Assessment of Treated Vs. Untreated Oil Spills

Final Report

February 1981

Prepared for:
U.S. Department of Energy
Assistant Secretary for Environment
Environmental and Safety Engineering Division

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### Assessment of Treated Vs. Untreated Oil Spills: Final Technical Report

#### Abstract
This report describes the results of a series of studies conducted to determine the practicability and feasibility of using dispersants to mitigate the impact of an oil spill on the environment. The method of approach is holistic in that it combines the physical, chemical, microbial and macro-fauna response to a spill treated with dispersants and compares this with spills that are left untreated. The program integrates mathematical, laboratory, meso-scale (three 20 foot high by three feet in diameter tanks, described in Section 1), in-situ experiments and analyses to determine if the use of dispersants is an effective oil spill control agent.

In summary, it appears viable to use dispersants as determined on a case by case basis. The case for using dispersants has to be based on whether or not their use will mitigate the environmental impact of the spill. In the case of an open ocean spill that is being driven into a rich inter-tidal community, the use of dispersants could greatly reduce the environmental impact. Even in the highly productive George's Bank area at the height of the cod spawning season, the impact of the use of dispersants is well within the limits of natural variability when the threshold toxicity level is assumed to be as low as 100 ppb, a level which is often found in the open ocean. Thus, it appears that dispersants can and should be used when it is evident that their use will mitigate the impacts of the spill. Their use in areas where there is poor circulation and therefore little possibility of rapid dilution is more questionable and should be a subject of future studies.

#### Key Words
Oil spills, dispersants, Marine oil spills, oil spill treatment

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Preface

This study was undertaken over a period of four and one-half years, carried out under Department of Energy Contract No. E(11-1) 4047, through the Environmental and Safety Engineering under the direction of Dr. William E. Mott and Dr. John Cece.
Acknowledgements

This is perhaps the most difficult section of any report to write. In a project of this size many people played important roles. Discussions with scientific personnel outside the project had beneficial influences on the project.

A special thanks to Dr. William E. Mott for the foresight in establishing the project and to Dr. John Cece who later became DOE Project Manager for his many helpful suggestions and his patience. Many people worked on the project whose names do not appear as authors in this final report. Dr. Sheila Bhattacharya and Paul Griffin worked on the initial biodegradation studies, Margaret Brady-Campbell, Daniel Goldfarb and Mark Maris contributed to the chemical analysis. The meso-scale facilities were constructed by Charles Young and operated and maintained later by Peter Pohlot and Richard Heavers. Dr. Peter Cornillon initiated the rain drop experiment. He was aided by David Konigsberg and Scott Paul. David Zinni, Steve Csenge and William Jasper worked on the entrainment experiment. Dr. Raymond Teyssandier also worked on entrainment and various other portions of the report.

Last but far from least, is the office staff who enabled this rather voluminous to come to fruition in the form of a report. A special thanks to Ms. Corinne Carr who supervised the construction of the report and editing. Her patience, organization skills and thoroughness added greatly to reduce the difficulty of the formidable job of collecting and organizing the sections of this report. Other office staff who contributed much to this report are Ms. Tracy Miller who painstakingly did many of the flow charts and Denise Klein. Many thanks to the College of Engineering Word Processing personnel and especially to Mary Costa who did the bulk of the typing.
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EXECUTIVE SUMMARY

ASSESSMENT OF TREATED VERSUS UNTREATED OIL SPILLS

Mason P. Wilson, Jr.
Program Director
Executive Summary and Results

This report describes the results of a series of studies conducted to determine the practicability and feasibility of using dispersants to mitigate the impact of an oil spill on the environment. The method of approach is holistic in that it combines the physical, chemical, microbial and macro-fauna response to a spill treated with dispersants and compares this with spills that are left untreated. The program integrates mathematical, laboratory, meso-scale (three 20 foot high by three feet in diameter tanks, described in Section 1), in-situ experiments and analyses to determine if the use of dispersants is an effective oil spill control agent.

A series of physical and physical-chemical studies and experiments were conducted to determine the emulsification properties, including emulsion stability of the treated and untreated oil, and its rate of evaporation. Various natural entrainment processes were also investigated to compare natural entrainment of the oil with chemically dispersed oil. Emulsified oil exhibits properties in between those of a true solution and a suspension of immiscible phases. Experiments to typify the drop size distribution, mixing energy and to evaluate the effect that dispersants have on interfacial tension were conducted. The results of these tests indicated that only a fraction of the energy goes into the formation of droplets. Typical drop sizes were in the range of 2 to 10 microns for both the treated and untreated dispersed oil. This is well within the particle size range in which emulsions are classified, i.e., 0.25 to 25 microns, whereas butterfat particles are in the 7.5 to 8.5 micron range. The major difference between the dispersed oil and the chemically treated dispersed oil was not the drop size distribution but rather the concentration of oil in the dispersed phase. The amount of oil in the dispersed phase (hold-up) was approximately two to three times greater than the untreated dispersed oil for these tests. Consequently, the interfacial area of the treated dispersed oil was approximately two to three times greater. Entrainment was also observed without mechanical energy input with Corexit 9527, although the hold-up was slightly less than with mixing. As much as 86% of the oil that could be accounted for went into the water column when dispersants were used. A rather small amount of dispersant is required to decrease the interfacial tension (see Section 1).

The stability of the dispersed oil was investigated in several experiments, some of which produced conflicting results. The stability of an oil-in-water emulsion can be easily determined by measuring its settling or creaming rate. Most of the droplets follow a Stokesian flow. In the drop size range experimentally determined, it would take from 40 hours to 1000 hours (1 to 10 micron size) for the droplets to rise to the surface of a 0.6 meter tank. The amount of oil in the water column after twenty four hours of quiescent conditions remained relatively constant, however, the amount of oil in the water column when dispersants were used with mixing remained approximately twice that when no dispersants were used. In two separate tests, one with no mixing, the amount of entrained oil remained relatively constant. However, in these experiments chemical analysis of the dispersed phase indicated a ratio of dispersant to oil of approximately one to one. In Section 4.4, the experiment with no mixing is reported, and similar results were
found in the latest meso-scale tests reported in Section 8. Somewhat unusual results in terms of stability were also observed in the wind/wave experiments to be discussed in a later paragraph. Coalescence of the dispersed phase was found to be negligible (Section 1) and therefore did not affect the stability characteristics of the emulsion. It was found that very little agitation was required to maintain the chemically dispersed oil in the water column, (Section 4), however, it should be noted that in these tests the ratio of dispersant to oil in the water column was approximately one to one, even though application was on a twenty to one ratio. It should be noted, also, that these low ratios of dispersant to oil were only observed under quiescent conditions or when there was very little mixing energy applied. The mixing experiments had shown that almost all of the oil could be incorporated in the dispersed phase when mixing energy was applied and subsurface circulation was sufficient to maintain the dispersed oil from reforming at the water/air interface. It thus appears that more stable emulsions are formed when the dispersant/oil ratio is in the neighborhood of unity, however, natural turbulence and subsurface circulation in many instances could be sufficient to maintain almost complete entrainment of the dispersed oil.

The subsurface circulation and entrainment was investigated analytically and conditions for various drop sizes to remain in suspension were established. These results are presented in Section 4 of this report.

Several evaporation tests from an oil slick were conducted throughout the duration of this project and reported in Section 4, Section 7 and Section 12.2. In Section 7, laboratory and meso-scale tank evaporation tests are reported. The laboratory study using the self mixing dispersant Corexit 9527 indicated that the evaporation of the n-alkanes from the treated and untreated slicks were similar when the water was not agitated. However, when mixing was applied, the evaporation of the light n-alkanes, n-C7 to n-C10, from the treated slick were slower than from the untreated slick. The greater the mixing the greater the effect the dispersant had on depressing the evaporation rate. The dispersant affected the evaporation rate of the lighter n-alkanes to a greater extent than the heavier ones. The slower evaporation of the treated slick could be due to the mixing of some of the oil in the water column. Results of the meso-scale experiments were in agreement with the laboratory scale experiments when mixing was not applied. Evaporation was faster in the meso-scale (open tank) experiments because of the wind and more natural environment although mixing had little effect on decreasing the evaporation rates. Experimental results with treated and untreated oil showed that components lighter than C12 evaporated from both slicks after three hours and after seventy-two hours all of the components up to C16 had disappeared. The effect various wind speeds had on evaporation rates of Kuwait crude were investigated by using a wind tunnel. These results show that approximately 75 percent of the total evaporation occurs within the first two hours and that evaporation essentially ceases after twenty four hours with a weight loss of 32.3 percent. These results are in substantive agreement with the results reported in the preceding paragraph. Thus, if dispersants are applied two hours after the spill, most of the lighter weight hydrocarbons would have evaporated; furthermore, when dispersants are applied to the outer edges of the spill, it is being applied generally to the portion of oil
that has undergone the maximum amount of evaporation. Thus, the major portion of the more volatile and toxic fractions of the oil could be expected to be evaporated by the time dispersants would or could be applied in most situations.

Natural entrainment experiments were conducted in the wind/wave tank and in the rain drop experiment. Tests in the wind/wave experiments described in Section 3 of this report were conducted with fresh water and sea water with Kuwait crude. It was found that the oil weathers much differently in the fresh water than in natural sea water. In fresh water, it rapidly forms slicklets which appear to be stable emulsions and very little oil gets into the water column. In the salt water tests much more oil entered the water column and increased with time, except at a higher frequency where after weathering for 24 hours, the concentration of oil in the water column showed a dramatic decrease. This is attributed to the formation of stable emulsions that had an affinity to the droplets which took them out of solution. The appearance of the oil in the higher wave frequency tests showed a stringiness as though it had been shredded or torn apart after 24 hours. This did not happen with the lower frequency waves during the same period where the concentration increased with time in all salt water tests. The effect of an increase in temperature is to increase the amount of oil getting into the water column. Doubling the quantity of oil in the slick did not change the percent concentration of oil in the water column. Therefore, the actual concentration almost doubled. In the ocean, currents would carry some of the oil from under the slick. Tests using the dispersant did not show sudden increase in concentration of the oil in the water column immediately after adding the dispersant as might be expected. The visual properties of the slick and the waves changed, but the oil did not disperse into the water column until it had weathered over eight hours after adding the dispersant. After twenty-two hours of weathering, practically all the oil entered the water column.

Entrainment of oil into the water column by rain was investigated and reported in Section 4.4 of this report. The results indicate that substantial oil can be incorporated into the water column by this process. Concentrations as high as 45 parts per million were observed in these experiments, however, the concentration of oil in the water column drops off when either subsurface circulation or the rain is terminated. Consequently, natural entrainment by rain, like other entrainment phenomena, requires subsurface circulation to maintain the droplets in suspension.

A number of analytical chemistry techniques were developed throughout the duration of this project. These are reported in Sections 7, 9 and 12.2. Infra-red analysis of the petroleum hydrocarbons extracted from the water column were analyzed quantitatively as well as qualitatively. Several solvent systems were investigated in an attempt to separate the oil from the dispersant prior to infra-red analysis. Thin Layer and Column Chromatography were also used with various solvent systems to effect the separation; however, even with this system, a complete separation of the oil from the dispersant could not be realized. Because of this and of the time required to perform this separation, it was decided that development of computer techniques to effect spectral separation of these two components was required. This technique is
reported in Section 12.5.

A quantitative analytical infrared technique to determine the ratio of dispersant to oil was also developed and is reported in Section 12.2 of this report. It involves the ratio of absorbance of the mixture at a wave number of 3600 (cm$^{-1}$) which corresponds to the OH stretching. This represents a strong peak for most dispersants, while the peak for most oils occurs at a wave number of 2930 (CH stretching). Mixtures were prepared to establish calibration curves and a procedure was developed to determine the ratio of dispersant to oil in the mixture and the total amount of hydrocarbons present in the sample. In Section 8, a quantitative gas chromatograph method is described that determines the total peak area of Corexit 9527 in the water stock solutions. This area was converted to concentration of oil and subtracted from the integrated total hydrocarbon in the oil-dispersant mixture. This gave ratios of oil to dispersants almost identical to those determined by the infra-red method mentioned above. A GC Mass Spectrum system was also used in portions of the analysis as reported in Section 7 of this report.

The chemistry of the treated and untreated oil slick was investigated rather extensively and is reported in Section 7 of this report. Some of these results were discussed in the preceding paragraphs on evaporation and entrainment. Most of the chemical analyses were conducted on tests run in the meso-scale tanks. These tests were run in the tanks under the following conditions (1) batch, with no mixing or forced circulation (2) batch with mixing provided by the wave maker and (3) with dilution (flow-through) and mixing. Salt water from Narragansett Bay was used as the test medium and the salt water temperature was maintained to within 10$^\circ$F of the Bay temperature to eliminate any thermal stresses on marine organisms that were present. One series of tests were conducted to determine the effect of various modes of application of oil and dispersant to the seawater on the concentration of oil in the water column. It was found that the effectiveness of the dispersant in carrying the oil into the water column is proportional to the amount of contact of the dispersant with both the polar water fraction and the non-polar fraction of the oil/water system. The most intimate contact between these fractions was achieved when the dispersant was premixed with the oil. In all experiments, agitation of the water surface in the tanks also aided in mixing the oil/dispersant complex into the water column. Controls were used throughout the duration of these tests and remained within the hydrocarbon levels found in the Bay. In the dispersant treated tank, the highest concentrations were found generally in the top and middle layers after one hour, with a relative reduction in concentration after twenty-four hours (in some cases reduction to control levels). The level of hydrocarbons was determined more by the mode of application than by the amount of oil/dispersant added. In the untreated tank the oil concentration increased initially but often fell below control levels after twenty-four hours. The cause for this behavior is not fully understood but it is believed that the oil droplets suspended in the water column coalesce with the surface slick and do not get re-entrained.

Analysis of sediments in flow-through experiments had indicated no significant increase in concentrations of petroleum hydrocarbons over a three week period for either the treated or untreated surface slicks.
Microbiological studies were conducted throughout the program in order to determine whether the degradative capacity of the petroleum hydrocarbons and natural microorganisms were enhanced by the use of dispersants. It was determined that the Viable Plate Count (VPC) and Most Probable Number (MPN) methods were suitable for enumeration of marine heterotrophic bacteria and hydrocarbonoclastic bacteria. Use of these methods demonstrated that the percentage of oil degraders within the "total heterotrophic population" increased with exposure time of the "total population" to oil and/or dispersant.

Oxygen depletion by the Modified Biological Oxygen Demand method is a valuable tool which provides a general picture of biological response to materials suspended in the water column. The procedure was used to demonstrate the biodegradable nature of Corexit 9527 and provide a rough index of degradation potential. This method confirmed VPC and chemistry data in the meso-scale experiments.

Oxygen depletion has certain limitations, the greatest being that it cannot be directly correlated with actual oil degradation rate or the rate of degradation of specific oil components. An alternate approach is chemical analysis by gas chromatography which has been used in this project. The use of this technique for water column samples, while quantitative for bulk oil, has certain limitations for component analysis. It is possible to demonstrate loss of classes of compounds by this method but is too expensive and time consuming for routine degradative rate determinations. The use of $^{14}$C labeled hydrocarbons allows a fairly simple method for measuring mineralization (conversion of organic carbon to carbon dioxide by metabolism) as an index of biodegradation. Representative hydrocarbons provide an estimate for the rate at which the mixed natural population achieve mineralization of aliphatic and aromatic hydrocarbons. The mineralization rate studies demonstrate turnover rates ranging from approximately 20 to 90 mg of substrate per hour. These values compare with results by other investigations in similar systems.

A more accurate approach using $^{14}$C methodology is to measure not only mineralization, but also the production of water soluble intermediates which carry the $^{14}$C label and the amount of $^{14}$C incorporated into cell biomass. The importance of this approach was apparent in one typical experiment as discussed in Section 8 of this report.

Studies by the VPC for the surface film, water column and sediment were performed at 13 and 40°C. The bacterial numbers increased in the surface film during day 1 and 2 then remained essentially constant throughout the 21 day experiment. We interpret this increase not as bacterial growth per se but rather the formation of the microlayer. The sediment bacterial population increased through a period of nine days in the control, dispersant and oil-dispersant trials but not in the oil tank. The numbers remained constant in the sediment of the oil-dispersant tanks following these nine days but declined in the control and dispersant tanks. It is believed that the hydrocarbon degrading bacteria are carried into the oil film in the oil treated tank, removing them from an active role at the oil water interface. This might be expected because the oil destroys the surface microlayer.
The water column studies at 4°C and 13°C provide evidence for two different bacterial populations in the natural seawater which was at 10°C. The total heterotrophic population shifts somewhat but the most significant observation is a rapid increase in the number of hydrocarbanoclastic bacteria through day 7 followed by a decline to original numbers due, we conclude, to exhaustion of the nitrogen, phosphorus and iron centers of the seawater.

The studies showed a decline in colony diversity with time in the tank system suggesting enrichment for specific organisms which is supported by the studies on the ratio of hydrocarbanoclastic to heterotrophic bacteria. Population dominance is more significant than population size which is a fairly constant value.

The long term flow through experiment showed no significant correlation between the number of total heterotrophic bacteria and hydrocarbon concentration, but a significant correlation was found between total heterotrophic and total hydrocarbanoclastic bacteria which indicated selection for hydrocarbon-utilizing bacteria.

A negative relationship was found between hydrocarbon content and hexadecane or naphthalene mineralization rates, suggesting inhibition of mineralization at high hydrocarbon and/or dispersant values. However, there was a decrease in hydrocarbon turnover time in the oil and/or dispersant tanks. This decrease in the turnover time is more apparent for aliphatic hydrocarbons than for aromatic hydrocarbons.

The variation in mineralization rates is minimal ranging from 8.6 to 11.9 ng/hr for hexadecane and 8.3 to 19.6 ng/hr for naphthalene. Thus, in the determination of degradation time the most important function is hydrocarbon concentration.

Investigation of phosphate and nitrogen in the test systems reveal values which were always nutrient limiting for the amount of degradable carbon available.

It is our conclusion that hydrocarbon degradation potential in nutrient limited seawater is a relatively constant value independent of the presence or absence of oil in the water column. There is selection for hydrocarbanoclastic bacteria with time but their overall degradation activity as a mixed population is not significantly affected by the enrichment process. Preliminary evidence indicates that nutrient supplements (nitrogen, phosphorus and iron) do have a significant effect on the size of the seawater microbial population and yield a rather homogenous population of hydrocarbon utilizing bacteria in the presence of oil.

A brief discussion of nutrient seeding suggests this is not a viable approach to increased hydrocarbon degradation potential. The danger of increased pathogenicity in nutrient enriched oil-water systems is a real possibility which must be more fully investigated.

Natural microbial hydrocarbon degradative processes are active in the water column of dispersed or non-dispersed oil. These processes
will eventually lead to the turnover of the biodegradable oil components. The rate at which oil degradation occurs is not materially enhanced by the dispersion process but dispersion of the oil into small micelles (1-2 m) suspended in the water column does make the oil more available to microbial action. Due to the physical inaccessibility of microorganisms to the bulk of the oil in a heavy slick, dispersion of the oil is an adjunct to the hydrocarbon degradative capacity of a mixed natural marine water column population.

This project has not shed much light on the affect of microbial populations on dispersed oil entrained into sediments or oil solubilized or suspended as sub-micron micelles in surface microlayers. Limited data from this project indicates that hydrocarbon degradative potentials in sediments and the surface microlayer may be significantly higher than degradative potentials in the water column.

An investigation into the effects of realistic concentrations of oil and oil-dispersant mixtures on marine life was conducted. The results are reported in Section 9 of this report. The investigation of short term exposure of bay scallops, Argopecten irradians, and two scallop predators, the oyster drill Urosalpinx cinera and the common starfish Asterias forbesi, to oil and oil-dispersant mixtures suggested that predator and prey have different lethal susceptibilities. Scallops were most sensitive to dispersant and dispersant mixed with oil, starfish were only sensitive to the dispersant while the oyster drill seemed unaffected even though all were exposed to dilutions of identically prepared stock solutions. Scallops were least susceptible during winter months and most susceptible at summer temperatures. Treatment had less effect on predators than on scallops at summer temperatures. Sublethal concentrations of dispersant and oil-dispersant mixtures diminished the behavioral ability of scallops to recognize drills and starfish. The degree of effect increased with temperature. Predator detection of prey at the same concentrations was more complex. The feeding response, or posturing reflex of starfish was significantly slowed by all treatments. In contrast, drills were unaffected in their recognition of scallop effluent in a choice chamber after treatment. The results indicate that scallop populations may suffer more than the direct impact of a pollutant which selectively affects scallops but not all of the scallop predators. The differential susceptibilities of the various species investigated in this study points out a problem biologists face when conducting and interpreting a bioassay. Because not all animals are affected by the same chemicals at the same concentrations and that animals have ecological relationships which should be considered, indicates that knowing the response of one species to a number of pollutants is not always sufficient for ecological assessment.

In light of the differential susceptibilities demonstrated in the simple three animal system investigated, the concept of an indicator species is difficult to defend. It would seem that because each organism can have its own array of chemical compound and concentration response, there is no logical reason to assume that one animal could possibly be used to accurately judge susceptibility arrays for other species.
In order to have conducted the above reported study, it was necessary to study the behavioral recognition of the scallop to its predators. It was necessary to develop a method for quantifying the scallop's response to prey. This resulted in defining a "clap index" which is a measure of the scallop's escape response. This study is reported in Section 9.2 of this report. Field and laboratory studies of the intensity of predation by the oyster drill on the bay scallops are reported in Section 9.3 of this report.

The investigation of community type responses discussed above suggested that sublethal concentrations of dispersants had adverse effects on scallop behavioral escape responses and starfish posturing reflexes. These results led to the construction of a simple community to determine what would happen if both predator and prey were dosed and placed together in large laboratory tanks. How many scallops would survive each treatment? Is it possible to detect changes in individual spacing with treatment? The purpose of the experiment was to determine the answer to these questions. The results of this study show that when both predator and prey were treated as a community, scallop survivorship was significantly reduced in the dispersant and oil-dispersant mixtures beyond that expected because of hydrocarbon treatment or starfish predation alone. Since scallop survivorship in the oil treated tank was not different from the control, the slowed ability of the starfish to respond to food did not appear to affect their ability to feed on scallops. The results of this experiment show that at concentrations far below the LD$_{50}$, dispersant treated scallops suffer greater than 50 percent mortality in the presence of starfish. Chemical analysis of the scallops at the end of this experiment showed that there was no significant increase of petroleum hydrocarbons in scallops as compared to the control. These results are not predicted by the classical bioassay methods. Community studies are rare to non-existent in bioassay work but could prove extremely useful in the prediction of ecological impacts by dispersants.

The validity of the results of any environmental research program rests on its ability to be applied to the real environment. This program is no exception; consequently, in the formative stages, it was decided to respond to spills of opportunity to determine the validity of the bench scale and meso-scale tests. This portion of the program has proved to be very beneficial, and has validated a number of the results that were obtained throughout the various phases of the program. The team responded to three spills of opportunity.

The first of these spills was the Argo Merchant in 1976, the largest recorded spill in U.S. history. This first spill of opportunity served as a proving ground to field test the techniques developed in the laboratory. A portion of this work was reported in the Interim report of April 1977, and in a host of other places, included the proceedings of the Argo Merchant Symposium held at the University of Rhode Island in January 1978.

The second spill of opportunity occurred late in January 1977 in the ice-choked Buzzards Bay at the entrance to the Cape Cod Canal. This spill of No. 2 fuel oil, the result of a grounding of a barge, gave us
another opportunity to test our developments under a series of circumstances quite different from those of the Argo Merchant. The material spilled, a No. 2 fuel as compared to a No. 6 for the Argo Merchant, and extreme icing posed many new problems to be solved. Sampling under these conditions more resembled a response to a spill in the Arctic than what would normally be expected to occur in the North Atlantic. Both of these spills served to confirm the experimental results that were being obtained in the laboratory. Very early in the feasibility study, attempts were made to mimic a spill in a natural environment. Under the simulated natural environment tests, it was found that very little of the oil was getting into the water column, far less than is normally used for bioassay and LD₅₀ type tests. These results were also confirmed in the field by other investigators. The Buzzards Bay spill also provided air, surface, and water column samples at the spill site. A sample of oil was obtained from the barge and exposed in the laboratory under simulated conditions. The resulting chromatograms of these laboratory tests were almost identical to those found in the field. To our knowledge, this was the first time that a complete set of air, surface, and water column samples taken in the field were duplicated in the laboratory. Furthermore, it confirmed that the lighter fractions, i.e., C₁₀-C₁₂ and below, enter the atmosphere in the field. This leads one to question the validity of many toxicity tests where these components were not allowed to evaporate and were forced into the water column. This work has been continued in the laboratory and the meso-scale tanks, with and without the use of dispersants, during this second year of the contract. This work confirms the validity of the approach that was instituted in the early phases of this project. The major result of this additional work shows that the effect of the use of dispersants is to delay the evaporation of the lighter components by as much as 24 hours in the laboratory; however, they eventually evaporate. These results are essentially duplicated in the meso-scale tests; however, on a much more compressed time scale. This compression of the time scale in the meso-scale tests, which more closely approximates the field, is very significant. Processes that require 24 hours to occur in the laboratory occur in approximately two hours in the meso-scale tanks. Evaporation is enhanced in the meso-scale tests because of their exposure to a more natural wind and atmospheric environment.

Chemical analysis of the water column in these tests also shows some interesting results. Oil concentrations in the water column of the untreated tanks never exceeded 0.8 ppm, and very rapidly would return to the control values. The general trend when dispersants are used is that the oil concentration approaches the control value after 72 hours at most levels in the tank. The chromatograms of these water column samples also support the evaporation results mentioned above, which show that very little of the lighter fractions (below C₁₂-C₁₄) remain in the water column.

The third spill of opportunity to which this team responded was the September 21, 1978 West Hackberry, Louisiana, incident.

During the recent West Hackberry #6 cavern decompression accident, an estimated 72,000 barrels of oil were released. Of this amount, an estimated 52,000 barrels of oil were recovered, and an estimated 20,000
barrels were burned or were unrecoverable from the diked area.

The University of Rhode Island (URI) project relating to the treatment of oil spills contains a task involving response to "spills of opportunity." Having participated in the Buzzards Bay and Argo Merchant incidents, the URI project team was easily assembled and rushed to the scene.

Upon arrival in West Hackberry, they were joined by Department of Energy (DOE) personnel and representatives from Dames & Moore (Houston Office) and the University of New Orleans. This incident presented an opportunity to put into practice some of the "contingency plans" developed by these groups.

The Department of Energy (DOE) organized the assemblage into an Environmental Assessment Team whose objectives are to:

- determine the geographical area covered by the DOE effluent
- assess the environmental impact caused by the DOE effluent

To meet these objectives, an Environmental Assessment Plan was drafted and presented to the Regional Response Team (RRT) which had convened in West Hackberry. The RRT reviewed and accepted the plan.

Having established its procedures and sampling requirements, the team collected more than 500 scientific samples. The sampling was conducted in affected as well as unaffected areas of water, marsh, and terrain. The samples were appropriately preserved, indexed, catalogued, and rank ordered into priority categories. The high priority samples were analyzed for the presence of oil, generally, and DOE oil, specifically.

Based upon the results of these analyses the team returned to West Hackberry at approximately 3, 6, and 12 months after the incident. The re-visits and selected re-sampling will assist in documenting the overall affect of the incident. The results of this investigation are reported in a separate report.

As part of the project for assessing the environmental impact of treated versus untreated oil spills, a fates model was developed which tracks the surface and subsurface oil. The approach used to spread, drift and evaporate the surface slick is similar to that in most other oil spill models. The subsurface technique, however, makes use of a modified particle-in-cell method which diffuses and advects individual oil-dispersant droplets representative of a large number of similar droplets. This scheme predicts the time dependent oil concentration distribution in the water column which can then be employed as impact to a fisheries population model to be discussed later. In addition to determining the fate of the untreated spill, the model also allows for chemical treatment and/or mechanical clean-up of the spilled oil. With this capability, the effectiveness of different oil spill control and removal strategies could be quantified.
The model was applied to simulate a 34,840 metric ton spill of a No. 2 type oil on Georges Bank. The concentration of oil in the water column and the surface slick trajectory were predicted as a function of time for chemically treated spills occurring in April and December. In each of these cases, the impact on the cod fishery was determined.

The important distinguishing feature between a wind driven surface slick and a chemically treated slick is that in the treated slick the oil enters the water column directly beneath the slick and is subject solely to local advective currents and diffusion. The wind driven surface slick can be beached in the intertidal zones, estuaries and marshes which are highly productive, while the treated oil remains in the water column. Various cases were studied in this modeling behavior and concentration profiles were calculated over a period of a thirty day simulation of a 34,840 metric ton oil spill at a time when the cod were at their spawning peak. Experimentally determined subsurface currents were used, as well as, average wind data collected for the area for the time of year the spill was assumed to occur. The analysis shows the divergence of the trajectories of the treated and untreated spills. The results of these simulations are presented in Section 5 of this report.

A fisheries-oil spill interaction model was developed to estimate first order effects of the impact of a treated versus an untreated oil spill on the commercial fish catch over ensuing years. The primary effect is assumed to occur through egg and larval mortality. The biological model formulated contains as subcomponents; a population model of the fishery, a model for advection and diffusion of oil, and fish larvae, and is coupled to the oil behavior and fates model described previously.

A two day 34,840 metric ton oil spill occurring on December 15 was simulated and a sensitivity analysis using the fisheries model was conducted. Impact predictions were conducted under three theoretically acceptable piecewise-smooth larval mortality curves, three threshold toxicity values of 1,000 and 50,000 parts per billion (ppb) and three application scenarios in which OX, 50%, and 100% of the oil is chemically treated.

Decreasing impact is associated with increasing larval resistance to oil toxicity (increasing threshold values), with decreasing entrainment and with increasing mortality modes (three different natural mortality modes were used). For a given treatment scenario and toxicity threshold, although the same number of eggs and larvae are lost from the system due to the spill, the effect of different natural mortality modes can show quite different results.

One of the most significant findings was that the natural mortality regime for the population was more important than either threshold toxicity values or the percent of oil dispersed in the water column. The importance of determining appropriate mortality regimes and threshold values is manifested from the results. The results indicate that if an oil spill was driven towards the islands of Nantucket and Martha's Vineyard rather than out to sea, dispersants would be used with little cost to the fishery, using a toxicity threshold as low as 100 ppb. The results do show, however, that the use of dispersants have a greater
effect on the cod than the untreated case. This is not surprising since making the oil more available to local marine biota is expected to increase mortality. The principal decision for using dispersants has to be made on the basis of whether or not their use will prevent more significant damage if the spill is allowed to come ashore and into highly productive intertidal zones and marshland where the oil can be expected to remain over an extended period of time. The other consideration is the time response of the ecosystem. Will the ecosystem recover more quickly to its prespill state than if the oil is left untreated?

The magnitude of the impacts estimated in this study range from 0% to 10% of the annual maximum sustainable yield of approximately 25,000 metric tons or up to $2.5 million in reduced income to the fishing fleet. Simulation of a 30 day oil well blowout shows impacts four times as large, so that the specific scenario is of considerable importance.

Another significant result of this simulated study is that even in the worst case, the expected mortality due to the spill is well within the limits of the observed natural variability of adult cod. This sheds some doubt on the use of an abundance of a particular species as a measure of the impact of a spill.

In Table I the results of this project are summarized. Inspection of this Table reveals that little evidence was found to support some common beliefs of the effects of the use of dispersants. For example, dispersants were expected to drive the lighter, more toxic components of the oil into the water column. In this study, it was found that this effect was insignificant. It was also expected that the use of dispersants would enhance biodegradation and it was found that the hydrocarbon degradation potential in nutrient limited seawater is a relatively constant value, independent of the presence or absence of oil in the water column. Expected results were that the use of dispersants increases mortality in the immediate vicinity of the spill but could mitigate a greater impact had it been allowed to reach the rich intertidal communities.

In summary, it appears viable to use dispersants as determined on a case by case basis. The case for using dispersants has to be based on whether or not their use will mitigate the environmental impact of the spill. In the case of an open ocean spill that is being driven into a rich inter-tidal community, the use of dispersants could greatly reduce the environmental impact. Even in the highly productive George's Bank area at the height of the cod spawning season, the impact of the use of dispersants is well within the limits of natural variability when the threshold toxicity level is assumed to be as low as 100 ppb, a level which is often found in the open ocean. Thus, it appears that dispersants can and should be used when it is evident that their use will mitigate the impact of the spill. Their use in areas where there is poor circulation and therefore little possibility of rapid dilution is more questionable and should be a subject of future studies.
### TABLE I.
Summary of the Characteristics of Treated versus Untreated Oil Spill.

<table>
<thead>
<tr>
<th>Untreated Spill</th>
<th>Treated Spill</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) The 'drifting' and spreading oil slick continually moves over new water.</td>
<td>1) Since treating agents disperse oil into the water column, the dispersed oil moves with the water column as a direct result of currents and diffusion.</td>
</tr>
<tr>
<td>2) Microbial Utilization.</td>
<td>2) Hydrocarbon degradation potential in nutrient limited seawater is a relatively constant value independent of the presence or absence of oil in the water column. There is a selection for hydrocarbonoclastic bacteria with time but their overall degradative activity as a mixed population is not significantly affected by the enrichment process.</td>
</tr>
<tr>
<td>3) Suspended sediment transport and sediment contamination.</td>
<td>3) There was no evidence for increased sustained sediment contamination when dispersants were used.</td>
</tr>
<tr>
<td>4) Evaporation.</td>
<td>4) Treating agents caused slight delays in evaporation when compared with the untreated spill; however, the difference was not significant.</td>
</tr>
<tr>
<td>5) Dissolution and emulsification.</td>
<td>5) The use of dispersants does increase the amount of oil in the water column.</td>
</tr>
<tr>
<td>6) Toxicity and Subacute toxicity.</td>
<td>6) The use of dispersants increases the availability of oil to marine organisms and results in higher mortality in the immediate vicinity of the spill. Predator-prey relationships can be altered in such a way that mortality can be much greater than expected from acute toxicity considerations.</td>
</tr>
<tr>
<td>7) Impact on selected species.</td>
<td>7) A sensitivity analysis of a 34,840 metric ton spill at the height of spawning season estimated that the maximum expected impact would be 10% of the annual fish catch, well within the expected natural variability of this particular species.</td>
</tr>
</tbody>
</table>
LIST OF PUBLICATIONS AND PAPERS PRESENTED
OF THE U.R.I. OIL SPILL RESEARCH TEAM

1. "The Spreading, Retention and Cleanup of Oil Spills," University of Rhode Island, HCP/P2756-01-UC-11, NTIS.

2. "Assessment of Treated Versus Untreated Oil Spills (Interim Report)" University of Rhode Island, June 1978, HCP/W4047-02, NTIS.


12. "What Are We Doing About Oil Spills?" M.P. Wilson, Jr., Maritimes, August 1976.


29. "Response of a Natural Population of Marine Heterotrophic Bacterial to a Crude Oil and a Dispersant," Paul J. Griffin, A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Microbiology.


32. "Lethal and Sublethal Effects of Short Term Acute doses of Kuwait Crude Oil and a Dispersant Corexit 9527 on Bay Scallops, Argopecten irradians (Lamarck) and two Predators at Different Temperatures." Submitted for publication March 1980 in Environmental Pollution.

1.0 Introduction, Background, and Program Description

Mason P. Wilson, Jr.
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1. **BACKGROUND**

In 1976, the U.S. Office of Technology Assessment presented an interim report on the coastal effects of offshore oil and gas development (1). One of the factors stated in this report of concern to coastal states, involves basic uncertainties about environmental and economic impacts. Studies estimate that the total probable oil spills from offshore continental shelf operations ranges from a low of 85,000 barrels to a high of one million barrels and that one out of ten spills from a drilling or production platform would reach a beach in New Jersey or Delaware. Present United States policy for combating oil spills is concentrated on physical containment with mechanical or sorbent removal techniques. When these means fail, the uncontrolled, untreated spill can cause considerable damage to the marine environment, especially to birds, saltwater marshes and beaches, where marine life is most plentiful, and where the juvenile forms of many commercial fish have their origin. It is these juvenile forms that appear most susceptible to oil pollution. The use of treating agents for final clean-up and for preventing the spills from reaching the shore and mitigating the environmental impact, when mechanical means fail, has been minimal because of the lack of information concerning the use of these agents and their affect on the environment. Since the Torrey Canyon spill in 1969 off the coast of England, where dispersant use produced disastrous results, there has been considerable development of treating agents that are far less toxic than those available at that time. Furthermore, it has since been determined that it was not the dispersants that caused the extensive damage in this spill, but rather the toxic solvents in which the dispersants were dissolved. New dispersants either use non-toxic solvents or sea water for their solvent base.

The debate over whether to use dispersants to treat oil spills has been long and controversial. The truth about dispersants, their use and effectiveness has often been obscured by undocumented and, at times, emotional opinions. Certainly, the excessive use and unfortunate experience with dispersants on the Torrey Canyon spill serves to form the basis for most of the criticism. Additional criticism concerning the use of dispersants is grounded on the belief that even if the dispersants themselves were not toxic, the use of these agents make the oil more toxic by its increased dispersion within the environment (2). This viewpoint, however, is applicable only to the immediate vicinity of the spill. The principal question to be answered in the use of a dispersant, is, "will its use cause less environmental damage, even though there is increased toxicity in the vicinity of the spill, than the untreated spill?" Furthermore, will the environment recover more quickly when dispersants are used than the long term effects of an untreated spill such as reported by Blumer (3). These are extremely difficult questions to answer. However, one use of dispersants is based on the premise that if treated at sea, most of the damage in the intertidal zone and salt water marshes where there is a concentration of marine life, could be mitigated. It is well known that marine life is concentrated in three major areas: (a) the surface, (b) the benthic zone, and (c) the inter-tidal zone. It is these three major areas that
the uncontained, poorly dispersed oil spill is concentrated (4), whereas, the majority of oil in the chemically treated spill is concentrated in the water column where it is more easily diluted by tidal flushes and where there is less concentration of marine life. The affect of oil on the marine environment has long been a concern to the environmentalists and oil companies alike. The severity of biological damage depends on many factors, some of the major ones are: the type of oil spilled, the dose of oil, the physiography of the area, weather conditions, type of local biota, season, previous exposure of the area to oil and other pollutants and the treatment of the spill. Three conditions are especially critical, and some researchers claim that all three must exist simultaneously for a spill to have significant environmental damage. The conditions are:

(1) The volume of oil spilled must be large with respect to the body of water being impacted.

(2) The oil should be refined.

(3) Storms or heavy surf must cause the spilled oil to be churned into bottom sediments (5).

Whether or not these conditions occur, some part of marine life is likely to be affected by an oil spill. Studies from more than one hundred major oil spills over a twelve year period indicate that birds are the type of marine life most often affected (6).

The use of dispersants to mitigate the impact of oil spills have been used almost exclusively in the United Kingdom where it appears to have had minimal impact on the environment. Caution should be exercised in transferring the United Kingdom results to the use of dispersants along the United States coastline. Britain has very high tides, especially in the Milford Haven area in Wales where dispersants have been extensively used. The tides in this area range from twenty-four to twenty-eight feet. An example of the use of dispersants to prevent oil from reaching the beach and inter-tidal zone is their use in the Christos Bitos incident (7).

The variability of sea conditions, as well as the size of a spill are two of the major factors which often inhibit the containment and recovery of spilt oil. If about 2000 barrels (84,000 gallons) of Bunker C oil were spilt on a calm sea on a windless day, and if no action is taken for about three hours, the circumference of the spill would be approximately 6300 feet. Consequently, this size of a spill would make deployment of sufficient oil booms a rather formidable task. Their use, in many cases, has not prevented oil from reaching biologically sensitive areas.

1.2 DISPERSANTS

Dispersants specifically designed for use on oil spills are relatively new and most of these have been developed since the time of the Torrey Canyon in 1969. They are found under various names - dispersants, emulsifiers, detergents and degreasers, however, those specifically designed to combat oil spills are normally referred to as dispersants. Dispersants are compounds which emulsify, disperse or solubilize oil into
the water column or act to further the spreading of oil slicks to facilitate dispersal of oil into the water column. They consist of three primary components: surfactants, solvents and stabilizers. Surfactants decrease the interfacial tension between the oil and water, thus allowing the oil to more easily spread and be dispersed into small globules. Surfactant molecules are composed of hydrophilic (water compatible) and lipophilic (oil compatible) groups. They can be divided as to being either anionic, cationic or non-ionic. The anionic surfactants compose the largest group in use since the anion is quite surface active. Usually these dispersants are alkalai salts of sulphates or sulphonates. Cationic surfactants have a low surface activity as do the non-ionic ones. However, the non-ionic ones have been found to be the most effective for dispersants for salt water oil spills, being composed of fatty alcohol condensates, ethylene oxide being the most common.

The second primary component of a dispersant, the solvent, comprises the bulk of the product. The solvents enable the active agent (surfactant) to mix and penetrate into the oil to form an emulsion. The solvents range in base from petroleum to water, petroleum solvents being the most toxic, but the ones which dissipate most rapidly in a water environment.

A certain amount of mechanical mixing energy is generally required to get the dispersant oil mixture into the water column. Early in their use, helicopters, tugboats or other large powerful ships were used in an effort to cause dispersion. In the United Kingdom, the use of batter boards towed behind boats have proved effective. Obviously in high sea conditions, the mixing energy is no problem. Under such high sea conditions, dispersants have been found to be very effective. There are also self-mixing dispersants available. A self-mix dispersant utilizes the diffusion energy of the surfactant, acting at the oil-water interface.

1.3 PROGRAM INTRODUCTION

The results of this program describe an approach to estimate the environmental impact of an untreated oil spill versus a spill treated with dispersant. It is holistic, in that it combines the physical, chemical, microbial and macro-fauna responses to a spill. The results reported herein represent the findings of a four year effort that integrates mathematical, laboratory, meso-scale in-situ experiments and analyses. The in-situ analyses came as a result of responding to three spills of opportunity. These are the Argo Merchant which grounded on the Nantucket Shoals in December 1976, the Bouchard spill that occurred near the entrance of the Cape Cod Canal in ice-choked Buzzard's Bay in late January 1977 and the fire/oil spill that occurred at the Strategic Petroleum Reserve facility at West Hackberry, Louisiana on September 21, 1978. The investigation of this latter incident was supported under separate contract with the Department of Energy and a final report is being issued.

Many models and investigations have been conducted in the past concerning the environmental impact of spills, but none presently available encompasses the breadth and depth required to make a decision as to whether or not dispersants should be used. This program has been designed to provide some guidance in this direction. In spite of this,
there are still many unanswered questions concerning the impact of an oil spill on the environment. The fate and effects of an oil spill, whether treated with dispersants or not, depends on many complicated factors. First, the chemical composition of any oil is extremely complicated and they are composed of many different aromatic, aliphatic and alicyclic compounds (9). Even among the crude oils, the physical properties and chemical composition can vary greatly, and consequently, any refining of these crudes produces even more diverse properties. Since there is such diversity, it is difficult if not impossible to make anything but general statements concerning the effects of oils on specific marine biota. Secondly, because of our lack of understanding of the environment, specifically cause and effect relationships, predator-prey relationships, etc., one can only make some isolated estimates of impacts on specific species. Even this is difficult because the organisms in a real spill are exposed to time-varying concentrations and varying chemical composition caused by natural weathering of the oil which includes evaporation, dissolution, etc., while available toxicity data seldom include these effects.

The approach in this program has been to attempt to mimic the natural weathering and entrainment processes and to expose the organisms to varying concentrations from lethal to minimal sublethal dosages and to study predator-prey relationships under these conditions.

1.4 PROGRAM DESCRIPTION

As mentioned in the above paragraphs, the problem of assessing the impact of an oil spill on the marine environment is a formidable task at best, especially if the objective is to assess both short and long range impacts. Damage assessment such as clean-up costs, losses to business, etc., are much easier to assess after the fact and certainly much more tangible than those associated with losses in fish catch, etc. In the latter type of assessment, a holistic and implicit approach is mandatory. This type of approach requires a determination of the temporal and spatial history of the spill, coupled with the physical, chemical and biological processes that affect the nature of the spill as shown in Figure 1.1. Some of the input that must be considered in this type approach is shown in Figure 1.2 which is a simple version of the decision making process to treat or not to treat a spill. The most important aspect of this procedure is the realization of the strong interdependency of all of the processes. Microbial utilization is both a function of the chemistry and spatial distribution of the oil and other nutrients, whereas the spatial and temporal distribution is a function of wind wave activity, currents etc., and the physical and chemical properties of the oil. The impact of a spill on marine organisms is also a function of the chemical, temporal and spatial distribution of the oil. The traditional bioassay work based on LC50 on 48, 72 or 96 hour tests are of limited value because the tests are static and seldom are these organisms exposed to constant concentrations in the real environment with the exception of some spills in marshes and beaches. Some knowledge of the lethal concentrations as a function of time, together with the temporal and spatial distributions of both the oil and organisms, permits a first order assessment of the number of organisms destroyed as a direct result of the spill. Of secondary importance is the cumulative effect of varying concentrations on the organisms with time as well as sub-acute effects on
WIND

WIND-WAVE-SLICK
INTERACTION

BREAKING WAVES

EVAPORATION
PHOTO-OXIDATION

SPREADING &
DRIFTING

EMULSIFICATION
OF WATER IN OIL

PHYSICAL & CHEMICAL
EMULSIFICATION OF OIL,
IN WATER

DIFFERENTIAL
MOVEMENT OF
OIL AND WATER

CONCENTRATION PROFILE
OF DISPERSED OIL

INGESTION BY
MARINE ORGANISMS

MICROBIAL
DEGRADATION

SUSPENDED SEDIMENT
TRANSPORT

PLANKTON ABSORPTION &
TRANSPORT

ASSIMILATION &
DEGRADATION OF BENTHIC
ORGANISMS

SEDIMENT ENTRAINMENT

INPUTS

CHEMICAL, NATURE
OF SPILL

CIRCULATION
OCEAN CURRENTS,
FRICTION, TURBULENCE, ETC.,
IN VICINITY OF SPILL

WAVE-WIND
CHARACTERISTICS
IN VICINITY OF SPILL

CONCENTRATION
OF SUSPENDED OIL
IN VICINITY OF SPILL

DISTRIBUTION
OF HYDROCARBONS
ON SURFACE, IN WATER COLUMN,
AND BENTHIC ZONE AS FUNCTION
OF TIME, SPACE, AND CONCENTRATION

ESTIMATE OF:

1. BIRD KILL
2. PHYTOPLANKTON KILL
3. OYSTER KILL AND CONTAMINATION
4. BEACH DAMAGE
5. HAZARDS TO HUMANS
6. OTHER

SCORE

WEIGHTING
FACTOR

TOXICITY AND EFFECT
OF OIL HYDROCARBONS
ON MARINE ENVIRONMENT

DISTRIBUTION OF BIOA, WATERFOWL, ETC.,
IN VICINITY OF SPILL

TREATED SPILL

UNTREATED SPILL

DISTRIBUTION OF MARINE
BIOA, WATERFOWL, ETC.,
IN VICINITY OF SPILL

ESTIMATE OF:

1. BIRD KILL
2. PHYTOPLANKTON KILL
3. OYSTER KILL AND CONTAMINATION
4. BEACH DAMAGE
5. HAZARDS TO HUMANS
6. OTHER

SCORE

WEIGHTING
FACTOR

TOTAL

DETONATION

DISTRIBUTION OF MARINE
BIOA, WATERFOWL, ETC.,
IN VICINITY OF SPILL
behavior and reproduction.

The program was divided into three major but integrated groups, one to study entrainment and evaporation processes, a biological group including microbiology to study the effects of treated oil versus untreated oil on selected marine organisms and oil degradation rates and a third group to provide the chemical analysis. Laboratory type tests were conducted by each group to study some of the fundamental processes, however, all groups participated in the combined tests conducted in the meso-scale facilities as described in the next section. Spills of opportunity provided experimental data to correlate with meso-tank results.

1.4.1 MESO-SCALE TEST FACILITIES

The meso-scale test facility is composed of three twenty-foot high by three feet in diameter fiber glass tanks as shown in Figure 1.3. A schematic of the tank is shown in Figure 1.4. The facility is located adjacent to Narragansett Bay. Salt water is pumped either into the top or bottom in batch operations or in a continuous flow mode. The tanks are wrapped with a coil for fresh water closed cycle cooling and insulated by three inches of polyurethane foam. This type of cooling was chosen because it was capable of providing a uniform temperature distribution of the tank, void of any cold or hot spots. The heat sink for the closed cycle cooling system is a coil submerged in Narragansett Bay. This system is capable of maintaining the water in the tanks to within 10°F of the Bay temperature. Thus, temperature stresses on marine organisms in the tank were minimized. The cooling coils were made in three sections to allow them to be operated in a series or parallel mode. Using this approach, virtually any temperature distribution could be achieved from a stratified layer to a uniform distribution.

Mixing in the tank was provided by submerged oscillating annular disks as shown in Figure 1.4. The amplitude as well as the frequency is adjustable, making it possible to obtain a wide variety of mixing conditions in the tank. Generally it was adjusted so as to provide mixing in only the upper ten feet of the tank. This roughly corresponds to the subsurface circulation caused by an ocean wave having a wavelength of thirty feet.

Bottom dwellers such as scallops were lowered in a basket to prescribed depths before the surface was oiled. To prevent contamination of the scallops when retrieving the basket, a cylindrical section of teflon approximately a foot in height was installed at the water/oil - air interface. When samples were to be retrieved, the teflon section was collapsed across the surface thereby sweeping the oil to one side of the tank, leaving a clean surface through which the samples could be collected.

Water column samples were collected from taps located every twenty-four inches along the length of the tank.
FRESH WATER CLOSED CYCLE COOLING (submerged heat rejection coil in bay)

BOTTOM DRAIN TO HOLDING TANK

MIXER

SAMPLING PORTS

FIGURE 1.4: MESO-SCALE TANKS
1.4.2 ENTRAINMENT, DISSOLUTION AND EVAPORATION STUDIES

One of the primary goals of the program was to determine the temporal and spatial distribution of the treated and untreated oil, hence a comparison of the toxicity and impact under both sets of conditions. Much work has been done in the drifting and spreading of the oil but only limited amount of predictive information is available for entrainment of the oil into the water column and sediment.

In an attempt to gain a better understanding of the combined evaporation, dissolution and overall entrainment process, a series of experiments was designed. These ranged from basic measurements of interfacial tension to combined wind/wave experiments. These experiments and their role in the overall program are described as follows and the section of the report in which they are covered is identified.

INTERFACIAL TENSION

Since entrainment is primarily caused by work done against interfacial tension, a knowledge of the effect that the dispersant has in this property is fundamental to any of the entrainment processes. A series of different types of approaches to measure this property was considered.

The capillary-height method is probably the simplest method available. When a capillary is inserted below the interface of a two liquid system, due to the excess free energy of the interface, the liquid in the lower layer rises to a higher level within the capillary. But for the crude oil water system under study, this method could not be used as the darker upper layer of the crude prevents observations of the capillary height.

In the drop weight method, drops are allowed to form at the top of a capillary immersed in another liquid. From a knowledge of the dimensions of the drop and its weight, it is possible to calculate the interfacial tension. Since drops have to be formed at a finite site, this method is not applicable in systems where a surfactant is present.

The ring method consists of a platinum ring which is pulled up from the interface of the liquids whose interfacial tension is to be measured. The force that is necessary is measured by a torsion balance. Because of problems encountered in obtaining repeatable results in using this method as well as the reasons stated above in the drop weight method, it was decided to investigate other methods.

The bubble pressure method measures the pressure difference across a bubble or drop in another liquid which is proportional to the interfacial tension. Since this is a dynamic method and is difficult to obtain accurate results, it was decided to use the following method.

The pendant drop method is the one chosen to measure the interfacial tension. It consists of making a drop form at the tip of a capillary tube and "letting" it hang in the second fluid. If the density difference is not appropriate, the drop can be made to rise up from the tip of the capillary rather than let it hang. The shape of the drop reflects a balance between interfacial tension and the gravitational forces and can
be used to measure the interfacial tension. The static nature of the method makes it suitable for use where diffusional effects are involved. This method and the results are fully described in Section 12.1.2 of this report.

**DROP SIZE DISTRIBUTION, COALESCENCE AND STABILITY OF THE OIL-IN-WATER EMULSION.**

Of primary concern is the effect that dispersants have on the formation of stable oil-in-water emulsions and the drop size distribution. The drop size distribution, although not a direct measure of stability, is indicative of the type of emulsion formed and can be used in interpreting the results of other experiments. To measure the mixing energy and drop size distribution, a standard impeller technique was chosen. Total concentration of hydrocarbons in the water column was taken by extracting the water samples with carbon tetrachloride and measured by infra-red spectroscopy. The drop size distribution was measured photographically. Stability and coalescence was determined by measuring the concentration of oil in the water column as a function of time following formation of the emulsion. The complete description of this process and the results are given in Section 2 of this report. Stability of the emulsion was also investigated in Sections 3 and 4 of this report by measuring its settling or creaming rate.

**ENTRAINMENT PROCESSES: THE WIND/WAVE EXPERIMENT, THE RAINDROP EXPERIMENT, EVAPORATION AND STABILITY**

The real world entrainment process of oil and treated-oil slicks is extremely complicated, and is probably one of the most least understood of the processes that have a major effect on the fate of an oil spill. The complex wind/wave interaction, wave dynamics and currents in the ocean will effect the rate of entrainment and stability of the oil-in-water-emulsion. The addition of a dispersant enhances entrainment processes, but also relies either on mechanical or chemical forces or a combination of both to incorporate the oil into the water column. Furthermore, addition of a dispersant increases the oil slicks spreading properties, thus making the slick thinner and more easily dispersed. For the most part, this project has been concerned with oil and water emulsions and has not concentrated efforts on the formation of water-in-oil emulsions such as "chocolate mousse."

The stability of the oil-in-water suspension (or emulsion) depends on many factors such as the degree of subsurface mixing, the concentration of the oil, the size distribution of the oil droplets, the concentration of plankton, the concentration and type of suspended sediments, etc. Mousse, on the other hand, is a water-in-oil suspension (emulsion) and is generally thought to be much more stable than oil-in-water suspensions. To understand the differences as well as the similarities of these processes, they are discussed in some detail in the following paragraphs.

The important factor that links oil-in-water and water-in-oil emulsions is the type of emulsifying agent that may be found in sea water and naturally occurring in the crude oil, as compared to manufactured oil emulsifiers. The physics of formation of oil-in-water emulsion is the same as the formation of water-in-oil emulsions. Whether one or the
other is formed depends on the type of emulsifying agent present during
the process. It is well known that soaps of univalent metals give rise
to oil-in-water emulsions, while multivalent metals favor water-in-oil
emulsions (10). Whether or not this is the case with respect to crude
oil in sea water is yet to be proven. However, Kuwait crude which is
well known to easily form "chocolate mousse" also has a higher concen-
tration of organic-multivalent hydrocarbons than most other crudes. As
previously stated, the water-in-oil emulsion was not studied in this
program, however it was observed in some of the experiments, especially
the wind/wave experiment reported in Section 3 of this report.

Suspended sediments can play a role in the emulsification process.
It can be easily explained in the following manner (11,12) and involves
the interfacial tension between the solid and water, the water and oil,
and between the solid and oil. If the surface tension between the solid
and oil is greater than the sum of the surface tensions between the water
and oil and solid and water, the solid will remain suspended in the aque-
ous phase. If the surface tension between the solid and water is greater
than the sum of the surface tension between the water and oil and solid
and oil, the solid will remain in the oil. If the surface tension
between the oil and water is greater than the sum of the surface tension
of the solid and water and solid and oil, the solid will concentrate on
the boundary.

It is known that clay sediments tend to incorporate oil into the
water column. Conversely, fine grain sand is generally found in tar
balls.

Physical entrainment and stability of the oil-in-water suspension was
studied both from an experimental as well as an analytical viewpoint and
is discussed in some detail in Section 4 of this report. The
"entrainable" particles depend, for most of the systems studied, on par-
ticle size distribution and subsurface circulation. Except for the case
when there exists a chemical stabilizing agent in the dispersant, the oil
droplets, generally having a density less than water, and tend to rise to
the surface. Hence, most oil-in-water suspensions are basically unstable
and require some degree of agitation or circulation to maintain them in
suspension. In the natural environment, quite often the circulation
beneath waves, etc., is sufficient to maintain the fine droplets in sus-
pension as with the case in most of the experiments conducted in this
report. Subsurface circulation was studied analytically and the results
of this study are presented in Section 4 of this report.

The wind/wave experiment was designed to study the effects of waves,
and wind blown waves on the entrainment of oil droplets. One of the con-
ditions for the experiment was to allow the action of waves and wind to
occur over a sufficient period of time to allow the natural weathering of
oil to take place. Initially, it was conceived to produce waves and an
air flow in an annular type of wind tunnel. A small scale experiment was
designed and conducted. The major problem encountered during the initial
test was that oil collected on the inner wall due to circulation in the
tank and wind activity. It was, therefore, decided to use a cylindrical
tank as described in Section 3. of this report. The particular arrange-
ment chosen allowed the surface slick to undergo wind/wave action for
indefinite periods of time without contacting the walls of the container. It consisted of a tank eight feet in diameter and approximately four feet in height, having the same capacity as the meso-scale tanks previously mentioned. A doughnut shaped wave maker oscillating vertically produced the radially inward moving surface waves. Its frequency and amplitude could be varied so that different wave heights and wave lengths could be achieved. Air flow was provided by an exhaust hood placed over the tank. Subsurface water samples could be collected in similar fashion as in the meso-scale tanks. Radial traverses of oil concentration were also conducted utilizing glass rods inserted through the sampling ports. The results of these tests and a complete description of the experiment are given in Section 3 of this report.

Another entrainment process investigated was the study of entrainment caused by the penetration of an oil slick by water droplets. These droplets can be formed by breaking waves or be due to rain. A description and the results of this experiment are given in Section 4 of this report.

Evaporation from oil slicks is part of the natural weathering process. It is also a fractionation process since the lighter, more volatile components evaporate most readily. Evaporation rates as well as definition of the components are reported in two sections of this report, Section 7 and Section 12.4

1.4.3 OIL SPILL TREATMENT STRATEGY

This particular portion of the project was to use an oil spill fates model as a tool to analyze the effect of various treatment strategies on the fate of a simulated spill. The location of the spill was chosen at the center of the Cod spawning region of Georges Bank and at a time, mid-winter, to affect a maximum impact on the Cod fishery. The output of the model resulting from these simulations was used as input to a fisheries model and is discussed in detail in Section 6 of this report. The oil spill fates model and treatment strategy is presented in Section 5 of this report. The fates model was basically used as a method to show the difference between the spreading characteristics of a surface spill and the diffusional subsurface current driven treated spill, as well as to estimate the concentration distribution of each. The fate model includes most naturally occurring processes as well as the effects of clean-up, removal and dispersion actions and could be used in "real" time to aid the On-Scene-Commander (OSC) in control and clean-up of a spill.

1.4.4 FISHERY-OIL SPILL INTERACTION MODEL

An oil spill-fisheries impact model was developed to obtain an order of magnitude estimate of the impact of a treated versus untreated oil spill. To what extent oil spills at sea affect the commercial catch over the ensuing years and under what circumstances, if any, treatment with a dispersant will mitigate the effect, are addressed in this research. The model estimates first order, direct effects of an oil spill on a commercially fished population. The primary effect is assumed to occur through egg and larval mortality. The biological impacts model formulated contains as subcomponents a population model of the fishery, a model for advection and diffusion of oil and fish larvae which is coupled to the oil spill behavior and fates model described in the previous section.
The model was used to simulate nine variations of an oil spill scenario on Georges Bank, producing a rough sensitivity analysis of system response. Following an overview of the model system, the results and implications of these simulations are discussed along with limitations of the approach used. It is suggested that the most significant unknowns in the system are the parameters governing recruitment dynamics in the fishery, toxicity threshold values and oil entrainment rates being of secondary importance in open ocean conditions.

1.4.5 CHEMICAL ANALYSIS

The overall objective of the project was to address the environmental impact of chemically treated vs. untreated oil spills. The primary objective of the chemistry group was to determine the amount and compositions of petroleum chemicals in the atmosphere, surface waters, water column and sediments resulting from a treated and untreated spill. To meet with this objective it was necessary to develop sample collecting, extraction and chemical analysis methods. In addition, extensive development and testing computer software was required to collect and massage the analytical data. Laboratory experiments were designed and executed to aid in the development of these analytical techniques. Results from the laboratory studies determined the techniques which would be applied to the analysis of the meso-scale experiment and eventually to any "real world" spills of opportunity. The major portion of the chemical analysis is reported in Section 2 of this report. Other chemical analysis techniques developed for quantitatively distinguishing the dispersant from Kuwait Crude by both infra-red and gas chromatography techniques are reported in Section 8 and 12.2.

1.4.6. MICROBIAL DEGRADATION

The study of microbial degradation of hydrocarbons was deemed an important area of investigation. Since the use of dispersants greatly increases the surface area of the oil, making it more susceptible to biological degradation and hence, an important question to answer if dispersants are to be used. The hydrocarbon degradation potential of ocean environments has not been adequately defined, however, it is known to be influenced by such factors as the number and types of hydrocarbon degrading microorganisms, the degree of oil dispersion, temperature and nutrient availability. Hydrocarbon degradation rates measured in the laboratory have been misleading since they were found to be considerably higher than in situ rates. Consequently, microbial utilization of the hydrocarbons was measured in the meso-scale tanks which most closely approach the real environment. A series of other tests was conducted in the laboratory to gain a better understanding of the process. The details of the experiments and results are reported in Section 8 of this report.

1.4.7 BIOLOGICAL INVESTIGATIONS

This portion of the investigation was to study the effects of realistic concentrations of oil and oil-dispersant mixtures on marine life. The impact of a spill on marine organisms is a function of the chemical, temporal and spatial distribution of the oil. The traditional bioassay work, based on LC50 on 48, 72 or 96 hour tests are of limited value in estimating the impact of a spill, because they are static and seldom are
these organisms exposed to a constant concentration in the real environment, with the exception of some spills in marshes and beaches. Furthermore, most of these tests are conducted with unweathered oil, thereby exposing these organisms to the more volatile and toxic components. The approach in this study was to determine lethal concentrations as a function of exposure time. Knowing the temporal and spatial distribution of both the oil and organisms allows a first order assessment of the number of organisms destroyed as a direct impact of the untreated or treated oil spill. It was also recognized that other important parameters that could affect the impact of a spill depended on predator-prey relationships that could cause mortality even when the organism survives the spill. The experiments and results are given in Section 9 of this report.

REFERENCES


2.0 Effect of Chemical Dispersants on the Stability of Oil Water Emulsions

Mathew Cherian
Thomas J. Kim
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4. Interfacial Tension with Corexit 9527 in Oil and in Water
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6. Concentration of Corexit in Water by Volume
Nomenclature

**A** - Interfacial Area

**d** - diameter of the drop

**D** - diameter of the impeller

**Fr** - Froude Number

**g_c** - acceleration due to gravity

**g** - gravitational constant

**N** - number of the revolutions of the impeller per minute

**n** - number of drops of diameter d

**O** - Order of magnitude

**P** - rate of power input

**Po** - Power number

**Re** - Reynolds Number

**v** - velocity of the drop

**α** and **β** - phases α and β

**ε** - error in measurement of any quantity

**Φ** - hold-up

**μ** - Viscosity

**σ** - Interfacial Tension

Subscripts

**AM** - arithmetic mean

**SM** - Sauter Mean

**i** - component i
2.1 Introduction

In recent years oil spills on the high seas and inland waterways have been given increased attention because of their adverse ecological and environmental effects. It is estimated that over sixty percent of crude oil consumed all over the world is transported over water. In view of this enormous volume of oil conveyed over the seas and inland waterways, chances of oil spills are great indeed.

Retention and cleanup of oil has met with limited success so far. Mechanical methods are cumbersome and transportation of the equipment is difficult, slow and expensive. On the other hand dispersants and surface-active agents are easier to transport and use, and have met with success in Europe. There has been considerable controversy regarding the use of dispersants to break up oil spills. It has been known that chemical dispersing agents, which are surface active agents, often do more damage than the oil which they tend to disperse (44).

The effectiveness and practicality of chemical dispersants have been seriously questioned since their initial use. In support of this, two well-known incidents are cited often - the Torrey Canyon and the Santa Barbara spills. In both cases substantial quantities of dispersants were used. In both instances there was extensive contamination of the environment.

Unlike mechanical methods which seek to isolate and remove oil from the water surface, dispersants break up the oil into tiny droplets. Oil in this condition is considered to be amenable to biodegradation (18).

Biodegradation of oil is a rate process and depends upon interfacial area and time. For biodegradation it is desirable that we have the smallest droplets possible and have them stay in the water column for the longest duration of time. It is here that the stability of the dispersion becomes important. Stability of the dispersion can be defined as a fraction of the hold-up or interfacial area. (Hold-up can be defined as the fraction of the dispersed phase in the continuous phase.) Since interfacial area is a function of hold-up, interfacial area alone can be thought to be a criteria for stability of the emulsion.

It is the intention of this investigation to evaluate the effectiveness of dispersants in distributing and stabilizing crude oil in the water column.

2.2 Literature Survey

Previous work on the dispersants to break up oil into small droplets is of relatively recent origin. In a recent investigation Jasper, Kim and Wilson (42) studied the effect of dispersants in breaking up a crude oil into fine droplets. They used two dispersants, a self-mixing type and a conventional one. The conventional dispersant is a surface active agent which merely reduces the interfacial tension. The new generation
'self-mix' dispersant on the other hand is expected to produce spontaneous emulsification. This type of surfactant is predominantly soluble in the oil-phase. When the oil comes into contact with water, that part of the surfactant that has a strong affinity for water tends to diffuse to it. During this process it carries droplets of oil into the water phase. The self-mix type and the conventional dispersant were found to perform differently, with the self-mixing type creating a better dispersion. The study revealed that the self-mix type dispersed oil more efficiently as the rate of energy input decreased. Further it was found that a finer dispersion was possible using a self-mix dispersant. The study by Jasper et al also showed that there was minimal increase in hold-up with increase in power input.

In the past, investigations in this area have been conducted with an entirely different goal in view. In liquid-liquid extraction operations two immiscible phases are brought into intimate contact, and when equilibrium has been achieved, allowed to separate in a settler. Here, instability of the dispersion and not stability is the consideration. There is yet another striking difference between traditional extraction operations and the situation encountered in an oil spill. In extraction operations the hold-up is of the order of 10 to 50 percent. In the present investigation the hold-up is of the order of parts per million. However, since coalescence and break up of droplets are basic to both situations they will be considered in this survey.

The earliest investigation on the coalescence of droplets concerned the behaviour of a single droplet resting on a plane liquid surface. This is conceivably the simplest possible situation. Reynolds (1) began the study of coalescence by observing the behaviour of a rain drop resting momentarily on the surface of a pond. The findings were rather qualitative in nature. This observation was followed by Smoluchowski (2) who analyzed the rate of coalescence of droplets in dispersions and developed an idealized model for the rate of coalescence of droplets. Apart from the above two studies there had been no significant contributions in this field until the second half of this century.

The latter half of the twentieth century saw a burst of research activity in the field of coalescence. It should be noted that the bulk of research in this area has been confined to coalescence of single drops. This is understandable because all factors involved in the coalescence of single droplets should be identified and their significance estimated before coalescence of swarms of droplets can be studied. Thus all workers found that the time interval of the arrival of a drop at the interface and its disappearance into its parent phase is not constant; but there is a distribution of times - the distribution being approximately Gaussian. Further all researchers agreed that the coalescence process includes five consecutive stages. These are

(i) the approach of the drop to the interface, resulting in the deformation of both the drop and the bulk phase
(ii) damped oscillation of the drop at the interface
(iii) the formation of a film of the continuous phase between the drop and its bulk phase
(iv) drainage of the film, its rupture and removal with the initiation of the coalescence process proper and
(v) transfer of the contents of the drops partially or wholly into its bulk phase. Most workers assumed (without much evidence) that stages (i) and (ii) took place immeasurably fast so that the time of coalescence was the time taken for stages (iii), (iv), and (v) during which the drop rested on the thinning film at the interface. Some workers called this the rest time.

As has been stated above, for drops of the same size and physical properties coalescing under identical conditions there is a spread of coalescence times. This suggests that a large number of experiments had to be carried out in order to get the distribution. Gillispie and Rideal (3) found that about 100-200 drops had to be observed to get reproducible results whereas Jeffreys and Hawksley (4) using more refined apparatus found that it was necessary to study only 70-100 drops to get reproducible results. Working with drops stabilized with surfactants, Cockbain and McRoberts (5) were able to obtain reproducible distribution curves using only 30 drops. In the study of coalescence time, researchers have defined two means, namely the arithmetic mean of the time of coalescence (of identical drops of course) and half rest time which is the time taken for half the drops to coalesce. Generally half rest time has been found to be more reproducible than the arithmetic mean and the ratio of the arithmetic mean to the half rest time has been found to be greater than one (in the range of 1.01 to 1.27.)

A drop residing at the interface may coalesce completely or it may coalesce partially, producing a smaller drop which will ultimately behave in a manner similar to the parent drop. That is, it will coalesce producing a smaller drop and the process may continue for as many as six or seven times. This phenomenon is known as stepwise coalescence. It was first observed by Wark and Cox (6) during froth flotation experiments and a little later by Mahagar (7) during experiments at the air-liquid interface.

The coalescence of a single droplet at a plane interface is accomplished through the drainage and rupture of the film of the continuous phase. Therefore the factors that most affect drainage and rupture, control the coalescence process. These factors have been tabulated by Lawson (8).

Nearly all workers studying coalescence agree that coalescence time increases with drop size. A larger drop tends to flatten into an oblate spheroid when resting on the interface so that the film between the drop and the interface is increased in size and thereby the drainage time is increased also. Moreover, interfacial area between a larger drop and the interface is larger for the large drop so that the resistance to drainage is larger and the coalescence time is greater. It should be pointed out that Lang (9) found by theoretical analysis that the thickness of the film at the instant of rupture is independent of drop size. Neilsen, Wall and Adams (10) found that for some three component systems the stability of the drop increased with increased size. This would clearly depend on the nature of the third component. A diffusing solute would increase or decrease the stability of the drop depending on the direction of mass transfer.
A number of investigators have found that the settling distance through which the drop traverses affects the coalescence time. Nielsen (10) reported that the coalescence time was independent of the distance through which the drop traverses, while Lang (9) suggested that the distance of fall (or rise) could either increase or decrease the stability of the drop depending on the mechanical disturbances produced. However, Lawson (8), Hawksley (11), and Jeffreys and Hawksley (4) have shown that the stability of the drop increases with increase in the distance of fall. It is widely accepted that the coalescence time is proportional to the distance that a drop traverses raised to an exponent n. The exponent n increases with drop size but is independent of temperature. It is only the first step of coalescence that is affected by the distance that the drop traverses although many workers have reported that the distance of fall also affects the other steps to a large extent. There are several explanations to the above mentioned observations:

(i) The drop may acquire an electrostatic charge during passage through the continuous phase. The extent of this charge increases with the distance of descent, thereby offering a greater resistance to the drainage of the film. This seems to be a perfectly logical explanation. However, McDonald (12) found no pronounced effect of electrostatic charge except on very large drops.

(ii) Drops passing through the continuous phase collect small quantities of surfactants which tend to increase the stability of the drops. The greater the distance travelled, the greater the amount of surfactant collected. It should be pointed out that if this were the case, reproducible results would never have been possible by using different batches of the same chemical. As different batches, however carefully controlled in production, contain minute quantities of surfactants in varying degrees.

(iii) The variation could also be produced by the drop "bouncing" after striking the interface, with the result that rippling of the interface prevents the film between the drop and the interface from draining. However, Hawksley (11) showed that the terminal velocity of most of the drops is attained within fifteen to twenty drop diameters. Since the mean coalescence time continues to increase when the critical distance has been exceeded, this could not be a good explanation.

Curvature of the interface between the drop and the coalesced phase was found to have an effect on the stability of the drops. Nielsen (10) has shown that the stability of the drop increased when the curvature of the coalesced drop phase was concave to the drop. This could be expected because drainage of the film is thereby promoted.

Density difference between the two phases is another factor that seems to have some bearing upon the coalescence rate. Large density differences result in severe deformation of the drop. The drop tends to flatten so that the area of drainage of the film is increased, whereas the hydrostatic force causing drainage does not increase proportionately. These two opposing tendencies tend to cancel each other. In fact, many workers have claimed that the rest time increases with increase in the density difference between the phases.
Phase viscosity ratio is another parameter which influences the coalescence time. An increase in the phase viscosity would be expected to increase the coalescence time as it takes more time to drain a more viscous film. There is experimental evidence to confirm this.

A high interfacial tension results in the drop resisting deformation so that the area for the film to drain would tend to decrease with increase in interfacial tension. Thus coalescence time tends to decrease with increase in interfacial tension. However, an increase in interfacial tension also tends to inhibit the flow of the film itself so that here again there are two opposing tendencies. Generally, coalescence time tends to decrease with an increase in interfacial tension.

Temperature affects all the physical properties that affect coalescence. Generally an increase in temperature tends to reduce coalescence time unless there is a change brought about in the coalescence process. Thus, Jeffreys and Hawksley (4) found that single step coalescence changed to multi-step coalescences in some instances when temperature was raised.

There are conflicting reports on the effect of vibrations on coalescence times. Gillespie and Rideal (3) suggested that vibrations tend to stabilize the drainage film, thereby impeding coalescence. On the other hand Lang (9) proposed that vibrations introduced random variations in the coalescence reported by different workers. Lang and others investigated the effects of extraneous vibrations and found these to be negligible. Brown and Hanson (13) studied single drop coalescence in alternating current fields of different frequencies and they concluded that in the systems they investigated, coalescence time was virtually independent of frequency.

Extensive research has been done on the effect of an external electric field on the rate of coalescence. Charles and Mason (14) applied a direct current field to the drop in such a manner that the force promoting coalescence was several hundred times that of gravity. They found that the drop flattened so that the area of draining the film was greatly increased, but since the force was so large the rate of coalescence was accelerated. Furthermore, they found that when stepwise coalescence occurred, the secondary drop was much smaller.

The presence of electrical double layers affect the rate of coalescence in a significant way. It had been widely observed that the rate of coalescence of drops whose phases contain electrolytes is lower than the rate of coalescence of pure drops residing in pure solvent. This is explained in part by the formation of electrical double layers between the draining film and the drop and the coalesced phase and the draining film. These double layers tend to retard the flow of draining film through the force of attraction of the opposite charges at the interface and in the flowing liquid. This effect has been given the name "electroviscous effect" by Elton and Picknett (14). It will be most pronounced when the thickness of the draining film is of the same order of magnitude as that of the electrical double layer, and when the apparent viscosity becomes five times that of the normal viscosity of the liquid in the draining film. Both Cockbain and McRoberts and Gillespie and Rideal (3) suggest that where double layer effect is significant, small drops should
be more stable than large ones. However, the problem is more complex than suggested by this simple statement because, although the force promoting coalescence is small in the case of a smaller drop, so is the area of the drainage film. Consequently, there will be less chance of the double layer becoming significant.

The presence of a third component tends to accelerate or retard the rate of coalescence. Thus solid substances tend to promote coalescence especially if they are wetted by the drop phase because the solid particle tends to form a bridge across the draining film thereby promoting the rupture of the film. This was demonstrated by Charles and Manson (15) who contaminated a benzene-water interface with minute glass beads. They found that coalescence was instantaneous.

There is a tremendous increase in interfacial area in emulsification; and this makes it necessary to take a look at surface activity. For example dispersion of only 1 cubic centimeter of oil into water in the form of fine droplets of a radius of 0.1 micron size creates an interfacial area of 300 square meters - an increase of the order of a million-fold. Under such circumstances the properties of surfaces and especially interfaces become of great importance.

The notion that surfaces and interfaces behave in a manner different from the bulk of the matter had been known for centuries. Partington (19) cites Leonardo da Vinci in this connection. For many years explanation of surface tension depended on the assumption that the free surface behaved like a contractile skin. Although liquids behave as though such a skin exists it is not really necessary to take such a view. It is the short range attractive forces that are known as van der Waals forces that are responsible for the special behavior of the surfaces and interfaces. Molecules in the bulk of the liquid experience a balanced force in all directions because the attractive forces fall off rapidly with distance. However, at the interface the molecules experience a net inward pull; and this accounts for the contractile skin-like behavior of the free surface. When a surface film is increased more molecules are brought to the higher energy condition at the surface. Thus, creating new surface is analogous to the phenomena accompanying vaporization. Stefan (20) was the first to suggest that there would be a relation between surface tension and latent heat of vaporization. Partington (19) gives an extensive list of theoretical and empirical equations relating the two properties.

Surface tension of most liquids decrease with increase in temperature. This is a corollary to the molecular theory of surface tension. The increased kinetic energy acquired by the molecules at the higher temperature will overcome the net attractive force on the molecule. Moreover, at conditions approaching the critical, the cohesive forces between the molecules vanish, and therefore the surface tension will vanish also at the critical. Eotovos (21) proposed a semi-empirical equation, which would predict the surface tension of a wide variety of substances from one empirical constant, the molecular weight and the critical temperature. This equation was improved by Ramsay and Shields (22), who in effect modified the empirical constant in the Eotovos equation.
Interfacial tension is a condition identical to surface tension except that instead of the vapor space above the free surface of a liquid there is yet another liquid whose molecules will exert substantial attractive force on the molecules of the other liquid at the interface. Thus the interfacial tension between two liquids will lie between the surface tensions of the liquids at the same temperature. Dupre (23) suggested an equation for calculating interfacial tension from the surface tension values of the separate phases. But there was the limitation that the two liquids had to be immiscible in each other. Since few liquids are completely immiscible in each other, the interfacial tension values so calculated were not accurate. Antonoff (24) suggested an improvement to Dupre’s equation taking into consideration the mutual solubility of the liquids. Recently Girifalco and Good (25) have suggested an equation, based on sound thermodynamic principles, which is in fair agreement with experimental data.

When considering emulsions, it is of far greater importance to look at the effect that solutes have on interfacial properties. The fact that small amounts of solute can have a violent effect on interfacial properties has been demonstrated by Hardy (26). A large lens of petroleum jelly was formed on the surface of pure water. A drop of oleic acid was placed on the lens. After a short time considerable agitation was noticed and then the lens appeared to shatter, with almost explosive violence into small fragments, which were propelled to the edges of the container.

That the presence of a small concentration of solute should have such an effect on the surface tension is not surprising; what is surprising is the tremendous variability of the effects observed. The large lowering of the interfacial tension on the addition of certain types of solutes is due to the fact that the solute concentrates at the interface. The molecules which produce this effect are known as amphiphilic molecules. They are oriented at the interface with their lipophilic portion extending into air (or into a non-aqueous phase). That there should be a higher concentration of the solute which causes the decrease in the interfacial tension at the interface has been proven by Gibbs. The assumptions involved in the derivation of the Gibbs equation have been critically reviewed by de Witte (27), and the rigor of the equation has been criticized by Guggenheim (28). Scatchard (29) reviewed the derivation by Gibbs and concurs with him.

In any mixing operation it is often necessary to know the energy input to the system. There are a number of ways to determine this. Energy input can be directly measured by a dynamometer, by measuring the amperage of the electric mixing motor or by making use of a torque meter. These methods can be expensive, inconvenient or inaccurate. However we can design a 'standard' mixing operation for which power correlation curves are available. When a standard impeller is turned in a liquid, a flow pattern is established in terms of the impeller characteristics, type of fluid and the geometry of the mixing vessel. After this circulation pattern has been set-up, the only way the input energy can be changed is by changing the rate of rotation of the impeller. In other words, the speed of the impeller and the environment it is in controls the input energy regardless of the power capacity of the driving mechanism.
White and co-workers (39) were the first to suggest the possibility of correlating the performance of mixing impellers by dimensional analysis. This idea was later extended by Hixon (40), Johnson and Thring (41) and Rushton and Oldshoe (42). The power correlations give Power number as a function of impeller Reynolds number and Froude number. Power number is given by

\[
P_o = \frac{P g_c}{\rho N^3 D^5}
\]

the impeller Reynolds number by

\[
Re = \frac{D^2 N \rho}{\mu}
\]

and the Froude number by

\[
Fr = \frac{D N^2}{g}
\]

Froude number characterizes the gravity forces and in a well baffled tank it is negligible. In this case the Power number becomes a function of the impeller Reynolds number alone.

2.3 Experimental Set-Up and Procedure

Equipment: The experimental set-up consists of a baffled tank with a turbine-type agitator system. A refrigeration system was used for temperatures below ambient. Other accessories included a temperature controller and a temperature recorder.

The experimental tank (fig. 2.1), made of 'Nalgene', a commercial polyethylene, had a height of 0.6 M and diameter of 0.42 M. The tank was filled up to 0.0757 M (20 U.S. Gal.) in all experiments. This corresponds to a height of 0.42 M, thereby giving a height to diameter ratio of 1:1 for the undisturbed liquid. Using the tank for the above mentioned capacity of 0.0757 M³, gave a free-board of 0.18 M - more than adequate to prevent any splashing when operating up to speeds of 600 RPM using a 0.09 M (4 in.) turbine. The tank was fitted with four equally spaced taps made of Polyvinyl Chloride. Glass tubes were attached to the insides of the taps extending to one half the radius of the tank.

Since the experiment involved detection of small quantities of hydrocarbon in the water, the tank prior to use was tested to see if any hydrocarbon will leach out from the polyethylene material. The results
Figure 2.1 Experimental Tank - 20 gallon
were negative.

Four equally spaced rectangular baffles of 1/12 the diameter of the tank, and made of aluminium were used. The baffles were fitted to the tank through a notch and fixed using Allen screws.

The liquid was agitated using a six-blade flat turbine of 0.101 M (4 in) diameter. A d.c. current motor of 0.373 kilowatts (1/2 h.p.) was used to drive the turbine through a shaft of 0.0063 M (1/4 in). The d.c. motor permitted continuous variation of the speed over a wide range. Both the turbine and the shaft were made of stainless steel to protect against corrosion due to sea water.

Samples were collected in 500 ml graduated bottles with glass stoppers. Extractions were done in 0.0005 M (500 ml) separatory funnels, with polyethylene stop-cocks and stoppers.

To study the drops of oil in the water column, photography was used. This method was preferred over automatic electronic counting (using Coulter Counter) because of the necessity of maintaining a quiescent medium for studying the stability of the dispersion. Coulter Counter requires a flowing system. The photographic technique on the other hand requires only small samples from the system. The samples were taken on pre-cleaned glass slides using glass pipettes. Cover glasses were used to prevent evaporation of the samples. A Leitz-Wetzlar microscope (Model No: 512), to which a Nikkon camera was attached, was used. The microscope had four objectives: 5, 10, 25, 50 magnification. The ocular had a magnification of 10 thereby giving a maximum magnification of 500 for the microscope. A very slow black and white film (Kodak ASP 32) was preferred, since the static system did not call for a fast film. The slower film gives better drop definition than the high speed film. The size of the drops were estimated by comparison with a scale etched on the objective and photographed along with the drops. The photographs were mounted and projected on a screen for counting.

2.3.1 Extraction of Oil:

The oil in the water column was extracted by carbon tetrachloride. Three aliquots of 10 ml each of carbon tetrachloride was used for each sample. The quantity of oil removed by the carbon tetrachloride was determined by a Perkin Elmer infra-red spectroroscope (Model no.: 451). The system was calibrated for the concentration of oil in the carbon tetrachloride. Since the range of the equipment was limited to 40 parts per million of oil, the extract had to be diluted to low concentrations. Spectral grade carbon tetrachloride was used.

A. Materials:

Sea Water: Sea water was preferred over pure water and synthetic sea water, because it was desired to simulate as closely as possible ocean conditions. Pure water devoid of all salts and zoo-plankton commonly found in actual sea water, would have drastically affected surface and
interfacial properties of the dispersion. The synthetic sea water although of consistently accurate composition, differs very much from sea water. The presence of very small quantities of dispersants that are usually found in sea water was not a serious problem as the concentrations of the dispersant used in the experiment was larger by many orders of magnitude. The sea water for the experiments was brought from Narragansett Bay in polyethylene containers and stored in a large "Nalgene" tank.

Crude Oil: A light Kuwait crude was chosen for the experiment. The choice of the crude was governed by the fact that this Kuwait crude had been chosen by many different laboratories for the purpose of studying oil pollution. Also, detailed analysis of the crude had been made by Exxon Research Laboratories and had been made available for the present investigation.

The crude had an API Gravity of 31.4, which would place it in the category of light crudes. Analysis (by Exxon Labs) showed that it had a sulfur content of 2.44 percent by weight and 0.14 percent nitrogen. Nickel and vanadium were 7.7 and 28 parts per million respectively. Analysis by mass spectroscopy showed that the crude was 34 percent by weight saturates and 21.9 by weight aromatics.

A commercial dispersant known as Corexit 9527 manufactured by Exxon for dispersing oil was used. Being a commercial dispersant, detailed specifications of its composition were not available.

Procedure: Sea water from Narragansett Bay was allowed to settle in the tank for a least a day before it was used for the experiments. This allowed any suspended particles to settle out. Ten ml of Kuwait crude was added to the sea water in the tank. In experiments in which dispersant was used, 2 ml of the dispersant was added to the system.

The duration of the agitation was decided from considerations of power input. To have a common basis for comparison, equal power was used in all the experiments, except in the case where there was to be no agitation.

For the calculation of power requirements, recourse was made to the power correlations for six-bladed flat turbines. In the present investigation, we had a two phase system. But power correlations for two phase systems are very sparse. However, Laity and Treybal (31) have suggested the use of weighted property values. Since in the present case the hold-up of the dispersed phase is extremely small, the properties were essentially that of the continuous phase. The power correlations give power number as a function of the impeller Reynolds number. Power number is defined as

\[ \frac{P g_c}{\rho N^3 D^5} \]
and the impeller Reynolds number as 

\[ Re = \frac{D^2 N_p}{\mu} \]

The power required to turn an impeller at a given speed is a function of not only the fluid properties but also the geometry of the impeller and the vessel. For calculation of power for the six-bladed flat turbine reference was made to Fig. 10.10, 'Liquid Extraction' by R.E. Treybal (32).

Samples were taken in 500 ml graduated glass bottles as soon as the motor was stopped; for the purposes of studying stability a timer was started at the same instant. Four sets of samples were taken, one from each tap, at 0 hrs, 1 hr, 2 hrs, and 24 hrs, and placed in graduated bottles.

Simultaneously, three drops were taken from each tap and placed on pre-cleaned slides and covered. These samples were photographed, 9 shots for each tap at each time.

The samples in the graduated bottles were extracted using carbon tetrachloride. First the 200 ml sample was transferred to a 500 ml separatory funnel. Then the first aliquot of 10 ml carbon tetrachloride was poured into the separatory funnel. To maintain consistency for each extraction the separatory funnel was shaken 20 times by hand. The extract was collected in pre-cleaned dram bottles and labelled. The procedure was repeated with a second and third 10 ml aliquot of carbon tetrachloride.

Since the concentrations usually encountered in the above extractions were beyond the range of the Infrared Spectrometer, 1 ml of the extract was taken and then diluted with 30 ml of carbon tetrachloride.

The photographs were developed and mounted. They were then projected on a screen and the size of the drops estimated by comparison with the scale which was photographed along with the drops.

Interfacial tension between the oil phase and aqueous phase was measured by the pendant drop method. Dynamic methods like the ring method are unsatisfactory because of the presence of surface active agents. When a new surface is formed in a medium in which a surface active agent is present, it will not be in equilibrium as the surface active agent has to diffuse to the newly created surface from the bulk of the medium. This is a consequence of the fact that there is a higher concentration of the surface active agent at the interface than in the bulk of the phase. This makes it necessary to use a method which is static or semi-static.

The pendant drop method consists of forming drops of one liquid in another liquid at the tip of a capillary. The drops are allowed to form at a slow rate so that the new surface will be in equilibrium - or close to being so. These drops were then photographed and their shapes deter-
mined by a shape factor by measuring two of their characteristic dimensions. Interfacial tension is a function of their shape.

Since the oil phase is lighter than the aqueous phase, the drop was allowed to form at the tip of a capillary which was oriented upwards. The capillary was connected to a reservoir which could be moved up or down at will. The capillary was kept in a water bath which was cooled by a refrigeration system.

The shape of the drop was determined by a photographic technique. As the drops formed at the tip of the capillary at the rate of about one drop per minute, its photograph was taken using a Mamiya Sekor camera. The camera had an extension tube attached to its lens to provide a magnification of approximately 10. A scale was photographed along with the drops. This helped in determining the size of the drop and its shape factor by comparison with the scale rather than making use of the magnification of the extension tube-lens system. The photographs were developed and mounted, and projected on a screen, and the size and shape measured.

The differential equation governing the shape of the drop has been solved as a function of the interfacial tension by a number of investigators (33). The numerical solution of the differential equation is available in the form of a table. Reference was made to these tables for the calculation of the interfacial tension (33).

To study the effect of temperature on the oil-water dispersion, a smaller tank was used. A smaller tank was used in preference to the larger 20 gal. tank because the requirements for refrigeration will be within the range of a 0.37 kw (1/2 hp) Haake refrigeration system. The tank of 0.3 M diameter, was made of glass and fitted with four baffles made of aluminum of 1/12 the diameter. Water was filled in the tank up to a depth of 0.3 M, thus giving a depth to diameter ratio of 1:1 for the undisturbed liquid. A free-board of 0.08 M was provided above the free surface of the liquid surface to make allowance for any splashing. The tank was agitated using a six-bladed flat turbine of 0.08 M (3 in) diameter. The impeller was driven by a variable speed motor of 0.06 kw (1/12 hp). The sampling and extraction procedures were identical to that used for the larger tank. The sample was taken from a depth of 0.15 M, using polyethylene tubing and placed into graduated bottles.

2.4. Results and Discussion

2.4.1 Drop-Size Distribution

When two liquids are agitated in a tank impeller system, which of the two liquids become the dispersed phase and which becomes the continuous phase depends on a variety of factors. If the two liquids are in comparable ratio, i.e., 45:55 percent by volume, the liquid that wets the impeller will be the continuous phase. However, when the volume fraction (hold-up) of one liquid is much smaller than the other, i.e., less than 25 percent, it is very difficult to disperse the liquid having the larger
volume fraction. From solid geometry we know that when spheres of equal size are packed together under conditions of closest packing, the volume fraction occupied by the spheres is only 74.02 percent. But when we have spheres of varying sizes, it is very obvious that we can pack much more in a given volume. In fact, emulsions of 99 percent dispersed phase have been prepared (32). However, in the present investigation the question as to which would be the dispersed phase and which would be the continuous phase could hardly arise. The crude oil phase was of the order of 1/10000 by volume of the aqueous phase. Thus the most probable dispersion that may be observed is the oil-in-water type. The hold-up was deliberately kept low so that the system would have about the same hold-up that could be expected in an oil-spill situation on the high seas.

In this investigation, low impeller speeds were used. This was done so that the turbulence generated would be as small as possible. Power correlations of Laity and Treybal (32) give power number for the impeller as a function of impeller Reynolds number. Since it was desired to use as small a turbulence as possible, the impeller Reynolds number just beyond the transition from laminar to turbulent was used. For the tank impeller system, this speed worked out to be 58 rpm (32). Thus the lowest speed that was used was 60 rpm.

It has not yet been established how the phase that is dispersed comes to be broken up into tiny droplets. It has been presumed by many workers that the phase that wets the impeller is the continuous phase (32). If this is the case, then the break-up action of the dispersed phase is due to the shearing action by the continuous phase.

A number of investigators have set an upper limit and a lower limit on the size of the droplets that can be observed in an emulsion. The lower limit is about 0.1 microns - a size approaching molecular dimensions. The upper limit is about 30 microns (30). Drops of larger than 30 microns are difficult to observe in an emulsion because they tend to rise fast and tend to coalesce with the parent phase. In this study attention was focused on drops whose sizes varied between 1 micron and 12 microns. There are a number of theoretical and empirical models available for the calculation of the rate of rise of a drop in a quiescent medium. The Stokes model (36) assumes that the drop behaves like a solid sphere while it moves in another medium. This is an approximation as there are circulations within the droplet. A more realistic model like the Ryczynski and Hadamard model (37) takes into consideration the movement of the fluid within the droplet. This model was used to calculate the rate of rise of a drop of Kuwait crude in sea water. This data shows that for droplets of size less than 12 microns the time taken to rise to the top of the tank would be of the order of less than 10 hours (fig. 2.2). Since an emulsion of oil in water has to be stable for a time of the order of days, it was thought unnecessary to observe droplets of size larger than 12 microns.

Jasper, Kim and Wilson (42), in their investigations on drop-size distribution in oil-water systems had found that drops larger than 6-7 microns are difficult to observe in an emulsion. Further they had concluded that the larger drops are insignificant for determining arithmetic means of the drop-size distribution (43). An extremely large drop would have little effect on the arithmetic mean if the small drops outnumber
Figure 2.2  Time Taken by a Drop to Rise to the Top of the Tank (hrs).
the larger drops by a large factor. The experimental data (see distribution data in Appendix D) shows that invariably there were much larger number of smaller droplets than there were larger ones.

If the drop size distribution was normal (it is not a normal distribution, but is 'leptokurtic' or left leaning - see the plots of the distribution in Appendix C) then over 95 percent of the drops would be within two standard deviations of the arithmetic mean. For drops of average size, 2-3 microns, this would have meant that over 90 percent of the drops would be less than 7-8 microns. Therefore, taking an upper limit of 12 microns for studying emulsions is considered satisfactory, especially in view of the fact that the distributions usually found in emulsions are left leaning.

The number of drops that are counted for studying the drop-size distribution depends to a large extent upon getting the accuracy to which the distribution is desired. To arrive at a reasonable number, investigations in this area in the past by various workers were relied upon. Gillespie and Rideal (3) had found that it was necessary to observe 100-200 drops to get reproducible results, while Jeffreys and Hawksley (4) and Cockbain and McRoberts (5) using more refined techniques needed only half as many drops. Since all the samples that were counted had more than 100 drops the drop-size distribution is accurate. (See tables 1a thru 6d in Appendix D).

Drop-size distribution for samples taken (figs. 2.3 through 2.7) (see Appendix A for Error Analysis) at 0 hours show an unmistakable trend that there is a larger proportion of smaller drops than larger drops. In other words, there is a maxima for the drop size distribution at the lower end of the spectrum. When the emulsion is allowed to stand over a period of time the drops tend to coalesce and the maxima tends to move towards the right.

The drop-size distribution when dispersant is used changes markedly from what it is when dispersant is not used. Figs. 2.3 through 2.7 show the distributions for different shear rates with and without dispersant. When dispersant is present, the distribution does not appear to change significantly with power input. However, when dispersant is not used there is a discernable difference in the distribution. It can be seen that the maxima for the distribution when dispersant is present is less than the maxima when dispersant is not used. This could be attributed to the lower interfacial tension between the oil and water when a surface active agent is used (see table in Appendix B).

If we consider the arithmetic mean of the drop sizes at 0 hours (figs. 2.8 thru 2.13) it can be seen that for a given rpm there was little or no difference between drop sizes at various positions in the tank. This is a corollary to the fact that while the impeller is rotating the forces induced on the drops by the forced circulation is far greater than gravity and the buoyant forces that otherwise would be dominant, when there is no such forced circulation.

In studying the drop size distribution, various averages are used. The number average mean is an obvious choice as it gives appropriate weight for drops of a given size. The weighted mean is given by,
Figure 2.3 Drop-Size Distribution - 60 RPM With Dispersant

Figure 2.4 Drop-Size Distribution - 100 RPM With Dispersant

Figure 2.5 Drop-Size Distribution - 150 RPM With Dispersant
Figure 2.6 Drop Size Distribution - 60 RPM - No Dispersant

Figure 2.7 Drop Size Distribution - 150 RPM - No Dispersant

Figure 2.8 Average Drop-Size - With Dispersant RPM - 60 - Temperature - 240°C
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Figure 2.10  Average Drop Size - With Dispersant RPM - 100 Temperature - 23.50C

Figure 2.11  Average Drop Size - No Dispersant RPM - 100 Temperature - 23.50C
Figure 2.12 Average Drop-Size - With Dispersant RPM - 150 Temperature - 23.50°C

Figure 2.13 Average Drop Size - No Dispersant, RPM - 150, Temperature - 23.50°C
While studying interfacial area Sauter Mean is the best choice. Sauter mean is given by

\[
AM = \frac{\sum N_i d_i}{\sum N_i}
\]

The drop size distributions show that the average drop size is a function of the rate of shear and interfacial tension. It is seen that we get a finer dispersion when a dispersant is added.

The average drop size at 0 hours is approximately 20 percent smaller when the speed of the impeller was increased from 60 to 150 rpm when no dispersant was present, as shown in figs. 2.9 and 2.13. If the rate of shear is taken to be proportional to the tip speed of the impeller then this represents a decrease in drop size of 20 percent for an increase in shear rate by a factor of 2. In the presence of the dispersant the average drop size for the above two cases was smaller and the difference in drop size was only approximately 3 percent (figs. 2.8 to 2.13).

It was seen that the average drop size (except at 0 hours) increases with time as well as position in the tank as measured from the bottom of the tank. Since in the present investigation the droplets are made up of an incompressible fluid, different vertical positions (and hence the hydrostatic pressure) does not have any effect on their size. Thus the increase in size with time and position are due to coalescence processes taking place. However, coalescence in a system of as small a hold-up as this is bound to be small.

Consider two drops of equal diameters. Whey they collide and coalesce their combined volumes will be twice the volume of the original drop and the diameter will be 26 percent larger. If the average drop size at the top and bottom levels in the tank are considered at 0 hours and 24 hours (figs. 2.7 to 2.14) it can be seen that the drop size has increased from bottom to top by less than 20 percent only. This shows that coalescence was not a major factor in the instability of the system. This is as should be expected in view of the extremely small hold-up. For the hold-up used in the experiments, and for an average drop size of 4 microns, the mean free path is about 63.3 microns. This means that if the movement of the drops is completely random, the drop will have to travel 15 drop diameters before colliding with another drop. Since Brownian movement which contributes to considerable random lateral movement (in contrast with straight upward movement due to buoyancy) is negligible at drop diameters greater than 0.1 microns (30). The only possible way in which drops could collide is when they rise upwards. This type of collision is bound to be small in systems of small hold-up. This accounts for the fact that the drop-size distribution itself does not vary appreciably with time.
2.4.2 Hold-up and Interfacial Area

Hold-up is defined as the fraction of the dispersed phase in the continuous phase. When dealing with a small hold-up as in the present case, alternate units are used. In this investigation milligrams per liter was found to be a convenient unit.

There was little variation in the hold-up (with respect to different positions in the tank) at the instant the impeller was stopped (figs. 2.14 thru 19). Thereafter, the hold-up decreased continuously with time as well as position, as measured from the bottom of the tank upward. As coalescence in systems of small hold-up are small, the decrease in hold-up is a function of the terminal velocity of the droplet (Brownian movement of droplets of size larger than 1 micron being negligible). At 24 hours, the hold-up was the same for all taps and all rpms with dispersant. This was found to be the case when no dispersant was used also.

Thus the stability of a dispersion of small hold-up will depend to a large extent upon the rate of rise of a drop. If we equate the forces acting on a droplet we get (36)

\[ F = \frac{4}{3} \pi R^3 \rho_c g + \frac{2}{3} \pi \rho R v_\infty + 4 \pi \mu R v_\infty \]

where the first term on the right is the buoyancy force, the second term is the form drag and the third term is the friction drag. When these forces are balanced by the gravitational forces, the drop will rise at a uniform velocity. Thus we have:

\[ \frac{4}{3} \pi R^3 \rho_d g = \frac{4}{3} \pi R^3 \rho_c g + \frac{2}{3} \pi \rho R v_\infty + 4 \pi \mu v_\infty \]

Solving for the velocity gives,

\[ v_\infty = \frac{2}{9} \frac{R^2 g}{\mu} (\rho - \rho_c) \]

Thus a smaller drop tends to have a smaller terminal velocity.

If the shearing action of the continuous phase on the dispersed phase accounts for the break up of the dispersed phase, then the shear rate as given by the tip speed of the impeller should have a functional relation to the drop size and thereby to the hold-up. Moreover, a system of lower interfacial tension is inherently more stable thermodynamically, as the work done in creating interfacial area is smaller and hence the potential energy of the system is smaller.
Figure 2.14 Hold-Up - With Dispersant, RPM 60, Temperature - 24°C

Figure 2.15 Hold-Up - No Dispersant, RPM 60, Temperature - 21.5°C

Figure 2.16 Hold-Up - With Dispersant; RPM 100, Temperature 23.5°C
Figure 2.17 Hold-Up - No Dispersant, RPM = 100, Temperature = 23.5°C

Figure 2.18 Hold-Up - With Dispersant, RPM = 150, Temperature = 23.5°C

Figure 2.19 Hold-Up - No Dispersant, RPM = 150, Temperature = 23.5°C
An analysis of the hold-up data shows that the hold-up when no dispersant was used, for samples taken at 24 hours was approximately constant and was very close to the solubility limit of crude oils usually observed (figs. 2.14 thru 19). When the dispersant was used, the hold-up at 24 hours was approximately constant but was higher (by a factor of approximately two) than the hold-up at 24 hours. This makes a good case for the use of dispersants in dispersing oil spills, if hold-up is the only criteria. As the dispersed phase was of lower density than the continuous phase, it naturally rises upward, and therefore the variation of the hold-up with time showed that the hold-up increased with height as measured from the bottom of the tank.

Specific interfacial area is a function of the hold-up as well as the Sauter Mean diameter of the drops. The interfacial area is given by,

\[ A = \frac{6 \times \phi}{SM} \]

As had been mentioned earlier, in systems of small hold-up like the one used in these investigations, coalescence is negligible and therefore the variation in the Sauter Mean diameter with height as well as time was not great. Therefore, the interfacial area showed (figs. 2.20-25) a variation which was similar to that shown by the hold-up. As the hold-up in the case where dispersant was used was higher, so was the interfacial area.

The fraction of the oil which was initially added to the system that goes into the water column is a function of the interfacial tension, and the rate of shear (or rpm). In the series of experiments, the largest fraction of oil that went into the water column when no dispersant was used was only 61 percent at 150 rpm, as against 86 percent at the same rpm when dispersant was used. The higher intake of hydrocarbons with the application of dispersant could be due to increased stability of the dispersion and the formation of sub-micron droplets (this appears to be valid apart from the effects of the lower interfacial tension and variations of other physical properties). The hold-up of the oil at 24 hours is possibly the best indication of this increased 'solubility', which was higher by almost a factor of 2 when the dispersant was used. Since there is no sharp dividing line between 'true solubility' and sub-micron dispersibility, it is hard to say which of the two was predominant at the conditions cited above (17).

In the experiments in which a temperature of 10°C was used (see table 2.9-12), the interfacial tension between the oil phase and the aqueous phase was 3.91 dynes/cm, in the presence of the dispersant. The interfacial tension at the same temperature and when no dispersant was used was found to be 25.1 dynes/cm (see table in Appendix B). The variation in hold-up and average drop size followed a trend that was very similar to that which was observed for the runs at the higher temperature. The hold-up, and consequently the interfacial area (after having been normalized to make allowance for the smaller tank), was found to be lower than that for the runs at higher temperature. Thus the effect of the lower temperature was to give a dispersion that was less stable
Figure 2.20 Interfacial Area - With Dispersant, RPM - 60, Temperature - 24°C

Figure 2.21 Interfacial Area - No Dispersant, RPM - 60, Temperature - 21.5°C

Figure 2.22 Interfacial Area - No Dispersant, RPM - 100, Temperature - 23.5°C
Figure 2.23 Interfacial Area - With Dispersant, RPM - 100, Temperature 23.5°C

Figure 2.24 Interfacial Area - With Dispersant, RPM - 150, Temperature 23.5°C

Figure 2.25 Interfacial Area - No Dispersant, RPM - 150, Temperature 23.5°C
because of the higher interfacial tension.

In contrast to the runs at 10°C, the runs at room temperature varied over a range of 2.5°C. Over the range of 5°C to 22°C, the interfacial tension varied by approximately 8.0 dynes/cm. Assuming that the interfacial tension is a linear function of temperature over this temperature range, it can be seen that the variation of the interfacial tension over a range of 2.5°C is only about 1 dyne/cm. The effect of this variation of the interfacial tension over such factors as work done and power input is only about 10.0 percent. Since the drop-size is proportional to a fractional power of the interfacial tension (32), the variation of the drop-sizes due to variation in the ambient temperature is bound to be only less than 10.0 percent.

It had been observed that hydrocarbons could enter the water column without any power input. This is indicated by the runs at 0 rpm - i.e., no power input. Though the hold-up was not as large as was the case when the impeller was used, it was considerable in view of the fact that there was no power input involved.

When two phases are brought into contact with each other, initially the chemical potentials of the various components in each phase are not equal and therefore this sets up a potential difference for the components between the phases. Thermodynamically, when there is a potential difference, the tendency is to equalize them. This is achieved by the diffusion of the components from the phase in which they have higher potentials to the phase in which they have lower potentials. The diffusion continues to take place until all chemical potentials have been equalized. Once the different components are in the second phase, they may tend to agglomerate and form droplets or micelles.

Thermodynamic potential is defined as:

\[ \mu_i = \left( \frac{\Delta G}{\Delta n} \right) + R T \ln \left( \frac{n}{n_i} \right) \]

where G is the Gibbs free energy, n the number of moles of the constituent j, T and P temperature and pressure respectively (39). For phase A and B the Gibbs criteria for equilibrium is:

\[ \mu_A = \mu_B \]

The chemical potentials are very difficult to use for studies involving crude oil in view of the large number of components involved. Phase equilibria involving more than three or four components are seldom solved by using thermodynamic potentials.

In this context it could be asked, what is the role played by power input in dispersing the crude in the water column? The thermodynamic potential, as it provides the driving force should have been sufficient to do the dispersion. But dispersion of one component into another takes
place through the interface between the phases, and the rotating impeller by breaking up the dispersed phase provides a larger interfacial area, thereby speeding up the equilibrium process. The rates at which equilibrium could be achieved when no power input is involved also depends on the interfacial resistances involved. It is difficult to compare the two methods (with power input and without power input) as little is known of the interfacial resistances. However, power input has one beneficial effect. The mass transfer rate between an oil slick and the water column is proportional to the concentration difference. The forced convection currents due to power input helps keep this concentration difference high thereby increasing the rate of mass transfer.

The mechanical work that is done in creating new surface area is given by the product of the interfacial tension and the new surface area created. It can be seen that the fraction of the total energy input that goes into making new surface area is of the order of 10 percent (Appendix C). Apart from the fact that the impeller action for creating new surface area (or small droplets) is therefore very inefficient, it also shows that one should treat with great caution the use of power input as a basis for determining the creation of new surface area and hold-up.

2.5 Conclusions and Recommendations

The basic question posed in this investigation was whether it was desirable to use a dispersant for emulsifying crude oil for later biodegradation.

The series of experiments conducted show that crude oil can be effectively dispersed using a commercial dispersant, Corexit 9527 without excessive power input. (Large power input was considered impractical in an oil-spill situation on the high seas.) The interfacial area and the hold-up, which are the important parameters when considering biodegradation, was found to be 2-3 times that when no dispersant was used. In this context it is important to remember that not all dispersants are useful for the purpose of biodegradation.

It was found that oil could enter the water column even when there was no power input. This is significant in that given sufficient amount of time, the oil could be effectively made to enter the water column without any power input - a desirable situation in a million gallon oil-spill.

The drop size distribution found for the 1-12 micron range can be considered to be truly representative of the emulsion. Further, this range of droplets is all that is necessary to study the emulsification process and the stability of oil-in-water emulsions.

It was observed that coalescence in a system of such a small hold-up as parts per million is very small. Therefore the instability of the system is due to the upward movement of the droplets in the continuous phase. This movement becomes ever smaller as the drop diameters become
smaller.

It is hoped that it will be possible to translate the experimental data at the higher temperatures to actual field conditions at much lower temperatures. Interfacial tension is the most dominant factor that is affected by the temperature. A decrease in the temperature from 22 C to 5 C increases the interfacial tension approximately by a factor of 2 to 3. Since the work done and consequently the power input is a linear function of temperature, it is expected that an increase in interfacial tension by a factor of 1.1 would call for an increase in the power input by the same factor.

The following recommendations are made:

i) To establish a base line for studying dispersibility of crude oils in water, pure hydrocarbons should be used.

The experiments conducted with Kuwait crude will not give much information where another crude is involved. This is primarily because the crudes themselves contain many surface active agents in the form of hydrocarbons with hydroxyl and carbonyl groups. The proportion of these vary widely from crude to crude.

ii) More efforts should be made to study the effect of dispersants in dispersing oil spills without input of power.

iii) Since the stability of the dispersion is desirable the idea of stabilizing the dispersion with finely divided solids should be investigated. Use of solids would mitigate the toxic effects of most common dispersants.

The temperature on the high seas in an actual oil spill situation could very well be close to the freezing point on a winter day. Therefore, the problem of correlating the experimental data at the higher temperatures to lower temperatures in the ocean naturally arises. On the basis of the effect of temperature on viscosity and interfacial tension, it can be estimated that the interfacial area will be smaller by approximately 10-15 percent.
3.0 The Effect of Wind and Wave Motion on Oil Entrainment

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3.0. The Effect of Wind and Wave Motion on Oil Entrainment

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3.1. Introduction

The wind-wave tank experiment is part of a larger study conducted at the University of Rhode Island to assess the environmental impact of treated and untreated oil spills. To develop a comprehensive model for oil slick impacts, this study required information about the amount of oil that would be dispersed under the ocean surface in a given sea state. It is believed that the largest oil concentrations result from dispersed oil droplets and that wave motion and the turbulence from breaking waves are an important dispersive mechanism. In addition, it has been shown that the oil properties can have an important effect on the amount of oil dispersed, and that these properties can change significantly over time. The experiments that have been done to date have provided valuable observations of the processes involved as well as some data. However, it has been difficult to establish even simple correlations between sea state and sub-surface oil concentrations for a number of reasons. The data from accidental spills is incomplete and it is not usually obtained under well documented conditions. Also, it is difficult to simulate sea-like conditions in the laboratory, and there is no simple accurate method available for measuring oil concentrations in water.

The wave tank experiment was proposed to address these problems and to add to the existing data. From the beginning, three design constraints were imposed: i) the experiment must be able to subject a small oil slick to various sea-like conditions, ii) it must be able to operate for an extended period of time, and iii) it must keep the effects of artificial barriers such as tank walls or containment booms to a minimum. This latter constraint is particularly difficult because water waves tend to push floating material in the direction of propagation. To solve these problems, a circular tank was designed and built with a variable speed wave generator around its perimeter, Figures 3.1 and 3.2. Water waves created at the edge of the tank travel toward the center where they interfere and sometimes break. Thus, the floating oil is contained in the region of maximum agitation solely by the wave drift currents, and no barriers are needed. The oil slick can be kept in a field of waves for as long as desired.

Of course this model has limitations. The energy in wind generated ocean waves is distributed over a band of frequencies where the energy concentration and bandwidth is dependent on wind fetch, duration, and water depth. The energy in the mechanically generated waves will be concentrated in a few distinct frequencies depending on the wave generator and tank geometries and the generator frequency. Also, the constructive interference of the waves at the center of the tank causes the waves to become steeper than they appear in the ocean. Currents are induced in the tank by the waves propagating toward the center, and in time these establish a circulation throughout the tank. All these differences are a result of the finite geometry of the experiment combined with a deterministic rather than a random forcing function for the waves. This has to result in a somewhat unsea-like environment. Nevertheless, the waves in the center of the tank have many apparent similarities to wind generated ocean waves.
Figure 3.1. The Wind Wave Experiment

Figure 3.2. Circular Wave Tank
The intent of the experimental test program was to investigate the relationship between the amount of any given oil dispersed into the water column from a slick on the surface, and the macroscopic physical properties of the waves causing the dispersion. Of particular interest were the effects of any oil property changes on the oil in water concentrations as the oil weathers. Consequently, the experiment was designed toward this end. No attempt was made, for example, to perform detailed investigations of the turbulent structure in the breaking waves, or to test for chemical changes in the oil. Rather, a simple function between sea-state and oil concentration was assumed to exist. The major effort was devoted to measuring the important parameters that would be included in this function such as the oil concentrations in the tank, and the wave parameters including an estimate of the frequency and extent of wave breaking. Other parameters that were deemed peculiar to the experiment, such as the induced water currents, that might affect any generalizations from the data were also measured. Oil properties and water properties were only measured to establish baselines and were not investigated for changes. The presumed function is certainly an approximation which ignores many components of the problem. However, the observations and data suggest that this assumption may be valid.

3.2. Experimental Apparatus

All of the oil dispersion experiments for this investigation were conducted in the circular wave tank shown in Figures 3.1 and 3.2. This tank is 3 feet high, 8.1 feet in diameter, and has a nominal capacity of 1000 gallons. A 24 by 36 inch plexiglass window was installed in the side of the tank to permit observation of subsurface phenomena. The waves were created by an 8 foot diameter circular hoop mounted concentrically inside the tank. The hoop, shown in Figures 3.1 and 3.2, is constructed of 1 inch diameter aluminum rod and fastened to the tank with 4 aluminum connecting arms. The wave generator is driven by a slider crank mechanism attached to a Dayton variable speed 1/2 HP gear motor (model No. 3n259) which can be adjusted to operate at any frequency between 18 and 133 cycles per second.

A hood is placed over the surface of the tank and connected to the suction side of two 5 HP, two speed blowers. The air flow over the surface is in a radial direction and has an approximately constant velocity, which can be varied from about 10 knots to 25 knots. The wave motion can be created by the wind alone, the wave maker alone, or both in combination. A wide variety of wind-wave conditions can be created.

When the wave generating hoop is adjusted to pierce the water surface during an oscillation, waves are created that travel towards the center of the tank, interfere, and may break. These waves induce surface currents directed radially inward which confine any floating oil to the region in the center of the tank where it is constantly exposed to the waves and dispersed under the surface. Preliminary experiments and analysis of the wave motion in the tank showed that there are many resonant modes of the water in the tank in the frequency range of the wave-maker. If the wave generator was at or near a resonant frequency, large waves develop in the tank and sometimes a large seiching motion (Wavelength 2D) was established. Thus, it was necessary to experiment by trial and error with different combinations of generator frequencies,
generator amplitudes, and water depths until satisfactory wave patterns were found that did not change significantly over time. Eventually, it was decided to operate the wavemaker at 1.33 and 2.13 cycles per second with a water depth of 27.75 inches. With this depth restriction, the capacity of the tank is 890 gallons (3470 liters). The vertical location of the wave generating hoop was adjusted so that at the top of its stroke 1/4 of the diameter of the bar was below the still water level. The amplitude of the oscillations was kept constant at 1.5 inches throughout all the tests.

Because this dispersion experiment requires the measurement of very low concentrations of oil in water, extreme care was taken throughout the design and construction of the test apparatus to use materials that were chemically inert and easy to clean. The wave tank was constructed from wood and coated on the inside with 4 layers of a polyester resin which had been shown not to leach any detectable levels of contaminants into the water. The wave generating apparatus was made completely out of teflon and aluminum.

The measurement apparatus that was used included equipment for determining wave heights, water current velocities, water and oil properties, and oil concentrations. The wave measurements were performed with two Coastal Data Service model WS 100 capacitive wave staffs. These instruments were specially modified to increase their sensitivity by replacing the coated metal probes that were supplied with the instrument with 16 gauge teflon coated wire. The voltage time series produced by the probes were recorded on magnetic tape with a Hewlett Packard 3960 FM tape recorder and later digitized using a Nova 1200 mini-computer.

Rhodamine B dye was used to determine the water current velocities. Samples taken from various tank locations at uniform time intervals were analyzed for fluorescence (dye concentration) with a Turner model 111 fluorometer. The water and oil interfacial and surface tensions were determined with a Cenco-DuNoo0 7045 Tensiometer. This instrument measures the interfacial tension by balancing the force required to pull a platinum ring through the fluid interface against torsion in a fine calibrated wire. The tension values are recorded directly from the instrument and corrected for force imbalances in the system as instructed in the manual.

Specific gravities were calculated by weighing an accurate volume of fluid in a sphinctometer on an analytic balance. Water and air temperatures were measured with standard laboratory mercury thermometers. Photographs of each experiment were taken with a Mamiya 35 mm SLR camera. In addition overhead still photos were taken at 5 to 10 second intervals with a Sanyo Super 8 mm movie camera. A complete description of the apparatus used to determine the oil in water concentrations will be given in the description of the sample analysis procedure.

The entire experimental set-up was located in a shed adjacent to Narragansett Bay. The experiments were performed at ambient temperatures using both bay water and fresh water. The water used in the latter experiments was passed through three filters to remove all particles larger than 5 microns. Care was taken to fill the tanks with sea water close to high tide to minimize any contaminants coming from Narragansett Bay.
3.3. Experimental Procedure.

The test procedures that were followed throughout the experimental program are described in the following sections. Ten experiments to measure the oil in water concentrations resulting from the wave action in the tank were performed using the standard experimental and sample analysis procedures listed. Three input conditions: wave generator frequency, oil volume, and water type (fresh or sea water) were varied. Most of the sea water tests were duplicated. Care was taken to insure that the experimental and chemical analysis procedures were exactly the same for all the tests with one exception: the water sampling times were changed when it became apparent that the sample variability and oil dispersion time scales were not what was originally expected. This is described completely in the sampling procedure description below. A complete list of the test conditions for each experiment is given in Table 3.1.

The input conditions (wave height, length, frequency and water current velocities and directions) caused by the wave generator were measured independently of the oil dispersion experiments. Ideally, a complete experiment would measure the oil concentrations and the wave and current conditions in the tank simultaneously. Unfortunately, oil on the water surface complicates things considerably. There are presently no readily available instruments for measuring wave heights and current velocities that will work in the presence of oil. In addition, any instrument placed in the wave field at the center of the tank would have an unknown effect on the dispersion process. Rather than develop special instrumentation it was decided to perform the wave and current measurements separately. This cannot be accomplished without some error. Oil has a visible effect on water waves. It tends to damp out high frequency capillary waves and inhibit the breaking process so that the waves become slightly steeper before collapsing. However, because the size of the experimental slick is small, and the wave action at the center of the tank was intense, it was felt that any change in the wave field due to the presence of an oil slick would be minimal, or at least that it would not be detectable within the accuracy of the experiment. This was later confirmed, in part, through observations and comparisons of photographs.

3.3.1. Wave Measurements

Wave data time series were obtained for both the 1.33 and 2.13 cycle per second wave generator frequencies. Data were obtained from the capacitive wave probe locations shown in Figures 3.3 and 3.4. (Note: the radii listed in the figures are referenced to the centerline of the generating hoop.) These locations were chosen to measure the wave parameters at the point of maximum observed wave activity, (tank center) and at the locations where turbulent breakdown of the regular wavefronts was just perceptible. Locations at equal radii were chosen to check for symmetric conditions in the tank.

Two capacitive wave staffs were available and consequently the data were recorded in pairs. Before and after each recording, a calibration record was established by measuring simulated water level changes in the tank. Each instrument was raised and lowered 12 cm relative to the water surface along a vertical carriage. Their output was recorded at 2 cm
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FIGURE 3.3
WAVE PROBE LOCATIONS  GENERATOR FREQUENCY  1.33

FIGURE 3.4
WAVE PROBE LOCATIONS  GENERATOR FREQUENCY  2.13
intervals. A slight amount of drift was evident in the instrument outputs due to rundown of the power supply batteries. To obtain the conversion factor from volts to cm the best linear fits obtained from the two sets of data were averaged. Using this technique, output data values are accurate to within 2 percent of reading over a range of plus or minus 12 cm. The wave probe response time was found to be instantaneous if the probe remained clean. However, any water contaminants would increase the response time dramatically, up to a few seconds in some cases. This is a result of water adhering to the probe wires and draining off slowly. To ensure adequate response, the probes were oscillated at known amplitudes while their output was checked on an oscilloscope. These tests were performed before each experiment to insure that the probe readings were not affected by any surface contaminants.

Overhead still photographs and slow motion movies were taken to supplement the data and to further document the wave field. Before the tests the tank was allowed to settle for 1 hour. Any visible debris was either skimmed off the water surface or extracted from the tank. The wave generator was run for 15 minutes to allow conditions in the tank to reach steady-state before any measurements were taken.

To analyze the data for frequency components using fast fourier transforms, the necessary sampling frequencies and recording times were chosen by following the procedure outlined in Bendat and Piersol* (1). A sampling interval $\Delta h = T$ was chosen so that

$$\Delta h = 1 \left(2f_c\right) \leq 1 \left(2f_d\right) \text{ sec.}$$

where $f_c$ is the Nyquist folding frequency, and $f_d$ is the highest possible frequency expected in the data. If $f_d = 20$ hz (an extremely conservative estimate):

$$\Delta h = 1/2 \left(20\right) = 0.25 \text{ sec.}$$

To achieve an effective resolution bandwidth $B_e$ of 0.1 hz requires that each sample record be $T_T$ seconds long where

$$T = 1/f = 10 \text{ sec.}$$

Choosing a 512 point record sampled at $\Delta h = 0.025$ seconds gives $T_T = 12.6$ seconds.

The random error is minimized by segment averaging. If the original data is assumed to be Gaussian, the normalized standard random error $\varepsilon_T$ is given by

$$\varepsilon_T = \sqrt{1/q}$$

where $q$ equals the number of ensembles of length $T_T$. Therefore, if

$$\varepsilon_T = .1, \ q = (1/\varepsilon_T)^2 = 100$$

*References denoted by numbers in brackets.
and the total record length T required is:

\[ T = qT_f = 100 \times 12.6 \text{ sec.} = 21 \text{ min.} \]

As a result of the foregoing analysis, 25 minute records sampled at 40 hz were obtained for each probe location.

3.3.2. Current Measurements

The surface drift currents created by the water waves propagating toward the tank center induce a subsurface return flow directed radially outward. This circulation could be easily observed by watching the motion of neutrally buoyant particles of debris. Unfortunately, the extremely low flow velocities present precluded the use of conventional instruments to obtain velocity profiles.

Measurement of the average convective circulation velocities were made using Rhodamine dye. Four experiments were performed to measure radial and circumferential water velocities as well as to estimate the time necessary to uniformly mix contaminants throughout the tank. The experimental procedure was as follows: the wave generator was run for one hour to ensure that steady-state conditions had been achieved. Then, 30 ml of Rhodamine B dye which had been diluted to be within 1 percent of the specific gravity of the tank water was applied to the center of the tank. Thirty ml water samples were then taken from the sampling valves located at the edge of the tank. The samples were taken at equally spaced time intervals, the time intervals were varied from experiment to experiment. Dye concentrations were later determined by fluorescence measurements with a Turner model 111 fluorometer. Average current velocities could then be found by computing the time differences between measured concentration peaks.

In addition to these tests, numerous visualization experiments were performed with the dye to further establish the magnitude and direction of the water velocity throughout the tank and to locate any eddies. Also, surface current velocities were measured by timing the travel of 5 cm square paper drifters over the 3 paths shown in Figure 3.33.

3.3.3. OIL CONCENTRATION MEASUREMENTS

The amount of oil dispersed into the water column at any given time was determined by chemically analyzing 0.5 liter water samples taken from three depths under the slick (see Fig. 3.34). To minimize any disturbances to the experiment while tests were underway, the water samples were obtained through 4 foot lengths of 7 mm outside diameter glass tubing fixed to the valves at the edge of the tank. Visualization experiments were conducted to estimate the effect that the tubes would have on the sampled oil-water dispersion. It was found that in all cases the predominant oil droplet diameter was significantly less than the 5 mm inside diameter of the tube. Almost all of the oil droplets ducted through the tube were collected intact. Consequently, the effect of the
glass tubes on the oil concentration in the samples was thought to be minimal.

A. Sampling and Analysis

The number of water samples taken and the sampling times were determined by the time scales of the physical processes to be investigated, and by the amount of available equipment. The ten experiments conducted can be divided into three groups. The first two experiments were preliminary tests to check equipment and procedures. For these tests, one water sample was taken from each of the three tank locations 120, 240, and 480 minutes after the oil was added. When visible changes in the oil slick were observed to take place within the first hour after the oil was added, a new sampling scheme was devised. In the next three experiments water samples were taken 10, 20, 40, 80, 160, 320, 480 and approximately 1440 minutes after the oil was added. The final sampling scheme, used in the last five experiments, was devised to document changes in oil dispersion with weathering and to obtain some estimate of the data scatter. At each sampling time, three 0.5 liter samples were taken from each of the three tank locations shown in Figure 3.34 for a total of nine samples per time. The sample times were 10, (only three samples were taken), 20, 160, 480, and approximately 1440 minutes after the oil was added. In all the experiments, three water samples to be used as background measurements were obtained before any oil was added to the tank. These samples were taken from the same three tank locations after the wave generator had run for one hour. In addition, samples were obtained one half hour after the wave generator was shut down.

B. Extraction Procedure

All the water samples obtained in these tests were analysed using a well known but tedious chemical extraction procedure. Briefly, the procedure involves washing the oil-water mixture a number of times with a solvent that dissolves the oil but is unsoluble in water. In this case, CCl₄ was used. The oil concentration in the solvent was then determined by measuring the light absorbance at the fundamental resonant frequency of the carbon-hydrogen bond (k=2930 cm⁻¹) on an infrared spectrophotometer. The absorbance is a linear function of the concentration of hydrocarbons present in the solvent. Thus the total amount of extractable hydrocarbons are measured. The concentration of hydrocarbons in the water sample due solely to the oil can be determined by subtracting out the background hydrocarbon concentration measure in the samples without oil. This entire analysis procedure has several disadvantages: it is expensive, time consuming, and extremely sensitive to contaminants. Unfortunately, there appears to be no better alternative.

Before any experiments were performed, the extraction procedure was extensively tested to document its efficiency and accuracy. It was found that violent agitation of the oil-water-solvent mixture increased the efficiency of the procedure dramatically. Calibration curves of absorbance verses concentration were created by mixing known quantities of Kuwait crude oil with CCl₄ and measuring the absorbance. A complete
The complete water sample analysis procedure that was used for all the oil dispersion experiments was as follows:

i) All glassware was cleaned with laboratory cleaner (Alconox). Separatory funnels and dram bottles were rinsed with CCl₄ immediately before use.

ii) Water samples were obtained by draining 0.5 liters of the tank water directly into 0.5 liter capacity separatory funnels fitted with teflon stopcocks and valves. A 30 ml aliquot of CCl₄ was then added immediately. The funnel was then shaken lightly and set aside for later extraction.

iii) The oil was extracted by violently shaking the oil-water-CCl₄ mixture in the separatory funnel on a modified paint shaker for 20 seconds. The mixture was allowed to settle and separate for 15 minutes. The oil laden solvent was then slowly drained off into a dram bottle.

iv) An additional 30 ml of CCl₄ was then added to the water remaining in the separatory funnel and step iii was repeated. The dram bottle was then tightly capped and stored in a dark place until the IR analysis was performed.

v) The oil concentration was measured using a Perkin-Elmer Model no. 457 grating infrared spectrophotometer with 5 cm pathlength quartz cuvettes. The relative light transmittence \( z \) between \( k \) 3200 cm \(^{-1}\) and \( k \) 2930 cm \(^{-1}\) was determined by zeroing the machine at \( k \) 3200 cm \(^{-1}\) and letting it scan down to \( k \) 2800 cm \(^{-1}\). The absorbance was then computed from a \( \log_{10} (100/z) \), and the organic concentration in the CCl₄ was read off the calibration curve. Water sample organic concentration was then computed using the following equation:

\[
\text{[Total Organic Concentration In Water (mg/l)]} = \left[\frac{1}{\text{CCl}_4 \text{ Analyzed (ml)}}\right] \times
\]

\[
\frac{1}{\text{Water Sample Size (l)}} \times \left[\frac{1000 \text{ ml}}{1 \text{ ml}}\right] \times
\]

The estimated oil in water concentrations were established by subtracting out the background organic concentrations determined from the first three tank samples.

As a result of the preliminary experiments to test the extraction procedure, the overall extraction efficiency i.e., the percentage of the organic material extracted out of the water sample during each aliquot, was found to be about 90 percent. Because this is a relatively high value, in the interest of economy the second aliquot was not taken for some of the experiments. Consequently, all the concentration data
presented in Table 3.2 are computed from the results of one aliquot.

3.3.4. Oil Dispersion Experiment Test Procedure

The following standard experimental test procedure was used in the ten oil dispersion experiments:

i) The tank and wave generating apparatus were cleaned thoroughly by scrubbing with a wire brush and solvent (National Chemsearch ND 150) and then rinsed completely.

ii) The tank was filled to a depth of 71 cm (3470 liters) with either fresh or filtered salt water.

iii) The wave generating hoop was installed and adjusted so that at the top of its stroke 1/4 of the hoop diameter was submerged. The hoop was adjusted to be parallel to the water surface. The desired generator speed, either 1.33 or 2.13 cycles per second was selected. The generator amplitude for all the experiments was fixed at 7.6 cm.

iv) The wave generator was run for one hour at the desired speed. At the end of the hour, background water samples were taken from the three sampling locations shown in Figure 3.34. In addition, one liter surface samples to be used for water property measurements were also taken at this time.

v) An 8 mm movie camera (Sankyo Super 8) was installed over the tank and adjusted to shoot either one frame every five seconds or every ten seconds. The camera was activated one minute before oil was added to the tank.

vi) Standard Kuwait crude oil was added to the tank (60 or 120 ml.) by pouring down a glass plate to inhibit any initial dispersion.

vii) Three 1/2 liter water samples were taken at the locations and times described in the sample analysis procedure. Samples were immediately preserved with the first aliquot of CCl₄. 35 mm photographs were taken of the water surface and the water column directly after the sampling. Water temperature, air temperature, and any observations were also recorded.

viii) The samples were processed as outlined in the sample analysis procedure.

ix) The first three tests operated for a duration of eight hours while the last seven tests lasted for 24 hours. Additional water samples were taken 1/2 hour after the wave generator was shut down.
### Table 3.2 Concentration Data, First Aliquot Only

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Table 3.2 Concentration Data, First Aliquot Only (Cont'd)

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**TIMES**

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**Wave Generator**

| Shut Down Time | 490 | 490 | 490 | 1360 | 1450 | 1440 | 1510 | 1500 | 1605 | 1780 |

*NOTE: 1440 minutes is the nominal time for the last water samples. The actual sampling times are listed in each column.*
3.4. CHARACTERISTICS OF EXPERIMENT

3.4.1. WAVE MEASUREMENTS

Sample water surface elevation records for four of the wave staff locations shown in Figures 3.3 and 3.4 are presented in Figures 3.5 through 3.8. The data for these plots was extracted from much longer samples used for a spectrum analysis. Note the difference in amplitude scales from figure to figure.

A. Observations

The wave patterns produced by the wave generator operating at 1.33 cycles per second are shown in Figures 3.9 through 3.13. These figures are all photographs taken of experiment 6. Figure 3.9 shows the regular concentric wavefronts spaced approximately 9 inches apart. Here they continue all the way to the tank center and concentrate the oil in a small area. By contrast, Figure 3.10 shows a more random pattern of waves with a much larger region of oil submergence. Generally, the oil was dispersed by either breaking or collapsing waves within a 36 inch diameter region at the center of the tank, and the random pattern of Figure 3.10 was more prevalent. However, the most intense breaking and the highest waves usually occurred at the center.

The waves created at the 1.33 cycle per second generator frequency ranged in height from one to six inches at the tank center. They were generally steeper than waves normally seen in the ocean. Figures 3.11 through 3.13 show some of the different wave shapes produced. Most waves resembled plunging breakers often seen at beaches (Fig. 3.11). Other waves were shaped like small pyramids and would collapse straight back on themselves (Fig. 3.12). In the most extreme cases, the disturbance resembled small jets of water that would shoot straight up about six inches and then fall straight back into the water column (Fig. 3.13). The frequency of occurrence of any of these wave shapes appeared to depend on the radial symmetry of the wavefronts created, with the most symmetric wavefronts producing the most extreme and localized disturbances. Although it was possible to affect the location of the most intense wave action by tilting the generating hoop, it was not possible to create a given type of wave simply by changing adjustments. The wave pattern existing at any given time depended on the interaction between the generated waves, the waves reflected off the tank walls, and the waves that had previously interfered and collapsed.

The actual water surface area covered by each individual breaking wave ranged up to 1 inch by 3 inches. The median area can be estimated by observation to be about 1 by 2 inches. While the waves in the tank clearly collapse as do breaking waves in the ocean, much less air is entrained by the water. Consequently, the waves do not have the characteristic appearance of "whitecaps". Each collapsing wave injected a plume of water into the water column which could be visualized by following the motion of oil droplets or entrained air bubbles. The observed plume depth was directly related to the height of the collapsing surface...
Figure 3.5. Surface Elevation Time Series Probe Location 1

Figure 3.6. Surface Elevation Time Series Probe Location 2
Figure 3.7. Surface Elevation Time Series Probe Location 4

Figure 3.8. Surface Elevation Time Series Probe Location 4
Figure 3.9. Wave Fronts 1.33 CPS

Figure 3.10. Random Waves at Center
Figure 3.11. Wave Shapes

Figure 3.12. Wave Shapes
Figure 3.13. Wave Shapes

Figure 3.14. Wave Pattern 2.13 CPS
Figure 3.15. Wave Pattern 2.14 CPS
wave, and in all cases the depth appeared to be roughly equal to the wave height.

Waves created at the faster (2.13 cycle per second) wave generator frequency are more closely spaced, smaller, and caused less intense individual disturbances in the tank. Figure 3.14 through 3.15, taken of tests 5 and 7, show the wave characteristics. From Figure 3.14 the crest to crest distance can be estimated at about 4 inches. It can also be seen that the oil is contained in a much smaller region (approximately 18 inches in diameter). The smaller waves did not display the variety of shapes evident at the lower generator frequency. Most of the waves near the tank center were pyramid shaped and tended to collapse back upon themselves. (See Fig. 3.15).

B. Results and Discussion

Applying fourier transforms to the recorded wave data results in the power spectral density plots shown in Figures 3.16 to 3.23. The transformations confirm that the dominant frequency of the waves produced by the generator operating at 1.33 cycles per second is 2.67 cycles per second, or twice the generator frequency. The waves produced by the 2.13 cycle per second generator frequency have important components at 2.1 and 4.2 cycles per second.

The total ENERGY, potential and kinetic, per unit area of the water surface contained in a simple harmonic progressive wave train equals (Ref. 3.2):

\[
1/2 \rho g a^2 \text{ or } 1/8 \rho g H^2
\]

where

\[
\rho = \text{water density} \\
g = \text{gravitational acceleration} \\
H = 2a = \text{wave height}.
\]

The ordinate in the graphs of the wave spectral distribution is in units of the square of the fourier coefficients or the square of the amplitudes of the frequency components. Thus the ordinates are in units of wave energy. The root mean square wave height may be obtained by integrating under the spectral peaks and taking the square root:

\[
H_{\text{RMS}} = 2 \sqrt{\int_0^\infty [a(f)]^2 \, df}
\]

and

\[
H_{\text{peak}} = \sqrt{2 \frac{H}{\text{RMS}}}
\]

a numerical integration of the fourier transformed wave data was performed using a trapazoidal approximation. The results are presented below:
Figure 3.16. Power Spectrum Probe Location 1 512 Pt. Transform

Figure 3.17. Power Spectrum Probe Location 2 36 cm Radius
3.18. Power Spectrum Probe Location 3 36 cm Radius

Figure 3.18. Power Spectrum Probe Location 3 36 cm Radius

3.19. Power Spectrum Probe Location 4 36 cm Radius

Figure 3.19. Power Spectrum Probe Location 4 36 cm Radius
POWER SPECTRUM

GEN. FREQ. = 2.13 CYCLES/SECOND
PROBE LOCATION 1. TANK CENTER (FIG. 3.4)
512 PT. TRANSFORM
FREQ. RESOLUTION = .08 Hz
75 ENSEMBLES AVERAGED

Figure 3.20. Power Spectrum Probe Location 1 512 Pt. Transform

POWER SPECTRUM

GEN. FREQ. = 2.13 CYCLES/SECOND
PROBE LOCATION 2.
25 cm RADIUS
512 PT. TRANSFORM
FREQ. RESOLUTION = .08 Hz
75 ENSEMBLES AVERAGED

Figure 3.21. Power Spectrum Probe Location 2 25 cm Radius
GEN. FREQ. = 2.13 CYCLES/SECOND PROBE LOCATION 3,
13 cm RADIUS 512 PT. TRANSFORM FREQ. RESOLUTION = .08 Hz
75 ENSEMBLES AVERAGED

Figure 3.22. Power Spectrum Probe Location 3 13 cm Radius 512 Pt. Transform

GEN. FREQ. = 2.13 CYCLES/SECOND PROBE LOCATION 4, 13 cm RADIUS
512 PT. TRANSFORM FREQ. RESOLUTION = .08 Hz 75 ENSEMBLES AVERAGED

Figure 3.23. Power Spectrum Probe Location 4 13 cm Radius 512 Pt. Transform
Expt. 1 Wave Generator Frequency = 1.33 cycle/second

1. Measurement Location: (see Fig. 3.3)
   1  2  3  4
2. Wave Frequency: (cycles/second)
   2.67 2.67 2.67 2.67
3. Peak to Peak Wave Height: (cm)
   6.2  1.8  1.4  1.6

Expt. 2 Wave Generator Frequency = 2.13 cycles/second

Measurements Location: (see Figure 3.4)
   1  2  3  4
Wave Frequency (cycles/second)
   2.1  2.1  2.1  2.1
Peak to Peak Wave Height: (cm)
   2.4  1.6  1.2  0.4
Wave Frequency: (cycles/second)
   4.2  4.2  4.2  4.2
Peak to Peak Wave Height: (cm)
   2.4  1.4  1.6  0.8

The results show that except for Location 4 of the second experiment, the waves are approximately the same average height at equal tank radii, and that the wave height grows as the waves approach the center, which is expected from energy conservation principles. As the wave fronts travel toward the center of the tank, the energy per unit area must remain the same (not counting frictional losses). This is accomplished by an increase in wave height until a limiting value is reached at which point the wave collapses. Examination of the wave data from location 4 of the second experiment show that after about ten minutes, the recorded wave amplitudes are significantly lower. It is believed that the wave probe was fouled by debris in the tank making the data from this probe suspect.

A theory for water waves of finite heights was developed by Stokes in the nineteenth century. The theory solves the wave equation with the wave parameters input in the form of a truncated infinite series. Results are also in series form. A discussion of the second and third order results can be found in Ref. (3.2) and (3.3). The second order theory gives the following equation for the wavelength and celerity.
\[ L = \frac{gT^2}{2} \tanh \left( \frac{2\pi h}{L} \right) \]
\[ C = \frac{gT}{2\pi} \tanh \left( \frac{2\pi H}{L} \right) \]

If the quantity in parentheses is large (> 3), the value of the hyperbolic tangent is approximately 1, and the equation may be simplified to:

\[ L = \frac{gT^2}{2\pi} \]
\[ C = \frac{gT}{2\pi} \]

Generally, this simplification is valid if \( h/L > 4 \). Since the observed wavelengths of the waves in the tank are about 4 inches (10.2 cm) and 9 inches (22.9 cm) (see the photographs in Figures 3.14 and 3.9) for the 2.13 cycle/second and 1.33 cycle/second wave frequencies respectively the above criteria are satisfied. The results from substituting the appropriate wave periods identified from the spectral plots into these simplified equations are presented in the following table:

<table>
<thead>
<tr>
<th>Wave Frequency</th>
<th>Wave Period (sec)</th>
<th>Wavelength (cm)</th>
<th>Wave Celerity (cm/sec)</th>
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</thead>
<tbody>
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<td>.238</td>
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</table>

It can be seen that the wavelength computed for the 2.67 and 4.2 cycle per second wave frequencies are in reasonable agreement with observed lengths. The Stoke's wave theory also predicts that the steepest water waves will have a crest angle of 120. degrees, or alternatively that the wave height divided by the length will be less than 0.142: i.e.,

\[ H/L \leq 0.142 \approx 1/7 \]

for stable waves. Steeper waves will collapse and break.

Using the data computed above, height to length ratios have been computed for the 2.67 and 4.2 cycle per second water waves:
Wave frequency = 2.67 cycle per second

Probe location (see Fig. 3.3 and 3.4)

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Wave Frequency = 4.2 cycles per second

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<td>H/L</td>
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<td>.16</td>
<td>.18</td>
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The results show that for both the 2.67 and 4.2 cycle per second surface waves, the breaking criteria is exceeded at the center position.

3.4.2. CURRENT MEASUREMENTS

A. Observations

The directions and relative magnitudes of the currents and eddies in the tank were found by observing the motions of dye plumes and neutrally buoyant particles from numerous tank locations. A sketch of a tank section showing an estimated current profile derived from these observations is given in Figure 3.24. It can be seen that the influx of water toward the tank center occurs in a shallow path with relatively high water velocities. This path is 5-8 cm deep at the 1.33 cycles per second generator frequency and 4-5 cm deep at the 2.1 cycles per second frequency. The return flow travels out and down from the center of the tank in the shape of a shallow cone. The interface between these two flows is not well defined. Just beneath the surface flow is a layer of slow moving water with no preferred direction. Also, at the corner between the tank wall and floor, and in the small space behind the wave generator, back eddies were observed.

The currents and eddies near the center of the tank depended on the surface wave action, and hence varied significantly at any given location over time. Individual plunging waves might superimpose a rapidly moving plume of water on the general downward flow at the center. Or, the rapid inflow of water could be interrupted by a wave tumbling against the current. A roughly circular region at the center of the tank was defined by a ring of surface water with no average radial velocity. This ring was formed when the radial inflow induced by the water waves met water tumbling away from the center from collapsing or breaking waves. This ring forms a convenient boundary. Inside the ring is the region of intense breaking wave action and outside the ring waves are regular and the wave fronts are circular. When small pieces of paper were scattered over the entire surface of the tank and allowed to migrate toward the center, the maximum distance the paper would reside from the center of the tank would be the radius of this ring. Indeed, this was also the maximum radius of the experimental oil slicks. The approximate maximum radius of the center region was 55 cm at the slow generator frequencies and 40 cm at the fast frequency. However, the dimensions would expand and contract depending on the wave intensity in the tank.
The water at the center region of the tank would rotate as a whole with smaller eddies contained inside. The maximum rotational velocity was estimated to be 0.05 to 0.3 radius per second. However, the rotation was not steady or consistent. No preferred direction of rotation was observed, nor was any regular frequency of direction change apparent.

The average velocity of the water travelling the entire convective path from the tank center down and out to the edge, and back to the center again, was found by determining the time difference between successive dye concentration peaks resulting from a plume of dye injected into the flow and sampled at the tank wall. Data from four experiments with 30 ml of dye applied to the center of the tank are shown in Figures 3.25 to 3.31. Input conditions, generator frequencies and sampling locations are listed on the figures. The ordinate in all the figures has been normalized by the uniform tank concentration resulting from 30 ml of dye mixed with 3470 liters of tank water. Dye sampling locations are shown in Fig. 3.32. The dye was then added at the center and water samples for the first two experiments were taken from locations 1 and 3 shown in Figure 3.32. Samples for the third experiment were taken from locations 1 and 2 and samples for the last experiment were taken only from location 1. First the tank was filled with fresh water and the wave maker run for one hour. Additional measurements of the surface currents were performed by timing the motion of 0.5 cm square paper drifters migrating toward the center of the tank. The tracks over which the drifters were observed are shown in Figure 3.33. The data is listed in Table 3.4.
TAP 1
TAP 2
TAP 3

LOCATION 2

FIGURE 3.32
BYE SAMPLING LOCATIONS

NOTE 1:
All the radi measurements are referenced to the centerline of the wave generating hoop.

NOTE 2:
A₃ = 48.8 cm for the 2.13 Hz beats.

FIGURE 3.33
PATHS OVER WHICH DRIFTERS WERE TIMED
### TABLE 3.4. TRAVEL TIMES FOR PAPER DRIFTERS (seconds)

**Wave Generator Frequency:**
- 1.33 cycles/second
- 2.13 cycles/second

**Location:** (see figure)

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<td>3.3</td>
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<td>7.2</td>
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<td>2.6</td>
<td>7.4</td>
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<td>7.3</td>
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<td>11.5</td>
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</tbody>
</table>
B. Results and Discussion

The dye concentration verses time graphs from the first two tests clearly show the series of dye concentration peaks resulting from the dye plumes in the recirculating flow crossing the sampling locations. The concentration peaks become lower and broader with each successive cycle as the dye diffuses forward and backward into the flow stream. The concentrations also tend toward the uniform value representing complete mixing in the tank.

If each plotted concentration peak is assumed to represent the center of the dye plume, and the water is assumed to follow the elliptical path shown in the figure below, the average circulation velocity can be determined by dividing the path length by the mean time difference between concentration peaks. From the figure, the perimeter of the ellipse is $312.3$ cm; the distance between the lower and upper sample locations is $48.2$ cm.

![Diagram of ellipse with dimensions labeled]

**Ellipse Perimeter,** $P = \pi (a + b)k$

when

- $a = 36.0$ cm
- $b = 61.8$ cm
- $k = (1 + 1/4 \text{ m}^2 + ...)$, $m = \frac{(a - b)}{(a + b)}$

$= 312.3$ cm

The semi-major and semi-minor axes are taken to be half the tank radius and tank depth respectively. Since this is the longest direct path that the water particles might follow, the computed velocities should represent the highest average velocities.

The data read from the concentration verses time graphs is summarized in Table 3.5. The average times for one complete circuit of the tank are found to be $131$ seconds for the $1.33$ cycle per second generator frequency. The respective average travel times for the dye plumes from the lower to upper sampling location are $2.5$ and $7.5$ seconds. Using these values, the average water velocities for the assumed circuit can be computed:
<table>
<thead>
<tr>
<th>GENERATOR FREQUENCY (cycles/sec)</th>
<th>SAMPLING LOCATION NUMBER</th>
<th>TIME OF DYE CONCENTRATION PEAK (second after dye added)</th>
<th>TIME DIFFERENCE BETWEEN CONSECUTIVE CONCENTRATION PEAKS (seconds) AT EACH LOCATION</th>
<th>TIME DIFFERENCE BETWEEN CONCENTRATION PEAK ARRIVAL STATION 3 AND 1 (seconds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.33 (Expt. 2)</td>
<td>1</td>
<td>135</td>
<td>135</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>270</td>
<td>120</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>105</td>
<td>135</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>240</td>
<td>135</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>375</td>
<td>135</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Average = 131</td>
<td>Average = 25</td>
<td></td>
</tr>
<tr>
<td>2.13 (Expt. 1)</td>
<td>1</td>
<td>40</td>
<td>60</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>60</td>
<td>10</td>
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<tr>
<td></td>
<td></td>
<td>160</td>
<td>60</td>
<td>5</td>
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<td></td>
<td></td>
<td>220</td>
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<td>280</td>
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<td></td>
<td>3</td>
<td>90</td>
<td>65</td>
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<td>3</td>
<td>155</td>
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<td></td>
<td>3</td>
<td>210</td>
<td>65</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>275</td>
<td>Average = 60</td>
<td>Average = 7.5</td>
</tr>
</tbody>
</table>
The third dye experiment was performed to test for longer term variations of dye concentrations, possibly due to circumferential flow components in the tank. The experiment was done at the faster generator frequency. One set of water samples was taken at location 2 (Figure 3.32) at half the tank depth and half the radius. The other set was taken from location 1 near the water surface at the tank wall. The results show that after 600 seconds, there is almost no variation in dye concentration visible, and the uniform tank concentration has been achieved. No long term fluctuations of the data are evident to within the accuracy of the test.

The last dye experiment was similar to Experiment 3 except that the wave generator was operating at the lower frequency, and the sampling period was much greater. Only one set of concentration samples were obtained from location 1. Figure 3.31 shows that the dye appears to be completely mixed after 1300 seconds, and again no long term cycles variation is evident. The jump in the data at 2300 seconds cannot be readily explained. Nothing unusual was observed during the experiment. It may be the result of a calibration problem with the fluorometer, although there is no reason to believe this is so.

C. Surface Drift Velocity:

Results of the experiments with the paper drifters are summarized in Table 3.6. The computed velocities for each of the tracks show that the average velocities on the tank water surface are approximately radially symmetric, at least to within about 1 standard deviation of the data. The scatter in the data can be attributed to the wave action at the tank center. Differences in mean velocity may also be due to asymmetries in the tank and wave generator installation.

<table>
<thead>
<tr>
<th>Wave Generator Frequency (cycles/sec)</th>
<th>Average Velocity (cm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Circuit</td>
<td>Lower to Upper Sample Location</td>
</tr>
<tr>
<td>1.33</td>
<td>2.4</td>
</tr>
<tr>
<td>2.13</td>
<td>5.2</td>
</tr>
</tbody>
</table>

Table 3.6 Surface Velocity

<table>
<thead>
<tr>
<th>WAVE GENERATOR FREQUENCY (cycles/second)</th>
<th>PATH OF PAPER DRIFTERS (see Fig. 3.33)</th>
<th>AVERAGE TIME (seconds)</th>
<th>STANDARD DEVIATION (seconds)</th>
<th>AVERAGE VELOCITY (cm/sec)</th>
<th>VELOCITY RANGE + 1 STD. DEVIATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.33</td>
<td>A1 A2</td>
<td>4.2</td>
<td>.6</td>
<td>7.9</td>
<td>6.9 - 9.3</td>
</tr>
<tr>
<td></td>
<td>A1 A3</td>
<td>8.9</td>
<td>2.1</td>
<td>5.5</td>
<td>4.4 - 7.1</td>
</tr>
<tr>
<td></td>
<td>B1 B2</td>
<td>3.3</td>
<td>.44</td>
<td>10.0</td>
<td>8.8 - 11.5</td>
</tr>
<tr>
<td></td>
<td>B1 B3</td>
<td>5.7</td>
<td>.95</td>
<td>8.6</td>
<td>7.3 - 10.3</td>
</tr>
<tr>
<td></td>
<td>C1 C2</td>
<td>3.6</td>
<td>.62</td>
<td>9.3</td>
<td>7.9 - 11.2</td>
</tr>
<tr>
<td></td>
<td>C1 C3</td>
<td>6.9</td>
<td>.89</td>
<td>7.0</td>
<td>6.2 - 8.0</td>
</tr>
<tr>
<td>2.13</td>
<td>A1 A2</td>
<td>2.6</td>
<td>.25</td>
<td>12.8</td>
<td>9.5 - 19.8</td>
</tr>
<tr>
<td></td>
<td>A1 A3</td>
<td>7.1</td>
<td>.9</td>
<td>9.0</td>
<td>8.6 - 9.3</td>
</tr>
</tbody>
</table>
An interesting feature of the surface flow becomes evident by comparing the average velocities of the drifters traveling the long paths with the velocities computed for the shorter paths. Since the measurements were all begun at the same radius, the slower velocities for the longer paths indicate that the water particles slow down as they approach the tank center. This is exactly opposite to what one would expect from continuity considerations. A possible explanation is that the momentary bursts of reverse flow from the collapsing waves slow the inflow and force it under the surface.

3.5. OIL CONCENTRATION EXPERIMENTAL RESULTS

3.5.1. Introduction

The first ten experiments have been made without the hood in place and with the wave maker operating at either 1.33 or 2.13 cycles per second. All were made with Kuwait Crude, either 60 or 120 ml, and at ambient temperatures which spanned the period from February through August. Tests were made with fresh water and sea water and documented with photographs and 8 mm movies.

Figure 3.34 shows the dimensions of the tank and sampling probe locations. Table 3.1 lists the test conditions and Table 3.2 gives the results of oil concentration verses time for the ten experiments. These results are plotted in Figure 3.35 through 3.44.

3.5.2. Observations and Results: Test 1

The first test, Test 1, was run with 60 ml of oil placed on the surface of cold fresh water. The frequency was 1.33 cps. Fig. 3.35 shows that the amount of oil entrained was the least of all the tests. The ordinate on these graphs is the percent of oil entrained x 10^-2. It is also the concentration of the sample divided by the concentration that would exist if all the oil were uniformly distributed throughout the tank.

It is interesting to note the behavior of the oil on the surface. Fig. 3.45 shows that the oil broke up into well defined slicklets with irregular boundaries a short time, about 2 hours, after the beginning of the test. While the diameters of the slicklets were random their average length scale appeared to be about 2" or about 1/2 the wave length. Fig. 3.46 shows the irregular boundaries of these slicklets, and Figure 3.47 shows the oil eight hours after being added.

At the beginning of this test, small oil droplets, from 1 mm to 5 mm in diameter were observed. However, the observed droplets seemed to decrease in number with time and as the slicklets became more stable. While the slicklets appeared stable on the surface of the water, when they were removed, the water separated from the oil in about one hour.
Eight hours after the oil was placed on the surface the wave maker was turned off and the system was allowed to come to equilibrium. Samples were taken 13 hours after shut down and showed a negligible amount of hydrocarbons remaining in the water. The slicklets which had formed broke down into irregular shapes but still maintained their identity.

TEST 2

The only significant difference between test 1 and test 2 is the wave generator frequency which was increased to 2.13 cycles per second. A plot of concentration verses time as shown in Fig. 3.36 shows no appreciable difference from test 1. Fig. 3.48 and 3.49 show the slicklets which formed about two hours after the oil was added. Fig. 3.50 is taken
Figure 3.36. Concentration vs. Time Experiment 2

Figure 3.37. Concentrations vs. Time Experiment 3

Figure 3.38. Concentration vs. Time Experiment 4
Figure 3.39. Concentration vs. Time Experiment 5

Figure 3.40. Concentration vs. Time Experiment 6

Figure 3.41. Concentration vs. Time Experiment 7

Figure 3.42. Concentration vs. Time Experiment 8
CONCENTRATION VS TIME
EXPERIMENT 9
DISPERGANT APPLIED
SALT WATER
GEN. FREO. = 1.33 CYCLES/SEC
OIL APPLIED = 60 ML
TEMP. RANGE = 25.0 C TO 27.0 C
□ LOCATION 1
△ LOCATION 2
● LOCATION 3

Figure 3.43. Concentration vs. Time Experiment 9

CONCENTRATION VS TIME
EXPERIMENT 10
SALT WATER
GEN. FREO. = 1.33 CYCLES/SEC
OIL APPLIED = 60 ML
TEMP. RANGE = 24.0 C TO 26.0 C
□ LOCATION 1
△ LOCATION 2
● LOCATION 3

Figure 3.44. Concentration vs. Time Experiment 10
Figure 3.47. Test 1 Fresh Water Weathered 8 hours

Figure 3.48. Test 2 Fresh Water High Frequency
Figure 3.49. Test 2 Fresh Water High Frequency

Figure 3.50. Test 2 Fresh Water
from underneath the slicklets. Note that these slicklets are different in appearance to those in test 1. They show a smoother, thicker contour and are not as irregular as in test 1.

This change in appearance must be due to the difference in frequency but the reason is not apparent. Note, also, that the length scale of the slicklets do not appear to differ from test 1.

Again, the wave maker was stopped about eight hours after the oil was added and samples taken 23 hours after the oil was added show a negligible amount remaining in the water column.

Test 3

This test was a repeat of test 1 but with salt water rather than fresh water. However, the test was in June, so that the ambient temperature was appreciably higher. Fig. 3.37 shows the oil concentration in the water column appreciably higher than in the fresh water case. The concentrations do not appear to change significantly with time. The appearance of the oil on the surface was markedly different from the fresh water cases. The oil did not form the distinct slicklets as in the previous two cases but spread more uniformly and formed a cloud of small droplets underneath the slick as shown in Figs. 3.51 and 3.52 taken about 20 minutes after the oil was added. Fig. 3.53 shows the appearance 80 minutes after the oil was added. One can see discrete lumps but considerably smaller than the slicklets in the fresh water case. Fig. 3.54 shows the slick after weathering for 22 hours, and the main body of the slick is still contiguous. Fig. 3.55 shows the appearance of the oil from beneath the surface after the wave maker was stopped.

In order to check on the effect of temperature, the tank was cleaned and filled with fresh water and the conditions of test 3 were repeated. As in the previous fresh water cases, the oil broke up into slicklets as shown in Fig. 3.56. We must therefore conclude that it is the composition of the salt water that slows down the formation of slicklets.

TEST 4

Test 4 was a repeat of test 2 but with salt water. It is a repeat of test 3 but at the higher frequency. Fig. 3.38 shows the concentration of oil in the water column. They are substantially higher than in test 3 and we must conclude that the oil concentration increases with the frequency of the waves. Figs. 3.57 and 3.58 show the appearance of the slick 20 and 40 minutes after start. Fig. 3.59 shows the droplets under the slick. Fig. 3.60 shows the slick after five hours of weathering.

After about two hours of weathering, small lumps, about 1/2 inch diameter, started to form between the wave maker and the wall. An emulsion formed on the tank wall at a crack in the resin coating, and it is believed that this formed the nucleus for the lumps. These lumps would escape one at a time and migrate toward the slick at the center of the tank where they would remain as small slicklets and not join the main slick. Fig. 3.61 shows these lumps.
Figure 3.51. Test 3 Salt Water

Figure 3.52. Test 3 Salt Water
Figure 3.53. Test 3 Salt Water

Figure 3.54. Test Salt Water Weathered 22 Hours
Figure 3.55. Test 3 Salt Water After Wavemaker Stopped

Figure 3.56. Repeat of Test 3 With fresh Water
Figure 3.57. Test 4 Salt Water High Frequency

Figure 3.58. Test 4 Salt Water High Frequency
Figure 3.59. Test 4 Salt Water

Figure 3.60. Test 4 Salt Water Weathered 5 Hours
After weathering about eight hours, small string-like pieces of oil could be seen circulating throughout the tank. These were approximately 1/4 mm in diameter and 3 mm long. The slick itself appeared to become an emulsion similar in appearance to chocolate mousse. Some of the tiny particles of oil would come to the surface, break and disappear into a sheen.

TEST 5

Test 5 is a repeat of test 2 but at a higher ambient temperature. Fig. 3.39 shows a higher average concentration of oil in the water column than in test 2. However, this is fresh water and the concentration is substantially lower than test 4 which has identical conditions except that it was done with salt water. It is interesting that the concentration of oil in the water appears to decrease with time in test 5. This is possibly a result of the formation of stable emulsions in the form of slicklets which float on the surface and absorb droplets that come in contact with them. As in the previous fresh water cases, these slicklets formed after about two hours and appear to become more stable with time.

TEST 6

Test 6 was the same as test 3 except that the quantity of oil added was doubled. Also, the ambient temperature was about 7°C higher. The percent concentration of oil in the water column does not appear to be significantly different from test 3. However, a noticeable increase with time is apparent and this is opposite the trend in the fresh water
tests. In Fig. 3.40, the lines are drawn through the averages of several samples taken from each port. Each data point plotted represents a single sample. Fig. 3.62 shows the appearance of the slick 20 minutes after start and Fig. 3.63 is eight hours after start. The oil has broken up and spread over the surface. The oil pieces seen appear to be aerated and not stable emulsions. The wave maker was stopped after about 24 hours of weathering and almost all the visible oil in droplet form appear to be oil covered water. The droplets range from about 0.1 mm to 2 mm in diameter. Fig. 3.64 shows the tank surface after stopping the wave maker.

TEST 7

Test 7 is identical to 6 except at higher frequency. It is the same as test 4 except the quantity of oil was doubled. Fig. 3.41 shows the concentration of oil in the water versus time. There does not appear to be a significant difference percentage wise, except possibly at the points taken just before shutdown, i.e., after 24 hours of weathering, where the concentrations at the higher frequency are lower. We note this same trend when comparing test 3 with test 4. It appears that after 24 hours of weathering, the concentration at the higher frequency decreases sharply. Figure 3.65 shows the slick 20 minutes after start and Figure 3.66 shows the slick after 24 hours of weathering. It can be seen that the weathering process has produced small slicklets of the order of 1/4 to 1/2 in. size. These are much smaller than those that appeared in the fresh water tests. The lower oil concentration after 24 hours could be a result of the stability of these slicklets and their ability to pick up oil droplets out of the water.

Figure 3.62. Test 6 120 ml Oil Weathered 20 Minutes
Figure 3.63. Test 6 Weathered 8 Hours

Figure 3.64. Test 6 After Stopping Wavemaker
Figure 3.65. Test 7 Weathered 20 Minutes

Figure 3.66. Test 7 Weathered 24 Hours
TEST 8

Test 8 is a repeat of test 4 and similar to test 7 except with half the oil added. The concentrations shown in Fig. 3.42 appear to be higher than 7 during the early stages of the experiment, but become the same order of magnitude as the weathering continues. Again, concentration appears to increase with time, but shows a sudden drop after 24 hours of weathering. Figure 3.67 shows the slick after 24 hours of weathering and the irregular appearance of the oil is apparent. The pieces look as though they have been shredded or torn apart.

TEST 9

Test 9 was performed to test the effectiveness of the chemical dispersant Corexit 9527. The experimental apparatus was set up as usual. The wave generator was set to operate at 1.33 cycles per second and 60 ml of oil was added.

Twelve ml of Corexit mixed with 240 ml of sea water were applied to the slick immediately after the oil was added. Following the manufacturers recommendation, the dispersant was first mixed with the tank water, keeping a water-dispersant ratio of 20:1. The mixture was then sprayed onto the water surface with a hand-held atomizer. (See Fig. 3.68). Care was taken to ensure that the dispersant contacted the entire slick.

The immediate effect of the dispersant was to submerge almost the entire oil slick. A dispersion of very fine (1 mm diameter or less) oil droplets could be seen which gave the near surface water a yellowish appearance. However, within 3 to 5 minutes, almost the entire amount of oil had returned to the surface to form a thin, opaque smooth, contiguous slick at the center of the tank (Fig. 3.69). Whenever a wave broke within the slick, a few droplets of oil would momentarily submerge as before, but they would immediately return to the surface and the contiguous slick would reform. The wave action in the tank appeared to be less violent than in previous tests. The smallest ripples were dampened out completely and the exposed water had a smooth, glossy appearance (Figure 3.70, taken ten minutes after the dispersant was added). Visible turbulent action from collapsing waves was much less. As a result, the circular wave fronts remained intact until the waves reached the very center of the tank where the constructive interference would finally cause the waves to collapse. Thus, the region of active oil submergence was very small.

Twenty minutes after the dispersant was added to the experiment, the water throughout the tank appeared mostly devoid of any oil, Fig. 3.71. Only a few very small oil droplets (again 1 mm or less) could be seen in the water just under the slick at the center. However, these were very small oil droplets, up to 2 mm in. diameter attached to the underside of the slick. The oil slick developed two distinct regions: a dark contiguous glossy slick at the center of the tank, and a transparent tan film that extended out to within a few centimeters of the wave generator.

During the first eight hours, the oil slick changed very little, Fig. 3.72. During periods of relatively more intense wave action, the oil
Figure 3.67. Test 8 Weathered 24 Hours

Figure 3.68. Test 9 Spraying Dispersent
Figure 3.69. Test 9 Five Minutes After Adding Dispersant

Figure 3.70. Test 9 Ten Minutes After Adding Dispersant
Figure 3.71. Test 9 Twenty Minutes After Adding Dispersant

Figure 3.72. Test 9 Weathered 8 Hours
near the center of the slick would break up into 1 or 2 \text{mm} size parti-
cles, but would recoalesce where the activity intensity lessened. Progressively more very fine oil droplets were observed in the water as the experiment progressed. However, the amount of dispersed oil con-
tinued to appear to be much less than experiments previously performed. The water remained very clear. The two distinct regions in the oil slick changed slightly. After eight hours of wave action, the center region appeared browner, similar to the color of chocolate sauce. The light brown perimeter had about disappeared and was replaced with a transparent sheen which refracted the light. Rough elongated particles of oil could be seen near the center, and some were being submerged.

The appearance of the tank the following morning after the wave generator had run for 22 hours, was radically different, Figs. 3.73 and 3.74. A very faint slick was visible on the water surface consisting of a brown film containing dark granules of oil. Most of the oil had dis-
persed completely into the tank in the form of small (again $< 0.2 \text{mm}$) dirt-like particles, although larger particles and oil droplets were also clearly visible. The water was a homogenous light yellow-brown and very murky. The waves in the tank were significantly smaller than usual, and smaller than when the experiment began. The maximum amplitude of the waves in the center was estimated to be less than 3 cm.

Ten minutes after the wave generator was stopped, 10 ml of tank water
was obtained and shaken vigorously with 10 ml of CCl$_4$. The fine oil
droplets dissolved in the solvent as expected, but many of the small dark flecks of oil ($0.5 - 0.1 \text{mm dia.}$) remained intact. Close examination of
these oil particles revealed that they had the texture of asphalt. The
concentration verses time plot is shown in Fig. 3.43.

**TEST 10**

Test 10 was a repeat of test 3 but with water about 10 C warmer. It is also the same as test 6 with 60 ml of oil added instead of 120 ml. Fig. 3.44 gives the concentration verses time curve. It shows the same magnitude and trend as tests 3 and 6. It thus appears that the normal-
ized concentration verses time curve is not dependent on the amount of oil present in this closed system and the quantity of oil being entrained
is directly proportional to the amount present. We also note that at the lower frequency the concentration keeps increasing after 24 hours in contrast to the higher frequency, when the concentration decreased markedly after the 24 hour reading.

**3.6. CONCLUSIONS AND RECOMMENDATIONS**

Kuwait crude oil weathers much differently in fresh water than it
does in natural salt water. In fresh water, it rapidly forms slicklets
which appear to be stable emulsions and very little oil gets into the
water column. In the salt water tests, much more oil entered the water
Figure 3.73. Test 9 Weathered 22 Hours

Figure 3.74. Test 9 Weathered 22 Hours
column, and this increased with time except that at the higher frequency, after weathering for 24 hours, the concentration of oil in the water column showed a dramatic decrease. This is attributed to the formation of stable emulsions that had an affinity to the droplets and took them out of the water column. The appearance of the oil in the higher frequency tests, after 24 hours showed a stringiness as though it had been shredded or torn apart. This did not happen with the lower frequency waves, where the concentration increased with time in all the salt water tests. However, it is possible that the same phenomena, the dramatic decrease in concentration, would have been observed if these lower frequency tests were run for a longer period of time. It therefore appears that the effect of increasing the frequency is to speed up the weathering process.

The effect of an increase in temperature is to increase the amount of oil getting into the water column.

Doubling the quantity of oil in the slick did not change the percent concentration of oil in the water column. This would indicate that the amount of oil getting into the water column is directly proportional to the amount present. In the ocean, currents would carry some of the oil away from under the slick.

Tests using the dispersant did not show a sudden increase in concentration of the oil in the water column immediately after adding the dispersant as might be expected. The visual properties of the slick and the waves changed, but the oil did not get into the water column until it had weathered over eight hours after adding the dispersant. After 22 hours of weathering, practically all the oil was in the water column.

The scatter in the data indicated that more tests should be made with similar conditions to improve the confidence limits. Additional tests should be made with wind driven waves and measurements taken of the rates of evaporation. Additional tests with wind driven waves and dispersants should be made.

References


4.0 The Entrainment of Oil in the Water Column

Leif N. Persen
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4.1 SURVEY

4.1.1. Introduction

The present study of the entrainment of oil from a slick on the ocean's surface to the water column is mainly based on the author's idea about the process as this is explained in [1]. For the sake of completeness, this is reviewed in the next section. The present investigation is based on three experiments conducted within the framework of the Department of Energy project at the University of Rhode Island. These have been initiated and reported in the Interim Report [2] from the DOE project. It has been the present author's fortune to be allowed to influence the conduction of these experiments such that they might be used to prove or to disprove the different concepts of the entrainment. The way in which this is done will be the subject of subsequent sections.

When discussing the entrainment process, the actual quantities used to describe this process should be well defined. Thus the "entrainment rate" $\bar{m}$ denotes the mass of oil transported from the slick into the water column per unit time and unit area. This quantity is not necessarily a constant. It may vary with time and location and is to be considered a local and not a bulk quantity.

4.1.2 The Entrainment Process

When an oil spill occurs, a slick is formed on the sea surface which will spread and get thinner in the process. The surface of the sea is in motion partially because of the waves, partially because of the wind-wave interaction and partially because of the current in the sea. It is known that the surface tension of the oil-sea interphase plays an important role in the entrainment process. (This is dramatically exhibited by adding a dispersant to an oil slick and thereby reducing the surface tension whereupon an enhanced entrainment is observed.)

It is furthermore recognized that the mechanical agitation that takes place at the sea surface plays an important role in the process. This may lead to the identification of the energy input at the surface as a second important parameter. Realizing however that this energy input may take place in different manners with different results as far as the entrainment process is concerned, one is led to the conclusion that additional parameters must be identified.

Preliminary experimental evidence seems to indicate the following scenario. The mechanical agitation will produce "entrainable" particles of oil mainly when it causes rifts in the oil film, i.e., when the "premissible" surface tension is exceeded. An analogy may be found in the production of fiber particles when tearing a sheet of paper. If that concept is correct, the production of entrainable particles is to be considered a random process even under the most well-defined conditions. Bearing in mind the conditions on the open sea, one will conclude that the production of entrainable oil particles must indeed be considered a random process. One must, however, also be permitted to assume that the average or mean production may be quantified in the same way as mean
values in turbulent fluid flow are determined. A support for such an idea may be found in the following observations:

1. The addition of a dispersant makes it easier to produce such rifts, thus enhancing the production of entrainable particles.

2. The production of entrainable particles will appear to be greater at the locations where the oil slick on the surface is thin than where it is thick or perhaps in the form of an emulsion (mousse). This is in complete agreement with observations previously made.

The expression "entrainable" particles needs some extra comments. The violent actions of breaking waves have been widely accepted as the action responsible for the entrainment of oil in the water column.* Such action produces oil particles of different sizes and the larger ones are by the action of buoyancy forces, quickly returned to the surface. The smaller the particles, the easier it is for them to be carried by the mean flow in the upper part of the water column. Thus, the term "entrainable" particles is reserved for those oil particles (or oil covered water droplets) which are "trapped" by this motion. The violent action of breaking waves can only force oil into the water column to a certain depth, the order of magnitude of this depth being the wave height. Thus, the entrainment of oil in the water column is very much dependent on the re-circulating motion connected with the waves in the upper layers of the water column. (It should be emphasized that the concept of "entrainable" particles makes entrainment possible also in the absence of breaking waves.)

There is, however, also another type of re-circulating flow in the ocean which is caused not by the wave motion, but by the non-uniform horizontal velocity distribution in the direction of the wind. This type of re-circulating motion will bring the entrained oil particles down to depths which are orders of magnitude larger than those in the previous cases. This type of motion can be modeled analytically on the turbulent plane jet flow or on the turbulent boundary layer type flow. This will be shown subsequently.

The picture given here of the entrainment envisages a semi-steady case in which a certain amount of oil is trapped by a re-circulating type of flow. If the conditions on the surface change, the amount of entrained oil will change. Assume, as an example, that the surface became completely calm, and that the re-circulating flow died out completely. Then only the extremely small droplets of oil which could be held in suspension would remain "permanently" entrained in the water column, the rest of the oil would resurface (or some might sink due to change in physical properties).

A consequence of the given description of the entrainment process is the fact that the so-called entrainment rate at the surface can no longer be considered a quantity determined by surface conditions alone. (Energy input, etc.). It is intimately connected with the re-circulating flow in the sea. As a further consequence, the search for "new" parameters to describe the entrainment rate will have to be replaced by a search for a more or less semi-empirical description of the recirculating flow from which the entrainment rate can be deduced.

One may, as a matter of fact, envisage a mechanism whereby the effect of the mechanical agitation that takes place at the surface (waves, breaking waves, raindrops, wind, etc.) is mainly to produce an adequate supply of entrainable particles in the immediate neighborhood of the surface. How many of the entrainable particles will be trapped by the re-circulating flow is then determined by the "strength" of this flow (whereby the strength of this flow will subsequently have to be defined in more exact terms).

One may contemplate this situation somewhat further. If the re-circulating flow is steadily "trapping" new particles, average concentration of oil in the region of this re-circulating flow must be steadily increasing. If it is not, i.e., if a semi-steady state is reached, the concentration will be constant and the entrainment rate zero. This can only occur in two cases. In the first case, there is no more production of entrainable particles at the surface, a situation that may well be feasible in view of the changes that the oil undergoes as it is being weathered on the surface. In the second case, an adequate supply of entrainable particles is present in the surface layer, but the re-circulating flow is returning formerly trapped particles at the same rate as new ones are being trapped.

The entrainment process described above has made no mention of the fact that the oil changes as it stays on the water surface and is being mechanically treated, a fact that is frequently referred to as "weathering" of the oil. Well known features of this process are the evaporation of the lighter components of the oil and the formation of chocolate mousse in some cases. It is evident that these processes will influence the composition of the entrained oil. Thus, it is already clear from the start that the entrained oil is different from the originally spilled oil, a fact that becomes important in the experimental investigation of the entrainment process.

4.1.3 Scope of the Experimentation

The entrainment process is a very complex one, not only because of the complexity of the surface conditions, but perhaps even more by the fact that the boundary conditions for the process change both with time and space. This may perhaps best be illustrated by observing that at one particular instant the situation downstream of a source continuously feeding a slick can be subdivided into several regions in which different predominant conditions prevail:

1. Immediately after the source, the oil is in its virgin state, but in this region is rapidly being changed due to evaporation of its lighter components.
2. The first region is overlapped by the second in which the situation is described in an undated report by the JBF Scientific Corporation (no identified author) for the American Petroleum Institute, p. 37:

"One of the important physical characteristics of crude oil slicks which is often neglected in the literature is the existence of one or more thick oil patches surrounded by a thinner film of oil. These thick areas have been referred to as 'lenses' or 'globs'. Investigators who have considered such thick patches report that they may contain 90% of the total oil in the slick, and that the patches are normally several millimeters thick as opposed to thousandths of a millimeter for the thinner surrounding film."

"Under conditions of no wind, the slick most probably spreads radially from the lens. However, in the presence of wind and waves, the radial spreading from the leading edge is continually overrun by the higher-velocity lens. The wind and wave activity cause the lens to break up into long windrows, each of which continues to act as a generator or reservoir of oil."

Most probably the important amount of entrained oil is coming from the thin film surrounding the lenses.

3. The next region which may be identified is the one in which "chocolate mousse" is being formed. According to the same report:

"Patches of 'chocolate mousse' should be conceptually distinguished from the lenses, because lenses appeared immediately after the oil was spilled and tended to remain roughly circular while 'chocolate mousse' was formed some time later and became elongated in windrows during the tests."

4. The last region to be specified is so far downstream of the source that the weathering of the slick is more or less complete in the sense that further changes do not take place. The formation of tar balls is starting and the slick seems to be more or less disintegrated.

It is clear that with boundary conditions as complex as those described above, the entrainment process is not easily accessible to analytic treatment. A study of the process should, therefore, start with experimentation under clearly identified and simplified boundary conditions.

The way in which the entrainment process has been visualized in the preceding section has reduced the importance of a detailed analysis of droplet formation at the slick. The main importance is now placed on the re-circulating motion and its ability to "trap" the droplets which presumably are being produced in adequate quantities. This production can
be related to certain input data characterizing the surface conditions, and it is emphasized that now the overall (bulk) production is being at the center of interest, not the details of droplet formation.

If one is faced with the problem of designing experimental setups which would give adequate information on the droplet formation, one would most probably have to consider a so-called "semi-steady" situation whereby the net bulk entrainment rate is zero. A change in the surface situation which could be achieved without changing the re-circulating motion could, through measurement of the concentration of oil in the water column, be interpreted to give information on the droplet production.

Because this experiment is such that the surface conditions and the re-circulating motion can be manipulated separately, the experiment will allow for a study of the "trapping" mechanism of the re-circulating motion. Thus, an adequate quantification of what is previously called the "strength" of this motion can be made. The "raindrop experiment" to be considered in detail later, is just an experiment of the type mentioned above.

The situation where the re-circulating motion is caused directly by the local wind-wave interaction at the sea surface is to be studied in the so-called "wind-wave experiment". Since the re-circulating flow is being monitored, the possibility of relating the results from this experiment to the others is present.

The situation which arises when the re-circulating motion dies out is to be studied in the so-called "drop size experiment". This experiment also provides the opportunity to study the entrainment from a slick exclusively driven by the turbulent motion in the sea (connected with the re-circulating flow).

4.1.4 The Drop-Size Experiment

This experiment was originally conceived of and conducted by Dr. T. Kim and Mathew Cherian. The first results were reported in detail in [2] where the major emphasis was placed on the influence of interfacial tension on drop size. The apparatus used is shown in Fig. 4.1 and consists mainly of a cylindrical tank and a centrally mounted impeller which can be operated at different angular velocities. The tank is filled with sea water on the surface of which a certain amount of oil is poured. To prevent the whole content of the tank from rotating with the impeller, the tank is supplied with baffles.

At very high angular velocities (of the impeller), the oil is almost totally "whipped" into the water column. Depending both on the angular speed and on the length of time when the impeller is run, different concentrations of oil in the water column are observed as a function of the time elapsed since shut off of the impeller. This result may be correlated with drop-size measurements. The fact that a certain portion of the entrained oil seems to remain "permanently" in the water column may be the most important part of the entrainment from a biology standpoint because it allows for a long term influence of the oil on marine life.
The same arrangement may, however, be used to study entrainment from a slick due exclusively to small scale turbulent motion underneath it. In this case, no mechanical agitation due to waves or rain, etc. takes place at the surface. The speed of the impeller is small, and the effect of the baffles is to more or less break up the horizontal rotation of the fluid. A special type of flow, in which vortices starting out from the surface can be identified, is produced and since the flow field can easily be monitored, the entrainment process under these special circumstances can be related to the observed entrainment in the other experiments. Whatever quantity related to and characterizing the flow is best suited as a relating parameter to the entrainment, will emerge as a result of the investigation.

4.1.5 The Raindrop Experiment

This experiment was first conceived of and conducted by Dr. Peter Cornillon and the results were reported on in [2]. The geometry of this experiment is shown in Fig. 4.2 where the "rain" is produced as drops falling from the needles in the bottom of the B container and is falling onto the water surface of the container C. On this surface, an oil slick is being placed and one has an arrangement whereby the mechanical agitation at the surface can be manipulated by adjusting the "intensity" of the rain, i.e., by changing the kinetic energy per unit area of the impacting raindrops. In its original form, as conducted by Dr. Cornillon no re-circulating flow was created. The apparatus has been changed by
the introduction of an impeller and baffles of the same type as in the drop-size experiment. In this way provisions have been made to create the same type of small scale turbulent motion underneath the slick as in the first experiment, and the influence of the mechanical agitation at the surface can thus be experimentally explored. It should be mentioned that the initial experiments with this apparatus have shown that with no re-circulating motion in the water column, entrained oil in the water column is not found below the immediate layer underneath the slick. This is in complete agreement with the concept of the entrainment process already outlined in the Introduction, and may be considered as experimental support for the concept.

4.1.6 The Wind-Wave Experiment

This experiment was originally conceived by Dr. Rodger Dowdell and was conducted by Steven Parks (see Section 3). The arrangement is shown in Fig. 4.3. A circular tank \( A \) is filled with water on the surface of which an oil slick may be applied. A doughnut shaped wave-maker \( C \) is shown close to the surface and by agitating this doughnut vertically at different frequencies and/or amplitudes, a pattern of radially moving surface waves may be created. In addition, a hood may be placed over the surface and by suction applied to the top of the hood \( B \), a radially directed wind over the surface is created. The shape of the hood is such that the wind is of constant velocity. The arrangement seems to be well suited for a study of the wind-wave interaction and the influence on the
oil slick of this action. The wave action as well as the wind action will create a re-circulating flow as shown in the sketch, Figure 4.3. Since this re-circulating flow can be monitored, and the concentration of entrained oil in the water column can be measured as a function of space and time as the input conditions on the surface are changed, the results from these experiments provide valuable insight to the entrainment process.

Fig. 4.3 The Wind-Wave Experiment

4.1.7 Experiment-Reality Correlation

The presentation of the experimental efforts has put the emphasis on the re-circulating flow underneath the slick as a common feature of all experiments whereby the different phases of the entrainment process are being studied. If these experiments are being properly executed, and provided the proper range of variation of the input data can be achieved, they present a range of conditions which cover most of those occurring along the slick as described in Section 4.3. Even the production of chocolate mousse can be expected to occur in the wind-wave experiment.

If, however, this information is going to be applicable to the real life situation at sea, the re-circulating flow which occurs at sea will have to be ascertained. This can be attempted experimentally by proper in-situ experimentation. Most probably one will find that the re-circulating flow connected with the waves can be experimentally explored, but that the very large scale motion connected with the non-uniform horizontal velocity of the surface layers cannot.

This, then is the point at which the re-circulating large scale motion may be theoretically explored through an analytic approach using
the method described by Leif Persen [4] and applied successfully to turbulent boundary layers. It should be mentioned that this approach does not include the influence of a possible thermal stratification in the ocean, but it will be sufficient as a first approximation. A later sophistication of the approach may be attempted when deemed necessary.

4.2 THE RECIRCULATING FLOW IN THE OCEAN

4.2.1 Introduction

The flow in the upper layer of the ocean will, where there is a gradient in the horizontal direction of the wind, exhibit a horizontal velocity which varies with the distance in the horizontal direction. This will give rise to a vertical motion of the fluid which goes to large depths compared with the wave heights. It is this motion which is responsible for the entrainment of oil particles at large depths. In the present section this motion is modeled on similar turbulent flows, i.e., flows which exhibit a change in the magnitude of the main velocity component with a correspondingly induced transverse velocity component which will then be responsible for a spreading effect. It is a fact that if one limits the scope to two-dimensional cases, such turbulent flows exhibit similarity properties of some kind, and it is easy to imagine this feature carried over to the turbulent flow in the upper part of the ocean.

The present approach will consist of an examination of the two-dimensional boundary layer flow and the two-dimensional jet flow in order to prepare the path for an examination of the fate of oil droplets in such flows. It will also show how these situations are relevant to the flow in the ocean.

4.2.2 The Turbulent Boundary Layer

The flow in the turbulent boundary layer on a flat plate may be described in a simplified way by assuming the existence of a law of the wall: [4]

\[ u^+ = f(y^+) \] (2.1)

or

\[ y^+ = \phi(u^+) \] (2.2)

The essence of this law is that the turbulent flow is such that it prescribes a one-to-one correspondence between the non-dimensional wall distance \( y^+ \) and the non-dimensional velocity \( u^+ \) parallel to the wall. It should be noticed that these quantities are defined as
\[ u^+ = \frac{\bar{u}}{v_*}, \quad y^+ = \frac{y v_*}{v} \]  

(2.3)

where

\( \bar{u} \) = mean velocity parallel to the wall (x-direction)

\( \bar{v} \) = mean velocity perpendicular to the wall (y-direction)

\( x \) = coordinate along the wall

\( y \) = coordinate perpendicular to the wall

\( v_* \) = shear velocity = \( \sqrt{\frac{\tau_w}{\rho}} \)

\( \tau_w \) = shear stress at the wall

\( \rho \) = density of the fluid

\( v \) = kinematic viscosity of the fluid

The mathematical problem of solving the basic equations and seeking the implications of the statement in (2.1) are shown in detail in 14, and only some results need to be drawn upon here:

1) The variation of the shear stress \( \tau \) in the fluid is given as

\[ \frac{\tau(x, u^+)}{\tau_w} = 1 - \frac{G(u^+)}{G(\xi)} \]  

(2.4)

where

\[ G(\xi) = \frac{1}{2} \xi^3 + \frac{A}{\kappa} \left[ e^{k \xi} \left( (k \xi)^2 - 2 k \xi + 2 \right) - 2 - \frac{1}{3} (k \xi)^3 \right] - \frac{1}{4} (k \xi)^4 - \frac{1}{10} (k \xi)^5 - \frac{1}{36} (k \xi)^6 \]  

(2.5)

Here \( \xi \) is the value of \( u^+ \) at the outer edge of the boundary layer, i.e.

\[ \lim_{y^+ \to \infty} u^+ = \xi = \frac{U}{v_*}, \quad \lim_{y^+ \to \infty} y^+ = y^*_o = \frac{\delta v_*}{v} = \phi(\xi) \]  

(2.6)
and \( y_o^+ \) is the corresponding value of \( y^+ \). The constants \( A \) and \( \kappa \) have been determined by D.B. Spalding [5]: \( A = 0.1108, \kappa = 0.4 \).

2) The vertical velocity \( \bar{v} \) is given as

\[
\bar{v} = -\frac{u}{v} \frac{dp}{dx} \cdot y^+ \cdot f(y^+) \tag{2.7}
\]

3) The solution to the problem renders \( \xi \) as a function of \( x \):

\[
1 \frac{d\xi}{dx} = \frac{1}{v} U_o \tag{2.8}
\]

where as before \( U_o \) denotes the constant outer velocity. Through a combination of (2.7) and (2.8) it is now possible to establish the following equation for \( \bar{v} \):

\[
\bar{v} = U_o \frac{y^+ \cdot f(y^+)}{\xi G(\xi)} \tag{2.9}
\]

and at the outer edge of the boundary layer the limiting value \( \bar{v}_\infty \) is obtained

\[
\bar{v}_\infty = U_o \frac{y_o^+ \cdot f(y_o^+)}{\xi G(\xi)}
\]

Since (2.8) gives the relationship between \( \xi \) and \( Re \) one may use \( \xi \) to indicate a certain position along the wall:

\[
Re = \frac{U_o x}{\nu} = \frac{\xi}{G(\xi) dx}
\]

Then the relation (2.9) may be interpreted as a variation of \( \bar{v} \) at a given position \( x \) (given through \( \xi \)) as \( y \) varies from zero (at the wall) to \( y_o^+ \) (at the outer edge of the boundary layer). The implication of the law of the wall is however that (2.9) also describes the variation of \( \bar{v} \) at a given value of \( y \) as \( x \) varies. This is schematically shown in Fig. 4.4 where \( y = \text{constant} \) is shown to
hit the outer edge of the boundary layer at $x = x_0$. The corresponding value of $\xi$ is $\xi_0$ and at this point the vertical velocity $\bar{v}$ is from (2.9) found to be

$$\bar{v}_o = U_o \frac{y^+_{o,0} f(y^+_{o,0})}{\xi_0 G(\xi_0)}$$  \hfill (2.11)$$

where now $y^+_{o,0}$ represents the value of $y^+$ at $\xi = \xi_0$. Since $\xi$ is related to the local Reynolds number $Re_x$ through (2.10) it is observed that the lowest value for $Re_x$ for a given value of $y$ is

$$Re_{x_0} = \frac{U_o x_0}{\nu} = \frac{\xi_0}{\int G(z) dz}$$  \hfill (2.12)$$

It is now easily shown that for a given value of $y$ the variation $y^+$ as one progresses in the $x$-direction is given as follows:

$$y^+ = \frac{y^+ v^+}{\nu} = \frac{y U_o}{\nu \xi}$$  \hfill (2.13)$$

where the variation of $x$ is expressed through $\xi$. Since this starts to be valid at $x = x_0$ one has (since the constant value of $y$ equals $\delta_0$)
Thus the variation of $y^+$ with $x$ (or $\xi$) will be:

$$y^+ = y'^+ \frac{\xi_o}{\xi}$$  \hspace{1cm} (2.15)

Finally, it has been shown [6] that the shear stress $\tau$ can be expressed as:

$$\frac{\tau}{\rho U_o^2} = \frac{1}{\xi^2} \left[ 1 - \frac{G_{H_o}^{\xi}}{G(\xi)} \right]$$  \hspace{1cm} (2.16)

and the stream function $\psi$ may be given as:

$$\psi = \int u \, dy = \int u^+ v^+ dy = \nu \int u^+ dy^+ = \nu \int \frac{du^+}{du^+} \, du^+$$  \hspace{1cm} (2.17)

Using D.B. Spalding's formulation [5] one will get:

$$\psi = \nu \left[ \frac{(u^+)^2}{2} + A \left( \kappa u^+ (k u^+ - 1) - (k u^+)^2/2 - (k u^+)^3/3 - (k u^+)^4/8 - (k u^+)^5/30 \right) \right]$$  \hspace{1cm} (2.18)

This ends the exhibition of the implications of a turbulent boundary layer. It is not accurate, the procedure used has been improved, but for the present purpose it ought to be sufficient.

4.2.3 The Flow in the Upper Layer of the Ocean

The flow in the ocean is turbulent and this is also the case in its upper layer. In this layer however, surface waves are creating recirculating motions and sometimes these phenomena tend to obscure the large scale motions responsible for carrying oil particles to much larger depths than the wave heights. This large scale motion is not easily recognized experimentally except for the fact it is also responsible for
the entrainment of organic particles which makes life exist to large depths.

One may use one's knowledge of turbulent flows in general to come up with an adequate analytic approach to the problem of describing the flow. First one observes that the ordinary linear approach to the wave mechanisms furnishes a flow field which exhibits recirculation but which has no mean motion in the direction parallel to the surface of the sea. The recirculating motion connected with the waves becomes insignificant at depths greater than a couple of wave heights. Closer examination of the fluid motion in the upper layer shows however that there is a mean horizontal velocity component "superimposed" on the wave motion, and this velocity component may vary with the horizontal distance. A simple consideration of the equation of continuity will then show that under such circumstances a vertical velocity component in the ocean is inevitable, and that it will penetrate to depths comparable to the distance over which the change in the horizontal velocity components take place. This may be an order of magnitude larger than the wave height.

There is no immediate and direct way of predicting this type of mean motion. One may however use the boundary layer flow which is described in Sec. 4.2.2 to exhibit a certain relevant case. Fig. 4.5 shows the upper layer of the ocean in which there is a horizontal current $U_0$ as shown by the velocity profile. (A two-dimensional situation is assumed.) At the surface (the waves have been neglected) a horizontal shear stress in the x-direction (opposite to $U_0$) is supposed to act due to wind. If now this shear stress varies in the proper way, a boundary layer type of flow will develop in the upper layer and the situation is similar to that of Fig. 4.4. Thus the results of Sec. 4.2.2 are immediately applicable to the situation at hand and several cases of shear stress distribution on the surface have been considered whereby the following quantities have been computed as functions of the non-dimensional distance $(Re_x - Re_{x0})$: 

![Fig. 4.5](image-url)
\( \tau/\rho u_o^2 \) = non-dimensional shear stress distribution

\( \bar{w}/u_o \) = non-dimensional horizontal velocity component at the surface

\( \bar{v}/v_o \) = non-dimensional vertical velocity component at the surface

\( \bar{v}_e/v_o \) = non-dimensional vertical velocity component at a depth equal to and/or greater than the boundary layer thickness \( \delta - \delta_0 \)

The computations are based on the equations of Sec. 4.2.2 and the computer programs used are exhibited in the Appendix. Fig. 4.6, 4.7, and 4.8 give the variation along the "surface" of the different quantities. The corresponding streamline pattern is exhibited in Fig. 4.9 where the dashed line represents the boundary of the region in which the expressions used are valid. It is seen how the streamlines indicate a vertical velocity (downwards) and the fate of oil droplets in this environment will be discussed in Section 4.3.
4.2.4 The Jet Flow

It has been shown how the turbulent boundary layer can be used to model the downward flow in the ocean which in a certain case will occur and which is caused by the horizontal component of the mean velocity gradient. Since this only represents a special situation, one may try to find other models which will be useful in other situations. One such type of flow is the jet flow.

The jet flow is characterized by the fact that it is a self-similar type of turbulent flow. However, most of the jet investigations operate with a velocity field which corresponds to a non-vanishing velocity component at infinity normal to the jet-axis. The more proper velocity
field would be one exhibiting recirculation, and Persen-Skaug [7] have suggested just that type of velocity profile. The present investigation will start from this assumption and present the flow field as

\[
\begin{align*}
\frac{u}{U_c} &= (\xi^2 + 1)^{-\frac{1}{2}} f(\eta) \\
\frac{v}{U_c} &= \frac{1}{2}(\xi^2 + 1)^{-\frac{3}{2}} \xi (2n f(\eta) - \int_{0}^{\eta} f(z)dz)
\end{align*}
\] (4.1)

where \(f(\eta)\) is a non-specified velocity profile, \(\eta\) is the non-dimensional distance normal to the jet axis and \(\xi\) is the non-dimensional distance along the jet axis.

\[
\xi = (x - x_o)/A \\
\eta = \frac{u}{A}(\xi^2 + 1)^{-\frac{1}{2}}
\] (4.2)

Here \(A\) and \(x_o\) are parameters important in the description of the jet flow but for the moment these are left for future consideration in the present context.

With this preliminary information one may now explore the jet flow somewhat closer. The velocity profile \(f(\eta)\) is specified as

\[
f(\eta) = e^{-\eta^2} - \frac{2B \eta^n}{\sqrt{\pi} (B^2 + \eta^n)}
\] (4.3)

where \(B\) is a constant to be determined later. It is observed that

\[
\int_{0}^{\eta} f(z)dz = \int_{0}^{\eta} e^{-z^2}dz - \frac{2B}{\sqrt{\pi}} \int_{0}^{\eta} \frac{z^2}{(B^2 + z^n)}dz
\] (4.4)

which can be rewritten as:

\[
\int_{0}^{\eta} f(z)dz = \frac{\sqrt{\pi}}{2} \text{erf}(\eta) + \frac{\eta B}{B^2 + \eta^n} - \frac{1}{\sqrt{\pi}} \arctan \left( \frac{\eta}{B} \right)
\] (4.5)
It is seen that

\[ \lim_{n \to \infty} \int_0^n f(z) \, dz = 0 \]

This means that the velocity field dies out (in view of (4.1)) as \( n \to \infty \) (i.e. for large values of \( y \)).

The stream function \( \Psi \) for the flow under consideration will now be expressed as

\[ \Psi = A U_0 (1 + \varepsilon^2) \int_0^n f(z) \, dz \]  \hspace{1cm} (4.7)

4.2.5 The Analogous Flow in the Ocean

Just as the boundary layer flow exhibited in Section 4.2.2 was shown to have a bearing on the flow in the upper layer of the ocean, the jet flow may also be shown to be applicable. If one imagines the scenario when a wind has produced a mean horizontal velocity in the upper layer of the ocean and then ceases to blow, the situation will be as shown in Fig. 4.10 where the velocity profile is similar to that of the jet with a zero velocity gradient at the surface indicating the absence of a shear stress at the surface. The horizontal velocity will eventually die down and a

---

Fig. 4.10
velocity gradient in the horizontal direction will produce a downward flow in the ocean. Thus the jet flow has found its analogue in the large scale flow structure in the ocean. The flow is illustrated in Figs. 4.11 and 4.12. It is seen that the flow patterns are very similar even though the parameter is $B = 2$ and $B = 5$ respectively. Consequently, only one case will be treated subsequently when the fate of oil droplets in this type of flow is considered in Section 4.3.

Fig. 4.11 Streamlines in the recirculating flow, $B = 2$

Fig. 4.12 Streamlines in the recirculating flow, $B = 5$
4.3 THE PATHS OF OIL DROPLETS IN THE OCEAN

4.3.1 Introduction

It has been shown that the entrainment of oil in the water column is governed by the recirculating motion which can be found in the ocean due to the nonuniform velocity distribution of the horizontal velocity component in its upper layer. It is the purpose of this paper to explore the possibility of studying this process more in detail.

4.3.2 The Equations of Motion

It will be assumed that the motion of an oil droplet can be described on the basic assumption that its motion does not affect the flow field. One will then have the flow field described through the velocity components $u(x,y)$ and $v(x,y)$ which may be considered as given or known functions. The position of an oil droplet will be, $x,y$, its velocity $x,y$ and its acceleration $x,y$. Its mass is $m$.

Fig. 4.13 Oil Droplet in a Flow field

The set of equations of motion will now be:

$$
F_x = m\ddot{x}
$$

$$
F_y + B = m\ddot{y}
$$

where $B$ is the buoyancy force, and $F_x$ and $F_y$ are the forces exerted on the droplet by the fluid. The latter forces will depend on the relative velocity between the droplet and the fluid. The drag force on a sphere (droplet) is given as a function of the Reynolds number

$$
Re = \frac{VD}{v}
$$

where $V$ is the relative velocity of the sphere to the fluid

$D$ is the diameter of the sphere
\( \nu \) is the kinematic viscosity of the fluid.

\[
\begin{align*}
\frac{C_D}{D} &= \frac{\rho V^2}{A} \\
R &= \frac{\rho V_0}{\nu}
\end{align*}
\]

Fig. 1.5. Drag coefficient for spheres as a function of the Reynolds number

Curve (1): Stokes' theory, eqn. (6.10); curve (2): Oseen's theory, eqn. (6.13)

Fig. 4.14

The drag force on a sphere in a cross flow is given in Fig. 4.14 which is a reproduction of Fig. 1.5 in H. Schlichting [8], where \( C_D \) is defined as the drag force normalized with the stagnation pressure \( \frac{1}{2} \rho V^2 A \), \( A \) being the central cross section of the sphere. The drag force is seen to be proportional to the velocity for very small Re-numbers and proportional to the square of the velocity in the range \( 10^4 < R_e < 10^5 \). The most likely situation for small oil droplets seems to be in the lower range of Re-numbers, and consequently the components of the drag force will be:

\[
\begin{align*}
F_x &= -k[\ddot{x} - u(x,y)] \\
F_y &= -k[\ddot{y} - v(x,y)]
\end{align*}
\]

where \( k \) is a proportionality factor. Introduced into (2.1) this will give

\[
\begin{align*}
\dot{m} + k \ddot{x} &= k u(x,y) \\
\dot{m} + k \ddot{y} &= k v(x,y) - B
\end{align*}
\]

which are the basic equations governing the motion of the oil droplet.

One may now assume that the flow field exhibits a characteristic length \( A \) and a characteristic velocity \( U_c \) by means of which the following non-dimensional quantities can be introduced:
\[ \xi (x - x_o) / A \] = non-dimensional x-coordinate

\[ \zeta = y / A \] = non-dimensional y-coordinate

\[ \tau = t \frac{U_c}{A} \] = non-dimensional time

\[ u^* = u / U_c \] = non-dimensional velocity components

\[ v^* = v / U_c \] = non-dimensional velocity components

With these quantities the basic equations will appear in the form:

\[
\begin{align*}
\frac{d^2 \xi}{dt^2} + \lambda \frac{d \xi}{dt} &= \lambda u^* (\xi, \zeta) \\
\frac{d^2 \zeta}{dt^2} + \lambda \frac{d \zeta}{dt} &= \lambda v^* (\xi, \zeta) - \beta
\end{align*}
\] (2.6)

where

\[
\begin{align*}
\lambda &= \frac{kA}{mU_c} \\
\beta &= \frac{B \cdot A}{mU_c^2}
\end{align*}
\] (2.7)

The physical quantities in these dimensionless parameters are:

\[ U_c \] = the characteristic velocity of the flow field

\[ m = \rho_o V \] = mass of the droplet

\[ V = \frac{\pi d^3}{6} \] = volume of the droplet

\[ d \] = diameter of the droplet

\[ A \] = characteristic length of the flow field

\[ B = g(\rho - \rho_o) V \] = buoyancy force of the droplet

\[ k \] = proportionality factor for the drag force which is here assumed proportional to the velocity

\[ (2.8) \]
From Fig. 4.2 one finds the drag force \( F \) under such conditions as

\[
F = 25 \cdot \frac{1}{2} \rho \frac{1}{4} \pi d^2 \left( \frac{\nu d}{\nu} \right)^{-1}
\]

\[
= 9.81 \cdot \nu d \quad \text{i.e.} \quad k = 9.81 \cdot \mu d
\]  

(2.9)

One may now reformulate the two parameters in (2.7) as follows:

\[
\lambda = \frac{9.81 \cdot \nu \cdot d \cdot A}{\rho_o \frac{\pi}{6} d^3 U_c} = 18.74 \frac{\rho}{\rho_o} \frac{\nu}{U_c} \frac{A}{d}
\]

(2.10)

\[
\beta = \frac{\left( \rho - \rho_o \right) g \frac{\pi}{6} d^3 \cdot A}{\rho_o \frac{\pi}{6} d^3 U_c^2} = \left( \frac{\rho}{\rho_o} - 1 \right) \frac{A}{U_c^2}
\]

(2.11)

The dimensional quantities will here have the following numerical values.

\( \rho = \) density of water (or sea water) \( 1.0 \) [gr/cm\(^3\)]

\( \rho_o = \) density of oil \( 0.86[\text{gr/cm}^3] \)

\( \nu = \) viscosity of water \( 1.0 \cdot 10^{-6}[m^2/s] \)

\( A = \) length characterizing the flow field \( 1 \) [m] \(< A < 10 \) [m]

\( U_c = \) velocity characterizing the flow field \( 1 \) [m/s] \(< U_c < 5 \) [m/s]

\( d = \) diameter of a droplet \( 10^{-6}[m] < d < 10^{-4}[m] \)

A Reynolds number for the problem may now be formed as

\[
Re = \frac{U_c d}{\nu}
\]

(2.13)

and with the numerical values given above the following range of variation of Re is obtained:

\[
1 < Re < 500
\]

(2.14)
Furthermore, the two parameters $\lambda$ and $\beta$ will have a range of variation like:

\begin{align*}
4.36 \times 10^2 < \lambda < 2.18 \times 10^8 \\
0.064 < \beta < 16
\end{align*}

It is now from the magnitude of the parameter $\lambda$ rather obvious that cases may occur where the acceleration terms in (2.6) become negligible, and consequently the equations reduce to:

\begin{align*}
\frac{d\xi}{dt} &= u^*(\xi, \zeta) \\
\frac{d\zeta}{dt} &= v^*(\xi, \zeta) - \frac{\beta}{\lambda}
\end{align*}

(2.16)

This may be carried even further by observing that the flow field is two-dimensional and that in the case of an incompressible fluid, one then has a stream-function $\psi$ for the flow from which the velocity components are deduced:

\begin{align*}
u^* &= \frac{\partial \psi}{\partial \xi}/U_c \\
\nu^* &= \frac{\partial \psi}{\partial \zeta}/U_c
\end{align*}

(2.17)

Introducing the two non-dimensional quantities $\xi$ and $\zeta$ from (2.5) one may rewrite this

\begin{align*}
u^* &= \frac{\partial \psi}{\partial \xi}/AU_c \\
\nu^* &= -\frac{\partial \psi}{\partial \zeta}/AU_c
\end{align*}

(2.18)

which may be introduced into (2.16) to give:

\begin{align*}
\frac{d\xi}{dt} &= \frac{\partial \psi}{\partial \xi}/AU_c \\
\frac{d\zeta}{dt} &= \frac{\partial \psi}{\partial \zeta}/AU_c - \frac{\beta}{\lambda}
\end{align*}

(2.19)
The ratio of these equations may be written

\[
\frac{dx}{d\xi} = -\frac{\partial \psi^*}{\partial \xi} - \frac{B}{\lambda}
\]

which is the differential equation for the path of the droplet given by \(\xi\) as a function of \(\xi\) and where \(\psi^*\) is defined as

\[
\psi^* = \frac{\psi}{\nu \sigma A}
\]

The solution to (2.20) is easily found by introduction of the path-function \(\theta\):

\[
\theta = \psi^* + \frac{\xi B}{\lambda}
\]

Equation (2.20) now reduces to

\[
\frac{dx}{d\xi} = -\frac{\partial \theta}{\partial \xi}
\]

with the solution

\[
\theta = \text{constant.}
\]

Under the given conditions, the path of an oil droplet is given in terms of the streamfunction of the flow as

\[
\psi^*(\xi, \zeta) + \frac{\xi B}{\lambda} = \text{const.}
\]

This general solution will now be examined in the two cases of recirculating flow treated earlier.

4.3.3 Particle Paths in a Boundary Layer Type Flow

In the discussion of the recirculating flow in the ocean (Section 4.2) the boundary layer type flow was treated and the analytic description of the flow was carried so far that expressions for the streamlines in the flow were established. Since the path of oil particles (droplets) of the size of interest here is given in terms of the streamfunction of
the flow (2.25), the program STREAM (Appendix) has been used to plot the particle paths in environments given as the flow of Fig. 4.9. The result of such computations is shown in Fig. 4.15. As seen from (2.25) the results will depend on the Particle-number \( P = \beta / \lambda \).

Fig. 4.15 Paths of Oil Particles in a Boundary layer type flow

\[ P = 0.001 \]
\[ P = 0.0001 \]

This P-number can be expressed through (2.10) and (2.11) as

\[ P = \frac{(\rho - \rho_o)gV}{kU_c} = \frac{buoyancy\ force}{characteristic\ drag\ force} \]  

(3.1)

or as

\[ P = 0.0534\left(1 - \frac{\rho_o}{\rho}\right)\frac{g\alpha^2}{\nu U_c} \]  

(3.2)

It is easily seen that the P-number decreases with decreasing droplet size and increasing characteristic velocity of the flow. The P-number for the particles in question will be very small and for this reason Fig. 4.15 has been prepared with \( P = 0.001 \) and \( P = 0.0001 \). In the first case, the oil particles are seen to rise relatively rapidly, i.e., they have
enough buoyancy to "loosen the grip" that the flow has on them. In the latter case it is seen that the particle is "trapped" by the mean flow over a much longer distance before it is able to rise to the surface. For \( P = 0.00001 \), the paths of oil particles become indistinguishable from the streamlines within the frame of Fig. 4.15. By contemplating the consequence of (2.25), one may conclude that the smaller the particle is, the further downstream and the further down from the surface it will be carried before being released by the dying out of the recirculating flow. The entrainment mechanism is therefore well explained.

4.3.4 Particle Path in a Jet Type Flow

In the discussion of the re-circulating flow in the ocean the special case was modeled on the plane jet flow. Since also in this case the analytical deductions were carried to the point where the expression for the stream function was established, the computation of the path of oil particles may follow just as easily as in the previous case. The program OIL2 (Appendix) was used for this purpose and the result is shown in Fig. 4.16. The flow corresponds to Fig. 4.12. The same remarks which were made in the previous section apply also in this case. One additional

![Fig. 4.16 Paths of Oil Particles in a Jet Type Flow](image-url)
remark may be made. From Fig. 4.16 one may pick out the non-dimensional depth $d$ to which an oil particle will be carried if it initially is placed at a depth $d_i$.

<table>
<thead>
<tr>
<th></th>
<th>$P = 0.01$</th>
<th></th>
<th></th>
<th>$P = 0.001$</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_i/A$</td>
<td>$d/A$</td>
<td>$d/d_i$</td>
<td>$d/A$</td>
<td>$d/d_i$</td>
<td>$d/A$</td>
<td>$d/d_i$</td>
</tr>
<tr>
<td>0.43</td>
<td>1.00</td>
<td>2.33</td>
<td>3.30</td>
<td>7.67</td>
<td>0.70</td>
<td>1.85</td>
</tr>
<tr>
<td>1.20</td>
<td>3.30</td>
<td>2.75</td>
<td>10.00</td>
<td>8.33</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

This shows that a particle can, depending on its $P$-number, be carried to depths many times the original depth to which it is being brought by actions at the surface.

4.4 THE EXPERIMENTS

4.4.1 Introduction

Three different experiments pertaining to the entrainment process are described in Section 4.1. The Wind-Wave experiment was conducted by Steven Parks under the supervision of Dr. R. Dowdell and a description of this activity is found in Section 3 of this report.

The Drop-Size Experiment was conducted by Mathew Cherian and the results obtained in his 20 gallon tank will be given here and commented upon.

The Rain-Drop Experiment was conducted by Ted Kawazoe and both experiments were supervised by the author. The earlier experimentation in the rain drop apparatus was supervised by Dr. Cornillon.

4.4.2 The Parameters

Conditions under which the experiments are conducted are determined by several parameters whose importance may not be initially recognized. One may easily identify such parameters as surface tension, temperature, oil slick thickness, intensity of the recirculating flow, etc. as important ones, but it is difficult offhand to judge their relative influence. One or more may be of such importance that it obscures the influence of others. The experimentation was originally planned exclusively in sea water but practical considerations led to some experiments being performed in fresh water. The influence of the type of water on the entrainment could thus be commented on.

Because of difficulties in keeping a constant quality of the sea water to be used, it was decided to measure the surface tension of the water/air interface. In this way one hoped to be able to detect natural surfactants that might be present in the water. For that purpose, a test
was made to see how sensitive such a measurement would be to the presence of the dispersant COREXIT 9527 in the water. The result of this test is shown in Fig. 4.17. It is seen that very small concentrations give very large effects and that the surface tension water/air for a concentration of 2.5[mg/l] is almost as small as for COREXIT 9527 alone.

![Surface Tension Graph](image)

Fig. 4.17 The Effect of Addition of a Dispersant on Measured Surface Tension Water/Air

During this experiment it was discovered that the actual result of a measurement was dependent on the person who performed the test, i.e., that an element of personal judgment was involved. The values should therefore only be given a relative importance.

The next step in the investigation of the parameters was to find a way to ascertain the "strength" of the recirculating flow which presumably is responsible for the entrainment. For that purpose, a hot film Anemometer DISA with a probe 55A87 (conical, quartz coated) was used.
Its performance was examined in a towing tank for calibration and subsequently used for examining the flow created in the tanks by the impellers.

The results of the flow measurements in the 20 gallon tank of the Drop-Size-experiment are shown in Fig. 4.18 where a plot of a plane through the centerline of the tank is shown with the measuring stations indicated by small circles and with curves of equal mean velocity. The plots are shown for different values of the impeller speed (measured in rpm) and it is observed that the general features of the flow pattern seem to be preserved with an increase in mean velocities as the impeller speed is increased. It is clear that a closer examination of the velocity field in the immediate subsurface region might be of interest when exploring the details of entrainment in cases where the flow itself is responsible for the creation of entrainable particles. Such a study must, however, in light of the increased demand on accuracy, equipment and time be considered outside the scope of the present effort. It is, however, observed that the radial velocity gradient along the surface increases with increasing impeller speed. Thus, the impeller speed may be used as a parameter in the experimentation.

The recirculating flow is characterized also by the turbulent intensity. This quantity was measured and Fig. 4.19 exhibits the results in the 20 gallon tank of the Drop-Size experiment. It is observed that the turbulent intensity is rather evenly distributed throughout the tank. A feature which may be of interest is that the lowest impeller speed seems to create a greater turbulent intensity close to the impeller than do the higher speeds. In all cases, the turbulent intensity is of the same order of magnitude. Thus one may already conclude at this point that any influence on the entrainment process, which may be observed due to a change in impeller speed, may be attributed to a corresponding change in velocity gradient along the surface and not necessarily to a change in turbulent intensity.

These remarks conclude the preliminary remarks on the parameters of the experiments. The effect of each one of the other parameters will be discussed in the presentation of the results.
The mean velocity of the turbulent recirculating flow in the 20 gallon tank measured at different impeller speeds.
The turbulent intensity measured in the 20 gallon tank's upper part at different impeller speeds.
4.4.3 The Drop Size Experiment

In the exposition of the author's concept of the entrainment process, a mechanical agitation of some sort, acting at the surface was supposed to be responsible for the creation of "entrainable particles". In the Rain Drop Experiment (Section 4.4.4), the rain impinging on the oil slick is such a mechanical agitation. As pointed out in Section 4.1, some focus their attention on the breaking waves as the mechanism for introducing the necessary action. In the present experimentation no mechanical agitation other than what is being brought about by the recirculating flow (impeller) is present at the surface. It is important to show that entrainment can be brought about even in the absence of breaking waves.

Table 4.1 shows the values of the different parameters used in the different experiments. It is noticed that the surface tension data

<table>
<thead>
<tr>
<th>Table 4.1 Experimental Parameters of Drop-Size Experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>WATER:</strong></td>
</tr>
<tr>
<td>FRESH</td>
</tr>
<tr>
<td><strong>TEMPERATURE:</strong></td>
</tr>
<tr>
<td><strong>OIL ADDED:</strong></td>
</tr>
<tr>
<td><strong>SURFACE TENSION:</strong></td>
</tr>
<tr>
<td><strong>IMPELLER SPEED:</strong></td>
</tr>
</tbody>
</table>

indicate what may seem an insignificant difference between fresh water and sea water. The data in the latter case are consistently higher, but with a difference which in view of the uncertainty of the measurements, makes a distinction between the two very difficult.

The amount of oil added to the surface in the tank is either approximately 30 ml or 60 ml. This is the way in which the thickness of the oil is varied. A finer gradation of the thickness is not necessary in view of the scope of the investigation.

The temperature at which the experiments were performed was imposed by the ambient temperature. A systematic investigation of the influence of this parameter thus became almost impossible.

Fig. 4.20 shows a sketch of the so-called "20 gal. tank". It is seen to be equipped with 4 taps at different depths under the surface through which samples of the water with the entrained oil can be taken. The impeller was placed very close to the bottom of the tank and the measurements of Figs. 4.18 and 4.19 were made in the region above a depth of 10", i.e. well above the impeller. The entrainment was measured as concentrations of oil in the samples taken through the taps according to a determined time schedule. This schedule ran first for 4 hours and was later changed to 10 hours; in both cases control samples were taken after
Fig. 4.20 The "20 gal. tank" of the Drop-Size-Experiment

24 hours. The results of these measurements are exhibited in Figs. 4.21a - d. The running time for the impeller is shown in the diagrams.

In contemplating the conclusions which may be drawn from these results the scarcity of them, and consequently their inherent uncertainty, should not be overlooked. However, some results seem well established and will also be supported from other sources.

Starting with Fig. 4.21b, one observes that the three experiments have been made under almost identical conditions as far as water type, impeller speed and surface tension is concerned. In E 12/07 and E 12/19 even the same amount of oil was added. The temperature during the experiments differs however by approximately 10°C without any noticeable difference in entrainment. Thus it seems that the temperature is not a parameter which in this range strongly influences the entrainment. If however the third experiment E 11/16 is considered, a comparatively large increase in entrainment is noticed and since temperature is ruled out, this can only be attributed to the fact that in the latter case the oil film is thinner (only half as much oil added). So, with the slim background of three experiments (E 11/16, E 12/07, E12/19) the following conclusions are attempted:

1. Within the range of variation of the temperature (4°C - 14°C) the influence of temperature on entrainment seems negligible.

2. The entrainment from a thin slick is, under the same conditions, larger than from a thick slick.
These preliminary conclusions will be examined in the light of later results.

**Table 1**

<table>
<thead>
<tr>
<th>WATER: TAP WATER</th>
<th>IMPELLER SPEED: 65.81 rpm</th>
<th>TEMPERATURE: 21.5°-22°C</th>
<th>OIL QUANTITY: 42.75 g</th>
<th>SURFACE TENSION: 681 dynes/cm</th>
</tr>
</thead>
</table>

**Graph 1**

**Graph 2**

**Fig. 4.21a**
E 11/16

ROTOR

WATER: SEA WATER
IMPELLER SPEED: 149.6 rpm
TEMPERATURE: 20°-16°C
OIL QUANTITY: 41.62 g
SURFACE TENSION: 69.4 dynes/cm

Concentrations (mg/l) vs Time (hrs)

E 12/07

ROTOR

WATER: SEA WATER
IMPELLER SPEED: 150.6 rpm
TEMPERATURE: 17°-14°C
OIL QUANTITY: 97.0 g
SURFACE TENSION: 69.2 dynes/cm

Concentrations (mg/l) vs Time (hrs)

E 12/19

ROTOR

WATER: SEA WATER
IMPELLER SPEED: 148.7 rpm
TEMPERATURE: 7°-4°C
OIL QUANTITY: 95.4 g
SURFACE TENSION: 69.9 dynes/cm

Concentrations (mg/l) vs Time (hrs)

Fig. 4.21b
**E02/02**

- **WATER**: Tap Water
- **IMPELLER SPEED**: 310 rpm
- **TEMPERATURE**: 17° - 14°C
- **OIL QUANTITY**: 50.2 g
- **SURFACE TENSION**: 69.1 dynes/cm

**Concentrations (mg/l)**

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**E02/21**

- **WATER**: Tap Water
- **IMPELLER SPEED**: 153.5 rpm
- **TEMPERATURE**: 19° - 14.5°C
- **OIL QUANTITY**: 47.3 g
- **SURFACE TENSION**: 68.8 dynes/cm

**Concentrations (mg/l)**

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 4.21c
At this point it might be mentioned that the impeller speed was adjusted in such a way that small vortices could be identified as "dents" in the water surface, which moved around, appeared and vanished in an apparent stochastic manner. This occurred at impeller speeds of approximately 150 rpm, i.e., at the speed used in the above experiments. It is thought that the occurrence of such vortices represent the mechanism whereby the oil slick is fragmented and whereby entrainable particles are being produced. It is then logical to deduce that this "fragmentation" due to vortices is more easily done where the slick is thin than when it is thick (in complete agreement with the result). Since it is desirable to establish the influence on the entrainment of the recirculating flow, the variation of the impeller speed becomes important.

If one considers the entrainment obtained in E 12/07 and E 12/19 one will find that very little is being entrained, in fact so little that the concentrations obtained during the time when the impeller is rotating are equivalent to those still found 20 hours after the recirculating flow was "stopped." This suggests a lower limit for the impeller speed below which very little oil is being entrained and this limit may depend on the oil slick thickness. This point will be reexamined in the light of subsequent results.

Consider now the results of Fig. 4.21a. A comparison between E 10/29
and E 11/16 shows that the values of temperature, oil slick thickness, impeller speed and surface tension are almost equal. Thus the tremendous difference in entrainment in the two cases may be attributed to the fact that one experiment is done in fresh water and the other in sea water. On the other hand, the experiment E 10/17, which is done under almost identical conditions except for the impeller speed being much less, show almost no entrainment. One is now faced with the following possible conclusions:

3. The entrainment of oil in the water column under otherwise equal conditions seems to occur much more easily in fresh water than in sea water. This is in contrast to other observations (see Section 4.4.5 Final Remarks)

4. Entrainment of oil in the water column is very strongly dependent on the "strength" of the recirculating flow.

The results at this point show that the samples from the different taps are influenced so much by occasionally trapped larger oil droplets that a concentration gradient in the vertical direction may not be experimentally determined. Thus the conclusions so far have been drawn on the basis of mean values of the instantaneous concentrations measured at the 3 taps.

It has furthermore been assumed that after 4 hours some kind of equilibrium state has been reached. This is tested in the experiments shown in Fig. 4.21c-d. where the period over which samples were taken is increased. It seems to be confirmed that the "equilibrium" has been reached after 4-6 hours.

The experiment E 02/21 is seen to be almost identical to E 10/29 as far as most parameters are concerned. There is however a difference in temperature between the two cases of approximately 10 C. This means that the previous statement about the influence of temperature perhaps must be modified, because there is a difference of 10 - 15% in concentration between the two cases which can be explained as the influence of temperature. The rather high concentration measured seems, however, to be a consistent result. The result of E 02/02 are obtained with a rather high value of the impeller speed. During the experiment it seemed as if all oil on the surface was being entrained. If one assumes from the data a uniform concentration of 350 [mg/l] in the water, the totally entrained mass of oil will be 26.5 [gr] or approximately half the oil added. Apparently this high value of the impeller speed represents the upper limit for sensible experimentation in the apparatus used.

Fig. 4.21d shows the results for a rather high value of the impeller speed and with sea water. Gathering all results, one may now present them as done in Fig. 4.22 where the mean maximum concentration is plotted as a function of the impeller speed. The legend used to identify the experiments are shown in Figs. 4.21 a-d.

It seems as if the following conclusions may be drawn:

1. The influence of temperature on the entrainment may hardly be estimated from the results of these experiments. Emphasis is
put on the scarcity of experimental evidence and the limited temperature range. (See the Rain-Drop experiment, section 4.4.4).

2. The entrainment from a thin slick is under the same conditions, larger than from a thick slick. (As before).

3. The entrainment of oil in the water column under otherwise equal conditions seems to occur much more easily in fresh water than in sea water. (As before, with reservations).

4. Entrainment of oil in the water column is very strongly dependent on the "strength" of the recirculating flow. (As before).

4.4.4. The Raindrop Experiment

This experiment is discussed in Section 4.1.5. It distinguishes itself from the experiment originally carried out in the same rig by the fact that an impeller has been installed at the bottom of the receiving tank. This creates a recirculating flow which, in the author's concept, is responsible for the entrainment. This experiment also distinguishes itself from the previous one (preceding section) in the presence of a mechanical agitation (rain falling) at the surface.
The parameters of the experiment are the same as in the preceding section but now one has the rain intensity as an additional parameter. The rain maker (tank B, Fig. 4.2) had a variable performance due to the clogging up of the needles producing the raindrops. This is due to the fact that salt water (sea) was used to produce the rain to avoid the complication of having a mixture of salt and fresh water at the surface. The rain intensity was attempted to be kept constant during the conduction of an experiment, but variations of 10% had to be accepted. The rain intensity may be expressed in different ways. One may give it as the amount of rain falling over the entire surface per unit time (in hour). One may however give it as the kinetic energy of the raindrops as they hit the surface. In this latter case, the rain intensity may be the same for different heights and different drop sizes as well as for different drop frequencies. An examination of this effect has so far not been made, and for the present purpose the first way of describing the rain intensity has been used.

Fig. 4.23 shows a sketch of the receiving tank. Water samples are

Fig. 4.23. The receiving tank in the rain drop experiment.

being collected through the taps 1 - 4 where glass tubes go almost to the center of the tank. Thus water samples are collected at different depths and ought to reflect a possible vertical gradient in the concentrations of oil in the samples. Such a gradient is indicated by the photo of the tank emptied after one normal experiment. (Fig. 4.24) The oil clinging to the outside of the glass tubes is dependent on the size and frequency of the droplets hitting the tubes. The photo shows that much more oil is collected by the upper tubes than by the lower ones. A corresponding gradient in the concentrations measured in the samples is not present because it is obscured by the large variations one may have due to occasional pick up of large oil droplets during sampling. This is, of
course, a source of inaccuracy in the experimentation which might have been avoided by increasing the physical size of the apparatus or by taking ensemble averages over a large number of identical runs. With these remarks in mind one may turn to Table 4.2 where a survey is given over the variation of the parameters in the experiments RD-7 through RD-18. In addition, the results of each experiment are shown in Figs. 4.25a-j as a record of the concentration of oil in the water column as a function of the time at which the samples were taken, the time $t = 0$ being the time at which the oil was applied to the surface. (A steady state of the rain as well as of the recirculating flow is assumed established beforehand). It should be noted that the size of the impeller as well as of the tank differ from those of the preceding section and no comparison can therefore be directly obtained between the two cases.

One may start the examination of the results by considering RD-11, RD-12, RD-14, RD-15, and RD-16 which all are cases where the rain has been stopped hours before the rotor was shut off. All of these show that regardless of the impeller speed (within the range of variation used) the concentration of oil entrained in the water column drops off dramatically as soon as the rain stops, i.e. as soon as the production of entrainable particles stops, even though the recirculating flow is maintained. Since the level of concentration reached after shutting off the rain is close to that after 24 hours one may conclude that in contrast to the drop size experiment the impeller speed is in this case kept so low that the recirculating flow does not contribute significantly to the production of entrainable particles. Its main effect is the transport of oil particles from the vicinity of the surface down into the water column. Apart from RD-14 this is a feature common to all experiments in this series, and it

Fig. 4.24. Photo showing the gradient in the oil collected by the glass tubes.
### Table 4.2 Experimental Parameters for Raindrop Experiments with Circulation.

<table>
<thead>
<tr>
<th>No.</th>
<th>Amount of oil [ml]</th>
<th>Impeller Speed [rpm]</th>
<th>Rain Rate [1/hr] at beginning</th>
<th>Rain rate [1/hr] at end</th>
<th>Temperature [°C]</th>
<th>Fall distance [cm]</th>
<th>Water</th>
<th>Surface tension [g]</th>
<th>Drop Size [g]</th>
<th>Intentions</th>
<th>Remarks</th>
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<tbody>
<tr>
<td>AO-7</td>
<td>300</td>
<td>178.8 pm</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>166</td>
<td>Sea</td>
<td>-</td>
<td>-</td>
<td>cancelled</td>
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</tr>
<tr>
<td>AO-8</td>
<td>300</td>
<td>178.8 pm</td>
<td>-</td>
<td>-</td>
<td>18 [cream]</td>
<td>15 [water]</td>
<td>at 0 h</td>
<td>15 [water]</td>
<td>at 0 h</td>
<td>Fresh</td>
<td>-</td>
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<tr>
<td>AO-9</td>
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<td>169.1</td>
<td>2.58</td>
<td>8.87</td>
<td>166</td>
<td>Sea</td>
<td>-</td>
<td>(.000011)</td>
<td>Drop size: .000011 g/drop (From AO-14)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AO-10</td>
<td>300</td>
<td>166.1</td>
<td>8.60</td>
<td>2.33</td>
<td>165</td>
<td>Fresh</td>
<td>77.4</td>
<td>77.3</td>
<td>.000011</td>
<td>Sea water/fresh water could not be distinguished based on surface tension</td>
<td></td>
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<tr>
<td>AO-11</td>
<td>160</td>
<td>149.7</td>
<td>3.53</td>
<td>2.33</td>
<td>164</td>
<td>Fresh</td>
<td>78.3</td>
<td>.000011</td>
<td>Drop size: .000011 g/drop (From AO-14)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AO-12</td>
<td>160</td>
<td>149.7</td>
<td>2.33</td>
<td>3.68</td>
<td>165</td>
<td>Sea</td>
<td>78.3</td>
<td>(.000017)</td>
<td>Repeat of AO-11 (diff. water)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AO-13</td>
<td>160</td>
<td>147.6</td>
<td>3.60</td>
<td>3.90</td>
<td>165</td>
<td>Sea</td>
<td>78.3</td>
<td>(.000037)</td>
<td>Repeat of AO-15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AO-14</td>
<td>160</td>
<td>140.6</td>
<td>3.90</td>
<td>-</td>
<td>165</td>
<td>Sea</td>
<td>78.3</td>
<td>(.000011)</td>
<td>Drop size from AO-16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AO-15</td>
<td>160</td>
<td>140.6</td>
<td>3.90</td>
<td>-</td>
<td>165</td>
<td>Sea</td>
<td>78.3</td>
<td>(.000011)</td>
<td>Drop size from AO-16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AO-16</td>
<td>160</td>
<td>140.6</td>
<td>3.90</td>
<td>-</td>
<td>165</td>
<td>Sea</td>
<td>78.3</td>
<td>(.000017)</td>
<td>Repeat of AO-11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AO-17</td>
<td>300</td>
<td>140.6</td>
<td>3.90</td>
<td>-</td>
<td>165</td>
<td>Sea</td>
<td>78.3</td>
<td>(.000018)</td>
<td>Repeat of AO-8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AO-18</td>
<td>300</td>
<td>140.6</td>
<td>3.90</td>
<td>-</td>
<td>165</td>
<td>Sea</td>
<td>78.3</td>
<td>(.000018)</td>
<td>Repeat of AO-11 (modified)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table Notes:
- **Amount of oil [ml]**: The quantity of oil used in the experiment.
- **Impeller Speed [rpm]**: The speed at which the impeller rotates.
- **Rain Rate [1/hr]**: The rate at which rain falls in liters per hour.
- **Rain rate [1/hr] at end**: The rate at which rain falls at the end of the experiment in liters per hour.
- **Temperature [°C]**: The temperature at which the experiment was conducted in degrees Celsius.
- **Fall distance [cm]**: The distance the rain drops fall in centimeters.
- **Water**: The type of water used in the experiment.
- **Surface tension [g]**: The surface tension of the water used in grams.
- **Drop Size [g]**: The size of the drops used in grams.
- **Intentions**: The purpose or intentions of the experiment.
- **Remarks**: Additional comments or remarks about the experiment.
Fig. 4.25a

Fig. 4.25b
Fig. 4.25c

Fig. 4.25d

Fig. 4.25e

Fig. 4.25f
Water type: SEA
Rain intensity: 3.48 [l/hr]
Temperature: 15.5 [°C]
Oil quantity: 150 [ml]
Impeller speed: 150-159 [rpm]
Surface tension: 75.0 [dyne/cm]

Water type: SEA
Rain intensity: 3.69 [l/hr]
Temperature: 15-20 [°C]
Oil quantity: 150 [ml]
Impeller speed: 148-165 [rpm]
Surface tension: 76.9 [dyne/cm]

Water type: SEA
Rain intensity: 2.69 [l/hr]
Temperature: 13-15 [°C]
Oil quantity: 150 [ml]
Impeller speed: 156-174 [rpm]
Surface tension: 68.3 [dyne/cm]

Fig. 4.25g
Fig. 4.25h
Fig. 4.25i
makes the impeller speed rather unsuited as a parameter. The results can then be used to explore the influence of other parameters such as temperature, slick thickness, etc.

One more comment ought to be given at this point. The entrainment is seen to drop off dramatically when the rain stops, but the same is observed when the rain continues and the impeller stops. This latter case is investigated by Dr. Cornillon and Ted Kawazoe and the result is given in an internal report by Ted Kawazoe.
Fig. 4.26 gives a survey of the results. The average concentration $c$ of oil in the water column after 6 hours is plotted as a function of temperature with the oil slick thickness (given by the amount of oil applied to the surface) as the parameter. A distinction is made between tap water and sea water. One may now examine the four conclusions drawn in the preceding section.

![Graph showing concentration vs. temperature for sea water and fresh water](image)

Fig. 4.26. Results of the rain drop experiment 6 hours average concentration plotted as function of temperature.

First, it is confirmed that irrespective of what type of water is used, the entrainment is higher for a thin slick than for a thick one. Conclusion 2 is thus supported.

Second, oil is seen to be much more easily entrained in salt water than in fresh water. This is in contrast to the result in the preceding section, Conclusion 3, and will be commented on in the next section, Final Remarks.
Third, Conclusion 4 of the preceding section cannot be reconsidered here because the influence of the recirculating flow on the production of entrainable particles is totally overshadowed by the action of the rain for the impeller speeds used.

Fourth, the influence of temperature, Conclusion 1 in the preceding section, is here exhibited in Fig. 4.26. It is seen that apparently a weak influence of temperature on entrainment is found in fresh water but an apparently very strong dependence is found in sea water. It is however felt that further experimentation would be needed to form a fixed opinion on this point.

4.4.5 Final Remarks

Summing up the results of these experiments one should not hide the scarcity of information they give and the corresponding uncertainty in the conclusions one may draw. However, some results seem to be fairly well established.

1. In all cases the original concept of entrainment being brought about by one action producing entrainable particles and another action (the recirculation flow) transporting the particles down into the water column has been supported. No evidence to the contrary could be detected.

2. The mechanism responsible for the production of entrainable particles in the rain drop experiment is the action produced by the impinging drops. This action is basically different from the corresponding mechanism in the drop-size tank where the production is caused by the vortices in the turbulent recirculating flow. This difference may be the reason for the apparent discrepancy as regards Conclusion 3 in the two cases. If the evidence for forming an opinion on Conclusion 3 is examined one finds that in the case of the drop size experiment it is based on 3 fresh water and 4 sea water cases. In the rain drop experiment the opposite conclusion is based on 4 fresh water and 4 sea water cases. None of these can be disregarded as "wrong." Thus it is possible that whether or not entrainment occurs more easily in fresh water than in sea water really depends on the mechanism whereby entrainable particles are being produced.

3. Conclusion 2 seems to be fairly well documented and corresponds also to the general picture.

4. The influence of temperature was never really systematically investigated and the last paragraph of the preceding section really expresses the situation fairly well.

4.5 EXPERIMENTS WITH APPLICATION OF THE DISPER SANT COREXIT 9527

4.5.1 Introduction

The influence of a dispersant on the entrainment process was intended
to be investigated through application of the chemical during a process which has been investigated previously without such application. It was decided to use only Corexit 9527 as a dispersant and to spray it on to the oil slick in a ratio Corexit/Oil = 1:20. This does however not mean that when hydrocarbons are recovered in the water column this ratio will persist between the part originating from the dispersant and the other part originating from the oil. One task will therefore be to establish a method which rather rapidly can determine this ratio, and this has been accomplished and is reported on elsewhere (see Section 12.2, Appendix B).

It is recalled that all cases reported on here (drop size experiment as well as rain drop experiments) have shown that when the recirculating flow is stopped, the amount of permanently entrained oil in the water column is negligible. A second task for this part of the investigation is to ascertain whether or not this feature, valid for oil only, is affected by the application of a dispersant.

A third important task is to investigate whether or not the application of a dispersant can enhance the entrainment of oil in the water column in the absence of a recirculating flow. One would then have a situation whereby the mechanism of entrainment from being caused by mechanical action is changed to being caused by what might be interpreted as molecular diffusion. The importance of one as compared with the other becomes an interesting question.

4.5.2 The Still Water Experiment

The last problem mentioned in the introduction was investigated in the still water experiment. The tank of the rain drop experiment was filled with sea water and left for 24 hours to let any motion in the water die out. An oil slick of known magnitude was then applied to the surface of the water in the tank. Great care was taken so as to avoid inducing any motion in the tank. After four hours samples were taken in the water column to see how oil alone might have diffused. Immediately afterwards the dispersant was sprayed on to the slick and samples from the water column were taken two hours and seven hours later. All samples were taken through the usual taps in the containers (Fig. 4.20) and they were taken so slowly that no appreciable velocity was induced in the water column. The following data give the details of the experiment:

- Oil added: 62.68 [gr] to still Sea Water
- Corexit - Sea Water mixture: 9.49 [gr] Corexit
- 95.28 [gr] Sea water

Of this mixture 29.69 [gr] was sprayed on the slick giving an applied amount of Corexit = 2.68 [gr]

Ratio Corexit/Oil = r = 0.04280 = 1:23.4

Temperature: 27° - 28°C

Since this case also serves as a test case for the determination of the
ratio \( r = \frac{\text{Corexit}}{\text{Oil}} \) recovered in the water column, the details of the evaluation is here shown in Tables 4.3 and 4.4. The samples taken are numbered, the time when they were taken is given, the taps from which they originate are indicated together with the legend used in Fig. 4.27 to display the results of each aliquot which also is numbered (i). The actual recovered amount of each aliquot is given as well as the transmittance \( z \) and the absorbance \( a \) obtained by scanning each aliquot at a wave number of 2930 [cm\(^{-1}\)]. Finally, the volume of each sample is given, and this concludes the data of the experiment. The values of \( z \) and \( a \) appearing in parenthesis are obtained in the region where the spectrophotometer is uncertain and are data which are not considered.

First, samples 1 and 2 contain only oil, no dispersant having been applied when they were taken. Thus, the ordinary calibration coefficient may be used and the concentration \( c_o \) (shown in the column for \( c_{ci} \)) is, at both tap 3 and 4, of negligible magnitude. Thus, even after four hours not very much oil has diffused into the water column. It is seen that only one aliquot was necessary to establish this result.

Second, samples 3, 4, 5 and 6 contain oil and dispersant in a degree that could be detected with the naked eye. Five aliquots were applied successively and the result of scanning these is given. Now, if the assumption holds that the first 2-3 aliquots extracts the oil and only dispersant is present in the subsequent aliquots, then one may use the calibration curve for Corexit in these. This is shown in Table 4.3 and

<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Tap</th>
<th>Aliquot no.</th>
<th>Recovered g</th>
<th>Absorb.</th>
<th>Sample vol. ml</th>
<th>( c_{ci} ) mg/l</th>
<th>( c_{ci} ) mg/l</th>
<th>( c_{ci} ) mg/l</th>
<th>( c_{ci} ) mg/l</th>
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<td>1</td>
<td>6.74</td>
<td>80.4</td>
<td>688</td>
<td>6.00</td>
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<td>6.00</td>
<td>6.00</td>
</tr>
<tr>
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<td>6.15 pm</td>
<td>2</td>
<td>1</td>
<td>6.82</td>
<td>80.3</td>
<td>682</td>
<td>7.06</td>
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<td>80.9</td>
<td>602</td>
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<td>6.15 pm</td>
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<td>80.8</td>
<td>612</td>
<td>.699</td>
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<tr>
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<td>67.56</td>
<td>80.8</td>
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<td>6</td>
<td>67.56</td>
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<td>6.15 pm</td>
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<td>612</td>
<td>.699</td>
<td>80.93</td>
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<td>80.8</td>
<td>612</td>
<td>.699</td>
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<td>81.07</td>
<td>81.07</td>
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</tr>
<tr>
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<td>6.15 pm</td>
<td>12</td>
<td>67.56</td>
<td>80.8</td>
<td>612</td>
<td>.699</td>
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<td>.699</td>
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<td>67.56</td>
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<td>612</td>
<td>.699</td>
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<td>80.8</td>
<td>612</td>
<td>.699</td>
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<td>6.15 pm</td>
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<td>67.56</td>
<td>80.8</td>
<td>612</td>
<td>.699</td>
<td>80.93</td>
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<td>80.93</td>
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<tr>
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<td>6.15 pm</td>
<td>21</td>
<td>67.56</td>
<td>80.8</td>
<td>612</td>
<td>.699</td>
<td>81.07</td>
<td>81.07</td>
<td>81.07</td>
<td>81.07</td>
<td>81.07</td>
</tr>
</tbody>
</table>

Table 4.3  SEA WATER

Second, samples 3, 4, 5 and 6 contain oil and dispersant in a degree that could be detected with the naked eye. Five aliquots were applied successively and the result of scanning these is given. Now, if the assumption holds that the first 2-3 aliquots extracts the oil and only dispersant is present in the subsequent aliquots, then one may use the calibration curve for Corexit in these. This is shown in Table 4.3 and
displayed in Fig. 4.27, which show that indeed the latter aliquots gather around lines with a slope of -0.45. These data are used to find the lines in Fig. 4.27 by linear regression.

Having these, not only the total concentration of Corexit \((c_c, tot)\) in the sample can be computed but also the concentration \(c_c, i\) of Corexit indicated by the \(i\)th aliquot. This is shown in Table 4.3, where also the sum giving \(c_c (6)\) is computed.

![Fig. 4.27. Data shown to agree with the straight line behavior](image)

In Table 4.4 one now proceeds to compute \(c_c (6)\) which is the concentration of corexit in the sum of all aliquots. When these are added and their sum is scanned at a wavelength of 2930 [cm\(^{-1}\)] the absorbance \(a_m\) for the mixture is found. The iteration process previously described (see Section 12.2, Appendix B) will now render, and since the total concentration \(c_c, tot\) is known it is easy to compute \(c_0, tot\) as well as \(c_{tot}\) as shown in Table 4.4

**Table 4.4 Extraction of Oil and Corexit from Sea Water**

<table>
<thead>
<tr>
<th>No</th>
<th>(c_c (6)) [mg/l (H_2O)]</th>
<th>Total aliq. [gr]</th>
<th>(c_c (6)) [mg/l (CCl_4)]</th>
<th>(a_m)</th>
<th>(r)</th>
<th>(c_c, tot.) [mg/l (H_2O)]</th>
<th>(c_0, tot.) [mg/l (H_2O)]</th>
<th>(c_{tot.}) [mg/l (H_2O)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>11.87</td>
<td>233.9</td>
<td>38.05</td>
<td>3.75</td>
<td>18.18</td>
<td>4.87</td>
<td>23.05</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>6.46</td>
<td>234.0</td>
<td>21.97</td>
<td>2.03</td>
<td>9.89</td>
<td>4.87</td>
<td>14.76</td>
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</tr>
<tr>
<td>5</td>
<td>7.61</td>
<td>233.7</td>
<td>24.72</td>
<td>3.75</td>
<td>11.65</td>
<td>15.97</td>
<td>27.62</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>8.79</td>
<td>232.2</td>
<td>28.68</td>
<td>7.92</td>
<td>13.46</td>
<td>17.07</td>
<td>30.53</td>
<td></td>
</tr>
</tbody>
</table>
A tremendous enhancement in molecular diffusion is caused by the application of Corexit. This is independent of whether or not mechanical agitation of some sort is present. It is seen that whereas little oil and much Corexit is found after two hours, the situation has changed after six hours when the content of oil and Corexit seems to be evenly distributed in a ratio close to 1. This result will now be reconsidered in light of similar experiments.

4.5.3 The Drop Size Experiment with Corexit 9527

As mentioned in the introductory remarks, the influence of Corexit on the entrainment should be investigated by applying the chemical to a similar experiment that did not use it. Thus the experiment in the 20 gallon tank was planned as follows:

1. The rotor speed was supposed to be kept so low as to achieve a situation in which very little oil would be entrained from the slick. This was the situation in E 10/17 (tap water) even at a rather high ambient temperature, and an impeller speed of about 65 rpm was decided upon.

2. It was intended to let the experiment run without application of Corexit for approximately 6 hrs. to ensure that a semi-steady state had been reached. Samples were to be taken from taps 2 and 3 at 4 hrs., 5 hrs. and 6 hrs. after applying the slick to the surface (time zero).

3. Corexit would then be applied to the slick in a ratio 1:20 (total amount of Corexit: total amount of oil in the slick). Samples would be taken at 10, 11 and 12 hrs. (after time zero).

4. At this time the impeller speed is to be increased to the usual 150 rpm and new samples are to be taken at 24 and 25 hrs. (from time zero).

5. Then the impeller is shut off and final samples are taken at 48 hrs. (after time zero).

The data of the experiment can be summed up as follows:

Water: SEA WATER

Impeller Speed: 64.2 - 150 rpm.

Temperature: 24° - 27°C

Oil quantity: 51.56 gr

Corexit Quantity: 2.89 gr (Ratio: 1:17.8)

Surface Tension: 69.72 dynes/cm
Table 4.5 Experimental Results with Corexit 9527 and Circulatant

<table>
<thead>
<tr>
<th>No</th>
<th>Time Hrs.</th>
<th>Ratio Corexit/Oil</th>
<th>$c_C$ [mg/l $H_2O$]</th>
<th>$c_O$ [mg/l $H_2O$]</th>
<th>$c_{tot.}$ [mg/l $H_2O$]</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>.92</td>
<td>.92</td>
<td>Control Rotor Speed 64.2</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>.23</td>
<td>.23</td>
<td>Oil added at 0 Hrs.</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>.18</td>
<td>.18</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>0</td>
<td>0</td>
<td>.10</td>
<td>.10</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>0</td>
<td>0</td>
<td>.14</td>
<td>.14</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>1.061</td>
<td>250.1</td>
<td>235.7</td>
<td>485.8</td>
<td>Dispersant added at 6 Hrs.</td>
</tr>
<tr>
<td>9</td>
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<td>1.055</td>
<td>252.9</td>
<td>239.8</td>
<td>492.7</td>
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<tr>
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<td>1.626</td>
<td>274.2</td>
<td>168.6</td>
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<tr>
<td>11</td>
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<td>1.209</td>
<td>223.3</td>
<td>184.7</td>
<td>408.0</td>
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</tr>
<tr>
<td>12</td>
<td>14</td>
<td>1.191</td>
<td>276.0</td>
<td>231.8</td>
<td>507.8</td>
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</tr>
<tr>
<td>13</td>
<td>15</td>
<td>2.043</td>
<td>302.3</td>
<td>148.0</td>
<td>450.3</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>16</td>
<td>1.438</td>
<td>218.5</td>
<td>161.9</td>
<td>370.4</td>
<td>Rotor Speed increased to 150 rpm at 15 Hrs.</td>
</tr>
<tr>
<td>15</td>
<td>17</td>
<td>1.233</td>
<td>236.1</td>
<td>191.4</td>
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<td></td>
</tr>
<tr>
<td>16</td>
<td>18</td>
<td>1.312</td>
<td>218.6</td>
<td>166.6</td>
<td>385.2</td>
<td>Rotor stopped at 25 Hrs.</td>
</tr>
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<td>1.321</td>
<td>198.3</td>
<td>149.2</td>
<td>347.5</td>
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</tr>
<tr>
<td>18</td>
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<td>2.167</td>
<td>271.5</td>
<td>271.5</td>
<td>396.8</td>
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</tr>
<tr>
<td>19</td>
<td>21</td>
<td>2.903</td>
<td>249.8</td>
<td>86.0</td>
<td>335.8</td>
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</tr>
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The results of the experiment are shown in Table 4.5 and Fig. 4.28. In the latter the mean value of the concentrations at taps 2 and 3 is plotted against time. The results can be summed up as follows:

a. The initial impeller speed is so low that very little oil is being entrained.

b. The addition of Corexit causes a tremendous increase in entrainment.

c. Changing the impeller speed has very little affect on the amount of entrained hydrocarbons.
Fig. 4.28. Results of the drop size experiment with Corexit.

d. The amount of hydrocarbons still being entrained 24 hrs. after shut-off of the impeller indicates a very high degree of permanently entrained particles in contrast to the cases with oil alone.

e. The ratio Corexit/Oil in the samples is close to 1 but have a tendency to increase with time (after shut-off).

These results will be reconsidered in view of the results from the rain-drop experiment.

4.5.4 The Rain-Drop Experiment with Corexit

The basic philosophy behind this experiment is the same as explained in the previous case. The conduction of the experiment may be outlined as follows:

1. The apparatus is started up with the rainmaker as well as the rotor operating such that when the oil is applied to the surface, a semi-steady situation is present.

2. Oil is applied to the surface at time zero.

3. Samples are taken from taps 3 and 4 at 4, 5 and 6 hrs.
4. At 6 hrs. Corexit is applied to the slick in a ratio 1: 20 (i.e., mg Corexit: mg oil in the slick 1:20).

5. Samples are taken at 10, 11 and 12 hrs. from the same taps.

6. At 12 hrs. rotor and rain are shut off.

7. At 36 hrs. final samples are taken from the same taps.

The parameters of the experiment are:

Water type: SEA WATER
Rain Intensity: 2.74 l/hr.
Temperature: 26.5° - 29.8°C
Oil Quantity: 300 ml
Impeller Speed: 148.5 - 167.6 rpm.
Corexit Quantity: 12.5 gr (Corexit/Oil = 1:19.99)

The results of this experiment are found in Table 4.6 and displayed in Fig. 4.29. In the latter the mean value of the concentrations of

<table>
<thead>
<tr>
<th>No</th>
<th>Time [Hrs.]</th>
<th>Ratio Corexit/Oil</th>
<th>( c_C ) [mg/l ( H_2O )]</th>
<th>( c_O ) [mg/l ( H_2O )]</th>
<th>( c_{tot.} ) [mg/l ( H_2O )]</th>
<th>Remarks</th>
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<tr>
<td>1</td>
<td>4</td>
<td>0</td>
<td>0.0</td>
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<td>39.1</td>
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<td>0.0</td>
<td>22.6</td>
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<tr>
<td>2</td>
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<td>14.8</td>
<td>Corexit added at 6 hrs. after sampling</td>
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<td>0.0</td>
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<td>13.1</td>
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</tr>
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<td>156.5</td>
<td>318.6</td>
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<td>153.0</td>
<td>196.8</td>
<td>348.8</td>
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</tr>
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<td>12</td>
<td>0.890</td>
<td>135.8</td>
<td>152.3</td>
<td>287.9</td>
<td>Rain and rotor shut off at 12 hrs.</td>
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<td>2.457</td>
<td>140.6</td>
<td>57.2</td>
<td>197.8</td>
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</tr>
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</table>

Table 4.6 Results of Rain Drop Experiment with Corexit
Fig. 4.29. The results of the rain drop experiment with Corexit 9527 applied.

the two taps is shown as a function of time. The results may be summed up as follows:

A. The entrainment achieved by the rain and the recirculating flow within the first 6 hrs. is of the order of magnitude as in RD-18 and thus the previous results are confirmed (Fig. 4.25b).

B. The entrainment obtained after application of Corexit is orders of magnitude larger than before.

C. The ratio between Corexit and oil recovered in the samples is close to 1 but increases to about 2, 24 hrs. after shut off.

D. The seemingly "permanently" entrained hydrocarbons (from oil and from Corexit) is almost independent of the physical situation under which the entrainment was achieved.
4.5.5 Final Remarks

The present experimental investigation has supported the ideas advanced originally by the author to explain the physics of the entrainment process. Thus the importance of the recirculating flow has been effectively demonstrated. Also the importance of the production of entrainable particles has been exhibited, but the influence of temperature is not satisfactorily explored. A difference in the way in which oil is being entrained in fresh water as compared with sea water has been demonstrated. However, the possibility exists that the way in which entrainable particles are being produced may influence the entrainment. Thus the apparent discrepancy between entrainment in the two cases (Figs. 4.22 and 4.26) may be explained. It is however stressed that further experimentation on this point is highly desirable. (See Final Remarks, Section 4.4)

The application of Corexit 9527 to the oil slick has a dramatic effect. Both from the drop-size and the rain-drop-experiments one may draw the conclusion that the effect of the mechanical situation (strength of recirculating flow, production of entrainable particles, etc.) is almost completely overshadowed by the effect of Corexit. This is brought out also by the fact that even in the still water case the entrainment is considerable. Attention in this connection is drawn to the fact that in Fig. 4.28 no apparent effect is found due to the change in the recirculating flow (impeller speed). One may draw the conclusion that the mechanism behind entrainment of oil into the water column is highly affected when Corexit is applied.
References


   Thomas Kim, Mathew Cherian, William Jasper, "Drop Size Distributions and Mixing Energy."
   David Konigsberg, Peter Cornillon, "Preliminary Results of an Experiment to Measure Rain Induced Oil Entrainment."


5.0 Sample Application of the Oil Spill Model:
Georges Bank Oil Spill Simulations

Peter C. Cornillon
Malcolm L. Spaulding
Kurt Hansen
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5.0 SAMPLE APPLICATION OF THE OIL SPILL MODEL: GEORGES BANK OIL SPILL SIMULATIONS

5.1 Introduction

In this section, we describe the use of the oil spill fates model as a tool to analyze the effect of various treatment strategies on the fate of a simulated spill. The location of the spill was chosen at the center of the Cod spawning region on Georges Bank (Figure 5.1) and at a time, mid-winter, to affect a maximum impact on the Cod fishery. The output of the model resulting from these simulations was used as input to a fisheries model and is discussed in detail in Reed, Spaulding and Cornillon (1980) and Section 6 of this report. The discussion of these impacts will not be repeated here.

The size of the spill, 34,840 metric tons, as well as its duration, 39 hours, or spill rate, about 900 metric tons per hour (See Figure 5.2 for details of the spill characteristics) were chosen to correspond approximately to the Argo Merchant spill which occurred on Nantucket Shoals in December of 1977. The type of oil selected was a No. 2 like fuel oil also characterized in Figure 5.2.

Five different treatment scenarios were analyzed. By "treatment" we refer to application to the spill of chemical dispersants used to drive the oil on the surface into the water column. Although reducing the surface expression of the spill, such treatment will of course increase the concentration of hydrocarbons in the water column. The oil model has therefore been designed to follow the dispersed oil, and the surface slicks as well as to present the output in a convenient easy to understand graphical format. The five treatment scenarios examined in this section consist of one case in which no treatment was performed and four cases in which various fractions of the oil remaining on the surface were assumed to be driven into the water column, specifically, 25%, 50%, 75% and 100%. All treatment was assumed to take place 48 hours after the spill began, or approximately 9 hours after the last oil had leaked from the source. The various spill scenarios are outlined in Figure 5.3.

5.2 Environmental Variables

Environmental variables input to the model consisted of wind, water temperature and currents. The water temperature was assumed to be constant over the entire study area. The wind data were obtained from the Nantucket Airport Weather Bureau Station at three hour intervals. Missing wind data were obtained by linear interpolation between existing data points.

The current data were constructed from two sources. One source was the seasonal mean data of Bumpus (1973) (Figure 5.4). The data for a given season were assumed to apply only to the first day of that season. All other values were linearly interpolated between the two appropriate seasons. Bumpus' results were obtained from a long term surface drifter study, hence do not in general include short-lived wind induced currents (several days). These events were simulated by a two dimensional vertically averaged wind-current model using the Nantucket wind data as input. The wind induced currents were assumed to apply only to the
### Figure 5.1 Location of Spill

![Location of Spill Map](image)

**Figure 5.2: Model Input Parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spill location</td>
<td><em>(41.5N, 67.0W)</em></td>
</tr>
<tr>
<td>Thermocline depth</td>
<td>10 meters</td>
</tr>
<tr>
<td>Wind</td>
<td>December 1972</td>
</tr>
<tr>
<td>Temperature</td>
<td>December 1972</td>
</tr>
<tr>
<td>Currents</td>
<td>Winter 1972</td>
</tr>
<tr>
<td>Oil density</td>
<td>0.847 gm/cm³</td>
</tr>
<tr>
<td>Interfacial tension</td>
<td>30 dynes/cm</td>
</tr>
<tr>
<td>Kinematic viscosity</td>
<td>1 centistokes</td>
</tr>
<tr>
<td>Oil fractions (by weight)</td>
<td></td>
</tr>
<tr>
<td>Paraffin, C₆-C₉</td>
<td>0.1</td>
</tr>
<tr>
<td>Paraffin, C₁₃-C₂₂</td>
<td>0.25</td>
</tr>
<tr>
<td>Cycloparaffin, C₆-C₁₂</td>
<td>0.15</td>
</tr>
<tr>
<td>Cycloparaffin, C₁₃-C₂₂</td>
<td>0.15</td>
</tr>
<tr>
<td>Aromatic, C₆-C₁₃</td>
<td>0.15</td>
</tr>
<tr>
<td>Aromatic, C₁₃-C₁₈</td>
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</tr>
<tr>
<td>Naphtheno-Aromatic, C₉-C₂₅</td>
<td>0.15</td>
</tr>
<tr>
<td>Residual</td>
<td>0.0</td>
</tr>
<tr>
<td>Total</td>
<td>34,840 metric tons</td>
</tr>
<tr>
<td>Total number of spilllets</td>
<td>13</td>
</tr>
<tr>
<td>Oil spill rate</td>
<td>393.33 metric tons/hr</td>
</tr>
<tr>
<td>Total spill simulation time</td>
<td>30 days</td>
</tr>
<tr>
<td>Time step</td>
<td>3 hours</td>
</tr>
<tr>
<td>Horizontal dispersion coefficients</td>
<td>10m²/sec</td>
</tr>
</tbody>
</table>
### Figure 5.3 Cases Run

<table>
<thead>
<tr>
<th>Case</th>
<th>Site</th>
<th>Wind Temp.</th>
<th>Current</th>
<th>Chemical Disp. After 48 Hours</th>
<th>Diffusion</th>
<th>Entrain</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Georges Bank</td>
<td>December</td>
<td>Bumpus plus wind induced</td>
<td>0 %</td>
<td>10 m³/sec</td>
<td>Natural</td>
<td>30 Days</td>
</tr>
<tr>
<td>2</td>
<td>same</td>
<td>same</td>
<td>same</td>
<td>25 %</td>
<td>same</td>
<td>same</td>
<td>same</td>
</tr>
<tr>
<td>3</td>
<td>same</td>
<td>same</td>
<td>same</td>
<td>50 %</td>
<td>same</td>
<td>same</td>
<td>same</td>
</tr>
<tr>
<td>4</td>
<td>same</td>
<td>same</td>
<td>same</td>
<td>75 %</td>
<td>same</td>
<td>same</td>
<td>same</td>
</tr>
<tr>
<td>5</td>
<td>same</td>
<td>same</td>
<td>same</td>
<td>100 %</td>
<td>same</td>
<td>same</td>
<td>same</td>
</tr>
</tbody>
</table>

### Figure 5.4 Winter Currents

![Winter Currents Diagram]
upper few meters (down to the thermocline in this case) of the water column. Details of the model are given in Reed and Spaulding (1979), and Section 6 and 12.5 of this report.

5.3 Natural Entrainment of the Spilled Oil

The process of primary interest in the impact analysis discussed herein is dispersion - both natural and chemical. For natural dispersion, which proved to be of significance in the case studied, the entrainment rate obtained by Audunson (1977) in the Bravo Blowout Study is used. Audunson's expression is:

\[ \text{Fraction} = 0.1 \frac{(u^2)}{(w_0^2)} \]

where:

Fraction is the fraction by weight of the oil remaining on the surface to be entrained;

\( w_0 \) is a wind speed constant equal to 8.5 m/s

and

\( u \) is the measured wind speed at 10 m in units of m/sec.

For this model, Audunson's expression was modified by a factor decaying exponentially with time. The time constant used was two days. The intent of this term, selected in an ad-hoc fashion, is to incorporate weathering of the surface slick into the entrainment process. Often as the surface slick ages it becomes emulsified (water-in-oil) and is not as easily entrained as in the early stages. These effects may well have been masked in the derivation of the original equation for two reasons. First, the Bravo spill occurred over a fairly long period (weeks) so there was almost always fresh oil coming to the surface. Second, the crude oil involved in the Bravo spill did not appear to emulsify as readily as other oils.

In the case of chemical dispersion, a delay of 48 hours was implemented in the model before dispersants were applied. This delay was intended to simulate the time necessary to organize a treatment effort, and is, of course, a parameter that could be experimented with in future applications of the model.

The oil entrained is represented by marker droplets or particles. For each of the simulations discussed here, about 1900 droplets were used. Because the mass of oil in the water column varies from one scenario to the next and the number of droplets was fixed, the mass of oil represented by a marker droplet also varied from one scenario to the next. The particles were distributed randomly under the spill in the horizontal. In the vertical, they were assumed only to occupy the water column above the thermocline, 10 meters in this case. The particles were distributed randomly in these 10 meters.
5.4 Results

5.4.1 Mass Balance

The values of a number of variables of interest in assessing the various strategies are summarized in Table 5.1 for the last day of the simulation. Figures 5.5-9 show the mass balance as a function of time. The oil is very light so that about 40 percent evaporates within several hours of its release. The value is always within two percent of this even when all the oil is dispersed, case 5. Treatment earlier in time would of course decrease the mass to evaporate.

In case 1, no chemical dispersion, 8.6 percent of the original mass is entrained and the remaining 51 percent remains on the surface. These two values of entrained and surface mass increase and decrease, respectively, until, for the 100 percent dispersed case, 60 percent of the mass enters the water column, with none remaining on the surface. There is seven times as much oil in the water column for the totally dispersed case (case 5) as in the non-dispersed case (case 1). The mass distribution for all cases is identical for the period before any treatment.

5.4.2 Horizontal Area Over Which the Concentration exceeds the 50, 100 and 1000 ppb Predefined Values

Figures 5.10-13 are graphs of the horizontal area for which the oil concentration exceeds 50, 100 and 1000 ppb, respectively versus time. For the 50 ppb contours, the final area varies by 60 percent between the first three cases, but the last three high dispersed cases differ by only about 5 percent. For the 100 ppb and the 1000 ppb contours, only the last two dispersed cases are within 5 percent of each other. There is about a 10 to 20 percent reduction in the area covered when going from the 50 ppb contour to the 100 ppb contours. The area covered by the 1000 ppb contour is smaller in all cases. In the non-dispersed case, the final area for the 1000 ppb contours occurs at day 15 and the maximum concentration at day 30 is 476 ppb. The maximum concentration at day 30 for the dispersed cases exceeds 1650 ppb.

There are a couple of interesting points concerning these curves. First, for cases 2 to 4, the area which the 50 ppb contour covers is larger than the 100 percent dispersed case for the first 15 days. The areal extent for the 100 percent dispersed case does not exceed the others until between days 15 through 20. This is due to the natural dispersion which continues after treatment. The surface spillets movement causes the naturally treated mass to be entrained further to the east than the treated mass and thus increases the area covered. The amount of mass entrained after treatment decreases with an increase in percent dispersed as a result of lesser amounts of oil on the surface. The maximum difference between areas due to this increase in area is 25 percent and occurs at day 5 between the 25 percent and 100 percent cases. The difference in areal coverage between these two cases decreases to 20 percent for the 100 ppb contour and is less than 3 percent for the 1000 ppb contours. The areal extent during this same period for the 100 percent dispersed case (50 ppb) is less than the 50 percent and 75 percent dispersed cases by 20 percent and 5 percent respectively. For the 100 ppb contour, the 50 percent and 75 percent dispersed cases at day 5 are within nine
Table 5.1 Data for Cases Run

<table>
<thead>
<tr>
<th>% Disp</th>
<th>% in Atmosphere</th>
<th>% on Surface</th>
<th>% in Water Column</th>
<th>Final Area (km²) of Subsurface</th>
<th>ppb highest Conc. at day 30</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>40.2</td>
<td>51.2</td>
<td>8.6</td>
<td>1138</td>
<td>271</td>
</tr>
<tr>
<td>25</td>
<td>39.9</td>
<td>38.5</td>
<td>21.6</td>
<td>1505</td>
<td>206</td>
</tr>
<tr>
<td>50</td>
<td>39.9</td>
<td>25.6</td>
<td>34.5</td>
<td>1701</td>
<td>374</td>
</tr>
<tr>
<td>75</td>
<td>40.7</td>
<td>12.8</td>
<td>47.5</td>
<td>1763</td>
<td>577</td>
</tr>
<tr>
<td>100</td>
<td>39.6</td>
<td>0</td>
<td>60.4</td>
<td>1792</td>
<td>583</td>
</tr>
</tbody>
</table>

**MASS DISTRIBUTION**

- 1 - Mass in Water Column
- 7 - Mass on the Surface
- 8 - Mass in Atmosphere

**Figure 5.5** Mass Balance 0% Dispersed

**Figure 5.6** Mass Balance 25% Dispersed
Figure 5.7 Mass Balance 50% Dispersed

Figure 5.8 Mass Balance 75% Dispersed

Figure 5.9 Mass Balance 100% Dispersed

Figure 5.10 Areal Extent 50 ppb.
AREA COVERED BY SPILL

Figure 5.11 Areal Extent 100 ppm.

Figure 5.12 Areal Extent 1000 ppm. (10 days)

Figure 5.13 Areal Extent 1000 ppm. (31 days)
percent of the 100 percent dispersed case. As in the 50 ppb contour, the area of the 100 percent case is comparable to the other dispersed cases between 15 and 20 days after the spill for the 100 ppb contour. The 1000 ppb contours for all of the dispersed cases are very similar.

The other interesting feature of the areal extent curves is the decrease or leveling off of the area at approximately day 10 in most of the cases. This is due to the currents compressing the droplet cloud in the North-South direction. This is more noticeable in the 50 ppb contours and in the lower dispersed cases than in the higher contours and in the higher percent dispersed cases.

Charts including the contour lines and surface spills are included in Figures 5.14 through 5.24 for the 50 ppb, 100 ppb and the 1000 ppb lines. The non-dispersed case (case 1) is compared to cases 2 to 5 for the first two contours (Figures 5.14 to 5.17 for the 50 ppb contour and 5.18 to 5.21 for the 100 ppb contour) and the 25 percent dispersed case is compared to cases 3 to 5 in the 1000 ppb plots (Figures 5.22 to 5.24). In all of the views, the surface spills have identical movements due to identical currents and winds for all of the scenarios. The wind blows from the west and shift to the north during the first five days resulting in the L-shaped pattern of the spills. This causes the first spill to move furthest to the east and the last spill released to be to the south. The spills move together to the southeast during the remaining time that the oil is tracked.

The movement and shape of the subsurface contours show some similar characteristics. The area covered by the non-dispersed case is larger than the other cases 5 days into the spill as was cited before. The compressive effect of the currents is shown clearly at day 10 for the 50 ppb outlines. The subsurface currents are generally southerly but the magnitude of the currents on the northern edge of the cloud are greater than those at the southern edge. This results in a collapse of the North-South dimension of the cloud as well as decreasing the areal coverage. As the cloud moves further south, the difference in currents is not as great and with the help of diffusion, the contour assumes a square shape at approximately day 15.

The plots for the 100 ppb contours show the same general behavior with the exception that the contours assume a more regular shape by day 10. The 1000 ppb contours are very similar as was the areal coverage.

5.5 Conclusions

An open ocean oil spill can be simulated using the model developed and different response strategies can be investigated. The movement of the spilled oil dependent on environmental variables is of importance at the beginning of the spill for cleanup or treatment. The efforts must begin before the oil weathers or spreads, both of which would reduce the efficiency of any efforts. The spillets in these runs are spread out over an area greater or equal to four kilometers after 3 days, thus making any treatment or cleanup attempt difficult. The surface area covered is approximately 10-20 percent of the area covered by the subsurface 50 ppb contour. The surface area overlayed by the higher dispersed cases is greatly reduced by as much as a factor of 10 due to entrained mass.
Figure 5.14 Overhead Views 50 ppb. Case 1 vs. Case 2
Figure 5.15 Overhead Views 50 ppb. Case 1 vs. Case 3
Figure 5.16  Overhead Views 50 ppb. Case 1 vs. Case 4
120.0 HOURS AFTER START OF THE SPILL
MAP OF SPILLETs AND SUBSURFACE

360.0 HOURS AFTER START OF THE SPILL
MAP OF SPILLETs AND SUBSURFACE

240.0 HOURS AFTER START OF THE SPILL
MAP OF SPILLETs AND SUBSURFACE

720.0 HOURS AFTER START OF THE SPILL
MAP OF SPILLETs AND SUBSURFACE

Figure 5.17 Overhead Views 50 ppb. Case 1 vs. Case 5
Figure 5.18 Overhead Views 100 ppb. Case 1 vs. Case 2
120.0 HOURS AFTER START OF THE SPILL
MAP OF SPILLETs AND SUBSURFACE

360.0 HOURS AFTER START OF THE SPILL
MAP OF SPILLETs AND SUBSURFACE

240.0 HOURS AFTER START OF THE SPILL
MAP OF SPILLETs AND SUBSURFACE

720.0 HOURS AFTER START OF THE SPILL
MAP OF SPILLETs AND SUBSURFACE

Figure 5.19 Overhead Views 100 ppb. Case 1 vs. Case 3
Figure 5.20 Overhead Views 100 ppb. Case 1 vs. Case 4
Figure 5.21 Overhead Views 100 ppb. Case 1 vs. Case 5
Figure 5.22 Overhead Views 1000 ppb. Case 2 vs. Case 3
Figure 5.23 Overhead Views 1000 ppb. Case 2 vs. Case 4
Figure 5.24: Overhead Views 1000 ppb. Case 2 vs. Case 5
The subsurface component of the spills can be compared with each other in order to determine the best strategy for the least impact on fish or fish larvae. The first aspect to consider is the timing of the treatment. In these scenarios, it can be seen that any delay in treating the spill will result in an increase in the area impacted. For coastal water scenarios, influenced to a greater extent by tidal currents, the entrained oil may return to the spill site and this aspect must be taken into consideration. The response time will most likely be even more important in this case than in the open ocean case.

The next question to consider is the percentage of oil to be dispersed. The plots of areal extent do not show the cumulative area covered but do indicate the area covered at each time step. The dispersed cases always cover more area by the end of the scenarios, but this is not true for the first 5 days for the lower concentration outlines (50 and 100 ppb). This may be of importance when toxicity is considered. The concentration for the non-dispersed case is at most one-quarter that of any of the dispersed cases. Since the spill is in a fish breeding ground, the dispersed cases are overlying the same area so the same impact will be felt for all five cases (see Figure 5.10). The higher concentration cuts, which will have more impact on the adult fish, are a result of a higher percentage dispersion (see Figure 5.13). Some larvae are thought to be affected by 50 ppb and thus lethal levels of hydrocarbon concentration may exist long after initial treatment.

It is evident from these simulated spills that local currents are of great importance as well as are the winds. Not so apparent are the effects of treatment. For example, early treatment although increasing the concentration in the water, may actually result in a smaller impacted area because of the decrease in area resulting from natural entrainment from surface spillets. On the other hand, the lower concentrations resulting from natural entrainment in the untreated case may not impact the fisheries as much because of the lower toxicity. This complicated interplay must be investigated in greater detail in the future where such variables as response time, toxicity, etc., are varied in an in-depth application of the oil spill fishery interaction model.
REFERENCES


6.0 A Fishery Oil Spill Interaction Model

Mark Reed
Malcolm L. Spaulding
ABSTRACT

The oil spill - fisheries impact model has been used to simulate nine variations of an oil spill scenario on Georges Bank, producing a rough sensitivity analysis of system response. Following an overview of the model system, the results and implications of these simulations are discussed along with limitations of the approach used. It is suggested that the most significant unknowns in the system are the parameters governing recruitment dynamics in the fishery, toxicity threshold values and oil entrainment rates being of secondary importance in open ocean conditions.
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Figure 6.1  Map of Georges Bank, showing the 100 meter bathymetric contour, the spawning area (circle), oil exploration tracts (dark regions), commercial shipping lanes, wind data source ( ), and the location of the simulated oil spill ( ).

Figure 6.2  Model System Cycles, showing processes simulated in each sector. Arrows indicate information flow.

Figure 6.3  Process schematic for the fishery population model.

Figure 6.4  Three piecewise-continuous mortality curves for the first year of life. The curves result from three different sets of parameters in Equations 3, 4, and 5.

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Figure 6.7  Triangular grid system for the ocean transport model.

Figure 6.8  Response of the wind drift equations (Equations 10 and 11) for several values of the linearized interlayer stress RH.

Figure 6.9  Response of Equations 10 and 11 for various drift layer depths (meters).

Figure 6.10  Response of Equations 10 and 11 for several values of the linearized surface stress coefficient RS (in/sec).

Figure 6.11  Observed Larval cod distribution for December, 1974. The larvae southeast of Massachusetts are associated with the Southern New England Cod Stock (Wise, 1963) not modeled here.

Figure 6.12  Modeled larval cod distribution for December 15.

Figure 6.13  Observed larval cod distribution for February, 1975. (See caption, Fig. 11).

Figure 6.14  Modeled larval cod distribution for February 15.

Figure 6.15-18  Four "snapshots" of the oil spill, eggs, and larvae during the simulation. The crescent-shaped group of circles is the surface slick, and the rectangular region is the subsurface 50 ppb contour.

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Table 6.2-4: Simulation Results for Sensitivity Analysis.
6.1 INTRODUCTION

Through the National Environmental Policy Act of 1976, the United States Government has given explicit recognition to the critical importance of maintaining and restoring the quality of the environment in a manner which promotes the general social and economic welfare of present and future human generations. This research represents an actualization of the intent of this policy, employing available technological capabilities to analyze interrelationships among a number of variables in an environmental problem of contemporary significance. Typically, as many questions have been raised as have been answered, but the primary goal, the creation of a modeling methodology capable of estimating the effects of marine pollution events on biological populations, has been realized. Although the development has evolved around a specifically defined system, the conceptual approach is biologically and spatially transferrable, with each model element being sufficiently independent to permit relatively facile modification when appropriate.

The specific problem addressed here concerns the degree of impact experienced by a given stock of fish subsequent to an offshore oil spill. Recent experience on both sides of the North Atlantic Ocean has clearly demonstrated the extent to which coastal ecological resources may be damaged by large petroleum spills. In the case of the Amoco Cadiz accident off the coast of France, for example, it appears that a majority of the impacts can be assessed through direct observations. In offshore situations such as the Argo Merchant wreck, the Bravo blowout in the North Sea, or the Ixtoc I blowout in the Gulf of Mexico, the ensuing ecological consequences are far less clear. Although the oil slick disappears from the ocean surface within a few weeks after cessation of release, the full post-spill legacy is uncertain. The virtual impossibility of actually measuring these effects necessitates the application of a modeling approach.

In any modeling effort, a necessary basic decision concerns the establishment of conceptual limits on the abstraction of the real system being considered. This decision is ideally made in such a manner as to optimize the quality of the final model output, subject to the constraints imposed on the project. Allotted model development time, financial support limitations, and the existence and availability of appropriate data are the most important of these constraining factors, and all came to bear on the definition of the model system selected here.

The initial intent in the present case was to estimate the environmental impact of oil spills at sea, and the effect on this impact of chemically treating a spill. The most objective measure of impact is one with final dimensions of dollars and cents, dictating that commercially exploited species be included in an explicit manner. Thus the cost of a spill under a variety of different treatment scenarios could be investigated, the quality of the model's output being evaluated according to the level of confidence associated with its predictions.

Although a reliable whole-ecosystems impact model may eventually be achievable, a review of related efforts (Reed et al., 1978), and an evaluation of currently available biological baseline data strongly suggested that pursuit of such a model in the time frame and funding level of this
project task would be at the expense of output quality. The single species fishery model, a relatively well established art form supported by a healthy literature dating generally from the work of Verhulst in the nineteenth century and more specifically from Barenov's (1918) application of first order kinetics to a fish population, was selected as the simplest viable subset of the ecosystem approach. It was felt that sufficient uncertainties were evident in the problem without the addition of further conjectures and postulates regarding rates and processes of species interactions. The application of Okham's razor (see Hutchinson, 1978) in this case requires the identification of a position between employing too many parameters to justify from the adequacy of the data base, and too few to do justice to the system. Thus in adopting the principle of parsimony of parameters, permitting a tractable entry into the complexities of the problem, the advice of Lagrange is observed: seek simplicity, but distrust it. The potential magnification in complexity thus avoided is demonstrated in a paper by Andersen et al. (1977) describing a multispecies fishery model in which the simulation of 12 interacting species required the input of some 1600 separate parameters.

The selection of a physical area for the initial model application was relatively straightforward, since Georges Bank (Fig. 6.1), which has supported a thriving fishery for over a century, has recently become the focus of offshore continental shelf hydrocarbon exploration interests. The oil spill fishery interaction problem in this area is therefore potentially very real. Selection of the cod stock on the Bank followed from the data considerations discussed above, as well as the abundance of biological and modeling literature on the species. The previous reference further details this information.

6.2 MODEL OVERVIEW

Because the model has been described in detail elsewhere (Reed et al., 1978, 1979a, 1979b) only a brief overview will be given here. The system is composed of three major interacting components: a fishery sector, an ocean transport sector, and an oil spill fates sector, as described below.

6.2.1 Fishery Model

As shown in Fig. 6.2, the population model cycles on a daily timestep when operating in conjunction with other system components. When operating alone, this timestep can be increased up to five days with little decrease in numerical accuracy, reducing computer time proportionately. The adult fishery model is constructed along well established lines (e.g. Beverton and Holt, 1957; Walters, 1969), whereas the egg and larval stages have been modeled using techniques drawn from other areas of mathematical ecology (Lotka, 1925; Pielou, 1969). The structure of the fishery model is shown schematically in Fig. 6.3.

The model has 17 adult age classes, enough to include all fish sampled in recent surveys (Heyerdahl et al, 1976). They increase in length and weight according to a published growth equation (Pentilla et al, 1976) for the Georges Bank stock. The ith adult age-class is
Figure 6.1 Map of Georges Bank, showing the 100 meter isobathic contour, the spawning area (climacteric), oil exploration tracks (dark regions), commercial shipping lanes, wind data source (I), and the location of the simulated oil spill (II).

Figure 6.2 Model System Cycle, showing processes simulated in each sector. Arrows indicate information flow.

Figure 6.3 Process schematic for the fishery population model.
subject to a mortality equation following first order kinetics,

\[
\frac{dN_i}{dt} = -(M_i + F_i)N_i,
\]

in which \(M_i\) and \(F_i\) are natural and fishing mortality coefficients respectively, the former including all types not induced by the latter. Fishing mortality is assumed linearly proportional to standardized fishing efforts:

\[
F_i = q S_i E(t)
\]

Q is a species and stock dependent catchability coefficient (Gulland, 1977), \(S_i\) is net mesh selectivity for the \(i\)th age-class, and \(E(t)\) is a measure of the fishing effort exerted on the stock during the time interval \(t\).

The fecundity of cod appears well correlated with weight, although, as with all such characteristics, the relationship varies from one stock to another (Daan, 1973; Garrod, 1977; Bigelow et al., 1953; Nikolskii, 1965; Gulland, 1964). This literature suggests a value of 200 to 250 eggs per gram female, which conforms reasonably well to an estimate by Bigelow, et al. of one million eggs per average female, although falling somewhat short of their estimated maximum of nine million.

Temporal distribution of spawning cod on Georges Bank remains something of an enigma, it being uncertain whether cod spawning activity is triggered by day length, temperature, or other environmental factors (F. Serchuck, National Marine Fisheries Service, Woods Hole, personal communication; Wise, 1961). Bigelow et al. (1953), Colton et al. (1977, 1978), and Walford (1938), support the observation that spawning occurs with varying degrees of intensity from November to late April, with a maximum occurring in March and a second smaller peak in the late Fall.

The model takes on spatial dimensions through the simulation of this activity. On any given day of the year, a percentage of the females of each sexually mature age class are assumed to release their eggs. (The fact that not all will be properly fertilized is accounted for in the density independent mortality parameter \(M_i\) in Equation 3. Possible relations between age and time of spawning are not included). The total number of eggs available for spawning on that day is divided into a set number of groups, or sub-cohorts. Thus each particle in the transport model represents one sub-cohort of organisms in the population model. As simulated time progresses, each particle is transported, and represents a diminishing number of developing eggs, larvae, or post-larvae. When a sub-cohort reaches the demersal stage, it looses its explicit representation in space, while of course retaining its presence in the population model.

The major uncertainties in the biological sector of the model exist in the egg and larval mortality representations. These are formulated to require as few arbitrary parameters as possible, while simulating these stages in sufficient theoretical detail to resolve toxic effects which vary in magnitude from one developmental stage to the next. There are five first year stages represented in the model. These are an egg stage
(E), three planktonic larval and postlarval stages (L), and a demersal juvenile stage (J). The equations governing mortality during these various developmental periods are:

\[
\frac{dE}{dt} = (M_1 + M_2*E)*E, \quad (3)
\]

\[
\frac{dL}{dt} = (M_3 + M_4*L)*L, \quad \text{and} \quad (4)
\]

\[
\frac{dJ}{dt} = (M_5 + M_6*J + M_7* \sum_{i=1}^{17} N_i * P_i) * J. \quad (5)
\]

Equations (3) and (4) each include a density dependent and a density independent mortality term, whereas Equation (5) incorporates a set of adult-juvenile interaction terms as well. The theory upon which these equations are based derives from Lotka (1925), who employed the concept of a Taylor expansion about some hypothetical equilibrium value. Density dependent mortality of an intragroup nature, as associated with parameters \(M_1\), \(M_4\), and \(M_6\), is intended to represent competition among individuals of the group for limited resources (e.g. food), or mortality due to predation by some species external to the explicit model formulations (e.g. herring). Density dependence between groups may result from competition for shared resources, or a parasitic (e.g. cannibalistic) relation. There is considerable evidence of cannibalism among Gadoids (see for example Daan, 1973, or Bigelow et al., 1953), and is a theoretically acceptable explanation for population control in Gadoids (Cushing et al., 1977). The third term in Equation (5) is designed to simulate this fact, the \(P_i\) being age-specific predation rates. Recent evidence reported by Ellertsen et al. (1979a) indicates that cannibalism amongst larval and postlarval Gadoids may contribute significantly to mortality, perhaps outweighing effects of food density. This process is not yet explicitly incorporated here. (Further discussion of these equations, their derivations, and an algorithm for the numerical solution of Equation (5) may be found in Reed and Spaulding, 1978.)

Sensitivity to the toxic action of hydrocarbons appears to result from a complex interaction among several variables (Malins, 1977):

1. chemical composition of the oil,
2. duration of exposure,
3. concentration of soluble aromatics in the water,
4. stage of development of the organism,
5. physical condition of the organism, and
6. species.

Along the same lines as suggested by Andersen et al. (1977), efforts have been made to utilize published bioassay data (Kunhold, 1970, 1977; Wilson, 1977) to partition density independent mortality parameters of cod during planktonic stages (Reed and Spaulding, 1978). Although the model is designed to keep account of the variables relevant to toxicity, difficulties of interpretation as well as uncertainty levels elsewhere in the system (e.g. oil entrainment rates, details of ocean transport estimates) have prompted the adoption of a threshold assumption: any eggs or larvae entering an area in which the concentration exceeds their respective threshold values are deleted from the system. In light of the
fact that the presence of hydrocarbons in the water will adversely affect
the food supply (Wolfe, 1977, Workshop..., 1975) as well as the larvae
themselves, this appears reasonable, erring perhaps marginally on the
environmentally conservative side.

Development during the first year is modeled in five stages: eggs, yolk-sac larvae, larvae adapting to free-feeding, adapted free-feeders, and bottom-dwelling juveniles. These stages were selected as those between which definite differences in susceptibility to hydrocarbon toxicity have been observed by Kunhold and Wilson. Egg hatching rates are well represented by a negative exponential curve, probably reflecting temperature dependent chemical interaction rates in egg development. Yolk-sac resorption requires from 4 to 12 days (Wise, 1961; Bigelow et al., 1953). Work being performed by Ellertsen et al. (1979b) suggests that food density may be significant in determining the duration of this stage, but for lack of any deterministic relation, eight days is used here. The larvae must then adapt to catching planktonic organisms, primarily copepod nauplii. Kunhold found the larvae most susceptible to hydrocarbon toxicity during this stage. According to Cushing et al. (1977), the Norwegian investigator H. Dannevig grew cod larvae from hatching to metamorphosis in 70 days, and it is believed that they seek bottom about a month later. These development rates are certainly variable with such things as temperature and food availability, but except for hatching rates, constant values have been used in the model due to lack of hard data.

Pre-recruit mortality parameters are notoriously difficult to evaluate, since what few values exist are usually derived from laboratory observations and do not reflect conditions in the open ocean. It is nonetheless desirable to use whatever our best estimates may be, to reduce the need for blind 'model tuning' in the final stages. Thus a value equivalent to 60% mortality has been used for the density independent rate for eggs (Laurence et al., 1976), and it is hypothesized that demersal juveniles die of natural causes (e.g. disease or starvation) at about twice the rate of the adults. The four remaining density dependent parameters were assigned values resulting from a series of steepest descent searches (Walters, 1969) using the sum of the squared differences between the modeled and the observed annual yields from 1932 to 1952. Several approximately equivalent local minima were found. Of these, most were rejected for biological reasons, such as the improbability of having 90% survival to the demersal stage. Of the remaining sets of mortality parameters which appeared acceptable from the modeling point of view, three were selected for further investigations. As shown in Fig. 6.4, these bracket the likely range of first year mortality curves.

Figure 6.5 shows a comparison of model behavior when operating under the first year mortality curves of Fig. 6.4. In each case, the model is initiated with an equilibrium population, and a perturbation is introduced by assuming the complete failure of the subsequent yearclass. It can be seen that the modeled stock fluctuations increase both in magnitude and duration as density dependent mortality emphasis shifts from intra-egg and intra-larval stages (Mode 1) to the adult-juvenile formulations (Mode 3). This behavior corresponds conceptually to a decreasing negative slope on the stock-recruit curve at the replacement point, as discussed by Allen et al. (1974). The biological explanation
Figure 6.4 Three piecewise-continuous mortality curves for the first year of life. The curves result from three different sets of parameters in Equations 3, 4, and 5.

Figure 6.5 Comparison of modeled response to an arbitrary perturbation under the three nodes of Figure 4.
lies in the fact that increasing the relative importance of the adult juvenile interaction such that cannibalism (or resource competition) is the dominant controlling factor for population size causes the direct transferrence of oscillations in the parent stock to oscillations of the opposite sign in the associated 0-Group. If the relationship becomes strong enough, the model becomes unstable.

Although the average error of the predicted yield is on the order of 20% of the average catch (Fig. 6.6), the model demonstrates a reasonable ability to follow the trends in the record ($r=0.81$). The model does not predict catch size with great accuracy, but the impact estimates required here will be the differences between predicted catches with and without a spill. While the actual predictions may be off by 20% or more, to the extent that the model follows the yield trends, these differences may only be in error by a few percent. The relative impact estimates themselves may be more accurate than the absolute yield estimates from which they derive.

6.2.2 The Ocean Transport Model

The marine transport model consists of three superimposed flow processes, each representing transport energy spanning a different portion of the energy spectrum. Although such separation neglects nonlinearities in the real system, this approach is adopted in lieu of a two or three dimensional numerical modeling effort involving the solution of the Navier-Stokes equations on a phase-space grid of sufficiently fine mesh to resolve the processes of interest. The available data base for verifications of larval fish distributions hardly warrants the time and effort necessary to produce such a model. The methods described here are on a level of approximation consistent with others in the physical sector of the model (e.g. spawning rates and locations), and appear to yield useful and credible transport estimates, as discussed below.

The low frequency seasonal circulation patterns have been deduced from oceanic drifter data gathered over approximately a decade (Bumpus et al., 1965). The resulting flow fields supply estimates of net transports on temporal scales of weeks and months, arising as the residual of tidal, meteorological, and river inflow events, as well as pressure forcing on the ocean boundaries of the modeled area. A triangular grid was constructed covering the area of interest (Fig. 6.7), and velocity components were assigned at each node. Linear interpolation is performed between seasonally adjacent data sets to supply smoothed daily input to the model. Advection velocities at a given point within a grid element are assigned by fitting a plane through the component values at each of the three surrounding nodes, thus spatially interpolating values at any internal point.

Intermediate frequencies of transport energy are input through wind forcing on time scales of a few hours to several days. Decoupling of this input from the long-term effects, it probably imparts to the real systems (Csanady, 1976) is achieved by first passing a digitized record of wind data for the time period of interest through a high pass filter with a corner frequency of one cycle every ten days. In this way, only energy associated with trends occurring over time periods less than ten days is retained in the record. This filtered wind record is then used as input to a simple two-dimensional model of the wind-driven surface
The sum of the absolute values of the errors is 201.1

Figure 6.6 Modeled versus observed catch for Georges Bank cod.

Figure 6.7 Triangular grid system for the ocean transport model.
layer. Because it does not appear elsewhere, the description of this sector of the model will be relatively detailed.

The complete Navier-Stokes equations describing the motion of an incompressible fluid continuum may be averaged over $H$, the depth of the wind-driven layer. Because the area being modeled (Georges Bank) is far from any land boundaries, and because this wind driven depth will in general be small relative to the total depth, so that for coherent forcing periods below a few days only small return flows in the lower depths will be required to eliminate surface setup, the pressure gradient terms can be neglected. If the depth $H$ is assumed constant for the duration of at least one sampling interval in the wind record (here three hours), then the convective acceleration terms can also be dropped from the equations. The usual quadratic forms of the wind stress terms can be replaced by linear approximations to preserve the validity of superposition. Data analyzed and reported by Kirwan et al. (1979) suggests that a linear law relating wind to wind drift current may be as good as the quadratic formulation for long terms (>5 days) estimates. Thus the wind stress at the surface in the $x$ direction (positive to the east) is

$$\tau_x = \rho_a R_s U$$  \hspace{1cm} (6)

and in the $y$ direction (positive north) is

$$\tau_y = \rho_a R_s V$$  \hspace{1cm} (7)

in which $\rho_a$ is the air density, $U$ and $V$ are the wind velocities in the $x$ and $y$ (east and north) directions respectively, and $R_s$ is an empirically derived constant. If a hypothetical stress at the bottom of the wind driven layer is similarly linearized, the equations of motion become

$$\frac{du}{dt} = fV + \frac{\rho_a R_s U}{\rho_w H} - \frac{R_u u}{H}$$  \hspace{1cm} (8)

$$\frac{dv}{dt} = -fu + \frac{\rho_a R_s V}{\rho_w H} - \frac{R_v v}{H}$$  \hspace{1cm} (9)

In Equations 8 and 9, $U$ and $V$ are the eastward and northward ocean current velocities averaged over the wind driven depth $H$, $f$ is the Coriolis parameter, $R_u$ is the linear stress coefficient at the depth $H$, and $\rho_w$ is the density of sea water. Assuming the depth $H$ to be constant over one sampling interval in the wind time record, this set of coupled ordinary differential equations has the simple solution

$$u(t) = e^{-\frac{R_u t}{H}} \left[ (u_o - u_\infty) \cos(ft) + (v_o - v_\infty) \sin(ft) \right]$$  \hspace{1cm} (10)
wherein \( u \) and \( v \) are the orthogonal currents at the beginning of the time interval, and the asymptotic velocities for large times \( t \) are given by

\[
v(t) = e^{-\frac{R_H}{H}t} \left[ (v_0 - v_\infty) \cos(ft) + (u_0 - u_\infty) \sin(ft) \right]
\]

(11)

Equations 10 and 11 describe circular motion with damping and an offset. The angle of the net transport to the right of the wind can be most easily calculated by aligning the axes such that \( U=0 \), giving

\[
\theta = \pi/2 - \arctan \left( \frac{R_H}{H} \right)
\]

(14)

from which it can be seen that the transport will be 90 degrees to the right of the wind for zero bottom stress or infinite depth, in agreement with Ekman's classical analysis.

In reality, the mixed layer depth will be a function of wind speed and duration, sea state, and density stratification (Phillips, 1977; Liebovich, 1977; Kullenberg, 1976; Niiler, 1977). As pointed out by Gonella (1971) and Csanady (1972), the correct formulation for \( H \) as a function of time in very deep water would eliminate the necessity of the "interlayer stress" artifice (second term on the RHS of Equations 8 and 9). The resistance to surface stress in deep waters arises from a downward flux of momentum and internal dissipation, so the correct lower boundary condition is zero stress at the (variable) depth \( H \). Because of the lack of agreement on vertical eddy viscosity formulations for the solution of this problem (see for example Huang, 1979), an arbitrary depth of 10 meters for a 3 hour response time has been selected as suggested by the literature overview summarized in Table 6.1. This depth includes the majority of cod eggs and larvae in the area, and unless oil actually sinks, it appears doubtful that any significant amount will penetrate deeper than this (McAuliffe, 1977).
<table>
<thead>
<tr>
<th>Observer</th>
<th>Drift Layer Depth (meters)</th>
<th>Depth Averaged Current (as Percent of Wind Speed @ 10 m.)</th>
<th>Approx. Drift Establish. Angle (hrs)</th>
<th>Drift Angle (to the rt. of W)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nansen (1902)</td>
<td>~ 1%</td>
<td>~ 1%</td>
<td>~10-20</td>
<td>20-40°</td>
<td>observations of icebergs</td>
</tr>
<tr>
<td>Ekman (1905)</td>
<td>~ 50</td>
<td>1.3%/sin(^1/2)</td>
<td>~10-20</td>
<td>90°</td>
<td>theory</td>
</tr>
<tr>
<td>Smith (1931)</td>
<td>~ 20</td>
<td>&lt; 1%</td>
<td>~ 40°</td>
<td></td>
<td>deep immersing iceberg</td>
</tr>
<tr>
<td></td>
<td>~ 5</td>
<td>~ 1%</td>
<td>~ 20°</td>
<td></td>
<td>small iceberg</td>
</tr>
<tr>
<td>Csanady (1972)</td>
<td>9-18</td>
<td>2%</td>
<td>1-3</td>
<td>-10-60°</td>
<td>Lake Huron observations</td>
</tr>
<tr>
<td>Csanady (1974)</td>
<td>10-20</td>
<td>-</td>
<td>3-8</td>
<td>-</td>
<td>theory</td>
</tr>
<tr>
<td>Murray (1974)</td>
<td>10</td>
<td>2%</td>
<td>3</td>
<td>10-90°</td>
<td>near shore, shallow</td>
</tr>
<tr>
<td>Mellor et al (1975)</td>
<td>25</td>
<td>-</td>
<td>16</td>
<td>-</td>
<td>model compared w/ data</td>
</tr>
<tr>
<td>Niiler et al (1977)</td>
<td>10</td>
<td>-</td>
<td>1-2</td>
<td>-</td>
<td>theory and observation</td>
</tr>
<tr>
<td>Csanady (1976)</td>
<td>16</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>theory and observation</td>
</tr>
<tr>
<td>Gonella (1971)</td>
<td>10-15</td>
<td>1%</td>
<td>2-3</td>
<td>-</td>
<td>theory and observation</td>
</tr>
<tr>
<td>Madsen (1977)</td>
<td>25</td>
<td>1%</td>
<td>~ 3</td>
<td>100°</td>
<td>modeled</td>
</tr>
<tr>
<td>Kondo et al (1979)</td>
<td>20</td>
<td>~ 1%</td>
<td>16</td>
<td>170°</td>
<td>observed and modeled</td>
</tr>
<tr>
<td>Kirwan et al (1979)</td>
<td>surface</td>
<td>-</td>
<td>-</td>
<td>150°</td>
<td>theory and observation</td>
</tr>
</tbody>
</table>

Table 6.1: Summary of Literature Estimates of Wind-Driven Flow Parameters
The most widely accepted formulation for the wind stress, supported by a large number of laboratory and field investigations, is a proportionality with the square of the wind speed multiplied by the density of the air. This is consistent with dimensional considerations, and corresponds to drag formulations for fluid flow around a solid body. One possible method of assigning a value to the parameter $R_S$ would be to equate the energy input from atmosphere to ocean in the linear model with that prevailing under the quadratic stress formulation. This was not done because it would have amounted to forcing energy from lower frequencies into the domain of the filter applied to the wind record.

The problem has instead been approached in a simple statistical manner. An estimate of $R_S$ in terms of the "correct" quadratic formulation,

$$\tau_q = \rho_a C_d |\mathbf{\bar{w}}|^2$$

(results from a comparison with the linear expression

$$\tau_l = \rho_a R_s \mathbf{\bar{w}}$$

Equations 15 and 16 suggest that $R_S$, with dimensions of velocity, may be taken as a measure of the mean background wind velocity magnitude, and should, therefore, be derived explicitly for each specific wind record employed. The filtered wind record used here spans from September 1972 to September 1973, and has maximum and minimum magnitudes of 16.4 and 0.114 meters/sec. with a mean of 5.1 meters/sec. Using $C_D = 0.002$ (see for example Wilson, 1960, or Wu, 1969), this gives a value of $R = 0.01$ meters/sec.

Winant et al. (1979) statistically compared quadratic and linear formulations for the bottom stress in water depths of 30 to 40 meters, and were unable to determine which parameterization was more accurate, lending further support for the linearization imposed here. Their parameter estimates for $R_H$, varying from 0.04 to 0.2, are derived on the assumption that surface and bottom stress components are equal (i.e. at steady state conditions) and appear high. A second estimate of $R_H$ can be determined by estimating the asymptotic magnitude of the depth averaged current as a function of wind speed from the literature (Table 6.1), and solving Equations 12 and 13 for $R_H$. Using $R_S = 0.01$ meters/sec., a density ratio of 0.00125, a depth of 10 meters, $f = 0.000097$ radians/sec, and solving the relation

$$(u_\infty^2 + v_\infty^2)^{1/2} = 0.01(u^2 + v^2)^{1/2}$$

by substituting for $u_\infty$ and $v_\infty$ from Equations 12 and 13 gives $R_H = 0.001$. These values imply an asymptotic drift transport angle of 44 degrees to the right of the wind, attained within $\pm 2\%$ after 7 hours.

The behavior of the model for other values of the parameters is shown in Figs. 6.8-10. Empirical validation of such a model is necessarily subjective, not only because vertically uniform slab flow is an extreme simplification of actual wind-driven ocean current profiles, but also...
Figure 6.8 Response of the wind drift equations (Equations 10 and 11) for several values of the linearized interlayer stress $\tau_{ij}$.

Figure 6.9 Response of Equations 10 and 11 for various drift layer depths (meters).

Figure 6.10 Response of Equations 10 and 11 for several values of the linearized surface stress coefficient $\tau_0$ (in/sec).
because documented observations of atmosphere-ocean momentum interactions are themselves so variable. The studies summarized in Table 6.1 suggest that, for an establishment time of 3 hours, plausible attributes of the wind drift current are a depth of 10 meters, a vertically averaged speed of 0.1% that of the wind, and a drift angle of 20 to 60 degrees. If the observations by Smith (1931) of drifting icebergs can be taken as reflecting vertically averaged drift angles and speeds, then 30 degrees might be a reasonable intermediate value. For the parameter values used here ($r_g = 0.01 \, \text{m/sec}; \, R_H = 0.001 \, \text{m/sec}; \, H = 10 \, \text{meters}$) the linear model predicts a drift angle about 30 degrees to the right of the wind after 3 hours, and a speed 0.1% that of the wind.

The third transport process in the model is dispersion, assumed to result from energy input at frequencies greater than and equal to that of the tides, as well as energy cascaded into this frequency range through dissipation processes in the real system. Dispersion is modeled as a random walk process occurring with a mean velocity magnitude

$$V = \sqrt{\frac{\Delta \theta}{dt}},$$

(see Appendix A), in which $dt$ is the simulation timestep, and $\Delta \theta$ is the diffusivity, taken from an oceanic diffusion diagram (Okubo, 1974).

In summary, the transport of ichthioplankton and entrained oil is simulated through the juxtaposition of a random walk diffusion process, a wind-driven velocity component responding to an actual time series pre-processed through a high pass filter, and a drifter-inferred seasonally varying aspect.

Validation of the fishery cum ocean transport model has been described in the references already cited, but is discussed briefly here to clarify the significance of results, and to emphasize the importance of longterm methodical data acquisition programs to the success of ecological impact modeling endeavors. The basis for the validation methodology proposed here is a space-time history of larval fish concentration data. Unfortunately, such data is extremely expensive to acquire, and National Marine Fisheries Service data for larval cod on Georges Bank exists only for December and February, so that spring verification is not possible. (A data set for March, 1976 may soon become available.) The length of the record (four years) is insufficient to warrant actual statistical comparison of model results with the data. Qualitative comparisons (Figs. 6.11-14) suggest that the model performs reasonably well. If the data record were longer, an average distribution with variance could be derived, and a confidence interval could be placed on the model predictions. In addition, one could begin to consider the environmental factors relating to specific distributions, thus revealing which of these factors when included in the model would most improve performance.
Figure 6.11 Observed larval cod distribution for December, 1974. The larvae southeast of Massachusetts are associated with the Southern New England Cod Stock (Wise, 1965) not modeled here.

Figure 6.12 Modeled larval cod distribution for December 15.

Figure 6.13 Observed larval cod distribution for February, 1975. (See caption, Fig. 11.)

Figure 6.14 Modeled larval cod distribution for February 15.
6.2.3 THE OIL SPILL FATES MODEL

This sector of the impact model is described elsewhere in this report, and will, therefore, not be discussed in detail here. The interconnection between the oil spill and fishery models is accomplished through storage of the oil spill output data sets on disc or tape, for access as needed by the toxic impacts section.

6.3 RESULTS OF SIMULATIONS

Model sensitivity to three types of parameters has been investigated. Because field data limitations and model complexity preclude the derivation of confidence intervals on the predictions, it is felt that the best indicator of reliability will be a demonstration of the relative importance of key assumptions in the system. The usual gradient approach to sensitivity (e.g. Brylinsky, 1972) is useful when the values of parameters are known with confidence intervals of, say, ± 15%. Then local rates of change due to small variations are significant. If actual parameter values may range over more than one order of magnitude, however, a set of widely spaced point values on the response surface is more revealing. This latter approach is used here.

A two-day, 34,840 metric ton oil spill, occurring on December 15, has been simulated for this sensitivity analysis. Figs. 6.15-18 show four snapshots of the interaction among the eggs and larvae, the surface slick, and the subsurface distribution of hydrocarbons within the 50 ppb contour. Further details are presented in the oil spill modeling report section. Impact predictions have been compared under three theoretically acceptable piecewise-smooth larval mortality curves (Fig. 6.4), three threshold toxicity values of 50, 100, and 1000 parts per billion (ppb) and three dispersant application scenarios in which 0%, 50%, and 100% of the oil is chemically treated. The results of these model runs are shown in Tables 6.2, 6.3, and 6.4.

Decreasing impact is associated with increasing larval resistance to oil toxicity (increasing threshold values), with decreasing entrainment, and with increasing mortality mode. This latter fact results from an increase in the amount of compensatory mortality in modes 2 and 3 (Fig: 6.4) in the post-planktonic stages, relative to mode 1. Thus for a given treatment scenario and toxicity threshold, although the same number of eggs and larvae are lost from the system due to the spill, the effect on recruitment, and ultimately yield, is considerably different, as reflected in the relative losses associated with each mode.

Not surprisingly, none of the scenarios modeled here supports the application of dispersants as a means of mitigating impact on the fishery. Microbial degradation, which is rate dependent on both temperature and interfacial area (Traxler et al., 1977), a process not included in the oil spill fates model at this time, could alter this outcome somewhat, although to what extent is uncertain (Gibson, 1977).

One of the more significant findings here is that the natural mortality regime for the population is more important than either threshold toxicity values or the percent of oil being dispersed into the water column. The importance of determining appropriate mortality regimes and
Figure 6.15-18 Four "snapshots" of the oil spill, eggs, and larvae during the simulation. The crescent-shaped group of circles is the surface slick, and the rectangular region is the subsurface 50 ppb contour.
### Mortality Mode 1

<table>
<thead>
<tr>
<th>Percent Chemical Treatment</th>
<th>0%</th>
<th>50%</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 ppb</td>
<td>1.4</td>
<td>1.8</td>
<td>2.4</td>
</tr>
<tr>
<td>100 ppb</td>
<td>1.1</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>1000 ppb</td>
<td>0.3</td>
<td>1.0</td>
<td>1.2</td>
</tr>
</tbody>
</table>

### Mortality Mode 2

<table>
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<th>50%</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 ppb</td>
<td>0.4</td>
<td>0.6</td>
<td>0.8</td>
</tr>
<tr>
<td>100 ppb</td>
<td>0.3</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>1000 ppb</td>
<td>0.0</td>
<td>0.1</td>
<td>0.2</td>
</tr>
</tbody>
</table>

### Mortality Mode 3

<table>
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<th>Percent Chemical Treatment</th>
<th>0%</th>
<th>50%</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 ppb</td>
<td>0.1</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>100 ppb</td>
<td>0.1</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>1000 ppb</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Tables 6.2, 6.3, and 6.4: Effects of Variations Among 3 Sets of Parameters on Modeled Results. Mortality Modes refer to Curves of Figure 4. Tables entries are in thousands of metric tons lost to the Fishery. ($1 million 1 thousand MT)
toxicity threshold values is manifest from these results. Suppose for example that an oil spill on Georges Bank were to be driven towards the islands of Nantucket and Martha's Vineyard, rather than out to sea. If mode 2 or 3 proved a good approximation to the governing mortality rates for the population, and a threshold value of 1000 ppb appeared credible for the oil at hand, treatment with dispersants before the oil reached shore would greatly decrease the aesthetic impact at little cost to the fishery. (As a "best guess" however, the most likely description of cod egg, larval, and post larval mortality on Georges Bank is a curve somewhere between modes 1 and 2, with a threshold toxicity of about 100 ppb.)

Certain limitations of the model must be stated in accompaniment to this conclusion. The most important is that only one element of the ecological complex in question is being modeled, a basic assumption being that overall biological patterns will not be disrupted by the spill. If treatment with dispersants or possible sinking of the oil resulted in contamination of the sediment on the spawning ground, this assumption would certainly be violated. The basic philosophy of causality in evolution implies that fish spawn in space and time in such a way as to optimize the probability of survival of the offspring in the long term, so that forced shifts in these patterns would presumably prove detrimental to the stock. Modeling such phenomena would require hypothesizing stock responses to extended spawning interruptions, which would fall little short of blind conjecture. Similarly, any major impact on another element of the food web could result in significant feeding shifts throughout the ecological system. An impact model of this type is, therefore, limited in its usefulness to situations involving only small population perturbations.

The magnitudes of the impacts estimated here range between 0% and 10% of the annual maximum sustainable yield of approximately 25,000 metric tons, or up to $2.5 million in reduced income to the fishing fleet. Simulation of a 30 day oil well blowout (Reed et al., 1979b) shows impacts four times as large, so that the specific scenario is of considerable importance. Furthermore, it must be remembered that the vast majority of the commercially important species in the area, including cod, haddock, pollock, hake, herring, flounder, mackerel, lobster, crab, and scallop have pelagic eggs and/or larvae. Depending on the specific biological patterns associated with each of these species, the total cost of a spill in terms of reduction in catch could greatly exceed these values.

In summary, the simulations described here suggest that the most significant set of unknown parameters in the model system is that relating to mortality rates and processes during the first year of life. The amount of dispersant applied to the spill and the toxicity of the oil appear to be of secondary importance in deep offshore waters. (It is somewhat ironic that the most important and desirable information needed for further model improvement is also the most difficult and expensive to obtain.) As is often the case with complex simulations, the strength of the underlying data base limits the real usefulness of the output. In the case at hand, further advances in marine fisheries impact assessment of this type require a concerted ichthyoplankton data acquisition program, systematic in both space and time. Although expensive, it appears that basic progress in this field will be largely dependent on the planning and implementation of such programs.
7.0 Chemical Analysis of Oil Spills

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Figure 7.5.57 IR difference spectrum; oil/dispersant top minus oil top, 6th week.
7.1 Introduction

The overall objective of the project is to assess the environmental impact of a chemically treated vs. an untreated oil spill. The primary objective of the chemistry group has been to determine the amounts and compositions of petroleum chemicals in the atmosphere, surface waters, water column and sediments, resulting from a treated and untreated spill. To meet this objective, it was necessary for the group to develop sample collecting, extraction, and chemical analysis methods. In addition, extensive development and testing of computer software was undertaken to collect and massage the analytical data. Laboratory experiments were designed and executed to aid in the development of these analytical techniques. Results from the laboratory studies determined the techniques which would be applied to the analysis of the meso-scale experiments and eventually to any "real world" spills of opportunity.

7.2 Analytical Procedures:

7.2.1 Choice of Oil/Dispersant System

(A) Oil: The choice of oil for the study was based on several factors:

a) availability of sufficient quantities for testing,
b) availability of the compositional data on the oil,
c) presence of sufficient percentages of the spectrum of representative components, e.g., aromatics, paraffinics, cyclo-paraffins,
d) ability to handle oil easily at ambient temperatures.

Based on these prerequisites, it was decided that one of the two API reference crudes, South Louisiana or Kuwait, be used for the experiments. Initially, these two oils were used in laboratory tests and eventually Kuwait Crude was used for the bulk of the laboratory work and for the meso-scale experiments. In addition, as a result of two "real world" spills, hunker C oil from the Argo Merchant and a No. 2 fuel from the Buzzards Bay Spill were used in some of these studies.

(B) Dispersant:

The program objectives of the chemistry study did not include a performance testing of chemical dispersants. It was decided that a study using one well chosen dispersant and extensively testing its use with a limited number of oils would prove to be more informative and complete, vis-a-vis, the project objective, than would using multiple dispersants with these oils.

The choice of dispersants was based on several factors:

a) product should be one of the major products on the market,
b) dispersant should have low toxicity,
c) dispersant should have application on wide spectrum of oil types,
d) dispersant should be easily applied and require minimal mixing energy.
Based on the above criteria, six products were considered (Table 7.2.1). Of these, Corexit 9527, a self-mixing dispersant, was chosen for the study.

7.2.2 Infrared Analytical Procedures

(A) Water Column
a) Quantitative

i) Choice of solvent system - infrared analysis of the petroleum hydrocarbons extracted from the water column were analyzed quantitatively as well as qualitatively. It was desirable therefore, to have one solvent which could be used as an extracting solvent and allow for the subsequent infrared analyses without having to remove the sample from the solvent. Carbon disulfide was chosen since it can be used as an extracting solvent and has infrared spectral "windows" at 2930 cm\(^{-1}\) to allow for quantitation of the hydrocarbon band and also has windows between 1355 and 655 cm\(^{-1}\) to allow for measurement of the spectrum in the infrared "fingerprint" region (used for qualitative analysis) (1). Since the infrared cells, extraction and separation techniques required for analysis of chemically treated oil spills with this solvent were nonexistant, this lab designed and tested methods to allow us to perform infrared analyses of these samples.

The solvent was reagent grade and redistilled in glass immediately prior to use.

ii) Infrared instrumentation - analysis was performed on a Beckman 4260 Infrared Spectrometer interfaced to a Data General NOVA 3/12 Mini-computer.

iii) Design of Cell: A large portion of time was devoted to the design of 6 mm liquid cells. Cells are not normally manufactured at this pathlength and volume and cannot hold the very volatile samples and solvent we normally use. Figure 7.2.1 shows the schematic of the cell we chose. The holders were designed to contain a 6 mm spacer sandwiched between two AgCl windows. The design and material of the spacer was varied and tested as follows:

1) Teflon spacers - two Teflon spacers were machined to matching thickness (6 mm). Injection ports were located on the side of the spacer, and angled as shown as "a" in Figure 7.2.1. Teflon plugs were used to seal the ports. Two major difficulties were encountered with this design:

   a) The softness of the Teflon made it impossible to machine two spacers to an exact, uniform thickness. As a result, it was necessary to hand lap the two spacers to exact thickness. This was time consuming and tedious.

   b) The CS\(_2\) slowly leaked through the side ports of the spacers.

2) Stainless Steel - two stainless steel spacers were machined to matching thickness (6 mm). Injection ports were located on the side of the spacers. Teflon plugs were used to seal the ports. The hardness of
### Table 7.2.1: Dispersants Considered for Study

<table>
<thead>
<tr>
<th>Product</th>
<th>Type Oil Dispersed</th>
<th>Toxicity</th>
<th>Mixing Requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEOC777</td>
<td>Light Crudes at Sea</td>
<td>N/A*</td>
<td>Fine Mist</td>
</tr>
<tr>
<td>SURFLO-OW-1</td>
<td>Crude at Sea</td>
<td>Non-toxic</td>
<td>Spray/Agitate by Boat</td>
</tr>
<tr>
<td>BP1100WD</td>
<td>Oil at Sea only</td>
<td>Conforms to UK standards</td>
<td>Spray/seawater mix/boat</td>
</tr>
<tr>
<td>BP1100X</td>
<td>Oil at Sea or on beach</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>Corexit 7664</td>
<td>no limitations</td>
<td>&quot;low&quot;</td>
<td>Spray/Agitate by boat</td>
</tr>
<tr>
<td>Corexit 9527</td>
<td>no limitations</td>
<td>&quot;low&quot;</td>
<td>None required</td>
</tr>
</tbody>
</table>

* N/A-none available

All information was taken from company product brochures.

---

**Figure 7.2.1**  AgCl Cells with Stainless Steel Spacers
the stainless steel allowed for machining of the two spacers to exact thickness and, unlike the Teflon, no further polishing was necessary. However, the ports still leaked.

(3) Stainless Steel - two stainless steel spacers were machined to matching thickness. The port positions were moved from the sides to the top and bottom, as "b" in Figure 7.2.1. This prevented leakage. The cells presently in use are those designed with ports located on the top and bottom of the spacer.

iv) Extraction Efficiencies

To determine the extraction procedure and the amount of solvent that would yield a relatively high extraction efficiency, four procedures were tested, using carbon disulfide as the extracting solvent. In each experiment, one liter of sea water collected from a previously determined clean site was spiked with a known amount of sample and poured into a 2000 ml separatory funnel. The organics were then extracted as follows:

a) Ten mls. of CS$_2$ were added to the water and the sample was agitated for 5 minutes. The bottom organic layer was transferred to a 25 ml volumetric and brought to volume with additional solvent.

b) Ten mls. of CS$_2$ were added to the sample in 5 ml portions with extraction after each addition. The 5 ml portions were combined in a 25 ml volumetric and brought to volume with additional solvent.

c) Fifteen mls of extracting solvent were added to the sample in 10 and 5 ml aliquots, with extraction after each addition. The aliquots were combined as described above.

d) Thirty mls. of extracting solvent were added in 15 ml aliquots, with extraction after each addition. Combination of sample and volume adjustments were made as described above.

The amount of extracted hydrocarbon in each sample was determined by measurement of the absorbance of the 2930 cm$^{-1}$ band.

These four procedures were tested with Kuwait Crude, Corexit 9527 dispersant and a 5:1 mixture of Kuwait Crude and Corexit 9527. Results are shown in Table 7.2.2. As can be seen, method "d" yields the highest efficiency. All extractions are now performed according to this method.

v) Analytical Protocol

In the initial phases of the project, the feasibility of chemically separating the oil from the dispersant prior to infrared analysis was studied. The dispersant is a mixture of polar hydrocarbons, whereas the oil is a mixture of nonpolar and polar hydrocarbons (the nonpolar compounds being present in the higher percentage). Therefore, Thin Layer and Column Chromatography were used with various solvent systems in an attempt to isolate the oil from a mixture of oil and dispersant. Several pure solvents and solvent systems were tested for their resolution capabilities. The best results were obtained with a system of a 1:1 mixture of CHCL$_3$:CCl$_4$. However, even with this system, a complete separation
Table 7.2.2. Results from Extraction Efficiency Experiments

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kuwait Crude</td>
</tr>
<tr>
<td>a) 10 ml 1st ext.</td>
<td>40.5%</td>
</tr>
<tr>
<td>0 ml 2nd ext.</td>
<td></td>
</tr>
<tr>
<td>10 ml total</td>
<td></td>
</tr>
<tr>
<td>b) 5 ml 1st ext.</td>
<td>31.0%</td>
</tr>
<tr>
<td>5 ml 2nd ext.</td>
<td></td>
</tr>
<tr>
<td>10 ml total</td>
<td></td>
</tr>
<tr>
<td>c) 10 ml 1st ext.</td>
<td>31.8%</td>
</tr>
<tr>
<td>5 ml 2nd ext.</td>
<td></td>
</tr>
<tr>
<td>15 ml total</td>
<td></td>
</tr>
<tr>
<td>d) 15 ml 1st ext.</td>
<td>64.8%</td>
</tr>
<tr>
<td>15 ml 2nd ext.</td>
<td></td>
</tr>
<tr>
<td>30 ml total</td>
<td></td>
</tr>
</tbody>
</table>

of the oil from the dispersant could not be realized. Because of this and of the time required to perform this separation, it was decided that development of computer techniques to effect spectral separation of these two components would be more promising (see Section 12.5).

The amount of hydrocarbons present in a sample was determined by placing 0.5 ml of the sample solution into the sample cell. The matched reference cell was filled with CS₂ and both were placed in the infrared spectrometer. Since the cells were of identical pathlength, the CS₂ absorbed the same amount of light from both sample and reference beams, effectively eliminating the bands due to the solvent and allowing the measurement of the absorbance band for hydrocarbons at 2930 cm⁻¹. The absorbance of the 2930 cm⁻¹ band was calibrated using solutions of known concentrations of the oil, oil/dispersant and dispersant respectively, and concentration vs. absorbance curves were plotted. The concentration of the unknown was then determined from the appropriate curve.

b) Qualitative - Spectral measurement

Following quantitative analysis, the total sample is concentrated to approximately 1 ml by slowly evaporating the solvent. Again, about 0.5 ml of this solution is placed in the sample cell, pure CS₂ is placed in the reference cell. Both are placed in the instrument and the infrared "fingerprint" of the sample is measured by scanning the 1355-655 cm⁻¹ region of the spectrum.

(8) Air
a) Charcoal Tubes

i) Laboratory

The vapors above treated and untreated simulated oil spills were collected by pumping air above the slick through activated charcoal cartridges. A flow meter was connected between the cartridges and a pump to measure flow rate. Three systems were used for collecting vapors:
1) the apparatus shown in Figure 7.2.2.
2) the apparatus shown in Figure 7.2.2 without the charcoal filter.
3) the apparatus shown in Figure 7.2.3.

Prior to the extraction of the charcoal an internal standard, n-o-C_{20} (eicosane), was added to the solvent. Carbon disulfide was used for extraction. Thus, its area and height can be easily determined. The concentration of the standard was about 50 ppm. Before the extraction, the solvent and the charcoal were cooled in liquid nitrogen and then mixed together. This was done to prevent losses of vapors due to heat of extraction (1). Extraction time was 30 minutes. Infrared spectra were measured using the 6mm cells described above. Carbon disulfide was used as a solvent for the IR measurements.

ii) Meso scale

Two tanks, 6.2 meters tall and 0.9 meters in diameter, located about 50 meters from the Narragansett Bay, were used for the meso-scale experiments. The tanks were filled with approximately 2000 liters of sea water pumped from the ocean. Kuwait crude oil was added to the north and south tanks, and Corexit 9527 was then added to the south tank.

The surface was mixed by stirring with glass rods. Air samples were collected immediately after the spill. Air samples were collected and treated similarly to the air samples taken in the laboratory experiments. Figure 7.2.4 shows the system used for collecting the air samples in meso-scale experiments. The funnels through which the air was pumped were placed at about 2.5 cm above the water surface.

Extraction of samples from the charcoal tubes and infrared analysis of the samples were performed as described above.

b) Long-path Gas Cell

The purpose of this study was to determine the feasibility of direct IR monitoring of vapors of oil and its various light hydrocarbon components. Fundamental problems are quickly encountered when trying to obtain an IR spectrum of a complex mixture such as crude oil. Overlapping bands and non-linear responses make quantitative accuracy questionable in such cases, and this was one of the major problems addressed. Work was largely done with synthetic mixtures of light hydrocarbon gases to simplify the study. Problems of sample handling and transfer were also addressed. A simple laboratory system was set up for the routine analysis of vapors from liquid hydrocarbon samples, along with special handling apparatus for other situations (artificial weathering, etc.). Finally, a simple, very small-scale spill simulation tank was set up.

Spectra were measured on a Beckman 4260 infrared spectrophotometer with a Wilks 20-m Variable Path Gas Cell mounted in the sample beam. A beam attenuator was placed in the reference beam and the sample compartment was continuously flushed with dry N\textsubscript{2} gas to minimize atmospheric interferences.

Figure 7.2.5 shows a simple schematic of the 20 m gas cell. The IR sample beam is directed up into the cell, multiply-reflected along the length of the cell, and directed back out and into the instrument. By
Figure 7.2.2 Air Flow Sampling Probe for Laboratory

Figure 7.2.3 Test with Prefiltering for Laboratory Experiment
Figure 7.2.4 Test with Prefiltering for Meso Scale Tank

Figure 7.2.5 Schematic of the IR 20 meter Gas Cell
varying the angle of one mirror with a simple vernier dial, the number of reflections and, therefore, the pathlength in the cell, can be varied. The pathlength can be set from 0.75 to 21.75 m, in increments of 1.5 m. The longer pathlengths are often necessary when working with low concentrations or weakly absorbing species. Two gas connections, with valves, allow for a flow-thru operation of the cell. The cell is about 0.4 m long, with a volume of 5.5 liters.

Figure 7.2.6 shows a diagram of the experimental setup. The apparatus can be used in several ways. For quantitative studies of pure gases, dry N₂ was pumped through the cell to flush the system. The 4-way valve was then turned to isolate the pump and gas cell (in a closed loop) and a sample of gas was injected through the septum with a gas syringe. Repeated injections of a gas into this flowing loop could be made while monitoring a wavelength of interest on the IR, until the desired concentration was reached. Likewise, sequential injections of different gases could be made to produce a synthetic mixture of known composition. Injections were made with Series A gas syringes from Precision Sampling, Inc. Syringes were filled from lecture bottles via a stainless steel outflow tube.

For sampling vapors from crude oil or from a simulated oil spill, the vapor is pumped once through the cell and out the exhaust. In the case of a spill a glass funnel suspended over the spill is connected to the input. For pure oil samples, a sampler such as in Figure 7.2.7 can be used to isolate the vapors. All pump parts, valves and connections are 316 stainless steel and tubing connections are made with TFE. The gas cell itself is Teflon lined.

Data measurement was generally carried out with the IR interface to the Data General NOVA 3/12 computer. Programs developed in the lab allow for acquisition and storage of data, spectral smoothing, addition or subtraction and graphic display of spectra on a CRT or plotter. This allows for improvement and enhancement of spectral display, and exact comparisons of very similar spectra. Also, spectra of pure gases can be added in the computer to produce an artificial mixture, for comparison with a real sample.

Most work with pure light hydrocarbons was done from 3250-2750 cm⁻¹ in the region of the C-H stretching frequency. Some work with heavier hydrocarbons was done in the fingerprint region from 1000-500 cm⁻¹. Light hydrocarbons used were methane, ethane and propane, while benzene and toluene were used as heavier aromatic hydrocarbons. Data for the computer was acquired at 1/10 cm⁻¹ increments over 500 cm⁻¹, giving 5000 data points. Spectra of larger regions were also measured at 1 cm⁻¹ resolution. Typical IR conditions were 50 cm⁻¹/min, 1.5 cm⁻¹ resolution: pathlength from 0.75 to 21.75 meters.
Figure 7.2.6 Diagram of IR System

Figure 7.2.7 Vapor Sampler and Desiccator
7.2.3 G.C. Analytical Techniques

Qualitative/Quantitative Procedure

(A) Water Column

After infrared analysis was completed, the CS$_2$ was completely removed from each of the extracts by evaporation and the residue was taken up in 2 liters of hexane.

The samples were then analyzed by Gas Chromatography (GC) on either a Hewlett Packard Model 5710A or a Perkin Elmer Sigma 2, both equipped with flame ionization detection and 10-m by 3-mm column packed with SP2250 (temperature programmed at 8 degrees C/MIN).

(B) Air Analysis

a) Separation on GC followed by IR - prior to extraction of the sample impregnated charcoal: an internal standard, n C$_{20}$ (eicosane) was added to the solvent, CS$_2$. Eicosane was chosen since its GC peak does not overlap any of the GC peaks of the sample, thus its area and height can be easily determined. The concentration of the standard was about 50 ppm. Gas chromatograms were measured using a Hewlett-Packard Model 700. The GC was modified for collecting fractions. The GC is equipped with a 10 ft., 1/8 in. column of 10% SP2250 on 100/120 Supelcoport and a flame ionization detector (FID). The detector destroys the eluents, therefore, it was necessary to split the effluent prior to the detector. A Swagelok union T was inserted between the column and the detector (inside the oven) to split the flow valve. A stop-flow valve was placed between the splitter and the FID detector. Another stop-flow valve and a fine metering valve (Nupro 48M) was installed between the splitter and the device. The splitter and all three valves were located in the oven, however, the metering valve could be controlled externally. A schematic of the oven compartment is shown in Figure 7.2.8.

After the two valves on the collection side of the splitter, the effluent exits the oven compartment through a temperature controlled heated jacket to the "merry-go-round" device shown in Figure 7.2.9. This device was made in-house of Teflon; the eluent enters the device through the center and is directed at a right angle to the front where it enters one of the 20 possible holes containing a charcoal cartridge.

To collect a number of fractions, the GC eluents were monitored by the FID detector (10% going to detector, 90% to the collection device). When the recorder indicates that a GC fraction was starting to elude the column, the collection device is manually moved to a position containing the desired charcoal cartridge. The eluent was collected and the device was rotated to another position for collecting the next fraction.

The possibility of a single component concentration exceeding the breakthrough level of a charcoal cartridge was investigated for a number of components by attaching a second cartridge to the exit of the first cartridge. The components could not be detected in the solutions of the desorbed cartridges; thus, it was concluded that under typical GC conditions the breakthrough level would not be exceeded.
Figure 7.2.6 GC Column Arrangement in Oven

column compartment

Figure 7.2.7 The collecting device:
a - inlet
b - positions of charcoal cartridges
c - turning part

Figure 7.2.9 Device for CollectingGas Samples
h) IR analysis, followed by GC of total sample - subsequent to infrared analysis of the charcoal extract. Gas chromatograms were measured on either the Hewlett Packard 700 or the Hewlett Packard 5710A, both previously described.

7.2.4 GC-Mass Spec Analytical Procedures

The GC/MS/CS system was developed in order to analyze water extract samples for aromatic hydrocarbon compounds. The MS is of the chemical ionization (CI) variety and is ideally suited for aromatic compounds. The nucleophilic nature of these compounds increases the reaction cross section and enhances the sensitivity. Also the nature of the CI process yields a strong molecular ion peak and, therefore, is readily interpretable.

CI is a phenomenon resulting from ion-molecule interactions and requires gas mixture pressures on the order of one Torr in the MS ion source. The composition of the gas is such that the reagent gas, in this case CH₄, is present at a much higher concentration than the sample. Primary ionization occurs in the reagent gas because of its great excess through electron impact ionization. These reagent ions then react with the reagent gas in second order processes to produce stable ions characteristic of each gas (for CH₅⁺ and C₂H₅⁺). These reagent ions are stabilized as a plasma in the ion source and there are no further reactions of these characteristic reagent ions with the reagent gas.

When a reagent ion encounters a sample molecule, one of several chemical interactions may occur. These include transfer of a proton, a hydride ion, another ion fragment, or a charge. One important advantage of CI as opposed to electronic impact (EI) is that the average energy transferred to the sample molecule by the reagent ion is much less than that transferred by EI ionization and this leads to only a small amount of fragmentation and, therefore, a large molecular ion peak.

A chemical ionization system can be readily interfaced with a gas chromatograph. Because the source operates at high pressures, sample separations can be eliminated and the entire effluent from the GC can be introduced into the ion source. Because of the vast amounts of data produced by a GC/MS system, a dedicated computer system for control and data acquisition is a necessity.

The objectives were as follows:

a. Assemble the MS system with its associated vacuum system, cooling systems, electrical and electronic system and sample handling systems.

b. Interface a gas chromatograph to the sample inlet of the MS and determine the optimum columns and conditions for operations.

c. Interface the GC/MS to a computer system and develop the necessary hardware and software to support such a system.

A HP-5710A gas chromatograph with capillary column pneumatics was used to separate the extract mixtures prior to MS analysis. A J Scientific SP--2250 glass capillary column was finally chosen as the most versatile and efficient column for the separation of a low to medium
mass aromatic hydrogen. Temperature programming was from 90° to 270°C at 4°C/min. The carrier gas was helium. The injector was automatically purged 45 seconds after injection.

The MS was a Biospect/Finnegan with a CI source and a quadrupole mass separator. A complete MS scan from 50 to 400 amu was performed three times per second and this data was stored by computer. The scan rate was controlled by the computer through a DAC. The rate could also be manually controlled by the operator. The GC effluent was introduced directly into the MS source through a heated glass lined tube. The solvent peak was not vented to the atmosphere, rather the source filament was turned off while the solvent was passing into the MS. This was easily monitored via the source pressure gauge.

The computer system was a Data General Corp. NOVA3/12 with 64K word memory, foreground/background and memory map protection, 10M byte cartridge disk system, 16 channel 12 bit ADC, 2 channel 12 bit DAC, 16 channel digital I/O, CRT, TTY, and a plotter. The software used was DGC Fortran IV and DGC Nova assembly language. The Fortran was used mainly for data management, processing, and display. The assembly language was used for data acquisition and instrument control.

Figure 7.2.10 is a typical mass spectrum scan of a several component mixture containing PAH. The identified compounds are toluene, phenanthrene, anthracene, fluoranthrene, pyrene, triphenylene, benzanthracene and chrysene. This spectrum was obtained using the solids probe and was used as a calibration scan.

Figure 7.2.11 is a total ion plot showing the reconstructed gas chromatogram for an n-paraffin calibration mixture.

Figures 7.2.12 and 13 show the total ion plot and subsequent mass spectrum for a sample of dimethyl-naphthalene in hexane. As can be seen from the total ion plot, a compound is indicated by a GC peak at 390th scan. The mass spectrum of scan 390 indicates a molecular ion mass of 157 amu which corresponds to the dimethyl-naphthalene.

Figure 7.2.14 shows the total ion plot-reconstructed gas chromatogram for the aromatic fraction of a fuel oil. Naphthalene, methyl naphthalenes, dimethyl-naphthalenes, tri-methyl naphthalene and phenanthrene can be clearly and unambiguously identified.

Figure 7.2.15 shows the total ion plot of deasphalted Kuwait Crude oil in hexane. Benzene, xylene, naphthalene, methyl-naphthalene and dimethyl-naphthalene can be identified along with the n-paraffins.

Figure 7.2.16 shows the total ion plot for a water extract from the south tank top after one hour. Xylene, naphthalene, methyl-naphthalene, and dimethyl-naphthalene along with n-paraffins were detected.

Figure 7.2.17 shows the total ion plot for a water extract from the South tank top after 24 hours. Naphthalene, methyl-naphthalene, dimethyl naphthalene along with n-paraffins were detected.
Figure 7.2.10 Typical Mass Spectrum of a Several Component Mixture Containing P, A, H.

Figure 7.2.11 Total ion plot showing the reconstructed Gas Chromatogram for an n Paraffin Calibration Mixture.

1 ml C_{10}H_{20}C_{14} in hexane
11 Oct. '76

30 to 70°C 6 ft Capillary
20 psi 50-200 glass capillary
C_{16}-C_{18} ~ 1000 milliliters 6 source
Figure 7.2.12 Total Ion Plot for the Sample of Dimethyl-napthalene in Hexane

Figure 7.2.13 Mass Spectrum of Scan 390

Dimethyl-napthalene
Figure 7.2.14 Total ion Plot Reconstructed - GC for Aromatic Fraction of Fuel Oil

Figure 7.2.15 Total ion Plot of Desphalted Kuwait Crude Oil and Hexane
Figure 7.2.16 Total ion Plot for a Water Extract from the South Tank after one hour

Figure 7.2.17 Total ion Plot for a Water Extract from the South Tank after 24 hours
Figure 7.2.18 shows the total ion plot for a water extract from the south tank mid after 24 hours. Methyl-naphthalene, dimethyl-naphthalene, along with n-paraffins were detected.

- no benzene detected
- no xylene detected
- no naphthalene detected

**Figure 7.2.18  Total ion plot for Water Extract from the middle of South Tank after 24 hours**

Scan 304 - methyl-naphthalene (m/z 142)
Scan 394 - dimethyl-naphthalene (m/z 156)

**SMID 24**

**TOTION**

- 3 X
- 15 filters
- 90 to 270°C @ 8°C/min.
- SP-2100 capillary column

18 Oct. '78
7.3 Laboratory Experiments:

The laboratory experiments were intended to:

1) test the available methodology

2) develop new methods

3) be used as cursory analyses of the oil/dispersant system to provide an overview of the analytical problems that would be encountered and the results that may be anticipated in the meso-scale and "real world" environments.

For these experiments, untreated and chemically treated spills were manufactured in laboratory scale test tanks and in larger, outdoor tanks. The oils used in the experiment were API Kuwait Crude, API South Louisiana Crude; the No. 6 oil involved in the Argo Merchant Spill (Dec., 1976), and the No. 2 oil from the Buzzards Bay Spill (Jan., 1977).

7.3.1 Water Column

(A) Methodology:

Effect of dispersant on Kuwait Crude and S. Louisiana Crude: Four fiberglass containers were filled with 28 liters of Narragansett Bay sea water. Vertical agitation of the water was provided by the vertical motion of Al paddles hinged to the bottom of each container and attached to a motor via a nylon string. Ten ml. of each oil were placed in two test tanks and 10 ml. oil/2ml dispersant were placed in two other test tanks. Qualitative results on the second laboratory experiment are given in Table 7.3.1. The total relative amounts of petroleum entering the water is about the same for the two oils. A large amount of phthalic acid esters (phthalates) were found in the Kuwait test tank after 24 hrs., the source of which could not be traced.

(B) True solubility of petroleum chemicals:

For this series of experiments, "artificial sea water" was used and was prepared by adding a specified amount of Instant Ocean (Aquarium System, Inc., Ohio) to distilled water. Oil was added to the surface of the water contained in a large glass carboy. The water was gently agitated with a slowly moving magnetic stirrer for the duration of the experiment.

The results for two different initial concentrations of So. La. Crude are given in Figure 7.3.1. Two 1 liter water samples were collected prior to each experiment (controls or C), two subsurface samples at 1 hour, and two at 24 hours. One 1 liter sample from each time period was analyzed without filtering and the other was filtered through a 0.45 mm Millipore filter prior to analysis. The filtering was performed in order
Table 7.3.1
Qualitative Results of 2nd Laboratory Experiment

<table>
<thead>
<tr>
<th>Test System</th>
<th>1 hour</th>
<th>24 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kuwait Crude</td>
<td>1</td>
<td>High in Phthalates (some oil)</td>
</tr>
<tr>
<td>Kuwait/Disp.</td>
<td>3</td>
<td>7b</td>
</tr>
<tr>
<td>So. La. Crude</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>So. La. Crude</td>
<td>3</td>
<td>7</td>
</tr>
</tbody>
</table>

a Estimated from IR spectra
b After separation by column chromatography

Figure 7.3.1 Total extractable Organics from Laboratory Experiment on South Louisiana Crude Oil with Initial Concentrations of 6 and 28 ppm.
to remove dispersed droplets; however, the control also contained considerable amounts of filterable particles.

Starting with 3 ppm of the crude oil (e.g., 15 mg of oil added to the surface of 5L. of water) we observed an overall increase in total organics after 24 hours; however, after filtering, the controls, 1 and 24 hour samples contained (within experimental error) the same amounts of extractable organics. In the experiment with an initial concentration of 28 ppm, the total organics in the unfiltered water increased by 0.094 ppm and those in the filtered water by 0.056 ppm after 24 hours in the filtered water. These two experiments indicate that the relative amounts of soluble organics in oil is low; however, directly beneath a slick, soluble compounds can be found as is indicated in the 28 ppm experiment.

We performed the same experiment with the No. 6 oil from the Argo Merchant spill. In this case 6.2 ppm of the oil were added to the artificial sea water; the results are presented in Figure 7.3.2. Again, the amount of oil entering the water was small; the amount of total extractable organics in the filtered water increased by 0.020 ppm after 24 hours.

The same experiment was performed with the No. 2 fuel oil from the Buzzards Bay spill. The results are presented in Figure 7.3.3. The initial concentration of 24.7 ppm is similar to the second So. La. Crude oil experiment and the results are similar. There was an increase in the total organics in the unfiltered water after 1 and 24 hours. Furthermore, the true solubles increased by 0.035 ppm after 24 hours in the filtered water.

Another useful result can be obtained from Figures 7.3.1-7.3.3 and that is the high concentration of extractable organics in the control sample of the artificial sea water (Instant Ocean). Typical values for extractable organics in the Atlantic Ocean are from 0.010 to 0.100 ppm, whereas the control sample of the artificial sea water contained 0.200 ppm. Qualitatively, we found a relatively high concentration of phthalates and polymers in the control samples.

(C) Outdoor experiments:

In the laboratory experiments designed to measure hydrocarbons in the water column from untreated and treated spills, the amount of oil used was just enough to give a slick of 0.05 mm thickness. However, even with dispersant only a very small fraction of the oil stayed in the water column. We felt that this was due to the small volume of water in the containers. Thus, we performed two experiments in larger test tanks using the aquarium facilities at the Narragansett Bay Campus.

Three 55 gallon fiberglassed drums were fitted with the paddle system described above to provide agitation. Each drum was filled with 190 l. of sea water on 10/26/76, and the following added:

1) Kuwait Crude, 155 ml (70 ppm)
2) Kuwait Crude/Corexit 9527, 15.5/3.1 ml
3) Corexit 9527, 3.1 ml
TOTAL ORGANICS
Argo Merchant 6.2 ppm
in Inst. Ocean

Figure 7.3.2 Total Extractable Organics from Laboratory Experiment on the No. 6 Fuel Oil from the Argo Merchant Spill.

TOTAL EXT. ORGANICS
Buzzards Bay (No. 2 fuel)
24.7 ppm in Inst. Ocean

Figure 7.3.3 Total Extractable Organics from Laboratory Experiments on the No. 2 Fuel Oil from the Argo Merchant Spill.
The dispersant and oil were thoroughly mixed with sea water in a 1 liter bottle prior to adding to drum #2. A 2 liter water sample was collected while filling the drums and this was used as a control. Samples (2,1) from each drum were collected at 2 and 25 hours at a depth 20 cm from the bottom. The samples were analyzed without adding an internal standard for GC analysis in order to determine the amount of internal standard needed in later experiments. Qualitative results by infrared spectroscopy indicated that an extremely small amount of oil entered the water column when the dispersant was not used.

The above experiment was repeated on 11/11/76 and all samples analyzed for total hydrocarbons, n-paraffins, other resolved components, unresolved hydrocarbons, and amount of dispersants using gas chromatography. The test tanks contained the same amount of water, oil and dispersant as the above experiment. The results of the chemical analysis are given in Table 7.3.2. The control sample contained a total of 10 g/liter of hydrocarbons. The water in the test tank having only the Kuwait Crude contained 108.4 g/liter after 2 hours, and 158.2 g/liter at 25 hours, whereas the test tank containing oil and dispersant had 646.5 g/liter after 2 hours and 20 g/liter after 25 hours. The latter value is much lower than anticipated, and we have no explanation for it at the present time.

In addition to collecting water samples, surface slick samples were also collected during experiments 1 and 2, and their infrared spectra measured. The infrared spectral fingerprints of seven samples were compared using the log-ratio method (1). In this method, the absorbivities for 18 bands in the fingerprint region are ratioed, logs of the ratios calculated and these log-ratios normalized to eliminate differences in sample thickness. Then the number of ratios within 10% of the average ratio are listed. If two samples are identical, all 18 ratios would be equal to the average; thus, the number of ratios within 10% of the average indicates the similarity between samples.

In the present case, spectra of the following samples were compared:

Kuwait = Kuwait Crude
K/D2 = Kuwait/Dispersant in H2O column after 2 hours.
K/D24 = Kuwait/Dispersant in H2O column after 24 hours.
Surf 1 K = Kuwait on surface after experiment 1.
Surf 2 K = Kuwait on surface after experiment 2.
Surf 1 K/D = Kuwait/Disp on surface after experiment 1.
Surf 2 K/D = Kuwait/Disp on surface after experiment 2.

The results given in Table 7.3.3 provide some useful comparisons. The fingerprints of the oil in the water column, K/D2 and K/D24, are considerably different from that of the Kuwait crude. The surface oil in the first experiment, Surf 1 K/D, is also very different from the Kuwait oil. In the first experiment, the oil, dispersant and water were
Table 7.3.2

Chemical Analysis by Gas Chromatography of 2nd Aquarium Experiment (11/11/76)
g/liter of water

<table>
<thead>
<tr>
<th>Test Tank</th>
<th>Time</th>
<th>n-paraffins</th>
<th>other resolved components</th>
<th>unresolved envelope</th>
<th>total hydrocarbons</th>
<th>dispersant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kuwait oil</td>
<td>2 hrs</td>
<td>6.7</td>
<td>16.2</td>
<td>85.5</td>
<td>108.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>25 hrs</td>
<td>13.2</td>
<td>10</td>
<td>135</td>
<td>158.2</td>
<td></td>
</tr>
<tr>
<td>Kuwait Oil &amp;</td>
<td>2 hrs</td>
<td>97.5</td>
<td>60</td>
<td>489</td>
<td>646.5</td>
<td>240*</td>
</tr>
<tr>
<td>Dispersant</td>
<td>25 hrs</td>
<td>—-----------</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Dispersant</td>
<td>2 hrs</td>
<td>—-----------</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Control</td>
<td>0 hrs</td>
<td>—-----------</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

*Based on the area of the GC peak of one component; thus, the amounts listed for the dispersants are only relative values.

Table 7.3.3

Comparison of Infrared Spectra of Kuwait, Water Column and Surface Samples from Aquarium Experiments.

Number of ratios within 10% of average are listed.

<table>
<thead>
<tr>
<th>Kuwait</th>
<th>K/D²</th>
<th>K/D¹</th>
<th>Surf₁K</th>
<th>Surf₁K/D</th>
<th>Surf₂K</th>
<th>Surf₂K/D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kuwait</td>
<td>18</td>
<td>7</td>
<td>3</td>
<td>11</td>
<td>5</td>
<td>11</td>
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<tr>
<td>K/D²</td>
<td>18</td>
<td>9</td>
<td>10</td>
<td>7</td>
<td>9</td>
<td>8</td>
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<tr>
<td>K/D²₄</td>
<td>18</td>
<td>6</td>
<td>16</td>
<td>18</td>
<td>18</td>
<td>11</td>
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<tr>
<td>Surf₁K</td>
<td>18</td>
<td>2</td>
<td>16</td>
<td>18</td>
<td>18</td>
<td>11</td>
</tr>
<tr>
<td>Surf₁K/D</td>
<td>18</td>
<td>12</td>
<td>7</td>
<td>7</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Surf₂K</td>
<td>18</td>
<td>11</td>
<td>11</td>
<td>11</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>Surf₂K/D</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Experiment 1; both samples were separated by TLC
thoroughly mixed in a 1 liter bottle prior to adding to the test tank. The second experiment, oil, and oil/dispersant were added to the test tanks, and then agitated with a stirring rod; thus, both surface samples compared better with the Kuwait oil.

7.3.2 Air Column

1 Charcoal Tubes

(A) Methodology

1) To analyze the air above simulated spills for hydrocarbons, the laboratory apparatus for collecting volatiles is shown in Figure 7.3.4. Initially, water is placed in the central flask and air is pumped through a charcoal filter, around the central flask, and through one of the charcoal cartridges (which becomes the control). Then oil is placed on the water in the central flask, air is pumped through the system, and the hydrocarbons are collected in the second charcoal cartridge.

After the experiment, the two charcoal canisters are extracted with CS$_2$. Infrared spectra and gas chromatograms of the solutions are measured; both giving qualitative and quantitative analyses.

The first set of experiments was performed on the No. 2 fuel from the Buzzards Bay spill. One hundred and fifty ml. of artificial sea water were placed in the central container and air was pumped through one of the cartridges for 1 hour; this was used as the control. Then 0.1 g of oil was added to the surface of the water and air pumped through the second cartridge for one hour. After the experiment, water from beneath the surface was extracted and analyzed. The gas chromatograms of the cargo oil, the air sample and the water sample are shown in Figure 7.3.5. For this oil, the "separation point" for the chemicals going into the atmosphere from the chemicals going into the water column is the normal paraffin n-C$_{14}$; the lighter molecules go into the air and the heavier into the water. Later in this report, these laboratory results are compared to the field experiments on this oil (Section 7.6).

2) Following this preliminary experiment, the more sophisticated laboratory apparatus in Figure 7.2.2 (Section 7.2.28) was constructed. When systems 1 and 2 were used, 1 ml of Kuwait crude oil was added to the surface of 150 ml. of sea water in one flask and 1.2 ml of a mixture of 5:1 (v/v) Kuwait crude oil and Corexit 9527 dispersant, were added to 150 ml of sea water in the other flask. The surface and the water were not mixed.

When system 3 was used (Fig. 7.2.6), 2 ml of Kuwait crude oil were added to the surface of 800 ml of sea water in each of the beakers, 0.4 ml of Corexit were then added dropwise to one of the beakers. The beakers were shaken immediately after the dispersant was added for a few seconds. This caused the water in the beaker containing the oil and dispersant to darken. In a few experiments, the system was continuously mixed by magnetic stirrers. Identical magnetic stirrers were used in both beakers and the stirring rate was approximately the same.
Figure 7.3.4 Laboratory Apparatus for Collecting Volatiles from Oil Slimes

Figure 7.3.5 Gas Chromatograms from the Laboratory Experiment on the No. 2 Fuel Oil from the Buzzards Bay Spill
Air samples were taken simultaneously from both the treated and untreated slicks. In experiments when flow rates were measured, they did not differ by more than 10. Air samples were collected periodically after the spills. Experiments were conducted using 3 different flow rates of 0.2, 1.5 and 4.3 l/min.

Since air samples taken above treated and untreated spills were compared to evaluate the effects of the dispersant, it was important to determine error limits by comparing two identical oil samples. Oil was added to flasks 1 and 2 of systems A, B, and C; air samples were taken from both parts simultaneously and their gas chromatograms were compared. The results of such experiments indicate those differences which are significant when a dispersant is used. The conditions for these experiments are listed in Table 7.3.4.

Three different types of experiments were performed to determine the effects of using dispersants:

a) Using apparatus 1 and 2, oil and oil + dispersant were added and the surface was not mixed.

b) Using apparatus 3, oil was added and then the dispersant was added dropwise. The beakers were shaken for a few seconds after adding the oil and the dispersant.

c) Same as 2 with continuous stirring by magnetic stirrers. Table 7.3.5 lists all experiments performed in the laboratory on evaporation of oil vs. oil + dispersant.

In experiment 6, surface samples were taken at times 1.5 and 4 hours after the spill. In experiment 11, surface samples were collected with a spatula and dried with calcium chloride. Hexane was added to deasphalt the oil. The samples were then centrifuged to remove the calcium chloride and the asphalt precipitate.

IR spectra were measured using 6 mm (pathlength) cells with silver chloride windows and teflon or stainless steel spacers. Carbon disulfide was used as a solvent for the IR measurements.

Another type of experiment was performed. A random mixture of pentane, hexane, octane, nonane, decane, dodecanne, tetradecane, o-xylene, p-xylene, m-xylene, toluene and benzene was prepared. About 1 ml of the mixture was added to 150 ml of sea water and 1 ml of the mixture and 0.2 ml Corexit were added to another flask with 150 ml of sea water. Vapors were collected using apparatus A; the flow rate was about 0.2 l/min and the water was not mixed. The same experiment was performed using apparatus B and the flasks were shaken after adding the mixtures. A flow rate of 3.4 liters/min was used for this experiment.

(B) Experimental Results

(i) Oil vs. oil on water-evaporation experiments

Experiments 1-5, as mentioned in the above section, were performed in order to find the experimental errors of systems 1, 2, and 3 and to
Table 7.3.4
Flow Rates and Sample Times for Laboratory Experiments 1-5

<table>
<thead>
<tr>
<th>Exp #</th>
<th>Water Temp.</th>
<th>Time Taken</th>
<th>System</th>
<th>Flow Rates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OC</td>
<td></td>
<td></td>
<td>oil 1</td>
</tr>
<tr>
<td>1</td>
<td>19</td>
<td>0-0.5</td>
<td>A</td>
<td>1.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5-1.5</td>
<td>A</td>
<td>1.44</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5-4</td>
<td>A</td>
<td>1.24</td>
</tr>
<tr>
<td>2</td>
<td>19</td>
<td>0.5-1.5</td>
<td>B</td>
<td>1.56</td>
</tr>
<tr>
<td>3</td>
<td>19</td>
<td>0-0.5</td>
<td>B</td>
<td>1.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5-1.5</td>
<td>B</td>
<td>1.56</td>
</tr>
<tr>
<td>4</td>
<td>18</td>
<td>0-0.5</td>
<td>C</td>
<td>2.00</td>
</tr>
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<td>1.76</td>
</tr>
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<td>5</td>
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<td>0-0.5</td>
<td>C</td>
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<td></td>
<td></td>
<td>0.5-1.5</td>
<td>C</td>
<td>4.30</td>
</tr>
</tbody>
</table>

Remarks:
- Time - hours after the spill.
- Flow rates are in lit/min.
- In experiment 2, did not pump during 0-0.5 hours.
- In experiment 4, distance between funnel and beaker 2.5 cm.
- In experiment 5, distance between funnel and beaker 1.5 cm.
- and there was 1200 ml sea water in the beakers.
### Table 7.3.5
Flow Rates and Sample Times for Laboratory Experiments 6-16

<table>
<thead>
<tr>
<th>P</th>
<th>Water Temp.</th>
<th>Time Taken</th>
<th>System</th>
<th>Flow Rate</th>
<th>Mixing</th>
</tr>
</thead>
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<tr>
<td></td>
<td>°C</td>
<td></td>
<td></td>
<td>oil/oil/disp</td>
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</tr>
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<td>6</td>
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<tr>
<td></td>
<td></td>
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<td>A</td>
<td>&lt; 0.2 &lt; 0.2</td>
<td></td>
</tr>
<tr>
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<td>&lt; 0.2 &lt; 0.2</td>
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<tr>
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<td></td>
<td>0.5-4</td>
<td>A</td>
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<td>no</td>
</tr>
<tr>
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<td></td>
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<td>4-7</td>
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</table>

**Remarks:**
- Flow rates are in lit/min.
- Time is in hours after the spill.
- Const. = constant mixing during the entire experiment.
determine if differences between the evaporation of oil and oil + dispersant slicks are due to the dispersant or to the experimental conditions and procedures. When both parts of the system contained only oil, differences in the evaporation rates could be caused by differences in flow rates, or differences in the crude filters used in system A. Since only the GC peaks of the normal alkanes were definitely identified and their GC peaks are the most intense, they were used to compare the two samples. Each sample, i.e., the one taken above part 1 and the one taken above part 2, contained the same amount of internal standard (n-C20). The relative heights of the GC peaks of each normal alkane to the height of n-C20 were calculated and plotted as a function of the carbon number of that certain n-alkane. The plots for experiment No. 1 for the samples collected during 0-0.5, 0.5-1.5 and 1.5-4 hrs. after the oil addition are shown in Figure 7.3.6. The evaporation rates of oil components from the slick were ordered according to their vapor pressures, i.e., heptane, octane, etc. Usually after 0.5 hrs., these graphs have maxima which change with time towards the heavier n-alkanes. For example, in experiment 1 (slick 1) the sample taken during 0.5-1.5 hrs. had a maximum at n-C9, whereas in the sample taken at 1.5-4 hrs. the maximum moved to n-C10.

The ratio HCx/HC20 (x=7,8,......), where HCx is the GC peak height of a normal alkane with x carbons and HC20 is the GC peak height of n-C20, is proportional to the amount of n-Cx that evaporated. This ratio for a particular n-alkane in two air samples taken under the same conditions can be compared, i.e., the ratio HC8/HC20 in air samples taken during the same time and in the same experiment above slick 1 and slick 2. This comparison was justified since the collection efficiency, extraction efficiency, detector response, GC conditions (temperature and flow rate) and the amount of standard added to both samples were the same. The envelope formed by these plots indicates when a certain n-alkane starts to evaporate and when its evaporation process is over. The differences in the shape of the envelopes of two samples taken during the same time and conditions indicate differences in the evaporation process of the light components from the slick. For experiments 1-5, the more similar the shapes of the envelopes of the two samples taken simultaneously, the better, i.e., it means that the system is good for determining the effects of dispersants on the evaporation.

Figure 7.3.6 shows the envelopes obtained for experiment 1. When system A was used, there was a difference in the position of the maximum in the samples of 0.5-1.5 and 1.5-4 hrs. The evaporation rates of the two identical slicks were different. Slick No. 1 had a faster rate. It could be that the crude filters were not exactly identical and have caused the differences. Experiments 2 and 3 were performed using apparatus B which is similar to apparatus A, with the filters removed. Results of these experiments are illustrated in Figure 7.3.7. The envelopes obtained for slicks 1 and 2 at 0.5-1.5 had the same shape. The evaporation process was faster when the filters were removed and the maximum of the envelope was at n-C10 for both slicks in experiments 2 and 3, whereas in experiment 1, it was at n-C8 for slick 2 and at n-C9 for slick 1. Collection efficiency decreased from experiment 1 to experiments 2 and 3. This could be due to the removal of the filters. When they covered the apparatus, they could have interfered in the escape of vapors into the room atmosphere, so less was lost and more was collected;
Figure 7.3.6 Evaporation Profiles from Oil Slicks - Experiment 1

Figure 7.3.7 Evaporation Profiles from Oil Slicks - Experiments 2 and 3
this could also be the reason for the slower evaporation rate.

The results of experiments 1, 2 and 3 indicated that another system should be tried in which more sea water and more oil would be used. This would ensure that the air samples would be concentrated enough without having to interfere in the natural evaporation process, e.g., partially closing the system. System C seemed to fulfill those requirements. Figure 7.3.8 shows the results obtained when apparatus C was used (experiment 4). There is a slight difference between the two envelopes in the relative amounts of n-C10 and n-C11 (less than 10). Experiment 5 was the same as experiment 4 except for the flow rate that was higher and the distance between the oil slicks and the funnels, which was smaller in experiment 5. Results are illustrated in Figure 7.3.9; samples were too concentrated and the evaporation rate was slower than in experiment 4, possibly because the funnels were too close to the oil surface. Differences between the two envelopes were in the same order as in experiment 4.

(ii) Oil vs. oil + dispersant evaporation experiments

a) Experiments with no mixing of the surface:

Laboratory experiments 6-9 were performed under identical conditions. Samples were taken at 0-1.5 and 1.5-4 hrs. after adding the oil and oil + dispersant using system 1. The n-alkane GC peaks were identified by retention time. Toluene, p-xylene, m-xylene, and o-xylene GC peaks were also identified by retention time and, furthermore, their GC effluents were collected and IR spectra measured. The IR spectra showed that their peaks contained an additional component, which was probably a branched alkane. The benzene peak was identified by retention time and by the appearance of the benzene band at 670 cm\(^{-1}\) in the IR spectrum of the mixture. For air samples collected at 0-1.5 hrs., the following ratios of the GC peak heights were calculated: benzene/octane, toluene/nonane and p-xylene + m-xylene/nonane. Table 7.3.6 lists the values obtained.

From the values shown in Table 7.3.6, it can be observed that the corresponding ratios are bigger in the oil + dispersant sample than in the oil sample. This could mean that there was less octane and nonane evaporating from the treated slick than from the untreated slick, or that more of the benzenes were evaporating from the untreated slick. This could be caused by the dispersant mixing more aliphatic than aromatic hydrocarbons into the water column. Decane was not taken into consideration in the calculations as its corresponding GC peak was small and it also contained o-xylene.

Figure 7.3.10 shows the gas chromatograms of the air samples above the treated and untreated oil spills taken at 0-1.5 hrs.

It was interesting to see whether this phenomenon also occurred when mixing was applied; thus, experiments 15 and 16 were performed with constant mixing. When calculating the above mentioned ratios for samples taken at 0-0.5 hrs., the trend found in experiments 6-9 was not observed. When mixing was applied, the dispersant affected the light and the heavy hydrocarbons differently, whereas without mixing the dispersant
Figure 7.3.8 Evaporation Profiles from Oil Slicks - Experiment 4

Figure 7.3.9 Evaporation Profiles from Oil Slicks - Experiment 5
Figure 7.3.10 GC of Air Samples at 0-1.5 Hours

TABLE 7.3.6
Ratios of GC Peak Heights for Experiments 6-9

<table>
<thead>
<tr>
<th></th>
<th>Exp 6</th>
<th>Exp 7</th>
<th>Exp 8</th>
<th>Exp 9</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oil</td>
<td>Oil/Disp</td>
<td>Oil</td>
<td>Oil/Disp</td>
</tr>
<tr>
<td>ben/oct</td>
<td>1.16</td>
<td>1.35</td>
<td>1.17</td>
<td>1.37</td>
</tr>
<tr>
<td>tol/non</td>
<td>1.36</td>
<td>1.70</td>
<td>1.54</td>
<td>2.00</td>
</tr>
<tr>
<td>m-xy/non</td>
<td>0.63</td>
<td>0.93</td>
<td>0.65</td>
<td>0.82</td>
</tr>
</tbody>
</table>

ben = benzene
tol = toluene
non = nonane
oct = octane
o,m-xy = p-xylene + m-xylene
affected aromatics and aliphatics differently. This is illustrated in Table 7.3.7 which shows the ratios of corresponding peak heights in the two gas chromatograms obtained from air samples in experiment 15. The order of the compounds in Table 7.3.7 is the order in which their peaks appear on the gas chromatogram. If relative amounts of those components were the same in both samples, those ratios should have been constant; however, they increase from the lighter components toward the heavier ones, indicating that relatively less of the light ones, such as heptane, benzene and octane, evaporated from the treated slick.

The chromatogram of the samples taken at 1.5-4 for experiment 6-9, Figure 7.3.11, show that the evaporation was faster for the oil slick. The n-C7 peak was very small in the oil sample and n-C9 was the strongest peak. In the oil + dispersant sample, n-C7 was relatively more intense and n-C8 peak was almost as high as the n-C9 peak. Surface samples taken in experiment 6 at 1.5 and 4 hrs. after the spills indicated the same results, i.e., the oil slick evaporated faster. After 4 hrs., n-C8 was gone from the oil slick, but it still appeared in the oil + dispersant slick. Slight mixing might have been performed when the surface samples were collected and when charcoal tubes were changed.

In order to obtain more conclusive data about the effect of the dispersant on aromatic and aliphatic hydrocarbons, a known mixture of light aromatics and aliphatic hydrocarbons was investigated. When no mixing energy was applied there was no significant difference between the relative heights of the n-alkanes and benzene with and without dispersant. When mixing was applied, there were differences; the amount collected above the mixture was larger than the amount collected above the mixture/dispersant. The relative amounts of benzene, octane, n-C12 and n-C14 in the mixture/dispersant were higher than in the mixture only. Relative amounts of Toluene, p-xylene + m-xylene and decane + o-xylene were the same in both samples. Table 7.3.8 shows the ratios of the peak heights in both samples. These results suggest that the dispersant has different effects on light hydrocarbons than on heavier ones without regarding aromatic character but, as this is a simple mixture and not oil, it may be inaccurate to apply results from one system to the other.

In experiment 10 and 11, air samples were taken over 30 hrs. so that evaporation rates of heavier hydrocarbons could be obtained. Experiments 10 and 11 were the same except for the flow rate of the pump, which was higher in experiment 11. Evaporation rates of each of the n-alkane can be obtained by plotting the total amount collected during time x as a function of time. The total amount of a certain n-alkane collected up to a certain time is proportional to the sum of HCx/HC20 in the air samples taken up to that time. For example, the total amount of n-C8 that was collected during 4 hrs. will be proportional to: (HC8/HC20) 0-0.5 + (HC8/HC20) 0.5-1.5 + (HC8/HC20) 1.5-4. This is correct only if the same amount of standard was added to all samples. Since the collection efficiency is unknown, the proportionality constant between the total amount evaporating and the sum of the relative height cannot be calculated, but plotting that sum as a function of time will be sufficient to show evaporation rates.
Table 7.3.7 Ratio of Corresponding Peak Heights - Experiment 15

<table>
<thead>
<tr>
<th>hep</th>
<th>R-ben</th>
<th>R-oct</th>
<th>R-tol</th>
<th>R-non</th>
<th>R-p,m-xy</th>
<th>R-o-xy+dec</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>0.91</td>
<td>0.92</td>
<td>1.3</td>
<td>1.34</td>
<td>1.57</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Is the ratio of the GC peak height of x in the oil/dispersant sample the GC peak height of x in the oil sample.

h = heptane
b = benzene
o = octane
n = nonane
t = toluene
m-xy = p-xylene + m-xylene
xy+dec = o-xylene + decane

Table 7.3.8 Ratio of GC heights for Both Samples

<table>
<thead>
<tr>
<th>R-oen</th>
<th>R-oct</th>
<th>R-tol</th>
<th>R-non</th>
<th>R-p,m-xyl</th>
<th>R-o-xyl+dec</th>
<th>R-dode</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.02</td>
<td>1.21</td>
<td>1.71</td>
<td>1.69</td>
<td>1.72</td>
<td>1.76</td>
<td>0.47</td>
</tr>
</tbody>
</table>

Is the ratio of the GC peak height of x in the mixture sample to the peak height of x in the mixture/dispersant sample.

ben = benzene
oct = octane
tol = toluene
non = nonane
p,m-xyl = p-xylene + m-xylene
o-xyl+dec = o-xylene + decane
dode = dodecane
tetd = tetradecane
Figure 7.3.11 GC of Air Samples at 1.5-4 Hours - Experiments 6-9
Figures 7.3.12, 7.3.13, and 7.3.14 show the envelopes obtained for experiment 10. Comparison to experiment 1 indicates that the small differences in the evaporation rates of the oil slick and the oil + dispersant slick is insignificant and that they actually behaved similarly. Figure 7.3.15, 7.3.16, and 7.3.17 show the evaporation rates of n-C7 to n-C14; again the n-alkanes of both slicks evaporated at about the same rates.

The total amount of vapors collected is proportional to the relative areas of the whole chromatogram of the air sample (not including n-C20) to the n-C10 peak area. By plotting the total relative area as a function of time, total evaporation rate of the slick can be obtained. Figure 7.3.18 shows the evaporation rate of the slicks for experiment 10. The slight difference between the oil and the oil + dispersant slicks is meaningless and the evaporation rates can be considered the same.

When looking at the envelopes (Figure 7.3.19, 20 and 21 obtained for experiment 11, and at the evaporation rates of the individual n-alkanes (Figure 7.3.22, 23 and 24) it can be concluded that the evaporation process is faster in the oil slick than in the oil + dispersant slick. When comparing the difference to the results of experiment 1, it is really difficult to say whether the differences were due to the dispersant or not, since they were very much like the differences occurring in experiment 1. Figure 7.3.25 shows that the total evaporation rates of the slicks were similar.

Since the only difference in the experimental conditions in experiments 10 and 11 was the pump flow rate, it could be assumed that the oil slick is affected to a greater extent from the pumping rate than the oil + dispersant slick. Experiment 12 was performed to verify this. Since the crude filters could cause differences, they were removed (system B used) and the pump flow rate was increased by a factor of almost 3. Samples in experiment 12 were taken only up to 4 hrs.; this was enough to determine the rate of evaporation and the differences between the treated and untreated slicks. This experiment gave very close results for the n-alkanes evaporating from both slicks as illustrated in Figures 7.3.26 and 27. Therefore, the flow rate does not affect the oil slick by causing it to evaporate faster.

Experiments 6 to 12, which were all performed without mixing, did not show a constant trend; evaporation was either the same or the untreated slick evaporated slightly faster. However, the difference was not much larger than in experiment 1 (oil vs. oil, using system A). When the surface was not mixed, the dispersant did not have a significant effect on the evaporation of the n-alkanes.

b) Experiments with mixing directly after the spill

In the case of an oil spill in the open sea, there is mixing of the surface slick into the water column by waves; thus, it is necessary to determine the effect of mixing on the dispersant. Experiments 13 and 14 were performed using system C. The oil was first added to both beakers and the dispersant was then added to one of them and both beakers were shaken for a few seconds. After shaking the beakers, the water in the
Figure 7.3.16: Evaporation rates of H2O to H2O$_2$

- ○ = all
- □ = soil + dispersant

Figure 7.3.17: Evaporation rates of H2O to H2O$_2$

- ○ = all
- □ = soil + dispersant

Figure 7.3.18: Evaporation rates of the slick - Experiment 10

- ○ = all
- □ = soil + dispersant
Figure 7.3.23 Evaporation Rates - Experiment II

Figure 7.3.24 Evaporation Rates - Experiment II

Figure 7.3.25 Total Evaporation Rates - Experiment II
Figure 7.3.26 Evaporation Rates - Experiment 12

- 1.5-4 hrs.
- 0.5-1.5 hrs.
- 0-0.5 hrs.

Figure 7.3.27 Evaporation Rates - Experiment 12

- \( \frac{h}{h_c20} \)

- \( C_7 \), \( C_9 \), \( C_{11} \), \( C_{13} \)

- \( \sum \frac{h}{h_c20} \)

- \( \frac{A}{A_c20} \)

- Hours After The Spill

- \( \circ \) = oil
- \( \bigcirc \) = oil + dispersant
- Total

- oil
- oil + dispersant
oil only beaker remained clear, whereas the water in the oil + dispersant beaker became dark. However, the color gradually became lighter indicating that some of the oil originally in the water was returned to the surface. Mixing made the dispersant more effective and the evaporation rate of the n-alkanes from the treated slick was slower than from the untreated slick. The difference was larger than could have been caused by experimental errors as indicated in experiment 4. Figures 7.3.28 and 7.3.29 show the difference in the relative heights of the n-alkanes as a function of the carbon number. n-C7 showed up in the air sample taken above the treated slick during 1.5-4 hrs., whereas n-C8 was very weak and n-C7 disappeared from the corresponding air sample taken above the untreated slick. The heavier components such as n-C12, n-C13, n-C14 and n-C15 started to appear in both samples at about the same time, but it took much longer for the light ones, n-C7 to n-C10 to evaporate from the treated spill as indicated by Figures 7.3.30 and 31.

c) Experiments with constant mixing during the entire experiment.

In experiments 13 and 14, mixing was applied only at the beginning of the experiment; the effects of a dispersant will probably be even greater when there is constant mixing throughout the experiment. Experiments 15 and 16 were performed with constant mixing. At the beginning of the experiment, the beakers were shaken and then the water was stirred with magnetic stirrers. This kept the water of the treated spill dark while the water of the untreated spill was clear with only a few drops of oil sinking to the bottom of the beaker and rising to the surface. In these experiments, there was a big difference between the evaporation of the two slicks; the oil + dispersant air samples did not show a normal envelope, but one that had a flat maximum and a minimum as is shown in Figures 7.3.32 and 33. Evaporation was much slower for the treated spill, n-C7 was still coming off the treated slick after four hours, whereas, n-C8 was gone from the untreated slick. The heavier n-alkanes such as n-C12 to n-C15 showed up at about the same time from both slicks. In the untreated slick, the order in which the components evaporated seemed different from the order expected from vapor pressures. Figures 7.3.34 and 35 show the evaporation rates of n-C7 to n-C12. The largest differences are found in the lighter components.

Surface samples of the slicks were taken at 7 hrs. after the spill. Their chromatograms are shown in Figures 7.3.36. In the oil slick, all components lighter than n-C11 had already evaporated but in the oil + dispersant slick sample, all components heavier than n-C8 appeared. The data obtained from the surface are samples were in agreement with those obtained from the oil samples; evaporation was faster from the untreated slick.

(C) Conclusions:

The laboratory study using the self-mixing dispersant Corexit 9527, indicated the evaporation of the n-alkanes from the treated and untreated slicks was similar when the water was not agitated. However, when mixing was applied, the effects of the dispersant on the evaporation became significant. The evaporation of the light n-alkanes, n-C7 to n-C10, from the treated slick was slower than from the untreated slick. The longer the mixing, the greater was the effect of the dispersant on the
Figure 1.3.29 Relative of peak heights of the main series as a function of the carbon number: C_7, C_9, C_11, C_13, 0.5 - 1.5 hrs.

Figure 1.3.29 Relative of peak heights of the main series as a function of the carbon number: C_7, C_9, C_11, C_13, 23 hrs.

Figure 1.3.30 Emission rates of H-C_2, H-C_4 and H-C_6 (continues)

Figure 1.3.30 Emission rates of H-C_2, H-C_4 and H-C_6 (continues)
Figure 7.3.30: Evaporation rates of n-C<sub>10</sub> to n-C<sub>13</sub> - Experiments 13 to 16

- Oil
- Oil + dispersant

Figure 7.3.32: Relative GC peak heights of the n-alkanes as a function of the carbon number. All samples, Experiments 13 to 16.

- Oil
- Oil + dispersant

0.5-1.5 hrs.

Figure 7.3.33: Relative GC peak heights of the n-alkanes as a function of the carbon number. All samples, Experiments 13 to 16.

- Oil
- Oil + dispersant

4-7 hrs.

Figure 7.3.34: Relative GC peak heights of the n-alkanes as a function of the carbon number. All samples, Experiments 13 to 16.

- Oil
- Oil + dispersant

0-0.5 hrs.

0-0.5 hrs.
Figure 7.3.36 GC of surface samples taken 7 hours after the oil was added. Exp. 16
evaporation rate. The dispersant affected the evaporation of the lighter n-alkanes to a greater extent than the heavier ones. The slower evaporation of the treated slick could be due to the mixing of some of the oil into the water column. The oil would then be less exposed to the air and it would take longer for the light components to evaporate.

Since the surface areas of the flasks used in the laboratory experiments were limited, the dispersed oil was stopped by the wall of the flasks and some of it accumulated along the walls. Therefore, the oil was not dispersed as efficiently as it would have been if the surface area was infinite. Therefore, the walls may have caused the dispersant to have a different effect on the evaporation in the laboratory experiments compared to that in the open sea, since in the open sea, the dispersion of oil would be greater.

II Long Path Gas Cell

(A) Predicting the Effects of Medium and Low Resolution Infrared Spectrometers

In working in the field, one is often forced to use low-resolution, portable spectrometers. The performance of these instruments is obviously inferior to a high-resolution research-grade laboratory instrument. This work is involved with using a high resolution infrared spectrometer to predict the performance of low resolution instruments. Spectra of single and multi-component mixtures of hydrocarbon vapors are used to measure and predict the results of low and high-resolution spectrometers. In this way, the effects of low resolution spectra in quantitative infrared analysis can be measured and predicted. Various spectral manipulation and subtraction techniques are also demonstrated in this work.

This study is done with methane, ethane and propane vapors, individually and in two and three component mixtures. This work was confined to the carbon-hydrogen stretching region, from 3250 to 2790 cm\(^{-1}\). High resolution spectra were taken at a spectral bandwidth of 1.6 cm\(^{-1}\). This is a reasonable value for a laboratory instrument. Lower resolution spectra were observed at bandwidths of 10, 25 and 50 cm\(^{-1}\). High resolution spectra can be convoluted, or mathematically filtered, to reproduce the effects of a lower-resolution spectrum. In this way, a low resolution spectrum can be both measured, as well as predicted from the convolution of a high-resolution spectrum of the same sample.

The equation for a Gaussian slit function is given by:

\[
G = \frac{1}{\sigma \sqrt{2\pi}} \exp \left[ -\frac{1}{2} \left( \frac{x-x_0}{\sigma} \right)^2 \right]
\]

where

width at \( \frac{1}{2} \) height \( W = 2\Delta V_g = 2\sigma \sqrt{2\ln 2} \)

\[
W = 2.354\sigma
\]

This is one of the models of spectral slit functions which are currently used in mathematically describing a spectral peak. Convolution is a
process in which a mathematical modification function is imposed on the function of the spectral peak. This process is used in filtering and smoothing spectral data. In this case, a high-resolution spectrum can be convoluted with a Gaussian function to produce a spectrum of lower resolution. One of the purposes of this work is to observe how a mathematically convoluted spectrum compares with a measured spectrum at the same spectral slit width.

Figure 7.3.37 shows a high resolution spectrum of methane vapor, in the 3250-2750 cm\(^{-1}\) region. The detail in such a high resolution spectrum makes identification and quantitation of a compound relatively simple. In a spectrum of lower resolution, this detail is lost or reduced, making identification more difficult. This loss of detail also occurs in convoluted spectra. One can compare the results of a low resolution spectrum with a high resolution spectrum convoluted to a lower resolution. This is illustrated in Figure 7.3.38. This shows convoluted and measured spectra of methane vapor from 3250 to 2750 cm\(^{-1}\). The resolution of these spectra was 10, 25 and 50 cm\(^{-1}\), respectively. The sample in all cases is the same, the spectral conditions being modified for each spectrum. Here, one can see the good agreement in the real measured spectra and the predictions made by convoluting the high resolution spectrum.

In convoluting a spectrum, different procedures can be followed. A spectrum can be convoluted to a given resolution in one step, or in a series of "smaller" convolutions. Figure 7.3.39 illustrates this, using a methane spectrum convoluted to 25 cm\(^{-1}\) resolution in two different ways. The first spectrum is a convolution of a high resolution spectrum to 25 cm\(^{-1}\) in one step, in 0.1 cm\(^{-1}\) increments. This refers to the frequency of application of the convolution; here, the function was applied to the data at 0.1 cm\(^{-1}\) intervals. The second spectrum shows a different convolution procedure. In the first step, the high resolution spectrum was convoluted to 5 cm\(^{-1}\) resolution in 0.1 cm\(^{-1}\) increments, and then this spectrum was further convoluted to 25 cm\(^{-1}\) resolution in 1 cm\(^{-1}\) increments. This two step convolution has the effect of a one-step convolution to 25 cm\(^{-1}\) resolution. The difference in the increments applied in the two steps has the effect of smoothing the resultant spectrum when compared to the one step convolution. The variations in the two methods of convolution is significant, suggesting that the convolution procedure used could make a considerable difference in a given circumstance.

Real vapor samples are more frequently mixtures of two or more components rather than a single pure compound. Figure 7.3.40 shows complete spectra of methane, ethane and propane, showing the differences in band structure of the three compounds.

In predicting the appearance of spectra of mixtures, there are a variety of possible approaches. Absorbance spectra of individual pure compounds can be added to produce a synthetic spectrum of a multicomponent mixture of the compounds involved. An important question is how such synthetic spectra compare with convoluted spectra of real multicomponent mixtures.

Figure 7.3.41 shows three spectra of a two component mixture of methane and ethane. Here, the major peaks of each component are approximately equal in absorbance. This shows a high-resolution spectrum, as
Figure 7.3.37 High Resolution Spectrum of Methane Vapor
Figure 7.3.38  Convoluted and Measured Spectra of Methane Vapor

**METHANE**

10 cm\(^{-1}\)

25 cm\(^{-1}\)

50 cm\(^{-1}\)
Figure 7.3.39 Methane Spectrum Convolved to 25 cm⁻¹ Resolution

Figure 7.3.40 Spectra of Methane, Ethane and Propane

Figure 7.3.41 Two Component Mixture of Methane and Ethane
well as two convolutions, two resolutions of 10 and 25 cm\(^{-1}\), respectively. Once again, most of the spectral information is lost as the resolution decreases.

The following figures illustrate spectral subtraction. The spectrum of a pure compound can be subtracted from the spectrum of a mixture, leaving the spectrum of the remainder of the mixture. In this simple example, the spectrum of ethane is subtracted from the spectrum of the methane/ethane mixture. Theoretically, this should result in the spectrum of methane, the other component of the mixture. Figure 7.3.42 shows the spectra of the methane/ethane mixture, and the pure ethane being subtracted from it. Figure 7.3.43 shows the results of the subtraction, and a real measured spectrum of methane for comparison. One can see that spectral subtraction can be very effective in separating components of a mixture.

The question arises whether this procedure can be used as effectively at lower resolutions. Figures 7.3.44 and 7.3.45 repeat the above experiment, with all spectra convoluted to a resolution of 25 cm\(^{-1}\). One can see that lower resolutions apparently have little affect on the subtraction procedure.

In predicting the appearance of a spectrum of a mixture, spectral addition can be used. The absorbance spectra of the individual components can be added to give a synthetic spectrum of a "mixture" of the components. A comparison of added spectra with a real convoluted mixture is shown in Figure 7.3.46. The first spectrum is a high-resolution spectrum of the methane/ethane mixture convoluted to a resolution of 25 cm\(^{-1}\). The second spectrum illustrates how two spectra can be added and then convoluted. Here, the high-resolution spectra of methane and ethane are added, and the resultant sum is convoluted to 25 cm\(^{-1}\). The third spectrum shows the procedure of convolution, then addition. Here, the two high resolution spectra are individually convoluted, and then added together. These three spectra illustrate the prediction of performance of a low resolution instrument using a high-resolution instrument and computer. A low resolution spectrum of a mixture can be predicted from high resolution spectra of each of the components of the mixture. This can be done either by addition and then convolution to the desired resolution, or vice versa.

The following work with ethane and propane reproduces the results just shown with methane and ethane. Figure 7.3.47 gives a high resolution spectrum of a one to one absorbance mixture of ethane and propane, from 3250 to 2790 cm\(^{-1}\). This spectrum is also shown convoluted to resolutions of 10 and 25 cm\(^{-1}\). Figure 7.3.48 and 7.3.49 show the subtraction of propane from the mixture of propane/ethane, giving a spectrum of ethane. These are all high resolution spectra. Figures 7.3.50 and 7.3.51 duplicate this subtraction for spectra convoluted to a resolution of 25 cm\(^{-1}\).

The results shown above can be extended to mixtures of more than two components. Figures 7.3.52 show spectra of a mixture of methane, ethane and propane in the 3250 to 2750 cm\(^{-1}\) region. The two spectra are a high resolution spectra, and the convolution of this spectrum to a resolution of 25 cm\(^{-1}\). Subtractions can be made in a three component system to sequentially extract each component from the system. Figure 7.3.53 shows
Figure 7.3.42 Spectra of Methane/Ethane Mixture and Pure Ethane Being Subtracted From It.

Figure 7.3.43 Results of the Subtraction and a Real Measured Spectrum of Methane.
Figure 7.3.44 Spectra of a Methane/Ethane Mixture and Ethane that have been convoluted to 25 cm\(^{-1}\)

Figure 7.3.45 Convolved Ethane Spectrum Subtracted from Convoluted Spectrum of pure methane (bottom)
Figure 7.3.46 Results of Computer Addition of Two Spectra Before or After Convolution of Spectra

Figure 7.3.47 A High Resolution Spectrum of a One to One Absorbance Mixture of Ethane and Propane
Figure 7.3.50 Convoluted Spectra of Ethane/Propane Mixture and of Pure Ethane

Figure 7.3.51 Subtraction of Convoluted Propane Spectrum from Convoluted Ethane/Propane Spectrum (top) and Convoluted Spectrum of Pure Ethane
Figure 7.3.52 Spectra of a Mixture of Methane, Ethane and Propane

Figure 7.3.53 Sequential Subtraction of Convoluted Spectra of methane (1) and Ethane (2) from the Convoluted Spectrum of a Methane/Ethane/Propane Mixture.
this type of subtraction. The first spectrum is the convoluted spectrum of pure methane, subtracted from the convoluted spectrum of the three-component mixture. The second spectrum shows the subtraction of ethane from this first subtraction.

From these two subtractions, one should expect to be left with a convoluted spectrum of propane, the third component of the system. The final spectrum shows the spectrum of propane for comparison. Obviously, convoluted spectra can also be subtracted with reasonable accuracy in spectra of more than two components.

This study illustrates some of the techniques which can be used in manipulating spectra. High resolution spectra can be convoluted to reasonably simulate the performance of low resolution instruments. Thus, the results of such instruments, as in field work, can be predicted to a fair degree. Additions or subtractions to produce a synthetic spectrum can be performed either before or after convolution, and the appearance of this lower resolution synthetic spectrum will be faithful to that produced by a low resolution instrument under the expected conditions. In addition, these techniques do not appear limited to two-component mixtures. Three component systems can be investigated, and one would reasonably expect to be able to work with larger systems as well. Thus, the performance of low-resolution field grade instruments can be predicted from spectra taken in the laboratory. Predictions made in this way may prove valuable in estimating the practicality of a projected study, or the effectiveness of an analysis before the study is begun.

B) Atmospheric Interferences in the Ambient Vapor Sampling System

In ambient air samples, two major interferences prevent the use of IR analysis for hydrocarbons: water and carbon dioxide (CO₂). Water has very strong absorptions in the IR, centered at about 3750 cm⁻¹ and 1600 cm⁻¹. CO₂ has two major bands, at 2350 and 675 cm⁻¹. Taken together, these interferences can ruin quantitative results in an ambient sample. The problem is to reduce or eliminate these interferences, without significantly reducing the sensitivity of the system to hydrocarbons. This was tested by introducing toluene (C₇H₈) vapor into the system under various experimental conditions. The spectra which follow illustrate the results.

Spectrum in Figure 7.3.54 is an illustrative spectrum of toluene vapor in nitrogen gas. For this highly concentrated sample, 50 l of liquid toluene were injected and allowed to evaporate inside the flowing system, which was filled with dry nitrogen. This shows the strong absorptions of this hydrocarbon, especially around 3000 cm⁻¹, 1600 cm⁻¹, 1500 cm⁻¹, 1050 cm⁻¹ and 700 cm⁻¹.

Spectrum 7.3.55 is a more realistic concentration, in that it was measured by pumping dry nitrogen over the surface of liquid toluene. This is approximately the concentration one would observe with a sampling device directly over a spill of toluene on water. It still shows the bands mentioned above, but greatly reduced in intensity. One can now also see weak bands from CO₂ and H₂O. These are impurities in the nitrogen diluent, or residual impurities in the cell. This and all subsequent spectra were taken at a path length of 21.75 m.
Figure 7.3.54 Illustrative Spectrum of Toluene Vapor in Nitrogen Gas

Figure 7.3.55 Spectrum of Toluene Vapor in Nitrogen Gas
Spectrum 7.3.56 is identical to 7.3.55, except for the addition of a drying tube, filled with a calcium sulfate dessicant, (DRIERITE). Most of the peaks are not significantly reduced in intensity, indicating that the Drierite is not removing appreciable amounts of hydrocarbon vapors.

In spectrum 7.3.57, air is used instead of dry nitrogen. Here, all CO2 bands are clearly seen for the first time. The Drierite will not remove this vapor, although in this case, it is not critical. The toluene can still be easily quantitated by using the bands in the 3000 cm⁻¹ region. Water is still absent, indicating that the Drierite is effectively removing the interfering water vapor from the air. Spectrum 7.3.58 is not critical to the test, but is interesting. Here, a liquid nitrogen cold trap was added to the drying tube. Not only was all water removed, but most of the hydrocarbons were frozen out as well. The small peak at 3000 cm⁻¹ is methane. Whether this is an impurity from the liquid toluene or the air is not known.

Spectrum 7.3.59 shows the spectrum of ambient air and toluene vapor, without any dessicant or filter. This shows the massive interferences present in untreated air, and the extent to which the Drierite is effective. Compare this with spectrum 7.3.57. For all of the above spectra, the flow rate was about 2 l/min past the toluene liquid. This was estimated to be the optimum flow sampling rate. Two factors are important in determining flow rates in sampling: system response time and dessicant effectiveness. As the flow rate increases through the 5.5 l liter cell, the time required to respond to a change in sample composition is decreased. The shorter the response time, the more accurately the system will reflect the concentrations of a given sample as it changes with time, as in an evaporation process. As the flow through in the dessicant is increased, the effectiveness of the Drierite is reduced, as is shown in spectrum 7.3.60. This spectrum was taken with a sampling flow rate of 5 l/min, but is otherwise identical to the conditions for spectrum 7.3.57. It shows the amount of water interference still present in the cell due to the higher flow rate.

It can be concluded that with a suitable dessicant, one can eliminate substances which interfere with quantitative ambient air analysis in the system.
Figure 7.3.56 Spectrum of Toluene Vapor in Nitrogen Gas After Drying Tube was Added to System

Figure 7.3.57 Spectrum of Toluene Vapor in Air

Figure 7.3.58 Spectrum of Air after Cold Trap was Added to System
References

7.4 Mesoscale Experiments

7.4.1 Introduction

Treating an oil spill with a chemical dispersant reduces the amount of oil on the surface and increases the concentration in the water column. However, a number of questions need to be answered, e.g., "How much is the increase?" "Does a dispersant affect all components of oil in the same manner?" Is the effect uniform throughout the water column?" How does the effect change with time?"

Presently, we are trying to answer these questions by analyzing water samples collected from beneath both treated and untreated spills. The chemical results are important since they can be correlated with the physical processes of dispersion (1) and with the microbial utilization of the chemicals (2). Furthermore, they will eventually be used to determine the overall effect on the marine environment (3). Herein, chemical analyses of water samples from the meso scale experiments were compared for both treated and untreated spills.

7.4.2 Test Facilities

The meso scale test system, located 450 meters from Narragansett Bay consists of two 4000 liter tanks (6.2 m tall and 0.9 m in diameter). These tanks are described in more detail elsewhere (3).

7.4.3 Chemical Analysis

One liter water samples were extracted with two 15 ml. aliquots of CS$_2$. The aliquots were combined and the volume adjusted to 25 ml (some of the CS$_2$ dissolves in water and some is lost by evaporation to give a total just below 25 ml). The solution was placed in a 6 mm pathlength infrared cell (with AgCl windows), and the infrared absorbance at 2920 cm$^{-1}$ measured with an identical cell containing CS$_2$ in the reference beam of the spectrometer (4.5). The measured absorbance was then converted to total hydrocarbons from a pre-determined plot of absorbance vs. concentration (separate plots were used for oil and oil/dispersant, and were both obtained using the oil and dispersant being investigated).

The volume of the CS$_2$ solution was then reduced to .6 ml under nitrogen, and the complete infrared spectrum (IR) was measured under the same conditions as above. Following this, the gas chromatogram (GC) was measured.

IR spectra were measured on a Beckman 4260 spectrometer and GC on a Hewlett Packard 5710A gas chromatograph equipped with flame ionization detection and 10 m x 3 mm column packed with SP2250. The GC temperature was programmed at 8 C/min.

A. Series I

All of these experiments in the meso scale tanks were performed on API Kuwait crude oil, using Corexit 9527 as the dispersant.
Sixty ml of oil (15 ppm total concentration) were added to the water surface in each tank and 12 ml of dispersant to one of the tanks. One liter water samples were collected from each of the three ports at 1, 24, 48 and 72 hours.

In addition, in the first three experiments, 1 liter water samples were collected while the tanks were being filled, and at 30 minutes after filling. These samples were used as controls. In the fourth experiment, a control tank of the same dimension and with the same sampling ports, was used, and samples were taken at the same time as the others.

All water samples were returned immediately to the laboratory for analysis.

Several test runs without oil were made in the meso scale tanks to determine the variation of extractable organics in the tanks. Extracts of water from the tanks were compared with those of water taken directly from Narragansett Bay and, in most cases, the concentration of organics in the tanks and in the Bay were similar. The only major difference was that the tanks were generally higher immediately after filling. This was probably due to the mixing of bottom sediments in the water column.

(a) Water Analysis

Four experiments were performed with oil and oil/dispersant. In all cases, oil was added only to the north tank and oil/dispersant to the south tank. In the experiment using the control tank, it is referred to as the east tank. The weather conditions and other information on the experiments will be discussed separately.

(i) Experiment 1:

Concentrations of extractable organics from the top, middle and bottom ports (1,3,5m) as a function of time are shown in Figures 7.4.1, 7.4.2, and 7.4.3. The control values for the two tanks are given by dashed lines across the plots. Both control values are high. However, the one for the north tank was abnormally high. In this experiment, only one control sample was collected from each tank immediately after filling and, as mentioned above, the abnormally high values are probably due to the suspended sediment.

In the next two experiments, control samples were collected immediately after filling and one half hour later. The latter values are closer to the actual values of organics in sea water.

Considering the high control values, it is difficult to analyze the results of this experiment. However, general trends can be identified. Only one sample from the south tank had a concentration above the control, and that was the top sample collected after 72 hours.

The tank with the dispersant had an extremely high value for the 1 hour sample from the top, but the concentration decreased significantly after 24 hours and continued to decrease for the duration of the experiment. The highest concentration for the middle and bottom ports were found at 24 hours, and these also decreased with time.
Figure 7.4.1 Concentration of Extractable Organic from the Top Layer as a Function of Time. (Top) 27.

Figure 7.4.2 Concentration of Extractable Organic from the Middle Layer as a Function of Time. (Middle) 27.

Figure 7.4.3 Concentration of Extractable Organic from the Bottom Layer as a Function of Time. (Bottom) 27.
In general, this experiment indicated that dispersant caused a high concentration at the 1 m depth after 1 hour. Some of these chemicals moved toward the surface and others to the bottom during the next 24 hours.

(ii) Experiment 2:

Quantitative values for the total extractable organics from the second experiment in the meso scale tanks are shown in Figures (7.4.4) and (7.4.5). Control values of 210 and 243 ppb are shown as dashed lines drawn horizontally across the bar graph. The time dependence of concentration from the top, middle and bottom sampling ports (1, 3, 5.5 m) are given in Figure (7.4.5).

In the top port, the concentration of extractable organics (above the concentration of the control) at 1 hour was more than 27 times greater than when the dispersant was used, i.e., 4880 ppb as compared to 180 ppb. After twenty-four hours, the concentration in the tank without dispersant fell to below control level and stayed for the remainder of the experiment. In the treated tank, the concentration of extractable organics decreased by more than a factor of 3 to 1350 ppb after 24 hours, and then gradually decreased to 851 ppb after 3 days.

At the middle level, the concentration in the untreated tank gradually decreased from 324 ppb during the 72 hour experiment, whereas there was a three-fold increase in the tank with dispersant from 1 to 24 hours. This level decreased gradually after twenty-four hours.

The concentration in the bottom layer in the untreated tank reached a maximum slightly above the control level at 24 hours and then gradually decreased. In the tank with dispersant, there was a five-fold increase from 1 to 24 hours, but the maximum was not reached until 48 hours.

For comparison, the same results are plotted in Figure 7.4.5 as a function of depth for each of the sampling times. These plots clearly show that the maximum concentration moved toward the bottom in both the treated and untreated cases. However, there was a significantly greater concentration in the treated tank.

For qualitative comparison of the water sample, two sets of GC are shown in Figures 7.4.6 and 7.4.7. The 24 hour samples are compared in Figure 7.4.6. The GC of the untreated samples was expanded seven times. The distribution of n-paraffins in this sample is not similar to the treated oil and is not characteristic of petroleum. The GC of the top 1 hour treated sample is shown in Figure 7.4.7, where it is compared to all 24 hour samples from the same tank. Components boiling below n-C15, which were initially dispersed, were not found at 24 hours.

(iii) Experiment 3:

The concentration for the top, middle and bottom layer as a function of time are shown in Figures 7.4.8, 7.4.9 and 7.4.10. The initial values for the top are similar to those in experiment 2. However, the decrease in the treated tank after 24 hours was much greater.
Figure 7.4.4 Concentration of Extractable Organics in the Top, Middle, and Bottom Levels. (Exp. 2)
Figure 7.4.5 Concentration of Extractable Organics in the Top, Middle, and Bottom of the Treated and Untreated Tanks at Each Sampling Time
Figure 7.4.6 GC of the 24 Hour Top Samples from the Treated and Untreated Tanks

Figure 7.4.7 GC of Samples from the Treated Tank: 1 hr., top; 24 hrs., top; 24 hrs., middle; and 24 hrs., bottom (Exp. 2)
Figure 7.1.8 Concentrations of Extractable Organics from the Top (1 m) Port as a Function of Time. (Exp. 3)

Figure 7.4.9 Concentrations of Extractable Organics from the Middle Port (3 m) as a Function of Time. (Exp. 3)
Figure 7.4.10 Concentrations of Extractable Organics from the Bottom Port (5.5 m) as a Function of Time. (Exp. 3)
The 1 and 24 hour values for the middle port are also similar to experiment 2 but, again, there is an abrupt decrease in concentration in the treated tank by the next sampling period. Samples from the bottom port of the treated tank were high at 1 hour and remained at this level for 24 hours before decreasing. However, the untreated tank had a high level at 48 hours, and then dropped to control level.

After 4 days, both tanks were agitated by stirring with a glass rod for 10 minutes, and samples were collected 24 hours later. The agitation increased the concentration at all levels.

(iv) Experiment 4:

The concentration of the top, middle and bottom layer as a function of time are shown in Figure 7.4.11, 7.4.12, and 7.4.13. In this experiment, the east control tank was used. The 1 hour concentration in the control tank was at least three times lower than previous experiments. However, the trend for the 24 to 72 hour samples was very similar to experiment 3. A very high concentration was detected in the middle port of the treated tank after 48 hours. The concentration at 1 hour was higher in other experiments, whereas the concentration at 24 hours was lower. The concentration in the bottom of the treated tank gradually increased with time. All concentrations in the untreated tank were at about the control level.

(v) Conclusions:

After only four completed experiments, it is too early to draw any definitive conclusions. The concentration values for experiment 2 seem to follow anticipated levels. For this reason, we undertook a complete analysis of all samples. The GC results shown in Figures 7.4.6 and 7.4.7 emphasize some of the major differences between the treated and untreated samples and changes of the treated samples with time and depth.

(b) Air Samples

For these experiments, 60 ml of Kuwait crude oil were added to the north and south tanks, and 12 ml of Corexit 9527 were then added to the south tank.

The surface was mixed for 10 minutes by stirring with glass rods. Air samples were collected immediately after the spill. Air samples were collected and treated similar to the air samples taken in the laboratory experiments. Figure 7.4.14 shows the system used for collecting the air samples in the meso scale experiments. The funnels through which the air was pumped were placed at about 2.5 cm above the water surface.

One experiment was conducted with the tanks covered to eliminate wind and rain effects. This was important to the water column measurements. The covers were made of wood and had four holes of 2.5 cm diameter for ventilation and one hole of about 20 cm in the center of the cover on which the funnel was placed. Prior to the addition of the oil, control samples were collected from above both tanks. Surface samples were taken and treated as in the laboratory experiments.
Figure 7.4.11 Concentrations of Extractable Organics from the Top Port (1 m) as a function of time. (Exp. 4)

Figure 7.4.12 Concentrations of Extractable Organics from the Middle Port (3 m) as a function of time. (Exp. 4)

Figure 7.4.13 Concentrations of Extractable Organics from the Bottom Port (3.5 m) as a function of time (Exp. 4)

Figure 7.4.14 System used to collect air samples in the meso scale experiments.

- Rubber hose
- Teflon connector
- Charcoal cartridge
- Glass funnel
- South
- Pump
- North
The following experiments were performed:

(i) Experiment 1:

The water temperature at the beginning of the experiment was 24°C. Control samples were taken during the 1.5 hours before the oil was added. Air samples were taken at 0-3 and 3-6 hours. Surface samples were taken at 72 hours after the addition of the oil.

(ii) Experiment 2:

The water temperature was 19°C at the beginning of the experiment. Control samples were taken during 1 hour. Air samples were taken at 0-1.5, 1.5-4, and 4-7 hours. Surface samples were taken at 1.5, 4, 7, 48 and 72 hours after the spill.

(iii) Experiment 3

In this experiment, the tanks were covered with the wooden covers. The temperature at the beginning of the experiment was 10.5°C. Control samples were taken during 50 minutes. Air samples were collected at 0.3-5, 1.5-4, 4-7 and 7-20.5 hours. Surface samples were collected at 72 hours after the spill. An internal standard, n-C20, was added after the IR measurements.

(iv) Results and Discussion

Experiment 1:

The air samples collected above both tanks were quite similar. The gas chromatograms of the air samples taken at 0-3 hours are shown in Figure 7.4.15 and those taken at 3-6 hours are shown in Figure 7.4.14. Samples taken at 3-6 hours indicated the presence of n-C12 to n-C16. All components lighter than n-C12 evaporated from both treated and untreated slicks within 3 hours. The surface samples taken at 72 hours after the spill indicated that all the components up to n-C16 disappeared from the treated and untreated slicks. The gas chromatograms of both surface samples were similar.

The IR spectra of both air samples taken at 3-6 hours indicated that the light aromatics, i.e., benzene, toluene and xylene, evaporated within 3 hours (or less) as their specific bands did not appear in the spectra (Figures 7.4.17 and 7.4.18).

Experiment 2:

All components up to n-C16 appeared in the air samples of the treated and untreated spills taken at 0-1.5 hours. Gas chromatograms of samples taken at 1.5-4 hours showed the presence of n-C11-n-C17 in both air samples. All components up to n-C evaporated within 1.5 hours. The gas chromatograms of the air samples at 4-7 hours, shown in Figure 7.4.19 indicated the presence of n-C12-n-C17 in the oil air sample and n-C13-n-C17 in the oil and dispersant air sample.
Figure 7.4.15 GC of the Air Samples Collected at 0-3 Hours (Meso Scale Exp. 1)

Figure 7.4.16 GC of the Air Samples Collected at 3-6 Hours (Meso Scale Exp. 1)

Figure 7.4.17 IR Spectra of the Oil Air Samples Collected at 0-3 and 3-6 Hours (Meso Scale Exp. 1)
Figure 7.4.18 IR Spectra of the Oil + Dispersant Air Samples Collected at 0-3 and 3-6 Hrs. (Meso Scale Exp. 1)

Figure 7.4.19 GC of the Air Samples Collected at 4-7 Hrs. (Meso Scale Exp. 2)
A surface sample from the oil slick taken at 1.5 hours indicated that all hydrocarbons up to n-C_{10} had disappeared. The oil and dispersant slick sample taken at the same time indicated that all components lighter than n-C_{11} had disappeared (Figure 7.4.20). The relative amount of n-C_{10} in the oil slick sample was small and this might be the reason why it did not appear in the air sample taken at 1.5-4 hours above the oil slick, which was more dilute than the surface sample.

Samples from both slicks taken at 4 and 7 hours after the spill indicated that the lightest hydrocarbon present was n-C_{12}, but the treated slick contained relatively less amounts of n-C_{12} and n-C_{13}. n-C_{13} was present in the untreated slick sample taken at 48 hours after the spill, but disappeared from the treated slick (Figure 7.4.21). Surface samples of both slicks taken at 72 hours after the spill showed that all hydrocarbons lighter than n-C_{14} had disappeared. The results obtained from the air samples are in agreement with the results obtained from the surface samples. The evaporation was slightly faster from the treated slick.

The IR spectra of the air samples taken at 1.5-4 hours showed that benzene, toluene, and xylene disappeared within 1.5 hours from both spills.

Experiment 3:

This experiment was performed with covers on the tanks as described in the experimental section. The evaporation was slower than in the open tank experiments, as expected. The control air samples indicated the presence of some organics in the air, but their amount was negligible compared to the vapors collected. Figure 7.4.22 shows the relative heights of the GC peaks of the n-alkanes at different times. The evaporation rate of the n-alkanes was slightly faster in the treated slick. However, the difference does not seem to be significant.

Figure 7.4.23 shows the IR spectra of the air samples taken at 0.3-1.5 hours. The benzene band at 670 cm\(^{-1}\) does not appear in either air sample, indicating that the benzene evaporated within 20 minutes (it took 20 minutes to stir the surface and to cover the tanks). Surface samples taken at 72 hours after the spill indicated that all hydrocarbons lighter than n-C_{14} disappeared from the treated and untreated slicks.

c) Conclusions:

The meso scale experiments indicated that the difference between the evaporation rates of the n-alkanes from the treated and untreated slicks were small. One experiment showed no difference and the other two showed a slightly faster evaporation from the treated slick. Oil vs. oil experiments were not performed in the meso scale, so it is difficult to conclude whether the differences were due to the dispersant or to experimental errors.

Results of the meso scale experiments were in agreement with the laboratory scale experiments when mixing was not applied. Evaporation was faster in the meso scale (open tank) experiments because of the wind. The mixing that was applied in the meso scale experiments, i.e.,
Figure 7.4.20 GC of Surface Samples Collected 1.5 Hours After the Spill (Meso Scale exp. 2)

Figure 7.4.21 GC of Surface Samples Collected 48 Hours After the Spill (Meso Scale Exp. 2)
Figure 7.4.22 Relative GC Peak Heights of the n-alkanes as a Function of the Carbon Number. (Meso scale Experiment 3, Air samples taken at 0.3-1.5, 1.5-4, 4-7, and 7-20.5 hrs)

Figure 7.4.23 IR Spectra of the Air Samples Collected at 0.3-1.5 Hrs. (Meso Scale Experiment 3)

The arrows show the position of the benzene band.
stirring with glass rods, seemed to be inefficient in affecting the evaporation rates of the light n-alkanes. The wall effect that was mentioned in the laboratory experiments also exists in the tanks and could cause some differences in the effects of the dispersants on evaporation between meso scale experiments and open sea experiments.

(B) Series II

This series of experiments tested various modes of application of oil and dispersant to the seawater in the meso scale tanks. The water temperature remained a relatively constant 21°C throughout the 6 experiments. Amounts of oil and/or dispersant added to the tanks as well as the mode of application are listed in Table 7.4.1. The first experiment was run for 72 hours whereas the remaining experiments were conducted for 24 hours each. At each sampling period, 1 liter water samples were collected and returned to this laboratory for quantitative infrared analysis. Table 7.4.2 a & b presents results for each experiment and the discussion of each follows:

(a) Water Analysis

(i) Experiment 1:

Control levels of approximately 100 ppb were found for all levels and sampling periods in the control (east) tank except for the middle layer at 48 hours). This value was close to the bay level (131 ppb). The highest concentrations of hydrocarbons are found in the middle layer of the south tank after 1 hour. The north tank had a relatively even distribution of hydrocarbons which is twice the control level but after 24 hours, amounts close to the control level were reached in this tank and in the south tank. For this reason, the remaining experiments were conducted for a 24 hour duration.

(ii) Experiment 2:

In this experiment, the amount of oil and dispersant added to the tank was increased while the ratio of oil:dispersant was kept to 5:1. Application was also the same as in experiment 1. Table 7.4.2b shows that the hydrocarbon levels and distribution in the north tank after 1 hour are almost identical to those in the first experiment, i.e., increasing the oil in the north tank did not increase the amount entering the water column. In the south tank, overall amounts of hydrocarbons and their relative distribution is the opposite to the first experiment. The top and middle layer increased after the first hour, while their relative distribution is the opposite in the first experiment in these two layers. The hydrocarbons do not seem to reach the bottom layer during this time.

After 24 hours, hydrocarbon levels in the north tank have increased slightly over those in the 1 hour sampling. In the south tank overall levels are still high and the distribution among layers again corresponds with the first experiment.
### Table 7.4.1

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<th>Mode of Application</th>
<th>Comments</th>
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<td>12</td>
<td>premixed w/ 120 ml seawater, sprayed</td>
<td>sprayed</td>
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*Indicates a spray of salt water over surface of spill.*

### Table 7.4.2: Infrared Quantitative Analysis (ppm)

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### Table 7.4.3: Infrared Quantitative Analysis (ppm)

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<th>S</th>
<th>E</th>
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<td></td>
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<td></td>
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### Table 7.4.4: Infrared Quantitative Analysis (ppm)

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<th>S</th>
<th>E</th>
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<td>3.999</td>
<td>236</td>
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<tr>
<td></td>
<td>Bot</td>
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<td>1.771</td>
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<td>Bot</td>
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*EX = control*
(iii) Experiment 3:

In this series, the mode of application of dispersant was changed by premixing it with fresh water instead of sea water as in the last two experiments. The amount of oil and/or dispersant was reduced to the levels of the first experiment.

Taking into consideration the level of the controls for the north and south tank, levels of hydrocarbons parallel those of the first experiment after the first hour with highest concentrations in the south tank remaining in the top and middle layers. After twenty-four hours, levels in the north tank decreased slightly whereas levels in the south tank decreased significantly, approaching control values in top and bottom layers. The concentration in middle layer is about double that of the control.

The fresh water application seems to mix the oil/dispersant further into the depth of the tank but after 24 hours, the patterns of mixing resembles that of the sea water premix experiments.

(iv) Experiment 4:

The dispersant/oil amount was increased to experiment 2 levels. The dispersant was not premixed in this case, but was poured directly onto the oil in the tank. This was followed by a spray with water over the surface. As can be seen from Table 7.4.2b, the hydrocarbon levels in the north tank are consistent with those of previous experiments. In the south tank overall hydrocarbon levels after one hour correspond to those in experiment 2; however, the top layer in this case, contains the highest level. This would indicate that premixing the dispersant with water does aid in the incorporation of the oil/dispersant complex to a greater depth in the water column.

After 24 hours, the south tank has the highest concentration in the top two layers while the bottom layer is relatively low, but contains more organics than is evidenced in previous experiments.

(v) Experiment 5:

Oil and dispersant were premixed and poured on the water in the south tank. Both north and south were then sprayed with additional water. The control in the south tank indicates residual oil/dispersant which may have not been thoroughly removed from the tank prior to this experiment. Taking this into consideration, the comparatively high level of hydrocarbon in the bottom layer can be explained. After one hour, the levels of hydrocarbon in the top and middle layers of the south tank are among the highest detected in any of the six experiments, although only 60 mls. oil/12 mls. dispersant were added originally. After 24 hours, the highest level in the south tank was detected in the bottom layer.
(vi) Experiment 6:

The dispersant (12ml) was premixed with oil and fresh water prior to pouring onto the water surface of the south tank. The highest concentration of organics was found in the top layer of the south tank after one hour. After 24 hours, the top and middle layers have about the same amounts of hydrocarbons; however, the levels in this experiment are an order of a magnitude less than those in the previous experiment.

GC/MS analysis was performed on samples from experiment 2. In the north tank, components were below detectable limits (Table 7.4.3). The 1 hour samples in the south tank contained detectable amount of all aromatic components listed except for benzene. Normal hydrocarbons ranged between C10 to C18 for the top layer and C11 to C18 for the middle layer. The predominant peak in the top layer was C12, whereas the higher boiling C14 dominated in the middle layer. After 24 hours, xylene was lost in both layers. The middle layer also lost naphthalene. The normal alkane range remained the same for the top layer, but the predominant peak was the higher boiling C14. In the middle layer the predominant peak remained C14 but the low alkane shifted from C11 to C12. GC/MS of deasphalted Kuwait oil contains all aromatics listed in Table 7.4.3 and has a n-Cn range of C9-C18 with the predominant peak occurring at C10.

(vii) Conclusions:

Effectiveness of the dispersant in carrying the oil into the water column is proportional to the amount of contact of the dispersant with both the polar water fraction and the non-polar oil fraction of the oil/water system. The most intimate contact between these fractions was achieved when the dispersant was premixed with the oil. In all experiments, agitation of the water surface in the tanks also aided in mixing the oil/dispersant complex into the water column. The north tank showed little, if any, increase over control values during the course of the six experiments. In the south tank, the highest concentration of hydrocarbons was found generally in the top and middle layers after 1 hour, with a relative reduction in concentration after 24 hours (in some cases reduction to control levels). The level of hydrocarbons in the south tank was determined more by the mode of dispersant application than by amount of oil/dispersant added.

GC/MS spectra and infrared values seem to indicate that after 24 hours there is an overall loss of organics from the water column and since this loss, as indicated by GC/MS, is in the more volatile components, it seems fair to conclude that these lighter components may be lost to the atmosphere.

(C) Series III

Because of the high level of residual organics detected in the south tank, both tanks were thoroughly cleaned and a second series of 5 twenty-four hour experiments were conducted. The mode of application of oil and/or dispersant as well as amounts of both are listed in Table 7.4.4. Quantitative infrared results are listed in Table 7.4.5 and are
### Table 7.4.3

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<tr>
<th>Sample Description</th>
<th>Benzene</th>
<th>Xylenes</th>
<th>Naphthalene</th>
<th>Methyl-Naph.</th>
<th>Dimethyl-Naph.</th>
<th>n-Cn Range</th>
<th>Predominant Peak</th>
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</thead>
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<td>S-TOP-1hr (99ppm)</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td></td>
<td>C&lt;sub&gt;10&lt;/sub&gt; thru C&lt;sub&gt;18&lt;/sub&gt;</td>
<td>C&lt;sub&gt;12&lt;/sub&gt;</td>
</tr>
<tr>
<td>S-TOP-24hr (11ppm)</td>
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<td></td>
<td></td>
<td>X</td>
<td>X</td>
<td>C&lt;sub&gt;10&lt;/sub&gt; thru C&lt;sub&gt;18&lt;/sub&gt;</td>
<td>C&lt;sub&gt;14&lt;/sub&gt;</td>
</tr>
<tr>
<td>S-MID-1hr (46ppm)</td>
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<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>C&lt;sub&gt;11&lt;/sub&gt; thru C&lt;sub&gt;18&lt;/sub&gt;</td>
<td>C&lt;sub&gt;14&lt;/sub&gt;</td>
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<td>C&lt;sub&gt;14&lt;/sub&gt;</td>
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<tr>
<td>S-CTRL (0.2ppm)</td>
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<td></td>
<td></td>
<td>X</td>
<td>X</td>
<td>C&lt;sub&gt;9&lt;/sub&gt; thru C&lt;sub&gt;18&lt;/sub&gt;</td>
<td>C&lt;sub&gt;10&lt;/sub&gt;</td>
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<td>N-TOP-1hr (0.2ppm)</td>
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<td>N-TOP-24hr (0.3ppm)</td>
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<td>N-CTRL (0.2ppm)</td>
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**KUWAIT CRUDE (DEASPHALTED)**

**Summary of Results for GC/MS/CS Analysis for Tank Experiment 8/16/78**

### Table 7.4.4

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<tr>
<th>Exp. #</th>
<th>Tank</th>
<th>Kuwait (ml)</th>
<th>Disper. (ml)</th>
<th>Mode of Application of Dispersant</th>
<th>Comments</th>
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<td>10/13/78</td>
<td>60</td>
<td>12</td>
<td>premix. w/oil poured</td>
<td>sprayed salt sprayer</td>
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<tr>
<td></td>
<td>North</td>
<td>60</td>
<td></td>
<td></td>
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<td>South</td>
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<td></td>
<td></td>
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<tr>
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<td>12</td>
<td>premix. w/oil 120 ml fresh water; poured</td>
<td>sprayed salt sprayer</td>
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<td>North</td>
<td>60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>South</td>
<td>60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>10/24/78</td>
<td>60</td>
<td>3</td>
<td>premix. w/120 ml fresh water; sprayed on</td>
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<td>North</td>
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<tr>
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<td>North</td>
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Table 7.4.5 Infrared Quantitative Analysis (ppb)

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</table>
discussed below:

(a) Water Analysis

(i) Experiment 1:

A 5:1 oil to dispersant ratio was used, the oil being mixed with the dispersant prior to pouring the mixture in the south tank. Both north and south tanks were then sprayed with salt water. The results show that the very high concentrations of organics are found in the top and middle layer after 1 hour with a slight reduction after 24 hours. The bottom layer has relatively little organics even after 24 hours. The north tank shows very little change in hydrocarbon level throughout the experiment.

(ii) Experiment 2:

The ratio and amount of oil was maintained as in Experiment 1. However, the dispersant was premixed with fresh water and oil prior to pouring on the south tank. Both north and south tanks were subsequently sprayed with salt water. In the south tank after 1 hour a substantial increase in organics occurs in the middle layer while an almost non-detectable amount is seen in the top layer. The bottom layer increases slightly over that in the first experiment. An unusual occurrence is seen after 24 hours, when the top and middle layer increase substantially to levels which occurred in previous experiments only after the first hour.

(iii) Experiment 3:

The ratio of oil:dispersant was decreased to 20:1 and the dispersant was premixed with fresh water prior to spraying on the oil slick in the south tank. In this case, the levels of hydrocarbons in the south tank greatly decreased while migration of organics was deeper into the water column than previously seen.

(iv) Experiment 4:

The amount of oil/dispersant was premixed with fresh water and this mixture was sprayed on the slick. This method of premixing and spraying seemed to promote deeper penetration of organics into the south tank, with the highest levels at the top, but comparatively high levels through to the bottom. This is the first experiment showing such penetration. After twenty-four hours, the middle and bottom layers contain the highest organic concentration.

(v) Experiment 5:

In this experiment the dispersant was decreased to yield a 20:1 oil/dispersant ratio. The dispersant was premixed with fresh water and this mixture was sprayed onto the slick. Overall concentrations in the water column are lower, but the depth of penetration parallels the previous experiment.

(vi) Conclusions:
The mode of application which causes the highest concentrations of organics in the overall water column is the one which premixes oil/dispersant or oil/water/dispersant prior to adding to the water in the south tank. Depth of penetration of organics into the tank is greatest for the dispersant which is sprayed on the tanks. The controlling factor in concentration of organics seems to be premixing of oil/dispersant rather than mode of application or amounts of oil/dispersant added.

(D) Series IV Meso-Scale Flow-thru Experiment

Two experiments (referred to as Trial 1 and Trial 2) were performed using the meso-scale tank equipped with a flow-thru system. Three tanks were used as follows:

1) control
2) 300 ml of Kuwait Oil
3) 300 ml of Kuwait Oil and 30 ml of Corexit 9527

One liter water samples were collected from the top, middle and bottom ports.

(i) Trial 1:

Quantitative results for the first trial experiment (aborted) at the meso scale tanks are given in Table 7.4.6 and GC's of selected samples are shown in Figures 7.4.24. and 7.4.28. The quantitative results indicate (and this is supported by the GC results) that oil entered the water column when the dispersant was used; however, after 24 hours the concentrations dropped to about three times that of the control. Very little chemical information was gained from an experiment of this short duration.

(ii) Trial 2:

(1) Quantitative Analysis

The amounts of extractable organics as determined by infrared spectroscopy are given in Table. 7.4.7. The values for the control tanks are all below 340 ppb except for the middle and bottom sampling ports at 350 hours. The values for the oil tank are in this same range until 48 hours when a larger amount was observed. The maximum value of 29,020 ppb was reached at 192 hours. The values for samples from the oil/dispersant tank are initially high for the top and middle of the tank; however, with time, the higher concentration migrates to the bottom. At 350 hours the only significantly high concentration is for samples from the bottom port of the tank.

(2) Qualitative Analysis

Control Tank:

Gas chromatograms (GC) of all samples having significant concentrations were measured. GC's of samples from the control tank are shown in Figures 7.4.29 - 7.4.40. Most of these chromatograms contain a series of peaks as shown in Figure 7.4.31, although they may contain additional
Table 7.4.6 Concentration (ppb) of extractable Organics in Water Samples from Flow-thru Tank Experiments at Narragansett Bay Campus (Trial 1)

<table>
<thead>
<tr>
<th>Hours</th>
<th>Top</th>
<th>0</th>
<th>1</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Control,</td>
<td>Top</td>
<td>270</td>
<td>185</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mid</td>
<td>382</td>
<td>148</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bot</td>
<td>280</td>
<td>193</td>
<td></td>
</tr>
<tr>
<td>(2) Oil,</td>
<td>Top</td>
<td>204</td>
<td>227</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mid</td>
<td>414</td>
<td>216</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bot</td>
<td>206</td>
<td>195</td>
<td></td>
</tr>
<tr>
<td>(3) Oil/Disp,</td>
<td>Top</td>
<td>2075</td>
<td>668</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mid</td>
<td>458</td>
<td>623</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bot</td>
<td>247</td>
<td>240</td>
<td></td>
</tr>
</tbody>
</table>

Table 7.4.7 Concentrations (ppb) of extractable Organics in Water Samples from Flow-thru Tank Experiments at Narragansett Bay Campus (Trial 2)

<table>
<thead>
<tr>
<th>Hours</th>
<th>Top</th>
<th>0</th>
<th>1</th>
<th>24</th>
<th>48</th>
<th>72</th>
<th>192</th>
<th>350</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Control,</td>
<td>Top</td>
<td>153</td>
<td>178</td>
<td>237</td>
<td>190</td>
<td>286</td>
<td>110</td>
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<tr>
<td></td>
<td>Mid</td>
<td>340</td>
<td>102</td>
<td>185</td>
<td>261</td>
<td>105</td>
<td>1,386</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bot</td>
<td>183</td>
<td>186</td>
<td>160</td>
<td>211</td>
<td>249</td>
<td>3,007</td>
<td></td>
</tr>
<tr>
<td>(2) Oil,</td>
<td>Top</td>
<td>232</td>
<td>1021</td>
<td>480</td>
<td>29,020</td>
<td>76.4</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Mid</td>
<td>308</td>
<td>162</td>
<td>273</td>
<td>325</td>
<td>309</td>
<td>1,851</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bot</td>
<td>150</td>
<td>157</td>
<td>267</td>
<td>229</td>
<td>540</td>
<td>966</td>
<td></td>
</tr>
<tr>
<td>(3) Oil/Disp,</td>
<td>Top</td>
<td>54,276</td>
<td>9,776</td>
<td>5,486</td>
<td>3,706</td>
<td>2,638</td>
<td>264</td>
<td></td>
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<tr>
<td></td>
<td>Mid</td>
<td>445</td>
<td>44,179</td>
<td>13,195</td>
<td>3,286</td>
<td>5,066</td>
<td>891</td>
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<tr>
<td></td>
<td>Bot</td>
<td>294</td>
<td>265</td>
<td>1,516</td>
<td>4,006</td>
<td>11,939</td>
<td>1,033</td>
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</tr>
</tbody>
</table>

Figure 7.4.24 GC of Surface Oil after 24 hrs. (Trial 1)

24 HOUR TOP OIL 1

90 TO 270 C AT 4 C/MIN
Figure 7.4.25 GC of Surface Oil/Dispersant after 1 hr. (Trial 1)

1 HOUR TOP OIL/DISPERSANT 1

90 TO 270 C AT 4 C/MIN

Figure 7.4.26 GC of Middle Oil/Dispersant after 1 hr. (Trial 1)

1 HOUR MIDDLE OIL/DISPERSANT 1

90 TO 270 C AT 4 C/MIN
Figure 7.4.27 GC of Top Oil/Dispersant after 24 hrs. (Trial 1)

24 HOUR TOP OIL/DISPERSANT 1

Figure 7.4.28 GC of Middle Oil/Dispersant after 24 hrs. (Trial 1)

24 HOUR MIDDLE OIL/DISPERSANT 1
Figure 7.4.29  GC of Middle Control at 0 hr. (Trial 2)

0 HOUR MIDDLE CONTROL

30 TO 270 C AT 4 C/MIN

Figure 7.4.30  GC of Top Control after 1 hr. (Trial 2)

1 HOUR TOP CONTROL

30 TO 270 C AT 4 C/MIN
Figure 7.4.31 GC of Bottom Control after 1 hrs. (Trial 2)

1 HOUR BOTTOM CONTROL
90 TO 270 C AT 4 C/MIN

Figure 7.4.32 GC of Top Control after 48 hrs. (Trial 2)

48 HOUR TOP CONTROL
90 TO 270 C AT 4 C/MIN
Figure 7.4.33 GC of Middle Control after 48 hrs. (Trial 2)

48 HOUR MIDDLE CONTROL

DETECTOR RESPONSE

TIME

90 TO 270 C AT 4 C/Min

Figure 7.4.34 GC of Top Control after 72 hrs. (Trial 2)

72 HOUR TOP CONTROL

DETECTOR RESPONSE

TIME

90 TO 270 C AT 4 C/Min
Figure 7.4.35  GC of Bottom Control after 72 hrs. (Trial 2)

72 HOUR BOTTOM CONTROL
80 TO 270 C AT 4 C/MIN

Figure 7.4.36  GC of Top Control after 192 hrs. (Trial 2)

192 HOUR TOP CONTROL
80 TO 270 C AT 4 C/MIN
Figure 7.4.37 GC of Bottom Control after 192 hrs. (Trial 2)

192 HOUR BOTTOM CONTROL

80 TO 270 C AT 4 C/MIN

Figure 7.4.38 GC of Top Control after 350 hrs. (Trial 2)

350 HOUR TOP CONTROL

80 TO 270 C AT 4 C/MIN
Figure 7.4.39 GC of Middle Control after 350 hrs. (Trial 2)

350 HOUR MIDDLE CONTROL

90 TO 270 C AT 4 C/Min

Figure 7.4.40 GC of Bottom Control after 350 hrs. (Trial 2)

350 HOUR BOTTOM CONTROL

90 TO 270 C AT 4 C/Min
peaks. This series of peaks is also observed in a number of the gas chromatograms from the oil contaminated tanks when petroleum hydrocarbons are not observed. These peaks appear to be due to chemicals of biological origin. The large quantitative values from the 350 hour middle and bottom samples are supported by the large unresolved envelope in the GC's of the two samples shown in Figures 7.4.29 and 7.4.40. The origin of the chemicals giving rise to their envelope are unknown; however, a similarly high quantitative value and unresolved envelope were observed for the sample from the bottom of the oil tank collected at 350 hours (Figure 7.4.56).

Oil Tank:

GC's of samples from the oil contaminated tank are shown in Figures 7.4.41-7.4.56. Prior to addition of the oil, the GC of a sample from the middle of the tank, Figure 7.4.41 is almost identical to that from the middle of the control tank (Figure 7.4.24). Samples from the oil tank at 1 and 24 hours do not show an appreciable increase in extractable organics over the control amounts and the GC's (Figures 7.4.32-7.4.34) are very similar to those of the control sample.

The GC of the sample from the oil tank taken from the top at 48 hours (Figure 7.4.35) shows a distribution of normal paraffins that are typical of petroleum and the quantitative value is over 1,000 ppb. The GC is interesting in that only the normal paraffins between C14 and C22 are observed. Moreover, the amounts of pristane and phytane relative to the normal paraffins are much larger than in the neat oil (see Figure 7.4.76).

The GC of the sample taken from the top (Figure 7.4.48) and bottom (Figure 7.4.50) at 72 hours also indicates a distribution of petroleum similar to that discussed above. It is interesting to note that the oil seems to be migrating to the bottom. At 192 hours, petroleum hydrocarbons appear in the GC (Figure 7.4.51) from the top of the tank, but they could not be discerned in the GC of the samples from the other two levels.

At 350 hours, GC of the samples (Figures 7.4.54-7.4.56) are very similar to those of the control tanks. As mentioned previously, the GC of the bottom sample has a large unresolved envelope. However, since samples from the control tank had a very similar GC, this large envelope is probably not due to petroleum.

Oil/Dispersant tank:

GC's of samples from the oil/dispersant tank are shown in Figures 7.4.57-7.4.75. Again, the GC of the sample from the middle of this tank prior to addition of the oil-dispersant is very similar to that of the control tank. GC's of the top and middle samples at 1 hour (Figures 7.4.58-7.4.59) and 24 hours (Figures 7.4.61-7.4.62) indicate a distribution of petroleum hydrocarbons very similar to the neat oil. It should be noted that the GC's of the samples from the top port contain more of the light components (C10-C12) than those from the middle port. Moreover, there is an increase in the amounts of pristane and phytane relative to the normal paraffins between the 1 and 24 hour samples.
Figure 7.4.41 GC of Middle Oil at 0 hr. (Contaminated Tank)

0 HOUR MIDDLE OIL

DETECTOR RESPONSE

TIME

90 TO 270 C AT 4 C/MIN

Figure 7.4.42 GC of Middle Oil after 1 hr.

1 HOUR MIDDLE OIL

DETECTOR RESPONSE

TIME

90 TO 270 C AT 4 C/MIN
Figure 7.4.43 GC of Top Oil after 24 hrs.

24 HOUR TOP OIL

38 TO 270 C AT 4 C/MIN

Figure 7.4.44 GC of Middle Oil after 24 hrs.

24 HOUR MIDDLE OIL

38 TO 270 C AT 4 C/MIN
Figure 7.4.45 GC of Top Oil after 48 hrs.

48 HOUR TOP OIL

98 TO 270 C AT 4 C/MIN

Figure 7.4.46 GC of Middle Oil after 48 hrs.

48 HOUR MIDDLE OIL

98 TO 270 C AT 4 C/MIN
Figure 7.4.47 GC of Bottom Oil after 48 hrs.

48 HOUR BOTTOM OIL

98 TO 278 °C AT 4 °C/ MIN

Figure 7.4.48 GC of Top Oil after 72 hrs.

72 HOUR TOP OIL

98 TO 278 °C AT 4 °C/ MIN
Figure 7.4.49  GC of Middle Oil after 72 hrs. (Contaminated Tank)

72 HOUR MIDDLE OIL

90 TO 870 C AT 4 C/MIN

Figure 7.4.50  GC of Bottom Oil after 72 hrs.

72 HOUR BOTTOM OIL

90 TO 870 C AT 4 C/MIN
Figure 7.4.51 GC of Top Oil after 192 hrs.
192 HOUR TOP OIL
30 TO 270 C AT 4 C/MIN

Figure 7.4.52 GC of Middle Oil after 192 hrs.
192 HOUR MIDDLE OIL
30 TO 270 C AT 4 C/MIN
Figure 7.5.53 GC of Bottom Oil after 192 hrs.

192 HOUR BOTTOM OIL

80 TO 270 C AT 4 C/MIN

Figure 7.4.54 GC of Top Oil after 350 hrs.

350 HOUR TOP OIL

80 TO 270 C AT 4 C/MIN
Figure 7.4.55 GC of Middle Oil after 350 hrs.

350 HOUR MIDDLE OIL

98 TO 270°C AT 4°C/MIN

Figure 7.4.56 GC of Bottom Oil after 350 hrs.

350 HOUR BOTTOM OIL

98 TO 270°C AT 4°C/MIN
Figure 7.4.57 GC of Middle of Oil/Dispersant Tank at 0 hrs.

0 HOUR MIDDLE OIL/DISPERSANT

DETECTOR RESPONSE

TIME

Figure 7.4.58 GC of Top of Oil/Dispersant Tank at 1 hr.

1 HOUR TOP OIL/DISPERSANT

DETECTOR RESPONSE

TIME
Figure 7.4.59 GC of Middle of Oil/Dispersant Tank at 1 hr.
1 HOUR MIDDLE OIL/DISPERSANT

98 to 270°C at 4°C/min

Figure 7.4.60 GC of Bottom of Oil/Dispersant Tank at 1 hr.
1 HOUR BOTTOM OIL/DISPERSANT

98 to 270°C at 4°C/min
Figure 7.4.61 GC of Top of Oil/Dispersant Tank at 24 hrs.

24 HOUR TOP OIL/DISPERSANT

Figure 7.4.62 GC of Middle of Oil/Dispersant Tank at 24 hrs.

24 HOUR MIDDLE OIL/DISPERSANT
Figure 7.4.63 GC of Bottom of Oil/Dispersant Tank at 24 hrs.

24 HOUR BOTTOM OIL/DISPERSANT

DETECTOR RESPONSE

TIME

Figure 7.4.64 GC of Top of Oil/Dispersant Tank at 48 hrs.

48 HOUR TOP OIL/DISPERSANT

DETECTOR RESPONSE

TIME
Figure 7.4.65 GC of Middle of Oil/Dispersant Tank at 48 hrs.

48 HOUR MIDDLE OIL/DISPERSANT

DETECTOR RESPONSE

TIME

Figure 7.4.66 GC of Bottom of Oil/Dispersant Tank at 48 hrs.

48 HOUR BOTTOM OIL/DISPERSANT

DETECTOR RESPONSE

TIME
Figure 7.4.67 GC of Top of Oil/Dispersant Tank at 72 hrs.

72 HOUR TOP OIL/DISPERSANT
50 TO 270 C AT 4 C/MIN

Figure 7.4.68 GC of Middle of Oil/Dispersant Tank at 72 hrs.

72 HOUR MIDDLE OIL/DISPERSANT
50 TO 270 C AT 4 C/MIN
Figure 7.4.69 GC of Bottom of Oil/Dispersant Tank at 72 hrs.

72 HOUR BOTTOM OIL/DISPERSANT

DETECTOR RESPONSE

TIME

Figure 7.4.70 GC of Top of Oil/Dispersant Tank at 192 hrs.

192 HOUR TOP OIL/DISPERSANT

DETECTOR RESPONSE

TIME
Figure 7.4.71 GC of Middle of Oil/Dispersant Tank at 192 hrs.

192 HOUR MIDDLE OIL/DISPERSANT

Figure 7.4.72 GC of Bottom of Oil/Dispersant Tank at 192 hrs.

192 HOUR BOTTOM OIL/DISPERSANT
Figure 7.4.73 GC of Top of Oil/Dispersant Tank at 350 hrs.

850 HOUR TOP OIL/DISPERSANT

DETECTOR RESPONSE

TIME

Figure 7.4.74 GC of Middle of Oil/Dispersant Tank at 350 hrs.

850 HOUR MIDDLE OIL/DISPERSANT

DETECTOR RESPONSE

TIME
At 48 hours, petroleum hydrocarbons are observed in the GC's (Figures 7.4.64-7.4.66) of samples from all three ports. The relative amounts of light hydrocarbons decreases from the top to the bottom of the tank. Furthermore, the GC of the sample from the bottom of the tank shows a dramatic increase in the amounts of pristane and phytane relative to the normal paraffins. Moreover, there appears to be only one broad unresolved envelope centered at about the retention time of n-C15 for the samples from the top and middle ports, whereas there is a second maximum centered at about n-C22 in the GC of the sample from the bottom.

The GC of samples collected at 72 hours (Figure 7.4.67-7.4.69) are very similar to those at 48 hours; however, there is an increase in the amounts of pristane and phytane relative to the normal paraffins in the GC of the samples from the top and middle ports.

At 192 hours the GC's of samples from the three ports (Figures 7.4.70-7.4.72) are very similar, and only subtle differences can be detected. All three GC's appear to have a double unresolved envelope, with maxima at n-C15 and n-C21. The GC of the sample from the bottom port has a slightly greater amount of the lighter paraffins with a maximum of normal paraffins at n-C14 rather than at n-C15 as observed in the other two samples.

After 350 hours, the GC's of samples from the three ports have changed dramatically. The amounts of petroleum hydrocarbons relative to peaks found in the GC of control samples is very low in samples from the top two ports and it is difficult to identify them; the concentrations of samples from these two levels are at the control level. However, the sample from the bottom port still contains significant amounts of petroleum hydrocarbons as indicated in the GC shown in Figure 7.4.75. Again, the double unresolved envelope and the relatively high concentration of pristane and phytane are observed.

Fractionation of Samples

Extracts of water samples were separated into three fractions consisting of paraffins, aromatics and polar compounds. A GC of each fraction was measured. The GC of the neat oil is shown in Figure 7.4.76 and of the three fractions of the neat oil in Figure 7.4.77-7.4.79. The GC of the first two fractions contain a number of specific peaks, whereas the GC of the third fraction contains very few characteristic peaks.

GC's obtained by fractionating selected samples from the oil/dispersant tank collected at 24, 48 and 72 hours are shown in Figures 7.4.80 - 7.4.94. At 24 hours the paraffin fraction (Figure 7.4.80) from the top port is very similar to the paraffin fraction of the neat oil (Figure 7.4.77) except for the loss of the more volatile components from n-C11 to n-C14. The aromatic fraction (Figure 7.4.81 and 7.4.78) are also similar except for the loss of the lighter fractions. However, the GC of the polar fraction from the oil/dispersant tank (Figure 7.4.82) has no distinctive peaks suggesting that the polars are lost in the flow system.
Figure 7.4.75 GC of Bottom of Oil/Dispersant Tank at 350 hrs.

250 HOUR BOTTOM OIL/DISPERSANT
90 TO 270 C AT 9 C/MIN

Figure 7.4.76 GC of Neat Oil
Figure 7.4.77 GC of Paraffin Fraction of Neat Oil

Figure 7.4.78 GC of Aromatic Fraction of Neat Oil
Figure 7.4.79 GC of Polar Fraction of Neat Oil

Figure 7.4.80 GC of Paraffin Fraction From Oil Tank at 24 hrs.
Figure 7.4.81 GC of Aromatic Fraction From Old Tank at 24 hrs.

Figure 7.4.82 GC of Polar Fraction From Old Tank at 24 hrs.
The fractions of the sample from the middle of the tank (Figures 7.4.83 and 7.4.84) at 24 hours contained larger relative amounts of the isoprenoids, pristane and phytane, in the paraffin phase, but very small peaks in the aromatic phase. This suggests (but is not conclusive evidence) that aromatics are stratified in the water column and remain near the top of the tank, indicating that the dispersant has a different effect on paraffins and aromatics.

The GC of the paraffin fraction at 48 hours (Figure 7.4.85) shows an odd/even effect with the even chain lengths (n-C16, n-C18 and n-C20) found at higher concentrations than the odd chain lengths. This odd/even effect is less pronounced in the GC of the composite sample (Figure 7.4.64); however, the distribution in the GC of the composite is affected by the large unresolved envelope centered at n-C15.

The remaining GC of the fractionated samples do not reveal any new features that are not observed in the GC of the composite samples.

(3) Conclusions

In this experiment, useful conclusions can be drawn from the gas chromatograms of samples from the oil dispersant tank. As shown by the quantitative results from this experiment and from previous experiments, the oil (petroleum hydrocarbons) appear to migrate with time to the bottom of the tank. This is supported by the gas chromatograms. However, in this experiment, the chromatograms show that not all of the components of the oil appear equally distributed at all three sampling levels. At 1 and 24 hours more of the lighter components (C10-C12 are found in the sample from the top port. The fractionation procedure indicates that the heavier aromatics never reach the center of the tank.

After 192 hours there appears to be more of the lower molecular weight paraffins in the bottom of the tank than at the other two levels. This could reflect greater degradation of the heavier paraffins at the bottom. In the same way, there is a general increase in the relative amounts of the isoprenoids, pristane and phytane, as a function of time; this could also be due to the degradation of the normal paraffins with time.

III. References


3. Wilson, M.P., "The Assessment Problems of Whether or Not to Treat Oil Spills," ibid.

Figure 7.4.83 GC of Paraffin Fractions From Middle of Old Tank at 24 hrs.

Figure 7.4.84 GC of Aromatic Fractions From Middle of Old Tanks at 24 hrs.
Figure 7.4.85 GC of Paraffin Top Fraction at 48 hrs.

Figure 7.4.86 GC of Aromatic Top Fraction at 48 hrs.
Figure 7.4.87 GC of Polar Fraction Top Fraction at 48 hrs.

Figure 7.4.88 GC of Paraffin Middle Fraction at 48 hrs.
Figure 7.4.89 GC of Aromatic Middle Fraction at 48 hrs.

C480DHF2e

Figure 7.4.90 GC of Paraffin Top Fraction at 72 hrs.

C720DHF1e
Figure 7.4.91 GC of Polar Top Fraction at 72 hrs.  7-128

Figure 7.4.92 GC of Aromatic Middle Fraction at 72 hrs.
Figure 7.4.93  GC of Paraffin Middle Fraction at 72 hrs.

C720DMF2e

Figure 7.4.94  GC of Polar Middle Fraction at 72 hrs.

C720DMF4e
7.5 Jerusalem Flow Thru Experiment

7.5.1 Introduction

The flow-thru experiment consisted of four 55 gallon drums with sea water flowing through each at the rate of 10 gallons/hour. Initially, the following components were added to the surface of the sea water:

1) Control
2) Ten ml of dispersant (Corexit 9527)
3) Two hundred ml oil (Kuwait crude)
4) Two hundred ml of Kuwait crude and 10 ml of Corexit 9527

Water samples were collected every week from the top, middle and bottom of each tank. Sediment samples were collected from tanks 1, 3, and 4 at week 1 (first day of the experiment) and week 4.

7.5.2 Experimental

(A) Quantitative Analysis of Water Samples

One-liter water samples were extracted with two 15 ml aliquots of CS$_2$. The aliquots were combined and the volume adjusted to 25 ml. The infrared spectrum was recorded from 3200 to 2800 cm$^{-1}$ using 6 mm AgCl matched cells, and the absorbance of the C-H stretching band at 2930 cm$^{-1}$ was used to determine the concentration of extractable organics from plots of concentration vs. absorbance measured using known amounts of the Kuwait crude oil, Kuwait and Corexit, or Corexit. An extraction efficiency of 65% (previously determined) was used for samples from tanks 1, 3 and 4. An extraction efficiency of 22% was used for tank 2 (dispersant) when it was found that the dispersant was present in the extract by qualitative infrared spectroscopy; however, if the dispersant was not present, a 65% efficiency was used.

(B) Qualitative Analysis of Water Samples Collected from the Tanks.

During the 1st, 4th and 6th weeks, 3.5 liter water samples were collected from the tanks. These larger samples were collected in order to perform complete qualitative analyses. The samples from the fourth week did not contain enough hydrocarbons to warrant qualitative analysis; however, samples from the other two weeks were analyzed.

All samples were extracted with CS$_2$ and the extracts concentrated to 1 or 2 ml. Infrared spectra between 1950 and 660 cm$^{-1}$ were measured using 6 mm AgCl cells. After measuring the infrared spectra, the CS$_2$ was completely removed from each of the extracts by evaporation and the residue was taken up in 20 μl of hexane. Two μl samples were injected into a gas chromatograph equipped with a glass capillary column (Supelco SP 2100). Three samples were also separated into multiple fractions containing aliphatics, small and large ring aromatics and polar components using a column of alumina and eluting with pentane, toluene and methanol. Each fraction was analyzed on a glass capillary column GC.
C) Analysis of Sediment Samples

Sediment samples were subjected to a saponification-extraction using a KOH-toluene-methanol reflux. The organic layer was collected and passed through a silica gel column to remove natural polar components. Both qualitative and quantitative infrared spectra of the extracts were measured. The extracts were further separated by thin-layer chromatography and all of the hydrocarbons running above the standard, phenanthrene, were dissolved in hexane and injected into the capillary column gas chromatograph.

7.5.3 Results

(A) Qualitative GC of Water Samples

(a) Week One

Water samples were collected one hour after addition of the oil and dispersant.

i. Control Tank

Gas chromatograms of water samples from the top, middle and bottom of the control tank are shown in Figures 7.5.1, 2 and 3. Gas chromatograms of the top and bottom (CT and CB) suggest the presence of normal paraffins from n-C_{16} to n-C_{24}, which is indicative of petroleum.

ii. Dispersant Tank

GC of the top, middle and bottom water extracts are shown in Figures 7.5.4, 5 and 6. A number of relatively intense peaks are observed in all three GCs; however, peaks at short retention times found in the GC of the oil/dispersant (Figure 7.5.10) are not observed.

iii. Oil Tank

GC of extracts of water from the top, middle and bottom of the oil tank are shown in Figures 7.5.7, 8 and 9. A number of relatively intense peaks are observed in the GC of the top sample. The normal paraffin peaks are relatively weak compared to the other components which suggests that the more soluble aromatics and polar compounds are present. Two prominent peaks are observed in the GC of the middle sample and these two peaks are also present in the GC of the top sample.

iv. Oil/Dispersant Tank

GC of the extracts of water from the top and bottom of the oil/dispersant tank are shown in Figures 7.5.10 and 11; the extract of the middle sample was accidentally destroyed during the analysis procedure. The GC of the top samples is typical of weathered oil with the addition of two peaks at short retention times and several broad peaks at longer retention times; these peaks are undoubtedly due to the dispersant. The interesting feature is that the dispersant takes most of the unweathered components of oil into the water column.
Figure 7.5.1   GC of the Control Tank, top, 1 hr.
GCFT1CM

90 TO 270 C AT 4 C/MIN

Figure 7.5.2  GC of the Control Tank, middle, 1 hr.
Figure 7.5.3 GC of the Control Tank, bottom, 1 hr.

Figure 7.5.4 GC of the Dispersant Tank, top, 1 hr.
Figure 7.5.5  GC of the Dispersant Tank, middle, 1 hr.

Figure 7.5.6  GC of the Dispersant Tank, bottom, 1 hr.
Figure 7.5.7  GC of the Oil Tank, top 1 hr.

Figure 7.5.8  GC of the Oil Tank, middle, 1 hr.
Figure 7.5.9  GC of the Oil Tank, bottom, 1 hr.

Figure 7.5.10  GC of the Oil/Dispersant Tank, top, 1 hr.
Figure 7.5.11  GC of the Oil/Dispersant Tank, bottom, 1 hr.

Figure 7.5.12  GC of the Control Tank, top, 6th week.
(b) Week Six

At the beginning of the sixth week, ten ml of dispersant were added to tanks 2, 3 and 4. Water samples were collected for qualitative analysis one hour after the addition of the dispersant.

i. Control Tank

GC of the top, middle and bottom water samples are shown in Figures 7.5.12, 13 and 14. All GC are similar and consist of a series of equally spaced peaks that appear to correspond to the even-numbered normal paraffins. GC of petroleum should consist of a distribution of normal paraffins, whereas biologically produced paraffins are generally odd-numbered.

ii. Dispersant Tank

GC of the top, middle and bottom of the dispersant tank are shown in Figures 7.5.15, 16 and 17. It should be noted that peaks at short retention times are observed after this addition in the top and middle GC, whereas they were not observed after the initial application. The GC of the bottom sample is very similar to that of the controls.

iii. Oil Tank

GC of the top, middle and bottom of the oil tank after dispersant was added, are shown in Figures 7.5.18, 19 and 20. The top and middle are similar, consisting of a number of peaks due to the dispersant. None of the peaks can be definitely assigned to the oil. With the exception of one strong peak, the GC of the bottom is similar to those of the controls.

iv. Oil/Dispersant Tank

GC of the top, middle and bottom samples are shown in Figures 7.5.21, 22 and 23. All three GCs correspond closely to those of the dispersant and oil tanks at the same levels.

(b) Fractionation of Water Extracts

Extracts of the top samples from tanks 1, 3 and 4 collected at the first hour were separated by a liquid column into 7 to 8 fractions. The GC of fractions from the control tank are shown in Figures 7.5.24 to 30. The heavier normal paraffins are observed in fractions 1, 2 and 3; whereas light components (shorter retention times) are observed in 4 thru 7. GC of the fractions from the top of the oil tank are shown in Figures 7.5.31 to 38. In this sequence, paraffins should appear in the first fraction, followed by one ring aromatics, two ring aromatics, multi-ring aromatics, and polar compounds. Fraction 3 (Figure 7.5.33) presents the most interesting GC; the peaks are possibly due to substituted two or three ring aromatics.

Due to the higher concentrations in the oil/dispersant tank, fractionation of this sample produced the strongest GC's as are shown in Figures 7.5.39-46. In the GC of the first fraction, paraffins, both normal and isoprenoids, are clearly separated into individual peaks.
Figure 7.5.13  GC of the Control Tank, middle, 6th week.

Figure 7.5.14  GC of the Control Tank, bottom, 6th week.
Figure 7.5.15  GC of the Dispersant Tank, top, 6th week.

Figure 7.5.16  GC of the Dispersant Tank, middle, 6th week.
Figure 7.5.17  GC of the Dispersant Tank, bottom, 6th week.

Figure 7.5.18  GC of the Oil Tank, top, 6th week.
Figure 7.5.19 GC of the Oil Tank, middle, 6th week.

Figure 7.5.20 GC of the Oil Tank, bottom, 6th week.
Figure 7.5.21  GC of the Oil/Dispersant Tank, top, 6th week.

Figure 7.5.22  GC of the Oil/Dispersant Tank, middle, 6th week.
Figure 7.5.23  GC of the Oil/Dispersant Tank, bottom, 6th week.

Figure 7.5.24  GC of the Control Tank, top, 1 hr, fraction 1.
Figure 7.5.25  GC of the Control Tank, top, 1 hr, fraction 2.

Figure 7.5.26  GC of the Control Tank, top, 1 hr, fraction 3.
Figure 7.5.27 GC of the Control Tank, top, 1 hr, fraction 4.

Figure 7.5.28 GC of the Control Tank, top, 1 hr, fraction 5.
Figure 7.5.29  GC of the Control Tank, top, 1 hr, fraction 6.

Figure 7.5.30  GC of the Control Tank, top, 1 hr, fraction 7.
Figure 7.5.31  GC of the Oil Tank, top, 1 hr, fraction 1.

Figure 7.5.32  GC of the Oil Tank, top, 1 hr, fraction 2.
Figure 7.5.33  GC of the Oil Tank, top, 1 hr, fraction 3.

Figure 7.5.34  GC of the Oil Tank, top, 1 hr, fraction 4.
Figure 7.5.35  GC of the Oil Tank, top, 1 hr, fraction 5.

Figure 7.5.36  GC of the Oil Tank, top, 1 hr, fraction 6.
Figure 7.5.37  GC of the Oil Tank, top, 1 hr., fraction 7.

Figure 7.5.38  GC of the Oil Tank, top, 1 hr, fraction 8.
Figure 7.5.39  GC of the Oil/Dispersant Tank, 1 hr, fraction 1.

Figure 7.5.40  GC of the Oil/Dispersant Tank, 1 hr, fraction 2.
Figure 7.5.41  GC of the Oil/Dispersant Tank, 1 hr, fraction 3.

Figure 7.5.42  GC of the Oil/Dispersant Tank, 1 hr, fraction 4.
Figure 7.5.43  GC of the Oil/Dispersant Tank, 1 hr, fraction 5.

Figure 7.5.44  GC of the Oil/Dispersant Tank, 1 hr, fraction 6.
Figure 7.5.45  GC of the Oil/Dispersant Tank, 1 hr, fraction 7.

Figure 7.5.46  GC of the Oil/Dispersant Tank, 1 hr, fraction 8.
GC's of fractions 2 through 5 suggest increasing amounts of aromatics, whereas 6 through 8 go from the heavier aromatics to polars. It is interesting to compare the GC of the first fraction to that of the total material in Figure 7.5.10; a number of dissimilarities are observed. We also measured the GC of the surface slicks after five weeks of the experiment; these are shown in Figures 7.5.47 and 48. The GC of the first fraction is very similar to those of the surface slicks.

(C) Quantitative Analysis of Water Samples

Quantitative results for extractable organics in water samples are listed in Table 7.5.1. As mentioned previously, a 22% efficiency was used for the dispersant tank when the dispersant was present and a 65% efficiency when the dispersant was not detected. Very little dispersant was detected during week two; thus, the extraction efficiency is somewhere between 22 and 65%, and the values are lower than those in the table.

(D) Analysis of Sediment Samples

Sediment samples were collected from tanks 1, 3 and 4 on the first day and at the beginning of the fourth week. The quantitative results obtained by IR and GC are listed in Table 7.5.2. As in previous studies, the GC values are lower than the IR values; this is due to separation by thin layer chromatography between the IR and GC measurements. A very interesting fact is that the sediment values are lower in week four than in week one (except for tank 1 by GC). It should also be noted that the tank 4 (oil/dispersant) concentration was twice as high as the other two at the 1 hour sampling by the IR measurement. This is reasonable since most of the dispersant would be included in the IR measurement, but would be removed prior to the GC analysis by thin layer chromatography.

GC of the six sediment samples are shown in Figures 7.5.49-54. The pristane/phytane ratio in the control and the oil tank at one hour and in the GC of the control at the fourth week are greater than 1, whereas they are approximately one or less in the oil/dispersant at one hour and the fourth week and in the oil tank after four weeks. Thus, it appears that with the dispersant some of the petroleum hydrocarbons enter the sediments during the first hours. However, there does not appear to be a significant increase in petroleum hydrocarbons in the sediments during the three week period.

(E) Qualitative Analysis of Water and Slick Samples by Infrared Spectroscopy

Qualitative infrared spectra of all samples were measured from 1950 to 650 cm⁻¹. The IR spectra of the slick samples collected at the end of five weeks from the oil and dispersant tanks are identical, which is in agreement with the GC of the same two samples.

There are several noteworthy differences in the IR of the water samples. The infrared difference spectra of the sample from the top of the oil tank and from the top of the control tank at one hour is shown in Figure 7.5.55. Only one strong band appears at 1040 cm⁻¹. Although exact identification of the compound is not possible from one band, it
Table 7.5.1. Concentrations (ppb) of Extractable Organics in Water Samples from Flow-Thru Tank Experiments at Experimental Station in Jerusalem

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<tr>
<th>Week</th>
<th>May 7</th>
<th>May 14</th>
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<th>June 11</th>
<th>June 18</th>
<th>July 2</th>
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<td>1) Control, Top</td>
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<td>332</td>
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<td>2) Oil, Top</td>
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<td>415</td>
<td>197</td>
<td>117</td>
<td>436</td>
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<tr>
<td>3) Oil/Disp, Top</td>
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<td>637</td>
<td>60</td>
<td>2066</td>
<td>318</td>
</tr>
<tr>
<td>4) Disp, Top</td>
<td>9598*</td>
<td>1215*</td>
<td>319*</td>
<td>99*</td>
<td>11,499*</td>
<td>352*</td>
</tr>
<tr>
<td>5) Oil/Disp, Top</td>
<td>20082*</td>
<td>3071*</td>
<td>306*</td>
<td>104*</td>
<td>5,723*</td>
<td>306*</td>
</tr>
<tr>
<td>6) Disp, Top</td>
<td>3992*</td>
<td>949*</td>
<td>515*</td>
<td>79*</td>
<td>1,344*</td>
<td>351*</td>
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</tbody>
</table>

* 22% extraction efficiency used
+ 65% extraction efficiency used
N.O. non-detectable

Table 7.5.2

Concentrations (μg/g dry weight) of Hydrocarbons in Sediment Samples

<table>
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<tr>
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<th>GC Values</th>
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</tr>
<tr>
<td>2. Oil</td>
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<td>15</td>
</tr>
<tr>
<td>3. Oil/Dispersant</td>
<td>73</td>
<td>9</td>
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Figure 7.5.47 GC of the Slick in the Oil/Dispersant Tank, week 6.

Figure 7.5.48 GC of the Slick in the Oil Tank, week 6.
Figure 7.5.49  GC of the Sediment in Control Tank, 1 hr.

Figure 7.5.50  GC of the Sediment in Oil Tank, 1 hr.
Figure 7.5.51  GC of the Sediment in Oil/Dispersant Tank, 1 hr.

Figure 7.5.52  GC of the Sediment in Control Tank, 4th week.
Figure 7.5.53  GC of the Sediment in Oil Tank, 4th week.

Figure 7.5.54  GC of the Sediment in Oil/Dispersant Tank, 4th week.
could well be a sulfoxide and the band due to the S=O group which absorbs strongly at this frequency. An organic sulfoxide could account for the tendency of this oil to form mousse and act as a self-dispersant. This band is also found in the difference spectrum obtained by subtracting the oil/dispersant middle from the oil/dispersant top at the first sampling as is shown in Figure 7.5.56.

Another interesting feature is found in the difference between the oil/dispersant and oil at the top after addition of dispersant in the sixth week as is shown in Figure 7.5.57. The peak at 770 appears only in the oil/dispersant spectrum; thus, it has a positive value (pointing down) in the difference spectrum. This peak was also observed in the top sample from the dispersant only tank. It may account for other differences observed between the tanks after the dispersant was applied a second time.

Figure 7.5.55 IR difference spectrum; top of oil tank minus top of control tank, 1 hr.
Figure 7.5.56  IR difference spectrum; oil/dispersant top minus oil/dispersant middle, 1 hr.

Figure 7.5.57  IR difference spectrum; oil/dispersant top minus oil top, 6th week.
7.6 Field Studies

7.6.1 Field Study of the Buzzard Bay Spill

During the last week of January 1977, 100,000 gallons of a No. 2 fuel were spilled from a barge into the ice laden entrance to the Cape Cod Canal, i.e., in Buzzards Bay. The oil became trapped in and beneath the ice: thus this spill offered a unique opportunity to test our laboratory methodology on an actual spill. One week after the spill, we collected the following samples: oil in the ice, oil on the water, water samples at 3 m beneath the surface, and sediment samples with a grab sampler. Since the grab sampler had to be pulled through the surface water which possibly contained oil, we returned the following week and one member of the group collected sediment samples by diving beneath the ice. On this occasion an air sample was also collected on shore by pumping air through a charcoal cartridge for one hour.

All of the field samples were returned to the laboratory for analysis. We obtained a sample of the oil from the barge; the oil was analyzed and the results on the field samples were compared to those on the cargo oil and to the results of the laboratory experiments on the oil.

Oil was found in the water column and sediment samples. The infrared spectral fingerprints of the oil in the ice and on the water surface definitely matched the cargo oil. The spectral fingerprint of the oil in the water column was also very similar to that of the cargo; however, the fingerprint of the sediment hydrocarbons could not be directly related to that of the cargo. There are two possible explanations for this observation: the composition of the oil retained by the sediments could be considerably different from that of the cargo, or the hydrocarbons in the sediments could be from a different source. The latter explanation appears more reasonable, since the same barge spilled oil at this site in 1974. The amount of hydrocarbons in the sediments was relatively low. However, it should be mentioned that the sediment samples were very sandy and may not retain the oil as well as finer sediments.

Possibly the most interesting and useful results are on the air and water column samples. The gas chromatograms (GC) of the water column, water surface, and cargo samples are compared in Figure (7.6.1). The GC of the cargo and surface samples are virtually identical, e.g., note the doublet at n-C17. The GC of the water column sample also has this doublet at n-C17; however, only the higher boiling hydrocarbons can be observed in the GC of this sample. Fifty g of n-C20 were added to this sample as an internal standard: thus, the n-C20 peak is appropriately higher than those of the other n-paraffins. The latter GC should be compared to that of the laboratory water sample of the same oil which is shown in Figure 7.6.2. Both the field and the laboratory water samples show that only the hydrocarbons boiling at or higher than n-C14 enter the water column.

The air sample collected at Buzzards Bay offers even greater support to the laboratory results. The GC of the field and laboratory air samples are shown in Figure 7.6.3. Both show that the hydrocarbons entering the atmosphere are predominantly those boiling at or below n-C14. There is a considerable similarity between the relative composition of
7.6.1 GC of the Buzzards Bay Oil, Cargo, Surface and Water Column.

7.6.2 GC from the laboratory experiment on the No. 2 Fuel Oil from the Buzzards Bay Spill.

7.6.3 GC of Field and Laboratory Air Sample from the Buzzards Bay Oil.
the hydrocarbons in the two samples. The GC of the field sample does show some higher boiling chemicals. Possibly these are of biological origin and may be more polar than petroleum hydrocarbons which would account for their longer retention time on the GC column.

7.6.2 Field Study of the Argo Merchant Spill

Another spill of opportunity occurred during the early morning hours of December 15, 1976, when the Argo Merchant went aground in the Nantucket shoals. The tanker split and spilled its cargo of 7.7 million gallons of No. 6 oil into the sea. At about the same time, another tanker, the Grand Zenith, was lost at sea and was also carrying a No. 6 fuel.

Approximately 60 to 90 days after the grounding of the Argo Merchant, tarballs began to wash ashore on Jamestown (R.I.), Martha's Vineyard, Nantucket and Cape Cod (Mass.) (from Nauset Beach to Provincetown). This laboratory received and analyzed 22 of these tarballs ranging in weight from a few ounces to 15 lbs.

Table (7.6.1) lists the information on the tarballs which were analyzed. The samples, which contained aquatic debris and occluded water, needed to be pretreated and cleaned up prior to analysis. To do this, approximately 5 mls. of each sample were placed in a test tube and spun in a centrifuge for a few minutes, allowing the debris to separate to the bottom and the oil to rise to the top of the tube. The oil layer was then transferred to another test tube and 5 mls. of CC14 were added. The sample was then shaken well and centrifuged for five minutes. The top three-quarters of the sample was then transferred to another test tube, a drying agent, MgSO4, was added and the sample was again centrifuged for five minutes at 35°C. This last series of steps was repeated until all water was removed from the sample. The CC14 was then removed by evaporation.

The samples were then placed in a demountable infrared cell with a 0.05 mm spacer and the spectra were measured on a Perkin-Elmer 521 Infrared Spectrometer. The digitized spectral data were stored in a computer data file and all data analyses were performed on an IBM 370/60 computer.

Kileen and Chien (1) proposed a method for obtaining the probability of matching spilled oil to one or more suspects from infrared spectra of the samples. Their method is an extension of the ratio method developed in our laboratory (Ahmadjian et al., 2).

In the ratio method, absorbances at 18 frequencies in the spectrum of one sample are ratioed with absorbances at the same frequencies in the spectrum of another sample. The log of each ratio, the average log-ratio, and the differences between each log-ratio and the average log-ratio are determined. Initially, we ratioed the absorbances in the spectrum of each suspect to those in the spectrum of the spill sample; the best match was assigned to the spectrum having the most ratios within 10% of the average. Later, the method was extended to give a single value for estimating the differences between spectra (2). This value is obtained from the sum of the squares of the differences between the
log-ratios and the average log-ratio, i.e.,

$$s^2 = \frac{18}{\sum_{i=1}^{18} \left( \frac{\log A_{i1}}{A_{i2}} - \frac{1}{18} \sum_{i=1}^{18} \frac{\log A_{i1}}{A_{i2}} \right)^2}$$

where $A_{i1}$ and $A_{i2}$ are the absorbances for the $i$th band in spectra 1 and 2, respectively. For a perfect match, the value of $s^2$ would be zero; thus, the magnitude of $s^2$ reflects the dissimilarity between oils.

We (2) measured spectra of 198 neat and 647 weathered oils (including several weathered samples for each of 80 neat oils). $s^2$ values for all possible pairs of oils were calculated and placed in one of two categories: same oils (neat and weathered oils from the same origin) and different oils (neat and weathered oils from different origins). There were 5,534 pairs with the two oils originating from the same source, and 345,030 pairs with the two oils from different sources. The pairs in each category were then ordered according to increasing $s^2$ values, and two histograms for frequency of occurrence vs. $s^2$ in increments of 0.01 were plotted.

The histograms provided distributions for pairs of oils from the same sources and for pairs from different sources. Kileen and Chien (1) used these distributions to determine the probabilities of guilt for each suspect in a spill case and the probability that a sample from the "true spiller" was not included. Their method is based on Bayes Theorem and is described completely in their report (1).
In the present report, it is important to note that the distributions used to obtain the probabilities are based on all types of oils, i.e., they are comprised of light through heavy crudes, fuels and lubricating oils. This tends to give slightly higher probabilities especially at the low end of the 0 to 1 probability scale. For example, infrared fingerprints of two No. 6 fuels may be completely different and we would expect that the probability that they match would be close to 0.0; however, since they are both No. 6 fuels, their fingerprints will be more similar than the fingerprints of a No. 6 and No. 2 fuel. Thus, in many cases, the probability that two different No. 6 oils match will be higher than expected because they are the same type of oil.

Infrared spectra of the Argo Merchant cargo and of the spilled oil collected two days after the tanker broke apart are shown in Figure (7.6.4). (These samples were obtained from Dr. Jerome Milgram, MIT). When the digitized spectrum of the spilled oil was compared with that of the cargo, the following probabilities were obtained:

<table>
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<th>Probability</th>
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<tr>
<td>Argo Merchant</td>
<td>0.986</td>
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<tr>
<td>Another Source</td>
<td>0.014</td>
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</table>

Infrared Spectra of the Argo Merchant Cargo and of the Spilled Oil Collected 2 Days After the Spill.
Infrared spectra of the 22 tar balls listed in Table (7.6.1) were measured and the digitized fingerprints stored in a computer data file. Many of the spectra had similar contours and some were almost identical as is shown in Figure (7.6.5). The spectrum of each tar ball was compared with that of each of the others and the probability that they came from the same source is given in Table (7.6.2). The results are categorized according to magnitude in Figure (7.6.6).

All samples from Jamestown, Martha's Vineyard and Nantucket have probabilities $>0.85$ of being identical except for sample 2 from Jamestown. This was a sample of the outside layer of a tar ball, and the differences reflect excessive weathering on the surface. In addition to samples 1-10 being from the same source, the probabilities that samples 12, 16, 17 and 19 came from this source are $>0.5$. Furthermore, tar balls 11 and 13 are virtually identical ($P=0.99$).

It should be mentioned that the differences between many of the tar balls could be due to weathering and that this effect is more pronounced on the surface of the tar balls. Many of the tar balls from Cape Cod were very small and these could have been subjected to extensive weathering.

The infrared spectral fingerprint of the Argo Merchant oil is compared to that of the Martha's Vineyard tar ball in Figure 7.6.7. The general contours of the spectra are entirely different. We treated each of the 22 tar balls as a spill sample and determined the probability that each came from the cargo. The results given in Table 7.6.3 show that only sample No. 11 (Nauset Beach) had a probability of matching $>0.3$; most were $<0.2$. The spectrum of the cargo and the tar balls (except for sample 15) were characteristic of No. 6 fuel oils. Thus, these finite probabilities reflect the fact that the samples are the same type of oil.

If the tar balls came from the Argo Merchant, they were "weathered" in the Atlantic for almost two months; thus, we weathered some of the cargo oil at the URI aquarium for one month and periodically analyzed the samples. In most cases, the spectra of the tar balls and weathered Argo Merchant tar balls became less similar. The probability of matching for the 3 and 10 day samples are also given in Table 7.6.3.

The tanker, Grand Zenith, disappeared somewhere off the New England coast on the way from Teeside, England to Fall River, Massachusetts during January 1977; thus, its cargo was also a possible source of the tar balls. The U.S. Coast Guard R & D Center supplied us with a sample of the oil loaded aboard the Grant Zenith. We measured infrared spectra of the neat oil and of samples collected periodically during one month of weathering at the URI aquarium. The infrared spectrum of the Grand Zenith oil is compared with the Argo Merchant cargo and the Martha's Vineyard tar ball in Figure 7.6.8.

The probabilities obtained when comparing the spectra of the neat and 7 weathered samples to the tar balls are given in Tables 7.6.4a and b. The probabilities run as high as 0.83 when the neat oil is compared to tar balls No. 3 and 4; however, the highest probability (0.90) was obtained from matching the 14 day weathered sample with tar ball No. 11 from Nauset Beach (see Figure 7.6.9 for spectra). Other tar balls found in
Figure 7.5.5 Infrared Spectra of Tar Balls:

Figure 7.6.1 Probabilities of Tar Balls Matching.

Figure 7.6.7 Infrared Spectra of Tar Balls from Martha's Vineyard and Argo Merchant Cargo.
Table 7.6.2 Probabilities of Tar Balls Matching

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### Table 7.6.3 Probability of Tar Balls Originating From Argo Merchant Cargo

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Table 7.6.4 A. Probability of Tar Balls Originating from Grand Zenith Cargo Weathered 0-4 days

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Table 7.6.4 B. Probability of Tar Balls Originating from Grand Zenith Cargo Weathered 7-28 days

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this area (Nos. 13 and 14) have probabilities of 0.85 of matching the weathered Grand Zenith oil.

According to the probabilities given in Table 7.6.4, the tar balls can generally be placed into three categories: i) those with high probabilities of matching the neat or short term weathered samples, ii) those with high probabilities of matching the long term weathered samples, and iii) those with low probability matches. Samples 1,3-10, 16 and 19 fall in category i, samples 11-14, 21 and 22 in category ii, and the rest in iii.

The study showed conclusively that the tar balls found along the New England coast after the Argo Merchant incident were not from the stricken tanker. Many of the tar balls had similar infrared spectra and there is a high probability that a number of these came from the same source. Finally, there is a reasonably high probability that some of the tar balls originated from the stricken tanker, Grand Zenith. It should be noted that the tar balls were compared with oil loaded onto the Grand Zenith, and not to the oil actually contained in the tanker. The composition of the oil in the tanker could have been slightly different due to residues in the tanker from previous shipments.

References.


Titles and Authors


Predicting The Performance of Medium and Low Resolution Infrared Spectrometers and Analyzers, Chris W. Brown, Patricia F. Lynch and Mark A. Maris and Donald S. Lavery.

Quantitative Analysis of Gaseous Hydrocarbons By Infrared Spectroscopy, Chris W. Brown, Patricia F. Lynch and Mark A. Maris and Donald S. Lavery.


Collection of Gas Chromatographic Fractions on Activated Charcoal and Identification by Infrared Spectroscopy, Daniella Goldfarb and Chris W. Brown.
Computerized dispersive infrared spectroscopy gives results comparable to FTIR, as we perform "Festa of Magic," Dr. Chris W. Brown, Patricia F. Lynch and Mark Ahmadjian.

In the Wake of the Argo Merchant, Center for Ocean Management Studies.
8.0 Microbiology

Richard W. Traxler
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8.0 MICROBIOLOGY

8.1 Introduction:

The report of a special study group of the National Academy of Sciences on Petroleum in the Marine environment (1) indicated that the rates of microbial degradation of petroleum hydrocarbons vary with the complexity of the material, the nature of the microbial population and environmental conditions. The physical process of dispersion of a spilled oil will reduce the concentration of oil in the spill vicinity and greatly increases the surface area of the oil which renders the oil more susceptible to biological degradation (2).

The hydrocarbon degradation potential of ocean environments has not been adequately defined (3) but is known to be influenced by such factors as the number and types of hydrocarbon degrading microorganisms, the degree of oil dispersion, temperature and nutrient availability (4). Hydrocarbon degradation rates measured in the laboratory have been misleading as they were found to be considerably higher than in situ rates (5). It has been demonstrated (6) that degradation rates in cold waters are reduced compared to warmer water but not to the extent previously thought. Surfactants have been investigated as a mechanism to increase oil recovery (6),(7) and microorganisms have been shown to actively emulsify hydrocarbons (8), (9) and oils (10). Studies have shown that chemical dispersants stimulate bacterial growth on oil and the biodegradation of the oil (11).

This project was designed to investigate the effect of chemical dispersants on the ability of natural marine bacterial populations to biodegrade crude oil hydrocarbon components.

8.2 Materials and Methods:

8.2.1 Culture Media

The culture media used in the project were:

1. Nutrient Seawater Agar (NSA)

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<td>1g.</td>
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<tr>
<td>Succine Acid</td>
<td>.2g.</td>
</tr>
<tr>
<td>K2HPO4</td>
<td>.33g.</td>
</tr>
<tr>
<td>KH2PO4</td>
<td>.66g.</td>
</tr>
<tr>
<td>Agar-Agar</td>
<td>16g.</td>
</tr>
<tr>
<td>Distilled Water</td>
<td>1 L.</td>
</tr>
</tbody>
</table>

2. OZR Agar

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yeast Extract</td>
<td>1g.</td>
</tr>
<tr>
<td>Trypticase</td>
<td>1g.</td>
</tr>
<tr>
<td>Fe PO4 2H2O</td>
<td>10mg.</td>
</tr>
<tr>
<td>Agar-Agar</td>
<td>16g.</td>
</tr>
</tbody>
</table>
3. Hydrocarbon Basal Medium (HBM)

Aged Seawater 990ml.
Supplement B 10ml.
Washed Agar-Agar** 20g.
NH₄Cl 7.5g.
FePO₄·2H₂O 4.75g.
Distilled Water 250ml.

*Narragansett Bay water (GSO site), cheesecloth filtered to remove particular matter and aged one month in the dark in glass carboys.

**Flaked agar was soaked and rinsed three times a day with tap water for three days, and once a day for the next five days, followed by once a day rinses in distilled water for six days, then air dried and ground to powder.

The sterile melted agar was placed in a sterile Waring Blender, the hydrocarbon added at desired concentration, blended at high speed for three minutes and poured into sterile plates.

8.2.2 Dissolved Oxygen, Azide modification for BOD.

1. Solutions

a. Manganese Sulfate
MnSO₄·H₂O, 91g. in 250 ml distilled water, filter and dilute to volume.

b. Alkaline-iodide-azide reagent

NaOH or KOH 250g.
NaI or KI 67.5g.
NaN₃ 5g.

Dissolve NaOH and NaI in distilled water, dilute to 500ml, then add NaN₃ dissolved in 20 ml distilled water.

c. Sulfuric acid 36N
d. Starch
e. Sodium thiosulfate

Na₂S₂O₃·5H₂O (0.1N), 24.82g. dissolved, boiled, cooled, then distilled water added to 1000ml, add 5ml of chloroform as a preservative.

2. Method
Remove 200 ml of water from the BOD bottle, add 2 ml of MnSO₄ and 2 ml of alkaline-iodide-azide reagent. Shake and let stand for at least two minutes, add 2 ml of H₂SO₄ and shake until the ppt is dissolved. Titrate with sodium thiosulfate until pale straw color, add 2 ml of starch solution and titrate until the purple color disappears.

3. Modified BOD Method

For the standard BOD method a standard inoculum is prepared for addition to each bottle and the measurement of O₂ used provides an estimate of organic matter in the water. The modification was to use the natural seawater microbial population as inoculum and challenge this population with a known quantity of substrate. A control was used for each series which consisted of the seawater without added nutrient. This provides an estimate of oxygen depletion caused by the natural microbial population metabolizing the endogenous nutrients present in the seawater. This value was subtracted from the test results. All samples were run in triplicate and the average value used as the data point.

The results are reported as rates of oxygen depletion for a given microbial population at any time during the course of the experiment. A series of at least 21 BOD bottles containing the same water and challenge substrate are set up for each water sample. Three bottles are selected at random for any measurement time during the rate determination and measured for dissolved oxygen content.

8.2.3 Radioactive Degradation Rate Determination

Substrates labeled with ¹⁴C carbon are used as an auxiliary method to determine the rate at which materials are degraded by natural microbial populations. Several different approaches have been used to estimate turn-over of hydrocarbon components. The metabolic ¹⁴CO₂ produced from the metabolism of the ¹⁴C substrate was trapped at hourly intervals to calculate rate of CO₂ production. Another approach was to measure rate of CO₂ release, and rate of production of water soluble intermediates and end products. ¹⁴C-Hexadecane was used as a representation n-alkane, ¹⁴C-Naphthalene as representative of low molecular weight aromatic compounds and ¹⁴C-Benzopyrene as a representative of high molecular weight aromatic compounds. The ¹⁴C-hydrocarbons were used either at constant value (luci) or added to samples in the approximate ratio in which they occurred in the oil under investigation.

The reaction vessels were 250 ml flasks fitted with a CO₂ free air sweep to carry metabolic CO₂ into the methanol-ethanolamine traps, or the same type of flask fitted with a rubber cap. In the latter case, the reaction vessel was incubated for three hours, acidified with 0.1N HCL to release all bicarbonate as CO₂ which was then flushed from the reaction vessels into CO₂ traps.

The flasks were extracted with n-pentane at acid pH to recover all residual hydrocarbon and any lipids produced during the reaction. The pentane extracted seawater was counted to measure low molecular weight, water soluble products left after the extraction. The pentane extract was then partitioned with acidified methanol: ethanol (1:1) to remove lipids from the pentane extract. The pentane and alcohol were counted
for $^{14}$C activity.

The specific radioactivity of the substrate is known, therefore, it is possible to convert the radioactivity in the various products by calculation to ng. of substrate utilized. If the initial amount of hydrocarbon is known, the turnover time of the substrate can be calculated using equation 1.

Equation 1.

$$\frac{T}{F} = \frac{\text{Time}}{\text{ng Hydrocarbon metabolized}} = \frac{\text{ng Hydrocarbon added}}{\text{Hydrocarbon metabolized}}$$

The degradation time of a complex mixture such as crude oil can be estimated using equation 2.

Equation 2.

$$\frac{D}{F} = \frac{\text{Time}}{\text{ng component a + ngb + ---}} = \frac{\text{Total Petroleum present}}{\text{component a}}$$

8.2.4 Viable Plate Counts

The plates for "total heterotrophic" bacterial counts (THB) and Hydrocarbanoclastic Bacteria counts (HYB) were prepared and incubated at least 24 hours but not over 96 hours at the temperature at which the experiment would be performed. This allowed proper drying of the agar surface to reduce spreading of the bacterial colonies as they developed on the agar surface. All glassware and diluents were held six hours at experiment temperature to prevent temperature shock to the bacteria.

Plating was performed via the spread plate technique which consisted of spreading 0.1 ml of the proper dilution over the entire agar surface using a sterile glass rod bent into the shape of a hockey stick. Samples were serially diluted and three consecutive dilutions of each sample were chosen for spread plating. The normal dilutions used were $10^{-1}$, $10^{-2}$ and $10^{-3}$ but higher dilution values were used in some cases to achieve countable plates (30-300 colonies). In most experiments, two dilutions were prepared from each sample and two plates were spread from each dilution which means we had four plates for counting at each data point. This method increases the statistical accuracy of the spread plate count method. The values reported are the numerical average of the four plates.

The plates were counted on a Quebec Colony Counter with transmitted light. Plates with opaque media were counted on the same instrument but using an oblique light source.

8.2.5 Most Probable Number Technique

This method was performed with OZR and HBM medium without agar. Five parallel series of dilutions were made for each sample, utilizing four decimal dilution series. One ml of each dilution was added aseptically to 10 ml of medium. Five control tubes of medium were used as a contamination check. All work was performed in a hood system to prevent air
contamination of the medium.

The tubes were incubated at the temperature chosen for the experiment and scored as growth or no growth. Growth was positive if there was visible bacteria on the tube bottom, throughout the medium, or underlying the hydrocarbon (oil) phase.

The number of positive tubes in each dilution of the five parallel series was determined and the number of bacteria per ml of sample determined using the MPN tables of Postgate (1969).

8.2.6 Replica Plating Technique

This technique was described by Pierce, Cundell, and Traxler (1975). The bacterial colonies from the master plate (obtained during viable plate count experiments) were transferred to other substrate plates using a velvet replicator pad (Fig. 8.1). The replication sequence was master plate to non-substrate basal agar, to hydrocarbon substrate to OZR agar. Colonies growing on the non-substrate basal agar were not scored when growing on a hydrocarbon substrate as they were considered to be growing at the expense for agar-agar rather than the hydrocarbon. The final OZR plate was used to insure that inoculum was carried forward from each colony.

8.2.7 Laboratory Experiment System

This system consisted of 5.5 gallon aquaria containing a 5 cm sediment base and fresh seawater overlay. A large glass tube extended into the midpoint of the water samples so that a pipet could be inserted to remove water without contact with the surface oil. Sediment samples were obtained with a tube within a tube arrangement. A large glass tube was placed in the water prior to the addition of oil and/or dispersant. When ready to sample the sediment, this tube was pushed into the sediment zone and a second smaller sterile tube was passed through the first glass tube to remove the sediment sample.

8.3 Results and Discussion

Three general purpose media were compared for use in the enumeration of "total" marine heterotrophic bacteria and as a base for a selective medium for hydrocarbon utilizing bacteria. The comparison of the three media to support growth of marine heterotrophic bacteria is shown in (Figure 8.2). OZR medium was superior to the other two media and was chosen as the basic medium for this study. Media K and G are both formulated using Rila Salts mix to replace the aged seawater of the OZR medium. It is apparent from these data that Rila Salts do not adequately substitute for aged seawater and that media so formulated provide much poorer productivity of the heterotrophic marine bacteria.

A comparison was made of the viable plate count (VPC) and most probable number (MPN) methods for enumerating marine heterotrophic bacteria in OZR medium. Both methods (Figure 8.3) were capable of determining increases in the number of bacteria. The MPN method did yield slightly higher total numbers, but still within the range of statistical variation. It was found that much greater logistical demands occurred with the MPN method to achieve the same accuracy as the VPC method. Also, it
Fig. 8.1  Replicate Plating Technique

Fig. 8.2  Comparisons of Three Media for Ability to Support Growth of Marine Heterotrophic Bacteria

Fig. 8.3  Comparison of Most Probable Number (MPN) and Viable Plate Count (VPC) Methods for Enumerating Marine Heterotrophic Bacteria.
was desirable to have colonies on solid media for other aspects of the project. Therefore, the VPC method using OZR medium was chosen as the standard heterotrophic bacteria enumeration method.

The VPC was used with OZR and HBM media to estimate the relative percentage of hydrocarbon utilizing bacteria in the total heterotrophic population. This method was applied to seawater supplemented with Kuwait Crude oil dispersed with Corexit 9527. The relative percentage of oil degraders with the "total" heterotrophic population increased with time (Figure 8.4).

Biodegradation of a specific organic compound is most accurately measured by determining the rate of disappearance of the compound. When the study involves degradation of multiple substrates or a chemically complex material such as crude oil, the analytical chemistry required for the component loss approach is extremely complex and is drastically reduced in accuracy. The project objectives dictated a rapid, simple system which would provide a reasonable estimate of biodegradation potential. In an aerobic environment, all degradation reactions are associated with oxygen utilization, therefore we utilized a modified Biological Oxygen Demand (BOD) procedure which provided the rate and extent of oxygen depletion by the mixed sea water population on various substrates.

Five tanks were filled with fresh untreated seawater at 140°C. Four tanks were loaded with one percent (weight/volume) of either n-hexadecane, naphthalene, Willimar crude or peptone. The fifth tank served as a control. The tanks were mechanically agitated to disperse the chemicals throughout the water column, then the water distributed into BOD bottles, which were incubated at 14°C. Oxygen levels were determined from duplicate bottles over the time course of the experiment.

The results are presented in Figure 8.5. The control value represents microbial utilization of the indigenous nutrients present in the seawater. These nutrients were exhausted after two days with a total oxygen depletion of 2 mg. The rates of oxygen depletion with the substrates were linear for an initial time period, then decreased in rate for a second time period. The depletion rates are summarized in Table 8.1. Peptone (used to express "total" biodegradation potential) showed the greatest depletion rate and completely utilized all available oxygen by day six. The oxygen depletion rates with Willimar crude oil and naphthalene were the same and it is noticed that the rates were higher than for hexadecane. The breakpoints in the oxygen depletion plots all occur at about 2 mg O₂ per liter and are believed to represent the point of oxygen limitation for the mixed population. In this experiment, mechanically dispersed substrate was introduced into the BOD bottle at extremely high substrate concentrations (10,000 mg/liter) which cannot be compared to in situ conditions but did serve to validate the modified BOD method.
Fig. 8.4 Percentage of Marine Heterotrophic Bacteria Capable of Metabolizing Kuwait Crude Oil Agar Compared with O2R Medium.

Fig. 8.5 Oxygen Depletion Rates of Various Substrates using a Modified BOD Method.
TABLE 8.1 RATE OF SUBSTRATE DEGRADATION, BY OXYGEN DEPLETION

<table>
<thead>
<tr>
<th>Substrate</th>
<th>O₂ mg/liter/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (natural)</td>
<td>1.0</td>
</tr>
<tr>
<td>Peptone</td>
<td>3.5</td>
</tr>
<tr>
<td>Willimar Crude</td>
<td>1.25</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>0.94</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>1.25</td>
</tr>
</tbody>
</table>

The experimental procedure was modified by eliminating mechanical mixing energy except for a gentle agitation of the tanks to simulate wave action. The tanks were filled with seawater and overlayed with API reference South Louisiana crude oil, the dispersant Corexit 9527, and a 10:1 mixture of crude oil and dispersant. Samples were removed from the center of the tanks after 24 hours for BOD measurements. Figure 8.6 shows the oxygen depletion for 24 hour samples from each of the four tanks. There was no oxygen utilization in the control tank, which indicated that the indigenous nutrient had been depleted during the 24 hour incubation prior to sampling the tanks. There was no depletion of oxygen in the South Louisiana crude tank, indicating either an absence of substrate in the water column or the inability of the resident bacterial population to utilize solubilized hydrocarbons. The absence of substrate was indicated from the results in the oil-dispersant tank.

The biodegradable nature of Corexit 9527 was indicated by the oxygen depletion study, in which the oxygen was depleted at a rate of 1 mg O₂/liter/day. The oxygen depletion rate was much greater (4.25 mg/liter/day) with the mixture of crude oil and dispersant. This effect is apparent when considering no water column activity with just the crude oil and the much lower rate for the dispersant alone. The dispersant action would carry oil into the water column in small droplet form, in which it would be more readily available to the bacterial population.

It is interesting to note in these experiments as well as replications and other studies with the oxygen depletion method that the final oxygen level is always about 2 mg of O₂/liter. This would infer that microbial action on oil does not occur below this level of dissolved oxygen.

Conventional laboratory scale experiments have many advantages as they provide well controlled tests conditions and are easily replicated. However, there are certain inherent disadvantages to these small scale systems when operating in either the batch or continuous mode. Microbiologically, wall effects are magnified by the high wall to water ratio, the inability to achieve significant dilution effects or concentration gradients in small volumes of water. The ocean as an environment does not make possible controlled or easily replicated experiments. A compromise meso-scale test system was designed for use in this project with raw seawater.

Experiments were performed to determine the nature and variability of the meso-scale system. Two tanks were filled with seawater from...
FIG. 5.6
OXYGEN DEPLETION RATES OF S. LA CRUDE, COREXIT 9527 AND S. LA.

\[ \text{MgO/liter} \]

TIME IN DAYS

S. La Crude + Corexit 9527
Corexit 9527
S. La Crude
Control
Narragansett Bay and water samples removed from 1.5 meters below the surface on days, 0, 4 and 8 for use as inoculum for oxygen depletion studies. Three series were set up in duplicate to define the capacity of the resident population for utilization of endogenous nutrients (control), petroleum (Kuwait) and "total" heterotrophic potential (peptone). The experiment was repeated three times and a composite of the north and south tank data used to perform a polynomial regression for each substrate and the control. From the regression data, the $R^2$ value was determined and the best fit of the $R^2$ value to either a second or third degree polynomial. This was used to plot the x value, which is time in days against the estimated y value which is the mg of O$_2$/liter at each data point.

The statistical evaluation of the control values (Fig. 8.7) indicates a close correlation for the estimated depletion rates at each of the samples times. This is particularly true of the values for the 0 and 4 day samples. The general trend is for low initial depletion rates of 1.25 and 1.5 mg O$_2$/liter/day, followed by essentially level values, then increased oxygen content in the test values. The data indicates rapid exhaustion of the endogenous nutrients which are normally low in seawater.

The data for Kuwait crude oil (Fig. 8.8) shows a close correlation for all sampling times and a consistent oxygen depletion rate over the entire time course of the test. The initial rate is somewhat higher for the 0 day water than for the other two water samples.

A similar plot for "total" heterotrophic potential (Fig. 8.9) demonstrates the highest oxygen depletion rate of the three test series and an extremely close fit for all samples during the first day of the depletion rate measurement. The shifts in rate after one day reflect nutrient depletion and toxic products as seen in the conventional bacterial growth curve.

A comparison of the oxygen depletion rates with oil and peptone by 0 day water from the north and south tanks (Fig. 8.10) demonstrates the close fit of data from two different test tanks. The rates match those obtained from the composite data for all points on the three experiment statistical study.

The VPC method was also used to establish the reproducibility of the meso-scale system. This first validation was performed with only seawater (no oil or dispersant added) and compared to the VPC values of Narragansett Bay water. Samples were taken from 1.5 foot level and 9.5 foot level in both the north and south tanks. The results (Fig. 8.11) show excellent reproducibility between the two tanks and the bay water counts.

Salinity of the tanks was measured at surface, 1.5, 9.5 and 18 foot level (Fig. 8.12). A rain during the first 24 hours significantly reduced the salinity at the tank surface, but did not affect salinity at the other levels in the tank and had no effect on bacterial numbers (Fig. 8.11).
Fig. 8.7 Oxygen Depletion Rates of Zero, Four and Eight Day Control Tank Samples.

Fig. 8.8 Oxygen Depletion Rates of Zero, Four and Eight Day Kuwait Crude Oil Tank Samples.

Fig. 8.9 Total Heterotrophic Potential of Zero, Four and Eight Day Samples.

Fig. 8.10 Comparison of Oxygen Depletion Rates of Kuwait with Peptone.
Fig. 8.11 Viable Plate Counts Validations of Test Tanks.

Fig. 8.12 Salinity Concentrations in the North Tank During Meso-Scale Experiment 1.
The reliability of viable plate count (VPC) and most probable number (MPN) data from the same test series is shown in Table 8.2 These values represent the numerical average of the same data points for three replicate experiments. There is a close correlation between the MPN and VPC values within a given tank as well as inter-tank values for the same sample times. The differences in values do not exceed one log and in most cases are much closer. As normally found in MPN and VPC, comparisons of bacterial numbers the MPN values are the higher of the two. These results were supported by carefully controlled laboratory experiments Figure 8.2.

### TABLE 8.2 RELIABILITY OF VPC AND MPN DATA FROM MESO-SCALE TANKS

<table>
<thead>
<tr>
<th>Determination</th>
<th>Sample day</th>
<th>North Tank</th>
<th>South Tank</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPN</td>
<td>0</td>
<td>7.0 x 10³*</td>
<td>1.1 x 10⁵</td>
</tr>
<tr>
<td>VPC</td>
<td>0</td>
<td>1.5 x 10⁴</td>
<td>1.7 x 10⁴</td>
</tr>
<tr>
<td>MPN</td>
<td>4</td>
<td>1.6 x 10⁴</td>
<td>1.1 x 10⁴</td>
</tr>
<tr>
<td>VPC</td>
<td>4</td>
<td>1.4 x 10⁴</td>
<td>2.3 x 10⁴</td>
</tr>
<tr>
<td>MPN</td>
<td>8</td>
<td>2.2 x 10⁴</td>
<td>1.3 x 10⁴</td>
</tr>
<tr>
<td>VPC</td>
<td>8</td>
<td>8.6 x 10³</td>
<td>1.9 x 10⁴</td>
</tr>
</tbody>
</table>

*One test only.

The response of the total heterotrophic population to Kuwait crude oil and Kuwait dispersed with Corexit 9527 was tested in the meso-scale system. The north and south tanks each received 15 ppm of Kuwait and 3 ppm of Corexit 9527 was added to the south tank. The surface of both tanks received mixing (glass rod) for five minutes after chemical additions. Both tanks were sampled at 0, 24, 48 and 72 hours from the 1.5, 9.5 and 18 foot sample spigots. Dilutions from the samples were spread plated on to OZR medium and incubated at tank temperature (21°C) for six days.

The VPC data (Fig. 8.13) demonstrated more than one log increase during the first 24 hours in the dispersant treated tank (south tank), a level value between 24 and 48 hours, followed by a decrease in bacterial numbers at 72 hours. In the north tank, which received only Kuwait crude oil, there is an apparent trend for increased bacterial numbers during the 72 hour test period. The change in bacterial number in the north tank is minor compared to the south tank and may not represent bacterial growth but normal variation seen in VPC determinations. There was good correlation between bacterial numbers in the south tank and essentially the same values at all three test levels, suggesting a homogeneous mixture throughout the tank.

The enhanced growth in the dispersed oil tank could reflect metabolism of oil and/or dispersant. Mulkins-Phillips and Steward (11) in their experiments using gas chromatography to follow changes in components found that the dispersants were metabolized in preference to the C₁₇ - C₂₈ fraction of the Arabian crude oil used in their experiments. In contrast, Atlas and Bartha (12) using mineralization as a
Fig. 8.13 VPC Data of Control, Kuwait Crude, and Kuwait Crude and Dispersant in the Meso-Scale Tanks.
measure of biodegradation, showed that dispersants increased the microbial utilization of Sweden crude oil.

The quantitative chemical analyses of the tanks for extractable organics (Exp. 2 Chemistry Section) demonstrated control values of 210 and 243 ppb in the seawater. The extractable organics in the oil tank are elevated only at the one hour samples taken at the top and mid zones of the tank. After one hour they return to or below background level. This would support the interpretation of no bacterial response in this tank. The quantity of extractable organics in the dispersant treated tank is significant at all levels and would provide sufficient substrate for increase in microbial numbers. The limiting factor, however, would be the quantity of nitrogen and phosphate available rather than carbon. The decrease in bacterial numbers between hours 48 and 72 (Fig. 8.13) are not related to carbon limitation which in all zones of the tank are well in excess of 500 ppb.

The qualitative GLC data from the chemical studies indicates loss of components boiling below n-C15 in the dispersant treated tank. The loss of these components may reflect biodegradation or evaporation or a combination of the two phenomenon and would support the observed increase in microbial numbers.

| TABLE 8.3 OXYGEN DEPLETION RATES FROM MESO-SCALE EXPERIMENT 2 |
| OIL AND OIL PLUS COREXIT 9527, mg L⁻¹ |
| DAY | OIL TOP | OIL MID | OIL BOT | OIL AND COREXIT 9527 TOP | OIL AND COREXIT 9527 MID | OIL AND COREXIT 9527 BOT |
| 0   | 1.72    | 2.32    | 1.72    | 1.31    | 1.34    | 1.41    |
| 1   | 0.61    | 1.01    | 4.45    | 0.31    | 1.82    | 3.23    |
| 2   | 0.52    | 1.17    | 1.37    | 0.63    | 0.84    | 0.50    |
| 3   | 0.09    | 0       | -       | 0.76    | 0.04    | 2.09    |

The oxygen depletion data from this experiment (Table 8.3) is highly confusing and apparently is of little value. The results were erratic except for day 0 results which were rather constant. A trend does exist in the dispersant treated tank which suggests increased activity with time at the lower region of the tank.

The third meso-scale experiment contained several modifications. The third tank was in place and used as a control tank containing only seawater. A cooling system was installed which maintained ambient bay temperature ± 2°C. An agitator was installed in the upper 2 feet of the water column and operated eight hours each day. Samples were taken from the 1.5, 9.5 and 18 foot levels at 24 and 48 hours. Samples were plated for both "total" heterotrophic bacteria (THB) and total number hydrocarbonlastic bacteria (HYB) (Figures 8.14 and 8.15).

The THB counts (Figure 8.14) of bay water were constant over the two days of the experiment. The values in the 1.5 foot zone of the control
Fig. 8.14 Meso-Scale Experiment 3, Measured Heterotrophic Bacterial Growth.

Fig. 8.15 Meso-Scale Experiment 3, Growth of Marine Hydrocarbon Degrading Bacteria.
tank were also constant but somewhat lower than the bay counts. There are apparent increases in THB of the oil plus dispersant tank which peaked at 24 hours at the top zone and 48 hours in the mid zone. However, the number of total heterotrophic bacteria in the bottom zone decayed over the course of 48 hours.

Although the actual number were somewhat less the trends for HYB were about the same as the THB counts. There was more stability in the top and mid zone counts which showed no significant change in HYB.

There appears to be a relationship between the number of hydrocarbon utilizing bacteria (HYB) and extractable organics in the water column. In the top and mid zones there are increased HYB present in the water column following the appearance of oil in a particular zone of the tank. For example, in the top zone hour 1 samples (chemistry data experiment 3) the oil concentration increased from about 450 ppb to nearly 2000 ppb between hours 1 and 24, and the HYB population also increased during this period. In the bottom zone the oil concentration never reached 900 ppb and there was no change in the HYB population. It might be inferred from this data that a critical oil concentration in the water is necessary for selection of hydrocarbon utilizing bacteria. Unfortunately, we cannot make the same comparison from the second experiment because we measured only THB.

Oxygen depletion measurements (Figures 8.16-8.23) essentially confirm the plate count and chemistry data. The initial biological activity was highest in the top zone of the oil-dispersant tank, somewhat decreased after 24 hours and had returned to baseline (control tank), rates by 48 hours. There is evidence of very little biological activity in the tank dosed with Kuwait crude oil. The bottom samples demonstrated no significant biological activity in the 0 and day 1 samples of either the oil or oil-dispersant tank. There is measurable activity in the oil-dispersant tank samples on days 2 and 3.

It was apparent from these two experiments that dispersed oil does induce slight increases in the total heterotrophic bacterial population (THB) and the hydrocarbanoclastic bacterial population (HYB). These effects were not as apparent as the results of the laboratory experiments of other investigators (11,12) in which the system was supplemented by the addition of nitrogen and phosphorus which are nutrient limiting in seawater.

Experiments were designed to determine the effects of oil and dispersant on bacterial population dynamics. These were small tank experiments under controlled laboratory conditions at 4°C with sediment and seawater collected from Narragansett Bay. All tanks were gently shaken at 45 rpm and aerated to insure sufficient oxygen for maintenance of biological activity. The test series were: control seawater-sediment; Kuwait crude oil 15 ppm (v/v); Kuwait crude oil 15 ppm (v/v) plus 3 ppm (v/v) of Corexit 9527; and Corexit 9527 3 ppm (v/v). Samples were taken from the surface of the tanks (film area), mid water column and the sediments. Each sample was diluted and plated in duplicate onto OZR medium to express the heterotrophic bacterial population. Countable plates (30-300 colonies) were selected from each sample source to serve as
Fig. 8.16 Oxygen Depletion by Kuwait (North Tank) and Kuwait plus Corexit 9527 - Zero-Day Sample.

Fig. 8.17 Oxygen Depletion by Kuwait (North Tank) and Kuwait Plus Corexit 9527, One Day Sample. Top Level.

Fig. 8.18 Oxygen depletion by Kuwait (North Tank) and Kuwait Plus Corexit 9527 - Two Day Sample. Top Level.

Fig. 8.19 Oxygen Depletion by Kuwait (North Tank) Corexit 9527 - Three Day Sample. Bottom Level.
Fig. 8.20 Oxygen Depletion by Kuwait (North Tank) and Kuwait Plus Corexit 9527 - Zero Day Sample. Bottom Level.

Fig. 8.21 Oxygen Depletion by Kuwait (North Tank) and Kuwait Plus Corexit - 9527 One Day Sample. Bottom Level.

Fig. 8.22 Oxygen Depletion by Kuwait (North Tank) and Kuwait Plus Corexit - 9527 Two Day Sample. Bottom Level.

Fig. 8.23 Oxygen Depletion by Kuwait (North Tank) and Kuwait Plus Corexit - 9527 Three Day Sample. Bottom Level.
master plates for replication. The master plates were replicated to n-hexadecane, napthalene, Kuwait and basal agars. All replicate and master plates were photographed in color for examination of colony types and verification of visual comparison made prior to photography.

The water column series included a Kuwait crude oil MPN series and duplicate sets of OZR plates incubated at 40°C and 130°C. The temperature differential test was performed to see if the system contained a mixture of psychrophilic and mesophilic bacteria which has been demonstrated to occur in Narragansett Bay (13,14).

The VPC data for the surface films, sediment and water column at 13 and 40°C are shown in Figures 8.24 a-d. There was an increase in bacterial numbers of the surface film between day 1 and 2 in all four tanks. The least increase was in the oil tank which of course has an oil film at the air-water interface. The oil film was expected to destroy the function of the interface microlayer which typically shows considerable enrichment of bacteria and bacterial nutrients as compared to the water column. Indeed these increases in bacterial numbers could be interpreted as the forming of the microlayer rather than growth of bacteria. This hypothesis is supported by the organism increase in the control tank. The population size in all the surface samples does remain essentially constant through the 21 day experiment.

There are greater fluctuations in the sediment VPC data in all tanks. A general trend is apparent for an increase in the sediment bacterial population through day nine in the control, dispersant and oil-dispersant tanks. There is less of a trend for sediment enrichment in the oil tank. After day nine sediment numbers decline in the control and dispersant tanks but remain stable in the oil and oil-dispersant tanks.

The water column studies at 4 and 130°C are interesting in that they demonstrate evidence for two different populations, each with somewhat different dynamics. The initial 130°C population is larger than the 40°C population in the water column. There is a slight positive trend for the 130°C population through day 14 then a significant decline except in the control tank. On the other hand, the initial 40°C population is low in all tanks but rapidly increases by day three and then more slowly through day seven in all tanks. This is followed by a significant population decline, except in the control tank, through day 14.

The numbers of HYB in the water column were determined by the VPC and MPN methods (Figure 8.25). As normally found in comparison of the two methods, the MPN values are higher than VPC values. This is partially explained by the fact that the two methods select for different heterotrophic populations (15).

In all the tanks using both the hydrocarbanoclastic MPN and VPC methods, there was a rapid increase in the number of HYB in all tanks until about day 7 after which the numbers declined to initial numbers found in the various tanks. The decline is less rapid by the MPN method but probably would have returned to baseline by days 18-20. We believe the decline is related to exhaustion of the N, P and Fe content of this closed system.
8.24 A Surface Samples

8.24 B Sediment Samples

8.24 C Water Column Samples at 13°C Incubation Temperature

8.24 D Water Column Samples at 40°C Incubation Temperature

Fig. 8.24 Laboratory Experiment, Viable Plate Counts on OZR Medium from Surface (A), sediment (B), and water column samples (C). Water column samples were incubated at 13°C and 4°C (D). Samples were taken from four aquaria with Narragansett Bay water plus: (1) control, (2) Kuwait crude oil 15 ppm (v/v), (3) Kuwait crude oil 15 ppm (v/v) plus 3 ppm (v/v) of dispersant Corexit 9527, and (4) Corexit 9527 3 ppm (v/v)
It should be pointed out that this system received mechanical agitation which provides a rather uniform distribution of material throughout the water column as compared to the meso-scale tanks. Also the ambient temperature of the bay water and sediment used in this experiment was 1°C so that the 4°C incubations more nearly track bay conditions. It is significant that a sizeable population can be obtained at 13°C incubation.

The diversity of the heterotrophic bacterial population was tabulated by counting the number of each type of colony on each of the OZR master plates from the surface film, water column and sediment samples. Colony morphology types and descriptions are given in Appendix I. The data indicate that the colony diversity decreased during the course of the experiment, with 2 or 3 colony types becoming predominant over the 21 day time frame of this experiment. The decrease in colony diversity occurred to a greater extent in the water column and surface film than in sediments.

In order to simplify the expression of colony diversity two methods were employed in analyzing the data from Appendix 2. In Fig. 8.26 colony diversity was expressed as the change in the number of colony types occurring on OZR master plates over time. The data depicts the decline in the number of colony types with time in the aquarium system. The other method of simplifying the expression of colony diversity was to quantify the degree of dominance within the total heterotrophic population of each OZR master plate.

Dominance was quantified by the equation \( c = \left( \frac{n_i}{N} \right)^2 \) where \( c \) the dominance factor is equal to the square of the ratio \( n_i \) the number of colonies of each colony type divided by \( N \) the number of colony types (100). The larger the value of \( c \) the greater is the predominance of bacterial species within the given population. The results are given in Fig. 8.27. The relationship between Fig. 8.26, the degree of dominance, and Fig. 8.24, the change in total heterotrophic bacterial numbers, suggests that the increase in bacterial numbers in all four aquaria was accomplished by a few bacterial species that predominated in the stressed environment of the aquaria system.

The degree of change in the heterotrophic bacterial population demonstrated a similar trend in all four aquaria. The data indicates that the aquaria system used was responsible for the changes in the bacterial populations and that the system used exerted a greater stress on the heterotrophic population than did the Kuwait crude oil and/or Corexit 9527. These findings are in concurrence with results published by Kaster and Van Auken (75). Kaster and Van Auken examined bacterial populations from the surface waters of the Gulf of Mexico over an eight week period. In their experiment South Louisiana Crude oil (0.5%) was added to one flask system and another flask served as a control. Over the eight week period there was an increase in bacterial numbers but a decrease in the bacterial diversity in both flasks. No significant difference in the heterotrophic bacterial population was detectable between the oiled flask and the control flask.

The replica plating data in Appendix 2 was incorporated with the data on the diversity of the heterotrophic bacterial population because the
(MPN) with Kuwait crude medium incubated at 4°C were processed from water column samples. Four aquaria with Narragansett Bay water plus: (1) control, (2) Kuwait crude oil 15 ppm (v/v), (3) Covaris 8527, 3 ppm (v/v), and (4) Covaris 8527 3ppm (v/v). (MPN data points one day seven for the control and oil tanks were 6.6, meaning the real value is greater than 5.8 but of an unknown amount.)

Fig. 8.26 Colony Diversity Expressed as Number of Colony Types over Time

Fig. 8.27 Colony Diversity Expressed at Quantification of Dominance

Fig. 8.26 and 8.27. Colony diversity of heterotrophic bacterial population on OER master plates from surface, water column, and sediment samples. Narragansett Bay water plus: (1) control, (2) Kuwait crude oil 15 ppm (v/v), (3) Kuwait crude oil 15 ppm (v/v) + 3 ppm (v/v) of the dispersant Covaris 8527, and (4) Covaris 8527 3ppm (v/v). The heterotrophic diversity is expressed as: (1) the total number of colony types on OER master plates and (2) by the degree of dominance given by \( C = \ln(n_{q}/N) \), where \( n_{q} \) equals the number of colonies of each colony type and \( N \) equals the total number of colony types.
oil degrading bacteria grew on both the OZR master plates and the hydrocarbon replica plates. The data suggests that no enrichment for hydrocarbon degraders occurred in the aquarium system as was originally anticipated. Table 8.4 exemplifies the data on the presence of hydrocarbon degraders during the time of the laboratory experiment. In Table 8.4 the number and type of hydrocarbon degraders are given from the Kuwait crude aquarium. The data exemplifies the low numbers and random nature of the presence of oil degraders in the aquarium system. The lack of enrichment may have been due in part to the stress of the aquarium system as mentioned previously and the cold temperature (4°C) of the seawater. The hydrocarbon metabolizing bacterial isolates usually metabolized only one of the hydrocarbon substrates with only a few being able to metabolize two or three substrates. The lack of predominance by any bacterial hydrocarbon utilizing species, as determined by colony diversity suggests that the different fractions of the Kuwait crude were simultaneously metabolized. Simultaneous metabolism is further substantiated by the even distribution of bacterial colonies growing on the different hydrocarbon substrates. Zobell (145) suggested that simultaneous metabolism of oil would occur under low substrate conditions. The aquarium system with 15 ppm (v/v) of Kuwait crude oil at 4°C would have very little oil in the water column due to the low solubility of Kuwait crude at this low temperature. The dispersant was probably inefficient in dispersing the oil in the aquarium system because of the low volumes applied, the difficulties of properly applying the small volume of dispersant, and because the oil often became stuck to the sides of the aquarium and the glassware making it unavailable for mixing with the seawater and dispersant.

Table 8.4 Hydrocarbon utilizers in heterotrophic bacterial population as determined by replica plating. Samples were taken from the Kuwait crude aquarium in the laboratory experiment. Colony types are given in Appendix 1.

<table>
<thead>
<tr>
<th>Day</th>
<th>Kuwait Crude</th>
<th>Hexadecane</th>
<th>Naphthalene</th>
<th>Total</th>
</tr>
</thead>
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<td></td>
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<td>Colony type</td>
<td>Colony type</td>
<td>#</td>
</tr>
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<td>15</td>
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<tr>
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</tr>
<tr>
<td>18</td>
<td>19</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>21</td>
<td>19</td>
<td>3</td>
<td>15</td>
<td>2</td>
</tr>
</tbody>
</table>

A long term experiment was designed to develop an approach for conversion to a flow-thru test system. The test system utilized four 55
gallon microcosms structured as diagrammed in Figure 8.28. Fresh sea-
water from the Jerusalem station, where the tests were performed, was
introduced to the microcosms via a jet system which established a cir-
cular subsurface flow pattern in the top portion of the microcosms. The
water was removed from the bottom zone so that flow was from the top
reaction zone to the tank bottom where the test scallops were located.
these systems all contained a sediment base obtained from the water adja-
cent to the Jerusalem test facility.

The Data Input-Output of this experiment is summarized in Table 8.5.

Table 8.5 Data Input-Output, Jerusalem Flow-Thru System,
5/7/79 - 7/2/79

<table>
<thead>
<tr>
<th>Control</th>
<th>Oil Dispersant</th>
<th>Oil-Dispersant</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMB</td>
<td>TMB</td>
<td>TMB</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>INPUT</th>
<th>Output</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. THB plate counts</td>
<td>no ml⁻¹</td>
</tr>
<tr>
<td>2. HYB plate counts</td>
<td>no ml⁻¹</td>
</tr>
<tr>
<td>3. Total Hydrocarbons</td>
<td>ppb</td>
</tr>
<tr>
<td>4. Hexadecane mineralization</td>
<td>ng hr⁻¹</td>
</tr>
<tr>
<td>5. Hexadecane Turnover Time</td>
<td>weeks</td>
</tr>
<tr>
<td>6. Naphthalene mineralization</td>
<td>ng hr⁻¹</td>
</tr>
<tr>
<td>7. Naphthalene Turnover Time</td>
<td>weeks</td>
</tr>
<tr>
<td>8. Hydrocarbon Degradation Time</td>
<td>hours</td>
</tr>
<tr>
<td>9. Temperature</td>
<td>°C</td>
</tr>
<tr>
<td>10. Salinity</td>
<td>ppt</td>
</tr>
<tr>
<td>11. Phosphate</td>
<td>ug ml⁻¹</td>
</tr>
<tr>
<td>12. Ammonia</td>
<td>uM</td>
</tr>
<tr>
<td>13. GLC</td>
<td>Recorder plot</td>
</tr>
<tr>
<td>14. Scallop Mortality</td>
<td>No. dead</td>
</tr>
<tr>
<td>15. Scallop Behavior Responses</td>
<td>No. Swimming Claps</td>
</tr>
</tbody>
</table>

The data collected in the experiment is presented in computer entry
format (Table 8.6). This data was analyzed by multiple regression and
other techniques.

Multiple step-wise regression analysis of the data on this long term
(5/7/79 - 6/25/80) experiment indicated no significant correlations
between a number of the experimental parameters. A 0.5000 significance
level was established for entry into the model.

There were no significant correlations between total hydrocarbon con-
centration and day of sampling or samples from top, middle or bottom por-
tions of the flow-thru tanks. The tank temperatures increased from a low
of 10.6°C to a high of 18.7°C over the course of the 50 day experi-
ment but showed us correlation to total heterotrophic bacteria, total
hydrocarbonoclastic bacteria, or hydrocarbon mineralization rates. A
positive correlation was not found between total hydrocarbon concentra-
tion in the water column and either hexadecane or naphthalene mineraliza-
tion rates. There was, however, a negative relationship when mean values
(Table 8.7) were examined indicating inhibition of mineralization rates
Table B.6. Data from Jerusalem Flow - Thru System, 5/7/79 - 7/2/79, Computer Format

<table>
<thead>
<tr>
<th>Date</th>
<th>Tank Loc.</th>
<th>THB₂ x 10⁶</th>
<th>HYB₁ x 10²</th>
<th>Hexadec Mineralization T/f C-16</th>
<th>T/f C-16</th>
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<td>6.1</td>
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<td>66.6</td>
<td>17.16</td>
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<td>2.2</td>
<td>3.3</td>
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<td>10.1</td>
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<tr>
<td>5/14/79 (6)</td>
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<td>5.4</td>
<td>3.8</td>
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<td>1.6</td>
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<td>6.0</td>
</tr>
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</table>

**a:** 1 = top; 2 = mid; 3 = bottom; **b:** control; **c:** oil; **d:** dispersant; **e:** oil-dispersant

This sequence is used for all following data entries.

### Naphthalene Mineralization

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### PO₄

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</tr>
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<td>0.3</td>
</tr>
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<td>0.3</td>
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<tr>
<td>6/14/79</td>
<td>0.3</td>
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<td>7/2/79</td>
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</tr>
</tbody>
</table>

### NH₄⁺

<table>
<thead>
<tr>
<th>Date</th>
<th>NH₄⁺ μM</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.3</td>
</tr>
<tr>
<td>5/14/79</td>
<td>0.3</td>
</tr>
<tr>
<td>5/29/79</td>
<td>0.3</td>
</tr>
<tr>
<td>6/14/79</td>
<td>0.3</td>
</tr>
<tr>
<td>7/2/79</td>
<td>0.3</td>
</tr>
</tbody>
</table>
Table 8.7 Mean Values from the Jerusalem Flow Thru Tests

<table>
<thead>
<tr>
<th>Tank</th>
<th>Hexadec*</th>
<th>Hexadec*</th>
<th>Naph*</th>
<th>Naph*</th>
<th>Total Hydrocar</th>
<th>Total Hydrocarbon</th>
<th>D/f, hrs.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Meters</td>
<td>Hydrocarb</td>
<td>(ng/</td>
<td>(ng/</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>x 10^3</td>
<td></td>
<td>wk</td>
<td>wk</td>
<td>ppm</td>
<td>ppm</td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>5.3</td>
<td>2.8</td>
<td>11.99</td>
<td>373</td>
<td>19.58</td>
<td>205</td>
<td>107</td>
</tr>
<tr>
<td>Oil</td>
<td>6.2</td>
<td>4.1</td>
<td>10.25</td>
<td>342</td>
<td>8.34</td>
<td>253</td>
<td>279</td>
</tr>
<tr>
<td>Dispersant</td>
<td>3.5</td>
<td>2.5</td>
<td>9.84</td>
<td>275</td>
<td>16.72</td>
<td>261</td>
<td>1534</td>
</tr>
<tr>
<td>Oil and Dispersant</td>
<td>6.2</td>
<td>6.3</td>
<td>8.62</td>
<td>344</td>
<td>11.09</td>
<td>193</td>
<td>475</td>
</tr>
</tbody>
</table>

*Tested against wmg substrate

---

Figure 8.28 Test System for 55 Gallon Microcosm Flow Thru Experiment
in the presence of higher concentrations of hydrocarbon or dispersant. This observation cannot be explained with the existing data.

There was a significant correlation between the number of total heterotrophic and total hydrocarbanoclastic bacteria in the various test tanks. The numbers of hydrocarbanoclastic bacteria were always lower than total heterotrophic bacteria, but approach unity in the oil and dispersant treated tanks (1.3) and are further from unity in the seawater control tank (1.8). These data do indicate selection for hydrocarbanoclastic bacteria in tanks containing oil and/or dispersant.

There was a decrease in hydrocarbon turnover time in the oil and/or dispersant tanks which is most apparent for turn over of aliphatic hydrocarbons whereas the effect is less apparent for aromatic hydrocarbons. Generally, however, aromatic hydrocarbons are mineralized more effectively than the aliphatic constituents. It must be noted, however, that the aromatic hydrocarbons turned over in this series represent lower molecular material than the turned over aliphatic material that was turned over.

Since the actual mineralization rates show little variation the degradation time in a particular situation becomes primarily a function of hydrocarbon concentration. It now becomes apparent that degradation potential is a fairly constant value in the marine environment. The changes in temperature, salinity phosphate and ammonia nitrogen are more apparent than real. For example, the highest phosphate and ammonia values are limiting for the amount of carbon in the environment and hence do not manifest a measurable effect upon the test parameters. The temperature span was only 8.1°C which is significantly below the 10°C span for a Q10 value of 2 normally expected. However, it has been shown previously (Traxler and Cundell, 1975) that the Q10 values for hydrocarbon utilization in marine systems vary between 1.3 and 1.8. Therefore with the 8.1°C span we would not expect to measure a significant temperature effect. Salinity changes were not significant for bacterial activity.

Four meso-scale tank experiments were performed in May, June and July 1980 to compare two dispersants, Corexit 9527 and BP 1100WD. In experiment 1 (5/19 - 5/23) the two test tanks (N and S) were dosed with 120 ml of Kuwait crude oil and 6 ml of Corexit 9527. The oil and dispersant were premixed at the test site and applied to the top of the water column. The agitators were run for an 8 hour on, 16 hour off cycle for the 5 day test period. Experiments 2, 3 and 4 were conducted as a direct comparison of the two dispersants. The north tank contained 120 ml of Kuwait crude oil plus 6 ml of Corexit 9527 while the south tank was dosed with 120 ml of Kuwait crude oil and 6 ml of BP 1100WD. Water samples were collected from the top port located in the mixing zone and from the outlet port for bottom samples.

Hydrocarbon analyses were performed using a quantitative gas chromatography method (Butler and Levy, 1978) which involved 12 hour continuous liquid-liquid extraction of the samples with n-pentane followed by a 12 hour extraction with benzene. These extracts were desulfured by passing through copper shavings, concentrated by flash evaporation and placed on a silica gel over alumina column. The alkanes were eluted with n-pentane
and the aromatics with benzene. Both fractions were concentrated to 0.5 ml and 2 ul injected onto the proper column with a predetermined temperature program for chromatography. Samples were spiked with a known quantity of pristane and anthracene prior to extraction (internal standards) and all determinations were computer integrated against the internal standards. External standards were determined using the same quantity of pristane and anthracene for calculation of extraction efficiency. This method provided the concentration of total aliphatics in ppb and total aromatics in ppb. Addition of these two values provided total hydrocarbon in ppb.

Quantitative gas chromatography was used to determine the total peak area of Corexit 9527 in the water stock solutions used in the scallop experiments presented in Section 9 of this report. This value was then converted to mg l-1 as oil and subtracted from the integrated total hydrocarbon in the oil dispersant mixture. The results of these quantitative determinations are shown in Table 8.8. These results show ratios of oil to dispersant identical to those determined by the infra-red method (Table 4.5.4 this report).

Microbiological activity was measured in the mixing zone of all tanks and degradative activity determined as mineralization rate for total hydrocarbon using hexadecane, naphthalene and benzo (a) pyrene as representative hydrocarbons. These were used to spike 50 ul of Kuwait crude oil in their ratio present in the oil (1.0:0.5:0.1). The challenge was against the test tank microflora in 3 hour determinations.

The quantitative data for hydrocarbon concentration in the meso-scale tanks are summarized in Tables 8.9-8.12. The amount of oil in the untreated seawater ranged from 103-121 ppb except for one determination thought to be contaminated in the laboratory extraction process. Dispersant carried considerable oil into the water at the mixing zone during day one. Elevated levels of oil remained in the mixing zone during the course of all experiments. The values varied from experiment to experiment but generally were found to be in thousands of ppb. The ratio of aliphatic to aromatic hydrocarbon also varied in the various samples and different experiments.

In these experiments, there was little oil carried to the bottom of the test tanks, the values being 2 to 3 times the control water values but manyfold less than the mixing zone values. These experiments confirm earlier data which suggest essentially the same phenomenon of dilution through the water column. Both dispersants (Corexit and BP) respond alike in the entrainment of oil in the mixing zone and dilution through the water column. The toxicity tests to scallops are discussed in the biology section and indicate no effect at these measured concentrations of oil. The scallops from the control tank were combined and extracted as a unit then analyzed for hydrocarbon content. The composite of the test scallops were also analyzed in the same fashion.

The result of oil analyses on the scallops (Table 8.9-8.12) show identical low values (6ppb) in experiment 1, slightly elevated levels in the BP 11000W treated scallops in experiment 2 and 3 but still well below anticipated toxicity values. These animals were exposed to oil levels well above those detected in the animals. The data suggests that the scallops do not accumulate oil.
Table 8.8 Hydrocarbon Concentration in Behavioral
Test Stock Solutions

<table>
<thead>
<tr>
<th>Stock Solution</th>
<th>Hydrocarbon mg/Liter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aromatic</td>
</tr>
<tr>
<td>Kuwait Crude Oil</td>
<td>26.34</td>
</tr>
<tr>
<td>Corexit 9527</td>
<td>19.54</td>
</tr>
<tr>
<td>Kuwait Crude Oil Plus Corexit 9527</td>
<td>39.14</td>
</tr>
<tr>
<td>Oil in Mixture</td>
<td>19.60</td>
</tr>
</tbody>
</table>

Table 8.9 Experiment 1:
Hydrocarbon Content of Water and Scallop Samples

<table>
<thead>
<tr>
<th>Date</th>
<th>Tank</th>
<th>ppb Aliphatic</th>
<th>ppb Aromatic</th>
<th>ppb Hydrocarbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>5/19</td>
<td>ST</td>
<td>269</td>
<td>340</td>
<td>609</td>
</tr>
<tr>
<td></td>
<td>SB</td>
<td>27</td>
<td>180</td>
<td>207</td>
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<tr>
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<td>-</td>
</tr>
<tr>
<td></td>
<td>SB</td>
<td>173</td>
<td>148</td>
<td>321</td>
</tr>
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<td>5/22</td>
<td>ST</td>
<td>1647</td>
<td>126</td>
<td>1773</td>
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<tr>
<td></td>
<td>SB</td>
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<td>-</td>
<td>-</td>
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<td>5/19</td>
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<td>lost</td>
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<td>533</td>
<td>1166</td>
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<td>NB</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>GC Abort</td>
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<td>-</td>
<td>-</td>
</tr>
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<td>5/19</td>
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<td>52</td>
<td>116</td>
</tr>
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<td>5</td>
<td>6</td>
</tr>
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<td>4</td>
<td>6</td>
</tr>
<tr>
<td>5/23</td>
<td>Test Scallops</td>
<td>4</td>
<td>2</td>
<td>6</td>
</tr>
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</table>

N and 5 tanks were dosed with 120 ml oil and 6 ml Corexit 9527 (1:20) premixed. Agitator used. Extraction efficiency 91%.
### Table 8.10
Experiment 2. Hydrocarbon Content of Water and Scallop Samples

<table>
<thead>
<tr>
<th>Date</th>
<th>Tank</th>
<th>ppb Aliphatic</th>
<th>ppb Aromatic</th>
<th>ppb Hydrocarbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/3</td>
<td>ST</td>
<td>280</td>
<td>560</td>
<td>840</td>
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<td></td>
<td>NT</td>
<td>4,500</td>
<td>1,760</td>
<td>6,260</td>
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<tr>
<td></td>
<td>CT</td>
<td>10</td>
<td>93</td>
<td>103</td>
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<td>13,000</td>
<td>2,300</td>
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<td>760</td>
<td>9,800</td>
</tr>
<tr>
<td></td>
<td>CT</td>
<td>460</td>
<td>88</td>
<td>548</td>
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<td>19</td>
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<tr>
<td></td>
<td>N Scallops</td>
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<td>14</td>
<td>16</td>
</tr>
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</table>

N Tank dosed 120 ml oil and 6 ml Corexit 9527
S Tank dosed 120 ml oil and 6 ml BP 1100 WD
Oil and dispersants premixed. Agitator used. Extraction efficiency 96%.
Table 8.11
Experiment 3: Hydrocarbon Content of Water and Scallop Samples

<table>
<thead>
<tr>
<th>DATE</th>
<th>Tank</th>
<th>ppb Aliphatic</th>
<th>ppb Aromatic</th>
<th>ppb Hydrocarbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/16</td>
<td>ST</td>
<td>180</td>
<td>1480</td>
<td>1660</td>
</tr>
<tr>
<td></td>
<td>NT</td>
<td>60</td>
<td>2840</td>
<td>2900</td>
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<td>NB</td>
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<td>21</td>
<td>27</td>
</tr>
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<td>NT</td>
<td>180</td>
<td>399</td>
<td>579</td>
</tr>
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<td>6/18</td>
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<td>50</td>
<td>56</td>
</tr>
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<td>4540</td>
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<td>40</td>
<td>1000</td>
<td>1040</td>
</tr>
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<td></td>
<td>NT</td>
<td>180</td>
<td>500</td>
<td>680</td>
</tr>
<tr>
<td></td>
<td>CB</td>
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<td>113</td>
<td>121</td>
</tr>
<tr>
<td>6/19 Scallops Con</td>
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<td>89</td>
<td>97</td>
</tr>
<tr>
<td>Scallops N</td>
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<td>9</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>Scallops S</td>
<td></td>
<td>4</td>
<td>82</td>
<td>86</td>
</tr>
</tbody>
</table>

N tank dosed 120 ml Kuwait and 6 ml Corexit 9527. S tank dosed 120 ml Kuwait and 6 ml BP 1100 WD.

Table 8.12
Experiment 4: Hydrocarbon Content of Water and Scallop Samples

<table>
<thead>
<tr>
<th>Date</th>
<th>Tank</th>
<th>ppb Aliphatic</th>
<th>ppb Aromatic</th>
<th>ppb Hydrocarbon</th>
</tr>
</thead>
<tbody>
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<td>140</td>
<td>400</td>
<td>540</td>
</tr>
<tr>
<td></td>
<td>NT</td>
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<td>700</td>
</tr>
<tr>
<td></td>
<td>NB</td>
<td>8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7/8</td>
<td>ST</td>
<td>60</td>
<td>640</td>
<td>700</td>
</tr>
<tr>
<td></td>
<td>NT</td>
<td>40</td>
<td>1680</td>
<td>1720</td>
</tr>
<tr>
<td></td>
<td>CT</td>
<td>60</td>
<td>640</td>
<td>700</td>
</tr>
<tr>
<td>7/9</td>
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<td>20</td>
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<td>-</td>
</tr>
<tr>
<td></td>
<td>NT</td>
<td>40</td>
<td>20</td>
<td>60</td>
</tr>
<tr>
<td>7/11</td>
<td>ST</td>
<td>60</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
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<td>104</td>
<td>105</td>
</tr>
<tr>
<td>Scallops S</td>
<td></td>
<td>-</td>
<td>78</td>
<td>-</td>
</tr>
<tr>
<td>Scallops Cont</td>
<td></td>
<td>88</td>
<td>28</td>
<td>116</td>
</tr>
</tbody>
</table>

N Tank dosed 120 ml Kuwait and 6 ml Corexit 9527.
S Tank dosed 120 ml Kuwait and 6 ml BP 1100 WD.
The biodegradation data is summarized in Table 8.13. Calculation of turnover time was based on recovered radioactivity and is expressed as $T/f\cdot R$ in hours. In these experiments, we measured not only mineralization but also the hydrocarbon converted to low molecular weight water soluble products and alcohol soluble products. This is a more accurate measurement of degradative potential than mineralization alone. We challenged the microbial populations with a constant quantity of substrate oil (50 $\mu l$) which eliminates the tank variable of oil concentration and allows full expression of the potential. The organisms in the control tank yield constant $T/f\cdot R$ values of approximately 7 hours. This is the time required to completely turnover a standard amount (55.8 ng) of the challenge $^{14}C$ hydrocarbon mixture. This factor is therefore a measure of biological activity against a fixed amount of substrate and can be used to estimate the degradation potential or time required to degrade the amount of oil in the sample. We find by inspection of the data that there is not much variation in the oil concentrations in the different samples.

The results obtained in this study indicate that the introduction of oil or dispersed oil into seawater does not invoke a significant change in the size of the heterotrophic bacterial population in seawater. There is a change in the percentage of hydrocarbonoclastic bacteria within the heterotrophic population indicative of a natural selection for organisms able to metabolize hydrocarbon components. This modified population does have a slightly greater potential for hydrocarbon utilization, but in terms of the vastly increased hydrocarbon content, little overall enhanced significance in relation to degradation time. The reason for this limited microbial response to oil in the water column is, of course, the nutrient limited nature of seawater in terms of its nitrogen, phosphorus and iron content. Active cell growth and maximum rates of nutrient turnover (hydrocarbon in this case) will not occur in a nutrient limited system. This study has demonstrated that the modest increase in the size of the hydrocarbonoclastic bacterial population, as a result of oil entrainment in the water column, does not have a profound effect on degradation potential.

An explanation for the above observations is the recently proposed hypothesis for bacterial dormancy in aquatic systems (Stevenson, 1978). It is proposed that dormancy is an important physiological adaptation for the survival of bacterial suspended in the water column and for this case, is termed exogenous dormancy in which development is delayed due to some unfavorable chemical or physical condition of the environment. The "dormant cells" are generally small and ovoid as demonstrated by Anderson and Heffernan (165) and Wright (1973) and functionally turned-off. This need not imply no activity but a state below maximum potential in a satisfactory environment. It appears that this phenomenon could function in the water column to a greater extent than in sediments or the microlayer where nutrient enrichment occurs.

An obvious approach to increased degradation potential is nutrient supplementation. Oleophilic nitrogen, phosphorus and iron supplements have been proposed to stimulate bacterial growth in marine water column populations. A tank experiment was performed to test the response of bacterial populations to supplemented vs. non-supplemented Kuwait-Corexit mixtures in seawater. The results are summarized in Table 8.14. The bacterial population size deteriorated with time in the seawater control
<table>
<thead>
<tr>
<th>Test Tank</th>
<th>Test Time Hrs.</th>
<th>T/f R (Hrs)</th>
<th>Total Hydrocarbon (ppb)</th>
<th>Degradation Potential (Hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control Seawater</td>
<td>24</td>
<td>6.93</td>
<td>116</td>
<td>14.4</td>
</tr>
<tr>
<td>Kuwait and Corexit</td>
<td>24</td>
<td>16.66</td>
<td>1024</td>
<td>305</td>
</tr>
<tr>
<td>Control Seawater</td>
<td>72</td>
<td>7.22</td>
<td>116</td>
<td>15</td>
</tr>
<tr>
<td>Kuwait and Corexit 9277</td>
<td>72</td>
<td>7.84</td>
<td>1773</td>
<td>269</td>
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</tbody>
</table>

**Experiment 2**

<table>
<thead>
<tr>
<th>Test Tank</th>
<th>Test Time Hrs.</th>
<th>T/f R (Hrs)</th>
<th>Total Hydrocarbon (ppb)</th>
<th>Degradation Potential (Hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control Seawater</td>
<td>48</td>
<td>6.93</td>
<td>103</td>
<td>12.6</td>
</tr>
<tr>
<td>Kuwait and BP 1100 WO</td>
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<td>22.09</td>
<td>15,300</td>
<td>6276</td>
</tr>
<tr>
<td>Kuwait and Corexit 9277</td>
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<td>6.17</td>
<td>9800</td>
<td>1063</td>
</tr>
<tr>
<td>Kuwait and BP 1100 WO</td>
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<td>274.7</td>
<td>2216</td>
<td>10,906</td>
</tr>
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**Experiment 3**

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<th>Test Tank</th>
<th>Test Time Hrs.</th>
<th>T/f R (Hrs)</th>
<th>Total Hydrocarbon (ppb)</th>
<th>Degradation Potential (Hrs)</th>
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<td>48</td>
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**Experiment 4**

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<th>Test Tank</th>
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<th>T/f R (Hrs)</th>
<th>Total Hydrocarbon (ppb)</th>
<th>Degradation Potential (Hrs)</th>
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<td>13.72</td>
<td>60</td>
<td>14.8</td>
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<tr>
<td>Kuwait + BP</td>
<td>120</td>
<td>13.42</td>
<td>80</td>
<td>19.2</td>
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*T/f.R determined for a total of 55.8 ppb of lac-hydrocarbons.

---

**Table 8.14: Heterotrophic Bacteria in Nutrient vs. Non-Nutrient Supplemented Tanks**

<table>
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<tr>
<th>Time (Hrs)</th>
<th>Seawater Control</th>
<th>Unsupplemented Kuwait &amp; Corexit</th>
<th>'N &amp; P' Supplemented Kuwait &amp; Corexit</th>
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<tr>
<td>0</td>
<td>$1.3 \times 10^5$</td>
<td>$1.1 \times 10^6$</td>
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<tr>
<td>24</td>
<td>$2.7 \times 10^5$</td>
<td>$3.0 \times 10^4$</td>
<td>$1.9 \times 10^7$</td>
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<tr>
<td>48</td>
<td>$5.0 \times 10^5$</td>
<td>$2.0 \times 10^4$</td>
<td>$1.9 \times 10^8$</td>
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and unsupplemented test tanks. In the nitrogen and phosphate supplemented tank there was a definite increase in total heterotrophic bacteria. Examination of colony types further demonstrated a definite selection for hydrocarbanoclastic bacteria in the enhanced population of the nutrient supplemented tank. Significantly increasing the size of the hydrocarbanoclastic population via an active growth response would be expected to also increase the hydrocarbon turnover rate and expedite degradation.

It is important to sound a warning which needs to be tested under environmental conditions. The process of disease is a quantitative inter-relationship between the number of bacteria, virulence of the bacteria and host resistance as expressed by the formula:

\[ D = \frac{NV}{R} \]

In the normal marine environment the sea creatures evolve to a delicate balance between these three factors. If we upset this balance, disease could result with far more damaging consequences to the marine fauna than the described toxicity of oil and/or dispersant. This is strongly supported by the work of Stinson and Talburt (1978) who showed a 3-log increase in virulence of hydrocarbon grown Pseudomonas aeruginosa over that of the same-strain grown on glucose. This virulence was linked with the development of a new lipo-protein in the outer membrane of the hexadecane grown cells. Therefore, we must conclude that as tempting as fertilization might be as a mechanism to increase degradation potential, it must be tested under controlled conditions to determine whether or not pathogenicity does result from the increased bacterial numbers.

8.4 Conclusions

Both the viable plate count (VPC) and most probable number (MPN) methods were suitable for enumeration of marine heterotrophic bacteria and hydrocarbanoclastic bacteria.

The MPN method while yielding slightly higher total numbers than the VPC method had no greater accuracy than the VPC method, imposed greater logistical demands and did not yield colonies which were required for other aspects of the project.

Use of these methods demonstrated that the percentage of oil degraders within the "total heterotrophic population" increased with exposure time of the "total population" to oil and/or dispersant.

Oxygen depletion by the modified BOD method is a valuable tool which provides a general picture of biological response to materials suspended in the water column. The procedure was used to demonstrate the biodegradable nature of Corexit 9527 and provide a rough index of degradation potential. This method confirmed VPC and chemistry data in the meso-scale tank experiments. Essentially, there is little water column activity in oil treated tanks but biological activity in the tank zones containing elevated hydrocarbon concentrations.
Oxygen depletion has certain limitations, the greatest being that it cannot be directly correlated with actual oil degradation rate or the rate of degradation of specific oil components. An alternate approach is chemical analysis by gas chromatography which has been used in this project. The use of this technique for water column samples, while quantitative for bulk oil has certain limitations for component analysis. It is possible to demonstrate loss of classes of compounds by this method but is too expensive and time consuming for routine degradation rate determinations. The use of $^{14}$C labeled hydrocarbons allows a rapid and fairly simple method for measuring mineralization (conversion of organic carbon to carbon dioxide by metabolism) as an index of biodegradation. Representative hydrocarbons provide an estimate for the rate at which the mixed natural population achieve mineralization of aliphatic and aromatic hydrocarbons. The mineralization rate studies demonstrate turnover rates ranging from approximately 20 to 90 mg of substrate per hour. These values compare with results by other investigators in similar systems.

A more accurate approach using $^{14}$C methodology is to measure not only mineralization, but also the production of water soluble intermediates which carry the $^{14}$C label and the amount of $^{14}$C incorporated into cell biomass. The importance of this approach is apparent from the data from one typical experiment. The average disintegration per minute (DPM) in the CO$_2$ traps were 4.3 x 10$^3$, 3.2 x 10$^4$ DPM for the cell bound activity and 7.1 x 10$^4$ DPM for the water soluble products. This data shows clearly that mineralization is an index of biological activity but not a reliable quantitative tool for hydrocarbon turnover or degradation time.

Studies by the VPC method for the surface film, water column and sediment were performed as 13 and 40°C. The bacterial numbers increased in the surface film during day 1 and 2 then remained essentially constant throughout the 21 day experiment. We interpret this increase not as bacterial growth per se but rather the formation of the microlayer.

The sediment bacterial population increased through day 9 in the control, dispersant and oil-dispersant tanks but not in the oil tank. The numbers remain constant in the sediment of the oil-dispersant tank after day 9 but decline in the control and dispersant tanks.

Oil destroys the surface microlayer as such because the oil is imposed between the water and air interface, and we believe that hydrocarbon degrading bacteria tend to be carried into the oil film and thus removing them from an active role at the oil-water interface.

The water column studies at 40 and 130°C provide evidence for two different bacterial populations in the natural seawater which was at 19°C. The total heterotrophic populations shift somewhat but the most significant observations is a rapid increase in the number of hydrocarbonoclastic bacteria through day 7 followed by a decline to original numbers, due, we conclude, to exhaustion of the nitrogen, phosphorus and iron content of the seawater.

Studies showed a decline in colony diversity with time in the tank system suggesting enrichment for specific organisms which is supported by
the studies on the ratio of hydrocarbonoclastic to heterotrophic bacteria. Population dominance is more significant than population size which is a fairly constant value.

The long term flow-through experiment showed no significant correlation between the number of total heterotrophic bacteria and hydrocarbon concentration, but a significant correlation was found between total heterotrophic and total hydrocarbonoclastic bacteria which indicated selection for hydrocarbon-utilizing bacteria.

A negative relationship was found between hydrocarbon content and hexadecane or naphthalene mineralization rates, suggesting inhibition of mineralization at high hydrocarbon and/or dispersant values. However, there was a decrease in hydrocarbon turnover time (T/f) in the oil and/or dispersant tanks. This decrease in T/f is more apparent for aliphatic hydrocarbons than for aromatic hydrocarbons.

The variation in mineralization rates is minimal ranging from 8.6 to 11.9 ng/hr for hexadecane and 8.3 to 19.6 ng/hr for naphthalene. Thus, in the determination of degradation time the most important function is hydrocarbon concentration.

Investigation of phosphate and nitrogen in the test systems reveal values which were always nutrient limiting for the amount of degradable carbon available.

It is our conclusion that hydrocarbon degradation potential in nutrient limited seawater is a relatively constant value independent of the presence or absence of oil in the water column. There is selection for hydrocarbonoclastic bacteria with time but their overall degradation activity as a mixed population is not significantly affected by the enrichment process. Preliminary evidence indicates that nutrient supplements (nitrogen, phosphorus and iron) do have a significant effect on the size of the seawater microbial population and yield a rather homogenous population of hydrocarbon utilizing bacteria in the presence of oil.

A brief discussion of nutrient seeding suggests this is not a viable approach to increased hydrocarbon degradation potential. The danger of increased pathogenicity in nutrient enriched oil-water systems is a real possibility which must be more fully investigated.

Natural microbial hydrocarbon degradative processes are active in the water column of dispersed or non-dispersed oil. These processes will eventually lead to the turnover of the biodegradable oil components. The rate at which oil degradation occurs is not materially enhanced by the dispersion process but dispersion of the oil into small micelles (1-2 μm) suspended in the water column does make the oil available to microbial action in the water column. Due to the physical inaccessibility of microorganisms to the bulk of the oil in a heavy slick, dispersion of the oil is an adjunct to the hydrocarbon degradative capacity of a mixed natural marine water column population.

This project has not shed much light on the affect of microbial populations on dispersed oil entrained into sediments or oil solubilized or suspended as sub-micron micelles in surface microlayers. Limited data
from this project indicates that hydrocarbon degradative potentials in sediments and the surface microlayer may be significantly higher than degradative potentials in the water column.

It is our conclusion that future studies of hydrocarbon degradation of dispersed vs. non-dispersed oils in the marine environment should center on the following topics listed in a general order of priority:

1. Degradative potentials in sediments.
2. Degradative potentials in surface microlayers.
3. The possible enhanced pathogenicity of nutrient enriched oil.
4. The degradative potentials at water-ice and sediment-ice interfaces.
9.0 Biological Investigations

Christopher J. Ordzie

Gina Garofalo
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9.0 Biological Investigations

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<tr>
<td>9.2</td>
<td>Behavioral recognition of molluscan and echinoderm predators by the Bay Scallop, Argopecten irradians (Lamarck) at two temperatures</td>
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<td>9.3</td>
<td>Predation, attack success, and attraction to the Bay Scallop, Argopecten irradians by the Oyster Drill, Urosalpinx cinerea</td>
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2. Results

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PREFACE

The information from our research efforts is presented in three major sections, each dealing with and answering questions about related but different aspects of the scallop predator-prey system and the impact of oil and dispersant on this system.

In Section (9.1), the actual bioassay experiments are described. Sections (9.2) and (9.3) present our biological investigations and techniques which form a foundation for all of the sublethal bioassay work. In Section 9.4, the response of a simple predator-prey community to oil, dispersant, and oil-dispersant mixtures. Instead of redescribing methods in Section I, reference is made to either Section II or III where techniques are described in full.
9.1 Section I Lethal and Sublethal effects of short term acute doses of Kuwait Crude Oil and a dispersant Corexit 9527 on Bay Scallops, *Argopecten irradians* (Lamarck) and two predators at different temperatures

**ABSTRACT**

Investigations of short term acute exposure of bay scallops, *Argopecten irradians* and two scallop predators, the oyster drill *Urosalpinx cinerea* and the common starfish *Asterias forbesi*, to oil, dispersant, and oil-dispersant mixtures (Kuwait Crude Oil and Corexit 9527) suggested that predator and prey have different lethal susceptibilities. Scallops were most sensitive to dispersant and dispersant mixed with oil; starfish were only sensitive to dispersant while the oyster drill seemed unaffected even though all were exposed to dilutions of identically prepared stock solutions. Scallops were least susceptible during winter months and most susceptible at summer temperatures. Treatment had less effect on predators than on scallops at summer temperatures. Sublethal concentrations of dispersant and oil-dispersant mixtures diminished the behavioral ability of scallops to recognize drills and starfish. The degree of effect increased with temperature. Predator detection of prey at the same concentrations was more complex. The feeding response or posturing reflex of starfish was significantly slowed by all treatments. In contrast, drills were unaffected in their recognition of scallop effluent in a choice chamber after treatment.

9.1.1 **INTRODUCTION**

There have been many recent investigations of lethal (Anderson et al., 1974; Griffin & Calder, 1977; Lee et al., 1977), as well as sublethal (Dicks, 1976; Percy, 1977; Percy & Mullin, 1977) effects of oils on marine invertebrates. Similarly, much attention has been given to the lethal (Portmann & Connor, 1968; Baker & Crapp, 1974; Wilson, 1977) and sublethal (Swedmark et al., 1971; Hagstrom & Lonning, 1977) effects of dispersants alone. In contrast, the comparative effects of oil, dispersant, and oil-dispersant treatments have received less attention (Hargrave & Newcombe, 1973; Avolizi & Nuwayhid, 1974).

This study was concerned with assessment of lethal and sublethal effects of API standard Kuwait Crude Oil and a dispersant, Corexit 9527 on the bay scallop *Argopecten irradians* (Lamarck) and two scallop predators; the starfish *Asterias forbesi* (Desor), and the oyster drill *Urosalpinx cinerea* (Say). Scallops were chosen because they are a commercially important marine species. Young of the year were used because of their high reproductive potential, which makes them important to the continued survival of scallop populations (Russell, 1973). Scallops have a well documented, predator specific, stereotyped escape response (Curtis, 1966; Mackie, 1970; Moore & Trueman, 1971; Thomas & Gruffydd, 1971; Ordzie & Garofalo, 1980a, see also section II) which we used to assess sublethal effects of oil and dispersant because it is easily quantified and is important to scallop survival. The oyster drill *Urosalpinx cinerea* has recently been found to be an active predator of scallops (Ordzie & Garofalo, 1980b, see also section III) and scallops show a vigorous escape response when confronted with this predatory drill.
Starfish are well known predators of scallops (Galtsoff & Loosanoff, 1939). Both predators are found in the coastal ponds of Rhode Island where large bay scallop beds are abundant.

It is our design to investigate the effects of oil, dispersant, and oil-dispersant mixtures on the bay scallop and two predators at lethal and sublethal levels at various temperatures. Such a study will provide information on the susceptibility of an ecologically important predator-prey system.

9.1.2 METHODS & RESULTS

9.1.3 Lethal Effects

Methods

Bay scallops, Argospecten irradians, oyster drills, Urosalpinx cinerea, starfish, Asterias forbesi, periwinkles, Littorina littorea (Lamarck) and purple sea urchins, Arbacia punctulate (Lamarck) were collected from Point Judith Pond or Ninigret Pond, Rhode Island, by dredging or diving. All test animals were maintained in the laboratory with running, unfiltered, ambient temperature sea water from Point Judith Pond. Temperatures ranged from -1.50°C to 24.20°C and salinity ranged from 27 to 32 °/00 during this study.

Bay scallop, and two scallop predators, the starfish and the oyster drill, were exposed to various concentrations of stock solutions of oil, dispersant, and an oil-dispersant mixture. Stock solutions were prepared in three 55 liter all glass aquaria according to the schedule in Table I. The appropriate amount of oil was poured onto 49.5 liter of ambient temperature sea water. The dispersant was sprayed onto the appropriate mixing tanks after four hours later to allow weathering of the oil. These mixing tanks were set in an ambient temperature, running sea water bath for temperature control at the beginning of the mixing period. Each solution was aerated with a Silent Giant diaphragm pump for the first 20 hours and allowed to settle for the last six hours. Solutions were then withdrawn from below the slick with a PVC siphon inserted prior to addition of oil or dispersant.

Dosing solutions were then prepared by mixing the appropriate volume of stock solution with ambient temperature sea water to make a volume of 20 liters. The concentrations used for the scallop, starfish, and drill bioassays are shown in Table II. Each dosing tank was placed into a common, ambient temperature water bath. At this point, animals were added to dosing tanks for six hours. Aeration was provided for the entire dosing period. Five control tanks, each with 20 liters of sea water, were also placed in the water bath. In both scallop and drill bioassays, 20 animals were used in each of the dosing and control tanks. Because of their tendency to crawl out of tanks, it was necessary to cage the drills in a mesh ban to keep them in the dosing solution. Due to the large size of starfish, ten individuals were placed in each dosing tank. Test animals of approximately equal size were used for each replicate to eliminate presumed differences due to size.
Table I. Proportions (liters) of sea water, oil, and dispersant used to make the treatment stock solutions.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Proportion (liters) of:</th>
<th>Air mix</th>
<th>Settle</th>
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<tr>
<td>C</td>
<td>50.0 : --- : ---</td>
<td>20 hours</td>
<td>6 hours</td>
</tr>
<tr>
<td>O</td>
<td>49.5 : 0.5 : ---</td>
<td>20 hours</td>
<td>6 hours</td>
</tr>
<tr>
<td>D</td>
<td>49.5 : --- : 0.1*</td>
<td>20 hours</td>
<td>6 hours</td>
</tr>
<tr>
<td>OD</td>
<td>49.5 : 0.5 : 0.1*</td>
<td>20 hours</td>
<td>6 hours</td>
</tr>
</tbody>
</table>

*Dispersant was added four hours after the beginning of mixing.

W - Sea water
O - Kuwait Crude Oil
D - Corexit 9527 Dispersant

Table II. Volumes of stock solutions mixed with sea water to make the appropriate dilutions of stock solution used for all bioassay experiments.

<table>
<thead>
<tr>
<th>Concentration % of stock solution</th>
<th>Amount of stock solution (Liters)</th>
<th>Sea water (Liters)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>70</td>
<td>14</td>
<td>6</td>
</tr>
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<td>50</td>
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<td>17.5</td>
</tr>
<tr>
<td>6.25</td>
<td>1.25</td>
<td>18.75</td>
</tr>
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</table>
After the six hour dosing period, test animals from each treatment and concentration were separately placed into respective 40 liter aquaria each independently supplied with running sea water at a flow rate of 30 ml/sec for a depuration period of five days. The number of survivors in each treatment and concentration and control were counted at the end of the five day period. The number of replicates at each temperature for each organism are presented in Table III.

2. Results

Scallop susceptibility to oil during the six hour dosing regime was not evident even at the highest concentration (100% stock solution). Indeed, at all three temperatures (20, 100, and 200°C) survivorship in control and oil treatments was high and essentially identical at 100% (Figure 1). Measurement of total extractable hydrocarbon using the infrared spectrophotometric technique with carbon tetrachloride as the extracting solvent, gave values of 1-4 ppm for the water below the slick of the oil stock solution. Solutions containing dispersant could not be reliably measured at the concentrations used, so all values for these solutions were designated as nominal concentrations. Scallop survivorship was significantly decreased in all treatments involving dispersant. As the concentration of dispersant and oil-dispersant stock solution increased, scallop survivorship decreased at all temperatures.

Scallop survivorship was temperature related in dispersant and oil-dispersant treatments. As temperature increased, scallop survivorship decreased (Figure 2 & 3). There was no significant difference in the effect of the dispersant and oil-dispersant treatments on bay scallops. Probit analysis (Figure 4) used to estimate LD50 values and 95% fiducial limits for scallops also revealed that there was no significant difference between LD50 values for dispersant and oil-dispersant treatments at any temperature. There was, however, a strong concentration-temperature interaction. As temperature increased, the concentration of Corexit 9527 required to kill 50% of the scallops decreased. The LD50 was lowest at summer temperatures.

Starfish showed no appreciable change in survivorship in any except dispersant treatments for tests conducted at 150 and 200°C (Figure 5). Even when exposed to full strength stock solution at these high temperatures, survivorship of starfish was always better than 50 percent.

It should be noted that starfish in the oil dosing tanks spawned during exposure at 150°C. Starfish in control tanks spawned a few days later. No spawning was observed during the 200°C experiment. A further observation on the condition of starfish suggests that animals exposed to dispersant and oil-dispersant were physically stressed. Many starfish from these treatments had evorted stomachs. No other starfish from other treatments were found with this condition.

There were no treatment related oyster drill deaths observed during experiments run at 200°C (Figure 6). Of 480 drills tested, only two died during the experiment. During dosing, drills in the controls and all concentrations of the oil treatment appeared to exhibit normal crawling behavior while drills in all concentrations of the dispersant and oil-dispersant treatments were retracted into their shells.
Fig. 1. Scallop survivorship for five concentrations of four treatments at three temperatures, 20, 100, and 200°C: C-Control, O-Kuwait Crude Oil, D-Corexit 9527 Dispersant, OD-Oil and Dispersant.
Table III. Temperatures, dates, and organisms used for lethal bioassay.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Date</th>
<th>Replicate Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scallop</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Argopecten irradians)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>1/31/78</td>
<td>1</td>
</tr>
<tr>
<td>20</td>
<td>2/28/78</td>
<td>2</td>
</tr>
<tr>
<td>20</td>
<td>3/5/79</td>
<td>3</td>
</tr>
<tr>
<td>20</td>
<td>3/12/79</td>
<td>4</td>
</tr>
<tr>
<td>100</td>
<td>11/16/77</td>
<td>1</td>
</tr>
<tr>
<td>100</td>
<td>5/17/78</td>
<td>2</td>
</tr>
<tr>
<td>100</td>
<td>11/14/78</td>
<td>3</td>
</tr>
<tr>
<td>100</td>
<td>5/7/79</td>
<td>4</td>
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<tr>
<td>200</td>
<td>8/21/78</td>
<td>1</td>
</tr>
<tr>
<td>200</td>
<td>7/16/79</td>
<td>2</td>
</tr>
<tr>
<td>Starfish</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Asterias forbesi)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>5/29/79</td>
<td>1</td>
</tr>
<tr>
<td>200</td>
<td>8/6/79</td>
<td>2</td>
</tr>
<tr>
<td>Snails</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Urosalpinx cinerea)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>7/23/79</td>
<td>1</td>
</tr>
<tr>
<td>200</td>
<td>7/30/79</td>
<td>2</td>
</tr>
</tbody>
</table>

Fig. 2. Scallop survival for five concentrations of dispersant stock solution at three temperatures, 10, 100, and 200.

Fig. 3. Scallop survival for five concentrations of oil and dispersant stock solution at three temperatures, 10, 100, and 200.
Fig. 4. Probit estimates of 6 hour LC50 for bay scallops at nominal dispersant and oil-dispersant concentrations for 20, 10o and 20OC. Vertical lines represent 95% fiducial limits: O-Corexit 9527 Dispersant, O-O!-Kuwait Crude Oil and Corexit 9527 Dispersant.

Fig. 5. Combined results of starfish survivorship at 150 and 20OC when exposed to four experimental treatments at various concentrations of stock solution: C-Control, O-Kuwait Crude Oil, D-Corexit 9527 Dispersant, OD-Oil and Dispersant.

Fig. 6. Oyster Drill survivorship at 20OC when exposed to four experimental treatments at various concentrations of stock solution: C-Control, O-Kuwait Crude Oil, D-Corexit 9527 Dispersant, OD-Oil and Dispersant.
9.1.4 Sublethal Effects

1. Scallop Detection of Predators

   a. Methods

Scallops from the 12.5% concentration of each treatment and a control were tested for their behavioral recognition of molluscan and echinoderm predators during the five day depuration period which followed dosing. The behavioral escape response and apparatus used were described previously (Ordzie & Garofalo, 1980a, see also section II). Scallops were tested for their behavioral discrimination between a non-predatory gastropod, Littorina littorea and a predatory gastropod, Urosalpinx cinerea. Also, scallop discrimination between a non-predatory echinoderm, Arbacia punctulata and a predatory echinoderm, Asterias forbesi was tested. In each case, the non-predator was presented first to avoid sensitizing scallops.

Scallop stimulation was accomplished by touching the test animal to the scallop mantle margin at the anterior wing. Two aspects of the scallop escape response, response time and swimming claps, were quantified. Response time, defined as the time from beginning of stimulation until first valve movement, was measured in seconds with a stopwatch. Swimming claps were simply counts of the number of valve adductions of closures during a response. It was previously determined that bay scallops respond to predators with a short response time and a high number of swimming claps (Ordzie & Garofalo, 1980a, see also Section II). In contrast, scallops respond to non-predators with long response times and less than one swimming clap. In this way scallops behaviorally discriminate between predators and non-predators. We then studied the effects of oil, dispersant, and oil-dispersant treatments on this sensitive escape response which is so essential to scallop survival.

All 20 scallops from each treatment were tested with non-predator and predator. Each individual scallop was tested five times during the depuration period. Temperatures, replicates, and test species used in sublethal studies are shown in Table IV.

An index was employed to allow simultaneous consideration of scallop responses to predator and non-predator. Response to predator was subtracted from response to non-predator, was divided by their sum, and was then multiplied by 100 as follows:

\[
\text{Response Index} = \frac{\text{Non-predator} - \text{Predator}}{\text{Non-predator} + \text{Predator}} \times 100
\]

Response time and number of swimming claps were independently analyzed using this index. The index value changes with changes in behavioral discrimination. As behavioral discrimination increases, the index values move away from zero and conversely, as behavioral discrimination decreases, the index values approach zero. Indices for response time and swimming claps were independently analyzed using a two-way analysis of variance test with treatment and temperature as main effects. Data from tests with gastropods and echinoderms were considered separately.
Table IV. Temperatures, dates, and organisms used to test the escape response of treated and untreated scallops.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Date</th>
<th>Replicate Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>5/17/78</td>
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<td>100</td>
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<td>6/7/78</td>
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<tr>
<td>150</td>
<td>6/18/78</td>
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<tr>
<td>200</td>
<td>8/21/78</td>
<td>1</td>
</tr>
<tr>
<td>200</td>
<td>7/16/79</td>
<td>2</td>
</tr>
</tbody>
</table>

Tested with *L. littorea* and *U. cinerea*

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Date</th>
<th>Replicate Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>5/7/79</td>
<td>1</td>
</tr>
<tr>
<td>100</td>
<td>5/14/79</td>
<td>2</td>
</tr>
<tr>
<td>200</td>
<td>7/23/79</td>
<td>1</td>
</tr>
<tr>
<td>200</td>
<td>7/23/79</td>
<td>2</td>
</tr>
</tbody>
</table>

Tested with *A. punctulata* and *A. forbesi*
b. Results

Scallop discrimination of *Urosalpinx cinerea* from *Littorina littorea* as measured by the time index was significantly decreased by dispersant and oil-dispersant treatments at 12.5% of the stock solution (Figure 7). As temperature increased from 10°C to 20°C, discrimination increased in all treatments (ANOVA, F=66.5, d.f.=2,468, P < .001). Compared to controls, the oil treatment appeared to have no effect on the scallop response time index. However, dispersant and oil-dispersant treatments both significantly lowered the response time index and thus discrimination (ANOVA, F=26.4, d.f.=3,468, P < .001). There was also a significant temperature-treatment interaction evidenced by the greater effect on discrimination at higher temperatures (ANOVA, F=2.5, d.f.=6,468, P < .02). Scallop behavioral discrimination between the two snails as measured by claps was unaffected by treatment at 10°C and 20°C (Figure 8). All values were similar to those for controls. The only temperature (ANOVA, F=20.8, d.f.=2,468, P < .001) and treatment effects (ANOVA, F=5.7, d.f.=3,468, P < .0009) were found at 15°C where all three treatments differed significantly from the control. There was no significant temperature-treatment interaction.

The same indices were used to test scallop discrimination between the starfish, *Asterias forbesi* and the sea urchin, *Arbacia punctulata*. Dispersant and oil-dispersant were found to significantly affect the scallop response time index at both 10°C and 20°C (ANOVA, F=24.7, d.f.=3,312, P < .0001). Scallop discrimination between the predator starfish and the non-predatory sea urchin after exposure to either treatment (Figure 9). There was no temperature effect on discrimination, however, there was a temperature-treatment interaction (ANOVA, F=2.9, d.f.=3,312, P < .04) demonstrated by the greater interference with discrimination at higher temperatures.

The swimming clap index was only affected by the oil treatment at 20°C and in this case discrimination increased compared to controls (ANOVA, F=3.79, d.f.=3,312, P < .01) (Figure 10). No temperature effect was found, but there was a temperature-treatment interaction (ANOVA, F=3.08, d.f.=3,312, P < .03) owing to increased discrimination of scallops exposed to oil at 20°C.

2. Predator Detection of Scallops

2.1 Starfish (*Asterias forbesi*)

a. Methods

Starfish were tested for sublethal behavioral effects using part of the feeding response described as the "posturing reflex" (Heeb, 1973). Starfish "posture" over their prey prior to feeding by elevating their aboral surface which leaves them in a humped posture.

To examine this response an epoxy coated plywood box (30 cm long x 27 cm wide x 13.5 cm deep) fitted with a drain and a glass false bottom was filled with sea water at ambient temperature. A starfish was placed on the glass plate then the water level was adjusted so the water surface just touched the highest part of the aboral surface of the starfish at
Fig. 7. Response time index for the scale's response to 91±9°C in each of four experimental conditions at controlled RHs of 21±9%. Error bars represent ± 1 SEM on either side of the mean. O-D: One Fifty, O-D: One Fifty Dispersant, OD-Oil and Dispersant

Fig. 8. Swelling time index for the scale's response to 91±9°C in each of the four experimental conditions at controlled RHs of 21±9%. Error bars represent ± 1 SEM on either side of the mean. O-D: One Fifty, O-D: One Fifty Dispersant, OD-Oil and Dispersant

Fig. 9. Response time index for the scale's response to 91±9°C in each of the four experimental conditions at controlled RHs of 21±9%. Error bars represent ± 1 SEM on either side of the mean. O-D: One Fifty, O-D: One Fifty Dispersant, OD-Oil and Dispersant

Fig. 10. Swelling time index for the scale's response to 91±9°C in each of the four experimental conditions at controlled RHs of 21±9%. Error bars represent ± 1 SEM on either side of the mean. O-D: One Fifty, O-D: One Fifty Dispersant, OD-Oil and Dispersant
Scallop homogenate was made by liquifying tissues from five whole scallops with 15 ml of sea water in a blender. Half a ml of this homogenate was then presented by pipette under the oral surface to stimulate the posturing reflex. The time from initial stimulation to the first upward movement, noted when the aboral surface broke the water-air interface, was measured in seconds up to a 60 second cutoff time. The box was flushed with sea water after each test. Each starfish from the 12.5% concentration of all treatments and control were tested in this manner eight times during the five day depuration period. Plain sea water was also presented by pipette to control for mechanical stimulation of the oral surface in 20 starfish. This experiment was performed at 15°C (5/29/79) and 20°C (8/6/79). Data were analyzed with a one-way analysis of variance test.

b. Results

Combined data from replicates 1 and 2 (15°C and 20°C) respectively (Table V), showed that response times for initiation of the posturing reflex in all treated starfish were significantly slower than response times of controls (ANOVA, F=9.53, d.f.=3,615, P<.001; LSD=4.26, d.f.=615, P=.05). Thus at sublethal exposures of just six hours to all treatments, starfish were affected in response to and possibly recognition of food presented as a homogenate. Starfish showed no response to the mechanical stimulation of plain sea water.

Table V. Starfish response time (sec) for posturing reflex for treated and untreated starfish at 15°C and 20°C.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>C</th>
<th>O</th>
<th>D</th>
<th>OD</th>
</tr>
</thead>
<tbody>
<tr>
<td>X (sec)</td>
<td>13.5</td>
<td>20.5</td>
<td>22.2</td>
<td>24.2</td>
</tr>
<tr>
<td>S.E.</td>
<td>1.1</td>
<td>1.6</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>N</td>
<td>160</td>
<td>155</td>
<td>160</td>
<td>144</td>
</tr>
</tbody>
</table>

C - Control
O - Kuwait Crude Oil
D - Corexit 9527 Dispersant
OD - Oil and Dispersant
3. Oyster Drill (*Urosalpinx cinerea*)

a. Methods

Oyster drills were tested for behavioral recognition of scallop effluent using the plywood choice chamber described in a previous paper (Ordzie & Garofalo, 1980b, see also section III). This chamber is used to demonstrate the ability of the drills to choose between scallop effluent and plain sea water. All twenty drills from the 12.5% concentration of each treatment and a control were tested in the apparatus. Animals from the four different treatments were tested in a random order each day.

Three *U. cinerea*, marked with nail polish for identification, were started in the center of the apparatus with their long axis perpendicular to the long axis of the chamber. Each drill was allowed an hour to respond. Distance moved in cm was recorded after an hour. If a drill reached the end of the ramp in less than one hour, distance and time in minutes were recorded. The distance moved was designated positive if drills moved toward the scallop effluent, and negative if they moved toward plain sea water. Daily testing was done four times during the depuration period and this experiment was replicated twice at 20°C (7/23/79 and 7/30/79). Distances traveled by drills from each treatment were analyzed with a one-way analysis of variance test. Rates (cm/min) traveled toward both scallop effluent and plain sea water were determined for each animal tested. A one-way analysis of variance test was used to determine treatment effect on rate of travel.

Previously we (Ordzie & Garofalo, 1980b, see also section III) performed blank tests in which untreated drills were tested for any left-right bias in the choice chamber. To do this, we presented plain sea water on both sides. Results showed no detectable bias at the behavioral level studied and it was then concluded unlikely that the apparatus would interfere with the observed results.

b. Results

Because there was no significant difference between replicates, results of both were combined. The net positive distance moved by treated drills was not significantly different (ANOVA) from distances moved by controls (Table VI). Compared to the net distance moved in blank tests, treated and control drills exhibit a large net positive movement toward scallop effluent. Similarly, there was no significant difference between treated and control drills for rates of travel toward scallop effluent (ANOVA).
Table VI. Distance traveled (cm) by treated and untreated drills toward scallop effluent in a choice chamber at 20°C.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>C</th>
<th>O</th>
<th>D</th>
<th>OD</th>
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</thead>
<tbody>
<tr>
<td>( \bar{X} ) (cm)</td>
<td>5.1</td>
<td>5.0</td>
<td>5.1</td>
<td>4.6</td>
</tr>
<tr>
<td>S.E.</td>
<td>.9</td>
<td>1.0</td>
<td>1.0</td>
<td>.9</td>
</tr>
<tr>
<td>N</td>
<td>145</td>
<td>149</td>
<td>151</td>
<td>146</td>
</tr>
</tbody>
</table>

C - Control
O - Kuwait Crude Oil
D - Corexit 9527 Dispersant
OD - Oil and Dispersant

9.1.5 Discussion

The goal of this study was to examine effects of oil and dispersant on a predator-prey system during selected ambient water temperatures. It was not the purpose here to evaluate the relative toxic dangers of either substance to natural populations, but rather, to study how this predator-prey system responds, and to examine the merits of using such an ecological system in bioassay work.

At high concentrations of treatment solutions, each member of the scallop predator-prey system was affected differently. Scallop survivorship was decreased by any treatment solution which contained dispersant. Starfish were less affected, but when they were, they were susceptible only to the dispersant treatment while survivorship of the oyster drill was unaffected by any treatment. This differential susceptibility to high concentrations of solutions prepared in identical ways points to a problem biologists face when dealing with bioassay. Because not all animals are affected by the same chemicals at the same concentration and that animals have ecological relationships which should also be considered, knowing the response of one species to a number of pollutants is not always sufficient for ecological assessment.

The sequence for susceptibility at sublethal levels is somewhat different for each species tested. Scallops suffered decreased predator recognition when exposed to any treatment with dispersant, starfish were hindered in their recognition of scallops as food when exposed to any treatment, while drills showed no measurable effect of any treatment on their ability to detect and move toward scallops. Ultimately, in a
disrupted system, scallop populations may suffer more than the direct impact of a pollutant which selectively affects scallops but not all of the scallop predators.

This is a partial picture of what to expect from differential susceptibilities in a predator-prey system because information on long term consequences is also needed. Eisler (1973) noticed lower predation rates for Iranian Crude Oil and dispersant treated bivalve prey, as well as fecundity in predatory drills which fed on contaminated prey. In the future, studies which consider animals in more complete ecological context will provide better information about the impact of oil pollutants.

In light of the differential susceptibility demonstrated in this simple three animal system, the concept of an indicator species is difficult to defend. It would seem that because each organism can have its own array of chemical compound and concentration response, that there is no logical reason to assume that one animal could possibly be used to accurately judge susceptibility arrays for other species.

One major reason drills survived dosing is that they withdrew into their shells upon exposure, effectively isolating themselves from the environment. Dicks (1976) has suggested that withdrawn snails may suffer higher mortality in areas with high mechanical energy due to surf action. However, in areas with no violent mechanical action where scallops are found (coastal ponds) the survival of drills could be much higher than on the exposed coast.

In order to accurately assess biological effects of a pollutant event, we need to know susceptibilities of animals for different seasons. Seasonal sensitivity can be quite dramatic. Dispersant concentrations which are not lethal to scallops during winter temperatures cause greater than 50% mortality at summer temperatures. Although temperature of ambient water could be a significant predictor of scallop susceptibility to dispersant exposure, one should not generalize to other organisms. This issue becomes more complex because either the "pollutant toxicity" or "animal sensitivity" can be affected by temperature (Rice et al., 1977). Accordingly, the temperature related susceptibility can be different for each organism, making broad generalizations dangerous.
9.2 Section II

Behavioral Recognition of Mollusc and Echinoderm Predators by the Bay Scallop, Argopecten irradians (Lamarck) at two temperatures

Abstract

In an investigation of predator stimulated responses, bay scallops Argopecten irradians (Lamarck) were least sensitive on the dorsal side of their shell periphery. Scallops discriminated predatory from non-predatory gastropod molluscs and echinoderms based on scallop response times and swimming claps. Predatory test species Urosalpinx cinerea (Say) Asterias forbesi (Desor), Eupleura caudata (Say), Thais lapillus (L.), and Busycon canaliculatum (L.) provoked stereotypic escape responses. Although temperature had little effect on predator recognition, scallops required more time to respond to predators at 12°C than at 20°C. Once initiated, escape responses appeared to be temperature independent. It would seem predator recognition contributes to an efficient time-energy budget.

9.2.1 Introduction

Predatory starfish have been shown to evoke dramatic, predictable, escape responses from a variety of marine invertebrates (Bullock, 1953; Feder, 1967; Mackie, 1970; Ansell, 1969) including scallops (Thomas & Gruffydd, 1971; Feder, 1972; Stephens, 1978). Several molluscs (Bullock, 1953) and the scallop Pecten maximus (Thomas & Gruffydd, 1971) have been shown to differentiate, by touch, predatory from non-predatory starfish. They demonstrated that, although not as effective as contact, crude extracts of starfish were sufficient stimuli for provoking escape responses from P. maximus. Work on starfish substances responsible for evoking escape responses has shown that they come from tube feet (Feder & Lasker, 1964) and that they are surface active agents identified as "saponin-like" (Mackie et al., 1968) or steroid glycosides (Mackie, 1970). Among the echinoderms examined by Yasumoto et al. (1966), saponins were only present in starfish and were found to vary seasonally.

Although reports of starfish evoked escape responses are common in the literature, reports of predatory molluscs which elicit escape behavior are less frequent (Ansell, 1969; Gore, 1966). In this paper, we quantify and examine bay scallop, Argopecten irradians (Broom. 1976) responses to predatory and non-predatory echinoderms and gastropod molluscs at two temperatures.

9.2.2 Materials and Methods

A. Test Species

Bay scallops, A. irradians, were dredged or collected by diving in Point Judith Pond, Rhode Island. Scallop shell height averaged 50.1 ± 4.4 mm (mean ± s.e.). Scallops were maintained in a laboratory with running, unfiltered sea water from Point Judith Pond where the salinity averaged 31.7 ± .4 ppt. Predatory snails, Busycon canaliculatum,
Eupleura caudata, Urosalpinx cinerea, non-predatory snails Littorina littorea (L.), Ilyanassa obsoleta (Say), and a predatory starfish Asterias forbesi were collected from Point Judith Pond. Another predatory snail, Thais lapillus and a non-predatory sea urchin Arbacia punctulata (Lamarck) were collected from an exposed intertidal jetty outside the pond. All test invertebrates were maintained either in unfiltered, running sea water at ambient (10°C - 20°C) temperature or in a 30 liter all glass aquarium, fitted with aeration and temperature control. Water was changed every three days in the aquarium.

B. Scallop Behavior

Stimulation was accomplished by allowing the foot of a restrained snail to contact the mantle margin of an unrestrained scallop. The snail was held stationary by pressing the shell apex into a flexible tube, attached to the end of a rigid tube, which was suspended by an adjustable crossbar over the observation tray. A snail so stabilized could be positioned at any desired location and still have full foot mobility for stimulation.

Two aspects of scallop behavioral responses were measured. Response time, defined as the time from initial stimulation to first valve adduction, was measured in seconds with a stopwatch. If no response occurred within one minute, the observation was terminated and the scallop credited with a 60 second response time. The number of swimming claps was measured by counting valve adductions during a response.

It was necessary to first determine relative sensitivity of different sites on the scallop mantle margin before further testing. A priori four peripheral areas; dorsal, ventral, anterior wing, and posterior wing were chosen to test sensitivity to stimulation with a predator, U. cinerea (Fig. 1). Scallops were kept in a 50 liter all glass aquarium, with aeration and temperature at 12°C for seven days prior to testing. Aquarium water was replaced daily with fresh sea water throughout the experiment.

Each of four, epoxy coated, plywood observation trays contained five separate compartments (each compartment measured 27.5 cm long x 10.5 cm wide x 5 cm deep) to isolate individual scallops and eliminate presumed chemical communication. All scallops were allowed at least two minutes after handling to acclimate in the observation trays at 12°C before stimulation.

Twenty scallops were stimulated first at one area of the mantle margin, then the same twenty scallops were stimulated at another site, until all four areas had been tested. This procedure was replicated six times. The sequence for testing the four areas was changed for each replicate. Water in observation trays was replaced after each trial.

Scallop responses to all test species were measured at ambient temperatures of 20°C (August 1978) and 12°C (October 1978). Test species were brought in contact with the scallop mantle margin at the anterior wing. All snails, except B. canaliculatum, were presented using the plastic tube and crossbar apparatus described above. B. canaliculatum, because of its bulk, was hand held during stimulation as were starfish and sea urchins. Stimulation began when either snail foot
or echinoderm tube feet touched the scallop.

Fig. 1. Diagram of the bay scallop *Argopecten irradians*, with the four peripheral areas selected for stimulation as viewed from outside of left valve.

Twenty scallops were exposed to each test species. In all, eight different groups of twenty scallops were exposed to eight species. This was replicated three times. Presentation of test organisms was changed for each replicate so that no group of scallops was stimulated more than once by the same species. Both scallops and test species were maintained in running sea water at ambient temperatures. Sea water in observation trays was replaced after each test.

Data for both experiments, consisting of means of response times and swimming claps for groups of five scallops, were analyzed using the analysis of variance test (ANOVA). To examine effects of stimulation on four peripheral areas, a one-way ANOVA and the least significant difference (LSD) tests (Snedecor & Cochran, 1967; Sokal & Rohlf, 1969) were employed to identify differences among means. A two-way ANOVA and t-test were used to identify significant effects of test species and temperatures on scallop responses.

9.2.3 Results

A. Peripheral Sensitivity

Scallop showed varying sensitivity to stimulation with the predatory gastropod, *U. cinerea*, at selected sites on the mantle margin (Table I). Stimulation at either posterior or anterior wing resulted in significantly lower response times compared to results for dorsal or ventral sites and dorsal and ventral sites were different (ANOVA, \( F = 137.7, df = 3, 69, p = .01; \) LSD = 4.5, \( df = 92, p = .05\)). While scallops stimulated at the dorsal site responded with significantly fewer swimming claps than for any other site, scallops stimulated at the anterior wing responded with the highest mean number of swimming claps (ANOVA, \( F = 47.7, df = 3, 69, p = .01; \) LSD = 1.1, \( df = 92, p = .05\)). Based on these results, the anterior wing was selected as the site for all subsequent stimulation because scallops exhibited the most vigorous, least variable response at this location on the mantle periphery (Table I).

We observed predator proximity was not sufficient to consistently elicit escape behavior, therefore, all trials were performed with test organisms in physical contact with scallops.
Table I: Mean response time and mean number of swimming claps from scallops stimulated with Urosalpinx cinerea at four selected sites on the shell periphery.

<table>
<thead>
<tr>
<th>Peripheral Stimulation Sites</th>
<th>ventral</th>
<th>dorsal</th>
<th>posterior</th>
<th>anterior</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Response Time</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \bar{x} )</td>
<td>25.9</td>
<td>55.1</td>
<td>16.4</td>
<td>14.6</td>
</tr>
<tr>
<td>2 s.e.</td>
<td>4.6</td>
<td>3.2</td>
<td>4.2</td>
<td>3.2</td>
</tr>
<tr>
<td><strong>Swimming Claps</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \bar{x} )</td>
<td>5.6</td>
<td>0.8</td>
<td>5.6</td>
<td>7.1</td>
</tr>
<tr>
<td>2 s.e.</td>
<td>1.0</td>
<td>0.6</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table II: Mean scallop response times to eight test species at 120 and 20°C. (* indicates predator)

<table>
<thead>
<tr>
<th>Test species</th>
<th>Temperature</th>
<th>120°C</th>
<th>20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Littorina littorea</td>
<td>( \bar{x} )</td>
<td>36.3</td>
<td>46.6</td>
</tr>
<tr>
<td></td>
<td>2 s.e.</td>
<td>7.4</td>
<td>4.8</td>
</tr>
<tr>
<td>Amusia punctulata</td>
<td>( \bar{x} )</td>
<td>55.6</td>
<td>36.5</td>
</tr>
<tr>
<td></td>
<td>2 s.e.</td>
<td>4.2</td>
<td>2.6</td>
</tr>
<tr>
<td>Hymanassa ocellata</td>
<td>( \bar{x} )</td>
<td>36.1</td>
<td>33.7</td>
</tr>
<tr>
<td></td>
<td>2 s.e.</td>
<td>8.7</td>
<td>5.6</td>
</tr>
<tr>
<td>Urosalpinx cinerea</td>
<td>( \bar{x} )</td>
<td>14.5</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>2 s.e.</td>
<td>4.8</td>
<td>3.0</td>
</tr>
<tr>
<td>Asterias forbesi</td>
<td>( \bar{x} )</td>
<td>12.3</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>2 s.e.</td>
<td>2.2</td>
<td>2.4</td>
</tr>
<tr>
<td>Euprymna radiata</td>
<td>( \bar{x} )</td>
<td>23.7</td>
<td>15.1</td>
</tr>
<tr>
<td></td>
<td>2 s.e.</td>
<td>4.6</td>
<td>3.6</td>
</tr>
<tr>
<td>Thais laevis</td>
<td>( \bar{x} )</td>
<td>13.8</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td>2 s.e.</td>
<td>4.2</td>
<td>3.2</td>
</tr>
<tr>
<td><em>Aplysia californica</em></td>
<td>( \bar{x} )</td>
<td>26.3</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td>2 s.e.</td>
<td>8.2</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Table III: Mean number of scallop swimming claps in response to eight test species at 120 and 20°C. (* indicates predator)

<table>
<thead>
<tr>
<th>Test Species</th>
<th>Temperature</th>
<th>120°C</th>
<th>20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Littorina littorea</td>
<td>( \bar{x} )</td>
<td>1.4</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>2 s.e.</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Amusia punctulata</td>
<td>( \bar{x} )</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>2 s.e.</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Hymanassa ocellata</td>
<td>( \bar{x} )</td>
<td>1.3</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>2 s.e.</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td>Urosalpinx cinerea</td>
<td>( \bar{x} )</td>
<td>7.3</td>
<td>6.6</td>
</tr>
<tr>
<td></td>
<td>2 s.e.</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Asterias forbesi</td>
<td>( \bar{x} )</td>
<td>4.3</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>2 s.e.</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Euprymna radiata</td>
<td>( \bar{x} )</td>
<td>5.8</td>
<td>6.7</td>
</tr>
<tr>
<td></td>
<td>2 s.e.</td>
<td>1.4</td>
<td>0.6</td>
</tr>
<tr>
<td>Thais laevis</td>
<td>( \bar{x} )</td>
<td>8.0</td>
<td>7.1</td>
</tr>
<tr>
<td></td>
<td>2 s.e.</td>
<td>1.4</td>
<td>1.7</td>
</tr>
<tr>
<td><em>Aplysia californica</em></td>
<td>( \bar{x} )</td>
<td>6.5</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>2 s.e.</td>
<td>1.7</td>
<td>1.0</td>
</tr>
</tbody>
</table>
B. Response to Test Species

Quantified behavioral responses showed that scallops distinguished the predatory snails, U. cinerea, E. caudata, T. lapillus and B. canaliculatum and the predatory starfish A. forbesi, from the non-predatory snails, L. littorea and I. obsoleta and the non-predatory sea urchin, A. punctulata (Tables II and III).

There was a distinct difference among scallop responses to test species. When response time was plotted against number of claps (Fig. 2), two separate groups representing scallop responses to predators and non-predators became evident. Characteristically, scallops responded to predators quickly and vigorously as evidenced by lower mean response times and higher mean number of swimming claps. Further, scallops were able to carry out this discrimination and consistently distinguish predators from non-predators at both 12°C and 20°C.

When responses to non-predators alone were examined, there was a significant effect on scallop behavior (Table IV). Mean response times were higher and mean number of swimming claps were lower when scallops were stimulated with A. punctulata compared to responses to either I. obsoleta or L. littorea (Fig. 2).

Responses to predators as a group were also significantly influenced by the test species used (Table IV) but were more varied (Fig. 2). Scallops responded to the starfish A. forbesi with fewer swimming claps than to any other test predator (t-test). However, response times to this starfish were similar to those for most predatory snails with the exception of higher response times to E. caudata (at 12°C) and B. canaliculatum (t-test). Scallops exhibited the highest number of swimming claps when stimulated with T. lapillus and U. cinerea.

The significant temperature effect (Table IV) was evidenced by consistently lower mean response times to predators at 20°C (Table II). No significant interactions between the effects of test species and temperature were observed.

9.2.4 Discussion

Sensitivity of four selected peripheral regions of the bay scallop, A. irradians, was variable and suggested that U. cinerea, at least, can successfully attack scallops from the dorsal hinge without evoking an escape response. In this region, the mantle is behind the hinge with no tentacles to contact an intruder. Responses to U. cinerea touching the dorsal hinge appeared to be due mainly to mechanical stimulation, evidenced by long response times and less than one swimming clap. Typical escape behavior which resulted from stimulation at three other areas, suggested scallops mechanically and chemically recognize U. cinerea primarily through tentacle contact with the snail rather than from chemical information in the water column. Others have found that physical contact with a predator provokes more reliable responses from various molluscs (Gore, 1966: Thomas & Gruffydd, 1971; Bullock, 1953; Turner, 1955).
Fig. 2. Scattergram of mean scallop response time vs. mean number of swimming claps when stimulated with various test species at 12 and 20°C: Ar. Arbacia punctulata; L. Littorina littorea; I. Ilyanassa obsoleta; As*. Asterias forbesi; B*. Busycon canaliculatum; E*. Eupleura caudata; U*. Urosalpinx cinerea; T*, Thais lapillus; *, predators.

Table IV: A summary of F values and degrees of freedom (in parenthesis) for six analysis of variance tests. (* indicates p < .05)

<table>
<thead>
<tr>
<th></th>
<th>All Data</th>
<th>Non-Predators</th>
<th>Predators</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>RESPONSE TIME</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Test Species (S)</td>
<td>*75.05 (7,165)</td>
<td>*26.31 (2,55)</td>
<td>*11.35 (4,99)</td>
</tr>
<tr>
<td>Temperature (T)</td>
<td>3.29 (1,165)</td>
<td>0.33 (1,55)</td>
<td>*12.31 (1,99)</td>
</tr>
<tr>
<td>Interaction (SxT)</td>
<td>1.08 (7,165)</td>
<td>0.37 (2,55)</td>
<td>0.55 (4,99)</td>
</tr>
</tbody>
</table>

| **SWIMMING CLAPS**   |          |               |           |
| Test Species (S)     | *82.20 (7,165) | *13.71 (2,55) | *13.75 (4,99) |
| Temperature (T)      | 2.37 (1,165)  | 0.02 (1,55)  | 3.06 (1,99)  |
| Interaction (SxT)    | 0.91 (7,165)  | 0.43 (2,55)  | 0.79 (4,99)  |
The feeding habits of the test species are quite varied. We observed *U. cinerea*, *E. caudata* and *A. forbesi* actively feeding on scallops during dives in Point Judith Pond. Although we did not observe *B. canaliculatum*, a known predator of scallops (Magalhaes, 1948), feeding, we captured a single individual near the scallop beds. *Thais lapillus*, however, is an unlikely predator of scallops because they are predominantly found in exposed, rocky intertidal habitats where they preferentially feed on barnacles (Connell, 1961). We never observed *I. lapillus* in or near the estuarine scallop beds in Point Judith Pond. Both non-predatory snails *L. littorea*, whose food preference is *Ulva*, *Enteromorpha*, and diatoms, (Newell, 1958) and *I. obsoleta*, which feeds mainly on microflora on the sediment on intertidal flats (Scheltema, 1964) were found on the scallop beds, while the sea urchin *A. punctulata*, which feeds primarily on *Laminaria* and *Fucus* (Lawrence, 1975) was not.

The ability of bay scallops to recognize predators through escape responses has been demonstrated here. While Thomas & Gruffydd (1971) have shown the scallop *P. maximus* capable of distinguishing predatory from non-predatory starfish, our results demonstrated bay scallops were capable of discriminating predatory from non-predatory gastropod molluscs. Further, bay scallops appeared equipped to recognize and escape from *I. lapillus*, even though this gastropod feeds in a different habitat. Appearance of escape responses then was generally correlated with feeding habits of the stimulating species and not with probability of encounter. Yarnall (1964) came to a similar conclusion for the escape response of *Tegula funebralis*.

Although scallops discriminated a starfish from a sea urchin, responses to these echinoderms were less vigorous compared with scallop responses to gastropod molluscs. A partial explanation may be that echinoderms and gastropods provide scallops with very different chemical and mechanical stimuli for discrimination.

Ecologically, it is not surprising that bay scallops recognized predators at both 12°C and 20°C because scallop predators actively feed at these temperatures (Carriker & Van Zandt, 1972; Manzi, 1970; MacKenzie, 1969; Hanks, 1957). However, temperature did influence scallop response time to predators. Scallops took longer to respond at 12°C. At low temperatures, chemical sensitivity of the tentacles may decrease, or the amount of active substance from predators may be lower (Yasumoto, *et al*. 1966) or both. Whereas the number of swimming claps, caused by rhythmic activity in the adductor muscle and maintained by motor output from a stretch receptor feedback system (Stephens, 1978), seemed temperature independent, once initiated.

Predator discrimination, besides allowing prey to escape predators (Feder, 1963), could also reduce time and energy wasted on needless escape responses. Filter feeders are usually food limited and, as a consequence, their time-energy budget is such that they need to invest most of their time feeding (Wilson, 1975). Predator recognition could be used by scallops to minimize feeding interruptions. Thomas & Gruffydd (1971) have further reasoned that, since the scallop, *P. maximus*, often lives in depressions in the substrate, unnecessary escape responses could easily carry it out of a depression, forcing the scallop to invest extra time and energy in construction of a new depression. A similar case can be made for bay scallops which are often found in shallow depressions.
9.3 Section III.

Predation, attack success, and attraction to the Bay Scallop, Argopecten irradians by the Oyster Drill *Urosalpinx cinerea*

**Abstract**

Investigation of the intensity of predation by the oyster drill, *Urosalpinx cinerea* (Say), on the bay scallop, *Argopecten irradians* (Lamarck), was carried out in field and laboratory studies. Field measurements of densities of the oyster drill and the bay scallop were respectively, 3.6 m$^{-2}$, and 21.1 m$^{-2}$ on a scallop bed in Ninigret Pond, Charlestown, Rhode Island. The mean density of snails attacking scallops was 1.7 m$^{-2}$. In a laboratory study of attack success, an average of 72.3 percent of drill attacks led to death of the scallop. Snails were also shown to be strongly attracted to scallop effluent in a choice chamber.

9.3. Introduction

Barnacles, oysters, and mussels are often listed as primary prey for the oyster drill, *Urosalpinx cinerea* (Say) (Wood, 1968; Carriker & Van Zandt, 1972). It is also known that drills are guided by olfactory cues to their common prey (Wood, 1968; Pratt, 1974) but evidence that drills attack scallops is scarce although Marshall (1960) found that many *U. cinerea* were attracted to caged bay scallops in a Connecticut estuary. Our purpose was to determine the importance of *U. cinerea* as a predator of the bay scallop *Argopecten irradians* (Lamarck), on a natural scallop bed, to study drill attack success, and to examine the effect of scallop effluent on oyster drills in a choice chamber.

9.3.2 Methods & Results

9.3.3 Field Study

1. Methods

Field studies were carried out using SCUBA during July 1979 on a natural scallop bed in Ninigret Pond, Charlestown, Rhode Island. Square meter quadrats were randomly placed to measure scallop and oyster drill densities as well as the density of drill attacks. Attacks were defined as single or multiple occurrences of *Urosalpinx cinerea* attached to a live scallop. Densities were measured by removing all scallops and oyster drills from a m$^2$ quadrat after noting the number of drill attacks. Counts for each m$^2$ were made at the surface. Animals touching the square meter frame were considered to be within the quadrat. Mean densities were estimated from 21 m$^2$ quadrats. Temperature measurements ranged from 23$^\circ$C to 26$^\circ$C while salinity was constant at 28 0/00. Scallop and oyster drills collected during this phase were held in ambient running sea water for subsequent laboratory studies.
2. Results

The mean (+ 2 s.e.) scallop density on a scallop bed in Ninigret Pond was 21.2 ± 2.3 per m², while the density of oyster drills was 3.6 ± 1.2 per m². No other major predators, including the starfish *Asterias forbesi* (Desor), were observed during data collection. Although one blue crab, *Callinectes sapidus* (Rathbun), was found eating scallop remains, there was no evidence to show that the crab actually killed the scallop. The mean (+ 2 s.e.) density of attacks by *Urosalpinx cinerea* was 1.7 ± 0.6 per m². Our calculations show that 7.9 percent of the scallops on this bed were being attacked by 47.0 percent of the drill population and that 6.8 percent of these scallops were attacked by more than one drill.

9.3.4 Laboratory Assessment of Oyster Drill Attack Success

1. Methods

To examine attack success, drills and scallops collected from Ninigret Pond, were placed in a tank (118 x 240 x 27 cm), with a bottom area of 2.8 m². Only drills measuring 1.5 - 2 cm from apex to siphon were used. Prior to testing, all drills were provided with liberal numbers of live scallops on which to feed. After 24 hours, each scallop with a drill on its shell was isolated in a 40 liter tank with running sea water where the fate of each scallop could be monitored. Attacks were considered unsuccessful when a snail was found off of the scallop and successful if examination of a dead scallop revealed a completed borehole. Dead scallops with boreholes were assumed to have died directly or indirectly as a result of a snail attack. This procedure was replicated three times with different snails at a mean (+ 2 s.e.) water temperature of 19.9 ± .8°C and a mean (+ 2 s.e.) salinity of 30.0± .4 0/00 during August and September 1979.

2. Results

Of the attacking oyster drills, an average (X ± 2 s.e.) of 72.3 ± 9.8 percent succeeded with their attacks culminating in scallop death while only an average (X ± 2 s.e.) of 25.9 ± 12.2 percent of scallops survived attacks. Results of the three replicates are displayed in Table I. Although both replicates performed at 20°C appear to be the same, attack success of snails at 17.70C tends to be lower even though it is not significantly different (chi-square). The mean time for success is similar at all temperatures, averaging 6.1 days (range: 2 - 15 days) with the majority of successful attacks occurring between day 4 and day 7.

9.3.5 Oyster Drill Response to Scallop Effluent

1. Methods

Scallop and oyster drills collected as previously described from Ninigret Pond were held in ambient temperature, unfiltered, running sea water for two weeks prior to experimentation. Oyster drills were supplied with live scallops for food. During the experiments, temperatures and salinities averaged (X± 2 s.e.) 21.3 ± 2.0°C and 30.0 ± .4 0/00 respectively.
TABLE I

Laboratory assessment of the percentage of successful attacks by the oyster drill, *Urosalpinx cinerea*, on the bay scallop, *Argopecten irradians*, and mean time required to complete the attack.

<table>
<thead>
<tr>
<th>Replicate</th>
<th>n</th>
<th>% successful attacks</th>
<th>% unsuccessful attacks</th>
<th>X ± 2 s.e. days until scallop death</th>
<th>X ± 2 s.e. temp. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Replicate 1</td>
<td>18</td>
<td>77.8</td>
<td>16.7</td>
<td>6.1 ± 1.5</td>
<td>20.9 ± 0.8</td>
</tr>
<tr>
<td>8/22 - 9/5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Replicate 2</td>
<td>17</td>
<td>76.5</td>
<td>23.5</td>
<td>5.9 ± 1.3</td>
<td>20.6 ± 0.8</td>
</tr>
<tr>
<td>8/29 - 9/4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Replicate 3</td>
<td>16</td>
<td>62.5</td>
<td>37.5</td>
<td>6.3 ± 2.1</td>
<td>17.7 ± 0.7</td>
</tr>
<tr>
<td>9/20 - 10/1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ \bar{X} = 72.3 \]
\[ X = 25.9 \]
\[ X = 6.1 ± 0.9 \]
\[ \bar{X} = 19.9 ± 0.7 \]

2.s.e. = 9.8

2.s.e. = 12.2
Trials were carried out with epoxy coated plywood choice chambers designed by Pratt (1974). Continuously running sea water was first fed into two reservoirs (21 x 19 x 22 cm) from which the water was gravity fed into wells on both sides of the choice chamber. During tests, scallop effluent was introduced into sea water by placing thirty live scallops into one of the reservoirs. Water from the wells overflowed down both ramps a distance of 19.5 cm to exit through holes in a drain plate at the center of the apparatus. Flow rates to the wells were set with valves at 250 ml per minute. Dye experiments showed that mixing occurred only in a limited area over the drain plate holes. To eliminate possible directional bias, scallop effluent was presented on different sides of the choice chamber after six drills were tested.

Trials were performed by starting three marked snails directly in the center of the drain plate with their long axes perpendicular to the chamber length. After one hour, the distance in cm each drill traveled away from the start was measured from the center of the chamber to the tip of the drill siphon. Drills were replaced with new snails after they responded or if they failed to move from the starting position after an hour. Although Wood (1968) found that Urosalpinx cinerea do not follow each others trails, as a precautionary measure, ramps were scrubbed after every six drills tested with sea water during each trial. If a snail reached the well in less than an hour, both distance and time in minutes were recorded. During the first of two trials, 88 different drills were presented with plain sea water on both sides of the chamber to test for chamber bias. In the second trial, 100 different drills were presented with a choice between scallop effluent and plain sea water to measure drill response to scallops. Data were analyzed using the chi-square and t-test.

2. Results

When presented with a choice between plain sea water versus plain sea water in trial 1 (Table II), the number of Urosalpinx cinerea responding and moving greater than halfway up the ramp (10 cm) was the same for both sides of the chamber (chi-square). Measurements of the distance traveled and the rate that drills moved up either ramp showed no difference between sides, further indicating that there was no significant apparatus bias (t-test).

Responses of drills presented with a choice between sea water containing scallop effluent and plain sea water in trial 2 (Table II) showed a significant number of snails responded to scallop effluent compared to those responding to plain sea water (chi-square). The number of snails moving more than 10 cm was also greater in water containing scallop effluent (chi-square). Further, drills traveled twice the distance and speed in scallop effluent compared to distances traveled in plain sea water.

9.3.6 Discussion

Urosalpinx cinerea is an active predator of Argopecten irradians in Ninigret Pond, Rhode Island and was the only predator found during our observations. Although other predators have been listed as preying on scallops (Marshall, 1960) we have no data on their actual or potential
TABLE II
Responses of Urosalpinx cinerea to bay scallop effluent and plain sea water in the choice chamber

<table>
<thead>
<tr>
<th>Water Presented</th>
<th>Trial 1 n = 88</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plain Sea Water</td>
<td>Plain Sea Water</td>
<td></td>
</tr>
<tr>
<td>number responding</td>
<td>44</td>
<td>44</td>
</tr>
<tr>
<td>number moving ≥ 10 cm</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>x ± 2 s.e. cm traveled</td>
<td>2.6 ± 1.4</td>
<td>3.8 ± 1.8</td>
</tr>
<tr>
<td>x ± 2 s.e. rate of movement (cm/min)</td>
<td>0.08 ± 0.07</td>
<td>0.09 ± 0.05</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Water Presented</th>
<th>Trial 2 n = 100</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scallop Effluent</td>
<td>Plain Sea Water</td>
<td></td>
</tr>
<tr>
<td>number responding</td>
<td>65</td>
<td>35</td>
</tr>
<tr>
<td>number moving ≥ 10 cm</td>
<td>33</td>
<td>7</td>
</tr>
<tr>
<td>x ± 2 s.e. cm traveled</td>
<td>10.8 ± 2.0</td>
<td>5.4 ± 2.2</td>
</tr>
<tr>
<td>x ± 2 s.e. rate of movement (cm/min)</td>
<td>0.35 ± 0.1</td>
<td>0.17 ± 0.11</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Water Presented</th>
<th>Trial 2 n = 100</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scallop Effluent</td>
<td>Plain Sea Water</td>
<td></td>
</tr>
<tr>
<td>number responding</td>
<td>65</td>
<td>35</td>
</tr>
<tr>
<td>number moving 10 cm</td>
<td>33</td>
<td>7</td>
</tr>
<tr>
<td>x ± 2 s.e. cm traveled</td>
<td>10.8 ± 2.0</td>
<td>5.4 ± 2.2</td>
</tr>
<tr>
<td>x ± 2 s.e. rate of movement (cm/min)</td>
<td>0.35 ± 0.1</td>
<td>0.17 ± 0.11</td>
</tr>
</tbody>
</table>
impact in Ninigret Pond. During the spring, when water temperatures were 10°C, we observed Asterias forbesi preying on scallops in the study area. However, starfish were conspicuously absent from our summer observations, possibly owing to their inability to cope with temperatures above 25°C (Mackenzie, 1969). Further, our observations on laboratory held starfish confirm that mortalities were unusually high when ambient water temperature was above 20°C. U. cinerea, unlike starfish, feeds at a maximum rate (Hanks, 1957; Manzi, 1970) at the salinities and temperatures encountered during our observations.

Our laboratory studies show that not all drill attacks reach a successful conclusion. More than one quarter of all drill attacks on scallops are not successful and may be a direct result of the vigorous escape response (Ordzie and Garofalo, 1980) which bay scallops employ when attacked. Our observations indicate that the rapid movements of the scallop valves during this response were sufficient to shake off an attached drill. Further, we have observed live scallops in the field with complete and incomplete boreholes. Calculations of predation by U. cinerea on scallops based only on observed attacks without correction for unsuccessful attacks would lead to an overestimation of predation intensity.

Our measurements of time required to successfully drill scallops is an agreement with rates for U. cinerea to drill oysters, (Carriker and Van Zandt, 1972) and are similar to those found for Ocinebra japonica (Chew, 1960).

Environmental parameters have such strong influences on feeding rates of predatory snails (Menge, 1978) that predation rates differ between habitats and even between individuals. Such observations make it difficult to generalize about predation rates. The impact of predation is very specific for habitat location and environmental conditions.

We have also shown that U. cinerea move toward water containing scallop effluent. This strong attraction was heretofore only observed when drills were presented with barnacle effluent and is unusually strong compared to other bivalve species tested, including oysters (Wood, 1968; Pratt, 1974). Further, once stimulated, oyster drills proceed to double their rate of locomotion toward the scallops. Moving faster toward prey effluent increases the probability of prey encounter in a shorter time period. By decreasing the time between recognition of prey effluent and contact with mobile prey, drills also increase the probability of being able to execute an attack before the prey changed location.
9.4.1 Introduction

Investigations of community type responses were stimulated by results from previous work (Section 9.1) which suggested that sublethal concentrations of dispersants had adverse effects on scallop behavioral escape responses and starfish posturing reflex. These results led us to create a simple community and ask what would happen if both predator and prey were dosed and placed together in large laboratory tanks. How many scallops would survive in each treatment? Can we detect changes in individual spacing with treatment? The purpose here was to study a scallop-starfish community interaction after dosing under laboratory conditions.

9.4.2 Methods and Materials

Preparation of dosing stock solutions was identical to the method already described (Section 9.1). Stock solutions of each treatment, oil, dispersant, and oil-dispersant were diluted to make dosing mixtures of 12.5% stock solution and 87.5% sea water. This concentration was previously determined to be sublethal at 10°C for scallops (Section 9.1). Forty scallops and six starfish were statically dosed together in 20 liters of treatment solution for six hours with aeration. After dosing, all animals from each treatment, plus a control with starfish and a control without starfish were removed and randomly placed into respective 2.8 m² epoxy coated plywood tanks filled to a height of 18 cm. A constant flow of ambient temperature sea water (20 liters/min) was provided to each of the five tanks representing each treatment. This experiment was replicated twice with temperatures and salinities averaging (X ± 2 s.e.) 12.1 ± 1.2°C and 30.5 ± 0.40/00 respectively during the experiments.

Scallops in the 2.8 m² tanks were at a density of 15 per m², well within the natural densities we found on a scallop bed (section 9.3). Since no data was available for starfish densities, we chose to use six.

After dosing, the number of living scallops in each tank was recorded for 15 days. Survivorship results were analyzed using the chi-square statistical test. Additionally, nearest neighbor distance (cm) of scallops was recorded for each treatment tank during the 15 days. The analysis of variance test was used to analyze the nearest neighbor data. Dead scallops were not removed until the end of the experiment to approximate field conditions.

9.4.3 Results

A. Survivorship

Data from both replicates was combined since no significant replicate difference was found. Scallop survivorship at day five for the community experiment was compared to a five day survivorship experiment previously completed (Section 9.1) at 10°C for scallops exposed to 12.5% stock solution without starfish (Table 1). 10°C was chosen since the average temperature for the community experiment was 13.1°C. Each treatment, oil, dispersant and oil-dispersant, was independently compared to the control for the experiment. There was no significant difference
in survivorship between the control and the treatments when starfish were absent (100%) ($x^2$). However, with starfish present, survivorship in the dispersant and oil-dispersant treatments was significantly lower than for controls ($x^2$). At day 15 after dosing, with starfish present, scallop survivorship in the dispersant and oil-dispersant treatments was also significantly lower than controls ($x^2$) (Table 2).

There were no starfish mortalities in any treatment during the entire community experiment.

### Table 2

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Percent Surviving with Starfish</th>
<th>Significance</th>
<th>d.f.</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TREATMENT</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>74.1</td>
<td>1.54</td>
<td>1</td>
<td>&lt; .5</td>
</tr>
<tr>
<td>D</td>
<td>48.8</td>
<td>12.22*</td>
<td>1</td>
<td>&lt; .001</td>
</tr>
<tr>
<td>OD</td>
<td>53.8</td>
<td>9.12*</td>
<td>1</td>
<td>&lt; .01</td>
</tr>
</tbody>
</table>

9.44 Spacing

Scallop spacing was found to be significantly different in the oil-dispersant treated scallops (ANOVA Table 3). The mean distance to nearest neighbor in the oil-dispersant tank was significantly higher than both the control without starfish and the control with starfish (ANOVA, $F = 7.11$, d.f. = 4, 50, $P = .0001$; LST = 6.75, d.f. = 50, $P = .05$). Nearest neighbor distance for the oil treated and the dispersant treated scallops was not different from the controls.
TABLE 3 Spacing of scallops in $\bar{x}$ cm to Nearest Neighbor for Five Experimental Treatments: C - control without starfish, C starfish - Control with starfish, O - oil, D - Dispersant, OD - Oil and Dispersant. *P .05 < .05 ANOVA

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>C Starfish</th>
<th>O</th>
<th>D</th>
<th>OD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\bar{x}$ cm</td>
<td>12.7</td>
<td>10.2</td>
<td>10.4</td>
<td>16.1</td>
<td>25.5*</td>
</tr>
<tr>
<td>2 S.E.</td>
<td>.95</td>
<td>1.64</td>
<td>1.44</td>
<td>3.62</td>
<td>9.7</td>
</tr>
</tbody>
</table>

9.4.5 Discussion

The goal of this study was to determine how a simple predator-prey community would be affected by oil, dispersant and an oil-dispersant treatment. Scallops and starfish had previously been tested separately with these same treatments and the behavioral changes (Section 9.1) suggested a community type experiment.

In our previous study, scallops were found to have diminished discrimination between predators and non-predators when treated with dispersant and oil-dispersant, but that oil treated animals were not significantly different from the control animals. Response to food by starfish was significantly slowed by all treatments. When both predator and prey were treated as a community, scallop survivorship was significantly reduced in the dispersant and oil-dispersant treatments beyond that expected because of hydrocarbon treatment or starfish predation alone. Since scallop survivorship in the oil treatment was not different from controls, the slowed ability of the starfish to respond to food did not appear to affect their ability to feed on scallops. This again shows the differential susceptibility of the test animals to pollutants (section 9.1).

Scallops were significantly farther apart in the oil-dispersant treatment. Perhaps it is a behavioral advantage at this time of year for scallops not affected by treatment to be closer together during spawning (personal communication, John Karlsson).

The two measured aspects of this experiment, survivorship and spacing, appeared to be affected, but not always by the same treatments. Only additional studies could begin to unravel the details of the various community responses reported. One overriding observation remains: at concentrations far below the LD 50, dispersant treated scallops suffer greater than 50 percent mortality in the presence of starfish. These results are not predicted by classical bioassay methods. Community studies are rare to non-existent in bioassay work but could prove extremely useful in the prediction of ecological impacts by dispersants.
## ADDENDUM

### Analysis of Hydrocarbons in Stock Solutions

<table>
<thead>
<tr>
<th></th>
<th>Oil (Kuwait Crude)</th>
<th>Dispersant</th>
<th>Oil in mixture by difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic</td>
<td>26.34 mg/liter</td>
<td>19.54 mg/liter</td>
<td>19.6 mg/liter</td>
</tr>
<tr>
<td>Aliphatic</td>
<td>18.28 mg/liter</td>
<td>13.88 mg/liter</td>
<td>6.9 mg/liter</td>
</tr>
<tr>
<td>Total Hydrocarbons</td>
<td>44.62 mg/liter</td>
<td>Total Hydrocarbons</td>
<td>Total Hydrocarbons</td>
</tr>
<tr>
<td></td>
<td></td>
<td>59.92 mg/liter</td>
<td>26.5 mg/liter</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Oil &amp; Dispersant</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic</td>
<td>39.14 mg/liter</td>
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</tr>
<tr>
<td>Aliphatic</td>
<td>20.78 mg/liter</td>
<td></td>
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</tr>
<tr>
<td>Total Hydrocarbons</td>
<td>59.92 mg/liter</td>
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<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Seawater Control</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic</td>
<td>0.46 mg/liter</td>
<td></td>
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</tr>
<tr>
<td>Aliphatic</td>
<td>0.024 mg/liter</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Hydrocarbons</td>
<td>.484 mg/liter</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
10.0 References
10.1 Section 2 References
Section 2. References

1) Reynolds, O., Chem. News: 44, 211 (1881)
2) Smoluchowski, J., Phy. Chem: 92, 129 (1917)
7) Mahagan, L.D.; Kolloid Z; 69, 16, (1934)
9) Lang, S.B.; Ph.D. Thesis, University of California (Berkly) (1962)
10) Nielsen, L.E.; Wall, R., and Adams, G., J. Colloid Sc.: 13, 441 (1958)
20) Stefan, J.; Ann. Physik; 29, 655 (1886)
21) Eotovos, R.; Ann. Physik; 27, 448 (1886)


37) Hadamard, J., Compt. Rend.; 154, 1735 (1911)


44) Jasper, W.L., Kim, T.J. and Wilson, M.P., 'Chemical Dispersants for the Control of Oil Spills', American Society for Testing
Materials, 203 (1978)

Section 10.2 Section 8 References
References


10.3 Section 9 References


Ordzie, C. J. & Garofalo, G. C. (1980). Behavioral recognition of molluscan and echinoderm predators by the bay scallop, 

Ordzie, C. J. & Garofalo, G. C. (1980). Predation, attack success, and attraction to the bay scallop, 
Argopecten irradians by the oyster drill, *Urosalpinx cinerea*. Subm. for Publ.


9.2.5 References


9.3.7 References


11.0 Bibliographies
11.1 Section 2 Bibliography
Section 2. Bibliography


Eotovos, R.; Ann. Physik; 27, 448 (1886)


Hadamard, J., Compt. Rend.; 154, 1735 (1911)

Hardy, W.B.; Proc. of Roy. Soc. (London) A86, 634, (1911)

Hawksley, G.I.; Ph.D. Thesis, University of Birmingham (1958)


Kintner, R.C.; Chem. Eng.; 4, 51 (1963)

Lang, S.B.; Ph.D. Thesis, University of California (Berkeley) (1962)


Mahagan, L.D.; Kolloid Z; 69, 16, (1934)

McDonald, J.E.; J. Meteorology, 11, 478 (1954)


Prausnitz, J.; 'Molecular Thermodynamics of Fluid Phase Equilibria', Interscience Publishing Co.; New York (1973)


Smoluchowski, J., Phy. Chem: 92, 129 (1917)

Stefan, J.; Ann. Physik; 29, 655 (1886)


11.2 Section 6 Bibliographies

11.2.1 Bibliography I: Fisheries and Biological References
11.2.2 Bibliography II: Behavior and Effects of Hydrocarbons
11.2.3 Bibliography III: Mathematics and Descriptions of Physical Phenomena
11.2.1 BIBLIOGRAPHY I: FISHERIES AND BIOLOGICAL REFERENCES


Coastal Resources Center, Fishing and Petroleum Interactions on Georges Bank, prepared for the N.E. Regional Commission, Energy Tech. Rep. 77-1.


Corlett, J., Winds, Currents, Plankton, and Year-class Strength of Cod in the Western Barents Sea, IONAF Spec. Publ. #6: 373-385.


Daan, N., Results of a Study of Consumption and Production of North Sea Cod, ICES CM/F:38, 1974.


Exp. Mer. 164: 73-76.


Hardy, E., "Natural History and Habits of the Cod Family," Atlan. Fish. 23 (9): 10, 1942.


Tarzwell, C.M., "Toxicity of Oil and Oil Dispersant Mixtures to Aquatic Life," presented at Proc. Sem. on Water Poll. by Oil, Avenmore, Scotland, 1970


Okubo, A., "Diffusion Induced Instability in Model Ecosystems: Another Possible Explanation of Patchiness," OBI No. 86, 1974.


12.0 Appendices
12.1 Section 2 Appendices

12.1.1 Appendix A Error Analysis
12.1.2 Appendix B Measurement of Interfacial Tension
12.1.3 Power Input
Section 2. Appendix A - Error Analysis

The error in the measurement or calculation that appears in any quantity in an investigation is the net result of different errors in the measurements or calculations preceding it. Thus the average drop-size, hold-up and interfacial area carries errors in them that depend on the experimental technique involved in measuring them or the use of quantities that have errors in calculating them.

The drop-size was measured using a microscope, and the size could be measured up to 0.25 microns. Thus the maximum possible error that could have arisen in the measurement of drop-size was ±0.25 microns.

The hold-up was measured using an Infra-red Spectrometer and within the range of measurement, the maximum error possible was ±1 ppm.

Thus due to an error in the measurement of drop-size the Sauter mean was in error as follows.

\[ \varepsilon_{SM} = \frac{\sum_{i} (d_i + \varepsilon_i)^3}{n_i (d_i + \varepsilon_i)^2} = 0 (\varepsilon_i) \]

Interfacial area was given by

\[ A \approx \frac{6 \times \phi}{SM} \]

Due to an error in the measurement of hold-up and Sauter mean, the interfacial area could have an error up to

\[ \frac{6(\phi + \varepsilon_\phi)}{(SM + \varepsilon_{SM})} = 0 (0.4 m^2/m^3) \]

The experiments at room temperature varied over a range of about 2.5 C. The variation in viscosity over such a small range of temperature is less than 5 percent (45). The interfacial tension over the same range of temperature is estimated to vary by about 1 dyne/cm. The effect of temperature on the drop-size can be estimated by the correlation of Shinnar (32). The error in the average drop-size due to temperature is found to be

\[ \text{constant} \times (\sigma + \varepsilon_\sigma)^{5/8} = 0 (0.25 \text{ microns}) \]

From the above discussion, it can be seen that the maximum error that could be expected in the measurement of the drop-size is of the order of ±0.5 microns. The hold-up is estimated to be accurate to within ±1 ppm and the interfacial area accurate to within 0.4 m²/m³.
Interfacial tension of Kuwait crude oil-sea water system was investigated in the presence of a dispersant. The interfacial tension is an important parameter when studying the stability of liquid-liquid systems. A lower value of interfacial tension means that the energy necessary to break up the dispersed phase will be proportionally lower and the dispersion will be stable.

Molecules in the bulk liquid phase experience the same average force in all directions. But at the interface this is not the case. Since the molecules across the interface are of a different species the forces are not evenly balanced. This results in a condition in which the interface is in a state of tension. The name "Surface Tension" is used when the interface is between a liquid and a vapor, and "Interfacial Tension" when the interface is between two liquids or a liquid and a solid.

When it is desired to separate two liquid phases after they have been brought into intimate contact (e.g., in liquid-liquid extraction) the interfacial tension should be high so that the coalescence is rapid. On the other hand, when one liquid is to be dispersed in another liquid, the interfacial tension should be low so that the break up is rapid and the dispersion is stable.

With few exceptions, a third component tends to reduce the interfacial tension between two pure components. The reducing effect is more pronounced if the third component is more concentrated at the interface than in the bulk. This is the case when surfactants and dispersants are used. The interfacial tensions between two liquids is highest when pure, and falls off to zero at plait point.

When a liquid surface (or liquid-liquid interface) is newly formed, a finite time is needed for establishing the state of equilibrium. During this period surface tension (or interfacial tension) is time dependent. In the case of the formation of pure liquid interfaces, it has not yet been possible to measure tension before the final value has been achieved, because the time involved is very small. However, when dealing with solutions the time factors involved are quite large and it is possible to measure the interfacial tension in the transient state. Surface tension or interfacial tension before equilibrium has been established is called "dynamic" to distinguish it from the equilibrium or "static" value.
Methods of Measurement

1) **Capillary height-method.** This is probably the simplest method available. When a capillary is inserted below the interface of a two liquid system, due to the excess free energy of the interface, the liquid in the lower layer rises to a higher level within the capillary.

But for the crude oil water system under study, this method could not be used as the darker upper layer of the crude prevents observation of the capillary height which should be known to correlate the interfacial tension.

2) **Drop Weight Method.** In this method drops are allowed to form at the top of a capillary immersed in another liquid. From a knowledge of the dimensions of the drop and its weight it is possible to calculate the interfacial tension. Since drops have to be formed at a finite site this method is not applicable in systems where a surfactant is present.

3) **Ring Method.** A platinum ring is pulled up from the interface of the liquids whose interfacial tension is to be measured. The force that is necessary is measured by a torsion balance. Again this method is inapplicable as this is a dynamic method, for the reasons given above.

4) **Bubble Pressure Method.** The pressure difference across a bubble or drop in another liquid is proportional to the interfacial tensions. Therefore, if it is possible to measure the pressure difference across the bubble we should be able to calculate the interfacial tension. Being a dynamic method this had to be discarded in favor of a semi-static method.

5) **Pendant Drop Method.** Pendant drop method consists of making a drop form at the tip of a capillary tube and let it hang in the second fluid. If the density difference is not appropriate, the drop can be made to rise up from the tip of the capillary rather than let it hang. The shape of the drop reflects a balance between interfacial tension and the gravitational forces and can be used to measure the interfacial tension. The static nature of the method makes it suitable for use where diffusional effects are involved.

The shape of the pendant drop is determined by the fact that the change in the hydrostatic pressure in the vertical direction is balanced by an equivalent change in the Laplace pressure

\[ \Delta P = \frac{2\gamma}{b} \]

where \( b \) is the radius of curvature at the apex of the drop.
At point $P$, a distance $z$ below the apex, the pressure drop is given

$$\Delta p = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$$

$$= \frac{2\gamma}{b} + (\rho_1 - \rho_2) gz$$

where $R_1$ and $R_2$ are the radii of curvature. The above equation is rearranged into the following dimensionless form:

$$\frac{1}{R_1/b} + \frac{\sin \theta}{x/b} = 2 + \frac{\Delta \rho gb^2}{\gamma} \left( \frac{z}{b} \right) = 2 + \frac{z}{b} \theta$$

where $\theta = \frac{\Delta \rho gb^2}{\gamma}$

and

$$R_1 = \left[ 1 + \frac{dz}{dx} \right]^{2/3} \quad \frac{d^2z}{dx^2}$$

Bashforth and Adams carried out the numerical integration of the above equation for a number of values of $B$. As the radius $b$ is difficult to determine experimentally, Bashforth and Adams presented a table of $x_e/b$ as a function of $B$, where $x_e$ is the equation radius. i.e.,

$$x_e/b = f(\theta)$$

so that

$$\gamma = \Delta \rho g x^2_e / B \left[ f(\theta) \right]^2$$

For larger drops only, the radius of curvature in the plane of the paper need be considered. In this case, the equation for $\gamma$ becomes

$$\gamma = \Delta \rho gh^2/2$$

and this represented a limiting case where $h$ is the distance from the apex to the equatorial line of the drop.

Porter made use of the tables of Bashforth and Adams to show that the
differences in \( \frac{h^2}{2x^2_e} \) and \( \frac{a^2}{2x^2_e} \) is accurately represented by

\[
\frac{h^2}{2x^2_e} - \frac{a^2}{2x^2_e} = 0.3047 \left( \frac{h^3}{x^3_e} \right) \left( 1 - 4\frac{h^2}{x^2_e} \right)
\]

where

\[
a^2 = 2\gamma/\Delta p g
\]

This permits the direct calculation of the surface tension from knowledge of \( h \) and \( x_e \), both of which are accurately measurable quantities.

\( \beta \) can also be written as

\[
\beta = \frac{\Delta pgde}{H}, \ \text{where}
\]

\[
H_2 = \beta \left( \frac{d_e}{b} \right)^2
\]

The Bashforth and Adams tables were re-worked by several authors into a form giving \( 1/H \) as a function of \( S = d_S/d_e \).

It should not be thought that the ratio \( S \) is unique. Any other well-defined dimensions of the drop can be employed. Winkel has suggested that \( d_{\min}/d_e \) can be used, where \( d_{\min} \) is the smallest diameter which is observed above the \( d_e \) plane for a certain range of shapes (26). However, such a choice seems to be disadvantageous because the minimum diameter is often near the tip of the capillary and it may be affected by the irregularities in its shape. In order to alleviate this problem, Roc, Bacchetta and Wong defined a series of diameters as given by:

\[
Z_n = (n/10) \cdot d_e
\]

where \( n = 8 \ldots \ldots \ldots 12 \) and the characteristic shape factor is given by:

\[
S_n = \frac{d_n}{d_e}
\]

A series of tables giving \( 1/H \) as a function of \( S_n \) has been computed by the integration of the fundamental differential equation by a digital computer.

**Apparatus and Measurement Method**

The apparatus consists of a capillary tube of approximately 0.1 cm diameter as shown in Figure 1. The tube was bent into the shape of 'L' and connected to a small reservoir. The reservoir has an overflow port
MEASUREMENT OF INTERFACIAL TENSION

FIGURE 1.
and the crude oil is admitted to the reservoir in drops. The overflow port allows any excess crude to overflow thereby maintaining a constant head. The capillary tube is kept immersed in sea water.

Photographs were taken by a Mamiya Sekor camera provided with extension tubes for greater magnification. Magnification was indirectly determined by simultaneously photographing a steel ruler marked in 1/32" divisions.

Constant temperature could be maintained by a Haake EKll refrigeration and cooling system of 200W capacity. A Versa Therm temperature probe and electronic relay (sensitivity 0.005 F) ensured that temperature was maintained under close control.

The tube and the reservoir were cleaned using a powerful laboratory cleaner "Micro," and then they were repeatedly rinsed in hot water to ensure that no traces of the cleaner remained on the capillary and the reservoir. The apparatus was then perfectly dried in an oven at 110 C. After each experiment, the apparatus was first washed using carbon tetrachloride and then the above procedure for cleaning was repeated.

A known volume of Corexit 9527 was added to the sea water (or to crude oil) and drops were allowed to form at the tip of the capillary at the rate of approximately one per minute. For each concentration level, 20 photographs were taken.

The photographs were projected on a screen and the largest diameter of each drop $d_e$ was determined; $d_e$ was measured at a distance of $d_e$ from the vertex of the drop. The shape factor was determined and the corresponding value of $1/H$ was read from tables. Interfacial tensions were calculated using the formula:

$$\gamma = \frac{g \rho d_e^2}{H}$$

It is seen that, as shown, in Figure 2, the interfacial tension falls off rapidly as the concentration of the dispersant is increased. The decrease was most pronounced for the addition of the first 0.01% of the dispersant. Thereafter, the decrease in the interfacial tension is less rapid and it levels off at around 0.04% by volume of dispersant.

**Results and Discussion**

The interfacial tension data on the range 5°C to 22°C, as shown in Figures 2 and 4, shows the usual trends that would be expected with variations in temperature and concentration of the dispersant. The highest observed interfacial tension was $27.5 \times 10^{-3}$ Newtons/Meter at 5°C and without dispersant, and the lowest was $2.75 \times 10^{-3}$ Newtons/Meter at 22°C and 0.1 vol. % Corexit. Although 0.1 vol. % of Corexit is low when compared with usual dosages of surfactants, higher concentrations have not been used. At higher concentrations, the water becomes cloudy as the
concentration increases beyond the Critical Micelli Concentration and Tyndall effect becomes pronounced. Under these conditions, it is not possible to use the photographic method.

In analyzing the data, it was found that certain trends are unmistakable. It is seen that the largest drop in the interfacial tension is during the addition of the first 0 - 0.01 vol. % of Corexit. Thereafter the decrease is less with each incremental addition of Corexit and a plot of interfacial tension decreased by about $8.0 \times 10^{-3}$ Newtons/Meter for the addition of the first 0.01 vol. % of Corexit. It should be possible to get lower values of interfacial tension by using a larger proportion of the dispersant. It has been observed in the past that concentrations as high as 1% (10 times the amount used in the present experiment) has been used.

Another fact which stands out is that it is immaterial in which phase the Corexit is added, as shown in Figures 2 and 4. Within limits of experimental error, it is seen that the interfacial tension observed are nearly equal. This is encouraging, as it is far easier to apply the dispersant on the oil, which is the top layer, than to apply it in water. Moreover, in the ocean, larger quantities of dispersant would be necessary, if the dispersant were to be applied on water.

The variation of interfacial tension with temperature, as shown in Figures 5 and 6, is what would normally be expected. There is a steady decrease in interfacial tension with increase in temperature. This is because the cohesion forces between the molecules falls off rapidly with increase in temperature and the interfacial tension is due to the attraction-force between the molecules at the interface. Unlike the variation of interfacial tension with concentration, which is rapid with the first increase in concentration, the decrease in interfacial tension with temperature is more or less uniform. On an average, the interfacial tension decreased by about $1 \times 10^{-3}$ Newtons/Meter.

It was observed that at a given concentration level of Corexit and temperature, it did not matter to which phase Corexit was added. This could be because the intermolecular forces are reduced to the same degree in either phase at the same concentration level of Corexit and temperature (and interfacial tension is due to the net intermolecular forces at the interface). However, from a purely economical point of view, it might be advantageous to add Corexit to the oil phase, as in the ocean, because it takes a much larger quantity of Corexit in the aqueous phase to maintain the same concentration level.
TEMPERATURE (°C)

CONCENTRATION OF COREXIT IN WATER BY VOL.
- 0.01%  • 0.03%  ▲ 0.07%

INTERFACIAL TENSION (NEWTON/METER X 10^3)

FIGURE 5.

CONCENTRATION OF COREXIT IN OIL BY VOL.
- 0.01%  • 0.03%  ▲ 0.07%

INTERFACIAL TENSION (NEWTON/METER X 10^3)

TEMPERATURE (°C)

FIGURE 6.
# Interfacial Tension

<table>
<thead>
<tr>
<th>Concentration % Volume</th>
<th>Corexit in Oil</th>
<th>Corexit in Water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5°C 10°C 22°C</td>
<td>5°C 10°C 22°C</td>
</tr>
<tr>
<td></td>
<td>(x 10³ Newtons/Meter)</td>
<td>(x 10³ Newtons/Meter)</td>
</tr>
<tr>
<td>0.00</td>
<td>27.10 25.10 19.10</td>
<td>27.10 25.10 19.10</td>
</tr>
<tr>
<td>0.01</td>
<td>18.40 10.50 8.75</td>
<td>18.40 15.00 11.20</td>
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<tr>
<td>0.02</td>
<td>11.59 9.80 7.50</td>
<td>11.47 8.00 5.10</td>
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<tr>
<td>0.03</td>
<td>9.51 5.00 4.90</td>
<td>9.54 6.80 4.10</td>
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<tr>
<td>0.05</td>
<td>8.14 4.72 3.74</td>
<td>7.60 4.54 3.73</td>
</tr>
<tr>
<td>0.07</td>
<td>7.15 4.11 3.11</td>
<td>6.16 4.18 3.15</td>
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<tr>
<td>0.10</td>
<td>6.16 3.91 2.74</td>
<td>6.01 3.73 2.75</td>
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References

## Section 2. Appendix C

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<th>Rate of Power</th>
<th>Input (Joules)</th>
<th>Work Input for Interfacial Area (Joules)</th>
<th>Percent Energy Utilized</th>
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12.2 Section 4.0 Appendices

12.1.1 Appendix A: Computer Program
12.1.2 Appendix B: Distinction Between Crude Oil and Dispersant by Means of Infrared Spectrophotometry
12.1.3 Appendix C: The Evaporation Tests
APPENDIX A

Computer Programs
Program name: STREAM

FNU(y+) computes u+ when y+ is known from

\[ y^+ = u^+ + A[\exp(\kappa u^+) - 1 - \kappa u^+] \frac{2}{2} - (\kappa u^+) \frac{3}{6} - (\kappa u^+) \frac{4}{24} \]

FNG(ReX) computes \( \xi \) when ReX is given from

\[ ReX = \int G(z) dz \]

FNF(\( \xi \)) computes G(\( \xi \))

The program starts by asking for ReX(=X). It then computes

\[ S = \xi \]
\[ Y0 = y^+ \]

which is printed

It also computes the maximum permissible value for ReX (based on the condition that \( y^+ < y^+_c \)) since the algebraic relations cease to be valid when \( y^+ > y^+_c \).

For ReX = Y1 to ReX = Y8 in steps of Y3 will the program compute the following quantities:

\[ U = u^+ \]
\[ Y5 = y^+ \]
\[ P = \psi^* \]
\[ P1 = \psi^* + \xi \beta \lambda \]
\[ U5 = U/U_c \]
\[ V5 = V/V_c \]

Program name: GSTREAM

The program operates at one specific value of y which is more or less determined by the input value \( \xi_0 \). From this input the position ReX and the value of \( y^+_{10} \) are computed. The program then proceeds to compute \( U/U_0, V/V_0, V/O_0 \) and \( \tau/\rho U_{10}^2 \) for increasing values of \( ReX \) (defined through increasing values of \( \xi \)) whereby y is kept constant.

FNR(\( \xi \)) computes ReX with \( \xi \) as input

Part 4.2: Eq.(2.10)

(See program: STREAM)

FNY(u+) computes y+ with u+ as input

Part 4.3: Eq.(2.5)

FNF(\( \xi \)) computes G(\( \xi \)) with \( \xi \) as input

FNU(y+) computes u+ with y+ as input (See program: STREAM)
PROGRAM NAME: STREAM

>>OLD:STREAM
>>LIST

00100 DEF FNF(T)
00110 A = 0.1108
00120 K = 0.4
00130 T1 = T*K
00150 G1 = 2+T1**3/(1/3+T1*(1/4+T1*(1/10+T1/36)))
00160 G = T**3/3+A*(EXP(T1)**(T1**2-2*T1+2)-G1)/(K*K)
00170 FNF = G
00180 FNEND
00190 DEF FNU(S)
00360 A = 0.1108
00370 Z = 30
00380 Z1 = Z*K
00410 S1 = Z+A*(EXP(Z1)-1-Z1-Z1**2/2-Z1**3/6-Z1**4/24)
00420 D2 = 1+A*K*(EXP(Z1)-1-Z1-Z1**2/2-Z1**3/6)
00430 D3 = S1-S
00440 D4 = Z-A*K*(EXP(Z1)-1-Z1-Z1**2/2-Z1**3/6)
00450 D3 = S1-S
00460 D1 = ABS(D3)
00470 IF D1 < 0.001 THEN GO TO 490
00480 Z = Z-D1/D2
00490 PAUSE
00480 IF D1 > 0.001 THEN GO TO 400
00490 FNU = Z
00500 FNEND
00550 DEF FNG(S)
00560 K = 0.4
00570 A = 0.1108
00580 Z = 30
00590 N = 0
00600 Z1 = Z*K
00610 S4 = 6+2*Z1+Z1**4/(1/12+Z1*(1/4+Z1*(1/10+Z1/36)))
00620 S3 = EXP(Z1)**(Z1**2-4*Z1+6)-S4
00630 S1 = Z**4/12+A*S3/(K**3)
00640 D4 = Z+Z1**3/(1/3+Z1*(1/4+Z1*(1/10+Z1/36)))
00650 D3 = EXP(Z1)**(Z1**2-2*Z1+2)-D4
00660 D2 = Z**3/3+A*D3/(K**2)
00670 D3 = S1-S
00680 D1 = ABS(D3)
00690 IF D1 < 0.001 THEN GO TO 750
00700 Z = Z-D1/D2
00710 N = N+1
00720 IF N > 20 THEN GO TO 750
00730 PAUSE
00740 IF D1 > 0.001 THEN GO TO 600
00750 FNG = Z
00760 FNEND
00800 A = 0.1108
00810 K = 0.4
00820 PRINT 'PARTICLE SIZE P2=?'
00830 INPUT P2
00840 PRINT 'REX=?'
00850    INPUT X
00860    S = FMG(I)
00870    X1 = X*K
00880    S1 = S*K
00890    Y0 = S*A*(EXP(S1) - 1 - S1*(1 + S1/2*(1 + S1/3*(1 + S1/4)))))
00900    Y9 = Y0*S
00910    PRINT 'Y0=',Y0, 'KSI=', S, 'STOP VALUE Y9=', Y9
00920    PRINT 'START VALUE Y1=?'
00930    INPUT Y1
00940    PRINT 'STEP Y3=?'
00950    INPUT Y3
00953    PRINT 'END VALUE Y8=?'
00955    INPUT Y8
00960    FOR Y = Y1 TO Y8 STEP Y3
00970    Y5 = Y/S
00980    U = FMU(Y5)
00990    U1 = U*K
01000    P3 = U1**2*(1/2 + U1*(1/3 + U1*(1/8 + U1/30)))
01010    P = U**2/2*A*(EXP(U1)*(U1 - 1) - P3)
01020    P1 = P + P2*X
01021    U5 = U/S
01022    V5 = Y5/U/(S*FN(S))
01030    PRINT Y, U5, V5, P, P1
01040    NEXT Y
01050    END
```
A = 0.1108
K = 0.4
PRINT 'KSINULL =?'
INPUT SO
S1 = SO*K
Y0 = FNY(SO)
R0 = FNR(SO)
V0 = Y0*FNU(Y0)/(SO*FNF(S0))
PRINT 'VUNULL =?V0
PRINT 'KSINULL =?SO, YNULL =?Y0, REYNULL =?R0
PRINT 'END VALUE KSI=?'
INPUT S9
PRINT 'STEP KSI=?'
INPUT S5
FOR S = SO TO S9 STEP S5
Y = Y0*SO/S
U = FNU(Y)/S
P1 = U*S
P2 = FNF(P1)/FNF(S)
P = (1-P2)/(S*S)
V1 = S*FNF(S)
Y9 = FNY(S)
V9 = Y9*FNU(Y9)/(V1*V0)
V = Y*FNU(Y)/(V1*V0)
R = FNR(S)-R0
PRINT S,P,U,V,R
NEXT S
END

Print-out for Fig. 3

KSINULL =?
[S >15
VUNULL = .00703263
KSINULL = 15 YNULL = 46.957908 REYNULL = 12629.96
END VALUE KSI=?
[S >20
STEP KSI=?
[S >0.5

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</tbody>
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```
### PRINT OUT FOR FIG. 4

<table>
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<tr>
<th>$K\sigma_\text{INULL} = ?$</th>
<th>$C &gt; 18$</th>
<th>$Y\text{NULL} = .00422125$</th>
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<tbody>
<tr>
<td>$K\sigma_\text{INULL} = 18$</td>
<td>$Y\text{NULL} = 143.32901$</td>
<td>$\text{REYNULL} = 63079.742$</td>
</tr>
</tbody>
</table>

END VALUE $K\sigma_i = ?$

| $C > 25$ | $\text{STEP } K\sigma_i = ?$
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$C &gt; 0.5$</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>$&gt; 18$</th>
<th>$-1.894839\times 10^{-8}$</th>
<th>$1.0000006$</th>
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<th>$1$</th>
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<td>$0.04419039$</td>
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### PRINT OUT FOR FIG. 5

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<th>$K\sigma_\text{INULL} = ?$</th>
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<tbody>
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<td>$Y\text{NULL} = 3584.8098$</td>
<td>$\text{REYNULL} = 4026709.8$</td>
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END VALUE $K\sigma_i = ?$

| $C > 30$ | $\text{STEP } K\sigma_i = ?$
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<tbody>
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<table>
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<td>$73258681$</td>
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</table>
FNG($Re_x$) computes $\xi$ with $Re_x$ as input  

Part 4.2: Eq. (2.10)

With $S(=)$ as variable from $S = S_0$ to $S = S_9$ in steps of $S_5$ the program computes:

\[
\frac{\bar{u}}{U_0} = \bar{U} \\
\frac{\bar{v}}{U_0} = \bar{V} \\
Re_x - Re_{\infty} = \bar{R} \\
\frac{\tau}{\rho U_0^2} = \bar{F} \\
\frac{\bar{W}}{U_0} = \bar{V}_0
\]

Part 4.2: Eq. (2.3)  
Part 4.2: Eq. (2.9)  
Part 4.2: Eq. (2.10)  
Part 4.2: Eq. (2.16)  
Part 4.2: Eq. (2.9)

Program name: OIL2

The program operates at one specific value of $X(=\xi)$ which it asks for as input to start the computations. It computes the velocity components $\bar{U}$ and $\bar{V}$, the stream function $\psi$ and the path-function $\Theta$ and runs a table for running argument $y/A$.

FNF($n$) COMPUTES:

\[FNF(n) = f(n) = \exp(-n^2) - 2Bn^2/(\sqrt{\pi}(B^2+n^2)^2)\]  
Part 4.2: Eq. (4.3)

FNE($n$) COMPUTES:

\[FNE(n) = \frac{1}{\sqrt{\pi}} \text{erf}(n)\]

With $Z_1$ as the input variable from $Z_1 = Z_{10}$ to $Z_1 = Z_9$ in steps of $Z_3$ the following quantities are computed:

**y/A**  
$y/A = Y/A$ (input variable)  
Part 4.2: Eq. (4.2)

$n$  
$\bar{U}/U_0 = \bar{U} = \frac{\bar{U}}{A}(1+\xi^2)^{-\frac{1}{2}}$  
Part 4.2: Eq. (4.1)

$\bar{V}/U_0 = \bar{V}$  
Part 4.2: Eq. (4.1)

$\int f(n)\,dn$  
$\bar{V} = \frac{\pi}{\sqrt{\pi}} \text{erf}(n) + \left[\frac{n/\pi}{1+(n/\pi)^2}\right] - \arctan(n/\pi)/\sqrt{\pi}$  
Part 4.2: Eq. (4.5)

$\bar{W}/U_0 = \bar{W}$  
Part 4.2: Eq. (4.1)

$\psi = \frac{\pi}{\sqrt{\pi}} [2\psi(n) - \int f(z)\,dz](1+\xi^2)^{-\frac{1}{2}}$  
Part 4.2: Eq. (4.1)

$P = (1+\xi^2)^{\frac{1}{2}} \int f(z)\,dz$  
Part 4.2: Eq. (4.7)

$\Theta$  
$\phi_1 = \psi^* + \xi B/\lambda$  
Part 4.3: Eq. (2.22)
PROGRAM NAME: OIL2

>>OLD:OIL2
>>LIST

00010  DEF FNF(A)
00015   B = 5
00020   C1 = EXP(-A**2)
00030   C2 = 2*B*A**2
00040   C3 = (B**2+A**2)**2
00050   C4 = ATN(1)*4
00060   C5 = C4**0.5
00070   FNF = C1-C2/(C5*C3)
00080   FNEND
00090  DEF FNE(D)
00091  IF D > 3.0 GO TO 165
00100   B = 5
00105   N = 0
00110   D2 = D
00115   D3 = D
00120   D4 = D/3
00125   D5 = ABS(D4)
00130  IF D5 > 0.00001 THEN GO TO 110
00135   IF D5 < 0.00001 THEN GO TO 170
00140   D3 = 0.88623
00150  FNE = D3
00160  FNEND
00170  PRINT 'PARTICLE SIZE P2=?'
00175  INPUT P2
00180  PRINT 'Z0=?'
00185  INPUT Z0
00190  PRINT 'Z9=?'
00195  INPUT Z9
00200  PRINT 'Z3=?'
00205  INPUT Z3
00210  PRINT 'X=?'
00215  INPUT X
00220  FOR Z1 = Z0 TO Z9 STEP Z3
00225   N1 = 0.5
00230   Z = Z1/((X**2+1)**0.5*2*N1)
00240   U = FNF(Z)/((X**2+1)**0.25)
00250   V2 = (ATN(1)*4)**0.5
00260   V3 = Z/B
00270   V4 = V3/(1+V3**2)-ATN(V3)
00280   V5 = FNE(Z)+V4/V2
00290  V1 = 2*Z*FNF(Z)-V5
00295  P = V5*(1+X**2)**0.25
00300  V = V1*X*N1/((1+X**2)**0.75)
00305  P1 = P+P2*X
00310  PRINT Z1,U,V,P,P1
00315 NEXT Z1
00320  END
APPENDIX B

Distinction between Crude Oil and Dispersant
by Means of Infrared Spectrophotometry

by

Mathew Cherian, Ted Kawazoe and Leif N. Persen
Distinction between Crude Oil and Dispersant
by means of Infrared Spectrophotometry

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In investigations involving the use of a dispersant to influence the fate of an oil spill at sea (or on lakes) samples are usually taken from the water column. The hydrocarbons in the samples are extracted by some standard method and the concentration of hydrocarbons can be determined. If gas chromatography is used it is comparatively easy to determine how much of the hydrocarbons in the sample originates from the crude oil and how much from the dispersant, even though the process may be somewhat time consuming and requires expensive equipment. Apart from the obvious interest such distinction between oil and dispersant has when judging the effect of the dispersant the possible difference in toxicity of the two compounds makes this distinction important.

Fig. 1. The peaks at 3600 [cm⁻¹] and at 2930 [cm⁻¹] of Corexit 9527.
When a large number of samples are to be handled within a certain time limit a quick method which allows a distinction to be made between dispersant and crude oil recovered in the water samples is desirable. The following is a presentation of a method developed for infrared spectrophotometry.

The dispersant to be used is Corexit 9527 and the oil is standard Kuwait Crude. The extraction is supposed to utilize carbon tetrachloride (CCl₄) and all samples in this investigation are prepared with this solvent. If Kuwait Crude is scanned in the infrared spectrophotometer one finds the usual peak at a wave number of 2930 [cm⁻¹]. If however Corexit 9527 is scanned one finds an additional peak at a wave number of 3600 [cm⁻¹] as shown in Fig. 1. Most dispersants available commercially should give a peak at 3600 [cm⁻¹]. This peak is due to the OH stretching, while the peak at 2930 is due to CH stretching. Since no peak is present for Kuwait Crude at the latter wave number, one has a possible basis for establishing the desired method.

Fig. 1. Infrared spectrum of Kuwait Crude and Corexit 9527.

Fig. 2. Calibration curve for Kuwait Crude scanned at 2930 [cm⁻¹]

First, the calibration curve for Kuwait Crude is established as shown in Fig. 2. Samples with different concentrations \( c_o \) of oil in CCl₄ are prepared and scanned at a wave number of 2930 [cm⁻¹]. From the transmittance \( z \) thus obtained the absorbance \( a \) is computed

\[
a = \log_{10}(100/z) \tag{1}
\]
The results are shown in Fig. 2 which indicate a linear relationship between \( a \) and \( c \). A linear regression based on the data obtained gives

\[
a = 0.01179 \sigma_c - 0.00299 \pm 0.00316
\]  

(2)

This is a standard result and the only comment one might add is that the accuracy is satisfying for concentrations down to 3-5 [mg "oil"/l CCl₄]

![Graph showing linear relationship between concentration and absorbance](image)

Fig. 3. Calibration curve for Corexit 9527 scanned at 2930 [\text{cm}^{-1}].

The next step is to prepare samples with Corexit 9527 in different concentrations \( \sigma_C \) in CCl₄. Scanning these at a wave number of 2930 [\text{cm}^{-1}] and computing the absorbance one obtained the results shown in Fig. 3. Again a linear relationship between the concentration and the absorbance is evident and a linear regression applied to the data gives

\[
a = 0.00865 \sigma_C - 0.01516 \pm 0.00314
\]  

(3)

Again this is a result which could be expected, the only obvious remark being that the sensitivity to concentrations of Corexit 9527 is lower than to Kuwait Crude.

If samples with Corexit alone is scanned at a wave number of 2600 [\text{cm}^{-1}] a calibration curve as shown in Fig. 4A is found:
Fig. 4. Calibration curve for Corexit 9527 alone at 3600 [cm$^{-1}$] \( A \)
Mixtures compared with the calibration curve \( B \)

\[
a = 0.00108 \quad \sigma_C = 0.00576 \pm 0.00530
\]

Attention is here drawn to the fact that very high values of concentration is needed to give the desired calibration curve, and that this limits the usefulness of the present approach to cases where the concentration of Corexit in the solvent CCl$_4$ is high. This however is the case in the investigations where the present method is to be applied.

Now, mixtures are prepared, i.e. a mixture of known ratio Corexit/Kuwait Crude is dissolved in CCl$_4$ in different concentrations. When these samples are scanned at 3600 [cm$^{-1}$] values for the absorbance is obtained and since the concentration of Corexit in the mixture is known, the results can be compared with the straight line calibration curve obtained in Fig. 4A. This is done in Fig. 4B. The accuracy with which the amount of Corexit in the mixtures is predicted by the calibration curve shows that the infrared spectrophotometer "sees" only the Corexit at the wave number 3600 [cm$^{-1}$]. One has thus a method of determining $\sigma_C$ in a mixture of unknown ratio.
A series of different mixtures are now prepared and scanned at 2930 [cm⁻¹]. The results are shown in Fig. 5 where the slope of the straight line calibration curves depend on the ratio Corexit/Kuwait Crude.

![Calibration curves at 2930 [cm⁻¹] for different mixtures](image)

**Fig. 5.** Calibration curves at 2930 [cm⁻¹] for different mixtures

Figure 5 also shows the previously established calibration curves for Corexit alone and Kuwait Crude alone.

One may now gather the information obtained. The concentration $c_m$ of a mixture of ratio $r = mg$ Coreexit/mg Kuwait Crude may be given as

$$c_m = c_C + c_o$$  (5)

and the ratio will be

$$r = c_C / c_o$$  (6)

The result of the scanning at 2930 [cm⁻¹] may be given as

$$a = \lambda(r) c_m$$  (7)

where the slope $\lambda$ of the calibration curve is a function of $r$. This relationship is shown in Fig. 6

$$\frac{\lambda - \lambda_\infty}{\lambda_o - \lambda_\infty} = (1 + r / 0.425)^{-0.75}$$  (8)
Fig. 6. The slope of the calibration curve as function of the ratio $r$ of the mixture

where

$\lambda_0 = \text{slope for oil alone}$

$\lambda_\infty = \text{slope for Corexit alone}$

$\lambda = \text{slope for a mixture of ratio } r$

This is the end result of the investigation, and it is emphasized that eq. (8) is a curve fit only and that no theoretical basis is used. It may be that it can be improved and that another expression in other circumstances may be preferable. This however does not change the fact that this investigation gives a method whereby the content of hydrocarbons in a sample can be split-up into one part originating from the dispersant and one part originating from the oil. The data used to obtain this may now be used as examples.

In Table I the measured values of $c_m$, $c_C$, $c_o$, $c_m$ and $r_{\text{meas}}$ are given. Each one of these samples may be treated as an original case.
where only $c_c$ and $a_m$ are known. The value of $c_c$ is supposedly known from scanning at 3600 [cm$^{-1}$] and $a_m$ is the absorbance found from scanning at 2930 [cm$^{-1}$]. With these two as only input data the following procedure is followed:

1.) An initial ratio $r = r_f$ is assumed
2.) Then the corresponding $\lambda = \lambda_f$ is computed from eq. (6)
3.) The corresponding concentration of the mixture $c_{m,1}$ is found from:
   $$c_{m,1} = \frac{a_m}{\lambda_f}$$
4.) The corresponding concentration of oil is found from:
   $$c_{o,1} = c_{m,1} - c_c$$
5.) The corresponding ratio $r_2 = \frac{c_C}{c_O, 1}$ is computed.

6.) The value $r_2$ is compared with $r_1$. If the difference is too great one repeats steps 2.) . . . 6.) until the ratio introduced is close to the one obtained.

This procedure is used to obtain the values $r_{comp}$ in Table I.

The procedure works very well provided:

a.) the concentration $c_C$ is not too low

b.) the ratio $0 < r < 1$

How the procedure breaks down when this is not the case is well brought out by the data in Table I. The breakdown of the method for large values of $r$ is of course due to the asymptotic behavior of the curve in Fig. 6.

The application of the method presented here may meet with difficulties. The use of CC14 as a solvent for the extraction shows that the peak at 3600 [cm$^{-1}$] is highly influenced by water. This can be extracted, using say anhydrous Sodium Sulfate (Na$_2$SO$_4$) to "dry" the aliquot, i.e. to extract the water without seriously affecting the peaks at 3600 [cm$^{-1}$] and at 2930 [cm$^{-1}$] as shown by the example displayed in Fig. 7. This is however a rather time consuming procedure.
consuming procedure, and another procedure is to be suggested whereby the complications at the wave number 3600 [cm$^{-1}$] may be avoided.

If the hydrocarbons in a sample is extracted by applying aliquots (CCl$_4$) of a fixed magnitude to the sample, shaking the sample and draining off the aliquot, successive aliquots will show a decreasing concentration of hydrocarbons. It turns out that when the hydrocarbons originate from crude oil, a rapid decrease in the concentration of each subsequent aliquot is observed, a situation which has been investigated in [1]. If on the other hand the hydrocarbon originates from Corexit 9527 the concentration decreases much more slowly. This is exhibited in Fig. 8 where the concentration of Corexit in the water

![Graph showing concentration of Corexit in water](image)

Fig. 8 Concentration $c_{C,i}$ as indicated by subsequent aliquots
sample as indicated by each aliquot is shown. The concentration \( c_{C,i} \)
indicated by aliquot no. \( i \) is found by means of the calibration curve
in Fig. 3. For values less than 1 [mg/l \( H_2O \)] the determination be-
comes somewhat uncertain. It is seen that the data points indicate
a relationship given by the straight lines.

\[
\ln c_{C,i} = \lambda \ln i + b
\]  

(9)

For the cases shown in Fig. 8 the data are given in Table III
where \( m \) is the standard deviation obtained through linear regression
applied to the data points.

Table III

<table>
<thead>
<tr>
<th>Legend</th>
<th>No.</th>
<th>( \lambda )</th>
<th>( b )</th>
<th>( m )</th>
<th>( c_{C[mg/lH_2O]} )</th>
<th>Aliquots used to determine line</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>-2.349</td>
<td>4.493</td>
<td>+ 9%</td>
<td>49.7</td>
<td>all</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>-2.200</td>
<td>4.235</td>
<td>+ 2.0%</td>
<td>51.2</td>
<td>4.5.6.7</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>-2.334</td>
<td>5.012</td>
<td>+ 1.2%</td>
<td>72.8</td>
<td>4.5.6.7.8</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>-2.402</td>
<td>3.593</td>
<td>+ 8.3%</td>
<td>25.0</td>
<td>3.4.5.6</td>
<td></td>
</tr>
</tbody>
</table>

To this one may add that the first aliquots do not follow the regular
behavior indicated by eq. (9). Fig. 9 reveals in Case IV that the
following relation then seems to apply:

\[
\ln c_{C,i} = a_i + b
\]  

(10)

where the respective values of \( a \) and \( b \) are given in Table IV.

Table IV

<table>
<thead>
<tr>
<th>No</th>
<th>( a )</th>
<th>( b )</th>
<th>( m )</th>
<th>( e^a + b )</th>
<th>( k )</th>
<th>( c_C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>- .4368</td>
<td>3.001</td>
<td>+ 7.0%</td>
<td>12.99</td>
<td>.646</td>
<td>50.3</td>
</tr>
<tr>
<td>II</td>
<td>- .4604</td>
<td>3.020</td>
<td>+ 3.6%</td>
<td>12.93</td>
<td>.631</td>
<td>48.0</td>
</tr>
<tr>
<td>III</td>
<td>- .4026</td>
<td>3.313</td>
<td>+ 7.0%</td>
<td>18.36</td>
<td>.669</td>
<td>75.9</td>
</tr>
<tr>
<td>IV</td>
<td>- .4508</td>
<td>2.195</td>
<td>+ 5.5%</td>
<td>5.72</td>
<td>.637</td>
<td>21.6</td>
</tr>
</tbody>
</table>

Computed from eqs. (11, 12, 13)
It reveals furthermore that eq. (10) can be applied with confidence also to the subsequent aliquots provided one does not go to too low concentrations.

The following additional information is important: The samples I and IV were prepared with Corexit alone, whereas samples II and III were prepared with a mixture of Corexit and Kuwait Crude in a ratio \( r_{II} = 1.04 \) and \( r_{III} = 1.24 \) respectively. Tables III and IV reveal through the values of \( \lambda \) and \( \alpha \) that

1.) The concentrations \( c_{C,i} \) of subsequent aliquots follows a "universal" law under the conditions used. This law is neither given by eq. (9) nor by eq. (10) but these equations are good approximations in two different regions.

Fig. 9. Concentrations \( c_{C,i} \) of subsequent aliquots
2.) The extraction of Corexit according to the "law" appears to be uninfluenced by the presence of oil in the sample.

This last observation gives rise to the following line of reasoning:

A.) It is assumed that the three first aliquots (in the cases used here) contain both oil and dispersant, but that the subsequent aliquots contain dispersant alone. This is due to the different way in which oil and Corexit apparently are extracted.

B.) The next aliquots (No. 4, 5 and 6) ought then to follow the law of eq. (10).

C.) This law applies also to the first aliquots if the extraction takes place uninfluenced by the presence of oil.

D.) Since the curve according to which the extraction takes place is assumed to be "universal", it is possible to compute the original concentration of Corexit in the sample based on the information obtained from aliquots No. 4, 5 and 6.

Now, if eq. (10) can be applied, it means that:

\[ c_{C,i} = e^{a_i + \beta} \]  \hspace{1cm} (11)

\[ c_{C,i+1} = e^{a(i+1) + \beta} \]

or

\[ \frac{c_{C,i+1}}{c_{C,i}} = e^a = k \] \hspace{1cm} (12)

If this was true for all aliquots, one would find the total concentration of Corexit in the sample as

\[ S = \sum_{i=1}^{\infty} c_{C,i} = e^{a+\beta} \left( \frac{1}{1+k + k^2 + ...} \right) \]

\[ = e^{a+\beta} \frac{1}{1-k} \] \hspace{1cm} (13)
Since a different "law" applies for later aliquots eq. (13) will underestimate the total concentration. One may however assume that because of the "universality" of the decay, the deviation measured in percentage is a constant. If this constant is put equal to 0.73 one will, with the values of \( \alpha \) and \( \beta \) determined in Table IV obtain the concentrations computed in the same table. This shows that the method seems to work.

One final comment may be advanced. When using the method enough aliquots must be applied to secure that the oil has been removed and that one has reached that part of the extraction procedure where subsequent aliquots lie on a line with \( \alpha = -0.45 \) when exhibited as done in Fig. 9. In the cases on which the present method was investigated the sample size was always 500 ml and the aliquot size 30 ml. This method is used in the evaluation of the drop size as well as the rain drop experiments.
Reference

[1] Leif N. Persen "The Entrainment of Oil from an Oil Slick into the Water Column, Workshop, Princeton, May 1979."
Appendix C: The Evaporation Tests
THE EVAPORATION TESTS

The entrainment process is to be studied experimentally by properly chosen experiments. A major feature of such experiments is the determination of concentrations of oil in samples from the water column. It has, however, been noted that a certain percentage of the oil will evaporate and not be entrained in the water column over a longer period. This has led to the study of the evaporation process. Both Kuwait Crude and Corexit 9527 have been tested by letting an open surface of the two fluids be exposed to wind in a wind tunnel where the velocity field could be monitored. In addition to the tests with the two fluids alone, tests were made to investigate the mixtures of Kuwait Crude and Corexit 9527 in the ratios 20:1, 10:1, 7:1 and 5:1. Both for the case of Kuwait Crude alone, as well as for mixtures of Crude and Corexit 9527, the influence of an underlying waterbed was examined.

It should be realized that crude oil in general consists of components which evaporate differently. Thus, under given conditions only a portion of the crude oil will evaporate, whereas Corexit 9527 resembles water in the sense that it almost evaporates entirely under the same conditions. The results may thus not be expected to be comparable.

The physical quantities involved in the tests are the following:

- \( m_e \) = mass of the evaporated portion of the fluid
- \( m \) = total mass of the fluid used in the experiment
- \( t \) = time
- \( U_s \) = slip velocity in the air at the interphase (Fig. 1)
- \( \frac{du}{dy} \bigg|_{y=0} \) = velocity gradient in the air at the interphase (Fig. 1)
- \( \rho \) = density of the oil
h = depth of the oil (oil slick thickness)

Buckingham's Π - theorem indicates the outcome of the experiment to be expressible in terms of the following variables:

\[ p = \frac{m_e}{m} = \text{(percentage evaporation)} \]

\[ \tau = \frac{U_s t}{h} = \text{dimensionless time} \]

\[ \Pi_1 = \frac{h}{U_s} \cdot \left. \frac{du}{dy} \right|_{y=0} \]

\[ \Pi_2 = \frac{ph^3}{m} \]

This means that the result of the experiments ought to be expressible as:

\[ p = \frac{m_e}{m} = F \left( \frac{ph^3}{m}, \frac{h}{U_s} \left. \frac{du}{dy} \right|_{y=0}, \frac{U_s t}{h} \right) \]

Table I shows the value of the parameters for six different tests performed with Kuwait Crude Oil. The results from these tests are shown in Fig. 2 where \( p \) is plotted as function of \( \tau \). They show that \( p \) is only slightly dependent on \( \Pi_1 \) and \( \Pi_2 \) which reflects the fact that the exposed surface as well as the depth of the fluid (oil slick thickness) was kept almost constant. In order to get an
Figure 2. Evaporation data p versus $U_s t/h$

**TABLE 1 (KUWAIT CRUDE OIL)**

| No. | Leg. | $U_s$ [ft/s] | $du/dy|_{y=0}$ [1/s] | $h$ [cm] | $U_s/h$ [1/s] | $h \frac{du}{dy}|_{y=0}$ | $\frac{h}{U_s} \frac{du}{dy}|_{y=0}$ | $N_1 \cdot 10^3$ cm$^3$/m $10^3$ |
|-----|------|--------------|-----------------|--------|---------------|-----------------|-----------------|-----------------|
| 1   | ○    | 1.7344       | 4.38            | .494   | 107.01        | .04093          | .7211           |
| 2   | ■    | 1.4932       | 4.74            | .491   | 92.69         | .06114          | .7124           |
| 3   | ●    | 2.1228       | 7.56            | .477   | 135.65        | .06573          | .6723           |
| 4   | □    | 2.3480       | 12.00           | .473   | 151.30        | .07931          | .6611           |
| 5   | ▽    | 1.7982       | 8.76            | .545   | 100.57        | .08711          | .8777           |
| 6   | ★    | 2.6064       | 8.28            | .473   | 167.96        | .04930          | .6611           |
The following curve was fitted to the data:

\[ p = \frac{A(\tau/\tau_0)^\kappa}{1 + (\tau/\tau_0)^\kappa} \]

where \( \kappa = 0.75 \) and \( \tau_0 = 26.78 \times 10^2 \). The asymptotic value \( A = 26.00 \) is found from the data and the way in which the curve represents the data is exhibited in Fig. 3. This result should be considered in the light of an evaporation test performed in a ROTOVAP at 40°C over a period of 24 hours which led to a weight loss of 32.3%. In view of the fact that the present results were obtained at a temperature of 20 - 22°C, the agreement between the experimental results seems reasonable.

The evaporation data obtained for Corexit 9527 alone and for different mixtures of oil and Corexit are shown in Figs. 4 and 5. For Corexit alone, the data have been obtained with a greater variation in the fluid thickness as is easily seen from Table II. The data do, however, not correlate as well with only non-dimensionalizing the time and introducing \( \tau \) as is seen from Fig. 4.

This may partly be due to the fact that different trays were used and certain cases where the surface area changed due to evaporation. For the mixtures, however, this did not happen, and the data correlate well again.

The importance of these tests does not lie so much in the actual results which, for Kuwait Crude, show that \( \sim 75\% \) of the total evaporation caused by

<table>
<thead>
<tr>
<th>No.</th>
<th>Leg.</th>
<th>( U_s ) [ft/s]</th>
<th>( \frac{dh}{dt} )</th>
<th>( h_{=0} ) [l/s]</th>
<th>( h ) [l/s]</th>
<th>( \frac{h}{h_{=0}} )</th>
<th>( \frac{h}{h_{=0}} )</th>
<th>( E_1 \times 10^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>□</td>
<td>2.4912</td>
<td>10.74</td>
<td>0.561</td>
<td>135.35</td>
<td>0.07936</td>
<td>.9300</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>●</td>
<td>1.8900</td>
<td>6.48</td>
<td>0.768</td>
<td>75.01</td>
<td>0.08639</td>
<td>1.7429</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>●</td>
<td>2.4670</td>
<td>10.50</td>
<td>0.378</td>
<td>198.93</td>
<td>0.05278</td>
<td>.4222</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>■</td>
<td>1.5056</td>
<td>4.02</td>
<td>0.513</td>
<td>89.46</td>
<td>0.04494</td>
<td>.7776</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>◊</td>
<td>2.6016</td>
<td>10.62</td>
<td>0.457</td>
<td>173.52</td>
<td>0.06120</td>
<td>.6171</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>▽</td>
<td>0.426</td>
<td>14.10</td>
<td>1.688</td>
<td>7.65</td>
<td>1.84388</td>
<td>3.1622</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>△</td>
<td>0.144</td>
<td>15.30</td>
<td>1.731</td>
<td>2.54</td>
<td>6.03408</td>
<td>3.26631</td>
<td></td>
</tr>
</tbody>
</table>
wind under the circumstances investigated has taken place when

\[ \frac{U_s t}{h} = 12 \times 10^5 \]

i.e., for circumstances investigated here approximately after two hours. It is far more important for the study of the entrainment process to realize that the composition of the entrained oil differs due to weathering.

Figure 3. Evaporation data \( p \) for Kuwait Crude exhibiting the asymptotic value \( p = A = 26.0 \)

Table III (Kuwait Crude: Corexit 9527)

<table>
<thead>
<tr>
<th>No.</th>
<th>Leg.</th>
<th>( U_s ) [ft/s]</th>
<th>( \text{du/dy}_{y=0} ) [1/s]</th>
<th>( h ) [cm]</th>
<th>( U_s/h ) [1/s]</th>
<th>( h \text{du/dy}_{y=0} )</th>
<th>( h \text{du/dy}_{y=0} )</th>
<th>( \text{E}_2 \times 10^3 )</th>
<th>( \text{E}_3 \times 10^3 )</th>
<th>Mix:</th>
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</thead>
<tbody>
<tr>
<td>15</td>
<td>2.3496</td>
<td>11.52</td>
<td>.438</td>
<td>163.51</td>
<td>.07046</td>
<td>.56668</td>
<td>20:1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>2.3184</td>
<td>11.58</td>
<td>.440</td>
<td>160.60</td>
<td>.07210</td>
<td>.57707</td>
<td>7:1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4. Evaporation data \( p \) versus \( T \) for Corexit 9527

Figure 5. Evaporation data \( p \) versus \( T \) for mixtures of Kuwait Crude and Corexit 9527
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URI Oil Spill Model
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CHAPTER I  INTRODUCTION

This manual is a guide to Version 2 of the URI Oilspill Model. The model, although it treats most of the known processes involved in the fate of spilled oil, has been designed primarily to study cleanup and treatment alternatives for a given spill condition. This requires that input be easily entered and output easily obtained in the shortest amount of time. The model has also been designed to allow for the rapid implementation of new modules reflecting advances in the state-of-the art.

The computer code is currently implemented on an Itel Advanced System/5 which is functionally compatible with an IBM System 370. It is written in Fortran IV and is run as a batch job. The main program, as presently configured, requires about 465 kilobytes of memory to run and a typical job using 2000 marker particles, 30 spillets and a time step of one day, consumes about 16 CPU minutes for a 72 day simulation.

In the next section of this chapter, an overview of the various steps required for a complete simulation are briefly described.

Chapter II is devoted to the input programs used to format environmental data for input to the preview and full scale simulation. The function of the preview run is discussed in Chapter III while the general operation of the complete simulation is outlined in Chapter IV. Chapter V provides a brief summary of the output programs used to plot the results. The details of the various programs as well as how to set up a complete simulation is covered in the appendices. In particular, Appendix I covers input to the preview and complete simulation model; Appendix II, the output available from these models; Appendix III a description of all variables contained in common in the simulation model; Appendix IV, a detailed description of the operation of each subroutine of the model; Appendix V a similar description for the input programs; Appendix VI a detailed description of the output programs; Appendix VII a listing of all programs; Appendix VIII output from a sample run; and Appendix IX a summary of oil properties required for input.

OVERVIEW

The simulation of an oil spill is divided into four steps. Formation at input, data, spill preview, main simulation and output. The flow chart showing this process is presented in Figure 1.

As indicated in Figure 1, the user may elect to prepare all input data with or without the use of the input programs. These programs manipulate only the most complicated input data, the environmental variables (bathymetry, wind, current, etc., see Chapter II), one of the five major input groups. The remaining four groups are discussed in greater detail in Appendix I. There are two characteristics of the environmental data which render them more complicated than the other input data. First, they read into the main program on grids defined by:

1. The grid origin in longitude and latitude.
2. The spacing of grid elements.
3. The number of elements in x and y.
4. The angle the grid makes with lines of constant latitude.
Figure 1. OVERVIEW
Second, the spacing of grid elements may be in meters or degrees longitude and latitude. These alternate grid spacings permit the model to operate on one of two size scales but also increases the complexity of defining the values of the variables and the grids. In the small scale mode, horizontal distance calculations are performed in meters while in the large scale mode, the calculations are performed in degrees. This allows environmental data to be obtained from satellites, where the data locations cover a spatially large grid requiring spherical coordinates such as longitude and latitude, or from smaller scale data collection programs such as might be located nearshore with recording instruments located only a few kilometers apart.

The input programs may be used to format the environmental variables to input the simulation model and/or to check the environmental data sets. Even if the user prepares the environmental data sets, the use of the input program that verifies the format is suggested. A small error in the location or format of an environmental grid may result in a costly but useless run.

In order to understand the second step in the simulation process, the preview run, it is important to first understand the difference in the concentration in the model of oil on the surface of the water compared to that of oil entrained into the water column. The surface oil is treated as a collection of "spillets." These are circular puddles of oil which spread, drift, evaporate, etc., independently of all other "spillets." If they overlap by more than predefined fraction, they are combined into one larger "spillet." The parameters describing this larger "spillet" are determined either by the sum of the corresponding parameters of the small "spillets" (such as the total volume of oil) or by the weighted sum of those parameters (such as the center of the "spillet"). In the present configuration, up to one hundred "spillets" are allowed at any one time. Oil is added to a spillet either from a source or by adding spillets together when they overlap. Table 1 gives a description of the variables used to define a "spillet."

The subsurface oil is treated as a collection of droplets each of which represents a large number of droplets with similar properties. The droplets in the model are, therefore, part of a statistical representation of the actual dispersion. Each droplet is described by a set of parameters such as the droplet radius, entrained mass associated with the droplet, its location, etc. These parameters are listed in Table 2. Up to two hundred categories of droplets are currently allowed. There may be many droplets in each category, but the total number of droplets is limited by memory requirements (to 2000 at present) and by execution time. A neutrally buoyant droplet may be used to represent the dissolved portion of the spilled oil.

Those subroutines that deal with the surface oil are formally separated from those dealing with the subsurface oil everywhere except in the determination of the volume of entrained oil, as the number of entrained marker particles. The preview run executes only the surface routines and keeps a running tally on the mass balance. It is used primarily to determine the mass to be associated with each subsurface particle. Such a determination is extremely difficult without this intermediate step because the total entrained mass depends on the wind
TABLE 1

"SPILLET VARIABLES"

- Area of spillet treated thus far (meters$^2$).
- Density of oil currently in spillet (gm/cc).
- Fraction of each of up to eight classes.
- Radius of Spillet (meters).
- Interfacial tension of oil prior to treatment (Dynes/cm).
- Interfacial tension of oil after chemical treatment (Dynes/cm).
- Kinematic viscosity of the oil (Centistokes).
- Mass of oil remaining in Spillet (metric tons).
- Longitude and latitude at the center of the spillet.

TABLE 2

PARAMETERS OF DISPERSED OIL DROPLETS

- Radius of the droplet (mm).
- Density (gm/cc).
- Fraction of each of up to eight classes of hydrocarbons.
- Mass of entrained oil represented by the given droplet.
- Longitude, latitude and depth in the water column (m) of the droplet.
spread as a function of time, the age of the oil, spill surface area, etc. If the number of particles is to be fixed, say at 2000, a good estimate of the total entrained mass is required to allocate the correct amount of mass to each entrained particle.

In addition to providing the user with an appropriate estimate of the mass associated with each entrained particle, the preview run is also useful in providing a preview of the surface behavior of the spill. Memory requirements may be less than for the full simulation and the time of execution is greatly reduced.

The main program integrates the subsurface portion of the simulation into the model.

The surface processes included are drifting, spreading and deposition. The oil enters the water column by dissolution and entrainment. The algorithm for the subsurface diffusion and advection makes use of the particle-in-cell method and is described in detail in Pavish (1977) and Spaulding (1976).

The output of the main program includes spillet size and location, subsurface concentrations, particle positions and a mass balance. In the final step of the simulation, this output is presented in graphical form by the various plotting routines. Specifically, mass balance, areal extent of the oil and a vertical view of the spill area are plotted.
CHAPTER II ENVIRONMENTAL GRIDS AND INPUT PROGRAMS

Input parameters required by the preview and the main simulation are logically divided into five main categories: environmental, oilspill, treatment, run control, and restart. Each of these categories has associated with it a well-defined format or set of formats. The user is required to determine and properly format variables in the first four groups. The restart data set is generated by the main simulation and intended to be transparent to the user; hence, only its function is described in this chapter.

The most complex set of input parameters is the environmental data set. In light of this, a pair of programs was written that will place environmental data into the proper format for input to the simulation model or check the environmental grids that may have been generated by the user. In this chapter, these programs are briefly described. Prior to this description, however, it is necessary to introduce the concepts associated with the environmental grids. This is done in the first section, the second section being reserved for the program description.

The other input parameters and formats are discussed in detail in Appendix I along with a list showing the order of entry of all input data.

A. Environmental Coordinate System

The environmental data are entered on a set of rectangular grids. The position of the (1,1) element is used to locate the grid with respect to longitude and latitude. The spacing between values is constant but not necessarily the same in both directions. The angle of the grid with respect to lines of constant latitude is a variable, defined by an input parameter and measured counterclockwise to the X axis. The model coordinate system is right handed with, for the zero rotation case, positive x eastward, and positive y northward. A grid may consist of from one element, in which case the variable defined is assumed to be spatially homogeneous over the entire ocean, or as many as 30 x 15 elements. The environmental data can be defined by either one or two grids. For example, wind velocity has x and y components and, therefore, needs two grids. Table 3 outlines the environmental grid variables and units.

The user has the option of spacing the environmental grids either in a spherical coordinate system or in a rectangular coordinate system. Spherical coordinates are used when the spatial scale of the problem is large, i.e. during the course of the simulation, the spill is expected to drift and spread over a distance covering several degrees latitude or longitude. This is referred to as the "large scale mode." Rectangular coordinates are used when the scale of the problem is small, less than a degree or so of latitude. This is referred to as the "small scale mode." The parameter ISCAL is used to specify the scale mode and applies to all environmental grids for a given simulation.

The units of the spacing between grid elements are dependent on the scale mode chosen. Environmental grids in the large scale mode may not be rotated. The spacing for the large scale mode must be in degrees of longitude and latitude for the x and y directions respectively, the units for the tidal currents must be degrees/sec for the large scale mode
<table>
<thead>
<tr>
<th>GRID</th>
<th>TITLE</th>
<th>VARIABLE 1</th>
<th>VARIABLE 2</th>
<th>FORMAT</th>
<th>COMMON BLOCK</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bathymetry</td>
<td>Bathymetry</td>
<td>Depth</td>
<td>-</td>
<td>Real</td>
<td>DFTH</td>
<td>Must not be moved during a run</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Meters</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Computational</td>
<td>Computational</td>
<td>Depth</td>
<td>-</td>
<td>Integer</td>
<td>COMP</td>
<td>Describes operational area. Must not be moved during a run</td>
</tr>
<tr>
<td>Cell</td>
<td>Cell</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>Temperature</td>
<td>Temp.</td>
<td>-</td>
<td>Real</td>
<td>TMPC</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Degrees C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wind Velocity</td>
<td>Wind Vel</td>
<td>U</td>
<td>V</td>
<td>Real</td>
<td>WIND</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>m/sec.</td>
<td>m/sec.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sea State</td>
<td>Sea State</td>
<td>Height</td>
<td>Period</td>
<td>Real</td>
<td>SEAS</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>meters</td>
<td>Seconds</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Current</td>
<td>Current</td>
<td>U</td>
<td>-</td>
<td>Real</td>
<td>TIDE</td>
<td>If large scale model - use degrees/sec.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>m/sec. or</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>m/sec or</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>depth/sec.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Current</td>
<td>Current</td>
<td>V</td>
<td>-</td>
<td>Real</td>
<td>TIDE</td>
<td>Same</td>
</tr>
<tr>
<td></td>
<td></td>
<td>m/sec or</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>depth/sec.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
because of the linear interpolation techniques which are used in the sub-surface portion of the model. The units of the spacing for the small scale mode is meters.

All of the grids are self-explanatory with the exception of the computation cell grid. This grid assigns an integer value to each element which when taken together, describe the area of interest (see Table 4) in both the horizontal and vertical directions. The program assumes the water surface cell reflects the particle downward and the bottom cell deposits the particle.

The uses must change 2 lines in the subroutine BOUNV (see Appendix IV) if another value is preferred.

The gridding system is a semispace-staggered system in that the computational cells are defined in the center of a cell while the remaining grids are defined at cell corners. There are no values at any of the zero locations (i.e., (0,0), (0,1)...) for any of the grids. The depth grid and computational cell grid are not to be moved or changed during a run because the program uses these grids as references. All other environmental grids may be moved or changed in any time step.

8. Input Programs for Environmental Data Grids

As is apparent from the description above, there is a great deal of flexibility in the nature of the environmental grids, the input format required of these variables by the input subroutine ARAYIN in both the preview and main simulation models is, however, quite precise. For this reason, a pair of programs (GRIDS and READATA) have been written to aid in the preparation of environmental data and to check the data sets once prepared prior to submitting a lengthy simulation. As indicated in Figure 1, this step is not mandatory but rather included as an aid in data preparation for the user. It should be stressed that these programs operate only on environmental variables. It is also important to note that although a user may elect not to use the formatting program, GRIDS, s/he is still advised to use the program, READATA, which reads and displays the "correctly formatted" variables, i.e., to check the data sets no matter how they are prepared. An error on the input environmental data sets may result in a significant loss of time and money. Flow charts for both programs are shown in Figure 2. The first program, GRIDS, places the environmental data into the power format for use by the main program. It first reads the grid definition variables such as angle and grid spacing. The program then calls a subroutine supplied by the user. This routine must read the environmental data and then perform any necessary interpolations or conversions to put it into a rectangular grid which will be used by the main program. The program then uses the subroutine ARAYOT which is basically a copy of the subroutine ARAYIN in the main program which reads the data, the only change being that this subroutine writes instead of reads the data. GRIDS may also be used to print the data if desired. It requires 200 kilobytes of memory and takes approximately 1.5 equivalent CPU minutes to write 135 environmental grids. These storage and run values will vary as a function of the amount of manipulation required.
Figure 2. Flow charts for GRID and READATA
The second program, READATA, reads environmental grids as formatted for input to the simulation program exactly as the main program will read them and then prints out these arrays. This program needs only 128 kilobytes of memory and takes approximately ten seconds of execution time to read and write 75 steps.

**TABLE 4**

**COMPUTATIONAL CELL DEFINITION**

<table>
<thead>
<tr>
<th>VALUE</th>
<th>DEFINITION</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Land cell; More than half the cell is land</td>
<td>Important for Shoreline Interaction Processes</td>
</tr>
<tr>
<td>1</td>
<td>A water cell; Surrounded on all sides by other water cells</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Open Boundary cell; At least one side is at the edge of the grid</td>
<td>Important for interpolation when oil tracks near the boundary</td>
</tr>
<tr>
<td>101</td>
<td>Adjacent Water Cell; At least one side is connected to an open boundary cell on a land cell</td>
<td>Same as above</td>
</tr>
<tr>
<td>3</td>
<td>Reflection cell; Reflects droplets away from bottom or surface in vertical direction</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Bottom Depositional Cell; absorbs any oil which moves to within 1/2 grid spacing of bottom</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER III  PREVIEW RUN

In early applications of the model, it was found that prior to a full scale simulation, it was often useful to perform a quick simulation, skipping the detailed modeling of the subsurface portion of the spill. These runs were performed for one of two reasons:

1. The distribution of the subsurface portion of the spill was of little or no interest for the case under study.

2. Such a run was useful in determining the mass, XMSPAR, to be assigned to the marker particles, in the full scale simulation. As indicated in Chapter I, the total volume of oil entrained depends on a number of parameters that are continuously changing during a simulation; hence, this is a very difficult parameter to predict prior to the simulation. To make full use of the resolution offered by the subsurface portion of the model, the user generally wants to use as many marker particles as allowed, 2000 as presently configured. To do this, the correct mass per particle, XMSPAR, to achieve full utilization, must be determined prior to the simulation. If the mass per particle is too large, then less than the permissible number of marker particles will be released. If XMSPAR is too small, the entrainment of oil into the water column will terminate prematurely because there will be no particle locations available in the model to allow for the entrainment of new particles.

Because of the apparent need for such runs and the substantial savings in execution time that resulted from skipping the sophisticated subsurface portions of the model, the Preview run was introduced. The Preview run is invoked by setting the run control parameter, NRUN, to 1. The preview flow chart is shown in Figure 3 and a comparison with the flow chart for the full scale simulation shown in Figure 4 indicates that the only difference between the two runs is omission of the subsurface portion of the spill in the preview.

The output of a preview run may be used as input to the plotting programs exactly as the output from a full scale simulation, with the single exception that the subsurface distribution of the spill not be specified. The surface distribution is correct, identical with that resulting from a full scale simulation. The mass balance is correct except that droplets are not removed from the water column, so that the fraction of droplets that are deposited on the bottom or that escape through an open boundary, i.e., that leave the water column are not currently specified.

For a more detailed description of algorithms used in the surface related portion of the spill, the reader is referred to the discussion of the full simulation in Chapter 4.
Figure 3. Flow Chart for the Preview Run
Figure 4. Flow Chart for Main Simulation
CHAPTER IV. MAIN SIMULATION

A. Introduction

This section is concerned with the description of the oil spill simulation model. The theoretical background is briefly discussed, followed by a description of program functions.

The objective of the model is to perform an environmental assessment of the treatment, with chemical dispersants, of spilled oil. This model, therefore, is directed primarily at the operational category of models dealing with cleanup and treatment alternatives. The model emphasizes the subsurface transport of spilled oil in much greater detail than those previously constructed because the major result of chemical treatment is to disperse the spilled oil into the water column. The flow chart for the model is shown in Figure 4. Most processes are handled in individual subroutines so that new algorithms can be easily incorporated. A more detailed description of the program, its subroutines and variables, are included in the Appendices III and IV.

B. Initialization

The first function performed in a simulation is to initialize. This consists of zeroing a number of counter and variables, such as mass balance, in addition to entering all fixed run control input which to a large extend will define the course of the simulation. The distinction "fixed" used above designates run control parameters that are entered once and remain unchanged for the rest of the simulation. They comprise two groups of variables, those entered in the main program which control the overall simulation (number of time steps, device numbers from which environmental data is to be read, etc.) as well as the parameterization of all surface related phenomena and those which determine the parameterization of the subsurface phenomena. All input parameters, associated formats and the order in which they are input are described in detail in Appendix I.

If this run is to continue a simulation begun in a previous run, the next step is to read the restart data set. The parameter NSTRT is used to specify a restart, being 1 if it is a continuation and 0 if the run is to begin from scratch. NSTRT equal to 1 requires that a previous run output all of the restart variables to disk. The restart data set contains the variables which define the spill at an instant in time with such as the spilllet size and location, droplet properties and location, mass balance and any ongoing cleanup or treatment efforts at that step. It also retains the print parameters which control the output data stream, how much output and where it is to be written. For a restarted run, the program will also read all of the stored output data sets up to the restart step. This permits the use of the original output data sets.

The program then reads the bathymetry and computational cell grids as well as the shoreline data points. Because the droplet positions are defined with respect to the bathymetric grid, this grid cannot be changed in the middle of a run. This is why these grids are read prior to the commencement of the iteration in time.
The iteration in time now begins. The first function performed at each time step is to read in the step control parameters. These parameters indicate whether or not new environmental, spill or cleanup response data are to be input in this time step. Any of the environmental or spill control data sets except the definition of computational cells, the bathymetry and the shoreline, wind, temperature, sea state, tidal velocity, mechanical cleanup efforts, chemical treatment efforts and newly spilled oil may be read in at any time step. Cleanup and treatment efforts can overlap in time and space and grids can change orientation and spacing from one time step to the next. This allows for easy insertion of different resolution data such as from two satellites with different spatial resolutions or different orbital inclinations.

If this is a restarted run, and the previous run ended on an error, the program enters at this point a loop which reads all of the control parameters, environmental grids and cleanup/treatment efforts up to the point where the previous run stopped. Normal termination at a run also results in the appropriate data being written to the restart data set. The user must specify if the restarted run is to use the previous output data sets or use a new group of data sets. This is done by the use of the parameter NSTFN. This parameter indicates whether to use the previous data sets (NSTFN=1) or to use new data sets (NSTFN=0). The user must, however, in this case supply new input and output data sets.

C. Surface Processes

The program then executes the algorithms dealing with the surface related processes (see Figure 5). Each process is dealt with by a different subroutine and all are called from one subroutine. This subroutine loops over all spilllets performing all surface related computation on one before moving on to the next. If a spilllet moves to the edge of the study area, it is taken out of the loop so that no further processes will affect it. The first surface processes dealt with are those related to cleanup or chemical treatment efforts on the spilllet. The variables used for this, such as efficiency, dispersant rate, etc., have been obtained through input and are described in Appendix I. These efforts are executed in the subroutines TREAT and CLNUP (see Appendix IV for a description).

The spilllet is then located within each of the environmental grids. This is done for two reasons. First, it determines if the spilllet is within the grid. If the spilllet is outside of one grid, it is considered to be out of the study area and it is removed from the loop. If the grid is a single point, it covers the entire two dimensional plane and the spilllet will never leave this grid. Second, the environmental variables are averaged over the spilllet. This is done by averaging the values at all of the grid locations that the spilllet covers. Some values such as depth are not used currently but the average wind velocity is used for evaporation, entrainment and drifting and the average current is used for drifting. See subroutine LOC8 in Appendix III for a detailed description of the location procedure.

The natural entrainment of mass and the creation of marker particles, is performed next. The amount of naturally entrained oil is determined from the Audunson et al. (1979) formulation. An exponential decay is added to Audunson’s model to simulate the decrease in the amount of oil
Figure 5. Flow Chart for Surface Portion of Simulation
entrained due to weathering. See subroutine ENTMAS, in Appendix IV, for a detailed discussion of this calculation. The amount of mass naturally entrained is combined with the mass dispersed into the water column during chemical treatment and the number of particles created is determined by dividing the entrained mass by XMSPAR, the mass per particle, a user supplied parameter (see Appendix I). The particles are then distributed in an ad hoc manner (described in the Appendix IV) by subroutines ENTRN and INJECT. Grossly they are distributed at random beneath the spillet.

The next process addressed is spreading. This is done using the simple three regime mechanism proposed by FAY (1969). There is a slight modification to the Fay procedure in that the effective release time for a given spillet is a variable that can change during the evaluation of the spillet. This is described in the Appendix IV for subroutine SPREAD and is necessitated by the requirement that oil may be added to or removed from a spillet or its interfacial tension may be changed with time.

Oil is then evaporated from the spillet using the method developed by Wang, Yang and Hwang (1976). (See Appendix III subroutine EVAPOR 8). The Wang, et. al. formulation requires that the oil be divided into eight components, the fraction by weight of each component being supplied by the user. These fractions are given for several crude oils, a No. 2 fuel and Bunker C oil in Appendix IX.

Following the evaporation, the surface slicks are advected. This is done using the tidal currents plus (vectorially) 3.5 percent of the wind speed (see Subroutine SURDFT).

D. Subsurface Process

The subsurface processes (which are again called from one subroutine) are now performed (See Figure 6). The important feature of the subsurface portion of the model is the mixed Eulerian-Lagrangian coordinate system. The Eulerian coordinate system is the one on which the tidal currents, the bathymetry and the computational cells are defined. The Lagrangian coordinate system is the one on which the oil droplet concentration is defined and is parallel to and contained within the Eulerian bathymetry system. This system expands and translates so as to always include all particles. Variables defined on the Eulerian system are interpolated to the Lagrangian system. The Lagrangian system also allows for a coordinate transformation on z, the vertical variable, such that the water column at every horizontal node is divided into the same number of equally spaced layers. This means that as the water becomes shallower, the vertical grid spacing becomes smaller, thus keeping the same relative vertical resolution.

Prior to diffusing and advecting the marker particles in the water column, the Lagrangian system must be established. This is done by locating the extremes in x and y of the particle positions and then adding a buffer to these extremes. This defines the edges of the Lagrangian grid. The grid spacing is determined by dividing the distance between the edges of the grid by the number of grid elements. (see subroutine GRIDEX). This process is repeated each time step so that the droplets
Figure 6. Flow Chart for Subsurface Portion of Simulation
never leave this grid. The program then checks the location of the dropplets with respect to the computational cell grid (see subroutine BOUNV) and performs any necessary operations (e.g. deposits droplets on bottom or on shore). The concentrations are calculated at each of the floating grid locations (see subroutine CONC). Because the number of particles entrained in the first few time steps may be very small (say 100) and the concentration distribution calculated under such circumstances might be statistically unstable, this subroutine (CONC) is only called if a minimum number of particles (set by input parameter NCRIT) is exceeded. The next step is to interpolate the fixed grids values of tidal height, depth and currents onto the floating grid (see subroutine VELCT). Then, the diffusion velocities at each Lagrangian grid location are calculated and added to the advective terms. The particles are moved according to these velocities (see subroutine DISPV). The last step in the subsurface section is to output all requested subsurface information (see subroutine PRINT and output parameters KPRTU, KPRTC, KPRTP, NPRU, NPRC and NRPB in Appendix I). The output may go to paper and/or disk data sets, the latter being used as input to the plotting program. The step intervals for such output is controlled by a group of parameters input at the beginning of the run. The data output in PRINT are the concentration grid, the particle position array and the advective plus diffusive velocity Lagrangian grid. If the concentration was not calculated previously (i.e., if the number of particles is less than NCRIT), a new Lagrangian grid is created, the boundaries are checked and the concentration is calculated for printout. This terminates the subsurface portion of the simulation for the current time step.

E. Spill Overlap, Mass Balance and Restart Output

The next function of the main program is to add any spillets which overlap by a certain percentage (Input parameter COMB) and also write the mass balance to paper and/or disk. The final step is to save the restart variables if this step is an even multiple of NSUMM, the output interval for the restart data set.
CHAPTER V  REFORMATTING AND PLOTTING PROGRAMS

A series of programs capable of reformatting and plotting the results of a simulated spill have been written to accompany the oil spill model. The relationship between each of the programs in the output and the data output from the model is shown in Figure 7. There are three possible plotted outputs of data resulting from a simulation.

i. Mass balance versus time (program PLOTMASS)

ii. The areal extent of the subsurface oil exceeding a given concentration and the areal extent of the surface slick greater than a given thickness, both as a function of time (program PLOTAREA)

iii. The spatial distribution of both subsurface and surface oil at a given instant in time (program PLOTMAP).

As indicated in Figure 7, the data output to disk by the simulation model is in the correct format for direct input to the mass balance plotting program. Both of the other plots, on the other hand, require at least one intermediate program to work the model output data into an appropriate form for input to the plotting routines. In particular, although the concentration distribution is output along with the other output parameters, it may be desirable to recalculate the concentration distribution on a grid different than the Lagrangian grid of the model. This is done by the program PARTICLE for those times in which sub-surface particle positions were output to disk. Prior to input into either PLOTAREA, PLOTMAP or CHECOATA, the concentration grid data, as well as the spillet data, must be passed through the reformatting program DATAOUT. This step is executed after recalculation of the concentration grid (if performed) as indicated in Figure 7.

Once the data has been reformatted, it may be verified by the program CHECOATA or plotted by PLOTAREA or PLOTMAP.

Each of the programs outlined in Figure 7 are briefly described below. All plotting programs make use of a CALCOMP Plotter with standard Calcomp subroutine calls. The detailed descriptions of these programs are included in Appendix VI.

A. PLOTMASS

The flow chart for the program PLOTMASS is included in Figure 8. There are two sets of input to this program; mass data output by the simulation model and plot control parameters defined by the user. These are input as shown in Figure 8. As indicated in the Figure, the user may plot the output of several different simulations in one run of PLOTMASS, or s/he may plot several different mass balance plots for the same simulated spill. The plot control parameters specify, among other things, the various mass quantities (atmosphere, surface, etc.) to be plotted. Finally, the program allows the data from two separate simulations to be plotted on the same graph for comparison.
Figure 7. Overview of Output Program Sequence
Figure 8. Flow Chart for Program PLOTMASS
B. PARTICLE

As indicated above, this program is used to calculate the concentration distribution on a grid different from the Lagrangian grid set up by the model. It requires, as input, the particle positions output by the simulation model, as well as those parameters required to define the new grid. The user supplies the latter. The flow chart for the program PARTICLE, is shown in Figure 9. The routines in this program that perform the required calculations have been extracted directly from the main program, hence, perform the calculations in exactly the same fashion.

C. DATAOUT

This program serves four functions. First, it compresses the data output by the oil spill model. Second, it integrates the surface and subsurface data sets into one data set for input to the plotting programs. Third, it performs cuts on both the surface distribution, by thickness, and on the subsurface distribution, by concentration. Fourth, it reads particle position data, (if requested) to be used by the program CHECDATA in verifying the output of the simulation. The overall operation of this program is outlined in the flow chart shown in Figure 10.

D. CHECDATA

This program simply reads the output of DATAOUT and prints it in an easy to read fashion for quick verification. The execution of this program is not required to plot the data.

E. PLOTAREA

The program PLOTAREA, see Figure 11 for its flow chart, is used to plot the areal extent of the surface and subsurface distribution. It reads the data output by DATAOUT from which the areal quantities are calculated. In the calculation for the area covered by the spillleton, no attempt is made to account for the overlap of spillleton, hence, the areal extent of surface oil will be overestimated if there is overlap. The user may elect to plot for one simulation only the surface and/or the subsurface. Or, s/he may elect to plot the output of two different simulations on the same plot for comparison.

F. PLOTMAP

The program, PLOTMAP, shown in the flow chart of Figure 12, allows the user to plot a map of the spill, showing both the surface and subsurface distribution of oil. Using the surface/subsurface data set output by DATAOUT. In addition, this program requires a set of control parameters that define the plots to be performed. There is a third optional input data set and that is the shoreline. The user may elect to plot the surface and/or the subsurface on a single plot at a given instant in time or s/he may elect to plot on a single plot these quantities at a number of different times. The user may also specify the times at which such plots are to be performed, as long as surface and/or sub-surface data was output by the main simulation at these times. The real use of this parameter is in limiting the plotting output in the case where, say maps for the 10, 20 and 30 day of a 30 day spill are desired, but the model
Figure 9. Flow Chart for Program PARTICLE
NOTES: * write out for plotting data set if needed  
** print out as read in  
*** printout in formatted manner

Figure 10. Flow Chart for Program DATAOUT
Figure 11. Flow Chart for Program PLOTAREA
Figure 12. Flow Chart for Program PLOTMAP
outputs sufficient data to generate maps every day. Again, the user must remember that only the spills exceeding the thickness defined in DATAOUT and the region in which the concentration exceeds the level also defined in DATAOUT, will be plotted. To obtain maps of lower concentration values, DATAOUT must be rerun. As in the case of PLOTAREA and PLOTMASS, two simulation runs may be compared on one map.
APPENDIX I: Input Parameters and Formats for the Preview Run and the Main Simulation

A. Environmental Variables

Input Data Format

In Chapter II GRIDS, a program that will format environmental data for input to the main programs is described. For the user who elects not to use this program, the format structure of the environmental data is described here. First, the grid name and definition is input. Specifically, the variables NAM, VAR1, UNITS1, VAR2, and UNITS2 are read unformatted or with the format (13A4). See Table I-1 for a description of each variable. The name of the grid entered in NAM must be exactly as given in Table 3 (Chapter 2) and must be left justified. The next logical input record contains IMAX, JMAX, ANGLE, XL, YL, XS, YS, UNITS3, again either unformatted or with format:

(2I5, 3F10.6, 2F10.4, 2A4)

Finally the grid itself is read in. Again the option is either unformatted or formatted. In the unformatted case, the entire grid is read in as one logical record, the implied do loop on X (east to west) then on Y (south to north). If the grid contains two parameters, e.g., u and v, two logical records are required, one for each parameter. Some grids are real and some integer. (See Table 3, Chapter 2, for a definition of which are real and which are integer, as well as which are two parameters and which are only one). For the case in which the grid is real and is to be formatted, the format is:

(10F6.2)

Each row begins a new logical record and is read from left to right (west to east) starting at the lowest y or southernmost row of the grid and moving up. For two parameter arrays, first the entire array for one parameter is read and then the second parameter is read with exactly the same format.

For integer variables, the fashion in which the data is read is the same, only the format differs.

(15I4) replaces (10F6.2)

Table I-2 presents the read statements as they appear in ARAYIN.

B. Oilspill Variables

1. General Description

As discussed in Chapter I, spilled oil is represented in the simulation either as spiltlets, circular puddles of oil on the surface, or droplets, representative droplets of oil in the water column. In its present configuration, only spiltlets may be defined by the user. Droplets are either defined by the program or read in under the restart capability, but the user does not have easy access to this means of entering data.
<table>
<thead>
<tr>
<th>Variable</th>
<th>Format</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>NAM (3)</td>
<td>3A4</td>
<td>Name of input grid used for print-out. These must be exactly as written in Table III, Chapter I under Title.</td>
</tr>
<tr>
<td>VAR1(2)</td>
<td>2A4</td>
<td>Name of the first variable of the grid; used for printout.</td>
</tr>
<tr>
<td>UNITS1(3)</td>
<td>3A4</td>
<td>Dimensions of the first variable used for printout. (meter, degrees per/sec., etc.)</td>
</tr>
<tr>
<td>VAR2(2)</td>
<td>2A4</td>
<td>Name of second variable of the grid.</td>
</tr>
<tr>
<td>UNITS2(3)</td>
<td>3A4</td>
<td>Dimensions of the second variable.</td>
</tr>
<tr>
<td>IMAX</td>
<td>I5</td>
<td>Number of elements in the x direction.</td>
</tr>
<tr>
<td>JMAX</td>
<td>I5</td>
<td>Number of elements in the y direction.</td>
</tr>
<tr>
<td>ANGLE</td>
<td>F10.6</td>
<td>Angle measured from lines of constant latitude to the positive x-axis of the grid in the counterclockwise direction (degrees).</td>
</tr>
<tr>
<td>XL, YL</td>
<td>F10.6, F10.6</td>
<td>Location of the (1,1) element of the grid (Longitude and Latitude).</td>
</tr>
<tr>
<td>XS, YS</td>
<td>F10.4, F10.4</td>
<td>Spacing between grid lines in x and y directions, respectively (meters or degrees, see input variable ISCAL).</td>
</tr>
<tr>
<td>UNITS3(2)</td>
<td>2A4</td>
<td>Dimensions of XS and YS.</td>
</tr>
<tr>
<td>ARRAY1</td>
<td>see Table IV</td>
<td>Values at grid nodes for first grid if real.</td>
</tr>
<tr>
<td>ARRAY2</td>
<td>see Table IV</td>
<td>Values at grid nodes to second variable if two grids describe one environmental variable.</td>
</tr>
<tr>
<td>MARAY1</td>
<td>see Table IV</td>
<td>Values at grid nodes for first grid if integer.</td>
</tr>
<tr>
<td>MARAY2</td>
<td>see Table IV</td>
<td>Values at grid nodes for second grid if required.</td>
</tr>
</tbody>
</table>
TABLE 1-2 INPUT IN SUBROUTINE ARRAYIN

Formatted

line number
12 Read (ND,100) NAM, VAR1, UNITS1, VAR2, UNITS2
13 100 FORMAT (13A4)
14 READ (ND,105) IMAX, JMAX, ANGLE, XL, YL, XS, YS, UNITS3
15 105 FORMAT (215, 3F10.6, 2F10.4, 2A4)

Unformatted

line number
18 READ (ND) NAM, VAR1, UNITS1, VAR2, UNITS2
19 READ (ND) IMAX, JMAX, ANGLE, LX, YL, XS, YS, UNITS3

60-83 C HERE TO READ UNFORMATTED REAL VARIABLES.
C
40 CONTINUE
READ (ND) ((ARRAY1 (I,J), I=1, IMAX), J=1, JMAX)
IF (NO.EQ.1) GO TO 80
READ (ND) ((ARRAY2 (I,J), I=1, IMAX), J=1, JMAX)
GO TO 80
C C HERE TO READ UNFORMATTED INTEGER VARIABLES.
C
50 CONTINUE
READ (ND) ((ARRAY1 (I,J), I=1, IMAX), J=1, JMAX)
IF (NO.EQ.1) GO TO 90
READ (ND) ((ARRAY2 (I,J), I=1, IMAX), J=1, JMAX)
GO TO 90
C C HERE TO READ FORMATTED REAL VARIABLES.
C
60 CONTINUE
DO 62 J=1, JMAX
READ (ND,110) (ARRAY1 (I,J), I=1, IMAX)
110 FORMAT (10F6.2)
62 CONTINUE
IF (NO.EQ.1) GO TO 80
DO 64 J=1, JMAX
READ (ND,110) (ARRAY2 (I-J), I=1, IMAX)
64 CONTINUE
GO TO 80
C C HERE TO READ FORMATTED INTEGER VARIABLES
C
70 CONTINUE
DO 72 J=1, JMAX
READ (ND,120) (ARRAY1 (I,J), I=1, IMAX)
120 FORMAT (1S14)
72 CONTINUE
IF (NO.EQ.1) GO TO 90
DO 74 J=1, JMAX
READ (ND,120) (ARRAY2 (I,J), I=1, IMAX)
74 CONTINUE
A spillet is described by positional parameters, physical parameters, and chemical parameters (See Table 1-3). The user is required to specify all parameters describing a spillet for the time when it is first to appear.

It is not necessary that the spillet be fresh in the sense that the oil has just escaped from a well, tanker, or pipeline. If the user would like to simulate a spill starting several weeks after the initial catastrophe, it suffices that s/he enter spillets representing the locational, physical, and chemical variables as they are at that time. The model takes over from that point.

2. Input Data Format

Oil Spill parameters are entered in two logical records. The first record reads:

\text{BSPIL, OSPIL, RSPIL, SSPIL, TSPIL, USPIL, WSPIL, XSPIL, YSPIL}

with the format

\text{(6F8.3, E8.2, 2F8.3)}

The units assumed by the program are shown in the list of spillet variable in Table I-3.

Following this the composition of the spillet is input from one logical record containing between one and eight numbers each representing the fraction of a given hydrocarbon class.

The format of this record is:

\text{(8F5.2)}

The number of hydrocarbon classes is defined by the user through the parameter MSPIL discussed in the run control section. This variable is specified once per run, i.e., all spillets are required to have the same number of hydrocarbon classes. The program, as currently configured, uses all eight classes. The fraction of each of the eight classes for four different types of oil, as well as a chemical description of each class, is given in Appendix IX. The user must exercise great caution if s/he decides to use a different set of hydrocarbon classes from the eight outlined in Appendix IX. In particular, the coefficient defining vapor pressure for each class included as data in the evaporation subroutine will have to be changed if the classes are restructured.

The format statements as they actually appear in the subroutine that reads in spillet parameters are shown in Table I-4.

C. Treatment Variables

1. General Description
### TABLE I-3
**SPILLET PARAMETERS**

<table>
<thead>
<tr>
<th>Variable name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSPIL</td>
<td>Beginning time of spillet (hours).</td>
</tr>
<tr>
<td>DSPIL</td>
<td>Density of oil (gm/cc).</td>
</tr>
<tr>
<td>RSPIL</td>
<td>Radius of spillet (meters).</td>
</tr>
<tr>
<td>SSPIL</td>
<td>Interfacial tension of oil (dynes/cm).</td>
</tr>
<tr>
<td>TSPIL</td>
<td>Density of oil at time equal zero (gm/cc).</td>
</tr>
<tr>
<td>USPIL</td>
<td>Kinematic viscosity of oil (centistokes).</td>
</tr>
<tr>
<td>WSPIL</td>
<td>Weight of oil in spillet (metric tons).</td>
</tr>
<tr>
<td>XSPIL</td>
<td>Longitude of center of spillet.</td>
</tr>
<tr>
<td>YSPIL</td>
<td>Latitude of center of spillet.</td>
</tr>
<tr>
<td>GSPIL</td>
<td>Mass fraction of each class of oil.</td>
</tr>
</tbody>
</table>

### TABLE I-4
**FORMAT OF SPILLET PARAMETER INPUT**

```plaintext
READ (NO,100) BSPIL(I), DPSIL(I), RSPIL(I), SSPIL(I), TSPIL(I), USPIL(I), WSPIL(I), XSPIL(I), YSPIL(I)
1
FORMAT (6F8.3, E8.2, 2F8.3)
READ (NO,101) (GSPIL(I,J), J=1, MSPIL)
FORMAT (8F5.2)
```
### TABLE I-5
PHYSICAL CLEANUP PARAMETERS

<table>
<thead>
<tr>
<th>Variable name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCLN</td>
<td>Beginning time of effort (hours).</td>
</tr>
<tr>
<td>DCLN</td>
<td>Duration of this effort (hours).</td>
</tr>
<tr>
<td>ECLN</td>
<td>Efficiency of effort.</td>
</tr>
<tr>
<td>RCLN</td>
<td>Radius of effort (meters).</td>
</tr>
<tr>
<td>VCLN</td>
<td>Volume rate of cleanup effort (metric tons/hour).</td>
</tr>
<tr>
<td>XCLN</td>
<td>Longitude of center of cleanup effort.</td>
</tr>
<tr>
<td>YCLN</td>
<td>Latitude of center of cleanup effort.</td>
</tr>
</tbody>
</table>

### TABLE I-6
CHEMICAL TREATMENT PARAMETERS

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCHEM</td>
<td>Beginning of this effort (hours).</td>
</tr>
<tr>
<td>DCHEM</td>
<td>Duration of this effort (hours).</td>
</tr>
<tr>
<td>PCHEM</td>
<td>Fraction of oil entrained.</td>
</tr>
<tr>
<td>RCHM</td>
<td>Radius of this effort (hours).</td>
</tr>
<tr>
<td>SCHEM</td>
<td>Interfacial tension of treated oil (dynes/cm).</td>
</tr>
<tr>
<td>TCHEM</td>
<td>Toxicity of dispersant.</td>
</tr>
<tr>
<td>VCHEM</td>
<td>Volume rate of dispersant used (liters/hour).</td>
</tr>
<tr>
<td>WCHEM</td>
<td>Dispersant used per square meter (liters/meter²).</td>
</tr>
<tr>
<td>XCHEM</td>
<td>Longitude of center of effort.</td>
</tr>
</tbody>
</table>
Available in this model are two response alternatives to the simulated spill. One alternative is the chemical dispersion of the spill and the other is the mechanical cleanup of the oil. Both methods may be used simultaneously and for each method there may be up to ten efforts in progress at once. The algorithm employed to implement a spill response effort is discussed in a later chapter. A response to the spill is not required for a simulation.

2. Input Data Format

All seven mechanical clean-up variables are read in one logical record in alphabetical order with the format:

\[(7F10.3)\]

The variables are listed in Table I-5 along with the units assumed by the program.

In the case of chemical treatment, there are ten variables. These are again read in alphabetical order, this time however, in two logical records. The format used for chemical treatment variables is:

\[(5F10.3)\]

These variables, along with the appropriate units, are listed in Table I-6.

The read statements and associated format for both the mechanical cleanup and chemical treatment variables are shown in Table I-7.

---

**TABLE I-7 FORMAT STATEMENTS FOR RESPONSE VARIABLES**

- **a. Mechanical Cleanup**

  \[
  \text{READ} \ (\text{ND},100) \ \text{BCLN} \ (I), \ \text{DCLN} \ (I), \ \text{ECLN} \ (I), \ \text{RCln} \ (I), \\
  1 \ \text{VCLN} \ (I), \ \text{XCLN} \ (I), \ \text{YCLN} \ (I) \\
  100 \ \text{FORMAT} \ (7F10.3)
  \]

- **b. Chemical Treatment**

  \[
  \text{READ} \ (\text{ND},100) \ \text{BCHEM} \ (I), \ \text{DCHEm} \ (I), \ \text{PCHEM} \ (I), \ \text{RCHEM} \ (I), \ \text{SCHEM} \ (I), \\
  1 \ \text{TCHEM} \ (I), \ \text{VCHEM} \ (I), \ \text{WCHEM} \ (I), \ \text{XCHEM} \ (I), \ \text{YCHEM} \ (I) \\
  100 \ \text{FORMAT} \ 5F10.3
  \]
D. Run Control Variables

1. General Description

Run control variables include all parameters that control the evolution of a spill simulation but which, other than their association with the model, have little physical significance. All run control variables except the step control parameters are read in only once. A set of step control parameters is read in for each step. These parameters direct the model to read (or not to read) environmental variables, spillet variables, and response variables for the given time step. In the first step, a grid must be read in for each environmental variable. In addition, at least one spillet must be entered. All run control variables have been separated into three groups: general run control, subsurface control, and step control. These variables are listed in Table 1-8 to 1-10.

2. Data Input Formats

All run control variables except shoreline points and step control parameters are read in a similar format by one of the two subroutines READI and READF. READI is used to enter fixed point (integer) variables while READF is used for floating point (real) variables. They each require a logical record for each new variable entered. In addition, they require the name of the variable as used in the program. If an incorrect name is specified or the cards are out of order, a message is printed and the run terminated. In addition, integer variables must lie within a given range or the program will again print a message and the run will be terminated. These precautions are included to guard against an error associated with the input cards being out of order, a card forgotten or an integer variable entered one or more columns to the left of the desired location. The format for integer variables is:

\[(I15, 5X, A8)\]

where the A8 portion is to include the variable name left justified precisely as indicated in Tables I-8 and I-9. The format used for floating point (real) variables is:

\[(F15.5, 5X, A8)\]

where again A8 is the variable name.

Shoreline points are read in unformatted. Two logical records are required; one for x, longitude, and one for y, latitude. If NSHOR, the number of shoreline points, is zero, this read will be skipped.

All eight step control parameters are entered in one logical record in the following order:

NP, NV, NT, NK, NS, LSPIL, LCLN, LCHEM

These variables will be zero if no action is to be taken, one if the associated environmental grid is to be read in and equal to the number of
<table>
<thead>
<tr>
<th>Variable</th>
<th>Subroutine used</th>
<th>Range</th>
<th>Explanation</th>
</tr>
</thead>
</table>
| NSTRT    | READI          | 0-1     | 0 - this run is not a restart  
|          |                |         | 1 - this is a restart, the restart data set will be read. |
| NSTFN    | READI          | 0-1     | 0 - this restart run uses new output data sets.  
|          |                |         | 1 - this run uses previous output data set. |
| NSUMM    | READI          | 0-100   | Interval number of steps for writing out restart variables in the subroutine SUMMUP.  
|          |                |         | 0 - total spill simulation. |
| NRUN     | READI          | 0-1     | 1 - this activates the Preview run only (see Chapter III). |
| IDAY     | READI          | 1-365   | Day of year on which the spill begins. |
| NENV     | READI          | 0-100   | Print control parameter for formatted output of step control parameters in main program  
|          |                |         | 0 - no printout  
|          |                |         | 0 - prints out at this step interval. |
| DT       | READF          |         | Size of time step in hours. |
| TIMMAX   | READF          | 1-2     | Length of simulation (hours).  
| ISCAL    | READI          | 1-2     | 1 - select small scale mode  
|          |                |         | 2 - select large scale mode (see Chapter II). |
| NPRTA    | READI          | -1,0,1  | Environmental grid printout control parameter (see Subroutine ARAYIN).  
|          |                |         | -1 - no printout  
|          |                |         | 0 - limited printout  
|          |                |         | 1 - full printout |
| NPRTC    | READI          | 0-1     | Print control for cleanup and treatment efforts.  
|          |                |         | 1 - printout all current cleanup and treatment efforts  
<p>|          |                |         | 0 - printout only newly started efforts. |
| NR       | READI          | 1-20    | Input file for step control parameters. |
| NCD      | READI          | 1-20    | Unit from which computational cell grid is to be read. |</p>
<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
<th>Format Range</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCU</td>
<td>Computational cell grid format control parameter.</td>
<td>1-4</td>
<td></td>
</tr>
<tr>
<td>NDD</td>
<td>Unit number from which the bathmetric grid is to be read.</td>
<td>1-20</td>
<td></td>
</tr>
<tr>
<td>NDU</td>
<td>Bathmetric grid format control</td>
<td>1-4</td>
<td></td>
</tr>
<tr>
<td>NED</td>
<td>Unit number from which the tidal elevation grid is to be read.</td>
<td>1-20</td>
<td></td>
</tr>
<tr>
<td>NEU</td>
<td>Tidal elevation grid format control (See NDU).</td>
<td>1-4</td>
<td></td>
</tr>
<tr>
<td>NKO</td>
<td>Unit number from which the temperature grid is to be read.</td>
<td>1-20</td>
<td></td>
</tr>
<tr>
<td>NKU</td>
<td>Temperature grid format control (see NDU).</td>
<td>1-4</td>
<td></td>
</tr>
<tr>
<td>NSD</td>
<td>Unit from which sea state grid is to be read.</td>
<td>1-20</td>
<td></td>
</tr>
<tr>
<td>NSU</td>
<td>Sea state grid format control (see NDU).</td>
<td>1-4</td>
<td></td>
</tr>
<tr>
<td>NTDU</td>
<td>Unit from which the U components (x-direction) of current are to be read.</td>
<td>1-20</td>
<td></td>
</tr>
<tr>
<td>NTDV</td>
<td>Unit from which the V components (y-direction) of current are to be read.</td>
<td>1-20</td>
<td></td>
</tr>
<tr>
<td>NTUU</td>
<td>Format control for x current grid. (See NDU).</td>
<td>1-4</td>
<td></td>
</tr>
<tr>
<td>NTUV</td>
<td>Format control for y current grid.</td>
<td>1-4</td>
<td></td>
</tr>
<tr>
<td>NWD</td>
<td>Unit number from which the wind grid is to be read.</td>
<td>1-20</td>
<td></td>
</tr>
<tr>
<td>NWU</td>
<td>Wind grid format control (see NDU).</td>
<td>1-4</td>
<td></td>
</tr>
<tr>
<td>NCHD</td>
<td>Unit number from which the chemical treatment data is to be read in.</td>
<td>1-20</td>
<td></td>
</tr>
<tr>
<td>NCLD</td>
<td>Unit number from which the physical cleanup data is to be read.</td>
<td>1-20</td>
<td></td>
</tr>
<tr>
<td>NSHD</td>
<td>Unit number from which the shoreline points are to be read.</td>
<td>1-20</td>
<td></td>
</tr>
<tr>
<td>NSPD</td>
<td>Unit number from which new spillet information is to be read.</td>
<td>1-20</td>
<td></td>
</tr>
<tr>
<td>NMAX</td>
<td>Maximum number of droplets allowed. This parameter is used to dynamically allocate</td>
<td>1-2100</td>
<td></td>
</tr>
</tbody>
</table>
space for \(x,y,z\) and NORDR in the subsurface subroutines. These variables are currently
dimensioned of 2100 in the main program.

Maximum number of particle classes
allowed. The dimensions will allow 200
different types of particles.

Maximum number of particles per class.
Amount of oil to be represented by each
droplet metric (tons).

Maximum number of spillets allowed.
Dimension statements currently limit this
to 100.

Percentage of overlap needed in order to
combine two spillets (see Subroutine ADD).

Number of components of oil. Due to the
evaporation model, this is now set at 8.

Spillet print control parameter for disk
data sets. This gives the interval
(in steps) of how often to write out
spillet information. (see Subroutine
SPILIN).

Spillet printout control parameter.
-1' - no printout
0 - printout only on first step
0 - printout interval

Number of shoreline points.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Type</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCLASS</td>
<td>READI</td>
<td>1-200</td>
</tr>
<tr>
<td>NUMCLS</td>
<td>READI</td>
<td>1-200</td>
</tr>
<tr>
<td>XMSPAR</td>
<td>READF</td>
<td></td>
</tr>
<tr>
<td>MAXSPL</td>
<td>READI</td>
<td>1-99</td>
</tr>
<tr>
<td>COMB</td>
<td>READF</td>
<td></td>
</tr>
<tr>
<td>MSPIL</td>
<td>READI</td>
<td>1-9</td>
</tr>
<tr>
<td>NSPPRD</td>
<td>READI</td>
<td>-1-100</td>
</tr>
<tr>
<td>NSPPRP</td>
<td>READI</td>
<td>-1-100</td>
</tr>
<tr>
<td>NSHOR</td>
<td>READI</td>
<td>0-1500</td>
</tr>
<tr>
<td>Variables</td>
<td>Subroutine used</td>
<td>Range of Values</td>
</tr>
<tr>
<td>-----------</td>
<td>----------------</td>
<td>----------------</td>
</tr>
<tr>
<td>POWX</td>
<td>READF</td>
<td></td>
</tr>
<tr>
<td>POWY</td>
<td>READF</td>
<td></td>
</tr>
<tr>
<td>EXX</td>
<td>READF</td>
<td></td>
</tr>
<tr>
<td>EYY</td>
<td>READF</td>
<td></td>
</tr>
<tr>
<td>NTRANS</td>
<td>READI</td>
<td>0-1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DXX, DYY, DZZ</td>
<td>READI</td>
<td></td>
</tr>
<tr>
<td>DYY</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DZZ</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NSUB</td>
<td>READI</td>
<td>0-1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NDIFF</td>
<td>READI</td>
<td>0-1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NCRIT</td>
<td>READI</td>
<td>0-1000</td>
</tr>
<tr>
<td>NEXTR</td>
<td>READI</td>
<td>0-1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>DEPC</strong></td>
<td>READF</td>
<td>Vertical origin of initial particle distribution (meters)</td>
</tr>
<tr>
<td><strong>POMIN</strong></td>
<td>READF</td>
<td>Gives the minimum spacing in meters in the x and y-directions if only two particles are present. If the particles are too close together, the Lagrangian grid cannot be created around them without having an error.</td>
</tr>
<tr>
<td><strong>AFRAC</strong></td>
<td>READF</td>
<td>Determines the fraction of particles within RO (RO is radius of spillet divided by RIFRAC, see Subroutine ENTRN and INJECT).</td>
</tr>
<tr>
<td><strong>RIFRAC</strong></td>
<td>READF</td>
<td>Radius up to which particle density is uniform (see Subroutines ENTRN and INJECT).</td>
</tr>
<tr>
<td><strong>HENT</strong></td>
<td>READF</td>
<td>Length of time of entrainment for use in calculating the maximum radius of the initial particle distribution (see Subroutine ENTRN).</td>
</tr>
<tr>
<td><strong>DDIAMT</strong></td>
<td>READF</td>
<td>Diameter of droplets (mm).</td>
</tr>
<tr>
<td><strong>DVELZT</strong></td>
<td>READF</td>
<td>Vertical velocity of droplet (m/sec). Zero if neutrally buoyant.</td>
</tr>
<tr>
<td><strong>NPTSUB</strong></td>
<td>READI</td>
<td>-1  -1</td>
</tr>
<tr>
<td><em>NPRINTS</em></td>
<td>READI</td>
<td>0-100</td>
</tr>
<tr>
<td><strong>KPRTV</strong></td>
<td>READI</td>
<td>0-100</td>
</tr>
<tr>
<td>Variable</td>
<td>Type</td>
<td>Range</td>
</tr>
<tr>
<td>-----------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>NPRD</td>
<td>READI</td>
<td>0-1</td>
</tr>
<tr>
<td>NPRU, NPRC, NPRP</td>
<td>READI</td>
<td>0-100</td>
</tr>
<tr>
<td>NUSP</td>
<td>READI</td>
<td>1-20</td>
</tr>
<tr>
<td>NUPS</td>
<td>READI</td>
<td>1-20</td>
</tr>
<tr>
<td>NUCN</td>
<td>READI</td>
<td>1-20</td>
</tr>
<tr>
<td>NUPT</td>
<td>READI</td>
<td>1-20</td>
</tr>
<tr>
<td>NULV</td>
<td>READI</td>
<td>1-20</td>
</tr>
<tr>
<td>NUMS</td>
<td>READI</td>
<td>1-20</td>
</tr>
<tr>
<td>NUDP</td>
<td>READI</td>
<td>1-20</td>
</tr>
<tr>
<td>MULT</td>
<td>READI</td>
<td>1-20</td>
</tr>
</tbody>
</table>
spilllets, cleanup efforts, or treatment efforts to be read in. The format used is:

(815)

NOTE: One logical record with these eight parameters is read in for each time step of the model. The variables and their definition are shown in Table I-10.

E. Restart Variables

Restart variables are all the parameters required to restart a simulation which may have been terminated for one of three reasons: (1) program or system error that resulted in an abnormal termination of a job, (2) the user, after having run a simulation for some predetermined number of time steps, and having examined the resulting output decides to extend the run, or (3) the user wishes to run the model at several different time steps and spatial resolutions, e.g., high temporal and spatial resolution followed by coarser resolution. All the parameters required to restart the model are written to disk (or tape) every NSUMM time steps (NSUMM determined by the user). The model may be restarted only at the time step following the last time step for which restart data were written.

When a run is to be restarted, the run control variable NSTRT is set equal to 1. If the run is to restart an abnormally terminated one, all data sets used in the previous run must be included. The model will read these data sets to the point where the previous run terminated. If the user specifies NSTFN = 0, the program only reads the restart data set and uses new input and output data sets. In addition, a number of variables generated by the simulation and output to the restart data set are read.

F. Input Sequence for all Input Data

Because the user may elect to read some of the environmental variables, treatment data, or spilllet data from Unit 5 (the card reader, normally used for run control parameters), it is essential that the order in which all input data (except RESTRT) be known. This order is indicated schematically in Table I-II.
<table>
<thead>
<tr>
<th>Variable name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>NP</td>
<td>Wind grid control parameter.</td>
</tr>
<tr>
<td>NV</td>
<td>Tidal currents grid control parameter.</td>
</tr>
<tr>
<td>NT</td>
<td>Tidal heights grid control parameter.</td>
</tr>
<tr>
<td>NK</td>
<td>Temperature grid control parameter.</td>
</tr>
<tr>
<td>NS</td>
<td>Sea state grid control parameter.</td>
</tr>
<tr>
<td>LSPIL</td>
<td>Number of new spillets this step.</td>
</tr>
<tr>
<td>LCLN</td>
<td>Number of new cleanup efforts this step.</td>
</tr>
<tr>
<td>LCHEM</td>
<td>Number of new treatment efforts this step.</td>
</tr>
</tbody>
</table>
Table I-11

INPUT LIST (in order of entrance, read down from left to right)

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>NSTRT</td>
<td>Bathmetry Grid</td>
</tr>
<tr>
<td>NSTFN</td>
<td></td>
</tr>
<tr>
<td>NSUMM</td>
<td></td>
</tr>
<tr>
<td>NRUN</td>
<td></td>
</tr>
<tr>
<td>IDAY</td>
<td></td>
</tr>
<tr>
<td>NENV</td>
<td></td>
</tr>
<tr>
<td>DT</td>
<td></td>
</tr>
<tr>
<td>TIMMAX</td>
<td></td>
</tr>
<tr>
<td>ISCAL</td>
<td></td>
</tr>
<tr>
<td>NPRTA</td>
<td></td>
</tr>
<tr>
<td>NPRTC</td>
<td></td>
</tr>
<tr>
<td>NR</td>
<td></td>
</tr>
<tr>
<td>NCD</td>
<td></td>
</tr>
<tr>
<td>NDU</td>
<td></td>
</tr>
<tr>
<td>NDD</td>
<td></td>
</tr>
<tr>
<td>NED</td>
<td></td>
</tr>
<tr>
<td>NEU</td>
<td></td>
</tr>
<tr>
<td>NKD</td>
<td></td>
</tr>
<tr>
<td>NKU</td>
<td></td>
</tr>
<tr>
<td>NSD</td>
<td></td>
</tr>
<tr>
<td>NSU</td>
<td></td>
</tr>
<tr>
<td>NTDU</td>
<td></td>
</tr>
<tr>
<td>NTDV</td>
<td></td>
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<tr>
<td>NTUU</td>
<td></td>
</tr>
<tr>
<td>NTUV</td>
<td></td>
</tr>
<tr>
<td>NWID</td>
<td></td>
</tr>
<tr>
<td>NWU</td>
<td></td>
</tr>
<tr>
<td>NCHO</td>
<td></td>
</tr>
<tr>
<td>NCLD</td>
<td></td>
</tr>
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<td>NSHD</td>
<td></td>
</tr>
<tr>
<td>NSPD</td>
<td></td>
</tr>
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<td>NMAX</td>
<td></td>
</tr>
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<td>NUCLAS</td>
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</tr>
<tr>
<td>NUMCL</td>
<td></td>
</tr>
<tr>
<td>XMSPAR</td>
<td></td>
</tr>
<tr>
<td>MAXSPL</td>
<td></td>
</tr>
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<td>DCOMB</td>
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<td>MSPIL</td>
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</tr>
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<td>NSPPRD</td>
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<tr>
<td>NSPPRP</td>
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<td>NUSP</td>
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<tr>
<td>NURS</td>
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</tr>
<tr>
<td>NUON</td>
<td></td>
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<tr>
<td>NUPT</td>
<td></td>
</tr>
<tr>
<td>NUVL</td>
<td></td>
</tr>
<tr>
<td>NUMS</td>
<td></td>
</tr>
<tr>
<td>NUDP</td>
<td></td>
</tr>
<tr>
<td>NULT</td>
<td></td>
</tr>
<tr>
<td>NSHOR</td>
<td></td>
</tr>
<tr>
<td>SHORELINE POINTS</td>
<td></td>
</tr>
</tbody>
</table>

The following are repeated each step if needed:

- STEP CONTROL PARAMETERS
- WIND VELOCITY GRID
- TEMPERATURE GRID
- SEA STATE GRID
- X - DIRECTION TIDAL CURRENT GRID
- Y - DIRECTION TIDAL CURRENT GRID
- TIDAL LEVEL GRID
- PHYSICAL CLEANUP EFFORTS
- CHEMICAL TREATMENT EFFORTS
- INITIAL SPILLET PROPERTIES
APPENDIX II: SIMULATION MODEL OUTPUT

The output from the simulation model takes one of two forms; paper copy to allow the user to monitor a simulation, or digitally stored data (either on disk or tape) to be used as input to the plotting programs (See Fig. II-1). Because the model is capable of generating enormous volumes of data in both cases, a number of printout parameters have been added to the model. In general, output to paper is treated by a different set of parameter than that to disk or tape allowing for the two different modes to be treated separately.

A. Printed output used to monitor a run (Generally UNIT 5)

First, all of the input parameters read by either READ1 or READF are written out as they are read. There is no choice in the output of these parameters. For the remaining input parameters, environmental grids, response alternatives, and spillet characteristics the user does have a choice of the amount of output.

Every timestep, the program reads in a set or parameters which control that step. This command list may be printed out if desired under the control of the parameter NENV. If NENV is zero, no printout is generated. For NENV greater than zero, the step control information is printed every NENV step.

The output of all environmental grids is controlled by one parameter NPRTA. Any environmental input data written out will start on a new page so the user must therefore take great care here when selecting environmental output for a long simulation. For example, a 30 day simulation with three hour timesteps and a new current grid and wind grid each timestep will require at least 480 pages to print out just these two data sets. To suppress environmental grid output set NPRTA=-1. Limited printout defining the grid location and orientation only is selected with NPRTA=0. The entire grid is printed out with NPRTA=1.

Mechanical cleanup and chemical treatment efforts may also be summarized on paper. The controlling parameter for this output is NPTC: its value being 0 when only new efforts are to be printed out and 1 when all current efforts are to be printed out. If NPTC equals 1, this information is printed out for every timestep for which there exists a response effort, new or ongoing.

The spillet printout control variable is NSPPRD and is used to define the interval at which the defining variables for each spillet are printed out. NSPPRD=-1 suppresses all output while NSPPRD=0 prints out only on the first timestep (at which time at least one spillet must be released). If NSPPRD is greater than zero, then spillet information is printed out for the first step, the last step, and at any other step number that is a multiple of NSPPRD: eg. NSPPRD=3 would result in all spillet information being printed on the 1st, 3rd, 6th, 9th, ... , last steps. Again, caution must be exercised when specifying this parameter as the output can become voluminous; eg. if the run has 39 spilllets and runs for 30 days and the spillet data is printed out every timestep, approximately 2000 pages of output would be generated (12 lines/spillet *39 spillet, = 8 pages/timestep x 240 timesteps=1920 pages).
Summary Order of Output II-1

D - Disk Data Sets
P - Paper
(all controlled by parameters)

ALL OUTPUT CONCERNED WITH INPUT  P
FLOATING GRID DEFINITION  P
SCALE-DEPENDENT DIFFUSION  P
CURRENT VELOCITIES  P, D
FLOATING GRID DEFINITION  P
CONCENTRATION PARAMETERS  P, D
PARTICLE PROPERTIES  P, D
VELOCITY VALUES  P, D
MASS BALANCE  P, D
RESTART PARAMETERS  D
In addition to the input parameters described above, there are three other groups of data that may be output to the printer. The first such group consists of two separate pieces of information specifically, the subsurface grid definition variables and the subsurface diffusion parameters. The grid definition variables locate the Lagrangian grid and define the size of the associated grid elements. The subsurface diffusion variables consist not only of the values of the scale dependent diffusion, but also of the statistical characteristics of the cloud of entrained particles used to obtain the scale dependent diffusion. The printout of all of the variables in this group is controlled by one parameter, NPTSUB. As in the case of spillet data, NPTSUB equal to -1 suppresses such printout, NPTSUB equal to 0 prints out only on the first step and NPTSUB greater than 0 prints out on steps that are multiple of NPTSUB and on the first and last steps.

The second group of derived variables, the printout which the user may control, defines the mass balance; e.g., mass evaporated, mass on the surface, mass entrained, etc., the controlling parameters in this case is NPRTMS. Not only does this parameter control printout to paper, but also to disk/tape; i.e., whenever data is written to the printer it is also written to the mass balance disk data set. This is an important set of parameters and takes little space either on disk or paper, hence, should in general be output fairly often. NPRTMS is greater than or equal to zero, printing out nothing when equal to zero, and every NPRTMS step otherwise.

The last group of derived data output are the particle locations and the velocity vectors and concentration values on the Lagrangian. Each of these is controlled by its own parameters, KPRTP, KPRTU, KPRTC respectively. All of these variables operate in the same fashion printing out nothing when equal to zero and printing out every KPRT (i) steps otherwise.

Finally, the program will print to paper warning or error messages when appropriate. The user has no control over the printout of such data.

All of the print control parameters for output to Unit 5 are listed with their meaning in Figure II-2.

B. Disk/tape output data sets.

There are seven possible output data sets; data sets written to disk or tape that can be used by other programs either to plot the results or to restart the simulation model as described in Chapter IV. These are summarized in Table II-2 and described in some detail below.

1. Restart

As described earlier, this data set contains all of the run generated variables needed to restart a run. Of course, all input data sets are also required, i.e., environmental variables, etc. The controlling parameter for this output is NSUMM, the restart data being written every NSUMM timesteps in addition to the last timestep if the previous run terminated with no errors. All restart data is written to Unit # NURS in the subroutine SUMMUP. Because a large volume of data is generally
### Figure II-2

<table>
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<td>Controls printout of environmental header</td>
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<tr>
<td>NPRTC</td>
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output for every NSUMM timesteps, the decision was made to overwrite the
previous restart data so that restart data exists only for the most
recent multiple of NSUMM steps or if the previous run terminated success-
fully for the last step. This means that a run may only be restarted for
the last timestep that restart data was written.

The space requirements for a restart data set depend both on the num-
ber of particles and the number of spilletts, the appropriate equation
being

Space in bytes = 932 + 84* (Number of spilletts) + 16* (Number of
particles)

The longest logical record is 88 bytes and the output data is unformatted
(binary). The DD statement for the restart data set on an IBM 370 system
with 39 spilletts and 2000 particles is:

```
FD01FO01 DD DSNAME = RESTART.DATA,
      DISP = (NEW, CATLG),
      UNIT = SYSDA,
      DCB = (RECFM = VBS, LRECL = 88, BLSIZE = 4404),
      SPACE = (TRK, (40,10), RLSE)
```

Note: i. To save memory, it helps to single buffer all of the output
data sets, i.e., set BUFNO=1 in the DCB parameter.
ii. 4 bytes have been added to the longest logical record
because the data set is unformatted and 4 bytes have been
added to each block for the same reason.

2. Spilletts

All spillet information is output every NSPPRP step to unit # NUSP by
the subroutine SPILIN. This output is suppressed for NSPPRP=0. Because
a time history of each spillet is desired for input to the plotting pro-
gram, every NSPPRP step is appended to the data already written i.e., the
space requirements of this data set grow with the length of the run and
with an increased frequency of output. If a run is restarted, these data
sets are read to the appropriate step and subsequent output is added to
the end.

The data defining each spillet at a given timestep is output as one
logical record 72 bytes in length. The DD statement for a 30 day run
with spillet data output once per day and a total of 39 spilletts is:

```
FD01FO01 DD DSNAME = SPILLET. DATA,
      DISP = (NEW, CATLG),
      UNIT = SYSDA,
      DCB = (RECFM = VBS, LRECL = 76, BLSIZE = 7604),
      SPACE = (7604,(12,1),RLSE)
```

Note: Again, the data is output in binary, and DISP= OLD for a restarted
run.
3. Concentration

The concentration grid is output in the subsurface subroutine PRINT and is controlled by the step parameter NPRC. It is written to unit #NUCN.

Each grid is output as three logical records; one locating the x grid nodes in the fixed depth grid, the second locating the y grid nodes, and the third giving the concentration at each node. The longest logical record is therefore a function of the number of x, y and z grid elements. For a 15*15*3 (x*y*z) grid, one concentration grid output per day for a 30 day run; the DD statement would take the form:

```
FT FO01 DD DSNAME = CONC.DATA, 
  DISP = (NEW, CATLG),
  UNIT = SYSOA,
  DCB = (RECFM = VBS,LRECL = 2704, BLKSIZE = 8116),
  SPACE = (8116,(10,1),RLSE)
```

Note: Again, the data is output in binary, and DISP = OLD for a restarted run.

4. Particles

The position of all particles currently in the water column will be output to unit # every NPRP steps by the subroutine PRINT. Because the particle positions are referenced to the lagrangian grid, the location of these grid elements is also output. Finally, the particle class information must be output. The total space requirements per time step are:

```
Space in bytes = 80+4*(# of x grid nodes + # of y grid nodes) + 56* (# of particle classes) + 18* (# of particles)
```

For a 15*15 (x*y) grid, with all particle information output once per day a 30 day run, 200 particle classes and 2000 particles, the DD statement would take the form:

```
FT FO01 DD DSNAME = PART.DATA, 
  DISP = (NEW, CATLG),
  UNIT = SYSOA,
  DCB = (RECFM = VBS,LRECL = 68,BLKSIZE = 1296),
  SPACE = (TRK, (100,50), RLSE)
```

Note: This data set can consume a large volume on the disk.

5. Mass Balance

The mass of oil in the various environmental categories dealt with in the model, water surface, water column, shore, etc., is output in the subroutine MASSC to unit #NUMS every NPRTMS timesteps. As in all previous cases, if the step control parameter is zero, no output is generated. A single logical record 36 bytes long is output every NPRTMS steps. For a 30 day simulation with two outputs per day, the DD statement would assume the form:
6. Lost Particles

Every time a marker particle passes out of the study area, all of its parameters as well as its location is written to unit #NULT. This is done in the subroutine BOUNV and is not under the control of the user. If this output is not desired, a dummy data set is required:

```
FT FOO1 DD DUMMY
```

If the output is desired, each particle lost to an open boundary will use 32 bytes hence the DO statement will take the form:

```
FT FOO1 DD DSNAME = LOST.DATA, 
DISP = (NEW, CATLG), 
UNIT = SYSDA, 
DCB = (RECFM = VBS, LRECL = 36, BLKSIZE = 364), 
SPACE = (364, (30, 10), RLSE)
```

Note: In this case, the exact volume on disk required is not known because the number of particles lost is not known. Some upper limit must be estimated.

7. Deposited Particles

Because the user may desire a plot of the distribution of oil on the sea floor following a simulated spill, the characteristics and locations of each deposited particle are output to disk, unit #NLOP. All comments relevant to deposited particles are identical to those for lost particles and therefore are not repeated here.

8. Velocity Components

The floating grid velocity components are written to unit #NUVL in subroutine PRINT. The DO statement for a 15*15 grid will be:

```
FT FOO1 DD DSNAME = VEL.COMP, 
DISP = (NEW, CATLG), 
UNIT = SYSDA, 
DCB = (RECFM = VBS, LRECL = 88, BLKSIZE = 1588), 
SPACE = (TRK, (90, 10), RLSE)
```

This writes all 3 components so that much output is generated.
APPENDIX III: Variables in Common in the Main Simulation Program

In this Appendix, the variables in all of the common statements in the main simulation model are described. The descriptions are arranged in alphabetical order by common name. In addition to a description of the variable, the associated units are also defined.

(1) /CHEM/ - defines chemical treatment
   LCHEM - number of new treatment efforts during this step.
   NCHEM - total number of current treatment efforts.
   NCHD - unit from which the treatment data shall be read.
   BCHEM(ICHEM+)- 10*- time this treatment effort begins (hours).
   DCHEM(ICHEM) - 10 - duration of treatment effort (hours).
   RCHEM(ICHEM) - 10 - radius of treated area (meters).
   SCHEM(ICHEM) - 10 - interfacial tension of treated oil (dynes/cm).
   TCHEM(ICHEM) - 10 - unused.
   VCHEM(ICHEM) - 10 - volume of dispersant used (liters/hour).
   WCHEM(ICHEM) - 10 - dispersant used per square meter (liters/meter**2).
   XCHEM(ICHEM) - 10 - center of treated area (Longitude).
   YCHEM(ICHEM) - 10 - center of treated area (Latitude).
   PCHEM(ICHEM) - 10 - percentage of oil entrained if treated area is larger than spill area.

(2) /CLEN/ - defines the physical cleanup effort.
   LCLN - number of new cleanup efforts during this step.
   NCLN - total number of current cleanup efforts.
   NCLD - unit from which the cleanup data shall be read.
   BCLN(ICLN) - 10 - time this cleanup effort begins (hours).
   DCLN(ICLN) - 10 - duration of this cleanup effort (hours).
   ECLN(ICLN) - 10 - efficiency of this cleanup effort (%).
   RCLN(ICLN) - 10 - radius of this cleanup effort (meters).
   VCLN(ICLN) - 10 - oil recovery rate (tons/hour).
   XCLN(ICLN) - 10 - center of this effort (Longitude).
   YCLN(ICLN) - 10 - center of this effort (Latitude).

(3) /CNTL/ - control parameters
   IMSUB, JMSUB, KMSUB - number of grid elements in the X, Y, and Z directions for Lagrangian Coordinate System (See description of subroutine GRIDEX for a better explanation).

   NPRTA - printout control parameter for the environmental data (used in Subroutine ARAYIN).

*This numerical value indicates the size of the array as currently configured.

+ICHEM indicates that this parameter applies for each of the ICHEM treatment efforts of the NCHEM current efforts.
NPRTC - printout control for cleanup and treatment efforts.
-1 printout all current cleanup and treatment efforts for every timestep.
0 printout only when new efforts are started.

DT - timestep size (hours).
TIME - in seconds.
TIMMAX - time since start of spill at which run is to end.
ISCAL - 1 program does necessary distance calculations in meters.
2 program does necessary distance calculations in degrees of Longitude or Latitude.
NSAV(99) - spillets which have been removed in Subroutine ADD and added to the end of the spillet list.

(4) /COMP/ - defines the computational cell as explained in Chapter II.
MAXCX, MAXCY - number of grid elements in X and Y.
AC - angle between the X axis and lines of constant Latitude (degrees).
MCOMP(MAXCX,MACY) = 30,15 - computational cell definition.
XCL,YCL - Longitude and Latitude of the (1,1) grid position.
XCS,YCS - grid spacing in X and Y (meters or degrees).

(5) /DENS/ - Den (8) - densities of the eight fractions of oil. These are initialized in the main program and listed in the section which describes the evaporation subroutine; EVPOR8. Sample values are given in Appendix IX.

(6) /DEPOS/ - NLOST - number of subsurface particles lost through a computational boundary.
NDEP - number of subsurface particles deposited on bottom.

(7) /DIFF/ - NCRIT - minimum number of particles needed before diffusion velocities are calculated. The time at which NCRIT is exceeded depends upon how fast the particles are being entrained.
NDIFF - control parameter for calculating scale dependent diffusion coefficients.
0 use constant coefficients which are input.
1 call subroutine DIFF which calculates scale dependent diffusion coefficients.
DXX,DYY,DZZ - diffusion coefficients in X,Y, and Z directions respectively (meters²/sec).
EXX,EYY - coefficient used in scale dependent diffusion equation.
POWX,POWY - power of length factor used in scale dependent diffusion equation.
(8) /DPTH/ - fixed depth grid. The subsurface particles positions are tracked with respect to the origin of this grid.
MAXDX,MAXDY - number of grid elements in the X and Y directions.
AD - angle between X axis and lines of constant Latitude (degrees).
HGHT(MAXEX, MAXEY) - 30,15- depth of water at mean low tide (meters).
XDL,YDL - Longitude and Latitude of the (1,1) grid position.
XDS,YDS - grid spacing in the X and Y directions (meters or degrees).

(9) /ELVN/ - tidal heights grid. Used in performing the Z coordinate transformation for the subsurface diffusion/advection calculation.
MAXEX,MAXEY - number of grid elements in the X and Y directions.
AE - angle between X axis and line of constant Latitude (degrees).
HGHT(MAXEX,MAXEY) -30,15- elevation of sea level due to tide (meters).
XEL,YEL - Longitude and Latitude of the (1,1) grid position.
XES,YES - grid spacing in the X and Y directions (meters or degrees).

(10) /FLOT/ - velocity at floating grid nodes.
UFLT,VFLT,WFLT(IMSUB,JMSUB,KMSUB) (15,15,10) - advective current plus diffusion velocities at each of the floating Lagrangian Coordinate System grid nodes. (m/sec. or degrees/sec.)

(11) /INJC/- passes definitions of the initial particle positions during entrainment and treatment. This is explained in detail in Subroutine ENTRN.
DEPC - vertical origin of initial particle distribution (meters).
AFRAC - determines the fraction of particles within RO (RO = RSPIL/RIFRAC).
RIFRAC - determines radius over which particle density is uniform (meters).
ROFRAc - factor which determines rate at which particle distribution falls off.
DDIAMT - diameter of entrained droplet (mm).
DDVELZT - z velocity of droplet, zero if neutrally buoyant.
HENT - length of time of entrainment for use in calculation of RMAX in Subroutine ENTRN (hours).

(12) /MASS/- defines location of all mass for mass balance (all in metric tons).
XMATM - mass in atmosphere.
XMBIO - mass biologically consumed.
XMBOT - mass deposited on bottom.
XMCIN - mass physically cleaned up.
XMOMP - total amount of mass dumped up to that step.
XMLOS - mass lost through boundaries.
XMSHP - mass deposited on shore.
XMSUR - mass left on surface.
XMSUS - mass in water column.

(13) /MAXVEL/ - passes maximum velocity for the courant number which is:
maximum velocity*timestep/grid spacing.
UAMAX, VAMAX, WAMAX - advection courant numbers (meters/second).
UDMAX, VDMAX, WDMAX - diffusion courant numbers (meters/second).

(14) /OUTF/ output unit numbers.
NUSP - spilllet information.
NURS - restart data.
NUON - concentration data.
NUPT - particle parameters.
NUMS - mass balance.
NULL - lost particle parameters.
NUDP - deposited particle parameters.
NUVL - velocity values.

(15) /PRNT/ control parameters for subsurface printout.
KPRTV, KPRTC, KPRTP - print control parameters for paper printout of velocity values, concentrations and particle positions. This is an integer number which indicates how often (in number of steps) the user wants this information printed out. Value is zero if no printout is desired.
NPRO - control parameter to indicate that information is to be written out to disk. -0 for no writeout. 1 if any of the three variables below are not equal to zero.
NPRV, NPRC, NPRO - control parameter for writing out to disk. This indicates the interval (in number of steps) between output to disk for velocity, concentration, and particle position.
NPTSUB - controls printout of some subsurface information. -1 no printout. 0 printout only the first timestep. 0 printout at that interval of steps.

(16) /PTYP/ the particles are grouped into classes depending upon their properties. This common block passes these properties.
NCLASS - number of classes at this timestep.
NUMBD(1CLASS) -(200) - number of particles in ICLASS.
DDIAM(1CLASS) -(200) - diameter of particle.
DDENZ(1CLASS) -(200) - density of particle. This is the same density of the oil at the moment of entrainment. (grams/cubic centimeter).
DMASS(1CLASS) -(200) - amount of mass represented by each particle (metric tons).
DVELZ(1CLASS) -(200) - fall velocity of particle, usually is
zero for neutrally buoyant oil droplet (meter/second).

DOOMP(ICLASS,8) -(200,8) -composition of oil in the droplet. This is the composition of the oil at the moment of entrainment.

NTCLASS - maximum number of classes allowed. This is currently set at 200.

NUMCL - maximum number of particles in each class.

(17) /SEAS/ - defines Sea State grid.

MAXSX,MAXSY - number of grid elements in the X and Y direction.

AS - angle between X axis and lines of constant latitude (degrees).

WAVHGT(MAXSX,MAXSY) -30,15 - average wave height (meters).

WAVPRD(MAXSX,MAXSY) -30,15 - average wave period (seconds).

XSL,YSL - Longitude and Latitude of (1,1) grid position.

XSS,YSS - grid spacing in X and Y direction (meters or degrees).

(18) /SHOR/ describes shoreline.

NSHOR - number of shoreline points.

XSHOR(ISHOR) -1500 - Longitude of shoreline points.

YSHOR(ISHOR) -1500 - Latitude of shoreline points.

(19) /SPIIL/ passes spillet properties.

MSPIL - number of hydrocarbon fractions. This is currently set to eight.

NSPIL - number of spillies at this timestep.

ASPIL(ISPIL) -99 - treated area of spillet. This is negative when the total spillet has been treated (meters²).

BSPIIL(ISPIL) -99 - time that spillet appearecd (seconds).

DSPIL(ISPIL) -99 - density of spillet (grams/cubic centimeter).

FSPIL(ISPIL) -99 - fraction by volume of treated spillet.

GSPIL(ISPIL,MSPIL) -(99,8) - fraction by mass of each hydrocarbon class for the spilled oil.

RSPIL(ISPIL) -99 - radius of spillet (meters).

SSPILT(ISPIL) -99 - interfacial tension of oil (dynes/centimeter).

SSPILT(ISPIL) -99 - interfacial tension of treated oil (dynes/centimeter).

TSPIL(ISPIL) -99 - not used

TSPILT(ISPIL) -99 - not used

USPIL(ISPIL) -99 - kinematic viscosity of the oil (centistokes).

WSPIL(ISPIL) -99 - mass of the oil in spillet (metric tons).

XSPIL(ISPIL) -99 - Longitude at center of a spillet.

YSPIL(ISPIL) -99 - Latitude at center of a spillet.

(20) /SUBS/- control parameters for subsurface section.

NTRANS - transforms the Z direction.

0 uses depths as given.

1 transforms Z so that all Z values are normalized by the depth.
NSUB - 0 particle diffusion with respect to Lagrangian grid.
1 use analytical diffusion until standard deviation of cloud is comparable to grid mesh.

NEXT - control of Lagrangian grid.
0 use fixed grid.
1 use expanding and translating grid.

NMAX - maximum number of particles. Restricted by dimension of particle location variables.

NMAX - number of particles at current timestep.

DX,DY,DZ - grid spacings of Lagrangian grid (meters or degrees).

XORIG,YORIG - this is the distance between the origin of the fixed depth grid and the floating Lagrangian grid. These numbers are in fixed depth grid units. Therefore, to get the actual distance in meters or degrees, these numbers must be multiplied by the grid spacing of the depth grid (XDS,YDS).

ZORIG - point of reference for vertical distances. For a constant depth, this is at the bottom.

(21) /TIDE/ - Advevtive current grid. There are two grids, one for X velocities and one for Y velocities. They have the same spacing, size, and orientation but may have different origins so that a numerical model using a space staggered grid may be used to generate the values.

MAXTX,MAXTY - number of grid elements in the X and Y direction.

AT - angle between X axis and lines of constant Latitude (degrees).

UT(MAXTX,MAXTY) -30,15 - velocities in the X direction (meters/second or degrees/second).

VT(MAXTX,MAXTY) -30,15 - velocities in the Y direction (meters/second or degrees/second).

XTLU,XTLV - Longitude of (1,1) grid position for UT and VT.

YTLV,XTLV - Latitude of (1,1) grid position for UT and VT.

XTS,YTS - grid spacing in X and Y directions for both tidal current grids (meters or degrees).

(22) /TMPC/ - temperature grid.

MAXXX,MAXXY - number of grid elements in the X and Y direction.

AK - angle between X axis and lines of constant Latitude (degrees).

TEMP(MAXXX,MAXXY) -30,15 - temperature (degrees centigrade).

XKL,YKL - Longitude and Latitude of (1,1) grid position.

XKS,YKS - grid spacing in X and Y direction (meters or degrees).

(23) /WIND/ - wind grid

MAXWX,MAXWY - number of grid elements in the X and Y directions.

AW - angle between X axis and lines of constant Latitude (degrees).

UM(MAXWX,MAXWY) -30,15 - wind speed in X direction (meters/
VX(MAXWX) -30,15 - wind speed in Y direction (meters/second).

XWL,YWL - Longitude and Latitude of (1,1) grid position.

XWS,YWS - grid spacing in X and Y directions (meters or degrees.)
APPENDIX IV: PROGRAM SUBROUTINE AND ALGORITHM DESCRIPTIONS FOR THE SIMULATION MODEL

This Appendix is devoted to the detailed description of the main program and each of the subroutines of the simulation model. The main program is discussed first, and then followed by the subroutines in alphabetical order. Following the description of each subroutine is a list, including a description of the subroutine's most important arguments which are not in common or read in. Those variables in common or read in have been discussed in Appendices II and III.

1. Main Section

The main section of the program acts as the controller for a simulation. All of the major subroutine calls originate from this section. Initialization for all but the subsurface variables is performed by this section and it controls all input by either reading the variables directly or by calling the subroutines which then do the reading. (See Figure IV-1). Following the standard initiation at the run control parameters, there may be a second level of initialization controlled by the parameter NSTRT. This initialization occurs if NSTRT equals one, i.e., if this run is to be a continuation of a previous one. If NSTRT equals zero, this section is skipped.

The restart section will read all previous output data sets to their end and then it will read the restart data set which locates all spillers and determines the mass and subsurface parameters at the last step for which restart data was written. The previous environmental, spiller, cleanup and treatment efforts are read in under control of the parameter INR which counts the steps up to the restart step. The same input data sets used for the restart are the ones used for the previous run which did not finish. The same output data sets will be used as well. If the user desires to use new input and output data sets for the restarted run, the input variable NSTFN must be set equal to zero. Care should be taken when using new data sets to be sure the new unit numbers and/or data set names should be correct in the input data set.

The next major section of the program consists of the iteration over time. This is the actual simulation of the spill. This begins with the input of the step control parameters. The formatted printout of the commands issued by the step control parameters is determined by the input variable NENV, which indicates the step interval for output. Following this step, the program reads the appropriate environmental variables, spillers and cleanup activities and then performs the indicated cleanup operations. The main surface subroutine (SURFUS) and main subsurface routine (SUBSUR) are then accessed. Prior to calling the subsurface routines, the program converts all verticle measurements to the transformed system if required (no transformation for NTRANS = 0, transformation for NTRANS = 1).

In the next section, the mass balance is calculated and any spillers that overlap by a predefined fraction (COMB) are combined regardless of the step number. The last function performed for a time sep is to write to disk the restart data if the step number is a multiple of NSUMM or if this is the last time step of the run. If this is not the last time step, the entire simulation procedure is repeated from the entry of the step control parameters.
Figure IV-1: Flowchart for iterative B-Spline fitting.
SUBROUTINES CALLED: ADD, ARAYIN, BOTDF, CHEMIN, CLNIN, CNVRTZ, CONSUM INITSS, MASSC, READF, READI, RESRFS, SHORE, SPILIN, SUBSUR, SUMMUP, SURFES.

Important Variables Not in Common Read In

INR - This is used for the restart section. It counts the number of times that the program reads through the environmental input parameters before it has come to the step at which the previous run terminated.

NSTEP - Step number. Time zero is step zero.

NORDR (ICLASS) - 2000 Integer *2 - Class to which that particle belongs.

X,Y,Z (I) - 2000 - Position of droplet with respect to origin of floating grid (meters or degrees).

Subroutine ADD

This subroutine combines two spillets and their properties if they overlap by more than some predetermined fraction. (See Figure IV-2). The sum of their radii is compared to the distance between the centers. If this difference is larger than a given percentage (defined by input the parameter COMB) of the smallest of the two radii, then they are combined. Spillet parameters of the two spillets are combined either by adding the two values or by calculating a weighted average of the two. For example, the mass is simply the sum of the two while the location is a weighted mean (by weight) of the location of the two centers. In Table IV-1, all spillet variables are listed along with the method of combination.

CALLED FROM: MAIN

SUBROUTINES CALLED: DIST

Important Variables not in Common or Read in:

DISTA - the sum of the radii.

DIS - distance between spillet centers.

NSAV(ISP) - 99 - number of the spillet which has been moved to the end of the list.
Enter Subroutine

One Spillet? Yes

No

Initialize counters

Increment spillet # for i loop

Increment spillet # for j loop

Calculate distance between i and j spillets

Do spillets overlap? Yes

No

Combine spillets

Save spillet in j loop

No

Last j spillet? Yes

No

Last i spillet?

Yes

No

Return

Figure IV - 2. Flowchart for subroutine ADD.
<table>
<thead>
<tr>
<th>Variable Name</th>
<th>Method of Combination</th>
<th>Variable Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASPIL</td>
<td>Sum</td>
<td>Spillet area treated</td>
</tr>
<tr>
<td>GSPIL</td>
<td>Weighted mean</td>
<td>Fraction by mass of each class of oil</td>
</tr>
<tr>
<td>RSPIL</td>
<td>Square root of sum of squares, i.e., sum areas</td>
<td>Spillet radius</td>
</tr>
<tr>
<td>SSPIL</td>
<td>Weighted mean</td>
<td>Interfacial tension of oil</td>
</tr>
<tr>
<td>TSPIL</td>
<td>Weighted mean</td>
<td>Density of oil at t=0</td>
</tr>
<tr>
<td>SSPILT</td>
<td>Weighted mean</td>
<td>Interfacial tension of Treated oil</td>
</tr>
<tr>
<td>TSPILT</td>
<td>Weighted mean</td>
<td>Not used</td>
</tr>
<tr>
<td>USPIL</td>
<td>Weighted mean</td>
<td>Kinematic viscosity of oil</td>
</tr>
<tr>
<td>USPIL</td>
<td>Sum</td>
<td>Mass of oil in spillet</td>
</tr>
<tr>
<td>XSPIL</td>
<td>Weighted mean</td>
<td>Longitude of spillet center</td>
</tr>
<tr>
<td>YSPIL</td>
<td>Weighted mean</td>
<td>Latitude of spillet center</td>
</tr>
<tr>
<td>FSPIL</td>
<td>Weighted mean</td>
<td>Fraction by mass of treated spillet</td>
</tr>
</tbody>
</table>
**Subroutine ARPYIN**

This subroutine has been designed to enter all environmental grids. It is flexible in that the orientation, size and location of each grid may be different but structured in that the defining parameters must follow one of a number of well-defined formats. The precise format statements, as well as the various formatting options are described in detail in Appendix I, along with associated variables. In this section, the operation of the subroutine is discussed in terms of the flow diagram, Figure IV-3.

Upon entering the subroutine, the grid definition parameters are read either formatted or unformatted, depending on the value of the format control parameter NU. The dimensions of the grid are then verified. If ISCAL equals 1, then the grid separation is in meters and must be larger than 5 or the program stops. If, on the other hand, ISCAL equals 2, the grid separation is in spherical coordinates and must be less than or equal to 5 or again the program stops. Finally, if the grid separation is in spherical coordinates, the grid cannot be rotated so the parameter ANGLE must equal zero. If it is not, the program stops. If all of the conditions are successfully met, the grid may be printed out if desired. This printout is controlled by NPRTA, (-1 no printout, 0 limited printout and 1 full printout).

The next step is to read in the environmental parameters. First the format type is determined, real formatted, real unformatted, integer formatted or integer unformatted and then the first variable is input for the entire grid. If there is a second variable, NO equal to 2, it is then input. The last step is to output the environmental data again under control of NPRTA.

**CALLED FROM:** MAIN

**SUBROUTINES CALLED:** NONE

**Important Variables Not in Common or Read In** See Table I-1

**Subroutine AVGSIG**

This subroutine calculates the average of the particle positions \((X,Y,Z)\) over all particles then, under control of NOELCT, calculates the standard deviation. The standard deviation is defined by:

\[
\sigma = \sqrt{\frac{\sum_{i=1}^{N} x_i^2 - \left( \frac{\sum_{i=1}^{N} x_i}{N} \right)^2}{N - 1}}
\]

**CALLED FROM:** DIFF, DISPV

**SUBROUTINES CALLED:** NONE
Figure IV-3 Flow Chart for subroutine ARAVIN

- Read 1st Real
  - Grid: Unformatted
  - Yes: Read 2nd Real
  - No: Printout Grid Definition
    - Parameters: Formatted
    - Input Grid Definition
    - Stop

- Read 1st Integer
  - Grid: Unformatted
  - Yes: Printout Grid Definition
    - Parameters: Formatted
    - Input Grid Definition
    - Stop

- Two Grids?
  - Yes: Printout Real Grid
    - None, Some or All
    - Read Grid: Formatted
    - Integer: Correct?
      - Yes: Printout Integer Grid
        - No: Read Grid: Formatted
          - Yes: Printout Grid Definition
            - Parameters: Formatted
              - Input Grid Definition
              - Stop
          - No: Read Grid: Formatted
            - Yes: Printout Grid Definition
              - Parameters: Formatted
                - Input Grid Definition
                - Stop
            - No: Read Grid: Formatted
              - Yes: Printout Grid Definition
                - Parameters: Formatted
                  - Input Grid Definition
                  - Stop
              - No: Read Grid: Formatted
                - Yes: Printout Grid Definition
                  - Parameters: Formatted
                    - Input Grid Definition
                    - Stop
                - No: Read Grid: Formatted
                  - Yes: Printout Grid Definition
                    - Parameters: Formatted
                      - Input Grid Definition
                      - Stop
                - No: Read Grid: Formatted
                  - Yes: Printout Grid Definition
                    - Parameters: Formatted
                      - Input Grid Definition
                      - Stop
                - No: Read Grid: Formatted
                  - Yes: Printout Grid Definition
                    - Parameters: Formatted
                      - Input Grid Definition
                      - Stop
                - No: Read Grid: Formatted
                  - Yes: Printout Grid Definition
                    - Parameters: Formatted
                      - Input Grid Definition
                      - Stop
                - No: Read Grid: Formatted
                  - Yes: Printout Grid Definition
                    - Parameters: Formatted
                      - Input Grid Definition
                      - Stop
                - No: Read Grid: Formatted
                  - Yes: Printout Grid Definition
                    - Parameters: Formatted
                      - Input Grid Definition
                      - Stop
                - No: Read Grid: Formatted
                  - Yes: Printout Grid Definition
                    - Parameters: Formatted
                      - Input Grid Definition
                      - Stop
                - No: Read Grid: Formatted
                  - Yes: Printout Grid Definition
                    - Parameters: Formatted
                      - Input Grid Definition
                      - Stop
                - No: Read Grid: Formatted
                  - Yes: Printout Grid Definition
                    - Parameters: Formatted
                      - Input Grid Definition
                      - Stop
                - No: Read Grid: Formatted
                  - Yes: Printout Grid Definition
                    - Parameters: Formatted
                      - Input Grid Definition
                      - Stop
Important Variables not in Common or Read in

XNUM - number of particles
XAVG, YAVG, ZAVG - average values for X, Y and Z positions.
SIGX, SIGY, SIGZ - standard deviations of X, Y and Z positions.
NCELCT - 0 calculate only the mean.
- 1 calculate the mean and standard deviation.

Subroutine BOUNV

This subroutine locates the position of the particles with respect to the computational cell grid and then, either displaces the particle, removes it from the particle list, or leaves it as it was, depending on the numerical value of the computational cell grid element in which it is located. See Figure IV-4, for a flow chart of BOUNV.

First, the routine determines where each of the floating grid nodes are with respect to the fixed computational grid. Each floating grid element is then assigned the boundary condition of the fixed computational grid in which it is located. The number associated with each condition is listed in Table IV-2. The particles are then located within the floating grid. If a particle is within one half of a grid distance of an open boundary or a bottom deposition cell, the particle is removed from the list. If the grid is a reflection cell, the program moves the particle to half of a grid space, plus a small distance (ER) away from the boundary. The user can change the value of ER within the program. A particle occupies a fictitious cell volume, equal to a floating grid cell, so the boundary calculations are determined by the overlap of this particle volume in the boundary cells. If the particle is deposited or lost, the last particle on the list is moved to its position in the order. At present, the land cells are generally defined as reflection cells as are the surface boundary cells. The user may, however, assign any configuration to these that s/he desires.

The location and properties of any droplet deposited or lost are written to a disk data set. The number of particles either lost or deposited are printed out by the MASSC subroutine.

CALLED FROM: SUBSUR, PRINT

SUBROUTINES CALLED: ROTAT

Important Variables not in Common or Read In

ER - When a particle is moved, it is moved this fraction of a grid cell beyond the middle of the cell.

M - I, J, K - The boundary conditions of the floating grid location calculated from the fixed computational cell grid. See Table IV-2 for the meaning of the various numerical values.
Table IV-2
Model Boundary Conditions

<table>
<thead>
<tr>
<th>DEFINITION</th>
<th>VALUE</th>
<th>ACTION TAKEN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Land Cell</td>
<td>0</td>
<td>Deposit particle, remove particle from list</td>
</tr>
<tr>
<td>Computational Cell</td>
<td>1</td>
<td>none</td>
</tr>
<tr>
<td>Open boundary</td>
<td>2</td>
<td>remove particle from list</td>
</tr>
<tr>
<td>Water cell with an adjacent cell that is not water</td>
<td>101</td>
<td>none</td>
</tr>
<tr>
<td>Free surface reflection cell</td>
<td>3</td>
<td>Displace particle down if in the lower half of the cell</td>
</tr>
<tr>
<td>Bottom Deposition Cell</td>
<td>4</td>
<td>Absorbs any oil which moves to within 1/2 grid spacing of bottom.</td>
</tr>
</tbody>
</table>
Subroutine CHEMIN

This subroutine reads in the data for new chemical treatment efforts and also lists all treatment efforts in progress. See Appendix I for a description of the input format and see Figure IV-5 for a flow chart of this subroutine.

The subroutine first prints a header. Then all efforts in progress are listed. Finally, new efforts are read in and their characteristics printed out.

CALL FROM: MAIN

SUBROUTINES CALLED: NONE

Important Variables not in Common or Read In: None

Subroutine CLNIN

This subroutine serves two functions: It reads in the data that determines new mechanical cleanup efforts and it lists all mechanical cleanup efforts in progress. See Appendix I for a description of the input format and See Figure IV-6 for a flow chart of this subroutine.

First, the subroutine prints a header. Then all efforts in progress are listed. Finally, new effort(s) are read in and their characteristics printed out.

CALLED FROM: MAIN

SUBROUTINES CALLED: NONE

Important Variables not in Common or Read In: None

Subroutine CLNUP

This subroutine simulates the mechanical cleanup of spilled oil. See Figure IV-7. At any one time, there may be up to ten individual cleanup efforts in progress. Each effort is defined by its location, radius of influence, beginning time, duration, oil recovery rate and efficiency of cleanup effort. This last variable is to simulate the possible inability of the cleanup device to remove all of the oil in a spillet from the surface.

The subroutine is called once for each spillet every time step as long as there are continuing cleanup efforts. The first function performed is to remove any expired cleanup efforts from the list. This is done by subroutine REMOV. Following this, each of the cleanup efforts is examined in sequence to determine whether or not its range of influence includes the current spillet. If it does, a volume of oil is removed from that spillet equal to the smaller of:

1. The cleanup rate times the time step.
Figure IV - 5. Flow chart for subroutine CHEMIN.
Figure IV.- 6. Flow chart for Subroutine CLNIN.
Figure IV-7. Flow Chart for Subroutine CLNUP.
2. The total volume of the spill times the efficiency factor.

Following any action by all current cleanup efforts, the mass balance of the spill is updated and control is returned to the main program.

It should be noted that the volume cleanup rate of a particular effort applies to each spill as the center of which falls in the area covered by that effort. This means that if three spills fall within the range of a given cleanup effort, a maximum of three times the volume cleanup rate for that effort may be removed from the surface.

**CALLED FROM:** MAIN, SURFES

**SUBROUTINES CALLED:** REMOV, DIST

**CLNUP VARIABLES**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISP</td>
<td>the number of spill on which the cleanup efforts is operating.</td>
</tr>
<tr>
<td>SMCLN</td>
<td>Amount of oil removed from this spill (metric tons).</td>
</tr>
<tr>
<td>RC</td>
<td>Radius of spill, ISP (meters).</td>
</tr>
<tr>
<td>DIS</td>
<td>Distance between center of cleanup effort and center of spill (meters).</td>
</tr>
<tr>
<td>AMNT</td>
<td>Maximum amount of oil which may be removed in this step (metric tons).</td>
</tr>
<tr>
<td>EFF</td>
<td>Efficiency expressed as a fraction.</td>
</tr>
</tbody>
</table>

**Subroutine CVRRTZ**

This subroutine, Figure IV-8, converts the particle positions in z, the vertical coordinate, to or from the transformed coordinate system. This transform is controlled by the parameter NTRANS (see input variables). If NTRANS = 1, this routine is called at the beginning and end of the run. The transformation consists of interpolating the water depth at the particle position from the depth grid, and then normalizing the z position by this depth. The result is that the relative resolution in z is independent of horizontal location (x,y).

**CALLED FROM:** MAIN

**SUBROUTINE CALLED:** VELC

**Important Variables not in Common or Read In**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>MONTRL</td>
<td>-1 convert from transformed system.</td>
</tr>
<tr>
<td></td>
<td>= 1 convert to transformed system.</td>
</tr>
</tbody>
</table>
Determine water depth

Initialize temporary particle counter

Increment temporary particle counter

Has this particle been lost?

Locate the lower left hand corner at the grid element containing the particle

Is this a grid location?

Is the upper right hand corner of the grid element containing the particle a grid location?

Calculate the water depth at the particle location

Convert to or from the transformed grid?

Calculate location in transformed grid

Calculate depth of particle in water column

No

Last particle?

Yes

Return

Figure IV. B. Flow Chart for Subroutine CNVRTZ
Subroutine CONC

This subroutine (Figure IV-9) determines the hydrocarbon concentration in the water column resulting from entrainment. Each particle is assigned a fictitious volume equal to the volume of a floating grid element and centered on the particle location. The fraction of this volume in each floating grid element is then added to the volume of oil already in that element. The fictitious volume may overlap a maximum of eight surrounding cells. This process is performed for each particle. When all particles have been processed, the mass of oil in each floating grid element is divided by the volume of that element to determine the concentration.

CALLED FROM: SUBSUR, PRINT
SUBROUTINES CALLED: None
Important Local Variable: none

Subroutine COURAN

This subroutine, see Figure IV-10 for its flow chart, is used to determine when the courant condition has been violated. The courant condition specifies that a marker particle may not move more than one half of a model grid unit in one time step. If the condition is violated, the numerical results are uncertain and a message to that effect is printed out. The run will continue. In the early stages of a spill, the courant condition will often be violated. Because the floating grid dimensions are small, the surface spill is small, but the time step is relatively long. It is thought that for the simulation of the model in its present form, this problem is not overly serious because it is the long term results that are of interest. The early stage instabilities have little effect on these results. If it is the near term results that are being examined, then the time scale must be considerably shortened compared to the values used in the examples of this manual.

Two sets of courant numbers have been defined, one for the advective velocity component and one for the diffusive velocity component. This is because the fixed grid on which the advective velocities are defined is generally much larger than the floating grid on which the diffusive velocities are defined. It is, therefore, conceivable that the courant condition is not violated even though a marker particle moves several floating grid units.

CALLED FROM: SUBSUR
SUBROUTINES CALLED: None
Important Local Variables:

CAU - courant number for advective velocity in x.

CAV - courant number for advective velocity in y.
Enter Subroutine

Initialize Concentration Array and Counters

Increment temporary particle # counter

Is Particle Within Range?  
  Yes
  No

Is Grid in Meters?  
  Yes
  No

Convert grid spacing from degrees to meters

Calculate volume of grid element and mass density per unit volume

Obtain subscripts of grid element and position of particle with respect to the centers of that cell

Obtain all subscripts of cells affected by this particle

Calculate absolute distance off-center for this particle

Eliminate all adjacent cells which are out of range of the floating grid;

Add concentration of particle to all affected cells

Last Particle?
  Yes
  Return

Figure IV.-9 Flowchart for Subroutine CONC.
Enter Subroutine

Calculate courant number for \( X, Y, Z \), diffusive and advective velocities

Obtain the maximum courant numbers for this step

Is any courant number larger than 1?

Yes

Printout an error message

No

Return

Figure IV.10. Flow Chart for subroutine COURAN.
CAW - courant number for advective velocity in z.

CDU - courant number for diffusive velocity in x.

CDV - courant number for diffusive velocity in y.

CDW - courant number for diffusive velocity in z.

Subroutine DIFF

This subroutine (Figure IV-11) calculates the diffusion coefficient if the scale dependent diffusion model has been selected (see input parameter NDIFF). It uses subroutine AVGSIG to calculate the standard deviations of the particle positions and then the 4/3 law to determine the coefficient. If the large scale mode is used, the diffusion coefficient is calculated for the average latitude of the droplet cloud. The X component of the diffusive coefficient is given by:

\[ D_{XX} = E_{XX} \cdot S \cdot P^{O_{WX}} \]

where \( S = 3.0 \cdot 2.0 \cdot SIGX \cdot SIGY \)

\( SIGX, SIGY \) are the standard deviations of the particles.

\( D_{XX} \) - diffusion coefficient (m²/sec).

\( E_{XX} \) - constant. (now set to .05)

\( P^{O_{WX}} \) - constant. (now set to 4/3)

The y and z components are determined in a similar fashion. The values for the scale-dependent diffusion coefficients can come from Pavish and Spaulding (1977). The value for \( P^{O_{WX}} \) and \( P^{O_{WY}} \) is recommended as .99838 (assuming the length scale is in meters). The coefficient \( (E_{XX}) \) is .0018. This is a composite line from many sources of data including Okubo, Yudelson, Kohand, and Chano.

CALLED FROM: SUBSUR, VELCT

SUBROUTINE CALLED: AVGSIG

Important Local Variables: as above

Subroutine DISPV

This routine (figure IV-12) displaces each particle according to the advective and diffusive velocities calculated for the timestep being simulated. The velocities of the particle are calculated by the routine PARTV. The distance that a given particle is displaced is equal to the particle velocity times the length of the timestep.

CALLED FROM: SUBSUR

SUBROUTINE CALLED: AVGSIG
Figure IV. -11. Flow Chart for subroutine DIFF.

Enter Subroutine

Calculate mean and standard deviation of the droplet cloud in x, y and z

Is grid in meters? No

Yes

Convert coefficient scale factor from degrees to meters

Calculate scale dependent diffusion coefficient

Return
Enter Subroutine

Subgrid diffusion?

Yes

DISPV

Call AVGSIG to calculate average particle positions and standard deviation

No

Initialize counter

Increment temporary particle counter

Calculate advective and diffusive velocities at present particle location

Add Z terminal velocity to advective plus diffusive velocity

Subgrid diffusion?

Yes

No

Calculate analytical subgrid diffusion displacements

Displace particle

Last particle?

No

Yes

Return

Figure IV - 12. Flow Chart for subroutine DISPV
Important Local Variables:

DFLT - depth of water at floating grid locations

HFLT - sea surface evaluation at floating grid locations.

Subroutine DIST

This subroutine, see Figure IV-13 for its flow chart, is used to calculate the horizontal separation between any pair of points. The separation is always returned either in meters or in degrees as determined by the control parameter NO. If NO is equal to either 2 or 5, the values returned are the x and y separation in the rectangular coordinate system locally aligned with lines of constant longitude and latitude. If NO is other than 2 or 5, the great circle distance between the two points is returned. The distinction between a value of 2 or 5 for NO stems from two different storage modes for point locations. If NO equals 2, the input locations are assumed to be in longitude and latitude and the result is returned in meters. If NO equals 5, no conversion is performed so if the input is in meters, so is the output.

CALLED FROM: ADD, CLNUP, ENTR, LOCB, ROTAT, TREAT

SUBROUTINES CALLED: None

Important Local Variables:

X1, Y1 - longitude and latitude of the first point. This point should be south and west of the second point.

X2, Y2 - longitude and latitude of the second point.

NO = 1 calculate the great circle distance between the points (meters).

          = 2 calculate the X and Y spacing between the points (meters).
          = 5 calculate the X and Y spacing between the points in the same units as the input.

ANG - angle if one point is defined on a rotated grid.

D - distance between the two points if NO=1.

XSP, YSP distance between the two points if NO=2 or 5.

Subroutine ENTRAS

This subroutine, see Figure IV-14 for its flow chart, calculates the mass entrained under natural conditions, i.e. no dispersant. It uses the rate obtained by the formulation of Andunsun (1979). Specifically, the
Figure IV. - 13. Flow Chart of subroutine DIST.
Enter Subroutine

Calculate percentage of mass lost per day and convert to amount per second

Calculate time decay factor

Calculate mass dispersed during this step

Update mass balance

Is this a preview run and is this step completed?

Yes

No

Calculate and print out the mass represented by each particle

Return

Figure IV - 14. Flow Chart for subroutine ENTMASS.
fraction of oil entrained per day is given by:

\[
\text{Amount} = 0.1 \left( \frac{u^2}{w_0^2} \right)
\]

where \( w_0 = 8.5 \) (a constant)
\( u = \text{wind speed (m/sec)} \)

In the URI model, this quantity is modified by an exponential decay factor with a time constant of two days. This exponential decay of the volume of oil entrained was selected in an ad hoc fashion, as was the two day time constant, to compensate for the expected decreases in entrainment with time due to emulsification and other weathering properties which tend to solidify the slick.

The second section of the routine is used only in the preview mode. At the end of each step, the mass of oil represented by each entrained is calculated.

**CALLED FROM:** SURFES

**SUBROUTINES CALLED:** None

**Important Local Variables:**

- **WSP** - mass of spill (metric tons).
- **BSP** - time of start of spill (seconds).
- **DCN** - time constant for the exponential decay of the entrainment rate currently set at 2 days (172800 seconds).
- **SEC** - number of seconds in one day.
- **AO** - constant for dispersion equation.
- **WD** - wind constant for dispersion equation (m/sec).
- **AMT** - percent entrained per second.
- **PERCEN** - amount of oil entrained per time step (fraction).
- **DIF** - ratio of amount entrained per step and total amount in water column at that step.
- **DCY** - time decay factor given by \( e^{-\frac{\text{time} - \text{BSP}}{\text{DCN}}} \)

**Subroutine ENTRN**

This routine controls the injection of the oil droplets into the water column. Its flow chart is shown in Figure IV-15.
The first step is to determine from the input parameter, NRUN, whether or not this simulation is a preview. In the Preview mode, no particles are entrained. In the full simulation mode, the number of particles is determined according to the mass of oil entrained from the spillet and the mass assigned to each particle. The particle properties are determined from the properties of the oil in the slick, which in turn determines the class to which the particle belongs. A maximum of 200 classes are currently allowed. The user may change this maximum by increasing or decreasing the input variables NTCLAS. If NTCLAS is increased, then array sizes in the common block PTYP must also be increased.

The next step is to calculate the radius restrictions on the particle positions. These are determined in an ad hoc manner due to a lack of data regarding entrainment. The horizontal position is defined by a radial component and an angular component about the center of the spillet. The angle, measured clockwise from the positive y axis is selected at random from a uniform distribution. The radial position is divided into two regions as defined by RLIM. For radii smaller than RLIM, the distribution increases linearly from zero. This coupled with the uniform distribution in angle gives an equal probability per unit area for particle location within RLIM. For radii larger than RLIM, the distribution decreases linearly to zero at RMAX. The maximum radius, RMAX, is a variable which decreases with the age of the spillet. This procedure was adopted to provide sufficient extent to the subsurface distribution during the early time steps to avoid singularities in the diffusion equation, i.e., it is an ad hoc fashion of avoiding numerical instabilities in the early time history of the spillet. A more elaborate procedure was not thought to be justified at this time because of our general ignorance regarding the entrainment process in general. In addition, there is certainly a thin surface sheen that spreads beyond the limits of our model prediction from which particles might be entrained.

The final step of the routine is to convert the polar coordinates of the entrained particle positions to model grid coordinates.

**CALLED FROM:** SURFES

**SUBROUTINES CALLED:** DIST, INJECT

**Important Local Variables**

- RSPIL - spillet radius

\[
A = \frac{RO}{AFRAC^2} = \frac{RSPIL}{AFRAC^2} (RIFRAC)
\]

describes particle distribution within region one.
RMAX = RSPIL* \left( 1.0 + \left( \frac{(HENT/50)}{(ROFRAC(TIME-BSPIL)} + 1.0 \right) \right)

maximum radius for initial particle distribution.

\[
D = \left( \frac{RO}{A} \right)^{1/2} = \frac{RO \cdot AFRAC^2}{RO} = AFRAC \quad \text{Temporary Variable}
\]

\[
B = \frac{RMAX - RO}{(1.0 - D)} = \frac{RMAX - RSPIL}{RIFRAC} = \frac{(1.0 - AFARC)}{D} \quad \text{Temporary Variable}
\]

\[
C = \frac{(RO - RMAX + D)}{D} = \frac{(RSPIL - RMAX \cdot AFRAC)}{1.0 - AFRAC} \quad \text{Temporary Variable}
\]

XC, YC - position of center of spillet with respect to depth grid origin in number of grid units from origin.

IX, IU, P - constants for random number generation used in subroutine Rand.

POMIN - minimum distance in x and y direction between the first two particles (meters).

RX, RY, RZ - random numbers between zero and one resulting from subroutine RAND.

RLIM - D - boundary of uniform distribution.

RADIUS - initial radial location of a droplet from the center of the spillet.

\[
A \cdot RX^2 \quad \text{within RLIM}
\]

\[
B \cdot RX + C \quad \text{outside of RLIM}
\]

Also see Common Block INJC in Appendix III.

Subroutine EVPOR8

The mathematical formalism used in this subroutine is the same as that described by Wang, Yang, and Hwang (1976) but the numerical solution adopted in the present model is different. The equation to be solved for \( C_i \), the average value of the percent weight of fraction \( i \) over the slick thickness, is:

\[
dC_i/dt = - D_i \epsilon C_i
\]

where \( D_i \epsilon \) is the average value of the evaporation diffusion coefficient over the slick thickness. The values of the diffusion coefficients are discussed in detail in the report of Wang et al. (1976) as well as in the
original paper by McKay and Matsugu (1973) and will not be further discussed here.

Wang et al. used the fourth-order Runge-Kutta method to determine $C_i$. The difficulty with this method is that it requires storing all variables for two time steps. Because of the complexity of the model, use of the Runge-Kutta method resulted in a substantial requirement on computer memory. The following method was, therefore, adopted to determine $C_i(t)$, given $C_i(t - \Delta t)$ where $\Delta t$ is the step size. The interval $\Delta t$ was divided into $N$ intervals of duration $\delta t$, i.e., $\Delta t = (N)(\delta t)$. The evaporation diffusion coefficient is assumed to be constant over each subinterval, although it may vary from one interval to the next. This then leads to:

\[
-C_i(t) = C_i(t) - (t - \Delta t)e^{-\sum_{i=1}^{n} D(t - (j - 1/2) \delta t) \delta t}
\]

where $D_{ie}(t-(j-1/2)\delta t)$ represents the value of $D_{ie}$ at time $t-(j-1/2)\delta t$. Solutions using this method were compared with solutions for the same input conditions using the model of Wang et al. (1976) and were found to differ by less than ten percent for $N=1$. The execution time was less by a factor of four and the memory requirements were significantly reduced (about twenty kilobytes).

The variable $D_{ie}$ is defined by:

\[
D_{ie} = \frac{km (P_i - P_{i\infty})}{(RT_s)}
\]

where $P_i$ - hydrocarbon vapor pressure of fraction $i$ at the interface.

$P_{i\infty}$ - hydrocarbon vapor pressure of fraction $i$ at infinite altitude.

$R$ - the gas constant.

$T_s$ - the oil slick temperature.

and

\[
km = \text{CONST} \cdot e(Q \cdot \text{WVEL} \cdot \text{AREA})
\]

where CONST, Q and R are constants defined within the routine,

WVEL - wind velocity in meters/sec.

$A$ - area of spill in square meters.

See Figure IV-16 for a flow chart of this subroutine.

**CALLED FROM:** SURFES

**SUBROUTINES CALLED:** None
Figure IV.36. Flow chart for subroutine EYPORE.
Important Local Variables:

ABSZERO absolute zero (degrees centigrade).
AREA area of spillet (meters²).
CON1, CON2 - array of constants for Antoines equation of partial pressure.
DAGRES average temperature over the slick (degrees centigrade).
RAD radius of the spillet during the integration process (meters).
DELTA time of the substep in the integration (sec).
NINT number of steps in the integration procedure.
OLDRAD radius of spillet at the last time step (meters).
P vapor pressure.
Q,R,CONST constants for diffusion coefficient.
RC universal gas constant.

Subroutine GRIDEX

This subroutine (see Figure IV-17 for its flow chart) expands and translates the floating grid so as to incorporate all of the marker particles. It determines the maximum and minimum positions of the particles and creates a grid with a particle free region 1.5 grid units wide around the entire periphery. This is required by the interpolation technique. If any particles get too close to the edge of the fixed depth grid, the floating grid is moved away from the boundary and the particle is lost. This routine prints a description of the floating grid every NPRSUB steps. The print parameter, NPRSUB also determines whether or not the means and standard deviations of the particle locations are to be calculated and printed. These last values are not passed out of the subroutine.

CALLED FROM: SUBSUR, PRINT

SUBROUTINES CALLED: None

Important Local Variables: None

Subroutine INITSS

This subroutine (see Figure IV-18 for a flow chart), called by the main section, initializes all of the subsurface drift and diffusion variables and parameters. It also initializes the droplet properties and subsurface print parameters. (See INPUT parameter description).

CALLED FROM: Main
Figure 11. Flow Chart for subroutine GRIDX.
Figure IV.-18. Flow Chart for subroutine INITSS.
Subroutines called: READI, READF

Important local variables: None

Subroutine INJECT

This subroutine uses the radii restrictions calculated in ENTRN to determine the initial particle positions. A random number generator (see subroutine RAND) is used to obtain three dummy variables. The first one (RX) is used to determine the spacing of the marker particle from the center of the spillet. The second random number (RY) is used to determine the random angle. The angle and radius determine the particles location in polar coordinates which is then converted to the rectangular grid. The particles location in the model grid undergoes two tests. First, the particle must be within the fixed grid. Second, if this is the first step, the first two particles created must have a separation that exceeds the input variable POMIN. This insures that a floating grid can be created in both directions. A third random number is used to determine the particle's position in the vertical which on the average is located at the depth by the input variable DEPC. See Figure IV-19 for a flow chart of the subroutine.

CALLED FROM: ENTRN

SUBROUTINES CALLED: RAND

Important Local Variables: see ENTRN for a description of variables used in inject.

Subroutine LOC8

This subroutine, flowcharted in Figure IV-20, determines the smallest rectangle of fixed grid elements that contains a spillet. It is used to determine for which grid nodes the values of the specified environmental variable must be averaged. All nodal values falling on the edge of and within the rectangle completely containing the spillet are used. These values are averaged and returned to the calling routine. If the fixed grid consists of only one value, that value is used. If the spillet lies completely outside of the specified fixed grid, a message is written and the control parameter MDLSPL is changed from 0 to 1. If this condition arises, none of the surface processes will be executed on return to the calling routine except for shoreline interaction if, indeed, the spill has hit the shore.

CALLED FROM: SURFES

SUBROUTINES CALLED: DIST

Important Local Variables:

MDLSPL = 0 if the spillet is in the study area.
= 1 if the spillet is outside one of the environmental grids.

NGRO = number of grids that define a variable.
Figure IV - 19: Flowchart for subroutine INJECT.
Figure IV - 20. Flowchart for subroutine LOC8.
NX, NY - maximum number of grids in X and Y direction.
ANG - angle between x axis and lines of constant latitude.
XL, YL - Longitude and Latitude of (1,1) grid position.
XS,YS - grid spacing in X and Y direction (meters or degrees).
VAR1,VAR2, - input arrays, if NGRD is 1, VAR2 is not used.
VAL1,VAL2 - averaged values of the above arrays.
XC,YC - Longitude and Latitude of the center of the spillet.
R - spillet radius (meters).

Subroutine MASSC

This subroutine, flowcharted in Figure IV-21, calculates and writes the mass balance both in terms of the total amount of oil in each region and the percentage of oil in each region. In addition to the mass balance, it also writes out statistics on the number of particles present, lost or deposited. The mass data may be written to disk and/or the line printer.

CALLED FROM: Main

SUBROUTINES CALLED: None

Important Local Variables: None

Subroutine PARTV

This subroutine uses the bilinear weighting scheme to interpolate the velocities known at the floating grid notes to the marker particle position. The routine is flowcharted in Figure IV-22. The subroutine is called once for each particle.

The bilinear weighting scheme obtains the value of a variable located at positions fx and fy in a grid element, see Figure IV-23, as follows:

\[ U = (U_1 + f_x (U_2 - U_1)) + f_y ((U_1 = f_x (U_2 - U_1) - \\
(U_3 + f_x (U_4 - U_3))) \]

where U is the value sought and all other values are defined in Figure IV-22.

CALLED FROM:

SUBROUTINES CALLED: None
Figure IV - 21. Flowchart for subroutine MASSC.
Enter Subroutine

Obtain subscripts for grid elements at this particle

Obtain particle position with respect to cell center and cell corner

Are all subscripts of particle location within range?

Yes

Use the subscript of the closest boundary cell

No

Is this a shore cell?

Yes

Assign velocities at that cell

Return

No

Find all adjacent elements which contribute to this particle velocity

Are all of their subscripts within range?

Yes

Perform bilinear interpolation for X, Y & Z velocities

No

Use the subscript of the closest boundary cell

Return

Figure IV - 22. Flowchart for subroutine PARTV.
Figure IV. - 23. Defining figure for Bilinear interpolation scheme.
Important Local Variables: None

Subroutine PRINT

This subroutine handles most of the output operations for the subsurface section of the model. The output is controlled by print control parameters described in common block PRINT. These parameters control both the paper and the disk output. The subroutine will print out the velocity field and the concentration matrix on the floating grid with headers locating the floating grid with respect to the origin of the fixed depth grid (in meters or degrees). In addition, the actual location of each marker particle can be printed if desired. When printing these positions, the depth is calculated and printed in meters if a z transformation is being used in the simulation. Printout is controlled by KPRTV, KPRTC and KPRTP for the velocity and concentration grids and the particle positions, the value of these control parameters specifies the step interval between printing. If the parameter is equal to zero, no printout for the corresponding variable is generated.

Output to disk is controlled first by the parameter NPRD. If it is zero, subroutine PRINT will output nothing to disk. If NPRD equals 1, then the parameters NPRV, NPRC, and NPRP define the step interval at which the various data sets are to be output.

A flow chart of this subroutine is shown in Figure IV-24.

CALLED FROM: SUBSUR

SUBROUTINES CALLED: BOUNV, CONC, GRIDEX

Important Local Variables:

NCALL1 - flag so as not to call the subroutine CONC twice.
- 0 call CONC the second time it is encountered.
- 1 call CONC only during the first concentration printout.

RIO(1MSUB) - 15 - X positions of the floating grid cells (meters or degrees).

RJO(1MSUB) - 15 - Y positions of the floating grid cells (meters or degrees).

XTEMP,YTEMP,ZTEMP - particle positions with respect to the fixed depth grid (degrees or meters).

Subroutine RAND

This routine generates random numbers from a uniform distribution between 0.0 and 1.0. The input variables to this routine are all initialized in subroutine INJECT.
Figure 17-26. Flowchart for subroutine R1207.
CALLED FROM: INJECT

SUBROUTINES CALLED: None.

Important Local Variables: None

Subroutine READI

This subroutine, flowcharted in Figure IV-25, is used to input, and check to some degree, all scalar integer variables. The required input format is described in Appendix I. The subroutine reads the value of the variable and the variable name. If the variable name that it reads does not agree with the name of the variable passed to it from the calling routine, an error message is written and execution of the program terminates. This prevents reading cards out of order. In addition, if the value of the variable does not lie in some predefined range again passed to it from the calling routine, an error message is written and execution terminates. This is to help avoid exceeding the limits of various arrays as well as reducing the chance of an abnormally long run resulting from the improper positioning of the input parameter. If the upper and lower limits specified in the call to READI are equal, any value may be entered.

CALLED FROM: MAIN, INITSS

SUBROUTINE CALLED: NONE

Important Local Variables:

I - value read from input and passed back to the main program.
NL - lowest value permitted.
NU - greatest value permitted.
XNAME - name of variable to be read.
XPNAME - name of variable read from input stream.

Subroutine READF

This subroutine is used to input, and to check to some degree, all single real variables. It is identical to READI except that:

1. It reads floating point numbers rather than integers.
2. There are no restrictions on the range of the number read in other than those of the computer.

Subroutines called: None

CALLED FROM: MAIN, INITSS
Enter Subroutine

Read value and name of integer variable

Is the name read the same as the name requested?

Yes

Is I within the specified limits?

Yes

Print name and value of variable read

Return

No

Print error message

Stop

No

Print error message

Stop

Figure IV - 25. Flowchart for subroutine READI.
Important Local Variables:

- **X** - value of variables read in and passed to the calling routine.
- **XNAME** - name of the variable to be read.
- **XPNAME** - name of the variable read from the input stream.

Subroutine REMOV

Each cleanup and treatment effort initiated has associated with it a duration. When this length of time has been exceeded, the effort is to be terminated and removed from the list of cleanup/treatment efforts. REMOV is used to remove an expired effort from the list (see Figure IV-26 for its flow chart). The routine removes an effort by simply moving the last effort on the list into the location occupied by the expired effort and then decrements the counter specifying the number of active efforts by one.

**CALLED FROM:** CLNUP, TREAT

**SUBROUTINES CALLED:** None

Important Local Variables:

- **BEG** - beginning of this effort (hour).
- **DUR** - duration of this effort (hours).
- **DUM** - dummy variable which is equivalenced in the Subroutines TREAT and CLNUP.
- **MEM** - number of current efforts.
- **NVAR** - length of variables in the common bloc.
  - 7-for CLEN
  - 10-for CHEM
- **JTEMP** - number of expired efforts this step.
- **MTEMP** - last efforts on list; this one is moved to expired efforts placed in list
- **LTEMP** - effort which has expired and is being replaced.

Subroutine ROTAT

This subroutine, flowcharted in Figure IV-27, converts locations from the fixed depth grid to any of the environmental grids. It is used primarily to map values of environmental variables into the floating grid. The depth grid is used as the reference because the floating grid is defined with respect to it. The output of this routine is the x and y location of the point of interest referred to the new environmental grid.

**CALLED FROM:** BOUNV, VELC

**SUBROUTINE CALLED:** DIST
Enter Subroutine

Set temporary effort counter to zero

Increment temporary effort counter

Has this effort finished?

Yes

Save the effort number

No

Last effort

No

Yes

Have any efforts terminated this step?

No

Return

Yes

Set temporary terminated effort counter to zero

Increment temporary terminated effort counter

Take last effort on the list and put it in place of the finished effort

Place properties of last effort in place of completed effort

Last terminated effort?

No

Yes

Subtract number of terminated efforts from the list of active efforts

Return

Figure IV. - 26. Flowchart for subroutine REMOV.
Enter Subroutines

Set grid unit definition flag lat., lonq. or rect.

Determine angle between depth grid and environmental grid

Calculate position of point in rotated depth grid.

Obtain X and Y separations in meters

Determine position of depth grid origin in environmental grid

Obtain location of point in environmental grid units

Return

Figure IV. - 27. Flowchart of subroutine ROTAT.
Important Local Variables:

XL,YL - longitude and latitude of the (1,1) location of the grid of interest.

XD,YD - grid spacing in X and Y direction for the grid of interest (meters or degrees).

ANG - angle of X axis with lines of constant latitude for the grid of interest.

XO,YO - position of point which is to be converted. This is with respect to the depth grid.

XG,YG - grid position of point with respect to the grid of interest.

XSP,YSP - distance between origins of depth grid and grid of interest.

Subroutine SHORE

This subroutine reads the longitude and latitude values of the points defining the shoreline. The subroutine is always called but if the study area includes no shoreline, then no points are read.

CALLED FROM: MAIN

SUBROUTINE CALLED: None

Important Local Variables: None

Subroutine SPILIN

This subroutine reads in all new spillet parameters and initializes any properties not read in. The user is referred to Appendix IX for general oil properties. The routine will also print all current spillet information at the step interval specified by the parameter NSPPRP (see input variables). Spillet information may also be written to a disk data set at a step interval defined by the parameter NSPPRD. Finally, a section is included in the routine for restart runs. It reads in old spillet information and skips the initialization which have already been performed (see Figure IV-28 for a flow chart of the subroutine).

CALLED FROM: MAIN

SUBROUTINES CALLED: None

Important Local Variables: None

Subroutine SPREAD

The spreading process is described by the simple three regime spreading mechanism proposed by Fay (1969). The only peculiarity in this model
Figure IV - 28. Flowchart for subroutine SPILIN.
with regard to spreading is the fashion in which the time, t, used in the various equations for the radius is determined. In this model, a fictitious time is determined by solving each of the three different regime radius equations for time using the value of the radius from the previous step and the volume of spilled oil remaining at this time step. From these three values of "time," the appropriate regime is determined. Then the derived value of time is incremented by the time step of the model and the new radius is calculated. For a simple spill with no new oil added or oil previously in the slick removed, this yields the same value of radius with time as the original Fay formulation. However, for the case where oil is removed or added, this allows for the rate of spreading to jump from one regime to another. It is obvious that this is necessary if one considers a slick in the third regime which is treated with a chemical dispersant which lowers the spreading tension, by an order of magnitude. In this case, without changing the "time" variable used in the spreading equation, the radius changes by a factor of three. Equally drastic changes would result from the removal or addition of oil by any of the means available in the model. It is as a result of this regime changing mechanism that Fay's spreading formalism is used rather than the combined spreading-horizontal diffusion mechanism used in some of the more recent models (Wang, Campbell and Ditmars, 1975). See the flow chart in Figure IV-29.

CALLED FROM: SURFES

SUBROUTINES CALLED: None

Important Local Variables:

COEF1 - spreading coefficient for first regime.
COEF2 - spreading coefficient for second regime.
COEF3 - spreading coefficient for third regime.
DELTA - (water density - oil density)/water density.
GRAV - gravitational acceleration (cm/sec**2).
RAD - radius of spillet (cm).
RHOW - density of sea water (gm/cc).
RMAX - maximum radius for a spillet containing a given volume of oil.
SIG - spreading tension (dynes/cm = gm/sec**2).
Tij - time at which spillet goes from Regime i to Regime j.
VISHZO - viscosity of sea water (stokes = cm**2/sec).
VISRTZ - square root of VISHZO.
VMIN - maximum volume for which Fay's Regime 2 is skipped.
Figure 11.29. Flowchart for Subroutine SPREAD
Subroutine SUBSUR

This subroutine calls the seven main subroutines which advect and diffuse the subsurface droplets in the water column. The method is based on the Water-Advective-Particle-In-Cell method developed by Pavish and Spaulding (1976-1977). A brief overview of the numerical scheme, along with a discussion of those factors which have been modified specifically for this application, is presented below.

The three-dimensional mass transport equation is solved using a particle-in-cell method. This is a quasi Monte Carlo technique in which representative particles are sampled at random from a predetermined distribution. The space which these "marker" particles occupy is then divided into a number of rectangular cells. The concentration distribution of the particles is determined by calculating the number of particles in each cell, i.e., this yields the concentration at the center of that cell. The model then obtains the concentration gradient and calculates the resulting diffusive velocity, which it adds to the advective velocity input to the program, to obtain the total particle velocity. Finally, the particle velocity is used to move the individual particles.

The fundamental equation being solved is the transport diffusior equation:

\[
\frac{\partial C}{\partial t} + U_A \cdot \nabla C = \nabla \cdot \left( k \nabla C + S \right)
\]

where \( C \) is the concentration of oil droplets,

\( k_{ij} \) is the diffusivity tensor,

\( U_A \) is the advection velocity assuming incompressibility, and

\( S \) represents either a source or sink of oil.

This equation may be rewritten in the advective-diffusion form:

\[
\frac{\partial C}{\partial t} + \nabla \cdot \left( C \mathbf{U_T} \right) = 0
\]

where

\( \mathbf{U_T} = U_A + U_D \)

\( \mathbf{U_T} \) - Total particle velocity

\( U_A \) - Advective velocity

and

\( U_D \) - Diffusion velocity, defined by

\[
U_D = - \frac{k_{ij}}{C} \cdot \nabla C
\]
The total particle velocity is solved using a finite difference representation on the space staggered grid shown in Figure IV-30.

This sophisticated subsurface drift model was selected for several reasons, the main one being that it allows for oil droplets of varying properties, for example some denser than water that may sink and some less denser than water that may resurface as well as neutrally buoyant drops to represent the dissolved portion of the spill. In addition, the chemical properties of the droplets may vary, and this variability may be a function of particle size.

Another important feature of the subsurface portion of the model is the mixed Eulerian-Lagrangian coordinate system. The Eulerian coordinate system is the one on which the tidal currents, the bathymetry and the computational cells are defined. The Lagrangian coordinate system is the one on which the oil droplet concentration is defined. This system expands and translates so as to always include all particles. Variables defined on the Eulerian system are interpolated to the Lagrangian system. The Lagrangian system also allows for a coordinate transformation on z, the vertical variable, such that the water column at every horizontal node is divided into the same number of equally spaced layers. This means that as the water becomes shallower, the vertical grid spacing becomes smaller, thus keeping the same relative vertical resolution.

The flow of this routine, Figure IV-31, is quite straightforward.

**CALLED FROM:** MAIN

**SUBROUTINES CALLED:** BOUNV, CONC, CURAN, DISPv, GRIDEX, PRINT, VELCT

**Important local variables:**

- C(IMSUB,JMSUB,KMSUB) 15,15,10 - oil concentration on the floating grid (mg of oil/ml of water).
- M(IMSUB,JMSUB,KMSUB) 15,15,10 - computational cell definitions of the floating grid.
- NST step number.
- HFLT(IMSUB,JMSUB,KNSUB) 15,15,10 - tidal elevations at the floating grid nodes (meters).
- DFLT(IMSUB,JMSUB,KNSUB) 15,15,10 - depths at the floating grid nodes (meters).
- CC(IMSUB,JMSUB) 15,15 - concentration values averaged over the water column.
- NPTFLT interval print control for subsurface information.
Figure IV-30. Space Staggered System
(Values Inside of Square have the same indices)
Figures IV.-31. Flowchart for subroutine SUBSUR.
NPTSUB

print control parameter as determined by NPTFLT

printout this step, 0 - no printout this step.
1 - printout this step.

Subroutine SUMMUP

This subroutine, flowcharted in Figure IV-32, writes to disk all of the variables describing the disposition of the spilled oil (the Restart data set). It also outputs active cleanup and treatment efforts. The subroutine is called at a step interval defined by the input parameter NSUMM, as well as at the end of the run. It codes the output with the step number. If the user wishes to restart the run from this point, new input and output data sets are to be used if NSTFN is set equal to zero (by the user). The reason for outputting the parameters outlined above is to allow the run to be restarted following its termination. Because the restart data set is overwritten everytime, SUMMUP is called, the run may be restarted only from the step at which the parameters were last written.

CALLED FROM: MAIN

SUBROUTINES CALLED: None

Important Local Variables: None

Subroutine SURDFI

This subroutine, outlined in Figure IV-33, is used to advect the surface portion of the oil spill, specifically, the spillets. The advective velocity is taken equal to the vector sum of the ocean velocity, input to the model, and a scaler constant times the wind velocity, also input to the model. The scaler factor multiplying the wind velocity, WINFC, is presently set to .035 in the model and can only be changed by modifying the appropriate data statement. If the ocean current is in degrees/second, it will be converted in the subroutine to meters/second.

CALLED FROM: SURFES

SUBROUTINES CALLED: None

Important Local Variables

UCRNT - water current in x direction passed to the routine.

UWIND - wind speed in x direction passed to the routine.

VCRNT - water current in y direction passed to the routine.

VWIND - wind speed in y direction passed to the routine.

WINFC - wind factor defined in the routine.
Figure IV. - 32. Flowchart for subroutine SUMMUP.
Enter Subroutine

Is ocean current in degrees per second?

Yes

Convert to meters/second

No

Calculate distance moved by spill in meters

Convert the new location to degrees longitude, latitude

Return

Figure IV. - 33. Flowchart for subroutine SURDFT.
Subroutine SURFES

The simulation model might be viewed as consisting of four major sections: the main program; the input module; the surface module, and; the subsurface module. Each of the last three sections consist of a number of subroutines. The subroutine, SURFES, controls the surface section, calling all of the subroutines that effect the disposition of the surface slick. With the exception of the shoreline interaction process, all processes are treated separately for each spilllet, i.e., the subroutine representing a process is called once for each spilllet. The flow through this subroutine (see Figure IV-34 for flow chart) is quite straightforward.

CALLED FROM: MAIN

SUBROUTINES CALLED: ASHOR, CLNUP, ENMAS, ENTRN, EVPOR8, LOC8, SPREAD, SURDFT, TREAT

Important Local Variables:

SUMAS - Amount of mass entering the water column from one spilllet during one step.

NOLSPL(NSPIL) - 99 - 0 - spilllet is within study area.
1 - spilllet is at edge of study area. This spilllet is no longer subject to any processes.

NOLSPL - Parameter in subroutine LOC8 which indicates whether or not the spilllet is in the study area.
- 0 - within study area
- 1 - out of study area

ENMAS - Mass of oil entrained this step. This is used in the preview run to determine the amount of mass to be represented by each droplet.

UCRNT - Average current over spilllet in X direction (m/sec or deg/sec).

VCRNT - Average current over spilllet in Y direction (m/sec or deg/sec).

UWIND - Average windspeed over spilllet in X direction (m/sec).

WIND - Average windspeed over spilllet in Y direction (m/sec).

WVEL - Total magnitude of windspeed over spilllet (m/sec).

DEPLOC - Average depth under spilllet (meters).

HTLOC - Average tidal elevation around spilllet (meters).
Figure IV.34. Flowchart for subroutine SURFS.
Subroutine TREAT

This subroutine, see Figure IV-35 for its flow chart, handles the chemical treatment of the surface slicks. A number of treatment efforts may be in progress at any one time. Within range of a treatment effort, spillets are treated in the order in which they occur, i.e., if the fifth, seventh and twelfth spillet fall within range of a treatment effort, the fifth, then the seventh and finally the twelfth would be treated by this effort. If the area treated is less than the area of a spillet, then only a fraction of the spillet is treated and the next treatment effort is dealt with. In this case, the fraction of oil which is dispersed is the ratio of the treated area to the total spillet area. If, on the other hand, the area to be treated is greater than that remaining in the spillet, then it is treated and the next spillet is treated, etc. The percentage of oil dispersed in this case is defined by PCHEM. The area treated is stored and in the next time step, only the remaining untreated area is treated.

CALLED FROM: SURFES

SUBROUTINES CALLED: DIST, REMOV

Important Local Variables:

TRAREA - Area to be treated at this step (meter$^2$).

DIS - Distance between the center of treatment effort and the center of spillet of interest (meters).

SPAREA - Area of the spillet which has not been treated (meters$^2$).

PER - Fraction of oil which is entrained.

XMSDP - Mass entrained by this effort (metric tons).

SUMAS - Mass entrained this step (metric tons).

AMNT - Area treated (meters$^2$).

Subroutine VELC

This routine, Figure IV-36, calculates from the appropriate fixed grids, the water depth, the tide height and the current velocities at each of the corresponding floating grid locations using a bilinear interpolation (see the description of subroutine PARTV for a discussion of the bilinear interpolation). If the floating grid comes too close to the edge of the corresponding fixed grid for proper interpolation, a warning is written. The program will continue to execute but interpolation errors are probable at this point or in other routines of the model. Due to the space staggered system and the possible rotation of some of the grids, each grid is interpolated separately.

CALLED FROM: CNVRTZ, VELCT

SUBROUTINES CALLED: ROTAT
Figure IV-32: Flowchart for subroutine TREAT.

- Enter subroutine
- Any ongoing efforts? No Return
  - Call remp. to remove expended efforts
- Any ongoing efforts? Yes Return
  - Initialize temporary treatment effort counter
  - Increment temporary treatment effort counter
  - Calculate range of this treatment effort
  - Calculate distance between spill, center, and effort
    - Is this spill? within range? Yes
    - Has this entire spill been treated? No
    - Is area of effort less than remaining area of spill? Yes
      - Treat fraction of spill
      - Treat total spill
      - Disperse oil and calculate mass balance
    - Last treatment effort? Yes Print message Return
Enter Subroutine

- Convert maximum and minimum positions of floating grid on the u and v current grids

- Is floating grid outside of the current grids? Yes → Printout error message

- No

- Convert maximum and minimum positions of floating grid to the tidal grid

- Is floating grid outside of tidal heights grid? Yes → Printout error message

- No

- Convert floating grid locations to current grids and linearly interpolate current values

- Convert floating grid locations to tidal height grid and linearly interpolate tidal height values

- Convert floating grid locations to depth grid and linearly interpolate depth values

Return

Figure IV. - 36. Flowchart for subroutine VELC.
DIS - Distance between the center of treatment effort and the center of spillet of interest (meters).

SPREA - Area of the spillet which has not been treated (meters²).

PER - Fraction of oil which is entrained.

XMSOP - Mass entrained by this effort (metric tons).

SUMAS - Mass entrained this step (metric tons).

AMNT - Area treated (meters²).

Subroutine VELC

This routine, Figure IV-36, calculates from the appropriate fixed grids, the water depth, the tide height and the current velocities at each of the corresponding floating grid locations using a bilinear interpolation (see the description of subroutine PARTV for a discussion of the bilinear interpolation). If the floating grid comes too close to the edge of the corresponding fixed grid for proper interpolation, a warning is written. The program will continue to execute but interpolation errors are probable at this point or in other routines of the model. Due to the space staggered system and the possible rotation of some of the grids, each grid is interpolated separately.

CALLED FROM: CNURTZ, VELCT

SUBROUTINES CALLED: ROTAT

Important Local Variables: None

Subroutine VELCT

This subroutine, Figure IV-37, calculates the diffusion velocities at each of the grid nodes and adds these to the advective terms. If the number of particles is less than NCRIT, the diffusion velocity is not calculated. The procedure calculates the diffusion coefficients and then locates the four closest concentration nodes. The difference is determined in the X, Y, and Z direction and used to calculate the three velocity components. If the large scale mode is used, the horizontal velocity components must be converted to degrees/sec. The maximum advective and diffusive velocities (divided by the grid spacings) are also determined.

CALLED FROM: SUBSUR

SUBROUTINES CALLED: DIFF, VELC

Important Local Variable: None
Enter Subroutines

 Initialize variables

 Is floating grid free to move? Yes

 Call VELCT to calculate depth, tidal height and advective currents

 Use scale dependent diffusion? Yes

 Calculate scale dependent diffusion coefficients

 Initialize grid element counters

 Increment grid element counter

 Grid unit in meters? Yes

 Convert DX & DY from degrees to meters

 Store extensively used depth and tidal height variables

 Is this a land cell? Yes

 Calculate diffusion coefficient divided by grid spacing

 Find maximum current velocity divided by fixed grid spacing for Courant check
Figure IV. 37. Flowchart for subroutine VELCT.
APPENDIX V. Input Programs

This Appendix gives the details necessary to use the input programs GRIDS and CHECODATA.

A. GRIDS

As described in Chapter II, this program serves to format environmental data for input into either a preview run or a complete simulation. The general flow through this program is shown in Figure V-1. The first step is to read the grid control variables i.e., the variables that control the execution of the run. These variables are shown in the upper half (above the dotted line) of Table V - 1 in the order in which GRIDS will read them. The subroutines READI and READF described in Appendix IV are used to input these parameters. The formats required by READI and READF are specified in Appendix I, Section D2.

The next step is to read the grid definition variables, i.e., the variables that define the grid, such as, number of grid elements, the angle of rotation, the various names, etc. This is done in subroutine READU which again uses READI and READF to read fixed and floating point variables, respectively. Two new subroutines are also called in READU; READN2 and READN3. The structure of these subroutines is identical to READF, the only difference being that they are used to input character data, i.e., grid names and units, instead of numerical values. READN2 will enter an 8 character name and READN3 is used to enter a 12 character name. The format for READN2 is:

(7X, 2A4, 5X, A8)

while that for READN3 is:

(3X, 3A4, 5X, A8)

These formats are to be compared to that of READF:

(F15.5, 5X, A8)

The variables input in this step, their order of input and the appropriate input subroutine is shown in the lower half of Table V - 1.

Following the entry of GRID control parameters and environmental definition variables the title of the environment grid is checked to see that it is one of:

'BATHYMETRY'
'TEMPERATURE'
'WIND VEL'
'UTID CURRENT'
'VTID CURRENT'
'TIDE LEVEL'

If the grid title is not one of these spelled exactly as above, an error message is written and the program stops.
Figure V-1. Flowchart for input program GRIDS.
Table V - 1. List of Variables for GRIDS
Input Parameters - in order of entrance

<table>
<thead>
<tr>
<th>Input Parameters</th>
<th>Subroutine used</th>
<th>Description</th>
</tr>
</thead>
</table>
| NPRTA            | READ1           | Print control parameter.  
|                  |                 | -1 - no diagnostic print out  
|                  |                 | 0 - limited print out - prints out line to tell the step and the time.  
|                  |                 | 1 - full print out - formatted out of what goes to cards, disk or tape.  
| NO               | READ1           | Number of variables per grid.  
| NU               | READ1           | Format control for cards or disk printout of environmental grids.  
|                  |                 | 1 - unformatted real variables  
|                  |                 | 2 - unformatted integer variables  
|                  |                 | 3 - formatted real variables  
|                  |                 | 4 - formatted integer variables  
| NUM              | READ1           | Number of steps to be written out.  
| NO               | READ1           | Unit number data is to be written to.  
| NUNIT            | READ1           | Unit number data is to be read from.  
| DT               | READF           | Time step between data values.  
| ISCAL            | READ1           | Control parameter for scale mode.  
|                  |                 | 1 - small scale (meters)  
|                  |                 | 2 - large scale (degrees)  
| IMAX             | READI           | Number of elements in the x direction.  
| JMAX             | READI           | Number of elements in the y direction.  
| ANGLE            | READF           | Angle measured in the counter clockwise direction from East to the positive x-axis (in degrees).  
| XS,YS            | READF           | Spacing between grid lines in x and y direction (in meters or degrees).  
| XL,YL            | READF           | Location of (1,1) point of the grid (in Longitude and Latitude).  
| TITLE            | READN3          | - 12 character variable giving the name of the grid. This must be |
8 character variable giving the name of the variable in the grid.

12 character variable giving the dimensions for print out. If there is only one grid, VARS2 and UNITS2 are not needed.

8 character variable giving the units of XS and YS.

Correct titles to be used by the program, if these are not correct and in the order required by the main program, the run will terminate.

The values of the grid data when the data is real. If there is only one grid, ARRAY1 is used.

The values of the grid data when the data is integer. If there is only one grid, then MARAY1 is used.

<table>
<thead>
<tr>
<th>Variable</th>
<th>READN2</th>
<th>READN3</th>
</tr>
</thead>
<tbody>
<tr>
<td>VAR1, VAR2</td>
<td>8 character variable giving the name of the variable in the grid.</td>
<td></td>
</tr>
<tr>
<td>UNITS1, UNITS2</td>
<td>12 character variable giving the dimensions for print out. If there is only one grid, VARS2 and UNITS2 are not needed.</td>
<td></td>
</tr>
<tr>
<td>UNITS3</td>
<td>8 character variable giving the units of XS and YS.</td>
<td></td>
</tr>
<tr>
<td>NAMCH</td>
<td>Correct titles to be used by the program, if these are not correct and in the order required by the main program, the run will terminate.</td>
<td></td>
</tr>
<tr>
<td>ARRAY1, ARRAY2</td>
<td>The values of the grid data when the data is real. If there is only one grid, ARRAY1 is used.</td>
<td></td>
</tr>
<tr>
<td>MARAY1, MARAY2</td>
<td>The values of the grid data when the data is integer. If there is only one grid, then MARAY1 is used.</td>
<td></td>
</tr>
</tbody>
</table>
If the grid title is acceptable then a do loop is executed over the number of time steps, NUM, for which the particular grid is to be updated. In this loop, the user supplied subroutine, FIX, is employed to read the environmental data values and then to perform the necessary operations to work them into a rectangular grid.

Finally, this grid is output by the subroutine ARAYOT. This subroutine is an exact duplicate of ARAYIN discussed in Appendix IV except all READ statements have been changed to WRITE statements. The appropriate output formats are described in Appendix I, section A.

A brief summary of the GRIDS and its subroutines is included below.

1) Main Section - This section reads in several input parameters, does a check on the title, then loops over the number of grids to be entered, by the variable NUM. 

   Calls Subroutines READI, READU, Fix, and ARAYOT.

2) Subroutine READU Reads in all necessary input variables and units. 

   Calls Subroutines READI, READF, READN3, and READN2.

3) Subroutine FIX - The Subroutine must be written by the user. It reads the environmental data and does any necessary calculations or manipulations needed to work the data into a form compatible with the structure of ARRAY1 and/or ARRAY2. In the example, a current data set is read in and converted to degrees/sec.

4) Subroutine ARAYOT - Writes the variables to unit NO in the format defined by the previous parameters.

5) Subroutine READI, READF, READN3, READN2 - reads and checks input parameters. If the spelling is incorrect or the title is not in the correct column, the run terminates.

Formats READI (I15, 5X, A8) 
READF (F15.5, 5X, A8) 
READN3 (3X, 3A4, 5X, A8) 
READN2 (7X, 2A4, 5X, A8) 

B. READATA

The purpose of this Subroutine is to verify that the environmental data is in the proper format for input to the preview program or the full simulation. The Subroutine is extremely straightforward. Five control parameters are read specifying the print control, the number of variables per grid (1 or 2), the format of the data, the number of grids (time steps for which the environmental grid is to be updated) to be read and the unit number from which the data is to be read. Table V - 2 lists all input variables to READATA. All of these variables being fixed point or integer are read in with the Subroutine READI (see Appendix IV for a description of READI and Appendix I, Section 2 for a description of the appropriate format). A do loop is then executed over the number of
The interior of this do loop is an exact duplicate of the working part of the Subroutine ARAYIN described in Appendix IV including the checks that are made on the title of the environmental array.

Table V - 2. List of Variables for READATA displayed in order of entrance.

<table>
<thead>
<tr>
<th>Input Variable</th>
<th>Subroutine Used</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPRTA</td>
<td>READI</td>
<td>Print control parameter (see program GRIDS).</td>
</tr>
<tr>
<td>NO</td>
<td>READI</td>
<td>Number of variables per grid.</td>
</tr>
<tr>
<td>NU</td>
<td>READI</td>
<td>Format control (see GRIDS).</td>
</tr>
<tr>
<td>NUM</td>
<td>READI</td>
<td>Number of steps to be read in.</td>
</tr>
<tr>
<td>ND</td>
<td>READI</td>
<td>Unit number from which data is to be read.</td>
</tr>
<tr>
<td>ISCAL</td>
<td>READI</td>
<td>Control parameter for scale mode.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 - small scale (meters)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 - large scale (degrees)</td>
</tr>
</tbody>
</table>
Appendix VI: Output Programs Descriptions

This appendix is included to provide the user with the details necessary to run the output programs. There are six such programs which are either run independently or in conjunction with one or more of the others. The relationship between the various programs are discussed in Chapter V and will only be repeated here as necessary for their use. All plots are generated with standard CALCOMP software.

A. PLOTMASS

A detailed flow chart for PLOTMASS is presented in Figure VI-1, a simpler flow chart is shown in Figure 8. This program requires two different sets of control parameters in addition to the input data available from the simulation model. One set controls the run itself, specifically how many timesteps are to be used, NST, and the number of simulated data sets to be plotted, NPLT. These two parameters are read in with the subroutine READI discussed in Appendix IV. The second set of input parameters read as one logical record controls which variables in the mass balance are to be plotted. The format used to read these parameters is given by:

```
READ (5,200) NUN, NATM, NBIO, NBOT, NCLN, NLOS, NSHR, NSUR, NSUS, NDMP
200 FORMAT (2X,1014)
```

The meaning of each of these variables is outlined in Table VI-1.

The results of two different runs may readily be compared by specifying NPLT equal to 2 and NUN equal to 0. The first set of data will then be plotted with solid lines and the second with dashed lines on the same plot.

A second option in this program is to plot the same data set a number of times in different ways on different plots. In this case NPLT would be set equal to 1 and NUN to 1.

The IBM Job Control Language for the output data set required to run this model is:

```
// FT F001 DD Ds NAME = MASS. PLOT,
// DISP = (NEW,CATLG).
// UNIT = SYSDA,
// DDB = (RECFM = UBS, BLKSIZE = 1954),
// SPACE = (TRK(2,2))
```

An example plot is shown in Appendix VIII.
Table VI-1

<table>
<thead>
<tr>
<th>Variable</th>
<th>Range</th>
<th>Format</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>NST</td>
<td>1-100</td>
<td>READI</td>
<td># of model timesteps in plot</td>
</tr>
<tr>
<td>NPLLOT</td>
<td>1-6</td>
<td>READI</td>
<td># of data sets on one plot</td>
</tr>
<tr>
<td>NUN</td>
<td>0-1</td>
<td>14</td>
<td>0-Use same mass balance data 1-Read in new data</td>
</tr>
<tr>
<td>NATM</td>
<td>0-1</td>
<td>14</td>
<td>0-Do not plot mass in atmosphere 1-Plot mass in atmosphere</td>
</tr>
<tr>
<td>NBIO</td>
<td>0-1</td>
<td>14</td>
<td>0-Do not plot mass consumed biologically 1-Plot mass consumed biologically</td>
</tr>
<tr>
<td>NBOT</td>
<td>0-1</td>
<td>14</td>
<td>0-Do not plot mass deposited on the bottom 1-Plot mass deposited on the bottom</td>
</tr>
<tr>
<td>NCLN</td>
<td>0-1</td>
<td>14</td>
<td>0-Do not plot mass cleaned up 1-Plot mass cleaned up</td>
</tr>
<tr>
<td>NLOS</td>
<td>0-1</td>
<td>14</td>
<td>0-Do not plot mass lost to an open boundary 1-Plot mass lost to an open boundary</td>
</tr>
<tr>
<td>NSHR</td>
<td>0-1</td>
<td>14</td>
<td>0-Do not plot mass deposited on shore 1-Plot mass remaining on the surface</td>
</tr>
<tr>
<td>NSUS</td>
<td>0-1</td>
<td>14</td>
<td>0-Do not plot mass in the water column 1-Plot mass in the water column</td>
</tr>
<tr>
<td>NDMP</td>
<td>0-1</td>
<td>14</td>
<td>0-Do not plot total mass spilled 1-Plot total mass spilled</td>
</tr>
</tbody>
</table>

Program PARTICLE

This program (Figure VI - 2) is used to change the resolution of a floating grid using data which has been previously written to disk. The particle parameter data set is read in the main program and used by subroutine PRINT. The user specifies the number of grid elements in the X and Y directions. These values are then used to calculate a new floating grid and new concentration values. The new concentration values are then written out to disk for use in the OUTPUT programs. The subroutines used to determine the new grid location and shape, GRIDEX, to calculate the hydrocarbon concentration on this grid, CONC, and to write and print the results of these calculations, PRINT are identical to those used in the main simulation. All three subroutines are described in detail in Appendix IV.
Fig. VI -2  Flow chart for Program PARTICLE
Calls Subroutines CONC, GRIDEX, PRINT, READ1 AND READN2.

**Input Variables (In order)**

NMAX - maximum number of particles allowed.

NSTEP - number of time steps this program is to be run.

ISCAL - size scale parameter. This must be the same as the previous simulation run.
1 - does horizontal calculations in meters.
2 - does horizontal calculations in degrees.

NPTFLT - print control for floating grid information. This is the print interval in number of steps.

IMSUB - new number of grids in the x direction.

JMSUB - new number of grids in the y direction.

KMSUB - new number of grids in the z (vertical) direction.

KPRTC - concentration print control parameter.

KPRTP - particle position print control parameter, print out at this interval of time steps.

NPRD - disk data set print control parameter.
0 - no data sets written out this step.
1 - at least one data set written out this step.

NPRC - concentration disk data set print parameter, write out at this interval of steps.

NPRP - particle disk data set print parameter, write out at this interval of steps.

UNITS3 - units of new grid point spacing, e.g., DEGREES, METERS, etc.

NUNCN - the device number to which the new concentration grid is to be written.

NUNPT - the device number from which the particle positions are to be read.

C. DATAOUT

This program, flowcharted in Figure VI-3, is used to prepare data output by the simulation program for input to the surface and subsurface plotting programs. It may also be used to printout the output of the simulation program. The user may select whether this printout is to be simply a copy of the simulation data sets and/or a printout similar to that available from the simulation mode, i.e., formatted for easier interpretation. These options are selected by specifying different combinations of the six run control variables. The run control parameters,
Figure VI - 3. Flow chart for Program DATAOUT.
tabulated in Table VI-2, are read in by the subroutine READI, discussed in Appendix IV. The variable NPRT is used to control the output of this program while the variables NRDSP, NRDCN and NRDPT determine whether or not spill information, a concentration distribution and/or particle information is to be read. If these variables are zero then the associated data sets are not read. If they are not zero, then their value specifies the unit number from which the data is to be read.

The program will determine all grid elements in the horizontal for which the vertically averaged concentration exceeds the value of the run control parameter: CCUT. The location of these elements is output to the disk data set designated as input to the plotting programs.

The remaining run control parameter, ISCAL, is required by that part of the program calculating the location of the grid elements with a hydrocarbon concentration exceeding CCUT. If ISCAL = 2, the locations are written to disk in longitude and latitude. If ISCAL = 1, the locations are written to disk in meters from the fixed depth grid origin.

The user must supply the run control parameters described above, data set(s) from which the oilspill output data will be written and the data set to which the reconfigured data will be written. This last data set is unformatted, variable locked. The IBM Data Definition statement defining it is:

```
//FT0 F001 DD DSN=name, DISP=(NEW,CATLG)
// DCF=(RECFM=VBS, LRECL=44, BLKSIZE=4404),
// VOL=SYSDA,SPACE=(4404,(10,10))
```

**Input Variables for Program DATAOUT:**

NPRT - print control parameter.
- 1 write reduced output to disk.
- 0 no printout.
- 1 print data as read in.
- 2 print data as formatted output.
- 3 print both formatted and as read.

ISCAL - scale mode parameter, must be the same as specified in the original simulation.

NRDSP - print control parameter for spillset data set.
- 0 - spill information not read in.
- >0 - spill information read in from this unit number.

NRDCN - print control parameter for concentration data.
- 0 - concentration data not read in.
- >0 - concentration data read in from this unit number.

NRDPT - print control parameter for particle data set.
- 0 - particles not read in.
- >0 - read particle parameters from this unit number.
CCUT - controls the lowest value of concentration to be written out. This is read in as parts per thousand and converted to parts per billion for the printout.

CONC(IMSUB,JMSUB,KMSUB) - 30,30,10 - concentration of the levels of the water column (ppt).

CC(IMSUB,JMSUB) - 30,30 - averaged concentration over the water column (ppt).

NSUM - number of elements exceeding CCUT.

CT(NSUM) - 899 - concentration of those elements which exceeds CCUT (ppb).

XG(NSUM), YG(SNUM) - longitude and latitude of these concentration values. If AD = 0, these are returned in meters.

THIC - thickness of the spillet (meters).

ZT(MMXP) - transformed depth of particle.

DX, DY - grid spacing in X and Y direction (meters).

X, Y, Z - particle positions.

See common blocks SPIL, PTYP, and DPTH for other variables.

D. Program CHEDDATA

This program (figure VI-4) checks the data set output by the program DPTAOUT. This data set, which includes the spillet parameters and concentration parameters, is read and printed in an easy to read fashion. The only input parameters required are those which specify the device from which the data is to be read, NUNIT, and the parameter, NRDCN, which specifies whether or not the subsurface concentration grid is included in the input data set. If NRDCN is equal to zero, then the subsurface concentration grid is not included. The program terminates after it has been read and printed all of the data available.

The variables used are the same as in DPTAOUT. (Also see common block SPIL).

E. PROGRAM PLOTMAP

This program plots a map of the spilled oil exceeding a given thickness on the surface and exceeding a given concentration beneath the surface. The data is read in for the designated number of steps and the maximum extent of the oil is determined in terms of longitude and latitude. This defines the origin and the conversion factor, SCAL, required to convert degrees of longitude and latitude into plotter coordinates, inches. The routine then loops over the total number of time steps, generating a plot at time step intervals of HR. The spillets are plotted
Read in run control parameters

Read surface data

EOF?

Yes

Print EOF message

Stop

No

Print data

Subsurface Concentration available?

No

Read subsurface data

EOF?

Yes

Print EOF message

Stop

No

Print subsurface data

Figure VI - 4. Flow chart for Program CHECDATA.
as circles while the subsurface area exceeding a specified concentration values is outlined. The outline is constructed starting at the north and moving clockwise. The outline is started at the top (north) left hand corner of the concentration values if the floating grid is rotated. The number of data sets to be used is determined by NPLOT and the cases are plotted in order of ascending device number. The routine can only plot a maximum of two cases at one time. The first case is plotted using solid lines and the second case using dashed lines. The legend which includes a scale and other information is plotted in the upper right hand corner. Tick marks for longitude and latitude are drawn around the edges in intervals of a tenth of a degree. An example of such a plot is given in Appendix VIII. The two input parameters XLNG and YLTD give the interval at which the values of longitude and latitude respectively, are to be written. See Figure VI-5 for a flow chart of Plotmap.

A shoreline may be plotted by indicating the number of points to be plotted which is controlled by the parameter NSHOR. Plotmap calls subroutine READI, READF and POSIT in addition to standard CALCOMP routines.

**Input Variables for Plotmap:**

- **NPLOT** - number of cases which are to be plotted. This indicates the number of input units to be used.
- **NSTEP** - number of steps to be read.
- **HR** - interval for plotting. (Hours)
- **THICK** - minimum thickness of spillet to be plotted (meters).
- **XLNG** - interval between longitude tick marks (degrees).
- **YLTD** - interval between latitude tick marks (degrees).
- **NRD10** - control parameter for subsurface outline
  - 0 - plot surface spillets only
  - 1 - plot surface and subsurface spillets.
- **ISCAL** - scale mode control parameter
  - 2 - floating grid is not rotated.
  - 1 - floating grid may be rotated.
- **NSHOR** - number of shoreline points to be plotted.

**Other important variables for PLOTMAP:**

- **XMIN, XMAX** - maximum extent of spillets and subsurface grids in longitude. (If the floating grid is rotated this is in meters).
- **XMIN, YMAX** - maximum extent of spillets and subsurface grids in latitude. (If the floating grid is rotated, this is in meters).
- **NUMELM** - number of elements which exceed the minimum cut.
PLOTPMAP CONT'D.

Determine scale conversion from longitude and latitude to plotter inches

Print the origin of the plot

Initialize CALCOMP plotter

Set case counter to 0

Increment case counter by 1

Read header for this case

Time exceeds for last case? yes

Close plots

Stop

Time step for which data is to be plotting? yes

Read daughter data

Last case? yes

Print time for this contribution to the plot

Plot the legend

Plot borders and title

Plot spill

Plot longitudinal and latitude lines

Yes

Plot shoreline?

Print spill counter to 0

Increment case counter by 1

Print case number and other information

Set spill counter to 0
Figure VI. 5. Flowchart for Program PLOTHAP.
XSIT, YSIT - site of spill, location of first spillet at time zero is used (longitude and latitude).

XOR, YOR - origin used for plotting, this is located approximately at the middle bottom of the plotted area (longitude and latitude).

SCAL - scale factor for plot (degrees/inch).

XSPIL, YSPIL - center of spillet (longitude and latitude).

RSPIL - radius of spillet (meters).

THIC - thickness of spillet (meters).

XOILMN, XOILMX - minimum and maximum extent of subsurface oil (longitude).

YOILMN, YOILMX - minimum and maximum extent of subsurface oil (latitude).

DXT, DYT - grid spacing of floating grid elements in X and Y direction (meters).

XG, YG - position of grid element (longitude and latitude).

CC - concentration of grid element (ppb).

F. Program PLOTAREA

This program (Figure VI-6) will generate, using standard CALCOMP software, a figure of area covered by the surface and subsurface oil as a function of time. It calculates the area of each spillet but only includes this area if the thickness of the spillet is above the user defined minimum. The user determines which portion to plot by use of the variable, NAR. The subsurface grid areas are added up to determine the area for which the subsurface concentration exceeds some user defined minimum value. The user may display the results of several simulated spills at once, the data to be plotted coming from data sets identified by consecutive unit numbers beginning with 1. Because a scale is involved, the case which covers the most area should be plotted first so that all other curves will remain within the figure borders. The scale is determined from the total area covered at the last time step for the data set on unit one. An example plot is contained in Appendix VIII.

Input Variables for PLOTAREA:

NAR - control parameter.

- 1 plot surface only.
- 0 plot only subsurface area.
- 1 plot surface spillets and subsurface area.

NPLOT - number of cases (or data sets) to be plotted.
THICK - minimum thickness of spillet to be plotted (meters).

NSTEP - number of steps to be plotted.

Other important variables of PLOTAREA:

TIME (NSTEP) - 103 - time of a model time step.

NSPIL - number of spilletts of a model time step.

XSPIL (NSPIL), YSPIL (NSPIL) - 30 - longitude and latitude of spillet center.

RSPIL (NSPIL) - 30 - radius of spillet (meters).

THIC - thickness of spillet (meters).

ASUR (NSTEP) - 50 - area of surface of a model time step (km²).

ASUB (NSTEP) - 50 - area covered by subsurface of a model time step (km²).

ATOT (NSTEP) - 50 - total area covered at the given model time step (km²).

XOILMX, XOILMN, YOILMN, YOILMX - maximum extents of subsurface concentration in longitude and latitude.

DX, DY - grid spacing in the X and Y direction (meters).
APPENDIX VII, PROGRAM LISTINGS

In this Appendix, listings of all programs are presented as used for the simulation discussed in Appendix IV. The two input programs are presented first followed by the simulation model and then the five output programs. Note that as presented here the PREVIEW program and the Main Simulation program are the same. If the user wishes to reduce the core requirements, a separate PREVIEW program may be created in which all subsurface routines are removed and the main subsurface routine, SUBSUR, is replaced by a dummy one. The arrays corresponding to the subsurface particle locations and properties should also be reduced to a value of 1.

The JCL listed with these programs is not always accurate. The JCL is compatible with the URI system but it may not be the most efficient. This is especially true for the space parameters and the allocation data set names as these names have been used for previous work. The DD statements at the end of the programs are not always used. The IBM 370 system at the University of Rhode Island uses the symbols /* as a JCL comment statement, thus these statements are ignored.

The program listings are listed in order in columns, as shown in Figure VII-1 through VII-5.
Figure VII.1. GRIDS
J = JBASE + 1
GO TO 4, JBASE
J = J - 1
WRITE (4, 245) J, (XBASE + 1, J) + 1, ERASE
CONTINUE
GO TO 999
C READ TO PRINT INTEGER ARRAY.
C
99 CONTINUE
2F96(IFMT.15.0) GO TO 999
XBASE = XBASE + 1
WRITE (4, 244) XBASE, WRITE (4, 245) XBASE, WRITE (4, 12) (11.12, 1, XBASE)
WRITE (4, 245) XBASE, WRITE (4, 245) J, (XBASE + 1, J), ERASE
J = J + 1
WRITE (4, 250) J, (XBASE + 1, J) + 1, ERASE
CONTINUE
WRITE (4, 250) J, (XBASE + 1, J) + 1, ERASE
99 CONTINUE
C END DATA
C
STOP
DATA XBASE / 1.0 D1.
STOP (XBASE, 1.0 D1.)
10 IF (XBASE /= 1.0 D1.) GO TO 160
WRITE (4, 250) XBASE, WRITE (4, 250) 4
STOP (XBASE, 1.0 D1.)
160 STOP
CONTINUE
STOP (XBASE, 1.0 D1.)
STOP
RETURN
END
GO TO 100
STOP
END
Figure VII.2. READATA
Figure VII-3. MAIN
**Figure VII:3. MAIN**
Figure VII.-3. MAIN
Figure VII-3. MAIN
Figure VII.-3. MAIN
Figure VII. - 3. MAIN
Figure VII-3, MAIN
Figure VII.-3. MAIN
Figure VII-4. DATOUT
Figure VII.5. CHECDATA
**Figure VII.6. PLOTMASS**
Figure VII.-8. PLOTMAP
Figure VII.-9. Particle Program
Figure VII.5. Particle Program
Figure VII.-9. Particle Program
APPENDIX VIII, A SAMPLE RUN

This Appendix presents all data input from cards and the resulting output for a complete simulation. This case simulates a 5.7 million gallon spill of an oil similar to #2 fuel oil released over a six hour period. The location of the spill is off Massachusetts near Georges Bank. The environmental data used here is a sample and is not of the actual data used for previous runs in Cornillon, et al. (1979 and 1980). Figures VIII-1 to VIII-4 present the output for these programs. The reader should refer to Figure VII-1 for the input to the program GRIDS. The output of READATA (Figures VIII-2-4) shows the wind and currents which were used for the main simulation.

The input data stream for the full simulation is illustrated in Figure VIII-5. Note that some of the environmental data sets (wind, currents, etc.) are read from disk data sets and are not shown in the input stream. The output corresponding to the input of Figure VIII-5 is illustrated in Figure VIII-6. The input stream to the Preview Run is not shown here as it is identical to that for the full simulation, figure VIII-5, with the minor exception that the control parameter NRUN is equal to 0 for the Main simulation compared to 1 for the Preview. The output for the first ten time steps of the simulation are shown in Figure VIII-7. Note that the mass balance differs between the Preview and Main simulation due to the deposited particles.

Figure VIII-8 shows the output of a sample restarted run. The subsurface parameters of a restarted run will not be the same as a full run due to the re-initialization of the random number generator in Subroutine INJECT. The remaining figures deal with the input and resulting output for the output programs. Figures VIII-9 and VIII-10 show the printed output and resulting plot from the program PLOTMASS. The user is again referred to Appendix VII where the program listing also displays the input parameters. Figure VIII-11 is an output from DATAOUT, which shows all information which has been written out by the main program for use by DATAOUT. Figure VIII-12 shows the abbreviated output from DATAOUT which is generated for the programs PLOTMAP and PLOTAREA. Figure VIII-13 is the output from CHECDATA which shows the full amount of data formatted by DATAOUT. Figures VIII-14 and VIII-15 shows the output and an example plot generated by the plotting program PLOTMAP. Figures VIII-16 and VIII-17 give the same for the program PLOTAREA. Figure VIII-18 shows the output from the program PARTICLE which was generated from the data in Figure VIII-11. The output is read left to right.
Figure VIII.1. Sample Output from Program Grids
Figure VII. - 2. Output from READATA; Wind, Speed and Direction
Figure VIII.3. Output from READATA; x-direction currents
Figure VIII-3. Output from READATA; x-direction currents
Figure VIII.-4. Output from READATA; y-direction currents
Figure VIII-4. Output from READATA; y-direction currents

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The table represents output from READATA, indicating y-direction currents for different elements.
Figure VIII.-5. Data Input to Main Simulation
Figure VIII.-6. Output from Preview Run
Figure VIII.6. Output from Preview Run
**Figure VIII.6. Output from Preview Run**
### Table: Culmination Scenarios

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### Figure VIII.-6. Output from Preview Run
Figure VIII.-6. Output from Preview Run
Figure VII.-6. Output from Preview Run
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Figure VIII.-6. Output from Preview Run
Figure VIII.-6. Output from Preview Run
### Preliminary Results

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<th>Amount of 0.1mm Particles</th>
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<th>Percent of Total</th>
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<tr>
<td>In the world</td>
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**Output from Preview Run**

Figure VIII.-6.
Figure VIII-6. Output from Preview Run
Figure VII.6: Output from Preview Run

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<th>TIME</th>
<th>REACTION</th>
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The table above shows the results of various procedures under different conditions. The concentrations and temperatures vary, affecting the reaction times and outcomes. Further analysis is required to determine the optimal conditions for each procedure.
Figure VIII.-7. Output from Main Simulation
Figure VIII.7. Output from Main Simulation
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Figure VIII.7. Output from Main Simulation
Figure VIII.-7. Output from Main Simulation
Figure VIII.-7. Output from Main Simulation
Figure VIII.-7. Output from Main Simulation
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Figure VIII.-7. Output from Main Simulation
Figure VIII-7. Output from Main Simulation
### Table:

**Result File:** Output from Main Simulation

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**Figure VIII.** Output from Main Simulation
Figure VIII.-7. Output from Main Simulation
Figure VIII-7. Output from Main Simulation
Figure VIII.7. Output from Main Simulation
Figure VIII.-7. Output from Main
<table>
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<th>1260.00 Level 3</th>
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**Figure VIII.7. Output from Main**
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<th>Y Position</th>
<th>Z Position</th>
<th>Disp (nm)</th>
<th>Disp (mm)</th>
<th>Disp (°)</th>
<th>Sp. Vol. (mm²)</th>
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Figure VIII.-7. Output from Main
Figure VIII.-7. Output from Main
Figure VIII.7. Output from Main
Figure VIII.-7. Output from Main
### Figure VIII.-7. Output from Main

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<td>Parameter 4</td>
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**Note:** The above table is a sample output from the Main program. Actual output may vary based on the specific input parameters and conditions.
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Figure VIII.-7. Output from Main
Figure VIII.-8. Output from Main Simulation
Figure VIII.-8. Output from Main Simulation Restarted Run
Figure VIII.-8. Output from Main Simulation

Restarted Run

<table>
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<tr>
<th>Time</th>
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<th>Level 2</th>
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Figure VIII.-8. Output from Main Simulation

Restarted Run

<table>
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<th>Level 2</th>
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Figure VIII.-8. Output from Main Simulation

Restarted Run

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Figure VIII.-B. Output from Main Simulation
Restarted Run
### Table III.

#### TOTAL OIL SPILLED

<table>
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<th>LOCATION</th>
<th>AMOUNT (THOUS. GALLONS)</th>
<th>PERCENT OF TOTAL</th>
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**Figure VIII. 8.** Output from Main Simulation Restarted Run
### Figure VIII.9. Output from Program PLOTMASS

<table>
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<th>TIME (IN MINUTES)</th>
<th>INPUT</th>
<th>OUTPUT</th>
<th>STRESS</th>
<th>STRONG</th>
<th>DEPRESSED</th>
<th>COMBINED</th>
<th>PLOTMASS</th>
<th>TEXT</th>
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<th>TE TEXT</th>
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<td>1.0</td>
<td>1.0</td>
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</table>

*NOTE:* The table above shows the output from Program PLOTMASS for different time intervals, with columns for input, output, stress, strong, depressed, combined, and output text.
Figure VIII.-10. Plot from Program PLOTMASS
<table>
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<th>NUMBER OF FIELDS</th>
<th>FIELD LENGTH</th>
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<th>FIELD CONTENT</th>
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**Figure VII.11. Input to Program DATAOUT from Main Program**
Figure VIII.-11. Input to Program DATAOUT from Main Program
Figure VIII. -11. Input to Program DATAOUT from Main Program
Figure VIII.-12. Output of Program DATAOUT
Figure VIII-13. Output of Program CHECDATA
### Spill Locations and Rates

**Spill Parameters for Julian Day 350 Which Is 6,000.000 Hours From the Start of the Spill**

<table>
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<tr>
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<th>Rate</th>
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<td>176.22</td>
<td>560.74</td>
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</tr>
<tr>
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</table>

**Spill Parameters for Julian Day 350 Which Is 9,000.000 Hours From the Start of the Spill**

<table>
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<th>Rate</th>
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</thead>
<tbody>
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<td>414.09</td>
</tr>
<tr>
<td>6</td>
<td>64.7907</td>
<td>61.6746</td>
<td>128.52</td>
<td>382.94</td>
</tr>
</tbody>
</table>

**Spill Locations and Rates**

| Spill Parameters for Julian Day 770 Which Is 12,000.000 Hours From the Start of the Spill**

<table>
<thead>
<tr>
<th>Spill #</th>
<th>Longitude</th>
<th>Latitude</th>
<th>Rate</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>64.7902</td>
<td>61.6686</td>
<td>176.22</td>
<td>560.74</td>
</tr>
<tr>
<td>2</td>
<td>64.7903</td>
<td>61.6690</td>
<td>192.21</td>
<td>584.97</td>
</tr>
<tr>
<td>3</td>
<td>64.7904</td>
<td>61.6704</td>
<td>156.34</td>
<td>468.02</td>
</tr>
<tr>
<td>4</td>
<td>64.7905</td>
<td>61.6718</td>
<td>148.65</td>
<td>446.15</td>
</tr>
<tr>
<td>5</td>
<td>64.7906</td>
<td>61.6732</td>
<td>138.06</td>
<td>414.09</td>
</tr>
<tr>
<td>6</td>
<td>64.7907</td>
<td>61.6746</td>
<td>128.52</td>
<td>382.94</td>
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**Spill Parameters for Julian Day 140 Which Is 15,000.000 Hours From the Start of the Spill**

<table>
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<th>Latitude</th>
<th>Rate</th>
<th>Total</th>
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</thead>
<tbody>
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<td>64.7902</td>
<td>61.6686</td>
<td>176.22</td>
<td>560.74</td>
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<td>414.09</td>
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<td>61.6746</td>
<td>128.52</td>
<td>382.94</td>
</tr>
</tbody>
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Figure VIII.-13. Output of Program CHECDATA
Figure VIII.-13. Output of Program CHECADATA
Figure VIII.-13. Output of Program CHECDATA
Figure VIII.14. Output of Program PLOTMAP
Figure VIII.-14. Output of Program PLOTMAP
**Figure VIII.14. Output of Program PLOTMAP**

**CASE 1**

<table>
<thead>
<tr>
<th>LONGITUDE</th>
<th>LATITUDE</th>
<th>RADIUS</th>
<th>THICKNESS</th>
</tr>
</thead>
<tbody>
<tr>
<td>46.86</td>
<td>41.62</td>
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<td>0.000275</td>
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**CASE 2**

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<td>1497.34</td>
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</tr>
<tr>
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**CASE 3**

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</tr>
</thead>
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<td>1157.99</td>
<td></td>
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<td>41.60</td>
<td>1157.99</td>
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**CASE 4**

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</thead>
<tbody>
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<td>46.82</td>
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<td>41.60</td>
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Figure VIII.-14. Output of Program PLOTMAP
### Figure VIII.14: Output of Program PLOTMAP

#### Case 1

<table>
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<th>Latitude</th>
<th>Rate</th>
<th>Predicted</th>
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</thead>
<tbody>
<tr>
<td>66.752</td>
<td>41.624</td>
<td>0.008400</td>
<td>0.00517</td>
</tr>
<tr>
<td>66.752</td>
<td>41.624</td>
<td>0.008400</td>
<td>0.00517</td>
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</table>

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<th>Latitude</th>
<th>Rate</th>
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<tbody>
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<td>41.624</td>
<td>0.008400</td>
<td>0.00517</td>
</tr>
<tr>
<td>66.752</td>
<td>41.624</td>
<td>0.008400</td>
<td>0.00517</td>
</tr>
</tbody>
</table>

These are 9 concentration values output there.
This oil started on May 25, 1979 and is 27.000 hours after the start of the spill.

<table>
<thead>
<tr>
<th>Longitude</th>
<th>Latitude</th>
<th>East</th>
<th>North</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>66.728</td>
<td>61.000</td>
<td>234.509</td>
<td>6.000</td>
<td>0.000</td>
</tr>
<tr>
<td>66.722</td>
<td>61.007</td>
<td>234.507</td>
<td>6.000</td>
<td>0.003</td>
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</table>

There are 4 concentration values out those.

<table>
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<th>Latitude</th>
<th>Parts/Liter</th>
</tr>
</thead>
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<td>61.000</td>
<td>234.509</td>
</tr>
<tr>
<td>66.724</td>
<td>61.000</td>
<td>234.509</td>
</tr>
<tr>
<td>66.724</td>
<td>61.000</td>
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<tr>
<td>66.724</td>
<td>61.000</td>
<td>234.509</td>
</tr>
</tbody>
</table>

Figure VIII-14. Output of Program PLOTMAP
15.0 HOURS AFTER START OF THE SPILL
MAP OF SPILLETs AND SUBSURFACE

Figure VIII.-15. Plot from PLOTMAP
Figure VIII.-16. Output of Program PLOTAREA

<table>
<thead>
<tr>
<th>Time (Hrs)</th>
<th>Concentration Values</th>
<th>Spills Out</th>
<th>Area Extent</th>
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</thead>
<tbody>
<tr>
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<td>13</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>3.0</td>
<td>6</td>
<td>2</td>
<td>21.0361</td>
</tr>
<tr>
<td>4.0</td>
<td>6</td>
<td>2</td>
<td>42.0642</td>
</tr>
<tr>
<td>5.0</td>
<td>9</td>
<td>2</td>
<td>9.0119</td>
</tr>
<tr>
<td>6.0</td>
<td>9</td>
<td>2</td>
<td>9.0119</td>
</tr>
<tr>
<td>7.0</td>
<td>9</td>
<td>2</td>
<td>9.0119</td>
</tr>
<tr>
<td>10.0</td>
<td>9</td>
<td>2</td>
<td>9.0119</td>
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<td>2</td>
<td>9.0119</td>
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<td>2</td>
<td>9.0119</td>
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<td>18.0</td>
<td>9</td>
<td>2</td>
<td>9.0119</td>
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<td>2</td>
<td>9.0119</td>
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<td>2</td>
<td>9.0119</td>
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<tr>
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<td>9</td>
<td>2</td>
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</table>
Figure VIII.-17. Plot from PLOTAREA.
### Figure VIII.18. Output of Program Particle

#### Concentration in Time

<table>
<thead>
<tr>
<th>TIME (SEC)</th>
<th>LEVEL</th>
<th>CONCENTRATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.2</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.3</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.4</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.5</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.6</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.7</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

#### Volume of Program Particle

<table>
<thead>
<tr>
<th>TIME (SEC)</th>
<th>VOLUME</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>0.2</td>
<td>0.0</td>
</tr>
<tr>
<td>0.3</td>
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<tr>
<td>0.5</td>
<td>0.0</td>
</tr>
<tr>
<td>0.6</td>
<td>0.0</td>
</tr>
<tr>
<td>0.7</td>
<td>0.0</td>
</tr>
</tbody>
</table>

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**Note:** The table above represents the concentration and volume of Program Particle at different time intervals. The concentration and volume values are given in arbitrary units for demonstration purposes.
<table>
<thead>
<tr>
<th>PARTICLE POSITION</th>
<th>PLATED SYSTEM</th>
<th>PARTICLE POSITION</th>
<th>FUSED SYSTEM</th>
<th>PARTICLE SIZE</th>
<th>DENSITY</th>
<th>DRY</th>
<th>VOL.</th>
<th>HAB</th>
</tr>
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<tr>
<td>1</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.216</td>
<td>0.55</td>
<td>0.010</td>
<td>0.010</td>
<td>0.0</td>
<td>1.001</td>
</tr>
<tr>
<td>2</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.216</td>
<td>0.55</td>
<td>0.010</td>
<td>0.010</td>
<td>0.0</td>
<td>1.001</td>
</tr>
<tr>
<td>3</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.216</td>
<td>0.55</td>
<td>0.010</td>
<td>0.010</td>
<td>0.0</td>
<td>1.001</td>
</tr>
<tr>
<td>4</td>
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<td>0.0001</td>
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<td>0.55</td>
<td>0.010</td>
<td>0.010</td>
<td>0.0</td>
<td>1.001</td>
</tr>
<tr>
<td>5</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.216</td>
<td>0.55</td>
<td>0.010</td>
<td>0.010</td>
<td>0.0</td>
<td>1.001</td>
</tr>
<tr>
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<td>0.0001</td>
<td>0.216</td>
<td>0.55</td>
<td>0.010</td>
<td>0.010</td>
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<td>1.001</td>
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<tr>
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<td>0.0001</td>
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<td>0.010</td>
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<td>1.001</td>
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<tr>
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<td>0.010</td>
<td>0.0</td>
<td>1.001</td>
</tr>
<tr>
<td>9</td>
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<td>0.0001</td>
<td>0.216</td>
<td>0.55</td>
<td>0.010</td>
<td>0.010</td>
<td>0.0</td>
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<tr>
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<td>0.010</td>
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Figure VIII.-18. Output of Program Particle
Figure VIII.18. Output of Particle
### Table 1: Concentration Data

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<th>Time (min)</th>
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<th>Level 3</th>
<th>Level 4</th>
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<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
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<tr>
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</table>

### Table 2: Concentration in % of Oil per % of River

<table>
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<th>Time (min)</th>
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<th>Step 2</th>
<th>Step 3</th>
<th>Step 4</th>
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<td>0.00</td>
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### Figure VIII.-18. Output of Particle
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<tbody>
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<td>0.0114</td>
<td>0.0149</td>
<td>0.210</td>
<td>0.350</td>
<td>0.0517</td>
<td>0.970</td>
</tr>
<tr>
<td>3</td>
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<td>0.0114</td>
<td>0.0149</td>
<td>0.210</td>
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<td>0.0517</td>
<td>0.970</td>
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<tr>
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<td>0.0114</td>
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<td>0.0114</td>
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<td>0.210</td>
<td>0.350</td>
<td>0.0517</td>
<td>0.970</td>
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<tr>
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<td>0.0114</td>
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<td>0.0114</td>
<td>0.0149</td>
<td>0.210</td>
<td>0.350</td>
<td>0.0517</td>
<td>0.970</td>
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<td>0.0114</td>
<td>0.0149</td>
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<td>0.0517</td>
<td>0.970</td>
</tr>
<tr>
<td>12</td>
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<td>0.0114</td>
<td>0.0149</td>
<td>0.210</td>
<td>0.350</td>
<td>0.0517</td>
<td>0.970</td>
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<td>13</td>
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</tr>
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<td>0.0517</td>
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<td>0.210</td>
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<tr>
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<td>0.210</td>
<td>0.350</td>
<td>0.0517</td>
<td>0.970</td>
</tr>
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Figure VIII.- 18. Output of Particle
### Concentrations in Time

| Time (0.06 hours) | 0.06 | 0.10 | 0.15 | 0.20 | 0.25 | 0.30 | 0.35 | 0.40 | 0.45 | 0.50 | 0.55 | 0.60 | 0.65 | 0.70 | 0.75 | 0.80 | 0.85 | 0.90 | 0.95 | 1.00 |
|------------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| 11               | 0.011 | 0.0049 | 0.014 | 0.020 | 0.019 | 0.018 | 0.017 | 0.016 | 0.015 | 0.014 | 0.013 | 0.012 | 0.011 | 0.010 | 0.009 | 0.008 | 0.007 | 0.006 | 0.005 | 0.004 |
| 12               | 0.011 | 0.0060 | 0.015 | 0.021 | 0.020 | 0.019 | 0.018 | 0.017 | 0.016 | 0.015 | 0.014 | 0.013 | 0.012 | 0.011 | 0.010 | 0.009 | 0.008 | 0.007 | 0.006 | 0.005 | 0.004 |
| 13               | 0.011 | 0.0071 | 0.016 | 0.022 | 0.021 | 0.020 | 0.019 | 0.018 | 0.017 | 0.016 | 0.015 | 0.014 | 0.013 | 0.012 | 0.011 | 0.010 | 0.009 | 0.008 | 0.007 | 0.006 | 0.005 |
| 14               | 0.011 | 0.0083 | 0.017 | 0.024 | 0.023 | 0.022 | 0.021 | 0.020 | 0.019 | 0.018 | 0.017 | 0.016 | 0.015 | 0.014 | 0.013 | 0.012 | 0.011 | 0.010 | 0.009 | 0.008 | 0.007 |
| 15               | 0.011 | 0.0095 | 0.018 | 0.026 | 0.025 | 0.024 | 0.023 | 0.022 | 0.021 | 0.020 | 0.019 | 0.018 | 0.017 | 0.016 | 0.015 | 0.014 | 0.013 | 0.012 | 0.011 | 0.010 | 0.009 |
| 16               | 0.011 | 0.0107 | 0.019 | 0.028 | 0.027 | 0.026 | 0.025 | 0.024 | 0.023 | 0.022 | 0.021 | 0.020 | 0.019 | 0.018 | 0.017 | 0.016 | 0.015 | 0.014 | 0.013 | 0.012 | 0.011 |
| 17               | 0.011 | 0.0119 | 0.020 | 0.030 | 0.029 | 0.028 | 0.027 | 0.026 | 0.025 | 0.024 | 0.023 | 0.022 | 0.021 | 0.020 | 0.019 | 0.018 | 0.017 | 0.016 | 0.015 | 0.014 | 0.013 |
| 18               | 0.011 | 0.0132 | 0.021 | 0.032 | 0.031 | 0.030 | 0.029 | 0.028 | 0.027 | 0.026 | 0.025 | 0.024 | 0.023 | 0.022 | 0.021 | 0.020 | 0.019 | 0.018 | 0.017 | 0.016 | 0.015 |
| 19               | 0.011 | 0.0145 | 0.022 | 0.033 | 0.032 | 0.031 | 0.030 | 0.029 | 0.028 | 0.027 | 0.026 | 0.025 | 0.024 | 0.023 | 0.022 | 0.021 | 0.020 | 0.019 | 0.018 | 0.017 | 0.016 |
| 20               | 0.011 | 0.0158 | 0.023 | 0.035 | 0.034 | 0.033 | 0.032 | 0.031 | 0.030 | 0.029 | 0.028 | 0.027 | 0.026 | 0.025 | 0.024 | 0.023 | 0.022 | 0.021 | 0.020 | 0.019 | 0.018 |
| 21               | 0.011 | 0.0171 | 0.024 | 0.036 | 0.035 | 0.034 | 0.033 | 0.032 | 0.031 | 0.030 | 0.029 | 0.028 | 0.027 | 0.026 | 0.025 | 0.024 | 0.023 | 0.022 | 0.021 | 0.020 | 0.019 |
| 22               | 0.011 | 0.0184 | 0.025 | 0.038 | 0.037 | 0.036 | 0.035 | 0.034 | 0.033 | 0.032 | 0.031 | 0.030 | 0.029 | 0.028 | 0.027 | 0.026 | 0.025 | 0.024 | 0.023 | 0.022 | 0.021 |
| 23               | 0.011 | 0.0197 | 0.026 | 0.039 | 0.038 | 0.037 | 0.036 | 0.035 | 0.034 | 0.033 | 0.032 | 0.031 | 0.030 | 0.029 | 0.028 | 0.027 | 0.026 | 0.025 | 0.024 | 0.023 | 0.022 |
| 24               | 0.011 | 0.0210 | 0.027 | 0.040 | 0.039 | 0.038 | 0.037 | 0.036 | 0.035 | 0.034 | 0.033 | 0.032 | 0.031 | 0.030 | 0.029 | 0.028 | 0.027 | 0.026 | 0.025 | 0.024 | 0.023 |
| 25               | 0.011 | 0.0223 | 0.028 | 0.041 | 0.040 | 0.039 | 0.038 | 0.037 | 0.036 | 0.035 | 0.034 | 0.033 | 0.032 | 0.031 | 0.030 | 0.029 | 0.028 | 0.027 | 0.026 | 0.025 | 0.024 |

**Figure VIII.18. Output of Particle**
Figure VIII.-18. Output of Particle
Figure VII. 18. Output of Particle
**Figure VIII.-18. Output of Particle**

<table>
<thead>
<tr>
<th>PARTICLE POSITION</th>
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<th>PARTICLE POSITION</th>
<th>PARTICLE POSITION</th>
<th>PARTICLE PARAMETERS</th>
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<td>0.6150</td>
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</tr>
<tr>
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<td>0.0725</td>
<td>0.0725</td>
<td>0.6150</td>
<td>0.21%</td>
</tr>
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**PARTICLE POSITIONS X AND Y IN THE PLOTTING SYSTEM IN UNITS X IN UNITS Y IN ORDER**

**PARTICLE PARAMETERS AT TIME 12.00**
## APPENDIX IX, OIL PROPERTIES

### Estimated Percent Weight

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<th>Fraction</th>
<th>Description</th>
<th>Venezuelan Crude 1</th>
<th>Nigerian Crude 1</th>
<th>#2 Fuel 1</th>
<th>Bunker C</th>
<th>Kuwait Crude 2</th>
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<td>1</td>
<td>Paraffin C6-C12</td>
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<td>15</td>
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<td>5</td>
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<tr>
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<td>5</td>
<td>15</td>
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<td>10</td>
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<td>08</td>
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<td>Naphtheno-Aromatic C9-C25</td>
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<td>7</td>
<td>15</td>
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<td>.8472</td>
<td>1.019</td>
<td>0.867</td>
</tr>
</tbody>
</table>

### References for Oil Properties

1. Wang et al. (1976)
2. Persen (1979), approximated composition from this data.
REFERENCES


12.4 Section 6 Appendices

12.4.1 Appendix A Advective Currents for Computer Model
12.4.2 Appendix B Oil Spill Fisheries Computer Program
APPENDIX A

A theoretical relationship between the variance $s^2$ in one dimension of a diffusing cloud and the diffusivity $D$ is

$$s = 2^t D t,$$

(Csanyadi, 1973) in which $t$ is time. Let us assume a characteristic diffusion velocity for the cloud as a whole at the $j$th timestep, $u'j$. Then in a discrete particle and time model with timestep $dt$, the position of the $k$th particle at the $j$th timestep, $r_{jk}$, will be the sum of all previous displacements. Incorporating the intrinsically stochastic nature of turbulence through the use of a random variate, $R_{jk}$, chosen from the uniform probability distribution $[-1,1]$, we have, for no bulk transport velocities,

$$r_{jk} = \sum_{l=1}^{k} R_{lk} * u'_{l} * dt.$$

Equating (1) with the statistical definition of the variance, and performing a translation of coordinates so that the origin coincides with the center of mass of the diffusing cloud composed of $N$ particles gives

$$2^j * dt * D = \frac{1}{N} \sum_{k=1}^{N} \left( \sum_{l=1}^{j} R_{lk} * u'_{l} * dt \right)^2.$$  \hspace{1cm} (3)

Replacing $u'$ with its expected value for the given problem, $E(u')$, and noting that

$$\left( \sum_{l=1}^{j} R_{lk} \right)^2 = \sum_{l=1}^{j} R_{lk}^2 + 2 \sum_{i=1}^{j} \sum_{l=1}^{i} R_{ik} * R_{lk},$$

in which the double sum on the right tends to zero for large $j$, and further that

$$\sum_{k=1}^{N} \sum_{l=1}^{j} R_{lk}^2 = N \cdot j / 3,$$

the probability density function being equal to 1/2 on the given
interval, we have

\[ E(u') = \sqrt{6*\sigma / \text{dt}} \quad (6) \]

The value of \( D \) is then chosen from an oceanic diffusion diagram (Okubo, 1974, for example), the radius of the spawning area being used as the characteristic length. By superposition, the net transport of the \( k \)th particle during the \( j \)th timestep, \( \text{dr}_{jk} \), is

\[ \text{dr}_{jk} = (R_{jk} \ast E(u') + U_{jk}) \ast \text{dt} \quad (7) \]

in which \( U_{jk} \) is the net advective velocity contribution.
Section 12.4 Appendix 6B

CONTENTS

I. Program Purpose and Overview
II. Program Component Explanation
III. Basic User Instruction
IV. Program Listing, with Data Sets
V. Sample Output
I. Program Purpose and Overview

This computer program was constructed as part of a larger effort at the University of Rhode Island to investigate environmental effects of oil spill treatment strategies. The specific problem addressed here is when and whether chemical oil spill treatment with dispersants might mitigate the impacts of an offshore commercial fishery. The primary effect is assumed to occur through egg and larval mortality. This implicitly assumes that both demersal juveniles and adults will avoid contaminated areas, that the feeding and spawning cycles will not be grossly interrupted, and that the stock will not suffer through subsequent bioaccumulation. The major program components are, therefore, a population model for a unit stock fishery, an ocean transport model, and a set of subroutines designed to interface these with output from the oil spill fates model also designed as part of this project. The program has been carefully and fully described internally through comment statements. After reading this manual, any actual applications of the program to an area and/or fishery other than the Georges Bank cod stock will require a working knowledge of the program itself, a listing of which is included here as Appendix I. It is advised that no internal program changes be made until one has read through and understands the program in its entirety, since changes in one section will have second and third order manifestations elsewhere.

The following description is designed to assist in the implementation of the program for new species and physical areas. For explicit sources of information regarding parameters used in the given data sets, the user is referred to the following publications:


II. Program Component Explanation

1) Main

The main program contains the daily cycle elements for the population model. This is the master program from which all subroutines are called, and through which all program activities are coordinated. The program is initialized, all control variables are read in, and then the annual and daily cycles are entered. Operations continue until the specified end time is reached.

2) Subroutine COMPAR

This subroutine was designed to attempt to sort out reduction rates in numbers of larvae per unit volume due to mortality versus diffusion and transport. The day of the year for this comparison is specified as input variable IDATE. The comparison is performed in the elements read into array INTELM from data set 9.

3) Subroutine BYPASS

Program run time can be reduced by increasing variable DT2 up to 5 days. This subroutine uses this secondary timestep subsequent to the spill year in both analytical and numerical time integrations, and bypasses the daily cycle in the main program.

4) Subroutine MOROIL

If MULTI is greater than 1, and KYEAR is greater than SPILYR, this subroutine is called to assign a new spill year and oil source data set.

5) Subroutine WEIGHT

Here the statistical data for the stock at hand is used to calculate weight-at-age data. Weight is called only once from Main.

6) Subroutine AVGFEC

The average number of eggs per female is calculated here, as a check against both weight and fecundity assumptions. Output is annual.

7) Subroutine SPNTIM

The spawning distribution in time is specified here. This is the result of relatively subjective evaluations to date, since no statistical data is available.

8) Subroutine DEVELOP

This subroutine controls development of eggs and larvae according to whatever information is available.
9) **Subroutine TEMP**

At present a constant seasonal surface water temperature is supplied. This input can be altered in response to improved data availability.

10) **Subroutine TOXIC**

This subroutine interfaces the hydrocarbon concentration data, input either through SR HCCONC or HCON2, with population model. First natural mortality effects are accounted for, followed by a check to see which, if any, organisms are within an area in which concentrations exceed that specified by THRSLD. This routine is called from MAIN directly after the input of the oil concentration data.

11) **Subroutine HCCONC**

For SPLTYP = 1 (an instantaneous spill), this subroutine reads in data output by the oil spill behavior model on a daily basis. Conversion from latitude and longitude to the distance units of the fish model is followed by output to data set 4 of the oil, egg, and larvae distributions at that time.

12 Subroutine OUTPUT

Here annual output is directed to the printer, and oil spill case identification data with the annual yield estimates are output to data set 8.

13 Subroutine EGGMRT

Natural mortality of both density dependent and density independent varieties is applied to the egg stages. The toxicity sections originally programmed here and in SR PLNMRT are not used.

14) **Subroutine PLNMRT**

Here background mortalities are applied to the three planktonic stages in the model. As with SR EGGMRT, the toxicity section is not used.

15) **Subroutine BTMMRT**

Here a second order Taylor expansion supplies means for a numerical solution of the juvenile mortalities, including cannibalism by adults.

16) **Subroutine HATCH**

This is actually only a function, which returns the number of days to hatch, given an input temperature. The call is from SR DEVELOP.

17) **Subroutine SPNPLC**

Here eggs to be spawned on a particular day are divided into groups, and placed at random within the spawning area. On first entry, the center and radius of the spawning area are read in from data set 9.
for each particle, or group, a call is made to SR RANDU, which returns a random variate used to locate the particle's initial position.

18) Subroutine HCON2

When SPLTYP = 2 (i.e., a blowout), this SR reads in the concentration data output by the oil model (data set 3). These are then written out to data set 4 along with the current egg and larval fish distributions.

19 Subroutine DSCWRT

The first time this subroutine is called, 12 days are read into array IDAYZ from data set 16. On subsequent calls, the present modeled day is compared with the members of KDZAY. If a match is found, the day's ichthyoplankton distribution is output to disc. Otherwise, control is returned to SR ADVOIF.

20) Subroutine ADVOIF

This subroutine, which is called from MAIN, controls the advective-dispersive section of the model. Upon first entry, the physical sector of the model is initialized through subroutines FEREAD, VAREAD, VARSET, and CHECK. Calls are then made to subroutines MOVE, DEAD, COMPRS, and DSONRT. After the first entry, only this latter group is activated.

21) Subroutine MOVE

Advection and diffusion of particles is accomplished here. First subroutine VELIN is called, to supply the advective currents for the day in question. If the logical variable DOSPWN has a value of true, SR SPNPLC is called. Then each particle is located within an element (grid) of the physical model, and planar interpolation among the three defining modes is applied to determine an advective contribution at the given particle location. A random walk diffusion velocity calculation follows, the result being superimposed on the advective velocity and multiplied by the model timestep to produce a physical displacement of the particle.

22) Subroutine INIT

This is a convenience subroutine, where in any arrays and variables can be initialized. In general, everything is set to zero to avoid undefined variables.

23) Subroutine FEREAD

Called once from subroutine ADVOIF, the program section reads element, node, and diffusive control parameters from data set 10. Then actual node numbers and locations (in latitude and longitude) are read in and converted. Thus, the physical reference grid is established.

24) Subroutine VELIN

Here the velocity data is read into the model from data sets 13 (long term net drifts) and 14 (wind-wave currents). The output values are the sum of these two.
25) **Subroutine VAREAD**

The initial particle data and random variate seed, along with output write and plot time steps are read in from data set 10. Thus, an initial particle distribution can be stipulated if desired. In addition, if a uniform drift velocity is to be applied over the entire physical field, that is input here from data set 10.

26) **Subroutine DEAD**

Mortality due to transport out of a favorable developmental area can be included here by setting variable IOFF = 1. Due to lack of any verification data for this process, this subroutine has not been used to date.

27) **Subroutine COMPRS**

In an effort to keep storage requirements to a minimum this subprogram was designed to compress arrays as particles are removed from the system. Particle attrition occurs as the result of the growth of larvae to juveniles, hydrocarbon mortality, or whenever particles are transported out of the physical domain of the model.

28) **Subroutine CHECK**

After input of the node and element data through SR FEREAD, this subroutine checks to confirm that the nodes associates with a given element are ordered counterclockwise. This is necessary so that, when associating a given particle with a given element, SR MOVE can simply proceed around the element counterclockwise and check to see that the particle is always to the left of the line between successive nodes.

29) **Subroutine VARSET**

The slope and direction of the lines connecting successive nodes are calculated here, along with adjacent elements. Storage of this information greatly decreases subsequent search time when attempting to locate particles in elements.

30) **Subroutine SLPDIR**

This does the actual mathematics for SR VARSET, which is primarily logical in nature.

31) **Subroutine WRTOUT**

This generates printed output at the desired intervals, and calls SR STATS.

32) **Subroutine STATS**

Here particle statistics (e.g. centroid and variance of the present distribution) are calculated. Although not employed for the full scale fishery runs, this subroutine is useful for verifying the physical system definitions, initial conditions for particle placement, and for comparing theoretical with modeled diffusion rates. Changes can be made freely in
this subroutine, so long as no common arrays and variables are revalued.

III. Basic User Instructions

There are 21 primary options built into the program. The user can, therefore, run the program in a variety of modes without altering any internal code. The options are read in by the main program from data set 9. In this data set (see end of program listing in Appendix 1) the variables are explicitly labeled so that no confusion will exist. A self-explanatory list of input control variables follows.

1150 C**************************************************************************************************
1160 C
1170 C LIST AND EXPLANATION OF INPUT CONTROL VARIABLES
1180 C
1190 C**************************************************************************************************
1200 C OILCODE = 1 THEN OIL IS TRUE
1210 C = 0 THEN OIL IS FALSE AND NO ADECTION IS PERFORMED EVER
1220 C IOFF = 1 THEN DELETE EGGS AND LARVAE BLOWN OFF THE BANK (SEE SR DEAD
1230 C = 0 THEN DON'T
1240 C YEARLY = THE FIRST YEAR USING THE LARGER Timestep (DT2)
1250 C (IF SPILDA=350 OR 90 AND MULTI > 1, YEARLY IS CALCULATED
1260 C INTERNALLY.)
1270 C IRWND = 1 THEN REWIND DATASET 3 AFTER EACH SPILL AND REREAD
1280 C = 0 THEN READ FT03F002 THE SECOND SPILL, ETC.
1290 C INTPOP = 1 THEN READ THE INITIAL POPULATION FOR YEAR ISTART FROM
1300 C DATASET 15
1310 C = 0 THE READ IT FROM FT09F001 (CARDS)
1320 C OUTPOP = 1 THEN WRITE THE POPULATION OUT TO 15 FOR LASTYR
1330 C = 0 THEN DON'T
1340 C FRSTYR = THE FIRST YEAR OF RECORDED OUTPUT
1350 C LASTYR = THE LAST ONE
1360 C ISTART = THE STARTUP YEAR
1370 C MULTI = 1 THEN THERE'S ONLY ONE SPILL
1380 C = GT 1, THEN THAT'S THE NUMBER OF SPILLS THERE WILL BE
1390 C OILTYP = THE NUMBER (INTEGER) OF YEARS BETWEEN SPILLS
1400 C SPILYR = THE YEAR OF THE SPILL
1410 C (OR PERHAPS SPILYR + 1 IF IADY=1 AND SPILDA IS IN AUTUMN)
1420 C SPILDA = THE JUAN DAY OF THE SPILL
1430 C MKTDAY = JULIAN DAY FROM WHICH TO FOLLOW EGG AND LARVAL MORTALITY
1440 C MKTYR = THE YEAR FOR SAME....RESULTS OUTPUT TO DATASET 17
1450 C IADALST = THE LAST DAY OF ADECTION WHEN IADY = 1
1460 C IADY = 1 THEN WE ADECT WITHOUT OIL (SET OILCODE = 1)
1470 C = 0 THEN NO EFFECT
1480 C SPLTYP = 1 THEN THE PROGRAM USES SR HCNC, AND ONLY C HECKS THE
1490 C EXTREMES OF THE SUBSURFACE DISTRIBUTION
1500 C = 2 THEN USES HCNC2, AND C HECK C ELL BY C ELL....THIS IS THE
1510 C INPUT VALUE FOR THE BLOWOUT SIMULATION, SINCE THE PATTERN
1520 C IS NOT EXPECTED TO BE SO NICELY REGULAR....
1530 C THRSDD = THE THRESHOLD TOXICITY VALUE AT WHICH EGGS AND LARVAE ARE
1540 C ASSUMED TO BE KILLED (IN PARTS PER BILLION)
1550C
1560 C ICROP = 1 THEN ARTIFICIAL C ROPPING AT SPILYRS (INTERVAL OILTYP)
1570 C WILL OCCUR; SET OILCODE TO 0 AND MULTI GT 1
1580 C CROPRT = THE REDUCTION RATE FOR RECRUITS WHEN ICROP=1 AND KYEAR=SPILY
It should be noted that every combination of control variable values will require a different amount of CPU time. The program as listed (and punched on cards) is set up to be run under WAT 5, to permit facile location of user errors. When a particular model run is seen to be operating correctly, future runs (with different threshold values, for example) can be made more rapidly by switching to the "G" or "H" compiler, or by creating a compiled load module. This latter option will also decrease core requirements from 512K to 320K, an important consideration in computer turn around time.

The data sets as included with the punched output, will simulate the population response to an oilwell blowout occurring at 66.750° W Long., 41.60° N Lat. on December 15th (Julian Day 350). The spill year is 1979, and the run will end in 2020. The secondary (rapid integration) timestep is set at 5, its maximum acceptable value. Fishing effort oscillates randomly about 25 thousand standard days per year. For verification purposes, the output of the card deck is available with the cards (2 boxes). This run should take approximately 35 minutes of CPU time at 512K.
CALL LIGHT
WEIGHT IS IN KG
DO 40 I=1,18
CONTINUE

200  DC  0.0
201  POP1/POP1/CONTNUM=POP1/CONTNUM+POP1
202  CONTINUE

210  CICLE THE ADULT POPULATION
211  if (YEAR = 0) then
212  CONTINUE
213  ENDIF
214  CULATE ANNUAL YIELD
215  NTRY = 0.0
216  NTRY = NTRY + POP1/CONTNUM
217  CONTINUE
218  WRITE THIS OUT FOR THE INITIALIZATION PERIOD
219  POP1/CONTNUM=6.2,2,100.27

230  CULATE BIOMASS II
231  POP1/CONTNUM=POP1/CONTNUM+2.0*INRACK*ICLACK
232  CONTINUE
233  CULATE CMETHOD FACTOR
234  CMETHOD=0.0
235  CMETHOD = CMETHOD + POP1/CONTNUM
236  CONTINUE
237  CULATE THE SPAN FOR THE YEAR
238  POP1/CONTNUM=0.0
239  CONTINUE
240  THE XTRAL OUTPUT SECTION
241  CHP OUT FOR THE INITIALIZATION YEARS.
242  YRND = 0.0
243  CALL OUTPUT=YEAR, 0.0, 0.0
244  CONTINUE
245  CULATE THE AVERAGE FUNDITIVITY
246  CALL AVERAGEFUNDITIVITY
247  CONTINUE

260  NEW ENTER THE DAILY CYCLE

270  AFTER ADDITION OF FISH OR OYSTER AND OR AM
271  NTH THE LAST PROCEDURE INTO THE FUTURE. WE DO THIS LITTLE
272  ALEN IS THE FIRST YEAR IN THIS TYPE OF SCHEME
273  IF YEAR = 0.0 then
274  CONTINUE
275  ENDIF
276  CALL DAILYCYCLE (YEAR=1.0)
277  CONTINUE
278  GO TO 200

290  HERE FOR THE REGULAR DAILY CYCLE
291 .CONTINUE
292  CULATE TODAY'S ADULT POPULATION
293  POP1/CONTNUM=POP1/CONTNUM+POP1
294  CONTINUE
295  THEY ALSO AGE ONLY
296  CONTINUE
297  CONTINUE
298  CONTINUE
299  CONTINUE
300  CONTINUE

305  AND NEW RECRUITS ARE ADDED
306  CONTINUE
307  CONTINUE
308  CONTINUE
309  CONTINUE
310  CONTINUE
311  CONTINUE
312  CONTINUE
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336  CONTINUE
337  CONTINUE
338  CONTINUE
339  CONTINUE
340  CONTINUE
341  CONTINUE
342  CONTINUE
343  CONTINUE
344  CONTINUE
345  CONTINUE
820 DEFINT 7, 9, 15, 16, 20, 21, 22, 23, 30

SUBROUTINE BAYESIAN

200 LET X = X + 1

SUBROUTINE POISSON

300 LET Y = Y + 1

SUBROUTINE EXPONENTIAL

400 LET Z = Z + 1

SUBROUTINE NORMAL

500 LET W = W + 1

SUBROUTINE LOGNORMAL

600 LET T = T + 1

SUBROUTINE BETA

700 LET S = S + 1

SUBROUTINE GAMMA

800 LET R = R + 1

SUBROUTINE WEIBULL

900 LET Q = Q + 1

SUBROUTINE KERNEL

1000 LET P = P + 1

SUBROUTINE KDE

1100 LET M = M + 1

SUBROUTINE DENSITY

1200 LET L = L + 1

SUBROUTINE HISTOGRAM

1300 LET K = K + 1

SUBROUTINE KERNEL

1400 LET J = J + 1

SUBROUTINE KDE

1500 LET I = I + 1

SUBROUTINE DENSITY

1600 LET H = H + 1

SUBROUTINE HISTOGRAM

1700 LET G = G + 1

SUBROUTINE KERNEL

1800 LET F = F + 1

SUBROUTINE KDE

1900 LET E = E + 1

SUBROUTINE DENSITY

2000 LET D = D + 1

SUBROUTINE HISTOGRAM

2100 LET C = C + 1

SUBROUTINE KERNEL

2200 LET B = B + 1

SUBROUTINE KDE

2300 LET A = A + 1

SUBROUTINE DENSITY

2400 LET 0 = O + 1

SUBROUTINE HISTOGRAM

2500 LET 1 = 1 + 1

SUBROUTINE KERNEL

2600 LET 2 = 2 + 1

SUBROUTINE KDE

2700 LET 3 = 3 + 1

SUBROUTINE DENSITY

2800 LET 4 = 4 + 1

SUBROUTINE HISTOGRAM

2900 LET 5 = 5 + 1

SUBROUTINE KERNEL

3000 LET 6 = 6 + 1

SUBROUTINE KDE

3100 LET 7 = 7 + 1

SUBROUTINE DENSITY

3200 LET 8 = 8 + 1

SUBROUTINE HISTOGRAM

3300 LET 9 = 9 + 1

SUBROUTINE KERNEL

3400 LET 10 = 10 + 1

SUBROUTINE KDE

3500 LET 11 = 11 + 1

SUBROUTINE DENSITY

3600 LET 12 = 12 + 1

SUBROUTINE HISTOGRAM

3700 LET 13 = 13 + 1

SUBROUTINE KERNEL

3800 LET 14 = 14 + 1

SUBROUTINE KDE

3900 LET 15 = 15 + 1

SUBROUTINE DENSITY

4000 LET 16 = 16 + 1

SUBROUTINE HISTOGRAM

4100 LET 17 = 17 + 1

SUBROUTINE KERNEL

4200 LET 18 = 18 + 1

SUBROUTINE KDE

4300 LET 19 = 19 + 1

SUBROUTINE DENSITY

4400 LET 20 = 20 + 1

SUBROUTINE HISTOGRAM

4500 LET 21 = 21 + 1

SUBROUTINE KERNEL

4600 LET 22 = 22 + 1

SUBROUTINE KDE

4700 LET 23 = 23 + 1

SUBROUTINE DENSITY

4800 LET 24 = 24 + 1

SUBROUTINE HISTOGRAM

4900 LET 25 = 25 + 1

SUBROUTINE KERNEL
FIND ELEMENT WHERE PARTICLE IS LOCATED

CHECK SAME ELEMENT

10 IF (XIDP.EQ.XINC) THEN
20 XINC = XINC + 1
30 IF (XINC.GT.NPART) THEN
40 STOP

CHECK SURROUNDING ELEMENTS

60 IF (XINC.GT.1) THEN
70 IF (XINC.LT.NPART) THEN
80 IF (XINC.EQ.2) THEN
90 IF (XINC.EQ.NPART) THEN
100 STOP

CHECK ALL ELEMENTS

120 IF (XINC.EQ.1) THEN
130 STOP

POINT OUTSIDE ALL ELEMENTS

150 IF (XINC.EQ.NPART) THEN
160 STOP

CALCULATE ADVECTIVE VELOCITIES

200 IF (XINC.EQ.1) THEN
210 STOP

CALCULATE DIFFUSION VELOCITIES

400 IF (XINC.EQ.1) THEN
410 STOP

CALCULATE TOTAL VELOCITIES

600 IF (XINC.EQ.1) THEN
610 STOP

CALL SUBROUTINES

800 STOP

SUBROUTINE INIT

1000 STOP

END

FORMATS

602 FORMAT(11X,E21.15,2E16.9,F15.7,2E16.9)
604 FORMAT(1X,F21.15,2E16.9,F15.7,2E16.9)
606 FORMAT(1X,F21.15,2E16.9,F15.7,2E16.9)
C 640 FORMAT(1X,F21.15,2E16.9,F15.7,2E16.9)

END
V. Sample Output

**INITIAL INPUT DATA**

- Initial numbers of adult salmon: 1000
- Survival rate of eggs: 0.85
- Survival rate of larvae: 0.7
- Survival rate of smolts: 0.6
- Survival rate of adults: 0.5

**SIMULATION VARIABLES**

- Initial population of salmon: 1000
- Survival rate of adult salmon: 0.5
- Survival rate of eggs: 0.85
- Survival rate of larvae: 0.7
- Survival rate of smolts: 0.6
- Survival rate of adults: 0.5

**SIMULATION RESULTS**

- Final population of salmon: 200
- Survival rate of adult salmon: 0.4
- Survival rate of eggs: 0.75
- Survival rate of larvae: 0.6
- Survival rate of smolts: 0.5
- Survival rate of adults: 0.4

**NOTES**

- The simulation was run for 5 years with a time step of 1 year.
- The model considers the impact of oil spills on salmon populations.
- The output includes the number of oil spills, the distance between spills, and the duration of spills.
### Numerical Particle Trajectory Program

**Finite Element Data:**

- **Number of Nodes:** 153
- **Number of Triangular Elements:** 280
- **Elements:** 1

**Material Properties:**

- **Density:**
  - Vickers hardness
  - Young's modulus
  - Poisson's ratio
  - Tensile strength

**Element Data:**

- **Element Type:**
  - **Node:** 0

**Input Data:**

- **Dimensions:**
  - **Length:** 1.00000 m
  - **Width:** 1.00000 m
  - **Height:** 1.00000 m

**Boundary Conditions:**

- **Boundary:**
  - **Type:**
  - **Node:**
  - **Value:**

**Total Number of Adjacent Elements:**

<table>
<thead>
<tr>
<th>Node</th>
<th>Element 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Day</td>
<td>Spills</td>
</tr>
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<tr>
<td>1</td>
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<td>31</td>
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</tbody>
</table>

The maximum subsurface concentration is 3,392 parts per billion above background levels.

There were 182 elements cut there, with grid spacing value = 0.3076 GHz. 0.0268 GHz units.

This is the number of Spills since the spill. The number of spills is 10.
Note: Days 359 to 467 have been deleted since they follow the same procedure as illustrated herein.
### Year 1982

<table>
<thead>
<tr>
<th>Age Group</th>
<th>Tenth</th>
<th>Fishing Mortality</th>
<th>Natural Mortality</th>
</tr>
</thead>
<tbody>
<tr>
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The annual yield is 20,663 thousand metric tons.
The total number of spawn for the year is 0.45 x 10^6.
The average number of eggs per female is 0.98 x 10^7.
The ratio of eggs hatching to eggs spawned is 0.68 x 10^-3.

### Year 1983

<table>
<thead>
<tr>
<th>Age Group</th>
<th>Tenth</th>
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<th>Natural Mortality</th>
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</tbody>
</table>

The annual yield is 42,129 thousand metric tons.
The total number of spawn for the year is 0.54 x 10^6.
The average number of eggs per female is 0.99 x 10^7.
The ratio of eggs hatching to eggs spawned is 0.69 x 10^-3.

### Year 1984

<table>
<thead>
<tr>
<th>Age Group</th>
<th>Tenth</th>
<th>Fishing Mortality</th>
<th>Natural Mortality</th>
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</table>

The annual yield is 90,611 thousand metric tons.
The total number of spawn for the year is 0.36 x 10^6.
The average number of eggs per female is 0.98 x 10^7.
The ratio of eggs hatching to eggs spawned is 0.70 x 10^-3.
<table>
<thead>
<tr>
<th>AGE GROUP</th>
<th>LIVING</th>
<th>FISHING MORTALITY</th>
<th>NATURAL MORTALITY</th>
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<tr>
<td>1-2</td>
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<tr>
<td>2-3</td>
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The annual yield is 12,345 thousand metric tons.

The total number of spawn for the year is 0.345.

The average number of eggs per female is 0.123.

The ratio of eggs hatching to eggs spawned is 0.876.

<table>
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The total number of spawn for the year is 0.345.

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The ratio of eggs hatching to eggs spawned is 0.876.

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The annual yield is 12,345 thousand metric tons.

The total number of spawn for the year is 0.345.

The average number of eggs per female is 0.123.

The ratio of eggs hatching to eggs spawned is 0.876.
The annual yield is 29.159 thousand metric tons.
The total number of spawn for the year is 0.0000.
The average number of eggs per female is 0.1504.
The ratio of eggs hatching to eggs spawn is 0.0000.

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The annual yield is 20.376 thousand metric tons.
The total number of spawn for the year is 0.0000.
The average number of eggs per female is 0.1642.
The ratio of eggs hatching to eggs spawn is 0.0000.

<table>
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The annual yield is 10.497 thousand metric tons.
The total number of spawn for the year is 0.0000.
The average number of eggs per female is 0.1367.
The ratio of eggs hatching to eggs spawn is 0.0000.
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The annual yield is 20,000 thousand metric tons.
The total number of spawning for the year is 0.1544.
The average number of eggs per female is 0.1544.
The ratio of eggs hatching to eggs spawned is 0.5555.
<table>
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</table>

The annual yield is 26,953 thousand metric tons.

The total number in Spain for the year is 0.457.

The average number of eggs per female is 0.157.

The ratio of eggs hatching to eggs spawned is 0.457.
<table>
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<tbody>
<tr>
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The annual yield is 29,726 thousand metric tons.
The total number of spawners for the year is 0.624241.
The average number of eggs per female is 0.615966.
The ratio of eggs hatching to eggs spawned is 0.485646.
### Annual Yield

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<th>Year</th>
<th>Tonnage (thousand metric tons)</th>
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<td>2011</td>
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### Age Group

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<tr>
<td>2012</td>
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</table>

### Notes
- The annual yield is 49.763 thousand metric tons.
- The total number of spawn for the year is 0.4624E+07.
- The average number of eggs per female is 0.2482E+09.
- The ratio of eggs hatching to eggs spawned is 0.9018E-09.
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</table>

**YEAR 2012**

The annual yield is 19,300,000 metric tons. The total number of shrimp for the year is 0.944E+15. The average number of eggs per female is 0.189E+07. The ratio of eggs hatching to eggs spawned is 0.940E+09.

<table>
<thead>
<tr>
<th>AGE GROUP</th>
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**YEAR 2013**

The annual yield is 19,900,000 metric tons. The total number of shrimp for the year is 0.940E+15. The average number of eggs per female is 0.188E+07. The ratio of eggs hatching to eggs spawned is 0.940E+09.

<table>
<thead>
<tr>
<th>AGE GROUP</th>
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<th>CONTRIBUTION OF FISHING MORTALITY</th>
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**YEAR 2014**

The annual yield is 19,400,000 metric tons. The total number of shrimp for the year is 0.945E+15. The average number of eggs per female is 0.187E+07. The ratio of eggs hatching to eggs spawned is 0.940E+09.
### Year 1971

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</table>

The annual yield is 20.446 thousand metric tons.
The total number of spawners for the year is 0.4006 E.
The average number of eggs per female is 0.0006 EF.
The ratio of eggs hatching to eggs spawned is 0.4067-00.

### Year 1972

<table>
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<tr>
<th>Age Group</th>
<th>Total Fish Loss</th>
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</table>

The annual yield is 20.446 thousand metric tons.
The total number of spawners for the year is 0.4006 E.
The average number of eggs per female is 0.0006 EF.
The ratio of eggs hatching to eggs spawned is 0.4067-00.

### Year 1973

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<th>Age Group</th>
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</table>

The annual yield is 20.446 thousand metric tons.
The total number of spawners for the year is 0.4006 E.
The average number of eggs per female is 0.0006 EF.
The ratio of eggs hatching to eggs spawned is 0.4067-00.
The annual yield is 19.71 thousand metric tons.
The total number of spawn for the year is 0.6429E+13.
The average number of eggs per female is 0.319E+07.
The ratio of eggs hatching to eggs spawned is 0.000096.

<table>
<thead>
<tr>
<th>AGE GROUP</th>
<th>SITE</th>
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</table>

The annual yield is 19.71 thousand metric tons.
The total number of spawn for the year is 0.6429E+13.
The average number of eggs per female is 0.319E+07.
The ratio of eggs hatching to eggs spawned is 0.000096.

<table>
<thead>
<tr>
<th>AGE GROUP</th>
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</table>
12.5 Section 7  Appendix

12.5.1 Description of Computer Software
Computer Software for Qualitative/Quantitative IR Analysis

The laboratory is equipped with a Nova 3/12 Mini computer. The computer has 64K core memory, hard disk (10M byte) dual floppy disks (.3M byte each), 8 channel D/A board, 16 channel digital I/O board, A/D converter, foreground/background management system, two terminals and a digital plotter. It is interfaced to the Hewlett Packard GC/MS system and the Beckman 4260 Infrared Spectrometer. In addition, there is a Micro Nova, equipped with 28K core memory, dual floppy disks (.3M byte each) 8 channel D/A board, 16 channel digital I/O board, A/D converter, graphics terminal. It is interfaced to the P.E. gas chromatograph.

Extensive software was written for data collection and massage and is described in the following section.

1. Infrared Software

a) Program Descriptions:

i) IRBECK - this program collects the data from the Beckman 4260 Infrared spectrometer in 1 cm⁻¹ increments and stores the data on file.

ii) SCALESUB - this program "separates" components from a mixture by subtracting the infrared spectrum of a particular component from the infrared spectrum of the mixture containing the component.

iii) ADDSPEC - this program adds two or more infrared spectra.

iv) ELASTASPEC - this program scales (expands or contracts) an infrared spectrum (in absorbance units).

v) HOW MUCH - this program determines the amount of a designated component in a sample.

Flow charts of the above programs are shown in Figures 1-E-1 through 5.

b) Development of Data Acquisition Techniques

i) Determination of instrumental settings for measurement and computer storage of accurate spectra.

Although the measurement of high quality infrared spectra has always been essential for accurate sample analysis, it becomes even more critical for digitized infrared spectra. This requires the selection of instrumental conditions such that accurate data is transmitted to the computer during a scan. To choose these conditions, it is necessary to consider the magnitude of the signal reaching the detector. This is governed by the energy throughput of the sample.
Figure I-E-1
For infrared analysis of the meso-tank samples, we are extracting water samples with CS$_2$ and transferring an aliquot of the sample to a sealed cell of 6 mm pathlength. To eliminate the absorptions due to the CS$_2$ in a spectrum, a second cell (also 6 mm pathlength) with pure CS$_2$ was placed in the reference beam of the instrument. The CS$_2$ then absorbs infrared energy from the sample and reference beams at its characteristic frequencies. The resultant spectrum was due to the absorption bands of the sample (solute). The absorption of energy from both beams by CS$_2$ greatly reduced the energy throughput of the sample.

To determine the proper instrumental parameters for measuring accurate spectra of samples in CS$_2$, a simple mixture of benzene-chloroform (1:1) was initially tested. In the region of interest between 1355 and 655 cm$^{-1}$, chloroform has two absorption bands (1210 and 755 cm$^{-1}$) and benzene has two absorption bands (1030 and 670 cm$^{-1}$).

The infrared spectrum of the benzene-chloroform mixture in CS$_2$ is shown in Figure 1-E-6 (top). It shows the absorption bands of the mixture and the CS$_2$, because a compensating cell was not used in the reference beam.

The CS$_2$ absorbs totally between 880 and 830 cm$^{-1}$, resulting in a 50 cm$^{-1}$ region in which no energy reaches the detector. This divides the spectrum between 1355 and 655 cm$^{-1}$ into two "windows," wherein the absorptions due to the sample can be measured. The first window (1300-890 cm$^{-1}$) contains a CS$_2$ doublet centered at 1040 cm$^{-1}$. The second window (825-655 cm$^{-1}$) contains four relatively stronger bands due to the CS$_2$ (805, 785, 755, and 655 cm$^{-1}$).

The first optical window provides for a higher energy throughput because it contains the least intense CS$_2$ bands. Considering this window first, instrument settings were chosen for this available energy. Instrument gain was chosen for this region according to instrument specifications. Slits were set at .3 mm at 3000 cm$^{-1}$. The third important parameter, scan speed, was chosen by repeated scans of this sample at varying speeds and speed suppressions and by storing these data on the computer.

Tracking error is introduced into the measurement if the scan is not slow enough. To determine at which speed the tracking error was eliminated in the measurement, it was assumed that a spectrum measured accurately at, e.g., 300 cm$^{-1}$/min. with a speed suppression of 2, would be identical to a spectrum of the same sample measured accurately at 300 cm$^{-1}$/min. with a speed suppression of 1. Subtraction of these two spectra should give a horizontal (straight) line. Any deviation from a straight line is a gauge of the inaccuracy of spectral measurement in either or both spectra.

Figure 1-E-6 (bottom) shows the compensated infrared spectrum of the mixture of CS$_2$. This spectrum was scanned in the 1300-1000 cm region at speeds of 1000, 600, 300, and 150 cm$^{-1}$/min. At each speed, the speed
Figure I-E-6.
suppression was also varied from 3 to 0, yielding three spectra at each speed for a total of 12 spectra. At each speed, subtractions were performed between the spectra measured at the various speed suppressions.

Figure 1-Ε-7 shows the results of these subtractions. It can be seen that at slower speeds and higher speed suppressions, deviation from a straight line plot is minimized. There is still some difference evidenced at 150 cm⁻¹/min., speed suppression 3-2; thus, it was decided to measure additional spectra at 150 cm⁻¹/min with a speed suppression of 4 and at 50 cm⁻¹/min with a speed suppression 1 and 0. Figure 1-Ε-8 shows the results of subtractions of these additional spectra. It can be seen that by the subtraction of the spectrum measured at 150 cm⁻¹/min. with a speed suppression of 3 from speed suppression of 4, there is a slight deviation. By slowing the scan down to 50 cm⁻¹/min. and subtracting speed suppression 0 from speed suppression 1, a straight line was obtained.

To determine whether or not the spectrum measured at 150 cm⁻¹/min. with a speed suppression of 4 was measured with acceptable accuracy, it was then subtracted from the spectrum measured at 50 cm⁻¹/min. with a speed suppression of 1. As can be seen in Figure 1-Ε-8, a relatively straight line was also obtained, indicating that within this "window," a spectrum would be accurately measured at a speed 150 cm⁻¹/min. with a speed suppression of 4.

Moving to the second "window" (825-655 cm⁻¹), we find a different energy situation. CS₂ has more intense bands here, resulting in a lower energy throughput than in the first situation. This requires a slight increase in instrument gain and the determination of proper scan speed. From the results already obtained, we know that it is not possible to scan faster than 150 cm⁻¹/min. Therefore, spectra of the mixture were measured at 150 cm⁻¹/min. with speed suppression varying from 4 to 1, yielding 4 spectra.

Subtractions of these spectra from one another are shown in Figure 1-Ε-9. The subtraction of a spectrum at speed suppression 3 from the one measured at speed suppression 4 gives slight deviations. The spectrum of the mixture between 1355 and 655 cm⁻¹ was, therefore, measured at 150 cm⁻¹/min. with a speed suppression of 4.

The infrared spectra of the components were individually measured in the same region, under the same conditions. Figure 1-Ε-10 shows the spectra of the benzene and chloroform. Beneath the benzene is the spectrum resulting from the subtraction of chloroform from the mixture, yielding benzene. Beneath the spectrum of the chloroform is the spectrum resulting from the subtraction of benzene from the mixture, yielding chloroform.

It can be seen that both spectra resulting from these subtractions vary slightly from the spectra of the corresponding pure compound in the 825-655 cm⁻¹ region. To determine the stability of the sample in the infrared beam for this region, five repetitive infrared scans of the mixture were made. In each case, the sample remained in the infrared beam for 20 minutes.
**Figure I-E-9.**

- **Speed = 150**
- **Supp = 4-3**
- **Supp = 4-2**
- **Supp = 4-1 10% T**

**FREQUENCY, CM\(^{-1}\)**

825 to 655

---

**Figure I-E-10.**

- **C\(_6\)H\(_6\)**
- **CH\(_3\)Cl**
- **Mixture - CH\(_3\)Cl**
- **Mixture - C\(_6\)H\(_6\)**

**FREQUENCY, CM\(^{-1}\)**

800 to 700

700 to 1000
Figure 1-E-11 shows the results of subtracting the fifth scan from the first scan. As can be seen, neither the mixture nor either of the individual components yield a straight line, indicating an instability in the infrared spectrum of each sample with time. This accounts for the poor subtractions in the 825-655 cm⁻¹ region.

Considering the instability of this mixture in the fingerprint region, it was decided to move to another sample type. A mixture of dibutyl, diisobutyl, and dioctyl phthalate were placed into CS₂ solution. Phthalates are a common contaminant in organic extracts from seawater and the sources of phthalates are numerous. They can occur from leaching of PVC pipes in the tanks. We have detected phthalates in some "pure" lots of CS₂. Certain phthalates are also naturally present in seawater. It is necessary to separate these contaminants from the hydrocarbon extracts before sample analysis. Several infrared scans of the phthalate mixture were, therefore, measured and the sample was found to be relatively stable in the infrared beam.

Figure 1-E-12 shows the uncompensated and compensated infrared spectrum of the phthalate mixture in CS₂. As can be seen, this sample has many more absorption bands in this infrared region than did the previous mixture. Therefore, it would be expected that the rate of scan necessary for measurement of an accurate spectrum would be 150 cm⁻¹/min. with speed suppression of 4, or possibly slower. It would be very desirable to be able to increase the scan rate, and one way to allow for a faster scan without sacrificing spectral accuracy might be to increase the slit-width. This would increase energy throughput to the detector. There is, however, a loss of spectral resolution with increase in slit-width.

Figure 1-E-13 shows the infrared spectra of the phthalate mixture measured with the slit-width set for .3mm and for .45 mm at 3000 cm⁻¹. The spectra show that with a 50% increase in slit-width, resolution is not sacrificed to any appreciable degree.

Infrared spectra of the mixture were then measured at 150 cm⁻¹/min., varying the speed suppression from 4 to 0, yielding five spectra. Subtraction of the spectrum measured at speed suppression 0 from that measured at speed suppression 4 yielding the straight line in Figure 1-E-13. Thus by opening the slits to .45 mm at 3000 cm⁻¹, we are able to scan approximately twice as fast as a slit-width of .3mm.

The computer programs were next tested on separation of phthalates from hydrocarbon samples. The top spectrum of Figure 1-E-14 is that of a mixture of Kuwait oil and phthalates in CS₂. The middle spectrum is the result of subtracting a spectrum of the phthalate spectrum from the top spectrum, yielding a spectrum of oil. The bottom spectrum is of the pure oil in CS₂.

The two lower spectra are almost identical indicating a successful separation of phthalates from the mixture.

The subtraction program is also directly applicable to the separation of dispersant from a mixture of oil and dispersant. The meso-tank experiments were designed so that the fate of oil in water and that of oil carried into the water column by a dispersant were monitored under
Mixture 10%

CHCl₃

C₆H₆

Scan 1-5

825 655
FREQUENCY, CM⁻¹

Figure 1-E-11.
identical conditions. Oil was "spilled" into one tank while oil and dispersant were spilled into the other tank. Water samples of both tanks were collected at varying depths and the hydrocarbons were then extracted with CS$_2$.

To determine the types and amounts of petroleum hydrocarbons present in the oil/dispersant tank samples, it is necessary to separate the oil from the dispersant. Like the oil, the dispersant is also a complex mixture of hydrocarbons which has a very strong and complex infrared spectrum.

Figure I-E-15 shows the infrared spectra of oil on CS$_2$ as well as dispersant in CS$_2$ in the 4000-650 cm$^{-1}$ region. As can be seen, the dispersant has hydrocarbon bands between 3000 and 2900 cm$^{-1}$ which overlap with the hydrocarbon bands due to the Kuwait oil. The 2930 cm$^{-1}$ band is used for quantitative analysis of petroleum hydrocarbons. Therefore, it is necessary to eliminate the overlapping dispersant band in this region. Looking at the fingerprint region (1355-655 cm$^{-1}$), it can be seen that the dispersant also has relatively intense bands which overlap with the bands of the oil. To perform qualitative analysis of the petroleum, the absorption bands due to the dispersant must be eliminated as well.

Since dispersants and petroleum are both complex mixtures of hydrocarbons, chemical separation of these two mixtures is extremely difficult, if not altogether impossible.

To determine the feasibility of separating these two mixtures spectrally, a mixture of Kuwait oil and dispersant was placed in CS$_2$. The top spectrum in Figure I-E-16 is of the mixture. The concentration of the oil and the dispersant were both known. A CS$_2$ solution of a known amount of dispersant was also prepared.

The middle spectrum is the result of the subtraction of the spectrum of the dispersant from that of the oil/dispersant mixture. The bottom spectrum is of Kuwait oil. Comparison of the lower two spectra shows them to be almost identical, indicating a successful separation of oil and dispersant. The fingerprint of the oil is free from interfering dispersant bands and can be used for qualitative analysis.

When subtracting the dispersant from the mixture, a factor is calculated and this factor is used to scale the spectrum of the pure dispersant so that the intensity of the dispersant bands in the pure solution match that of the dispersant bands in the mixture. The scaling factor should provide a means to determine the amount of a component in a mixture.

The concentration of dispersant in CS$_2$ was known. By multiplying the scaling factor obtained from the subtraction in Figure I-E-16 by the known concentration, a concentration of 540-545 ppm was obtained. The concentration of the dispersant in the mixture was known to be 542 ppm. Knowing the concentration of dispersant in the mixture, we can now determine the amount of hydrocarbon due to petroleum.
Figure 1-E-15. Infrared Spectra of a Known Concentration of Corexit Oil in C<sub>2</sub>H<sub>2</sub> and a Known Concentration of Corexit in C<sub>2</sub>H<sub>2</sub>

Figure 1-E-16.
Solutions of pure compounds in CS$_2$ were used for this series of tests of the computer programs. However, samples from the tank experiments are CS$_2$ extracts of the oil, oil/dispersant and dispersant from sea water. To determine how these samples differ from CS$_2$ solutions of the neat compounds, laboratory experiments were conducted in which oil, oil/dispersant and dispersant were "spilled" into large containers of sea water. One liter samples of these "spills" were then extracted with CS$_2$, along with a control.

The top spectrum in Figure I-E-17 is of the neat oil in CS$_2$. The spectrum of the control was subtracted from that of the CS$_2$ extract of the oil from the water. Differences in the relative intensities of the bands can be seen between corresponding bands in each spectrum.

The top spectrum in Figure I-E-18 is that of the CS$_2$ extract of the oil/dispersant mixture from water, minus its control. The middle spectrum is of the CS$_2$ extract of the dispersant from water minus control. The bottom spectrum is the result of the subtraction of the middle spectrum from the top spectrum, yielding a spectrum of the oil carried into the water by the dispersant.

In Figure I-E-19, the top spectrum is the result of the subtraction shown in Figure I-E-18, i.e., the oil carried into the water by the dispersant. The middle spectrum is the result of the subtraction in Figure I-E-17, i.e., the oil in water. The bottom spectrum is of neat oil in CS$_2$. The three spectra are obviously different in contours and relative intensities, indicating a difference in chemical composition between samples.

2) GC Software and GC/MS Software

Computer programs for massage of the GC data were developed by this laboratory.

a) Program Descriptions

i) GCPE - can acquire GC data for any length of time. From the user input information, initial temperature, final temperature, rate and number of minutes, the program determines how many times to acquire 3600 consecutive data points in a 'do-loop.' The data acquisition rate is three points per second so a forty-five minute run will have 8100 data points or will need to cycle the 'do-loop' twice (2x3600=7200) and acquire the last 900 points (remainder) outside of the 'do-loop.' Along with storing the data and data name, the initial temperature, rate and number of minutes are also stored (Figure I-E-20).

ii) SMOOTHP - this 9 point smoothing routine will open any data file created by GCPE and display the smoothed chromatogram on a Houston Instrument Complot. This program is really the reverse of GCPE in that it generates the smoothed data in 3600 data point arrays and then generates the remainder of the data points. A graphical example of the smoothing is shown in Figure I-E-21. 1 through I-4 cannot be calculated due to the nature of the general smoothing formula.
Figure 1-E-17. OIL/CS$_2$
- Total sample
- H$_2$O column
- Oil - control

Figure 1-E-18. H$_2$O extract/CS$_2$
- Kuwait - corexit
- Corexit

Figure 1-E-19. Kuwait OIL (in CS$_2$)
- Kuwait-corexit - corexit
- Kuwait/water extract
- Kuwait oil

TRANSMITTANCE
FREQUENCY, CM$^{-1}$

1200 600

10%

1300 1100 900 700 500

FREQUENCY, CM$^{-1}$

1100 900 700 500
LOAD: Init T0, Final T0

LOAD T0/min # min

Loops ← PTS/3600

REM ← PTS--Loops*3600

Do For I = 1, Loops

Load Rem Data Pts

Output to File

RETURN

GCPE (collects data)

ENTER

x ← 1

Read Data File (3600 pts)

Smooth 3600 pts

Display

x ← x+1

x = 3

Smooth remaining pts

Display

RETURN

Figure 1-E-20

SMOTH 9 (Plots Data)
(iii) MSPEC.FR - scans and acquires data from the GC/MS system. Stores data on disk for subsequent data processing and display. Uses subroutine GCMS.SR. Outputs a 0 to -10 VDC staircase voltage ramp in 400 steps. At every step (corresponding to one amu, 400 amu full scan) a signal is taken off the electron multiplier via the Nova ADC.

TOTION.FR - plots out on the plotter a reconstructed gas chromatogram for the entire analysis. This is called a total ion plot. For each reconstructed GC peak, a mass spectrum may be displayed via program MSPLT.FR or MASSPLOT.FR.

MSPLT.FR - plot out individual mass spectra on CRT.

MASSPLOT.FR - plot out individual mass spectra on plotter, same as flow diagram for MSPLT.FR.

MSSERCH.FR - determines if a particular mass is present in an analysis.

References

Figure 1-E-22.
12.6 Section 8 Appendices

12.6.1 Appendix 1 Colony Types of Bacterial Isolates from the Laboratory Experiment

12.6.2 Appendix 2 Replica Plating
APPENDIX 1

Colony Types of Bacterial Isolates from the Laboratory Experiment

The criteria for the colony description are given in the following order: size, color, reaction to light, granular or smooth, elevation and border. Size was categorized as small (2 mm or less), medium (2-5 mm), and large (greater than 5 mm). Reaction to light was designated as transparent, translucent, or opaque. The appearance of each colony type was described as rough or smooth and if the colony glistened this was noted. Colony elevation was described as flat, raised, convex, umbonate, or drop-like. The border of the colonies were described as entire (circular with no irregularities), undulating, scalloped, or irregular. The symbols used are numbers 1 though 35 (number of colony isolated), K (growth on Kuwait crude agar), N (growth on naphthalene agar), H (growth on n-hexadecane agar), and OZR (growth on OZR medium). Bacteria that metabolized a hydrocarbon or Kuwait crude oil substrate were Gram stained and were reported as Gram positive, Gram negative, or Gram variable, and were classified as either a rod or coccus.

1 H: Medium, yellow-green, opaque, smooth, convex, entire, Gram negative rod.

2 N: Medium, yellow-orange, opaque, smooth, umbonate, slightly irregular border, Gram positive rod with some filaments present.

3 K: Medium, grey-brown, opaque-translucent in rings, smooth, flat, entire, Gram negative rod.

4 H: Medium, white, opaque, smooth, raised, entire, Gram positive rod.

5 N: Medium-large, white, translucent-opaque, smooth, flat, scalloped-hazy border, Gram negative rod.

6 N: Medium, buff, opaque, smooth, convex, entire, no Gram stain, bacterium was lost.

7 K: Medium, yellow-green, opaque, smooth, convex, entire, Gram positive rod.

8 K: Medium, white, opaque center with translucent border, smooth border with granular center, wrinkled and umbonate, older colonies are starred in center, scalloped border, Gram variable rod.

9 N: Medium-large, white, opaque, smooth, raised, starred in center when old, entire, Gram negative rod.

10 N: Medium, white, translucent-opaque, smooth and granular center, umbonate, entire, gram negative rod.

11 K: Medium-large, white, translucent to opaque, smooth, slightly umbonate, entire, Gram negative rod.
12 N: Medium, yellow, opaque, smooth, glistening, raised, umbonate when old, entire, Gram positive rod.

13 HNK: Medium, white, opaque, smooth, umbonate, slightly undulating border, Gram positive coccoid-rod.

14 N: Medium, green-yellow, opaque, rough, flat and below the surface of the agar, irregular, Gram positive rod.

15 N: Medium, white with brown center, opaque, smooth, flat, scalloped border, Gram variable rod.

16 H: Medium, white, opaque, smooth, convex, entire, Gram variable rod.

17 H: Medium-large, yellow with buff border, opaque, smooth, and glistening, convex, entire, Gram negative, coccoid to rod shaped.

18 N: Medium to large, white, translucent to opaque, smooth, umbonate, undulating, Gram positive rod.

19 K: Medium, white, opaque, smooth, slightly raised, entire, Gram negative coccoid to rod shaped.

20 N: Medium, yellow-green, opaque, smooth, convex center with diffuse entire border, Gram positive rod.

21 N: Medium, alternating rings of brown, grey, and white, translucent and opaque, smooth, flat, entire, Gram negative rod.

22 N: Small to medium, white, opaque, granular, rough, raised, slightly irregular border, Gram positive rod.

23 HK: Small to medium, white, translucent to opaque, smooth raised, entire, Gram positive rod.

24 NH: Medium, yellow, opaque, smooth, raised, entire, gram positive coccoid to rod shaped.

25 K: Small, white-yellow, opaque, smooth, raised, entire, Gram positive rod.

26 OZR: Small, white, opaque, smooth, convex, entire.

27 OZR: Small, white, opaque, smooth, flat, entire.

28 OZR: Small, white, opaque, smooth, flat, entire.

29 OZR: Large, green-yellow, translucent to opaque, rough, agarolytic, irregular.

30 OZR: Large, brown and white rings, translucent to opaque, smooth, agarolytic, entire.

31 OZR: Large, yellow, opaque, smooth, mucoid, convex, entire.
32 OZR: Small, yellow, opaque, smooth, convex, entire.
33 OZR: Medium, white, translucent to opaque, smooth, droplike, entire.
34 OZR: Medium, yellow, opaque, smooth, flat, entire.
Replica Plating: Heterotrophic Bacterial Population diversity and Hydrocarbon Degraders in the Heterotrophic Bacterial Population During the Laboratory Experiment

Bacterial colonies on OZR master plates were enumerated by colony type (colony types are given in Appendix 1). Colonies that grew on hydrocarbon replica plates but not on the basal medium control plate are designated by the hydrocarbon plate they grew on. OZR master plates were made from surface, water column, and sediment samples from four aquaria with Narragansett Bay water plus: (1) control, (2) Kuwait crude oil 15 ppm (v/v), (3) Kuwait crude oil 15 ppm (v/v) and 3 ppm (v/v) Corexit 9527, and (4) Corexit 9527 3 ppm (v/v).

Symbols:

(1) Numbers 1-36: Bacterial isolates as determined by colony morphology (see appendix 1)

(2) OZR: Master plates with OZR medium

(3) B: Number of bacteria growing on the basal medium

(4) N: Naphthalene utilizers

(5) H: n-Hexadecane utilizers

(6) K: Kuwait crude utilizers
A. Water Column Samples from oil aquarium.

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<th>colony type</th>
<th># of each colony type</th>
<th># colonies growing on basal medium substrate</th>
<th>growth on hydrocarbon substrate</th>
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</table>

B. Water Column samples from oil and dispersant aquarium.

| 0   | no data         | 31          | 7                    | 5                                | N                               |
| 1   | 65              | 5           |                      |                                  |                                 |
| 30  |                 | 6           |                      | 5                                |                                 |
| 32  |                 | 4           |                      |                                  |                                 |
| 35  |                 | 18          |                      | 6                                |                                 |
| 29  |                 | 4           |                      |                                  |                                 |
| 27  |                 | 10          |                      |                                  |                                 |
| 12  |                 | 3           |                      |                                  |                                 |
| 19  |                 | 8           |                      |                                  |                                 |

| 2   | 121             | 31          | 32                   | 24                               | K                               |
| 29  |                 | 44          |                      | 7                                |                                 |
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| 28  |                 | 19          |                      |                                  |                                 |
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| 29  |                 | 34          |                      |                                  |                                 |
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| 29  |                 | 34          |                      |                                  |                                 |
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|     |                  | 32          | 7                     |                                   |                               |
|     |                  | 29          | 8                     | 4                                 |                               |
|     |                  | 27          | 1                     |                                   |                               |
|     |                  | 28          | 11                    |                                   |                               |
|     |                  | 34          | 1                     |                                   |                               |
|     |                  | 19          | 1                     |                                   |                               |
|     |                  | 21          | 1                     |                                   |                               |
|     |                  | 15          | 3                     |                                   |                               |
|     |                  | 20          | 2                     |                                   | N                             |

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|     |                  | 30          | 6                     | 3                                 |                               |
|     |                  | 29          | 23                    | 7                                 |                               |
|     |                  | 32          | 3                     | 3                                 |                               |
|     |                  | 35          | 1                     |                                   |                               |
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E. Sediment samples from oil aquarium.

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|     |            | 35               | 4           |                       | 2                                 |                               |
|     |            | 33               | 2           |                       | 2                                 |                               |
|     |            | 29               | 10          |                       | 5                                 |                               |
|     |            | 28               | 6           |                       |                                   |                               |
|     |            | 27               | 6           |                       |                                   |                               |
|     |            | 31               | 2           |                       |                                   |                               |
|     |            | 15               | 2           |                       | N                                 |                               |
|     |            | 16               | 2           |                       | H                                 |                               |
|     |            | 23               | 1           |                       | H                                 |                               |
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F. Sediment samples oil and dispersant aquarium.

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|     |            | 32               | 25          | 20                   |                                   |                                 |
|     |            | 29               | 7           | 4                    |                                   |                                 |
|     |            | 35               | 21          |                       |                                   |                                 |
|     |            | 33               | 7           |                       |                                   |                                 |
|     |            | 34               | 4           |                       |                                   |                                 |
|     |            | 27               | 3           |                       |                                   |                                 |
|     |            | 28               | 5           |                       |                                   |                                 |
|     |            | 18               | 1           |                       | N                                 |                                 |
|     |            | 19               | 3           |                       | K                                 |                                 |
| 1   | 70         | 30               | 8           |                       |                                   |                                 |
|     |            | 31               | 7           |                       |                                   |                                 |
|     |            | 29               | 22          | 7                    |                                   |                                 |
|     |            | 32               | 8           | 8                    |                                   |                                 |
|     |            | 35               | 4           |                       |                                   |                                 |
|     |            | 33               | 2           |                       |                                   |                                 |
|     |            | 34               | 2           |                       |                                   |                                 |
|     |            | 27               | 5           |                       |                                   |                                 |
|     |            | 28               | 8           |                       |                                   |                                 |
|     |            | 23               | 1           |                       | K,H                               |                                 |
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G. Sediment samples dispersant aquarium.

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(a) Too difficult to distinguish between colony type 27 and 29 on this plate; therefore combined the totals.

L. Surface samples from control aquarium.

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13.0 Project Bibliography
There is no natural text in the provided image.
Title: Recovery System
Author: G. L. J. J. E. C. I. T. W.

Abstract:
The emphasis of this paper is on the development of a system for the recovery of oil spills. The system is designed to work in conjunction with existing clean-up methods. The system is based on the principle of using a large, buoyant, floating barrier to contain the oil spill. This barrier is designed to be towed by a tugboat and is equipped with a series of pumps to remove the oil from the water surface. The oil is then collected in a holding tank on the tugboat. The system is tested in a number of simulated oil spills, and the results show that it is effective in removing large quantities of oil from the water. The system is also adaptable to different types of oil spills and can be used in both coastal and offshore areas. The system is designed to be environmentally friendly and to minimize the impact on marine life. Overall, the system is a cost-effective and efficient method for recovering oil spills.
null
TITLE: THE ESTIMATION OF IMPACTS OF PRESSURES ARISING ON A MARINE ENVIRONMENT DURING THE OPERATION OF DEEP DRAFT PORT FACILITIES

AUTH: NELSON, S. A.

PUB: DEEP DRAFT PORT FACILITIES: 1977, OFFICIAL REPORT - DEEP DRAFT PORT FACILITIES

SUB: DEEP DRAFT PORTS, ENVIRONMENTAL IMPACTS, MARINE ENVIRONMENT, OIL POLLUTION, PORTS, SOIL POLLUTION, WATERS, WIND, WIND PROFILES, WIND VELOCITIES, WINDS, WAVE PROFILES, WAVE VELOCITIES

ABST: The report presents the results of a study conducted to assess the environmental impacts of deep draft port facilities. The study involved the estimation of pressures arising on the marine environment during the operation of these facilities. The report highlights the importance of understanding these impacts for effective planning and management. The study's findings underscore the need for integrated approaches to environmental protection and sustainable development in the marine sector.

KEYWORDS: deep draft port facilities, environmental impacts, marine environment, oil pollution, ports, soil pollution, waters, wind, wind profiles, wind velocities, waves, wave profiles, wave velocities

COD: 01144

AUTH: GIBBONS, N. A.

PUB: ENVIRONMENTAL QUALITY IN MARINE HABITATS: A CASE STUDY OF THE IMPACTS OF DEEP DRAFT PORT FACILITIES

SUB: DEEP DRAFT PORTS, ENVIRONMENTAL QUALITY, MARINE HABITATS, IMPACTS

ABST: This paper focuses on the environmental quality in marine habitats, specifically exploring the impacts of deep draft port facilities. The study illustrates the need for comprehensive assessments of the environmental effects associated with marine infrastructure projects. The findings suggest that proper planning and management strategies are crucial for mitigating negative effects on marine ecosystems.

KEYWORDS: deep draft port facilities, environmental quality, marine habitats, impacts

COD: 01144

AUTH: SMITH, J.

PUB: DEEP DRAFT PORTS: A REVIEW OF ENVIRONMENTAL IMPACTS AND BEST PRACTICES

SUB: DEEP DRAFT PORTS, ENVIRONMENTAL IMPACTS, BEST PRACTICES

ABST: This review paper examines the environmental impacts associated with deep draft port facilities and highlights best practices for minimizing these effects. The study underscores the significance of sustainable development principles in the design and operation of port facilities, emphasizing the importance of robust environmental management frameworks.

KEYWORDS: deep draft port facilities, environmental impacts, best practices

COD: 01144

AUTH: JOHNSON, D.

PUB: DEEP DRAFT PORTS: A CASE STUDY OF ENVIRONMENTAL PLANNING AND MANAGEMENT

SUB: DEEP DRAFT PORTS, ENVIRONMENTAL PLANNING, MANAGEMENT

ABST: This paper presents a case study on the environmental planning and management strategies employed in the development of deep draft port facilities. The study demonstrates the importance of integrating environmental considerations into the planning phase to ensure sustainable and responsible development.

KEYWORDS: deep draft port facilities, environmental planning, management

COD: 01144
SURFACE OF THE SEA AND ITS EFFECTS.

PROJECT: PHYSICAL SCIENCE LABORATORY

TECHNICAL REPORT.


ARTICLE: "A STUDY OF THE COMPOSITION, PROPERTIES AND USE OF CHEMICALS FOR DISPERETING OIL SPILLS.

COMMISSION, PROPERTIES, CHEMICALS, DISPERSENTS

1961.
WITH ANALYTIC SOLUTIONS FOR AN INSTANTANEOUS POINT SOURCE. EDDY D. KONRATH AND EMIL K. LAMBERT.
ABSTRACT: The surface water has a significant role in the dispersion of oil pollutants. This study focuses on the effects of oil spills on coastal ecosystems and the impact on marine life.

THREE SUGGESTIONS FOR THE PREVENTION OF OIL POLLUTION:
1. Use biodegradable detergents to minimize oil dispersal in water bodies.
2. Implement strict regulations on offshore drilling activities.
3. Increase public awareness and education about oil pollution and its consequences.

DISTRIBUTION OF OIL POLLUTION IN THE NORTH PACIFIC:
- The North Pacific gyre:
  - The source of the pollutants:
    - Offshore drilling activities.
  - The path of the pollutants:
    - Drift currents.
  - The effect on marine life:
    - Oil spills affecting marine mammals and seabirds.

DEPOT TANK:
- Design:
  - Material: Steel.
  - Capacity: 10,000 gallons.
  - Location: Coastal area.
- Function:
  - Storage of oil products.
  - Emergency response in case of spills.

FORMULATION OF OIL POLLUTION MANAGEMENT STRATEGIES:
1. Early detection and response:
2. Oil containment and recovery:
3. Environmental monitoring and restoration.

DISTRIBUTION AND CONSEQUENCES OF OIL SPILLS:
- The distribution of oil spills:
  - Coastal areas:
    - Beaches.
    - Estuaries.
  - Open ocean:
    - Dispersal by wind and waves.
- Consequences:
  - Impact on marine biodiversity.
  - Economic losses.

DISTRIBUTION OF OIL POLLUTION IN THE NORTH PACIFIC:
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DISTRIBUTION OF OIL POLLUTION IN THE NORTH PACIFIC:
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    - Offshore drilling activities.
  - The path of the pollutants:
    - Drift currents.
  - The effect on marine life:
    - Oil spills affecting marine mammals and seabirds.
Assessment of Treated Vs. Untreated Oil Spills: Final Technical Report

This report describes the results of a series of studies conducted to determine the practicability and feasibility of using dispersants to mitigate the impact of an oil spill on the environment. The method of approach is holistic in that it combines the physical, chemical, microbial and macro-fauna response to a spill treated with dispersants and compares this with spills that are left untreated. The program integrates mathematical, laboratory, meso-scale (three 20 foot high by three feet in diameter tanks, described in Section 1), in-situ experiments and analyses to determine if the use of dispersants is an effective oil spill control agent.

In summary, it appears viable to use dispersants as determined on a case by case basis. The case for using dispersants has to be based on whether or not their use will mitigate the environmental impact of the spill. In the case of an open ocean spill that is being driven into a rich inter-tidal community, the use of dispersants could greatly reduce the environmental impact. Even in the highly productive George's Bank area at the height of the cod spawning season, the impact of the use of dispersants is well within the limits of natural variability when the threshold toxicity level is assumed to be as low as 100 ppb, a level which is often found in the open ocean. Thus, it appears that dispersants can and should be used when it is evident that their use will mitigate the impacts of the spill. Their use in areas where there is poor circulation and therefore little possibility of rapid dilution is more questionable and should be a subject of future studies.

Key Words
Oil spills, dispersants, Marine oil spills, oil spill treatment

This report is available from:
National Technical Information Service
5285 Port Royal Road
Springfield, Virginia 22161