

**Literature Review of Chemical Oil Spill Dispersants and  
Herders in Fresh and Brackish Waters**

**For**

**U.S. Department of the Interior  
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## **Executive Summary**

The purpose of this research is to document what is currently known about the use of dispersants and chemical herders in fresh and brackish waters to assist decision makers when they are confronted with these conditions.

An extensive review of worldwide scientific and technical journals has been undertaken to identify relevant literature on the use of chemical treating agents for oil spill response in fresh and brackish water.

Numerous laboratory-scale, meso-scale and field studies, dating back to the late seventies, have been conducted to study the effect of water salinity on the effectiveness of oil spill chemical dispersants. The consistent significant finding of all of these tests is that dispersant designed for use in marine environments (30 to 35 ppt salinity) are considerably less effective when the salinity falls below about 20 ppt or above 40 ppt.

Dispersants have been formulated for use in fresh water and these have also been tested for effectiveness over a range of water salinities, although not as extensively as the marine dispersants. The effectiveness of the freshwater dispersants have been shown to generally be much better than the marine products in freshwater but often achieve their best results in waters between 10 and 20 ppt salinity.

In theory, water salinity should have only a small influence on the effectiveness of herding agents. Tests using herders in fresh, brackish and salt water consistently have confirmed that salinity has a minimal effect on their performance.

France is the only country to have published information on dispersant use policies and criteria for their use specific to freshwater and it appears to be the only nation to have a list of dispersant products specifically approved for use in fresh water.

In the United States a number of guides to spill response in fresh water have been published (e.g., NOAA and API 1994). As far as dispersants are concerned, the NOAA/API guidelines are very general, directing the user to use dispersants in “open waters and large rivers with sufficient depth and volume for dilution”, when the potential impact of floating oil exceeds that of oil mixed into the water. However, the document lacks a decision guide and specific criteria for dispersant use and fails to provide information on integrating dispersant use with other counter measures.

In the UK, oil spill cleanup practices in fresh water are described in the Energy Institute publication, “Inland waters oil spill response.” The publication makes no reference to dispersant use.

In Canada a number of federal and provincial agencies have responsibility for specific aspects of spill response and planning. Environment Canada provides guidelines for dispersant use and a procedure for “acceptance” for use in Canadian waters, including procedures for effectiveness and toxicity testing. Most of the guidelines refer to marine waters, however, a very few scattered remarks clearly address freshwater. As in the United States there is a lack of a decision guide and specific criteria for dispersant use in fresh water.

The regional Dispersant Steering Committee for the Azerbaijan region of the Caspian Sea made the following recommendations for dispersant use in this inland body of brackish water (12 ppt).

1. Dispersants should be considered as a viable option for responding to an oil spill in the Azerbaijan sector of the Caspian Sea.
2. Dispersants considered for use must be evaluated for effectiveness, toxicity and environmental effects.
3. Dispersants could be a primary response option; typically in areas where water depths exceed 10 metres and distances from shorelines exceed 5 kilometres.
4. Dispersants should be considered as a secondary option in other areas (areas less than 5 km from shore and depths less than 10 metres).

The Baltic Sea is a brackish inland sea (6 to 8 ppt) located in Northern Europe, bounded by Sweden, Finland, Russia, Estonia, Latvia, Lithuania, Poland and Denmark. All sources of pollution in the Baltic are subject to the HELCOM convention that states that oil combating operations in the Baltic Sea Area should use mechanical means as far as possible and dispersant use should be limited as far as possible.

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## **1. Background**

The past use of chemical dispersants in response to oil spills in the United States has been limited primarily to offshore marine waters where water salinities are high. As the use of dispersants is becoming more accepted there is more interest in their use in locations nearer shore where the water can be fresh or brackish due to high river outflows or in ice-infested waters where melt water can significantly reduce the surface water salinity. Most dispersants have been formulated to work in relatively high salinity water and some are known to lose their effectiveness when applied in fresh or brackish water. The purpose of this research is to document what is currently known about the use of dispersants and chemical herders in fresh and brackish waters to assist decision makers when they are confronted with these conditions.

## **2. Objectives**

The objective of this research is to complete a comprehensive literature review and technical evaluation on the use of dispersants and chemical herders in fresh and brackish water.

## **3. Methods**

An extensive review of worldwide scientific and technical journals has been undertaken to identify relevant literature on the use of chemical treating agents for oil spill response in fresh and brackish water. The focus has been on chemical dispersants but chemical herders were also investigated. The effectiveness of these chemicals in fresh and brackish waters has been documented based on reported laboratory and tank test results as well as from documented uses of the products in the field. The current practices, guidelines and regulations of major government and private response agencies (world-wide) with regard to the use of chemical treating agents in fresh or brackish marine environments have been

investigated and documented. The literature has been reviewed from a technical perspective to build a knowledge base.

The online database search services of the Canada Institute for Scientific and Technical Information (CISTI) have been used to identify and acquire the relevant scientific documents from around the world. This agency has access to most international scientific and technical journals and publications. CISTI is a founding member of WorldWideScience.org, a global science gateway to enable federated searching of national and international scientific databases. The search strategies used to identify relevant articles is provided as [Appendix A](#). The library holdings of Environment Canada's Environmental Science and Technology Centre, an agency that has maintained an impressive library of marine oil spill related documents for the past 30 years and our own library that holds numerous research papers and journal articles on oil spill chemical treating agents have also been used to gather relevant research papers.

## **4. Dispersant Effectiveness in Fresh and Brackish Water**

### **4.1 General**

Numerous laboratory-scale studies, dating back to the late seventies, have been conducted to study the effect of water salinity on the effectiveness of oil spill chemical dispersants. Various bench scale swirling and rotating flask, air and water flow tests have been used in this analysis. Researchers who investigated dispersant effectiveness over a range of more than three salinities include Belk et al.1989, Blondina et al.1997 & 1999, Brandvik & Daling 1992, Byford et al. 1983, Fingas et al. 1991 & 2005 & 2006 and Moet 1995. The consistent significant finding of all of these tests is that dispersant designed for use in marine environments (water salinity in the 30 to 35 ppt range) are considerably less effective when the salinity falls below about 20 ppt or above 40 ppt (Fingas and Ka'ahue, 2005).

The data from all of these researchers (with the exception of Fingas 2005 & 2006) have been summarized and re-graphed in Fingas and Ka'ahue, 2005. A number of oils,



dispersants and test methods have been used in this body of testing. Because each oil and dispersant combination results in a unique dispersant effectiveness (DE) assessment that is also dependent on the type of small scale test that is used, it is difficult to directly compare the absolute dispersant effectiveness values arrived at from one test program to another and to differentiate the effects of salinity on the results from other factors. In an attempt to provide a more direct comparison of salinity effects, alone, on the dispersant effectiveness (DE) values measured in each of the test programs cited above, the results from each program have been normalized and re-graphed. The dispersant effectiveness values determined in each individual data set (dispersant and oil combination at a given temperature) have been divided by the highest DE value achieved in the set to provide a graph that illustrates the change in effectiveness at different water salinity levels when compared to the maximum achieved in the test. This type of normalization of the data is not appropriate where the test results indicate virtually no dispersant effectiveness is achieved at any water salinity. Data sets where the maximum dispersant effectiveness achieved did not exceed an arbitrary value of 15% have not been considered in this re-analysis of the historical data. Test results with water salinities higher than 40 ppt have also not been included as ocean salinities seldom reach such high values. The presentation of the results using this type of normalization also masks the absolute relative performance of different dispersants tested under similar conditions. The main purpose of this discussion is to isolate the effect of salinity on the performance of each dispersant not to discuss the relative performance of one dispersant against another.

## **4.2 Effectiveness as a Function of Water Salinity: Normalized Data Results**

The most common dispersants considered for use in the United States are Corexit 9500 and Corexit 9527 and much of the research on dispersant performance has included these two dispersants. For these reasons the normalized test results for these two dispersants are discussed first.

The work completed on DE with salinity variation by Fingas et al. (1991, 2003, 2005 and 2006) has been normalized and graphed in Figures 1 through 4. All Figures have been placed at the bottom of the report in [Appendix B](#) and have been hypertext linked in the digital version for easy access.

In [Figure 1](#), the Corexit 9527 results are plotted using a triangle data symbol. In these tests Corexit 9527 achieved maximum effectiveness at 35 ppt or higher on all of the oils and performance dropped off sharply to about 20% of the maximum at 20 ppt water salinity for all but the Adgo oil. The Enersperse 700 dispersant exhibited a similar trend and the Citrikleen dropped to zero effectiveness at 20 ppt.

The darker lines in [Figure 2](#) refer to the tests on Alaska North Slope (ANS) crude oil, the lighter lines Alberta Sweet Mixed Blend (ASMB) crude. In this work both Corexit 9527 (triangle data symbol) and Corexit 9500 (diamond data symbol) dispersants show maximum effectiveness at 20 to 33 ppt water salinity for both oils and effectiveness drops off in all tests when the salinity dropped below 20 ppt, but not as dramatically as in the 1991 data set. In the tests completed in 2005 ([Figure 3](#)) on ASMB crude, Corexit 9500 achieved maximum effectiveness at 20 ppt and higher water salinities and exhibited a sharp decline in performance at lower salinities. The Corexit 9500 results on ANS ([Figure 4](#)) reveal a maximum effectiveness at 25 ppt water salinity for this oil with a significant reduction in effectiveness (30% loss) when the salinity dropped to 20 ppt. These two data sets also illustrate oil type can influence the sensitivity of a dispersant to water salinity. Temperature also appears to have an influence on the effectiveness at different salinities. The data trends from these tests suggest that these two dispersants work somewhat better at lower salinities when the water temperature is warmer and are more effective at high salinities when the water is colder. It also appears that Corexit 9500 maintains a higher effectiveness over a wider range of brackish water salinities (20 to 35 ppt: [Figures 3](#) and [4](#)) than does Corexit 9527 (30+ ppt: [Figure 1](#)).

Moet et al. (1995) completed tests on one oil using Corexit 9527 and achieved very similar results ([Figure 5](#)) with Corexit 9527 achieving a maximum effectiveness at 30 ppt water salinity and then dropping off to about 40% of maximum effectiveness at 20 ppt.

The work by Blondina (1997) using Corexit 9527 ([Figure 6](#)) and Corexit 9500 ([Figure 7](#)) also show similar trends for all but one of the seven oils studied (Forcados). The Corexit 9500 again achieved maximum effectiveness over a wider range of brackish waters (20 to 35 ppt: [Figure 7](#)) and effectiveness did not fall as fast as with Corexit 9527 ([Figure 6](#)) below 30 ppt. Corexit 9527 showed maximum effectiveness at 35 ppt and dropped to 35% of its peak when the salinity dropped to 20 ppt.

Byford et al. (1983) studied the effects of water salinity on the effectiveness of seven dispersants on weathered Lago Medio, weathered North Slope and fresh North Slope crude oils. The dispersants used in the testing were named in the original report but the test results were reported using random letter designations for confidentiality purposes. Fingas and Ka'aihue (2005) present some of the Byford data with the specific dispersant names attached to the data and this association is maintained in Figures 8 through 10 and the following discussion. Byford's results deviate somewhat from those previously discussed in that for 4 of the 7 dispersants tested on weathered Lago Medio crude ([Figure 8](#)) and for all of the dispersants on weathered North Slope crude ([Figure 9](#)) the measured effectiveness generally did not drop off sharply until the water salinity dropped below 5 ppt. In the tests on weathered Lago Medio crude ([Figure 8](#)) Corexit 9527 again achieved its best performance at 33 ppt salinity and had a near linear drop in efficiency to 20% of maximum with fresh water. Corexit 9527 was one of the three dispersants that did not perform as well over a wide range of brackish water salinities on this oil. Both Corexit 9527 and 9550 performed as well over a range of salinities between 5 and 33 ppt on the weathered North Slope crude. Only two dispersants were tested on fresh North Slope crude oil. Both Arochem D609 and Corexit 9527 achieved their highest effectiveness at 33 ppt water salinity and effectiveness dropped linearly to about 60% of maximum at 5 ppt followed by a rapid drop to 20% of maximum in fresh water ([Figure 10](#)).

Belk et al. (1989) tested four dispersants formulated for marine conditions on two oils (Warren Spring (WS) test oil and Prudhoe Bay (PB) crude) at two temperatures (10 and 20 °C). The dispersants were not identified by name in these tests. [Figures 11](#) and [12](#) show the results for the marine formulation dispersants at 20 °C and 10 °C, respectively. The heavy lines on these graphs show results for the Prudhoe Bay crude oil and the light lines for the Warren Spring test oil. Effectiveness trends were very similar for both temperatures so the following discussion applies to both sets of results. Of the marine dispersants tested, dispersant C showed the best results over a wide range of water salinities with effectiveness remaining above 40 to 60% of maximum effectiveness over the full range of salinities tested (fresh to 35 ppt). Most of the marine dispersants tested achieved maximum effectiveness in 35 ppt water on both of the oils with a drop in effectiveness to 10 to 20% of maximum as the salinity decreased to zero. Dispersants A and B achieved best results on the Prudhoe Bay crude oil at about 20 ppt and effectiveness dropped off at both higher and lower salinities. These two dispersants were more effective than the others at lower salinities but less effective at higher salinities.

### **4.3 Effectiveness Data for Specific Freshwater Formulations**

Dispersants have been formulated for use in fresh water and these have also been tested for effectiveness over a range of water salinities, although not as extensively as the marine dispersants. The effectiveness of the freshwater dispersants have been shown to be much better than the marine products in freshwater but often achieve their best results in waters between 10 and 20 ppt salinity (Belk, 1989). The fresh water dispersants tested by Belk achieved peak performance at around 20 ppt and maintained at least 60% of maximum effectiveness on these two oils over a salinity range of 5 to 35 ppt ([Figures 13](#) and [14](#)). Their performance in fresh water varied from about 35 to 75% of their maximum performance levels achieved at about 20 ppt salinity.

Brandvik et al. (1995) conducted screening tests on fourteen dispersants at two salinities (5 and 35 ppt) and selected five of these for more detailed investigation based on their initial performance results over a range of salinities. Of these five dispersants selected

two were fresh water dispersants Dasic FW and Inipol-IPF. Figures 15 through 20 show the results of this testing. Because only two salinities were used in the test program only a general statement of effectiveness of these dispersants in typical marine conditions (35 ppt) and in low-salinity conditions (5 ppt) can be made. However, the results are useful in that they do show that dispersants can be nearly as effective in low-salinity conditions as they are in high salinity water. Tests were conducted on both weathered and emulsified (50% water content) Oseberg, Gullfaks, Veslefrikk crudes and IFO 30.

For the weathered oils ([Figures 15, 16 and 17](#)) the freshwater dispersant Inipol IPF dispersant always achieved its highest performance at the low salinity and experienced a 60 to 70% drop in effectiveness at the high salinity. The Dasic FW dispersant maintained a similar performance level over all salinities. However, it is important to note that this dispersant achieved consistently lower absolute effectiveness values at all salinities than the other dispersants tested. There were more varied results with the marine dispersants on the different weathered oils. In some cases the dispersants were nearly as effective at both salinities (with only a 10 to 20% loss in effectiveness), in others the effectiveness dropped by as much as 60% at the lower salinity. Overall the dispersants selected for detailed testing in this program worked relatively well at both salinities on the weathered oils.

For the emulsified oils ([Figures 18, 19 and 20](#)) the freshwater dispersant Inipol IPF dispersant achieved its highest performance at the low salinity for two of the three emulsions and experienced a 60 to 90% drop in effectiveness at the high salinity. The Dasic FW dispersant achieved about 60% better performance at the high salinity for two of the emulsions tested and was 20% better at the lower salinity for the third emulsion. All of the marine dispersants performed better at high salinities on the IFO 30 emulsion with a 90+% drop in effectiveness at the low salinity ([Figure 20](#)). On the Oseberg ([Figure 18](#)) and Veslefrikk ([Figure 19](#)) emulsions: Enersperse 700 was 25 and 7% less effective at the low salinity, Inipol IPC was 40 and 50% less effective at the low salinity, and OSR 52 was about 30% less effective at the high salinity.

Wrenn et al. (2009) studied experimental dispersant formulations in a baffled flask test to determine which surfactants provided the best dispersion of a single crude oil (MARS crude). Dispersant formulations were identified that were as effective on this oil in fresh water as the best commercial products were in marine conditions.

George-Ares et al. (2001) studied the effectiveness of Corexit 9500 and a modified Corexit 9500 that was blended with calcium chloride using the EXDET test. The modified product out-performed standard Corexit 9500 in freshwater tests for four different crude oils, including Alaska North Slope crude. These researchers also tested three freshwater dispersant formulations (Dasic Freshwater, Enersperse 1037 and Inipol IPF) and found similar effectiveness results with these dispersants as recorded with the modified Corexit 9500. Effectiveness values greater than 70% were recorded in some tests, indicating that dispersants can be effective in freshwater on some oil types.

Brown and Goodman (1989) reported results of effectiveness testing in fresh water at 5 and 10 °C using a number of commercially available dispersants. Effectiveness values of up to 90% were reported on Norman Wells crude oils using the Mackay-Nadeau-Steelman (MNS) test. Corexit 9550, 7664, 9600 and 8667, MP 900 and W-1911 dispersants were tested.

Payne et al. (1985) tested four dispersants on EPA-standard Prudhoe Bay crude oil at three salinities (0, 18 and 33 ppt) and two temperatures (1 and 10 °C). A full data set is not published in the citation but effectiveness values of greater than 50% were reported for Corexit 9550 in the fresh water tests.

Wells and Harris (1979) conducted MNS tests on Lago Medio crude in 1.5 °C water. Corexit 9527, Corexit 8666, BP1100X, Oilsperse 43 and Drew OSE 71 were tested in fresh water and 30 ppt salt water. All dispersants were more effective in salt water than in freshwater. The freshwater effectiveness values reported were all below 5% in these tests.

#### **4.4 Large-Scale Tests / Field Use**

A field program was conducted in fen lakes using Corexit 9550 on crude oil in the mid 1980's (Brown and Goodman 1989, Brown et al 1990). The chemically treated oil was no longer present on the lake surface after a few days in this test program. Untreated oil was visible on the lake for more than a month indicating that the chemical treatment was successful in the field trial. Corexit 9550 was selected for use based on preliminary testing of 9 dispersants that were commercially available at the time of the tests.

Quaife et al. (1986) tested Corexit 9550 on Norman Wells crude oil in freshwater sloughs. Drop-size measurements showed that the chemically treated oil was effectively dispersed into the water column.

Simulated freshwater streambed tests were completed by Clayton et al. (1989) using Corexit 9550 and OFC D-60 dispersants and Prudhoe Bay crude oil. The treated slicks resulted in more oil in the water column and sediments and less on the surface indicating that the dispersants were successful in the freshwater system.

No documented field uses of dispersants in fresh or brackish water were found in the literature search.

### **5. Effect of Water Salinity on Herding Agents**

The use of specific chemical surface-active agents, sometimes called oil herders or oil collecting agents, to clear and contain oil slicks on a water surface is well known (Garrett and Barger 1972, Rijkwaterstaat 1974, Pope *et al.* 1985, MSRC 1995). These agents have the ability to spread rapidly on a water surface into a monomolecular layer, as a result of their high spreading coefficient, or spreading pressure (the best agents have spreading pressures in the mid-40 mN/m range, whereas most crude oils have spreading pressures in the 10 to 20 mN/m range). Consequently, small quantities of these surfactants (about 5 L per kilometre) will quickly clear thin films of oil from large areas of water surface.

Applying a chemical herder around the periphery of spilled oil can contract the oil into a thicker slick.

Langmuir (1933), proposed that the thickness of a lens of non-spreading oil on water can be calculated from:

$$h^2 = \frac{-2F_s \rho_w}{g \rho_o (\rho_w - \rho_o)} \quad (1)$$

Where:  $F_s \equiv$  Spreading force [dynes/cm = mN/m]  
 $= \gamma_w - \gamma_o - \gamma_{o/w}$

Garrett and Barger (1970) rewrote Equation 1 to allow for the calculation of the thickness of an oil lens contained by a monolayer of surface-active herding agent on the water surrounding the oil lens:

$$h^2 = \frac{-2(F_o - F_m) \rho_w}{g \rho_o (\rho_w - \rho_o)} \quad (2)$$

Where:  $F_o \equiv$  Spreading force of oil on water [dynes/cm]  
 $= \gamma_w - \gamma_o - \gamma_{ow}$   
 $F_m \equiv$  Spreading pressure of monolayer on water [dynes/cm]

Numerical values of  $F_m$  are obtained experimentally with interfacial tensiometers using the following relationship from Canevari (1973):

$$F_m = \gamma_w - \gamma_{w/m} \quad (3)$$

Where:  $\gamma_{w/m} \equiv$  surface tension of water with monolayer on it [dynes/cm]

The surface tension (or water/air interfacial tension) of pure water is 72.75 mN/m at 20°C. This increases to 73.75 mN/m for a solution of 28.4 ‰ NaCl in water (CRC 1972). Thus, there is a very small effect of salinity on water surface tension in the equations above. Measurements on literally hundreds of different crude and product oils show that there is also only a very small effect of water salinity on oil/water interfacial tension (see [http://www.etc-cte.ec.gc.ca/databases/OilProperties/oil\\_prop\\_e.html](http://www.etc-cte.ec.gc.ca/databases/OilProperties/oil_prop_e.html)) with the freshwater measurement being at most 2 or 3 mN/m higher than the seawater measurement



(generally with a value in the 15 to 25 mN/m range). In theory, water salinity should have only a small influence on the effectiveness of herding agents.

Garrett and Barger (1972) undertook the first major scientific study of oil herding agents. They conducted hundreds of experiments with dozens of potential herders in both fresh and saline water, including field applications in rivers, harbours and offshore. There were no adverse effects of salinity variation on the herder performance noted.

In the early 1970's, a 5-ton oil slick was chemically herded and maintained thick for 5 hours in the North Sea (30+ ‰ saline water) (Rijkwaterstaat 1974).

In a series of experiments with three different herding agents in laboratory tests, Pope *et al.* 1985 concluded that there was no measurable difference when the agents were applied on tap water or simulated seawater.

In a review of chemical treating agents for oil spill response (MSRC 1995) no mention is made of water salinity as a factor in the application of herding agents.

A number of studies (SL Ross 2004, 2005, 2007) have been conducted to test the use of herders applied in loose broken ice to thicken slicks for *in situ* burning. First, a very small scale (1 m<sup>2</sup>) preliminary assessment of a shoreline-cleaning agent (Corexit 9580) with oil herding properties was carried out to assess its ability to herd oil on cold water and among ice (SL Ross 2004). Water salinity did not significantly affect the action of this herding agent that was only slightly more effective on 35-‰ saline water than on fresh water.

Further tests (SL Ross 2005) were conducted in 35 ‰ saline water to explore the relative effectiveness of three oil-herding agents in simulated ice conditions, at different scales, under wind and wave conditions; and, to perform small-scale *in situ* ignition and burn testing. One herder formulation (denoted USN) proved to be the best suited for the cold conditions.

The next series of tests (SL Ross 2007) involved larger scales and more realistic conditions using the USN herder. This entailed:

1. A two-week test program at a scale of 100 m<sup>2</sup> at the US Army CRREL Ice Engineering Research Facility Test Basin in Hanover, NH. The tank was filled with fresh water doped with 10-‰ urea (used to create ice with scaled physical properties). A laboratory study prior to these tests showed that the USN herder worked just as well on fresh water and urea-doped water as on full salinity seawater.
2. Experiments were carried out at Ohmsett in February 2006 to explore the use of herders on spreading oil slicks in free-drifting ice fields at a scale of 1000 m<sup>2</sup>. The water salinity during the experiments was 35-‰. The artificial ice blocks used in these experiments were grown at CRREL using 10-‰ urea-doped fresh water.
3. Burn experiments were conducted in the fall of 2006 at Prudhoe Bay, AK at the scale of 30 m<sup>2</sup> in a specially prepared pool containing fresh water drawn from a frozen lake nearby. The ice blocks used in the tests were grown from 15-‰ water obtained from Prudhoe Bay. The mid-scale basin tests showed that the USN cold-water herder significantly contracted fluid crude and refined oil slicks on cold open fresh water, in the presence of saline brash ice and in saline slush ice with concentrations of up to 70% ice coverage.

The performance of the USN herder remained consistent throughout the three test series that were completed under various water and ice salinities.

In conclusion, theory predicts and research has shown that there is little or no difference in the efficacy of herding agents on fresh or salt water.

## **6. Existing Policies and Guidelines for Dispersant Use in Fresh and Brackish Waters**

This section provides an overview of policies and guidelines for dispersant use in inland waters or for jurisdictions where the water bodies under consideration are either fresh or brackish.

### **6.1 Freshwaters**

#### **6.1.1 France**

France was the first to publish information on dispersant use policies for freshwater and apparently it is the only nation to have a list of dispersant products specifically approved for use in fresh water (<http://www.cedre.fr/en/response/dispersant.php>). Merlin et al. (1991) was perhaps the first to develop a strategy for using dispersants in fresh water, pointing out that criteria for dispersant use would be different from those for use at sea. Merlin argues that, for spills in rivers, dispersing the spill into the water column would best protect the environment. It assumed that in doing so the oil would quickly be diluted, settle to the river bed at low concentrations over a large area and quickly degrade rather than remaining on the river surface where it would contaminate the river banks precipitating large costs for cleanup and restoration.

Merlin's paper addressed both effectiveness and environmental protection. One part of the policy is a dispersant testing procedure that considers the effectiveness, toxicity and degradability of the product, as follows.

1. Product effectiveness is evaluated using the same testing method (AFNOR No. 90-345) for dispersants to be used at sea with the following changes to make results more relevant to the freshwater environment:
  - a) Freshwater with a mineral content (total hardness= 25) would be used instead of saltwater;
  - b) The mixing energy produced by the wave beater would be reduced by half to reflect lower mixing energy regimes assumed present in inland waters; and

- c) Diesel fuel would be used as the reference pollutant in the test as the oils most commonly encountered in inland water would be diesel oil, domestic fuel oil or kerosene.
2. Product toxicity must be low so that the toxicity of the dispersant-produced emulsion is not greater than that of an emulsion of the same oil produced by physical means. The paper describes a method for producing physically generated emulsion using an ultrasound beam.
3. Product must itself meet biodegradability standards and must not inhibit degradability of a specified oil.

The other part of Merlin's protocol addressed the effectiveness and capability of dispersion to provide environmental protection. It suggested that dispersants be used when mechanical recovery methods are not feasible, such as when flow in rivers exceeds limits for booms and skimmers. The following decision criteria were suggested.

- a) Dispersants should be used only in flowing water with a minimum speed of 0.3 m/s. Waters with less current do not have sufficient mixing energy to maintain the dispersed oil in suspension and the oil would resurface. Streams with less flow would be cleaned by mechanical means.
- b) Dispersants should be used only under conditions where the spill size and river flow rate (and presumably river width/depth) are such that initial oil exposure concentrations would be low and would be quickly reduced to background by dilution. The authors performed short-term toxicity tests exposing freshwater species to dispersed oil at high initial oil concentrations for brief periods. They concluded that, based on limited preliminary information, initial exposures should not exceed 100 ppm.

The authors also argued that the load of sediment in a river would also contribute to the river's capacity to hold dispersed oil in suspension in the water column and transfer it to the river bottom. However, they offered no guidance as to how information concerning sediment load might be used in decision-making.

### **6.1.2 United States**

In the US, dispersant use in fresh and brackish waters was permitted under the Oil Pollution Act of 1990, requiring that decisions on dispersant use be made on a case-by-case basis. Planning for spills in inland and brackish estuarine waters, in general, has received considerable attention in the US, (e.g, NOAA and API 1994), but dispersant use in these environments has received very limited attention, apparently due to widely held reluctance to use dispersant in inland waters of any kind (Nichols, pers. comm.) The US Environmental Protection Agency has sponsored semi-annual Freshwater Spills Symposia since 2000 to encourage spill responders from industry and government to exchange information on problems of freshwater oil spills. However, these symposia have not addressed dispersant use in freshwater.

A number of guides to spill response in fresh water have been published (e.g., NOAA and API 1994). These discuss the environmental protection value of many countermeasures in a variety of freshwater habitats (large, lakes, streams, marshes). As far as dispersants are concerned, the NOAA/API guidelines are very general, directing the user to use dispersants in “open waters and large rivers with sufficient depth and volume for dilution”, when the potential impact of floating oil exceeds that of oil mixed into the water. It cautions users of the risks to benthos if used in shallow water and the risks associated with the use of dispersants near water intakes. However, the document lacks a decision guide and specific criteria for dispersant use and fails to provide information on integrating dispersant use with other counter measures. Text from NOAA and API 1994 appears to be reprinted in some area contingency plans.

In addition to the above, the American Society for Testing and Materials offers guidance for dispersant use in fresh water environments including rivers, lakes ponds and swamps. These were originally published in 1989, but remain on the books today. General guidance includes the following.

1. It is important to recall that from an environmental perspective, dispersant use decision-making is one of making trade-offs.

2. Human uses of rivers include sources of potable water for domestic and industrial use.
3. In most cases, the mortality of individuals (of a wildlife species) is of less concern than the destruction of habitat. The repopulation of areas after a spill will occur naturally after the spill.

In addition, specific guidance for dispersant use in particular freshwater environments (e.g., rivers, large lakes, ponds) are provided in Table 1.

| Table 1. ASTM Recommendations for use of dispersant in freshwater bodies                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                                                                          |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Rivers and Creeks (ASTM 2008c)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | Large Lakes and Water Bodies (ASTM 2008b)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | Ponds and Sloughs (ASTM 2008a)                                                                                                                                           |
| <ol style="list-style-type: none"> <li>1. Dispersants should be considered for use in rivers and creeks if a spill poses a threat to wildlife or its habitat.</li> <li>2. The turbulence of flowing waters may be adequate for initial dispersion of the spill and for keeping dispersed oil droplets in suspension.</li> <li>3. In some cases river waters may be shallow enough for dispersed oil to reach the bottom and may cause an impact on the benthic community.</li> <li>4. The use of dispersants near water intakes is not recommended. Dispersant application should take place far enough upstream of water intakes to allow for dilution of the dispersed oil.</li> <li>5. Dispersants are recommended for reducing the risk from spills to waterfowl.</li> <li>6. Dispersed oil is known to pose some hazard to eggs, larvae juvenile and adult fish. Care should be taken to avoid dispersing oil in their habitats.</li> </ol> | <ol style="list-style-type: none"> <li>1. Dispersants should be considered for use in large lakes if a spill poses a threat to wildlife or its habitat.</li> <li>2. Since large waves can be generated in these bodies, these supply the turbulence needed for initial dispersion of the spill and for keeping dispersed oil droplets in suspension.</li> <li>3. In some cases lake waters may be shallow enough for dispersed oil to reach the bottom and may cause an impact on the benthic community.</li> <li>4. The use of dispersants near water intakes is not recommended. Dispersant application should take place far enough from water intakes to allow for dilution of the dispersed oil.</li> <li>5. Dispersants are recommended for reducing the risk from spills to waterfowl.</li> <li>6. Dispersed oil is known to pose some hazard to eggs, larvae juvenile and adult fish. Care should be taken to avoid dispersing oil in their habitats.</li> </ol> | <ol style="list-style-type: none"> <li>1. Dispersants should be considered for use in rivers and creeks if a spill poses a threat to wildlife or its habitat.</li> </ol> |

### 6.1.3 United Kingdom

In the UK, oil spill cleanup practices in fresh water are described in the Energy Institute (2004) publication, “Inland waters oil spill response.” That publication makes no reference to dispersant use.

#### **6.1.4 Canada**

In Canada a number of federal and provincial agencies have responsibility for specific aspects of spill response and planning. Environment Canada has responsibility for the environmental protection aspects of spill response, including dispersants, under the Canadian Environmental Protection Act (1999) (CEPA), (Dewis, 2003). Under CEPA, “The Minister may issue guidelines and codes of practice respecting the prevention of, preparedness for and response to an environmental emergency and for restoring any part of the environment damaged by or during an emergency.” Environment Canada’s policy regarding dispersant use in marine, estuarine and fresh waters is contained in the 1984 Environment Canada document, “Guidelines on the Use and Acceptability of Oil Spill Dispersants (2<sup>nd</sup> Edition)”. The document includes guidelines for dispersant use and a procedure for “acceptance” for use in Canadian waters, including procedures for effectiveness and toxicity testing. Most of the document provides general guidance and considerations clearly concerning marine waters. However a very few scattered remarks clearly address freshwater (e.g., “effectiveness is decreased when applied to oil spills on fresh or brackish waters.” (page 5) and “dispersants generally should not be used in any waters where such use may adversely affect surface water usage, i.e., drinking water” (page 2)). At least one region has developed a handbook addressing inland spills, on both water and land (Environmental Emergencies, Quebec Region, 1995). Dispersant use is not mentioned in this book, except where it cautions about the potential adverse impacts of using dispersants on spills on land.

### **6.2 Brackish Waters**

#### **6.2.1 Caspian Sea (Azerbaijan Sector)**

The Caspian Sea is the world’s largest inland water body and is variously classed as the world’s largest lake or a full-fledged sea. The Danube River provides most of its input and it has no outflow. Water salinity in the oil development areas of the Caspian Sea is 10 to 12 ppt, well below full marine salinity of 30 to 35 ppt. The regional Dispersant Steering Committee (Abbasova et al, 2005) made the following recommendations after



considering a) effectiveness of dispersant products in waters of 12 ppt salinity; b) toxicity of chemically dispersed Azerbaijan crude oil against Caspian Sea species; and c) the net environmental benefits of dispersant use in Azerbaijan waters.

5. Dispersants should be considered as a viable option for responding to an oil spill in the Azerbaijan sector of the Caspian Sea. Commercially available dispersants formulated for marine conditions are effective on Azerbaijan crude oils in the Caspian waters with 12 ppt salinity.
6. Dispersants considered for use must be evaluated for effectiveness, toxicity and environmental effects. The composition and salinity of waters in the Caspian Sea are very different from the ocean waters that are the basis used to formulate most dispersant products. Simple laboratory tests can evaluate the relative effectiveness and toxicity of various dispersants under a variety of test conditions and for a range of oil types.
7. Dispersants could be a primary response option in some areas. Environmental tradeoffs favor dispersant use as a primary response option in regions where mixing and dilution can rapidly reduce concentrations of dispersed oil to levels that are no longer a threat to aquatic organisms. This typically occurs in areas where water depths exceed 10 metres and distances from shorelines exceed 5 kilometres.
8. Dispersants should be considered as a secondary option in other areas (areas less than 5 km from shore and depths less than 10 metres). Net environmental benefits here will depend in the value of the nearshore environmental resources being threatened by any spill (wildlife, sea grass, sensitive intertidal habitats coastal marshes) and the potential for persistence of the oil in the area or redistribution of the oil to other areas. A more detailed and site-specific assessment of the trade-offs may show that dispersing the oil could provide an overall benefit to the environment even though such action may pose a short-term increase in risk to aquatic life in these shallow nearshore areas.

## 6.2.2 Baltic Sea Region

The Baltic Sea is a brackish inland sea located in Northern Europe, bounded by Sweden, Finland, Russia, Estonia, Latvia, Lithuania, Poland and Denmark. The Baltic Sea's salinity is much lower than that of ocean water, as a result of abundant freshwater runoff from the surrounding land. The open surface waters of the central basin have salinity of 6 to 8 ppt. Each nation on the Baltic has its own national oil spill response policy and capability. However, all sources of pollution in the Baltic are subject to a single convention, signed originally in 1974 and updated in 1992. The governing body of the Convention is the Helsinki Commission, or HELCOM, or Baltic Marine Environment Protection Commission.

HELCOM Recommendation 18 addressed dispersant use. The policy adopted in 1980, recommended that Governments of the Contracting Parties to the Helsinki Convention in oil combating operations in the Baltic Sea Area should use mechanical means as far as possible and see to it that the use of dispersants is limited as far as possible and that any such use is subject to authorization, in each individual case, by the competent national authorities.

However, in response to a in 2005-6 recommendation, HELCOM undertook a project to access the latest information and the best knowledge within the field of dispersants in order to develop revised recommendations that promote the best environmental practices and best available technique within oil spill response. As per M. Stankiewicz<sup>1</sup> (pers com, 2009), HELCOM has tasked Sweden with considering the new knowledge related to dispersants and their use in the Baltic Sea. At its September 2009 meeting, the HELCOM Response Group decided to re-examine its dispersant policy once the Sweden report has been submitted, possibly as early as its February 2010 meeting. However, major changes are not anticipated to HELCOM dispersant policy, as “even with the results of the Swedish investigation, we still don't have enough knowledge on dispersants' effectiveness and impact in the Baltic Sea”. Therefore the Group concluded that until such knowledge

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becomes available, HELCOM policy to use mechanical means for oil recovery remains unchanged as included in HELCOM Recommendation 22/2 "Restricted use of chemical agents and other non-mechanical means in oil combating operations in the Baltic Sea Area". This HELCOM Recommendation can be found in Appendix 1. The national policies of the HELCOM nations are summarized in Table 2.

| Table 2. National Dispersant Policies of Baltic Countries      |                                                                                                                                                                                                                                                                                                                                                                           |
|----------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Sweden                                                         | Dispersants are not used in Sweden <sup>a</sup> .                                                                                                                                                                                                                                                                                                                         |
| Finland                                                        | Dispersants are not used in Finland <sup>b</sup> .                                                                                                                                                                                                                                                                                                                        |
| Russia                                                         | Dispersants are permitted in larger spills, but must be pre-approved by the Ministries of Natural Resources and Health and the Fisheries Committee <sup>b</sup> .                                                                                                                                                                                                         |
| Estonia                                                        | Dispersant use is permitted with the approval of the Estonian Environmental Inspectorate <sup>b</sup> .                                                                                                                                                                                                                                                                   |
| Latvia                                                         | It is not foreseen that dispersants would be used in Latvian waters <sup>b</sup> .                                                                                                                                                                                                                                                                                        |
| Lithuania                                                      | Spill response policies are not fully defined <sup>b</sup> .                                                                                                                                                                                                                                                                                                              |
| Poland                                                         | The use of dispersants is limited as per the Helsinki Commission and requires specific permission from the relevant Director of Maritime Office <sup>b</sup> .                                                                                                                                                                                                            |
| Germany                                                        | The use of dispersants is limited to a minimum in the coastal regions; their application is less restrictive on the open sea, but, weather permitting, mechanical recovery has priority in all cases. In the Baltic Sea, Germany has objections to dispersant application because this sea has poor water exchange and is shallow in wide areas <sup>a</sup> .            |
| Denmark                                                        | In principle, the discharge of dispersants is prohibited. The Danish EPA is only inclined to accept the use of chemical dispersants if human beings are in danger or if larger concentrations of sea fowl or particularly valuable coastal areas are threatened by severe oil pollution incidents or if it is the only way to protect other valuable areas <sup>a</sup> . |
| a. From Bonn Agreement website. b. From ITOPF Country Profiles |                                                                                                                                                                                                                                                                                                                                                                           |

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## **Appendix A: Search Strategies Used by CISTI**

### ***Dispersants – Effectiveness***

#### **Databases:**

##### **AQUATIC SCIENCES AND FISHERIES ABSTRACTS**

(AQUASCI; FILE COVERS 1978 TO 1 May 2009 <20090501/ED>)

##### **AQUALINE**

(FILE COVERS 1960 TO DATE, LAST UPDATED: 2 JUN 2009 <20090602/UP>)

##### **CHEMICAL ABSTRACTS**

(CAPLUS; FILE COVERS 1907 – DATE FILE LAST UPDATED: 8 Jun 2009 <20090608/ED>)

##### **ENVIRONMENTAL ENGINEERING ABSTRACTS**

(ENVIROENG; 1990-DATE, LAST UPDATED: 28 MAY 2009 <20090528/UP>)

##### **PASCAL**

(FILE COVERS 1977- DATE FILE LAST UPDATED: 8 JUN 2009 <20090608/UP>)

##### **POLLUTION ABSTRACTS**

(POLLUAB; FILE COVERS 1970 TO 1 May 2009 <20090501/ED>)

##### **WATER RESOURCES ABSTRACTS**

(WATER; FILE COVERS 1967 TO DATE, FILE LAST UPDATED 2 JUN 2009 <20090602/UP>)

#### **Search strategy:**

**((DISPERSANT# OR HERDER# OR ((DISPERS? OR COLLECT? OR HERDING) WITHIN TWO WORDS IN ANY ORDER (AGENT# OR CHEMICAL# OR COMPOUND#)))**

**AND**

**((OIL OR OILS) WITHIN TWO WORDS IN ANY ORDER (CRUDE OR DIESEL OR SPILL? OR SLICK? OR DISCHARG? OR POLLUTION OR POLLUTANT#))**

**AND**

**(FRESHWATER# OR BRACKISHWATER# OR MARSH OR MARSHES OR RIVER OR RIVERS OR STREAM OR STREAMS OR NEARSHORE OR NEAR(W)SHORE OR LOW(W)SALINITY OR ((FRESH OR BRACKISH OR INLAND) WITHIN TWO WORDS IN ANY ORDER (WATER#)) OR (ESTUARINE NOT MARINE)**

**AND**

**(EFFECTIV? OR EFFICACY)**

**NOT**

**OIL WITH SPILL WITH CONFERENCE LIMITED TO SOURCE FIELD**

## ***Dispersants – Policies***

### **Databases:**

#### **AQUATIC SCIENCES AND FISHERIES ABSTRACTS**

(AQUASCI; FILE COVERS 1978 TO 1 May 2009 <20090501/ED>)

#### **AQUALINE**

(FILE COVERS 1960 TO DATE, LAST UPDATED: 2 JUN 2009 <20090602/UP>)

#### **CHEMICAL ABSTRACTS**

(CAPLUS; FILE COVERS 1907 – DATE FILE LAST UPDATED: 8 Jun 2009  
<20090608/ED>)

#### **ENVIRONMENTAL ENGINEERING ABSTRACTS**

(ENVIROENG; 1990-DATE, LAST UPDATED: 28 MAY 2009 <20090528/UP>)

#### **PASCAL**

(FILE COVERS 1977- DATE FILE LAST UPDATED: 8 JUN 2009 <20090608/UP>)

#### **POLLUTION ABSTRACTS**

(POLLUAB; FILE COVERS 1970 TO 1 May 2009 <20090501/ED>)

#### **WATER RESOURCES ABSTRACTS**

(WATER; FILE COVERS 1967 TO DATE, FILE LAST UPDATED 2 JUN 2009  
<20090602/UP>)

### **Search strategy:**

**((DISPERSANT# OR HERDER# OR ((DISPERS? OR COLLECT? OR HERDING)  
WITHIN TWO WORDS IN ANY ORDER (AGENT# OR CHEMICAL# OR  
COMPOUND#)))**

**AND**

**((OIL OR OILS) WITHIN TWO WORDS IN ANY ORDER (CRUDE OR DIESEL  
OR SPILL? OR SLICK? OR DISCHARG? OR POLLUTION OR  
POLLUTANT#))**

**AND**

**(FRESHWATER# OR BRACKISHWATER# OR MARSH OR MARSHES OR  
RIVER OR RIVERS OR STREAM OR STREAMS OR NEARSHORE OR  
NEAR(W)SHORE OR LOW(W)SALINITY OR ((FRESH OR BRACKISH OR  
INLAND) WITHIN TWO WORDS IN ANY ORDER (WATER#)) OR  
(ESTUARINE NOT MARINE)**

**AND**

**(POLICY OR POLICIES OR (GOVERNMENT OR NATIONAL OR  
INTERNATIONAL OR FEDERAL OR PROVINCIAL OR STATE OR  
REGIONAL)(2A) (LAW OR LAWS OR LEGISLATION OR REGULATION# OR  
STANDARD OR STANDARDS)**

**NOT**

**OIL WITH SPILL WITH CONFERENCE LIMITED TO SOURCE FIELD**

***Dispersants – Policies (freshwater concept not required)***

**Databases:**

**AQUATIC SCIENCES AND FISHERIES ABSTRACTS**

(AQUASCI; FILE COVERS 1978 TO 1 May 2009 <20090501/ED>)

**AQUALINE**

(FILE COVERS 1960 TO DATE, LAST UPDATED: 2 JUN 2009 <20090602/UP>)

**CHEMICAL ABSTRACTS**

(CAPLUS; FILE COVERS 1907 – DATE FILE LAST UPDATED: 8 Jun 2009  
<20090608/ED>)

**ENVIRONMENTAL ENGINEERING ABSTRACTS**

(ENVIROENG; 1990-DATE, LAST UPDATED: 28 MAY 2009 <20090528/UP>)

**PASCAL**

(FILE COVERS 1977- DATE FILE LAST UPDATED: 8 JUN 2009 <20090608/UP>)

**POLLUTION ABSTRACTS**

(POLLUAB; FILE COVERS 1970 TO 1 May 2009 <20090501/ED>)

**WATER RESOURCES ABSTRACTS**

(WATER; FILE COVERS 1967 TO DATE, FILE LAST UPDATED 2 JUN 2009  
<20090602/UP>)

**Search strategy:**

**(DISPERSANT# OR HERDER# OR ((DISPERS? OR COLLECT? OR HERDING)  
WITHIN TWO WORDS IN ANY ORDER (AGENT# OR CHEMICAL# OR  
COMPOUND#)))**

**AND**

**((OIL OR OILS) WITHIN TWO WORDS IN ANY ORDER (CRUDE OR DIESEL  
OR SPILL? OR SLICK? OR DISCHARG? OR POLLUTION OR  
POLLUTANT#))**

**AND**

**(POLICY OR POLICIES OR (GOVERNMENT OR NATIONAL OR  
INTERNATIONAL OR FEDERAL OR PROVINCIAL OR STATE OR  
REGIONAL)(2A) (LAW OR LAWS OR LEGISLATION OR REGULATION# OR  
STANDARD OR STANDARDS) LIMITED TO TITLE AND INDEX TERM  
FIELDS**

**NOT**

**OIL WITH SPILL WITH CONFERENCE LIMITED TO SOURCE FIELD OR  
PREVIOUSLY RETRIEVED POLICY REFERENCES**

## Appendix B: Figures

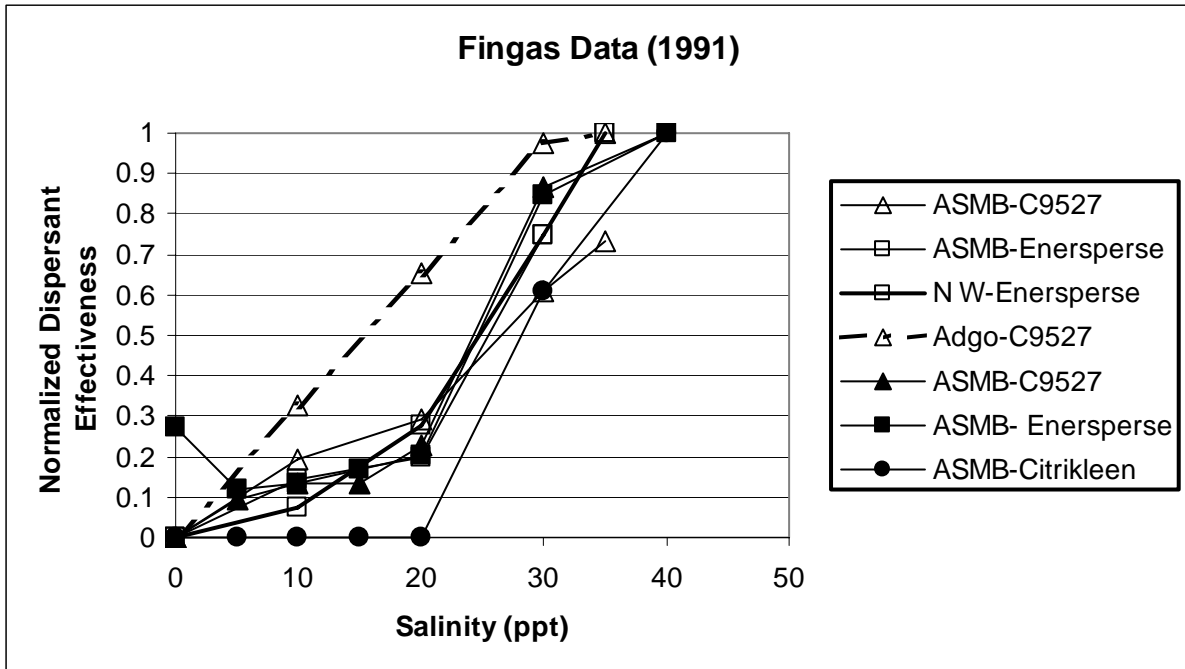


Figure 1. Normalized Dispersant Effectiveness Results adapted from Fingas et al. 1991.  
(note: only data for 40 ppt salinity and lower were used in this plot)

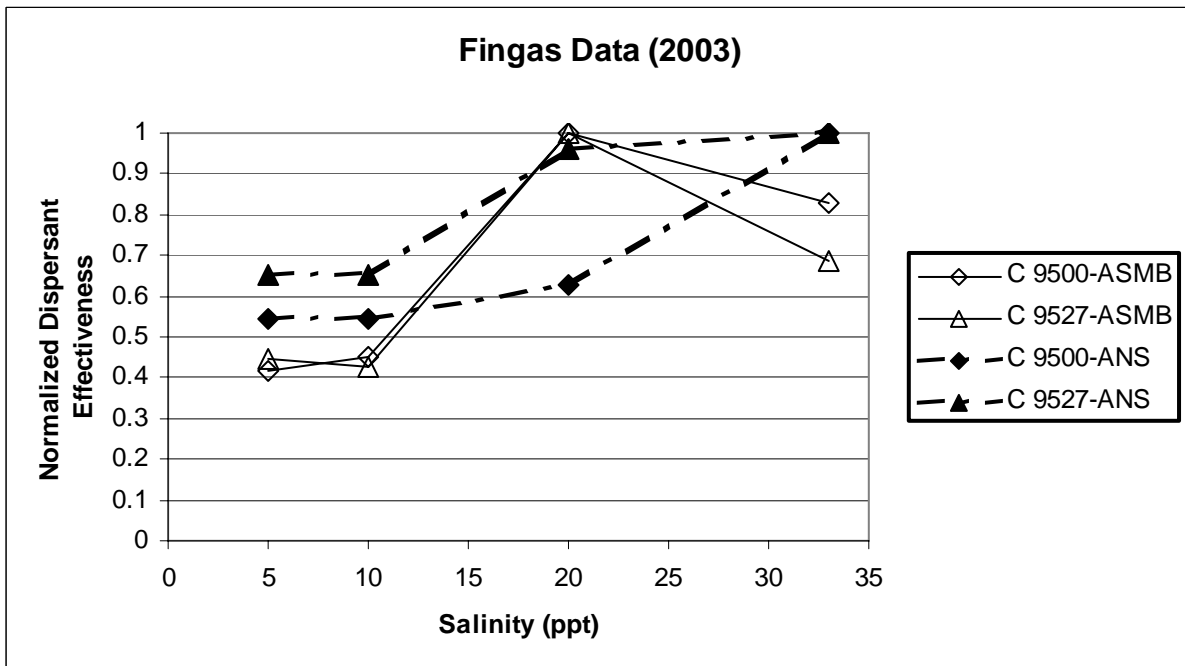


Figure 2. Normalized Dispersant Effectiveness Results adapted from Fingas et al. 2003.  
(note: this data was presented in Fingas and Ka'ahue 2005 where it was referenced as Fingas et al. 2003 data, original source unknown)

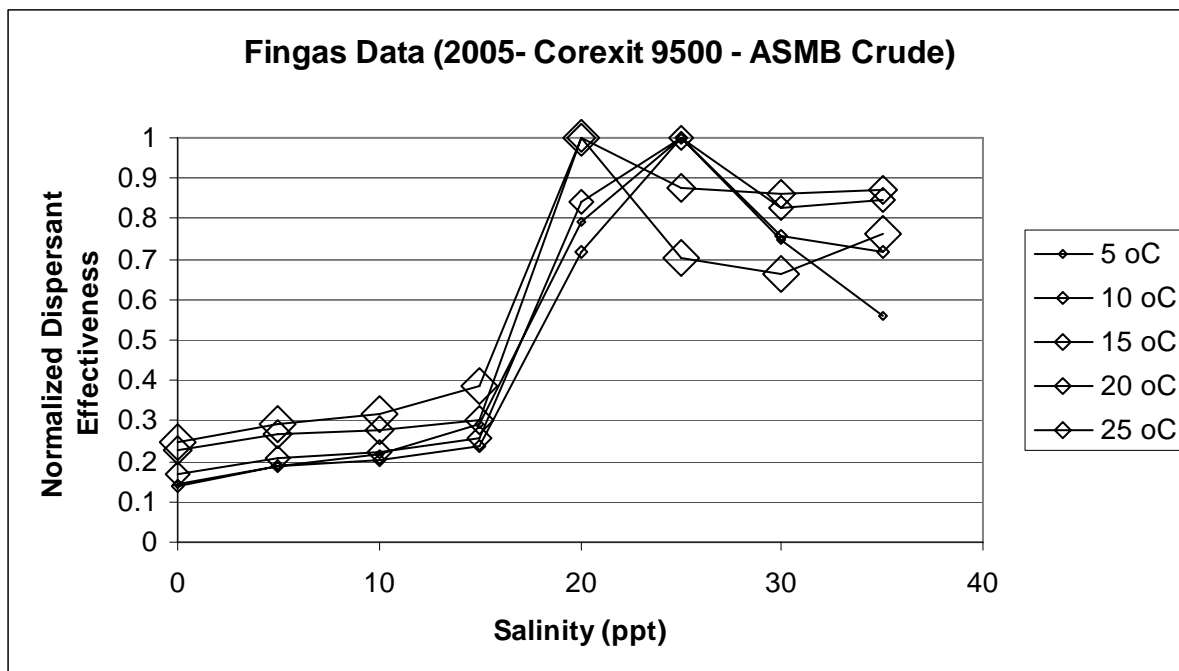


Figure 3. Normalized Dispersant Effectiveness Results adapted from Fingas et al. 2005.

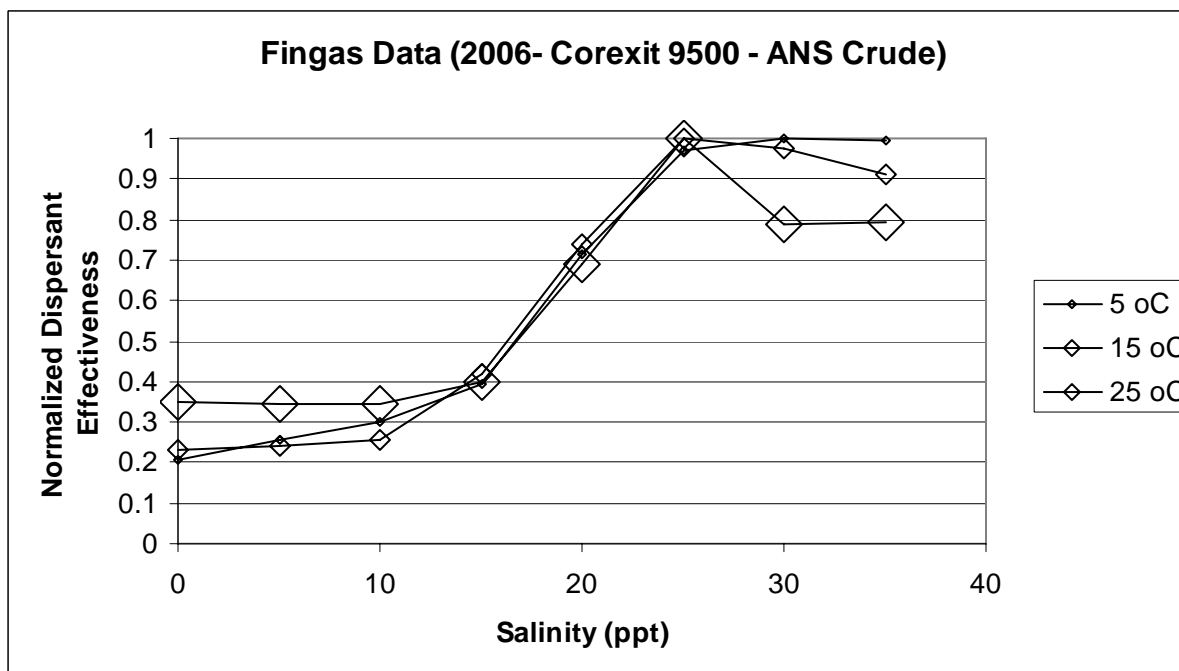


Figure 4. Normalized Dispersant Effectiveness Results adapted from Fingas et al. 2006.

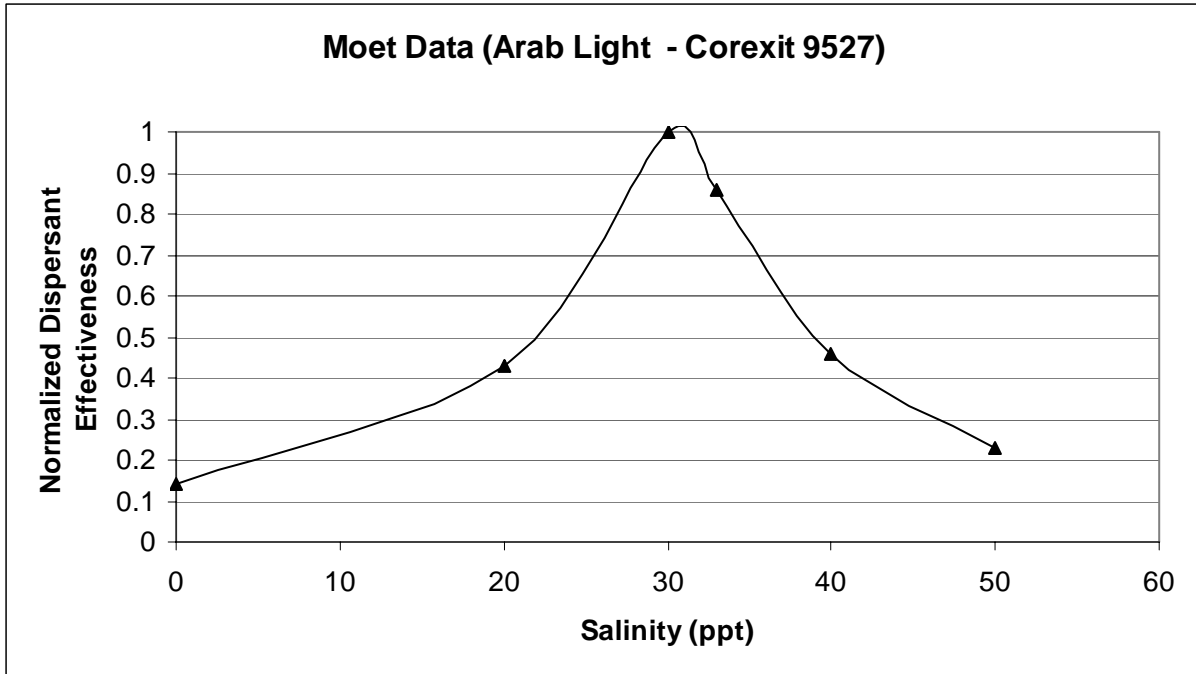


Figure 5. Normalized Dispersant Effectiveness Results adapted from Moet et al.1995.

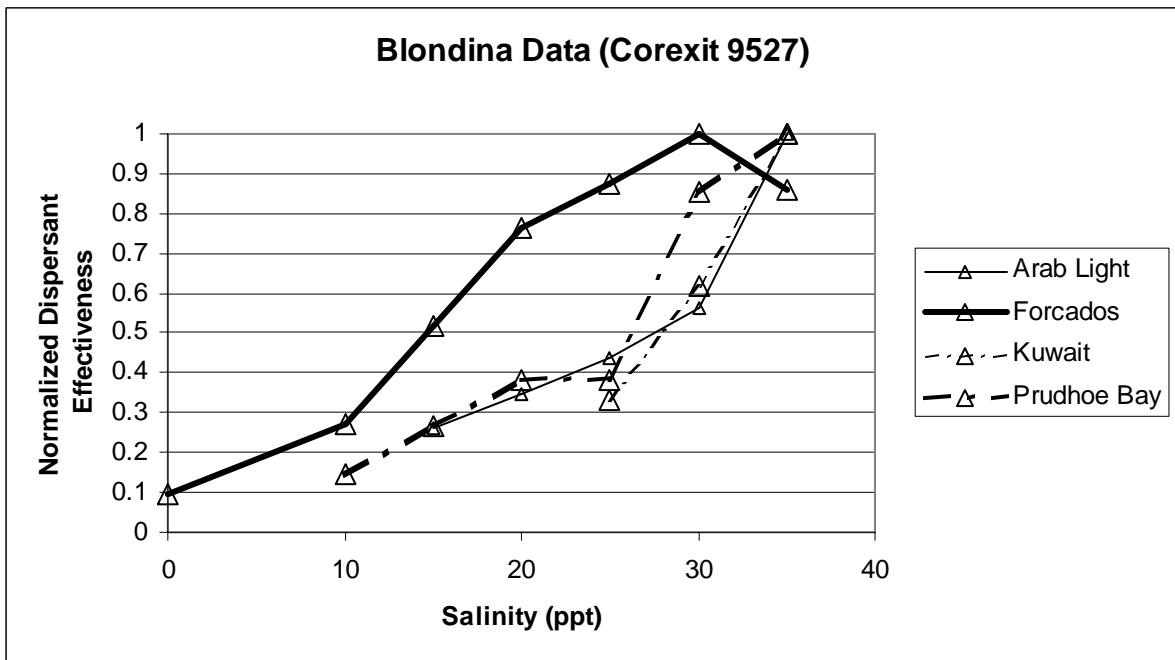


Figure 6. Normalized Dispersant Effectiveness Results adapted from Blondina et al.1997.



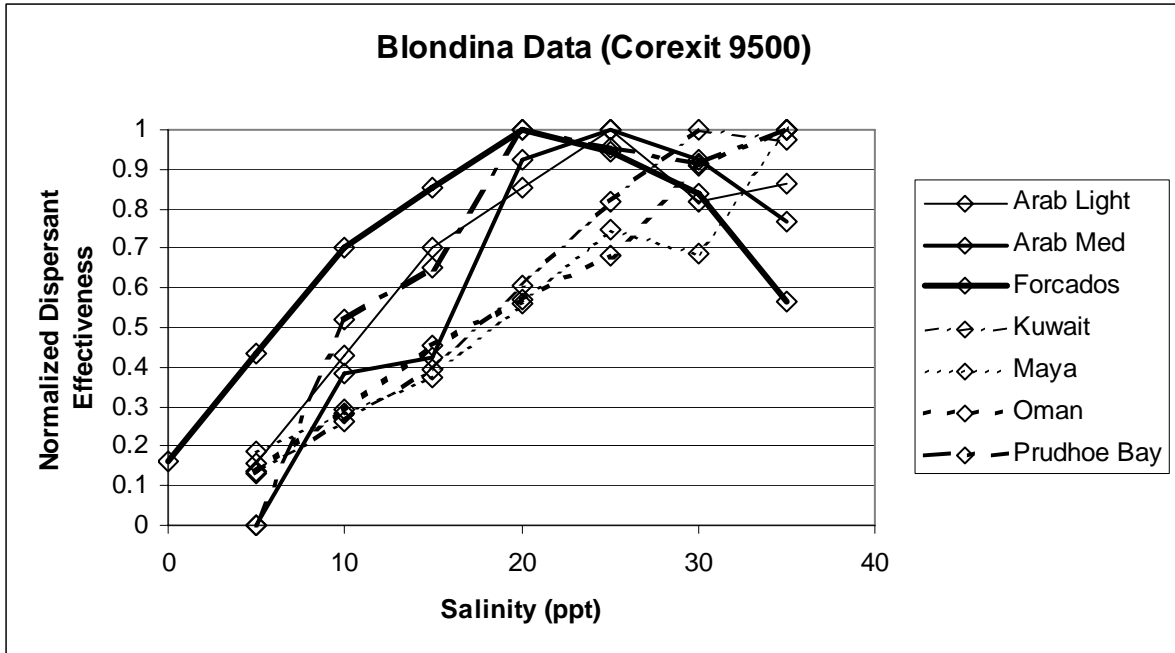


Figure 7. Normalized Dispersant Effectiveness Results adapted from Blondina et al.1997.

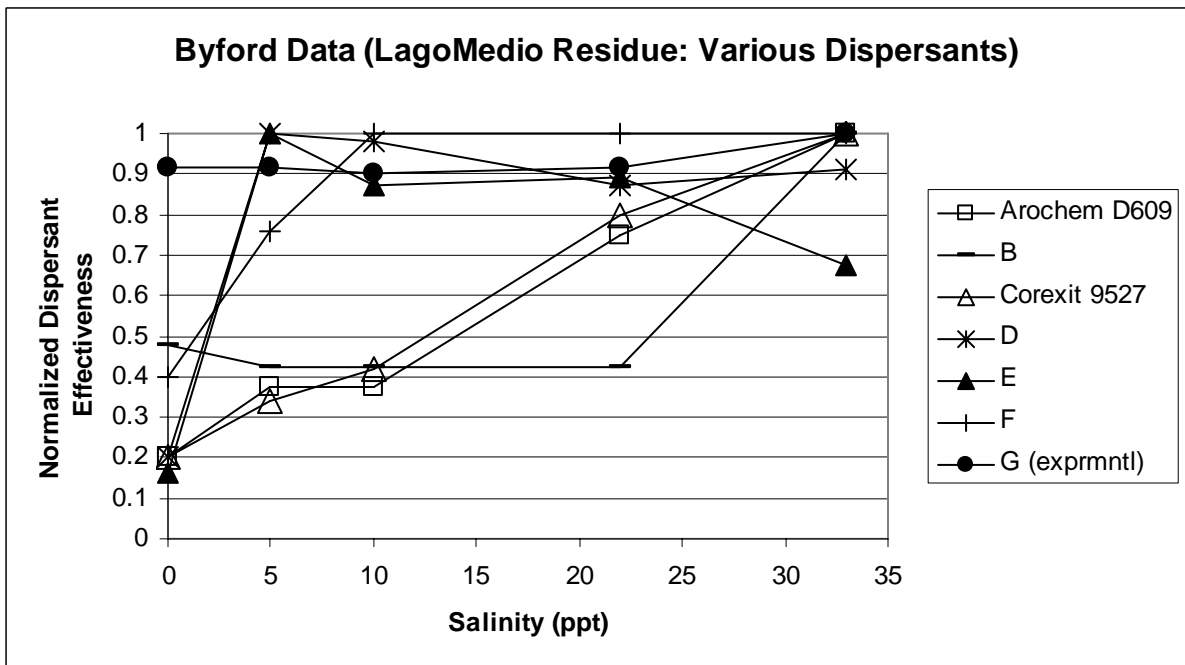


Figure 8. Normalized Dispersant Effectiveness Results for Weathered Lago Medio Crude adapted from Byford et al.1983.

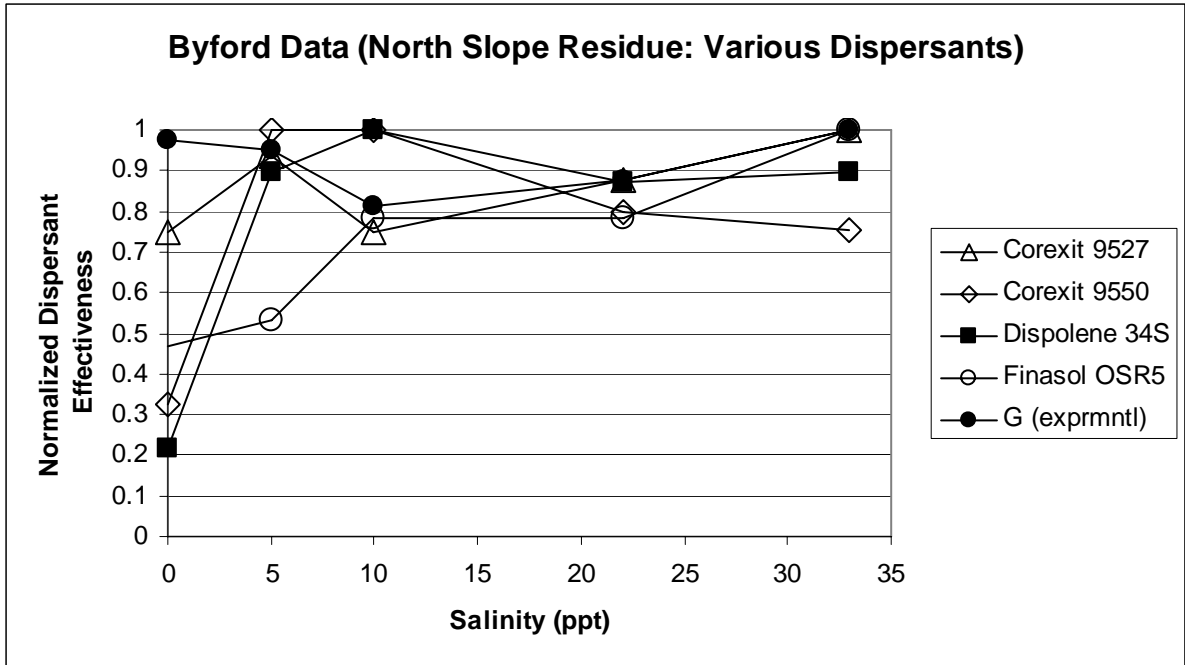


Figure 9. Normalized Dispersant Effectiveness Results for Weathered North Slope Crude adapted from Byford et al.1983.

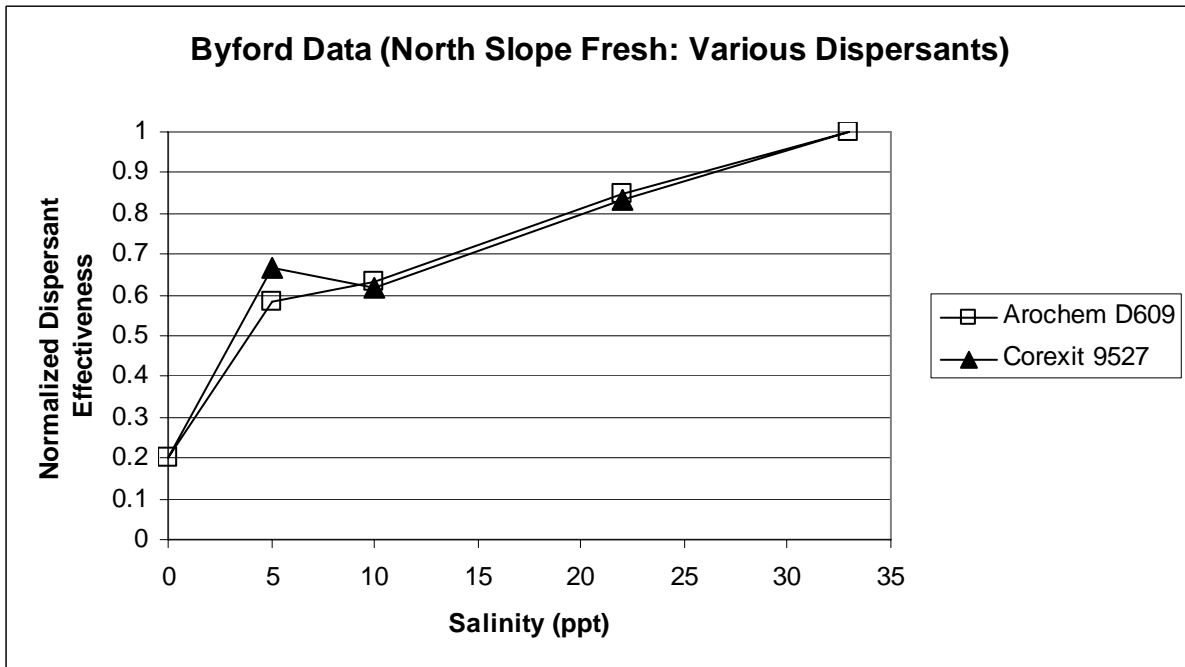


Figure 10. Normalized Dispersant Effectiveness Results for Fresh North Slope Crude adapted from Byford et al.1983.

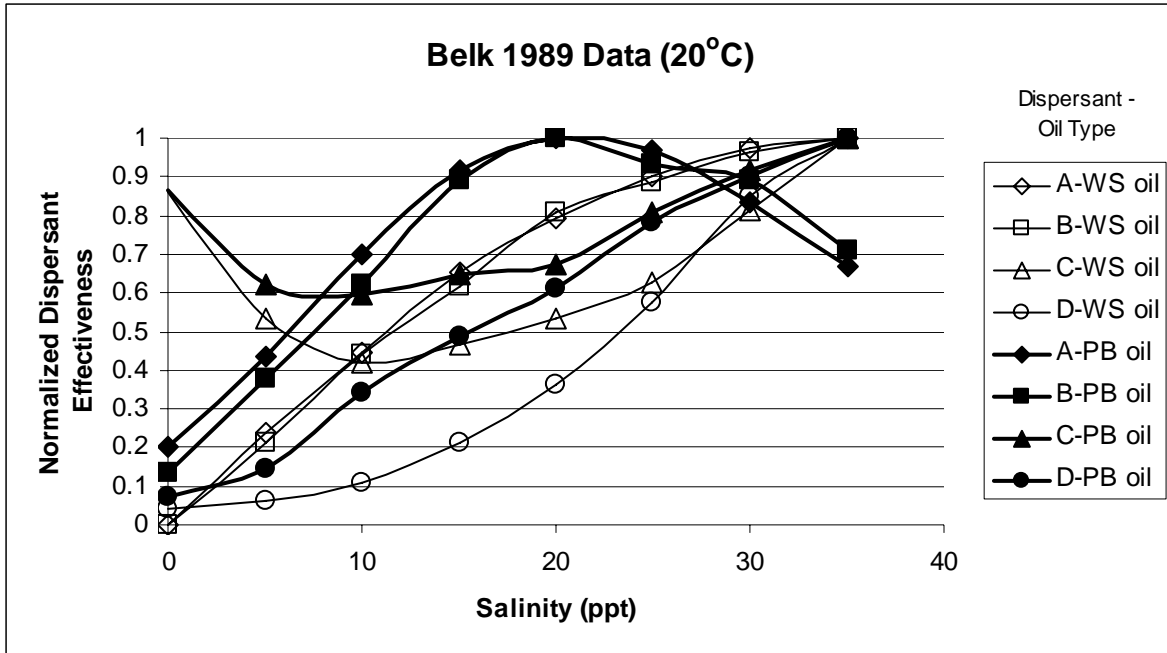


Figure 11. Normalized Dispersant Effectiveness Results for Marine Dispersants at 20 °C adapted from Byford et al.1983.

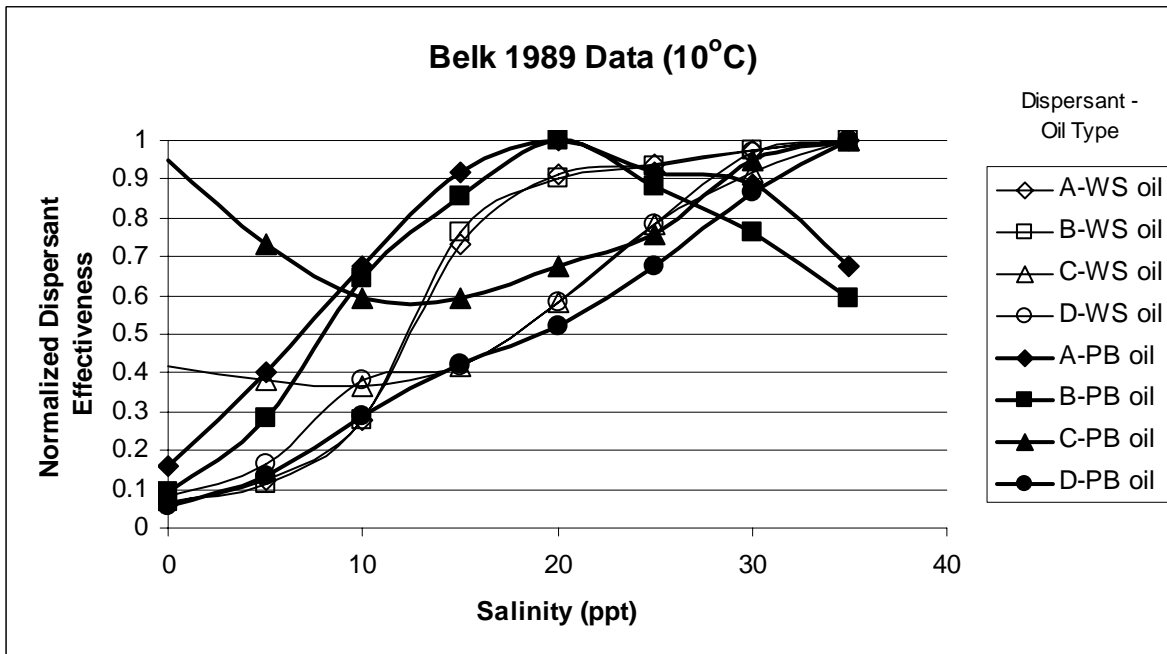


Figure 12. Normalized Dispersant Effectiveness Results for Marine Dispersants at 10 °C adapted from Byford et al.1983.

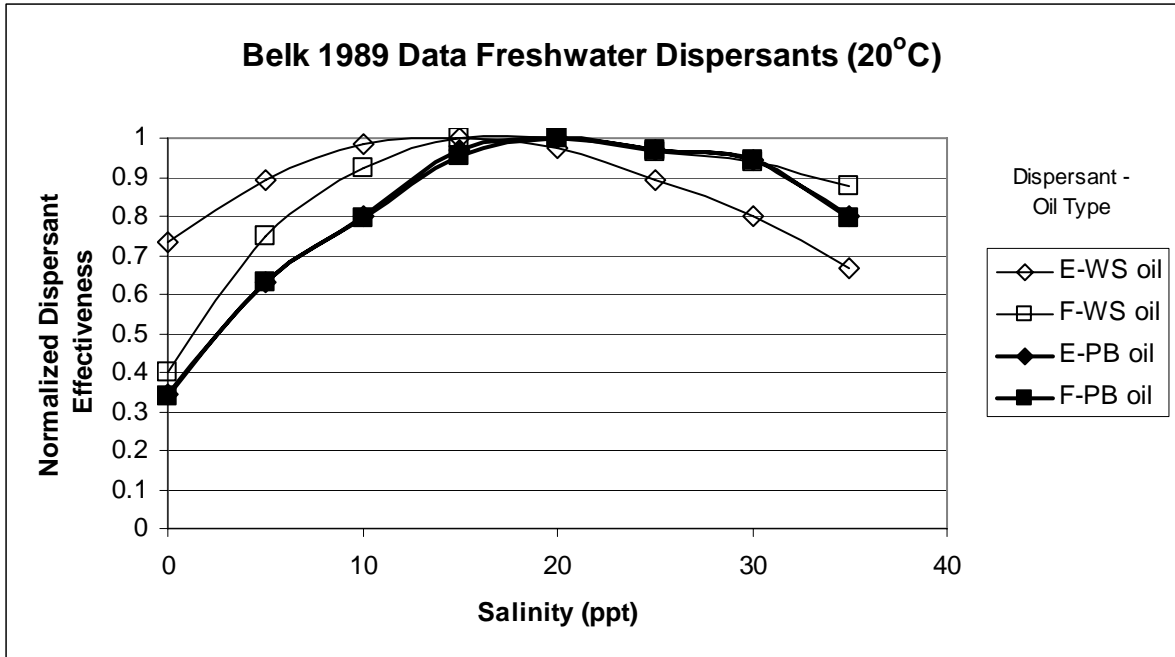


Figure 13. Normalized Dispersant Effectiveness Results for Fresh Water Dispersants at 20 °C adapted from Byford et al.1983.

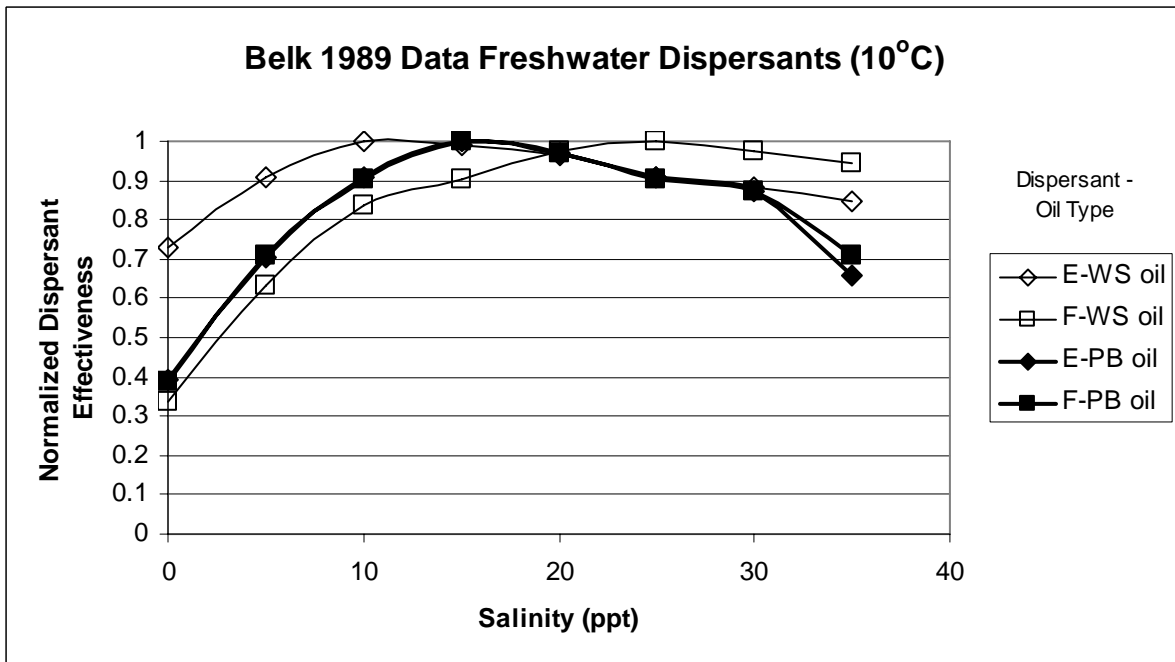


Figure 14. Normalized Dispersant Effectiveness Results for Fresh Water Dispersants at 10 °C adapted from Byford et al.1983.

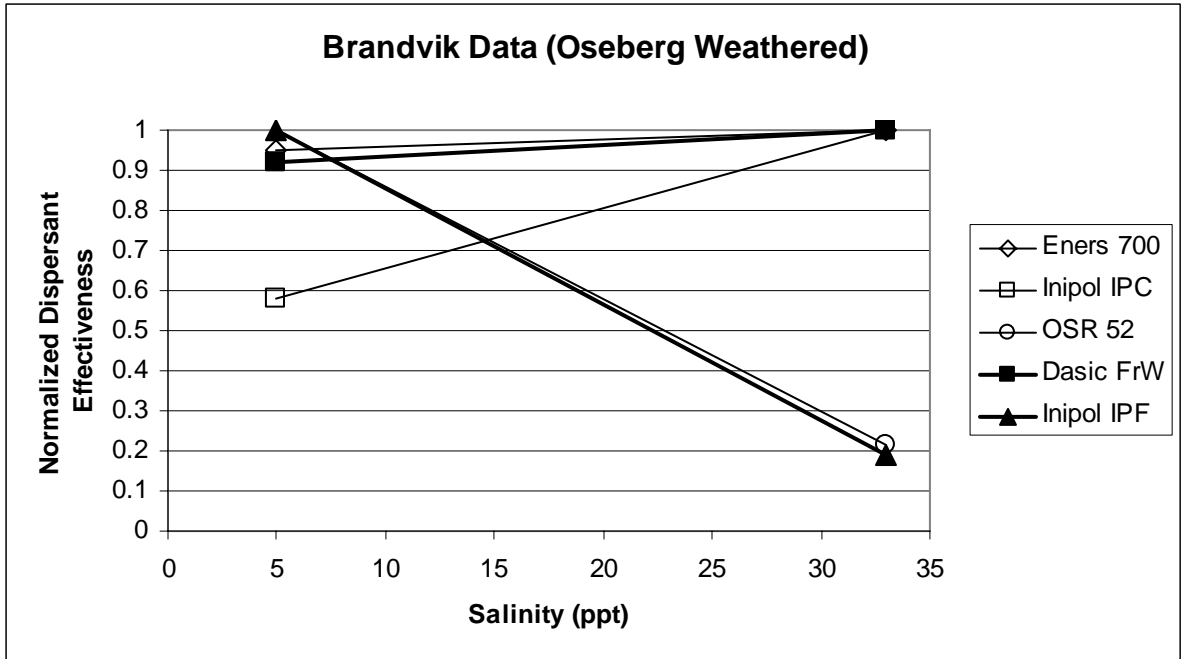


Figure 15. Normalized Dispersant Effectiveness Results on Weathered Oseberg Oil adapted from Brandvic & Daling 1992.

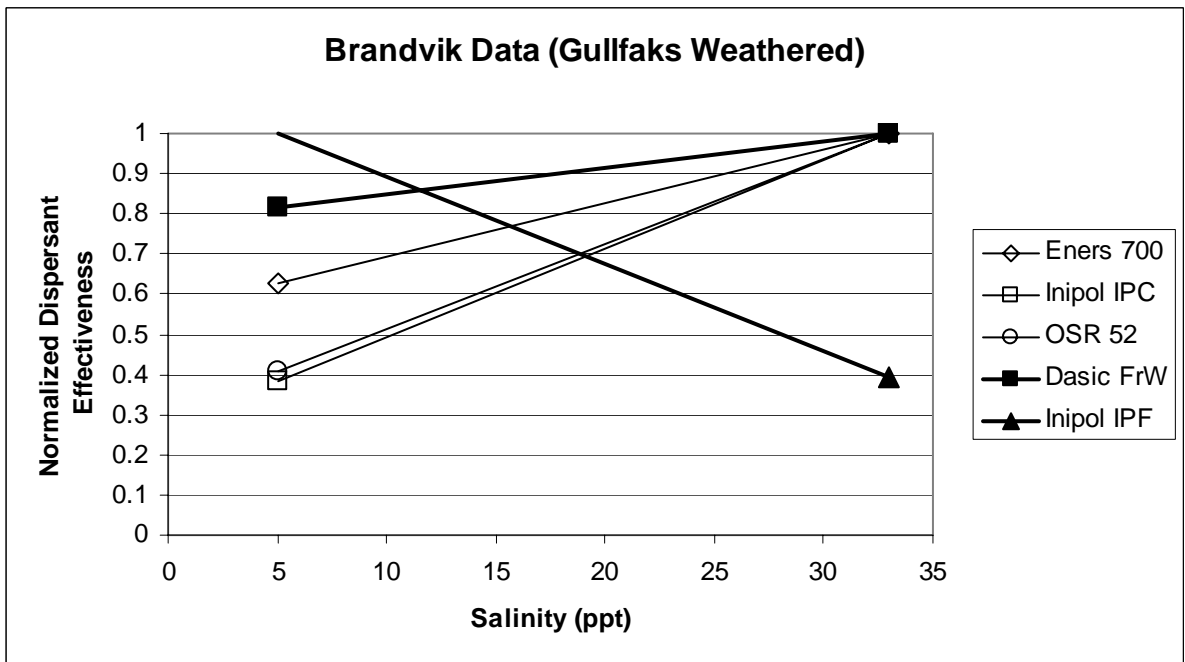


Figure 16. Normalized Dispersant Effectiveness Results on Weathered Gulfaks Oil adapted from Brandvic & Daling 1992.

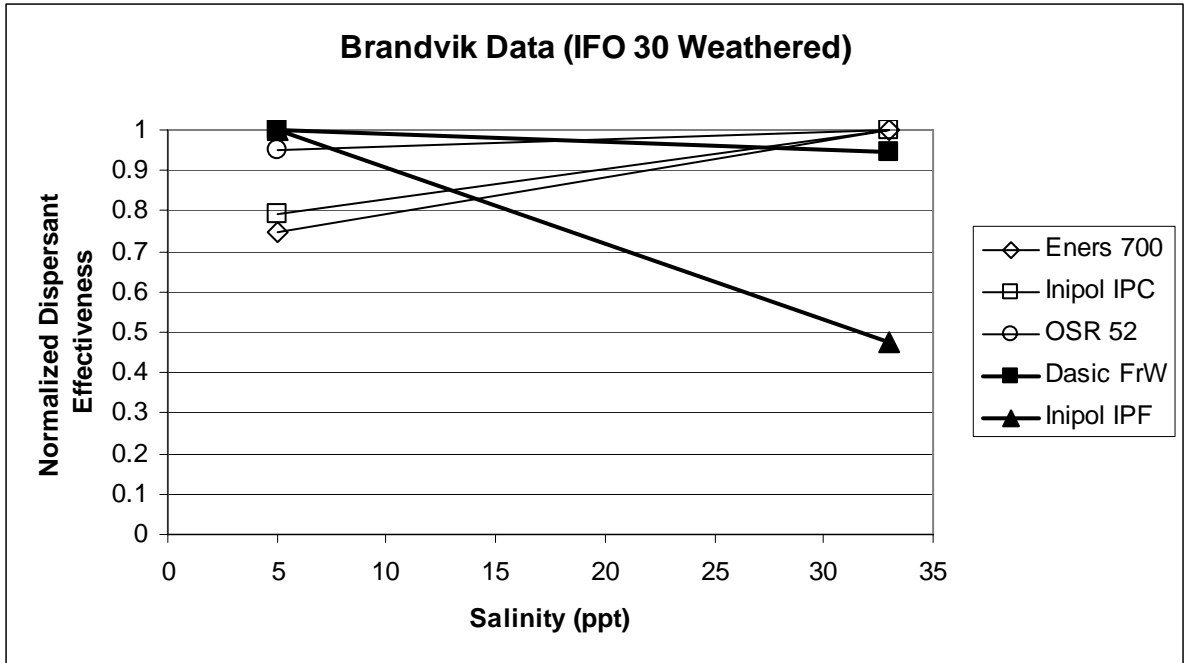


Figure 17. Normalized Dispersant Effectiveness Results on Weathered IFO 30 adapted from Brandvic & Daling 1992.

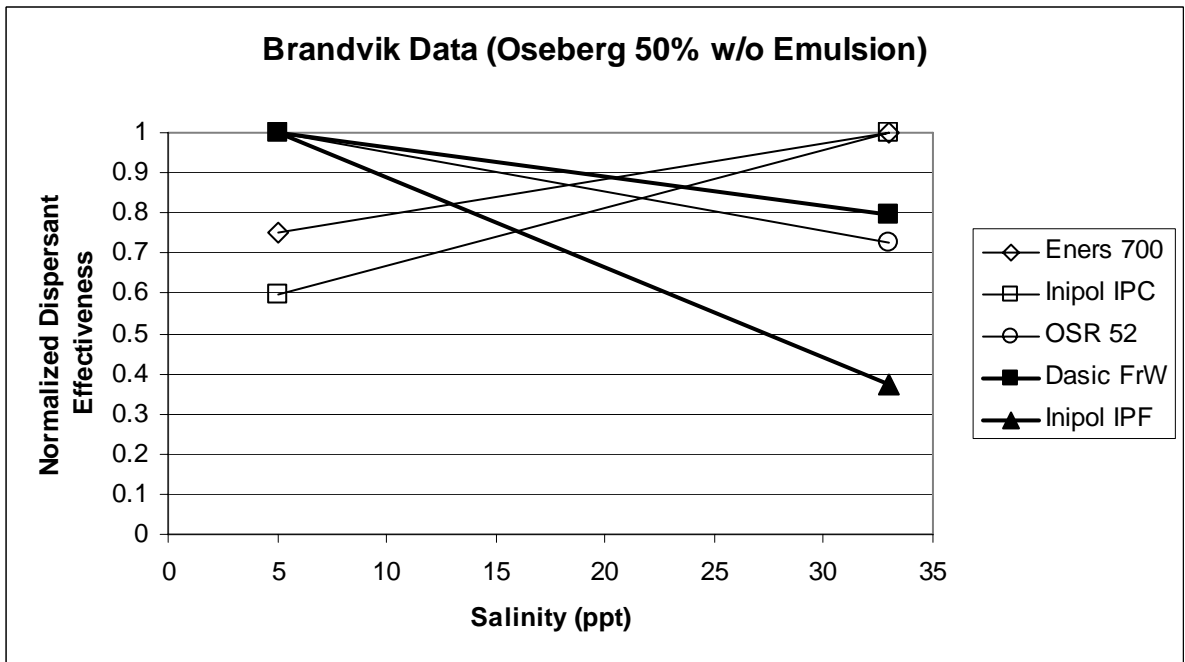


Figure 18. Normalized Dispersant Effectiveness Results on Emulsified Oseberg Oil adapted from Brandvic & Daling 1992.

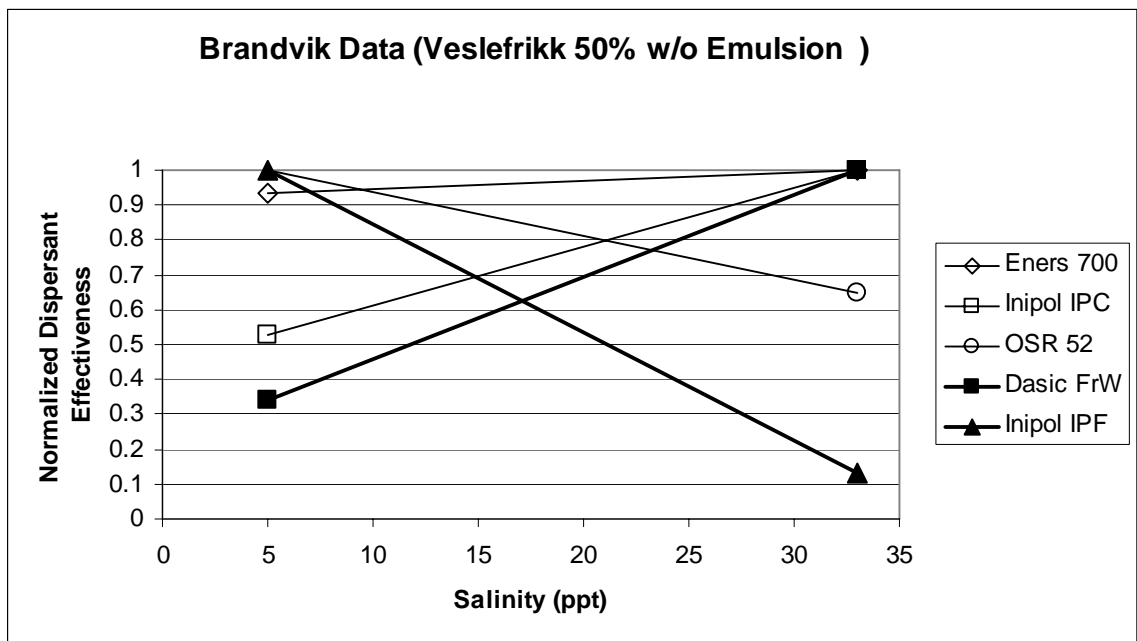


Figure 19. Normalized Dispersant Effectiveness Results on Emulsified Veslefrikk Oil adapted from Brandvic & Daling 1992.

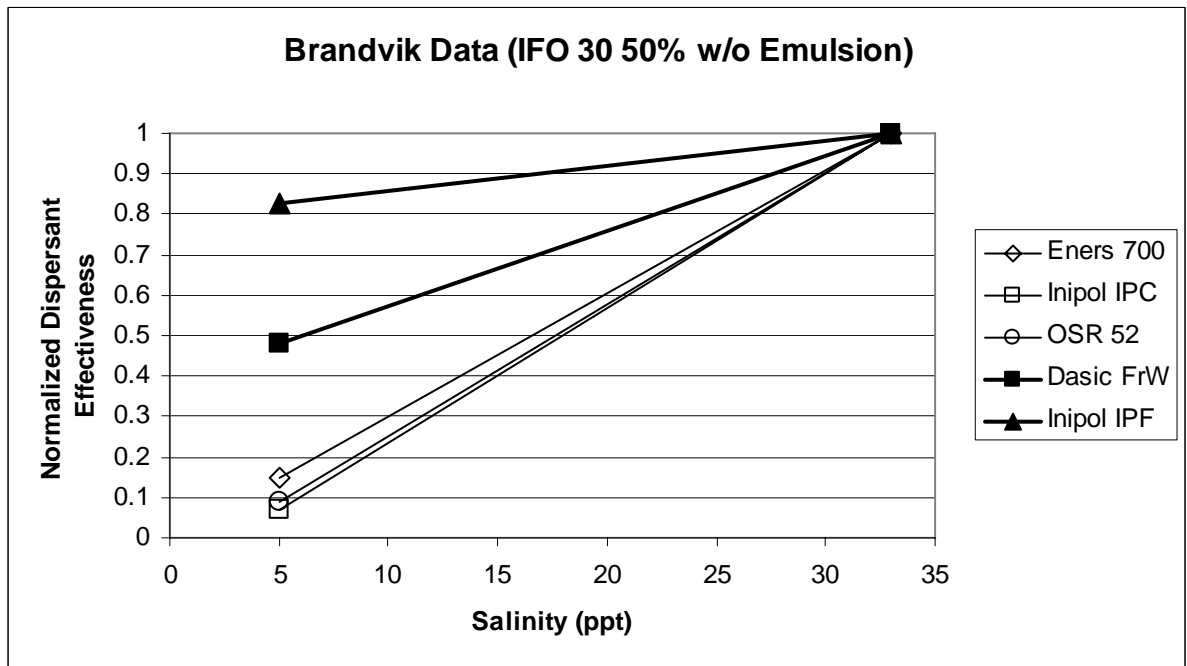


Figure 20. Normalized Dispersant Effectiveness Results on Emulsified IFO 30 adapted from Brandvic & Daling 1992.

## Appendix C: Annotated Bibliography

### Effect of Water Salinity on Chemical Dispersant Effectiveness

Barton, K., J. Michel, D. Fritz, E. Owens, A. Steen. 1995. Options for Minimizing Environmental Impacts of Freshwater Spill Response. 1995 International Oil Spill Conference, American Petroleum Institute. Washington, DC, pp. 987-989.

- Report indicates that dispersants “may cause the most adverse habitat impact” if used on light or medium crude oils or gasoline in small river and stream environments.

Belk, J.L., D.J. Elliott and L.M. Flaherty, "The Comparative Effectiveness of Dispersants in Fresh and Low Salinity Waters", in Proceedings of the 1989 International Oil Spill Conference, American Petroleum Institute, Washington, DC, pp. 333-336, 1989.

- Labofina tests using 4 marine dispersants and two freshwater dispersants at salinities from 0 to 35 ppt on WSL test oil and Prudhoe Bay crude oil. Dispersants were not named.
- Good data set for salinity effect on dispersant performance
- Tested dispersants in water with different electrolyte solutions and concentrations as well as freshwater with calcium hardness variation. One of the marine dispersants worked well in high calcium hardness fresh water but poorly in “soft” fresh water. The freshwater dispersant performed poorly in the hard water when compared to distilled. It was concluded that water hardness should be taken into account when assessing potential dispersant performance.
- Authors note that WSL test was developed for offshore conditions and energy levels in freshwater environs may be lower those in offshore. Lower energy testing may be more appropriate for freshwater studies.

Blondina, G.J., M.L. Sowby, M.A. Ouano, M.M. Singer and R.S. Tjeerdema, "Comparative Efficacy of Two Corexit Dispersants as Measured Using California's Modified Swirling Flask Test", in Proceedings of the Twentieth Arctic Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, ON, pp. 561573, 1997a.

- Modified (California protocol) swirling flask effectiveness tests of Corexit 9500 and 9527 on Prudhoe Bay, Kuwait and Arab medium oils.
- Good data collected on effectiveness vs salinity (use the SSTB report below for results from a wider range of oils)
- Corexit 9500 maintained performance over a wider range of salinities than Corexit 9527



Blondina, G.J., M.L. Sowby, M.T. Ouano, M.M. Singer and R.S. Tjeerdema, "A Modified Swirling Flask Efficacy Test for Oil Spill Dispersants", *Spill Science and Technology Bulletin*, 4, pp. 177-185, 1997b.

- No fresh or brackish water effectiveness testing in this report
- Report discusses analytical and other modifications to standard swirling flask test

Blondina, G.J., M.M. Singer, I. Lee, M.T. Ouano, M. Hodgins, R.S. Tjeerdema and M.L. Sowby, "Influence of Salinity on Petroleum Accommodation by Dispersants", *Spill Science & Technology Bulletin*, 5(2), pp. 127-134, 1999.

- Modified (California protocol) swirling flask effectiveness tests of Corexit 9500 and 9527 on 10 oils
- Good data collected on effectiveness vs salinity (this report includes the data from the 1997 AMOP paper above)
- Corexit 9500 exhibited better performance on most oils over the full range of salinities (the one exception was Forcados crude)
- Authors suggest that Corexit 9500 a better choice for application in areas where water salinity variations may occur
- Effectiveness variation in varying salinity waters is a function of both the oil and the dispersant

Brandvik, P.J. and P.S. Daling, "Laboratory Testing of Dispersants Under Arctic Conditions", in *Proceedings of the Fifteenth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, ON, pp. 123-134, 1992.

- IFP dilution testing: A) 14 dispersants and 2 weathered and emulsified (50% water) oils (Oseberg & Gullfaks) at 5 and 35 ppt salinities; B) 5 dispersants on 4 oils both weathered and emulsified and 5 and 35 ppt salinities; C) 2 dispersants with salinities ranging from 5 to 35 ppt (one oil??)
- A few of the dispersants tested were ones designed for low salinity (Inipol IPF was best of these at low salinity but its performance was poor below 12.5 ppt)
- No dispersant worked well in both fresh and high salinity water.

Brandvik, P.J., O.O. Knudsen, M.O. Moldestad and P.S. Daling, "Laboratory Testing of Dispersants Under Arctic Conditions", in *The Use of Chemicals in Oil Spill Response*, STP 1252, American Society for Testing and Materials, Philadelphia, PA, pp. 191-206, 1995.

Same as AMOP paper above:

- IFP dilution testing A) 14 dispersants and 2 weathered and emulsified (50% water) oils (Oseberg & Gullfaks) at 5 and 35 ppt salinities; B) 5 dispersants on 4 oils both weathered and emulsified and 5 and 35 ppt salinities; C) 2 dispersants with salinities ranging from 5 to 35 ppt (one oil??)

- A few of the dispersants tested were ones designed for low salinity (Inipol IPF was best of these at low salinity but its performance was poor below 12.5 ppt)
- No dispersant worked well in both fresh and high salinity water.

Brown, H.M. and R.H. Goodman, "Dispersants in the Freshwater Environment", in *Oil Dispersants: New Ecological Approaches*, STP 1018, American Society for Testing and Materials, Philadelphia, PA, pp. 31-40, 1989.

- Report of activities from the Freshwater Oil Spill Research Group
- EPS Env. Can. Tested 9 commercial dispersants for effectiveness on Norman Wells crude oil in fresh water in Mackay apparatus (MNS). Corexit 9550 was deemed a suitable freshwater dispersant based on these tests.
- Tests identified products that dispersed as much as 90% of the oil
- Toxicity testing was also completed on freshwater species
- A Field program (also see Brown et.al. 1990 below) was conducted in fen lakes using Corexit 9550 and Norman Wells crude oil. Oil initially covered between 5 and 10% of lake surfaces. The treated lake had no surface oil after a few days. The untreated lake had surface oil for more than a month. It was concluded that the oil spills (untreated and treated) had only temporary effects on the lakes. There were no significant biological impacts to the lakes either from the treated or untreated spills.

Brown, H.M., J.S. Goudey, J.M. Foght, S.K. Cheng, M. Dale, J. Hoddinott, L.R. Quaife and D.W.S. Westlake, "Dispersion of Spilled Oil in Freshwater Systems: Field Trial of a Chemical Dispersant", *Oil and Chemical Pollution*, 6, pp. 37-54, 1990.

- Norman Wells crude (3m<sup>3</sup>) spilled into two fen lakes. One spill treated with Corexit 9550
- Dispersed oil had little or no detectable short- or long-term effects on water quality or microbial populations in water or sediments
- Untreated oil caused more damage to floating and shoreline vegetation but this vegetation quickly re-grew and seasonal re-growth was normal (over two seasons)
- Authors concluded that no cleanup was best option but if spill posed a threat to indigenous wildlife dispersants might be an effective response in isolated fen lakes.

Buckley, J., B. De Lange Boom, E. Reimer. *The Physical Oceanography of the Cape Hatt Region, Eclipse Sound, N.W.T.*, *Journal of the Arctic Institute of North America*. Volume 40, Supplement 1. pp. 20-33. 1987

- Salinity data measured for the BIOS project where oil was dispersed in a nearshore arctic environment
- Salinity in spring and summer in the test Bays increased linearly from about 20 ppt at surface to 32 ppt at 5 m depth

Byford, D.C., P.J. Green and A. Lewis, "Factors Influencing the Performance and Selection of Low-Temperature Dispersants", in Proceedings of the Sixth Arctic Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, ON, pp. 140-150, 1983.

- In arctic environments surface water salinities should be considered for dispersant operations due to melting of low salinity ice and lower surface water salinities
- Labofina or WSL dispersant tests were completed at salinities of 5.5 to 33 ppt
- Medium fuel oil, weathered Lago Medi crude and weathered North Slope residue were tested with 7 unnamed dispersants
- Wide variations in performance with salinity as a function of both oil and dispersant type
- The effectiveness of one commercial dispersant was insensitive to salinity change but overall effectiveness was low
- The effectiveness of one experimental dispersant (G) was insensitive to salinity change and had a very good overall effectiveness rating
- Tests were also completed in the BP wave tank but only at full ocean salinity- the results did not correlated well with the WSL results

Chapman, H., K. Purnell, R. Law, M. Kirby. 2007. The use of dispersants to combat oil spills at sea: A review of practice and research needs in Europe. *Marine Pollution Bulletin*, 54 (2007) pp. 827-838.

- As of date of publication Europe had no statutory product approval process for effectiveness or toxicity... all procedures designed for full marine salinity
- Use of dispersants in low-salinity environments still an issue from effectiveness and impact standpoint
- This article speaks more to the policies of dispersant use

Clayton, I.R., G.H. Farmer, J.R. Payne, G.D. McNabb, P.C. Harkins, J.S. Evans, N.P. Rottlunda, C.R. Phillips and M.L. Evans, "Effects of Chemical Dispersant Agents on the Behavior and Retention of Spilled Crude Oil in a Simulated Streambed Channel", in *Oil Dispersants: New Ecological Approaches*, STP 1018, L.M. Flaherty (ed.), American Society for Testing and Materials, Philadelphia, PA, pp. 4-24, 1989.

- Artificial streambeds were constructed and natural stream water was routed through the channels.
- Chemically treated (Corexit 9550 and OFC D-60 premixed at 1:10) and untreated Prudhoe Bay crude oil were introduced to the stream and sediment samples were taken at locations of different sediment size and hydraulic conditions in the artificial streambed.
- Untreated slicks traveled through the artificial streams with only minor large drop dispersion at the highly turbulent areas along the stream. Treated slicks shed oil droplets more readily and much less oil was present on the surface at the end of

- the test beds. With Corexit 9550 the oil droplets had a greater tendency to be advected down into the water and to the sediments suggesting it is a better dispersant in the freshwater than the OFC D-60.
- More oil was detected in the sediments in the Corexit 955 tests than in the OFC D-60 and both dispersant applied tests resulted in considerably more oil in sediments than the untreated case.
  - It was concluded that the use of dispersants in freshwater streams should be done in conjunction with a knowledge of the characteristics of the spilled oil, the specific streambed environment and the location of sensitive biological communities
  - “For areas characterized by either relatively low sediment porosities (for example, Site 6 in this study) or high water turbulence levels (Site 10), dispersant application would appear to be useful because oil concentrations in sediment areas with these characteristics in this study were actually reduced with pre-spill additions of dispersants to the oil. However, application of dispersants in areas with sand or gravel matrices and only moderate turbulence levels must be approached with caution because such areas in this study were typically characterized by higher oil loadings with dispersants.”

Clayton, J.R., Jr., J.R. Payne, S.-F. Tsang, V. Frank, P. Marsden and J. Harrington, "Chemical Oil Spill Dispersants: Update State-of-the-Art on Mechanism of Action and Laboratory Testing for Performance", EPA/600/S-92/065, United States Environmental Protection Agency, Cincinnati, OH, 6 p., 1992.

- Primarily a comparison of different bench scale test results (IFP – dilution, Swirling flask pre-mix, EPA 10 min and 2 hr.)
- No data on salinity effects although importance of salinity as a variable mentioned.
- Full reports mentioned in this summary document.

Clayton, Jr., J.R., J.R. Payne and J.S. Farlow, Oil Dispersants: Mechanisms of Action and Laboratory Tests, C.K. Smoley for CRC Press, Boca Raton, FL, 103 p., 1993.

- A review of the effect of water salinity on dispersant effectiveness is provided as a section of this document.
- All of the references used in this review are included in this bibliography.

Eriksson, F. 1992. A Comparative Study of Oil Spill Dispersants in Brackish Water. Department of Physical Chemistry. Abo Akademi University, Abo, Finland. Paper presented in “Seminar: Combating Marine Oil Spills in Ice and Cold Conditions, Helsinki, Finland. December, 1992.

- Tested effectiveness of 31 commercial dispersants in 5 ppt salt water on fresh and weathered Russian crude oil using a modified WSL test.

- Flask was not rotated but shaken, efficiency measured at 2 and 10 minutes after mixing was stopped.
- Six dispersants were selected from the initial screening tests for a full analysis at two temperatures 0 and 15 oC and three DORs (1:10, 1:25, 1:50).
- Since only one water salinity was used the effect of salinity on effectiveness cannot be commented on from this data set alone.
- The modifications made to the WSL protocol for determination of effectiveness also makes it difficult to compare the results of this testing to other research.

Fingas, M.F., B. Kolokowski., E.J. Tennyson 1990. Study of Oil Spill Dispersants Effectiveness and Physical Studies. ",Proceedings of the 13th Arctic Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, ON, pp. 265-287, 1990.

Results in this paper are a sub-set of those reported in the 1991 IOSC conference paper below.

- Swirling flask tests on Alberta Sweet Mixed Blend, Norman Wells, Adgo crude oil with Corexit 9527, Enersperse 700 and Citrikleen dispersants with salinities between 0 and 100 ppt. All tests completed with pre-mixed dispersant and oil.
- Freshwater effectiveness was low for all dispersant and oil combinations
- Maximum effectiveness was achieved at 40 to 45 ppt and fell sharply with either a decrease or increase in salinity

Fingas, M.F., I. Bier, M. Bobra and S. Callaghan, "Studies on the Physical and Chemical Behaviour of Oil and Dispersant Mixtures", Proceedings of the 1991 International Oil Spill Conference, American Petroleum Institute, Washington, DC, pp. 419-426, 1991.

- Swirling flask tests on Alberta Sweet Mixed Blend, Norman Wells, Adgo crude oils with Corexit 9527, Enersperse 700 and Citrikleen dispersants with salinities between 0 and 100 ppt. All tests completed with pre-mixed dispersant and oil.
- Freshwater effectiveness was low for all dispersant and oil combinations
- Maximum effectiveness was achieved at 40 to 45 ppt and fell sharply with either a decrease or increase in salinity

Fingas, M.F., D.A. Kyle and E.J. Tennyson, "Dispersant Effectiveness: Studies Into the Causes of Effectiveness Variations", in The Use of Chemicals in Oil Spill Response, STP 1252, American Society for Testing and Materials, Philadelphia, PA, pp. 92-132, 1995.

Note: the effectiveness versus salinity data in this document are the same as those provide in Fingas et.al. 1991 IOSC.

- Report on laboratory scale testing completed at Environment Canada on dispersant effectiveness variation versus energy input, dispersant amount, oil characteristics, water salinity, and dispersant composition (HLB).
- Salinity results showed maximum effectiveness at 40 ppt with reduction at lower and higher salinities.
- Dispersants used were Corexit 9527, Enersperse 700 and Citrikleen.
- Oils tested were Alberta Sweet Mixed Blend, Norman Wells and ADGO.
- It was concluded that effectiveness of present-day dispersants in fresh water is low...however ...the results provided are for dispersants formulated for marine applications.

Fingas, M., L. Ka'ahue. 2005a. A literature Review of the Variation of Dispersant Effectiveness with Salinity. ",Proceedings of the 28th Arctic Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, ON, pp. 377-389, 2005.

- Conclusions of this review were as follows:
  - a) In waters with a salinity of 0 ppt conventional and currently available dispersants have a very low effectiveness or are sometimes even completely ineffective. This is consistent with physical studies in the surfactant literature.
  - b) Dispersant effectiveness peaks in waters with a salinity ranging from 20 to 40 ppt This may depend on the type of dispersant. Corexit 9500 appears to be less sensitive to salinity, but still peaks at about 35 ppt Corexit 9527 is more sensitive to salinity and appears to peak at about 25 ppt with some oils and at about 35 ppt with others.
  - c) There is a relatively smooth gradient of effectiveness with salinity both as the salinity rises to a peak point of effectiveness and after it exceeds this value. The curves for this salinity effect appear to be Gaussian.
  - D) While there is some evidence for a temperature-salinity interaction as noted in the data of Moles et al, 2002, there is not enough data to make solid conclusions.
  - e) Recent data are almost exclusively measured using Corexit 9527 and 9500. Since these have the same surfactant packages, there is a concern that the results may be more relevant to these formulations than to all possible formulations.
  - f) Observations on two field trials in freshwater appear to indicate that the laboratory tests are correct in concluding very low dispersant effectiveness in freshwater.
  - g) There were few studies on the biological effects of varying salinity and given oil exposure. There are not sufficient data to reach conclusions.
  - h) The findings in the dispersant literature reviewed here are in agreement with those in the theoretical and basic surfactant literature. The effect of ionic strength and salinity on both hydrophilic-lipophilic balance and stability is the reason for the decreased effectiveness noted at low salinities and the same decrease at high salinities above a certain peak of about 20 to 40 ppt.

Fingas, M., B.Fieldhouse, Z.Wang. 2005b. The Effectiveness of Dispersants under Various Temperature and Salinity Regimes. ",Proceedings of the 28th Arctic

- Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, ON, pp. 1043-1083, 2005b.
- Swirling flask tests on Alberta Sweet Mixed Blend crude and Corexit 9500 at 5 temperatures and 8 salinities.
  - Study showed an inter-relationship between temperature, salinity and effectiveness
- Fingas, M., B. Fieldhouse, Z. Wang. 2006. The Effectiveness of Dispersants on Alaska North Slope Crude Oil under Various Temperature and Salinity Regimes. ",Proceedings of the 29th Arctic Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, ON, pp. 821-827, 2006.
- Swirling flask tests on Alaska North Slope crude and Corexit 9500 at 3 temperatures and 8 salinities.
  - Study showed an inter-relationship between temperature, salinity and effectiveness
- Flaherty, L.M., W.B. Katz and S. Kaufman, "Dispersant Use Guidelines for Freshwater and Other Inland Environments", in Oil Dispersants: New Ecological Approaches, STP 1018, L.M. Flaherty (ed.), American Society for Testing and Materials, Philadelphia, PA, pp. 25-30, 1989.
- A general discussion of the need for guidelines for dispersant use in inland waters.
  - Discussion of some scenarios where dispersant use may be appropriate but no research data is provided on use of dispersants in freshwater.
- Fritz, D.E., A. Steen. 1995. Information to Minimize Impacts from Freshwater Oil Spills, Proceedings of the 1995 International Oil Spill Conference, American Petroleum Institute, Washington, DC, pp. 965-966, 1995.
- Mentions guide developed by API Inland Spills Working Group for best practices for freshwater oil spills.
  - Mentions annotated bibliography for freshwater spills.
  - Mentions decision tree for chemical use in freshwater systems.
- Fritz, D.E., "Effect of Salinity on Chemical Effectiveness", in Proceedings of a Workshop on the Use of Chemical Countermeasures Product Data for Oil Spill Planning and Response, NOAA, Seattle, WA, pp. 75-81, 1995.
- States that dispersants work best at 30 to 40 ppt and salinity can have a significant effect on the performance of most dispersants.
  - Uses the figures developed by Fingas in 1991 IOSC paper to support this.

George-Ares, A., R.R. Lessard, K.W. Becker, G.P. Canevari and R.J. Fiocco, "Modification of the Dispersant Corexit 9500 for Use in Freshwater", in Proceedings of the 2001 International Oil Spill Conference, American Petroleum Institute, Washington, DC, pp. 1209-1211, 2001.

- Indicates that France is only country with an approval process for fresh water dispersants.
- Exdet tests on Hydra, Escalante and Canadon Seco crude oils were completed using a calcium chloride modified Corexit 9500, standard Corexit 9500, Dasic freshwater, Enersperse 1037, and Inipol IPF dispersants.
- River and de-ionized water were used in tests.
- The calcium chloride modified Corexit 9500 worked better in the fresh and de-ionized water than C 9500. Dasic freshwater provided best effectiveness across all oils.

Guyomarch, J., S. Le Floch and F.-X. Merlin, "Effect of Suspended Mineral Load, Water Salinity and Oil Type on the Size of Oil-Mineral Aggregates in the Presence of Chemical Dispersant", *Spill Science and Technology*, 8, pp. 95-100, 2002.

- This study of clay-oil flocculation in chemically dispersed systems showed a decrease in oil removal by clay-oil flocculation / settling with salinities above 10 ppt. This was more pronounced with low clay concentration.

Lane, P.M., Crowell, D. Patriquin, I. Buist. 1987. The Use of Chemical Dispersants in Salt Marshes. Environmental Studies Research Funds Report No. 070. 1987.

- Field study was completed where oil was sprayed onto a tidal marsh plots and then sprayed with Corexit 9527 and monitored. No water salinity was reported but a water density of 1.025 g/cc was noted.
- A conclusion was that the use of dispersants in salt marshes is not a viable countermeasure as it did not remove the oil from the vegetation and was more toxic to the vascular plant communities than the oil.

Lee, K., P. Stoffyn-Egli, E. Owens. 2001. Natural Dispersion of Oil in a Freshwater Ecosystem: Desaguadero Pipeline Spill, Bolivia. Proceedings of the 2001 International Oil Spill Conference, American Petroleum Institute, Washington, DC, pp. 1445-1448, 2001.

- A report on natural OMA removal of oil in a freshwater ecosystem.
- No chemical dispersion connection

Lehtinen, C.M. and A.M. Vesala, "Effectiveness of Oil Spill Dispersants at Low Salinities and Low Water Temperatures", in *Oil Spill Chemical Dispersants: Research, Experience and Recommendations*, T.E. Allen (ed.), STP 840, American Society for Testing and Materials, Philadelphia, PA, pp. 108-121, 1984.



- MacKay dispersant effectiveness tests completed on a fresh and slightly weathered Russian crude oil using a standard marine dispersant and two freshwater formulations using 3, 7 and 12 ppt water at 4, 10 and 15 oC.
- Reduced effectiveness will all dispersants as salinity and temperature decreased
- The marine dispersant outperformed the two freshwater in all but the 3ppt weathered oil tests

Martinelli, F.N. and B.W.J. Lynch, "Factors Affecting the Efficiency of Dispersants", LR 363 (OP), Warren Spring Laboratory, Stevenage, 18 p., 1980.

- Oil and dispersant type, temperature and agitation studied but no testing with salinity variation

Mackay, D., "Effectiveness of Chemical Dispersants Under Breaking Wave Conditions", in *The Use of Chemicals in Oil Spill Response*, STP 1252, American Society for Testing and Materials, Philadelphia, PA, pp. 310-340, 1995.

- Laboratory scale tests using the EXDET test method resulted in little dispersion difference using Corexit 9527 in water with salinity ranging from 5 to 32 ppt on 10 and 20% weathered Alaska North Slope crude oil.
- Comment: Dispersant and oil were pre-mixed and this may be the reason for no variation in effectiveness as a function of water salinity.

McAuliffe, C.D., "The Use of Chemical Dispersants to Control Oil Spills in Shallow Nearshore Waters", STP 1018, American Society for Testing and Materials, Philadelphia, PA, pp. 49-72, 1989.

- Discussion of potential concentrations of oil in the water column due to dispersed oil slicks in the nearshore and the possible biological effects of these events.
- No discussion or data presented related to fresh or brackish water implications in the nearshore.

Moet, A., M.Y. Bakr, M. Abdelmonim and O. Abdelwahab, "Factors Affecting Measurements of the Efficiency of Spilled Oil Dispersion", Preprints - Symposium on General Papers and Poster Session for the Division of Petroleum Chemistry, 210 National Meeting, American Chemical Society, Vol. 40, pp. 564-566, 1995.

- Used WSL test method to study the effect of water salinity, settling time, mixing energy and dispersant to oil ratio. Used Corexit 9527 dispersant and Arab Light crude oil.
- Effect of salinity on results was similar to other research with max effectiveness at about 30 ppt with decreasing effectiveness at both lower and higher salinities.

Moles, A., L. Holland and J. Short, "Effectiveness in the Laboratory of Corexit 9527 and 9500 in Dispersing Fresh, Weathered and Emulsion of Alaska North Slope Crude Oil Under Subarctic Conditions", *Spill Science and Technology Bulletin*, 7, pp. 241247, 2002.

- Swirling flask testing of fresh, weathered and emulsified ANS crude at 3, 10 and 22°C and 22 and 32 ppt salt water
- Found reduced effectiveness at the 22 ppt salinity in the colder water tests for fresh ANS
- Found increased or similar effectiveness at low salinities and all temperatures for emulsions of ANS, but this may have been because the emulsions were made with 32 ppt water and then tested in lower salinity waters
- Author acknowledges that the low energy level in the swirling flask test may not be a good representation of environmental conditions

Merlin, F., C. Bocard, R. Cabridenc, J. Oudot. 1991. Toward a French Approval Procedure for the use of Dispersants in Inland Waters. *Proceedings of the 1991 International Oil Spill Conference*, American Petroleum Institute, Washington, DC, pp. 401-404, 1991.

- Concluded that dispersants would only be effective in running ( $> 0.3$  m/s) and turbulent fresh waters.
- Sediment in fresh water trapped 20 to 80% of the dispersed oil and this sediment would settle out once it reached calm water.
- Many products effective in salt water are not effective in fresh water so dispersants must be tested for use in fresh water.
- France was establishing a procedure for the approval of dispersant use in fresh water.

Michel, J., A. Walker, D. Scholz, J. Boyd. 2001. Surface-Washing Agents: Product Evaluations, Case Histories and Guidelines for Use in Marine and Freshwater Habitats. *Proceedings of the 2001 International Oil Spill Conference*, American Petroleum Institute, Washington, DC, pp. 805-813, 2001.

- Researchers developed summaries of mechanisms of action, when to use, health and safety issues, limiting factors and environmental issues for surface washing agents (SWAs).
- Summarized product-specific information on use, toxicity, effectiveness in salt and fresh water, stockpiles and production capabilities etc.
- Suggest monitoring plans and strategies for use of SWAs.

Nagy, E, B. Scott, J. Hart. 1981. The Fate of Oil and Dispersant Mixtures in Freshwater. National Water Research Institute, Canada Centre for Inland Waters. Env. Canada. EPS 4-EC-81-3.

- Artificial ponds were constructed and filled with lake water and allowed to form biological communities over a period of two months
- Oil only and oil premixed with Corexit 9527 were added to two ponds and the ponds were monitored for a one-year period.
- Dispersed oil was a brown-cloud so effectiveness was not an issue – pre-mixed C 9527 worked in the fresh water system.
- Ponds underwent similar changes regardless of oil-dispersant treatment.
- Dispersant did not appear to alter the characteristics of the oil
- Less oil was accounted for in the dispersant treated pond than the oil only.

Paddock, A. 1987. A Major Inland Spill Case History Viewed as a Candidate for Dispersant Use. Proceedings of the 1987 International Oil Spill Conference, American Petroleum Institute, Washington, DC, pp. 621, 1987.

- No dispersant was used in this inland spill.
- The article discusses how dispersant might have been used to improve the spill response in this fast flowing river environment.
- Article concludes that dispersants could have been used to treat streamers of oil along the mid-channel of the fast-flowing river to prevent this oil from eventually being herded to thick shoreline accumulations.

Payne, R., C. Phillips, M. Floyd, L. Flaherty. 1985. Estimating Dispersant Effectiveness Under Low Temperature-Low Salinity Conditions. Proceedings of the 1985 International Oil Spill Conference, American Petroleum Institute, Washington, DC, pp. 638, 1985.

- Effectiveness of 4 commercial dispersants were determined on Prudhoe Bay crude oil using EPA standard test (swirling flask) at 0, 18 and 33 ppt salinities and 1 and 10 °C temperatures
- Dispersants were Corexit 9550, Finasol OSR-7, ECO AtlanTol AT-7 and OFC D-609.
- Corexit 9550 was most effective of the four at 0 ppt, OFC D-609 was better than Corexit 9550 at 18ppt and the two were equally effective at 33 ppt. The other two dispersants were less effective under all conditions.

Peabody, C.H., "Freshwater Dispersant Study", Proceedings of the Fifth Arctic Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, ON, pp. 265-274, 1982.

- No actual research data is provided.
- This is just an overview of what the researchers were planning to do to study use of dispersants in fresh waters.

Quaife, L., C. Peabody, H. Brown, R. Goodman. 1986. Freshwater Oilspill Research Program – Field Trial. Proceedings of the 9th Arctic Marine Oilspill Program Technical Seminar, Environment Canada, Ottawa, ON, pp. 601-621, 1986.

- This is a report on the field trial described in Peabody, above.
- 3 sloughs with maximum depths of 2 m were used in the field program
- One was a control, one had Normal Wells crude oil only applied and in the final slough oil was laid down and then sprayed with Corexit 9550 by helicopter with a design dose of 1:10
- The ponds were monitored by remote sensing and water and vegetation sampling.
- Drop-size measurements showed that the chemically treated oil effectively dispersed into the water column
- The botanical and microbiological program results indicated that neither the oil nor the oil and dispersant treated mixtures caused any beneficial or deleterious effects to the water bodies.

Scott, B.F., E. Nagy, J.P. Sherry, B.J. Dutka, V. Glooschenko, N.B. Snow and P.J. Wade, "Ecological Effects of Oil-Dispersant Mixtures in Fresh Water", in Proceedings of the 1979 International Oil Spill Conference, American Petroleum Institute, Washington, DC, pp. 565-571, 1979.

- This is a second report on the work by Nagy et. al. 1981 above that provides more details on the ecological effects of the oil or oil-dispersant mixtures placed in the artificial ponds.
- The short-term (55 days) results showed that the dispersant-oil mixture affects the zooplankton, phytoplankton bacteria, fungi, and dissolved oxygen to a greater degree than oil only

Sergy, G., P. Blackall. 1987. Design and Conclusions of the Baffin Island Oil Spill Project. Journal of the Arctic Institute of North America. Volume 40, Supplement 1. pp. 1-9. 1987.

- Overview of BIOS project conducted in near shore Arctic waters of Cape Hatt, Baffin Island.
- Two spills, one spill was oil only and the other was premixed dispersant and oil: both released in near shore waters and allowed to move to shore.
- 75 drums spilled at each site
- Oil-dispersant and water were pre-mixed and released through a discharge header so dispersant effectiveness was not studied.
- The biological monitoring results from the control and dispersed oil sites provided no ecological reasons to prohibit the use of dispersants on oil slicks in near shore areas similar to the experimental site used in the study.

Sterling, C., J. Bonner, A. Ernest, C. Page, R. Autenrieth. 2004. Chemical dispersant effectiveness testing: influence of droplet coalescence. Marine Pollution Bulletin 48 (2004) 969-977.

- Studied droplet coalescence in a range of water salinities (10, 30 and 50 ppt) for pre-mixed oil and dispersant systems.
- Salinity effects were not significant in the effectiveness studies due to pre-mixing
- Coalescence kinetics were found to possibly be important in laboratory scale dispersant tests and coastal systems.

Walker, A., J. Kucklick, A. Steen, D. Fritz. 1995. Oil Spill Chemicals in Freshwater Environments: Technical Issues. Proceedings of the 1995 International Oil Spill Conference, American Petroleum Institute, Washington, DC, pp. 373-379, 1995.

- Review of chemical dispersant effectiveness in fresh water is not discussed in this article
- Main concern is with other chemical treating agents (herders, shoreline cleaners, de-emulsifiers, solidifiers)
- Main focus is on identifying test procedures for effectiveness and toxicity testing for the various chemical treating agents in freshwater

Wells, P.G. and G.W. Harris, "Dispersing Effectiveness of Some Oil Spill Dispersants: Testing with the 'Mackay Apparatus'", Spill Technology Newsletter, 4, pp. 232-241, 1979.

- Used Mackay Dispersant Effectiveness Apparatus to study effectiveness as a function of DOR, salinity, dispersant batch type, and dispersant temperature.
- Four dispersants (Corexit 9527, BP1100X, Corexit 8666, Drew O.S.E. 71 and Oisperse 43) were tested in fresh and seawater at ODRs of 10:1 and 10:5 using Venezuelan Lago Medio crude oil.
- Corexit 9527 performed best and was much more effective in sea water than in fresh (40% vs 4%).
- All dispersants worked better in seawater.
- Both Corexit 9527 and BP100X had reduced effectiveness when the dispersant was cooled prior to application

Wolfe, M.F., G.J.B. Schwartz, S. Singaram, E.E. Mielbrecht, R.S. Tjeerdema and M.L. Sowby, "Effects of Salinity and Temperature on the Bioavailability of Dispersed Petroleum Hydrocarbons to the Golden-Brown Algae, *Isochrysis galbana*", Archives of Environmental Contamination and Toxicology, 35, pp. 268-273, 1998.

- No data or discussion on the issue of dispersion effectiveness as a function of water salinity.

Wrenn, B., A. Virkus, B. Mukherjee, A. Venosa. 2009. Dispersibility of crude oil in fresh water. Environmental Pollution 157 (2009) 1807-1814.

- A good description of surfactant chemistry as it pertains to oil dispersion is provided.
- Studied experimental dispersant formulations with varying HLB's to determine which surfactants and HLB's provide best dispersion of a single crude oil (MARS crude) in fresh water.
- Measured oil drop size distributions generated in baffled flask test to determine effectiveness.
- Dispersant formulations were found that were as effective in fresh water as the best commercial products are in marine conditions.

## **Effect of Water Salinity on Chemical Herder Performance**

Buist, I. and Morrison, J. 2005. Research on using oil herding surfactants to thicken oil slicks in pack ice for in situ burning. Proceedings of the Arctic and Marine Oilspill Program Technical Seminar No. 28, Vol. 1, Environment Canada, Ottawa, pp 349-375.

- (see SL Ross 2004 below)

Buist, I., Potter, S., Zabilansky, L., Meyer, P. and Mullin, J. 2006. Mid-scale test tank research on using oil herding surfactants to thicken oil slicks in pack ice: An update. Proceedings of the Arctic and Marine Oilspill Program Technical Seminar No. 29, Vol. 2, Environment Canada, Ottawa, pp 691-709.

- (see SL Ross 2007 below)

Buist, I. 2007. Using Herding Surfactants to Thicken Oil Slicks in Pack Ice for In Situ Burning. Proceedings International Oil & Ice Workshop 2007, Minerals Management Service. Herndon, VA

- (see SL Ross 2007 below)

Buist, I., Potter, S., Nedwed, T. and Mullin, J. 2007. Field research on using oil herding surfactants to thicken oil slicks in pack ice for in situ burning. Proceedings of the Arctic and Marine Oilspill Program Technical Seminar No 30, Vol. 1, Environment Canada, Ottawa, pp 403-425.

- (see SL Ross 2007 below)

Buist, I., T. Nedwed and J. Mullin. 2008. Herding Agents Thicken Oil Spills In Drift Ice To Facilitate In Situ Burning: A New Trick for an Old Dog. 2008 International Oil Spill Conference Proceedings, May 4 - 8, Savannah, Georgia, American Petroleum Institute, pp.673-680.

- (see SL Ross 2007 below)
- Garrett, W. and W. Barger. 1970. Factors Affecting the Use of Monomolecular Surface Films to Control Oil Pollution on Water. Environmental Science and Technology. Vol. 4, No. 2 February, 1970.
- Advanced the theory of how herders work by reducing water surface tension
- Garrett, W.D. and W.R. Barger, 1972, Control and Confinement of Oil Pollution on Water with Monomolecular Surface Films. Final Report to U.S. Coast Guard, Nov 1971, Project No. 724110.1/4.1 (also reprinted as U.S. Navy Naval Research Laboratory Memorandum Report 2451, June 1972, AD 744-943)
- first scientific study of oil herding agents
- experiments in both fresh and saline water, including field applications in rivers, harbours and offshore, with no adverse effects of salinity noted
- Langmuir, I. 1933. Oil Lenses on Water and the Nature of the Monomolecular Expanded Films. J. Chemical Physics. Vol. 10, November, 1933.
- Seminal paper on monomolecular films and reduced surface tension
- Marine Spill Response Corporation, 1995, Chemical Oil Spill Treating Agents, MSRC Technical Report Series 93-105, Herndon, VA
- Summary report reviewing herding agents
- Pope, P., A. Allen and W. G. Nelson, 1985, Assessment of Three Surface Collecting Agents during Temperate and Arctic Conditions. Proceedings of the 1985 Oil Spill Conference, API/EPA/USCG, Washington, DC, pp 199-201.
- In a series of experiments with three different herding agents in laboratory tests, concluded that there was no measurable difference when the agents were applied on tap water or simulated seawater
- Rijkwaterstaat, 1974, Shell Herder Trials, Report to the Dutch Ministry of Transport, Gravenhage, Holland
- Kept a 5-ton slick from spreading for 5 hours by applying Shell Oil Herder
- SL Ross Environmental Research, 2004, Preliminary Research On Using Oil Herding Surfactant To Thicken Oil Slicks In Broken Ice Conditions, Report to ExxonMobil Upstream Research, Houston , January 2004
- Water salinity did not significantly affect the action of Corexit 9580. The herder was only slightly more effective on 35 ‰ saline water than on fresh water.

SL Ross Environmental Research, 2005, Small-Scale Test Tank Research on Using Oil Herding Surfactants to Thicken Oil Slicks in Broken Ice for In situ Burning, Report to ExxonMobil Upstream Research, Houston, TX

- Tests were carried out on 35 ‰ salt water to explore the relative effectiveness of three oil-herding agents in simulated ice conditions; conduct larger scale (10 m<sup>2</sup>) quiescent pan tests to explore scaling effects; carry out small-scale (2 to 6 m<sup>2</sup>) wind/wave tank testing to investigate wind and wave effects on herding efficiency; and, perform small-scale in situ ignition and burn testing. One herder formulation proved superior on cold water.

SL Ross Environmental Research, 2007, Mid-scale Test Tank Research on Using Oil Herding Surfactants to Thicken Oil Slicks in Broken Ice, Report to MMS, ExxonMobil Upstream Research Company, Agip Kashagan North Caspian Operating Company, Sakhalin Energy Investment Company and Statoil ASA, Herndon VA.

- Report on mid-scale tests of herders in pack ice at three facilities:
  1. A two-week test program at a scale of 100 m<sup>2</sup> at CRREL on water doped with 10 ‰ of urea .
  2. Experiments carried out at Ohmsett on 35-‰ salt water to explore the use of herders on spreading oil slicks in free-drifting ice fields at a scale of 1000 m<sup>2</sup>.
  3. Burn experiments at the scale of 30 m<sup>2</sup> in a specially prepared pool containing broken sea ice on fresh lake water at Prudhoe Bay, AK.

### **Existing Policies and Guidelines for Dispersant Use in Fresh and Brackish Waters**

Abbasova A., K. Bagirova, G. Campbell, J. Clark, R. Gallagher, N. Garajayeva, A. Georges-Ares, L. Huseynova, D. Nelson, B. Roddie, and R. Tair. 2005. Evaluation of dispersants for use in the Azerbaijan Region of the Caspian Sea. International Oil Spill Conference 2005 pp. 247-252.

- The study addressed the usefulness of dispersants for treating spills in the low salinity waters of the Caspian Sea. Authors: tested effectiveness of six dispersants against a locally produced crude oil in Caspian Sea water; measured the toxicity of the six dispersants and oil dispersant mixtures against locally important species of aquatic organism; discussed net environmental benefits of dispersants for local spills; and made recommendations concerning dispersant use for spills in the Azerbaijan region of the Caspian.

American Society for Testing and Materials. 2008a. Standard Guide for Ecological Considerations for the Use of Oil Spill Dispersants in Freshwater and Other Inland Environments, Ponds and Sloughs Designation: F1209-08. American Society for Testing and Materials, March 2008.



- Suggests some basic considerations in using dispersants in small, shallow bodies of fresh water.

American Society for Testing and Materials. 2008b. Standard Guide for Ecological Considerations for the Use of Oil Spill Dispersants in Freshwater and Other Inland Environments, Large Lakes and Water Bodies. Designation: F 1210-08. American Society for Testing and Materials, March 2008.

- Suggests some basic considerations in using dispersants in large lakes.

American Society for Testing and Materials. 2008c. Standard Guide for Ecological Considerations for the Use of Oil Spill Dispersants in Freshwater and Other Inland Environments, Rivers and Creeks. Designation: F 1231-08. American Society for Testing and Materials, March 2008.

- Suggests some very basic considerations in using dispersants in flowing waters small and large.

Energy Institute and Environmental Agency of England and Wales. 2004. Inland Waters Oil Spill Response: A Guidance Document for Incorporating the Strategies and Techniques for Responding to Inland Surface Water Oil Spills in the United Kingdom. Energy Institute, London.

- This is the standard guide/policy for cleanup of oil spills in inland water in the United Kingdom. Dispersants are not mentioned.

Helsinki Commission. 1992. Helcom Recommendation 22/2: Restricted Use Of Chemical Agents And Other Non-Mechanical Means In Oil Combating Operations In The Baltic Sea Area. Helsinki Commission.

- This provides some basic guidance regarding the use of countermeasures (e.g., dispersants, in-situ burning, sinking agents, sorbents) other than mechanical cleanup. With respect to dispersants, international codes of practice (e.g. IMO dispersant guidelines) are named and dispersant use considerations, such as effectiveness limitations and net environmental benefit analysis, are mentioned.

Merlin, F. C. Bocard, R. Cabridenc, J. Oudot, and E. Vindiniam. 1991. Toward a French approval procedure for the use of dispersants in inland waters. International Oil Spill Conference 1991, pp. 401-404.

- This paper assessed the potential for using dispersants to treat spills in inland waters in France and recommended certain guidelines. It concluded that dispersant use is appropriate only in running and turbulent waters and provided certain other guidance. It also developed a draft approval procedure for dispersant

products to be used in fresh water that considered effectiveness, toxicity and degradability.

NOAA and American Petroleum Institute. 1994. Inland Oil Spills: Options for Minimizing Environmental Impacts of Freshwater Spill Response. NOAA and American Petroleum Institute. September 1994.

- This is a generic guide for cleanup of oil spills in inland water in the United States. With respect to dispersants, certain basic considerations regarding dispersant use in inland waters are mentioned, but it contains no guidelines and provides no help in decision-making or planning.