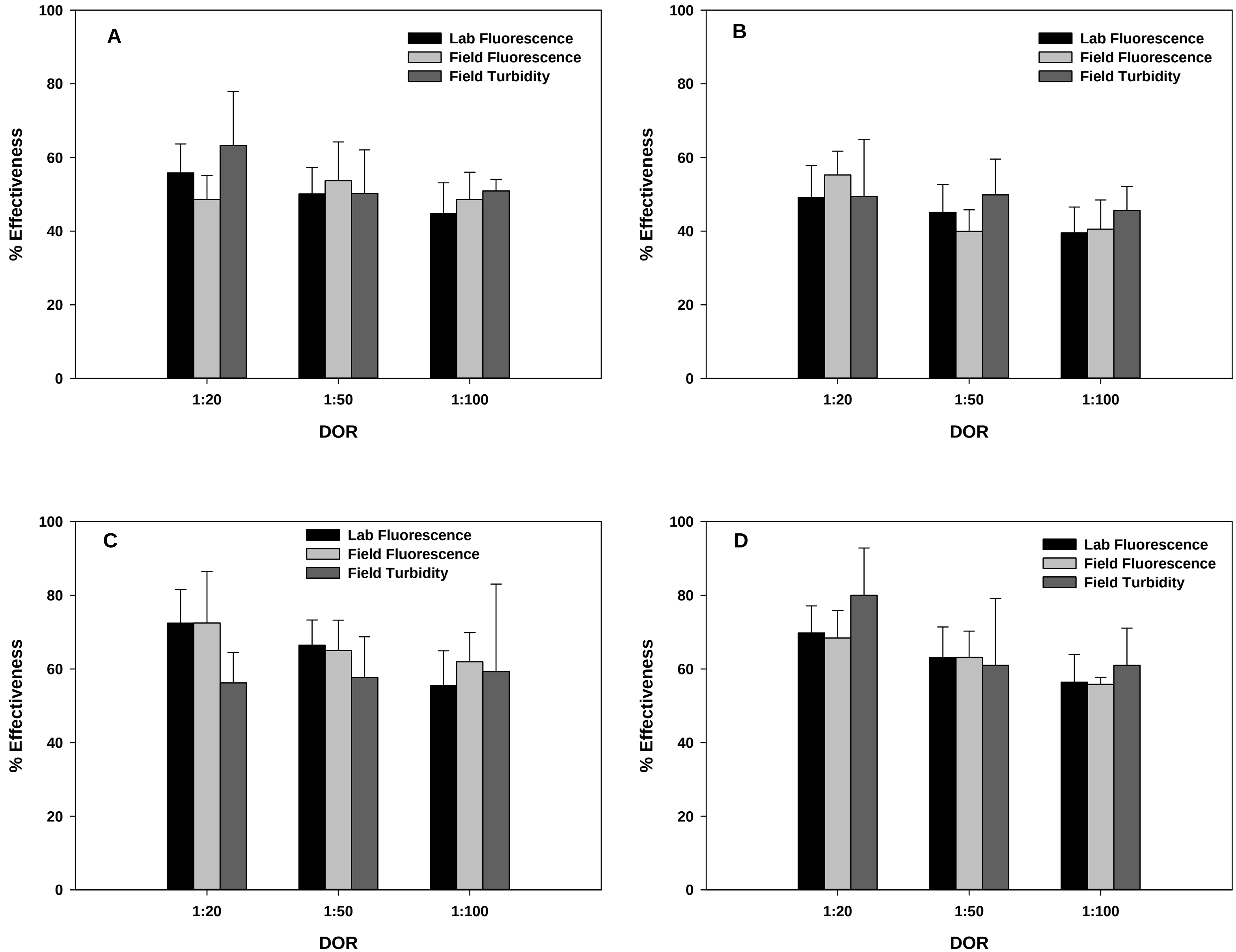

Figure 15. Average percent effectiveness for North Slope crude baffled flask study at 23°C with 150 rpm and 0% weathering (A), 150 rpm and 10% weathering (B), 200 rpm and 0% weathering (C), and 200 rpm and 10% weathering (D).

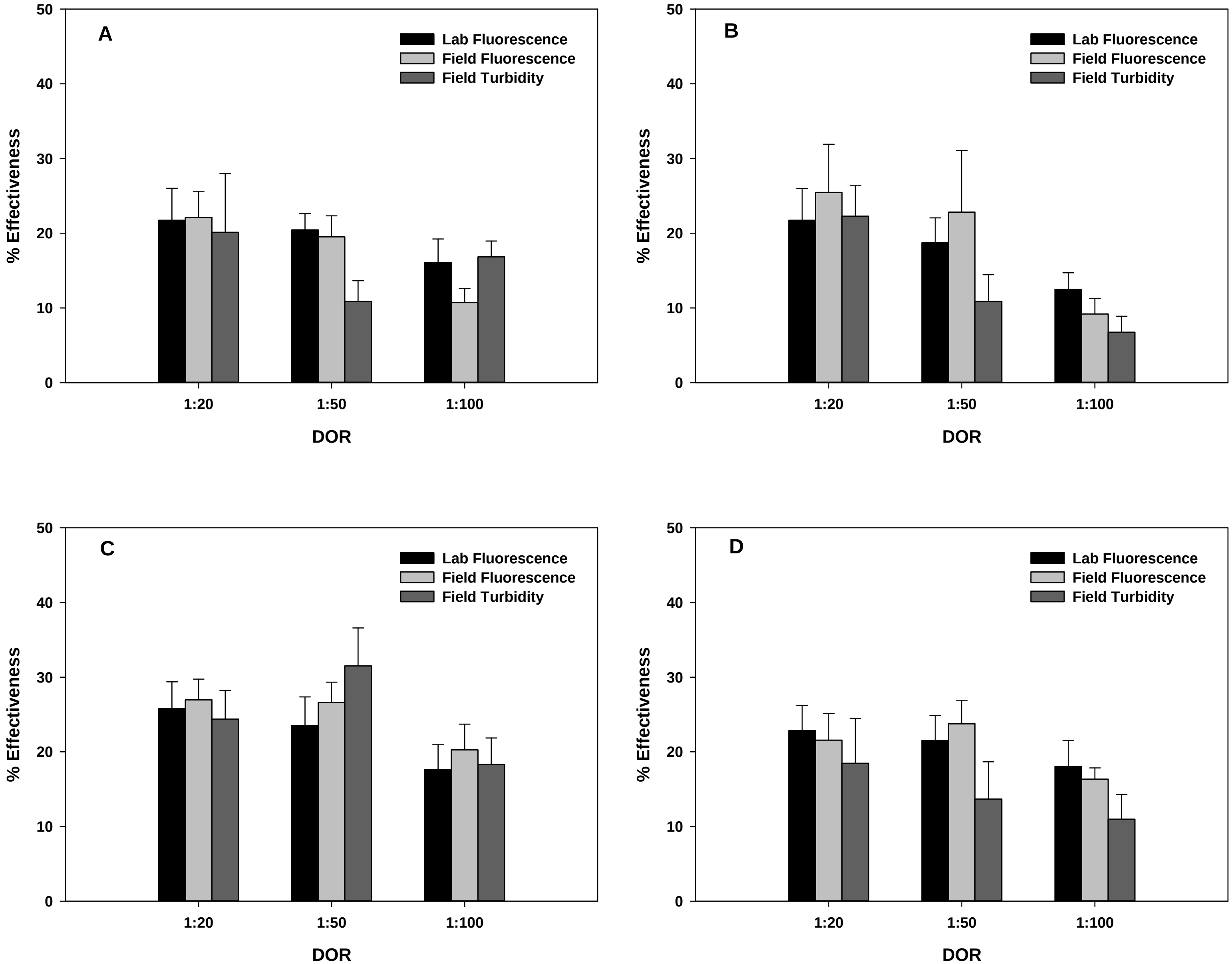

Figure 16. Average percent effectiveness for Hondo crude baffled flask study at 5°C with 150 rpm and 0% weathering (A), 150 rpm and 10% weathering (B), 200 rpm and 0% weathering (C), and 200 rpm and 10% weathering (D).

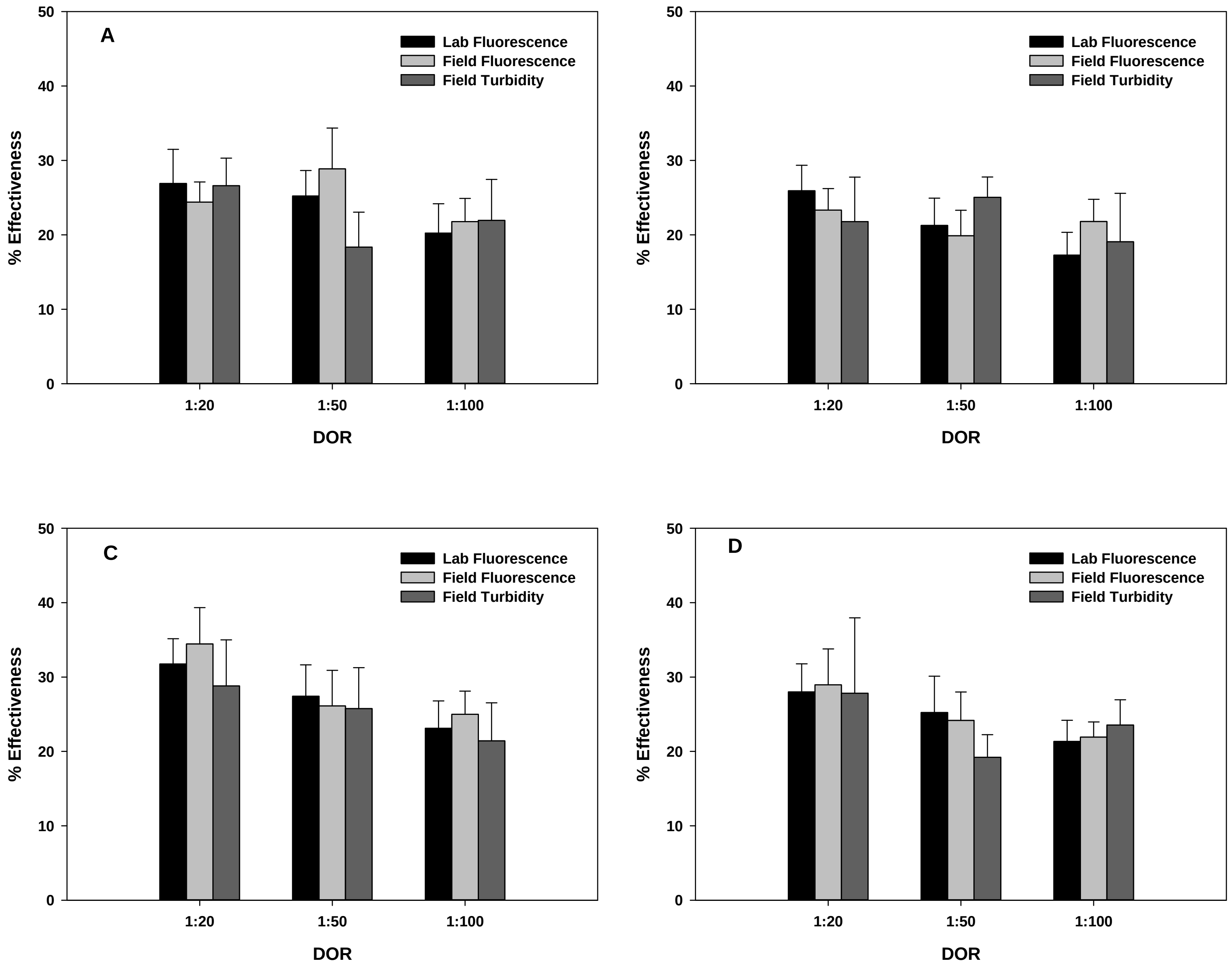

Figure 17. Average percent effectiveness for Hondo crude baffled flask study at 23°C with 150 rpm and 0% weathering (A), 150 rpm and 10% weathering (B), 200 rpm and 0% weathering (C), and 200 rpm and 10% weathering (D).

Task #4: 1-Day Dispersant Workshop

The investigators developed and organized a 1-day dispersant workshop at NOAA's Gulf of Mexico Disaster Response Center (GMDRC) located in Mobile, Alabama. The workshop was held on January 7, 2016. The objective of the workshop was to allow participants to review and evaluate project results, then make recommendations concerning dispersant strategy planning to predict the efficacy of dispersant application during oil spill cleanup operations. A total of 19 United States Coast Guard (USCG) Gulf Strike Team (GST) members and NOAA representatives were in attendance at the GMDRC in Mobile, AL. A total of 18 Bureau of Safety and Environmental Enforcement (BSEE) and National Oceanic and Atmospheric Administration (NOAA) personnel participated via WebEx. A list of personnel attending the 1-day workshop is displayed in table 4. A PowerPoint presentation was given at the start of the workshop outlining and highlight results from the BSEE project. The participants reviewed the completed project and commented if the portable 1-L BFT would be a valuable tool for enhancing the SMART protocol and oil spill responder capabilities. Following the PowerPoint presentation, the investigators gave USCG GST personnel in attendance an opportunity to participate in a hands-on 1-L BFT exercise. WebEx participants were allowed to follow the activity via WebEx cam. LSU personnel walked the attendees through 1-L BFT setup and analysis of actual South Louisiana crude oil. USCG attendees took readings with the Cyclops-7 field probe and made necessary calculations to determine percent dispersant effectiveness. The percent effectiveness was calculated to be 67.3%, which is 6.9% greater than laboratory-based results at the same environmental conditions.

Table 4. List of Personnel Attending the 1-Day Dispersant Workshop

	Name	Affiliation	Location
1	CDR Kevin Lynn	USCG	GMDRC
2	LCDR Tedd Hutley	USCG	GMDRC
3	LCDR Murphy	USCG	GMDRC
4	CWO Beltran	USCG	GMDRC
5	LTJG Gabriel Klaff	USCG	GMDRC
6	CWO Estrada	USCG	GMDRC
7	CWO Hinsch	USCG	GMDRC
8	PO1 Chris Wilborn	USCG	GMDRC
9	PO1 Jeff Medlin	USCG	GMDRC
10	LT Steve Ober	USCG	GMDRC
11	LT Ron Campbell	USCG	GMDRC
12	Chief Sheridan McClellan	USCG	GMDRC
13	BM1 Kenny Tucker	USCG	GMDRC
14	LT Jim Litzinger	USCG	GMDRC
15	CPO Clifford Brack	USCG	GMDRC
16	Six (6) attendees from USCG Chemical Division & Chem Shop	USCG	GMDRC
17	LTJG Steve Wall	NOAA	GMDRC
18	Mr. Adam Davis	NOAA	GMDRC
19	Mr. Timothy Steffek	BSEE	Sterling, VA
20	Dr. Jim Farr	NOAA	Seattle, WA
21	Dr. Robert Jones	NOAA	Seattle, WA
22	Ms. Catherine Berg	NOAA	Anchorage, AK
23	Dr. Alan Mearns	NOAA	Seattle, WA
24	Mr. John Tarpley	NOAA	Seattle, WA
25	Mr. Scott Lundgren	NOAA	Silver Springs, MD
26	Mr. Steve Lehmann	NOAA	Boston, MA
27	Dr. Paige Doelling	NOAA	Houston, TX
28	Mr. Ed Levine	NOAA	New York, NY
29	Mr. Gary Shigenaka	NOAA	Seattle, WA
30	Ms. Ruth Yender	NOAA	Seattle, WA
31	Mr. Jordan Stout	NOAA	Alameda, CA
32	Mr. Brad Benggio	NOAA	Miami, FL
33	Mr. Doug Helton	NOAA	Seattle, WA
34	Mr. Frank Csulak	NOAA	Highlands, NJ
35	Lt. Greg Scheitzer	NOAA	Clevland, OH
36	LTJG Rachel Pryor	NOAA	Seattle, WA
37	Dr. Scott Miles	LSU	GMDRC

GMDRC - Gulf of Mexico Damage Response center

The workshop participants also discussed and made recommendations concerning future research and method development. Recommendations and comments were recorded in the form of a survey. The following questions were included in the survey:

1. Would the 1-L Baffled Flask Kit be useful to oil spill responders?
2. Could the 1-L Baffled Flask Kit be incorporated into the SMART protocol?
3. Would you use this kit prior to an oil spill?
4. Ease of operations?
5. Is kit cost effective?
6. Additional comments?

Below are some of the comments received following the workshop:

“The presentation was great and after seeing it, I was somewhat intrigued but not quite sure if I could use it. But then watching you perform the field test and walk us through all of the steps and answering all of our questions just made it much more relatable. Watching the whole thing along with hearing the presentation provides a much better context for interpreting the results.”

“I think the kit would be very useful to responders if enough time were allowed prior to full-scale dispersant applications. It was a real plus to be able to predict effectiveness at different environmental conditions”

“This kit would be a good addition to our chem. shop. It is fairly inexpensive and seems easy to operate and make calculations”

“I would use this if I had it because I think it would provide a greater comfort level to the spill responders and the IMT in understanding the efficacy in real time. The field test and scale provides more information and a better understanding on the dispersability than just looking at the test jars”

“This kit could possibly be incorporated into the SMART protocol since it doesn’t require a lot of time to setup or sophisticated equipment/glassware to operate. Like that you take a single measurement and use one calculation to determine percent efficiency”

“Excited the method’s simplicity and ease of use during field operations, but would like to see field probe calibrated to different oils and temperatures. We see a lot more oils coming into the United States from South America and Canada that could be tested with this device”

SUMMARY OF KEY RESULTS AND RECOMMENDATIONS

A comparison of the results from the Aqualog spectrophotometer’s two analytical methods (fluorescence and UV-Vis) indicated there was no significant difference in the results from either method. The excellent correlation between results of the two analytical methods allow oil spill investigators to choose either method, depending on which is more available, without sacrificing reproducibility or accuracy. The UV-Vis method is somewhat more robust than the fluorescence method, being less sensitive and not requiring an unreasonable amount of dilutions.

The 1-L pressure vessel study results showed that temperature and DOR significantly affected the dispersant effectiveness in SLC, NSC, and HC under the test conditions. Results from the statistical analysis indicated there was no significant effect from changes in pressure for all three oils. The dispersant effectiveness results varied from 36.8% to 57.0% for SLC over the experimental temperature and pressure range. The dispersant effectiveness results varied from 35.8% to 56.4% for NSC over the experimental temperature and pressure range. The dispersant effectiveness results varied from 8.35% to 16.1% for HC over the experimental temperature and pressure range. The lack of change in dispersant effectiveness at different pressures can be explained by the mechanisms involved with the chemical dispersion of oil.

The 1-L baffled test study showed there was no significance mean difference between the laboratory-based fluorescence and field probe percent effectiveness results for South Louisiana, North Slope, and Hondo crude oils. The investigators' objective for this experiment was to develop an in-situ method for predicting the percent effectiveness of chemical dispersants in field conditions and be comparable to laboratory-based fluorescence results. The experiment clearly showed the 1-L BFT was capable of producing percent effectiveness results comparable to laboratory results. The 95% prediction interval for South Louisiana, North Slope, and Hondo crude oil were ±7.59%, ±6.52%, and ±9.48% dispersant effectiveness, respectively.

The 1-day workshop had a higher than expected turnout. The workshop was attended by 21 personnel from BSEE, NOAA, or the USCG GST via on-scene or WebEx. The hands-on 1-L BFT exercise was very successful and gave responders a good idea of the 1-L BFT's capabilities. The investigators received many positive comments from both the on-scene and WebEx participants. Many of the participants thought the 1-L BFT was a useful tool, but requested more oils be entered into the oil library.

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APPENDIX

Table A1. 150-ml Baffled Flask Percent Effectiveness Results (fluorescence) at 5°C and 150 rpm.

Oil	Weathering (%)	DOR	% Effectiveness of replicate samples R1	R2	R3	R4	R5	Average % Effectiveness	Standard Deviation	Coefficient of Variance
South LA Crude	0	0	4.9	4.7	3.8	3.6	5.3	4.5	0.7	16.0
		20	54.0	69.1	50.9	66.3	61.3	60.3	7.8	12.9
		50	56.7	49.4	63.9	45.4	52.8	53.6	7.1	13.2
		100	38.5	48.0	51.6	37.5	39.9	43.1	6.3	14.6
	10	0	3.5	2.7	3.8	3.8	3.3	3.4	0.5	13.4
		20	45.6	38.1	39.4	48.9	35.2	41.4	5.7	13.6
		50	37.3	30.1	43.5	33.0	34.4	35.6	5.1	14.3
		100	28.6	33.8	38.3	30.9	35.6	33.4	3.8	11.4
North Slope Crude	0	0	2.6	3.3	3.8	2.9	3.6	3.2	0.5	14.6
		20	54.5	53.4	45.5	55.9	41.2	50.1	6.4	12.8
		50	53.1	37.0	47.8	53.2	39.3	46.1	7.6	16.4
		100	34.5	48.0	37.5	47.9	34.2	40.4	7.0	17.2
	10	0	2.7	3.6	3.2	3.5	3.4	3.3	0.4	10.8
		20	49.8	38.6	41.2	45.8	44.6	44.0	4.3	9.8
		50	42.8	47.4	36.3	41.8	42.1	42.0	3.9	9.4
		100	31.3	39.9	39.6	43.7	38.9	38.7	4.5	11.7
Hondo Crude	0	0	2.3	2.1	1.6	2.1	2.1	2.0	0.3	13.3
		20	19.1	28.3	26.8	28.9	28.1	26.2	4.1	15.4
		50	26.1	22.1	20.4	19.1	23.8	22.3	2.8	12.4
		100	16.0	22.2	18.8	15.5	19.3	18.4	2.7	14.9
	10	0	1.8	2.3	1.9	2.2	2.3	2.1	0.2	11.0
		20	24.3	21.5	28.2	23.4	27.1	24.9	2.8	11.1
		50	24.9	18.4	20.4	21.2	25.4	22.1	3.0	13.5
		100	18.0	16.0	12.9	17.5	13.7	15.6	2.3	14.5

Table A2. 150-ml Baffled Flask Percent Effectiveness Results (fluorescence) at 5°C and 200 rpm.

Oil	Weathering (%)	DOR	% Effectiveness of replicate samples R1	R2	R3	R4	R5	Average % Effectiveness	Standard Deviation	Coefficient of Variance
South LA Crude	0	0	7.4	6.0	6.6	6.1	8.0	6.8	0.8	12.42
		20	89.9	89.3	70.9	73.1	94.6	83.6	10.8	12.89
		50	74.7	86.4	77.8	90.4	87.6	83.4	6.8	8.13
		100	77.9	55.3	62.0	52.9	64.7	62.6	9.8	15.73
	10	0	5.8	6.6	5.4	5.6	7.0	6.1	0.7	11.12
		20	86.3	66.1	74.2	75.5	77.4	75.9	7.2	9.50
		50	67.0	84.1	74.8	82.7	72.3	76.2	7.2	9.45
		100	67.9	75.7	58.2	53.9	63.8	63.9	8.5	13.29
North Slope Crude	0	0	5.4	4.1	3.9	3.8	5.0	4.4	0.7	15.90
		20	67.7	71.2	79.1	76.8	63.2	71.6	6.5	9.09
		50	67.1	63.4	76.3	77.6	79.3	72.7	7.0	9.7
		100	53.3	68.5	54.8	67.9	67.4	62.4	7.6	12.25
	10	0	3.1	4.0	4.1	4.2	3.2	3.7	0.5	14.48
		20	77.9	64.6	69.4	83.2	79.8	75.0	7.7	10.27
		50	70.8	51.1	64.0	74.0	58.2	63.6	9.3	14.63
		100	55.5	51.4	64.1	53.7	47.1	54.4	6.3	11.53
Hondo Crude	0	0	1.8	2.2	1.7	1.5	1.6	1.8	0.2	13.88
		20	26.1	33.3	27.7	33.4	34.4	31.0	3.8	12.30
		50	27.5	29.2	21.5	25.3	27.2	26.2	2.9	11.23
		100	23.9	16.7	21.3	17.7	23.2	20.6	3.2	15.65
	10	0	2.2	1.6	1.9	1.9	2.1	1.9	0.2	11.39
		20	26.7	22.1	28.4	24.3	27.0	25.7	2.5	9.65
		50	20.2	27.7	24.7	27.4	27.3	25.4	3.2	12.49
		100	16.2	23.9	20.3	21.9	20.5	20.6	2.8	13.8

Table A3. 150-ml Baffled Flask Percent Effectiveness Results (fluorescence) at 23°C and 150 rpm.

Oil	Weathering (%)	DOR	% Effectiveness of replicate samples R1	R2	R3	R4	R5	Average % Effectiveness	Standard Deviation	Coefficient of Variance
South LA Crude	0	0	6.4	5.4	5.2	5.9	6.6	5.9	0.6	10.32
		20	68.7	67.1	76.5	82.7	73.0	73.6	6.3	8.57
		50	52.1	69.2	70.4	75.4	73.3	68.1	9.3	13.64
		100	61.0	48.6	56.2	53.5	51.5	54.2	4.7	8.73
	10	0	5.4	4.2	3.9	3.6	5.0	4.4	0.8	17.57
		20	54.9	60.1	49.1	47.7	45.7	51.5	5.9	11.45
		50	45.6	57.6	49.2	43.3	58.6	50.9	7.0	13.69
		100	52.9	43.8	36.3	39.6	36.5	41.8	6.9	16.49
North Slope Crude	0	0	3.9	3.3	4.7	4.6	4.8	4.2	0.6	14.92
		20	57.6	71.4	58.4	62.2	73.1	64.5	7.3	11.30
		50	50.4	51.8	67.5	58.5	60.4	57.7	6.9	12.0
		100	61.1	45.5	45.3	55.6	49.5	51.4	6.8	13.29
	10	0	4.9	3.4	4.6	4.9	3.5	4.3	0.8	17.89
		20	45.5	62.1	60.5	48.7	61.9	55.8	8.0	14.33
		50	50.3	57.5	42.4	52.2	43.0	49.1	6.4	13.06
		100	52.2	42.4	38.4	50.1	48.1	46.2	5.7	12.27
Hondo Crude	0	0	2.1	1.5	2.0	2.0	1.8	1.9	0.3	13.73
		20	34.7	27.6	26.9	27.1	34.5	30.2	4.0	13.39
		50	27.2	25.5	32.8	23.9	30.7	28.0	3.7	13.14
		100	27.2	23.4	19.0	21.2	23.6	22.9	3.1	13.36
	10	0	2.3	1.9	2.0	2.4	2.3	2.2	0.2	9.83
		20	31.6	24.5	29.6	28.9	28.6	28.7	2.6	9.11
		50	25.9	20.3	26.5	21.3	24.6	23.7	2.8	11.69
		100	20.6	23.4	16.3	22.1	20.3	20.5	2.7	13.02

Table A4. 150-ml Baffled Flask Percent Effectiveness Results (fluorescence) at 23°C and 200 rpm.

Oil	Weathering (%)	DOR	% Effectiveness of replicate samples R1	R2	R3	R4	R5	Average % Effectiveness	Standard Deviation	Coefficient of Variance
South LA Crude	0	0	9.8	8.6	8.7	8.0	8.3	8.7	0.7	7.94
		20	92.6	84.0	98.8	96.3	78.6	90.1	8.5	9.46
		50	79.5	87.0	92.5	82.4	72.7	82.8	7.5	9.06
		100	80.3	86.4	73.5	88.1	77.4	81.1	6.1	7.53
	10	0	7.81	7.16	6.34	6.53	8.04	7.2	0.8	10.46
		20	91.7	83.6	81.2	70.7	90.1	83.5	8.4	10.02
		50	89.0	68.6	76.3	78.0	89.1	80.2	8.8	11.02
		100	65.5	69.6	82.4	64.8	82.3	72.9	8.8	12.08
North Slope Crude	0	0	6.5	5.1	5.6	4.6	6.2	5.6	0.8	13.70
		20	90.8	74.3	76.1	70.3	70.9	76.5	8.3	10.90
		50	66.4	79.8	76.4	72.9	72.8	73.7	5.0	6.74
		100	53.1	71.9	64.0	60.4	69.1	63.7	7.4	11.60
	10	0	5.1	4.4	3.9	3.9	4.5	4.3	0.5	11.38
		20	73.7	83.1	71.3	63.2	61.4	70.5	8.8	12.41
		50	73.8	75.9	60.6	60.1	84.0	70.9	10.4	14.61
		100	54.3	68.8	64.4	61.9	66.2	63.1	5.5	8.76
Hondo Crude	0	0	2.8	2.2	2.0	2.2	2.7	2.4	0.3	14.12
		20	35.2	37.2	30.5	39.2	34.6	35.4	3.3	9.25
		50	27.6	35.4	30.6	26.0	36.0	31.1	4.5	14.51
		100	31.1	26.6	21.8	22.2	30.6	26.4	4.4	16.76
	10	0	2.8	2.0	2.5	2.0	2.6	2.4	0.4	15.55
		20	30.0	34.2	29.0	33.2	33.6	32.0	2.3	7.27
		50	27.3	33.2	24.8	29.2	24.9	27.9	3.5	12.53
		100	27.3	24.1	21.7	23.0	27.3	24.7	2.5	10.28

Table A5. 150-ml Baffled Flask Percent Effectiveness Results (UV-Vis) at 5°C and 150 rpm.

Oil	Weathering (%)	DOR	% Effectiveness of replicate samples R1	R2	R3	R4	R5	Average % Effectiveness	Standard Deviation	Coefficient of Variance
South LA Crude	0	0	4.5	4.4	5.6	3.6	3.7	4.4	0.8	18.7
		20	68.4	61.4	55.0	58.4	56.5	59.9	5.3	8.8
		50	51.0	66.3	57.2	51.6	52.2	55.7	6.4	11.6
		100	45.1	42.4	45.8	43.9	40.7	43.6	2.1	4.7
	10	0	3.1	3.6	3.6	2.9	3.1	3.3	0.3	9.6
		20	44.0	44.5	36.7	36.2	39.4	40.2	3.9	9.7
		50	35.8	28.8	41.0	39.6	39.2	36.9	4.9	13.3
		100	30.2	30.3	34.4	30.7	35.3	32.2	2.4	7.6
North Slope Crude	0	0	2.6	3.0	3.3	3.5	3.0	3.1	0.4	11.8
		20	50.4	47.4	61.2	38.8	48.1	49.2	8.0	16.3
		50	51.0	43.5	44.4	42.9	45.3	45.4	3.3	7.2
		100	30.9	44.9	36.3	38.4	40.5	38.2	5.2	13.6
	10	0	3.6	3.2	2.9	3.1	3.3	3.2	0.3	8.2
		20	48.7	36.6	38.8	43.0	48.5	43.1	5.5	12.9
		50	41.7	45.5	32.9	48.1	39.5	41.5	5.9	14.1
		100	38.3	38.3	35.3	42.3	33.9	37.6	3.2	8.6
Hondo Crude	0	0	2.2	2.1	1.4	2.0	1.8	1.9	0.3	15.8
		20	27.2	27.2	24.7	23.3	24.1	25.3	1.8	7.1
		50	23.7	21.6	18.9	19.9	19.1	20.6	2.0	9.7
		100	15.0	21.6	18.3	19.0	19.5	18.7	2.4	12.9
	10	0	1.6	2.2	1.7	2.1	1.6	1.9	0.3	15.7
		20	23.2	20.9	26.8	25.2	22.0	23.6	2.4	10.1
		50	23.4	24.8	19.2	17.3	22.2	21.4	3.1	14.4
		100	15.9	14.9	11.4	15.5	13.4	14.2	1.8	13.0

Table A6. 150-ml Baffled Flask Percent Effectiveness Results (UV-Vis) at 5°C and 200 rpm.

Oil	Weathering (%)	DOR	% Effectiveness of replicate samples R1	R2	R3	R4	R5	Average % Effectiveness	Standard Deviation	Coefficient of Variance
South LA Crude	0	0	6.7	6.4	6.3	6.1	5.9	6.3	0.3	4.86
		20	86.2	86.1	75.4	85.6	81.2	82.9	4.7	5.66
		50	79.8	78.2	75.8	84.8	88.5	81.4	5.1	6.31
		100	70.0	53.0	67.2	53.5	64.5	61.6	7.9	12.83
	10	0	5.5	6.4	6.0	5.7	6.0	5.9	0.4	6.09
		20	80.7	69.9	78.7	75.6	65.0	74.0	6.5	8.73
		50	70.0	79.8	72.8	64.3	84.3	74.2	7.9	10.68
		100	62.9	71.4	54.5	65.6	62.3	63.3	6.1	9.70
North Slope Crude	0	0	5.2	4.0	3.7	4.2	4.2	4.3	0.6	13.54
		20	62.1	65.4	77.2	72.9	69.9	69.5	6.0	8.58
		50	62.5	79.6	73.8	73.2	66.3	71.1	6.7	9.5
		100	61.2	60.3	69.4	59.6	63.4	62.8	4.0	6.34
	10	0	3.0	3.8	3.7	4.1	4.0	3.7	0.4	11.94
		20	70.7	79.2	66.2	75.3	78.9	74.1	5.6	7.53
		50	67.6	70.0	60.1	67.0	54.3	63.8	6.5	10.12
		100	53.7	45.6	61.7	68.2	50.2	55.9	9.1	16.22
Hondo Crude	0	0	1.6	2.0	1.9	1.6	1.5	1.7	0.2	14.01
		20	35.1	30.0	34.4	29.9	29.8	31.8	2.7	8.40
		50	26.2	27.6	20.9	29.1	25.1	25.8	3.1	12.07
		100	22.7	16.2	19.3	19.5	21.0	19.7	2.4	12.05
	10	0	2.1	1.4	1.9	1.9	1.7	1.8	0.3	14.62
		20	25.6	21.1	27.7	26.6	22.8	24.8	2.7	11.06
		50	28.7	26.1	21.8	25.8	26.2	25.7	2.5	9.54
		100	25.2	22.1	19.1	18.6	16.0	20.2	3.5	17.5

Table A7. 150-ml Baffled Flask Percent Effectiveness Results (UV-Vis) at 23°C and 150 rpm.

Oil	Weathering (%)	DOR	% Effectiveness of replicate samples R1	R2	R3	R4	R5	Average % Effectiveness	Standard Deviation	Coefficient of Variance
South LA Crude	0	0	6.0	5.1	5.1	5.8	5.8	5.5	0.4	7.82
		20	65.7	79.3	69.7	72.1	73.1	72.0	5.0	6.95
		50	67.1	66.0	64.8	77.5	58.0	66.7	7.0	10.49
		100	57.4	46.8	49.6	63.6	60.0	55.5	7.1	12.74
	10	0	5.2	4.0	3.6	4.9	3.7	4.3	0.7	16.77
		20	53.6	57.5	46.8	50.8	52.6	52.3	3.9	7.48
		50	50.4	52.1	47.1	49.3	41.9	48.2	4.0	8.24
		100	40.5	42.9	34.6	49.9	37.8	41.1	5.8	14.05
North Slope Crude	0	0	3.6	3.9	4.4	3.5	4.0	3.9	0.3	8.84
		20	71.7	65.1	52.9	57.6	67.2	62.9	7.6	12.01
		50	64.4	50.0	62.2	52.0	53.8	56.5	6.4	11.3
		100	58.8	43.9	51.6	53.8	49.9	51.6	5.5	10.56
	10	0	4.7	3.3	4.3	4.2	4.1	4.1	0.5	12.30
		20	52.2	57.3	53.6	52.0	52.1	53.4	2.3	4.27
		50	48.6	51.8	39.0	49.1	52.2	48.2	5.4	11.11
		100	48.2	50.9	55.5	44.9	41.4	48.2	5.4	11.26
Hondo Crude	0	0	1.9	1.4	1.9	1.8	2.0	1.8	0.2	12.82
		20	31.1	34.7	25.6	31.6	31.4	30.9	3.3	10.63
		50	25.4	24.5	31.4	25.4	26.0	26.5	2.8	10.39
		100	24.1	22.4	27.1	19.0	19.6	22.4	3.3	14.86
	10	0	2.1	1.7	2.2	1.9	2.0	2.0	0.2	9.30
		20	29.5	23.6	27.0	27.6	29.5	27.5	2.4	8.81
		50	24.3	19.2	24.9	27.2	27.3	24.6	3.3	13.34
		100	19.9	21.5	25.0	19.0	17.9	20.6	2.8	13.38

Table A8. 150-ml Baffled Flask Percent Effectiveness Results (UV-Vis) at 23°C and 200 rpm.

Oil	Weathering (%)	DOR	% Effectiveness of replicate samples R1	R2	R3	R4	R5	Average % Effectiveness	Standard Deviation	Coefficient of Variance
South LA Crude	0	0	9.4	8.6	8.1	8.7	7.4	8.4	0.7	8.67
		20	88.0	82.3	90.3	102.2	84.3	89.4	7.8	8.70
		50	77.1	83.2	85.0	81.4	76.0	80.5	3.9	4.82
		100	78.7	76.3	78.5	78.0	87.7	79.8	4.5	5.62
	10	0	6.99	6.49	7.00	6.68	7.23	6.9	0.3	4.24
		20	81.4	81.9	73.1	85.9	84.1	81.3	4.9	6.03
		50	83.8	80.3	73.7	82.4	82.5	80.5	4.0	4.98
		100	73.9	67.7	74.8	77.3	68.7	72.5	4.1	5.67
North Slope Crude	0	0	6.3	4.9	5.3	4.6	6.4	5.5	0.8	14.59
		20	83.1	71.5	69.5	76.3	73.3	74.7	5.3	7.07
		50	63.6	74.3	67.5	75.5	80.5	72.3	6.7	9.31
		100	58.3	66.1	61.4	63.2	60.2	61.8	3.0	4.79
	10	0	4.5	4.1	3.5	3.8	4.3	4.1	0.4	9.58
		20	70.3	77.2	65.3	76.2	63.6	70.5	6.2	8.77
		50	65.3	73.5	68.1	70.6	72.4	70.0	3.3	4.78
		100	62.2	66.7	62.3	49.0	64.9	61.0	7.0	11.46
Hondo Crude	0	0	2.6	2.2	1.9	2.5	2.1	2.3	0.3	12.43
		20	33.9	34.1	38.7	37.8	35.5	36.0	2.2	6.08
		50	36.2	33.4	29.1	31.9	24.1	30.9	4.6	14.93
		100	28.6	24.6	29.4	26.7	26.2	27.1	1.9	7.05
	10	0	2.6	2.0	2.2	2.4	1.9	2.2	0.3	12.78
		20	28.3	31.9	36.9	33.4	28.9	31.9	3.5	10.96
		50	24.8	30.7	23.9	29.7	31.5	28.1	3.5	12.50
		100	26.6	22.9	20.5	30.5	25.4	25.2	3.8	15.05

Table A9. 1-L Pressure Vessel Percent Effectiveness Results (A) 5°C @ 200 psi and (B) 5°C @ 2000 psi

A

Oil	DOR	% Effectiveness of replicate samples R1	R2	R3	Average % Effectiveness	Standard Deviation	Coefficient of Variance
SLC	0	2.7	3.1	3.0	2.9	0.2	7.75
	20	53.2	48.1	43.6	48.3	4.8	9.90
	50	43.8	44.5	45.3	44.5	0.8	1.78
	100	36.4	37.2	39.2	37.6	1.4	3.76
NSC	0	2.5	2.4	2.2	2.4	0.2	6.86
	20	49.4	41.9	44.0	45.1	3.9	8.54
	50	35.3	43.0	36.8	38.4	4.1	10.7
	100	36.9	34.7	35.9	35.8	1.1	3.09
HC	0	1.9	2.3	2.1	2.1	0.2	9.53
	20	14.1	15.8	13.6	14.5	1.1	7.82
	50	13.2	13.8	11.5	12.8	1.2	9.24
	100	8.2	9.5	7.4	8.4	1.1	12.8

B

Oil	DOR	% Effectiveness of replicate samples R1	R2	R3	Average % Effectiveness	Standard Deviation	Coefficient of Variance
SLC	0	2.5	3.2	2.9	2.9	0.3	11.5
	20	48.8	47.2	50.6	48.9	1.7	3.48
	50	43.8	42.2	50.7	45.6	4.5	9.88
	100	35.3	36.5	38.6	36.8	1.7	4.54
NSC	0	2.3	2.3	2.5	2.4	0.1	4.94
	20	45.1	46.4	42.7	44.7	1.9	4.2
	50	42.5	36.6	36.4	38.5	3.5	8.97
	100	41.9	35.0	31.7	36.2	5.2	14.40
HC	0	1.6	2.0	2.2	2.0	0.3	14.4
	20	12.7	15.6	13.5	13.9	1.5	11.0
	50	13.6	12.1	11.4	12.4		0.0
	100	7.7	8.9	8.5	8.4	0.6	6.9

Table A10. 1-L Pressure Vessel Percent Effectiveness Results (A) 23°C @ 200 psi and (B) 23°C @ 2000 psi

A

Oil	DOR	% Effectiveness of replicate samples R1	R2	R3	Average % Effectiveness	Standard Deviation	Coefficient of Variance
SLC	0	3.42	4.02	3.75	3.7	0.3	8.1
	20	60.4	57.9	52.7	57.0	3.9	6.9
	50	50.3	57.5	53.8	53.9	3.6	6.7
	100	50.9	49.8	54.5	51.7	2.5	4.8
NSC	0	2.89	3.21	2.51	2.9	0.4	12.2
	20	56.1	49.3	54.3	53.2	3.5	6.6
	50	42.9	50.6	43.8	45.8	4.2	9.2
	100	40.1	38.7	42.5	40.4	1.9	4.8
HC	0	2.39	2.84	2.55	2.6	0.2	8.8
	20	15.8	17.5	14.3	15.9	1.6	10.1
	50	14.7	16.2	12.4	14.4	1.9	13.3
	100	10.5	11.9	9.7	10.7	1.1	10.4

B

Oil	DOR	% Effectiveness of replicate samples R1	R2	R3	Average % Effectiveness	Standard Deviation	Coefficient of Variance
SLC	0	3.2	3.9	3.6	3.6	0.4	10.3
	20	59.4	50.9	56.4	55.6	4.3	7.7
	50	53.6	57.7	48.9	53.4	4.4	8.3
	100	48.6	44.3	41.8	44.9	3.4	7.6
NSC	0	2.5	2.9	3.3	2.9	0.4	12.8
	20	51.2	63.5	54.5	56.4	6.4	11.3
	50	44.9	48.9	42.1	45.3	3.4	7.6
	100	39.3	36.2	41.1	38.8	2.5	6.3
HC	0	2.0	2.5	2.8	2.4	0.4	17.5
	20	15.3	15.1	17.8	16.1	1.5	9.4
	50	12.9	14.0	13.4	13.4	0.6	4.1
	100	12.5	8.4	9.4	10.1	2.2	21.4

Table A11. 1-L Baffled Flask Percent Effectiveness Results (laboratory fluorescence) 5°C @ 150 rpm.

Oil	Weathering (%)	DOR	% Effectiveness of replicate samples			Average % Effectiveness	Standard Deviation	Coefficient of Variance
			R1	R2	R3			
South LA Crude	0	0	4.7	4.4	3.8	4.3	0.5	10.7
		20	52.0	68.0	50.0	56.7	9.9	17.4
		50	53.0	47.0	63.0	54.3	8.1	14.9
		100	38.0	46.0	48.0	44.0	5.3	12.0
	10	0	3.5	2.5	3.6	3.2	0.6	19.0
		20	45.0	37.0	39.0	40.3	4.2	10.3
		50	36.0	30.0	43.0	36.3	6.5	17.9
		100	28.0	33.0	36.0	32.3	4.0	12.5
North Slope Crude	0	0	2.5	3.3	3.6	3.1	0.6	18.1
		20	53.0	50.0	43.0	48.7	5.1	10.5
		50	51.0	36.0	47.0	44.7	7.8	17.4
		100	34.0	45.0	36.0	38.3	5.9	15.3
	10	0	2.6	3.4	3.1	3.0	0.4	13.3
		20	49.0	36.0	41.0	42.0	6.6	15.6
		50	40.0	47.0	36.0	41.0	5.6	13.6
		100	31.0	38.0	37.0	35.3	3.8	10.7
HONDO	0	0	2.2	2.0	1.5	1.9	0.4	19.0
		20	19.0	27.0	26.0	24.0	4.4	18.2
		50	25.0	22.0	20.0	22.3	2.5	11.3
		100	15.0	21.0	18.0	18.0	3.0	16.7
	10	0	1.7	2.3	1.8	1.9	0.3	16.6
		20	23.0	20.0	28.0	23.7	4.0	17.1
		50	24.0	18.0	20.0	20.7	3.1	14.8
		100	17.0	15.0	12.0	14.7	2.5	17.2

Table A12. 1-L Baffled Flask Percent Effectiveness Results (laboratory fluorescence) 5°C @ 200 rpm.

Oil	Weathering (%)	DOR	% Effectiveness of replicate samples R1	R2	R3	Average % Effectiveness	Standard Deviation	Coefficient of Variance
South LA Crude	0	0	6.9	5.8	6.3	6.3	0.6	8.70
		20	88.0	87.0	70.0	81.7	10.1	12.39
		50	71.0	85.0	77.0	77.7	7.0	9.04
		100	74.0	55.0	60.0	63.0	9.8	15.63
	10	0	5.8	6.2	5.0	5.7	0.6	10.78
		20	82.0	66.0	74.0	74.0	8.0	10.81
		50	63.0	82.0	71.0	72.0	9.5	13.25
		100	66.0	71.0	56.0	64.3	7.6	11.87
North Slope Crude	0	0	5.2	4.1	3.8	4.4	0.7	16.88
		20	66.0	70.0	79.0	71.7	6.7	9.29
		50	63.0	62.0	73.0	66.0	6.1	9.2
		100	50.0	67.0	53.0	56.7	9.1	16.01
	10	0	2.9	3.7	4.1	3.6	0.6	17.13
		20	77.0	62.0	69.0	69.3	7.5	10.83
		50	67.0	51.0	63.0	60.3	8.3	13.80
		100	52.0	49.0	61.0	54.0	6.2	11.56
HONDO	0	0	1.7	2.1	1.7	1.8	0.2	12.60
		20	25.0	32.0	26.0	27.7	3.8	13.68
		50	26.0	29.0	21.0	25.3	4.0	15.95
		100	23.0	16.0	20.0	19.7	3.5	17.86
	10	0	2.1	1.5	1.8	1.8	0.3	16.67
		20	25.0	21.0	28.0	24.7	3.5	14.24
		50	20.0	26.0	24.0	23.3	3.1	13.09
		100	16.0	23.0	20.0	19.7	3.5	17.9

Table A13. 1-L Baffled Flask Percent Effectiveness Results (laboratory fluorescence) 23°C @ 150 rpm.

Oil	Weathering (%)	DOR	% Effectiveness of replicate samples R1	R2	R3	Average % Effectiveness	Standard Deviation	Coefficient of Variance
South LA Crude	0	0	6.0	5.3	5.0	5.4	0.5	9.44
		20	64.0	65.0	76.0	68.3	6.7	9.74
		50	52.0	65.0	66.0	61.0	7.8	12.80
		100	58.0	48.0	53.0	53.0	5.0	9.43
	10	0	5.1	4.0	3.5	4.2	0.8	19.49
		20	53.0	59.0	47.0	53.0	6.0	11.32
		50	44.0	56.0	49.0	49.7	6.0	12.14
		100	52.0	42.0	36.0	43.3	8.1	18.65
North Slope Crude	0	0	3.8	3.2	4.6	3.9	0.7	18.16
		20	54.0	68.0	57.0	59.7	7.4	12.35
		50	50.0	49.0	63.0	54.0	7.8	14.5
		100	58.0	45.0	43.0	48.7	8.1	16.74
	10	0	4.7	3.4	4.4	4.2	0.7	16.34
		20	44.0	59.0	57.0	53.3	8.1	15.27
		50	50.0	56.0	42.0	49.3	7.0	14.24
		100	52.0	41.0	38.0	43.7	7.4	16.88
HONDO	0	0	2.0	1.4	1.9	1.8	0.3	18.20
		20	34.0	27.0	25.0	28.7	4.7	16.49
		50	26.0	24.0	31.0	27.0	3.6	13.35
		100	26.0	22.0	18.0	22.0	4.0	18.18
	10	0	2.3	1.9	2.0	2.1	0.2	10.07
		20	31.0	24.0	29.0	28.0	3.6	12.88
		50	25.0	19.0	26.0	23.3	3.8	16.23
		100	20.0	22.0	16.0	19.3	3.1	15.80

Table A14. 1-L Baffled Flask Percent Effectiveness Results (laboratory fluorescence) 23°C @ 200 rpm.

Oil	Weathering (%)	DOR	% Effectiveness of replicate samples R1	R2	R3	Average % Effectiveness	Standard Deviation	Coefficient of Variance
South LA Crude	0	0	9.2	8.2	8.1	8.5	0.6	7.16
		20	97.0	83.0	95.0	91.7	7.6	8.26
		50	75.0	85.0	91.0	83.7	8.1	9.66
		100	77.0	86.0	73.0	78.7	6.7	8.46
	10	0	7.7	6.9	6	6.9	0.9	12.39
		20	91.0	78.0	76.0	81.7	8.1	9.97
		50	86.0	66.0	73.0	75.0	10.1	13.53
		100	65.0	69.0	80.0	71.3	7.8	10.89
North Slope Crude	0	0	6.2	4.9	5.6	5.6	0.7	11.69
		20	89.0	74.0	71.0	78.0	9.6	12.36
		50	65.0	77.0	74.0	72.0	6.2	8.67
		100	51.0	68.0	64.0	61.0	8.9	14.57
	10	0	4.8	4.2	3.7	4.2	0.6	13.01
		20	73.0	82.0	67.0	74.0	7.5	10.20
		50	69.0	75.0	58.0	67.3	8.6	12.80
		100	53.0	67.0	62.0	60.7	7.1	11.69
HONDO	0	0	2.6	2.2	1.9	2.2	0.4	15.72
		20	35.0	37.0	30.0	34.0	3.6	10.60
		50	26.0	34.0	29.0	29.7	4.0	13.62
		100	29.0	26.0	21.0	25.3	4.0	15.95
	10	0	2.7	1.9	2.4	2.3	0.4	17.32
		20	30.0	34.0	27.0	30.3	3.5	11.58
		50	26.0	33.0	24.0	27.7	4.7	17.08
		100	27.0	23.0	21.0	23.7	3.1	12.91

Table A15. 1-L Baffled Flask Percent Effectiveness Results (probe fluorescence) 5°C @ 150 rpm.

Oil	Weathering (%)	DOR	% Effectiveness of replicate samples R1	R2	R3	Average % Effectiveness	Standard Deviation	Coefficient of Variance
South LA Crude	0	0	3.9	3.5	3.2	3.6	0.4	9.9
		20	46.1	64.1	60.5	56.9	9.5	16.7
		50	50.5	48.9	51.4	50.3	1.3	2.5
		100	46.2	37.3	51.0	44.8	6.9	15.5
	10	0	4.3	3.1	3.4	3.6	0.6	17.0
		20	41.0	43.0	45.6	43.2	2.3	5.3
		50	41.3	32.7	40.3	38.1	4.7	12.4
		100	35.5	28.1	34.2	32.6	4.0	12.2
North Slope Crude	0	0	3.0	2.8	3.5	3.1	0.4	12.4
		20	61.6	55.1	51.6	56.1	5.1	9.1
		50	50.0	38.2	42.3	43.5	6.0	13.8
		100	39.3	43.2	42.5	41.6	2.1	4.9
	10	0	2.9	3.3	2.6	2.9	0.3	10.6
		20	48.9	44.8	50.4	48.0	2.9	6.0
		50	40.2	40.3	39.0	39.8	0.8	1.9
		100	38.0	31.2	43.0	37.4	5.9	15.9
HONDO	0	0	2.2	1.7	1.9	1.9	0.3	13.7
		20	21.2	28.4	26.9	25.5	3.8	15.0
		50	27.9	20.6	24.7	24.4	3.6	14.9
		100	15.2	19.8	17.1	17.4	2.3	13.3
	10	0	2.1	2.4	2.1	2.2	0.1	6.2
		20	27.9	21.2	23.9	24.3	3.4	13.9
		50	24.3	18.9	21.9	21.7	2.7	12.5
		100	12.5	11.3	14.9	12.9	1.8	14.1

Table A16. 1-L Baffled Flask Percent Effectiveness Results (probe fluorescence) 5°C @ 200 rpm.

Oil	Weathering (%)	DOR	% Effectiveness of replicate samples R1	R2	R3	Average % Effectiveness	Standard Deviation	Coefficient of Variance
South LA Crude	0	0	7.5	5.7	7.4	6.9	1.0	14.90
		20	78.4	72.7	83.0	78.1	5.2	6.60
		50	79.1	77.0	81.0	79.0	2.0	2.53
		100	64.2	61.4	50.8	58.8	7.1	12.06
	10	0	6.7	6.6	4.9	6.1	1.0	16.35
		20	77.4	68.8	90.0	78.7	10.7	13.53
		50	68.4	89.0	66.2	74.5	12.6	16.85
		100	62.1	76.0	68.6	68.9	6.9	10.07
North Slope Crude	0	0	3.9	4.9	4.5	4.4	0.5	11.70
		20	77.6	71.7	70.7	73.3	3.7	5.09
		50	63.4	69.1	61.5	64.7	3.9	6.1
		100	42.3	57.9	59.2	53.1	9.4	17.70
	10	0	3.6	2.9	3.8	3.4	0.5	13.39
		20	76.5	59.6	60.9	65.7	9.4	14.31
		50	70.5	52.4	64.7	62.5	9.3	14.80
		100	58.0	48.0	51.0	52.3	5.1	9.83
HONDO	0	0	2.0	1.6	2.0	1.9	0.2	12.35
		20	26.3	28.5	31.8	28.8	2.8	9.68
		50	28.1	31.2	26.3	28.5	2.5	8.66
		100	22.3	18.4	25.7	22.1	3.7	16.50
	10	0	1.9	1.6	1.7	1.7	0.2	9.15
		20	27.4	20.1	22.4	23.3	3.7	15.93
		50	22.1	26.6	27.8	25.5	3.0	11.85
		100	17.0	19.6	17.6	18.1	1.4	7.6

Table A17. 1-L Baffled Flask Percent Effectiveness Results (probe fluorescence) 23°C @ 150 rpm

Oil	Weathering (%)	DOR	% Effectiveness of replicate samples R1	R2	R3	Average % Effectiveness	Standard Deviation	Coefficient of Variance
South LA Crude	0	0	5.9	6.1	4.5	5.5	0.9	15.91
		20	67.4	63.6	75.2	68.7	5.9	8.62
		50	63.4	66.1	61.3	63.6	2.4	3.78
		100	46.0	60.4	47.5	51.3	7.9	15.42
	10	0	4.3	4.4	3.4	4.1	0.5	13.40
		20	44.6	54.5	49.4	49.5	5.0	10.05
		50	56.3	46.2	51.9	51.5	5.1	9.84
		100	43.8	35.0	42.9	40.6	4.8	11.92
North Slope Crude	0	0	4.6	4.1	3.7	4.1	0.5	10.96
		20	46.5	53.1	58.6	52.7	6.1	11.49
		50	49.0	55.5	68.9	57.8	10.1	17.5
		100	55.0	59.0	44.0	52.7	7.8	14.75
	10	0	4.2	3.4	3.9	3.8	0.4	10.31
		20	65.0	60.2	52.0	59.1	6.6	11.13
		50	41.9	50.0	39.4	43.8	5.5	12.66
		100	52.0	45.1	36.0	44.4	8.0	18.09
HONDO	0	0	2.0	1.5	2.1	1.9	0.3	17.10
		20	29.3	23.5	26.0	26.3	2.9	11.19
		50	29.1	26.0	37.1	30.7	5.7	18.63
		100	20.3	24.5	26.2	23.7	3.1	12.95
	10	0	2.3	1.7	1.9	2.0	0.3	16.12
		20	28.6	24.9	22.4	25.3	3.1	12.35
		50	24.7	17.7	23.2	21.9	3.7	16.99
		100	21.1	26.4	23.8	23.8	2.7	11.24

Table A18. 1-L Baffled Flask Percent Effectiveness Results (probe fluorescence) 23°C @ 200 rpm.

Oil	Weathering (%)	DOR	% Effectiveness of replicate samples R1	R2	R3	Average % Effectiveness	Standard Deviation	Coefficient of Variance
South LA Crude	0	0	8.4	7.6	8.6	8.2	0.5	6.45
		20	90.3	84.0	87.9	87.4	3.2	3.67
		50	79.1	86.0	77.7	80.9	4.5	5.51
		100	90.8	70.6	67.7	76.4	12.6	16.48
	10	0	6.6	7.2	5.1	6.3	1.1	17.02
		20	88.5	78.2	65.7	77.5	11.4	14.74
		50	69.6	87.7	63.3	73.5	12.6	17.20
		100	71.4	69.4	75.0	71.9	2.8	3.95
North Slope Crude	0	0	5.2	5.9	4.8	5.3	0.6	10.38
		20	83.4	62.5	87.5	77.8	13.4	17.29
		50	74.5	61.4	75.0	70.3	7.7	10.94
		100	62.0	63.9	75.9	67.3	7.5	11.23
	10	0	4.8	4.7	3.8	4.5	0.5	11.85
		20	64.8	75.6	78.2	72.9	7.1	9.75
		50	69.8	73.9	59.2	67.6	7.6	11.21
		100	61.4	61.9	57.5	60.3	2.4	4.00
HONDO	0	0	2.6	1.9	2.3	2.2	0.4	16.34
		20	38.5	40.3	31.3	36.7	4.8	13.03
		50	24.7	33.3	27.1	28.4	4.4	15.59
		100	30.3	27.6	23.8	27.2	3.2	11.93
	10	0	2.4	2.1	2.9	2.5	0.4	16.55
		20	36.3	26.4	31.6	31.4	5.0	15.89
		50	22.2	28.4	29.3	26.6	3.9	14.60
		100	26.1	21.8	25.3	24.4	2.3	9.35

Table A19. 1-L Baffled Flask Percent Effectiveness Results (turbidity) 5°C @ 150 rpm.

Oil	Weathering (%)	DOR	% Effectiveness of replicate samples R1	R2	R3	Average % Effectiveness	Standard Deviation	Coefficient of Variance
South LA Crude	0	0	5.2	3.9	3.1	4.0	1.1	26.3
		20	64.4	67.9	51.5	61.3	8.6	14.1
		50	70.6	55.3	82.4	69.4	13.6	19.6
		100	38.0	67.5	66.5	57.3	16.8	29.3
	10	0	3.2	2.6	3.0	3.0	0.3	11.4
		20	61.5	44.2	51.1	52.3	8.7	16.6
		50	45.1	42.7	58.8	48.8	8.7	17.8
		100	38.3	41.7	49.9	43.3	6.0	13.8
North Slope Crude	0	0	2.4	2.9	3.7	3.0	0.6	20.5
		20	64.0	48.1	33.3	48.5	15.4	31.7
		50	66.0	36.7	42.4	48.4	15.5	32.1
		100	24.5	56.2	38.1	39.6	15.9	40.0
	10	0	2.8	3.4	2.3	2.9	0.5	18.8
		20	64.0	43.1	36.9	48.0	14.2	29.6
		50	38.0	26.0	35.9	33.3	6.4	19.2
		100	42.0	29.8	47.0	39.6	8.9	22.4
HONDO	0	0	1.7	2.2	1.7	1.9	0.3	16.4
		20	12.8	27.3	25.9	22.0	8.0	36.4
		50	15.0	13.7	9.5	12.7	2.9	22.7
		100	20.9	17.2	18.0	18.7	1.9	10.3
	10	0	1.4	2.0	2.1	1.8	0.4	21.0
		20	22.9	28.7	20.7	24.1	4.2	17.3
		50	14.7	8.8	14.7	12.7	3.4	26.8
		100	5.8	10.6	9.3	8.6	2.5	29.0

Table A20. 1-L Baffled Flask Percent Effectiveness Results (turbidity) 5°C @ 200 rpm.

Oil	Weathering (%)	DOR	% Effectiveness of replicate samples R1	R2	R3	Average % Effectiveness	Standard Deviation	Coefficient of Variance
South LA Crude	0	0	7.5	5.3	7.7	6.8	1.4	19.85
		20	97.6	93.8	64.3	85.2	18.2	21.38
		50	65.5	115.4	105.7	95.5	26.5	27.72
		100	105.8	73.8	57.9	79.2	24.4	30.79
	10	0	6.5	7.6	4.5	6.2	1.6	24.98
		20	91.7	80.2	103.6	91.8	11.7	12.74
		50	58.2	90.7	89.7	79.5	18.5	23.25
		100	66.6	68.1	63.6	66.1	2.3	3.46
North Slope Crude	0	0	4.1	5.1	2.8	4.0	1.2	29.35
		20	63.0	59.7	71.0	64.6	5.8	9.01
		50	69.4	55.7	78.0	67.7	11.2	16.6
		100	42.7	72.2	34.0	49.6	20.0	40.33
	10	0	2.6	3.6	2.9	3.0	0.5	15.95
		20	61.1	66.3	75.5	67.6	7.3	10.75
		50	54.7	66.2	76.1	65.7	10.7	16.34
		100	62.0	57.2	69.5	62.9	6.2	9.81
HONDO	0	0	1.5	1.8	1.7	1.7	0.1	8.23
		20	23.6	30.6	24.0	26.1	3.9	15.04
		50	29.3	39.1	31.2	33.2	5.2	15.67
		100	22.3	21.8	16.0	20.0	3.5	17.52
	10	0	2.7	1.8	1.7	2.1	0.6	27.25
		20	21.4	14.1	26.1	20.5	6.0	29.41
		50	11.6	15.2	20.5	15.7	4.5	28.54
		100	10.0	13.7	15.3	13.0	2.7	21.1

Table A21. 1-L Baffled Flask Percent Effectiveness Results (turbidity) 23°C @ 150 rpm.

Oil	Weathering (%)	DOR	% Effectiveness of replicate samples R1	R2	R3	Average % Effectiveness	Standard Deviation	Coefficient of Variance
South LA Crude	0	0	3.9	5.4	3.2	4.2	1.1	27.57
		20	54.8	76.1	54.0	61.6	12.5	20.35
		50	53.4	51.0	88.8	64.4	21.2	32.87
		100	37.4	54.3	64.3	52.0	13.6	26.14
	10	0	3.4	2.0	3.7	3.0	0.9	30.84
		20	53.4	57.0	41.5	50.6	8.1	15.99
		50	42.6	55.2	63.2	53.6	10.4	19.38
		100	37.6	38.3	42.5	39.5	2.6	6.69
North Slope Crude	0	0	4.8	3.9	3.8	4.2	0.5	12.53
		20	52.5	81.1	68.6	67.4	14.3	21.21
		50	48.7	46.9	67.7	54.4	11.5	21.1
		100	59.2	53.8	52.3	55.1	3.6	6.62
	10	0	3.4	2.6	4.1	3.4	0.8	22.39
		20	41.8	69.8	46.7	52.7	15.0	28.38
		50	49.6	63.4	46.7	53.2	8.9	16.80
		100	51.9	52.8	42.1	48.9	5.9	12.08
HONDO	0	0	2.0	1.3	1.8	1.7	0.4	21.06
		20	29.1	24.0	31.8	28.3	4.0	14.05
		50	15.4	24.0	20.8	20.1	4.4	21.81
		100	24.8	28.3	17.9	23.7	5.3	22.41
	10	0	2.5	1.6	1.3	1.8	0.6	35.65
		20	18.0	24.1	28.7	23.6	5.3	22.66
		50	30.5	24.2	25.9	26.9	3.3	12.12
		100	14.3	25.8	22.6	20.9	5.9	28.46

Table A22. 1-L Baffled Flask Percent Effectiveness Results (turbidity) 23°C @ 200 rpm.

Oil	Weathering (%)	DOR	% Effectiveness of replicate samples R1	R2	R3	Average % Effectiveness	Standard Deviation	Coefficient of Variance
South LA Crude	0	0	7.7	4.7	7.3	6.6	1.6	24.80
		20	105.9	92.5	79.0	92.5	13.5	14.57
		50	89.1	81.4	93.9	88.2	6.3	7.12
		100	71.5	63.1	55.9	63.5	7.8	12.27
	10	0	6.3	7.1	5.635	6.3	0.8	11.87
		20	97.5	86.4	95.0	93.0	5.8	6.27
		50	57.9	116.1	91.4	88.5	29.2	32.97
		100	70.5	72.1	64.1	68.9	4.3	6.18
North Slope Crude	0	0	6.2	3.9	6.2	5.4	1.3	24.02
		20	71.5	58.2	55.3	61.6	8.6	13.99
		50	51.9	71.4	66.1	63.1	10.1	15.92
		100	38.0	76.2	79.9	64.7	23.2	35.85
	10	0	4.8	4.5	4.4	4.6	0.2	4.88
		20	92.9	91.2	69.5	84.6	13.0	15.41
		50	61.1	85.5	50.1	65.5	18.1	27.68
		100	56.8	76.4	63.4	65.6	10.0	15.23
HONDO	0	0	3.1	1.9	1.5	2.2	0.9	39.31
		20	35.4	34.5	23.1	31.0	6.8	22.00
		50	33.2	21.5	29.1	27.9	5.9	21.18
		100	25.1	18.0	27.7	23.6	5.0	21.29
	10	0	1.7	1.7	2.5	2.0	0.4	22.76
		20	37.5	33.0	18.9	29.8	9.7	32.59
		50	20.0	18.4	25.1	21.2	3.5	16.52
		100	23.5	23.1	30.0	25.5	3.8	15.01

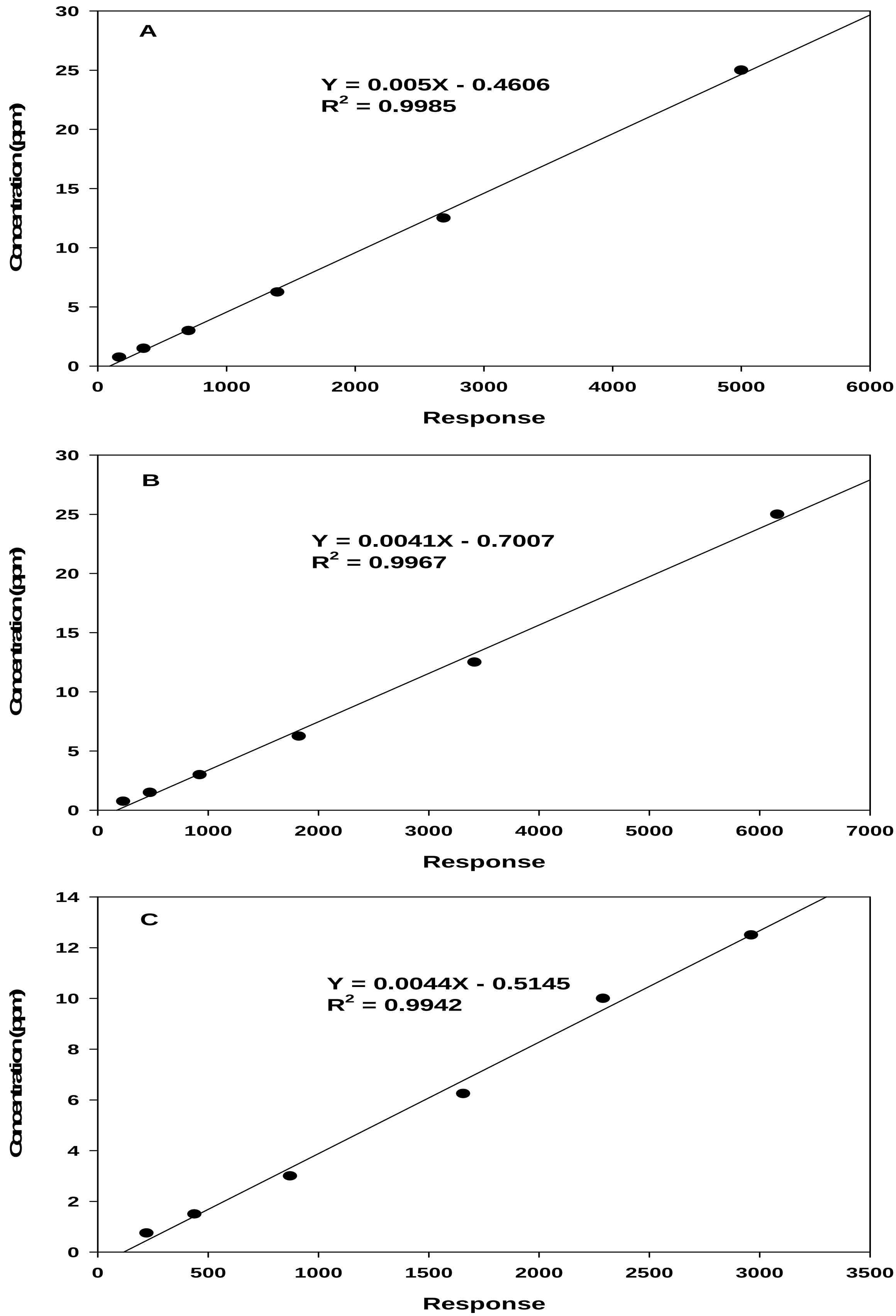

Figure A1. Laboratory Fluorescence Curves: (A) South Louisiana crude, (B) North Slope crude, and (C) Hondo crude.

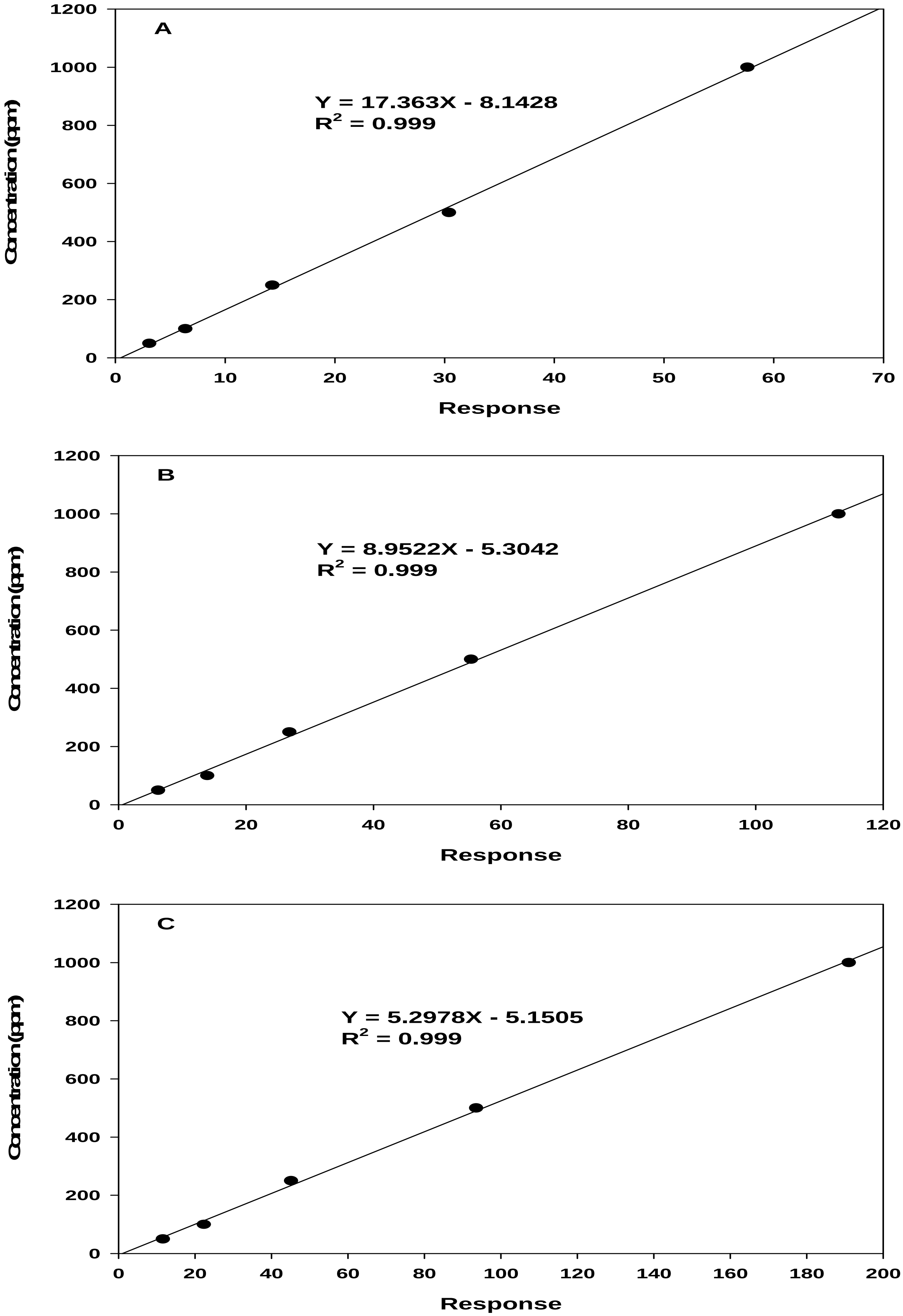

Figure A2. Laboratory UV-Vis Curves: (A) South Louisiana crude, (B) North Slope crude, and (C) Hondo crude.

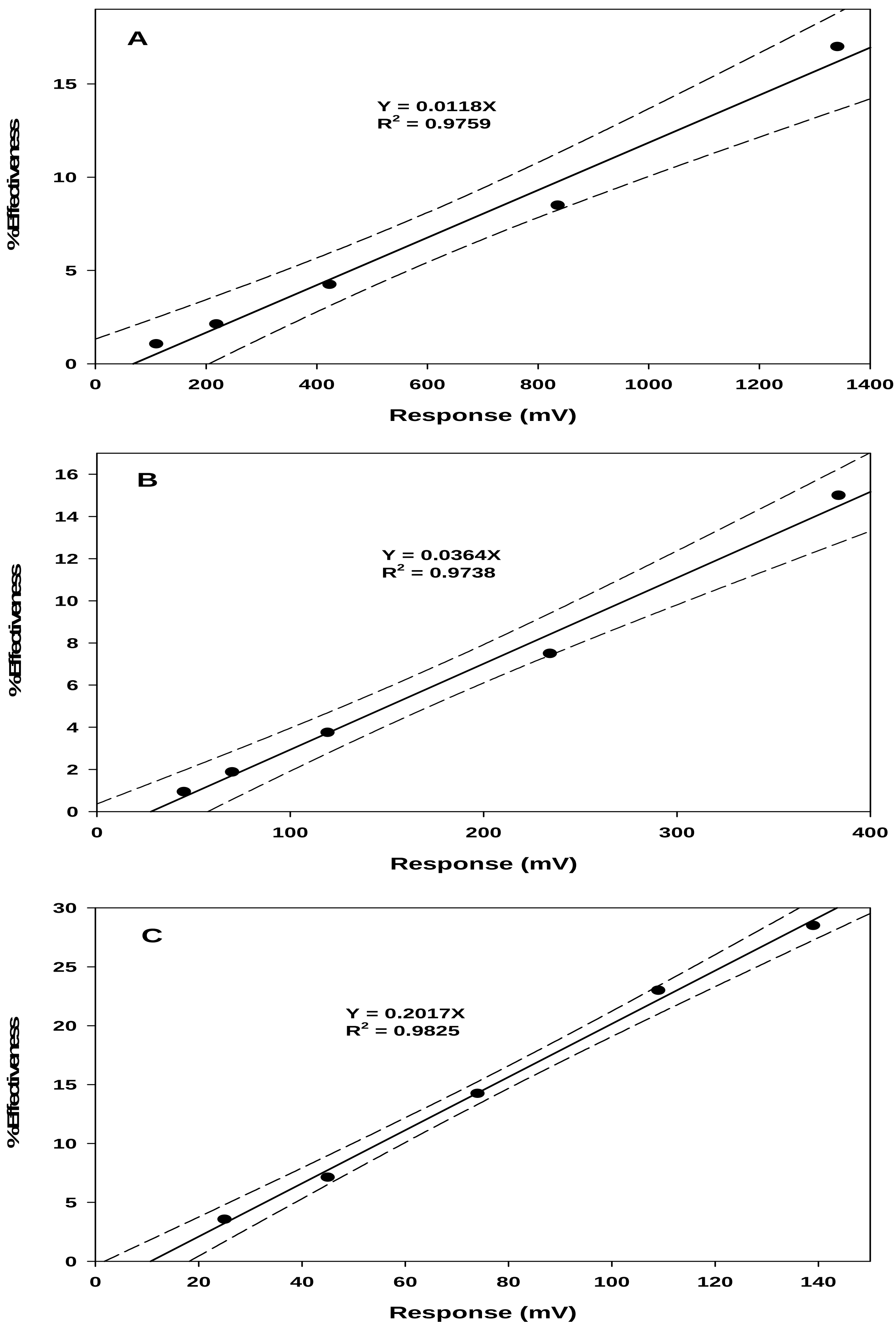

Figure A3. Field Probe Calibration Curves: (A) South Louisiana crude, (B) North Slope crude, and (C) Hondo crude. Baseline: DOR=1:20, 23°C, and 150 rpm.

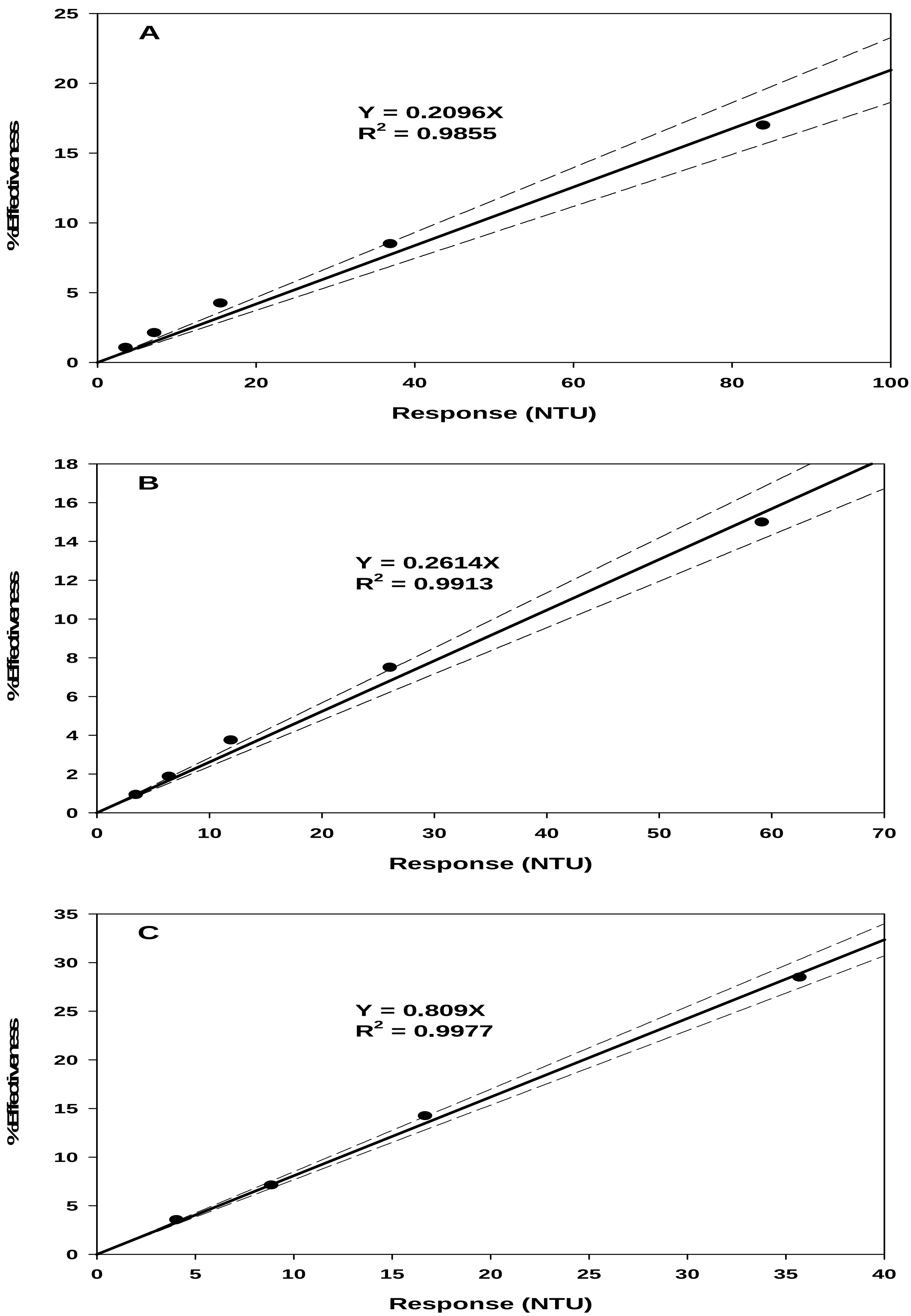

Figure A4. Turbidimeter Calibration Curves: (A) South Louisiana crude, (B) North Slope crude, and (C) Hondo crude. Baseline: DOR=1:20, 23°C, and 150 rpm.