Dispersants, Salinity and Prince William Sound

for

Prince William Sound Regional Citizens' Advisory Council (PWSRCAC)
Anchorage, Alaska

by

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December, 2004

Abstract

This paper is a summary of the effects of water salinity on chemical dispersion, especially those effects related to effectiveness. Surfactants are the active ingredient in dispersants. The surfactant is more lipophilic, or oil-loving, in freshwater and increases in hydrophilicity (or water-loving) as the salinity rises. The stability of the resulting droplets is also dependent on salinity. This is due to the increasing ionic strength of the water as salinity rises. As the salinity rises above a certain point, which depends on the particular type of surfactant, this increased force results in more surfactant molecules leaving the oil drop entirely. While the theoretical possibility of freshwater dispersants exist, the stability of dispersions in less saline waters would be less.

This report reviews several older dispersant tests. Data from these tests were separated from more recent data because older testing procedures and analytical methods are not as accurate as today's methods. Newer testing is reviewed as well. This testing is marked by the use of analysis by chromatography and very strict protocols in operating the dispersant tests themselves. These tests are marked by having standard deviations less that 10% and often less than 5%. The conclusions from both recent and older studies are the same.

The general surfactant literature was reviewed for the effects of salinity on surfactants and surfactant phenomena. There is a body of literature on the use of surfactants for secondary oil recovery. There are some commonalities among the many findings. Recovery efficiency falls off at both high and low salinities. The salinity at which surfactant efficiency peaks is very dependent on the structure of the specific surfactant. Several studies on the interaction of specific hydrocarbons and surfactants were reviewed. The consensus of these papers is that the solubility of the hydrocarbon increases with increasing salinity and is low at low salinities. The interfacial tension of water and oil changes with surfactant and salinity. The interfacial tension is higher at lower salinities. The optimal interfacial tension is generally achieved at salinities of between 25 to 35 o/oo. A number of physical systems involving surfactants and salinity changes are reported in the literature. Included in these is the finding that the stability of microemulsions is greater at salinities of 25 to 35o/oo. Some workers found that the stability of systems was very low in fresh water or in water with salinities of < 10 o/oo.

Some field studies of dispersant application were conducted in the freshwater environment. While effectiveness was not specifically measured, it was noted in both series of studies that effectiveness may have been low. In the one study, the investigators noted that the surfactants had poor effectiveness and stability in freshwater. In this particular case, the dispersion lasted only for about an hour and the dispersion was limited to a few centimetres. In another case, it was noted that there was oil around the edges of the dispersed pond within a short time of dispersant application.

Some effects studies were conducted under varying salinity conditions. In one study, naphthalene and a,b napthol sulphate uptake were studied under different salinity conditions. There were no significant differences at different salinities, although, naphthalene uptake was somewhat higher under low salinity conditions. Another study examined the induction of hsp60 protein in golden-brown algae. It was found that greater salinity reduced the effects of the simulated oil spills on the algae.

The varying salinities of the waters in Prince William Sound were described and summarized. There are areas around the Sound of low salinity. Dispersant applications in these areas would result in reduced dispersant effectiveness.

The following are the overall conclusions of this study.

a) The effectiveness of conventional and currently available dispersants is very low at 0 o/oo or sometimes they are even completely ineffective. This is consistent with physical studies described in the surfactant literature.

b) Dispersant effectiveness peaks at 20 to 40 o/oo. This may depend on the type of dispersant. Corexit 9500 appears to be less sensitive to salinity but still shows a peak at about 35 o/oo. Corexit 9527 is more sensitive to salinity and appears to peak at about 25 o/oo with some oils and with others at about 35 o/oo.

c) There is a relatively smooth gradient of effectiveness with salinity both as the salinity rises to a peak point of effectiveness and as it exceeds this value.

d) While there is some evidence for a temperature-salinity interaction, as noted in the data of Moles et al., 2002, there are not enough data to make solid conclusions.

e) Recent data are largely taken using Corexit 9527 and Corexit 9500. Since these have the same surfactant packages, there is a concern that the results may be more relevant to these formulations than to others.

f) Observations on two field trials in freshwater appear to indicate that the laboratory tests are correct in concluding very low freshwater effectiveness.

g) There were few studies on the biological effects of oil with varying salinity. There are not sufficient data to reach conclusions.

h) The findings in the dispersant literature summarized in this study are in agreement with the theoretical and basic surfactant literature.

i) The salinity of the waters in Prince William Sound is typically high in the centre of the Sound, but is sometimes low, especially near river outfalls, and in fjords with tidewater glaciers. The salinities in these areas, often less than 15 o/oo, will result in lower dispersant effectiveness.

Summary and Issues

Overall

The relationship between salinity and overall effectiveness of dispersants is reviewed in this document.

Specific Issues

The following is a summary of the specific issues and technical concerns related to salinity and dispersants.

1. It is very clear that salinity changes the effectiveness of conventional oil spill dispersants. In water with low salinity, these products have low effectiveness, even approaching zero.

2. There is very clear agreement on the effect of salinity and the relative changes this causes in dispersant effectiveness. There are a few exceptions, but these are all in the older literature and relate to studies with questionable analytical methods.

3. There are several outstanding questions: whether or not salinity changes any toxicity thresholds and whether there is an interaction between temperature and salinity.

Conclusions

The following are the overall conclusions of this study.

a) In waters with a salinity of 0 o/oo, conventional and currently available dispersant 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 o/oo. This may depend on the type of dispersant. Corexit 9500 appears to be less sensitive to salinity but still peaks at about 35 o/oo. Corexit 9527 is more sensitive to salinity and appears to peak at about 25 o/oo with some oils and at about 35 o/oo 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 Corexit 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 o/oo.

i) The waters in Prince William Sound are sometimes low in salinity, often less than 15 o/oo, especially near river outfalls and in bays. This will result in lower dispersant effectiveness.

List of Acronyms

ANS - Alaska North Slope - Usually referring to the crude oil mixture at the end of the pipeline

ASMB - Alberta Sweet Mixed Blend - a type of crude oil

CTAC - Cetyltrimetyl ammonium bromide (a surfactant)

CTAB - Cetyltrimetyl ammonium chloride (a surfactant)

Corexit 9527 - Brand name of a dispersant from Exxon

Corexit 9500 - Brand name of a dispersant from Exxon

DLVO - Derjaguin Landau Verway Overbeek - A reference to a theory on surfactant stabilization, with each letter referring to the author of the original theory.

DO - Dispersed oil

EPA - US Environmental Protection Agency

EXDET - An Exxon laboratory test for dispersants

GC - Gas Chromatograph, a chemical analytical technique

HLB - Hydrophilic-lipophilic balance

IFP - The French Petroleum Institute - Usually used here as a description of their laboratory test

IFT - Interfacial tension

PAH - Polynuclear Aromatic Hydrocarbons

PWSRCAC - Prince William Sound Regional Citizens' Advisory Council

RSD - Relative standard deviation

WAF - Water-Accommodated Fraction - The sum total of oil in a water sample including physically dispersed and soluble oil

Acknowledgements

The author thanks Lisa Ka’aihue of the Regional Citizens’ Advisory Council of Prince William Sound, who is the contract manager for this project. The author also thanks Jennifer Charles for her editorial work and Lloyd Gamble for collecting the references necessary for this report.

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1. Introduction

1.1 Objective

The objective of this paper is to address the issue of the effectiveness of dispersants in waters of various salinities, such as are found in Prince William Sound.

1.2 Scope

This paper covers the literature from the inception of the oil spill concern to August of 2004 and focuses primarily on issues related to variations in dispersant effectiveness caused by salinity.

1.3 Organization

The paper begins with a summary and outline of the issues. The overall effects of salinity on dispersant effectiveness are reviewed in Section 2. Laboratory testing or colorimetric measures used in older studies are reviewed in Section 3, while more recent laboratory testing is discussed in Section 4. Section 5 reviews the surfactant literature for studies on the effects of salinity. Field studies and effects studies are discussed in Section 6. The varying salinities found in the waters of Prince William Sound are discussed in Section 7. Section 8 consists of the summary and Section 9, the conclusions of this report.

The tables and figures referred to in the text have been placed at the end of the text, before Section 10, which lists the References.

2. Review of Salinity and Dispersant Effectiveness

Dispersant effectiveness is defined as the amount of oil that the dispersant puts into the water column versus that which remains on the surface. Effectiveness as used in this report will be constant throughout.

Surfactants have varying solubilities in water and varying actions toward oil and water. The parameter used to characterize surfactants is the hydrophilic-lipophilic balance (HLB) (Becher, 1977). HLB is determined using theoretical equations that relate the length of the water-soluble portion of the surfactant to the oil-soluble portion of the surfactant. A surfactant with an HLB between 1 and 8 promotes the formation of water-in-oil emulsions and one with an HLB between 12 and 20 promotes the formation of oil-in-water emulsions. A surfactant with an HLB between 8 and 12 may promote either type of emulsion, but generally promotes oil-in-water emulsions. Dispersants have an HLB in this range.

Dispersants are oil spill treating agents formulated to disperse oil into water in the form of fine droplets. Typically, the HLB of dispersants ranges from 9 to 11. Ionic surfactants can be rated using an expanded scale and have HLBs ranging from 25 to 40. Ionic surfactants are strong water-in-oil emulsifiers, very soluble in water and relatively insoluble in oil, which generally work from the water onto any oil present. Such products disappear rapidly in the water column and are not effective on oil.

Because they are readily available at a reasonable price, however, many ionic surfactants are proposed for use as dispersants. These agents are better classified as surface-washing agents. Some dispersants contain ionic surfactants in small proportions, yielding a total HLB closer to 15 than 10. No studies have been done on the specific effect of this on effectiveness or mode of action. A typical dispersant formulation consists of a pair of non-ionic surfactants in proportions to yield an average HLB of 10 and some proportion of ionic surfactants. Studies have been done on this mixture, one of which used statistical procedures in an attempt to determine the best mixture of the three ingredients.

It is well known in surface science that the hydrophilic portion of a surfactant is strongly affected by the salinity (Becher, 1977). This is a result of ionic strength. The greater the salinity, the greater the ionic strength and thus the greater the stability of the surfactant-stabilized droplet.

Dispersants have long been noted as being less effective in less saline waters. Martinelli and Lynch (1980) noted this as a factor to be considered. Despite this knowledge, several workers presumed that effectiveness was the same or similar in less saline water. Peabody (1982) proposed dispersant use in freshwater and noted that the concerns might be the different toxicity to aquatic species. McAuliffe (1989) developed scenarios for the use of dispersants in the nearshore environment to protect the ecosystem from surface oil damage. The assumption is that there is no reduction in effectiveness with decreasing salinity and that the effectiveness is 100%. Flaherty et al. (1989) reviewed the development of guidelines for using dispersants in fresh water and also did not note any concern about the decrease in effectiveness with decreasing salinity. This indicates that the effect of salinity was not necessarily well known among all oil spill workers, particularly those not involved in full-time research.

3. Older Laboratory Testing or Colorimetric Measures

While studies were conducted on the effectiveness of dispersants early in the history of oil spill dispersants (Martinelli and Lynch, 1980), proper quantitative methods did not appear until the mid-90s. Early methods using colorimetric analysis are in question (Fingas, 1995a). One older colorimetric method of measuring laboratory dispersant effectiveness uses a small aliquot of the dispersion test water, extracts the oil, usually with methylene chloride, and then measures the colour at a specific wavelength. This value is compared to a standard curve and effectiveness calculated. The standard curve was traditionally prepared by injecting the appropriate amount of oil directly into the methylene chloride and measuring colour density. It was found that the traditional approach of preparing standard curves was somewhat in error because the simple addition of water to the extraction process produced some colouration in the methylene chloride, despite drying the extract. This results in inflated effectiveness values.

Experiments comparing correct chromatographic methods and colorimetric methods showed that the latter could yield errors as much as 300 o/oo. More typical medium oils showed errors of only a few percent, but heavy oils again showed significant error because of the different wavelengths at which they are absorbed. Gas chromatography is the only accurate means to analyze for dispersant effectiveness. Many values from effectiveness tests conducted in the past using colorimetric methods are questionable. For this reason, the data relating salinity and effectiveness are separated into those obtained by colorimetric and chromatographic methodologies. All literature surveyed in Sections 3 and 4 is summarized in Table 1. It should be noted that much of the older literature reported data in graph form and not in tables. The numeric data was estimated from the graphs and subsequently re-plotted.

Belk et al. (1989) studied the effectiveness of dispersants in the Labofina laboratory apparatus. They tested several dispersants at a range of salinities and found that all dispersants were less effective at lower salinities. Belk et al. also tested freshwater dispersants and found that these showed similar behaviour and were less effective at lower salinity. These researchers also found that the ionic strength and the type of ion changed the effectiveness of freshwater dispersants. The data for several oils are given in Table 2 and re-plotted as shown in Figure 1. The dispersants tested are not named but are noted alphabetically.

Most of the dispersants show the same tendency, that is the effectiveness decreases to low values near zero salinity. The dispersant tendency also decreases after achieving a maximum of about 20 to 25 degrees salinity. One dispersant, designated ‘c’, did not behave in quite the same manner, but the authors note that this dispersant is neither typical nor common. Although these data will be compared to recent data, the tendency is the same throughout the data reported in this paper. Figure 2 shows the data for freshwater dispersants. This shows that even the freshwater dispersants have low effectiveness at low salinities and peak at a salinity of about 10 o/oo.

Fingas et al. (1991) studied the effectiveness of dispersant-oil combinations under a variety of salinity conditions using the swirling flask test and colorimetric measurement. They found that the effectiveness peaked at between 40 to 45 o/oo and then dropped rapidly to low values. These data are given in Table 3 and illustrated in Figure 3. This is one of the few data sets to include salinities beyond about 40 o/oo.

Clayton et al. (1992, 1993) reviewed the effect of salinity in the literature and summarized many of the old data. Fritz (1995) also reviews these data. The first numeric results were by Wells and Harris (1979) who report a sharp effect in going from fresh to saltwater. The results are summarized in Table 4 and illustrated in Figure 4 (also includes data from Byford et al., 1983 and Lehtinen and Vesala, 1984). These older data generally show the same tendencies as described by other workers later, although the data are much noisier as would be expected. Byford et al. employed the Labofina test and Lehtinen, the Mackay test.

Brandvik and Daling (1992) and Brandvik et al. (1995) studied the effectiveness of dispersants at low temperatures and salinity for application in the Arctic. They used the IFP test and found that most dispersant-oil combinations showed a large decrease in effectiveness at lower salinities. One dispersant intended for use in freshwater, Inipol IPF, showed the opposite tendency. These data are given in Table 5 and shown in Figures 5 and 6. Most dispersant-oil combinations showed very low effectiveness at low salinities.

Fingas et al. (1994, 1995b) studied the effectiveness of dispersant-oil combinations under a variety of salinity conditions and produced a salinity curve similar to that noted above. They found that the effectiveness peaked at between 30 to 40 o/oo and then dropped rapidly to low values. These data are given in Table 6 and illustrated in Figures 7. This is a data set that again shows a decrease in effectiveness after a peak at about 30 o/oo.

MacKay (1995) reported on tests conducted at Exxon using the Exdet tests. Effectiveness was reported as staying constant, although rising somewhat from the salinity values of 5 through to 35 o/oo. The effectiveness was also reported to be very low in freshwater. These tests were done for Prudhoe Bay crude and Corexit 9527.

Moet et al. (1995) tested the effectiveness of Corexit 9527 on light Arabian crude over a series of salinities, using the Labofina or Warren Springs test. The salinity effect was the same as found by Fingas et al., 1992, 1994, 1995b. The effectiveness peaked at about 33 o/oo and then again decreased. These results are shown in Table 7 and illustrated in Figure 8. Moet's results show the same tendency as results from Fingas et al. (1992, 1994, 1995b) in that the effectiveness peaks at about a salinity of 30 o/oo and then falls rapidly as salinity increases.

George-Ares et al. (2001) tested the effectiveness of various dispersants in river water, distilled water, and water with calcium chloride added. The Exdet apparatus was used to carry out the tests. The lowest effectiveness was found in the distilled water and the effectiveness was higher in the river water. Adding calcium chloride to the dispersant increased the effectiveness above that of the river water. These results, as shown in Table 8, are generally consistent with those noted previously in that a decrease in effectiveness is noted with a decrease in salinity.

Guyomarch et al. (2002) tested the effect of dispersants and variables such as salinity on the aggregate formation with clay. They found that the aggregate particle size increased with increasing salinity.

4. Recent Laboratory Testing

The effectiveness of dispersion at different temperatures and salinity has been measured using various tests. Blondina et al. (1997a, b) measured the effectiveness of dispersing Prudhoe Bay crude at 20ºC and 20‰ as 23% for Corexit 9500 and 13% for Corexit 9527, using the EPA swirling flask method. The results also show that, for the same tests, the use of colorimetry as much as doubled the apparent effectiveness. It was concluded that the chromatographic method showed less bias to oils as dependant on their compositions. The results are shown in Table 9 and illustrated in Figure 9. These results are consistent with previously measured results noted in Section 3, namely that dispersant effectiveness is less with lower salinity.

Blondina et al. (1999) also measured the effectiveness of the dispersants Corexit 9527 and Corexit 9500 on several oils. The results are summarized in Table 10 and illustrated in Figure 10 for Corexit 9500 and Figure 11 for Corexit 9527. Blondina and coworkers concluded that the interaction between the salinity of the receiving water and the ability of surfactant-based dispersants to enhance petroleum accommodation into the water column can be both oil- and dispersant-specific. They found that Corexit 9500 was more effective than Corexit 9527 on most oils at most salinities, but the opposite was true in some cases. Corexit 9500 maintained its effectiveness over a wider range of salinities. Blondina et al (1999) concluded that decisions should be made on a specific situation based on the oil, the dispersant, and the salinity of the receiving water.

Moles et al. (2001, 2002) conducted a series of measurements on Alaska North Slope (ANS) oil at lower temperatures and lower salinity. For Corexit 9500 at a temperature of 10ºC and 22 º/oo, the effectiveness was 8% for fresh ANS and 2% for weathered ANS. Under the same conditions, Corexit 9527 showed an effectiveness of 10% for the fresh ANS and 5% for the weathered ANS. The effectiveness of Corexit 9500 and Corexit 9527 was tested on Alaska North Slope crude oil at various salinities and temperatures representative of conditions found in Southern Alaskan waters. The oil was weathered to different degrees. Tests were conducted in a swirling flask at temperatures of 3, 10, and 22ºC with salinities of 22 and 32 º/oo. Analysis was by GC. The authors concluded that, at the common temperatures found in the estuaries and marine waters of Alaska, the dispersants were largely ineffective. They also found that there was an interactive effect between temperature and salinity. A high effectiveness for ‘emulsion’, an uncharacterized mixture of oil and water, was attributed to ‘osmotic shock’ because of the difference in the salinity of the preparation (33 º/oo) and the test salinity. At the combinations of temperature and salinity such as might be typical for Alaska, dispersant effectiveness in the test was less than 10%. The results are summarized in Table 11. The data for the fresh ANS are plotted in Figure 12 for Corexit 9527 and in Figure 13 for Corexit 9500. Both figures generally show the decrease in effectiveness with decreasing salinity. There may be a relationship between temperature, salinity, and effectiveness as shown in these data.

The Moles data (Moles et al., 2001, 2002) were tested for ability to form a consistent relationship between temperature and salinity. This was carried out by correlating the three-dimension factors of effectiveness, salinity, and temperature. The results show that there is a high correlation for the fresh ANS and less so for the weathered and emulsified products. Table 12 shows the three-dimensional linear equation used to identify correlation. This shows that there is a good correlation between all factors, less so for the weathered and emulsified oils. A simple linear equation is good for the fresh oil case but poor for the weathered and emulsified cases. Figures 14 to 17 show the linear correlations for the six oils. These figures show the three-way correlations as a plane surface or surface of best fit. Individual values are shown as circles and line extensions indicate whether these values are above or below the plane of best fit. It is important to note that such correlation as attempted here would be most valid if there were more data points.

Fingas et al. (2003) studied the effect of resurfacing of dispersed oil. As part of this study, a series of standard tests were conducted with Alberta Sweet Mixed Blend (ASMB) and Alaska North Slope (ANS) crude oils and the dispersants Corexit 9527 and Corexit 9500. Results are shown in Table 13 and illustrated in Figure 18. The same tendencies as Moles et al. (2001, 2002) found for ANS were found in this study, namely that the effectiveness of Corexit 9500 with ANS increases as salinity increases and that of Corexit 9527 generally does as well, but this is variable. The effectiveness of Corexit 9527 appears to peak at a salinity of 25 o/oo. It is not yet known why ANS has shown this tendency in these studies. The ASMB and most other crudes shows the tendency throughout this study that the effectiveness is Gaussian with the peak in this case coming at about 20 o/oo.

Sterling et al. (2004) studied the coalescence of dispersed oil droplets. Theoretical studies were conducted using DLVO theory and kinetic studies were conducted using a laboratory apparatus. Sterling et al. came to the following conclusions.

1. For salinity and pH values found in natural waters, the ζ- potential values of chemical dispersed crude oil were slightly negative. The ζ- potential is a measure of charge between particles and is relevant to dispersants in that a higher ζ- potential indicates a more stable particle and could imply a higher effectiveness. For a fixed pH value, ζ- potential values become marginally more negative with increased water salinity. This is shown in Figure 19. Using DLVO theory, no significant electrostatic energy barrier to droplet coalescence was present. This implies that oil dispersions (including those with dispersants) are unstable over time.

2. Within the tested experimental conditions, the collision efficiency parameter, α, (the probability of successful particle-particle collision) was significantly greater than 0. This result suggests that coalescence kinetics were important in estimating dispersant efficiency in laboratory-scale protocols and may be important in coastal spills. This is shown in Figure 20. The shear rate was the dominant parameter in estimating observed coalescence rates and dispersant efficiencies. This implies that the effectiveness is very dependent on shear rate, but that the resulting emulsions will also be unstable and in fact coalescence occurs faster under some energetic conditions.

3. Salinity had a limited influence on effectiveness values measured in this study. Sterling et al. suggest that salinity has a strong overall effect and thus, because salinity shows a lesser effect on coalescence, that salinity must have a greater effect on initial droplet formation.

5. Salinity Effects in Surfactant Literature

A literature search was conducted of the body of literature on surface chemistry. This search focussed on the effects of salinity on various aspects involving the use of surfactants. The papers are summarized in Table 14 and, where available, numeric results are given in Table 15. The values in Table 15 are given in terms of relative values compared to the value at 0 o/oo.

Davis (1994) reviews the basic surfactant chemistry and physics. He notes that interfacial tension of an oil-water system varies widely with salinity and is generally at a minimum at 15 ppt for many surfactant systems. Davis also provides information on the typical phase changes with changing salinity, including the effects of alkane change length and water fraction. Ysambertt et al. (1997) describes the phase behaviour of emulsions noting that salinity was an important factor in describing phases.

Several authors have studied oil recovery and the effectiveness of surfactants with respect to the salinity of the pore water. Sayyouh et al. (1993) studied the effect of salinity on a surfactant-oil-brine system and found that the stability of the system increased up to the salinity of about 3.8o/oo and then decreased as the salinity rose to 23o/oo . Fjelde and Austad (1994) studied the analysis of salt-tolerant and non-salt-tolerant surfactants, noting that ethoxylated anionic surfactants can tolerate high salinity water. These types of surfactants are not used in oil spill dispersants.

Several authors have tested oil reservoir recovery chemicals and found that increasing salinity increases performance of these surfactants (Austad et al., 1994; Fjelde et al., 1995; Austad and Strand, 1996. Wu et al. (2004) developed a new performance index for surfactants named the relative solubility index. This was used to examine a series of different surfactants at various salinities for oil recovery applications. Drummond and Israelachvili (2002) studied the fundamentals of surface forces and wettability, noting that recovery would be improved with increases in salinity. They also noted that recovery via natural surfactants is improved in high saline waters. Babadagli (2003) found that increasing salinity increased recovery with and without a surfactant. Zhang et al. (2004) studied natural surfactants and found that the recovery from reservoirs was increased with increasing salinity. Liu et al. (2004) studied the effectiveness of oil recovery and noted that increasing salinity increased the partition of surfactant into water. Al-Roomi et al. (2004) studied the use of surfactants to improve the flow properties of oil. Surfactants are used to emulsify oil into the water. Al-Roomi and co-workers found that the dispersion and viscosity reduction improved as surfactant content increased.

Several authors studied the effect of salinity on oil or specific hydrocarbons. Song and Islam (1994) studied the use of surfactant washing for cleaning petroleum from soil. They found that increasing salinity increased the removal or the effectiveness of the surfactant. Watt et al. (1998) studied the formation of a water-in-oil emulsion with a cationic surfactant and diesel oil. They found that the formation tendency increased with salinity up to about 30o/oo salinity and then decreased. Li and Chen (2002) studied the solubilization of PAHs into water with surfactants and found that increasing salinity decreased the cloud point, increased the apparent solubility, and reduced the hydrodynamic radius. Li and Kunieda (2003) studied the effect of having a cationic and an anionic surfactant to dissolve oil and found that salinity increased the effectiveness of the surfactants. Ghannam and Chaalal (2003) tested a vacuum oil recovery system which also used the surfactant Triton X-100. They found that increasing salinity greatly increased recovery. Moosai and Dawe (2003) studied the theoretical aspects of the use of gas flotation for oily wastewater cleanup. They noted that the flotation improves with salinity and surfactant amount. Chen et al. (2004) studied the change in interfacial tension between hexane and an ionic surfactant. The interfacial tension decreased sharply with a small amount of salinity and rose again slightly and peaked at about 10 ppt. Mollet et al. (1996) also studied interfacial tension but with paraffin oil and sodium linoleate and an in-situ formed surfactant. They found that the optimal IFT occurred with salinities between 10 and 30 ppt.

Some authors studied the solubilization of specific compounds. Chooro et al. (1996) studied the miscellization and adsorption of a zwitterionic surfactant, n-dodecyl betaine, with salt concentrations. These researchers found that the adsorption of the surfactant onto silica gel depended little on temperature, but very much on the salt concentration. Yu et al. (2004) studied the extraction of a bacterial toxin from water using a cationic surfactant. They found that increasing salinity increased the partition of the water portion of the extract. Park and Bielefeldt (2003) studied the partitioning of pentachorophenol into a mineral oil with varying amounts of a nonionic surfactant and found that a higher ionic strength increased the partitioning.

The effects on physical systems of surfactants and varying salinity were investigated by various authors. Abuin et al. (1993) studied the formation of microemulsions with ionic surfactants and found that stability increased with salinity for most CTAC surfactants and decreased if CTAB was the majority surfactant. Hou and Papadopoulis (1996, 1997) studied three-way emulsion droplets and found that the stability of these droplets with surfactant increased significantly with increasing salinity. Kaczmarski et al. (1999) studied the influences of surfactant and salinity on the viscosity of a polymer thickness. The viscosity of the thickener decreased with increasing salinity.

Kjøniksen et al. (1999) studied the formation of gels of ethyl (hydroxyethyl) cellulose with the surfactant sodium dodecyl sulphate (SDS) and found that the intermolecular structure of the gel is increased with increasing salinity. Prosser and Franses (2003) used a thermodynamic/electrostatic model to study sodium dodecyl sulfate/sulfonate systems. They concluded that salinity increases stability by lowering interfacial tension. Sabatini et al. (2003) studied the effect of linker molecules with surfactants in solubilization. They found that solubilization with naphthalenic sulfonates was very saline-dependent and governed the solubility/surfactant concentration relationship.

6. Field Studies and Effects Studies

Some studies focussed on examining the effects of oil dispersed into the freshwater environment. Scott et al. (1979) studied the effects of a freshwater dispersal into a pond. The authors noted that there were significant similarities between the dispersed oil and the non-dispersed oil. The dispersed oil remained in a 3 to 5 cm milky layer only for about an hour after which it separated and formed a slick similar to that of the oil-only pond. This indicates a relatively poor dispersant effectiveness.

Brown and Goodman (1989) report on an extensive study of the effects of oil in the freshwater environment. Several toxicity and behavioural tests are described, but these are not compared to similar species in the saltwater environment. Brown et al. (1990) describe a major field trial of dispersants in the freshwater environment. Three cubic metres of Norman Wells crude oil were spilled on each of two fen lakes. The slick on one lake was treated with the dispersant Corexit 9500. The workers claimed that the dispersant was effective at removing oil from the surface of the one lake but also reported the appearance of thick clumps of oil near the edge of the same pond. The impact of the oil on the fen appeared to be lessened by the use of the dispersant, gauged primarily by the impact on floating vegetation. After one month, there was little impact on either fen. This study concluded that the best response to a spill in such a lake was no response at all.

Clayton et al. (1989) studied chemical and mechanical dispersion in an artificial stream bed. They concluded that the value of added dispersant was tempered by various factors including viscosity of the oil, degree of exposure of sediment surfaces to the oil, sediment substrate characteristics, and water flow characteristics.

Wolfe et al. (1998) studied the uptake of naphthalene by an algae. The oil was Prudhoe Bay crude and the dispersant was Corexit 9527. It was found that the dispersant significantly affected the uptake of naphthalene (by as much as 50%). Salinity, however, did not affect this uptake significantly. The results are shown in Table 16 and Figures 21 and 22. These data show that the uptake of naphthalene and a,b naphthol sulphate are relatively unaffected by salinity. Wolfe et al. (1999) also studied the heat shock protein in *Isochrysis galbana*, a golden-brown algae and primary producer in marine food chains. Wolfe et al. found that the organism efficiently induced the heat shock protein hsp60 in response to elevated temperatures and exposure to low concentrations of petroleum hydrocarbons after a model oil spill and dispersant use. Differences in salinity were found to influence the induction of hsp60 by elevated temperature, WAF and DO preparations, and naphthalene. Increased salinity appeared to decrease the sensitivity of *I. Galbana* to hsp60 induction after exposure to these agents. They suggest that the hsp60 induction may serve as an adaptive function in *I. Galbana* to deal with exposures to oil and dispersants. This also suggests that dispersants/oil may be more toxic at low salinities.

7. Salinity in Prince William Sound

The waters in Prince William Sound vary in salinity (Vaughn et al., 2001; Gay and Vaughn, 2001; Bang and Mooers, 2003). The data generally indicate that the salinity in the middle of the Sound is about 33 o/oo. As one enters areas influenced strongly by river outfalls, however, the salinity drops to that of freshwater. While the range of salinities in the Sound certainly raises concern, the salinity is generally higher than 20 o/oo in the centre of the sound where dispersants are likely to be used.

Figure 23 shows Prince William Sound and the detailed sampling stations. Figure 24 shows varying salinities at the Zaikof Bay station. This figure shows that surface salinities often are 28 o/oo and range only as high as 31.5. This is typical of most of the central portion of the Sound. Figure 25, on the other hand, shows the salinity profiles at Eaglek Bay. The water salinity in this area, which is typical of most of the fringe regions of Prince William Sound, ranges from 20 to 31.5 o/oo. A similar profile is seen in the Whale Bay data as shown in Figure 26. Table 17 shows recent salinity testing results. This data, from Tony Parkin, shows that the outfalls of creeks are very low in salinity. The smaller bays are also very low in salinity. Dispersant application should not be considered in or near such regions where salinity is below 20 o/oo. It must be noted however that salinity varies very much with season and location.

In Alaska, there are three distinct dispersant use zones (Annex I to the Alaska: RRT Dispersant Use Guidelines for Alaska). Zone 1 delineates an area where dispersant use has been preapproved. The On-Scene Coordinator (OSC) is not required to consult with any other agencies prior to the use of dispersants in this zone. In Zone 2, dispersant use can be approved by the OSC, but only with the concurrent approvals from the Environmental Protection Agency (EPA) and the State of Alaska. The use of dispersants is not recommended in a Zone 3 but can be used on a case-by-case basis. Prior to use in a Zone 3, the OSC is required to consult with the Regional Response Team and obtain approvals from the EPA and the State of Alaska.

Generally, Zone 1 in Prince William Sound runs through the center and entrance of the Sound, what is commonly referred to as the "tanker lane." Zone 1 also runs along the southern edge of the entrance to the Sound. The Gulf of Alaska is a Zone 2. Much of the Eastern and Western areas are a Zone 3. Port Valdez is unique in that it has seasonal designations, that change it from a Zone 1 to a Zone 2 depending upon the season, although the eastern edge of the Port is always a Zone 3.

Alaska is unique in the United States in that it has a preapproval zones so close to the nearshore. Many of the preapproval zones in the other states are beyond three nautical miles. This is of concern with respect to salinity, as many of these pre-approval zones are in low salinity zones and the effectiveness of dispersants would be very low in these areas.

8. Summary

Surfactants are the active ingredient in dispersants. Surfactants work to sustain oil droplets in the water by maintaining a portion of the molecule in the oil (lipophilic) and in the water (hydrophilic). The ratio of lipophilic to hydrophilic depends on the ionic strength of the water which relates directly to the salinity. The hydrophilic portion of the surfactant is more soluble in water with a higher salinity. As salinity rises past a certain point, the surfactant becomes too soluble in the water and has a stronger tendency to partition to the water phase completely. Thus, in theory, the surfactant is more lipophilic in freshwater and increases in hydrophilicity as the salinity rises. The stability of the resulting droplets also depends on salinity due to the increasing ionic strength of the water as salinity rises. This increasing ionic strength results in greater molecular force. Again, as the salinity rises above a certain point, this point being dependent on the particular type of surfactant, this increased force results in more surfactant molecules leaving the oil drop entirely.

There is a theoretical scale of hydrophilic/lipophilic balance or HLB. This is calculated by the type of surfactant present. A surfactant with an HLB of 10 is a dispersant, that is the force of the molecule is equally balanced between hydrophilic and lipophilic tendencies. A surfactant of much greater than 10 is said to form oil-in-water emulsions (dispersions) and one of much lower than 10 can promote the formation of water-in-oil emulsions. The HLB of a surfactant changes with salinity. A low salinity lowers the HLB and vice versa. Thus, it is theoretically possible to design a dispersant with surfactants for lower salinity waters. While this possibility exists, it should be noted that the stability of dispersions is less in less saline waters. Furthermore, it should be noted that there are no recent measurements on freshwater dispersants, indicating that the industry has not pursued this avenue.

This report reviews several older dispersant tests beginning at 1979. These were separated from more recent data because both testing procedures and analytical methods used at that time are not as accurate as today's methods. Some older methods may, in fact, not yield data with sufficient accuracy to discriminate salinity effects. However, for the most part, this review shows that the older data, with a few exceptions, are entirely consistent in the generic conclusions of modern data, while not consistent in the actual numbers.

The following are the findings of several workers.

a) In waters with a salinity of 0 o/oo, most dispersants have a very low effectiveness or are sometimes even completely ineffective.

b) Dispersant effectiveness peaks in water with a salinity from 20 to 40 o/oo.

c) There is a relatively smooth gradient of effectiveness with salinity both as the salinity rises to a peak point of effectiveness and as it exceeds this value.

d) Some early works showed data anomalies, which may have resulted from measurement limitations and difficulties.

e) Studies published earlier than about 1989 are not highly accurate and contain the most anomalies.

Newer testing is also reviewed in this report. This testing is marked by the use of chromatography for analysis and the use of very strict protocols in operating the dispersant tests. These tests are marked by having standard deviations of less that 10% and often less than 5%. These are less than an order-of-magnitude of standard deviations in previous testing.

The followings are the conclusions of the authors of these newer studies.

a) In waters with a salinity of 0 o/oo, most dispersants have a very low effectiveness or are sometimes even completely ineffective.

b) Dispersant effectiveness peaks in water with a salinity from 20 to 40 o/oo. This may depend on the type of dispersant used. Corexit 9500 appears to be less sensitive to salinity, but still peaks at about 35 o/oo. Corexit 9527 is more sensitive to salinity and appears to peak at about 25 o/oo with some oils and at about 35 o/oo 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 as it exceeds this value. The curves for this salinity appear to be Gaussian as shown in Figures 3, 7, and 8.

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 Corexit 9500 and, 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) The values found in recent tests are much lower than the older tests, however, the trends are the same.

The general surfactant literature was reviewed for salinity effects on surfactants and surfactant phenomena. There is a body of literature on the use of surfactants for secondary oil recovery. There are several commonalities among the many findings. Recovery efficiency falls off at both high and low salinities. The salinity at which surfactant efficiency peaks is very dependent on the structure of the specific surfactant.

Several studies on the interaction of specific hydrocarbons and surfactants were reviewed. The consensus of these papers is that the solubility of the hydrocarbon increases with increasing salinity and decreases at low salinities. The interfacial tension of water and oil changes with surfactant and salinity. The interfacial tension is higher at lower salinities. The optimal interfacial tension is generally achieved at salinities of between 25 to 35 o/oo.

A number of physical systems involving surfactants and salinity changes are reported in the literature. Included in these is the finding that the stability of microemulsions is greater at salinities of 25 to 35 o/oo. Some workers found that the stability of systems was very low in fresh water or waters of salinities of < 10 o/oo. Similar effects were found with gels, polymer thickeners, and linker-molecule solubilization.

Some field studies of dispersant application were conducted in the freshwater environment. While effectiveness was not specifically measured, it was noted in both series of studies that effectiveness may have been low. In the one study, the investigators noted that the surfactants had poor effectiveness and stability. In this particular case, the dispersion lasted only about an hour and the dispersion was limited to a few centimetres. In another case, it was noted that in the dispersed pond, there was oil around the edges within a short time of dispersant application. Effects were monitored in both cases, but could not be compared and were not compared to similar applications at sea.

Some effects studies were conducted under varying salinity conditions. In one study, naphthalene and a,b napthol sulphate uptake were studied under different salinity conditions. There were no significant differences for different salinities, although naphthalene uptake was somewhat higher under low salinity conditions. Another study examined the induction of hsp60 protein in golden-brown algae. It was found that greater salinity reduced the effects of the simulated oil spills to the algae.

The salinity of the water in different parts of Prince William Sound was summarized. There are areas of low salinity where dispersant application would result in reduced dispersant effectiveness.

9. Conclusions

The following are the overall conclusions of this study.

a) In waters with a salinity of 0 o/oo, 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 o/oo. This may depend on the type of dispersant. Corexit 9500 appears to be less sensitive to salinity, but still peaks at about 35 o/oo. Corexit 9527 is more sensitive to salinity and appears to peak at about 25 o/oo with some oils and at about 35 o/oo 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 Corexit 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 o/oo.

i) The waters of Prince William Sound are sometimes low in salinity, often less than 15 o/oo, especially near river outfalls. This could result in lower dispersant effectiveness.

Table 1 Summary of Testing of Salinity Effects on Dispersant Effectiveness

Author	Year	Dispersant Type (s)	Specific Surfactant	Type of Test	Generic Results
Wells and Harris	1979	Commercial	Corexit 9527	Mackay	Effectiveness decreased very much from saltwater to freshwater.
Byford et al.	1983	Commercial	Several commercial dispersants	Labofina effectiveness	Saltwater andf freshwater dispersants decreased in effectiveness going down to zero salinity and decreased after 20 o/oo.
Lehtinen and Vesala	1984	Commercial	Two unidentified dispersants	Mackay	Decreased in effectiveness going down to low salinity.
Belk et al.	1989	Several	Designated A to F, both saltwater and freshwater dispersants	Labofina effectiveness	Saltwater and freshwater dispersants decreased in effectiveness going down to zero salinity and decreased after 20 o/oo.
Fingas et al.	1991	Commercial	Corexit 9527 & Enersperse 700	Swirling Flask	Commercial dispersants decreased in effectiveness going down to zero salinity and decreased after about 35 o/oo.
Brandvik and Daling	1992	Several	Several commercial dispersants	IFP	Saltwater and freshwater dispersants decreased in effectiveness going down to 5 0/00 salinity and decreased after 20 o/oo. One Labofina product showed opposite tendency.
Fingas et al.	1994, 95b	Commercial	Corexit 9527 & Enersperse 700	Swirling Flask	Commercial dispersants decreased in effectiveness going down to zero salinity and decreased after about 33 o/oo.
Brandvik et al.	1995	Several	Several commercial dispersants	IFP	Saltwater and freshwater dispersants decreased in effectiveness going down to 5 0/00 salinity and decreased after 20 o/oo. One Labofina product showed opposite
Moet et al.	1995	Commercial	Corexit 9527	Labofina effectiveness	Commercial dispersant decreased in effectiveness going down to zero salinity and decreased after about 33 o/oo.
Mackay	1995	Commercial	Corexit 9527	Exdet	Effectiveness in distilled water was very low but didn't change much after salinity increased past 5 o/oo.
Blondina et al.	1997 a,b	Commercial	Corexit 9527 and Corexit 9500	Swirling Flask	Effectiveness increased fromsalinity of 10 up to salinity of 30 for Corexit 9500 and up to 20 o/oo and then decreased otherwise.
George-Ares et al.	2001	Commercial	Corexit 9500 Enersperse 1037 Basic Freshwater Inipol IPF	Exdet	Effectiveness in distilled water could be improved by the addition of calciumchloride.
Moles et al.	2001	Commercial	Corexit 9527	Swirling Flask	Effectiveness increased fromsalinity of 10 up to salinity of 30 for Corexit 9500 and up to 20 o/oo and then decreased otherwise.
Guyomarch et al.	2002	Commercial	Inipol IP90	Special - 250 mL beaker	The aggregate size of particles increased with salinity.
Fingas et al.	2003	Commercial	Corexit 9527 and Corexit 9500	Swirling Flask	Effectiveness increased fromsalinity ot 10 up to salinity of 30 for Corexit 9500 and up to 20 o/oo and then decreased otherwise.

Table 2 Data from Belk et al. (1989)

Actual Values Taken from Graph

Effectivness for Warren Spring Oil at 10°C					**Effectivness for Prudhoe Bay Oil at 10°C**				
Salinity	**Disp A**	**Disp B**	**Disp C**	**Disp D**	**Salinity**	**Disp A**	**Disp B**	**Disp C**	**Disp D**
0	5	5	25	5	0	10	4	35	3
5	10	8	23	10	5	25	12	27	7
10	23	20	22	23	10	42	27	22	15
15	60	55	25	25	15	57	36	22	22
20	75	65	35	35	20	62	42	25	27
25	77	67	47	47	25	57	37	28	35
30	80	70	55	58	30	55	32	35	45
35	82	72	60	60	35	42	25	37	52

Effectivness for Warren Spring Oil at 20°C					**Effectivness for Prudhoe Bay Oil at 20°C**				
Salinity	**Disp A**	**Disp B**	**Disp C**	**Disp D**	**Salinity**	**Disp A**	**Disp B**	**Disp C**	**Disp D**
0	0	0	37	2	0	12	6	32	3
5	17	11	23	3	5	26	17	23	6
10	32	23	18	5	10	42	28	22	14
15	47	32	20	10	15	55	40	24	20
20	57	42	23	17	20	60	45	25	25
25	65	46	27	27	25	58	42	30	32
30	70	50	35	40	30	50	40	34	37
35	72	52	43	47	35	40	32	37	41

Effectivness for Warren Spring Oil at 10°C			Freshwat	**Effectivness for Warren Spring Oil at 20°C**			Freshwater dispersants
Salinity	**Disp E**	**Disp F**		**Salinity**	**Disp E**	**Disp F**	
0	62	25		0	55	32	
5	77	47		5	67	60	
10	85	62		10	74	74	
15	84	67		15	75	80	
20	82	72		20	73	80	
25	77	74		25	67	77	
30	75	72		30	60	75	
35	72	70		35	50	70	

Effectivness for Prudhoe Bay Oil at 10°C			Freshwater d	**Effectivness for Prudhoe Bay Oil at 20°C**			Freshwater dispersants
Salinity	**Disp E**	**Disp F**		**Salinity**	**Disp E**	**Disp F**	
0	25	24		0	24	23	
5	45	44		5	44	43	
10	58	56		10	56	54	
15	64	62		15	68	65	
20	62	60		20	70	68	
25	58	56		25	68	66	
30	56	54		30	66	64	
35	42	44		35	56	54	

Ionic Strength Effects for Dispersant E			**Ionic Strength Effects for Dispersant F**		
Ionic strength mol l-1	**Mg**	**Ca**	Ionic strength mol l-1	**Mg**	**Ca**
0.05	40	64	0.05	72	72
0.1	50	68	0.1	76	66
0.2	65	70	0.2	78	60
0.3	80	72	0.3	79	56
0.4	85	72	0.4	76	56
0.5	80	68	0.5	72	58
0.6	72	56	0.6	60	62

Table 3 Dispersant Effectiveness Data from Fingas et al., 1991

Salinity o/oo	ASMB Corexit	ASMB Enersperse	Norman Wells Enersperse	Adgo Corexit
0	0	0	0	0
10	8	8	3	14
20	12	11	11	28
30	25	41	30	42
35	30	55	40	43
40	38	68	48	44
50	39	73	39	35
60	41	13	12	33
70	32	6	7	23
80	12	5	5	16
90	9	2	2	7

Table 4 Results of Older Salinity Testing

Oil and Temperature	Dispersant	Effectiveness % at a given salinity Salinity o/oo				
Data from Byford et al., 1983		**0**	**5**	**10**	**22**	**33**
Lago Medio Residue 0°C	Arochem D609	8		11	18	25
	Corexit 9527	10	12	18	30	35
North Slope Crude 0°C	Arochem D609	12	30	34	46	51
	Corexit 9527	12	35		48	52
North Slope Residue 0°C	Corexit 9550	22	61	62	52	50
	Dispolene 34S	15	60	62	58	62
	Finasol OSR5	15	17	20	19	21
	Corexit 9527	25	29	25	26	27
	Experimental	78	70	68	70	79
Data from Lehtinen and Vesala, 1984		**3**	**7**	**12**		
Fresh Russian Crude 15°C	A	60	62	65		
	B	60	55	62		
	C	45	40	47		
Fresh Russian Crude 4°C	A	20	21	30		
	B	10	8	9		
	C	10	12	9		

Table 5 **Results of Salinity Testing from Brandvik and Daling, 1992**

		Effectiveness at Given Salinity %					
Oil and Temperature	**Dispersant**	**33 o/oo**	**5 o/oo**	**Oil and Temperature**	**Dispersant**	**33 o/oo**	**5 o/oo**
Oseberg 0^{o}C	Dasic NS	80	5	IFO 0^{o}C	Enersperse 700	67	48
	IKU-9	78	10	Weathered	Inipol IPC	42	37
	Inipol IPC	76	48		OSR 52	58	54
	E-700	76	55		Dasic Freshwater	37	38
	Dasic LTS	62	12		Inipol IPF	25	45
	E-1075	59	55	Veslefrikk 0^{o}C	Enersperse 700	58	54
	Dasic Freshwater	38	45	w/o	Inipol IPC	80	40
	Corexit 9527	36	5		OSR 52	10	15
	Disp. 365	30	7		Dasic Freshwater	30	8
	Corexit 9550	29	20		Inipol IPF	8	60
	OSR 52	26	28	Oseberg 0^{o}C	Enersperse 700	68	58
	Inipol IPF	24	50	w/o	Inipol IPC	68	44
	Disp. 385	20	24		OSR 52	25	35
	OSR 5	15	4		Dasic Freshwater	30	35
Oseberg 0^{o}C	Enersperse 700	70	69		Inipol IPF	20	50
Weathered	Inipol IPC	68	40	IFO 0^{o}C	Enersperse 700	30	4
	OSR 52	20	65	w/o	Inipol IPC	50	4
	Dasic Freshwater	25	23		OSR 52	30	4
	Inipol IPF	18	70		Dasic Freshwater	24	10
Oseberg 0^{o}C	Enersperse 700	82	55		Inipol IPF	36	28
Weathered 2	Inipol IPC	86	30				
	OSR 52	80	30				
	Dasic Freshwater	65	58				
	Inipol IPF	25	70				

Dispersant	**Salinity**	**Effectiveness**
IPF Inipol	0.5	38
	1.25	58
	2	78
	2.75	80
	3.5	70
IPC Inipol	0.5	85
	1.25	80
	2	25
	2.75	21
	3.5	18

Table 6 Dispersant Effectiveness Data from Fingas et al., 1994, 1995b

Salinity o/oo	ASMB Corexit 9527	ASMB Enersperse	Norman Wells Enersperse 700	Adgo Corexit
10	8	9	4	14
20	12	11	11	29
30	25	41	31	42
33	32	57	35	39
40	38	68	48	44
50	39	73	39	36
60	41	13	12	35
70	32	6	7	24
80	12	5	5	16
90	10	3	2	6

Table 7 Data from Moet et al., 1995

Salinity	Effectiveness (%)
0	3
20	6
30	16
33	14
40	7
50	3

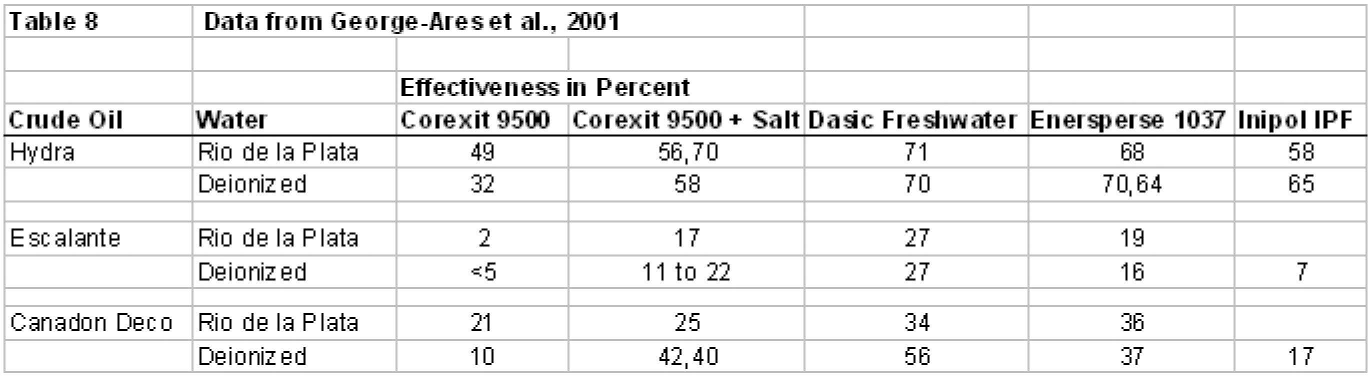

Table 8 Data from George-Ares et al., 2001

		Effectiveness in Percent				
Crude Oil	**Water**	**Corexit 9500**	**Corexit 9500 + Salt**	**Dasic Freshwater**	**Enersperse 1037**	**Inipol IPF**
Hydra	Rio de la Plata	49	56,70	71	68	58
	Deionized	32	58	70	70,64	65
Escalante	Rio de la Plata	2	17	27	19	
	Deionized	<5	11 to 22	27	16	7
Canadon Deco	Rio de la Plata	21	25	34	36	
	Deionized	10	42,40	56	37	17

Table 9 **Dispersant Effectiveness Measured by Blondina et al., 1997a, b**

Oil Type	Effectiveness in % at given salinity Salinity (o/oo)					
Prudhoe Bay	**35**	**30**	**25**	**20**	**15**	**10**
Corexit 9500	23	21	22	23	15	12
Corexit 9527	34	29	13	13	9	5

Table 10 **Dispersant Effectiveness Measured by Blondina et al., 1999**

Corexit 9500 **Oil Type**	Effectiveness in % at given salinity Salinity (^{0}/oo)							
	35	**30**	**25**	**20**	**15**	**10**	**5**	**0**
Arabian Light	38	36	44		31		7	
Arabian Medium	20	24	26	24	11	10		
Forcados	21	31	35	37		26		6
Kuwait	37	38	31		15		5	
Maya	16	11	12		6		3	
Oman	22	20	15		10		3	
Prudhoe Bay	23	21	22	23	15	12		

Corexit 9527 **Oil Type**	Effectiveness in % at given salinity Salinity (^{0}/oo)						
	35	**30**	**25**	**20**	**15**	**10**	**0**
Arabian Light	23	13	10		6		
Arabian Medium	10	5	7	6	6	3	
Forcados	54	63	55	48		17	6
Kuwait	21	13	7				
Maya	5	4					
Oman	7	5	6				
Prudhoe Bay	34	29	13	13	9	5	

Table 11 Data from Moles et al., 2001, 2002

Oil Type	**Temperature**	**Corexit 9527**		**Corexit 9500**	
		Effectiveness in percent			
		Salinity		**Salinity**	
	°C	**22 ^{0}/oo**	**32 ^{0}/oo**	**22 ^{0}/oo**	**32 ^{0}/oo**
Fresh ANS	*3*	8.5	1	10	10
	10	7.9	15	10	22
	22	35	31	16	18
20% evap. ANS	*3*	6.3	6.5	6.3	6.3
	10	1.7	4.1	4.5	2.6
	22	6.3	6.3	6.3	6.3
emulsified' ANS	*3*	26	20	13	23
	10	73	32	42	29
	22	17	20	24	14

Table 12 Prediction of Temperature and Salinity Interrelationship (Data from Moles et al., 2001, 2002)

Equation: Effectiveness = a + b*temperature + c*salinity

Dispersant	**Oil**	**a**	**b**	**c**	**Linear r_2**	**Best r_2**
9527	fresh ANS	2.6	1.5	-0.15	0.92	0.94
9500	fresh ANS	-2.2	0.34	0.47	0.57	0.72
9527	weathered	2.6	0.026	0.09	0.07	0.85
9500	weathered	6.8	0.025	-0.06	0.07	0.85
9527	emulsion	77	-0.52	-0.15	0.19	0.61
9500	emulsion	37	-0.1	-0.43	0.06	0.68

Table 13 Salinity and Effectiveness (Data from Fingas et al., 2003)

Oil	Dispersant	Salinity	Effectiveness	Std. Dev
ASMB	Corexit 9500	5	21.9	3.4
ASMB	Corexit 9500	10	24.1	1.3
ASMB	Corexit 9500	20	52.8	1.3
ASMB	Corexit 9500	33	43.8	6.5
ASMB	Corexit 9527	5	24.1	2.1
ASMB	Corexit 9527	10	23.3	2.2
ASMB	Corexit 9527	20	54.2	5.5
ASMB	Corexit 9527	33	36.6	3.5
ANS	Corexit 9500	5	19.4	1.1
ANS	Corexit 9500	10	18.8	0.7
ANS	Corexit 9500	20	21.9	1.9
ANS	Corexit 9500	33	34.8	4.7
ANS	Corexit 9527	5	17.1	0.8
ANS	Corexit 9527	10	17.2	1.7
ANS	Corexit 9527	20	24.6	0.8
ANS	Corexit 9527	33	25.9	2.8

ASMB = Alberta Sweet Mixed Blend

ANS = Alaska North Slope Blend

Table 14 Summary of Authors and Findings from Surfactant Literature

Author	Year	Surfactant Type	Specific Surfactant	Type of Test	Generic Results
Abuin et al.	1993	Ionic	CTAB and CTAC	Microemulsion stabilization	Stabilization increases with salinity except for one surfactant
Al-Roomy et al.	2004				
Austad and Strand	1996	Ionic	Exxon RL-3011	Oil behaviour	Salinity has large effect
Austad et al.	2004				
Babadagli	2003	Nonionic	Oxyethanol ethyoxylate	Recovery from reservoir	Recovery increases with salinity
Chen et al.	2004	Ionic	CTAB	Interfacial tension	IFT decreases and then increases
Chooro et al.	1996	Zwitteronic	N-dodecyl Betaine	Relative solubility	RSD decreases with salinity
Davis	1994	Most		Reviews basics	IFT decreases with salinity
Drummond & Israelachvili	2002	Various		Surface forces	Surface forces decrease with salinity
Fjelde and Austad	1994				
Fjelde et al.	1995	Dual ionic	6EOS & DDBS	Recovery from reservoir	Recovery increases with salinity
Ghannam and Chaalal	2003	Nonionic	Triton X-100	Oil spill recovery	Recovery increases with salinity
Hou and Papadopoulis	1996	Nonionic	Tween 80 & Span 80	Droplet stability	Drop stability increases with salinity
Hou and Papadopoulis	1997	Nonionic	Tween 80 & Span 80	Droplet stability	Drop stability increases with salinity
Kaczmarski et al.	1999	Dual ionic & nonionic	SDS & Triton 100	Thickener viscosity	Viscosity lower as salinity increases
Kjøniksen et al.	1999	Ionic	SDS	Gel structure	Salinity increases molecular associations
Li and Chen	2002	Nonionic	Tergitol 15-S-X, Triton X-100, Tween 20, Tween 80	Partitioning of org. into oil	Partitioning increases with salinity
Li and Kunieda	2003	Mixed	Anionic and cationic	Relative solubility	RSD decreases with salinity
Liu et al.	2004				
Mollet et al.	1996	Ionic	Sodium linoleate	Interfacial tension	IFT decreases and then increases
Moosai and Dawe	2003	Various	Various	Gas flotation	Wastewater cleanup improved with salinity
Park and Bielefeldt	2003	Nonionic	Tergitol NP-10	Partitioning of org. into oil	Partitioning increases with salinity
Prosser and Franses	2003	Ionic	SDS & SDSn	Model of IFT equilibrium	Salinity decreases IFT
Sabatini et al.	2003	Ionic	Naphthalene sulphonates	Solubilization	Very salinity-dependent
Sayyouh et al.	1993	Ionic	Sulphonates	Phase behaviour of oil-surfactant-brine	Stability increases up to 3.8% and then decreases as salinity goes to 23%
Song & Islam	1994				
Watt et al.	1998	Cationic	CTAB	Water-in-oil emulsion	Formation improves up to about 30% salinity
Wu et al.	2004	Nonionic	Brij 30	Relative solubility	RSD decreases with salinity
Wu et al.	2004	Nonionic	Tween 20	Relative solubility	RSD decreases with salinity
Wu et al.	2004	Nonionic	Igepol CO210	Relative solubility	RSD decreases with salinity
Ysambertt et al.	1997	Most		Reviews basics	Winsor states affected by salinity
Yu et al.	2004	Cationic	Aliquat-336	Extraction effectiveness	Extraction increases with salinity
Zhang et al.	2004	Natural	Acid fractions	Recovery from reservoir	Recovery increases with salinity

Table 15 Quantitative Data on Salinity Change from Surfactant Literature
(all data converted to relative effectiveness compared to 0 salinity)

Author and Details	Salinity o/oo	Increase in Effect (from 0)	Change in Solubilty	Reduction in IFT	Notes
Wu et al., 2004	50		4.1		
nonionic	100		5.8		
	50		2.7		
	100		3		
	50		3.4		
	100		5.2		
Chen et al., 2004	1			99.7	
ionic	2			99.4	
	5			99.3	
	7			99.2	
	9			99.1	
	11			99.2	
	15			99.6	
Mollet et al., 1996	5			22	
	10			44	
	20			38	
	30			35	
Kaczmarski et al.,	20	64			surf = .01
1999	30	84			surf = .01
	20	48			surf = .025
	30	77			surf = .025
	20	50			surf = .05
	30	90			surf = .05
Li and Chen, 2002	0.5	50			partitioning
	5	75			partitioning
	10	100			partitioning
	0.5	5			reduced radius
	5	10			reduced radius
	10	17			reduced radius
Ghannam and Chaalal,	10	5			still water
2003	20	150			still water
	30	260			still water
	10	5			circulated water
	20	16			circulated water
	30	36			circulated water
Sayyouh et al., 1993	5			20	
	10			90	
	15			3	
	20			60	
Guyomarch et al.,	10	0			
2002	25	166			
	35	200			
	50	566			

Table 16 Results of Metabolite Uptake (from Wolfe et al., 1998)

	Metabolic Uptake (as percentage recovered)			
	A,b Napthol Sulphate		Napthalene	
Sample	22 o/oo	34 o/oo	22 o/oo	34 o/oo
20 C WAF - Control	1	2	98	96
20 C WAF - Exp. Med.	5	8	93	90
20 C WAF - Algae	4	1	80	85
20 C Disp. oil - Control		2	99	96
20 C Disp. oil - Exp. Med.	3	3	96	95
20 C Disp. oil - Algae			95	92
12 C WAF - Control	6	1	91	98
12 C WAF - Exp. Med.	6	3	91	96
12 C WAF - Algae			92	92
12 C Disp. oil - Control	4		94	99
12 C Disp. oil - Exp. Med.	5	3	93	96
12 C Disp. oil - Algae			90	95

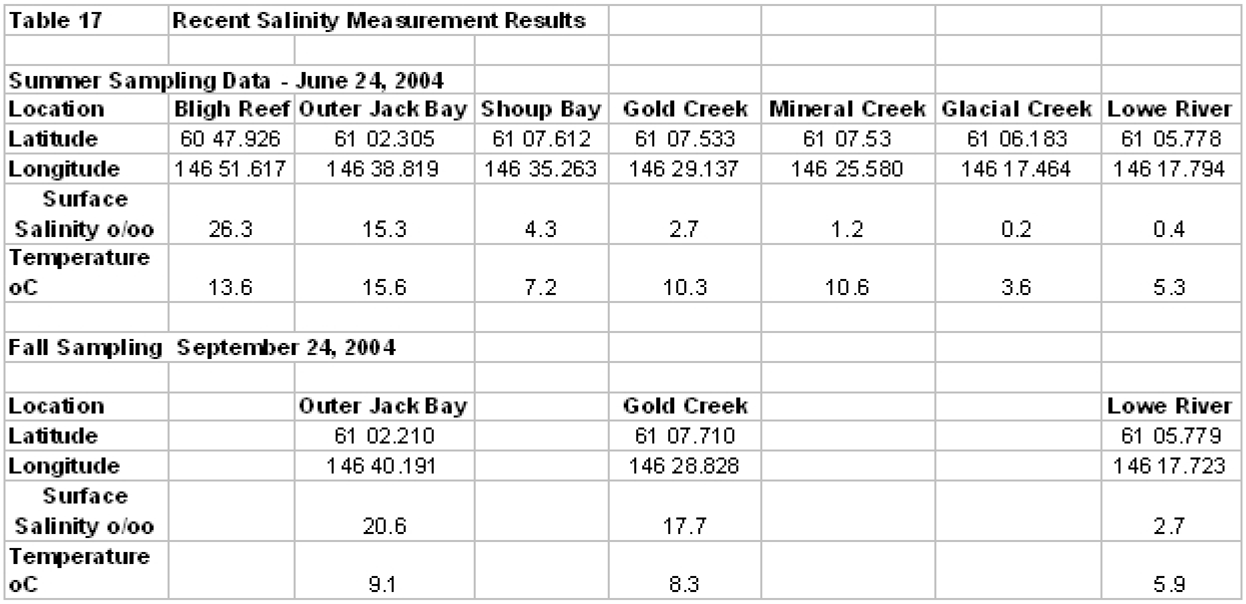

Table 17	Recent Salinity Measurement Results						
Summer Sampling Data - June 24, 2004							
Location	**Bligh Reef**	**Outer Jack Bay**	**Shoup Bay**	**Gold Creek**	**Mineral Creek**	**Glacial Creek**	**Lowe River**
Latitude	60 47.926	61 02.305	61 07.612	61 07.533	61 07.53	61 06.183	61 05.778
Longitude	146 51.617	146 38.819	146 35.263	146 29.137	146 25.580	146 17.464	146 17.794
Surface Salinity o/oo	26.3	15.3	4.3	2.7	1.2	0.2	0.4
Temperature oC	13.6	15.6	7.2	10.3	10.6	3.6	5.3
Fall Sampling September 24, 2004							
Location		**Outer Jack Bay**		**Gold Creek**			**Lowe River**
Latitude		61 02.210		61 07.710			61 05.779
Longitude		146 40.191		146 28.828			146 17.723
Surface Salinity o/oo		20.6		17.7			2.7
Temperature oC		9.1		8.3			5.9

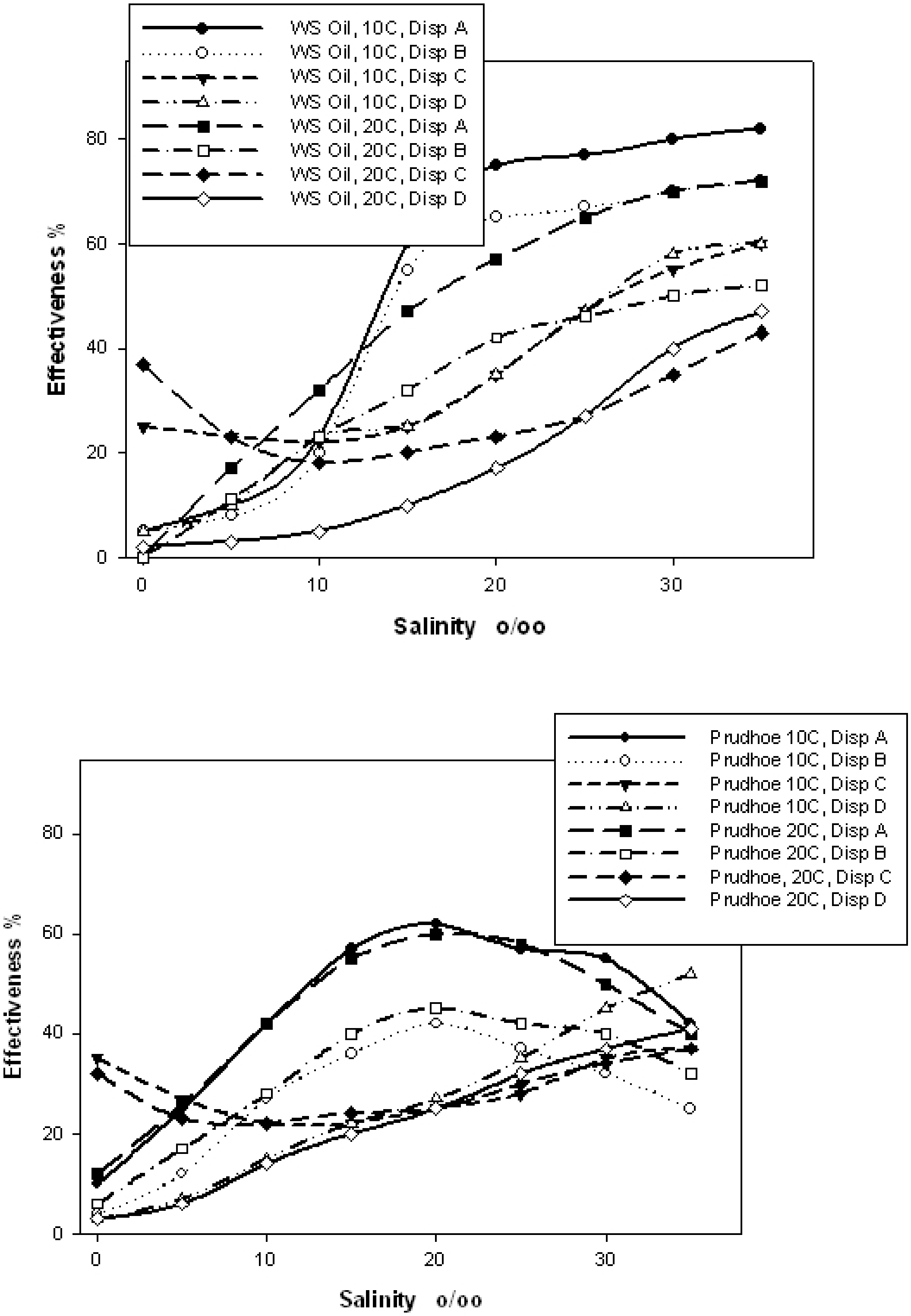

Figure 1 Salinity and Dispersant Test Results from Belk et al., 1989, Warren Springs Oil, Upper Plot: Prudhoe Bay Oil Lower Plot

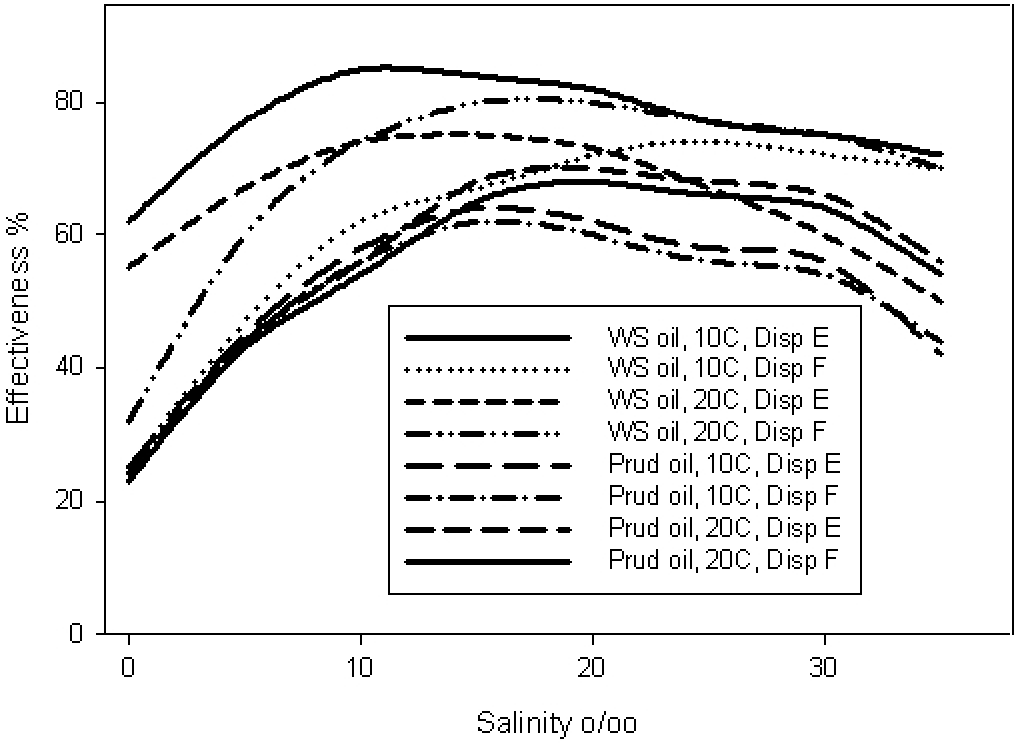

Figure 2 Dispersant E and F Data from Belk et al., 1989

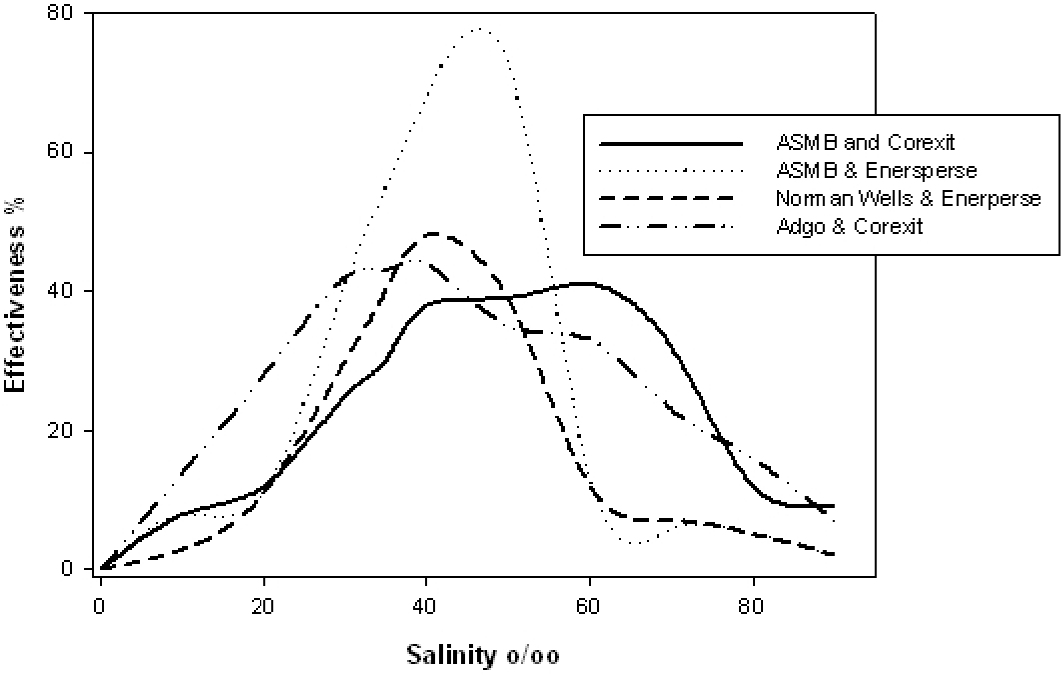

Figure 3 Dispersant Effectiveness with Salinity from Fingas et al. 1991

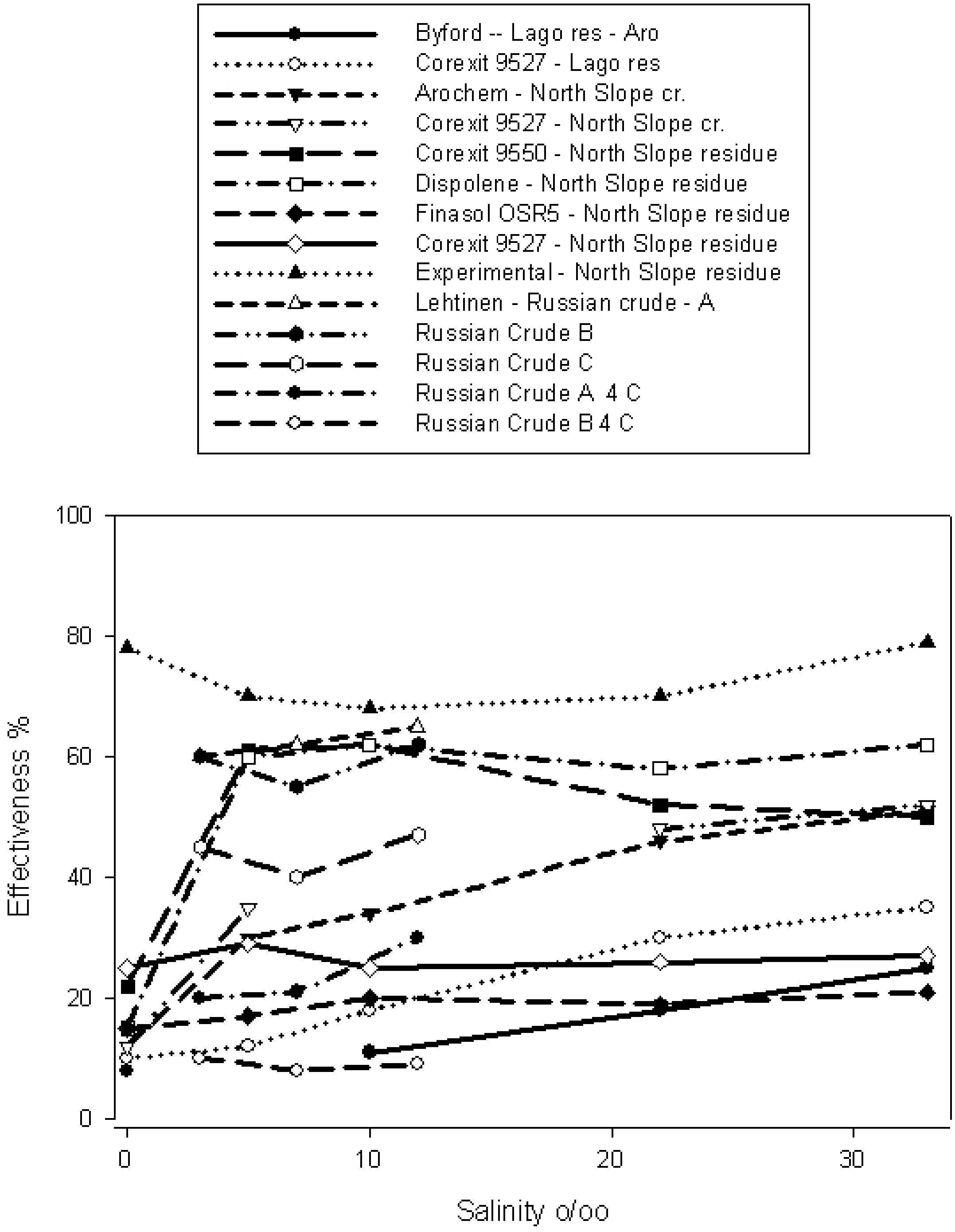

Figure 4 Salinity and Dispersant Effectiveness Data from Byford et al., 1983 and Lehtinen and Vesala, 1984

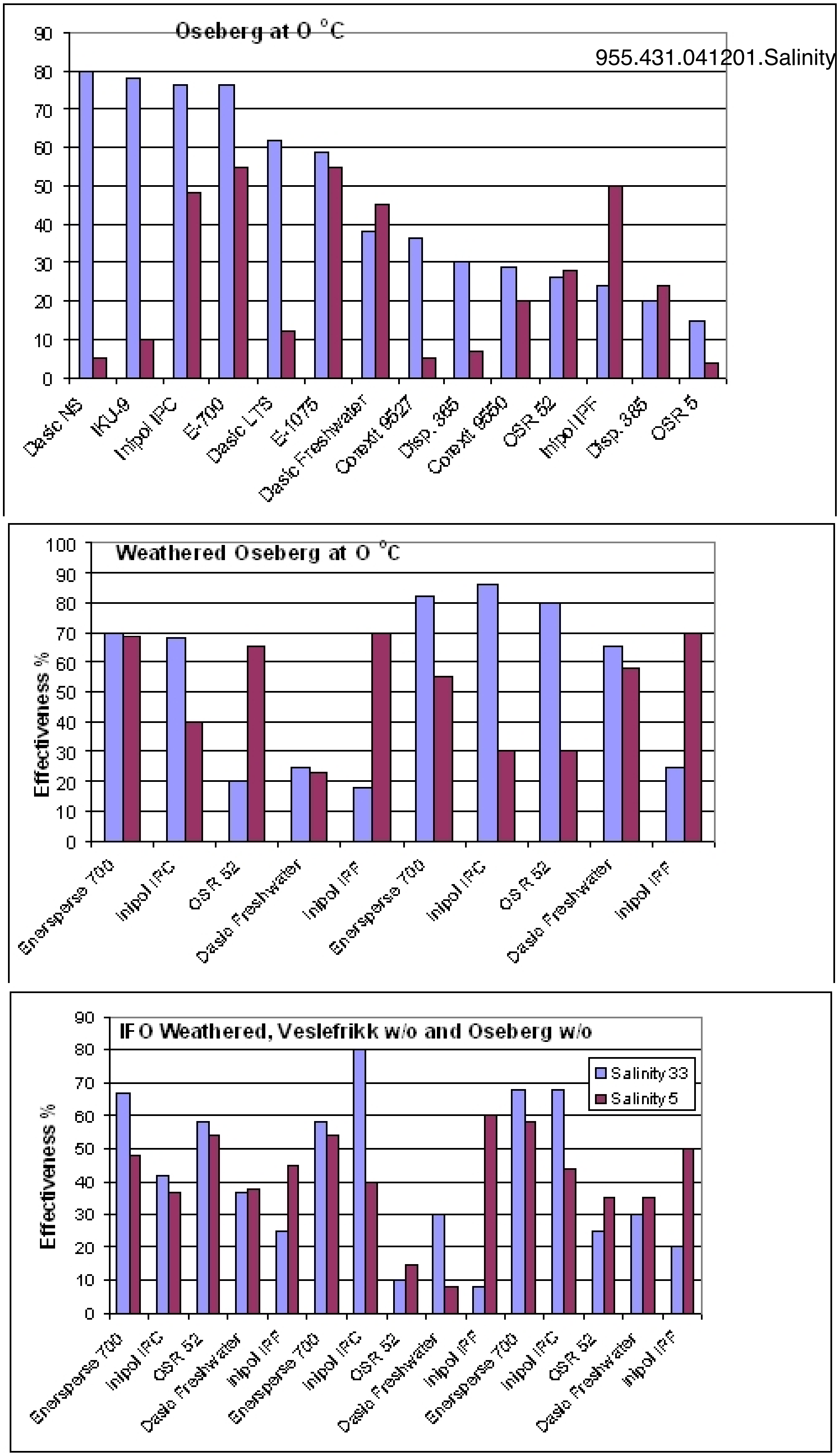

Figure 5 Dispersant Effectiveness with Salinity from Brandvik et al. 1995

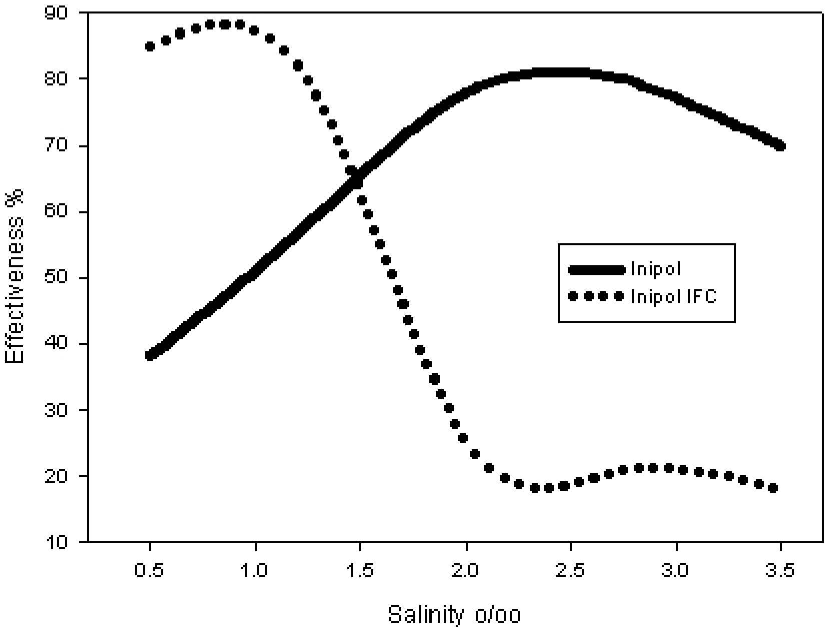

Figure 6 Dispersant/Salinity Test on Two Inipol dispersants - Inipol IFC was a Special Freshwater Dispersant (Data from Brandvik and Daling, 1992)

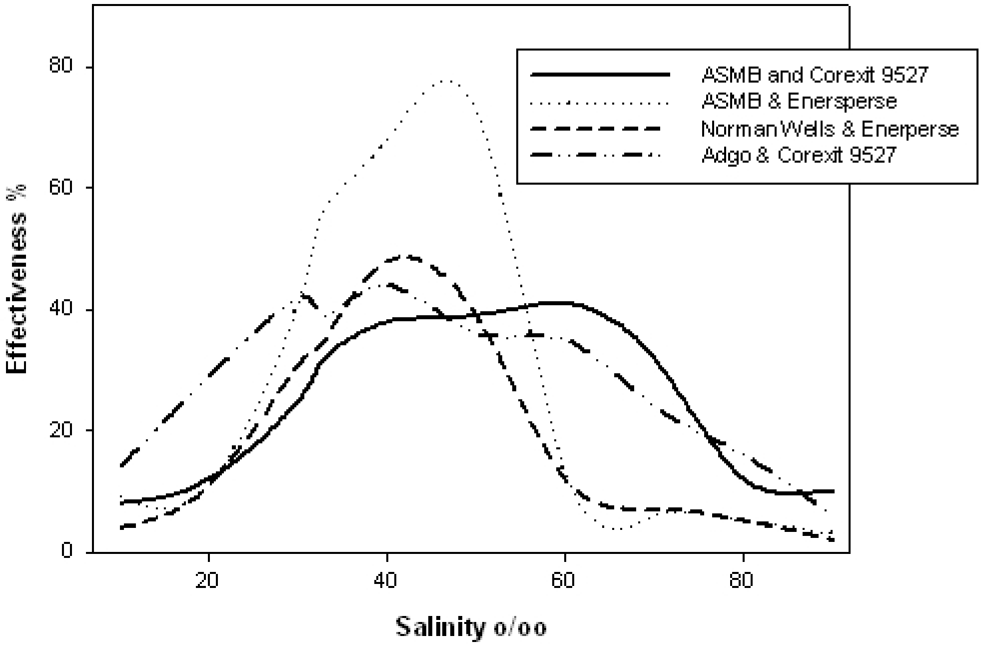

Figure 7 Tests on Dispersant Effects with Varying Salinity (Data from Fingas et al., 1994)

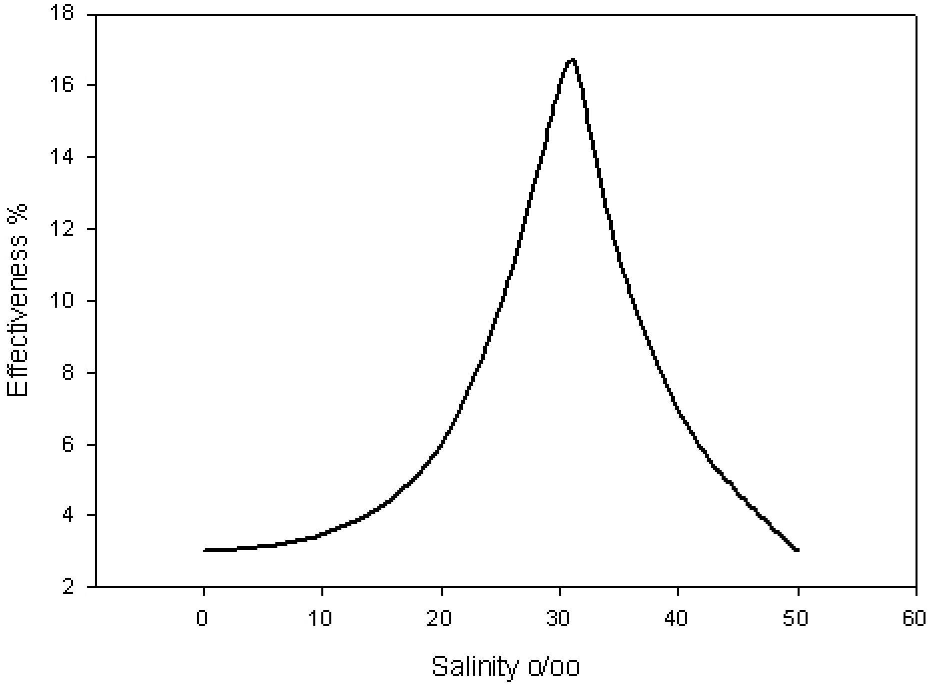

Figure 8 Dispersant Effectiveness Data for Corexit 9527 and a Light Arabian Crude (Data from Moet et al., 1995)

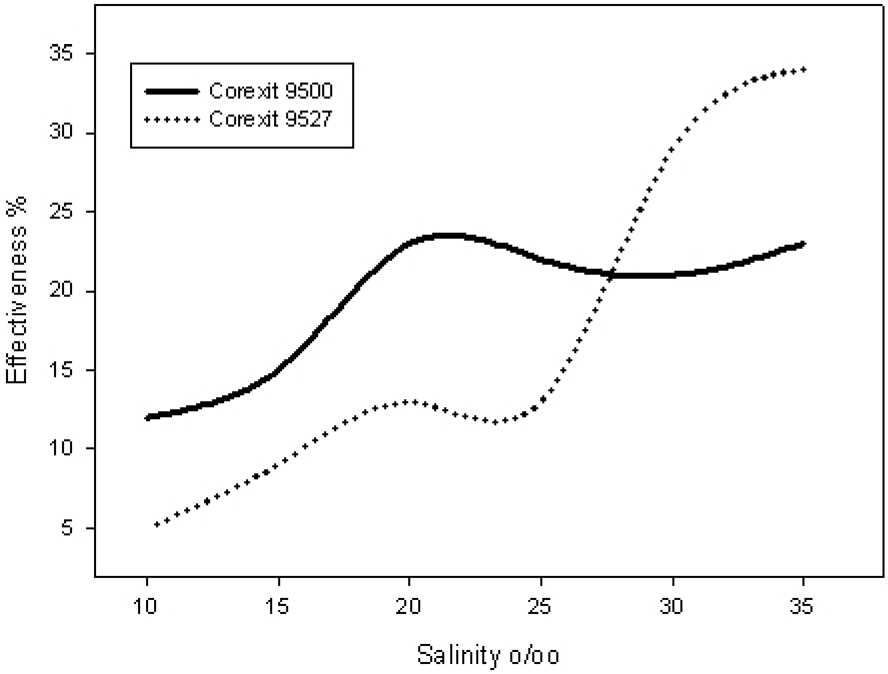

Figure 9 Dispersant Effectiveness Data on ANS Crude (Data from Blondina et al., 1997 a,b)

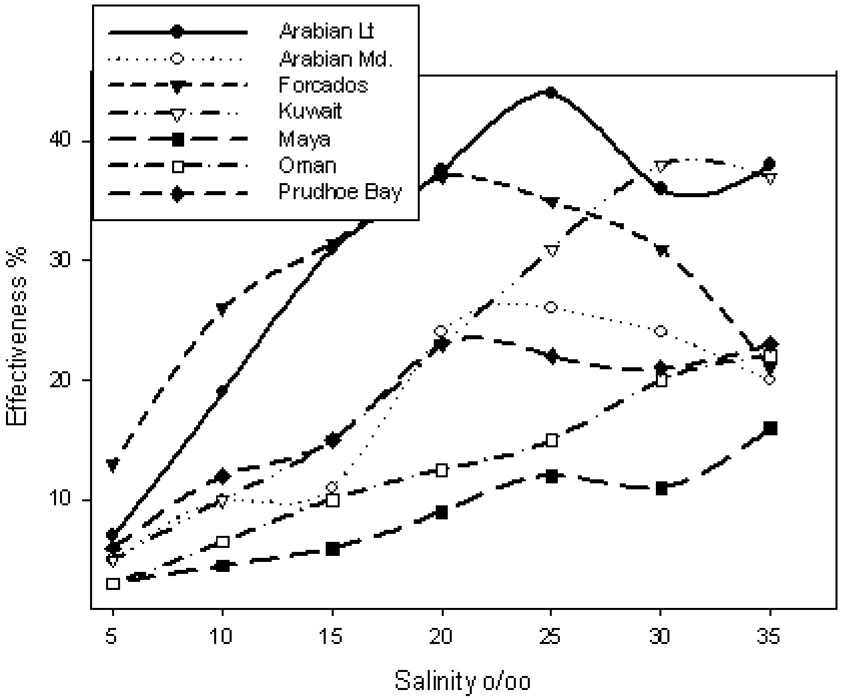

Figure 10 Effectiveness of Corexit 9500 with Salinity (Data from Blondina et al., 1999)

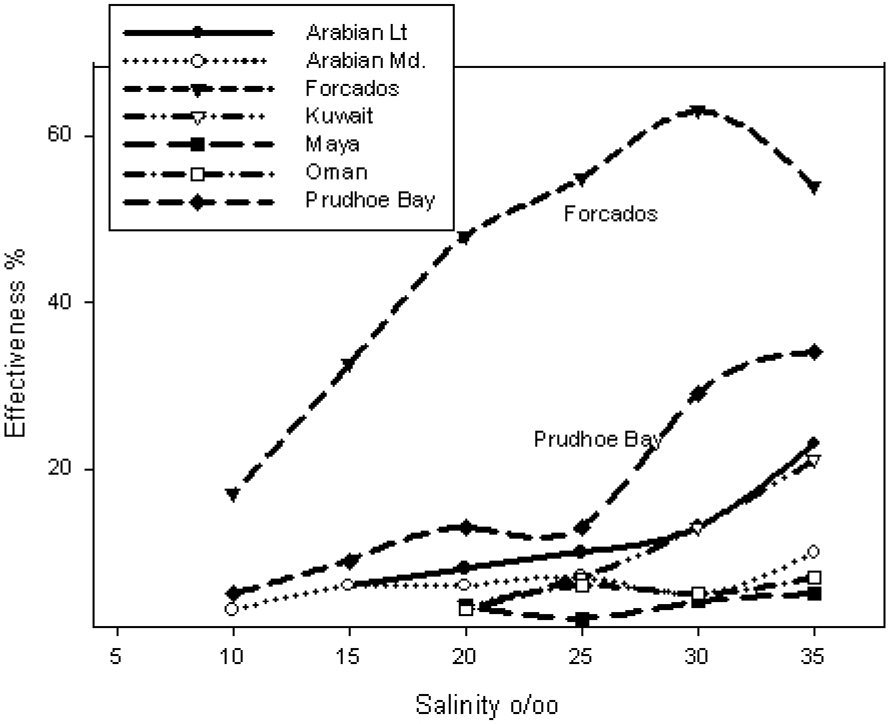

Figure 11 Effectiveness of Corexit 9527 with Salinity (Data from Blondina et al., 1999)

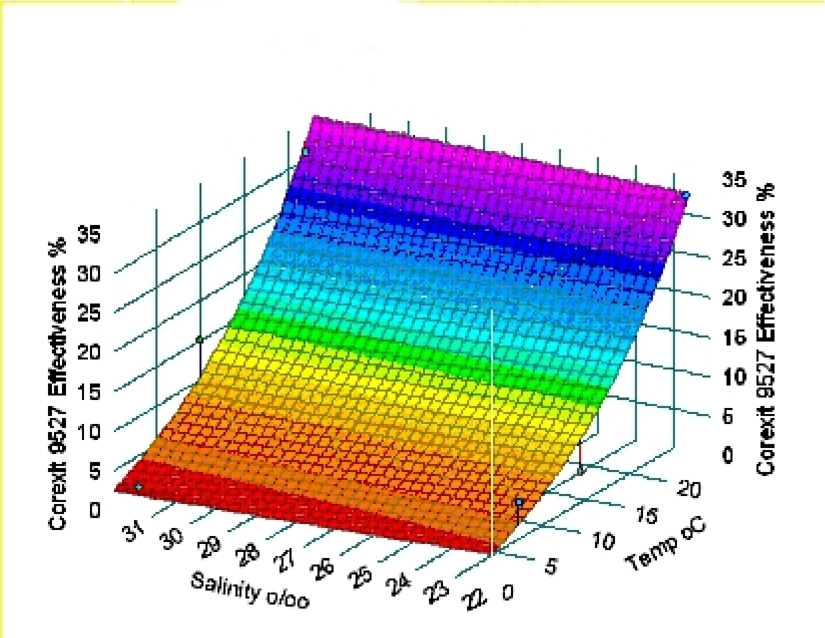

Figure 12 Three-way Relationship of Effectiveness, Salinity, and Temperature for Corexit 9527 and Fresh ANS (Data from Moles et al., 2002)

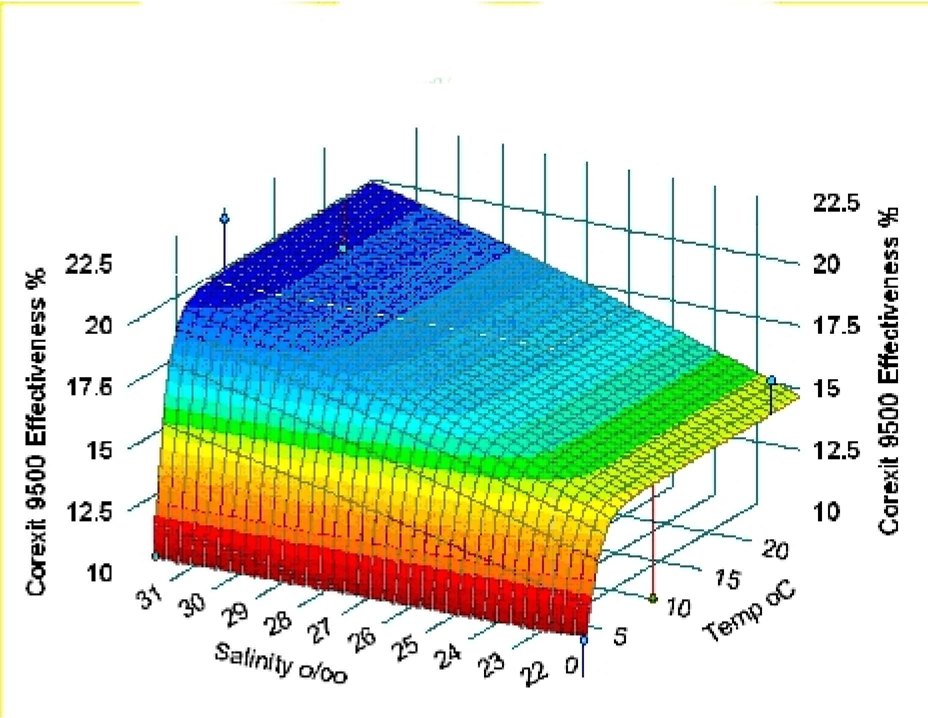

Figure 13 Three-way Relationship of Effectiveness, Salinity and Temperature for Corexit 9500 and Fresh ANS (Data from Moles et al., 2002)

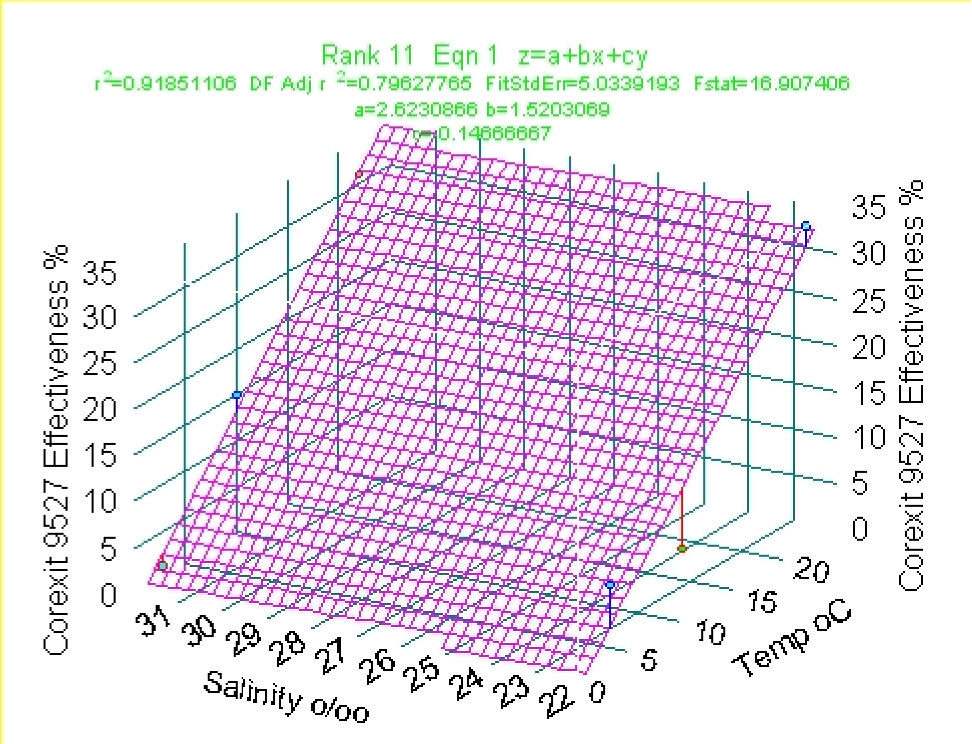

Figure 14 Three-Way Correlation of Corexit 9527 Effectiveness with Fresh ANS (Moles et al., 2002)

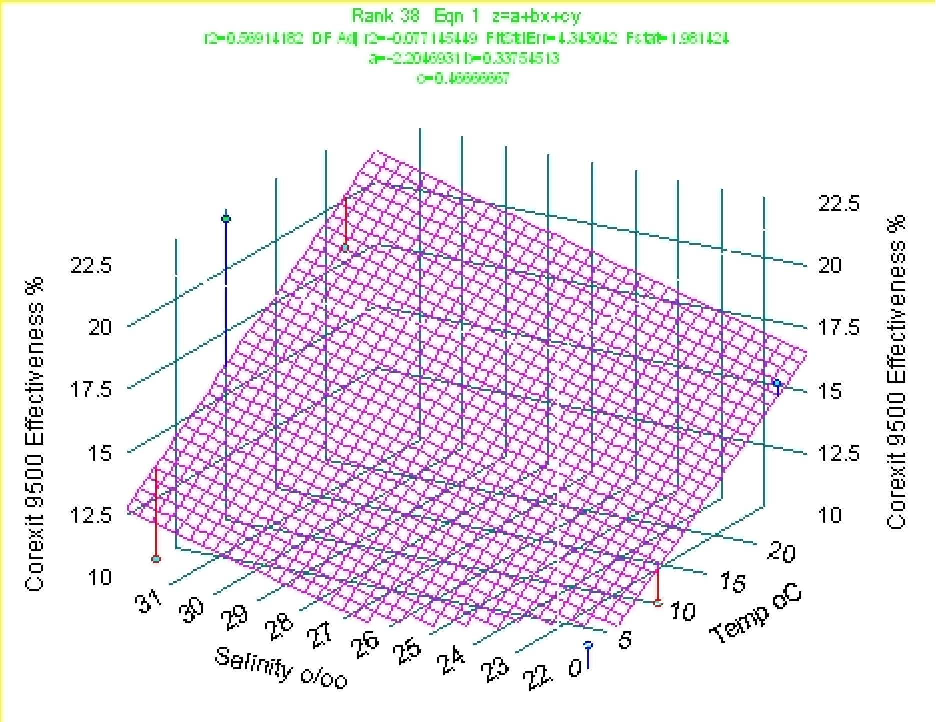

Figure 15 Three-Way Correlation of Corexit 9500 Effectiveness with Fresh ANS (Moles et al., 2002)

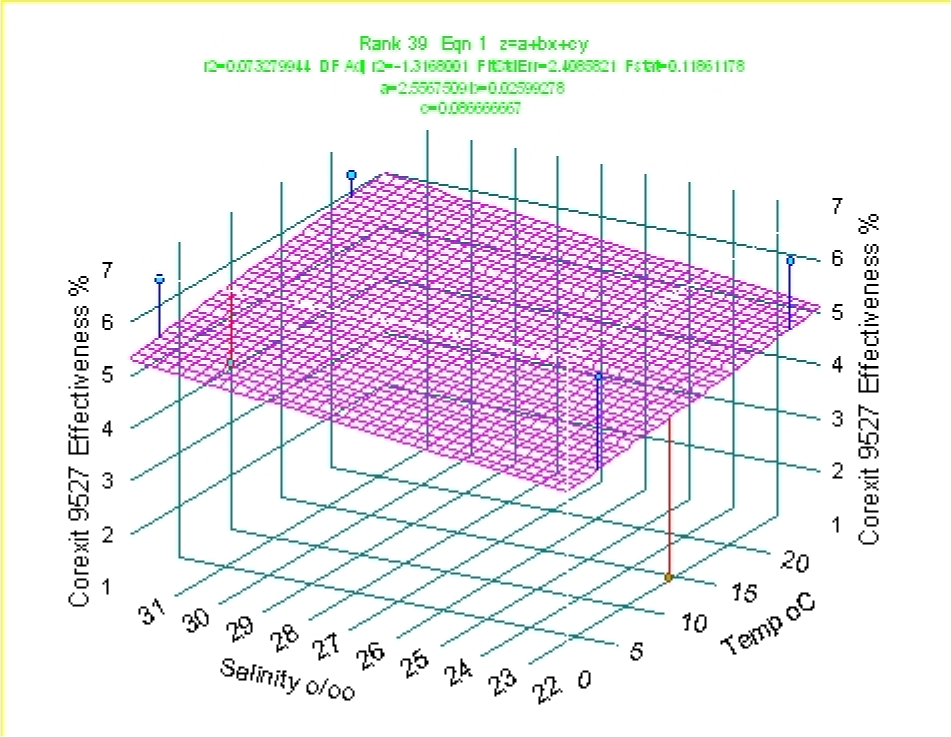

Figure 16 Three-Way Correlation of Corexit 9527 Effectiveness with Weathered ANS (Data from Moles et al., 2002)

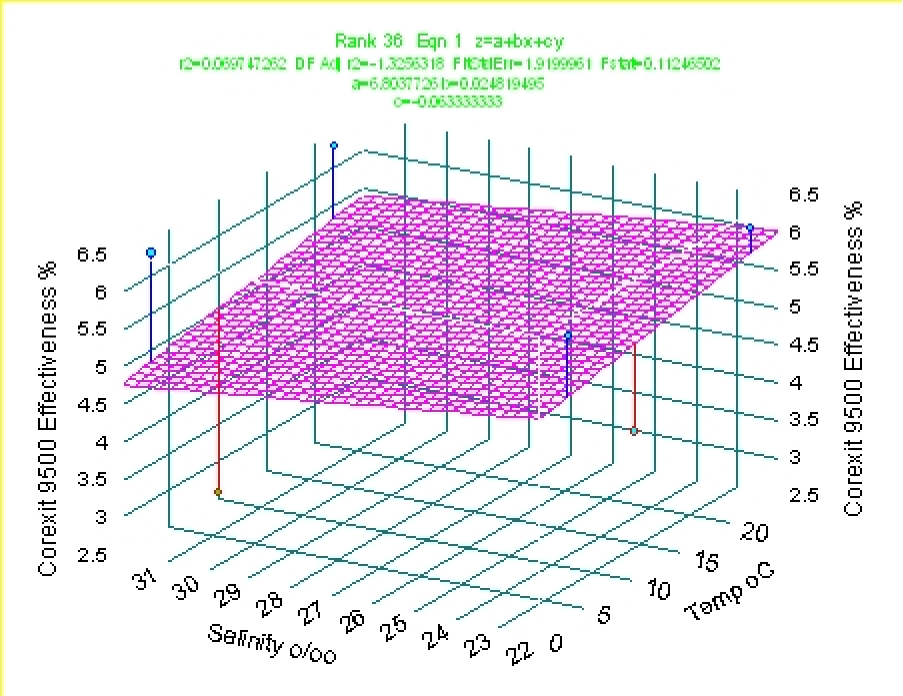

Figure 17 Three-Way Correlation of Corexit 9500 Effectiveness with Weathered ANS (Data from Moles et al., 2002)

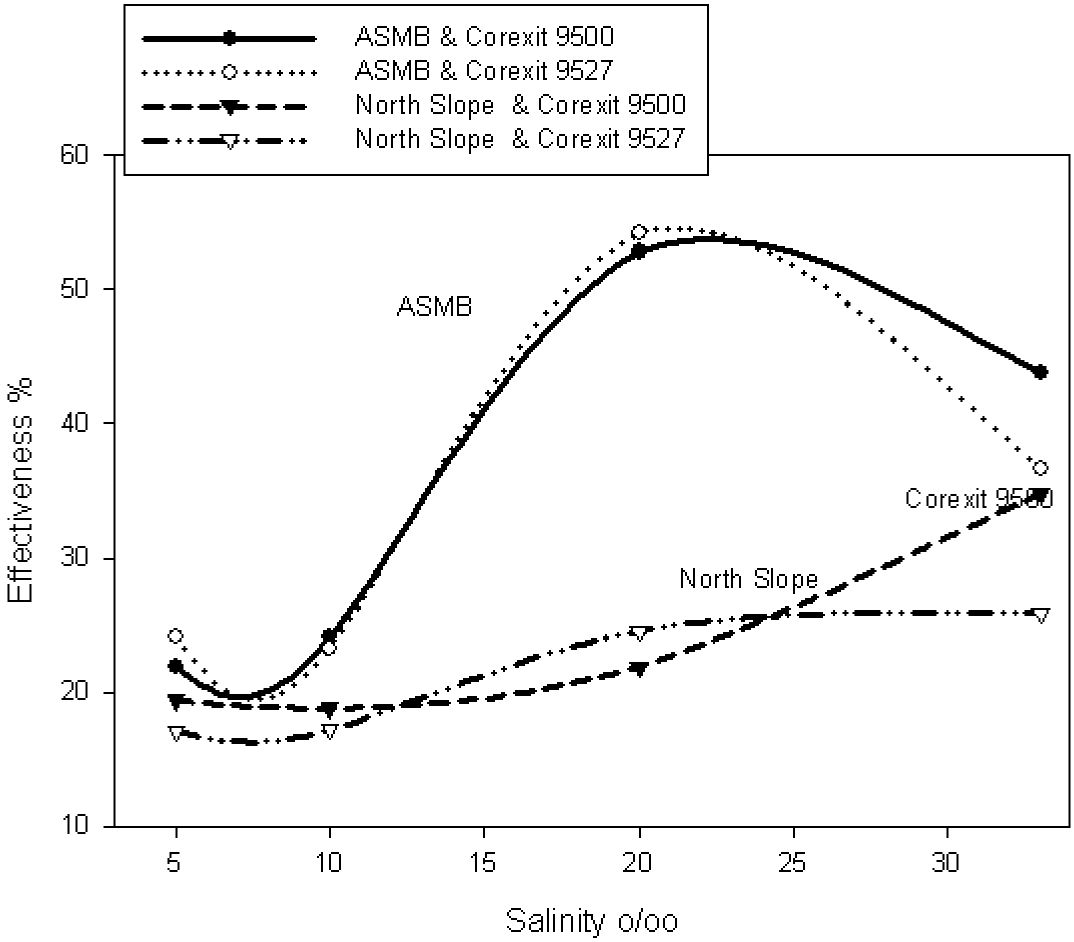

Figure 18 Variation of Dispersant Effectiveness with Salinity (Data from Fingas et al., 2003)

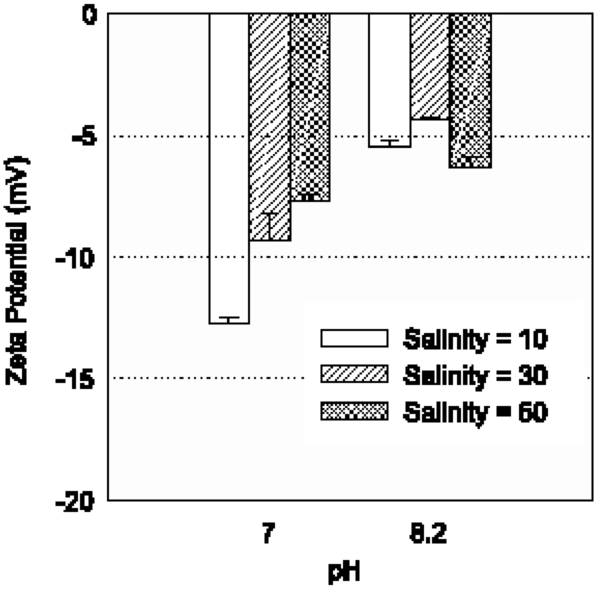

Figure 19 Measured Zeta Potential Values of Chemically Dispersed Crude Oil Droplets at Selected pH Values (Data from Sterling et al., 2004)

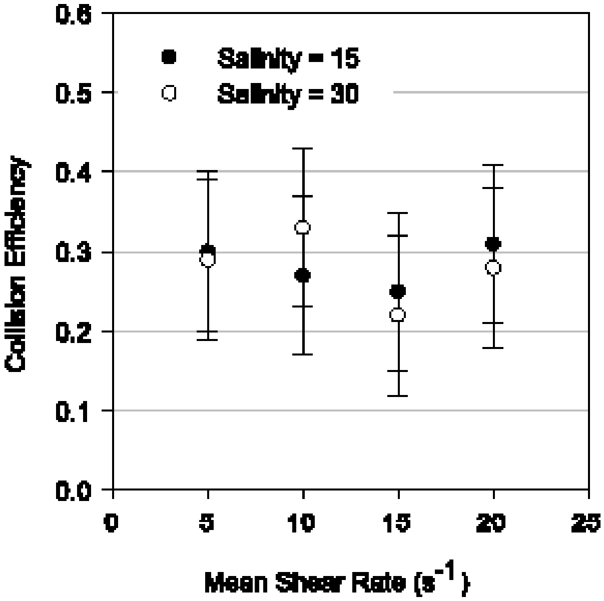

Figure 20 Effect of Shear Rate on Collision Efficiency (Data from Sterling et al., 2004)

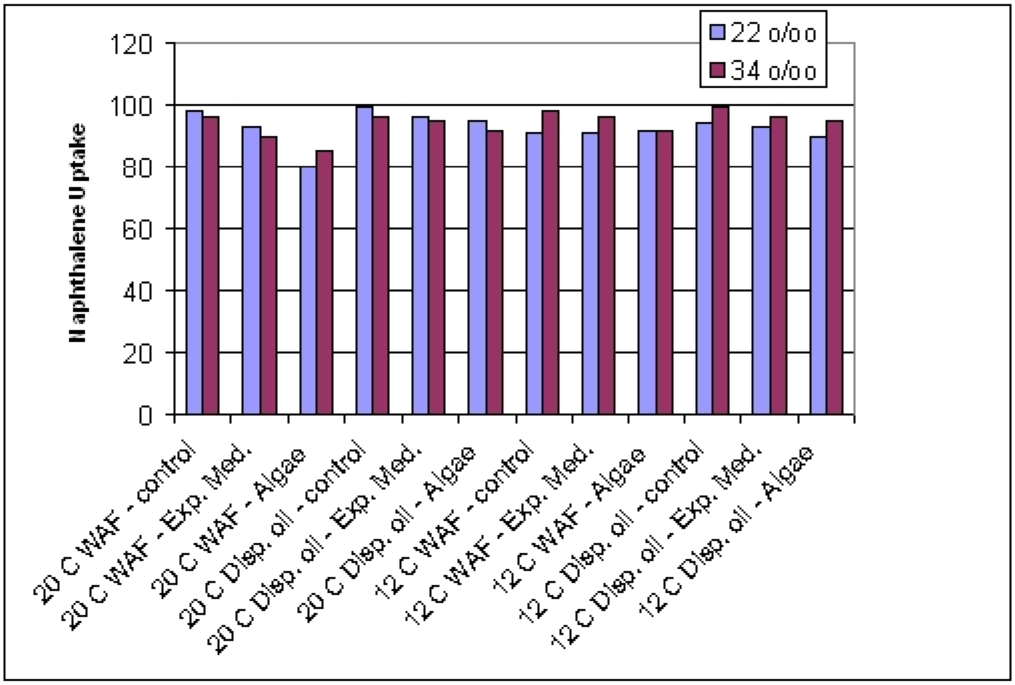

Figure 21 Variation in Uptake of Naphthalene by Algae (Data from Wolfe et al., 1998)

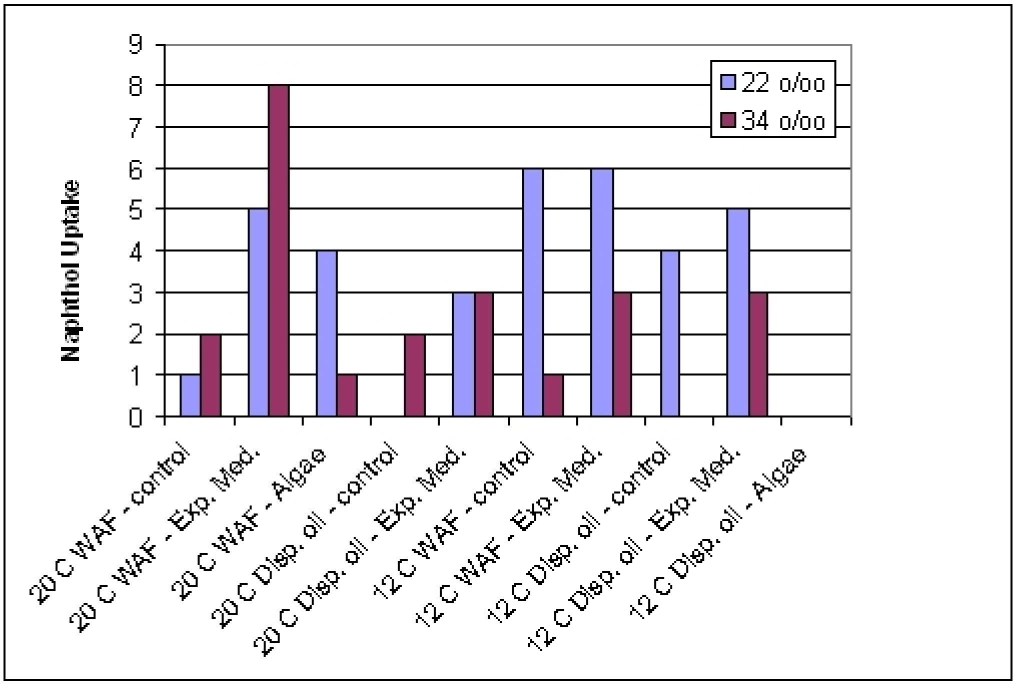

Figure 22 Variation in Uptake of a,b Naphthol Sulphate by Algae (Data from Wolfe et al., 1998)

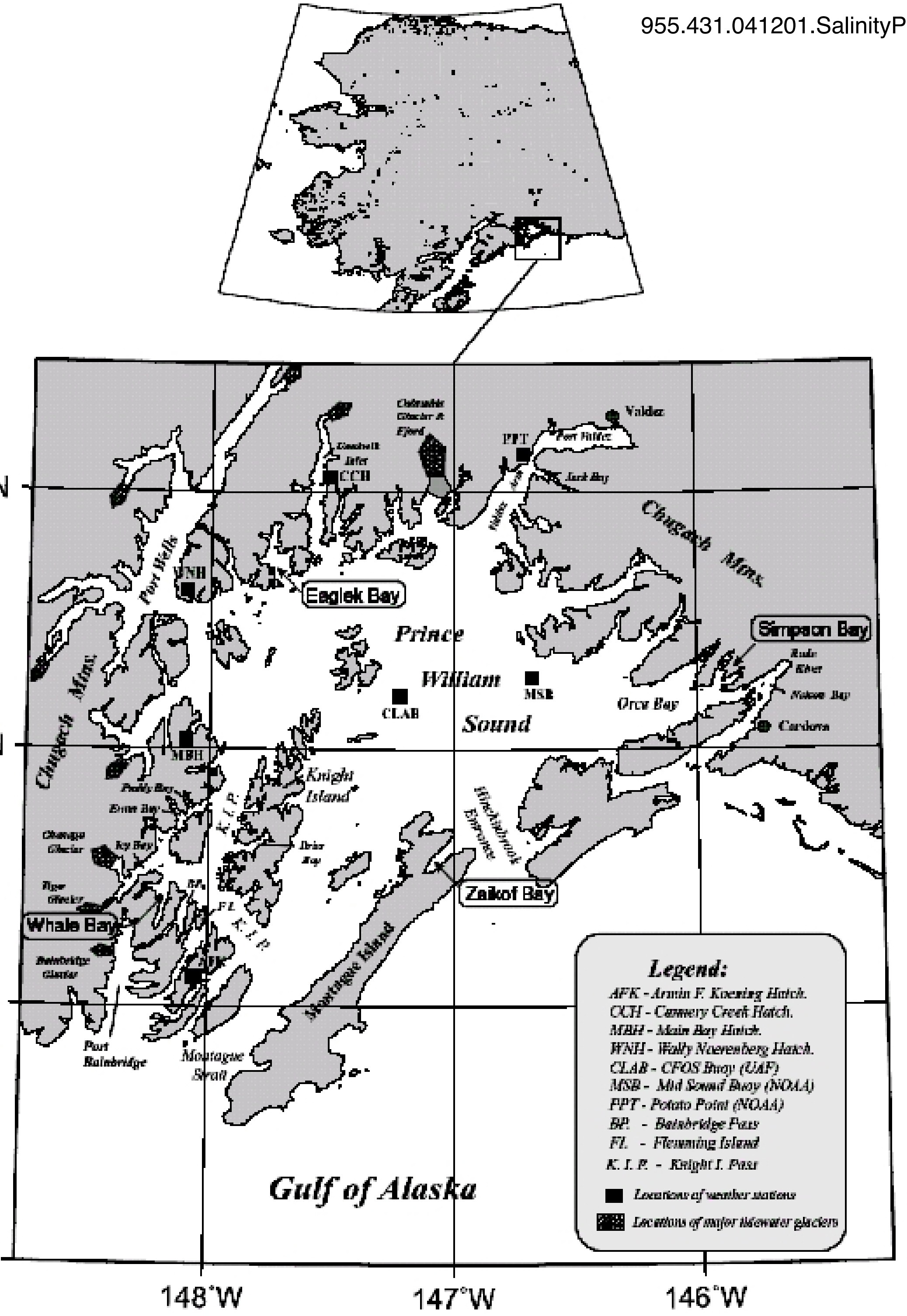

Figure 23 An Overview of Prince William Sound Showing Detailed Sample Sites

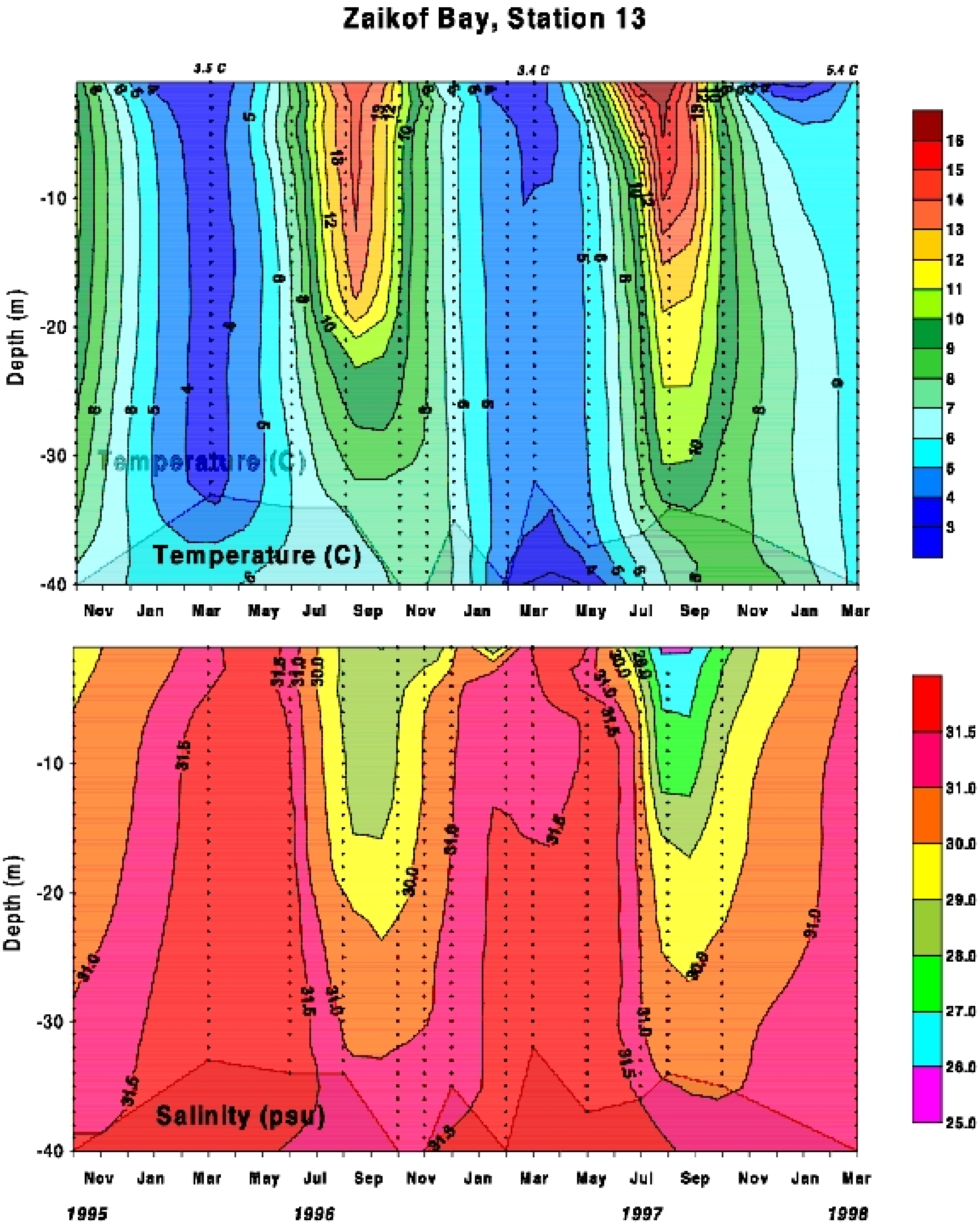

Figure 24 A Temperature/Salinity Graph from Zaikof Bay Sampling Site (Vaughn et al., 2001)

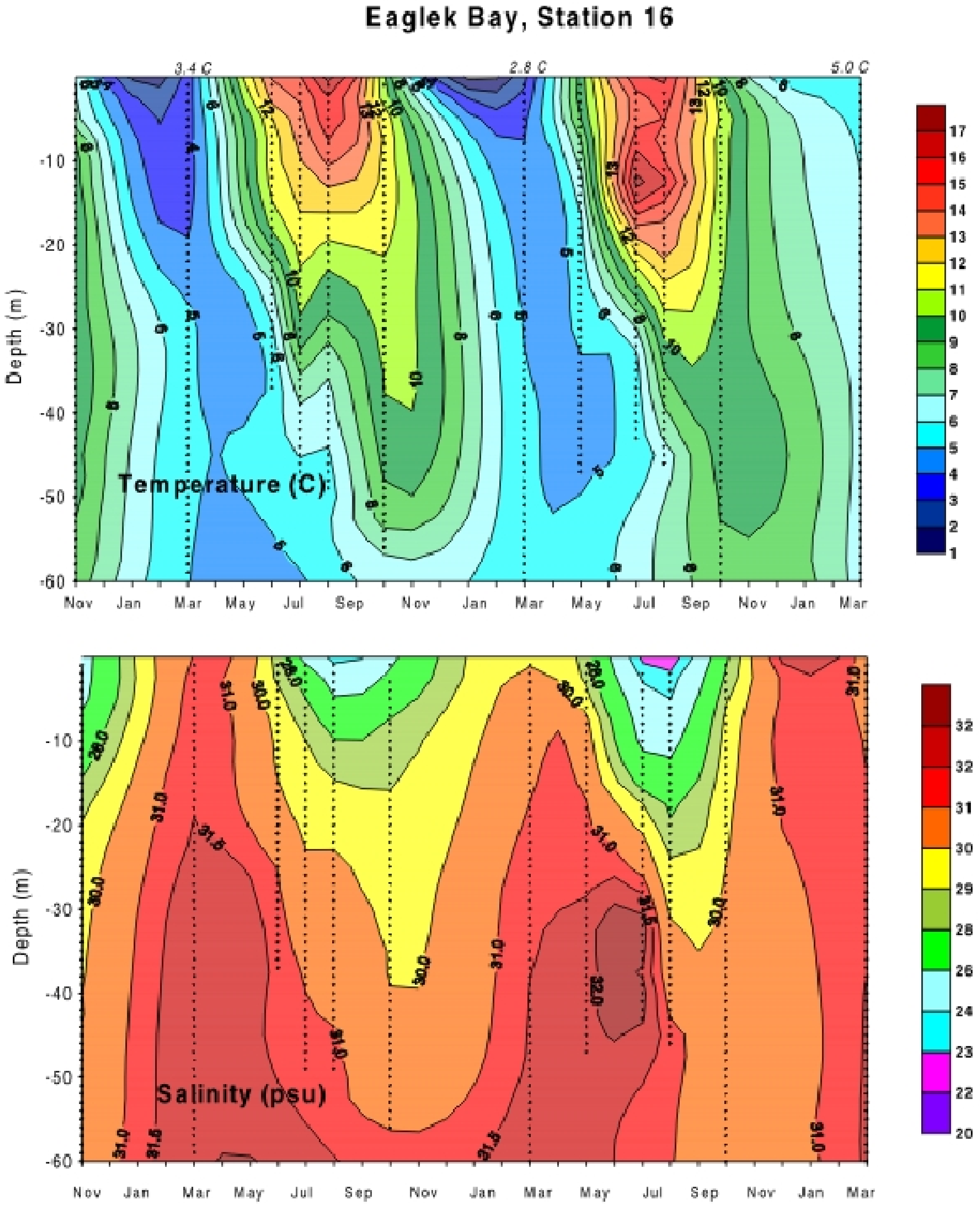

Figure 25 A Temperature/Salinity Graph from Eaglek Bay Sampling Site (Vaughn et al., 2001)

955.431.041201.SalinityPWS.pdf

Whale Bay, Station 11

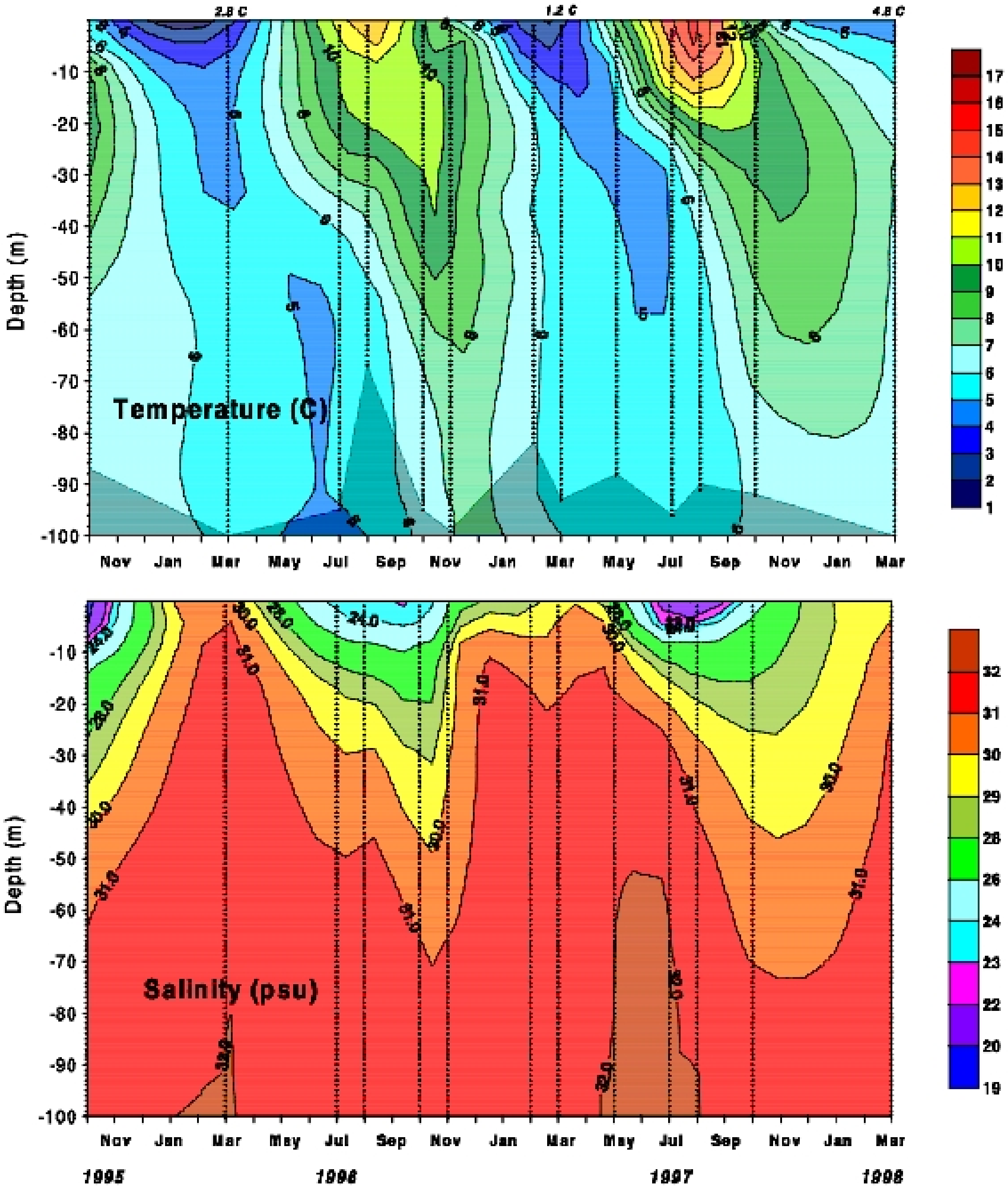

Figure 26 A Temperature/Salinity Graph from Whale Bay Sampling Site (Vaughn et al., 2001)

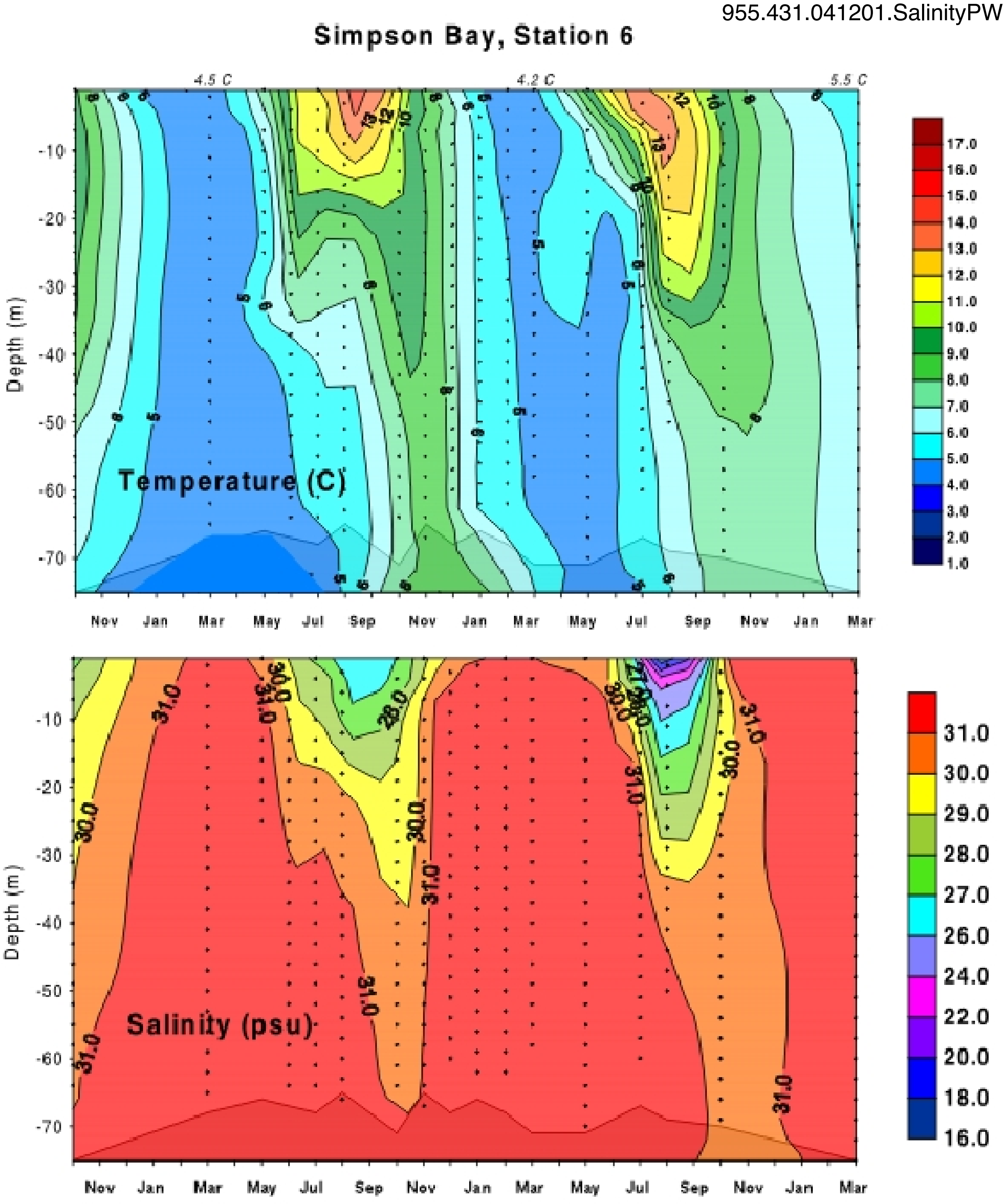

Figure 27 A Temperature/Salinity Graph from Simpson Bay Sampling Site (Vaughn et al., 2001)

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