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086 Prototype, Mesoscale Simulator for the Study of Oil Weathering Under Severe Conditions

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PROTOTYPE, MESOSCALE SIMULATOR FOR THE STUDY OF OIL WEATHERING UNDER SEVERE CONDITIONS

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SUMMARY

As long-term, open-sea tests on oil weathering could be difficult and experiments in ice in the field even impossible to manage, we chose to develop a low-cost simulation tank with which to study the long-term fate and behaviour of crude oil under severe weather conditions and also in the presence of ice cover. As a prototype, we constructed a protected, outdoor tank with the surface of the contained sea-water exposed to natural weather conditions but with the water column protected from extreme temperature variations. The desing included such experimental features as a conical bottom, sediment trap, deck, and a small instrument room. This prototype represents a compromise between an indoor tank where physical parameters, such as air temperature and light exposure, can be fully controlled and an unprotected outdoor tank where climatic conditions are generally beyond control and with the possibility of sea-water overheating in summer or tank rupture because of freezing at low temperatures.

This report gives a full technical description of the prototype, mesoscale simulator and describes the results of three long-term weathering experiments conducted in 1986 and 1987 using chemically dispersed (Corexit 9527) crude oil. In the course of this work we also examined stability of oil dispersions at near- or sub-zero temperatures, and the relative role of evaporation and biodegradation in weathering of surface emulsions and water column oil.

The results from these experiments highlight some interesting fundamental features about the long-term fate of dispersed oil under these particular experimental conditions of low temperature:

1) The seawater temperature is not a determining factor in the dispersion stability. Instead the presence of ice reduced strongly the effectiveness of the dispersant because of wave damping by the ice.
2) In the absence of diffusion and/or convection, the main mechanism controlling the oil concentration in the contained water column is buoyancy.
3) Within a few days after the initial dispersion, the rising of oil droplets can be described with a simple mathematical relationship, the Stokes' equation. This relationship implies that contributions from other physical mechanisms to the removal of oil from the water column, such as flocculation and dissolution, were negligible.
4) The long-term stability of a dispersion (i.e., the dispersant effectiveness) can be evaluated by plotting the calculated droplet size versus the measured concentration of dispersed oil.
5) Dispersed oil droplets were degraded rapidly in the water column by micro-organisms for sea-water temperature greater than 3°C. Bacterial degradation of hydrocarbons was much reduced at lower temperatures and below an ice cover.
6) Evaporation was the main weathering process for surface emulsions, whereas biodegradation for these emulsions was almost negligible.
7) In the fall experiment, the effects of both processes (evaporation and biodegradation) on the chemical composition of dispersed oil were easily detected by GC analysis. However, their relative contributions to the total removal of oil from the water column are not yet clear.

Recommendations for further studies on oil biodegradation at near- or sub-zero temperatures and for further development of mesoscale tanks for outdoor studies are made.

RÉSUMÉ

Comme il serait difficile de mener des études sur le vieillissement du pétrole à long terme en mer et même impossible de réaliser des expériences sur les champs de glace, nous avons choisi de développer un bassin de simulation à un coût modeste avec lequel on pourrait étudier le comportement et le sort à long terme de l'huile brute dans des conditions difficiles de température et aussi en présence d'une couverture de glace. Comme prototype, nous avons construit un réservoir extérieur protégé dont la surface de l'eau de mer est exposée aux intempéries naturelles mais dont la colonne d'eau est protégée contre les variations extrêmes de température. Ce modèle dispose de certaines facilités expérimentales comme un fond conique, une trappe à sédiment, un pont de travail et une petite salle d'instrumentation. Ce prototype représente un compromis entre un bassin intérieur où les paramètres physiques, comme la température de l'air et la photopériode, peuvent être entièrement contrôlés et un bassin extérieur non protégé où les conditions climatiques sont généralement hors contrôle en cas de surchauffe de l'eau de mer en été ou de rupture du bassin causée par le gel à basse température en hiver.

Ce rapport fournit une description technique complète du simulateur prototype et décrit les résultats de trois expériences de vieillissement à long terme effectuées en 1986 et en 1987 utilisant de l'huile brute dispersée chimiquement (Corexit 9527). Au cours de ce travail, nous avons aussi étudié la stabilité des dispersions d'huile à des températures tout près ou sous zéro ainsi que le rôle relatif de l'évaporation et de la biodégradation dans le vieillissement des émulsions de surface et de l'huile dans la colonne d'eau.

Les résultats de ces expériences mettent en lumière quelques données fondamentales intéressantes sur le comportement à long terme de l'huile dispersée dans ces conditions expérimentales particulières à basse température:

1) La température de l'eau de mer n'est pas un facteur déterminant pour la stabilité de la dispersion. Cependant, la présence de la glace réduit fortement l'efficacité du dispersant à cause de la réduction des vagues causée par la glace.
2) En l'absence de diffusion et/ou de convection, le principal mécanisme contrôlant la concentration de l'huile dans la colonne d'eau du bassin est le crèmage.
3) Quelques jours après la dispersion initiale, la remontée des gouttelettes d'huile peut être décrite par une relation mathématique simple; l'équation de Stoke. Cette relation implique que les contributions des mécanismes physiques, comme la floculation et la dissolution, à l'enlèvement de l'huile de la colonne d'eau furent négligeables.
4) La stabilité à long terme d'une dispersion (soit l'efficacité du dispersant) peut être évaluée en traçant la dimension calculée des gouttelettes en fonction de la concentration de l'huile dispersée.
5) Les gouttes d'huile dispersées furent rapidement dégradées dans la colonne d'eau par les microorganismes pour une température d'eau de mer supérieure à 3°C. La dégradation bactérienne des hydrocarbures fut fortement réduite à basse température et sous la couverture de glace.
6) L'évaporation fut le principal processus de vieillissement des émulsions de surface, tandis que la biodégradation des ces émulsions fut presque négligeable.

7) Au cours de l'expérience d'automne, les effets des deux processus (évaporation et biodégradation) sur la composition chimique de l'huile dispersée furent facilement observées par analyse CG. Cependant, leurs contributions relatives au nettoyage complet de l'huile dans la colonne d'eau ne sont pas encore évidentes.

Des recommandations pour de nouvelles études sur la biodégradation de l'huile à des températures très près ou sous zéro ainsi que pour le développement de réservoirs d'échelle moyenne pour des études à l'extérieur ont été énoncées.

INTRODUCTION

Environmental studies associated with oil exploration and exploitation in extreme weather conditions have received an increasing attention during the last decade (Hillman 1985). Much research and several development projects have addressed many practical problems caused by sea ice in the field application of classical countermeasure techniques. However, chemical dispersion of oil slicks in the presence of broken or slush ice or underneath ice cover has received little attention, mainly because the low effectiveness of most commercial dispersants at low temperatures and also because the long-term behaviour of crude oil dispersed in the water column at low temperatures is almost unknown. Numerous studies on the biodegradation of crude oil in sea-water have been reported in the last 15 years (Table 1). Nevertheless, few have been conducted at temperatures below 5°C, and none below 0°C. Thus, information about biodegradation rates and their controlling factors in subarctic and arctic marine environments are sparse and often highly speculative because they lack direct observations. Therefore, we undertook a study of crude-oil degradation in natural sea-water under near-freezing and freezing conditions.

As long-term, open-sea tests and experiments in ice in the field could be difficult or even impossible to manage, we chose to develop a low-cost simulation tank, which could be used to study the long-term fate and behaviour of crude oil under severe weather conditions and also in the presence of ice cover. This report gives a full technical description of the simulator prototype and describes the results of three, long-term, weathering experiments conducted in 1986 and 1987 using chemically dispersed (Corexit

TABLE 1

Experimental set-up of selected studies on oil biodegradation in marine environment

Volume of sea-water (L)	Temperature (°C)	Oil and additives	Period (days)	References
0.25	20 (controlled)	Arabian light	60	Oudot 1984
0.125	20 (controlled)	Oil and surfactants	2-3	Robichaux and Myrick 1972
10.2 X 10^3	0.5-2.5 (_in situ_)	Ekofisk crude	14	Laake, Tjessem and Rein 1984
20 X 10^3	variable (_in situ_)	Oil and dispersants	120	Marty _et al_. 1979
0.10	15 and 25(control.)	Libyan crude	45	Olivieri _et al_. 1976
Continuous flow-through	2-11 (_in situ_)	Oil and fertilizers	50	Horowitz and Atlas 1977
15.7 X 10^3	??? (_in situ_)	Oil and Corexit 9527	20	Tjessem, Pedersen and Aaberg 1984
75	3-8 (_in situ_)	Oil and fertilizers	21	Tramier and Sirvins 1983
65 X 10^3	12-17 (_in situ_)	Oil and Corexit 9527	24	Wong _et al_. 1984
66 X 10^3	11.6-12.8 (_in situ_)	" " "	15	Cretney _et al_. 1981
0.2	8 (controlled)	" " "	84	Foght, Fedorak and Westlake 1983 Foght and Westlake 1982 Fedorak and Westlake 1981

Table 1 (continued)

Volume (L)	Temperature (°C)	Oil and additives	Period (d)	References
0.5	4 and 14(control.)	Kuwait residue	315	Gibbs 1975 Gibbs, Pugh and Andrews 1975
0.1	5, 10 ,15 and 25 controlled	Sweden oil	60	Atlas et Bartha 1972a,b,c
2	4 and 30(control.)	Crude oil	21	Jobson, Cook and Westlake 1972
300	??? (*in situ*)	Oil and dispersants	25	Gatellier *et al*. 1973
14-15 X 10^3	0-2 (uncontrol.)	No.2 fuel oil	23	Gearing and Gearing 1982
"	20-21	" "	18	" "
"	17-19	" "	8	" "
"	21-23	" "	5.6	" "
60 X 10^3	12 (*in situ*)	Aromatics and oil	10	Lee *et al*. 1978
8.0 X 10^3	14-19 (uncontrol.)	Tia Juana crude	17	Gordon *et al*. 1976
	21-25	" "	10	" "
	24-5	" "	79	" "
	19-16	Guanipa crude	101	" "
	12-3	" "	32	" "
8.0 X 10^3	??? (*in situ*)	North Sea oil and dispersant	160	Linden *et al*. 1987

9527) crude oil. In the course of this work we also examined stability of oil dispersions at near- or sub-zero temperatures, and the relative role of evaporation and biodegradation in weathering surface emulsions and water column oil. We chose to construct a protected, outdoor tank with the surface of the contained sea-water exposed to natural weather conditions but with the water column protected from extreme temperature variations caused by cold, winter winds and hot, summer sunshine. This prototype allows also such experimental features as a conical bottom, sediment trap, deck, and a small instrument room.

MATERIALS AND METHODS

APPARATUS

The prototype simulator (Figure 1) was constructed at field-laboratory facilities located on the south shore of the St. Lawrence estuary, near Rimouski (Quebec). Modelled on the Mackay-Nadeau-Steelman (MNS) apparatus (Mackay and Szeto 1980), the simulator consists of a double-walled, steel tank, with either ambient sea-water or coolant circulating through the outer chamber or annulus. The conical bottom was specially designed to collect particles settling from the inner water column. To minimize metal contamination from walls and for ease in final clean-up, the inner cylinder (1.20 m i.d.) was built of stainless steel and the inside wall was coated with a white, adhesive Teflon film (Bytac, type VF-81, 1.6 mm thick). The total volume of the inner chamber is 1.80 m^3, and the sea-water volume used in each experiment was about 1.50 m^3. The contained sea-water can be protected from contamination (rain, snow, dust) by a transparent, plexiglass sheet (3 mm) allowing the transmission of about 80% of the sunlight.

To avoid the complete freezing of the water volume or rupture of the tank during the winter months, and also to control as far as possible sudden temperature changes due to cold wind or sunshine, the simulator was carfully sheltered with insulating glass wool. The outer chamber was filled with a 70:30 % mixture of water and ethylene glycol, which was thermo-regulated (+1°C) with a water-bath circulator (Haake model G). Extra heat was provided when necessary by a heater fan located at the bottom section of the simulator (see Figure 1).

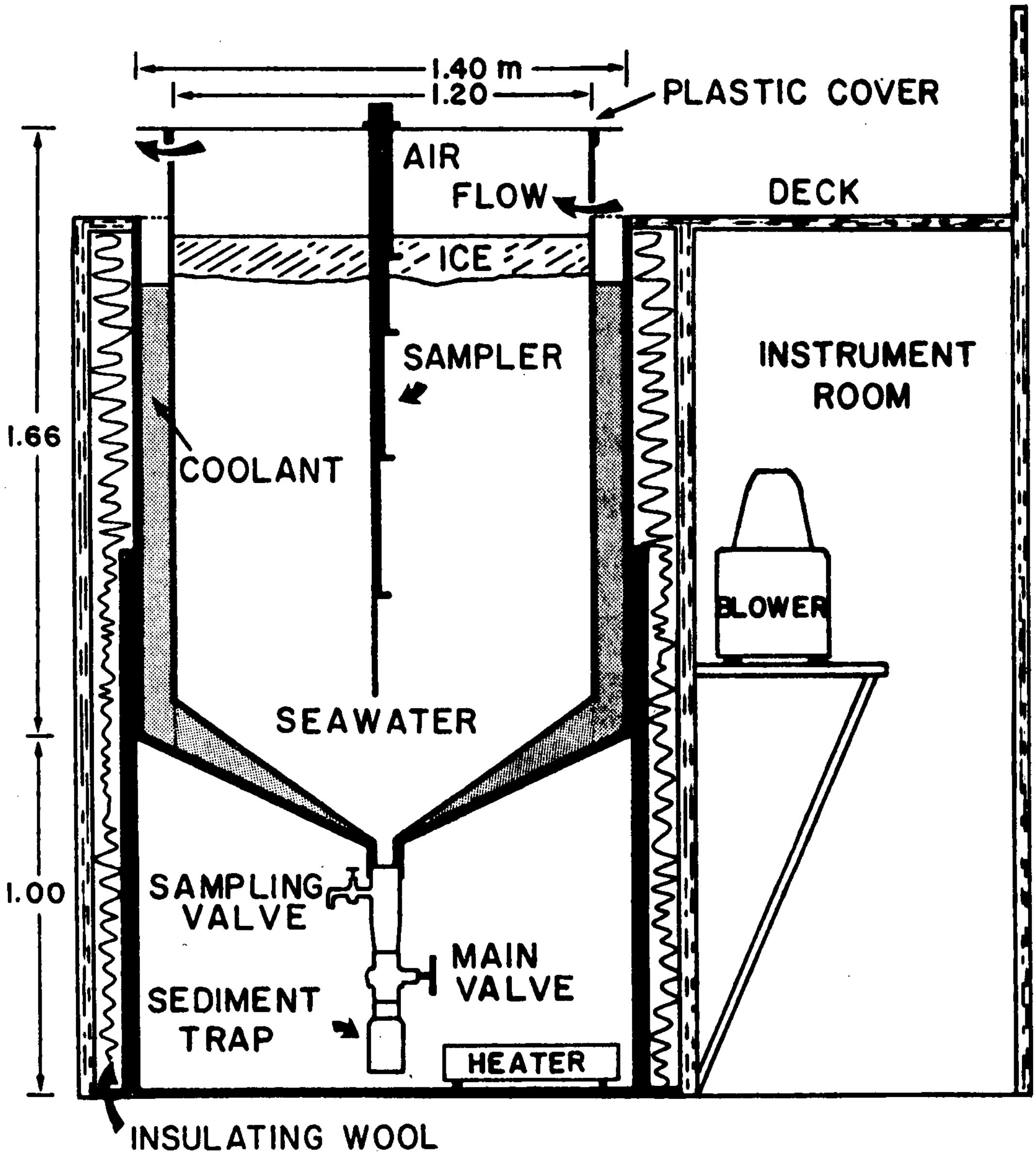

FIGURE 1. Side-view diagram of the prototype, mesoscale simulator.

The water circulation system was modelled on the MNS apparatus and used the same industrial vacuum-cleaner fan (Shop Vac, model 775-01) to force cold air over the surface of sea-water. The air stream hits the surface at an angle of about 20°, inducing 2-cm ripples, and generating a slow rotation of the contained water column (Figure 2). This gentle stirring maintained the homogeneity of the water column in absence of ice cover during the fall experiment. An air bubbler and a temperature thermocouple were attached to the sampling device at 60 cm and 1.3 m, respectively, below the surface (Figure 3). Temperature read out (Digitron model 3754) gave a precision of ±0.1°C.

Two sampling devices were installed. A sediment trap in the bottom of the simulator allowed sampling of particles settling from the water column. A sampling valve allowed the collection of large water volumes when required (Figure 1). All these fittings were constructed of non-corrosive, thermoplastic PVC. The water column could be sampled at various depths (0.1, 0.3, 0.6, 1.0, and 1.3 m) using five Tygon tubes (3.2 mm i.d.) of appropriate lengths suspended in the centre of the cylinder (Figure 3). Water samples for bacterial counts, hydrocarbon analysis, and nutrient concentrations could be collected in this way by drawing water up into sterile, 50-cc syringes. Samples for oxygen determination were collected directly below the surface with Biological Oxygen Demand (BOD) bottles.

Attempts to set up a device that could generate small waves for studies the incorporation of dispersed oil droplets into brash ice and slush were unsuccessful. The use of the small Mackay-Nadeau-Steelman (MNS) apparatus was found much more useful for such studies.

FIGURE 2. Overview of the tank showing the air stream output and the oil slick shortly after starting an experiment.

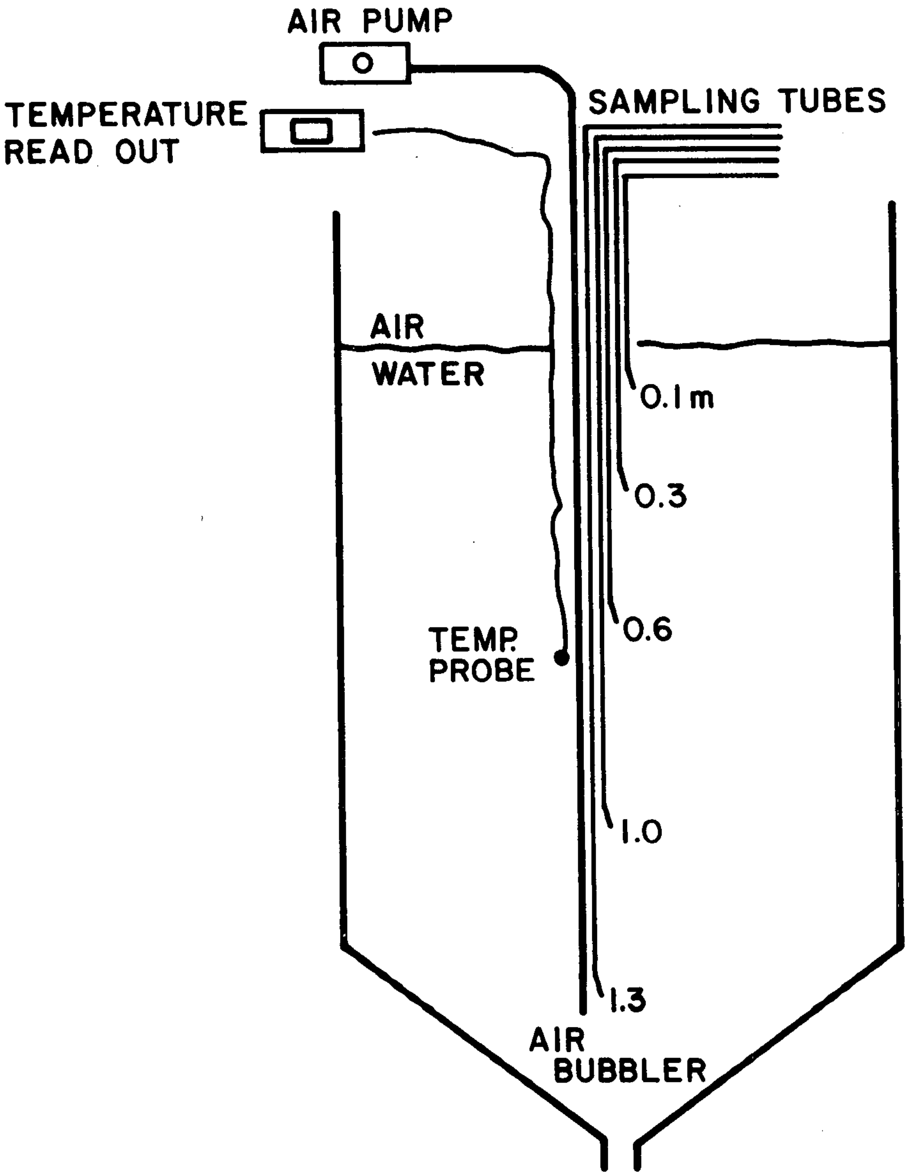

FIGURE 3. Sampling set-up.

EXPERIMENTAL PROCEDURE

Three long-term experiments were run covering one autumn and two winter periods (Table 2). At the start of each experiment, the simulator tank was filled with unfiltered, ambient sea-water (1500 L for each run) containing naturally occurring biota (zooplankton, phytoplankton and microplankton). Twenty-four hours were allowed before beginning the experiment to allow for settling of the largest particles and for temperature equilibration of the whole apparatus. Chemical and physical properties of crude oil and commercial dispersant used these experiments are given in Table 3.

The method for the addition of oil and its chemical dispersion was similar to the technique proposed by Mackay and Szeto (1980) for the study of dispersant effectiveness. The airflow was turned on a few minutes before oil was added. A large containment ring (30 cm diameter and 15 cm height) was positioned on the water surface at the centre of the simulator and 565 cc of crude oil was then added slowly inside the ring (Figure 4). After 5 min, 56.5 cc of the chemical dispersant was sprayed over the oil surface and 5 min later the ring was lifted allowing the treated oil to spread out over the water surface.

Under these conditions, the dispersion process began slowly, under the combined mixing action of the air flow and the rotation of the water column (Figure 2). During experiments 1 and 2, an apparent homogeneous dispersion through the entire water column was observed after 6 to 12 h. In experiment 3, the mixture of oil, dispersant, seawater and surface slush ice was stirred for few minutes with a wooden paddle because the air flow was insufficient to mix the water column.

TABLE 2

Experimental conditions for weathering studies of dispersed crude oil in the mesoscale simulator

Experiment no.	Dates	Water temp.(°C) start	end	Water salinity (°/oo)	Initial bacterial (counts/ cc)	Notes
1	18 Nov. 85- 26 March 86	3.4	0.3	28.0	311	90 days with ice cover
2	17 Aug. 86- 20 Oct. 86	11.0	3.3	25.5	2400	No ice
3	16 Dec. 86- 20 April 87	-1.7 (ice)	3.0	28.0	7286	100 days with ice cover

TABLE 3

Chemical and physical properties of crude oil and commercial dispersant used in all experiments

Crude oil	Dispersant
Type: Western Sweet Blend crude oil	Commercial name: Corexit 9527
Density: 0.839 g cc^{-1}	Specific gravity at 15.6°C: 0.995
Flash point: 7°C	Flash point: 72°C
Viscosity at 15°C: 9.2 Pa·s	Viscosity at 15.6°C: 60 Pa·s
% Aliphatics: 69.5	Contains a mixture of surfactants (Tween, Span and AOT) dissolved in hydrocarbon-based solvent (Isopar M)
% Aromatics: 28.0	
% Asphaltenes: 2.5	
Provided by: Environmental Protection Service, Environment Canada.	Provided by: Exxon Chemical Americas Houston, Texas.

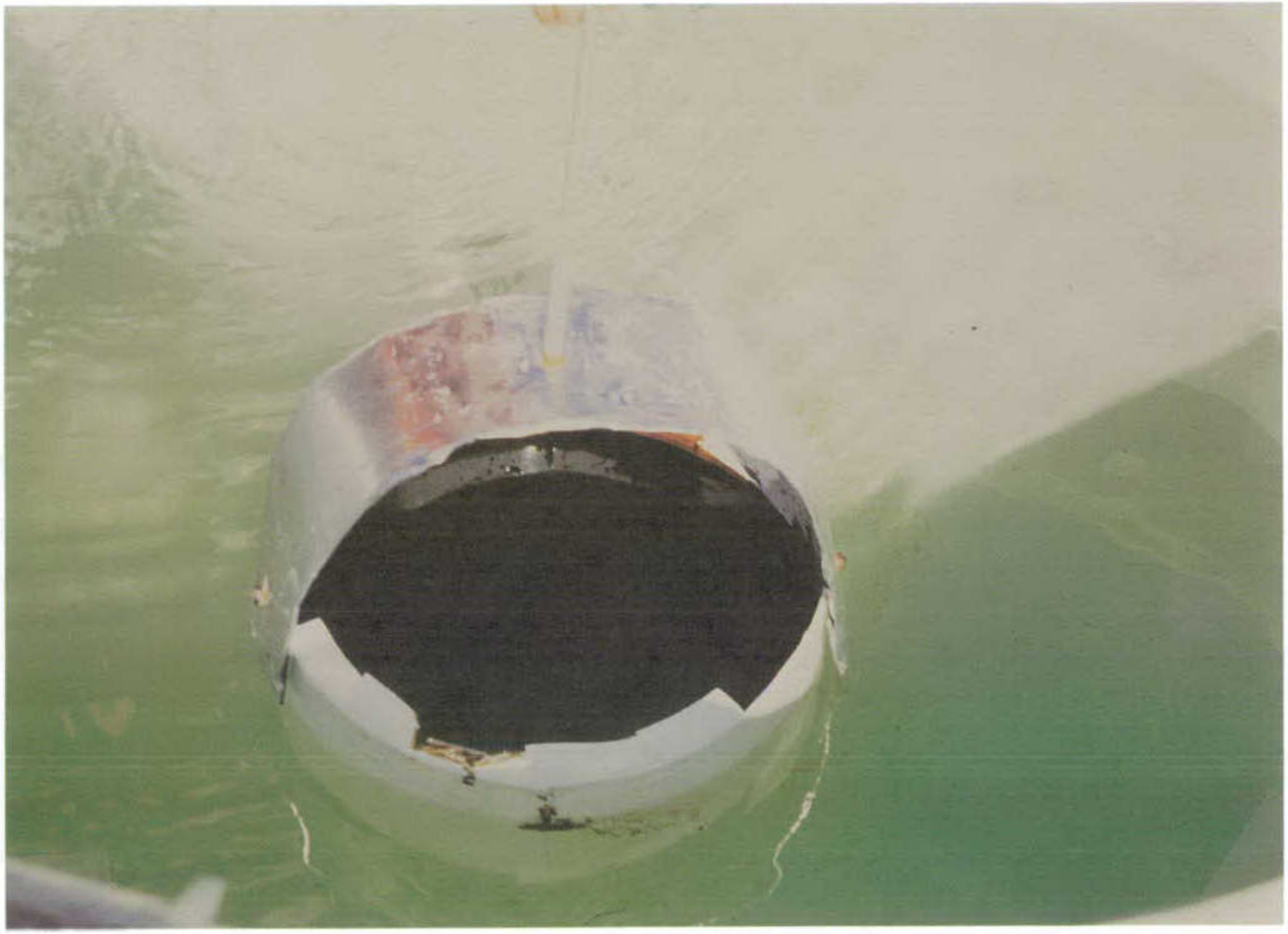

FIGURE 4. Containment ring positioned on the water surface at the centre of the simulator.

SAMPLING AND ANALYSES

During each experiment, water samples, floating oil mousse, and oil particles, as well as settling particles, were collected periodically for chemical analyses (Table 4). During the winter experiments (1 and 3), the presence of sea ice prevented water sampling at levels 0.1 m and 0.3 m. Some problems were also encountered when ambient air temperature went down to -10°C and seawater froze rapidly in the sampling tubes.

Salinity was determined using a salinometer (Guildline 8400 Autosal Model), with salinity values calculated from conductivity tables. Samples for the determination of reactive nitrate and phosphate were collected in 50-cc plastic bottles, previously washed with HCl (10% w/w) and deionized water. Nutrient samples were run on an auto-analyser (Technicon) using standard procedures. Dissolved oxygen in sea-water was measured with a YSI oxygen probe (Orion 97-08 Model) used directly in the BOD bottles. Samples for O_2 determinations were taken about 15 cm below the water surface in the absence of ice and through the regular sampling device in the presence of an ice cover.

To assess potential microbial degradation of dispersed oil, total viable counts of heterotrophs were determined by incubation on 100-mm petri dishes containing marine agar 2216. Triplicate petri dishes were incubated at 24.0°C for 72 h. The colonies were enumerated and the mean value was expressed as the total viable counts of bacteria per cc.

The entire scheme for hydrocarbon analysis is given in Figure 5. All samples were treated first with 200 cc of dichloromethane to extract all organic compounds from the aqueous phase. The concentration of oil in the extract was estimated by UV/visible spectrophotometry using the method

TABLE 4

Sampling volumes and measurements performed during each experiment.

Samples	Measurements
500 cc sea-water sampled at levels 0.1, 0.3, 0.6, 1.0, and 1.3 m.	Determination of % dispersed oil by UV/vis and GC traces.
50 cc sea-water at level 0.6 m	Bacterial counts
2 x 25 cc sea-water at level 0.6 m	Titration of nitrate and phosphate
1-2 g surface emulsion (when possible)	GC traces
Settled particles in the sediment trap (few mg)	% trapped oil by UV/vis and GC traces
Surface particles at the end of each experiment (few g)	GC traces

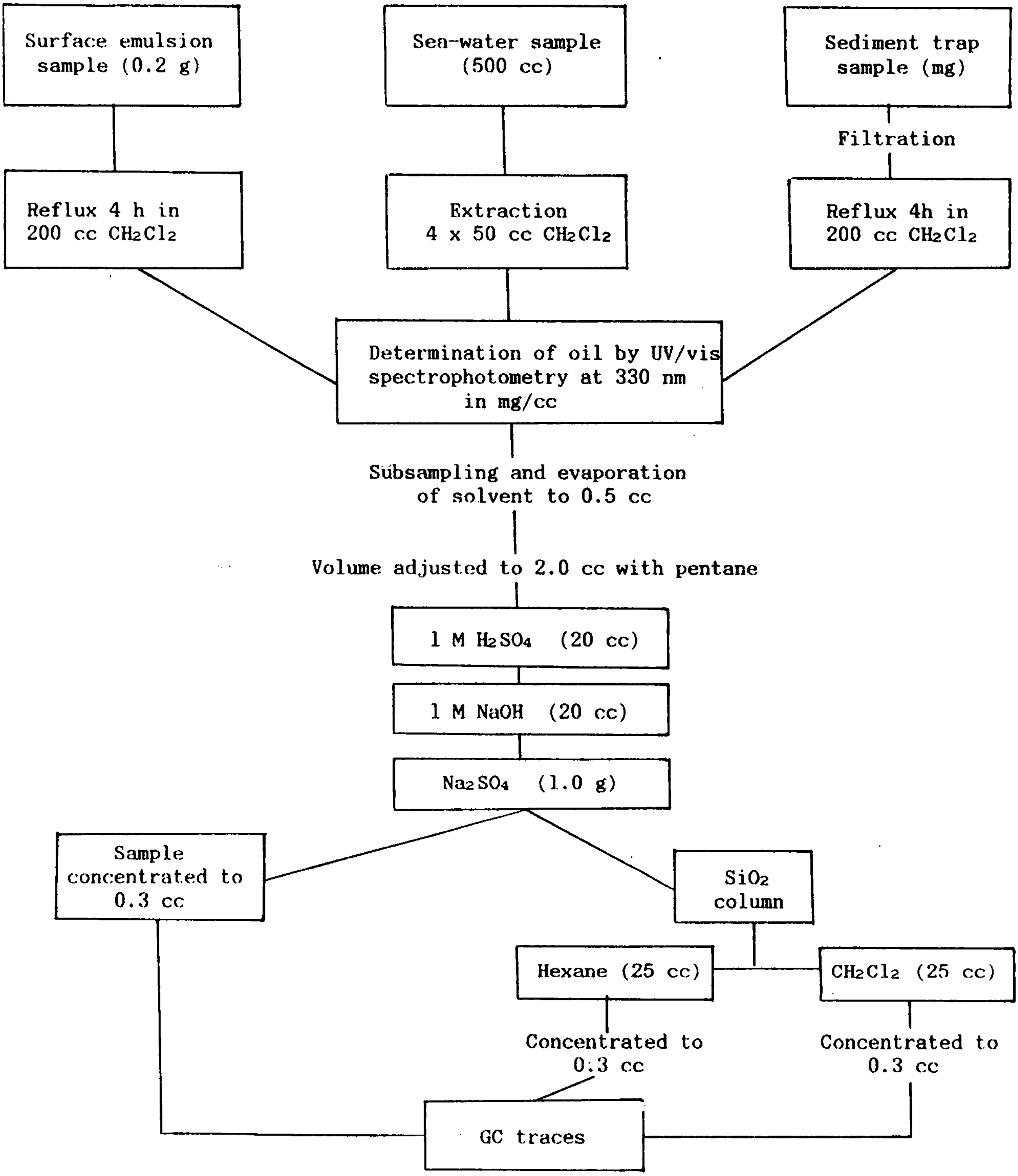

FIGURE 5. Analytical scheme for hydrocarbons.

proposed by Mackay and Szeto (1980). A known aliquot (containing about 2.0 mg hydrocarbons) was then subsampled into pentane for gas chromatography. The total volume was adjusted to 2.0 cc with pentane, which causes most asphaltenes to precipitate. The sample washed successively with sulphuric acid (20 cc) and sodium hydroxide (20 cc). This treatment eliminated most acid-soluble lipids and other biogenic compounds, and reduced strongly the complexity of gas chromatographic (GC) traces (Boehm <u>et</u> <u>al</u>. 1982). The clean sample was then dried over anhydrous sodium sulphate. At this point, the sample was either evaporated to 0.3 cc under a nitrogen stream and directly submitted to GC analysis or passed through a silica-gel column for the separation of aliphatics (F1) and aromatics (F2). The column (0.9 x 15 cm) was prepared with hexane using silica gel (70-230 mesh from Merch) previously activated 24 h. at 250°C. Aliphatics were eluted with 25 cc of hexane and aromatics with 25 cc of dichoromethane. Both fractions were evaporated up to 0.3 cc and were submitted to GC analysis.

A Varian 4270 gas chromatograph equipped with a temperature-programmable, on-column injector and a flame-ionization detector (320°C) were used for all analyses. Volatile compounds were eluted on a 30-m, glass capillary column (0.25 um) coated with a low-polarity stationary phase (DB1). The carrier gas was helium at a flow rate of 30 cc/min. The GC was coupled to a Varian 4270 integrator which was interfaced to a microcomputer Compaq Deskpro for storage and statistical treatment of chromatographic data. Two different temperature programs for the on-column injector and the column were used depending on the nature of the sample (Figure 6). Procedure A was specially designed for the resolution of compounds with low boiling points, mainly small, aromatic molecules, and was used for oil samples not pre-treated on silica gel column. Procedure B was used for the separation of

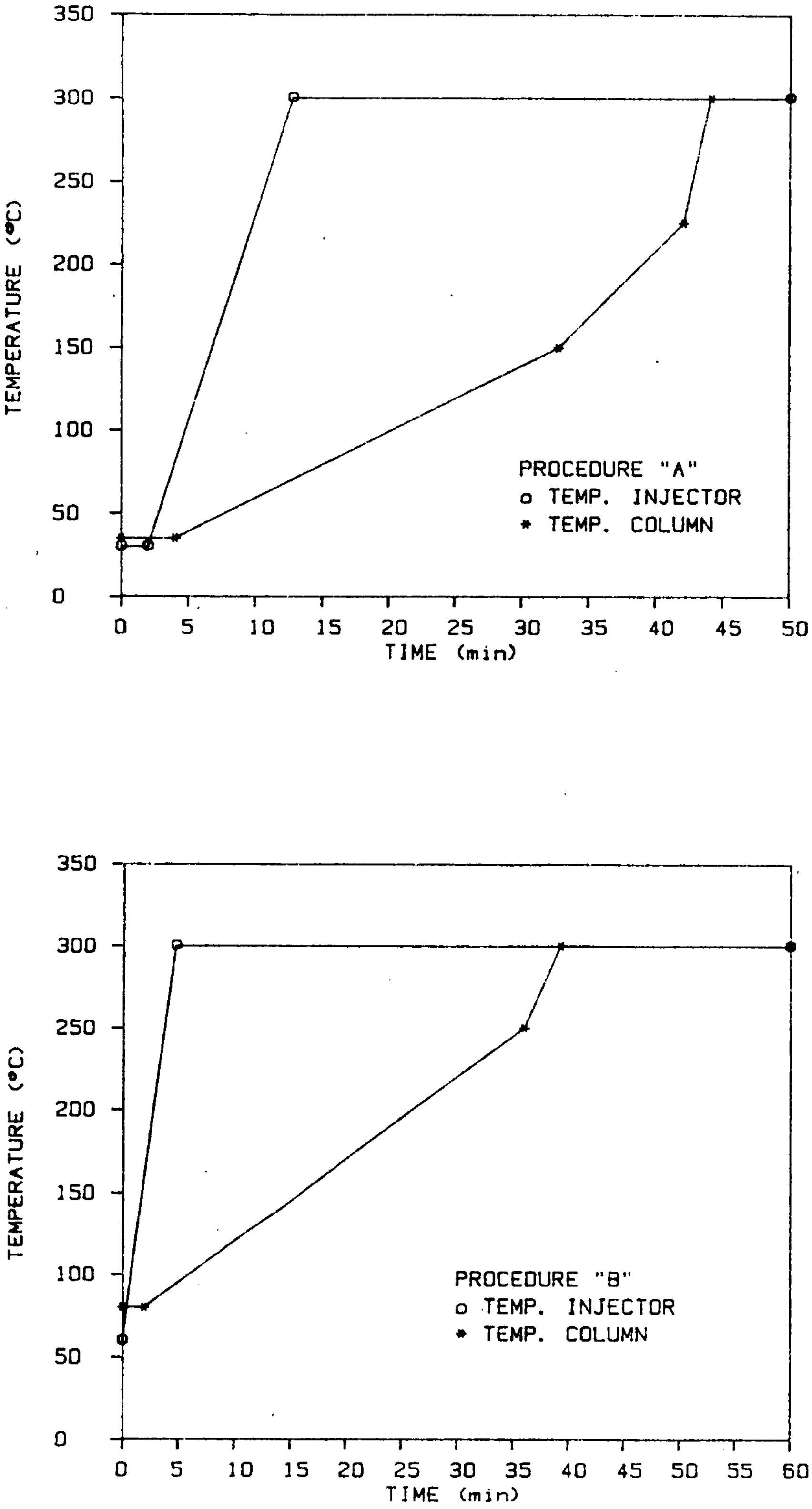

FIGURE 6. Temperature programs used for the on-column injector and the column oven.

the alphatic fraction (F1). In this procedure, the temperature of the on-column injector was raised rapidly to 300°C to obtain a maximum resolution for n-C_{10} to n-C_{35} alkanes.

WEATHERING RATIOS

The presence of light n-alkanes and isoprenoids in the dispersed oil allows the calculation of weathering ratios. The alkane/isoprenoid ratio (ALK/ISO) is used in connection with C17/pristane and C18/phytane ratios (C17/PRI and C18/PHY) to measure the relative contribution of microbial degradation to the weathering process. ALK/ISO approaches zero as linear alkanes are preferentially depleted in relation to biodegradation-resistant isoprenoids (Boehm et al. 1982).

The saturated hydrocarbon weathering ratio (SHWR) is used to evaluate the loss by evaporation by measuring the relative abundance of low-boiling and high-boiling linear alkanes, as follows:

$$\mathrm{ALK/ISO} = \frac{\sum C_{14} \text{ to } C_{18}}{\sum 5 \text{ ISOPRENOIDS}} \qquad \mathrm{SHWR} = \frac{\sum C_{10} \text{ to } C_{25}}{\sum C_{17} \text{ to } C_{25}}$$

RESULTS AND DISCUSSION

TEMPERATURE VARIATIONS AND ICE FORMATION

The prototype simulator discussed in this report represents a compromise between an indoor tank in which physical parameters, such as air temperature, and light exposure, can be fully controlled (Martin _et al._ 1976) and an unprotected outdoor tank for which climatic conditions are generally beyond control. In an outdoor tank, sea-water can overheat in summer and the tank can rupture because of freezing at low temperatures in winter (Gordon _et al_. 1976).

Temperature variation is reported in Figures 7, 8, and 9 for experiments 1, 2, and 3 respectively. Each graph gives the temperature of the sea-water column and the daily maximum and mimimum air temperatures recorded at the weather station located on the campus of the Université du Québec à Rimouski, near the experimental site.

In experiment 1, the initial water temperature decreased slowly over the first three weeks. Ice cover was formed after 25 days and persisted during most of the experiment. The large variability of the air temperature had little effect on the temperature profile of the water column.

In experiment 2 (Figure 8), no attempt was made to control the sea-water temperature and the variation observed is the result of the effects of continuous decrease the air temperature. It therefore appears that the thermal inertia of the system is quite good and only very large fluctuations can induce detectable variations in the sea-water temperature such as usually observed at sea.

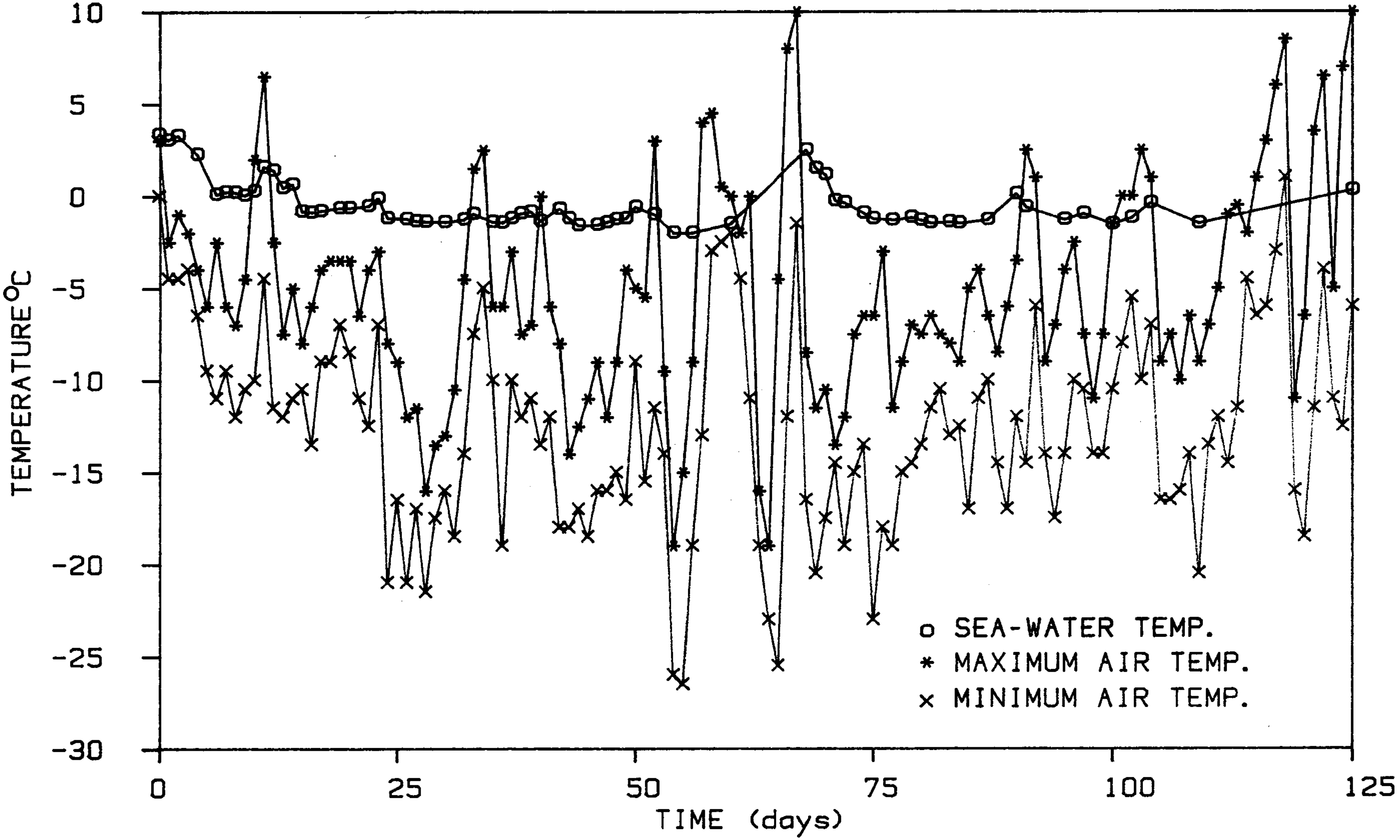

FIGURE 7 Temperature recording in experiment 1.

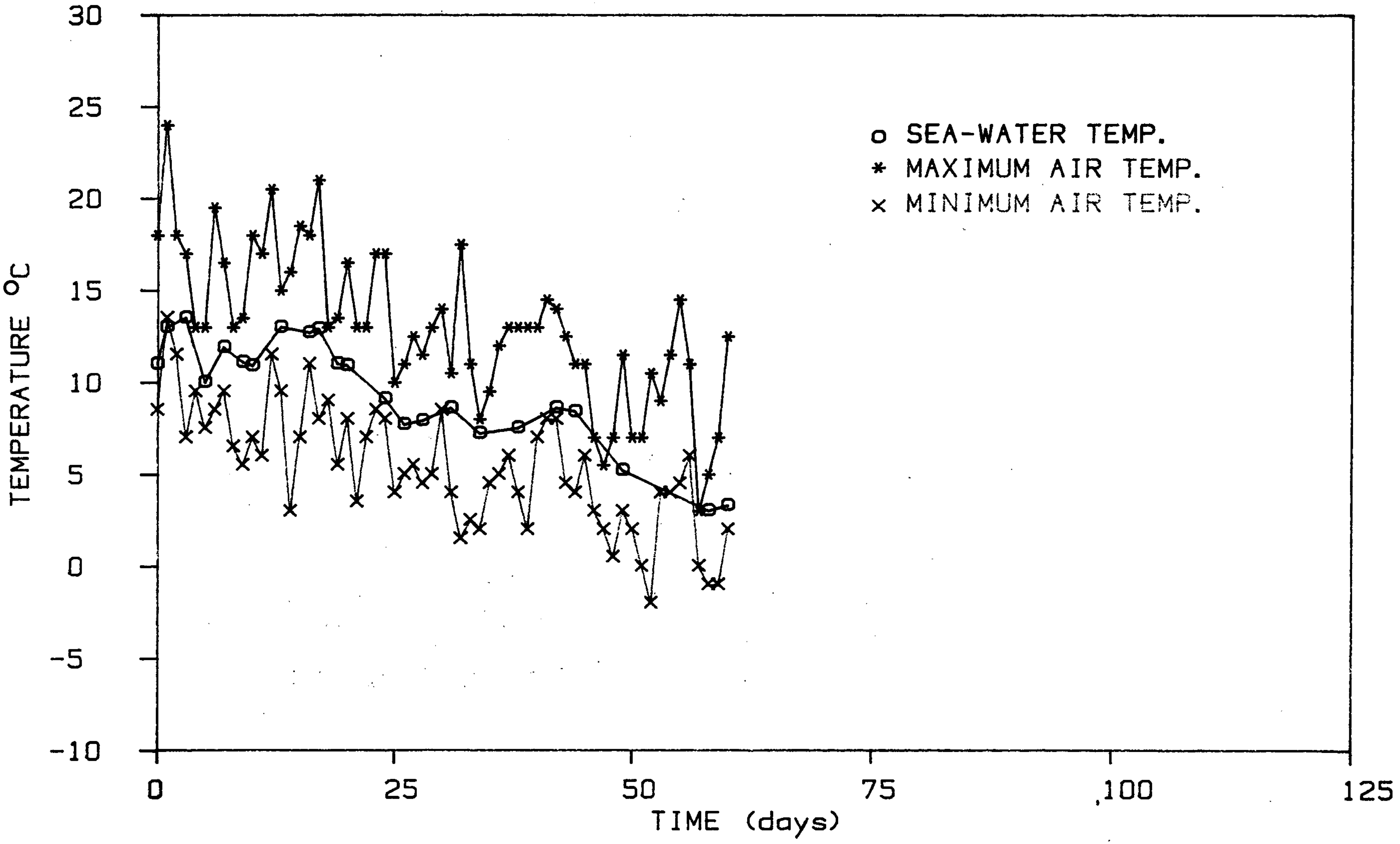

FIGURE 8 Temperature recording in experiment 2.

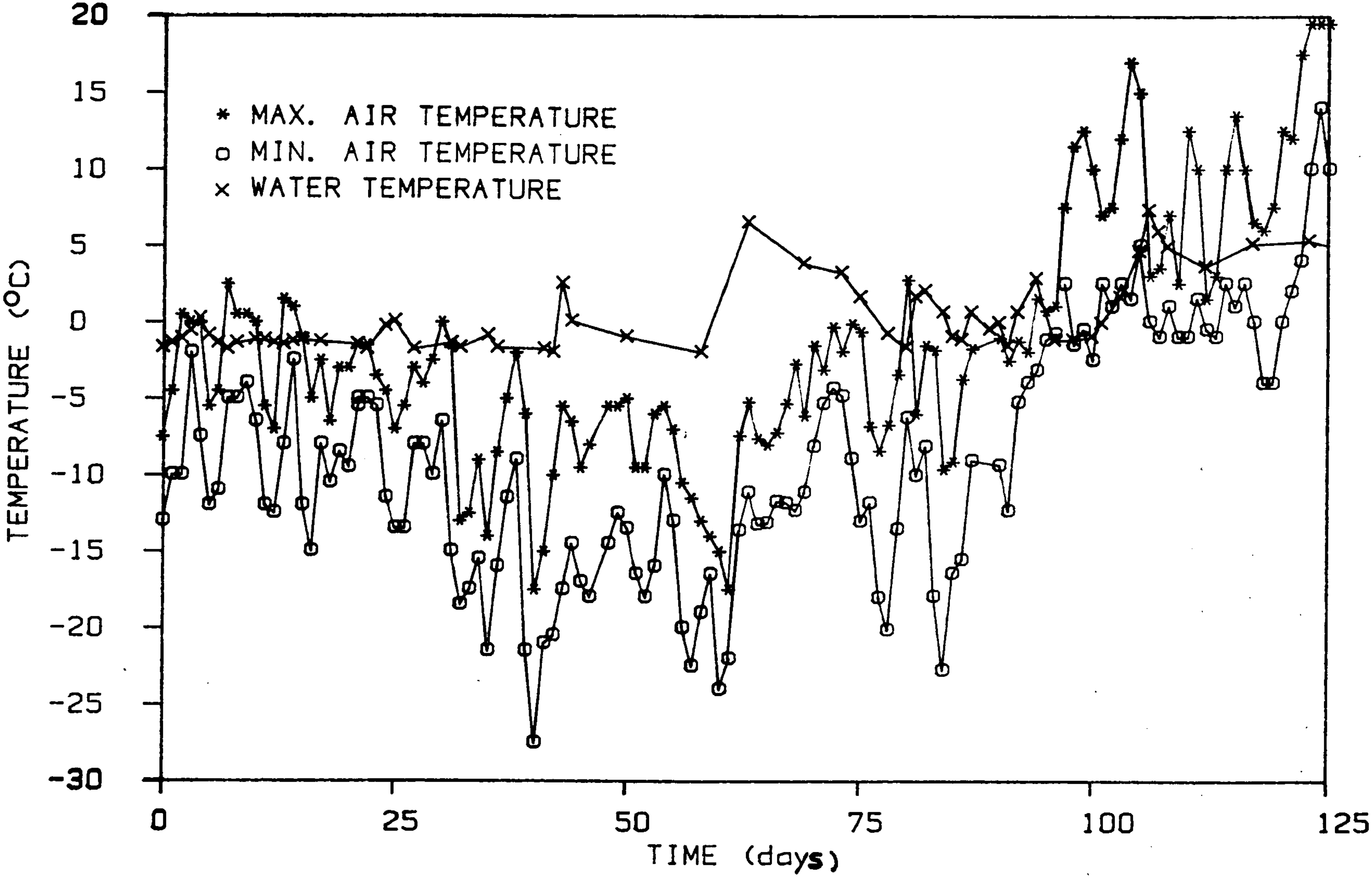

FIGURE 9 Temperature recording in experiment 3.

The third experiment was started in the presence of slush ice which consolidated into an ice cover up to end of the run. At day 58, the sea water temperature was raised accidently to about 7°C for a few hours because of a malfunction of the thermoregulation system. However, the ice cover did not melt and the temperature returned slowly to normal during the days following. The thickness of the ice cover reached 30-40 cm during the coldest period of the winter.

MICROBIAL ACTIVITY

As expected at low temperatures, the initial bacterial count in experiment 1 was very low. Again, as expected,it was about one order of magnitude higher at the beginning of experiment 2 (Table 2) because run 2 started at the end of the summer with a water temperature of 11°C. In contrast, the initial count in experiment 3 was suprisingly high for the season, especially with the very low water temperature. Accidental contamination of the sample is excluded because high counts were also observed for several days following.

Bacterial counts observed in the course of experiments 1, 2, and 3 are reported in Figure 10. The development of the microfauna was very slow in the first 50 days of experiment 1. This feature may be attributed to a low concentration of oxygen in the water column because the air bubbler was only installed on day 48 in this experiment, whereas nutrient concentration (nitrate and phosphate) was monitored and controlled by regular additions from the beginning. Bacterial grew very rapidly in experiment 2 and the population reached 10^6 colonies per cc only 5 days after the beginning of the run, doubling in the following 14 days. Then the population began to

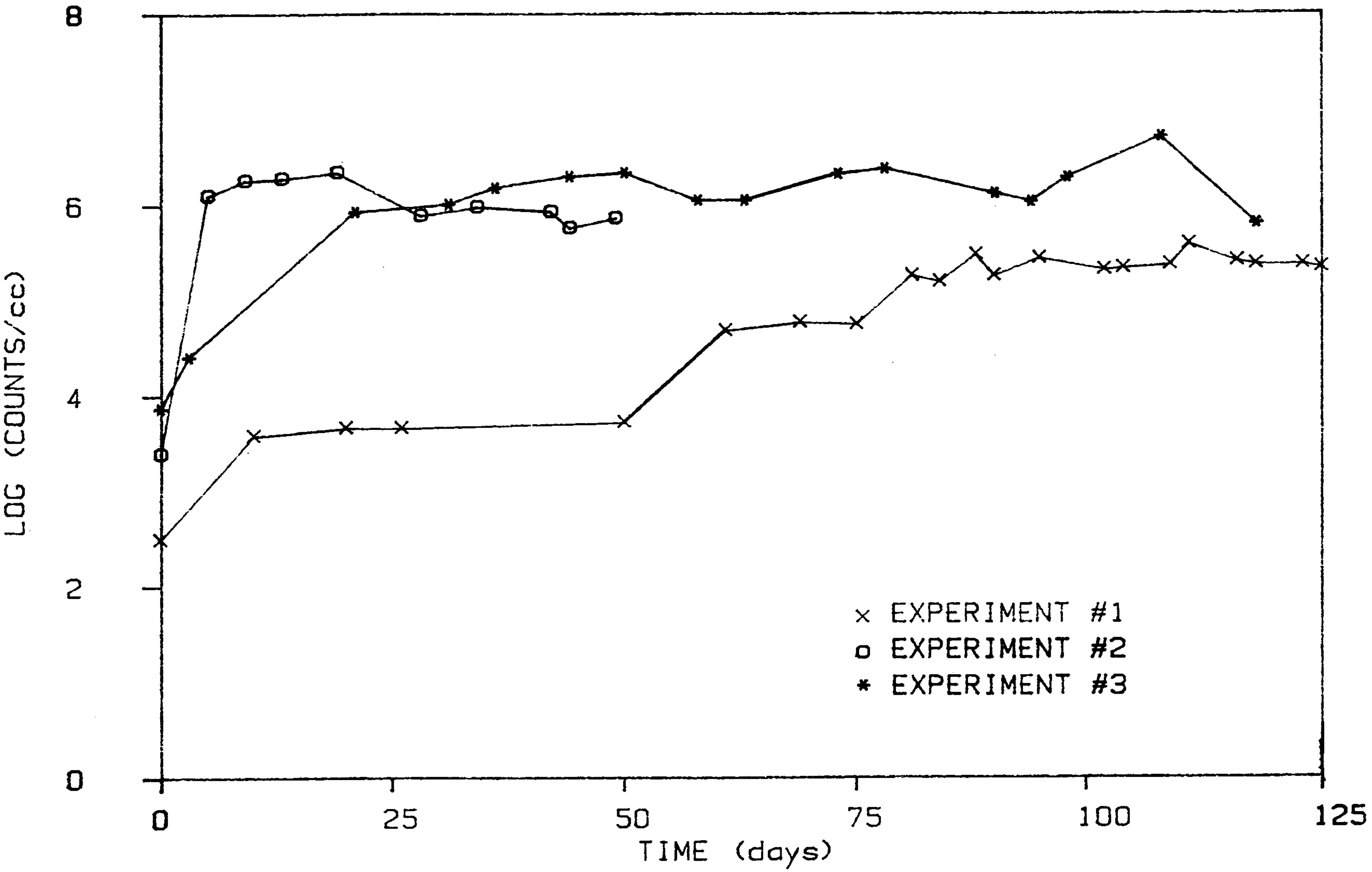

FIGURE 10. Bacterial counts in experiments 1, 2, and 3.

decline slowly up to the end of the experiment, possibly as a result of reducted concentration and changes in the quality of hydrocarbons.

In experiment 3, the bacterial counts increased much more rapidly than in experiment 1 (both during winter) and reached values even higher than the maximum count observed in experiment 2. This intense microbial activity is attributed to the availability of nutrients and oxygenation in the water column throughout the experiment.

The rate of nitrate consumption has been estimated for each experiment using the concentration measured before each addition and the amount of nitrate required to simulate the natural nutrient replenishment (15-20 μmole/cc) (Table 5). In all experiments, the maximum consumption rate seems to be related to the maximum activity of the microfauna but is not correlated to the maximum bacterial count reached in each run. Thus, the nitrate consumption of bacterial population between day 20 and day 40 of experiment 2 is much lower than the consumption in experiment 3 for the same period, with about an equal number of colonies.

RESURFACING PROCESS

One of the objectives of this project was also to evaluate the long-term effectiveness of a chemical dispersant at low temperature by estimating the stability of the dispersion. Figure 11 reports the percentage of dispersed oil remaining in the water column compared to the initial amount used for the dispersion. The percent dispersed oil was calculated from the oil concentration measured at sampling level 3 (0.6 m below the surface) assuming a homogeneous distribution of oil within the contained water column. In experiments 1 and 2, excellent initial

TABLE 5

Nitrate consumption in the contained sea-water column

Period (days)	Experiment 1 (µmole/day)	Experiment 2 (µmole/day)	Experiment 3 (µmole/day)
0-20	0.77	1.90	1.22
20-40	1.23	0.1	0.64
40-60	1.09	0.1	0.84
60-80	2.18	----	1.33
80-100	3.71	----	1.21
100-120	1.12	----	n.a.[a]

[a] not available

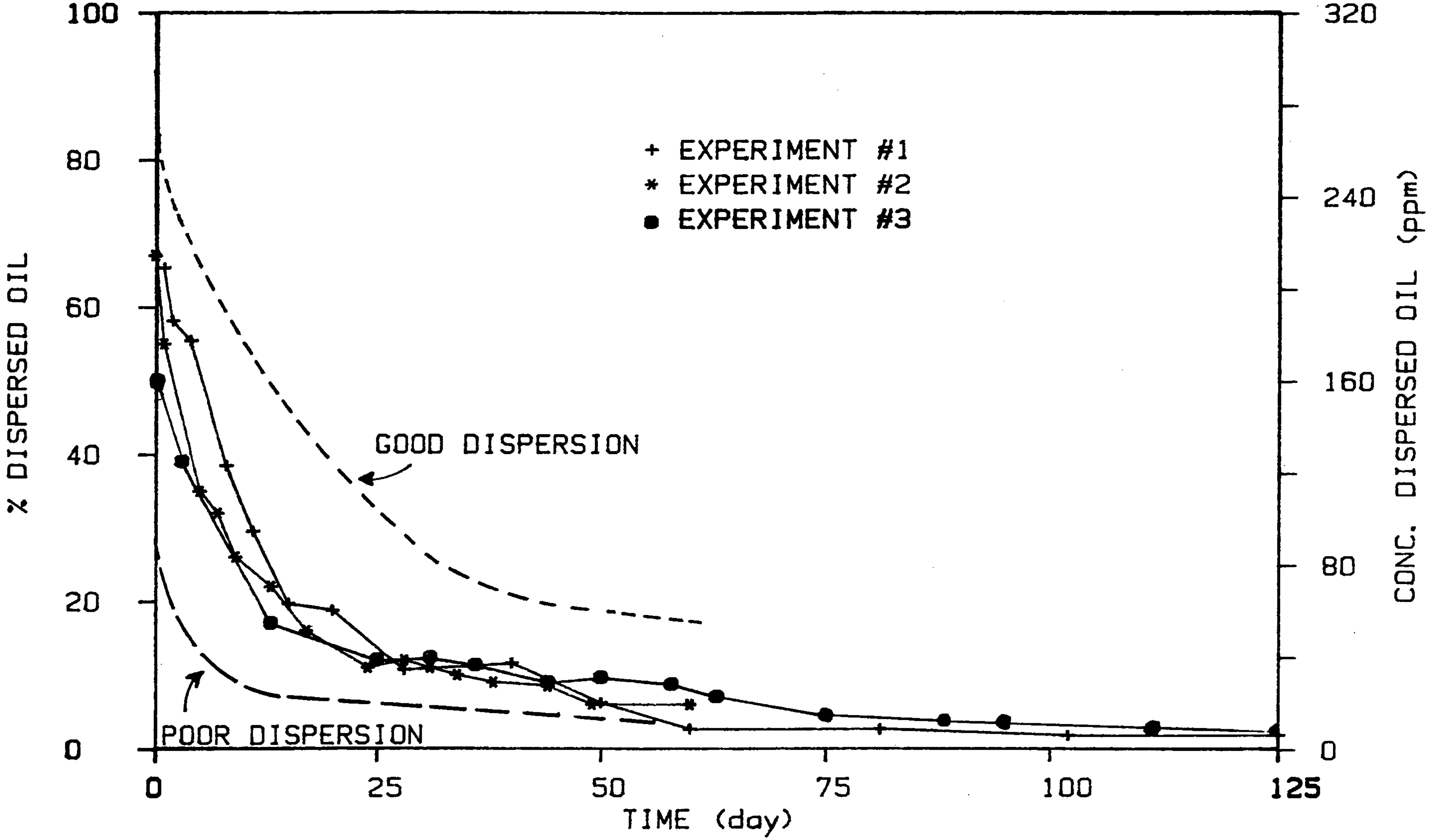

FIGURE 11. Percentage of dispersed oil measured in the water column in the experimental tank.

dispersions were obtained (reaching 70% in both cases) using only the low energy provided by the air stream blowing over the water surface. In experiment 3, the dispersion was conducted in the presence of slush ice (5-7 cm) and it was necessary to stir the oil/ice/water mixture moderately to ensure a relatively good dispersion of 50%.

The most striking feature evident in Figure 11 is the relative similarity of all experimental curves, regardless of the initial dispersion level or of water temperature. This behaviour indicates that the same physical process, working independently from the initial experimental conditions, regulates the amount of dispersed oil in the water column.

In a mesoscale tank of the size used in this experiment, the motion of oil droplets is controlled by buoyancy rather than by diffusion. The rate of particle settling is given by Stokes' law:

$$4/3\,\pi a^3 \Delta\rho g = 6\pi\eta a v \qquad \text{Eq. 1}$$

The derivation of Stokes' law assumes that (1) the motion of the spherical particles is very slow to avoid local turbulence generated by particles and to minimize the friction, (2) the suspension is very dilute to avoid interactions between particles, and (3) the particles are much much larger than the molecules of the medium. Keeping in mind these restrictions, eq. 1 can then be used to estimate the diameter of oil droplets rising slowly to the surface:

$$a = \sqrt{\frac{9\eta_W v}{(\rho_W - \rho_o) g}} \qquad \text{Eq. 2}$$

where:

a = diameter of oil droplet

η_w = viscosity of sea-water $\simeq$ 1 Pa·s

v = velocity of the droplet ($m \cdot s^{-1}$)

g = 9.81 $m \cdot s^{-2}$

ρ_w = density of sea-water = 1020 $kg \cdot m^{-3}$

ρ_o = density of crude oil = 839 $kg \cdot m^{-3}$

For a given velocity (i.e., v = 1 $m \cdot day^{-1}$), the size of oil droplets travelling from the bottom of the tank up to the sampling level 3, located about 1 m above the bottom, can then be estimated at 5.4 µm. Figure 12 gives the distribution of oil-droplet sizes rising to the surface as calculated by Stokes' equation for the experimental conditions observed in the simulator.

The similarity between experimental curves shown in Figure 11 and the calculated distribution (Figure 12) indicates a possible direct relationship between the amount of oil in the water column, an experimental parameter, and the calculated size of oil droplets. This relationship is highlighted by data presented in Table 6 and Figure 13. The linearity of the relationship is not observed immediately at the beginning of the experiments, but becomes evident within a few days after the initial dispersion (from day 3 to day 8), mainly because of restrictions to the application of Stokes' law already mentioned. Regression equations, calculated for data enclosed in large square brackets (Table 6), give the droplet size as a function of the oil concentration in the water column. The correlation coefficient (r) is also given.

The slope of these straight lines can be related to the stability of the dispersion, i.e., for a given amount of oil, the average size of droplets in a less stable dispersion should be larger (yielding a steeper slope) than

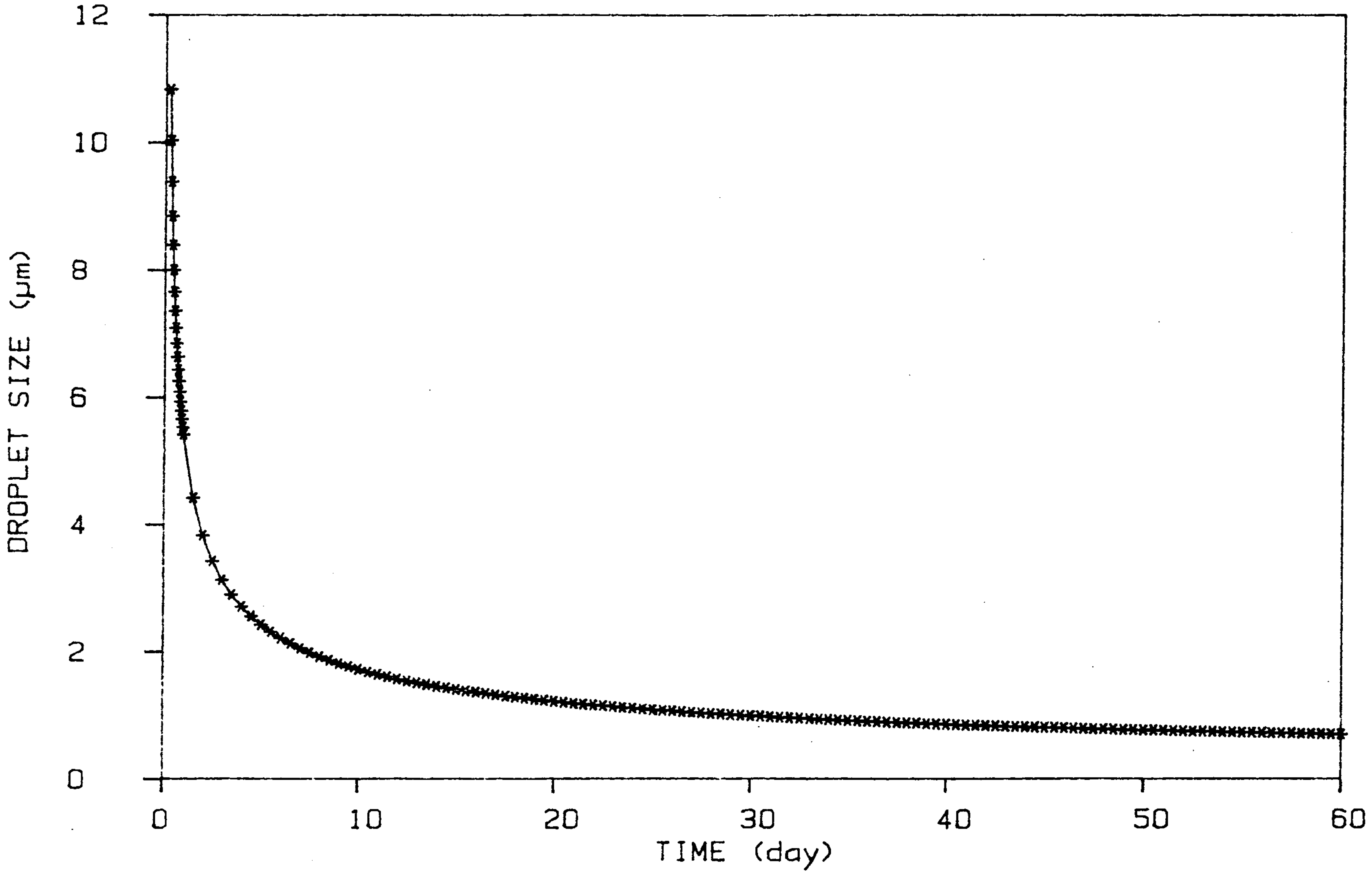

FIGURE 12. Distribution of oil-droplet size as calculated from the Stokes' equation.

TABLE 6

Correlation between calculated droplet size and measured oil concentration in the simulator.

Day	Oil concentration (ppm)	Droplet size (µm)	
EXPERIMENT 1 (Nov. 85 - March 86)			
0.25	296	10.8	
1	213	5.4	
2	206	3.8	
8	139	1.9	Regression equation:
11	106	1.6	
15	70	1.4	$Y(\mu m) = 0.5 + 1.03\ 10^{-2} X(ppm)$
20	67	1.2	
40	42	0.9	$r = 0.982$
50	23	0.8	
EXPERIMENT 2 (Aug. 86 - Oct. 86)			
0.25	211	15.3	
1	174	5.4	
5	110	2.4	
7	101	2.0	
9	83	1.8	
13	68	1.5	
17	52	1.3	Regression equation:
24	35	1.1	
28	37	1.0	$Y(\mu m) = 0.4 + 1.75\ 10^{-2} X(ppm)$
31	35	1.0	
34	32	0.9	$r = 0.993$
38	30	0.9	
44	27	0.8	
49	20	0.8	
60	21	0.7	
EXPERIMENT 3 (Dec. 86 - April 87)			
3	124	3.1	
13	59	1.5	
25	39	1.1	Regression equation:
31	39	1.0	
36	36	0.9	$Y(\mu m) = 0.04 + 2.49\ 10^{-2} X(ppm)$
44	29	0.8	
50	30	0.8	$r = 0.999$
58	28	0.7	

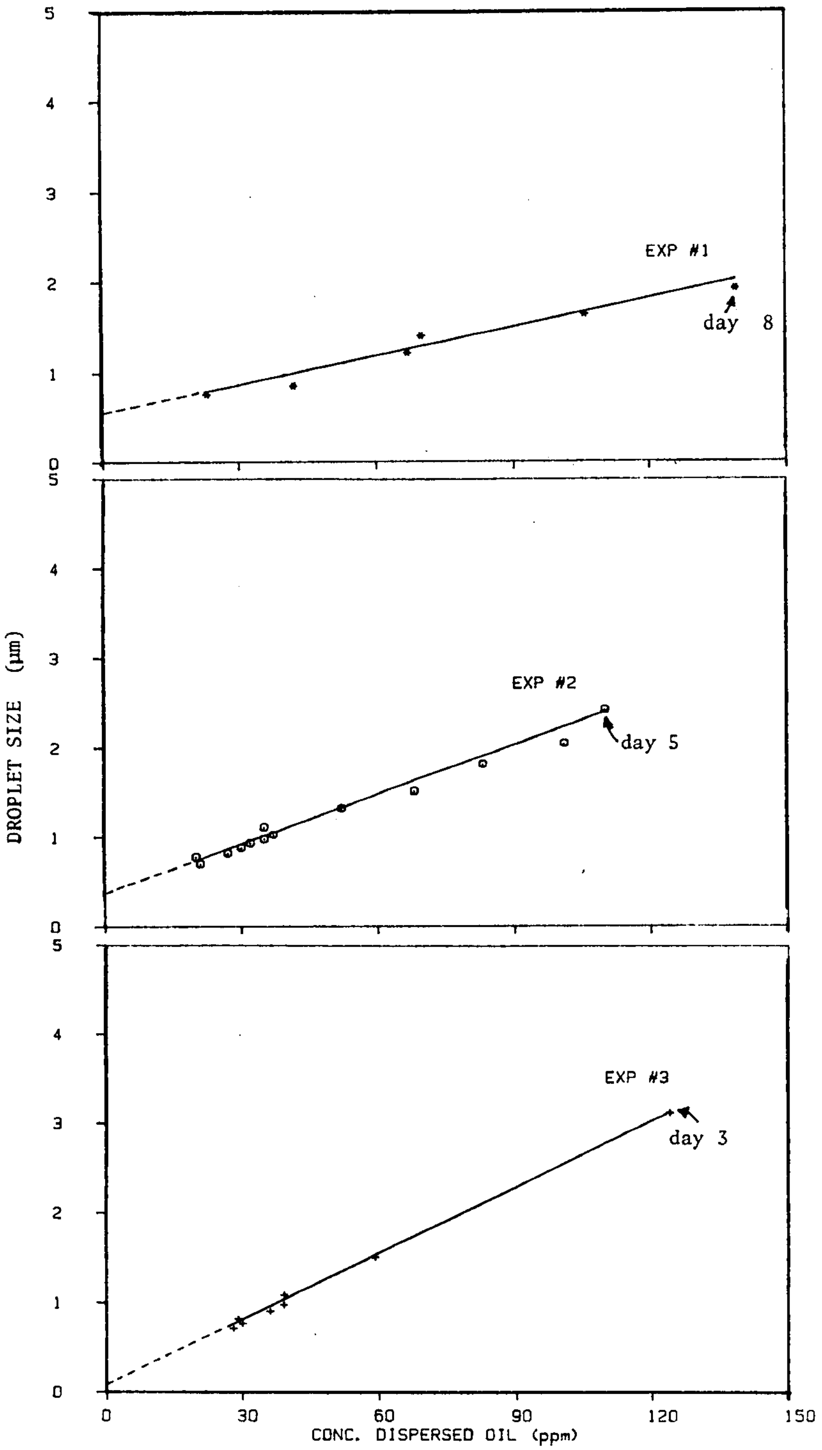

FIGURE 13. Distribution of oil-droplet size versus oil concentration observed in experiments 1, 2, and 3.

droplets from a good dispersion (lower slope). This feature is clearly illustrated using the simulated curves for poor and good dispersions in (Figure 11). A good dispersion gives a slope that approaches zero (i.e., slow change in the droplet size). In contrast, in a poor dispersion the slope is steeper, and with a displacement of the straight line towards lower values (Figure 14).

The experimental data in Table 6 give slopes relatively close together because the same commercial dispersant and the same crude oil were used throughout all experiments. The dispersion in experiment 3 was less stable mainly because of the presence of slush ice on the surface and the sub-zero sea-water temperature. As expected, the experimental slope observed for experiment 3 (Table 6) is almost twice the average slope of experiments 1 and 2. The correlation in the experiment 3 was the best of all (r = 0.999) mainly because the water column was rapidly covered by ice shortly after the dispersion and no further external factors could influence the slow resurfacing of droplets.

These results highlight some interesting fundamental points about the long-term fate of dispersed oil under these particular experimental conditions of low temperature.

a) Seawater temperature is not a determining factor in dispersion stability. Instead, the presence of ice reduces strongly the dispersant effectiveness because of the wave damping induced by the ice.

b) In the absence of diffusion and/or convection, the main mechanism controlling the oil concentration in the contained water column is buoyancy.

c) Within a few days after the initial dispersion, the rising of oil droplets

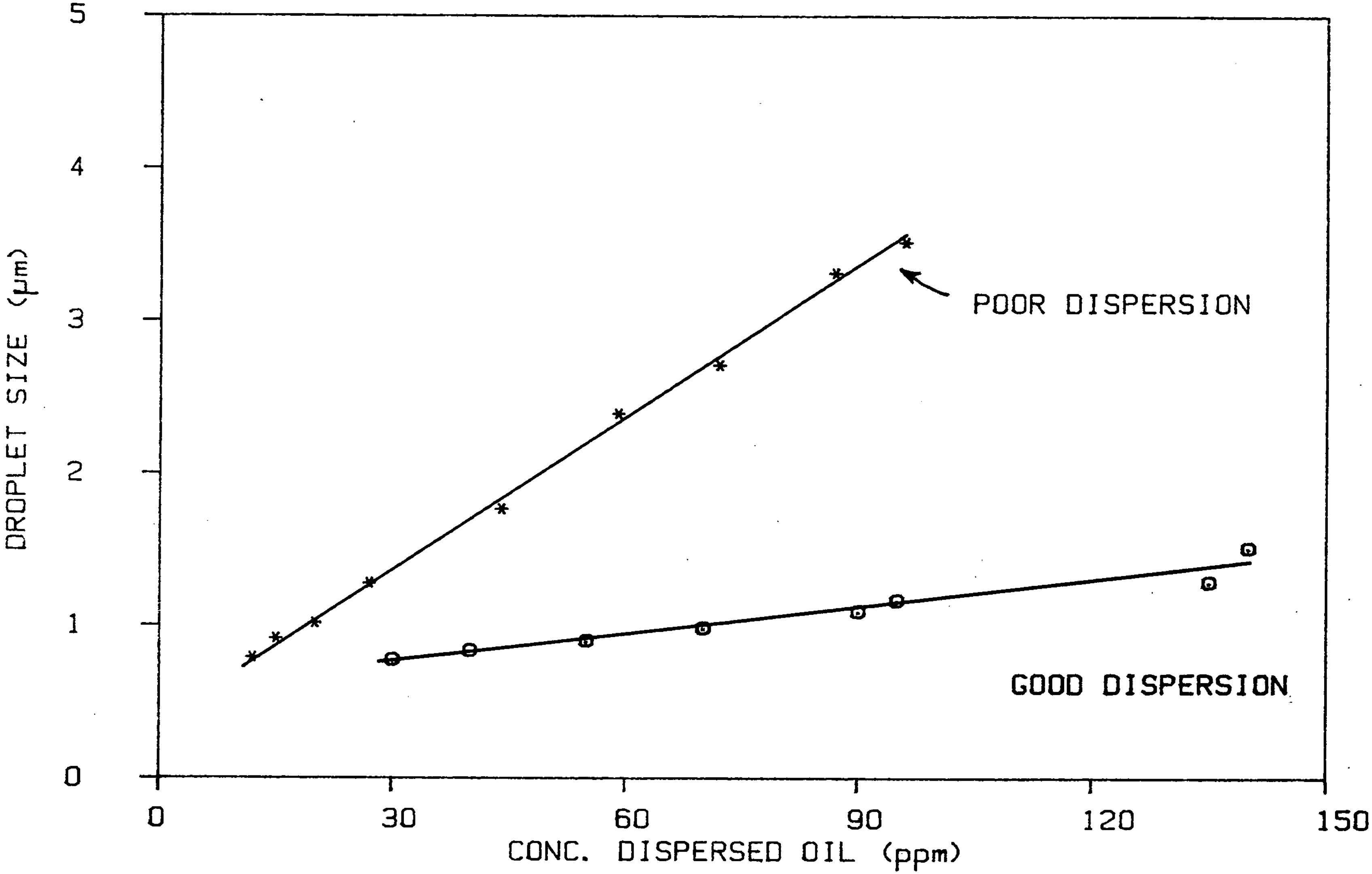

FIGURE 14. Distribution of oil-droplet size versus concentration of dispersed oil for good and poor dispersions.

can be described with a simple mathematical relationship; the Stokes' equation. The implication is that contributions from other physical mechanisms to the removal of oil from the water column, such as flocculation and dissolution, are negligible.

d) Long-term stability of a dispersion (i.e.,the dispersant effectiveness), is evaluated by plotting the calculated oil-droplet size versus the concentration of dispersed oil, which gives a linear relationship. Thus, in the absence of external disturbance, the experimental period could be reduced to 3 weeks without loss of accuracy.

EVAPORATION AND BIODEGRADATION PROCESSES

Among other factors affecting the concentration of oil in the water column, evaporation and biodegradation were monitored by regular gas chromatographic (GC) analysis of different hydrocarbon fractions of dispersed oil.

Gas chromatographic traces of surface mousse and dispersed oil are compared to unweathered crude oil in Figure 15. The EPS standard crude oil used in these experiments is a light oil and the compositional pattern of alkanes is clean and easily identified (Figure 15, top trace).

Weathering ratios (Table 7) show the effects of chemical dispersion on the oil weathering. These results suggest that the oil droplets in the water column were not exposed to the air and, thus, the light, linear alkanes were not lost by evaporation (high SHWRs), conversely, the surface emulsions remained in contact with air for several weeks to months, losing most light hydrocarbons (low SHWRs).

Microbial degradation is clearly indicated by the ratios of ALK/ISO,

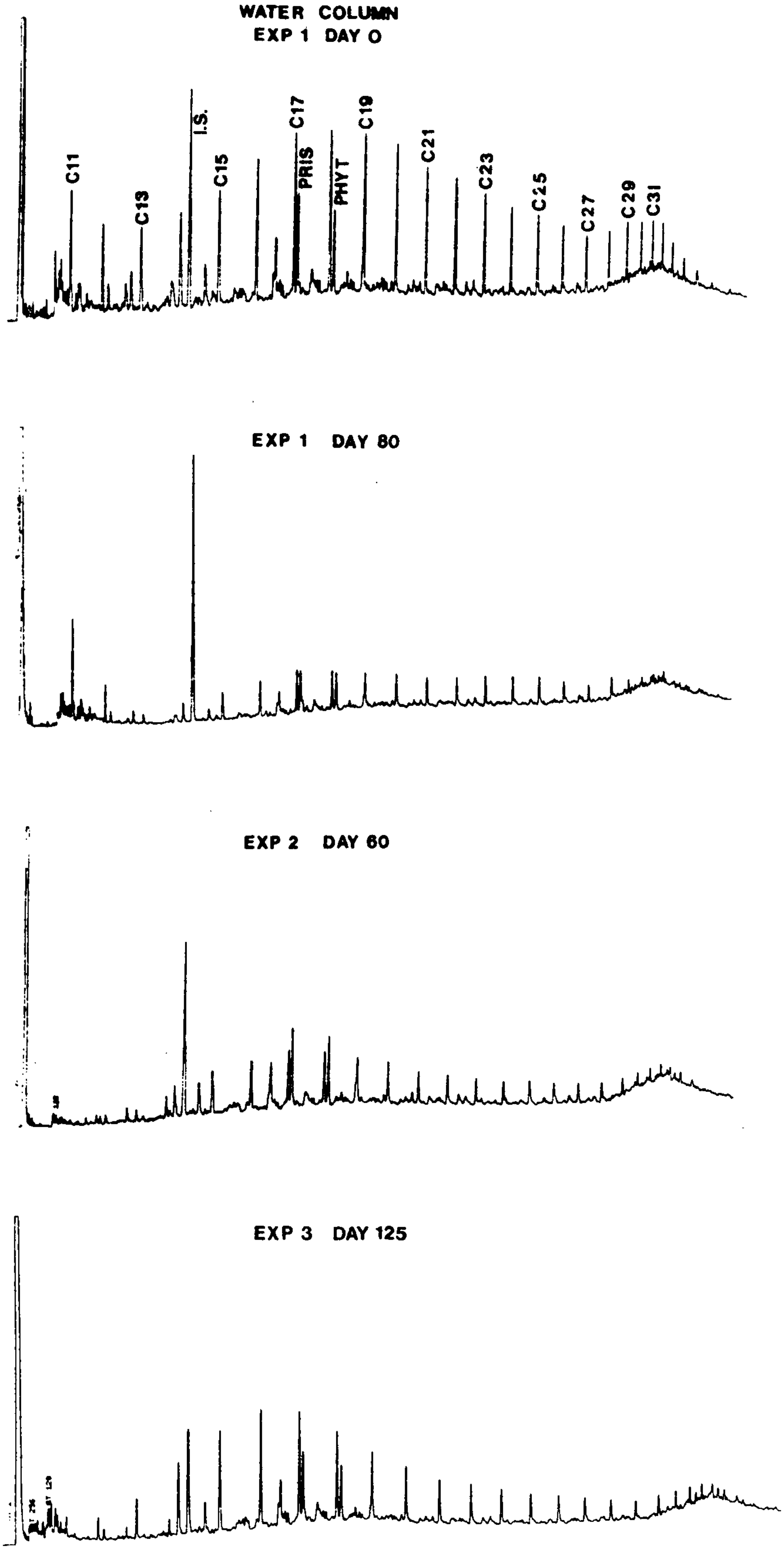

FIGURE 15. GC traces of aliphatic hydrocarbons extracted from the water column and the surface emulsion. The internal standard (I.S.) is hexamethyl benzene.

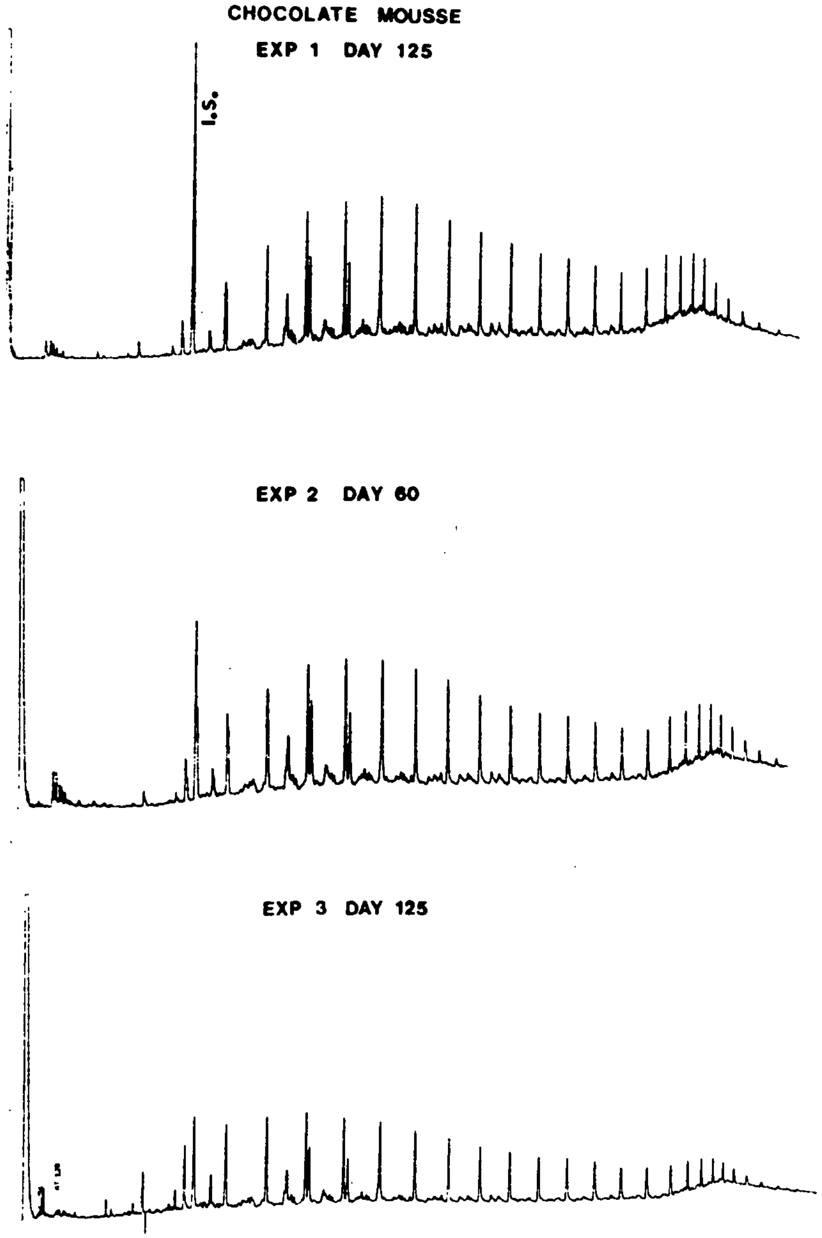

FIGURE 15. (continued).

TABLE 7

Weathering ratios calculated from chromatographic traces shown in Figure 15

a) Water column dispersion

	Before dispersion	Exp. 1 (day 80)	Exp. 2 (day 60)	Exp. 3 (day 125)
SHWR*	1.77	1.69	1.50	1.61
ALK/ISO	2.03	0.84	1.01	1.92
C17/PRI	1.60	0.75	0.77	1.49
C18/PHY	1.82	0.88	0.85	1.40
PRI/PHY	0.98	1.36	0.93	0.87

b) Surface emulsion

	Before dispersion	Exp. 1 (day 80)	Exp. 2 (day 60)	Exp. 3 (day 125)
SHWR	1.77	1.21	1.21	1.34
ALK/ISO	2.03	1.82	1.85	2.08
C17/PRI	1.60	1.48	1.41	1.61
C18/PHY	1.82	1.70	1.60	1.81
PRI/PHY	0.98	1.10	0.92	0.97

* Saturated Hydrocarbon Weathering Ratio

C17/PRI, and C18/PHY ratios in the water column of experiments 1 and 2, but dispersed oil droplets in experiment 3 seem almost undegraded. Similarly, surface emulsions are only slightly biodegraded in experiments 1 and 2. In experiment 3, ratios were left unchanged, presumably because the presence of ice during 100 days completely restricted the bacterial activity and biodegradation.

The pristane-to-phytane ratio (PRIS/PHY) was not affected by the weathering processes in surface emulsions but was abnormally high in water column in experiment 1, which could result from to the presence of plankton in the contained water column. The PRI/PHY ratio is equal to 1.0 in EPS crude oil. Usually, this ratio would increase as more biogenic pristane is produced relative to the petrogenic phytane.

These results emphasize four important features.

a) Dispersed oil droplets were rapidly degraded in the water column by micro-organisms in sea-water at temperaturesgreater than 3°C. Bacterial degradation of hydrocarbons was strongly reduced at lower temperatures and below an ice cover.

b) Evaporation was the main weathering process for surface emulsions, whereas biodegradation for these emulsions was almost negligible.

c) In the fall experiment, the effects of both processes (evaporation and biodegradation) on the chemical composition of dispersed oil were easily detected by GC analysis. However, their relative contributions to the total removal of oil from the water column are still unclear.

SEDIMENTATION PROCESS

The sedimentation process was studied by regular sampling of the sediment trap at the bottom of the simulator. The nature of the material found in the trap was not studied in detail but some chemical extractions have been carried out and a typical GC trace of the aliphatic fraction is shown in Figure 16. This profile shows no evidence of a selective biodegradation of light alkanes in settling. The amount of oil removed from the water column by the sedimentation process was estimated to about 3 to 5% in experiments 1 and 3 but was negligible in experiment 2. The role and the importance of sedimentation in the whole weathering process of dispersed oil in winter are not yet clearly understood.

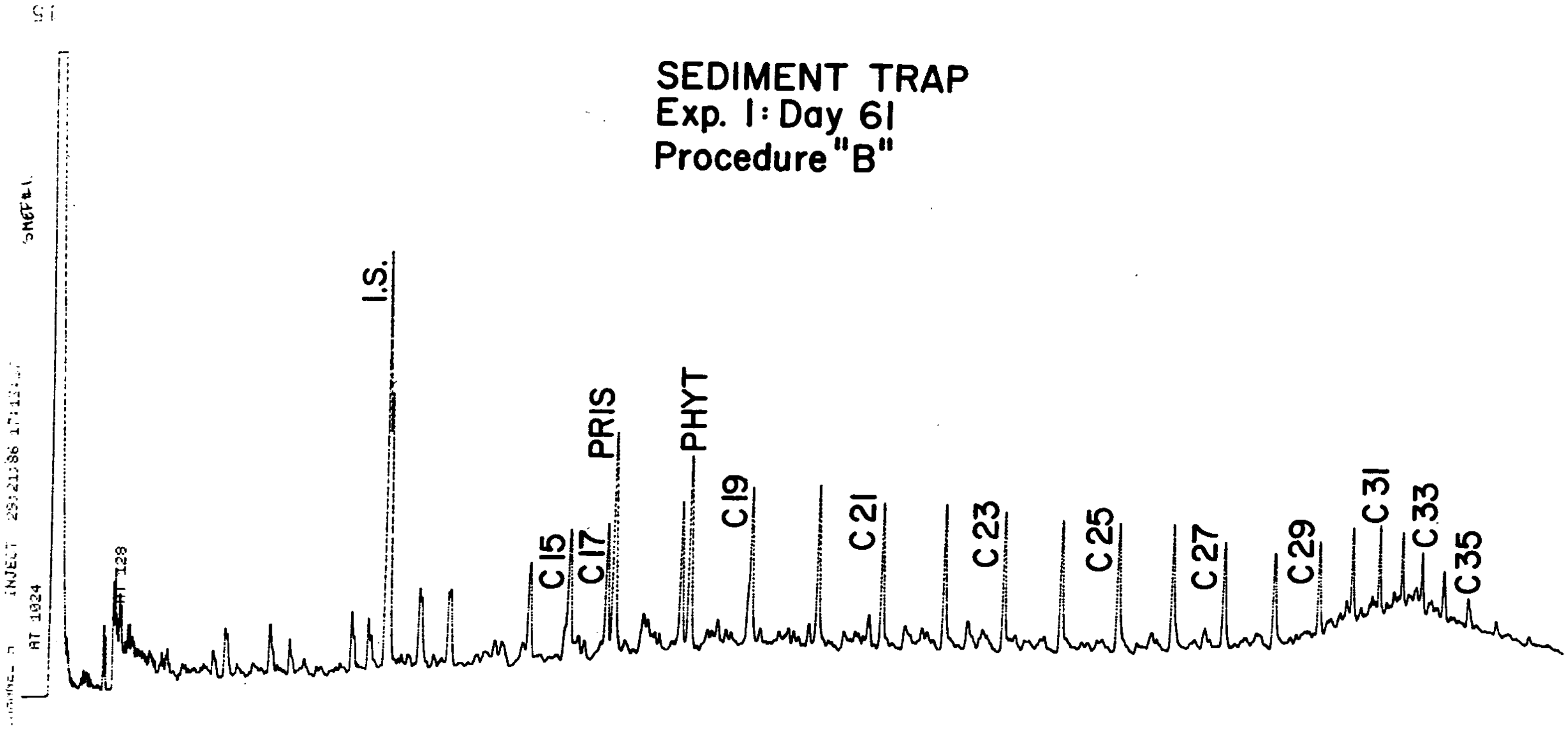

FIGURE 16. GC trace of aliphatic hydrocarbons extracted from settling particles in sediment trap.

CONCLUSION

In a recent study on the effects of oil and oil dispersants in an enclosed marine ecosystem under summer conditions, Linden and co-workers (1987) concluded that the long-term effects of the use of oil dispersants "may prove to be less severe than the dispersion of oil by natural processes." This conclusion is not supported, for winter conditions, by results of the present study since natural processes seem to lead to formation of stable, surface emulsions which are very resistant to natural biodegradation. Clearly more studies of these effects are required.

Based on the experimental results and observations, the mesoscale tank should provide all experimental requirements for long-term studies under fall and winter conditions. The simulator prototype fulfilled the main task of this project and only a few technical problems were encountered. Many of the weathering data presented in this report are new and original and show clearly the feasibility of experimental work in a protected outdoor tank during winter and also the relevance of the data obtained.

RECOMMENDATIONS

Concerning the future development of mesoscale tanks for controlled outdoor studies, we recommend the following:

- inclusion of an automatic data acquisition system to record temperature, oxygen, nutrients, turbidity, pH, and other routine physical data;
- Installation of a sampling device on the side of the simulator so as to avoid disturbance of the water surface and the freezing of samples inside sampling tubing during winter;
- further testing of simulator tanks under various summer and winter conditions to evaluate the stability of the system, i.e., time required to reach a significant deviation from the natural environment; and
- experimentation a series of experiments in which one tank would be a control and four tanks could be used in a cascade-dilution process where a highly contaminated solution is diluted progressively so that the environment becomes less toxic.

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