FINAL REPORT

EFFECTIVENESS TESTING FOR COREXIT 9500 ON ALASKA NORTH SLOPE CRUDE OIL IN PRINCE WILLIAM SOUND SEAWATER AT 8 ^{o}C

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Executive Summary

The objective of this project was to test dispersant effectiveness under certain fundamental and operational variables relevant to conditions in Prince William Sound (PWS). Two laboratory testing methods were used to compare a range of test conditions and dispersant to oil ratios using PWS seawater at 8 ^{o}C, Alaska North Slope crude oil, and Corexit 9500. In addition, a literature review was conducted to evaluate dispersant test methods in laboratory and field conditions.

In general, laboratory methods are criticized because different test methods can yield inconsistent results using the same dispersant and oil. The inconsistent results are largely a function of the different protocols called for in test methods. Field effectiveness measurements, however, are very expensive, time consuming, and provide results that are difficult to interpret since the weather and oceanic mixing phenomenon can neither be controlled nor fully understood. In order to address the inconsistent results that different laboratory methods produce, all testing was first conducted with the modified swirling flask method and then repeated with the modified Exxon Dispersant Effectiveness Test (EXDET). The second method was selected to represent a different mixing mode than the swirling flask. Results of the two methods tested were remarkably similar.

Three dispersant to oil ratios (DOR) were tested, 1:10, 1:20 and 1:50. It was found that in most cases, the dispersant effectiveness was directly proportional to the DOR. For each DOR, dispersant effectiveness was measured at four contact times (time between dispersant application to a spill and start of mixing) and five weathering times (time between oil spill and dispersant application). Corexit 9500 was able to disperse Alaska North Slope crude oil at 8 ^{o}C in PWS seawater to differing degrees, depending on the test conditions. The results indicated that in general, the greatest relative dispersion occurred when the weathering time was minimized and the dispersant was allowed to contact the oil prior to the onset of mixing. In addition when the test conditions were optimal dispersant effectiveness was directly proportional to the DOR (within the range 1:50 to 1:10).

Summary of Need and Objectives

Application of chemical dispersants to an oil spill is a response option that evokes continual controversy. Since the effectiveness of dispersants is a function of environmental and operational variables, the "when, where, and how" dispersants are used is debatable. Concerns about dispersant effectiveness are compounded by the unknown impact of cold temperatures prevalent in Alaska's waters. Two time periods are important to the effectiveness of dispersants, the weathering time and the contact time. The weathering time is that time between when the oil has spilled and the dispersant is applied. The contact time is that time between when the dispersant is applied and the time surface mixing occurs. For example, if a dispersant cannot be added immediately, will it be effective if added 12 hours, one day or two days after an oil spill? What if there is significant turbulence or no turbulence at all on the ocean surface when the dispersant is added? Will it be effective or should application wait until the seas calm? What is the cost of waiting? The effectiveness of a dispersant is not only dependent on when it is applied and when mixing occurs, but also the amount applied, expressed as the dispersant to oil ratio (DOR). If a spill has occurred and dispersant is needed, how much should be added? Does the amount of dispersant added depend on the weathering and contact times?

This project was designed to address the relative effectiveness of Corexit 9500 applied to ANS crude oil under a combination of 5 weathering times, 4 contact times, and three DORs. In addition, since it has been shown that laboratory methods for testing dispersant effectiveness can provide contradictory results, two different methods were used to test all conditions. In order to get statistically significant results, each test was conducted with 5 replicates resulting in a total of 600 individual tests. All studies were conducted with Prince William Sound (PWS) seawater at 8 ^{o}C with salinity between 31 and 32 ppt and TSS of 200 mg/L.

Dispersant effectiveness testing was previously conducted by members of the Chemical Response to Oil Spills: Ecological Effects Research Forum (CROSERF). Participating laboratories within CROSERF include: Texas A&M University; Exxon Biomedical Services, Inc.; SINTEF Applied Chemistry; Chevron Research and Technology, Inc.; Entrix, Inc.; Louisiana State University; University of California, Santa Cruz; National Oceanic and Atmospheric Administration; Scietex Corporation; University of South Florida; and the University of Alaska Fairbanks. The University of Alaska Fairbanks research team joined CROSERF in order to ensure that work conducted at UAF was consistent with national and international efforts. The research conducted at UAF was essential to fill a "cold regions" gap in the CROSERF's research on dispersant use.

Project Tasks

The project was divided into 8 individual tasks. The tasks were identified according to the nature of the work conducted, rather than equal proportions.

Task 1: Literature review for dispersant effectiveness testing alternatives: The UAF research team undertook an extensive literature review of methods used to evaluate dispersant effectiveness in laboratory and field environments.

Task 2: Examination of field efficiency measurements: The UAF research team undertook an extensive literature review of field dispersant effectiveness measurement methodologies.

Task 3: Set-up and testing of apparatus: The research team set-up testing equipment duplicating, as much as possible, other test systems already in use by CROSERF laboratories.

Task 4: Determination of appropriate energy levels: The research team reviewed literature for comparing the energy levels observed in laboratory tests with conditions at sea.

Task 5: Modified swirling flask (SF) efficiency experiments: A complete suite of tests was run for the modified SF method and an alternative method (modified EXDET) for a matrix of the following variables:

Variable	**Values tested**
Dispersant to oil ratio (DOR)	1:10, 1:20. 1:50
Weathering time (time between spill and dispersant application)	0, 12, 24, 48, 72 hrs.
Contact time (time from dispersant application to energy input)	0, 12, 24, 48 hrs.
Energy input method	Swirling flask

Task 6: Efficiency measurements of an alternate technique: The same conditions were tested as in Task 5 with the exception of the energy input method

Variable	**Values tested**
Dispersant to oil ratio (DOR)	1:10, 1:20. 1:50
Weathering time (time between spill and dispersant application)	0, 12, 24, 48, 72 hrs.
Contact time (time from dispersant application to energy input)	0, 12, 24, 48 hrs.
Energy input method	Wrist action shaker

Task 7: Preparation of Draft and Final Reports

Task 8: Coordination with other CROSERF laboratories: Project researchers have attended all CROSERF meetings since the beginning of the project.

Literature Review (Tasks 1 and 2)

An extensive literature review containing the following topics is included in Appendix A:

- Oil spills at Sea,
- Characteristics of Oil Spills at Sea,
- Environmental Effects,

- Oil Spill Response Options,
- Dispersant Properties,
- Factors that Affect Dispersant Effectiveness,
- Laboratory Methods for Testing Dispersant Effectiveness,
  - MNS Method
  - Warren Springs Laboratory Method
  - Exxon Dispersant Effectiveness Test
  - Swirling Flask Method
- Comparison of Laboratory Test Methods, and
- Field Dispersant Effectiveness Methods

Materials and Methods (Tasks 3-6)

Modified Swirling Flask Technique (modified SF)

A full description of the swirling flask technique is described in ESD (1997). A description of the modified SF technique used in this project is described below.

Sample Preparation

The entire procedure was carried out in a room refrigerated to 8^{o} C. 120 mL of filtered PWS seawater was measured with a graduated cylinder and added to a 125 mL Erlenmeyer flask. With a plastic tipped micropipette, 100 μL ANS crude oil was added to the surface of the seawater to reach an oil/water ratio of 1:1200. After adding oil to the seawater, the flask was set aside so as not to disturb the distinct circular oil slick that formed on the water surface. The flask was covered with foil and left to stand for a period of between 0 to 72 hours. At the end of this *weathering time,* the dispersant, Corexit 9500, was applied dropwise to the center of the oil slick using a hypodermic needle to establish a dispersant to oil ratio (DOR) of 1:10, 1:20 or 1:50. The fresh oil reacted instantly when adding dispersant while at longer weathering times, the initial dispersion was slower. The oil and dispersant in the flask were allowed to sit undisturbed for a *contact time* of 0, 12, 24 or 48 hours.

Sample Mixing

At the end of the contact time, the flasks were attached to a Zerbach brand rotating table with a 2 cm orbital diameter and rotating speed at 130 rpm. The rotational mixing lasted for 20 minutes, after which the flasks were removed from the table and set aside to settle for 10 minutes to allow droplets to stabilize. A disposable pipette was used to draw 50 mL of the sample from 1 inch below the surface. 10 mL was wasted, and 40 mL was added to a clean 25 mm cuvette.

Fluorometer Setup and Procedure

A Turner Designs Model 10-AU-005-CE Fluorometer was used to measure the extent to which the oil was dispersed in the water. The fluorometer was equipped with a Long Wavelength Oil optical kit (10-302R), and a 25 mm cuvette holder in the sampling chamber. The fluorometer was turned on and left on during the entire project. The calibration protocol in the User's Manual was followed together with a calibration of an unknown standard of approximately 80% of the highest concentration of any sample. The high concentration range setting was used with a span setting of 20% and the fluorometer was set to read raw units. Before every five readings, a blank of filtered PWS seawater was analyzed to control the response drift.

The 25 mm cuvette holding a 40 ml sample was immediately placed in the sampling chamber at the end of the settling time. The fluorometer reading was taken as soon as the reading was stable for 10 seconds.

Wrist Action Shaker Method (modified EXDET)

The wrist action shaker (WAS) method used was based on the EXDET test used by Nalco/Exxon Energy Chemical, L.P. (Clayton *et al*., 1993). The EXDET technique was modified slightly, as described below, to be compatible with the laboratory's existing equipment.

Sample Preparation

The entire procedure was carried out in a room maintained at 8 ^{o}C. 250 mL of filtered Prince William Sound seawater was added to a 250 mL separatory funnel; the 250 mL fill line is approximately the widest point of the funnel. With a plastic tipped micropipette, oil was added to the surface of the seawater to reach an oil to water ratio of 1:1200. After adding oil to the seawater, the funnel was left in place to prevent disturbance of the distinct circular oil slick formed at the center of the water surface. The funnel was covered with foil and allowed to weather for a time of 0, 12, 24, 48 or 72 hours. At the end of the *weathering time*, the dispersant, Corexit 9500, was applied drop-wise to the center of the oil slick with a hypodermic needle to establish a DOR of 1:10, 1:20 or 1:50. The fresh oil reacted instantly when dispersant was added while at long weathering time, the initial dispersion was slower. The oil and dispersant mixture on the surface was allowed to sit undisturbed for a *contact time* of 0, 12, 24 or 48 hours.

Sample Mixing

The funnels were attached to a Burrell Model 75 Wrist Action Shaker at a setting of "1". The funnels were placed such that the water surface was 30 cm above the axis of rotation of the shaker arm and the speed was set to produce a standing wave in the funnel (approximately 4 Hz). A schematic of the experimental set-up is shown in Figure B1 (Appendix B). Vessels were closed with a glass stopper, mixed for 20 minutes and then allowed to settle for 10 minutes to allow droplets to stabilize and to be consistent with procedures used in the modified SF method. Opening the stopcock on the funnel allowed the sample to drain. After the first 20 mL drawn were wasted, 40 mL were collected in a 25 mm clean cuvette.

Fluorometer Setup and Procedure

Fluorometer setup and procedure for the WAS method was identical to that described for the modified SF technique.

Comparison of the two methods

In terms of sample preparation and analysis, the two methods were executed identically. The modified SF technique was generally easy to perform and the method created a small waste volume. The dispersed oil was kept from the sides of the Erlenmeyer flask because of the rotational movement, however, the mixing created in the flask did not seem to represent waves in nature. In the WAS method the wave action was more vigorous, but the oil and dispersant mix left more oil stuck to the sides of the funnel. The funnel set up made it easy to draw a sample from the vessel.

Results and Discussion

Relative impact of the test procedure

The overall objective of this project was to compare the effects of contact time, weathering time and DOR on dispersant effectiveness in Prince William Sound (PWS) seawater at 8 ^{o}C and with Alaska North Slope (ANS) crude oil and Corexit 9500. The long-standing criticism of laboratory methods is that different methods produce different results. To address this potential problem, all tests were repeated using modifications of two common laboratory methods for testing effectiveness. A total of 600 individual tests were run, 300 using each method (i.e., the swirling flask method and wrist action shaker method).

In order to compare the two methods for testing dispersant effectiveness, the net dispersion observed using the modified SF method was plotted vs. the dispersion observed using the WAS method for each test condition (see Figure 1). The SF and WAS methods produced approximately the same result for each test. Each of the 60 points plotted in Figure 1 is the mean of 5 replicates accompanied by the 95% confidence interval. Each point represents one test condition (e.g., DOR 1:10, contact time = 0 hours, weathering time = 0 hours). The best linear fit through all points and passing through (0,0) showed that dispersion in the WAS method was in a 0.9:1 ratio to dispersion observed in the modified SF method. The linear curve was fit with an R^2 of 0.77. A simple quadratic passing through the point (0,0) fit the data slightly better with an R^2 of 0.83. In addition to the test results being consistent, the repeatability of tests was similar. In the modified SF method, one standard deviation was, on average, 18% of the mean for each of 5 test replicates. For the WAS method, one standard deviation was, on average, 20% of the mean of 5 replicates.

In previously published research, the Labofina (a wrist action shaker method), swirling flask, flowing cylinder and MNS methods were compared using a number of different types of oils (Fingas *et al*., 1990). For Prudhoe Bay crude oil and Corexit 9527, the Labofina method produced the highest degree of dispersion for the same conditions used in the other tests. It was found, however, that the variation in test results was a function of the different dispersant to oil ratios, oil to water ratios and settling times required by the different tests. When these factors were corrected for (by modifying the test methods to be consistent), all tests produced roughly the same result for the same oil and dispersant. Only in naturally dispersing oils did the Labofina method produce more dispersion than the swirling flask method.

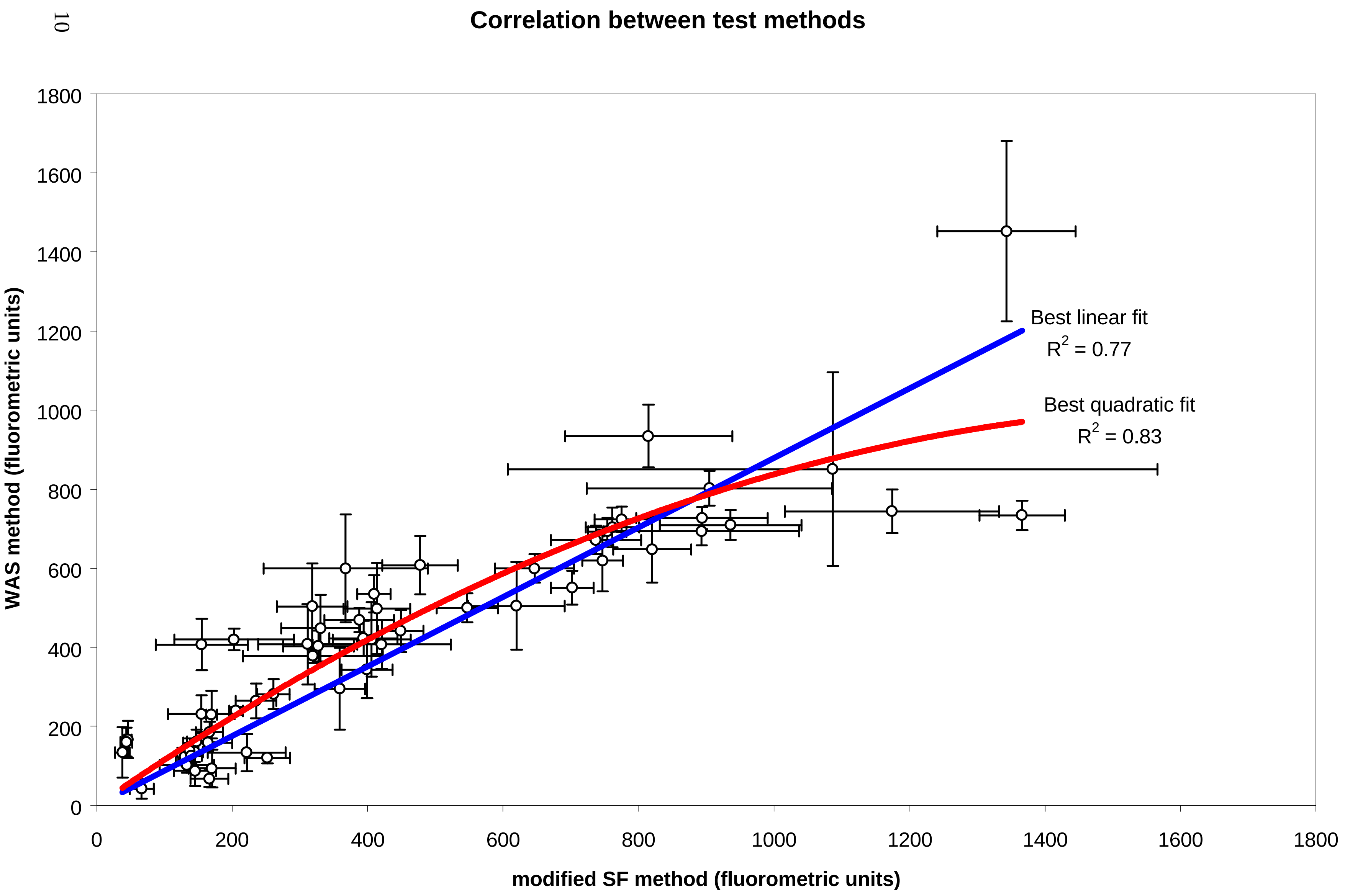

Correlation between test methods
WAS method (fluorometric units)
modified SF method (fluorometric units)
0
200
400
600
800
1000
1200
1400
1600
1800
Best linear fit
R^2 = 0.77
Best quadratic fit
R^2 = 0.83

Figure 1

The results obtained at UAF are consistent with those of Fingas and others (1990). The modified SF and WAS methods were modified to have consistent settling times and oil to water ratios. For the same DOR, ANS crude oil, and Corexit 9500, the results for the two laboratory tests were consistent. This was expected since no natural dispersion was measured in tests without dispersant. Also consistent with Fingas and others (1990), the UAF research found the WAS method to be slightly less reproducible than the modified swirling flask method.

Relative impact of the DOR

For each mixing regimen, three different dispersant to oil ratios (DOR) were used to evaluate the relative benefit to the amount of dispersant applied. In past research, it was shown that when more dispersant was applied, more dispersion was observed as long as the DOR was less than 1:5 (Clayton *et al.*, 1993). If dispersant was applied at a DOR greater than 1:5, no incremental benefit was observed from the added dispersant. It was also shown, however, that at a DOR of less than 1:60 very little dispersion occurred (Fingas *et al.,* 1990). In this research, DORs of 1:50, 1:20 and 1:10 were tested to evaluate the relative benefit to adding more Corexit 9500 dispersant to ANS crude oil in PWS sea water at 8 ^{o}C.

For each test method, 100 tests were conducted for each dispersant to oil ratio. Figure 2 was produced by averaging all tests conducted at a given DOR by a given test protocol. Each point is bracketed by 95% confidence intervals. The best line fit passing through (0,0) for each method had an R^2 of 0.97 or better. This result shows that, on average, the more dispersant, the more effective the application within the range tested. Although the averages of all tests conducted at each DOR were fit well by a linear model, individual results were strongly affected by the contact and weathering times.

Contact and weathering time results

The most important task of this research was to determine the relative effectiveness of dispersants under different application strategies. A matrix style experiment was designed to test the relative dispersion of oil at different DORs, different *weathering times* (time between oil spill and dispersant application) and different *contact times* (time between when the dispersant is added to the oil and the mixing is initiated). The factorial experimental set-up was designed to look at combinations of weathering times of 0, 12, 24, 48 and 72 hours and contact times of 0, 12, 24, and 48 hours at DORs of 1:10, 1:20, 1:50. Results are summarized in Figures 3 and 4. Bar charts of the data for each test conducted are in Figures B2-B11 (Appendix B).

Each plot in Figure 3 represents test results for one DOR from the modified SF method. Three regions appear significant in all three plots. First, the region of highest dispersion coincides with 0 weathering time and contact times greater than 0 hours. This is expected since dispersants are generally most effective prior to oil weathering (Daling *et* al., 1998).

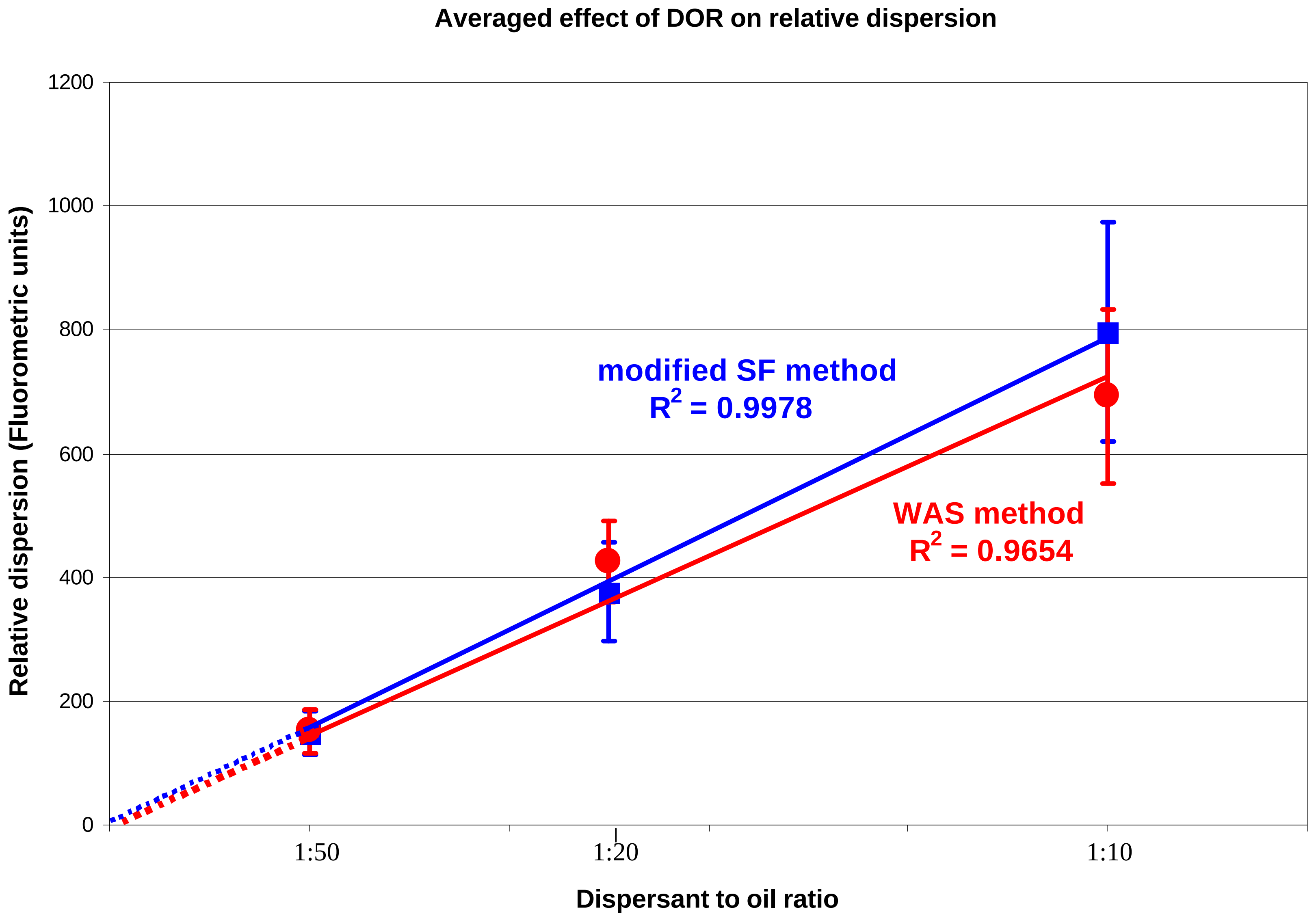
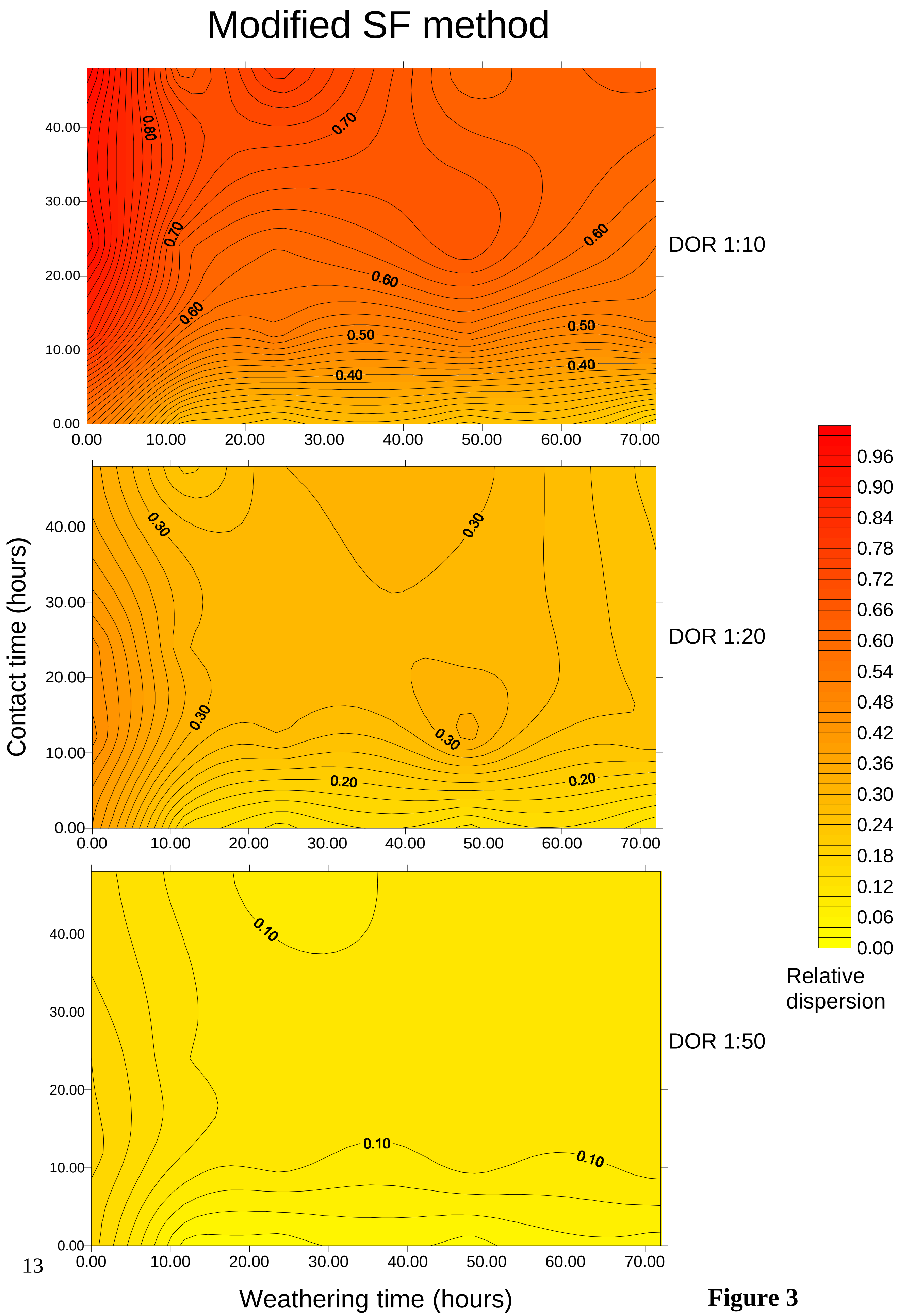

Averaged effect of DOR on relative dispersion
1200
1000
800
600
400
200
0
Relative dispersion (Fluorometric units)
modified SF method
R2 = 0.9978
WAS method
R2 = 0.9654
1:50
1:20
1:10
Dispersant to oil ratio

Figure 2



Modified SF method
DOR 1:10
0.80
0.70
0.70
0.60
0.60
0.60
0.50
0.50
0.40
0.40
DOR 1:20
0.30
0.30
0.30
0.30
0.20
0.20
DOR 1:50
0.10
0.10
0.10
Contact time (hours)
0.00
10.00
20.00
30.00
40.00
Weathering time (hours)
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
0.96
0.90
0.84
0.78
0.72
0.66
0.60
0.54
0.48
0.42
0.36
0.30
0.24
0.18
0.12
0.06
0.00
Relative dispersion

Figure 3

The second notable region in the plots of Figure 3 is that representing the least dispersion. This occurs primarily along the x-axis, or the region corresponding to 0 contact time. This also is expected since the dispersant must spread throughout the oil in order to be effective. Since the dispersant was added to the center of the oil slick, the dispersant and oil are not intimately mixed at first. If mixing occurs at the instant the dispersant is applied, much of the dispersant may pass through the oil and enter the water column, having little dispersing effect on the oil. Minimal dispersion was observed at all weathering times corresponding to a contact time of 0 hours. As the contact time increased, however, so did the oil dispersion.

The third notable region in Figure 3 is the central region, or that representing a weathering time and contact time greater than 12 hours. In this region there were no steep gradients indicating that changes in the contact or weathering time did not significantly effect the dispersant performance.

In the WAS method (Figure 4), a similar result was observed as for the modified SF method. The greatest dispersant effect was observed when the weathering time was 0 hours and the contact time was 24 hours. The least dispersion was observed at the shortest contact time and the longest weathering time.

With the WAS method, the results for DORs of 1:20 and 1:50 were similar to that for a DOR of 1:10. The longer the weathering time, the poorer the dispersant performance. Unlike the results observed at a DOR of 1:10, the results from DORs of 1:20 and 1:50 did not show a maximum dispersion at a 24-hour contact time. With all DORs plotted on the same scale, it is easy to see the relative performance of the dispersant at different DORs. The impact of contact and weathering times at a low DOR (e.g., 1:50) are less pronounced than the dispersion obtained at a DOR of 1:10.

Discussion of fluorometric measurements

The objective of this project was to provide field observers insight into the performance of dispersants in Prince William Sound seawater based on laboratory experiments. Field measurements of oil in water are measured in real time using a flow-through fluorometer. As such, the field decision-maker must interpret raw fluorometric measurements. This research compared the effect of many variables on dispersant effectiveness using fluorometry. Although raw fluorometric measurements are not easily reported as actual concentration of oil, they need not be for the purpose of determining the effects of certain treatments on relative dispersant effectiveness.

Discussion of mixing energy in the laboratory and field

The question of how much mixing energy is delivered to the water in laboratory methods compared to field conditions has received a great deal of attention from engineers and scientists around the world. Many scientists conclude that it is impossible to model field mixing energy in a laboratory vessel. A number of investigators have begun to study the relationship between mixing energy and the size of oil droplets generated in solutions. Recent results suggest that microscale turbulence is an important mechanism for creating dispersed oil droplets in a certain size range in the laboratory as well as the sea (Lunel, 1995). Perhaps the development of oil droplet characterization will allow future laboratory mixing energies to be compared to field mixing energies.

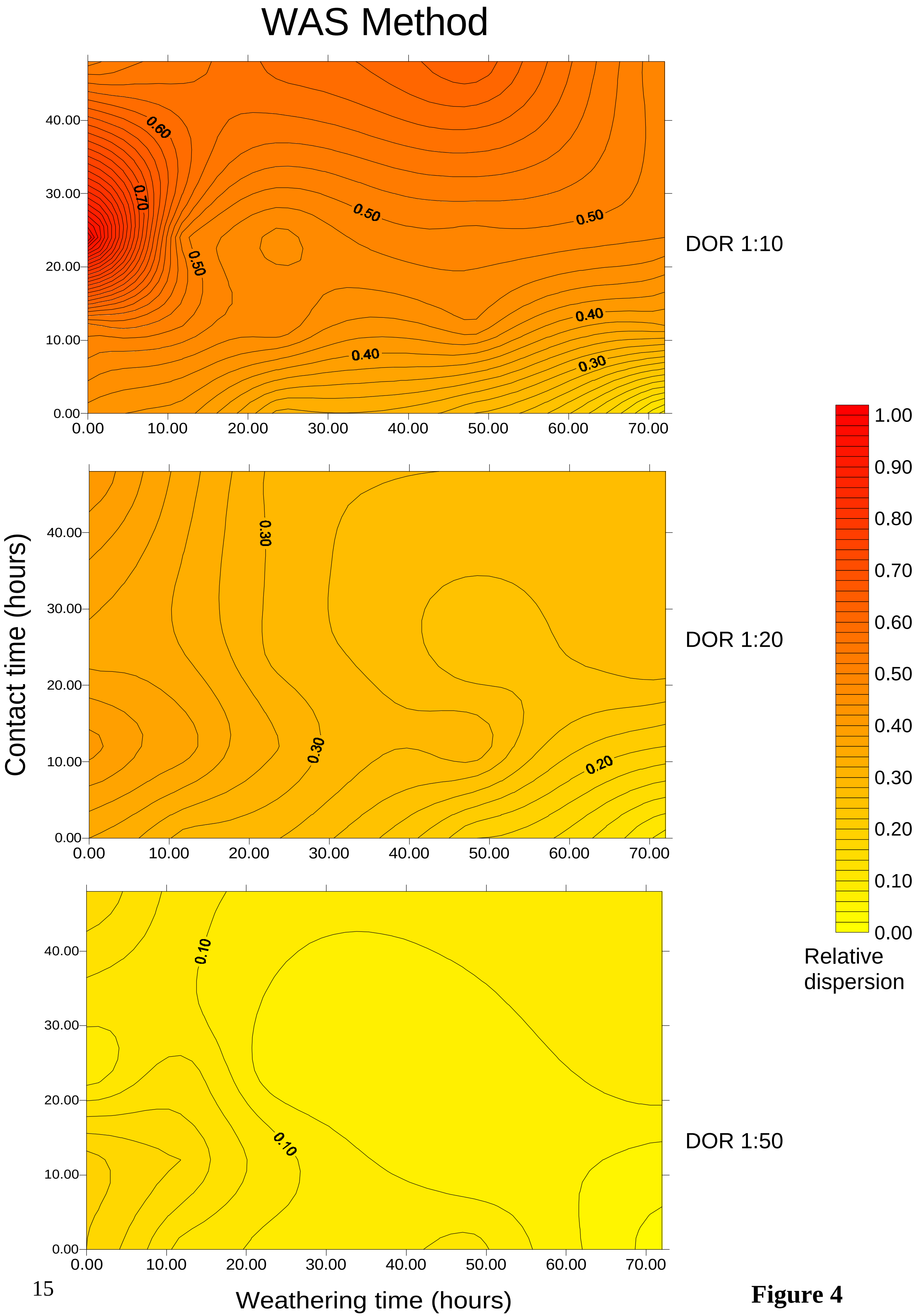

WAS Method
DOR 1:10
DOR 1:20
DOR 1:50
0.60
0.70
0.50
0.50
0.50
0.40
0.40
0.30
0.30
0.30
0.20
0.10
0.10
Contact time (hours)
0.00
10.00
20.00
30.00
40.00
Weathering time (hours)
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
Relative dispersion

Figure 4

Project conclusions

In order to address the results that different laboratory methods produce, all testing was conducted by both the modified SF method and a WAS method. The WAS method was selected since it produces a different mixing regime than the swirling flask method. Results of the two methods tested, however, were similar. The two methods tested produced results in almost a 1:1 ratio for the tests conducted. This result was consistent with previous research (Fingas *et al*.,1990).

Three dispersant to oil (DOR) ratios were tested, 1:10, 1:20 and 1:50. It was found that in most conditions, the dispersant effectiveness was directly proportional to the DOR. For each DOR, dispersant effectiveness was measured at four contact times and five weathering times. The results indicated that in general, the greatest relative dispersion occurred when the weathering time was minimized and the dispersant was allowed to contact the oil prior to the onset of mixing.

The two methods tested produced roughly the same results. If one method were to be used in the future, it is suggested that the modified swirling flask method be used. The method produced slightly less variability, is somewhat simpler to set-up and run, and produced less waste.

Literature Cited

Clayton, J.R., J.R. Payne, and J. S. Farlow, 1993. Oil Spill Dispersants, Mechanical Action and Laboratory Tests., CK Smoley, Boca Raton, FL.

Daling, P.S., P.J. Brandvik and M. Reed, 1998. “Dispersant Experience in Norway: Dispersant Effectiveness, Monitoring and Fate of Dispersed Oil”, In, B. K. Trudel (ed.), Proceedings of the conference: Dispersant Application in Alaska: A technical update,” Anchorage, Alaska, March 1998, Prince William Sound Oil Spill Recovery Inst., Alaska.

ESD, 1997, “Standard Method for Dispersant Effectiveness Testing by the Swirl Flask Procedure”, Environment Canada.

Fingas, M.F., B. Kolokowski, and E.J. Tennyson, 1990. “Study of Oil Spill Dispersants Effectiveness and Physical Studies. In: Proceedings of the Thirteenth Arctic Marine Oil Spill Program Technical Seminar, Edmonton, Alberta, Environment Canada, Ottawa, Ontario, pp. 265-287.

Lunel, T., 1995. “Creating an appropriate energy regime in laboratory dispersant effectiveness tests”, In: Scientific and Environmental Associates, Inc. (eds). Workshop Proceedings: The use of chemical countermeasures product data for oil spill planning and response, Vol. II, April 4-6, Leesburg, VA, pp. 83-182.

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APPENDIX A: Literature Review (Tasks 1 and 2)

Oil Spills at Sea

Consumption and transportation of petroleum products around the world has created the potential for spills of oil or its by-products into the environment. Ocean going tankers are the most common means of transporting crude oil from producers to consumers. The oil spills of Torrey Canyon in England and the Exxon Valdez in Alaska, are two examples of oil spills at sea caused by tanker accidents. Although many spills of petroleum are crude oil, other incidents involve the release of crude oil by-products such as diesel, bunker, and jet fuel. The spill of Bunker C fuel from the Kuroshima in Alaska is a recent example of such a spill.

Offshore drilling and production platforms are another potential source of oil spills at sea. Although technological advances have reduced the potential release of oil from these activities, the largest oil spill at sea is attributed to a blowout incident from the Ixtoc Offshore Platform in the Gulf of Mexico in 1979 and 1980. This incident reportedly released 3.1 million barrels of oil into the Gulf of Mexico (NRC, 1989). Human error is considered to be the most common cause of oil spills. For example, the Exxon Valdez oil spill incident could have been prevented by better judgement by the tanker captain. Human error is also suspected to have been a factor in the recent Kuroshima spill in Alaska

Characteristics of Oil Spills at Sea

Oil spills at sea can affect the water surface column, sediments, and shorelines. The water surface is affected due to the presence of an oil film. Oil initially forms a slick at the water surface due to its immiscibility. Water and wind actions disrupt the oil/water interface, resulting in the formation of oil droplets that enter the water column. Sinking of heavier hydrocarbons can impact the bottom sediments. Oil carried onshore by tides can impact the shorelines.

Spills at sea may spread tens or hundreds of miles from their original spill locations. Often, they may even impact land by being washed on shore by tides. For instance, the oil slick from the Exxon Valdez reached Kodiak Island in Alaska, which is hundreds of miles away from the spill site. Oil spills at sea will more likely spread over a large area if a quick response is not initiated. Oil spills at sea can occur in remote locations making response efforts more challenging. Hence, careful spill response planning and preparedness are essential for successful response to oil spills at sea.

Environmental Effects

Oil spills at sea can also impact marine life, especially sea mammals, which spend a considerable amount of time near the water surface. Marine mammals can be affected both internally and externally. Oil can adhere to the coat of fur-bearing sea mammals resulting in the loss of their furs insulating qualities. In cold waters, this could lead to severe problem for these animals, including fatalities. Oil toxicity is another factor that may affect the internal organs of sea mammals.

The effects of oil spills on birds can be as detrimental as they are on sea mammals. Seabirds coated with oil can be thermally affected and can carry the contamination to their nest, which may also effect their broods.

Oil Spill Response Options

In general, there are three major response options for cleanup of oil spills at sea: mechanical response, in-situ burning, and the use of chemical dispersants (NRC, 1989). Since there are laws that mandate cleanup of spilled oil, natural attenuation is not an option.

Mechanical recovery is a cleaning process that involves efforts to physically remove the oil from the water. This cleanup method is the most socially acceptable response to oil spill incidents. Mechanical recovery requires the deployment of booms for containment and diversion. Skimmers, floating pumps, and sorbent booms and pads are used for the removal of the oil from the water surface. High-pressure water and air jets may also be used to divert or “herd” the spilled oil to the desired locations. The success of the mechanical response to oil spills, however, can depend on water conditions (rough seas) and the quantity of the oil spilled. Rough seas can make it difficult or impossible to operate response vessels. Large oil spills may need mobilization of numerous response vessels, which could be a limiting factor during the initial stages of an oil spill response.

In-situ burning of oil is a partial cleanup process during which only part of the oil is burned or vaporized. The portion of oil that is neither burned nor vaporized remains in the water as oil or residue. In-situ burning of spilled oil amounts to transforming and transferring the pollution from water to air. This method of response may require the spilled oil to be herded by fire booms so that a sufficient thickness of oil is available for successful burning (Clayton *et al.*, 1993). Rough seas, therefore, may pose a challenge to this endeavor.

The application of chemical dispersants is an oil response option intended to enhance the dilution of the oil in the water column. Dispersants reduce the interfacial tension the between oil and water. The reduced interfacial tension results in bonding between the water and oil molecules and the formation of small oil droplets. As small oil droplets are formed, they separate from the oil slick on the water surface and disperse into the water column. Dispersed oil droplets have high surface area and are more amenable to biodegradation.

The application of dispersants can be planned and implemented in a shorter time than it would take to recover oil by mechanical means. Although rough seas and big waves could be limiting factors in mechanical recovery and in-situ burning, these conditions can improve dispersant effectiveness. Choppy seas provide mixing energy for the dispersant-oil mixture. The wave energy provides a favorable contact and mixing environment between the oil, dispersant, and water.

The first major spill to which dispersants were applied was the Torrey Canyon spill off the southwest coast of England in 1967. In that spill, 11 million liters of dispersants were applied to about 1 million barrels of spilled oil. The liberal use of dispersants on the water surface, and the impacted shorelines resulted in extensive ecological damage. Although large quantities of dispersant were used in that incident, large quantities of oil remained undispersed (Environment Canada, 1997). Since then, extensive research has been conducted in manufacturing dispersants that are substantially less toxic. In addition, many laboratory test methods have been developed for determining the effectiveness of different dispersants on different types of oil. There have also been a number of field studies to investigate the effectiveness of dispersants on spilled oil. The Beaufort Sea dispersant trial is an example of such efforts (Swiss, 1988).

Dispersant Properties

Dispersants are chemicals that assist in the breaking down of oil into small droplets, which are mixed in the upper layer of the water column. They also prevent the oil droplets from coalescing and reforming an oil slick (NRC, 1989). Oil spilled in warm water spreads to a thin layer, with a thickness of about 0.1 mm, in a relatively short time. It is estimated that a 1000-barrel oil spill can cover an area of about 0.6 square miles. In colder climates the oil layer may be somewhat thicker (Canevari *et al*., 1986). It has been estimated that dispersing a 0.1 mm thick oil slick within the top one meter of water would produce a petroleum hydrocarbon concentration of about 100 parts per million (ppm). The oil concentration would drop to 10 ppm, if the dispersed oil droplets were mixed in the top 10 meters of the water column (Canevari *et al*., 1986).

Dispersants are generally a mixture of three components: surfactant, solvents, and additives. The surfactant portion is the most important component of a dispersant. The surfactant molecules consist of a water-soluble (hydrophilic) portion and an oil-soluble (lipophilic) portion. The molecular structure of a dispersant is such that when it is introduced into a petroleum-water mixture, the molecules align themselves so that the hydrophilic segment of the molecule is dissolved in the water and the lipophilic segment is dissolved in the oil. The solubility of surfactant in both oil and water phases tends to reduce the interfacial surface tension between these two phases, and therefore, enhance the dispersion of oil in water (Brochu *et al*., 1987). The hydrophilic quality of dispersed oil will also reduce the possibility of these small droplets from adhering to solid surfaces, such as sediments or rocks. Solvents are mainly used to dissolve the surfactant and additives and enhance the ability to apply a dispersant uniformly on an oil spill. One of the reasons for including additives in dispersants is to enhance the biodegradability of the dispersed oil. Typical solvents could be water, water-soluble hydroxyl compounds, or hydrocarbon solvents with low aromatic content. (Brochu *et al*., 1987; Fingas, 1991).

The dispersants' solubility in an oil-water mixture depends on the specific molecular structure of the surfactant. Hydrophilic-lipophilic balance (HLB) is a parameter that is used to characterize the solubility of dispersants (Fingas and Tennyson, 1991; Griffin, 1954). HLB values range from 1 to 20 and describe the tendency of the non-ionic surfactant to dissolve in either oil or water based on its chemical structure. Surfactants with an HLB of between 1 and 8 have a higher tendency to dissolve in oil, and surfactants with an HLB of between 12 and 20 have a tendency to dissolve in water. For example, a surfactant with an HLB of 4 is lipophilic and has the tendency to form water-in-oil emulsions. A surfactant with an HLB of 15 is hydrophilic and has the tendency to from oil-in-water emulsions (Fingas and Tennyson, 1991).

Factors that Affect Dispersant Effectiveness

Although HLB is an important criterion in selecting a dispersant, other factors such as water temperature, salinity, mixing energy and oil properties are a few other important parameters which can also impact the effectiveness of a dispersant.

Temperature

Temperature impacts the effectiveness of dispersants. Lower water temperatures increase the viscosity of both the oil and the dispersant. As oil gets more viscous due to low water temperature or weathering, the energy requirement for mixing the dispersant and oil also increases (Clayton *et al*., 1993). In the Arctic and the subarctic regions, this would be the most likely scenario. Clayton *et al*., (1993) states that some dispersants that contain ethoxylated surfactants are more soluble at lower temperatures.

Higher water temperatures usually increase the solubility of dispersants in water. Higher water temperatures will also affect the spilled oil temperature. Rising oil temperatures can reduce oil viscosity and, hence, improve dispersion. At low temperatures, dispersants may not be readily mixed with viscous oils (Clayton *et* al., 1993).

Mackay *et al*. (1980), Byford *et al*. (1983), Lenthinen and Vesala (1984), and Fingas *et al.* (1991) conducted studies on the impact of water temperature on the effectiveness of dispersants on spilled oil. Studies conducted by Mackay *et al*. (1980) and Fingas *et* al. (1991) indicated an increase in dispersion with an increase in temperature. The experiments of Mackay *et* al. (1980) involved tests at various temperatures and in the presence of ice mixed with Alberta crude oil (Clayton *et* al., 1993).

Based on the literature indicated above, there have been conflicting results in the trend of dispersant effectiveness with either increasing or decreasing water temperature. Experimental results from studies performed by Lenthinen and Vesala (1984) and Byford and others (1983) varied from those conducted by Mackay and others (1980) and Fingas and others (1991). Byford and others (1983) conducted studies on the effectiveness of dispersants at conditions that might represent those encountered in the Arctic and subarctic environment. Byford and others (1983) performed tests at low temperatures with low energy input. These experiments were performed using the Labofina rotating flask test. The experimental results indicated that a decrease in temperature from 10 °C to O °C generally resulted in a slight increase in the degree of dispersion. Similar experiments by Byford *et* al. (1994) indicated better dispersion at 20 °C than 0°C (Clayton *et* al., 1993).

Salinity

In general, increasing salinity will decrease the solubility of dispersants in water resulting in more surfactant being available to interact and mix with the oil. Experimental studies have demonstrated a general increase in dispersant effectiveness with increasing salinity (Clayton *et* al., 1993).

Byford and others (1983) performed tests to determine the effect of salinity on dispersant effectiveness under low temperatures and low energy conditions using the Labofina rotating flask test method. These tests were conducted using seven different dispersants and two types of crude oil. The test conditions were such to simulate those commonly found in the Arctic environment. Experimental results indicated an overall increase in dispersion with an increase in salinity in five of the dispersants tested. The tests on the other two dispersants either showed no significant increase or no increase at all in dispersion with increased salinity (Clayton *et al*., 1993).

Fingas and others (1991) studied the role of salinity on the effectiveness of three dispersants on three types of crude oil using the swirling flask test method. These tests showed an increase in dispersion with an increase in salinity from 0 to 45 parts per thousand (ppt). A decline in dispersion was observed at salinities greater than 45 ppt (Clayton *et al*., 1993). A water salinity of 45 ppt is higher than those found in all oceans, as such, it appears that this study was conducted to determine if dispersant effectiveness continues to increase with increasing water salinity.

Mixing Energy

After dispersants have been added to the oil at sea and after small oil droplets have formed, mixing energy is required to further disperse these small droplets in the water column. Further dispersion of oil droplets will reduce the concentration of petroleum hydrocarbons to levels not believed to cause environmental damage. In order for the dispersion process to be successful, oil droplets must stay submerged in the upper layer of the water column and not return to the surface to form an oil slick. As reported by Clayton and others (1993), the application of dispersants reduces the interfacial tension between oil and water, which results in the formation of oil droplets. Actual dispersion of oil in the water column depends on mixing energy provided by wave action at sea.

Clayton and others (1993) report that experimental studies performed by a number of scientists indicated that the sizes of the oil droplets are inversely related to the amount of mixing energy input into test vessels (Delvigne, 1987; 1989). Jasper and others (1978) conducted experiments that indicated dispersion reduces the size of the oil droplets. Smaller oil droplets are less likely to coalesce and are more likely to biodegrade. Therefore, it is reasonable to assume that a choppy or rough sea would be preferred over a calm sea-state during dispersant application. It should be noted, however, that windy conditions might make aerial spraying of dispersants difficult since some of the dispersants may not land on the areas targeted for dispersant application (Clayton *et al*., 1993). The correlation between the mixing energy in the laboratory and the mixing in the ocean is a question that has been discussed for many years. Laboratory tests are often not designed for field conditions and the trend has been to use smaller test vessels, which create less waste and allow multiple tests in a short time period. When it comes to comparing mixing in the laboratory to ocean mixing, recent research suggests that the microscale turbulence plays an important roll in creating dispersed oil droplets in a certain size range in the solution (Lunel, 1995). Research in process also attempts to measure the turbulent energy of mixing in physical units (Fingas, 1998).

Oil Properties

Oil properties play an important role in the degree of dispersant effectiveness. Oil properties that have the most pronounced effect in the selection of dispersants are viscosity, pour point, boiling point, and surface tension.

Crude oils that have low viscosity generally disperse easier and require less input energy than high viscosity oils. The pour point of crude oil is the lowest temperature at which oil stops flowing (Environment Canada, 1997). After a spill incident, crude oil will lose its lower molecular weight compounds due to evaporation. The higher molecular weight compounds, which do not readily evaporate, have a higher pour point. When the water temperature is lower than the pour point of oil, the oil will demonstrate solid characteristics (Environment Canada, 1997).

Surface tension is the force that attracts molecules at a liquid's surface. The lower the surface tension, the weaker the attracting forces, and the easier the liquid will spread (Environment Canada, 1997). Dispersants reduce the oil-water interfacial tension and thus promote the break down of the oil slicks.

Laboratory Methods for Testing Dispersant Effectiveness

Fingas (1991) reports that there are about fifty different laboratory test methods available for determining the effectiveness of dispersants on oil. The laboratory tests can be categorized into four general groups: tank tests, rotating flask tests, interfacial surface tension tests, and flume tests (Clayton *et al*., 1993).

The tank tests usually require a large volume of water. The EPA tank test method requires a 130-liter stainless steel tank. The Mackay-Nadeau-Steelman (MNS) method is another example of the tank test method. A description of the MNS tank test method is provided in Mackay and Szeto (1981), Mackay and others (1984), Clayton and others (1993), and NRC (1989). The MNS method requires 6 liters of water in a 20-liter closed-glass vessel.

Examples for the rotating flask method are the Warren Spring Laboratory (WSL) test method, the swirling flask test method, and the Exxon dispersant effectiveness test method. All three tests in this category involve shaking or rotating flasks containing oil, water, and dispersants. The sizes of laboratory vessels used in these experiments are 250 ml, 125 ml, and 250 ml, respectively. The WSL method and the swirling flask test method are two of the most common laboratory methods used to determine the effectiveness of dispersants on oils. The WSL method is a modified version of the Labofina test method (Martinelli, 1984). Environment Canada developed the swirling flask test method. A description of this method is listed in Fingas and others (1991).

The interfacial surface tension tests measure the dispersant critical micelle concentration (CMC) and reductions in the oil-water interfacial surface tension. Micelles are surfactant molecules arranged with the hydrophobic portion of the molecules facing inward and the hydrophilic portions facing outward, towards the aqueous phase. Above the CMC level additional surfactant molecules will form new micelle (NRC, 1989). The drop-weight test is the most common test method in this category.

The drop-weight test is a method that determines the effectiveness of a dispersants based on measurements of the oil-water interfacial surface tension (Rewick *et al*., 1984). This test requires adding oil drops to a premixed dispersant-water solution placed in a 20 cc serum vial. The amount of the oil added is measured by weighting the syringe that contains oil before and after adding oil drops to the dispersant-water mixture. This test is carried out at different dispersant concentrations varying from 0 to 100 ppm. Dispersant concentrations are then plotted against the weight of oil drops needed to create a CMC curve. The weights of the oil drops are then calculated at 0 ppm and the CMC concentration. This method can be used to determine the lowest dispersant concentration at which complete surface coverage of the oil and water interface can be achieved (Clayton *et al*., 1993).

The flume test methods involve flow or movement of water in the testing vessel. The cascading weir test described by Mackay and others (1984) and the Delft hydraulics test are both flume test methods. The flume tests, especially the Delft hydraulics method, use specialized equipment, which may require specifically trained technicians. For instance, this method requires a laser doppler velocity meter and a particle sizer (Clayton *et al*., 1993). A more detailed description of the cascading weir test will be presented in the following pages.

Details of Specific Tests

MNS Method

The MNS test method requires a closed-glass vessel placed in a temperature controlled water bath. The oil and dispersant are added to the system through individual ports on the lid of the glass vessel. There are a total of six ports on the lid of the apparatus. These ports allow for immersion of a thermometer into the water, flow of an air stream into the system, collection of oil samples, exhaust of excess air, and the addition of oil and dispersant into the system. The oil and dispersants are added to the surface of the water through a plunger-shaped containment ring. The containment ring prevents the spreading of oil over the water surface before dispersants are added to the oil. This procedure was adopted to allow better reproducibility of the oil slick on the water surface (Mackay and Szeto, 1981; Mackay *et al*., 1984).

The MNS system requires the addition of six liters of water into the test vessel. The tests are conducted at specified temperature and salinity. The air valve is then turned on, allowing airflow into the system. Adjusting the pressure drop across an orifice plate that is designed to respond to various energy levels controls the airflow onto the water surface. Oil is added to the system after the wave motion created by airflow has reached a steady state. Oil is added on the surface through a containment ring that is half immersed in the water. The dispersant drops are then added to the oil surface within the containment ring. The ring is removed a minute and half after the dispersant is added to the oil. The system is then allowed to agitate for ten minutes after the containment ring has been lifted from the water. While the air is still flowing through the system, a 500-ml water sample is collected through the designated port. The airflow is then stopped, and after five minutes, another 500-ml water sample is withdrawn from the system. Oil analyses are performed on 20 to 40-ml aliquots that are extracted by methylene chloride (Mackay and Szeto, 1981; Mackay *et al*., 1984).

The MNS tests require six liters of water. This may create a waste disposal obstacle to laboratories that intend to conduct hundreds of such experiments. The apparatus used for this experiment must be custom-made (Mackay *et al*. 1984). Mackay and others (1984) report the occurrence of wave dampening during some of the tests. This phenomenon can result in low dispersant effectiveness due to the reduction of mixing energy input into the system. Increasing the airflow rate, however, may reduce the wave dampening effect. It is also reported that the wave dampening effect could be a function of the apparatus. Similar phenomenon, however, may occur at sea and in the other laboratory methods that use an air stream to provide the required mixing energy. Mackay and others (1984) also report that reducing the mixing time to three minutes will exclude the effects of wave dampening, since most of such phenomenon was observed after three minutes. Byford and Green (1984) list the complexity of the apparatus setup of the MNS test as a disadvantage of this method.

The advantages of the MNS system are its capability to produce waves and turbulence that are similar to actual at-sea conditions. The use of a containment ring allows reproducibility of the oil surface to which the dispersant is added. Byford and Green (1984) have reported that reproducibility of test results from the MNS tests are good and a number of tests can be completed in a day using this method. These authors also report that modifying the orifice plate resulted in good data reproducibility at the British Petroleum Research Centre, Sunbury. Byford and others (1984) also believe that introducing the air stream tangentially spreads the oil into a thin film layer, which would further assist the mixing of the oil and dispersant.

Warren Springs Laboratory Method

The Warren Spring Laboratory test was developed based on a previously developed revolving flask method that was referred to as the Labofina test method. After developing this laboratory method, the Warren Spring Laboratory conducted many sea trials. The laboratory and sea trial indicated a correlation between the two tests. In order to determine the reproducibility of the results, three different laboratories conducted tests using the standardized Warren Spring Laboratory method. The results of that study indicated a generally good reproducibility between the tests at the same laboratory. The results among the three laboratories, however, were not as close (Martinelli, 1984). Byford and Green (1984) report that using 250-ml long flasks that are long and narrow, results in a higher efficiency rating than using shorter, wider flasks. The authors suggest that a better transfer of the mixing energy occurs in the long, narrow flasks. Therefore, they suggest reporting the test vessel dimensions and specifications with the experiment results.

The Warren Spring Laboratory test is performed by adding a total of 0.2 ml of dispersant drop-wise to a measured volume of water with a temperature of 10 °C in a 250-ml conical separating funnel. The volume of seawater used in this experiment is 250 ml. The separating funnel is then rotated about a horizontal axis for 2 minutes at a speed of 33±1 revolutions per minute (rpm). After two minutes of rotation has elapsed, the vessel is allowed to stand for one minute, after which a 50-ml aliquot is removed from the bottom of the funnel. The aliquot is extracted by using chloroform and analyzed by a spectrophotometer. (Martinelli, 1984).

The Warren Spring Laboratory test is very easy to setup and operate. The tests are easy to conduct, and it is possible to perform as many as sixteen tests in a day (Byford and Green, 1984). The correlation of laboratory tests and sea trials have been demonstrated to be good (Martinelli, 1984).

The Warren Spring Laboratory test method requires collecting an oil aliquot after one minute of standing has elapsed. This practice may render the test time-dependent (Byford and Green, 1984). The same authors also report that during some of the tests different amounts of oil adhered to the flask walls, therefore affecting the efficiency rating.

It should be noted that “wall effect” is a phenomenon that may impact the majority of the laboratory test methods. This affect may be more pronounced in tests that utilize smaller volume vessels since there exists a greater opportunity for the oil to come into contact with the testing vessels’ walls.

Exxon Dispersant Effectiveness Test

The Exxon dispersant effectiveness test can be categorized as a shake flask laboratory method. This method, in principal, is similar to the Warren Springs Laboratory test method. The Exxon dispersant effectiveness test procedures involve adding a 1 ml oil-dispersant solution to 250 ml of seawater in a 250-ml separatory funnel. A wrist-action shaker then agitates the separatory funnel for 15 minutes at a pre-determined rate. The energy input creates a one-inch standing wave in the test vessel. After 15 minutes of shaking has elapsed, a square sorbent pad, with a size of 1.5 inches, is placed in the separatory funnel, and the apparatus is allowed be shaken for an additional 5 minutes. The sorbent is expected to adsorb the oil. At the completion of the test, the oil in the water, on the walls inside the vessel, and the sorbent pad are extracted by chloroform. The extracts from this test are then analyzed by a spectrophotometer (Becker *et al.*, 1991; Clayton *et al.*, 1993).

The Exxon dispersant effectiveness test apparatus appears to be relatively low cost to assemble and easy to operate. Another advantage of this test method is the use of a sorbent pad to adsorb the oil that has not been dispersed. This procedure assists in the estimation of the amount of oil dispersed in the water.

The Exxon method requires the extraction of the entire 250 ml of water in the separatory funnel. This practice may more accurately report the quantity of oil dispersed. The disadvantage of the Exxon effectiveness test may be its requirement to perform an additional extraction on the sorbent pad, prolonging the total testing time.

Swirling Flask Method

The swirling flask test is another test method in the shake flask category. The equipment required to perform the swirling flask test is readily available in most laboratories, and the tests are relatively simple to conduct. The swirling flask method was developed by the Environment Canada (Fingas, 1987).

This method is conducted by adding dispersant to the oil on the water surface in a 125-ml Erlenmeyer flask. The Erlenmeyer flask should have a sampling tube that can be used to collect sample aliquots without disturbing the non-dispersed oil on the water surface. A shaking table provides the mixing energy, thus the swirling motion, to the test vessel. The shaking table should have an adjustable rotation rating of up to 150 rpm (Fingas, 1987; Clayton *et al.*, 1993).

The swirling flask test procedures require the addition of 120 ml of seawater to an Erlenmeyer flask. A 0.1 ml of oil-dispersant mixture is then added to the water surface, and mixed for 20 minutes. The mixture is then allowed to settle for 10 minutes, after which a 30-ml aliquot is collected through the Erlenmeyer flask’s side spout. The oil in the sample aliquot is extracted by dichloromethane and quantified spectrophotometrically.

There are two modified versions of the swirling flask test method: one-drop and two-drop versions (Fingas et al., 1991). The one-drop version of the method requires the addition of 100 μl of oil in the middle of the water surface then a 10 μl drop of dispersant is placed in the middle of the oil slick. There are no other changes in the remainder of the test procedure as described above. The two-drop version requires adding the dispersants in two 5-ml drops to the surface of the oil slick. Each of the drops should be added one-third of the diameter into the oil slick on either side. These two methods will enable scientists to investigate the herding effect of a dispersant on an oil slick.

In addition to its simplicity, the swirling flask test method may provide less oil contact with the flask walls since the water moves in a swirling motion. The limitation of this method can be the lack of wave action. This may effect the correlation between laboratory and field results.

Cascading Weir Test

The cascading weir test is categorized as a flume test. This test method requires an 8-m long glass-sided flume with a width of 20 cm, and a water depth of 7 cm. The flume is installed with an incline of 1 in 20 or 1 in 100 (vertical:horizontal). Water flowing down the flume and over weirs is used to simulate wave action. Water is fed to the flume at a steady rate of 300 ml/s. Oil is then discharged at a continuous rate of 10 ml/s over the water surface producing an oil slick that spreads over the entire length of the flume. Dispersant is then sprayed onto to the oil slick at a specified rate, usually at 1 ml/s. The glass-sided flume allows researchers to observe and photograph the oil slick and the effect of the dispersant on it. The oil and dispersant discharge rates could be changed to adjust the dispersant to oil ratio (DOR). By adjusting the oil and dispersant discharge rate, researchers can determine the quantity of non-dispersed oil that is floating on the water surface at the end of the flume. This method allows collection of water samples for determining dispersant effectiveness (Mackay *et al.,* 1984).

The cascading weir test method can be used to determine the effectiveness of spraying dispersants on an oil spill from boats. The glass-sided flume allows visual observation of oil droplet movement in turbulent water (Clayton *et al*., 1993). The continuous water flow and experimental apparatus is such that it can closely simulate mixing at sea.

The equipment needed for this method must be custom-made. This may increase the overall cost of conducting the experiments. Adhesion of oil droplets to the flume walls can be a concern in this method. This concern is due to the total surface area of the apparatus that has the potential to come in contact with the oil. The volume of waste generated can also be a concern if a laboratory intends to conduct hundreds of experiments.

Comparison of Laboratory Test Methods

The rotating flask test methods such as the swirling flask test generally cost less than other laboratory tests. The low operating cost of rotating flask test methods stems from the simple equipment that is need to perform these tests. It is also possible to conduct a number of these tests simultaneously. For instance, the shaker table in the swirling flask test method can easily be used to agitate a number of flasks at the same time. The flume tests, on the other hand, appear to be more complex than other laboratory test methods. They also require more time to complete and obtain results. The complexity of the flume test method is due to the type of equipment used.

Although vessel volume varies considerably among different test methods, the quantity of dispersant required for a test depends on the volume of oil added to the test vessel. As such, the dispersants are used in relatively small quantities; therefore, dispersant volumes are not a significant factor in selecting a laboratory test method. All laboratory test methods listed in this report require relatively small quantities of oil. As such, the volume of oil required for the tests is also not a significant factor in selecting a laboratory test method. The laboratory waste generated depends on the volume of water extracted by a solvent to quantify the amount of dispersed oil. This factor also does not appear to be significant since the difference in the volume of water extracted among different test methods does not appear to vary considerably. The Exxon dispersant test method, however, requires the extraction of the entire 250-ml of the oil-water mixture. The volume of water extracted for this test is considerably more than other test methods. In summary, the rotating flask tests appear to be the simplest methods to assemble and operate. The potential for conducting multiple tests deems the rotating test methods an attractive option for laboratory efficacy testing.

Field Dispersant Effectiveness Methods

The laboratory test methods allow ranking of dispersants on various oils under conditions simulated in the laboratory. The relative effectiveness of a dispersant determined in a laboratory does not necessarily mean that an identical result can be obtained if the dispersants are applied to the same type of oil at sea. One of the factors that limit correlations between laboratory and field tests is the control volume. While a laboratory vessel provides a means to replicate a similar testing environment, exact replication is hard to achieve in field tests. Sea currents may provide different mixing conditions for tests conducted on the same day. Such natural occurrences complicate any meaningful correlation between results from different field tests.

Since oils that are spilled at sea undergo chemical and physical changes, it is crucial that rapid test methods are identified that can be used to determine the effectiveness of a dispersant shortly after a spill has occurred. In addition, it is imperative that field tests are simple to assemble and operate, and easy to transport. The field test methods should be capable of providing results in a relatively short period of time and with an acceptable range of accuracy (Clayton *et al.*, 1993).

The EPA field dispersant effectiveness test, the Mackay simple field test, and the Pelletier field test are a few examples of field dispersant effectiveness tests.

EPA Field Dispersant Effectiveness Test

The apparatus for the EPA field dispersant effectiveness test requires a 0.5-inch test tube, a tape measure or a ruler, a stopwatch, and a flashlight. Initially, using the ruler, a distance of 5 cm from the bottom of the tube is measured and marked. Synthetic seawater is then added to the test tube to the height of 5 cm. This is followed by adding 10 drops of oil and 1 drop of dispersant, sequentially, into the seawater. As such, the oil-drop to dispersant-drop ratio is 10:1. A solid rubber stopper is then placed in the opening of the test tube, and the vessel is agitated in a vertical plane at the rate of 120 cycles with 4-inch strokes. This piston-type agitation is continued for 1 minute, after which, the tube is allowed to stand in a vertical position for 10 minutes. The test tube is then placed on top of the flashlight. The flashlight is fitted with a shield that has an 0.5-inch opaque opening. An O-ring is then slid along the length of the test tube to a point at which the light cannot be seen from the side through the test tube. The distance of the O-ring from the bottom of the test tube is measured (L, cm). This measured distance, L, is plugged into the equation listed below to estimate the efficiency of the dispersant (Clayton *et al*., 1993):

$$D\ (\%) = \{(5 - L)/5\} \times 100 = \text{Percent dispersion}$$

The equipment for this field test method is inexpensive and easy to transport. This method's oil to dispersant ratio, however, is drop-wise rather than volumetric. This may complicate the potential reproducibility of the test results, as the volume of different oil and dispersant drops may vary. Clayton *et al*. (1993) also reports that the intensity of light passing through the oil-water mixture can also be a limiting factor in this method. Diaz (1987) provides a description of the EPA field dispersant effectiveness test.

The EPA field dispersant effectiveness test and other such rapid field tests are intended to provide the On-Scene Coordinators with information regarding potential effectiveness of a dispersant on the spilled oil.

Mackay Simple Field Test

This field test method requires 10 ml of oil collected from the slick. The Mackay simple field test requires a 1-liter standard flask, a 10-ml measuring cylinder, a 1-ml graduated cylinder, and pipettes (Abbott, 1983).

In this field test method, it is important to maintain the water to oil ratio at 10 to 1. Oil-water interface levels are marked on the tape for comparison before and after dispersant applications. One liter of seawater is added to the vessel; 10 ml of oil is then measured with the measuring cylinder and added to the surface of the seawater. One ml of dispersant is added to the oil by a pipette. At this point, the locations of the oil-air, oil-water interfaces are marked on the masking tape; a solid rubber stopper is placed in the flask opening; and the vessel is then allowed to stand for 1 minute. The flask is then turned 140 degrees and kept in that position until the oil and air trapped in the neck of the bottle float to the surface. The bottle is then returned to a vertical position. This routine is repeated 30 times, and at the completion of this procedure, the bottle is returned to a vertical position. Changes in the oil-water interface layer are observed at specified time intervals for 15 minutes. The volume of the oil visually observed in the water after 3 minutes is used to estimate the effectiveness of the dispersant. For instance, observing a 3-ml oil layer in the water after 3 minutes can imply dispersion of 7 ml of oil (Abbott, 1983).

The dispersant performance is estimated by plotting the depth of the oil layer observed in the water as a function of time. The volume of oil remaining in the water after 3 minutes is determined from the plot volume versus time. This value is then used in the following equation to estimate dispersant effectiveness (E) Abbott (1983).

$$E = (10-V)/10.$$

Abbott (1983) reports that the test procedure for this method has been tested in a laboratory with oil and dispersants that have been subject to established test procedures. This author also reports that the results were consistent, indicating that the field test results can be relied upon to give an indication of the potential effectiveness of a dispersant.

This field test method requires moving the oil layer 30 times from one end of the test vessel to the other. This may introduce a potential concern of oil sticking to the wall of the vessel. Overall, this test is easy to perform, and the required equipment can readily be acquired.

Pelletier Screen Test

The Pelletier screen test was developed by Pelletier (1987). This method relies on visual observations for estimating the dispersant effectiveness. The test procedure for this field test method requires the addition of 20 ml of seawater to a 25-ml vial followed by 0.1 ml of oil. The vial is then placed on top of a magnetic stirrer, and the seawater-oil mixture is stirred until a vortex with a depth of 1 cm is created in the mixture. At this point, 0.05 ml of dispersant is added to the middle of the vortex with a syringe, and the stirring rate is increased to 2000 rpm for 1 minute. The vial is then allowed to stand for 1 minute. The performance of the dispersant is visually estimated and categorized in a range from complete dispersion that is denoted as A to no dispersion that is denoted as E (Clayton *et al*., 1993).

The Pelletier screen test relies on visual observation to estimate and categorize the extent of dispersion. As such, the test depends on the judgment of the observer, which renders the dispersion estimates subjective. This test, however, is easy and quick to perform.

In-situ Field Tests of Dispersants Effectiveness

Fingas (1991) reports that there were 107 test spills within 12 years prior to 1991. The purpose of these tests was to study the effectiveness of dispersants on oil spills. Out of the 107 spills indicated above, 23 were control spills. The range of the claimed dispersant effectiveness, for the 25 spills that reported such values, is between 0-100 percent, with an average of about 30%. The dispersant effectiveness, in the majority of the tests, was determined by measuring the oil concentration in the water column and comparing it with the concentration in the oil slick. There is no defined correlation between the oil slick and undercurrent movement, which is the major limitation of this approach. One of the methods that has been investigated for determining the dispersant effectiveness in water is the use of remote sensing (Goodman and MacNeill, 1984). The remote sensing equipment, using either ultraviolet or infrared sensors, can be mounted on a helicopter or an airplane to track the movement of oil slicks.

Since remote sensing may not provide information pertaining to the oil slick's depth, collecting and analyzing water samples is still an integral part of determining dispersant effectiveness. Clayton and others (1993) cite a few concerns with field dispersant trials. The limitations of field dispersant tests are that most field tests involve minor spills. Rapid dissipation of oil in minor spills limits the opportunity to observe dispersion phenomenon over a prolonged period of time. Obtaining surface and subsurface samples that correlate is difficult. Clayton and others (1993) also point out that most field dispersant effectiveness tests calculate the dispersant-oil ratio by using the total amount of oil spilled. More accurate estimates would be obtained if it were practical to use the actual amount of oil that was sprayed with dispersant. In general, it is expensive to stage and conduct field dispersant effectiveness tests. The following is an example of a field dispersant trial in the Canadian Arctic.

Beaufort Sea Dispersant Effectiveness Testing

Swiss and Vanderkooy (1988) described the details of the Beaufort Sea dispersant effectiveness trial that was conducted in 1986. The purpose of the field test was to simulate, as realistically as possible, the dispersant applications at sea. One of the goals of the field test was to reapply dispersants to the oil slicks that did not disperse during the first stage of dispersant application. The other goal of the project was to formulate the most effective operational procedures for applying dispersant during oil spills.

The field test was conducted in open seas, where water depth was approximately 20 m and distance to shoreline was 40 km. The oil used in this trial was Alberta Sweet mixed blend, which was weathered to remove 15-20% of its volume. Exxon's CRX-8LT and British Petroleum Enersperse 700 were the two types of dispersant used. The field tests involved releasing 10 cubic meters (m^3) of oil at four different locations with 2.5 m^3 of oil at each location. One of the oil slicks was used as a control and no dispersant was sprayed on it (C). The second oil slick (C1) was sprayed only once with Enersperse 700, with an oil to dispersant ratio of 10 to 1. At this ratio, it was determined that 250 liters of dispersant was required to completely spray the oil slick. Since it had been determined that not all the dispersant would land on the oil slick, 416 liters of dispersant was applied to ensure complete coverage of the slick. Over all, 2,536 liters of dispersants was added to the oil slicks with dispersant to oil ratios ranging from 1:2.5 to 1:10. The third oil slick (T1) was sprayed 3 times with Enersperse 700. The fourth oil slick (T2) was sprayed three 3 times with CRX-8LT.

Spills T1 and T2 were monitored by an aircraft equipped with remote sensing equipment. Areas of the slick that appeared to have thick oil lenses were sprayed twice more at intervals ranging from half an hour to an hour. An aircraft equipped with remote sensing equipment using infrared imagery monitored the effectiveness of the dispersants. The effectiveness of the dispersants was evaluated by dispersion of oil lenses with a thickness of greater than 100 μm. The test procedures also called for analyzing subsurface water samples with a towed fluorometer. Due to damage to the fluorometer, however, no subsurface samples were analyzed.

The list of equipment utilized for this test was extensive: two marine vessels, two helicopters, and two aircraft. The oil was released from one of the ships and the other ship was used as a visual observation platform. The dispersants were sprayed by helicopter. The other helicopter was also used for command, photography, and regulatory purposes. The two aircraft were used for infrared and ultraviolet remote sensing of the oil slick.

The results from this study indicated that there was not a significant difference between dispersion rate of the control spill, and the slicks that were sprayed. In fact, it was reported that sprayed slicks did not dissipate as quickly as the control slick. As noted by Swiss and Vanderkooy (1988) it is imperative that remote sensing of spill dispersion be coupled with the collection of subsurface water samples. Interpretation of data collected 48 hours into the spill, however, indicates all four slicks had lost over 90% of their surface area. It should be noted that the cost of this field trial was $ 636,000 Canadian.

Comparison of laboratory test methods to actual field test methods

It is reasonable to expect laboratory results conducted by the same laboratory to be similar. For instance, Martinelli (1984) reports that tests were conducted at three laboratories using the WSL method. The comparison of interlaboratory results indicated reproducibility in the range of ±5% and ±10%. Intralaboratory results, however, were not as close as those obtained in interlaboratory analysis.

The laboratory tests are intended to determine the relative effectiveness of dispersants on different types of crude under known conditions. The laboratory tests can be used to rank the dispersants based on their effectiveness under the condition that the tests were performed. The results obtained from laboratory tests are no indication that the same results will be obtained if the same dispersants were used at sea on the same oil. The laboratory tests provide a better understanding of what actually takes place at sea when dispersants are sprayed on oil (Cormack, 1987).

Although considerable effort has been placed on simulating field conditions in the laboratory, the actual water currents, wave action, and dilution that takes place at sea are nearly impossible to replicate. The laboratory tests provide an opportunity to conduct tests at a fraction of the cost that it would take to conduct the tests at sea. The laboratory tests also provide an opportunity to study such factors such as the effect of dispersants' droplet-size or oil viscosity on the overall effectiveness of the dispersants. The small scale of the laboratory tests is ideal for controlling the factors that are the focus of the research.

The advantage of field tests is the opportunity they provide for observing actual oil dispersion at sea. These tests can demonstrate how oil disperses in the water column. Surface and subsurface currents at sea can move independent of each other; because of this the dispersion that occurs at sea is challenging to replicate in the laboratory. Such field observations enable the scientist to design the laboratory methods so that the test methods more realistically simulate the actual phenomenon that takes place at sea. Field tests can also assist the response teams in fine-tuning their dispersant application method so that it is as effective as it can be. For instance, field tests can aid in estimating or determining the number of times an oil slick should be sprayed so that it is completely dispersed (Swiss and Vanderkooy, 1988).

In summary, laboratory tests are practical and cost-effective tools for determining which dispersant is most efficient on crude oil under controlled conditions. Laboratory tests can be planned so that the effects of physical and chemical factors such as oil viscosity and oil composition on the effectiveness of the dispersants can be studied. It is impractical, if not impossible, to conduct such studies at sea. Field tests, on the other hand, provide an insight into what actually happens when dispersants are applied to oil slicks at sea. Field tests are expensive; therefore, they require extensive planning.

Laboratory tests are generally simple to conduct after the apparatus has been set up, and they offer the opportunity to conduct numerous tests at a fraction of the cost of field tests.

References cited in literature review

Abbott, F.S. 1983. A simple field effectiveness test for dispersion. Spill Technology Newsletter, September-October 1983. Environment Canada.

Brochu, C., E. Pelletier, G. Caron, and J.E. Desnoyers. 1986-1987. Dispersion of crude oil in seawater: The role of synthetic surfactants. Oil & Chemical Pollution. Vol. 3. Pp. 257-279.

Byford, D.C., P.J. Green, and A. Lewis. 1983. Factors influencing the performance and selection of low-temperature dispersants. Proceedings sixth Arctic Marine oil spill Program Technical Seminar, 14-16 June 1983. Edmonton, Alberta, Canada. Environmental Protection Service, Environment Canada. Pp. 140-150.

Byford, D.C., and P.J. Green. 1984. A view of the Mackay and Labofina laboratory tests for assessing dispersant effectiveness with regard to performance at sea. In oil Spill Chemical Dispersants: Research, Experience, and Recommendations. T.E. Allen ed. American Society of Testing and Materials. STP 840. Philadelphia, PA. p. 69-86.

Canevari, G.P., J.P. Fraser, S.A. Horn, L.J. Kazemireczak, A.H. Lasday, W.R. Leek, G.P. Lindblom, C.D. MacAuliffe and J.L. Siva. 1986. The Role of Chemical Dispersants in Oil Spill Control. Americam Petroleum Institute. Pp. vii

Clayton, J.R., J.R. Payne, and J. S. Farlow, 1993. EPA Technical Project Monitor. Oil Spill Dispersants, Mechanical Action and Laboratory Tests. pp.5, 42-3, 55-87.

Cormack, D.B., W.J. Lynch, and D.B. Dowsett. 1986/1987. Evaluation of dispersant effectivness. Oil & Chemical Pollution. Vol. 3, Pp. 87-103

Delvigne, G.A.L.. 1987. Droplet size distribution of naturally dispersed oil. In: Fate and Effects of Oil in Marine Ecosystems. Kupier, J. and W.J. Van den Brink, eds., Martinus Nijhoff Publishers, Dordrecht, The Netherlands. Pp. 29-40.

Delvigne, G.A.L.. 1989. Measurements of natural dispersion. In: Oil Dispersants: New Ecological Approaches, Astm STP 1018. Flaherty, L.M., ed. American Society for Testing and Materials, Philadelphia, PA. Pp. 194-206.

Diaz, A. 1987. A field dispersant effectiveness test. Final report submitted to Hazardous Waste Engineering Research Laboratory, Office of Research and Development, United States Environmental Protection Agency, Cincinnati, Ohio from Mason & Hanger-Silas Mason Co., Inc. Leonardo, NJ. Report No. EPA/600/2-87/072. 41 pages.

Environment Canada, Environment Emergencies Section. March 1997. Oil Spill Dispersants. 16 pages.

Fingas, M.F., K.A. Hughes, and M.A. Schweitzer. 1987. Dispersant testing at the Environmental Emergencies Technology Division. Proc. Tenth Arctic Marine oil Spill Program Technical Seminar, 9-11, June 1987, Edmonton, Alberta, Canada. Conservation and Protection, Canada. p. 343-356.

Fingas, M., 1988, Dispersant Effectiveness at Sea: A Hypothesis to Explain Current Problems with Effectiveness, In Proceedings of the Eleventh Annual AMOP Technical Seminar, Environment Canada, Ottawa, Ontario, Pp. 455-479, 1988

Fingas, M. 1991. Dispersants: A Review of Effectiveness Measures and Laboratory Physical Studies. In Proceedings of the Alaska RRT Dispersant Workshop, U.S. Minerals Management Service, Anchorage, Alaska. 37 pages

Fingas, M.F. and E.E. Tennyson, 1991. A review of Oil Spill Dispersants and Their Effectiveness, Environment Canada, and the U.S. Mineral Management Service. 78 pages.

Fingas M.F., I. Bier, M. Bobra, and S. Callaghan. 1991. Studies on the physical and chemical behavior of oil and dispersant mixtures. In Proceedings 1991 International Oil Spill Conference, 4-7, March 1991. San Diego, CA. American Petroleum Institute, Washington D.C. Pp. 411-414.

Goodman, R.H. and M.R. MacNeill. 1984. The use of remote sensing in the determination of dispersant effectiveness. In: Oil Spill Chemical Dispersants: Research Experience and Recommendations, ASTM STP 840, T.E. Allen, ed. American Society of Testing and Materials, Philadelphia, PA. pp. 51-55.

Griffin, W.C., “Calculation of HLB values of nonionic surfactants.” Journal of Society of Cosmet. Chemists.

Jasper, W.L., T.J. Kim, and M.P. Wilson. 1978. Drop size distribution in a treated oil-water system. In: Chemical Dispersants for the Control of Oil Spills, ASTM STP 659, L.T. McCarthy, Jr., G.P. Lindblom, and H.F. Walter, eds., American Society for Testing and Materials, Philadelphia, PA. Pp. 203-216.

Lentinen, C.M., and Aino-Maija Vesala. 1984. Effectiveness of oil dispersants at low salinities and low water temperatures. In: Oil Spill Chemical Dispersants, Research Eperince and Recommendatios, ASTM STP 840. (T.E. Allen, ed.) American Society of Testing and Materials, Philadelphoia, PA. Pp. 108-121.

Mackay, D. and F. Szeto. 1981. The Laboratory Determination of Dispersant Effectiveness: Method Development and Results. In Proceedings 1981 Oil Spill

Conference, 2-5 March, 1981. Atlanta, GA. American Petroleum Institute, Washington D.C. pp. 11-17.

Mackay, D., A. Chau. K. Hossain, and M. Bobra. 1984. Measurements and Prediction of the Effectiveness of Oil Spill Chemical Dispersants. In: Oil Spill Chemical Dispersants, Research Experience and Recommendations. American Society of Testing and Materials, Philadelphia, PA. Pp. 38-54.

Martinelli, F.N.. 1984. The Status of Warren Spring Laboratory's Rolling Flask Test. In: Oil Spill Chemical Dispersants, Research Experience an Recommendations, ASTM 840. T.E. Allen, ed., American Society of Testing and Materials, Philadelphia. P. 55-68

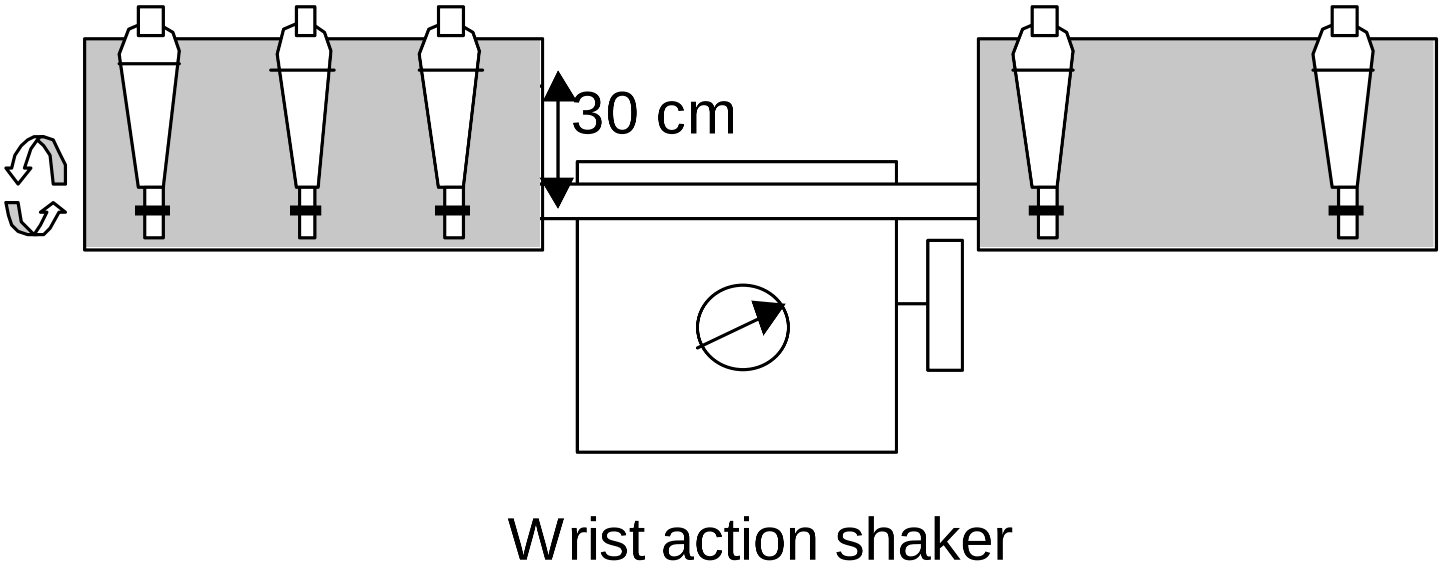
National Research Council. 1989. Using Oil Spill Dispersants on the Sea, National Academy Press, Pp.1. 10, and 28-31, and 70-80.

Pelletier, E.. 1986-1987. Dispersion of crude oil in seawater: The role of synthetic surfactants. Oil & Chemical Pollution, Vol.10. Pp. 631-662.

Rewick, R.R., K.A. Sabo, and J. H. Smith. 1984. The drop-weight interfacial tension method for predicting dispersant performance. In Oil Spill Chemical Dispersants: Research, Experience, and Recommendations, T. E. Allen. ed. STP 840, Philadelphia, PA. American Society of Testing and Methods. p. 94-107.

Swiss, J., and N. Vanderkooy. July 1988. Beaufort Sea Dispersant Trial. Dome Petroleum, Calgary, Canada. Environmental Studies Research Fund Report No. 100. 44 pages.

APPENDIX B: Additional Figures



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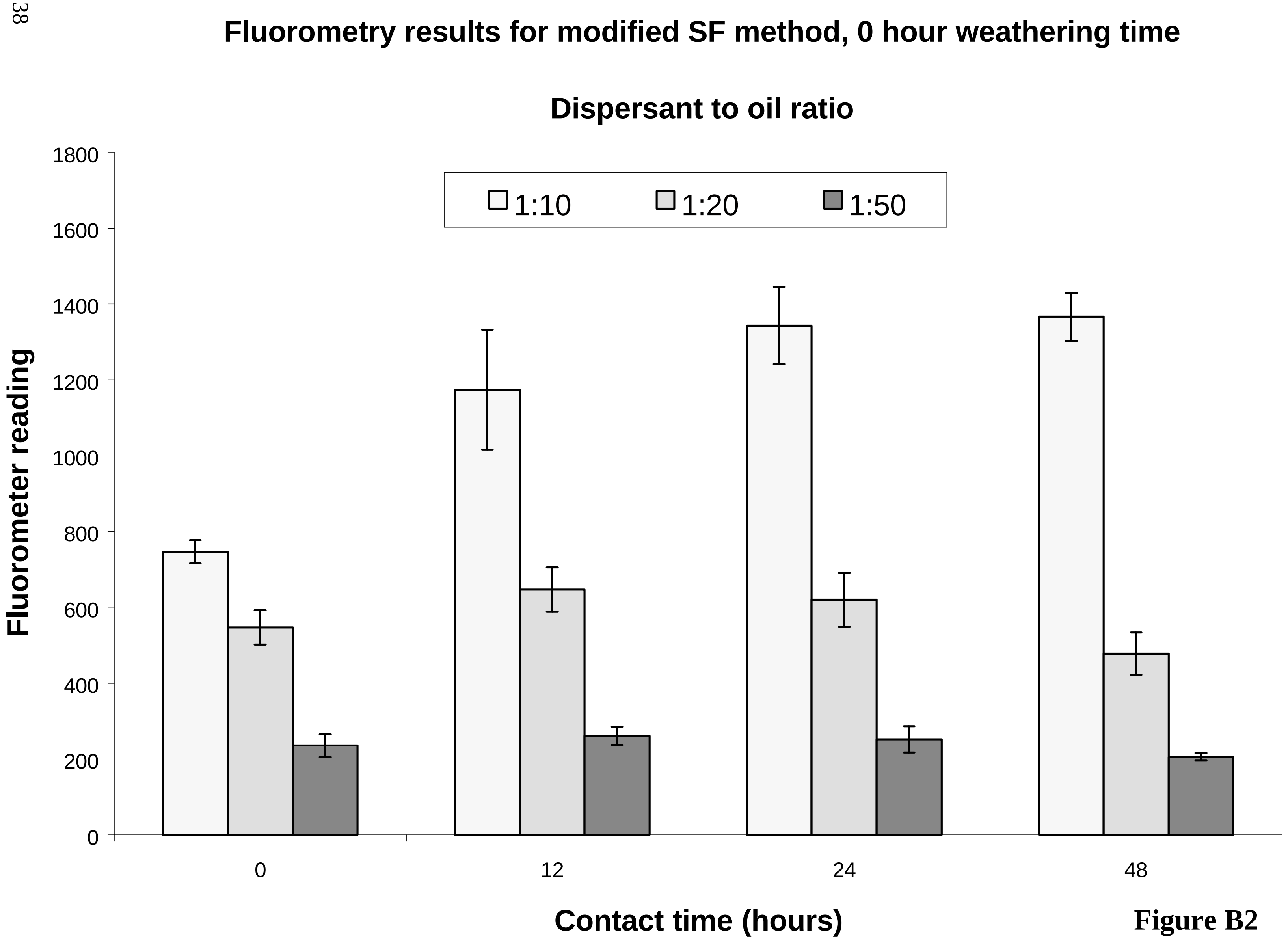
Fluorometry results for modified SF method, 0 hour weathering time
Dispersant to oil ratio
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□ 1:20
■ 1:50
Fluorometer reading
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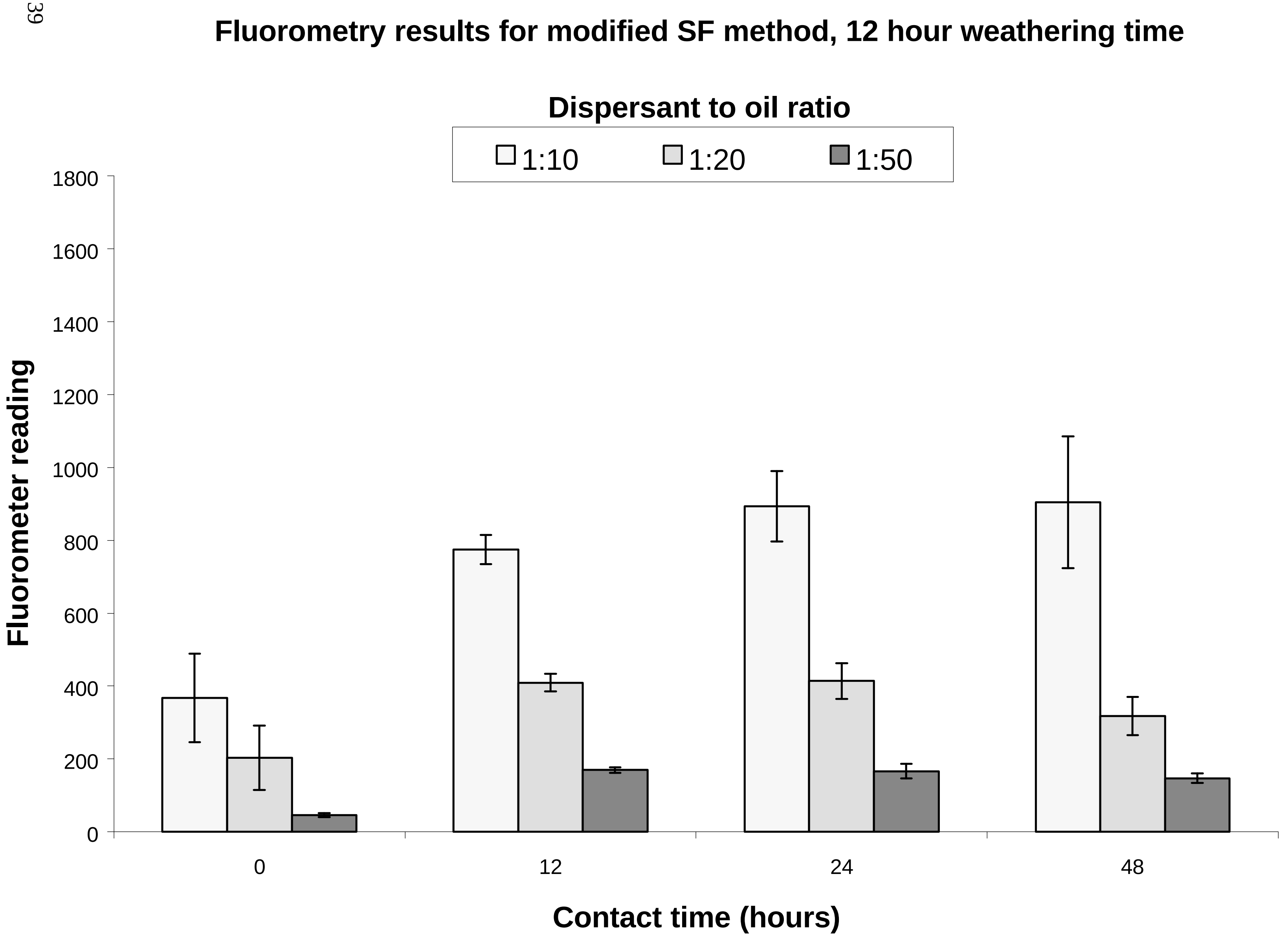
1400
1200
1000
800
600
400
200
0
0
12
24
48
Contact time (hours)

Figure B2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Dispersant to oil ratio
1:10
1:20
1:50
Fluorometer reading
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1600
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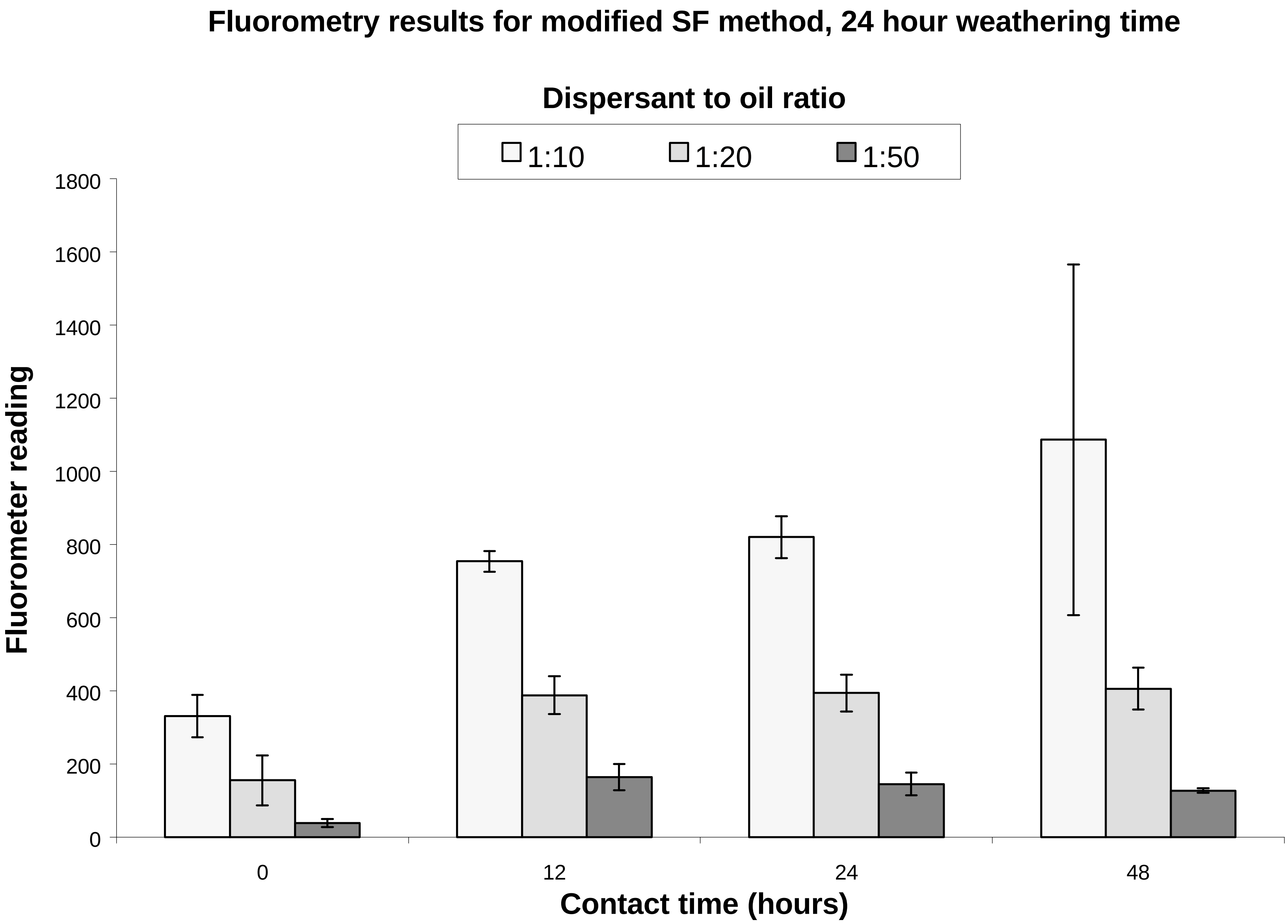
800
600
400
200
0
0
12
24
48
Contact time (hours)

Figure B3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Dispersant to oil ratio
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1:20
1:50
Fluorometer reading
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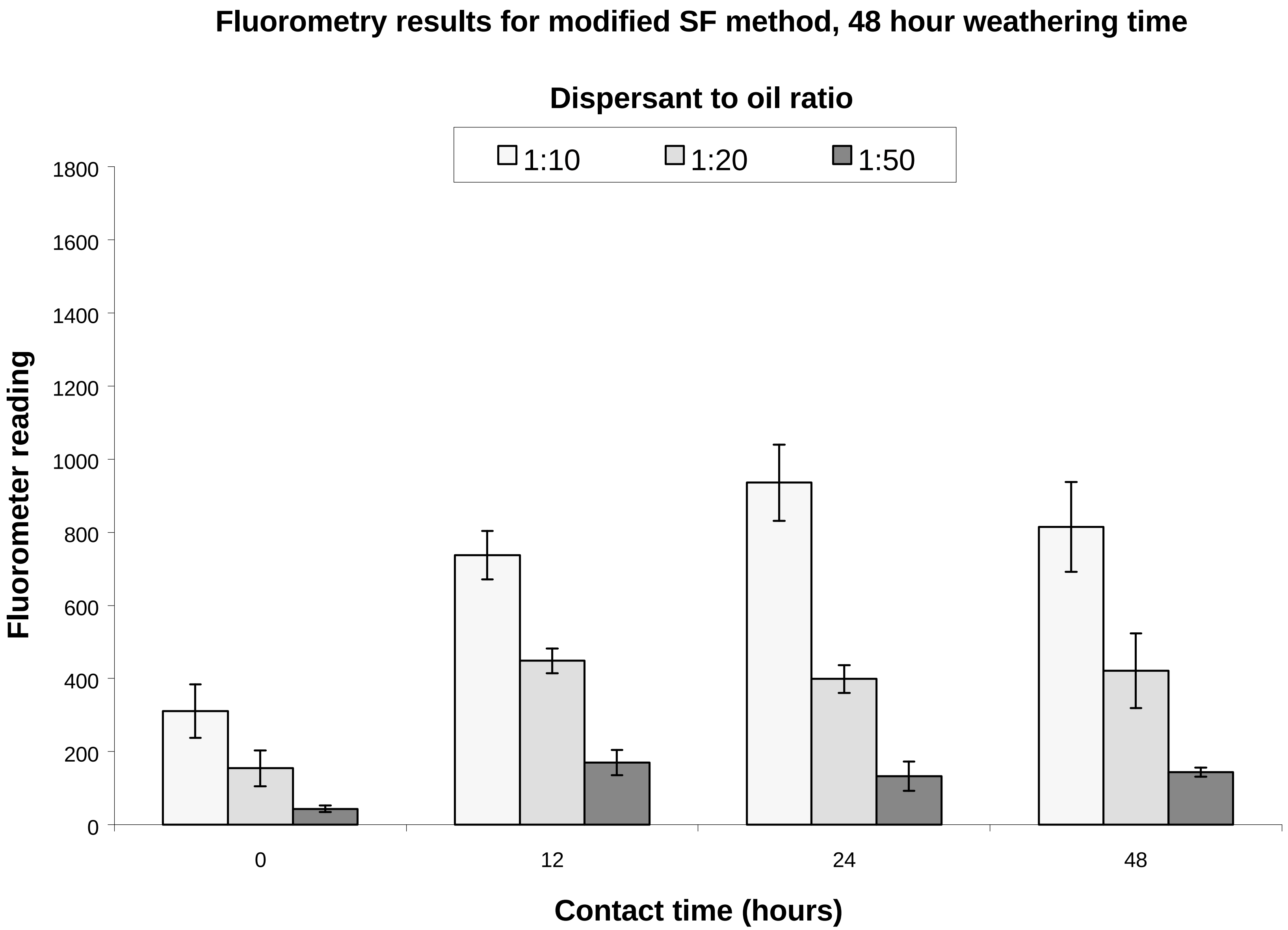
1200
1000
800
600
400
200
0
0
12
24
48
Contact time (hours)

Figure B4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▨ 1:20
■ 1:50
Fluorometer reading
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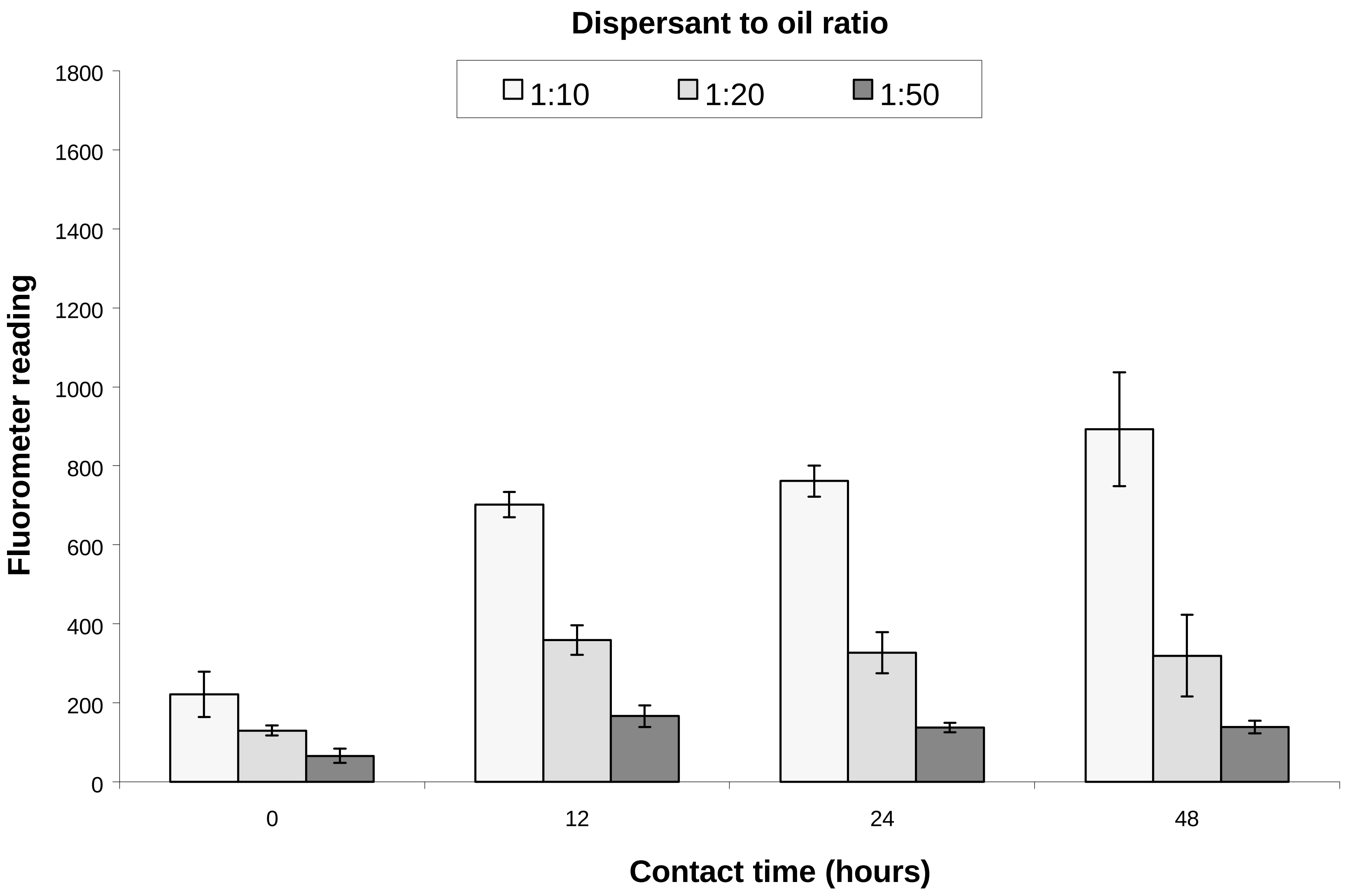
1400
1200
1000
800
600
400
200
0
0
12
24
48
Contact time (hours)

Figure B5

Fluorometry results for modified SF method, 72 hour weathering time



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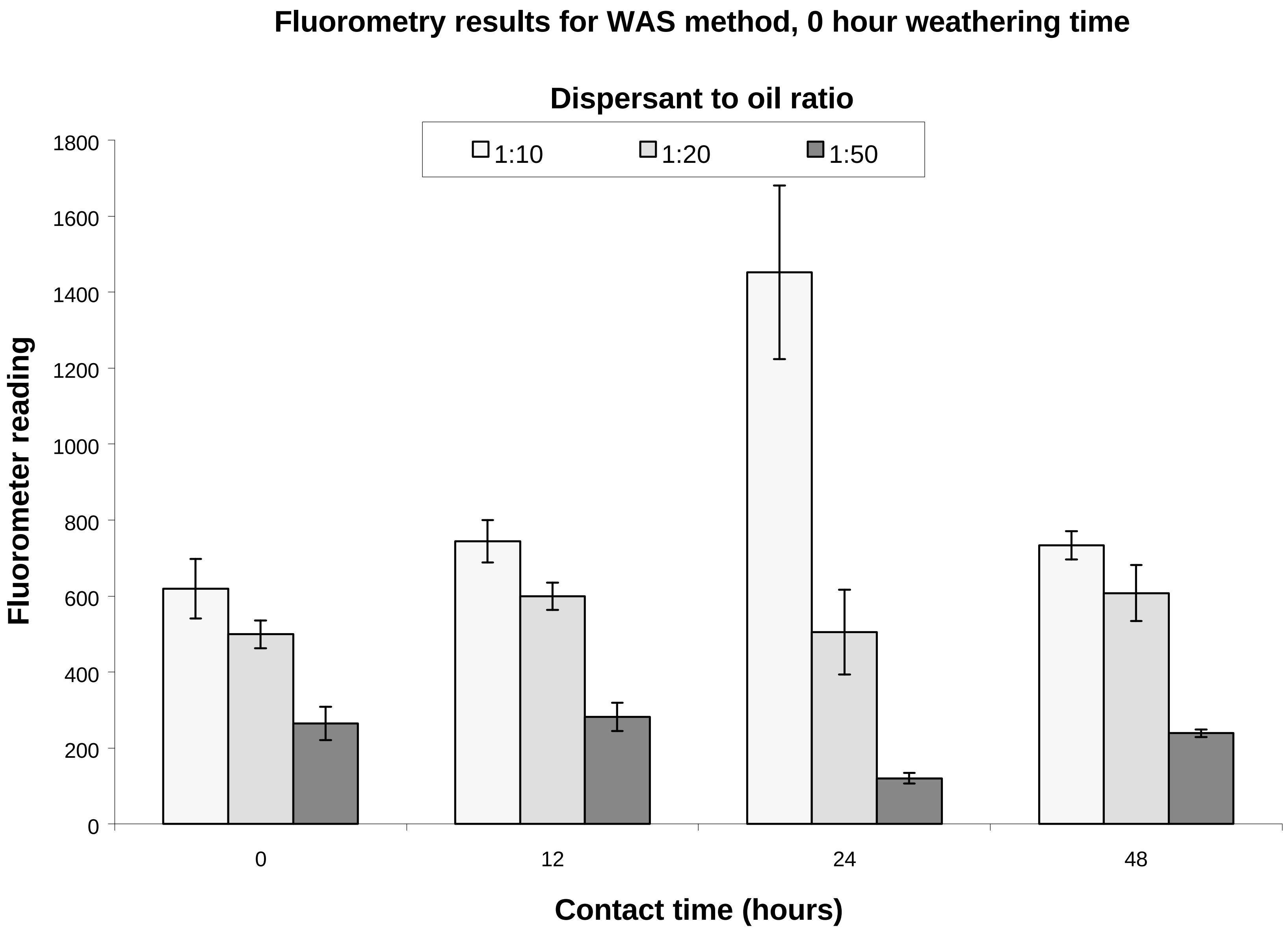
Fluorometry results for WAS method, 0 hour weathering time
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1:20
1:50
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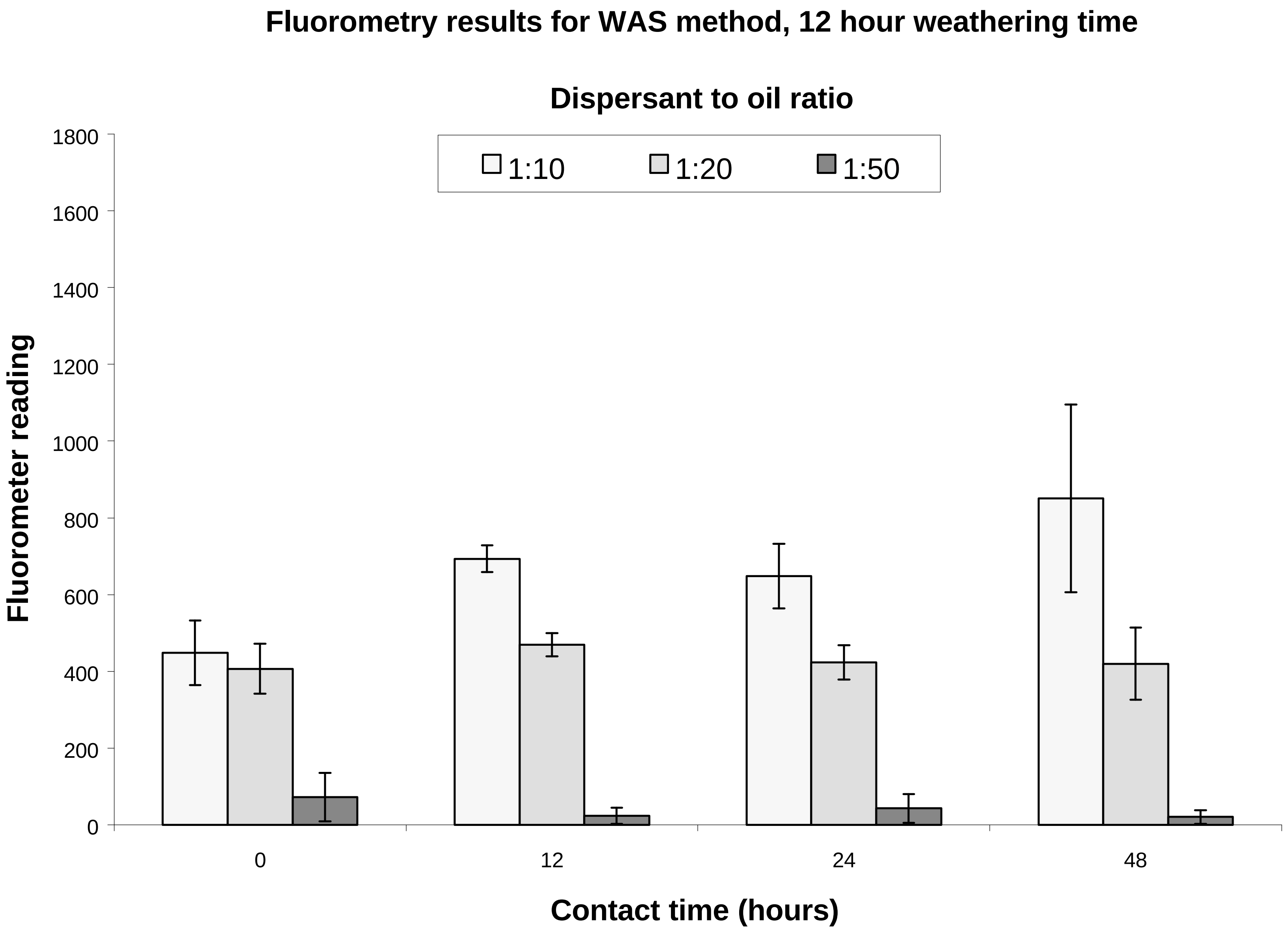
1200
1400
1600
1800
0
12
24
48
Contact time (hours)

Figure B7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Dispersant to oil ratio
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▨ 1:20
■ 1:50
Fluorometer reading
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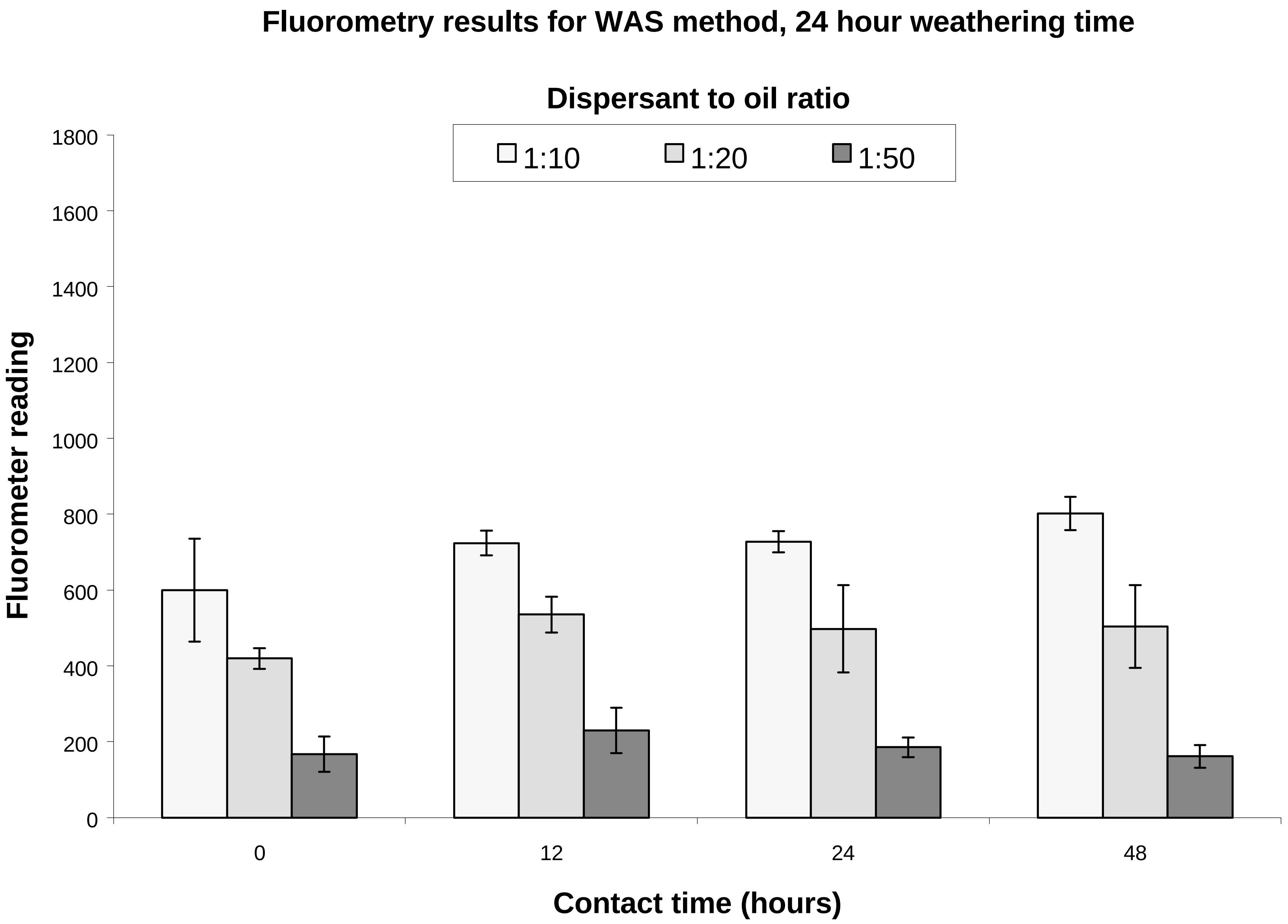
1600
1400
1200
1000
800
600
400
200
0
0
12
24
48
Contact time (hours)

Figure B8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Dispersant to oil ratio
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▨ 1:20
■ 1:50
Fluorometer reading
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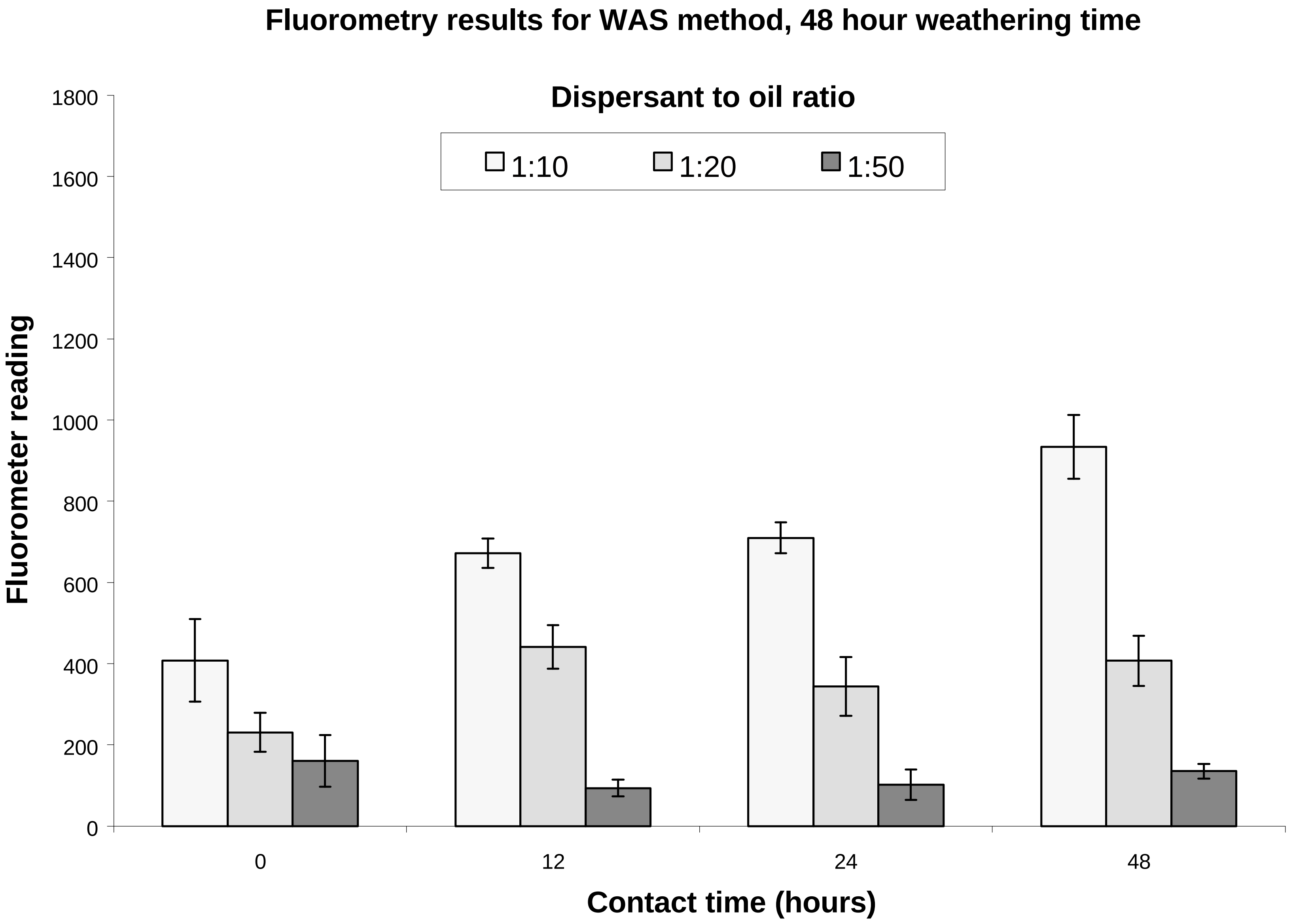
1600
1400
1200
1000
800
600
400
200
0
0
12
24
48
Contact time (hours)

Figure B9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Dispersant to oil ratio
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▨ 1:20
■ 1:50
Fluorometer reading
1800
1600
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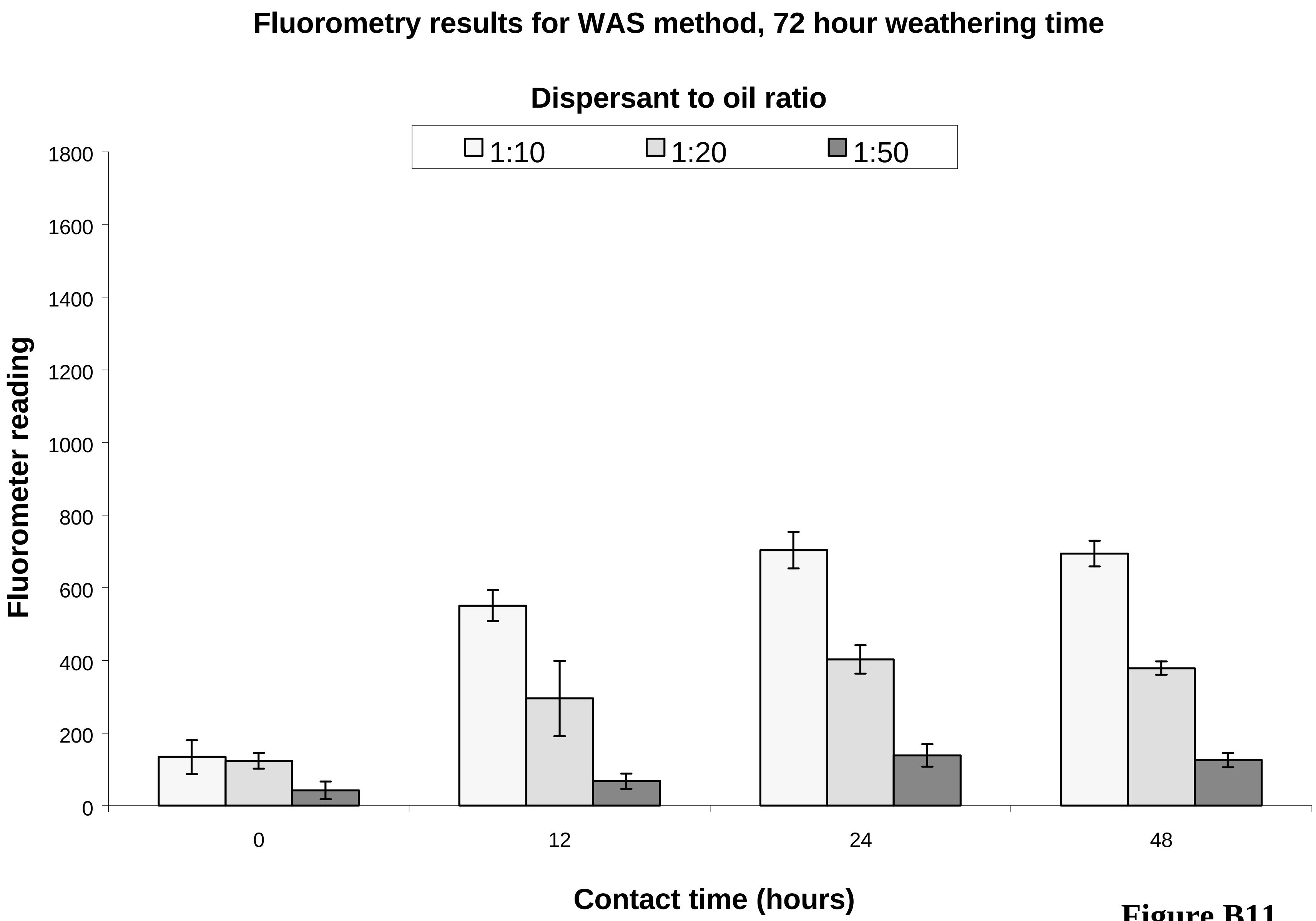
1200
1000
800
600
400
200
0
0
12
24
48
Contact time (hours)

Figure B10


Fluorometry results for WAS method, 72 hour weathering time
Dispersant to oil ratio
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▨ 1:20
■ 1:50
Fluorometer reading
1800
1600
1400
1200
1000
800
600
400
200
0
0
12
24
48
Contact time (hours)

Figure B11