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

Annotated Bibliography

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Effect of Water Salinity on Chemical Dispersant Effectiveness


- 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.


- 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.

• 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


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


• 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


• 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.

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??)
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- 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.


- **Norman Wells crude (3m³)** 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.

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


• 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


- 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.”


- 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.

- 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.


- 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 °C 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.


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


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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.


• 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.


- 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


- 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


- 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.


- 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.


• 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.


• Indicates that France is only country with an approval process for freshwater 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, Enerperse 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.


• 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.


• 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.

- No chemical dispersion connection.


- 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 °C.
- 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.


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


- 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.


- 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.

- 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.


- 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


- 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.

• 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.


• 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 he 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.


• 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.


• 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 9950 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.

- 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.


- 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.


- 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


- 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.


• 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.


• 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


• 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


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


- 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


- (see SL Ross 2004 below)


- (see SL Ross 2007 below)


- (see SL Ross 2007 below)

• (see SL Ross 2007 below)


• (see SL Ross 2007 below)


• Advanced the theory of how herders work by reducing water surface tension


• 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


• Seminal paper on monomolecular films and reduced surface tension


• Summary report reviewing herding agents


• 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 m²) quiescent pan tests to explore scaling effects; carry out small-scale (2 to 6 m²) 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 m² 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 m².
  3. Burn experiments at the scale of 30 m² 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**


• 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.


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


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


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


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


- 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.

- 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.


- 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.