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The Fate of Oil and Dispersant Mixtures in Freshwater

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THE FATE OF OIL AND DISPERSANT MIXTURES IN FRESHWATER

by

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ABSTRACT

A series of man-made ponds, with a fine-gravel sediment and containing mesotrophic water, were used to compare the fate, distribution and composition of oil/dispersant mixtures. Oiled and controlled conditions were established, using Norman Wells crude oil and Corexit 9527 as the dispersant. The 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.

RÉSUMÉ

Dans les étangs mésotrophes artificiels, à substrat de gravier fin, nous avons comparé le devenir, la répartition et la composition de mélanges de brut de Normal Wells et d'un dispersant (Corexit 9527). Pendant un an, nous avons prélevé systématiquement des échantillons de l'eau de surface, de l'eau sous-jacente, des sédiments, des parois et des organismes qui y étaient fixés. Durant la plus grande partie de l'expérience, la colonne d'eau n'a contenu qu'un peu de brut, car le brut dispersé a remonté rapidement en surface pour finalement couler au fond. Nous avons examiné les caractéristiques chimiques et la composition des pellicules huileuses; les pellicules minces contenaient plus de groupements carbonyles et plus de dispersant que les épaisses. Le bilan final du brut a révélé qu'on avait perdu trace de plus de brut dans les étangs qui contenaient les mélanges de brut et de dispersant que dans l'étang sans dispersant. Rien ne permet de croire que le dispersant a transformé la composition du brut au cours de l'expérience, et dans tous les étangs, celui-ci s'est transformé de façon similaire, indépendamment du traitement.

FOREWORD

This study was undertaken by E. Nagy, B.F. Scott and J. Hart of the National Water Research Institute, for the Environmental Protection Service. Mr. C. Ross of EPS acted as scientific authority for the project.

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1 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 when mechanical methods cannot be deployed or when nesting grounds need protection, dispersant use may be contemplated. The use of dispersants in such situations is contingent upon their passing certain laboratory tests which allow substances to be ranked according to their effectiveness and toxicity. This also forms the basis for an acceptability list (EPS, 1973). What the testing does not provide, is information on the long-term effectiveness as well as on the fate and effect of the oil/dispersant mixture.

This study was initiated to observe the fate and ecological effect of an oil/dispersant mixture in a selected freshwater system over an extended period of time. Also, the effectiveness of the dispersant under the test conditions and the ability of the system 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, DO, ATP), phyto-plankton, periphyton, fungi, bacteria, protozoa, zooplankton, and zoobenthos. This report deals exclusively with the composition, distribution and fate of the oil and oil/dispersant mixtures.

2 METHODS

The site of the ponds was at the University of Toronto's Institute for Environmental Studies Field Station at Baie du Doré, near Douglas Point Nuclear Power Plant on Lake Huron (see Figure 1). Four large I-beams divided a rectangular pit 22.5 by 9 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 are shown in Figure 2. Water from nearby Lake Huron was pumped into 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 in several other studies (Snow and Scott, 1975; Hellebust et al., 1975; Scott and Shindler, 1978).

In the oil-treated pond, 6 L of oil were poured onto the water surface from a height of 1 m. One litre of the dispersant (Corexit 9527) was added to 6 L of oil, hand-stirred with 13 L 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 L 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 formed over the ponds, 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.

Lake Huron

BAIE DU DORÉ
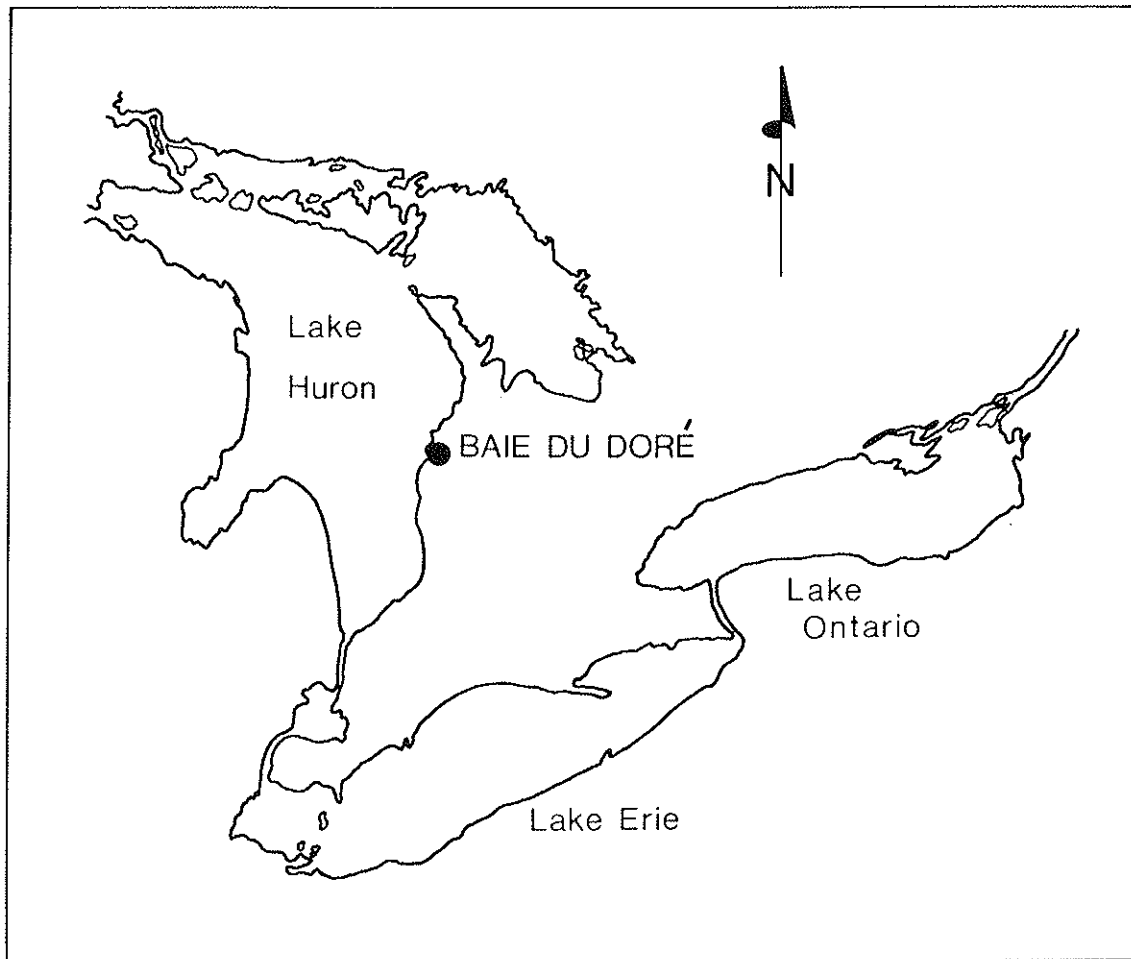
Lake Ontario

Lake Erie

N

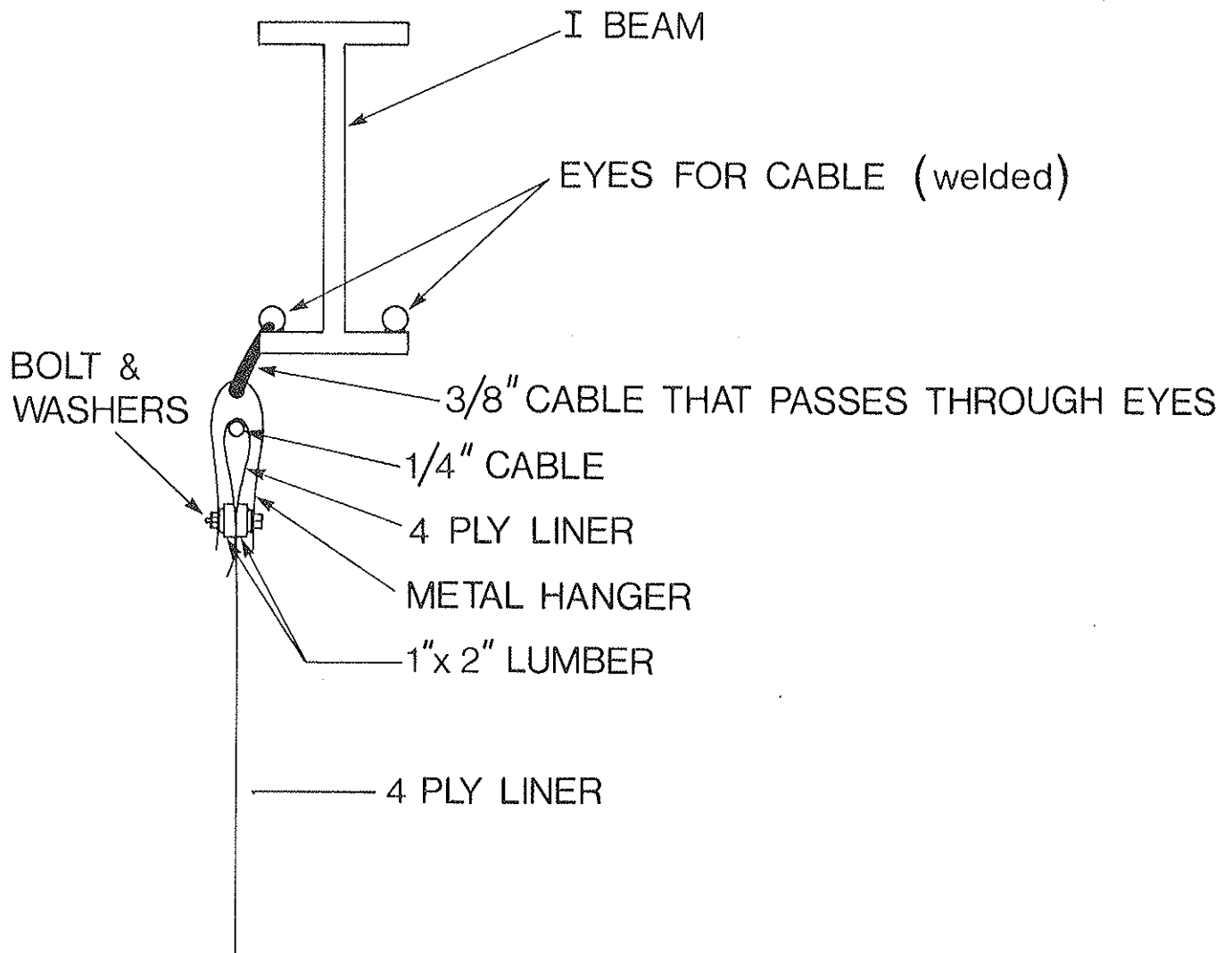FIGURE 1   LOCATION OF EXPERIMENTAL PONDS

FIGURE 2   REPRESENTATION OF LINER ATTACHMENT

Surface slicks, whether in the form of thick oil (streamers or lenses) or thin films (sheens), were sampled by placing a 100 by 100 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 infrared (IR) and ultraviolet (UV) spectroscopy, as well as column chromatography (see appendices). 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 slick 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 L 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 litre of the contents was placed in a 2 L separatory funnel to which 300 g sodium chloride (NaCl) was added. Ten mL carbon tetrachloride (CCl_4) was added and the mixture was then 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. Infrared 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 removed by gently scraping the liner and transferring the material to a small storage bottle. The material was analyzed in the laboratory after the 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 1.4 L empty juice can fastened to the end of a 3 m long pole. Replicate samples were not taken until the end of the study period, so that the benthic community would not be destroyed. The sediment samples were placed in 1 L 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 the dry weight (see 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

6

PLAN OF FINAL SAMPLING OF POND SEDIMENT

o – JULY 24, 1979
□ – AUG. 28, 1979

CATWALK

#1   #2   #3   #4

SLOPE

METRES 0   2   4   6
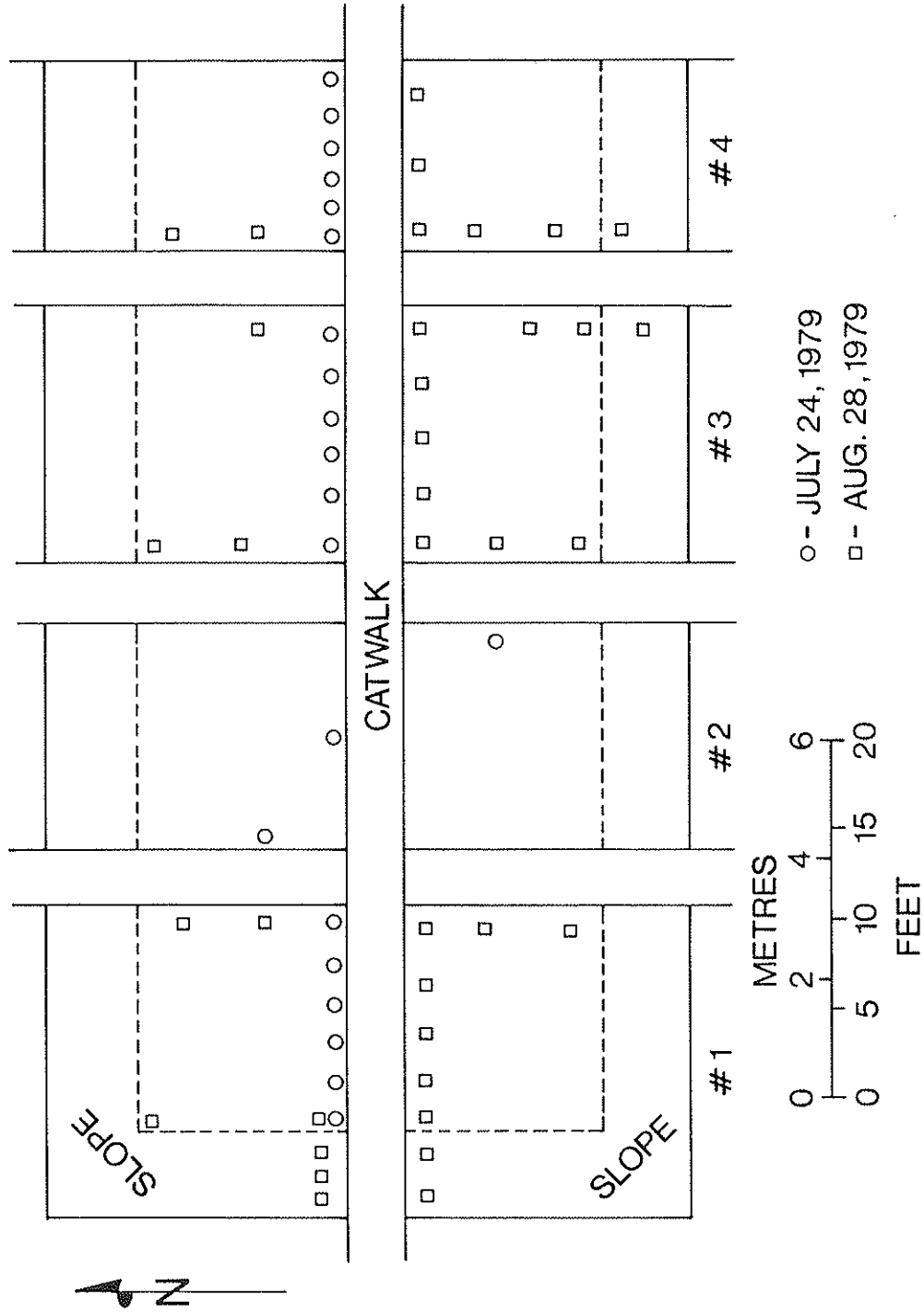FEET   0   5 10 15 20

FIGURE 3   SEDIMENT SAMPLING LOCATIONS

that date, samples were removed on a line parallel to the catwalk at 0.6 m 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 the same as the 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 (Skoog and West, 1969). The selection of this method resulted from preliminary studies using benzene, naphthalene and anthracene solutions shown in Appendix III.

Column chromatography was performed by filling a 20 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. Thirty 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. Gas chromatographic operating conditions are shown in Table 1.

Water chemistry parameters of dissolved organic carbon and dissolved reactive silica were determined using standard methods (IWD, 1974).

TABLE 1   GAS CHROMATOGRAPHIC CONDITIONS

Instrument:	Hewlett-Packard 5750 equipped with dual column
Column:	1.8 m x 0.31 cm, 5% OV-1, AWMCS 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

3   RESULTS AND OBSERVATIONS

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

3.1   Distribution and Concentrations

3.1.1   Oil-Treated Pond (Pond 4).

At the time of the spill, the oil spread from the point of addition and within an hour, surface oil of varying thicknesses covered the entire pond.   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 thicknesses 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 is given in Section 3.2.

The concentrations of oil in the water column plotted as a function of time are depicted in Figure 5.   The concentration was highest one hour after the treatment, and it decreased rapidly to 1 ppm within one day.   Concentrations of about this level were measured during the remainder of the experiment.   As shown in Figure 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 it 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.

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 the qualitative studies on oil composition given in Section 3.2. 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, where the oil and dispersant concentrations recovered from the sediment samples of all ponds during the experiment are listed.   The values from the treated ponds were usually greater, by an order of magnitude, than the background hydrocarbon levels of the control pond.   The
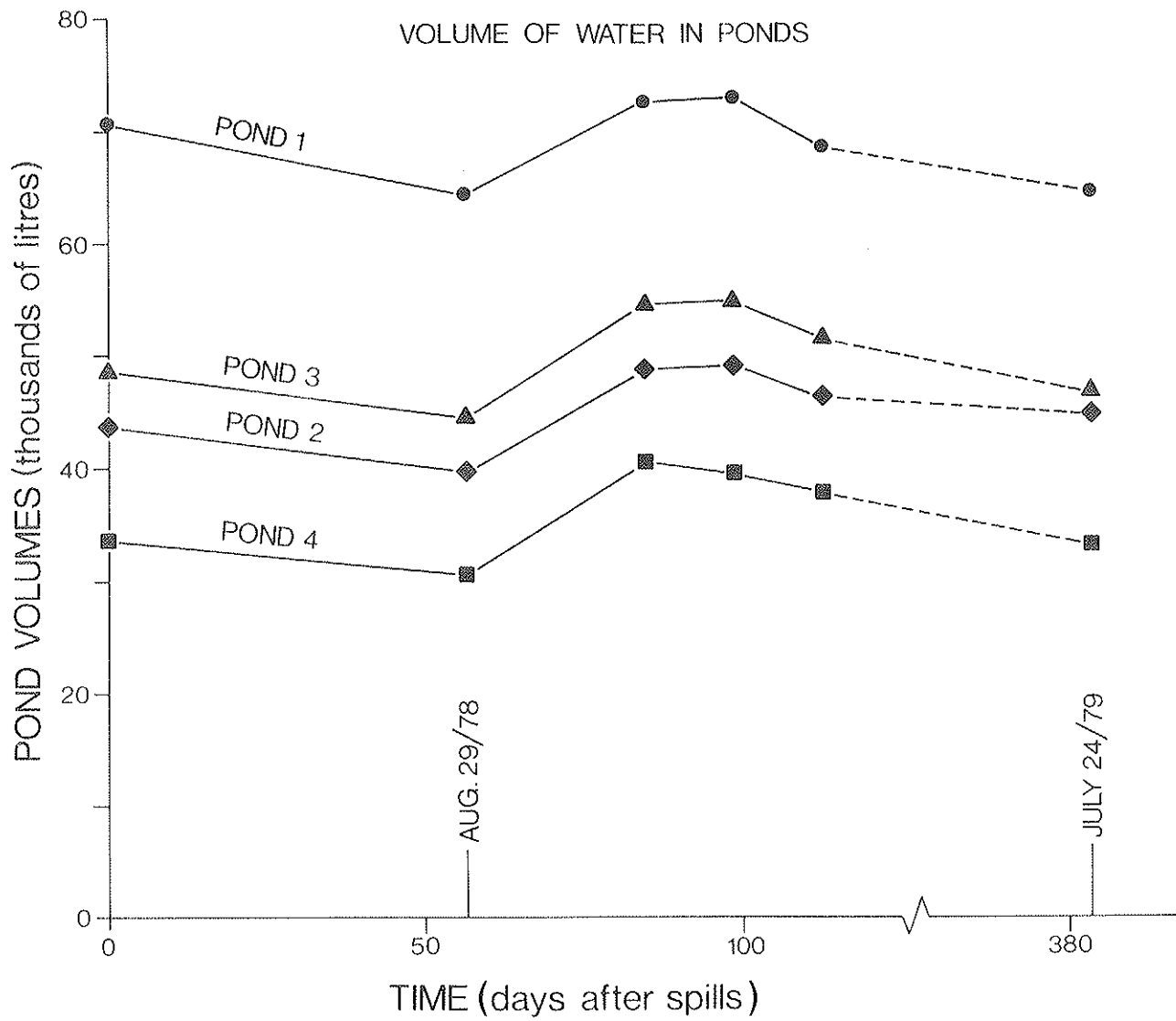
FIGURE 4   WATER VOLUMES IN PONDS

TABLE 2   SLICK THICKNESS MEASUREMENTS

Time after "spill"	Oil pond (Pond 4)	Measured thickness (micrometres) 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 26.2 316.0	5.6 17.5 354.0	0.35 43.2 355.0
7 days	10.8 346.0	31.7 147.9	30.2 223.2
14 days	0.43 101.0	7.5 41.1	0.85 55.6
27 days	0.21	0.075	0.65 47.8
41 days	0.136	0.043	0.189
55 days	0.05	0.1	0.09
69 days	0.051	0.006	0.022
83 days	0.062	none	none
97 days	0.006	none	none
111 days	none	none	none

- multiple values indicate the presence of different slicks on any given sampling date.

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. On 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
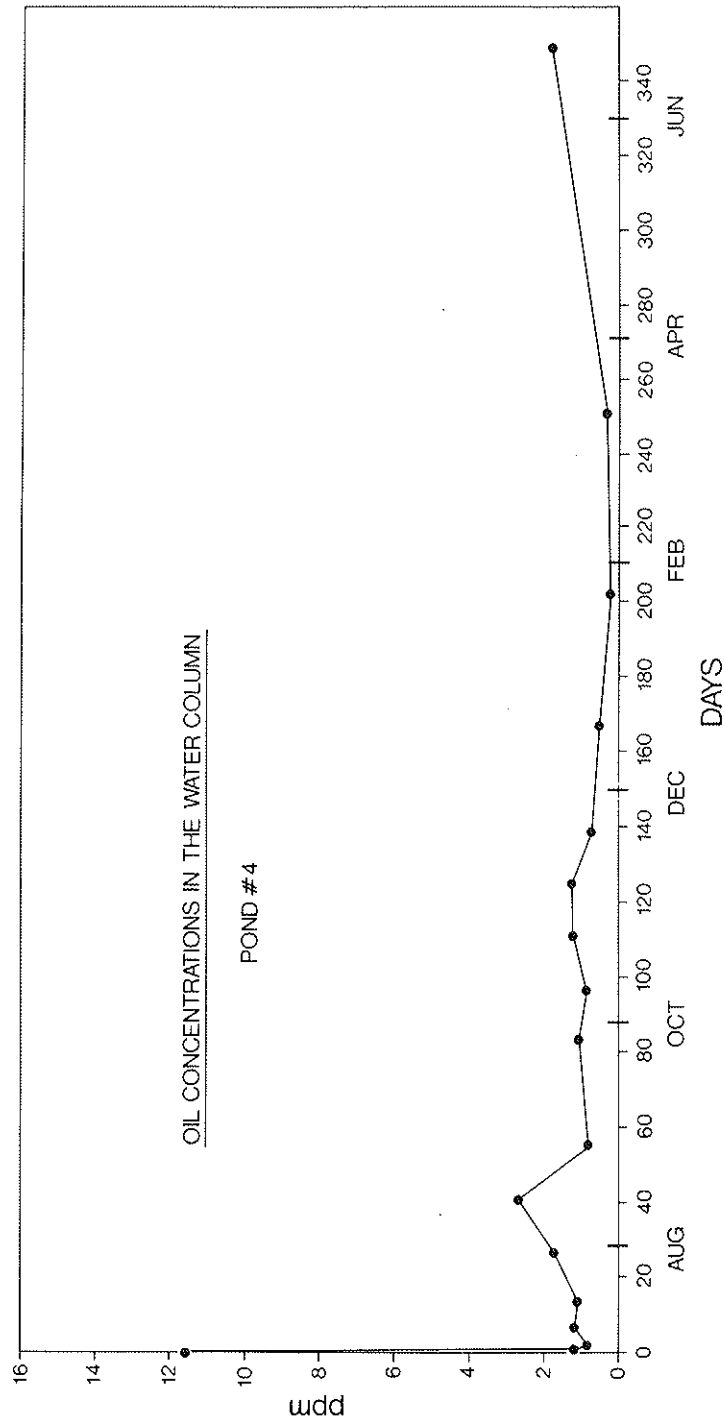
FIGURE 5   OIL CONCENTRATIONS IN THE WATER COLUMN OF
THE OIL- TREATED POND

TABLE 3   CONCENTRATION OF OIL OR OIL PLUS DISPERSANT IN SEDIMENT SAMPLES

Time (days)	Pond 1 oil and dispersant (mg/g)	Pond 2 control (mg/g)	Pond 3 oil and dispersant (mg/g)	Pond 4 oil (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	4.410
125	0.029		0.028	2.210
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

layers of sediment. Figure 6 shows the distribution of oil on the north-south axis of the ponds and Figure 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 there, 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 examining 0.3 m 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.

FIGURE 6   OIL DISTRIBUTION IN SEDIMENTS SHOWN ALONG THE
            NORTH-SOUTH AXIS

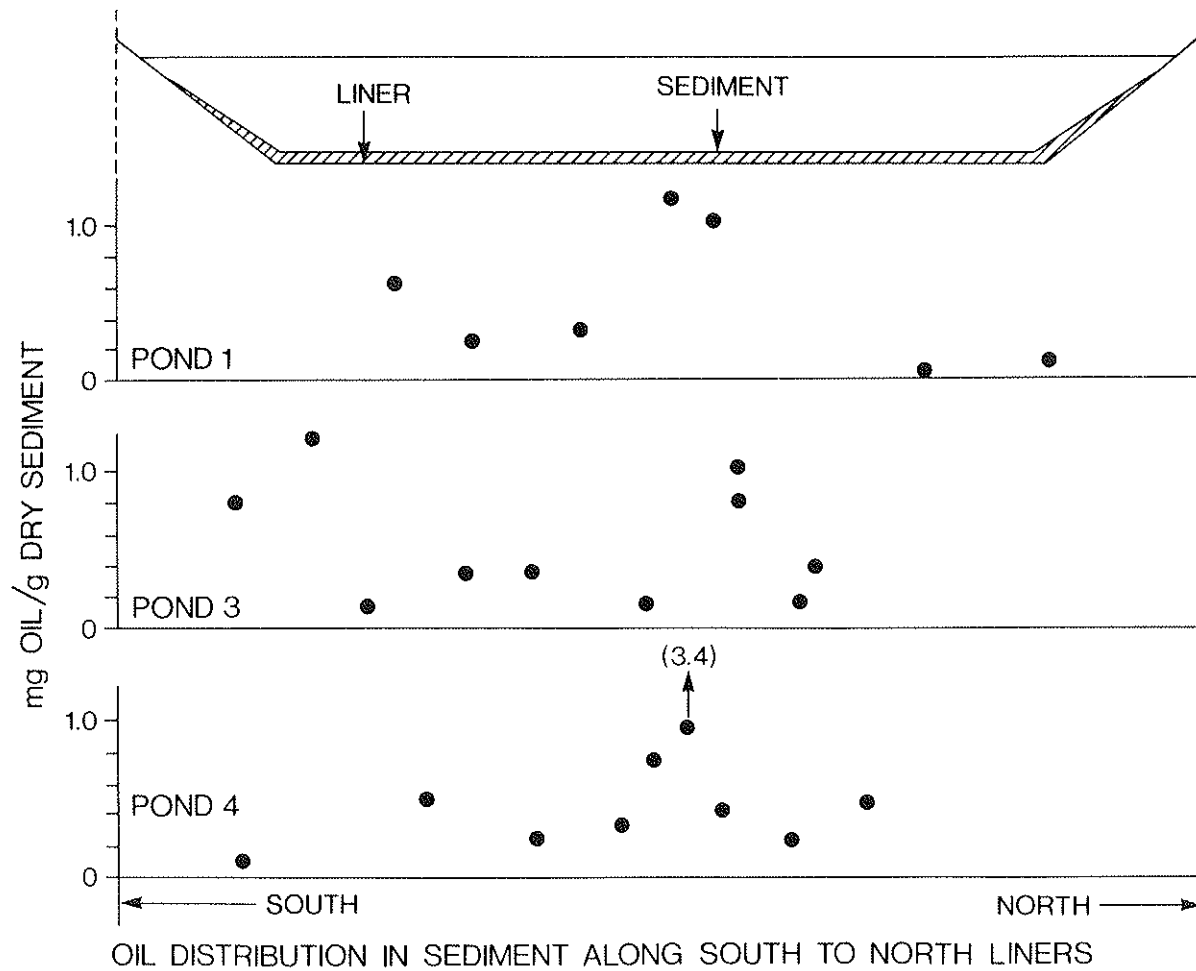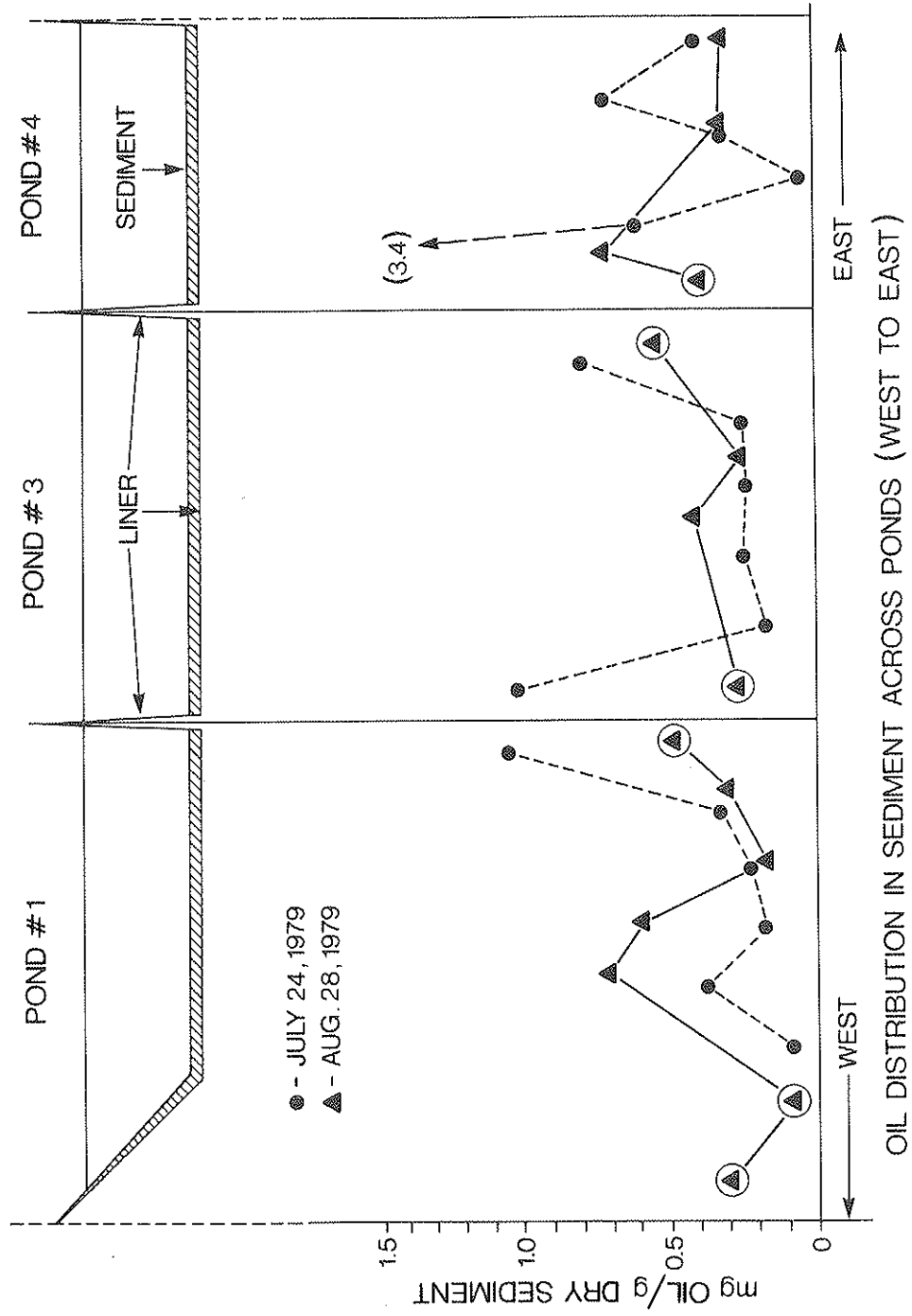FIGURE 7   OIL DISTRIBUTION IN SEDIMENT SHOWN ALONG THE EAST-WEST
AXIS (Ⓐ indicates an average of several values).

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.

The method used for this study was a simulated GLC distillation technique previously reported (Hart, unpubl. report, 1974). 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.

3.1.2   Oil/Dispersant Ponds (Ponds 1 and 3). The dark brown oil-in-water emulsion introduced at the centre of the 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 that was 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.

The surfacing of the oil during the first hour after treatment, left the top 5 to 10 cm of the water milky in appearance. This "milkiness" extended halfway 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 were visible to the naked eye 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 Figure 8. As anticipated, because of the larger volume of Pond 1, the values for this pond were slightly lower than those from Pond 3; the interior pond. There was an initial increase in the oil and dispersant concentration after the treatment. However, this slowly decreased to Day 111, when the oil concentrations were below 1 ppm in both ponds as were dispersant concentrations. The ratio of oil:dispersant in the water column was generally lower than the 5:1 value initially added.

TABLE 4a   FINAL OIL AND DISPERSANT ON POND LINER

Pond 1

Sample Number	Sample Location	Oil Found (mg/m²)	(mg/cm)	Dispersant Found (mg/m²)	(mg/cm)
203	east side, top, including 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:	Total Oil (g)	Dispersant (g)	B) From Linear Measurements: Total Length (cm)	Total Oil (g)	Dispersant (g)
Number	Total Area (m²)					
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 (mg/m^2)	(mg/cm)	Dispersant Found (mg/m^2)	(mg/cm)
206	west side, top, including water line	1412	6.46	52	0.24
207	west side, mid-section	–	–	482	1.84
208	west side, bottom	1535	4.8	83	0.42
209	east side, top half	1694	12.05	33	0.24
210	east side, bottom half	1851	16.86	(trace)	(trace)

Total Quantities in Pond

	A) On Area Basis	Total		B) From Linear Measurements	Total	
Number	Total Area (m^2)	Oil (g)	Dispersant (g)	Total Length (cm)	Oil (g)	Dispersant (g)
206	4.30	6.1	0.2	940	6.1	0.2
207	3.58	–	1.7	940	–	1.7
208	3.13	4.8	0.3	617	4.8	0.2
209	12.80	21.7	0.4	1800	21.7	0.2
210	5.64	10.4	–	617	10.4	–
Totals:		43.0	2.6		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, including 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

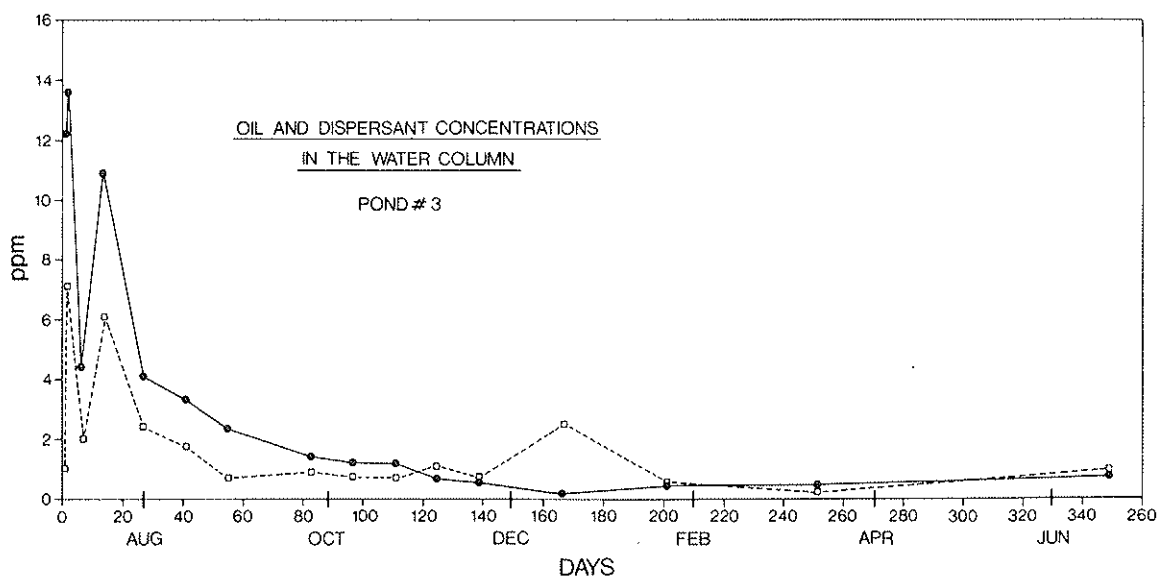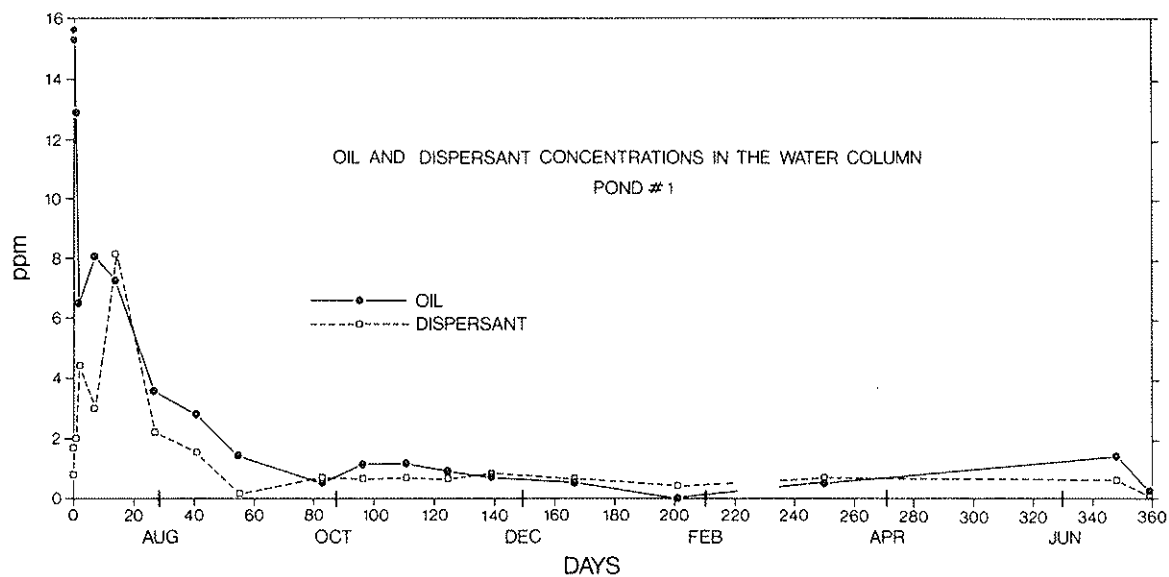| A) On Area Basis:			B) From Linear Measurements	
Number	Total Area (m^2)	Total Oil (g)	Total Length (cm)	Total Oil (g)
211	2.7	11.5	900	7.8
212	0.9	24.3	900	30.8
213	4.4	16.0	738	12.3
214	4.5	7.7	1520	18.2
215	0.9	1.3	738	8.3
Totals:		60.8		77.4

Average: 69.1 g oil

FIGURE 8   OIL AND DISPERSANT CONCENTRATIONS IN THE WATER COLUMNS
OF THE OIL/DISPERSANT TREATED PONDS

Figure 9 shows the results of the dissolved organic carbon measurements. For the oil/dispersant ponds, these values were much higher than the hydrocarbon values obtained from the IR spectroscopy technique (Figure 8). It is noteworthy that after Day 28, both parameters followed the same trends. After the initial decrease in concentrations from Day 28 to Day 138, there was 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 from 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 0.7 m; 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 much different from those found prior to freeze-up.

Twenty water quality parameters were monitored regularly in the ponds. Some have been previously reported (Scott et al., 1979) 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 at about Day 75 as shown in Figure 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 IV, were carried out to investigate the possible release of silica from the sediment by the dispersant. The results indicated that no such release occurred.

Oil:dispersant ratios, calculated from extractions of sediment samples taken during the experiment, are shown in Figure 11. Large variations between successive samples from the same pond may be caused by the heterogeneity in the sediment. The trend of the results, however, indicates 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 Figures 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.
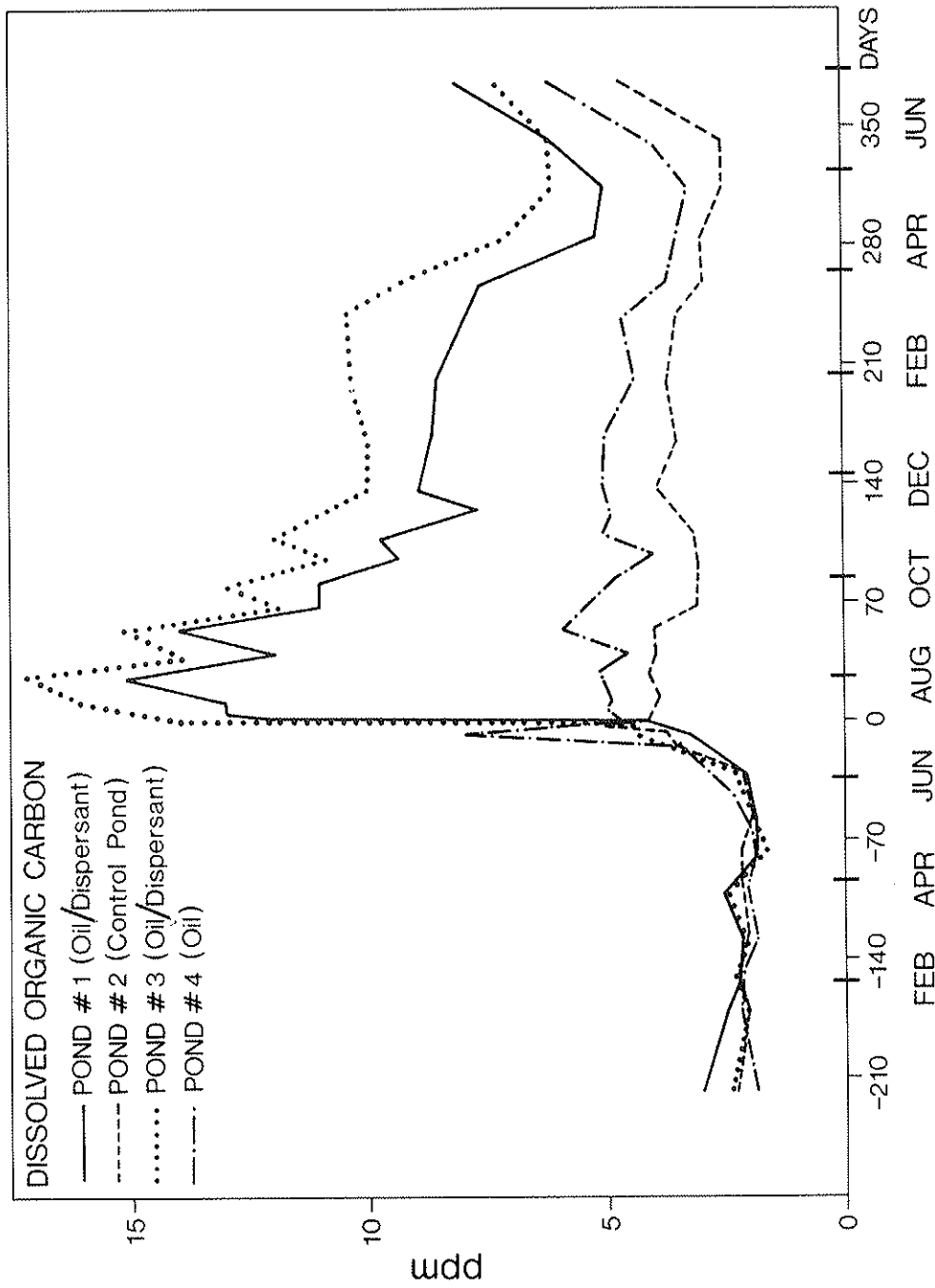
FIGURE 9   DISSOLVED ORGANIC CARBON CONCENTRATIONS IN WATER
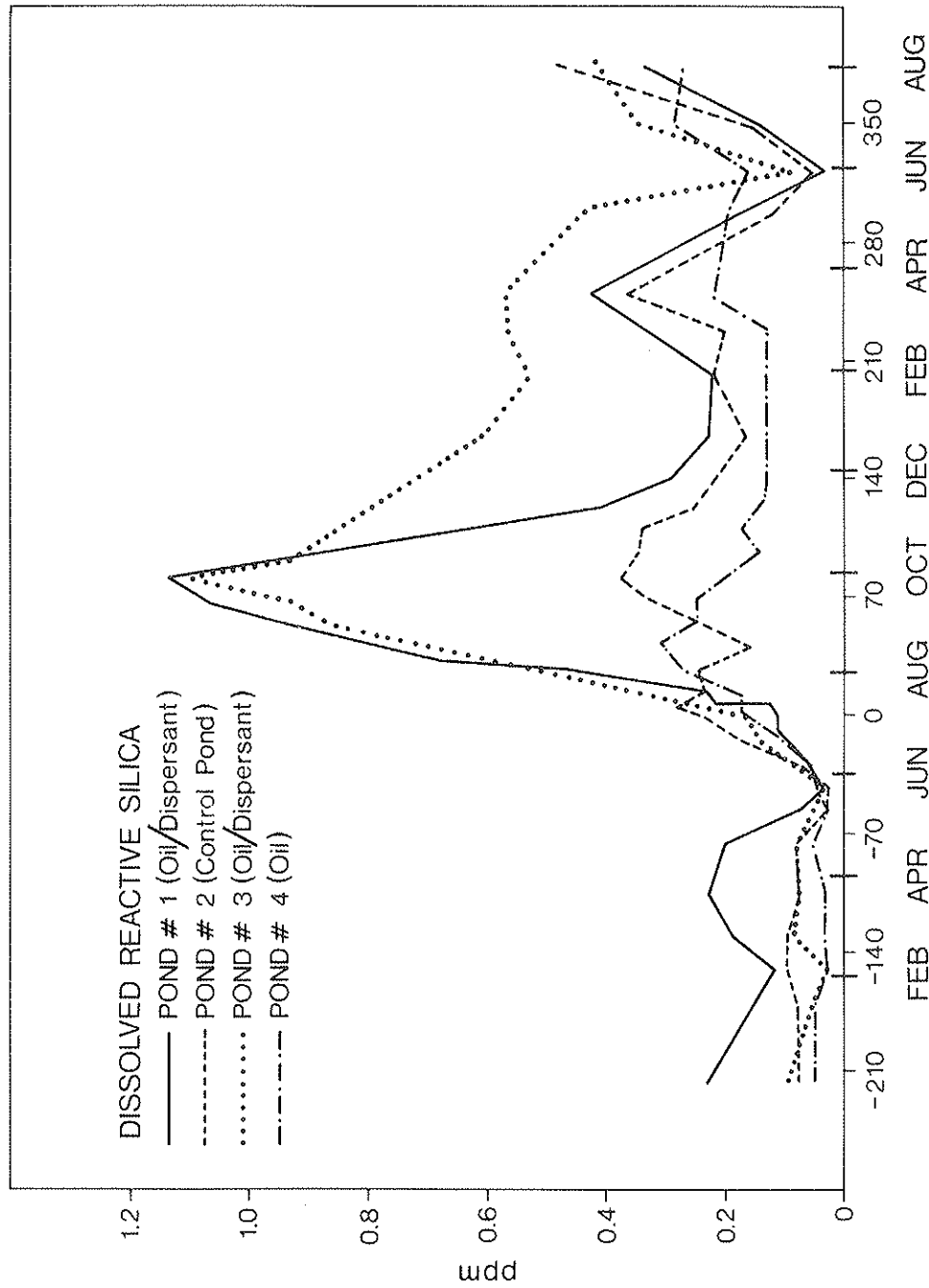COLUMNS OF EXPERIMENTAL PONDS

FIGURE 10   DISSOLVED REACTIVE SILICA CONCENTRATIONS IN WATER
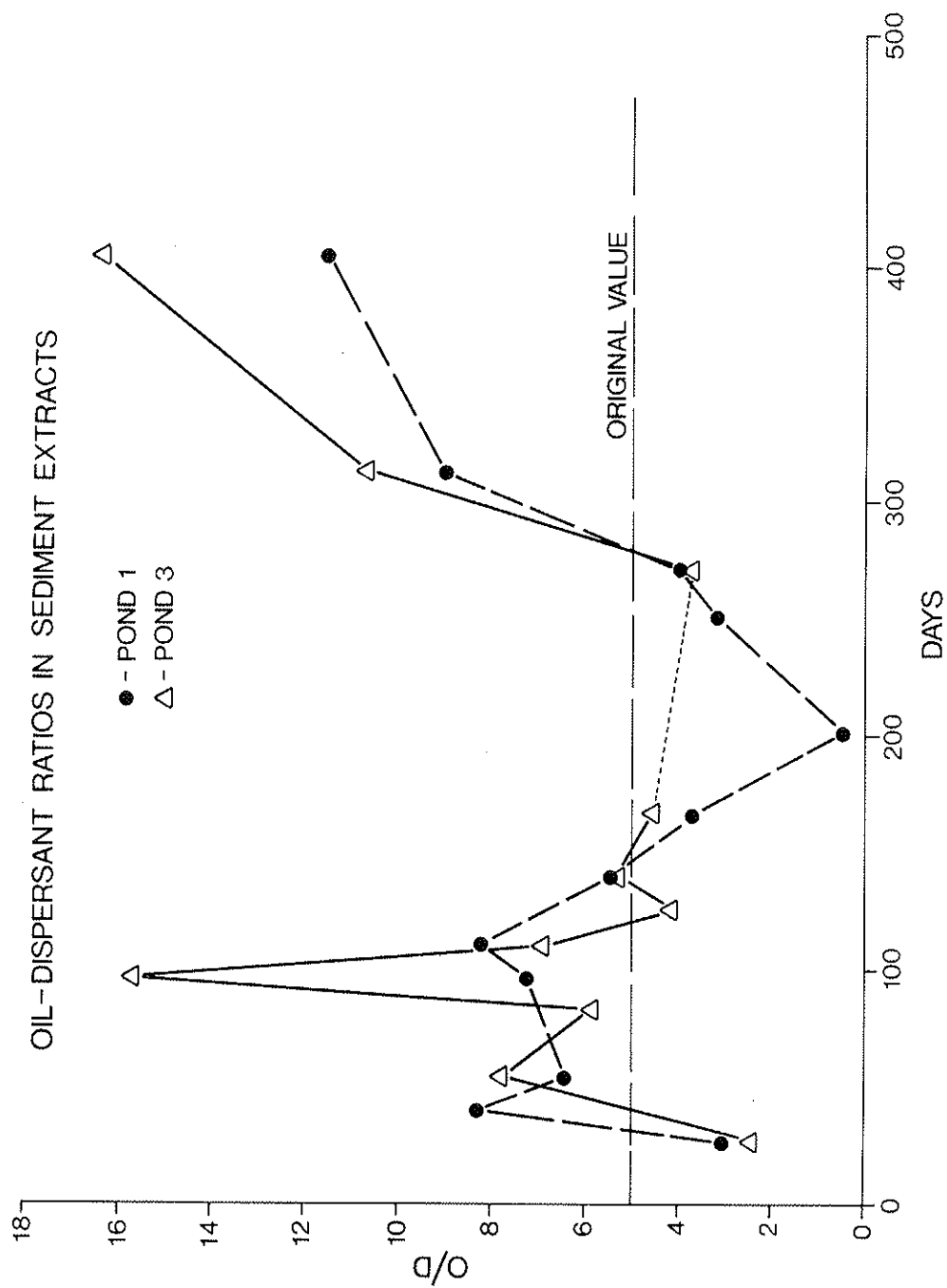COLUMNS OF EXPERIMENTAL PONDS

FIGURE 11   OIL:DISPERSANT RATIOS RECOVERED FROM SEDIMENT SAMPLES

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 pond. The amount of biotic material on the liner and over the bottom, was greater than that found in the oil-treated pond (Appendix III). Listed in Table 4 are the values of the oil and dispersant recovered from the liner.

TABLE 5   OIL AND DISPERSANT IN ATTACHED ALGAE

| Date (day after treatment) | Pond | Estimated Weights per Pond, (g) | | |
		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

The degree of evaporation of the oil in Ponds 1 and 3 was approximately 20%.

3.2   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 of the oil/dispersant ponds sampled on the same day.

The persistence of surface films is depicted in Figure 12, where the dashed line is an idealized representation of the diminishing areal extent of thin films in the 0.01 to 10 μm range. Films in this thickness range were observed throughout the period, but they became intermittent and generally smaller as time increased. As indicated in Figure 12, slicks on the oil/dispersant ponds disappeared earlier than on 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
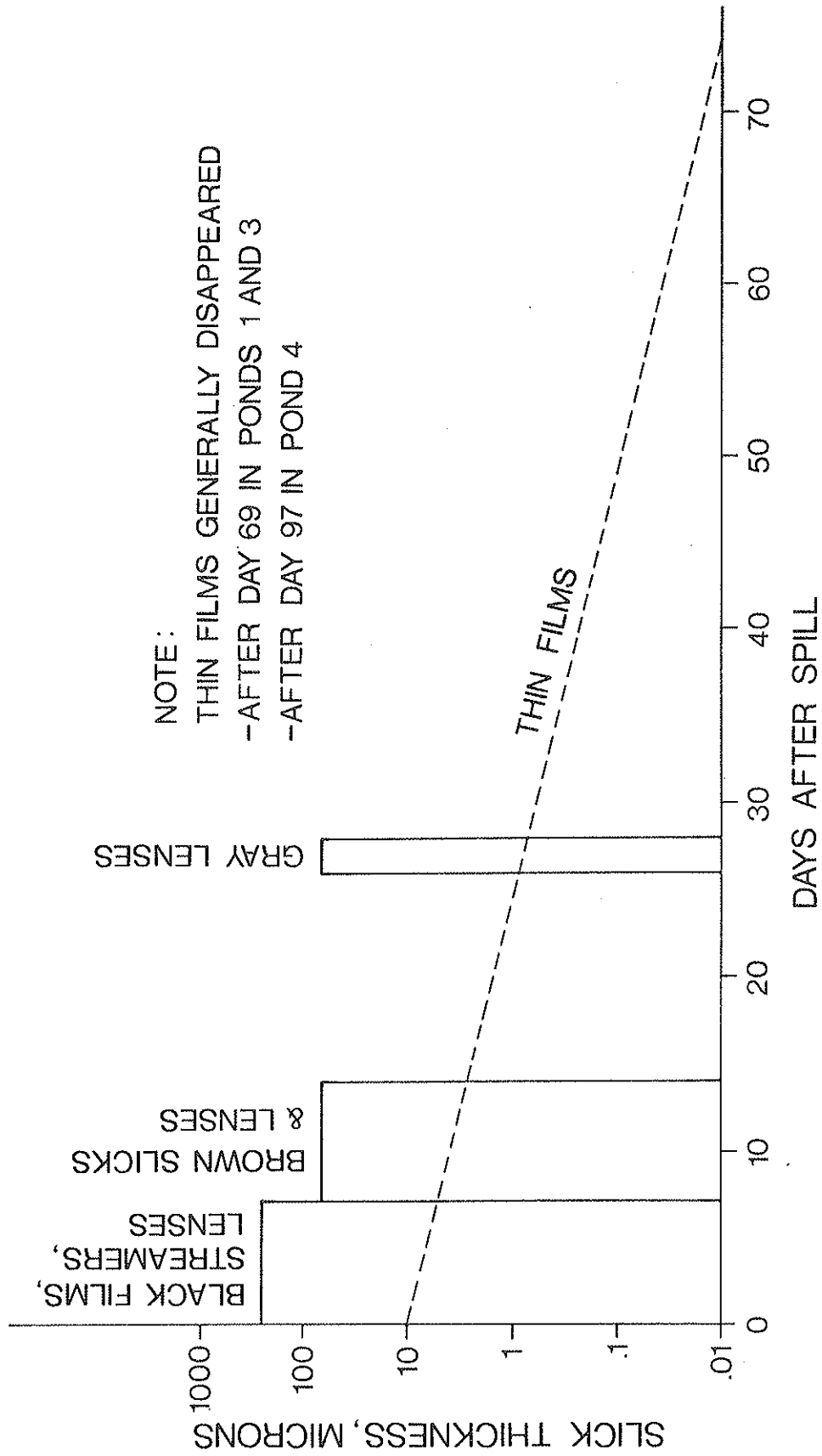
FIGURE 12   PERSISTENCE OF SURFACE FILMS

Ponds 1 and 3. The description of the slicks shown in Figure 12 is elaborated further in Figure 13, which shows the appearance of various slicks as a function of film thickness. Our observed colour-to-thickness relationship agrees with reported values, (Horstein, 1972) which are shown in the lower part of Figure 13.

Figure 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 is in the slick relative to the amount added and the thicker slicks contain predominantly oil released from the emulsified state.

Figure 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, Figure 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; however, it 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.

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. Figure 17, which illustrates the specific absorbances at 280 nm, shows a maximum at Day 125, after which the values level off. Measurements of the carbonyl group from the sediment samples using IR spectroscopy showed no overall trends.

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

Figure 19 illustrates the results obtained from sediment extracts treated by column chromatography. Results 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

FIGURE 13   APPEARANCE OF SURFACE FILMS
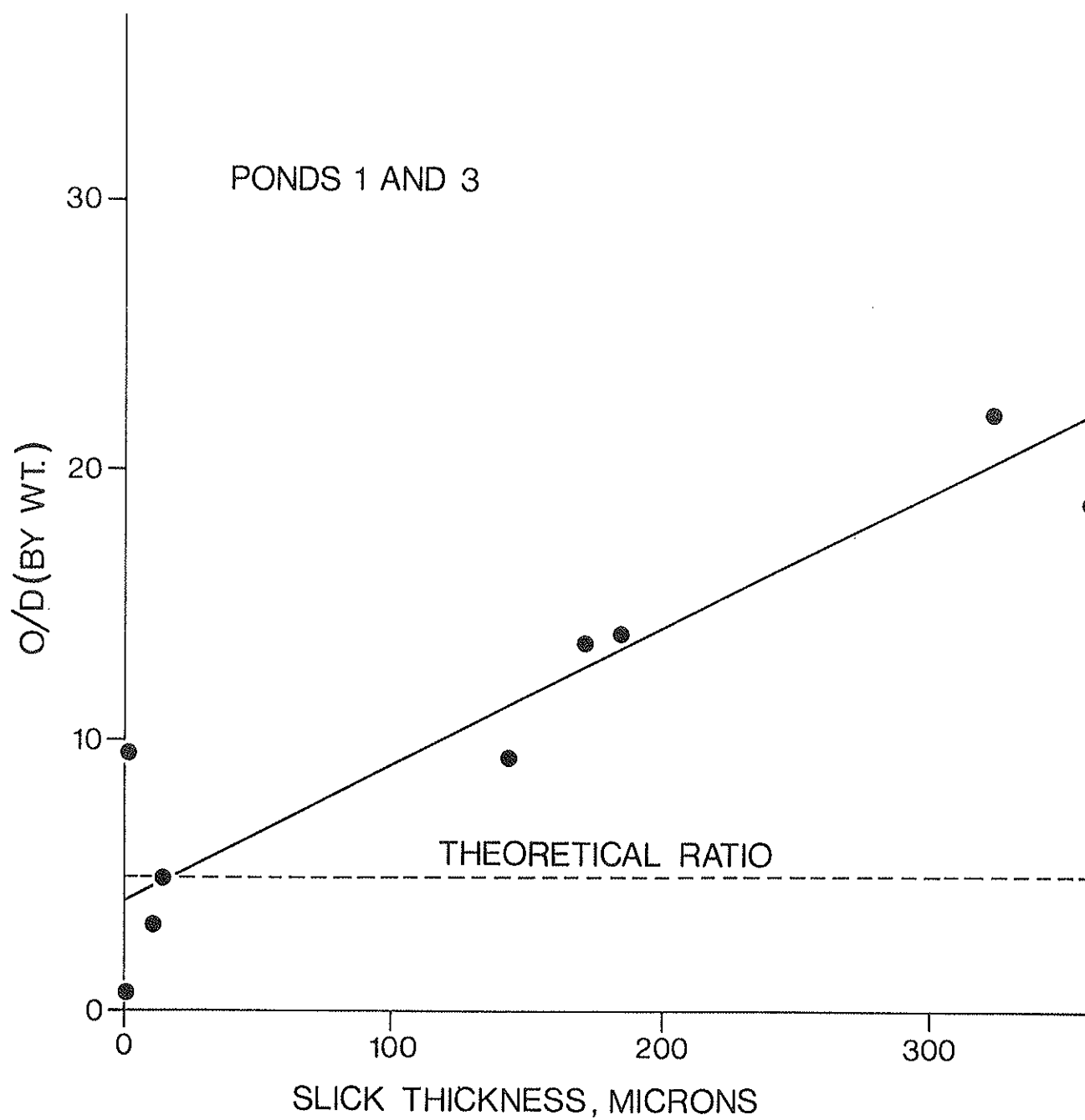
FIGURE 14   INITIAL OIL:DISPERSANT RATIOS OF SURFACE FILMS AS A
FUNCTION OF THICKNESS

30
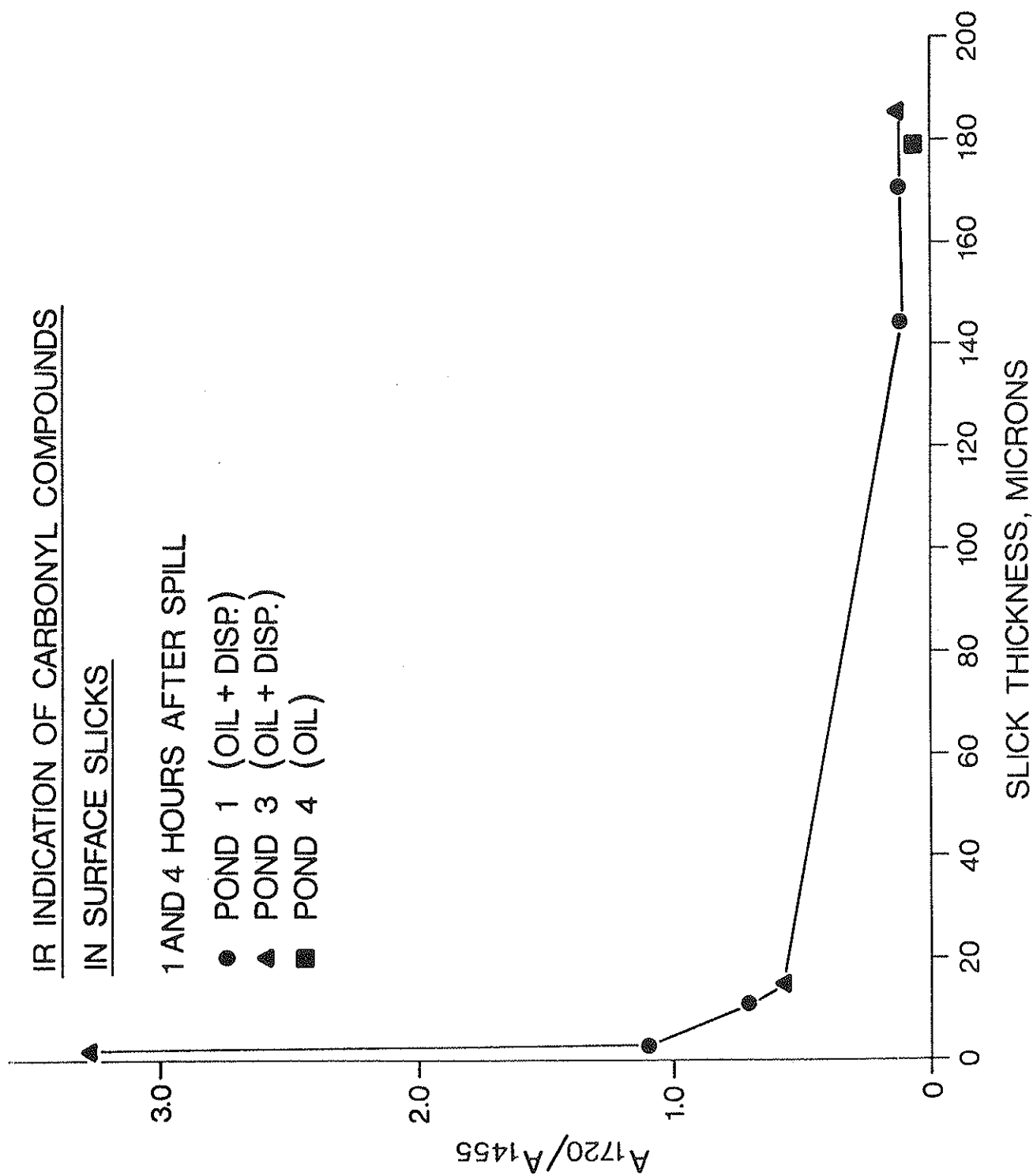
FIGURE 15   CARBONYL STRETCH ABSORPTION OF SURFACE FILMS
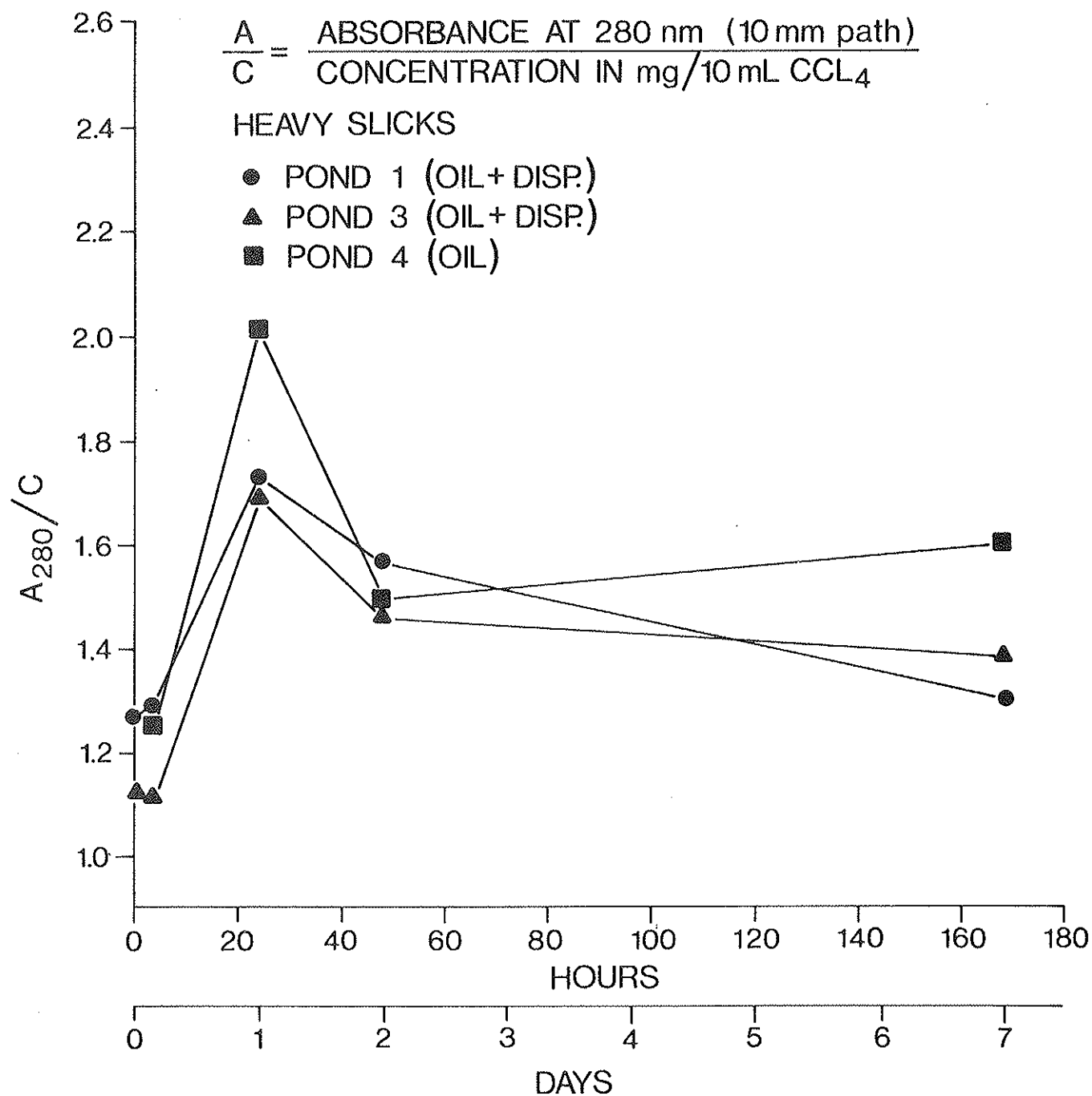
FIGURE 16   UV ABSORBANCE OF SURFACE FILMS (C is the concentration as determined by IR spectroscopy)
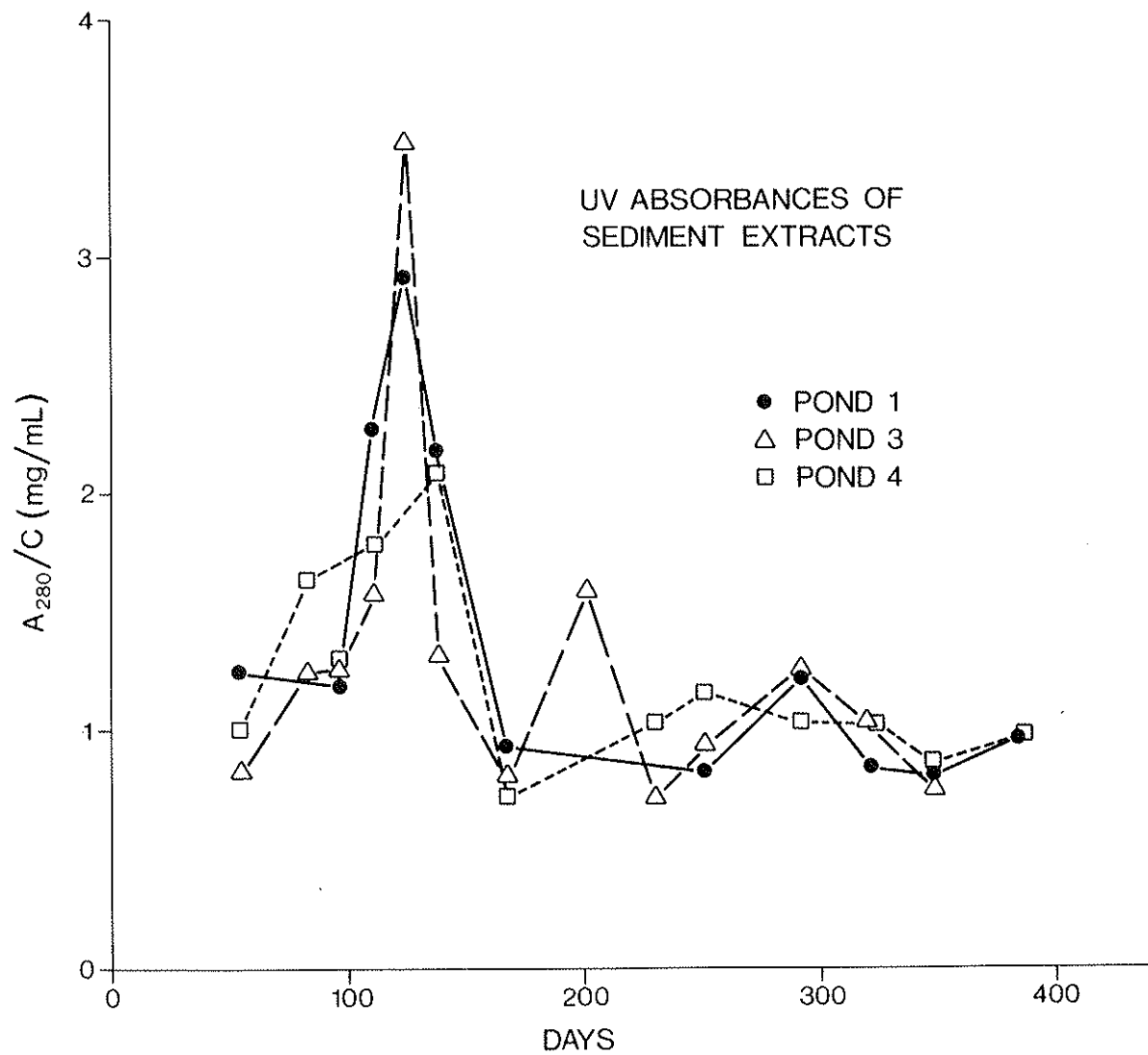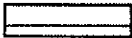
FIGURE 17   UV ABSORBANCE OF SEDIMENT EXTRACTS (C is the concentration as determined by IR spectroscopy)

LC FRACTIONATION OF OILS

HEXANE ELUATE

BENZENE ELUATE

COLUMN RESIDUE, RECOVERED BY
SOXHLET EXTRACTION WITH BENZENE

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)

0   20   40   60   80   100

PERCENTAGE OF RECOVERED OIL

FIGURE 18   LIQUID CHROMATOGRAPHIC FRACTIONS OF SOME
PETROLEUM PRODUCTS

LIQUID CHROMATOGRAPHIC SEPARATION OF SEDIMENT
EXTRACTS
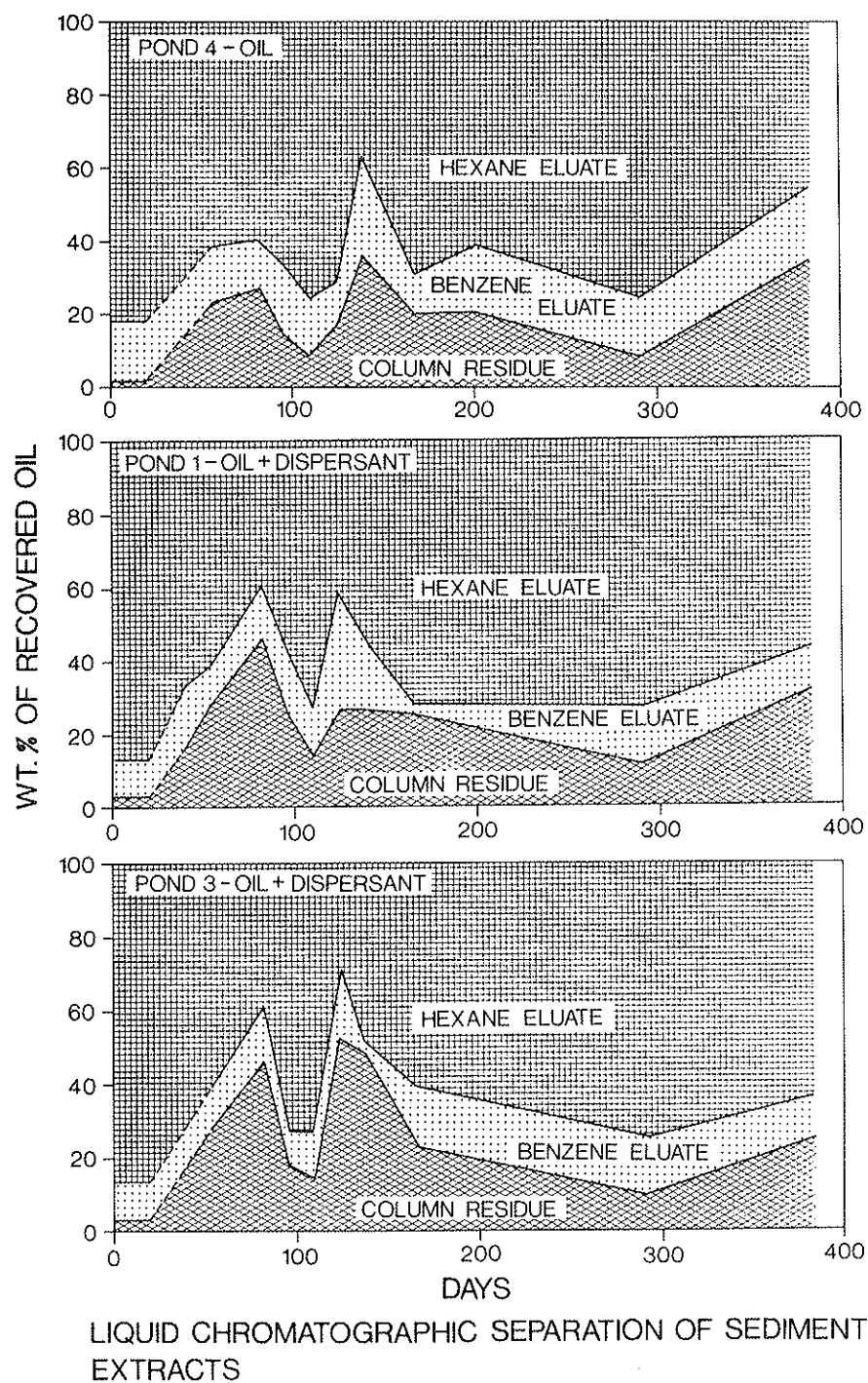
FIGURE 19   LIQUID CHROMATOGRAPHIC FRACTIONS OF SEDIMENT EXTRACTS
PLOTTED AS A FUNCTION OF TIME

derived from the interim samples follow a complex pattern that is essentially similar for each treated pond.

4   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 is found in Appendix I. The standard errors in the IR analysis are within the 2 to 5% range reported in the literature (Mallevialle, 1974; Lingren, 1957). 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 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 c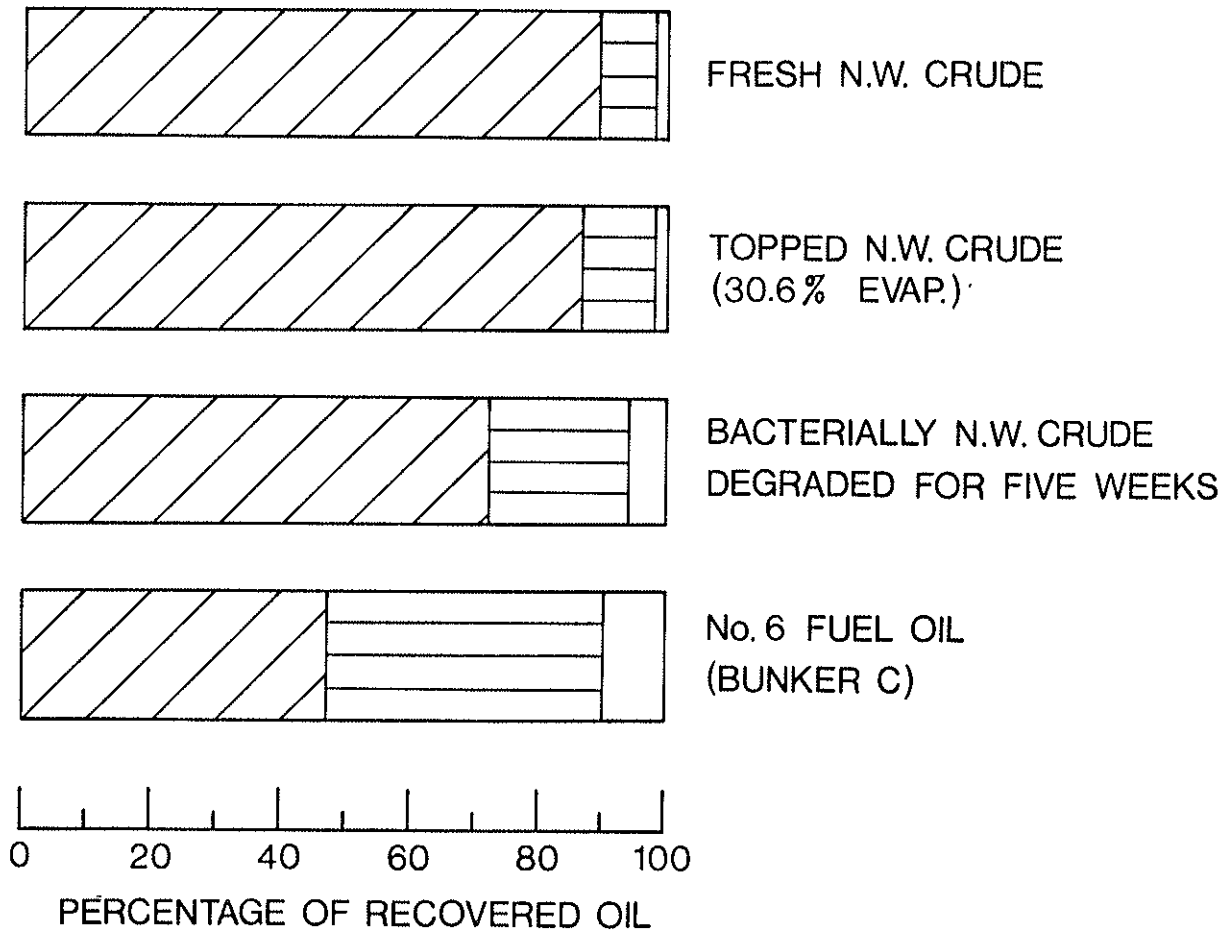onfirmed these observations, and showed that the highest oil concentrations found in the water, shortly after the treatment, were less than 20% of the design concentration. During the first weeks of the experiment, the slicks in the oil/dispersant ponds appeared to be as extensive as those in the undispersed 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 (Scott et al., 1979).

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

[1] initial value based on amounts added = 5.00

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

NS - no slick

N/A - not available

A possible clue to this turbidity phenomenon may be the presence 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 IV). The presence of airborne particulates kept in suspension by the dispersant, remains a possibility (Acres Consulting Services, 1975).

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 the 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 remaining oil and dispersant was 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 these 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 (Atlas and Bartha, 1973). To our knowledge, the extent of such degradation processes has not been reported for systems such 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 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 (Miget et al., 1969; Horowitz et al., 1975). If this was the only, or the most significant process for oil degradation in our system, then we would expect a
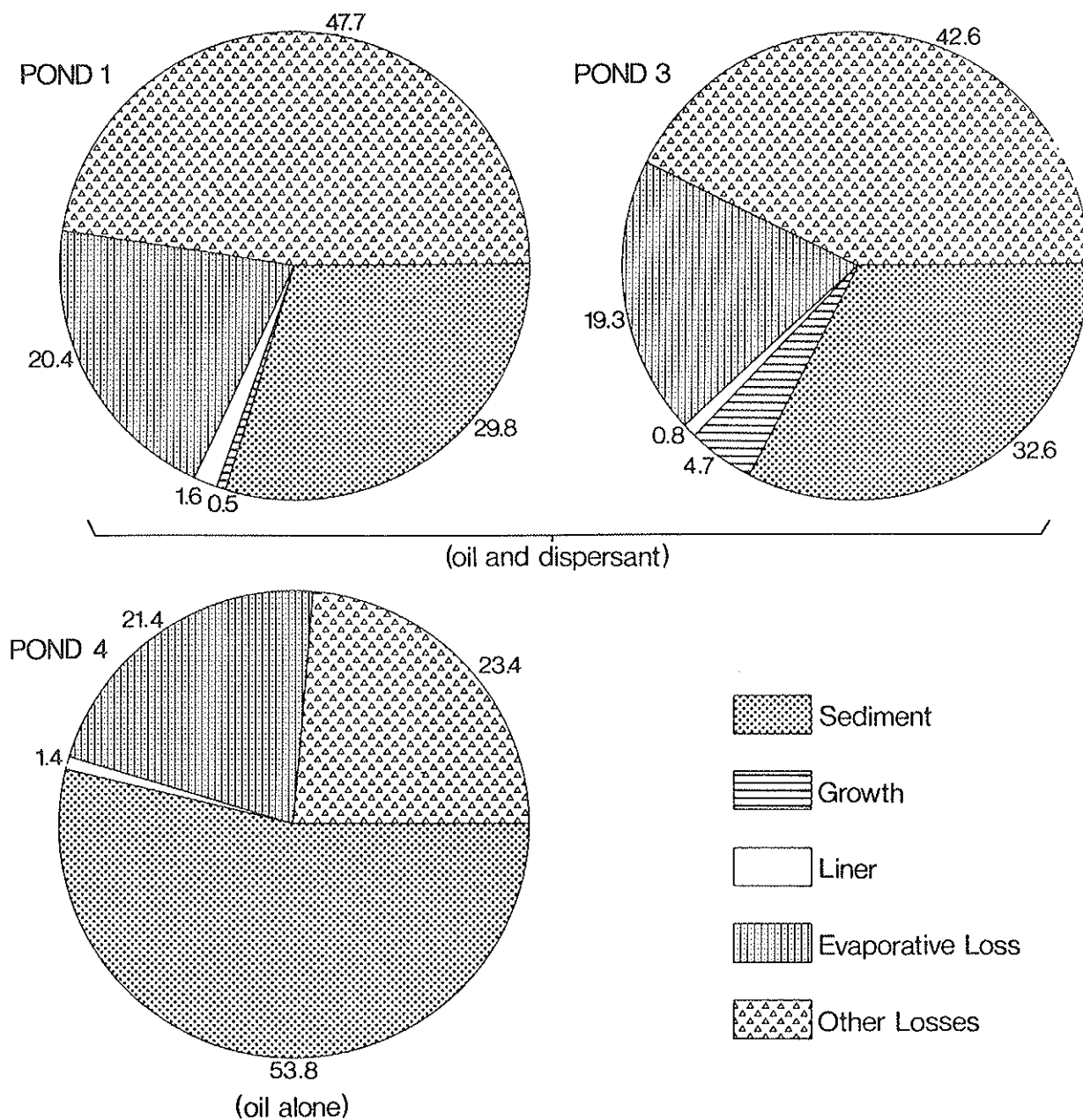
FIGURE 20   FINAL DISTRIBUTION OF OIL IN TREATED PONDS
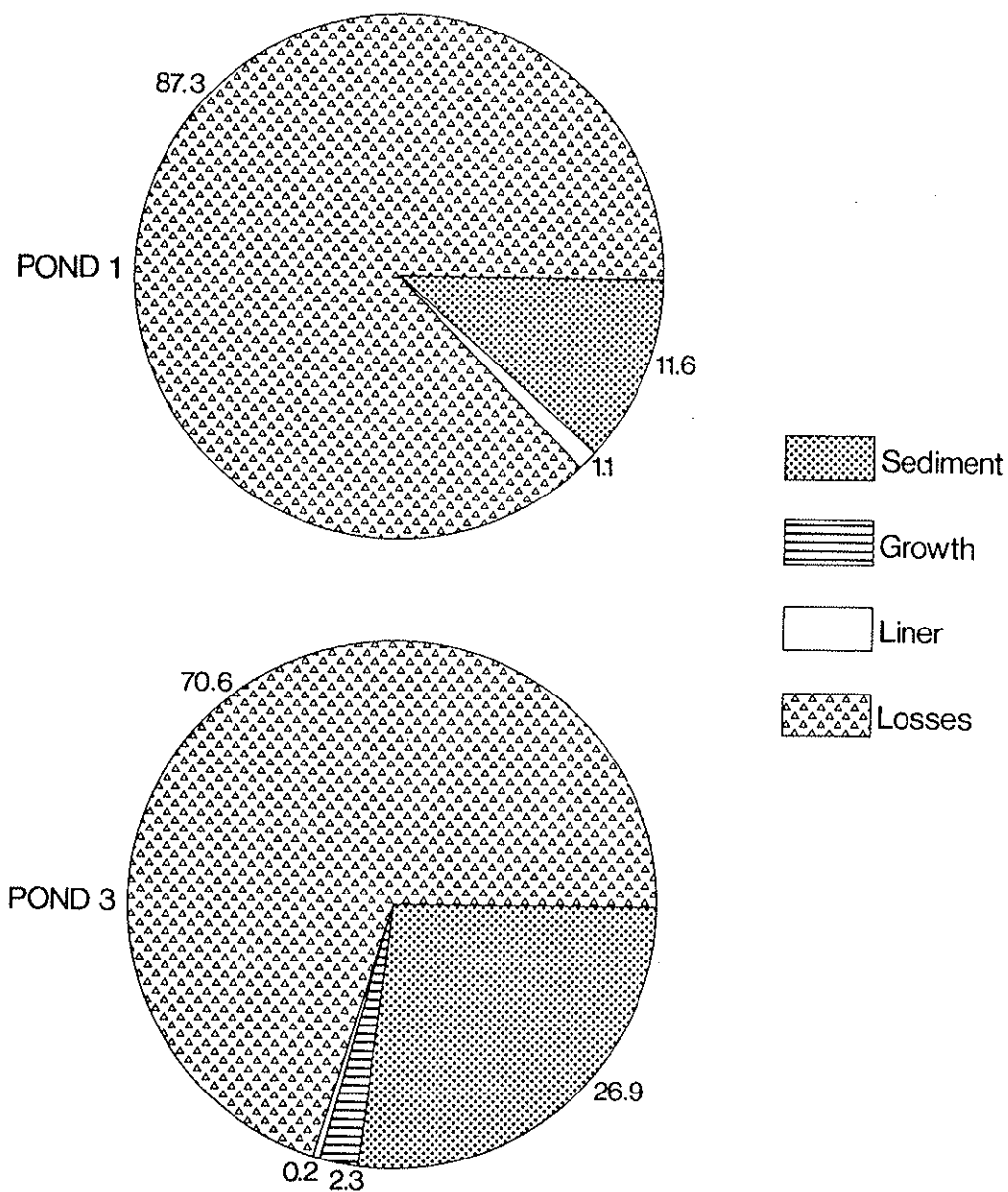
FIGURE 21   FINAL DISTRIBUTION OF DISPERSANT IN OIL/DISPERSANT
TREATED PONDS

continuous increase of the 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 (Figure 19) showed the predominance of different processes or pathways at different times during the experiment. We must note 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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APPENDIX I

A INFRARED METHOD OF OIL AND DISPERSANT ANALYSIS

B THE USE OF THE IR METHOD IN THE ANALYSIS OF FIELD SAMPLES

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 contained 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. 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.

TABLE I-A   SUMMARY OF IR CALIBRATION DATA

	Crude Oil 2920 cm^{-1}	Dispersant	
		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)	0.9993	0.9990	0.9994

C = 50.6 A_{2920}
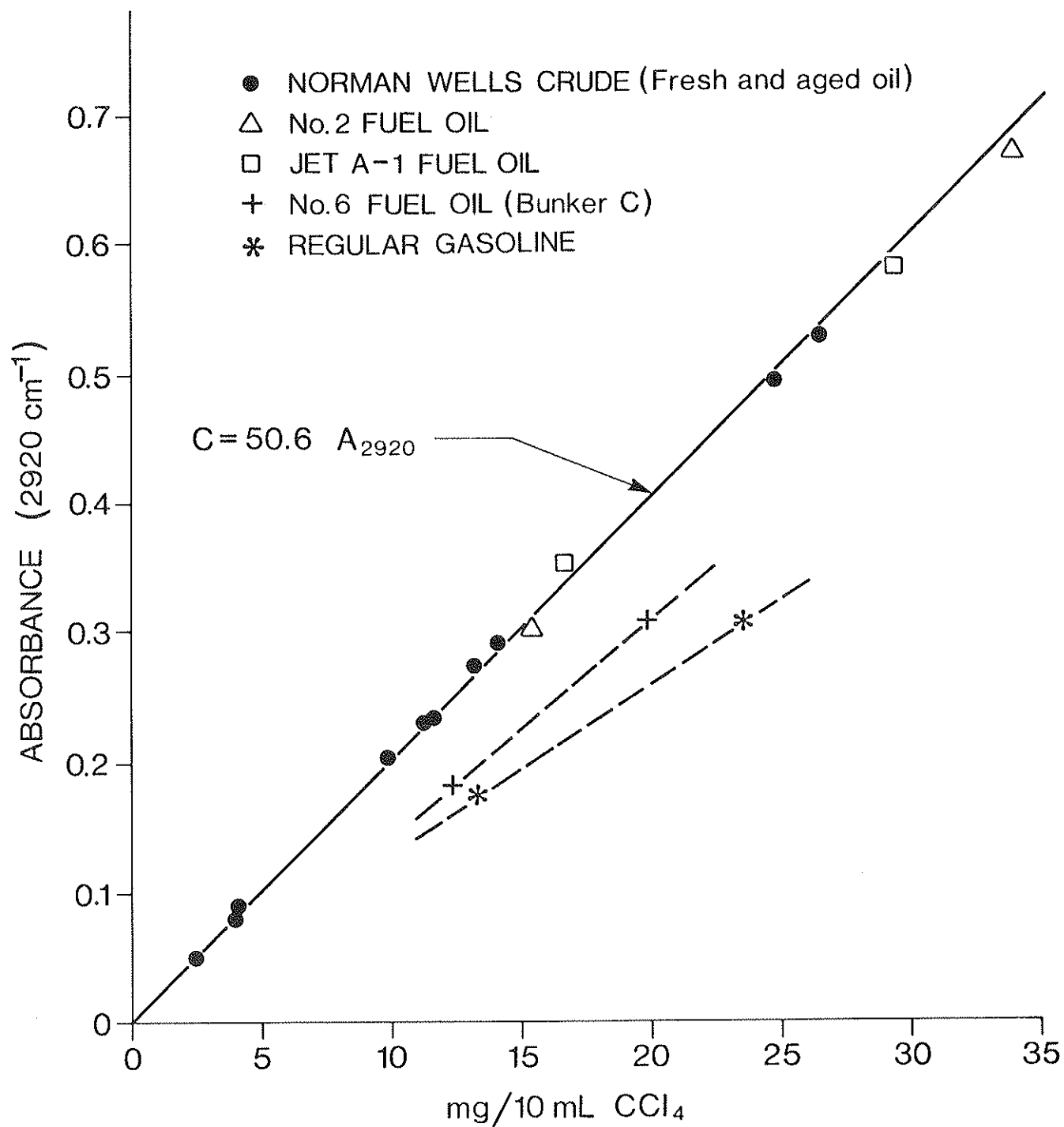
FIGURE I-1   CONCENTRATION ABSORBANCE RELATIONSHIPS FOR SELECTED PETROLEUM PRODUCTS

$$C_{OIL} = 49.3 \, A_{2920}$$
$$C_{DISP.} = 122.1 \, A_{1050}$$
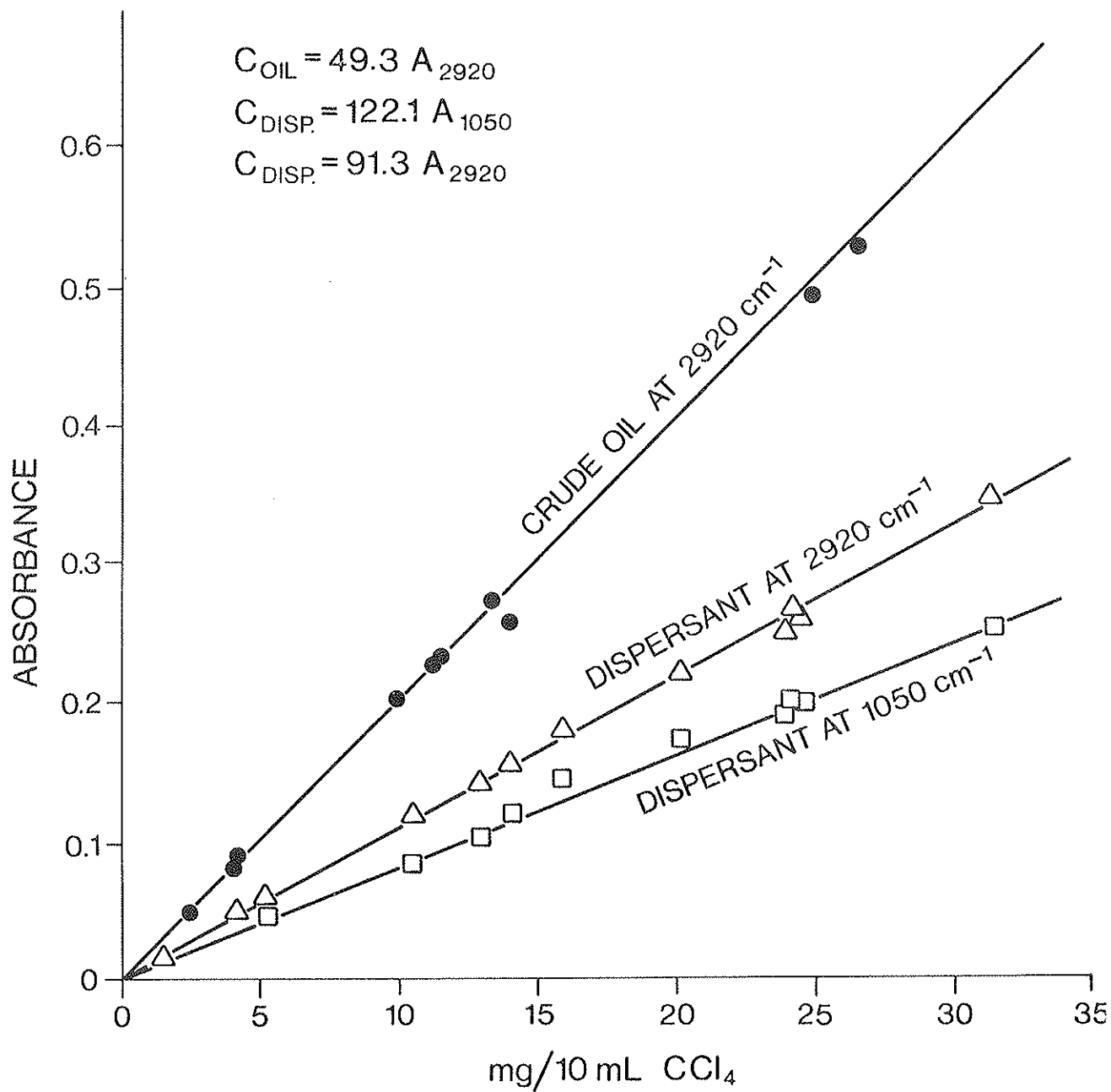$$C_{DISP.} = 91.3 \, A_{2920}$$

FIGURE I-2   CALIBRATION PLOTS FOR OIL AND DISPERSANT CONCENTRATIONS

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

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

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

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

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 subscript. In solutions containing oil alone or dispersant alone, the concentrations are calculated from only one of the above equations: (1) for oil, and (2) or (3) for the dispersant. In the analysis of oil/dispersant mixtures, the dispersant concentration is calculated from (3), while the oil concentration is given by:

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

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

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

Water samples: One litre aliquots of the water samples collected with a Van Dorn bottle were transferred into a 2 L separatory funnel immediately upon collection. After dissolving 300 g of NaCl in the sample, it was extracted by shaking with 10 mL of CCl_4 for one minute. The mixture was allowed to separate for five 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 mL) 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 L jars, each containing 400 to 600 g 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 mL 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 to 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 subsequent 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 mL of CCl_4 into the jars with the blotting paper and intermittently (five to six times) hand-shaking the jar for one hour. The extracts were free of water and were analyzed directly by the IR method. A laboratory evaluation of the method was carried out. Oil films of known thicknesses were produced by placing measured 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 an 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 in relation to the size of the absorbent pad.

TABLE I-B   LABORATORY TESTS OF SEDIMENT EXTRACTION METHOD

Dry Weight of Sediment (g)	Oil Added (mg)	Concentrations in CCl_4 (mg/10 mL)		
		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

Average recovery,   x = 95.7%

Standards deviation,   s = 3.40

Dry Weight of Sediment (g) Recovered	Dispersant Added (mg)	Concentrations in CCl_4 (mg/10 mL)		
		Calculated	Found	%
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

Average recovery,   x = 94.2%

Standards deviation,   s = 1.79

TABLE I-C   LABORATORY EVALUATION OF SAMPLING AND ANALYSIS OF SURFACE FILMS

| No. | Film Thickness, (μm) | | 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 weight x Oil density/area

APPENDIX II
UV ANALYSIS OF THE FIELD SAMPLES

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-I. The concentrations producing these spectra indicate that UV absorbances of these products increase in the order: gasoline; No. 2 fuel oil; crude oil; and 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 Figure 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, for example 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 the 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.

UV SPECTRA OF SOME PETROLEUM PRODUCTS

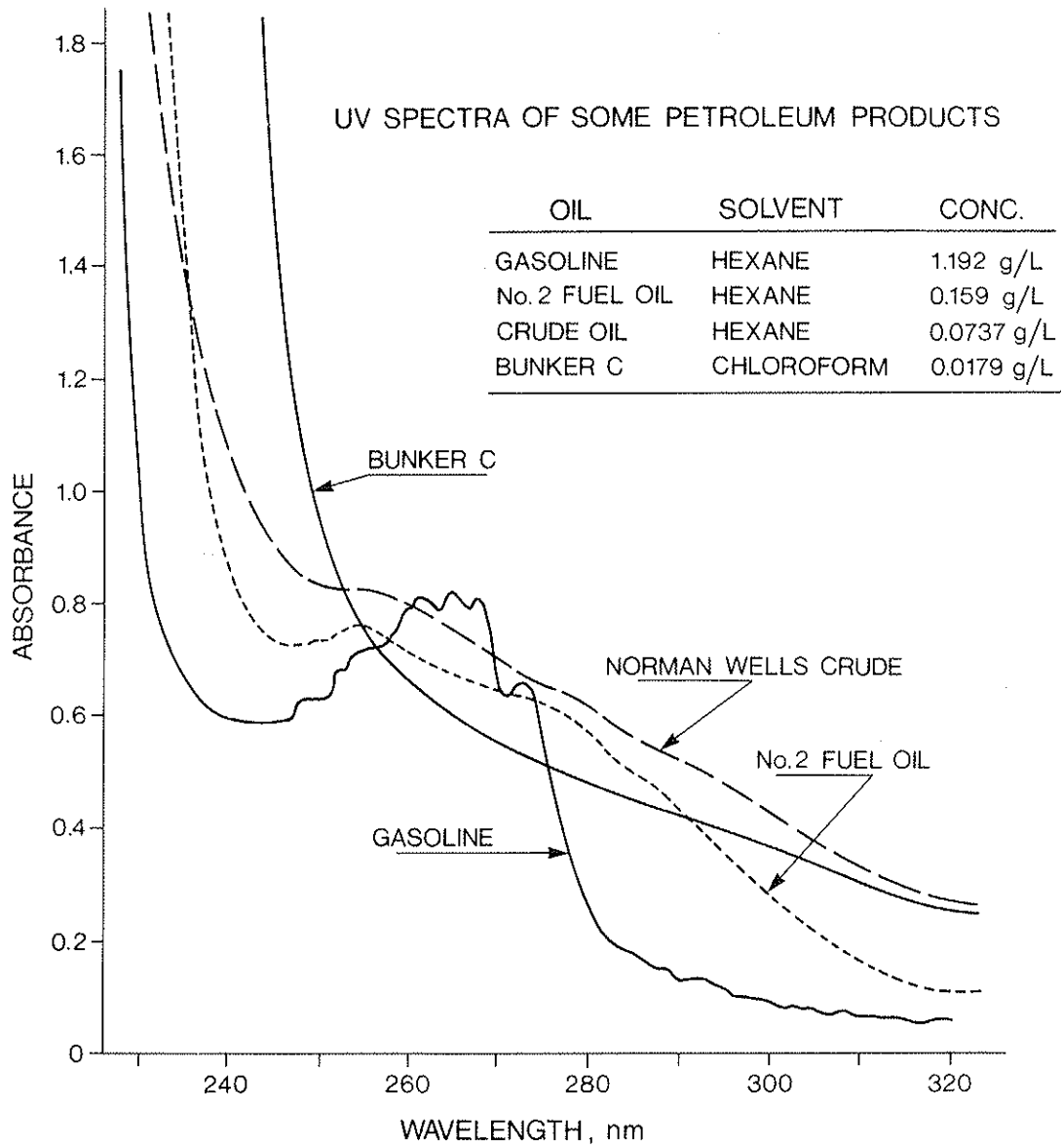| OIL	SOLVENT	CONC.
GASOLINE	HEXANE	1.192 g/L
No. 2 FUEL OIL	HEXANE	0.159 g/L
CRUDE OIL	HEXANE	0.0737 g/L
BUNKER C	CHLOROFORM	0.0179 g/L

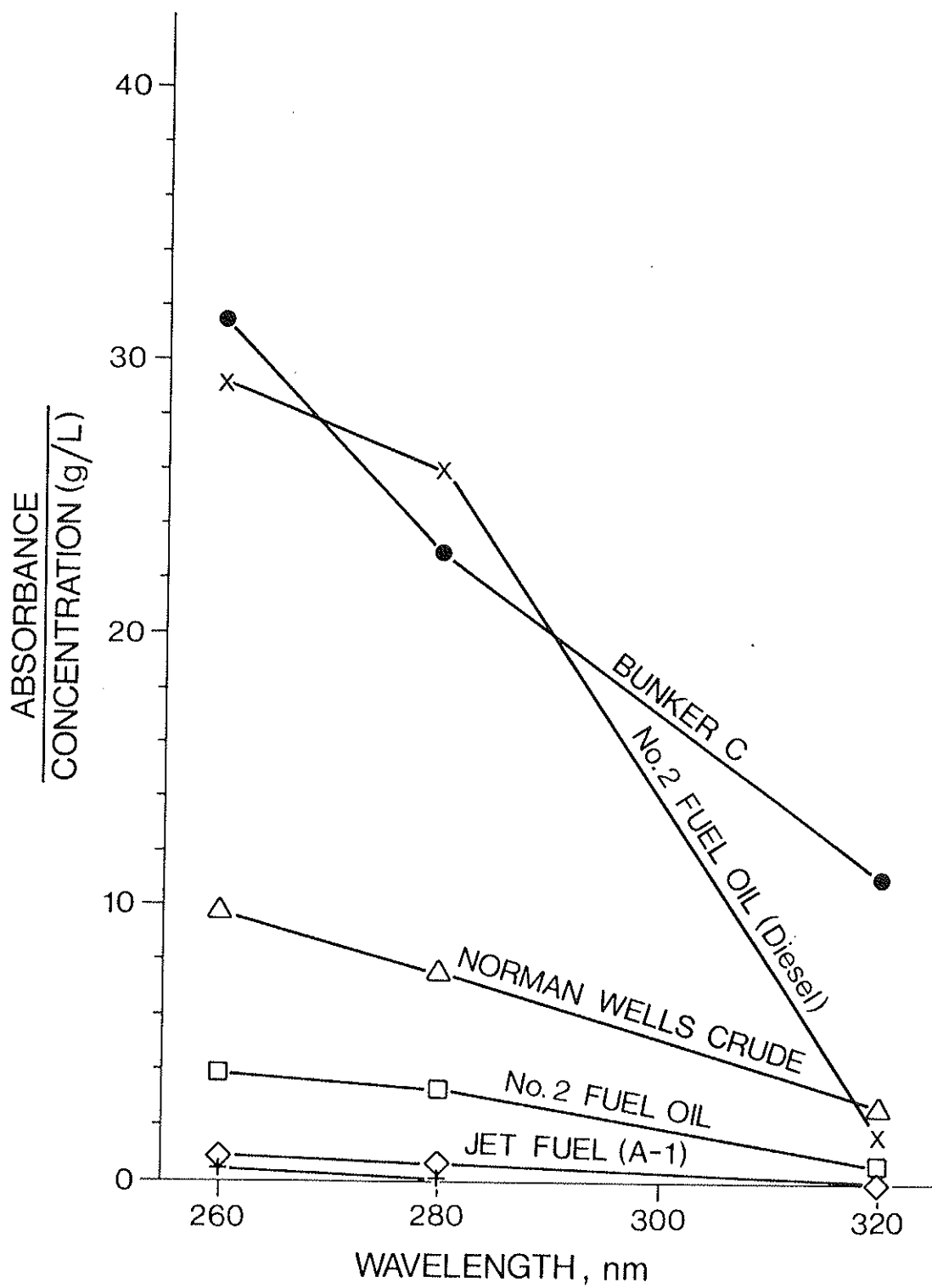FIGURE II-1   UV SPECTRA OF SOME PETROLEUM PRODUCTS

FIGURE II-2   ABSORPTIVITY OF SOME PETROLEUM PRODUCTS
AT SELECTED WAVELENGTHS

APPENDIX III
PERIPHYTON MEASUREMENTS

APPENDIX III   Periphyton Measurements

The dry weights and the ash weights of the attached material in the ponds are listed in Table III-A.   These materials were obtained from vertically-supported sand-blasted plexiglass plates in the bottom of all ponds.   Each plate had dimensions of 7 by 7 by 0.5 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 (Saraceni and Ruggiu, 1969).   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 the 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 two 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.

-    C. Saraceni and D. Ruggiu, 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 (1969).

TABLE III-A   WEIGHT OF PERIPHYTON PER UNIT AREA (g/m^2)

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

APPENDIX IV   Dissolved Reactive Silica Studies

Shortly after treatment of the ponds used in the oil/dispersant system 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 grams of sediment material sieved through a 2 mm mesh, were 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 DRS.

Filtered pond water (2.5 L, 0.45 µm) 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 time 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 controls. Aliquots (50 mL) were withdrawn, filtered and analyzed for DRS at the same times as were 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 had 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.

TABLE IV-A   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											
No Treatment	0.004	0.003	0.005	0.010	0.009	0.008	0.010	0.010	0.004	3	6.7
Dispersant	0.007	0.005	0.007	0.030	0.036	0.022	0.020	0.040	0.007	3	6.8
Sediment	0.497	0.599	0.675	0.760	0.861	0.928	0.937	0.917	0.497	3	6.7
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											
No Treatment	0.315	0.321	0.330	0.345	0.397	0.376	0.375	0.370	0.315	2	7.2
Dispersant	0.313	0.316	0.335	0.375	0.416	0.384	0.365	0.375	0.315	2	6.8
Sediment	0.675	0.793	0.876	1.01	1.10	1.11	1.09	1.07	0.677	3	7.0
Dispersant + Sediment	0.639	0.734	0.822	0.915	1.08	1.07	1.08	1.08	0.628	3	7.4