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# **A Study of the Solubility of Oil in Water**

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**A STUDY OF THE SOLUBILITY OF OIL IN WATER**

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ENVIRONMENT PROTECTION SERVICE  
DEPARTMENT OF THE ENVIRONMENT**

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## **ABSTRACT**

Experiments were conducted to determine the total solubility of oil in water. Three oils were employed; Number 2 fuel oil, medium bunker fuel, and western crude oil. The total solubilities of these oils were determined by dissolution tests and by static equilibrium tests; both testing procedures attained similar results. The maximum solubilities and the lengths of time in which these were attained were found to be of the following orders of magnitude; Number 2 fuel oil, 7.5 ppm, attained in 5 days; medium bunker fuel, 2.3 ppm, attained in 2 days; and western crude oil, 46 ppm, attained in 8 days. The rates of removal of the dissolved components from solution in water, were also investigated. It was observed that the time duration of removal was analagous to the time duration for the attainment of maximum concentration. Traces of soluble hydrocarbons were found to persist for at least 13 days after their introduction into solution.

## RÉSUMÉ

Des expériences ont été faites pour déterminer la solubilité totale de l'huile dans l'eau. Trois huiles furent employées: mazout numéro 2, huile de soute moyenne et huile brute d'Alberta. La solubilité totale de ces huiles fût déterminée par des essais de dissolution et d'équilibre statique; les deux procédures d'essais ont donné des résultats semblables. La solubilité maximum et la durée requise pour l'atteindre étaient de l'ordre de magnitude suivante: mazout numéro 2, 7.5 ppm, atteinte en 5 jours; huile de soute moyenne, 2.3 ppm, atteinte en 2 jours; huile brute d'Alberta, 46 ppm, atteinte en 8 jours. Le taux d'enlèvement des composantes dissoutes dans une solution dans l'eau fût étudiée. Il fût observé que la donnée requise pour l'enlèvement était analogue à la durée requise pour atteindre la concentration maximum. On a constaté que des traces d'hydrocarbures solubles persistaient pour au moins 13 jours après leur introduction dans la solution.

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## **FOREWORD**

The work in this study was performed under contract to the Environmental Emergency Branch, Environmental Protection Service, Department of the Environment, in accordance with the following terms of references:

- (a) To provide a determination of the persistence and maximum concentration of dissolved oil in water in a closed system;
- (b) To evaluate the nature of the dissolved materials by means of boiling point range, aromatic and non-aromatic components;
- (c) To determine the rates of dissolution and the rates of removal of the dissolved matter.

## **1 INTRODUCTION**

In recent years the old adage, "Oil and Water do not mix", has become somewhat inappropriate. It has been observed that some hydrocarbons are soluble in water and that oil can be dispersed into the water column. These phenomena have attracted the attention of environmental scientists who are studying not only the fate of oil in water but also its effects on the ecosystem.

The purpose of this paper is to investigate one aspect of these phenomena, the solubility of oil in water. The term, solubility of oil in water, implies not only the physical solubility factor, but also the time relationships involved, the persistence, and the analysis of the components which are in solution. In order to narrow the scope of this study the analysis of the soluble components was omitted. Instead, a method that determined the total volatile organic matter was used. This method was then applied to determine the maximum dissolved concentration, the length of time until this maximum was reached, and the time - concentration relations for the loss of the dissolved oil in an open system.

## **2 LITERATURE SURVEY OF METHODS FOR THE ANALYSIS OF DISSOLVED OIL IN WATER**

In the literature, a number of articles are available dealing fully or partly with the problem of solubility of oil in water. The work of McAuliffe (1,2,3,4) deals with the solubility of pure hydrocarbons in water, and hydrocarbon mixture in subsurface waters and subsurface brines. Other relevant works include Zarrella et al (5), Jettes and Veldink (6), Boylan and Tripp (7), and Demayo (8). There are two main steps involved in the study of oil solubility in water.

- (a) To dissolve oil and oil products in water
- (b) To analyze the water solution

The major problem lies with the analysis of the water layer, as the concentration of the dissolved organic compounds is very low. In the literature, gas chromatographic techniques are frequently used for analyzing hydrocarbons dissolved in water. These techniques are briefly reviewed in this section since the analysis of water samples in this investigation has also been performed by gas chromatography (GC).

### **2.1 Direct Analysis of Saturated Water Samples**

**2.1.1** Direct injection of sample -- After a sample is collected, it is directly injected into a gas chromatograph. Because a flame ionization detector is used in most cases, the presence and amount of water is undetected, and only the hydrocarbon contents in the sample are recorded. However, due to the presence of unknown interfering peaks (6), difficulties are usually encountered with this method.

**2.1.2** Using a carrier gas saturated with water vapor--The difficulties encountered with the direct injection method are caused by the water. However when the carrier gas is saturated with water vapor, no interfering peaks occur. This method has been used by Saraf and Witherspoon (9) for the determination of diffusion coefficients of hydrocarbons in water (ethane to n-butane). It is not known whether this method is suitable for analyzing hydrocarbons of higher molecular weights.

**2.1.3** Removal of water prior to GC analysis--In order to avoid interfering peaks caused by water, some workers (1,5) have removed water from the sample by using a drying agent before the sample enters the analytical column. In this method, only the hydrocarbons entering the column are detected. It is possible, however, that during the water removal procedure, some of the high boiling components may be also removed by the drying agent.

## 2.2 Extraction Method

Due to the analytical difficulties encountered by the presence of water, many workers have employed an extraction method (5,6,7,8). Hydrocarbons are extracted from the water sample by the addition of an immiscible solvent, such as iso-octane (5), nitrobenzene (6), pentane (7), or n-heptane (8). An extraction is performed and the immiscible organic layer is analysed using a gas chromatograph.

One of the drawbacks of this method is that the excess amount of the solvent causes an instability in the baseline, thus decreasing the sensitivity of the method. In order to increase the amount of hydrocarbons in the solvent, a large amount of water (one to two liters) is usually used in the extraction procedure. Another drawback of this method is that polar compounds of crude oils may not be extracted by the non-polar solvent (7). Possible errors may also be caused by the increase in the number of operational steps and in the time duration of the analysis.

The selection of a suitable solvent is not a simple task. If a solvent with a low boiling point is used, those hydrocarbons which have elution times similar to the solvent will not be detected because their small peaks will be masked by the large solvent peak. This is an important point for consideration, because the low boiling fractions of oil are generally the most soluble ones. On the other hand, if a solvent with a high boiling point is chosen, the analysis of the sample will take a greater length of time, and the high boiling fractions of the dissolved oil will not be easily detected in the analysis.

## 2.3 Gas Equilibration Method

This method (4) is based on successive gas chromatographic analyses after repeated equilibrations of a gas (e.g. helium) with an aqueous sample containing the dissolved hydrocarbons. Gas chromatographic data on the gas used in the equilibrations are plotted, and back-extrapolated to obtain the hydrocarbon concentration in the original aqueous sample. McAuliffe (4) reported that for hydrocarbons such as alkanes, 96% or more was carried into the gas phase from the aqueous sample. When water containing dissolved hydrocarbons is equilibrated with an equal volume of gas (air), the percentage of hydrocarbons in the gas phase has been reported as follows (3):

n-butane	98.0%
n-pentane	98.4%
n-hexane	98.6%
n-heptane	98.9%
n-octane	99.2%
Cyclopentane	88.5%
Cyclohexane	88.2%
Benzene	18.5%
Toluene	21.0%

These amounts depend on the vapor pressure and the solubility of the hydrocarbons concerned. This method has been used for determining hydrocarbon content of subsurface brines (3), as well as for the determination of the solubility of pure n-alkanes up to C<sub>14</sub>(2). Details of this method are available in the literature (4).

The short duration of this study and the number of experimental determinations required, necessitated a fast, simple but reliable method of analysis. A method, previously developed in this laboratory for the determination of total dissolved organic matter, was adapted to this investigation. This new method combines some of the aspects of the methods described above (2.1.2 and 2.3). Details of this method are presented in the Experimental Section of this report.

### 3 EXPERIMENTAL

#### 3.1 Oil Samples

Three petroleum oil products, supplied by Imperial Oil, were provided by the Center of Spill Technology, Environmental Protection Service, Environment Canada for this investigation. In the preliminary stage of this investigation, a sample of No. 2 fuel oil was obtained from the Imperial Oil Terminal in Ottawa. All the oil samples are identified and listed below:

- (A1) No. 2 fuel oil as specified by ASTM D-396-67 (obtained in Ottawa)
- (A2) No. 2 fuel oil as specified by ASTM D-396-67
- (B) Crude oil with gravity ( $^{\circ}$ API) 30-43; and residuum (100 $^{\circ}$ F) of 30 volume per cent minimum
- (C) Medium bunker fuel oil with viscosity (SSF at 122 $^{\circ}$ F) of 150-200

Some analytical test results on these oil samples, as performed by Imperial Oil, were received from Environment Canada (10). These results are reproduced in Table 1.

**TABLE 1 Analytical Information Received From the Centre of Spill Technology on the Three Oil Samples Studied in this Investigation**

No. 2 Fuel Oil	(FURNACE FUEL)	Medium Bunker Fuel	(FUEL OIL C)
API Gravity	35.5	API Gravity	14.8
Flash Pt.	136	Flash Pt.	172 $^{\circ}$ F
Cloud Pt.	+10		
Pour Pt.	-25 Dep.	Pour Pt.	+40
Viscosity	2.21 cs at 100 $^{\circ}$ F	Viscosity SF at 122 $^{\circ}$ F	184
Sulphur Wt. %	0.28	Sulphur Wt. %	1.38
BS & W	Nil	BS & W	0.1
Dist. IBP	324	Ash Wt. %	0.02
5%	352	MNI	4.5
10%	366	Sediment by HF	0.03
50%	478		
90%	610		
95%	637		
FBP	662		
CCR 10% Btms	0.04	<b>MIXED BLEND CRUDE</b>	
Acid No.	0.03	API Gravity	38.6
Mercaptan No.	1.3	Flash Pt.	Room Temp.
Colour ASTM	1.5	Viscosity at 100 $^{\circ}$ F SU	37.6
Suspended Sed.	0.2	Sulphur Wt. %	0.62
		BS & W	0.02

### 3.2 Description of Apparatus

A schematic diagram of the apparatus used in the investigation for the determination of dissolution rates in a closed system is depicted in Figure 1. It consisted of a glass tube G with an inside diameter of 14.87 cm (cross sectional area = 173.7 cm<sup>2</sup>). This glass tube was fitted into steel lids S<sub>1</sub> and S<sub>2</sub>, and sealed by teflon rings T<sub>1</sub> and T<sub>2</sub>. The vessel was equipped with a stirrer M, which rotated at two (2) revolutions per minute. The blade of the stirrer was constructed of stainless steel, and was 12.5 cm long, 0.65 cm wide and 0.15 cm thick. The stirring rod could be raised or lowered so that the blade of the stirrer cut through the interface layer as shown in Figure 1. The purpose of this arrangement was to prevent the concentration of polar-molecules at the interface, which would have prevented the dissolution of other components from the oil phase into the water layer (11). With this arrangement the interface was regenerated slowly, thus no oil droplets were dispersed into the water layer. The surface regeneration simulated reality, as during an actual oil spill, the interface between water and oil is regenerated by wind and currents. No stirrer was provided for the water layer, but a provision was made in the apparatus for taking water samples through a stainless steel capillary, C, which was equipped with a stainless steel valve, V. The position of the upper end of the capillary, C, could be adjusted so that samples could be taken from different levels. The complete vessel was immersed in a thermostatic water bath, B, which was maintained at 25 ± 0.01°C.

### 3.3 Experimental Procedure

In the determination of dissolution rates, the glass tube, of the apparatus, was filled with about 3 liters of water and 350 ml of the oil sample. Unless otherwise stated, all samples were taken at a level of 10 cm from the oil-water interface. Water samples (15 ml per sample) were taken at suitable intervals into 15 ml hypovials and immediately analyzed by the method described in Section 3.4.

At the end of the dissolution rate study, the water layer, now saturated with the dissolved hydrocarbons, was transferred into a 1000 ml beaker (10.5 cm in diameter with a cross sectional area of 86.6 cm<sup>2</sup>), which was then placed into another thermostatic water bath also maintained at 25 ± 0.01°C. The beaker was not covered. Samples for the determination of the rates of removal of dissolved matter were taken from a constant level of 3 cm below the water surface with a hypodermic syringe.

Although maximum concentrations of dissolved oils in water could be established from the dissolution rate studies, additional and independent determinations were carried out in this investigation in the following manner.

Oil samples were placed together with water into 125 ml hypo-vials (25 ml of oil with 100 ml of water). The hypo-vials were closed with teflon coated septums, inverted into the water bath mentioned above, and after about twenty-four (24) days of immersion, the vials were removed from the water bath. Prior to analysis the septum was dried. The vial was slightly pressurized by air admitted through an inserted hypodermic needle, then a sample was withdrawn using a different hypodermic syringe and was immediately analyzed. In this manner, the possibility of partial vaporization of the dissolved matter, caused by the creation of a vacuum during the sampling procedure, was avoided.

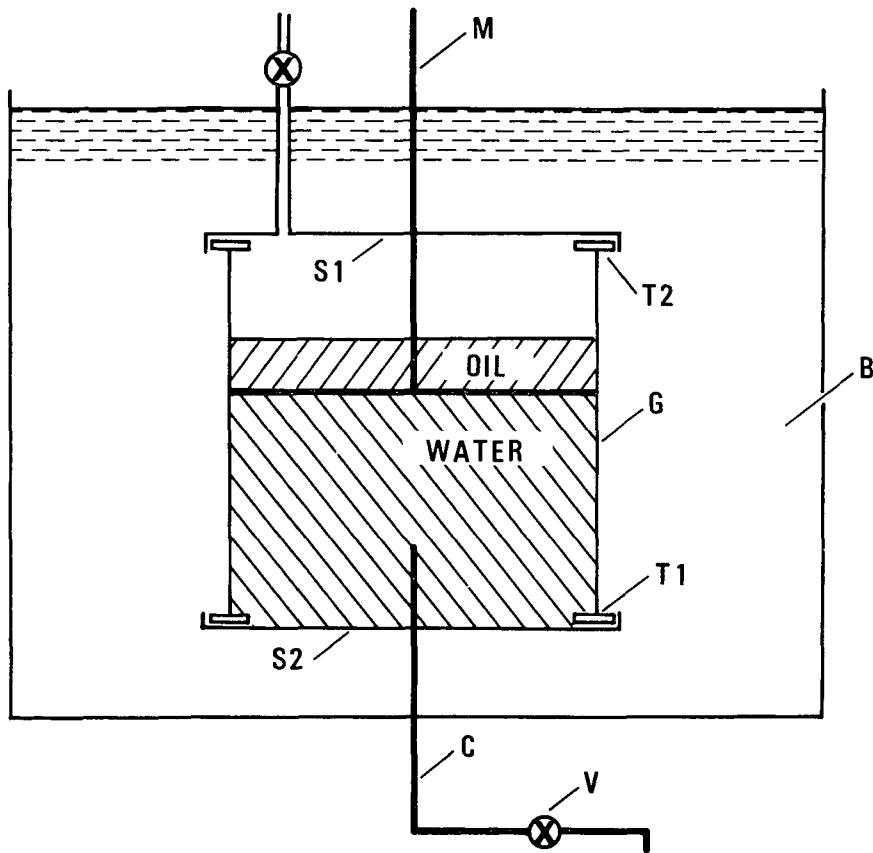
Distilled water was used in all the experimental determinations.

### 3.4 Analytical Method

The analytical method used in this investigation was the method for the determination of total volatile matter dissolved in water. It was particularly suitable for the determination of maximum concentrations of dissolved oil in water and for the determination of the dissolution and removal rates of the dissolved matter. In our preliminary studies of this work, it was observed that aging of the samples produced unreliable results, and that the analysis should be carried out immediately after sample collection. This observation further supported the adoption of this analytical method.

FIG.1 A SCHEMATIC DIAGRAM OF APPARATUS FOR THE DETERMINATION OF RATES OF DISSOLUTION OF OIL IN WATER

- B = WATER BATH
- C = SAMPLING CAPILLARY
- G = GLASS TUBE (I.D. 14.87cm)
- M = STIRRER
- S1, S2 = STAINLESS STEEL LIDS
- T1, T2 = TEFLON SEALING RINGS
- V = SAMPLING VALVE



In this investigation, a Hewlett Packard gas chromatograph Model 5750B, equipped with a flame ionization detector, was used. During the analysis, a stream of helium gas was bubbled through a vial of distilled water prior to entering the GC. This procedure was performed to establish stable conditions for the GC detector and a stable baseline. The helium stream was then switched to bubble through the sample and carried a portion of the dissolved organic matter into the GC for analysis. The amount of the organic matter carried by the helium gas decreased with time, corresponding to the depletion of dissolved matter in the water. Thus, a sharp surge appears initially at the detector of the GC, then the curve tapers off and approaches zero exponentially. A typical response to the presence of organic compounds in water sample, as found in this study, is shown in Figure 2. The area under the curve is integrated and printed out by an electronic digital integrator at intervals of about five (5) minutes for one hour. A Hewlett Packard model 3373B integrator was used in this investigation.

An equation was developed to represent the area under the portion of the exponential curve as follows:

$$A = a(e^{bt} - 1) \quad (1)$$

in which A is the area under the curve, a and b are the coefficients which are evaluated from the readings obtained from the digital integrator by means of a least-squares method. This equation is not used for the initial area under the GC curve, but for the estimation of the total area under this curve as time approaches infinity. The sum of the area obtained in this manner together with the area obtained during the initial response of the GC detector was proportional to the total amount of organic matter present in the sample. In order to evaluate the absolute amount of the organic matter present in the sample, a detector response factor was determined. In this investigation, this factor was obtained by calibrating the detector with samples saturated with n-hexane and benzene. Solubilities of these pure substances in water have been previously determined by means of an extraction method. The response factor of these solutions varies  $\pm 6.4\%$ . The response factor also varies  $\pm 5\%$  with the organic substance used. The overall uncertainty of the proposed method is therefore in the vicinity of  $\pm 10\%$  for concentrations above 0.1 ppm.

A sample calculation of this method is given in Table 2. The data used was that obtained from the determination of total volatile organic matter dissolved in water for a No. 2 fuel oil (sample A2, run No. 3) at 25° C. During the initial period, (the total elapsed time in minutes from the beginning of the experiment, 45.03 minutes), the area under the detector response curve is  $0.4282 \times 10^7 \mu\text{V-seconds}$ . The total area under the exponential curve from 45.03 minutes to infinity, as calculated by Equation 1, is equal to  $0.0231 \times 10^7 \mu\text{V-seconds}$ .

The sum of the areas under the detector response curve is therefore  $0.413 \times 10^7 \mu\text{V-seconds}$ . From the detector response factor ( $0.233 \times 10^{-10} \text{ g}/\mu\text{V-seconds}$ ) the total amount of the dissolved matter is calculated to be  $0.105 \times 10^{-3}$  grams. The total weight of the sample is 17.6377g. Therefore the concentration of the dissolved matter in sample is 5.96 ppm. In this calculation, the values of the coefficients a and b are as follows:

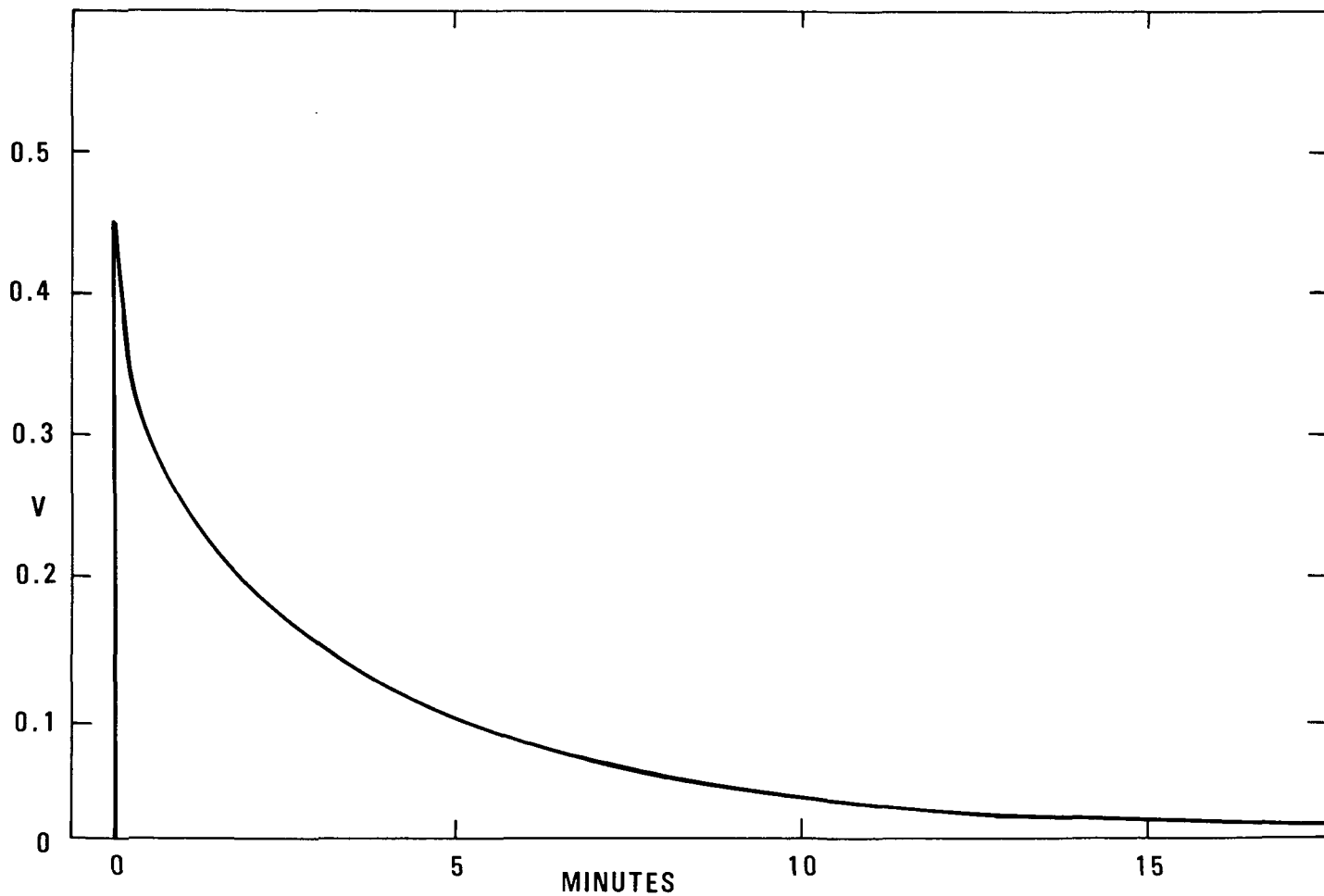
$$\begin{aligned} a &= -0.23128 \times 10^6 \\ b &= -0.37626 \times 10^{-1} \end{aligned}$$

It is also obvious from Equation 1 that, because of the negative value of the coefficient b, the total area under the exponential curve as time approaches infinity can be represented as follows:

$$\lim_{t \rightarrow \infty} A = -a$$

All the calculated concentrations reported in the Results and Discussion Section of this report were obtained in this manner.

FIG.2 A TYPICAL GC DETECTOR RESPONSE TO THE PRESENCE  
OF ORGANIC COMPOUNDS IN SAMPLE





**TABLE 2 A Sample Calculation For The Evaluation of Total Dissolved Organic Matter In Water From The GC Detector Response**

Hours from the Start	72.00			
Days from the Start	3.00			
Sample Weight	17.6377 gm.			
GC Response Factor	0.233D-10			
Calculated Coefficients:				
A =	-0.23128D 06	B =	-0.37626D-01	
EXPERIMENTAL			CALCULATED	
TIME	AREA	SUM (AR)	SUM (AR)	DEV. %
13.23	0.3590D 07	0.3590D 07	0.3590D 07	0.0
18.77	0.2719D 06	0.3862D 07	0.3862D 07	0.0
25.32	0.1678D 06	0.4030D 07	0.4030D 07	0.0
32.41	0.1154D 06	0.4145D 07	0.4145D 07	0.0
38.45	0.7225D 05	0.4217D 07	0.4217D 07	0.0
45.03	0.6440D 05	0.4282D 07	0.4282D 07	0.0
50.93	0.4631D 05	0.4328D 07	0.4328D 07	-0.01
56.69	0.3582D 05	0.4364D 07	0.4364D 07	0.00
63.28	0.3264D 05	0.4397D 07	0.4397D 07	0.00
			ST. FRR.	0.01
Total Calculated Area:	0.4513D 07			
Wt. of Dissolved Matter:	0.10515D-03 gm.			
	or	5.962 ppm		

In Table 2, the standard error is defined by Equation 2 as follows:

$$\text{st. err.} = \sqrt{\frac{\sum \left( \frac{A_{\text{calcd}} - A_{\text{exptl}}}{A_{\text{exptl}}} \times 100 \right)^2}{n - 2}} \quad (2)$$

where n is the number of experimental points used in the calculation.

Although no attempt was made to establish the limiting sensitivity of the method, which is mainly controlled by the sensitivity of the detector, it is believed that the sensitivity of the method is better than 0.01 ppm.

This method is restricted to the detection of volatile organic compounds. The applicability of the method depends on the vapor pressure and solubility of the species concerned. However, as in general, the low boiling (volatile) fractions of oil and oil products are the most soluble in water, the errors involved in the analytical method do not seriously effect the reported results. The method used is as accurate as the methods reviewed in the Literature Survey Section, and is simpler and faster.

## 4 RESULTS AND DISCUSSION

### 4.1 Maximum Concentrations of Dissolved Oil Samples in Water

Maximum solubilities of the three oil samples in water at 25°C are listed in Table 3. The concentrations are expressed in parts per million by weight (ppm). Two sets of values are reported; the first set is obtained from the dissolution curves of these three oil samples in water at 25°C. These curves are presented in Figures 3, 4, and 5 for No. 2 fuel oil, crude oil and bunker oil respectively. Numerical values of these results, expressing the dissolved matter in water in units of ppm as a function of the elapsed time, are listed in Tables 4 to 6. As mentioned earlier, all these dissolution studies have been carried out in a closed system. The other set of maximum solubility values of the same oil sample in water at 25°C is that obtained from the static equilibrium determinations as described in Section 3.3. A remarkable agreement was obtained between the two sets of values as shown in Table 3.

In the dissolution rate studies the maximum concentration is reached in about 5 days for No. 2 fuel oil, 2 days for the crude oil, and 8 or 9 days for the bunker oil. In the static equilibrium studies, a duration of 24 days, or the immersion of samples in water, was employed.

**TABLE 3 Values of Maximum Solubilities of Oil Samples in Water at 25°C**

Oil Sample	Maximum Solubility, in parts per million by weight	
	From dissolution curve	From static equilibrium
Fuel Oil <sup>a</sup>	9.7	
Fuel Oil <sup>b</sup>	7.0	7.87 ± 0.23
Bunker Oil	2.4	2.16 ± 0.13
Crude Oil	44.0	48.8 ± 3.7

<sup>a</sup> Sample A1

<sup>b</sup> Sample A2

Because it is believed that No. 2 fuel oil contains the least, if any, polar compounds, there is little possibility of having polar-molecules concentrated at the interface (see Section 4.2) thus, a slight modification of the experimental procedure was adopted for this sample. The experiment was carried out at room temperature (23°C) using another vessel and no stirring was provided at the interface. However, the dissolution curve obtained as shown in Figure 3 for sample A2 is not significantly different from the results obtained in our preliminary study of sample A1. This curve is perhaps slightly lower than it should be. This may be due to the fact that the room temperature was slightly lower than 25°C, and to the difference in the composition of the two samples. It may also be seen from Table 3 that the maximum solubility value obtained from the dissolution curve (Figure 3) is slightly lower than that obtained in the static equilibrium study at 25°C.

It is significant that the maximum solubilities of these three oil samples decrease in the following order.

Maximum Solubility of Crude oil > No. 2 fuel oil > Bunker oil

It is also interesting that during the study, the maximum concentration of the dissolved matter varied little with time indicating the persistence of the dissolved matter in the closed system.

FIG.3 DISSOLUTION OF NO.2 FUEL OIL IN WATER AT 23° C

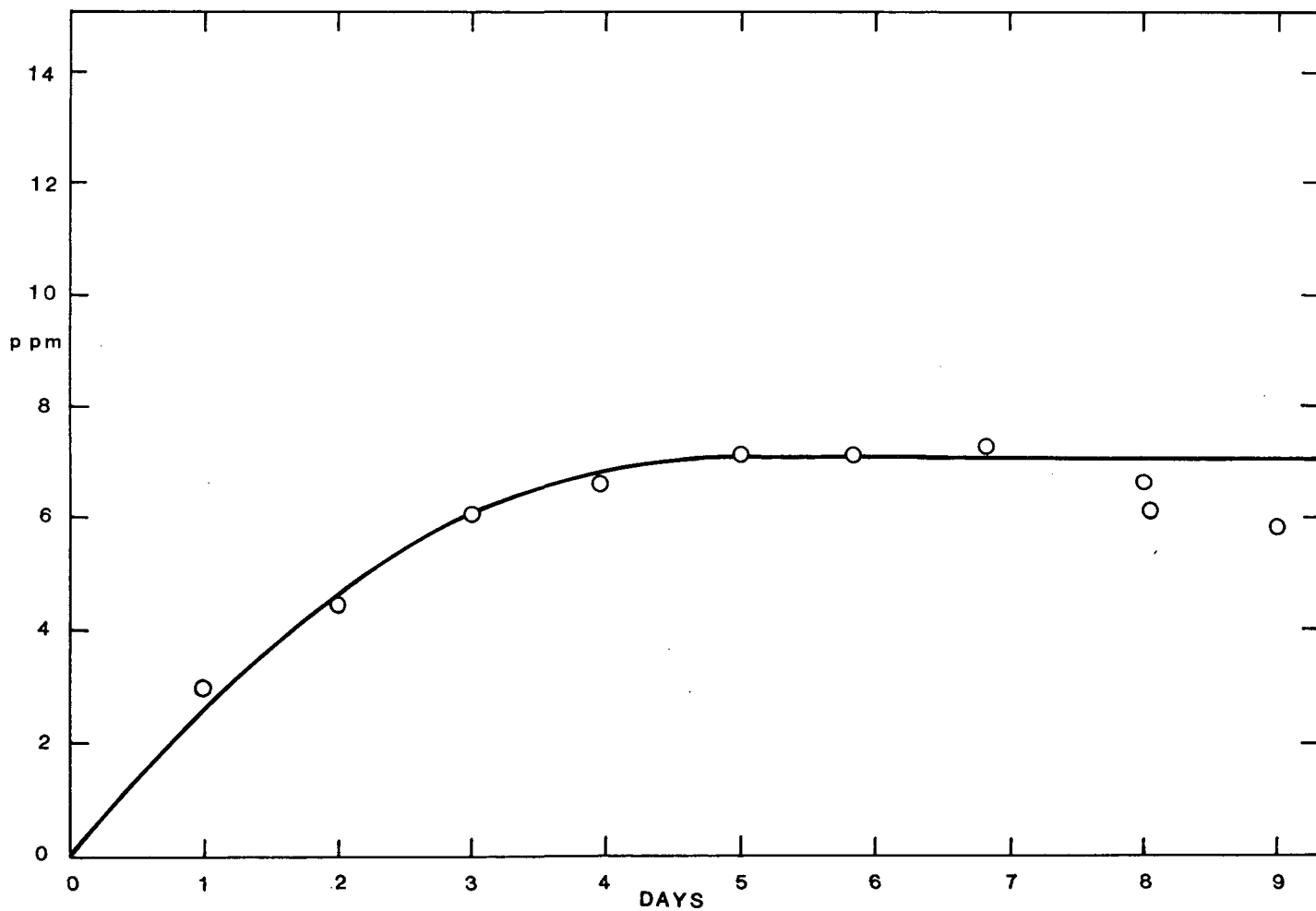


FIG.4 DISSOLUTION OF CRUDE OIL IN WATER AT 25° C

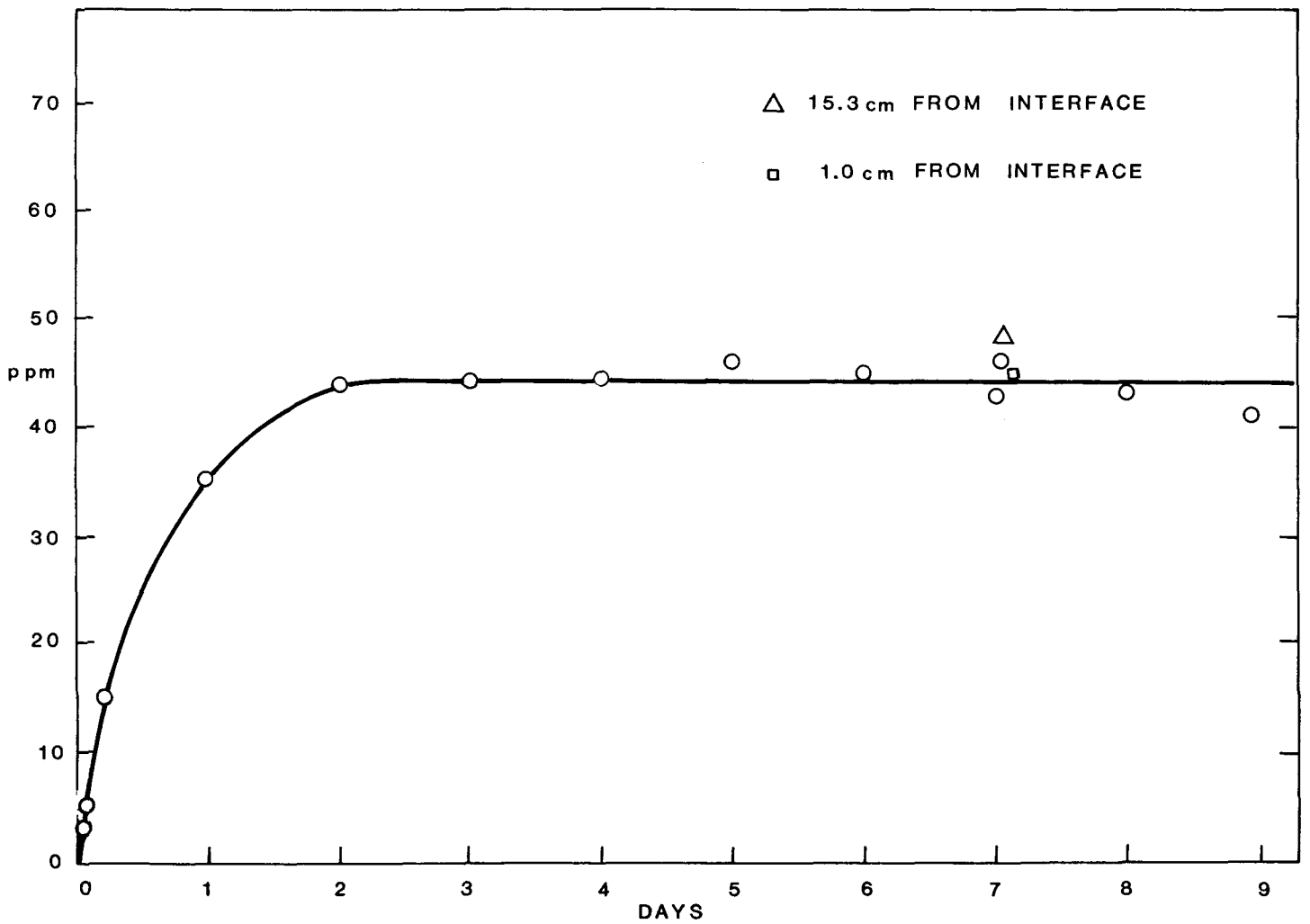
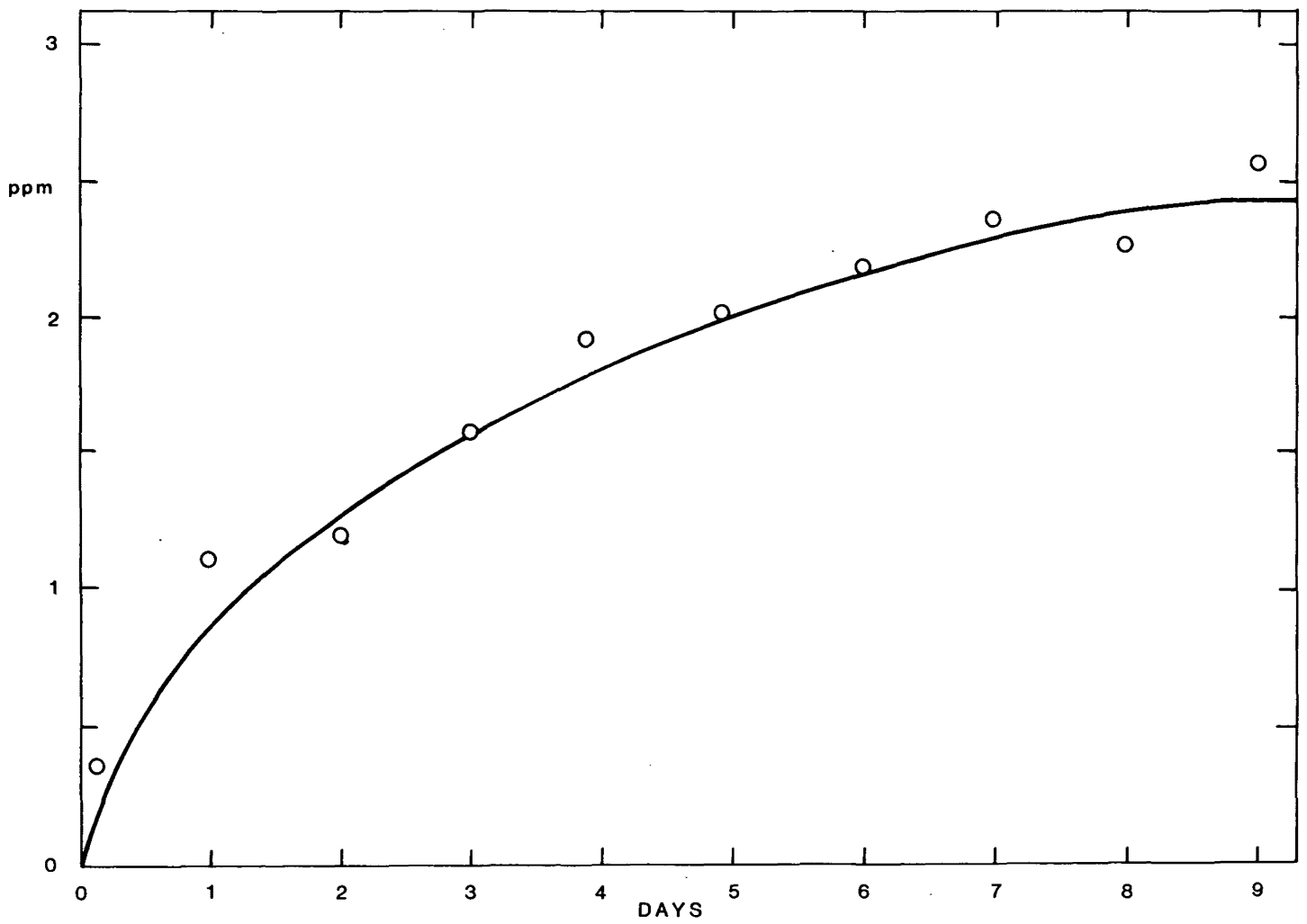


FIG.5  
DISSOLUTION OF BUNKER OIL IN WATER AT 25° C



**TABLE 4 Dissolution of No. 2 Fuel Oil\* in Water at 23°C**

Run No.	Elapsed time		Volatile matter in liquid, ppm
	hrs	days	
1	24.0	1.00	2.91
2	48.0	2.00	4.38
3	72.0	3.00	5.96
4	96.0	4.00	6.49
5	116.0	4.83	7.10
6	140.0	5.83	7.11
7	164.0	6.83	7.24
8	192.0	8.00	6.54
9	193.0	8.04	6.04
10	216.0	9.00	5.80
11	240.0	10.00	7.86
12	264.0	11.00	7.18
13	336.0	14.00	5.96
14	360.0	15.00	6.72
15	384.0	16.00	6.12

\* Sample A2

#### 4.2 Nature of Dissolved Materials

In order to make a reasonable correlation between the total amount of materials and the nature of the materials dissolved in water, one must know the properties and composition of the oil samples under investigation. The only information available on the properties of the oil samples is that reported in Table 1, in which the compositions of the oil samples are not given. The furnace fuel referred to in Table 1 is the No. 2 fuel oil, the fuel oil C referred to in the same table is the bunker oil sample.

The crude oil (mixed blend crude of Table 1) has an odour indicating the presence of soluble sulfur compounds. While polar sulfur compounds are very soluble, the high sulfur content of the bunker oil does not seem to have any effect on the solubility. Perhaps the sulfur compounds present in the bunker oil are not polar in nature, or are of higher molecular weights.

It may also be seen from Tables 1 and 3 that the lower the flash point of the oil sample; the higher the solubility of the sample in water at 25°C.

In order to understand the nature of the dissolved materials in a quantitative manner, a more detailed and thorough study over a longer period would be desirable.

#### 4.3 Rates of Dissolution and Rates of Removal of the Dissolved Matter

The experimental results for the dissolution of the three oil samples in water have been briefly mentioned in Section 4.1. The duration of these studies was as follows:

- Dissolution of No. 2 fuel oil (sample A2) in water at 25°C - 16 days
- Dissolution of crude oil in water at 25°C - 10 days
- Dissolution of bunker oil in water at 25°C - 10 days

**TABLE 5 Dissolution of Crude Oil in Water at 25°C**

Run No.	Elapsed time		Volatile matter in liquid, ppm
	hrs	days	
16	1.0	0.04	2.66
17	2.0	0.08	5.20
18	5.0	0.21	15.18
19	24.0	1.00	34.9
20	48.0	2.00	43.9
21	72.0	3.00	43.9
22	96.0	4.00	44.2
23	120.0	5.00	45.7
24	144.0	6.00	44.5
25	168.0	7.00	42.3
26	169.0	7.04	45.8
27	170.0	7.08	48.1*
28	171.0	7.13	44.1**
29	192.0	8.00	42.8
30	215.0	8.96	40.7
31	239.0	9.96	42.4

\* Sample taken at the bottom of the vessel, (15.3 cm from the interface)

\*\*Sample taken 1.0 cm from the interface

**TABLE 6 Dissolution of Bunker Oil in Water at 25°C**

Run No.	Elapsed time		Volatile matter in liquid, ppm
	hrs	days	
32	3.0	0.13	0.36
33	24.0	1.00	1.09
34	48.0	2.00	1.18
35	72.0	3.00	1.57
36	93.0	3.88	1.90
37	118.0	4.92	2.00
38	144.0	6.00	2.17
39	168.0	7.00	2.37
40	192.0	8.00	2.26
41	216.0	9.00	2.55
42	240.0	10.00	2.30

As previously mentioned, all these dissolution studies have been carried out in a closed system. The results are graphically presented in Figures 3 to 5 with numerical values reported in Tables 4 to 6. The concentrations of the dissolved volatile materials are expressed in parts per million (ppm).

At the end of each of the dissolution studies, the water layer was used for determining the rates of removal of the dissolved matter in an open system, with the exception of the bunker oil (see footnote of Table 9). The duration of these studies was as follows:

- Removal of dissolved No. 2 fuel oil (sample A1) from water at 25°C - 13 days
- Removal of dissolved crude oil from water at 25°C - 9 days
- Removal of dissolved bunker oil from water at 25°C - 7 days

The results are graphically presented in Figures 6 to 8 with numerical values reported in Tables 7 to 9. It was observed that several days are required to decrease the amount of the dissolved matter to one percent of the maximum concentration.

It was observed that the initial concentration as indicated in Figure 8 and Table 9 is less than the maximum concentration reported in Table 3. This difference may be caused by the absorption of the dissolved matter by the bottle used in the preparation of the sample in the static method. It is also possible that the dissolution of bunker oil in water has not reached the true equilibrium state or that the distribution of the dissolved matter in water is not uniform.

For the purpose of estimating the amount of materials dissolved in water per unit area of the interface between the oil sample and the water layer as a function of time, an attempt has been made to estimate the rate of dissolution by means of the following equation:

$$r = \frac{dm}{dt} \quad (3)$$

in which  $r$  is the rate of dissolution,  $m$  is amount of the material dissolved per square meter of the interface and  $t$  is the dissolution time. The rate, expressed in terms of the unit of  $\text{mg m}^{-2} \text{day}^{-1}$ , may provide useful information for actual oil spills. There are two difficulties encountered in the evaluation of the quantity,  $m$ . First, the concentration gradient of the dissolved materials in the water phase is not known. Such a gradient must exist, especially during the initial period of the determinations, because the water layer was not stirred during the experiment. This difficulty can only be resolved by extending the experiments for longer periods, and by taking samples at various levels. Secondly, the volume of the water layer was not kept constant due to the necessity of removing samples.

For these reasons, the concentration determined for the samples taken 10 cm from the interface was assumed to be equal to the mean concentration of the water layer. This distance of 10 cm is approximately equal to two-thirds of the total height of the water layer. In addition, the average of the initial and the final volumes of the water layer was used for the evaluation of the quantity  $m$ , which is expressed by

$$m^\infty - m = c e^{dt} \quad (4)$$

where  $m^\infty$  is the maximum amount of the dissolved materials present in the water layer. Hence

$$r = \frac{dm}{dt} = -c d e^{dt} \quad (5)$$

The values of  $c$  and  $d$  of Equation 5 were calculated by a least-squares analysis of the results, and are listed below:



FIG.6 REMOVAL OF DISSOLVED NO. 2 FUEL FROM WATER AT 25° C

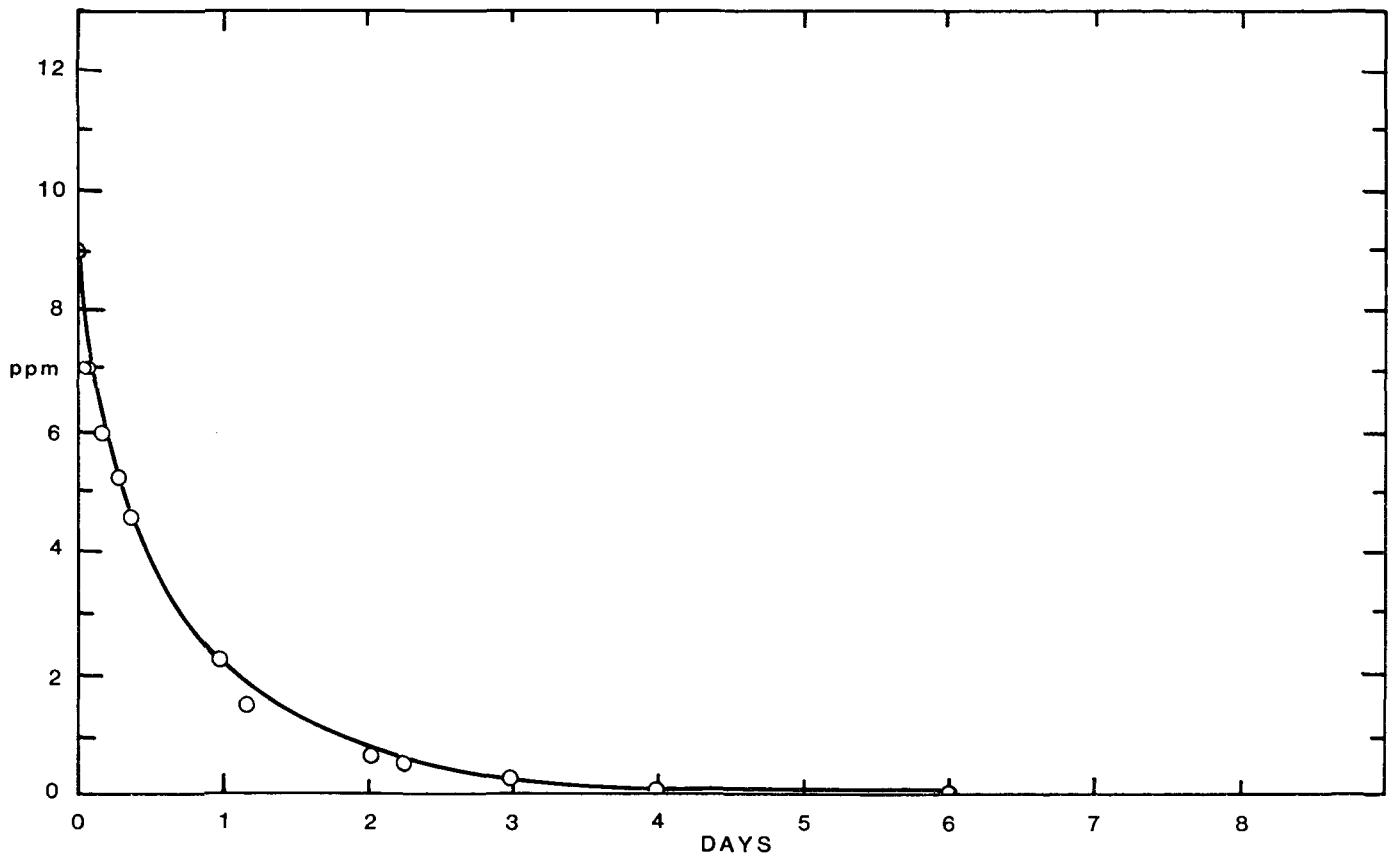
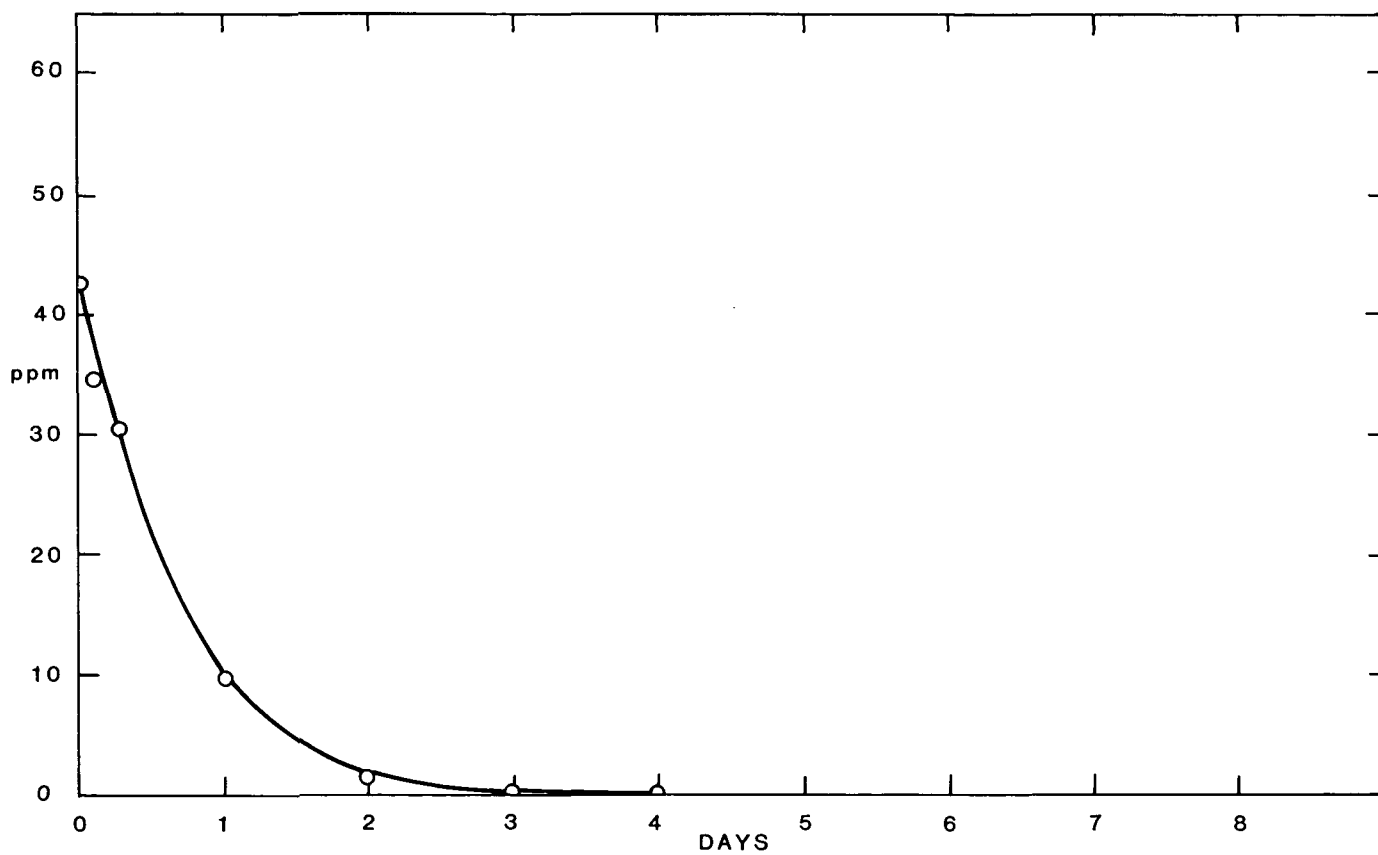


FIG.7 REMOVAL OF DISSOLVED CRUDE OIL FROM WATER AT 25° C



**TABLE 7 Removal of Dissolved No. 2 Fuel Oil\* from Water at 25°C**

Run No.	Elapsed time		Volatile matter in liquid, ppm
	hrs	days	
43	0.0	0.00	8.90
44	1.0	0.04	7.10
45	2.0	0.08	7.20
46	4.0	0.17	6.03
47	7.0	0.29	5.26
48	8.0	0.33	4.63
49	24.0	1.00	2.29
50	29.75	1.24	1.52
51	49.0	2.04	0.73
52	54.0	2.25	0.58
53	72.0	3.00	0.36
54	97.25	4.05	0.03
55	144.0	6.00	0.04
56	168.0	7.00	0.07
57	192.0	8.00	0.02
58	216.0	9.00	0.02
59	316.0	13.17	0.01

\* Sample A1

**TABLE 8 Removal of Dissolved Crude Oil from Water at 25°C**

Run No.	Elapsed time		Volatile matter in liquid, ppm
	hrs	days	
60	0.0	0.00	42.4
61	2.0	0.08	34.8
62	6.0	0.25	30.5
63	24.0	1.00	9.93
64	48.0	2.00	1.99
65	73.0	3.04	0.30
66	96.0	4.00	0.08
67	168.0	7.00	0.01
68	192.0	8.00	0.03
69	216.0	9.00	0.01

**TABLE 9 Removal of Dissolved Bunker Oil From Water at 25° C**

Run No.	Elapsed time		Volatile matter in liquid, ppm
	hrs	days	
70	0.0	0.00	0.81*
71	5.0	0.21	0.66
72	23.0	0.96	0.15
73	48.0	2.00	0.04
74	73.0	3.04	0.04
75	96.0	4.0	0.02
76	120.0	5.0	0.02
77	144.0	6.0	0.01
78	168.0	7.0	0.01

\*Oil sample was kept in a closed plastic bottle at 25°C for 16 days without stirring

	Dissolution Rate Constants	
	c	d
	mg m <sup>-2</sup>	day <sup>-1</sup>
No. 2 fuel oil	1043	-0.423
Crude oil	8915	-2.380
Bunker oil	459	-0.503

The calculated rates of dissolution of the three oil samples in water at 25°C are listed in Table 10 and graphically shown in Figure 9.

Similarly, Equation 5 has been used for expressing the removal rates, using the same units for the constants. The calculated rates of removal of dissolved oils from water at 25°C are listed in Table 11 and graphically presented in Figure 10. The values of c and d used in these calculations are listed as follows:

	Removal Rate Constants	
	- c	d
	mg m <sup>-2</sup>	day <sup>-1</sup>
No. 2 fuel oil	391	-0.846
Crude oil	1651	-0.981
Bunker oil	36.5	-0.746

Because an exponential function has been selected to express the rates, linear plots are obtained using semi-log paper as shown in Figures 9 and 10.

It is seen from these figures that the initial rates of dissolution and rates of removal follow the same order as that for the maximum solubilities of these oil samples (see Section 5.1).

Due to the preliminary nature of this work the reported rate values should be treated qualitatively, and used only for the purpose of comparison and for making estimates.

FIG.8 REMOVAL OF DISSOLVED BUNKER OIL FROM WATER AT 25° C

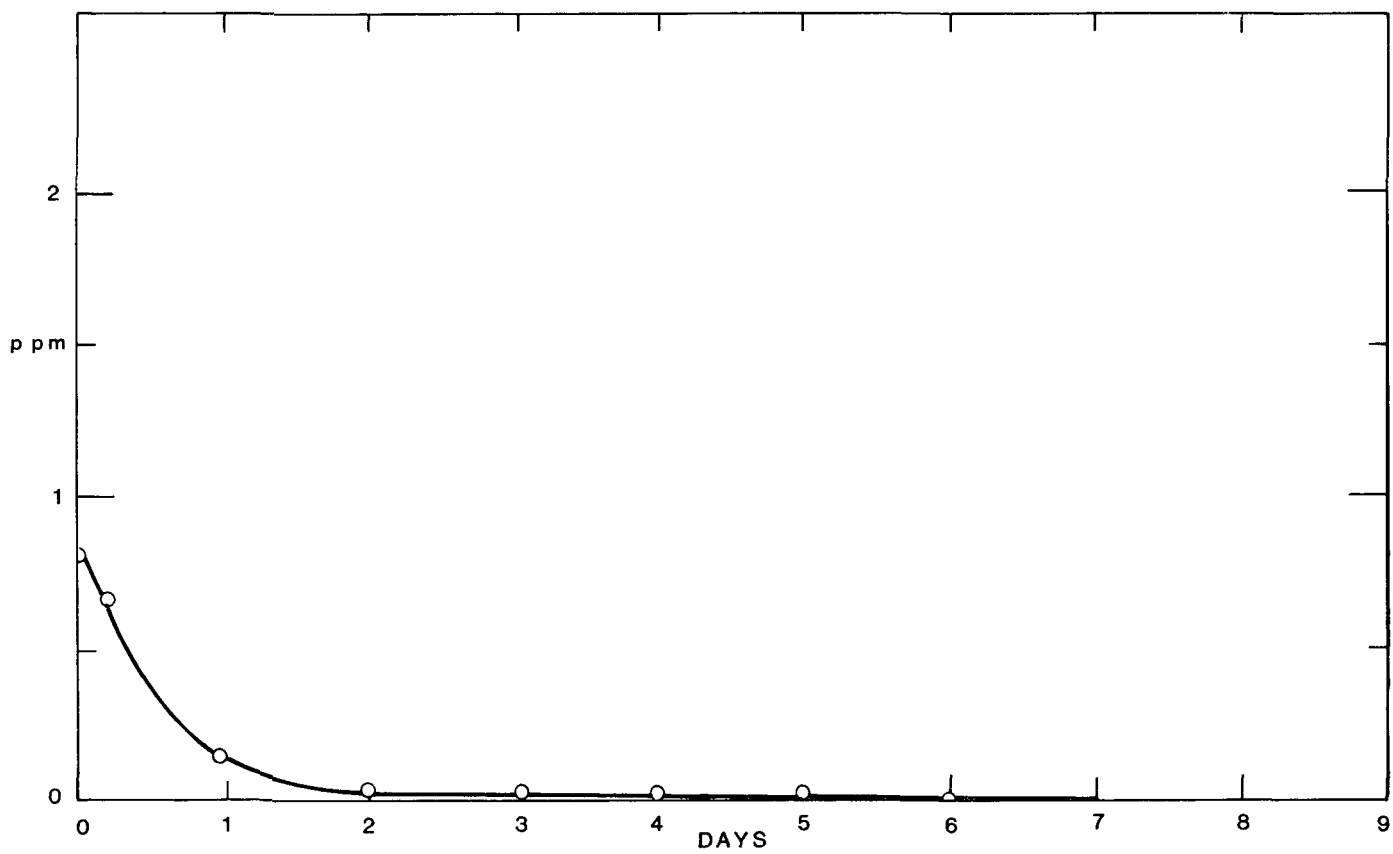
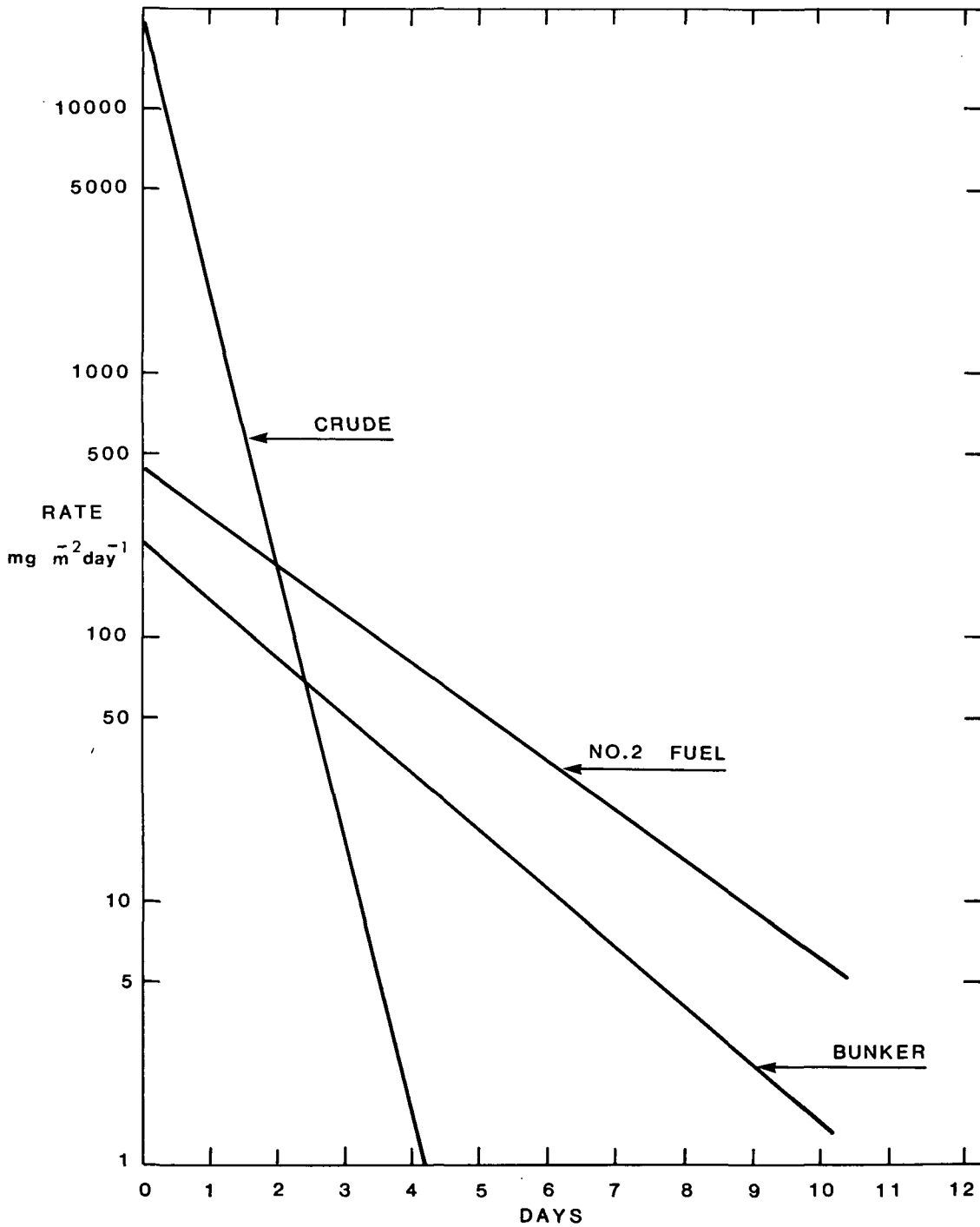


FIG.9  
RATES OF DISSOLUTION OF THE THREE OIL SAMPLES IN WATER AT 25° C



**TABLE 10 Calculated Rates of Dissolution of Oil Samples in Water at 25°C**

time , days	Rate		
	(mg m <sup>-2</sup> day <sup>-1</sup> )		
	Fuel Oil	Crude Oil	Bunker Oil
0	441	21218	231
0.25	397	11703	204
0.5	357	6455	180
0.75	321	3560	158
1.0	289	1964	140
2.0	189	182	84
3.0	124	16.8	51
4.0	81	1.56	31
5.0	53	0.14	19
6.0	35	0.01	11
7.0	23		7
8.0	15		4
9.0	10		2.5
10.0	6		1.5

## 5 CONCLUSIONS AND RECOMMENDATIONS

The rates of dissolution of three oil samples in water at 25°C in a closed system and the rates of removal of the dissolved oil from water at 25°C in an open system were investigated. In addition, maximum concentrations of dissolved oils were obtained from static equilibrium determinations, and compared with those values obtained from the dissolution rate studies.

The results of this study provide useful information on the fate of oil and oil products during the first few days of an oil spill. The dissolution studies, which were carried out in a closed system, represent the limiting case when sufficient oil is spilled on the water surface and no evaporation or adsorption takes place. The removal-rate studies also represent a limiting condition because all the oil layer was removed in the experiments.

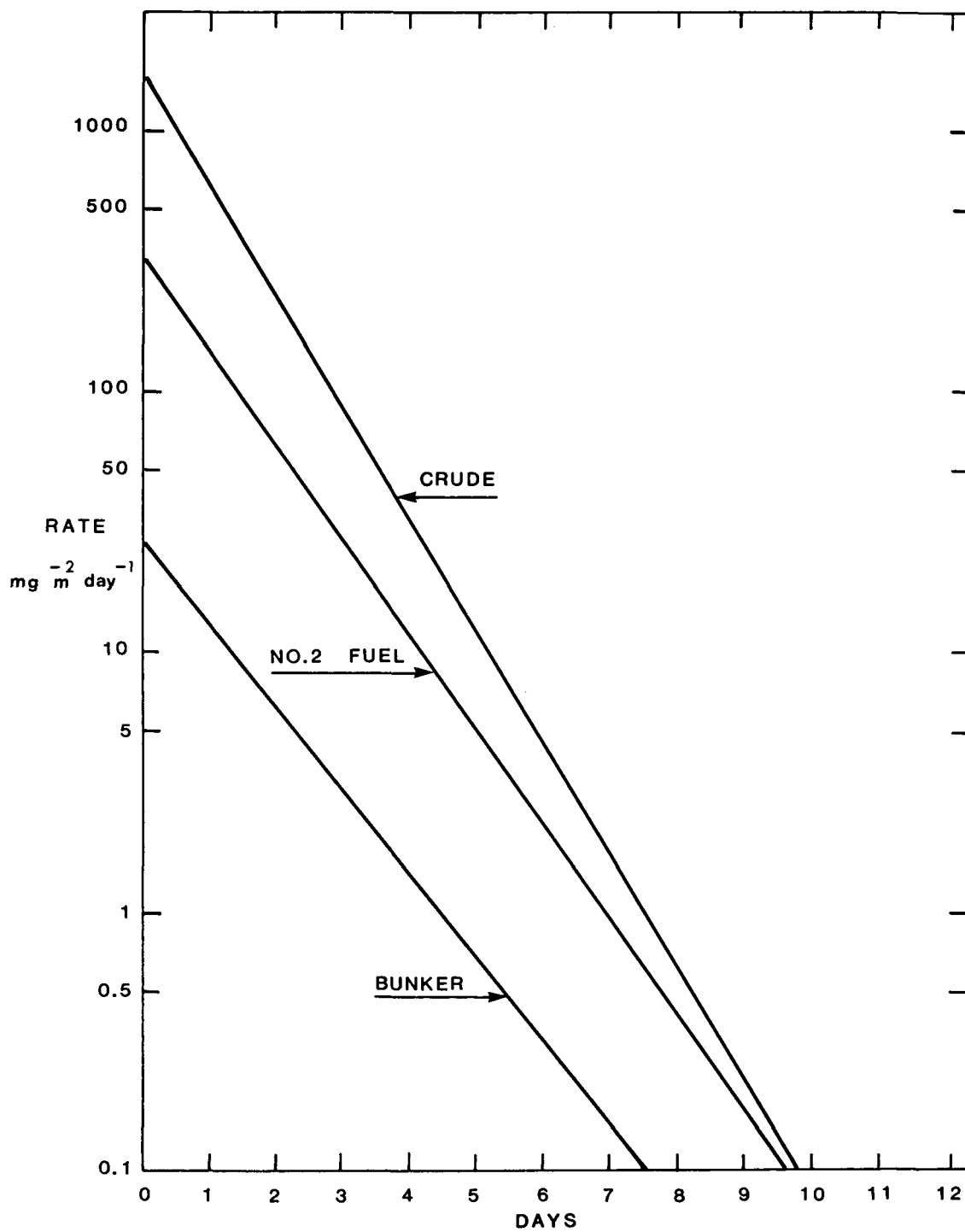
The amount and the rate of oil dissolving in water varied significantly with the type of the oil. It took about 2.5 days to reach maximum solubility in the case of the crude oil, but at least 9 days in the case of the Bunker oil.

The maximum solubilities of the three oil samples, the initial rates of dissolution and the initial rates of removal of the dissolved oil follow the same order. Namely  
Crude oil > No. 2 fuel oil > Bunker oil

The results of the removal rate studies indicate that small traces of the dissolved materials in water are very persistent and remain in the water solution even after a long period of time.

FIG.10

RATES OF REMOVAL OF DISSOLVED OILS FROM WATER AT 25° C





**TABLE 11 Calculated Rates of Removal of Dissolved Oil Samples from Water at 25°**

time , days	Rate		
	(mg m <sup>-2</sup> day <sup>-1</sup> )		
	Fuel Oil	Crude Oil	Bunker Oil
0	331	1620	27.2
0.25	268	1267	22.6
0.5	217	992	18.7
0.75	175	776	15.6
1	142	607	12.9
2	61	228	6.1
3	26	85	2.9
4	11.2	32	1.4
5	4.8	12	0.65
6	2.1	4.5	0.31
7	0.9	1.7	0.15
8	0.4	0.6	0.07
9	0.2	0.2	0.03
10	0.1	0.1	0.02

## 6 RECOMMENDATIONS FOR FUTURE WORK

The experimental determinations were conducted at only one temperature, the number of oil samples studies was rather limited, the nature of the dissolved materials was not thoroughly explored and the amount of the dissolved non-volatile materials was not determined. The effect of aging, the fate of the dissolved oil and the behaviour of the oil-water system over longer periods are of value to further the knowledge and the understanding of the fate of the oil dissolved in water after a spill.

For these reasons, continuation of investigations in this area is desirable. The following recommendations are therefore suggested for work in the immediate future:

- (a) To determine persistence and maximum concentration of oil in water in an open system;
- (b) To determine maximum solubilities of oil in water at more than one temperature;
- (c) To determine the rate of dissolution and the rate of removal of the dissolved oil at more than one temperature;
- (d) To determine the amount of non-volatile components of the dissolved oil in water;
- (e) To determine the fate of dissolved oil and behaviour of the oil-water system over a longer period of time.

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