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THE FATE OF OIL AND DISPERSANT MIXTURES
IN FRESHWATER ECOSYSTEMS

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ABSTRACT

A series of man-made ponds, with a fine-gravel sediment and containing meso-trophic water, were used to compare the fate, distribution and composition of oil-dispersant mixtures with oiled and controlled conditions, using Norman Wells crude oil and Corexit 9527 as the dispersant. Surface, water column, sediment, liner and attached biota were sampled systematically for a year. The water column contained only a small amount of the oil during most of the experimental period as dispersed oil quickly surfaced and eventually sank to the sediment. The chemistry and composition of the slicks were examined; thinner slicks had a greater carbonyl content and more dispersant relative to thicker slicks. Final distribution analysis revealed that more oil was unaccounted for in the oil-dispersant ponds than in the oil-treated pond. There was no evidence to suggest that the dispersant altered the composition of the oil during the experiment, and the oil in all ponds underwent changes that were similarly independent of treatment.

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INTRODUCTION

Dispersants are viewed as an adjunct to the successful control of oil spills, the primary control being dependent on mechanical methods. Under certain conditions, such as inability to deploy mechanical methods or the need to protect nesting grounds, dispersant use may be contemplated. The use of dispersants in such situations is contingent upon their passing certain laboratory tests related to their effectiveness and toxicity. The tests rank these substances both in effectiveness and toxicity, and form the basis of an acceptability list (1). What the testing does not provide is information on long-term effectiveness as well as on the fate and effect of the oil-dispersant mixture.

The present study was instituted to answer the question of the fate and ecological effect of an oil-dispersant mixture in a selected ecosystem over an extended period of time. Also, the effectiveness of the dispersant under the test conditions and the ability of the ecosystem to recover, if adversely affected, were investigated.

Large outdoor ponds with their indigenous biota were utilized, and results from ponds treated with an oil-dispersant mixture were compared to those from oil-treated and control ponds. The chemical and biological components of the system which were monitored were oil and dispersant, water chemistry (e.g., nutrients, D.O., A.T.P.), phytoplankton, periphyton, fungi, bacteria, protozoa, zooplankton, and zoobenthos. This report deals exclusively with the composition, distribution and fate of the oil and oil-dispersant mixtures.

METHODS

The site of the ponds was at the University of Toronto's Institute for Environmental Studies Field Station at Baie du Dore, near Douglas Point Nuclear Power Plant on Lake Huron (Fig. 1). Four large I-beams divided a rectangular pit 22.5 m X 9 m by 2 m deep into five approximately equal ponds. These ponds were lined with four layers of 6-mil black polyethylene sheeting, strung between the beams. Sufficient liner was used in each pond to drop vertically from the beams to the bottom of the respective ponds and to cover the bottom so that each pond was a closed system. Details of the lining attachment to the beams is shown in Fig. 2. Water from nearby Lake Huron was pumped onto the five ponds to a depth of 1.7 m and the polyethylene at the edges was anchored with gravel. Sufficient fine gravel-silt mix was then added to the ponds to provide a 5-cm sediment layer. A catwalk was constructed down the centre of the ponds along the east-west axis to facilitate sampling. One end pond was designated as a reserve.

The ponds were allowed to stabilize initially for several months to allow the biological systems to equilibrate before treatment. The spills were carried out on July 5, 1978, in the afternoon.

The oil used was Norman Wells crude oil which has been utilized for several other studies (2,3,4). In the oil-treated pond, six liters of oil were poured onto the water surface from a height of one meter.

The dispersant used was Corexit 9527. One liter of this was added to six liters of oil, hand-stirred with 13 liters of pond water to produce a dark brown oil-in-water emulsion and poured onto the surface of two ponds. As the interior ponds contained approximately 41×10^3 liters of water, the above quantities would produce nominal concentrations of about 100 ppm oil and 20 ppm dispersant in the water phase assuming complete mixing. The exterior pond contained significantly more water and the effective concentration was 70 ppm oil and 15 ppm of dispersant.

Samples of sub-surface water were withdrawn at 0, 1, 4, 24, 48 hours, one week, two weeks, and fortnightly thereafter until ice formation over the pond, six months after treatment. During and after the period of ice-cover, samples were withdrawn once a month. Surface slicks were taken at the same sampling dates for the first 100 days. Sediment samples were removed at monthly intervals after treatment. Attached algae were occasionally sampled for oil and dispersant concentrations.

Surface slicks, whether in the form of thick oil (streamers or lenses) or thin films (sheens), were sampled by placing a 10 cm x 10 cm by 0.4 mm blotting paper (general office use) directly on the sampling area and removing it immediately after the top had become completely wetted. The paper was then placed in a jar and returned to the laboratory for extraction by CCl_4 and subsequent analysis by IR (Appendix I) and UV spectroscopy (Appendix II), as

well as column chromatography. Surface concentrations of oil or oil and dispersant were determined by the IR method and were expressed as slick thickness. As the area was known, the thickness was determined by using a density of 0.9 for the oil.

Water Column Samples containing oil or oil and dispersant were removed from the desired depth of the water column by using a clear 2 liter plexiglass Van Dorn bottle. During the first weeks after treatment, two samples were withdrawn to determine any differences in the distribution between the top and bottom water layers. Generally only one sample was required and this was taken at mid-depth. One liter of the contents was placed in a 2-liter separatory funnel to which 300g NaCl was added. Ten ml CCl_4 was added and the mixture shaken for one minute and allowed to separate. The CCl_4 layer was centrifuged to remove any water droplets and then returned to the laboratory in vials. IR analysis was used to determine the oil and dispersant concentrations as shown in Appendix I. Other water column samples were filtered on site and returned cold for analysis in the Water Quality (Ontario) Laboratories.

"Beached" oil material on the liner was generally removed by gently scraping the liner and transferring the material to a small storage bottle. The material was analyzed in the laboratory after CCl_4 extraction. On the day of the final sampling, vertical strips of liner were removed from all sides of each pond. These strips were further divided, extracted and analyzed.

Oil in the sediment was sampled at selected locations by using a 48 oz empty juice can fastened to the end of a 3-meter pole.

Care had to be taken not to destroy the benthic community so replicate samples were not taken until the end of the study period. The sediment samples were placed in 1-liter glass jars with 1 cm excess water over the solid material. Within 24 hours, each sample was dosed with 100 ml of CCl_4 and extracted on a reciprocal shaker for one hour. The CCl_4 phase was separated, centrifuged, and analyzed. The sediment was air dried and then oven dried at 100°C to determine dry weight. The details of this method are reported in Appendix I. On July 24, 1979 (approximately one year) when the biological sampling was completed, a more thorough sampling of the sediment was initiated. On that date, samples were removed on a line parallel to the catwalk at 0.6 meter intervals. One month later, after reviewing the results of the analyses, additional samples were removed. These sediment sampling positions are shown in Figure 3.

Oil in Attached Biota was determined occasionally when there was a thick cover of periphyton over the sediment and liner. Samples were removed noting the approximate area of cover, shipped back to the laboratory unpreserved, and treated as the above sediment samples.

IR Analysis was performed on a Perkin-Elmer 457 IR recording spectrophotometer using NaCl cells. The absorbance at 1050 cm^{-1} was used to measure the dispersant concentration and the dispersant contribution to the absorbance at 2920 cm^{-1} was calculated. From the corrected absorbance at 2920 cm^{-1} , the concentration of the oil could be determined. The precision of this method is shown in Appendix I. Since crude oil does not contain any carbonyl groups,

the carbonyl absorbance at 1720 cm^{-1} was used as a qualitative indication of oil oxidation. These values were normalized by dividing by the methylene absorbance at 1455 cm^{-1} .

UV Analyses were made on a Unicam SP 1800 Ultraviolet recording spectrophotometer using SiO_2 cells. The solvent was CCl_4 and the absorbance at 280 nm was measured to determine the degree of aromaticity, expressed as the absorptivity (5). The selection of this method resulted from preliminary studies on benzene, naphthalene and anthracene solutions shown in Appendix III.

Chromatography

(a) Column chromatography was performed by filling a 20 cm x 0.85 cm i.d. chromatographic column with dry silica gel. The sample was introduced at the top of the column by dissolving 0.1 to 0.5 g of sample in 10 ml of hexane and initiating the elutions with hexane. 30 ml of this solvent was passed through the column, followed by 30 ml of benzene with all liquid being retained.

The silica gel was removed from the column and the residue removed by Soxhlet extraction with benzene. The extracts were air dried, taken up in CCl_4 and analyzed by IR spectroscopy for hydrocarbon concentration.

(b) GLC operating conditions are shown in Table 1.

Water Chemistry Parameters of dissolved organic carbon and dissolved reactive silica were determined using standard methods (6).

RESULTS AND OBSERVATIONS

The volumes of water in the ponds, calculated from measurements of the pond geometry, are shown in Fig. 4 plotted against time. This figure shows similar fluctuations for all ponds reflecting dry and wet periods.

A. Distribution and Concentrations

1. Oil Treated Pond (Pond 4)

(a) Surface. At the time of the spill, the oil spread from the point of addition and surface oil of varying thickness covered the entire pond surface within an hour. Most of the oil was then swept by the wind into a corner of the pond, leaving surface sheens and streamers over the rest of the pond surface. After four hours, the oil, which had impacted along the liner, radiated streamers of oil which covered an estimated 10% of the water surface. The oil continued to be moved about the pond by subsequent wind action but some oil was found to remain adhering to the liner. As shown in Table 2, which lists the thickness of the slicks and sheens, only small quantities of thick oil and streamers were noticeable on the water surface after fourteen days. A more thorough description of the slicks will be given in Section B.

(b) Water Column. Depicted in Fig. 5 are the concentrations of the oil in the water column plotted as a function of time. The concentration was highest one hour after the treatment, and decreased rapidly to 1 ppm within one day. Concentrations about this level were measured during the remainder of the experiment. As shown in Fig. 4, the water level decreased for several weeks after treatment as there was no significant rainfall during this period. This decrease did not noticeably affect the concentration in the water column but stranded small amounts of oil at various levels on the liner. The late-summer rains raised the water levels significantly and left some of the oil on the liner below the water surface. Cyanophyceae were observed growing on the liner in discrete bands where the oil was stranded.

(c) Sediment. During the course of the experiment, a limited number of samples were taken of the sediment to avoid excessive disturbance of the benthic biota. Samples that were taken were used for qualitative studies on oil composition given in Section B. Although oil was found in all samples, the variation of the oil distribution would not permit quantitative estimates. This variation is shown in Table 3 which lists the oil and dispersant concentrations recovered from the sediment samples for all ponds during the experiment. The values from the treated ponds were usually greater by an order of magnitude than the background hydrocarbon levels of the control pond.

The winter samples, collected from under an ice-cover, contained very little oil, probably as a result of the same positions being used at each sampling in each pond. At the final sampling dates, July and August 1979, a sufficient number of samples was taken to provide quantitative data on the amount and distribution of the oil. "Shallow" and deep" sediment samples exhibited no enrichment of oil (or dispersant) in either surface or deeper layers of sediment. Fig. 6 shows the distribution of oil on the north-south axis of the ponds and Fig. 7, on the east-west axis. Higher oil concentrations were found on the east side of the pond near the catwalk, corresponding to the heavier concentrations of surface oil observed earlier in the experiment. The sediment surface did not show any visible oiliness or particulate oil, even in these areas. The total amount of oil in the sediment was calculated by considering 0.3m strips along the north-south axis and then summing for the pond. This calculation showed that 53.8% of the oil initially added to the pond was still in the sediment. Visual and microscopic examination of the sediment did not reveal the presence of oil (or dispersant) droplets. Occasional slight disturbances of the sediment released small quantities of oil into rainbow-coloured or colourless sheens which, in total, were calculated as being less than 1% of the oil in the sediment.

(3) Liner and Attached Biota. On the last sampling date, strips of liner were removed and analyzed and the resulting liner-surface oil concentrations are shown in Table 4. The biotic material attached to the liner in this pond was insufficient for reliable sampling.

(e) Evaporation. The method used for this study was a simulated g.l.c. distillation technique previously reported (7). Within the first few days, analyses by this method indicated that about 18% of the oil had evaporated. Chromatograms of the oil recovered from the sediment showed that a total of 21% of it had evaporated.

2. Oil-Dispersant Ponds (Ponds 1 and 3)

(a) Surface. The dark brown oil-in-water emulsion introduced at the centre of ponds spread almost uniformly in all directions, with the entire surface layer of water being coloured a light brown within 10 minutes. During the first few hours, some of the oil came out of the emulsified state and formed long ribbons and small lenses (10 cm diameter) which impacted on the liners by wind action. The oil at this time was not as dark or cohesive as found in the oil treated pond. The water not covered by ribbons or lenses appeared milky.

The measured thicknesses of ribbons and sheens are given in Table 2. These values indicate that thick oil, generally observed as ribbons, was present from July to September; surface sheens persisted into October, and no measurable amount of surface oil was found after that time. Dispersant was found in conjunction with the oil in all samples.

(b) Water Column. With the surfacing of the oil during the first hour after treatment, the top 5 to 10 cm of the water was left milky. This milkiness extended half-way down the water column (0.8 m) within 24 hours and appeared uniformly distributed throughout the water column within the first week. Only a few water samples were collected at this time to avoid excessive turbulence in the water. No zooplankters visible to the eye were found in the milky layer at the 24-hour sample collection, but some were observed in the clear water below.

Concentrations of the oil and dispersant are shown in Fig. 8. As anticipated, because of the larger volume of pond 1, the values for this pond are slightly lower than those from pond 3, the interior pond. There is an initial increase in the oil and dispersant concentration after the treatment but this slowly decreases to day 111 where the oil concentrations are below 1 ppm in both ponds as are dispersant concentrations. The ratio of oil:dispersant in the water column is generally lower than the 5:1 value initially added.

Fig. 9 shows results of the dissolved organic carbon measurements. For the oil-dispersant ponds, these values are much higher than the hydrocarbon values obtained from the IR technique (Fig. 8). It is noteworthy that after day 28, both parameters follow the same trends. After the initial decrease in concentrations from day 28 to day 138, there is a leveling-off of values followed by another decrease starting on day 224. The leveling-off was probably caused by ice formation condensing the organics in the water column; the subsequent decrease could have arisen by dilution by the melting ice.

From the time of treatment until freeze-up, the water turbidity in both ponds was sufficient to produce an estimated Secchi depth of less than .7m; the bottoms of the ponds could not be seen. The turbidity was significantly reduced after the thaw of 1979 (day 280) although dispersant concentrations were not too different from those found prior to freeze-up.

Twenty water quality parameters were monitored regularly in the ponds. Some have been previously reported (8) and others will be incorporated in later reports. The results from the dissolved reactive silica (DRS) measurements showed the greatest variation with treatment of the non-nutrient parameters. Shortly after treatment, the DRS concentrations increased in both oil-dispersant ponds, reaching a maximum about day 75 as shown in Fig. 10. By freeze-up, the values had decreased and after the spring thaw, the concentrations were similar and low in all ponds. Additional laboratory studies, detailed in Appendix V were carried out to investigate the possible release of silica from the sediment by the dispersant. The results indicated that no such release occurred.

(c) Sediment. Oil:dispersant ratios calculated from extraction of sediment samples taken during the experiment are shown in Fig. 11. Large variations between successive samples from the same pond may be caused by the heterogeneity in the sediment. However, the trend of the results indicate that during the ice-free periods, the oil-dispersant ratios were greater than the initially added value of 5:1.

As in the oil treated pond, a more complete sampling of the sediment was undertaken at the conclusion of the experiment and the results are shown in Figs. 6 and 7. In both oil-dispersant ponds, the highest concentrations of oil and dispersant were found near the liners. The west slope of pond 1 was extensively sampled to investigate the possibility that oil and dispersant accumulated in that area during the water level decrease in the summer of 1978. No enhanced concentrations of oil or dispersant were found in this part of the sediment.

(d) Liner and Attached Biota. Ponds 1 and 3 appeared to have a continuous cover of attached filamentous material on the liner and over the sediment within a month after the treatment. After May, 1979, this material was sampled and analyzed for oil and dispersant. These results are listed in Table 5, along with those from the oil treated ponds. From another part of this study, the amount of biotic material on the liner and over the bottom were greater than was found in the oil treated pond (Appendix V). Listed in Table 4 are the values of the oil and dispersant recovered from the liner.

(e) Evaporation. The degree of evaporation of the oil in these two ponds was approximately 20%.

B. Chemical Composition and Physical Measurements of the Oil

With the sample size employed and the number of components in each sample, it was not possible to distinguish any variation in the oil composition between the samples of the oil-treated and oil-dispersant ponds sampled on the same day.

(a) Surface. Fig. 12 depicts the persistence of surface films, where the dashed line is an idealized representation of the diminishing areal extent of thin films in the 0.01 to 10 μ range. Films in this thickness range were observed throughout the period but became intermittent and generally smaller as time increased. As indicated in this figure, slicks on the oil-dispersant ponds disappeared earlier than in the oil-treated pond. This may have resulted from the thick oil on the liner of pond 4 being taken back onto the water surface, whereas there were less such deposits observed on the liners of ponds 1 and 3. The description of slicks shown in Fig. 12 is elaborated further in Fig. 13, which shows the appearance of various slicks as a function of film thickness. Our observed colour-to-thickness relationship agrees with reported values (9) which are shown on the lower part of Fig. 13.

Fig. 14 is a plot of oil-dispersant ratios versus the thickness of the slick. From the relationship shown on the plot, the thicker the slick is, the more oil or less dispersant in the slick relative to the amount added and the thicker slicks contain predominantly oil released from the emulsified state.

The next figure, Fig. 15, illustrates that oxidation occurs on the surface films to a considerable degree, even after short exposure times. From this figure, it is evident that the thinner the film, the greater the carbonyl content.

Finally, by utilizing the absorbance at 280 nm as an indicator of aromaticity, Fig. 16 illustrates the changes that do occur in the thicker surface films on a short-term basis. Surface oil from all treated ponds exhibited an increase in aromaticity during the first twenty-four hours, then a decrease, but maintained a value greater than that found in the original oil. The shape of this graph can be explained by considering the initial increase as arising from a concentrating effect on the benzenoid structures by the evaporation of the front ends of the oil; the subsequent evaporation of the simpler aromatics decreases the total aromaticity but leaves the higher aromatics which would absorb more strongly.

(b) Sediment. Unlike the surface slick samples which were available for only a few months after treatment, results from the sediment samples encompass a much longer period of time. Spectroscopic measurements of the sediment extracts show an interesting pattern. Fig. 17, which illustrates the specific absorbances at 280 nm, had a maximum at day 125, and after this the values level off. IR measurements of the carbonyl group from the sediment samples showed no over-all trends.

The sediment extracts were subjected to column chromatography when the sample size permitted. In this method, the material was separated into three fractions (hexane eluate, benzene eluate and column residue) of increasing polarity. Typical results obtained by this method are shown in Fig. 18. They indicate that aged or residual oils contain increasing amounts of polar material at the expense of the less polar components.

Fig. 19 illustrates the results obtained from sediment extracts treated by this technique. They show a net decrease in the amount of oil in the hexane eluate and an increase in the residue between the initial and final samples. The data derived from the interim samples follow a complex pattern that is essentially similar for each treated pond.

DISCUSSION

Prior to commenting on the distribution and composition of the oil in the ponds, the reliability and the limitations of the analytical methods must be demonstrated. The calibration of the methods has already been referred to and are found in Appendix

I. The standard errors in the IR analysis are within the 2 to 5% range reported in the literature (10,11). The extraction efficiency was found to be greater than 98% from water and better than 96% from the sediment samples. The uptake of surface films by blotting paper and the subsequent extraction was also 96% efficient. In short, we feel that the oil and dispersant concentration measurements are reliable.

Special efforts were made to ensure the dispersant's effectiveness in the experimental system. The oil:dispersant ratio chosen, 5:1, was lower than the generally recommended range (about 10:1). Previous lab studies indicated that lower ratios would be better for freshwater use. The oil-dispersant mix was stirred into a small amount of pond water to produce a fine oil-in-water emulsion, and was then poured into the ponds in that form, so that additional turbulence in the ponds was not needed for the initial oil dispersion. In spite of this precaution, our observations and measurements indicated a limited effectiveness of the dispersant even at the favourable ratio used. Visual observation showed that considerable amounts of oil were released from the dispersed state in the water column onto the surface within one hour of the treatment. The concurrent milky-white appearance of the water also suggested that only a small

fraction of the oil remained in the water. Analyses of water samples confirmed these observations, and showed that the highest oil concentrations found in the water, shortly after the treatment, were less than 20% of the design concentration. During the first weeks of the experiment, the slicks in the oil-dispersant ponds appeared to be as extensive as those in the undispersed oil pond. Another illustration of the oil release from the dispersed state is given in Table 6 which shows low oil:dispersant ratios in the water column, but high values in surface slicks and in sediments.

The turbidity of the water column in the oil-dispersant ponds, which persisted until freeze-up, could not be ascribed to the presence of the dispersant alone. The dispersant concentrations were low during most of that period and were similar to those measured in the following spring when there was no turbidity. This behaviour could not be related to phytoplankton growth as the pond did not exhibit corresponding trends in populations or biomass (8).

A possible clue to this turbidity phenomenon may be the observation of high "dissolved reactive silica" concentrations in the water phase of the turbid oil-dispersant ponds. The dispersant in these ponds may have produced stable suspensions of either sediment material or airborne particulates. The first of these possibilities had to be discounted after the dispersant failed to re-suspend any pond sediment material in a laboratory study. (Appendix V) The presence of airborne particulates (12), kept in suspension by the dispersant, remains a possibility.

The results of the final sampling and analysis of the pond sediments allow some comparisons between the undispersed and dispersed

oil ponds. The oil distribution patterns in the sediment near the liners suggest that a significant portion of the oil, in all three treated ponds, surfaced first, and sank later to the bottom near the liners, where surface slicks had been commonly observed. This possible pathway of the oil was apparently unaffected by the presence of the dispersant. Another interesting finding is that the evaporation losses of the oil in the final samples were remarkably similar in all ponds. This would again indicate that the "history" of the oil, such as its physical state, location, or its residence time on the water surface, was similar for both the dispersed and undispersed oil.

The final material balances for the oil and the dispersant, given in Figures 20 and 21, show that at the conclusion of the experiment most of the oil and the dispersant still present were found in the sediment. The dense growth of periphyton in the oil-dispersant ponds, the liners, and the water column contained only minor quantities of oil or dispersant. The results also show that a significant portion of the oil was lost from all ponds, exclusive of the evaporative losses, and that a fraction of the dispersant was also missing from the oil-dispersant ponds. Nothing is known of the relative amounts of losses due to chemical, photochemical, or biological processes, nor indeed whether all such processes were important. It is noteworthy, however, that the sum of these losses was significantly higher in the oil-dispersant ponds than in the oil-treated pond. This observation should be emphasized considering that one of the classical arguments

for the use of oil spill dispersants is that they may increase the biodegradation rates of spilled oil (13). To our knowledge, the extent of such degradation processes has not been reported in ecosystems as large or as diverse as those used in this study.

Evaluating data on oil composition is difficult as oil is a complex mixture of several hydrocarbon classes, and its composition will change during environmental exposure because of several possible processes. Such processes that will produce changes may occur simultaneously or consecutively and include evaporation, photochemical reactions, biological degradation processes and organic-sediment interactions. The presence of carbonyl compounds in the surface slicks within the first few hours of exposure is an indication of the potency of photochemical reactions in thin organic layers. The maximum and then subsequent leveling off of the carbonyl absorption in the oil may be caused both by a decrease of oxidative activity and by effective processes for the removal of carbonyls. The latter may include reactions with other oil components or with natural organics, irreversible adsorption on the sediment, or further oxidation. A better understanding of such behaviour may require an exhaustive identification of all possible degradation products, either in pond studies such as these, or in studies in smaller and simpler systems, or both.

The "aromaticity" of the oil exhibited an initial maximum followed by a leveling off period. Reports of bacterial degradation of oil generally show the removal of aliphatic components (14, 15). If this was the only, or the most significant process for oil

degradation in our system, then we would expect a continuous increase of relative aromaticity as the more readily degradable aliphatics are removed. Since this was not observed, the changes in aromaticity must be taken as an indication that other pathways exist for oil degradation.

The liquid chromatographic fractionation of the oil gave the most striking indication of the complex behaviour of the oil. The trends in the composition (Fig. 19) show the predominance of different processes or pathways at different times during the experiment. We must note also that the main trends were similar in all three ponds, suggesting that the dispersant did not introduce significantly different pathways of oil degradation.

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TABLE 1
Gas Chromatographic Conditions

Instrument: Hewlett-Packard 5750 equipped with dual column

Column: 1.8 m x 0.31 cm, 5% OV-1, A.W.M.C.S. 80-100 mesh

Detector: FID. Injector Temperature: 280°C. Detector Temperature: 320°C

Initial Temperature: 80°C for 0.0 min.

Final Temperature: 260°C for 45 min. Programmed at 10°C/min.

Carrier Gas: Helium. Flow rate: 37 ml/min at 80°C

Hydrogen Flow Rate: 36 ml/min. Air Flow Rate: 480 ml/min.

TABLE 2
Slick Thickness Measurements

Time after "spill"	-----Measured thickness in microns-----		
	Oil pond (Pond 4)	Oil-dispersant ponds (Pond 1)	(Pond 3)
1 hour		11.65 143.8 171.2	15.7 186.4
4 hours	178.5 299.4	3.1 359.2	2.3 324.5
1 day	51.8 265.9	36.7 334.1	56.7 270.3
2 days	26.37 26.2 316	5.6 17.5 354	.35 43.2 355
7 days	10.8 346	31.7 147.9	30.2 223.2
14 days	.43 101	7.5 41.1	.85 55.6
27 days	.21	.075	.65 47.8
41 days	.136	.043	.189
55 days	.05	.1	.09
69 days	.051	.006	.022
83 days	.062	none	none
97 days	.006	none	none
111 days	none	none	none

Footnote: Multiple values indicate the presence of different slicks on any given sampling date.

TABLE 3

Concentration of Oil or Oil Plus Dispersant in Sediment Samples

Time (days)	Oil & Dispersant	Control	Oil & Dispersant	Oil
	Pond 1 (mg/g)	Pond 2 (mg/g)	Pond 3 (mg/g)	Pond 4 (mg/g)
55	0.229	0.033	0.105	0.170
83	0.033	0.007	0.239	0.298
97	0.232	0.012	0.300	0.301
111	0.148	0.023	0.860	4.41
125	0.029		0.028	2.21
139	0.110	0.081	0.142	0.028
167	0.293	0.016	0.117	0.156
202		0.007	0.007	0.105
230	0.041	0.073	0.041	0.037
251	0.365	0.009	0.095	0.017
293	0.271	0.023	0.315	0.138
322	0.155		0.321	0.474
349	0.107		0.181	0.142
384	0.399	0.014	0.522	0.915

TABLE 4a: Final Oil and Dispersant on Pond Liner

Pond 1

Sample Number	Sample location	Oil found		Dispersant found	
		mg/m ²	mg/cm	mg/m ²	mg/cm
203	East side, top, incl. water line	22907	58.20	4220	9.85
204	East side, mid section	1744	7.98	(trace)	(trace)
205	East side, bottom section	1289	9.16	(trace)	(trace)

Note: In Pond 1, the liner on the west side was covered with sediment.

Total Quantities in Pond

A) On area basis:				B) From linear measurements:			
Number	Total area, m ²	Total grams of		Number	Total length, cm	Total grams of	
		Oil	Dispersant			Oil	Dispersant
203	2.74	62.76	11.56		1084	63.09	10.70
204	4.94	8.61	(trace)		1084	8.65	(trace)
205	5.61	7.23	(trace)		788	7.22	(trace)
Totals:		78.60	11.56			78.96	10.70

Averages: 78.8 g oil, 11.1 g dispersant

Table 4b: Final Oil and Dispersant on Pond Liner

Pond 3

Sample Number	Sample Location	Oil found		Dispersant found	
		mg/m ²	mg/cm	mg/m ²	mg/cm
206	West side, top, incl. water line	1412	6.46	52	.24
207	West side, mid section	-	-	482	1.84
208	West side, bottom	1535	4.8	83	.42
209	East side, top half	1694	12.05	33	.24
210	East side, bottom half	1851	16.86	(trace)	(trace)

Total Quantities in Pond

A) On area basis			B) From linear measurements		
Number	Total area, m ²	Total grams of Oil Dispersant	Number	Total length, cm	Total grams of Oil Dispersant
206	4.30	6.1		940	6.1
207	3.58	-		940	-
208	3.13	4.8		617	4.8
209	12.80	21.7		1800	21.7
210	5.64	10.4		617	10.4
Totals:		43.0			43.0
					2.3

Averages: 43.0 g oil, 2.45 g dispersant

Table 4c: Final Oil on Pond Liner

Pond 4

Sample Number	Sample Location	-----Oil found-----	
		mg/m ²	mg/cm
211	West side, top third	4252	8.64
212	West side, mid third, incl. water line	26967	34.20
213	West side, bottom third	3640	16.64
214	East side, top section	1717	12.19
215	East side, bottom section	1473	11.25

Total Quantities in Pond

A) On area basis:			B) From linear measurements:	
Number	Total area, m ²	Total grams of oil	Total length, cm	Total grams of oil
211	2.7	11.5	900	7.8
212	.9	24.3	900	30.8
213	4.4	16.0	738	12.3
214	4.5	7.7	1520	18.2
215	.9	1.3	738	8.3
Totals:		60.8		77.7

Average: 69.2 g oil

TABLE 5
Oil and Dispersant in Attached Algae

Date (Day after treatment)	Pond	Estimated weights per pond, grams		
		Algae, dry wt.	Oil	Dispersant
May 23, 1979 (322)	1	3283	121.1	14.6
	3	7256	77.4	8.8
June 19, 1979 (349)	1	8326	135.1	12.8
	2 (Control)	822	-	-
	3	4255	73.5	4.1
July 24, 1979 (384)	1	56900	22.9	(trace)
	3	55600	236.0	23.8

TABLE 6
Oil/Dispersant Ratios in Pond Samples^{1,2.}

Sampling time (Day after treatment)	Water column	Surface slicks	Deposits on liner	Sediment extracts
27	1.65	2.83	3.35	2.76
41	1.95	8.97	7.52	11.48
55	3.35	(NS)	7.86	7.09
69	N/A	(NS)	6.32	N/A
83	1.55	(NS)	N/A	5.85
97	1.71	(NS)	7.79	11.48
111	1.57	(NS)	7.09	7.53
Final sampling, on Day 384	N/A	(NS)	12.3	7.64

¹Initial value based on amounts added = 5.00

²The values in the table are averages for Ponds 1 and 3

NS - no slick

N/A - not available.

Figure 1. Location of Experimental Ponds.

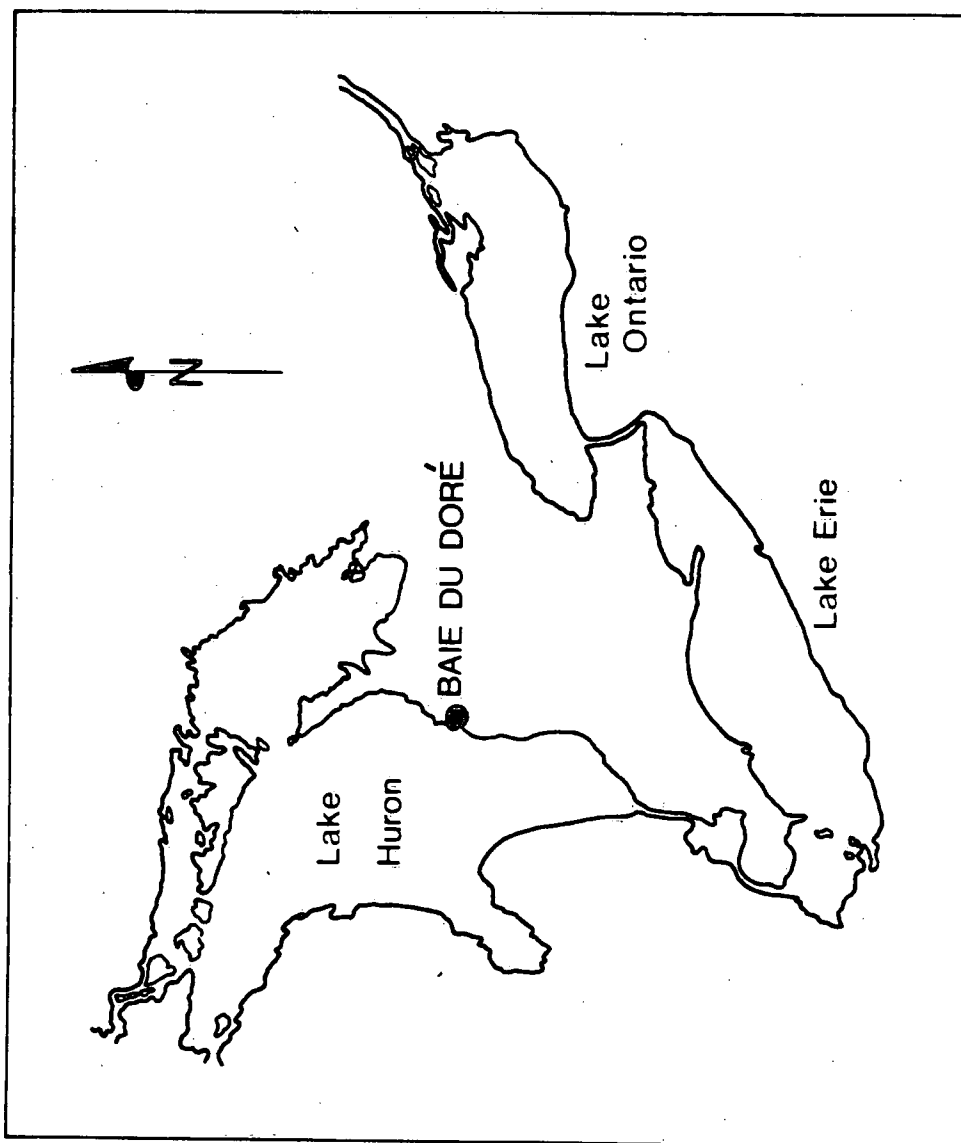


Figure 2. Representation of liner attachment.

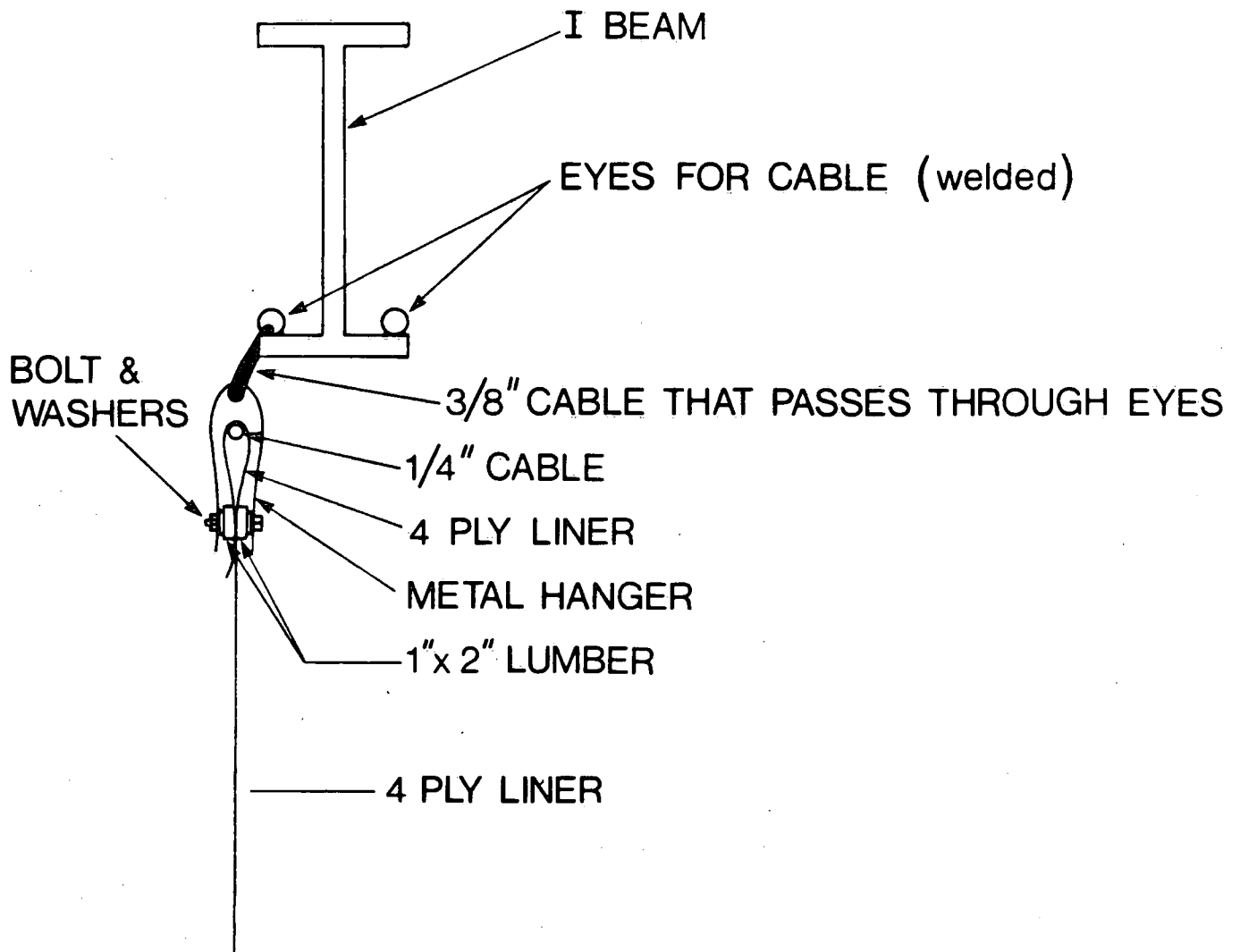


Table 3. Sediment sampling locations

PLAN OF FINAL SAMPLING OF POND SEDIMENT

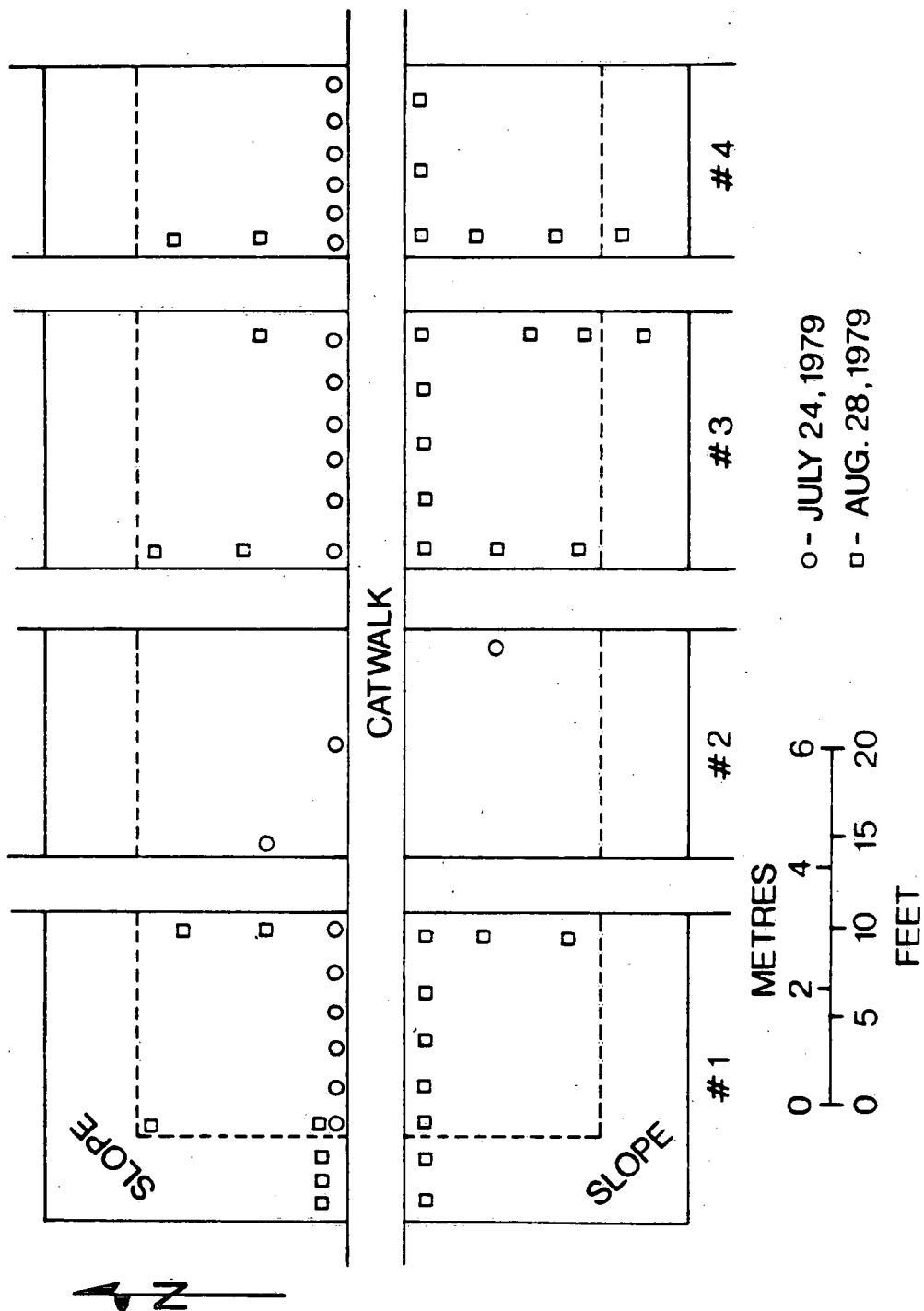


Figure 4. Water volumes in ponds.

POND VOLUMES (thousands of litres)

VOLUME OF WATER IN PONDS

TIME (days after spills)

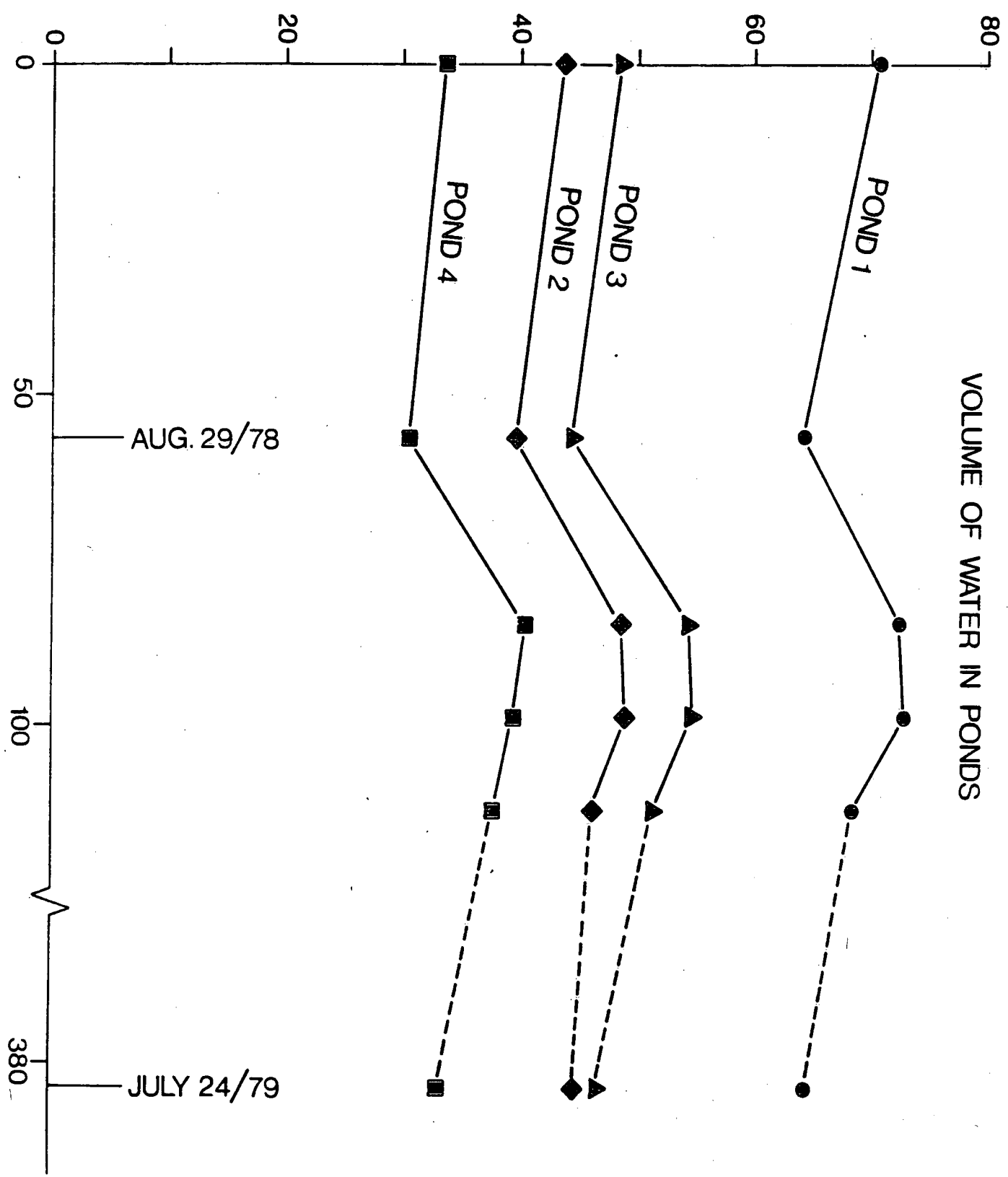


Figure 5. Oil concentrations in water column of oil-treated pond.

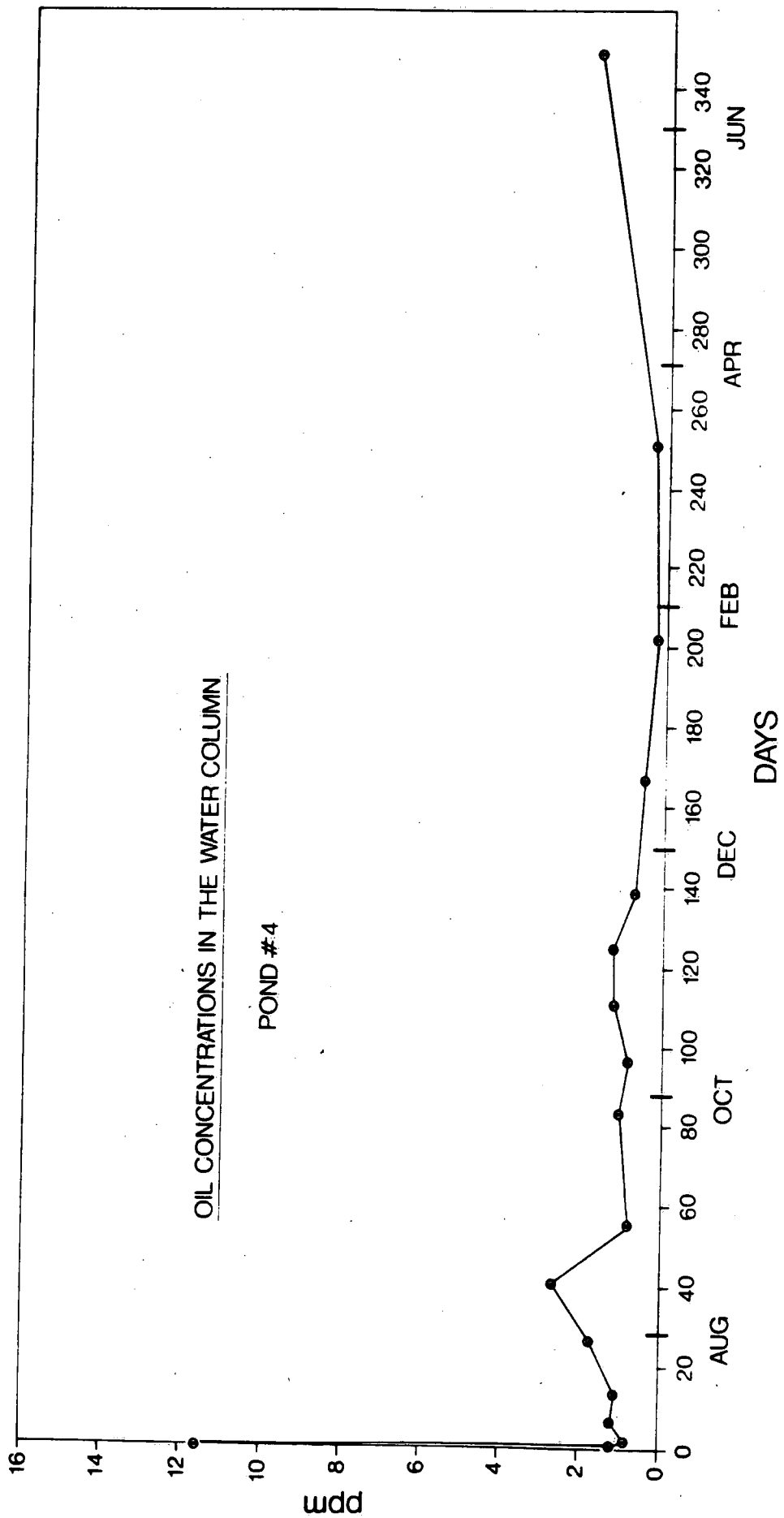
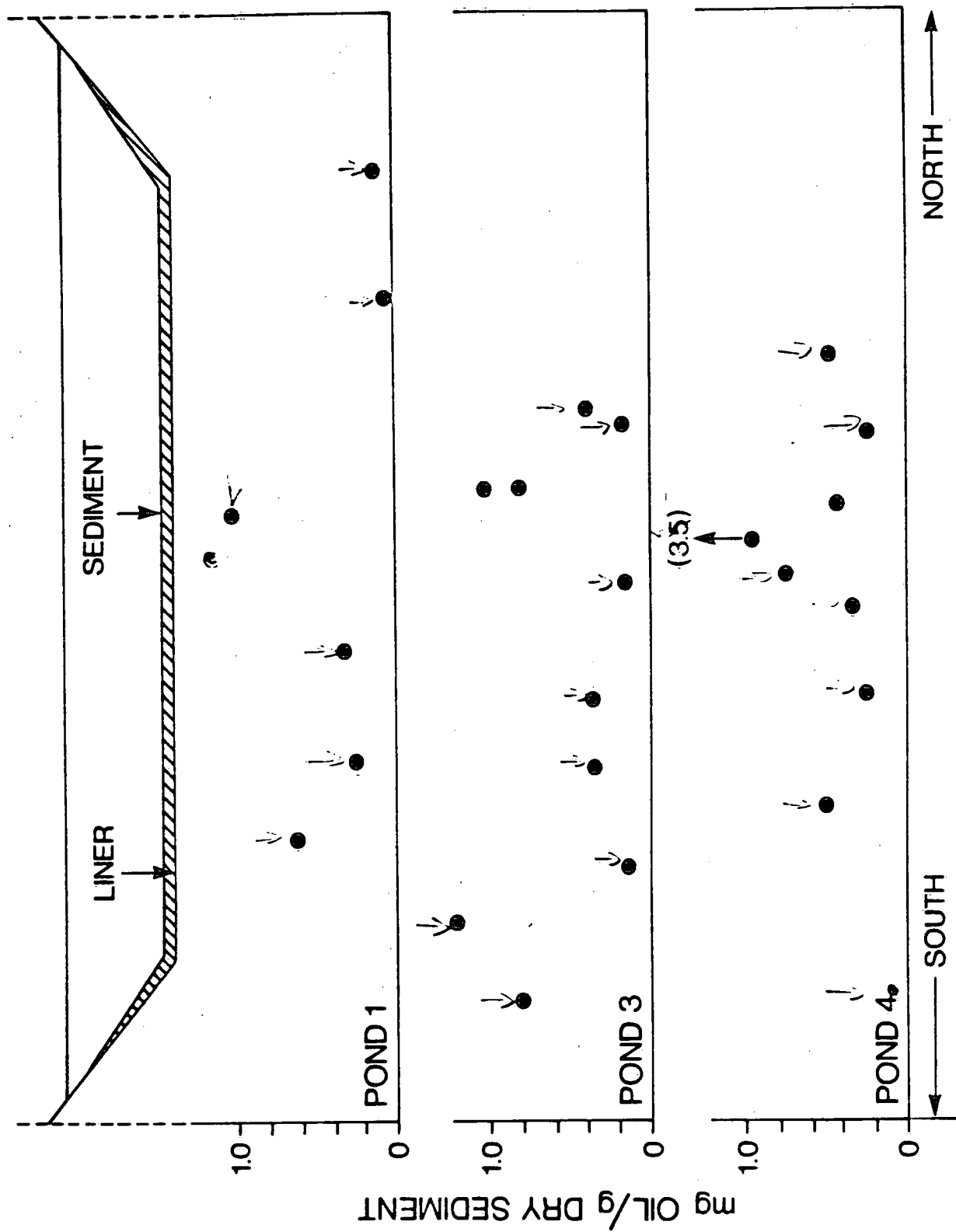


Figure 6. Oil distribution in sediments shown along the north-south axis.



OIL DISTRIBUTION IN SEDIMENT ALONG SOUTH TO NORTH LINERS

Figure 7. Oil distribution in sediment shown along the east-west axis where Δ indicate an average of several values

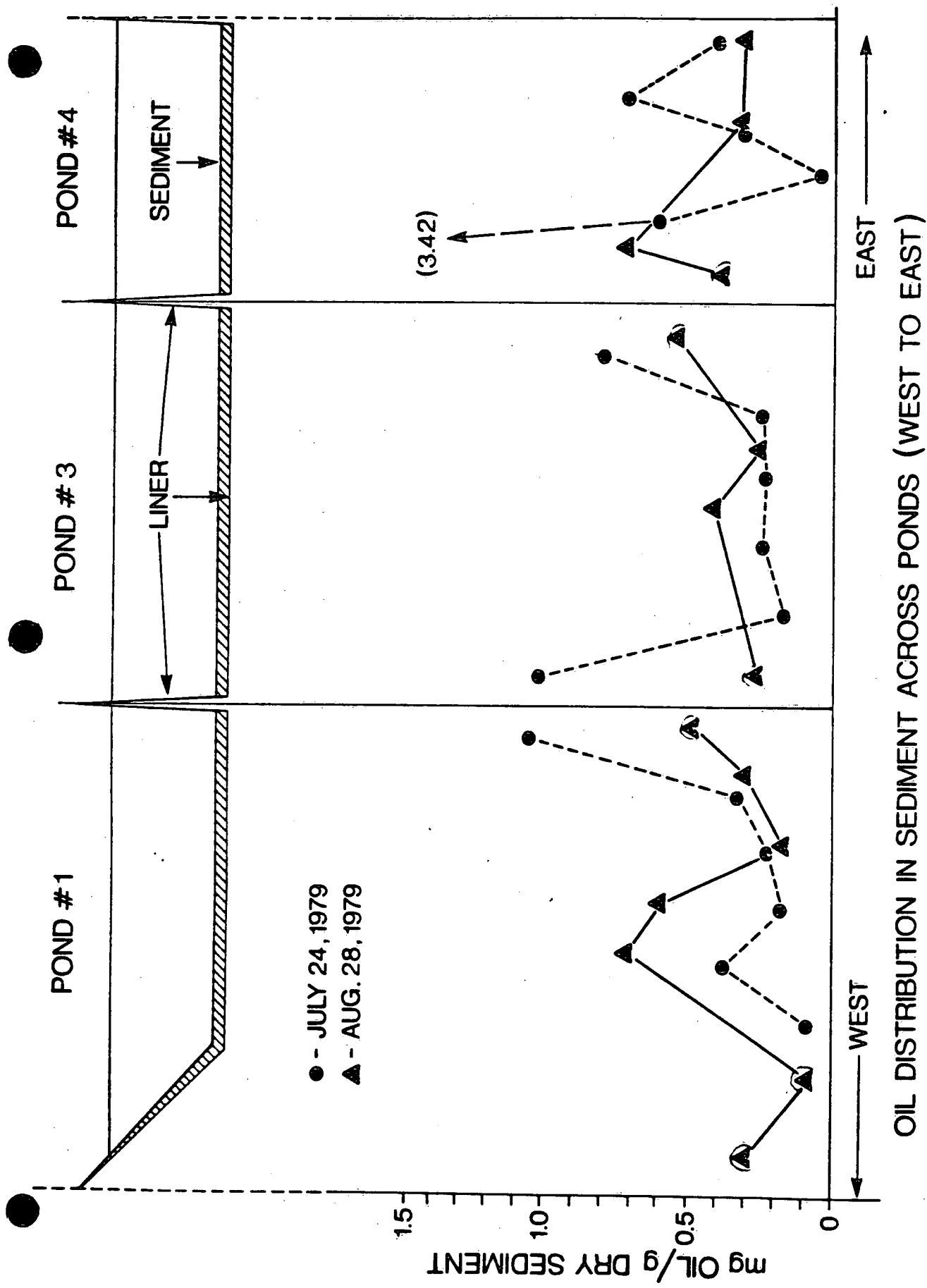


Figure 8. Oil and dispersant concentrations in the water columns of the oil-dispersant treated ponds.

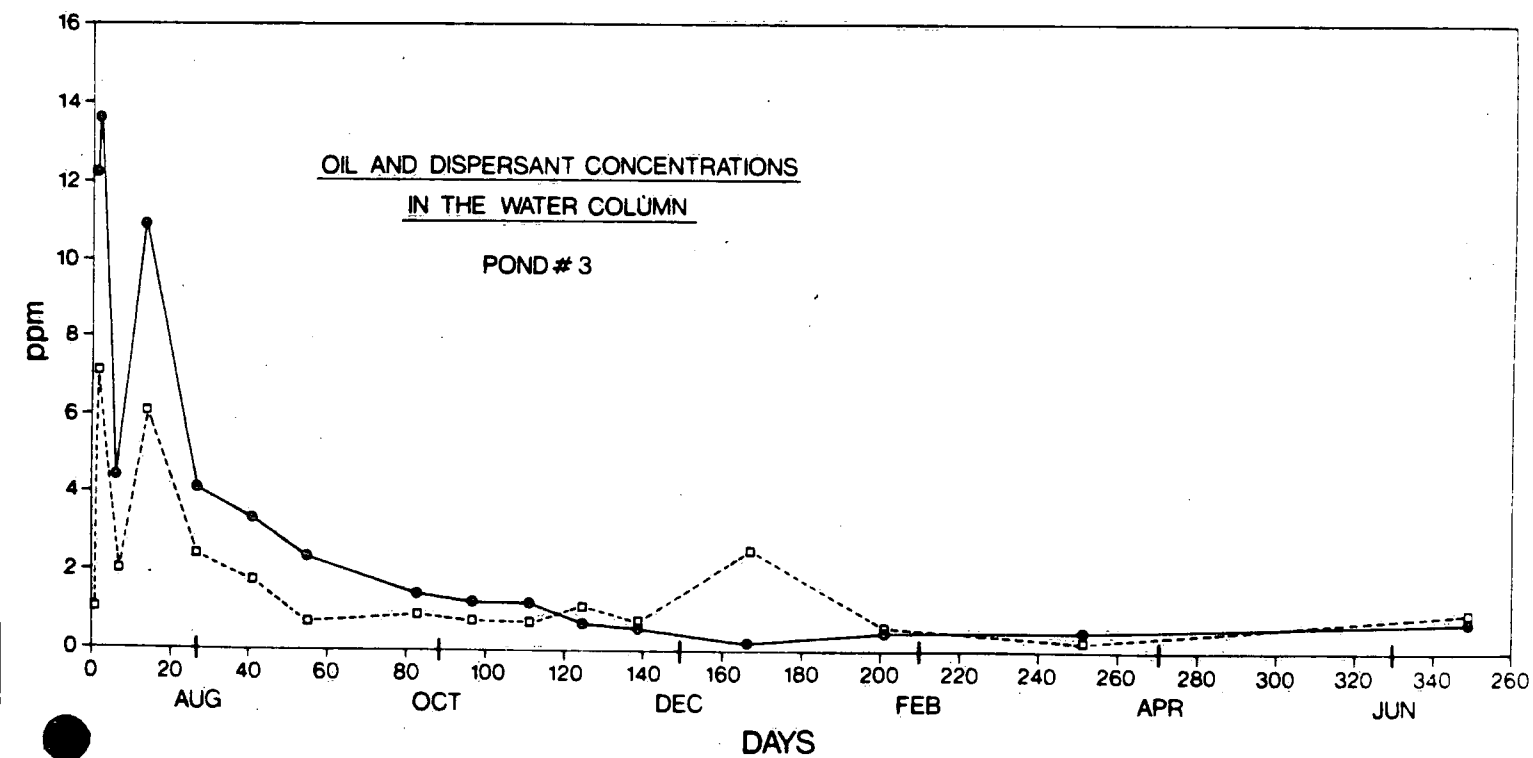
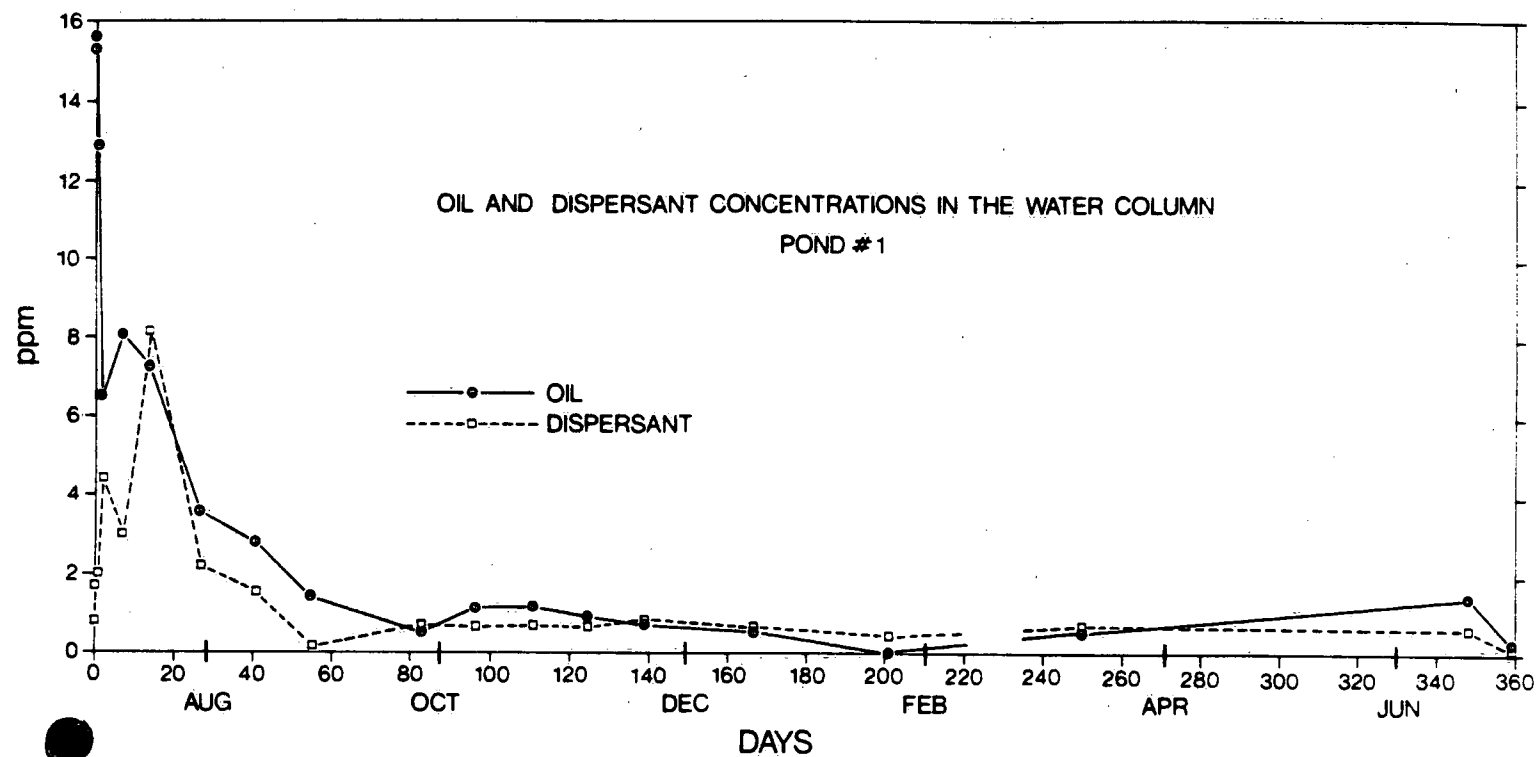


Figure 9. Dissolved organic carbon concentrations in water columns of experimental ponds.

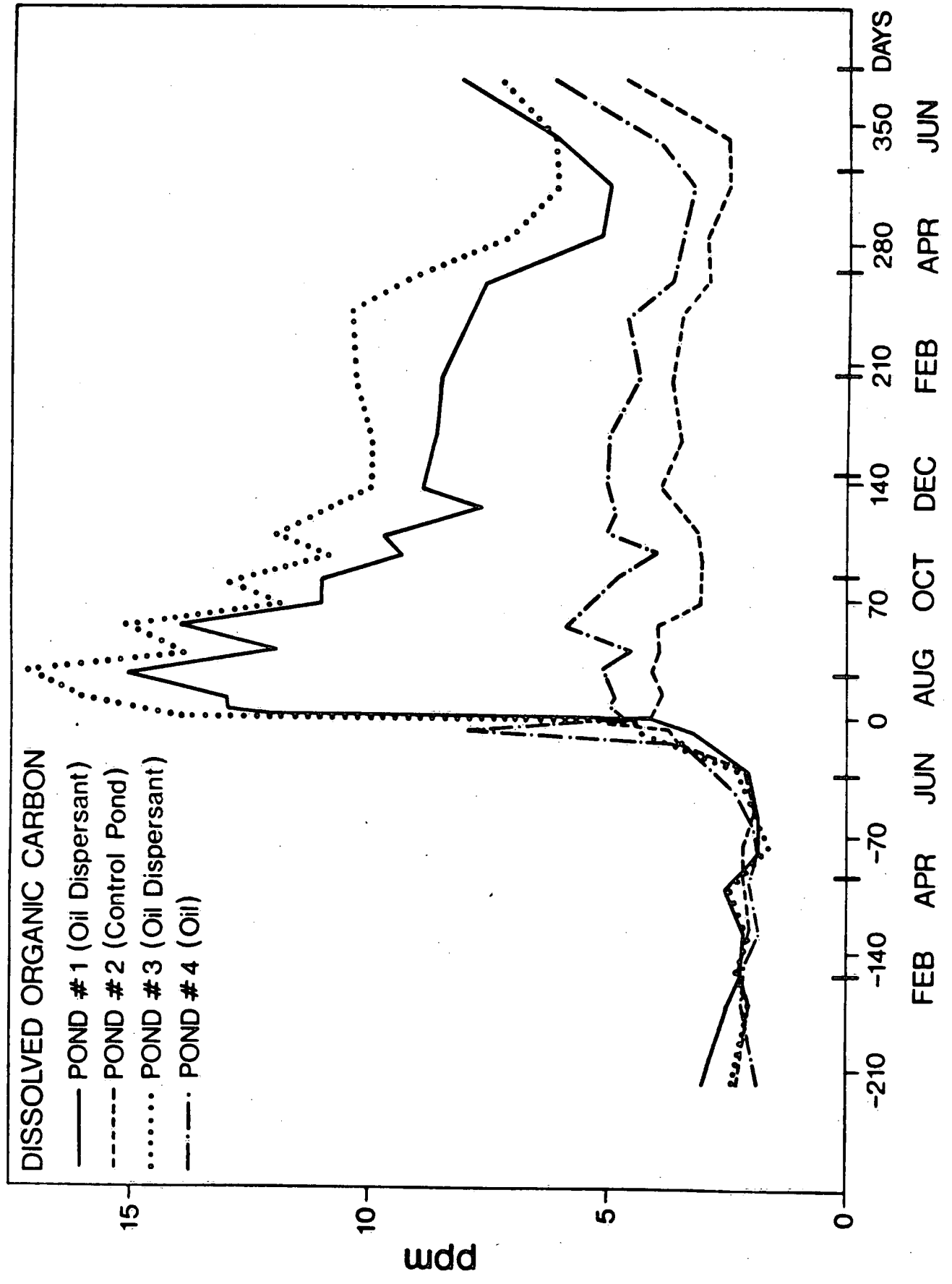


Figure 10. Dissolved reactive silica concentrations in water columns of experimental ponds.

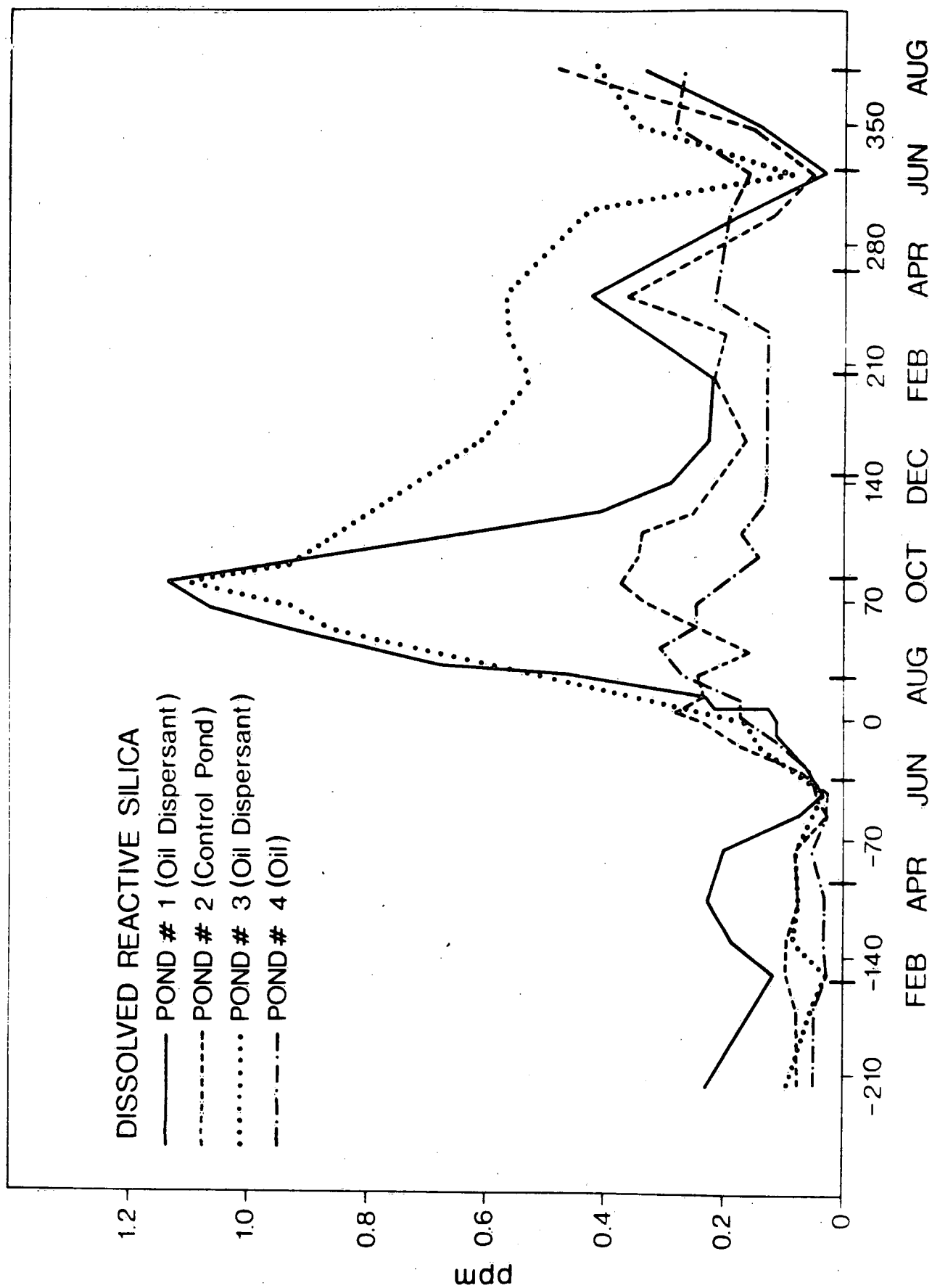


Figure 11. Oil:Dispersant ratios recovered from sediment samples.

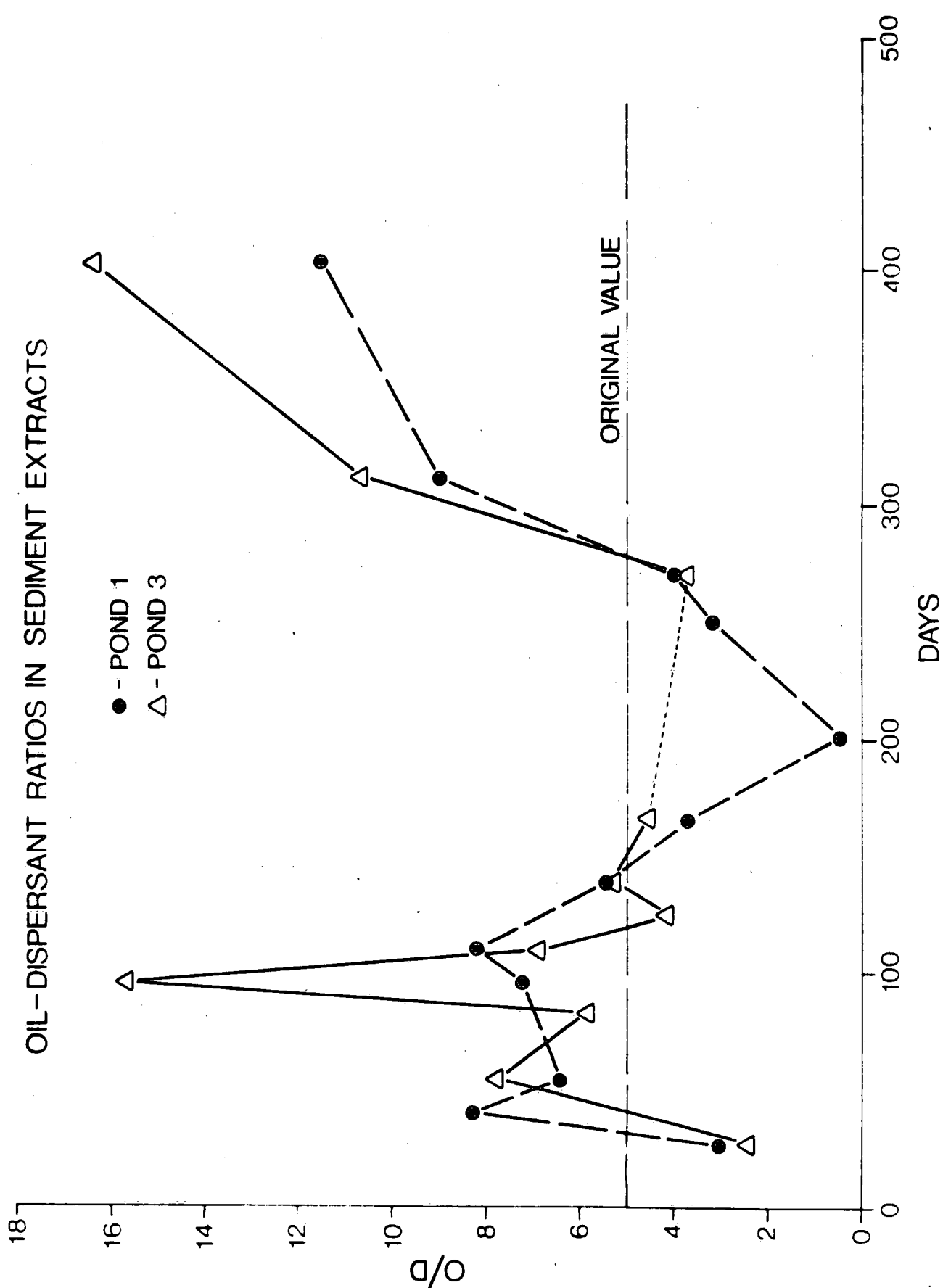


Figure 12. Persistence of surface films.

PERSISTENCE OF SURFACE FILMS IN PONDS 1, 3 AND 4

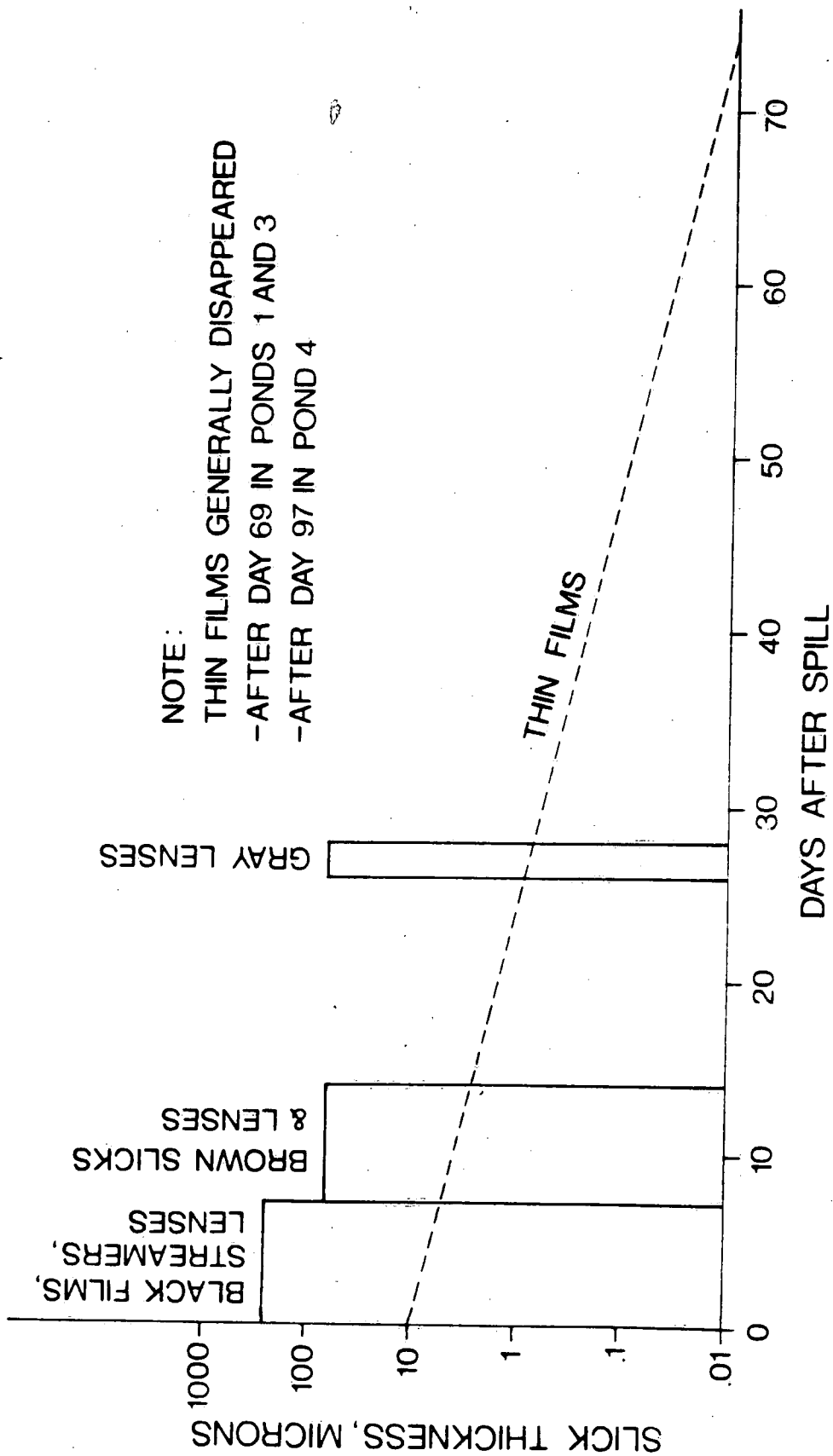
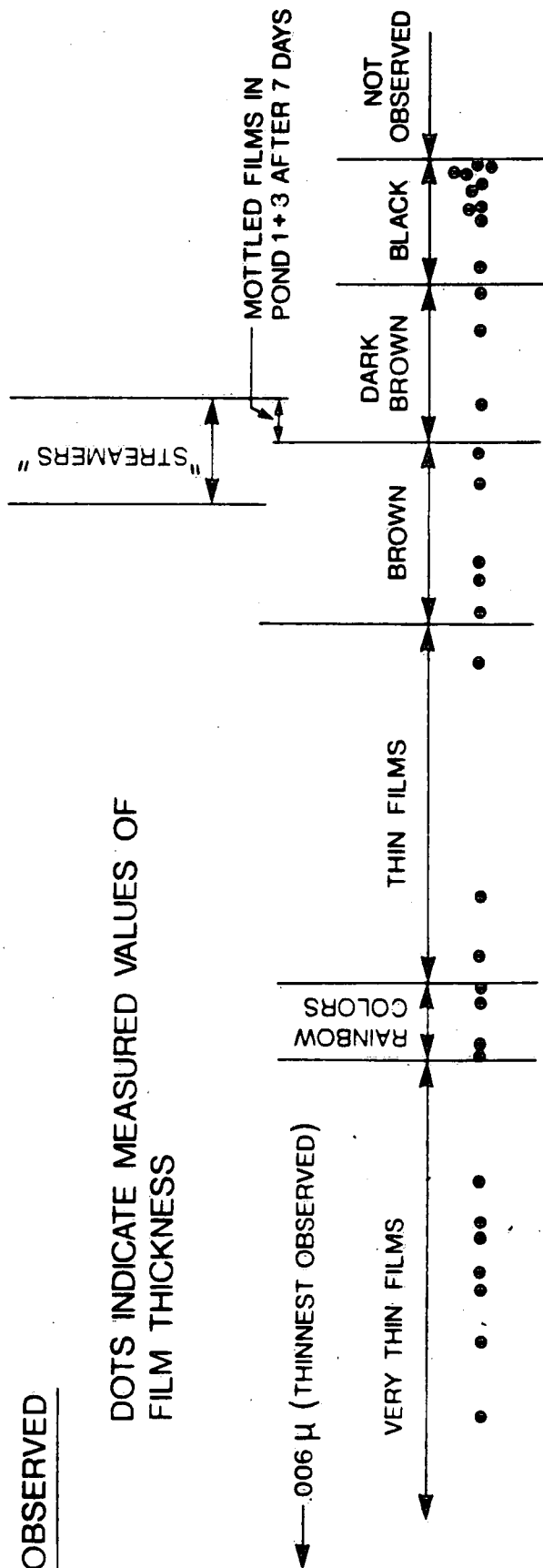


Figure 13. Appearance of surface films.

APPEARANCE OF SURFACE FILMS IN PONDS 1, 3 AND 4

(a) OBSERVED

DOTS INDICATE MEASURED VALUES OF
FILM THICKNESS



(b) LITERATURE (Horstein, 1972)

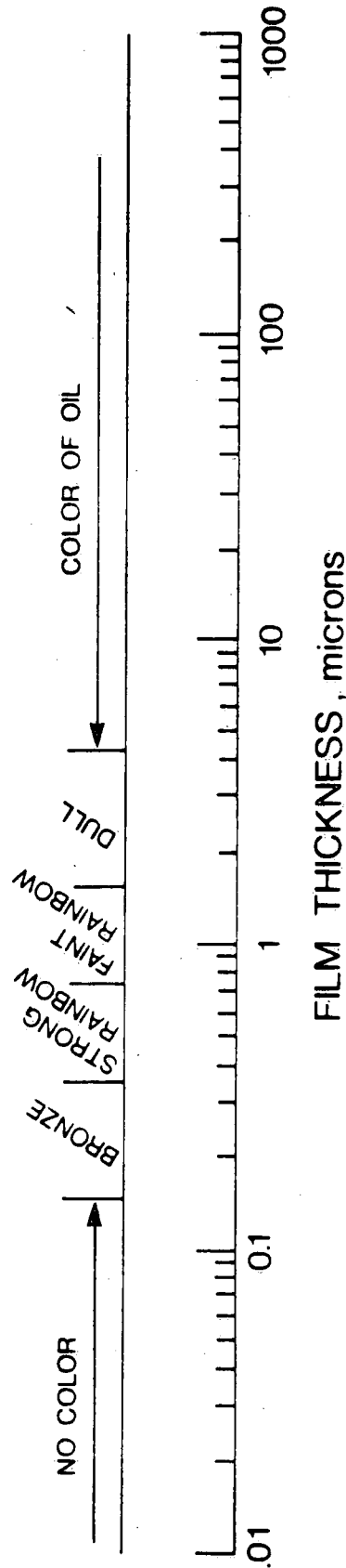


Figure 14. Initial oil:dispersant ratios of surface films as a function of thickness.

INITIAL OIL/DISPERSANT RATIOS IN
SURFACE SLICKS

PONDS 1 AND 3

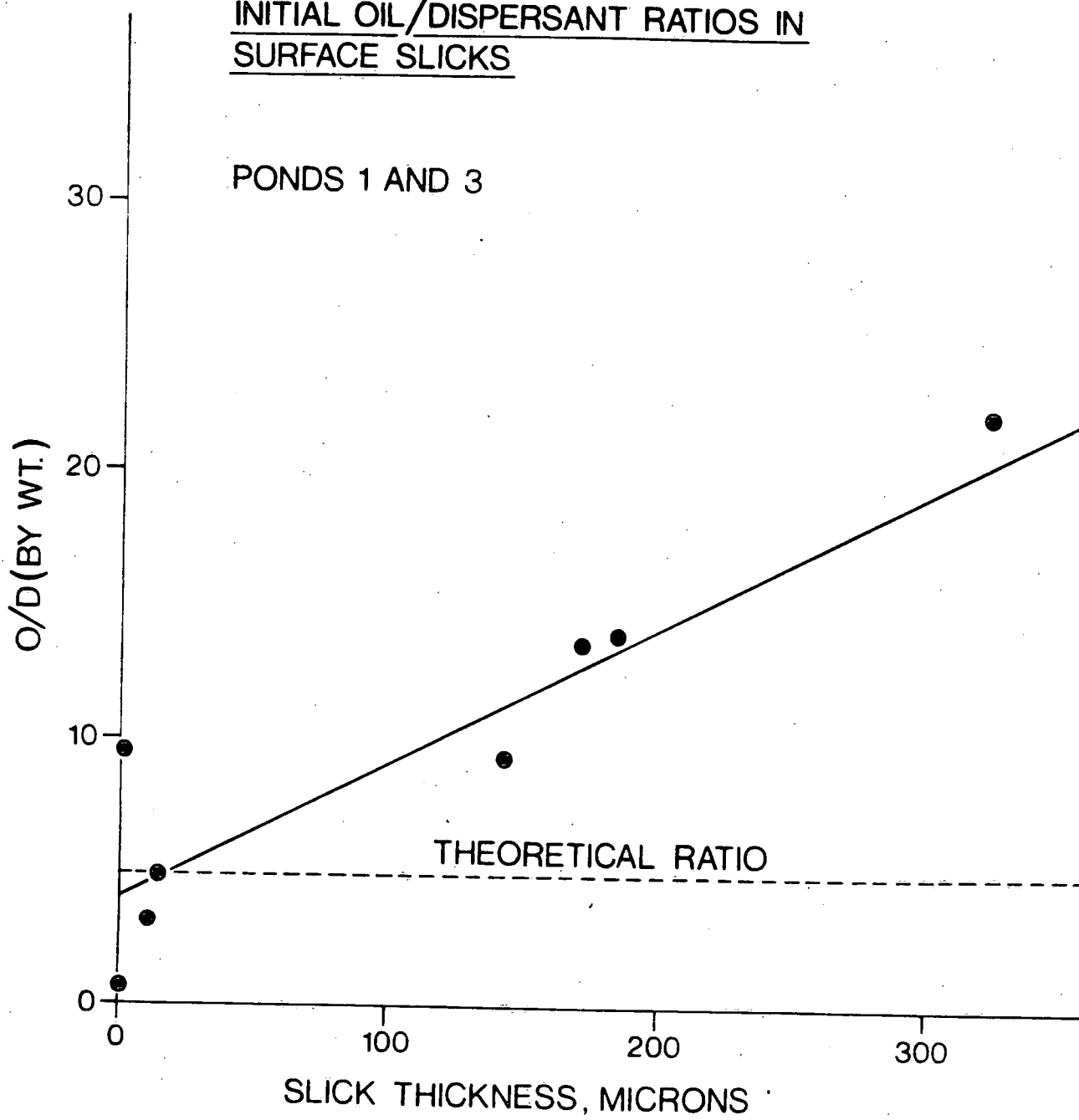


Figure 15. Carbonyl stretch absorption of surface films

IR INDICATION OF CARBONYL COMPOUNDS

IN SURFACE SLICKS

1 AND 4 HOURS AFTER SPILL

- POND 1 (OIL + DISP.)
- ▲ POND 3 (OIL + DISP.)
- POND 4 (OIL)

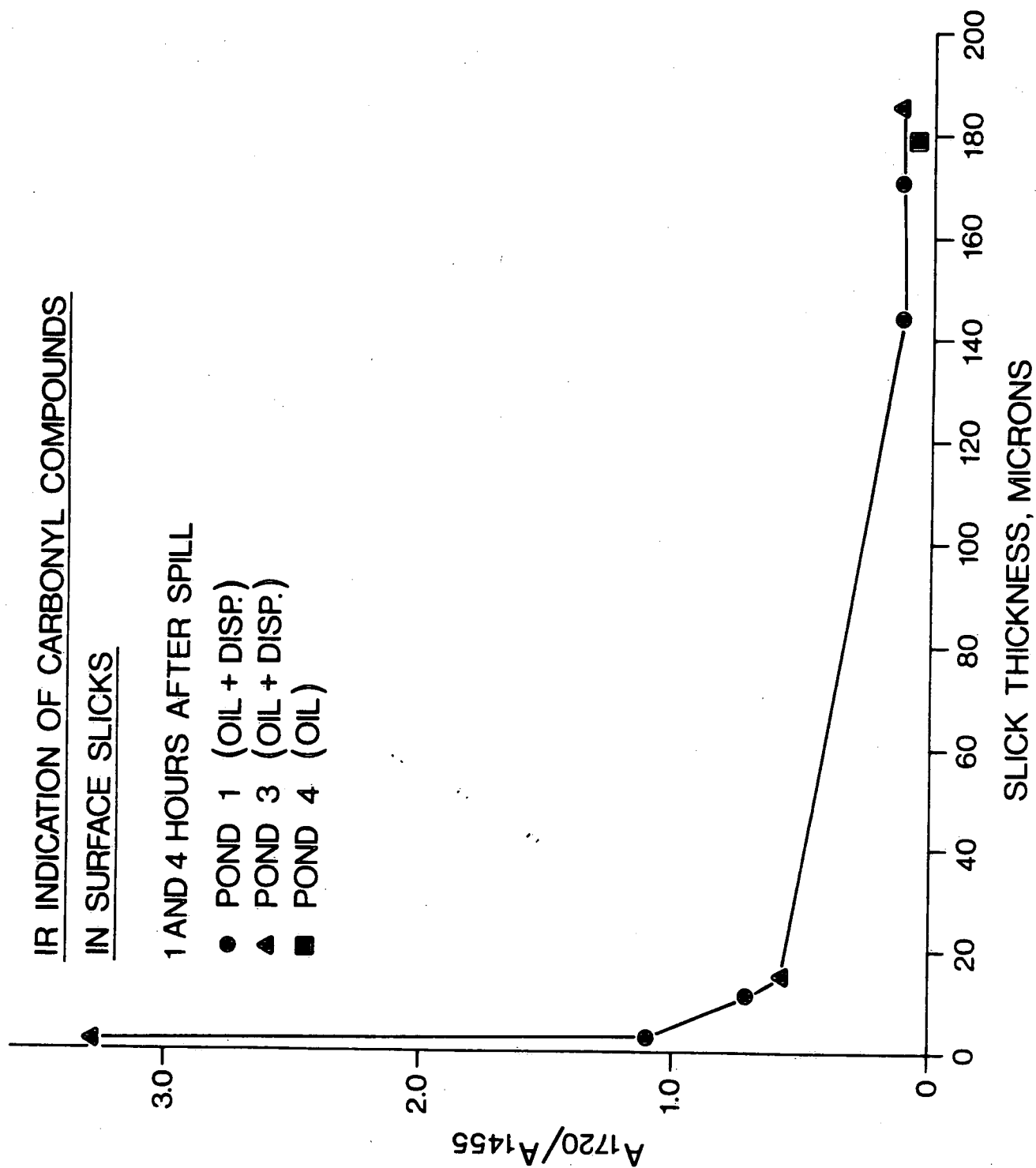


Figure 16. UV absorption of surface films. C is the concentration by IR (Appendix I).

AROMATICS IN SURFACE SLICKS

$$\frac{A}{C} = \frac{\text{ABSORBANCE AT 280 nm (10 mm path)}}{\text{CONCENTRATION IN mg/10 mL CCL}_4}$$

HEAVY SLICKS

- POND 1 (OIL + DISP.)
- ▲ POND 3 (OIL + DISP.)
- POND 4 (OIL)

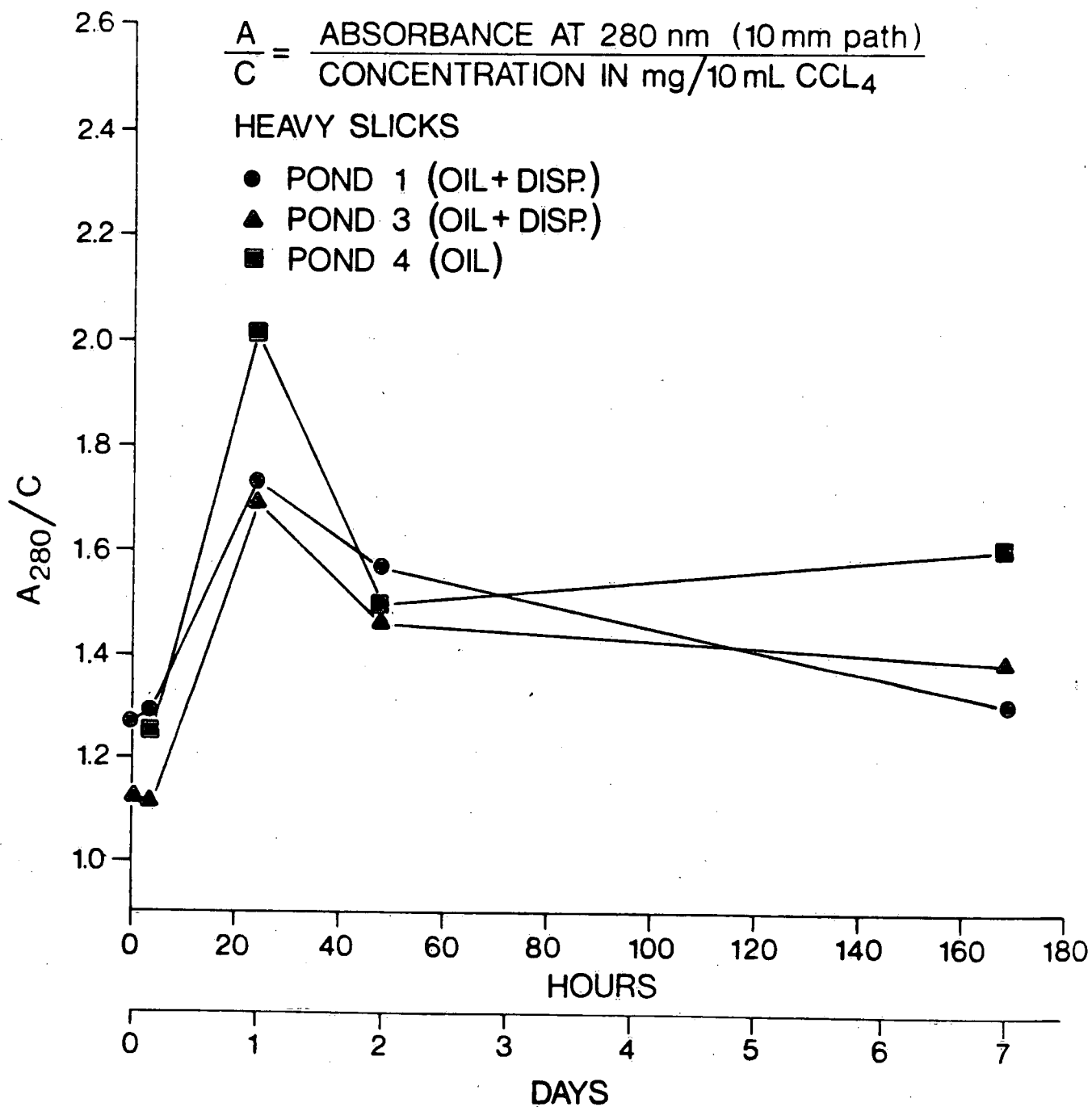


Figure 17. UV absorbance of sediment extracts. C is concentration as determined by IR.

UV ABSORBANCES OF
SEDIMENT EXTRACTS

- POND 1
- △ POND 3
- POND 4

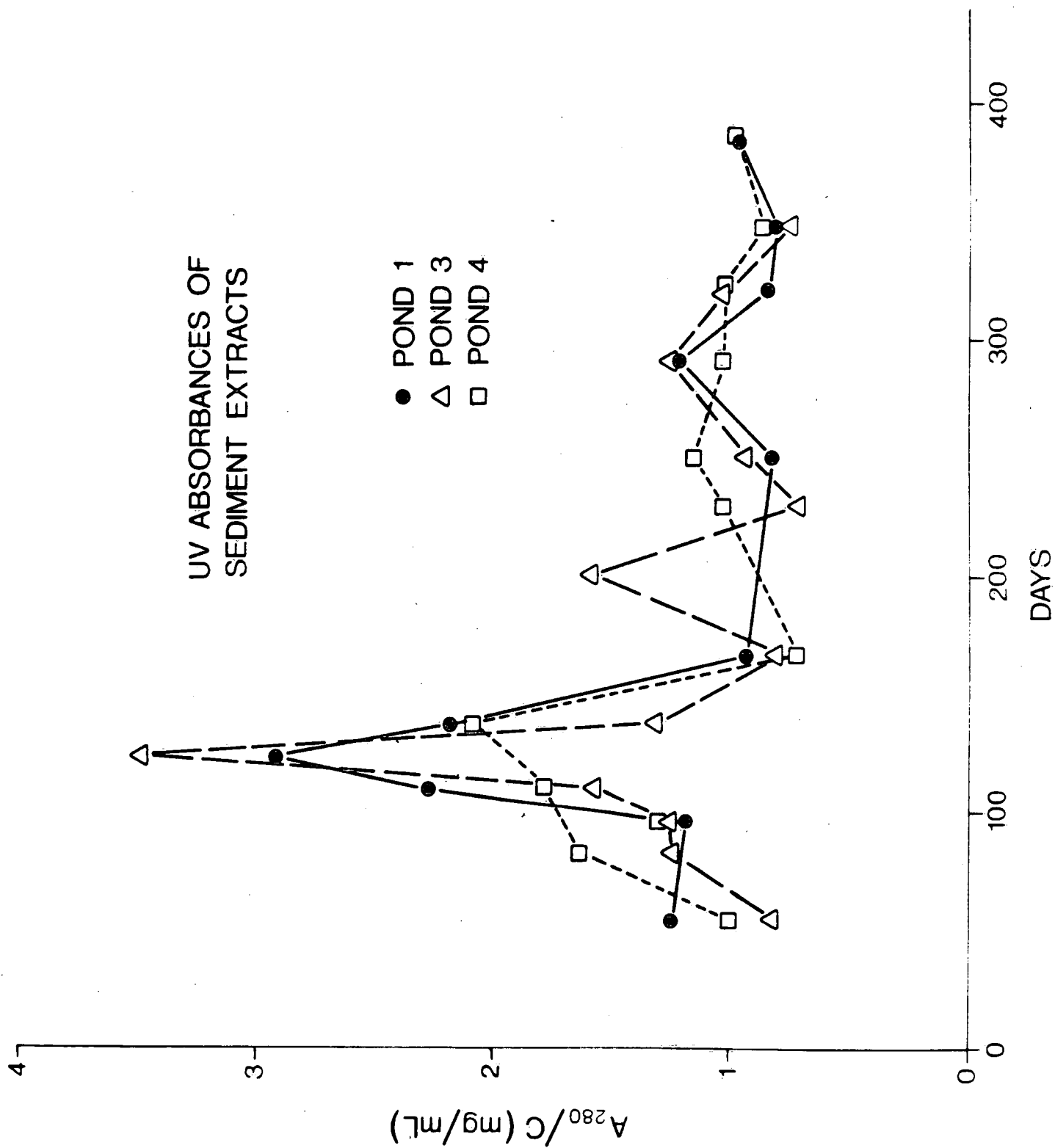
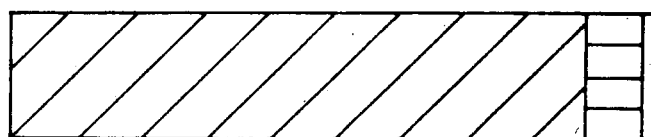
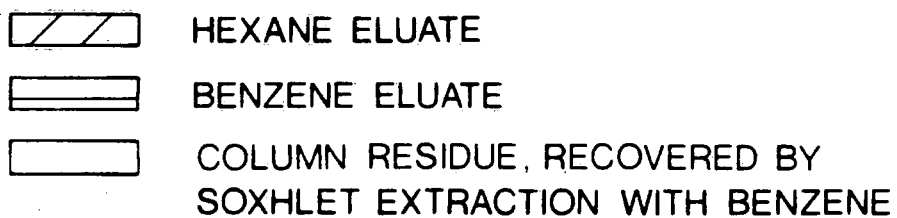
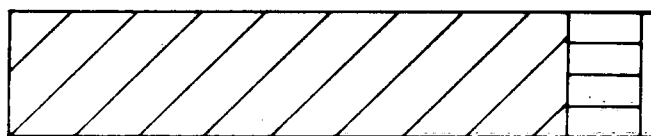


Figure 18. Liquid chromatographic fractions of some petroleum products.

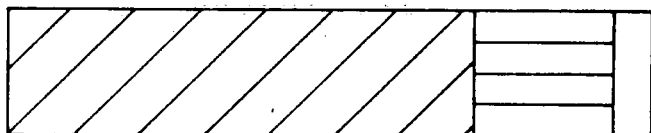
LC FRACTIONATION OF OILS



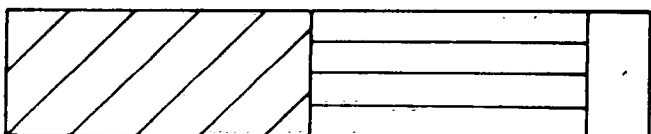
FRESH N.W. CRUDE



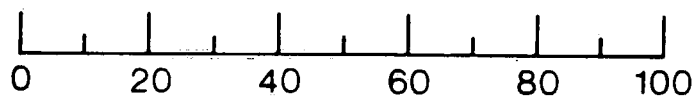
TOPPED N.W. CRUDE
(30.6% EVAP.)



BACTERIALLY N.W. CRUDE
DEGRADED FOR FIVE WEEKS

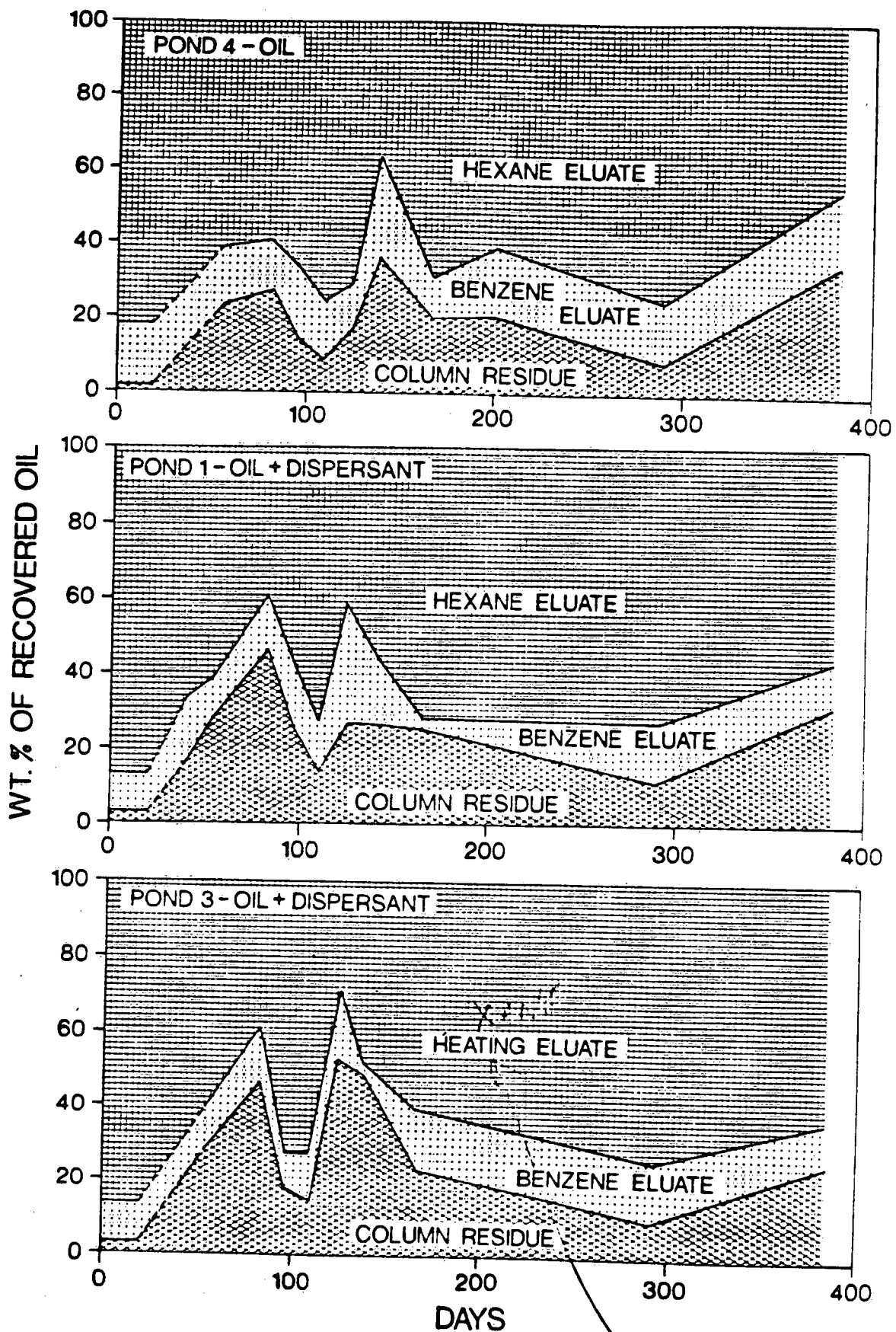


No. 6 FUEL OIL
(BUNKER C)



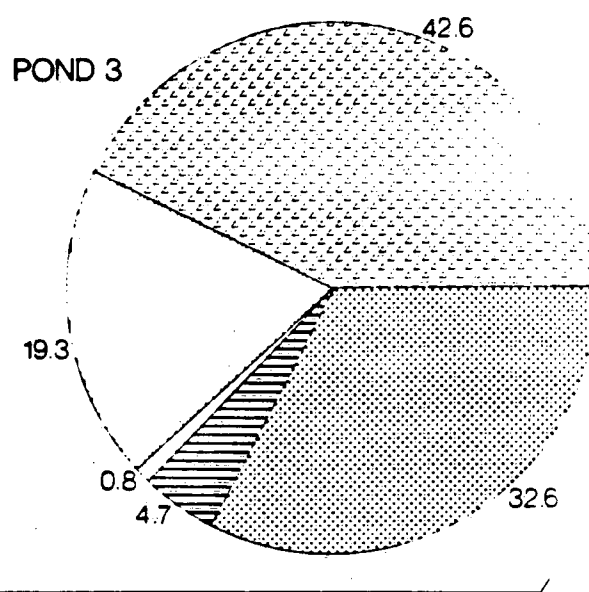
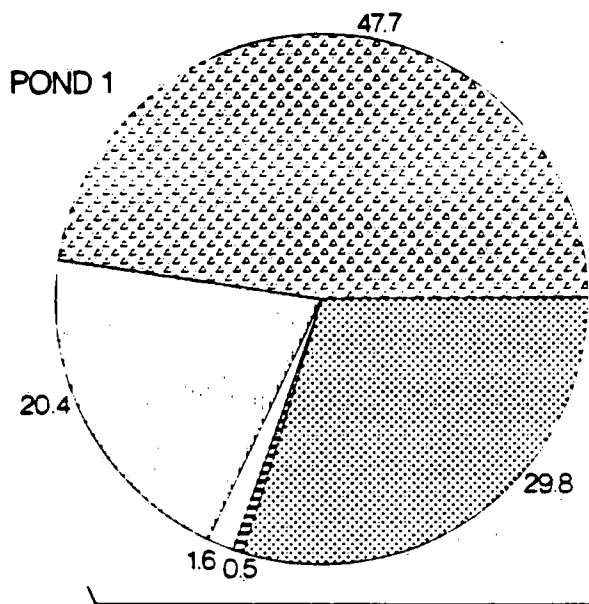
PERCENTAGE OF RECOVERED OIL

Figure 19. Liquid chromatograph fractions of sediment extracts plotted as a function of time.

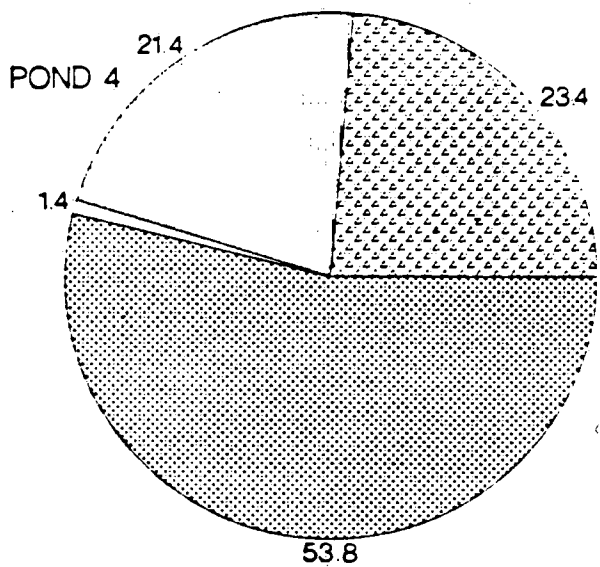


LIQUID CHROMATOGRAPHIC SEPARATION OF SEDIMENT EXTRACTS

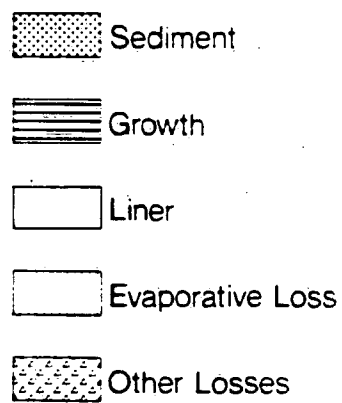
Figure 20. Final distribution of oil in treated ponds.



(oil and dispersant)

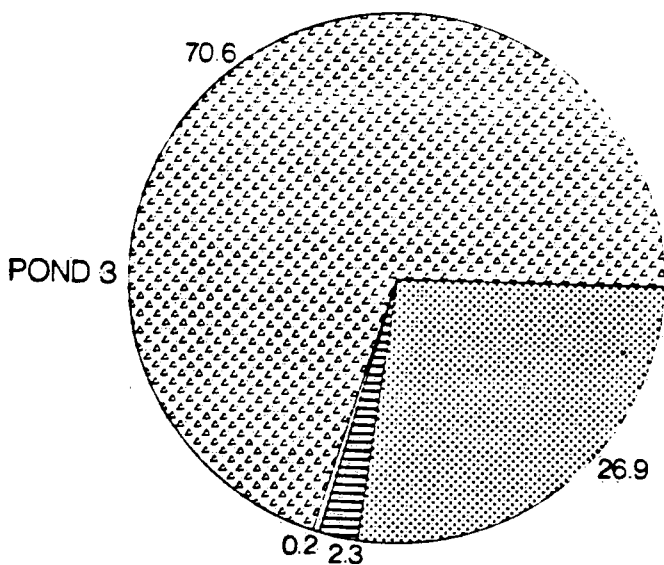
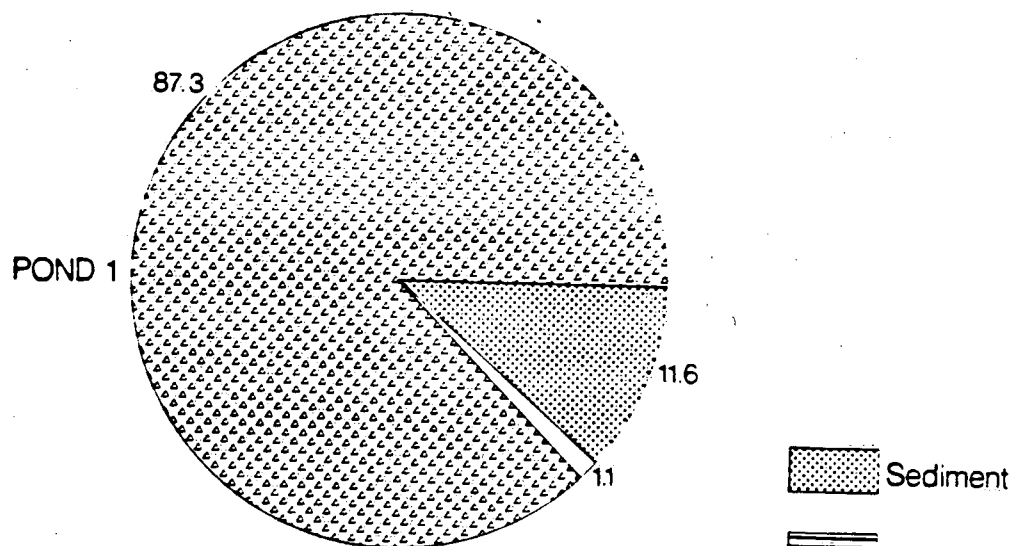


(oil alone)



FINAL OIL DISTRIBUTION IN PONDS (Expressed as percent of added oil)

Figure 21. Final distribution of dispersant in oil-dispersant treated ponds.



FINAL DISPERSANT DISTRIBUTION IN PONDS (Expressed as percent of added dispersant)

APPENDIX I

A. Infrared Method of Oil and Dispersant Analysis

The determination of oil and dispersant concentrations in all water, slick, and sediment samples was based on extraction of the samples with CCl_4 , and on obtaining the IR spectrum of the extracts. A Perkin-Elmer 457 grating IR spectrophotometer with matched NaCl cells of 1 mm path length was used, the reference cell containing the pure solvent.

Oil concentrations were calculated from the absorption at 2920 cm^{-1} . Analysis of oil-dispersant mixtures utilized both the above C-H stretch absorption as well as that assigned to C-O stretch at 1050 cm^{-1} . The results of the calibration are summarized in Table I-A, and graphically shown in Figures I-1 and I-2, indicating that Beer's Law is valid for this system in the 0 to 3500 mg/l concentration range. The calibration constant apparently was not affected by evaporative aging of the crude oil and the values obtained for a "topped" crude oil which had lost about 30% of its weight by evaporation of the most volatile oil components, could not be distinguished from those of fresh oil. Two light fuel oils tested, No. 2 fuel oil and Jet A-1 fuel, gave calibration values similar to those of the crude oil. A very light and a very heavy petroleum fraction, namely a gasoline and No. 6 fuel oil (Bunker C), on the other hand, would require their own calibration curves.

The equations used to calculate oil and dispersant concentrations in the solvent are

$$C_{oil} = 49.3 A_{2920} \dots \dots \dots (1)$$

$$C_{disp.} = 91.3 A_{2920} \dots \dots \dots (2)$$

$$C_{disp.} = 122.1 A_{1050} \dots \dots \dots (3)$$

where the C's are concentrations in mg/10 ml CCl_4 and the A's are the measured absorbances at the wavelengths shown in the subscripts. In solutions containing oil alone or dispersant alone, the concentrations are calculated from only one of the above equations: Eq (1) for oil, and Eq (2) or (3) for the dispersant. In the analysis of oil-dispersant mixtures, the dispersant concentration is calculated from Eq (3), while the oil concentration is given by

$$C_{oil} = 49.3(A_{2920} - 1.337 A_{1050}) \dots \dots \dots (4)$$

where the second term in the parentheses is the dispersant's contribution to the observed absorbance at 2920 cm^{-1} .

TABLE I-A

Summary of IR Calibration Data

	Crude Oil	Dispersant	
	2920 cm^{-1}	2920 cm^{-1}	1050 cm^{-1}
Calibration constant, (C/A)	49.3	91.3	122.1
No. of data points, (n)	10	18	15
Correlation coefficient, (r)	.9993	.9990	.9994

Figure I-1. Concentration - absorbance relationships for selected petroleum products

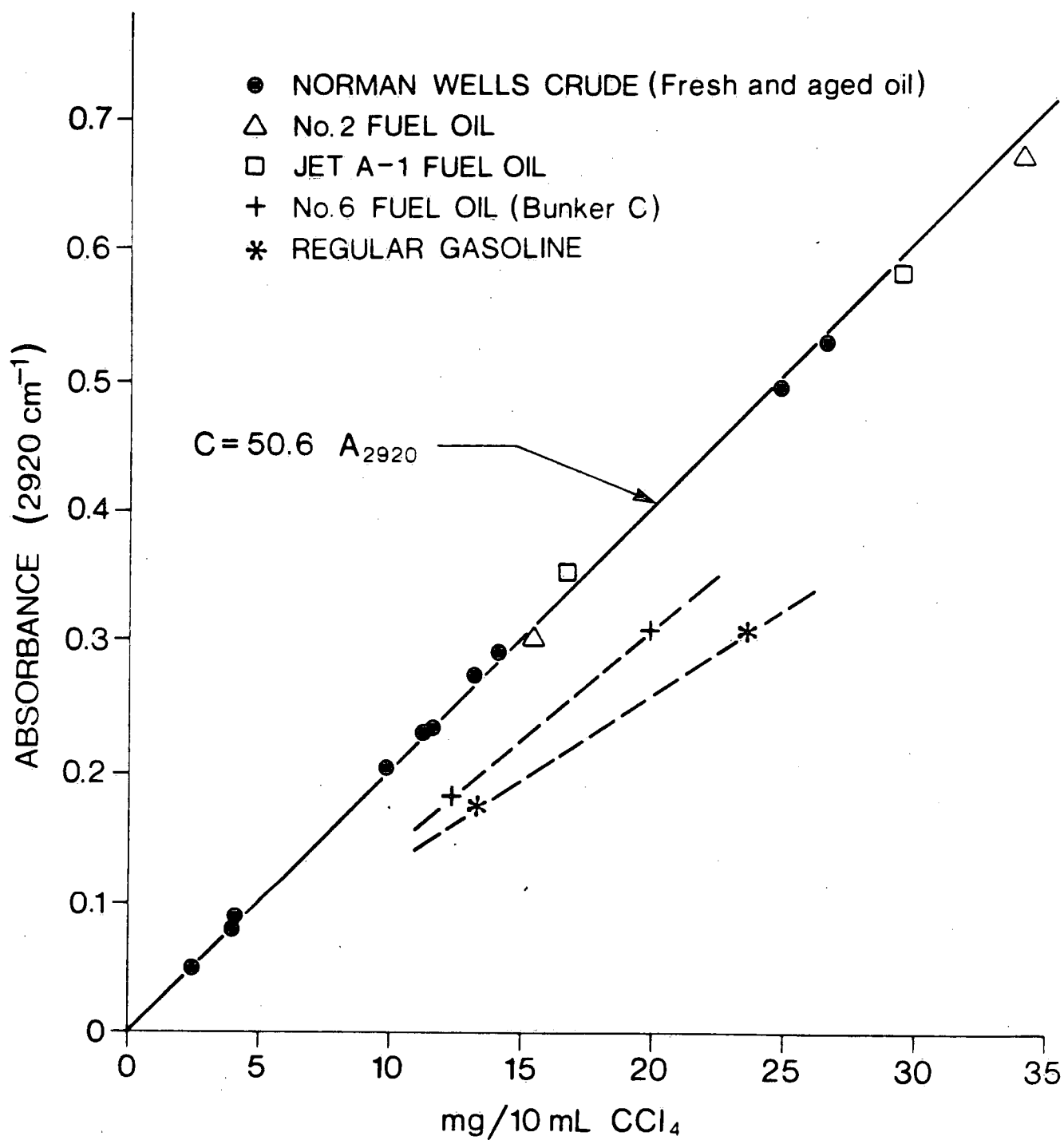
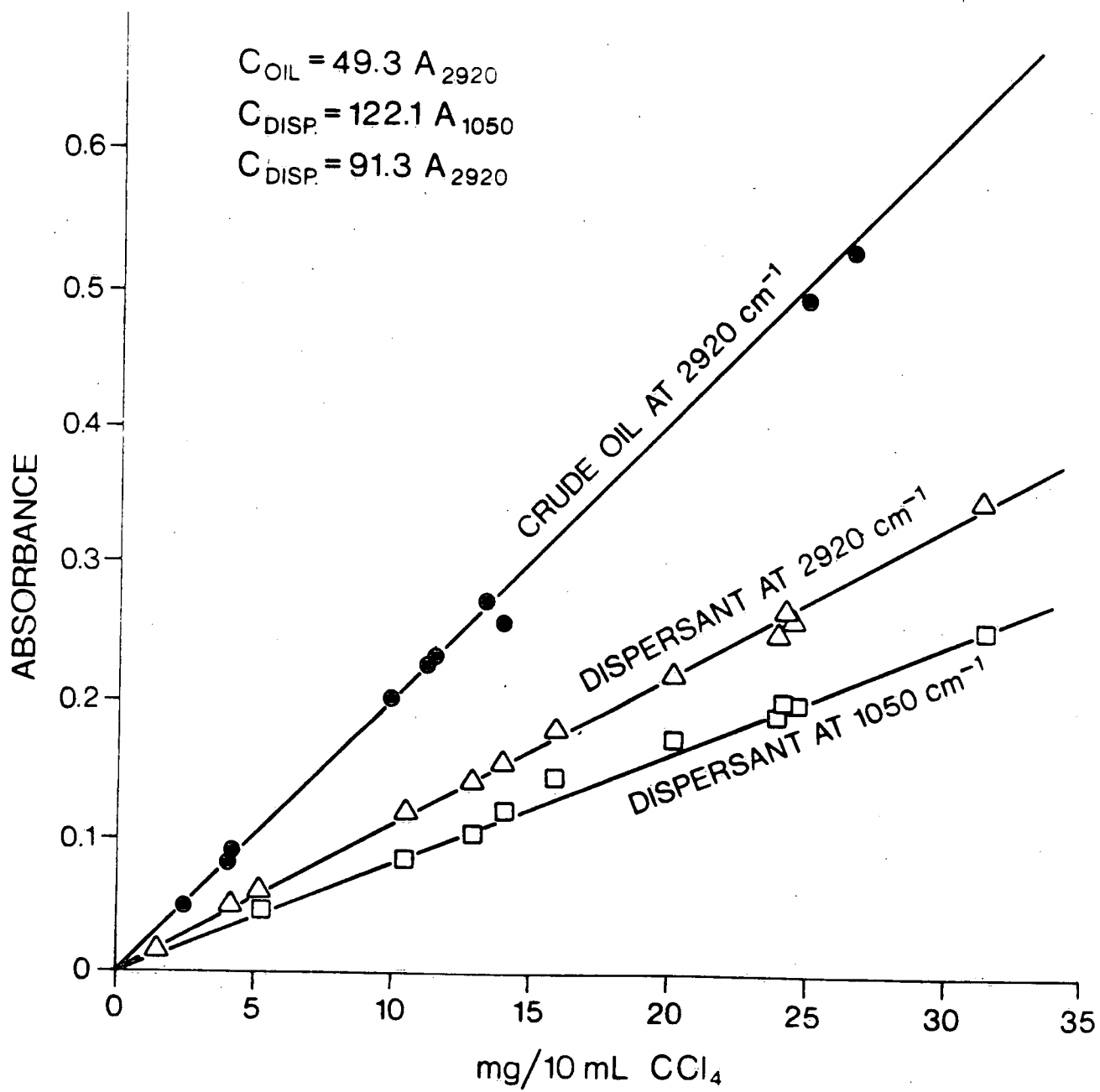


Figure I-2. Calibration plots for oil and dispersant concentrations



B. The Use of the IR Method in the Analysis of Field Samples

Water samples: One-liter aliquots of the water samples collected with a Van Dorn bottle were transferred into a 2-liter separatory funnel immediately upon collection. After dissolving 300 g of NaCl in the sample, it was extracted by shaking with 10 mls of CCl_4 for one minute. The mixture was allowed to separate for 5 minutes, resulting in an organic layer containing emulsified water. This layer was removed from the funnel and was centrifuged at approximately 1500 rpm until the solvent phase was clear (10 to 15 minutes). Most of the solvent layer was then transferred with a small pipette into a vial, (5 to 8 mls) and was returned to the laboratory for analysis. No attempts were made to quantitatively separate the solvent phase and the fraction in the vial was assumed to be representative of the 10 ml solvent phase added. In preliminary laboratory tests, this assumption was shown to produce recoveries of about 98% for both oil and dispersant.

Sediment samples: The samples were collected at the site in 1-liter jars, each containing 400 to 600 grams of dry solids. The solids settled to produce a visible sediment-water interface within a minute, and the samples were then transported to the laboratory with 1 cm free water layer above the sediment material. Extractions were performed by adding 100 ml of CCl_4 to the bottle and agitating on a reciprocal shaker for one hour. Disposable pipettes were used

to remove 20 to 30 mls of the solvent phase from the sediment interstices. This was then centrifuged, as in the case of the water extracts, to remove both moisture and fine solids from the solvent phase. The clarified solvent phase was then subjected to IR analysis and for any subsequent tests such as gas-liquid chromatography and liquid chromatography. The extraction efficiency was tested in the laboratory by spiking sediment material from the pond site with the oil and extracting, as above, after allowing it to stand for two days. The results, illustrated in Table I-B, show that the extraction was over 95% efficient. Preliminary tests with dispersant in the sediment indicated similar recoveries.

Surface slick samples: Surface slicks were sampled by lowering 10 x 10 cm squares of ordinary office type blotting paper, attached to the end of a stick with a thumbtack, onto the water surface, allowing it to be wetted through to the top, and transferring it to a small jar for later analysis. In the case of very thin surface sheens, several squares were used in the area to be tested, and these were extracted together. The extraction was accomplished by adding 50 mls of CCl_4 into the jars with the blotting paper and intermittently (e.g., 5 to 6 times) hand-shaking the jar for one hour. The extracts were free of water and were analyzed directly with the IR method. A laboratory evaluation of the method was carried out by producing oil films of known thicknesses by placing known weights of crude oil on top of distilled water in Petri dishes of known surface areas. These

films were then sampled by the field method, except that smaller squares of the blotting paper were used. The results in Table I-C show average recovery of 96.2%. The losses are probably due to incomplete extraction from the paper, which was indicated by a residual greyish color in the paper after extraction. Additional contact with fresh solvent for a 24-hour period did not recover additional oil from the pads, nor did it remove the grey residual colour. The observed scatter in the results is probably due to uncertainties in the actual adsorption step. Occasionally, small areas of the paper appeared oil-free, indicating either inhomogeneities in the oil film, or, more probably, hydrophilic impurities in the paper. It is important to note that many of the laboratory films were non-homogeneous, containing blotches, streamers, heavy oil concentrations, or thin spots. This apparently did not affect the measurements as the irregularities were small relative to the size of the absorbent pad.

TABLE I-B

Laboratory Tests of Sediment Extraction Method

Dry wt. of Sediment (g)	Oil added (mg)	Concentrations in CCl ₄		
		----- (mg/10 mls) -----		
		Calculated	Found	% Recovered
500.2	305.0	30.50	30.91	101.3
500.3	269.4	26.94	25.75	95.6
500.0	279.1	27.91	25.75	92.3
500.7	292.8	29.28	27.94	95.4
500.0	274.3	27.43	25.75	93.9

Recovery statistics:

$$n = 5$$

$$\text{Ave. recovery, } \bar{x} = 95.7\%$$

$$\text{Std. deviation, } s = 3.40$$

Dry wt. of Sediment (g)	Dispersant added (mg)	Concentrations in CCl ₄		
		----- (mg/10 mls) -----		
		Calculated	Found	% Recovered
500.3	223.0	22.3	21.67	97.2
500.0	241.6	24.16	22.48	93.0
500.3	175.6	17.56	16.29	92.7
500.0	214.2	21.42	20.09	93.8
500.0	249.5	24.95	23.55	94.4

Recovery statistics:

$$n = 5$$

$$\text{Ave. recovery, } \bar{x} = 94.2\%$$

$$\text{Std. deviation, } s = 1.79$$

TABLE I-C

Laboratory Evaluation of Sampling
and Analysis of Surface Films

No.	Film thickness, μ		Oil in pad, mg		
	Calculated	Measured ¹	Calculated	Found	% Recovery
1	17.3	16.8	54.7	53.1	97.0
2	6.1	6.7	16.8	18.5	110.1
3	4.8	4.7	10.8	10.5	97.2
4	4.1	4.2	62.5	63.7	101.9
5	3.0	3.0	11.5	11.9	103.5
6	6.4	5.7	20.3	17.9	88.2
7	12.0	10.6	42.2	37.4	88.6
8	4.8	4.4	17.6	16.2	92.0
9	9.4	8.3	34.8	30.7	88.2
10	13.2	12.1	48.1	44.2	91.1
11	20.2	18.9	88.2	82.7	93.8
12	48.9	51.8	213.6	226.4	106.0
13	102.9	92.9	449.8	405.9	90.2
14	78.5	79.4	342.9	347.3	101.3
15	224.7	196.0	982.1	856.5	87.2
16	25.1	26.5	109.7	115.8	105.6
17*	47.8	44.4	307.1	285.4	92.9

Statistics of % recovery values:

n = 17

Average, n = 96.2%

Standard deviation, s = 7.2%

* Single test with Bunker C

¹ Thickness = Oil wt. x Oil density/Area

APPENDIX II

UV Analysis of the Field Samples

All UV spectra were obtained with a Unicam SP 1800 spectrophotometer using a 10 mm silica cell. While some of the preliminary tests were made of the crude oil and of some petroleum products in hexane or chloroform, the field samples were all analyzed in carbon tetrachloride solvent versus air.

The spectra of Norman Wells crude oil and three petroleum products are shown in Figure II-1. The concentrations producing these spectra indicate that UV absorbances of these products increase in the order: gasoline No. 2 fuel oil crude oil Bunker C. Since the UV absorbances in this region may be related to aromatic structures, the "aromaticity" of these products is also presumed to increase in the same order. A plot of the absorbance/concentration values (A/C), at selected wavelengths is given in Fig. II-2 where the A/C term may be considered as a measure of relative aromaticity. At a given wavelength this ratio may be used to compare the aromaticity of different oils, or to follow changes in the aromaticity of one oil as a function of degradation processes. A comparison of the absorbances at higher wavelengths, e.g., 280 and 320 μm , could provide clues about the nature of the aromatic content of the oils since the absorbances at higher wavelengths are normally indicative of condensed aromatic compounds.

In the field study, the large number of samples and analyses limited our survey to the measurement of absorbances at 280 nm. The A_{280}/C ratios were then considered as indicators of changes in the aromaticity of the oil during the experiment.

Figure II-1. UV spectra of some petroleum products.

UV SPECTRA OF SOME PETROLEUM PRODUCTS

OIL	SOLVENT	CONC.
GASOLINE	HEXANE	1.192 g/L
No. 2 FUEL OIL	HEXANE	0.159 g/L
CRUDE OIL	HEXANE	0.0737 g/L
BUNKER C	CHLOROFORM	0.0179 g/L

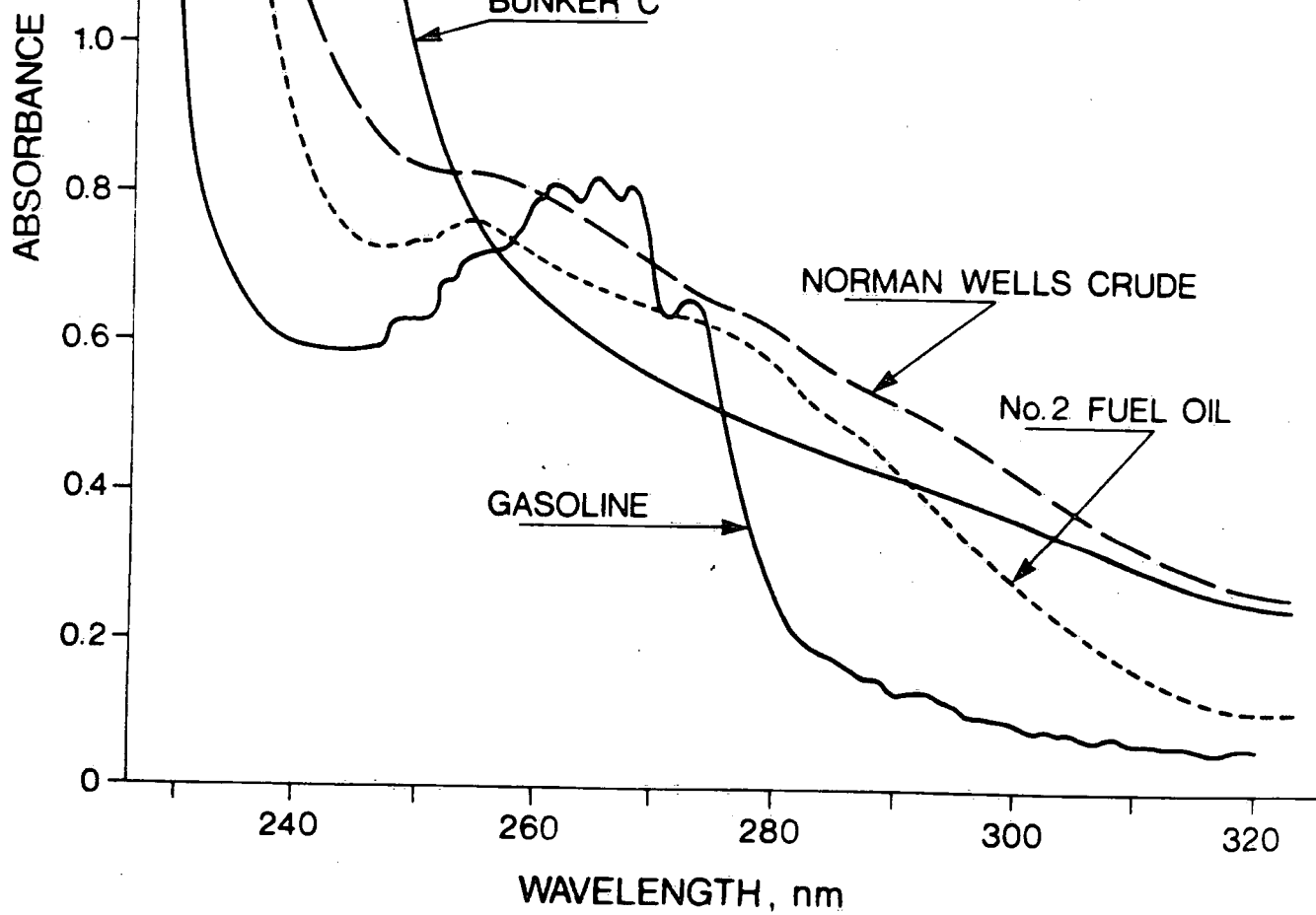
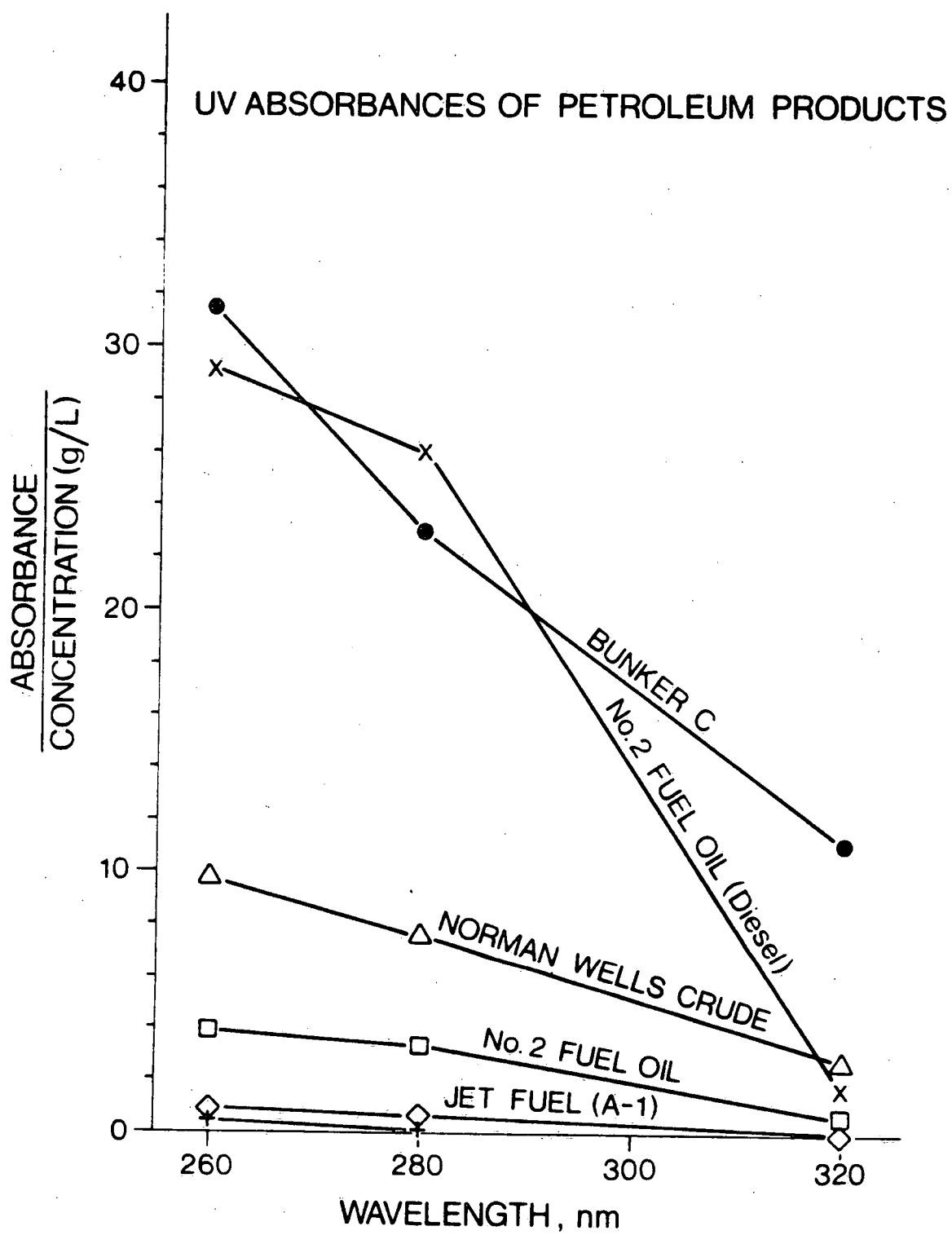


Figure II-2. Absorptivity of some petroleum products at selected wavelengths.



APPENDIX III

Periphyton Measurements

Table III-A lists the dry weights and the ash weights of the attached material in the ponds. These materials were obtained from vertically-supported sand-blasted plexiglass plates in the bottom of all ponds. Each plate had dimensions of 7 cm x 7 cm x .5 cm and at least two were collected at each sampling time (as denoted in the table) from each pond. The periphyton was brushed off the plate by first using a soft-bristled toothbrush, then rinsed into a wide-mouth 250 ml bottle containing 3 ml of modified Lugol's solution (1). The more strongly adhering material was brushed into the same bottle with a "hard-bristled" toothbrush. After returning the samples to the laboratories, the filamentous material and water were placed individually in a Vitreous blender for one minute and then transferred back into the original sample bottle with final volume being adjusted to 200 ml. An aliquot was then passed through a pre-washed, pre-heated (500°C) and pre-weighed filter paper (Whatman GF.C). The residue was left overnight in a drying oven set at 85°C and weighed for the dry weight. The filter paper was then dried for 2 hours at 500°C and the filter paper weighed again after cooling in a dessicator to obtain the ash-free weight.

After treatment, the results from the oil-treated pond were similar to those from the control pond. The weights from pond 3, one of the oil-dispersant ponds, were several times higher than those in the control or oil-treated ponds. The weights from pond 1, the other

oil-dispersant treated pond were several times higher than those from pond 3. Although the results from pond 1 were similar to those from the oil-treated and control ponds after a year, the values taken from pond 3 (oil-dispersant) were still significantly higher than any other pond.

- (1) C. Saraceni and D. Ruggiu, in "A Manual on Methods for Measuring Primary Production in Aquatic Environments, R.A. Vollenweider Ed., IBP Handbook No. 12, Blackwell Scientific Publications, Oxford, London, Edinburgh, Melbourne, 2nd Edition, p. 7.

TABLE III-A

Weight of Periphyton per Unit Area
(g/m²)

Date	Day	Pond 1		Pond 2		Pond 3		Pond 4	
		Dry Weight	Ash Weight	Dry Weight	Ash Weight	Dry Weight	Ash Weight	Dry Weight	Ash Weight
28/6/78	-7			20.78	15.16	7.08	3.41	9.33	4.92
1/8/78	28	14.2	9.18	10.79	6.92	27.77	14.85		
28/8/79	55	89.53	27.96	21.09	11.56	39.03	8.26	14.63	6.54
26/9/78	83	642.1	564.2	54.25	42.07	123.1	61.68	29.96	14.38
24/10/78	111	708.5	617.9	48.33	30.51	183.2	124.6	40.36	27.52
21/11/78	139	927.2	792.8	52.82	32.55	224.5	137.9	23.79	11.91
13/3/79	251	647.5	549.4	59.65	36.75	206.5	97.99	65.26	35.92
22/5/79	322	120.0	91.15	112.2	67.34	365.4	217.9	75.88	42.68
23/7/79	385	64.2	31.40	68.2	46.1	229.2	124.1	67.1	33.5

Pond 1 and 3 Treated with Oil + Dispersant

Pond 4 Treated with Oil

Pond 2 Control

APPENDIX IV

Dissolved Reactive Silica Studies

Shortly after treatment of the ponds used in the oil-dispersant-ecosystem studies, high concentrations of dissolved reactive silica (DRS) were measured in both oil-dispersant treated ponds but not in the oil-treated or control ponds. To investigate the possibility that the dispersant was interacting with the sediment, two series of laboratory tests were initiated. Both tests made use of the sediment material in the ponds and the dispersant, Corexit 9527, but one series used distilled water and the other used filtered pond water.

Twelve large polyethylene pitchers were filled with 2.5 l of distilled water. Fifty g of sediment material sieved through a 2 mm mesh was added to six of the vessels and all pitchers were covered with large, clear, polyethylene bags ("Baggies") to prevent evaporation. After two weeks, the vessels were divided into four sets of three pitchers each - two sets with sediment and two without. To one set with sediment and one set without, sufficient dispersant was added from a stock solution to give a concentration of 10.1 ppm of dispersant in each of the six vessels. Just prior to the dispersant addition and on days 7, 14, 21, 35, 49, 63, 70, and 85, 50 ml aliquots were withdrawn, filtered and then analyzed for DSR.

2.5 L of filtered (0.45 μ) pond water was placed into eight other large polyethylene pitchers, and 40 g of sediment was sieved into six of these. Two smaller polyethylene pitchers were filled with 1.25 L of filtered pond water and were used as controls. All vessels were covered with clear polyethylene bags for the duration of the experiment. After two weeks, which allowed the sediment to settle, dispersant (10.1 ppm) was added to three vessels with sediment and to two without. This arrangement gave three vessels with sediment and dispersant, three with sediment only, two with dispersant only, and two smaller vessels as control. 50 ml aliquots were withdrawn, filtered and analyzed for DSR at the same times as the distilled water tests outlined above. The analyses were carried out by Ship Support Services, Water Quality Branch (Ontario Region), EMS.

The pH was checked at the conclusion of the experiment and there were no major differences between the various sets of vessels using water from the same source. Also, the dispersant was found to remain mainly in the aqueous phase after 84 days.

The results are presented in Table IV-A. Pond water has higher DRS values than the distilled water and the vessels with added sediment had higher DRS values than those without. However, addition of dispersant had no effect on the DRS concentrations.

Dissolved Reactive Silica Concentrations (ppm)

Treatment	Days After Addition of Dispersant										n	Final pH
	0	7	14	21	35	49	63	70	85			
(a) Distilled Water												
i) No Treatment	0.004	0.003	0.005	0.010	0.009	0.008	0.010	0.010	0.004	3	6.7	
ii) Dispersant	0.007	0.005	0.007	0.030	0.036	0.022	0.020	0.040	0.007	3	6.8	
iii) Sediment	0.497	0.599	0.675	0.760	0.861	0.928	0.937	0.917	0.497	3	6.7	
iv) Dispersant + Sediment	0.474	0.575	0.653	0.750	0.837	0.862	0.890	0.897	0.474	3	6.5	
(b) Pond Water												
i) No Treatment	0.315	0.321	0.330	0.345	0.397	0.376	0.375	0.370	0.315	2	7.2	
ii) Dispersant	0.313	0.316	0.335	0.375	0.416	0.384	0.365	0.375	0.315	2	6.8	
iii) Sediment	0.675	0.793	0.876	1.01	1.10	1.11	1.09	1.07	0.677	3	7.0	
iv) Dispersant + Sediment	0.639	0.734	0.822	0.915	1.08	1.07	1.08	1.08	0.628	3	7.4	

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