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Mathematical Model of the Behaviour of Oil Spills on Water with Natural and Chemical Dispersion

Economic and Technical Review Report
EPS-3-EC-77-19

Environmental Impact Control Director

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Cat. No: En 46-3/77-19

ISBN 0-662-01217-8

TD 182
R46
3/EC/77/A
ex. 1

#12403

MATHEMATICAL MODEL OF THE BEHAVIOUR OF OIL SPILLS ON WATER
WITH NATURAL AND CHEMICAL DISPERSION

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A Report Submitted to:

Research and Development Division
Environmental Emergency Branch
Environmental Impact Control Directorate
Environmental Protection Service
Department of Fisheries and the Environment

EPS-3-EC-77-19
October, 1977

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ABSTRACT

A mathematical model of the behaviour of an oil spill on water has been assembled and solved on a digital computer to yield data on the oil slick size, thickness, properties and composition; on the amounts of oil evaporated, dissolved and dispersed; and on the concentration history of the hydrocarbon dissolved in the water column. To undertake the calculation, a simulated oil composition is used which enables various oil volatilities and aqueous solubilities to be reproduced. The processes quantified are evaporation; dissolution; oil slick spreading (both as patches of thickness 1 to 10 mm and as surface tension slicks of thickness ca. 10 μm , characterized by the Blokker Equation); horizontal diffusion in the water column; vertical diffusion in the water column to a diffusion floor, typically at a depth of 10 m; and natural and chemically induced dispersion. The model permits variation in oil composition, sea state, windspeed, temperature, and time of artificial dispersion to be investigated.

A total of 34 model spills were computed and the results presented in tabular and graphical form with discussion. The importance of evaporation as a mechanism of oil slick loss in the early stages of the spill is confirmed, especially in the first 12 hours. The quantities of hydrocarbon present in the water column resulting from natural dispersion are about two orders of magnitude greater than those from direct dissolution from the slick. The rate of natural dispersion is of critical importance in determining the effect of the spill on aquatic biota and should be further investigated. Examination of the effect of artificial dispersion at various times shows the desirability and feasibility of delaying dispersion until the hydrocarbon concentration increases only by an amount sufficient to achieve (1) a concentration which had been previously experienced in the water column, but by a smaller volume of water, or (2) a concentration which is judged to be of toxicological significance. The sensitivity of the results to changes in temperature, sea state, spreading constants, mixed water column depth, dispersion time and values of the various rate constants has been tested.

It is hoped that the model will be of value in elucidating the conditions under which artificial dispersion can be used as an oil spill countermeasure in determining which rate processes are worthy of future study and quantification, in designing large-scale experiments, and generally in contributing to the understanding of physical and biological effects of oil spills on water.

RESUME

Un modèle mathématique simulant un déversement d'hydrocarbures a été élaboré et analysé par ordinateur numérique afin de recueillir des données sur la dimension, l'épaisseur et la composition de nappes; sur la quantité d'hydrocarbures évaporée, dissoute et dispersée; et sur les modifications de concentration d'hydrocarbures dans les couches d'eau inférieures. La composition des hydrocarbures est simulée afin de reproduire les différents coefficients de tension de vapeur et de solubilité dans l'eau. Les processus étudiés sont: l'évaporation; la dilution et l'étalement des nappes (en tant que nappes de 1 à 10 mm d'épaisseur et en tant que pellicules de tension superficielle d'environ 10 μm d'épaisseur, caractérisées par l'équation de Blokker); la diffusion horizontale et verticale vers le bas dans l'eau sous-jacente dans ce dernier cas jusqu'à un palier de 10 m; et la dispersion naturelle ou chimique. Avec ce modèle, il est possible de faire varier la composition des hydrocarbures, l'état de la mer, la vitesse du vent, la température, le temps requis pour disperser la nappe de façon artificielle.

Au total, 34 déversements ont été simulés. Les résultats sont présentés sous forme de tableaux ou de graphiques et commentés. Il a été établi que c'est peu après le déversement, et plus particulièrement au cours des douze premières heures, que l'évaporation est importante. En outre, la quantité d'hydrocarbures dispersée naturellement dans l'eau dépasse par environ deux ordres de grandeur la quantité dissoute. La vitesse de dispersion naturelle s'est révélée déterminante pour ce qui est des effets des déversements sur la vie aquatique et devrait, par conséquent, faire l'objet d'une étude plus approfondie. L'étude des effets de la dispersion artificielle a montré, à plusieurs reprises, qu'il est préférable de retarder cette dispersion jusqu'à ce que la concentration des hydrocarbures soit: (1) égale à l'une de celles qui ont été observées dans l'eau sous-jacente, mais dans un volume d'eau moindre; ou (2) soit jugée toxique. La sensibilité des résultats aux variations de la température, de l'état de la mer, des coefficients d'étalement, de la profondeur de mélange dans l'eau, du temps de dispersion et des divers coefficients physico-chimiques, a été vérifiée.

Le modèle devrait contribuer à déterminer les conditions dans lesquelles la dispersion artificielle peut servir en cas de déversement; à discerner les processus physico-chimiques qui méritent d'être étudiés davantage et d'être quantifiés; à mettre sur pied des expériences à grande échelle; et à mieux connaître, en général, les répercussions physico-biologiques des déversements dans l'eau.

FOREWORD

This study was undertaken by the University of Toronto under contract to the Environmental Emergency Branch of the Department of Fisheries and the Environment. Mr. C.W. Ross of this Branch supervised the work as scientific authority.

TABLE OF CONTENTS	PAGE
FOREWORD	iii
ABSTRACT	i
RESUME	ii
TABLE OF CONTENTS	v
LIST OF FIGURES	vi
LIST OF TABLES	vii
1 INTRODUCTION	1
2 QUANTIFICATION OF OIL SPILL PROCESSES	2
2.1 Oil Properties and Simulated Composition	2
2.2 Evaporation	2
2.3 Vertical Diffusion in Water Column	4
2.4 Dissolution	5
2.5 Emulsification or Dispersion	6
2.6 Evaporation from Solution and Other Processes	7
2.7 Spreading of the Oil Slick	8
2.8 Horizontal Diffusion	9
2.9 Dissolution Rate of Dispersed Oil	12
3 RESULTS	17
4 DISCUSSION	49
5 CONCLUSIONS AND RECOMMENDATIONS	55
NOMENCLATURE	57
REFERENCES	59
APPENDIX A: DISTRIBUTION OF INDIVIDUAL COMPONENTS OF SIMULATED OIL AFTER A SPILL ON WATER	60
APPENDIX B: SCALE-UP TO 1,000-TON SPILL	70
APPENDIX C: WINDSPEED, BEAUFORT SCALE AND SEA STATE	75
APPENDIX D: COMPUTER PROGRAM LISTING AND DOCUMENTATION	78

LIST OF FIGURES	PAGE
1. ASTM D86-67 DISTILLATION CURVES OF VARIOUS NATURAL CRUDE OILS AND THE SIMULATED OIL	10
2(a) VISCOSITY OF NORMAN WELLS CRUDE OIL	11
(b) DENSITY OF NORMAN WELLS CRUDE OIL	11
3. RADIUS vs TIME ($K_r = 216$)	13
4. RADIUS vs TIME ($K_r = 108$)	14
5. RADIUS vs TIME ($K_r = 432$)	15
6. FATE OF OIL SPILLED ON WATER (SS = Low, $T = 5^{\circ}\text{C}$, $K_r = 216$)	18
7. FATE OF OIL SPILLED ON WATER (SS = Medium, $T = 5^{\circ}\text{C}$, $K_r = 216$)	19
8. FATE OF OIL SPILLED ON WATER (SS = High, $T = 5^{\circ}\text{C}$, $K_r = 216$)	20
9. FATE OF OIL SPILLED ON WATER (SS = Very High, $T = 5^{\circ}\text{C}$, $K_r = 216$)	21
10. FATE OF OIL SPILLED ON WATER (SS = Medium, $T = 15^{\circ}\text{C}$, $K_r = 216$)	22
11. FATE OF OIL SPILLED ON WATER (SS = Medium, $T = 0^{\circ}\text{C}$, $K_r = 216$)	23
12. FATE OF OIL SPILLED ON WATER (SS = Medium, $T = 5^{\circ}\text{C}$, $K_r = 108$)	24
13. FATE OF OIL SPILLED ON WATER (SS = Medium, $T = 5^{\circ}\text{C}$, $K_r = 432$)	25
14. SLICK THICKNESS vs TIME	26
15. CONCENTRATION OF DISSOLVED AND DISPERSED HYDROCARBONS vs TIME	29
16. CONCENTRATION vs TIME	30
17. CONCENTRATION IN WATER COLUMN IMMEDIATELY AFTER CHEMICAL DISPERSION vs DISPERSION TIME	31
18. RATIO OF CONCENTRATION AFTER DISPERSION TO CONCENTRATION BEFORE DISPERSION vs DISPERSION TIME	32
19. VISCOSITY OF OIL (NORMAN WELLS CRUDE) REMAINING IN SLICK	34
20. CONCENTRATION DISTRIBUTIONS FOR A CYLINDRICAL SOURCE	35
21. CONCENTRATION vs TIME (1 HOUR) AFTER CHEMICAL DISPERSION	37
22. CONCENTRATION vs TIME (12 HOURS) AFTER CHEMICAL DISPERSION	38

23.	CONCENTRATION vs TIME (24 HOURS) AFTER CHEMICAL DISPERSION	39
24.	CONCENTRATION vs TIME (48 HOURS) AFTER CHEMICAL DISPERSION	40
B1	RADIUS vs TIME ($K_r = 216$, $V = 1,425 \text{ m}^3$)	71
B2	FATE OF OIL SPILLED ON WATER (SS = Medium, $T = 5^\circ\text{C}$, $K_r = 216$)	72
B3	CONCENTRATION OF DISSOLVED AND DISPERSED HYDROCARBONS vs TIME	73
B4	VISCOSITY OF OIL (NORMAN WELLS CRUDE) REMAINING IN SLICK	74
C1	CORRELATION OF SEA STATE, BEAUFORT NUMBERS AND WIND VELOCITY	76

LIST OF TABLES	PAGE
1 COMPOSITION OF SIMULATED CRUDE OIL	3
2 SOLUBILITY ENHANCEMENT FACTORS	6
3 PARAMETER VALUES - 34 MODEL SPILLS	27
4 PARAMETER VALUES - CHEMICAL DISPERSION TIMES	41
5 CONCENTRATION AT TIME t (SS = Low, $T = 5^{\circ}\text{C}$, $K_r = 216$)	42
6 CONCENTRATION AT TIME t (SS = Medium, $T = 5^{\circ}\text{C}$, $K_r = 216$)	43
7 CONCENTRATION AT TIME t (SS = High, $T = 5^{\circ}\text{C}$, $K_r = 216$)	44
8 CONCENTRATION AT TIME t (SS = Very High, $T = 5^{\circ}\text{C}$, $K_r = 216$)	45
9 CONCENTRATION AT TIME t (SS = Medium, $T = 5^{\circ}\text{C}$, $K_r = \text{Varying}$)	46
10 CONCENTRATION AT TIME t (SS = Medium, $T = 5^{\circ}\text{C}$, $K_r = 216$)	47
11 CONCENTRATION AT TIME t (SS = Medium, $T = \text{Varying}$, $K_r = 216$)	48
A-1 SIMULATED OIL DISTRIBUTION 1 HOUR AFTER A SPILL ON WATER	61
A-2 SIMULATED OIL DISTRIBUTION 3 HOURS AFTER A SPILL ON WATER	62
A-3 SIMULATED OIL DISTRIBUTION 6 HOURS AFTER A SPILL ON WATER	63
A-4 SIMULATED OIL DISTRIBUTION 12 HOURS AFTER A SPILL ON WATER	64
A-5 SIMULATED OIL DISTRIBUTION 24 HOURS AFTER A SPILL ON WATER	65
A-6 SIMULATED OIL DISTRIBUTION 24 HOURS AFTER CHEMICAL DISPERSION	66
A-7 SIMULATED OIL DISTRIBUTION 48 HOURS AFTER A SPILL ON WATER	67
A-8 SIMULATED OIL DISTRIBUTION 72 HOURS AFTER A SPILL ON WATER	68
A-9 SIMULATED OIL DISTRIBUTION 96 HOURS AFTER A SPILL ON WATER	69
C-1 DESCRIPTION OF THE BEAUFORT SCALE	77

1. INTRODUCTION

It is well established that hydrocarbons dissolved or emulsified in the water column during spills of crude oils or petroleum products have a toxic effect on aquatic biota. This effect is dependent on the species, the hydrocarbon concentrations to which they are exposed, and exposure time.

The extent to which hydrocarbons are incorporated into the water column is dependent on oil slick thickness, oil composition, oil solubility, surface waves and turbulence, wind speed, oil evaporation history, the presence of surface active agents, spreading characteristics, surface currents, and the depth of the sea bottom or to the thermocline. This complex assembly of interacting processes has been reviewed by the National Academy of Sciences (1975) and by McAuliffe (1976).

This report addresses the problem of calculating the extent of hydrocarbon dispersion or dissolution in the event of an oil spill on the sea surface, thus exposing marine biota to possibly toxic conditions. Environmental factors vary from spill to spill and it is unlikely that such a calculation could ever be precise. It is hoped, however, that by calculating (and later verifying experimentally) the concentrations which might exist in the water in the vicinity of a spill, the likely toxic effect in marine organisms could be determined with acceptable accuracy. This model could be used as a tool to investigate the effect of artificial (chemical) dispersion, and thus contribute to the decision-making process on whether or not dispersants should be used in a given spill situation.

A simple model of oil spill dispersion has been assembled from a number of rate processes, expressed in suitable mathematical form, using values for the rate constants from the literature where possible. The computation, using this mathematical form, gives the concentration of the hydrocarbons in the water column during the history of the spill, and related data such as the volume of the water column exposed to concentrations above a certain value (judged to be of biological significance) and the duration of this exposure. The computation is also performed to yield data on oil slick dimensions, oil composition and property changes.

A mathematical model is a set of differential equations which describe the system under study and in simple cases, or after simplifications, analytical solutions can often be found. An oil spill on water, however, is an extremely complex system and an analytical solution is not feasible. It is suggested here that numerical solutions of the equations for evaporation, dissolution, and dispersion, combined with solutions of the spreading and horizontal diffusion equations as empirical correlations, might yield reasonable results.

2. QUANTIFICATION OF OIL SPILL PROCESSES

2.1 Oil Properties and Simulated Composition

To assign reasonable volatility and dissolution characteristics to the oil, and to obtain an estimate of the effect of these processes on the oil composition and properties, a simulated crude oil of the composition and properties given in Table 1 is used in the simulated spills (Leinonen, 1976). This oil has a ASTM D86-67 distillation curve similar to that of other natural crude oils as shown in Fig. 1. The total aqueous solubility is also similar to that of natural crude oils. The use of an oil of known simulated composition enables its vapour pressure and solubility to be calculated using standard physical chemical relationships such as Raoult's Law. Data on the dependence of viscosity and density on degree of weathering are available (Mackay et al, 1975) as shown in Fig. 2.

2.2 Evaporation

The evaporative flux of a given component from the oil spill is given by equation (1):

$$N_i^e = K_e x_i P_i^S / RT \quad (\text{mol cm}^{-2} \text{ sec}^{-1}) \quad (1)$$

where N_i^e = evaporative flux of component i

K_e = evaporative mass transfer coefficient (MTC) (cm sec^{-1})

x_i = concentration of i in the oil (mole fraction)

P_i^S = pure component vapour pressure of i (torr) at the oil temperature

R = gas constant ($\text{cm}^3 \text{ torr/mol K}$)

T = air temperature above the slick (K)

The value of the evaporative MTC was estimated from the correlation of Mackay and Matsugu (1973). For evaporation from pans, they showed that the MTC was proportional to the 0.78 power of the wind speed. This same proportion is used here with MTC's at 10, 32, 77 and 88 km/hr being 0.4, 1.0, 2.0 and 2.2 cm sec^{-1} respectively.

It is assumed that Raoult's Law applies to the hydrocarbon mixture and that evaporation proceeds into the atmosphere, which is considered to be an infinite reservoir of zero concentration. To calculate the vapour pressure of the evaporating hydrocarbons, it is also assumed that the oil layer is the same temperature as the water.

TABLE 1 COMPOSITION OF SIMULATED CRUDE OIL

Component No.	Compound	Mole Fraction	Volume Fraction	M.Weight	M.Volume (cm ³ /mol)	V.P. at 25°C (torr)	Solubility (ppm)
1	n-butane	0.07	0.033	58	101	1725	136
2	n-hexane	0.15	0.091	86	132	121	12.6
3	n-octane	0.1	0.075	114	164	10.6	0.66
4	n-decane	0.15	0.135	142	196	1.50	0.052
5	n-dodecane	0.1	0.104	170	228	0.075	0.008
6	n-hexadecane	0.15	0.202	226	293	3.43×10^{-4}	0.006
7	benzene	0.005	0.002	78	89	95.2	1760
8	toluene	0.015	0.007	92	107	28.4	515
9	naphthalene	0.005	0.003	128	126	0.23	32
10	phenanthrene	0.005	0.004	178	182	3.44×10^{-3}	1.3
11	"inert"	0.25	0.344	300	300	0	0

2.3 Vertical Diffusion in the Water Column

As is discussed later, oil may enter the water column in dissolved or dispersed (particulate or emulsion) form. It will then be subject to vertical and horizontal diffusion. These processes are critically important since they control the volumetric extent of oil contamination of the water column and the concentrations achieved. Horizontal diffusion is discussed in Section 2.8.

The model assumed here is that of a well-mixed (no concentration gradient) upper-water layer about 10 m deep. The resistance to dissolution mass transfer lies in a stagnant layer of thickness of the order of 1 mm underlying the oil. The resistance of this layer is characterized by a mass transfer coefficient discussed in Section 2.4. The "diffusion floor" may be a thermocline or bottom or region of low vertical diffusion. The justification for this model lies in the observation that vertical eddy diffusivities in this upper 10-m layer are sufficiently large that any concentration gradient established is likely to decay in a time shorter than the times in question. Alternatively, the problem could be regarded as determining which resistances of the two series dominate - either the resistance at the oil-water interface or the resistance of the 10-m water column. An analogous problem has been solved for heat transfer in which a surface heat transfer resistance can be compared with a body thermal conductivity.

It has been shown (Kreith, 1967) that in bodies whose shape resembles a flat plate, the error introduced by the assumption that the concentration at any instant is uniform, will be less than 5% when the internal resistance to mass (or heat) transfer is less than 10% of the external surface resistance. That is:

$$B = K_1 L / E_d < 0.1 \quad (2)$$

where L = characteristic length in the system, i.e. thickness of the slab

K_1 = mass (or heat) transfer coefficient

E_d = mass (or thermal) diffusivity in the slab

This ratio is called the Biot number. When the Biot number for dissolution of hydrocarbons from an oil slick into a water column was calculated, it was found that the mass transfer coefficient model will be adequate for the purpose of this work, and that no advantage is gained by using the more complex and time-consuming diffusion equation model.

The values of the parameters used in determining the Biot number are as follows:

$$K_1 = 2.36 \times 10^{-4} \text{ cm sec}^{-1}$$

$$L = 1,000 \text{ cm (10 m)}$$

$$E_d = 13.8 \text{ cm}^2 \text{ sec}^{-1}$$

The resulting Biot number using these values is 1.7×10^{-2} , which is a factor of 6 less than 0.1.

This conclusion greatly simplifies the model in avoiding the necessity for a multi-layer model. The conclusion is valid for dissolution, but may be invalid for dispersion shortly after dispersal in that 5 to 10 minutes may lapse before oil dispersed at the surface penetrates to the floor. Within this context, however, such a time factor is short.

2.4 Dissolution

Dissolution rates can be calculated by two methods: either the solution of the diffusion equation with appropriate boundary conditions, or the use of an MTC model as in the case of evaporation. It is believed that the simpler MTC model is preferable to the diffusion equation model which is considerably more complex. Some difficulties with the diffusion equation model include the lack of data on vertical diffusivity close to the oil-water interface and the use of excessive computation time.

The MTC model assumes a well-mixed water layer with most of the resistance to mass transfer lying in a hypothetical stagnant region close to the oil. The dissolution flux is calculated using equation (3) below:

$$N_i^d = K_d(e_i x_i C_i^S - C_i^W) \text{ (mol cm}^{-2} \text{ sec}^{-1}) \quad (3)$$

where N_i^d = dissolution flux

K_d = dissolution MTC (cm sec⁻¹)

e_i = solubility enhancement factor having values given
Table 2 (Leinonen and Mackay, 1977)

x_i = oil phase mole fraction

C_i^S = pure component solubility (mol cm⁻³)

C_i^W = bulk water phase concentration of i

TABLE 2 SOLUBILITY ENHANCEMENT FACTORS

Hydrocarbon	e_i
alkanes	1.4
cycloalkanes	1.4
aromatics	2.2
olefins	1.8

A dissolution MTC of $2.36 \times 10^{-4} \text{ cm sec}^{-1}$ is used in the simulations. This value was obtained experimentally in ponds by Leinonen (1976). There is, however, considerable doubt about the actual values of the MTC, especially as a function of wind speed or surface roughness.

2.5 Emulsification or Dispersion

Dispersion by two methods is included in the model. The first is natural dispersion (formation of an water-in-oil emulsion) which occurs at a rate determined by turbulence conditions, the presence of natural surfactants, and the oil properties. This is approximated by equation (4), which is a simple first-order expression:

$$D = k V \text{ cm}^3 \text{ sec}^{-1} \quad (4)$$

where D = rate of dispersion of the oil spill

k = dispersion constant (sec^{-1})

V = volume of oil in the slick (cm^3)

It has been estimated that k typically ranges from 10 to 60% per day depending on the sea state (Holmes, 1977; Blaikely, 1977). For the simulations here, values of 15, 25, 35 and 45% per day are used, corresponding to low (2), medium (4), high (7), and very high (7+) Beaufort sea states respectively.

The presence of dispersed oil particles will, of course, add considerably to the hydrocarbon concentration in the water column. Calculations based on theoretical considerations (Section 2.9) show that half the soluble material will dissolve from a $10\mu\text{m}$ oil particle within eight seconds. Since this process is fast, it is assumed instantaneous, and for the purposes of calculating the concentration driving force for the dissolution flux, dispersed hydrocarbon is not to be considered any differently from dissolved hydrocarbon. Thus, C_i^w , in equation (3) is the sum of dissolved and dispersed hydrocarbon concentration.

The second method of dispersion which is considered here is dispersion through the use of a chemical surface-active agent. At some predetermined time in the model spill, the slick is treated with chemical dispersant and disperses completely and immediately. In practice the process is not instantaneous, but depending on surface turbulence and waves, occurs within several minutes or more. For simplicity, this short lag time is not considered since it is believed that evaporation and dissolution will not seriously alter the spill characteristics during this short time period.

2.6 Evaporation From Solution and Other Processes

Evaporation of dissolved hydrocarbons directly from the water body to the atmosphere is not considered in the model, although it is possibly an important mechanism by which the dissolved volatile hydrocarbons are lost from the water column (Leinonen and Mackay, 1975). Neglecting this process is justified by the fact that the contaminated water column will lie mainly under the oil slick, at least prior to chemical dispersion. It is also well established (Leinonen and Mackay, 1975) that evaporation of the lower molecular weight hydrocarbons from the oil slick is much more rapid than dissolution, and that the concentration of these compounds in the water column is likely to be low. That is not to say, however, that low concentrations of the lighter aromatics are innocuous to marine organisms.

Another process not included in the model, but of possible importance, is the production of a water-in-oil emulsion or "chocolate-mousse", as has been observed in many spills of crude and heavier fuel oils, particularly in colder water. This production results in thick patches of a very viscous water-in-oil emulsion containing a large percentage of water. Once the oil is in this form, it is possible that other processes such as evaporation, spreading, and dispersion of oil into the water column would be seriously curtailed. Quantification of this process, however, is extremely difficult and weathering rates of chocolate-mousse are not well understood.

Other processes such as biodegradation, sedimentation, chemical and photochemical oxidation are not considered in this model as well, since they are thought to be slow when compared with other processes quantified here or that they affect only a small fraction of the oil mass.

2.7 Spreading of the Oil Slick

Of the several available models of oil slick spreading, the Blokker model given in equation (4) was selected:

$$r_t = \sqrt[3]{r_o^3 + \frac{3 K_r t V (\rho_w - \rho_o) \rho_o}{\pi \rho_w}} \quad (5)$$

where r_t = radius of the slick at time, t , after the spill (cm)

r_o = radius at zero time (cm)

K_r = Blokker constant

t = time (sec)

V = original volume of the spill (cm³)

ρ_w and ρ_o = densities of seawater and spilled oil respectively

In the model being developed here, the oil is considered to spread symmetrically. In real spills, however, an elongated shape is almost always adopted in the presence of wind and surface currents. Because this shape is not easily predicted, the circular slick model is used in this instance. It is believed that few differences would result between an assumed circular or elongated spill.

A further complication arises from the observation that oil slicks move with the wind at a rate of approximately 3% of the wind velocity. This effect has not been considered in the model, but would serve to dilute the dissolved or dispersed hydrocarbon.

In testing this spreading model, the hypothetical spill selected was similar to the experimental spill in the North Sea described by Jeffrey (1973). The spill was taken to be 120 tons of API gravity 33.5° crude oil, i.e. 142.5 m³ of oil with a density of 0.8575 g cm⁻³. The parameters for the Blokker equation were those obtained by Jeffrey:

$$K_r = 216$$

$$r_o = 1.125 \times 10^4 \text{ cm}$$

$$V = 1.425 \times 10^8 \text{ cm}^3$$

$$\rho_o = 0.8575 \text{ g cm}^{-3}$$

$$\rho_w = 1.025 \text{ g cm}^{-3}$$

It has been reported (NAS, 1975; Jeffrey, 1973) that an oil slick has two distinct regions: a "thick" region and a "thin" region. About 90% of the oil, by volume, is found in the thick slick, which is only a small fraction of the total area. From Jeffrey's illustrations it was found that the thick region occupied, on the average, about 1/8 of the total area of the slick. For the purpose of the model, therefore, it was decided that the overall slick would spread according to the Blokker equation with $K_r = 216$; the thick slick would be located in the centre of the spill and would always be 1/8 of the total slick (i.e. radius of thick slick = $r_t/\sqrt{8}$). It is assumed that 90% of the spilled oil would originally be in the thick slick, with the remainder being in the thin slick. This situation corresponds to an initial 2.58 cm thick oil layer surrounded by a thin slick, 0.04 cm in thickness. It is further assumed that there is no transfer of oil from the thick slick to the thin slick or vice versa and that these slicks remain coherent.

2.8 Horizontal Diffusion

A key question in examining the horizontal movement of the oil is the relative velocity of spreading on the surface, as opposed to spreading by horizontal diffusion in the upper layers of the water column.

From experimental dye-patch studies it has been shown that the apparent horizontal diffusivity varies with the scale of diffusion (Okubo, 1971). The scale of diffusion is defined by Okubo to be that area within which 95% of the dye can be found, or, more simply, the size of the dye patch. The following correlation for the scale of diffusion, L , (cm) is presented by Okubo:

$$L = 0.155 t^{1.17} \quad (6)$$

where t = time in seconds after the release of an instantaneous point source of dye

L = radius of the scale of diffusion (cm)

Murthy and Okubo (1977) have shown that data for large lakes are similar to oceanic data.

The horizontal diffusion of dissolved and dispersed oil from an oil slick is somewhat more complex than dye-patch spreading. In this model it is assumed that most of the dissolved and dispersed hydrocarbon in the water column comes from the thick portion of the slick. This seems reasonable because 90% of the oil mass is in the thick slick and if a 10 μm layer of oil is completely dispersed in, say, 10 m of water, the water concentration will be about 1 ppm. In practice, only a fraction of oil is dispersed and the concentrations achieved may be much lower, possibly 10 to 100 ppb.

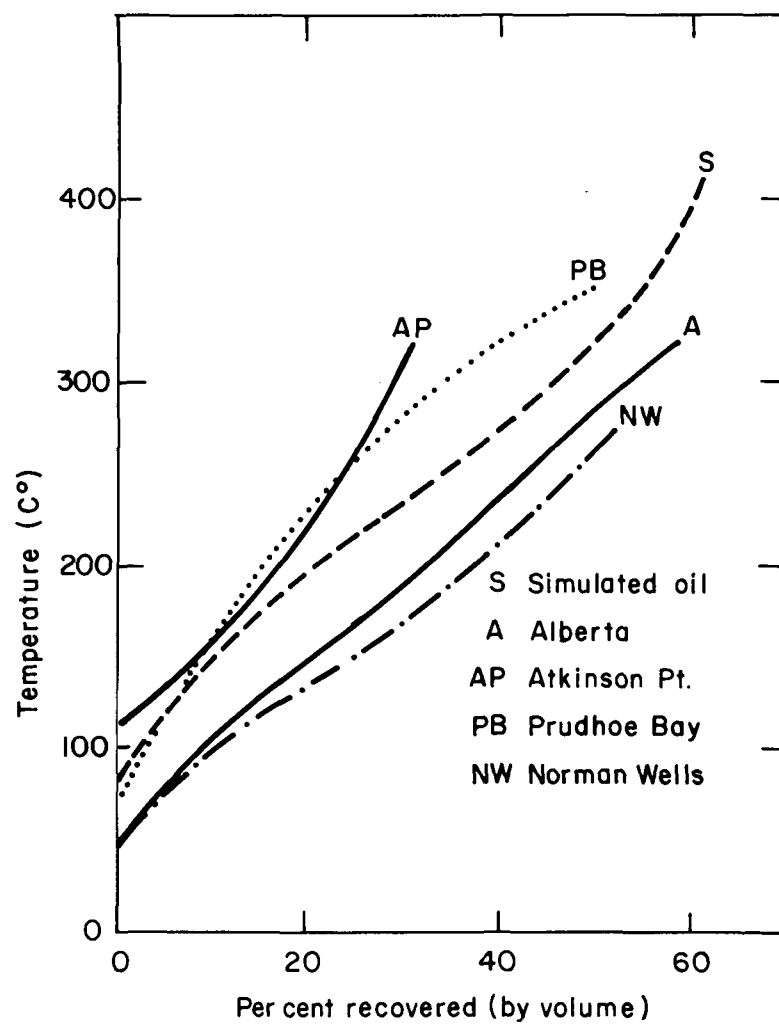


Fig.1 ASTM D86-67 Distillation curves of various natural crude oils and the simulated oil

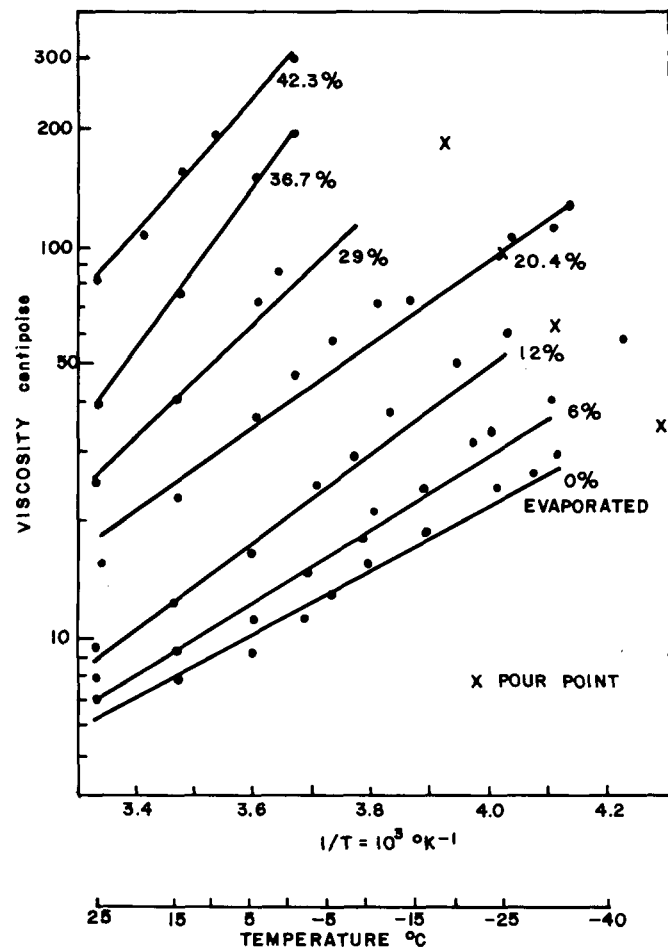


Fig. 2a Viscosity of Norman Wells crude oil

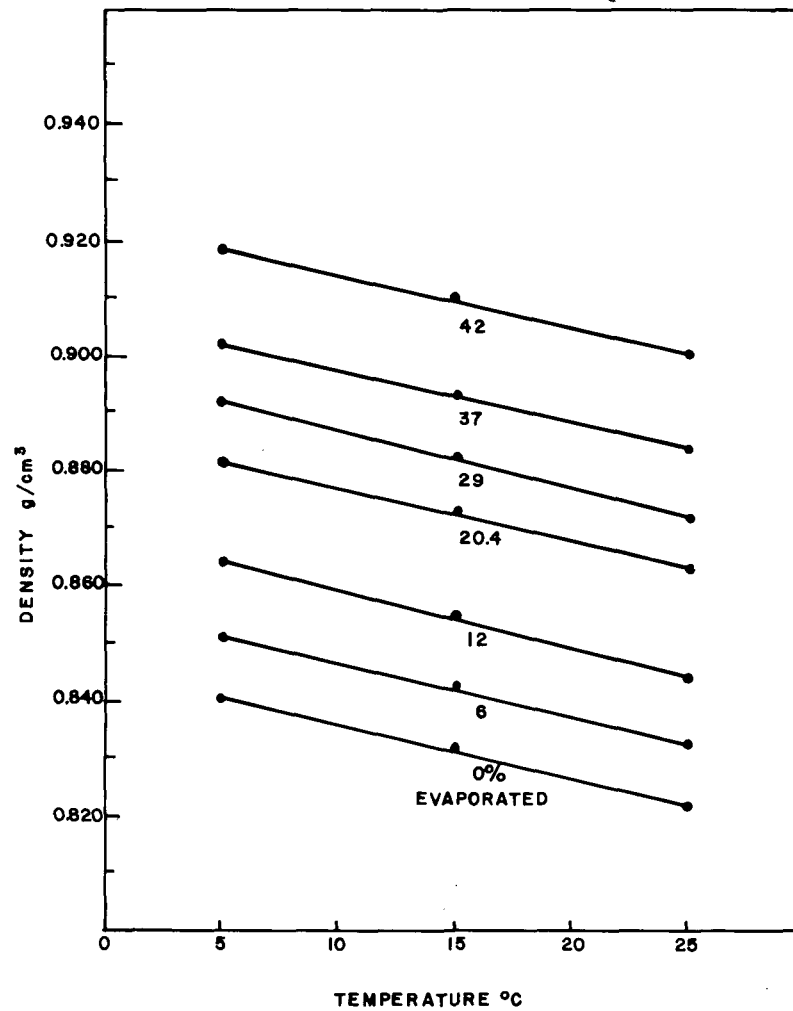


Fig. 2b Density of Norman Wells crude oil

If the spreading velocity of the oil slick is compared with the rate of increase of the scale of diffusion, (i.e. the diffusion velocity) initially the slick will spread more rapidly than the diffusion cell. As the diffusion cell increases in size, however, it expands more rapidly and eventually its velocity will exceed that of the spreading slick. Since it is assumed that the water beneath the slick is well mixed, the diffusion cell must necessarily expand at the same velocity as the oil slick until a diameter is reached when horizontal diffusion in the water column becomes more rapid than the slick spreading rate. This is illustrated in Figure 3, which shows spreading behaviour. For an initial thick slick radius of 39.8 m and a Blokker constant of 216, it is found that horizontal diffusion overtakes slick spreading about 46 minutes (2,770 seconds) after the spill when the thick slick has a radius of about 83 m. After this, the diffusion cell is larger than the thick slick. Similar curves are given in Figures 4 and 5 for Blokker constants of 108 and 432 respectively.

For simplicity, it is assumed that the concentration is uniform throughout the entire diffusion cell, although it is recognized that the concentration will be lower near the edges, and the peak concentration at the centre of the slick will be somewhat higher than the calculated average.

At the time of chemical dispersion it is assumed that the concentration of dissolved and dispersed hydrocarbon will be uniform across the entire scale of diffusion. To follow the decrease of hydrocarbon concentration with time, two approaches are possible. The first is simply to continue to use the correlation of Okubo for scale of diffusion and to assume that the hydrocarbon concentration is uniform across the entire diffusion cell. Again, this is a simplification and the concentration will be lower near the edges and higher near the centre. The second approach is to solve the diffusion equation in cylindrical coordinates. The difficulty here is that the diffusivity increases with time. If it is assumed that the diffusivity remains constant at the value it had at dispersal, the problem is soluble analytically and an approximate solution is obtained. This is a "worst case" solution because if the diffusivity increases with time, the concentration in the water column will decrease faster than that of constant diffusivity. Therefore, the model slightly overestimates concentration and underestimates the volume of water which is contaminated.

2.9 Dissolution Rate of Dispersed Oil

The dispersed oil is clearly subject to faster dissolution than the oil slick because of the high area-to-volume ratio of the droplets. It is interesting to estimate how fast these oil droplets dissolve and, thus, whether (and how) this process should be included in the model. An analysis based on some elementary mass transfer theory follows.

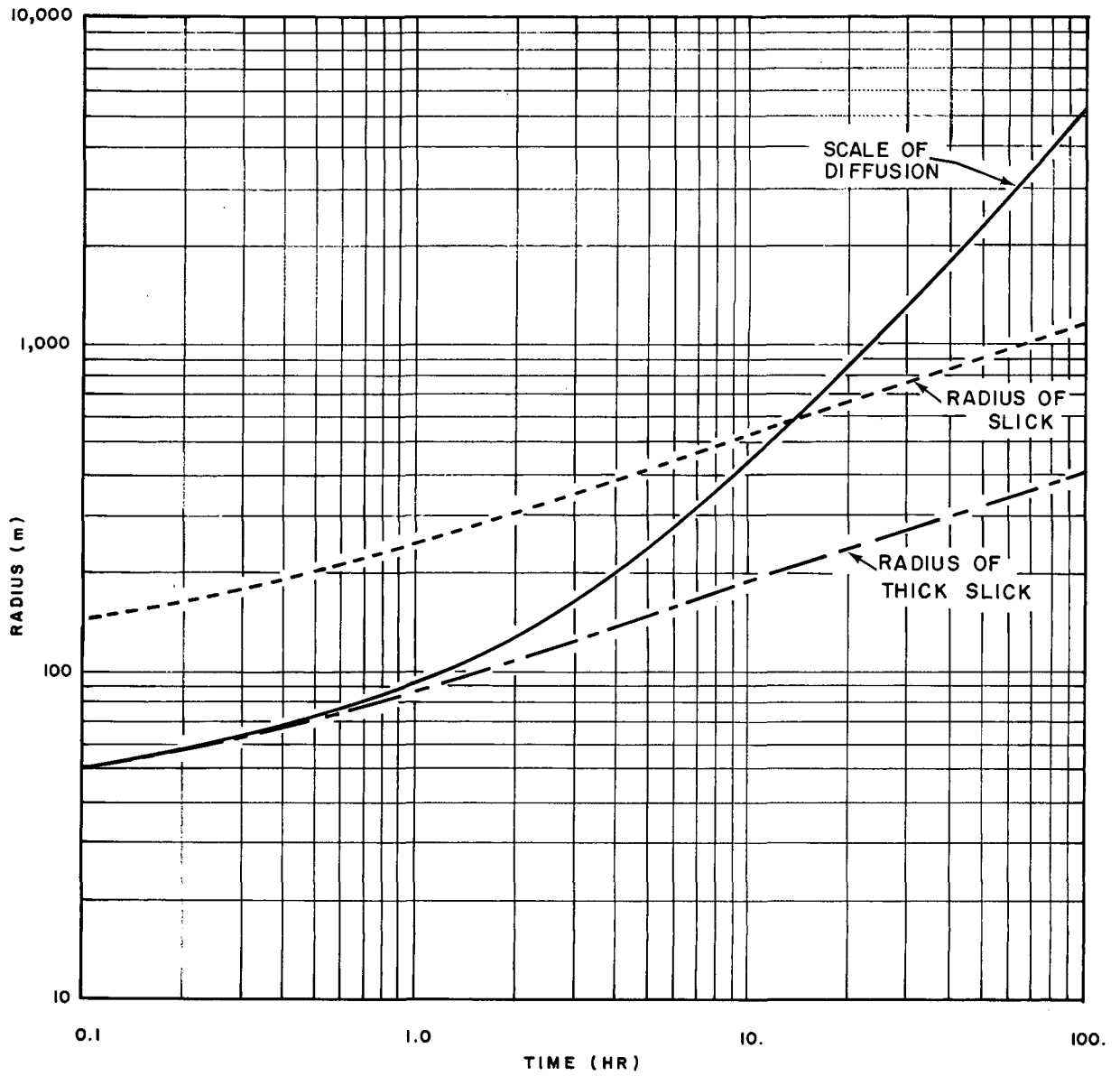


Fig. 3 Radius v Time ($K_r = 216$)

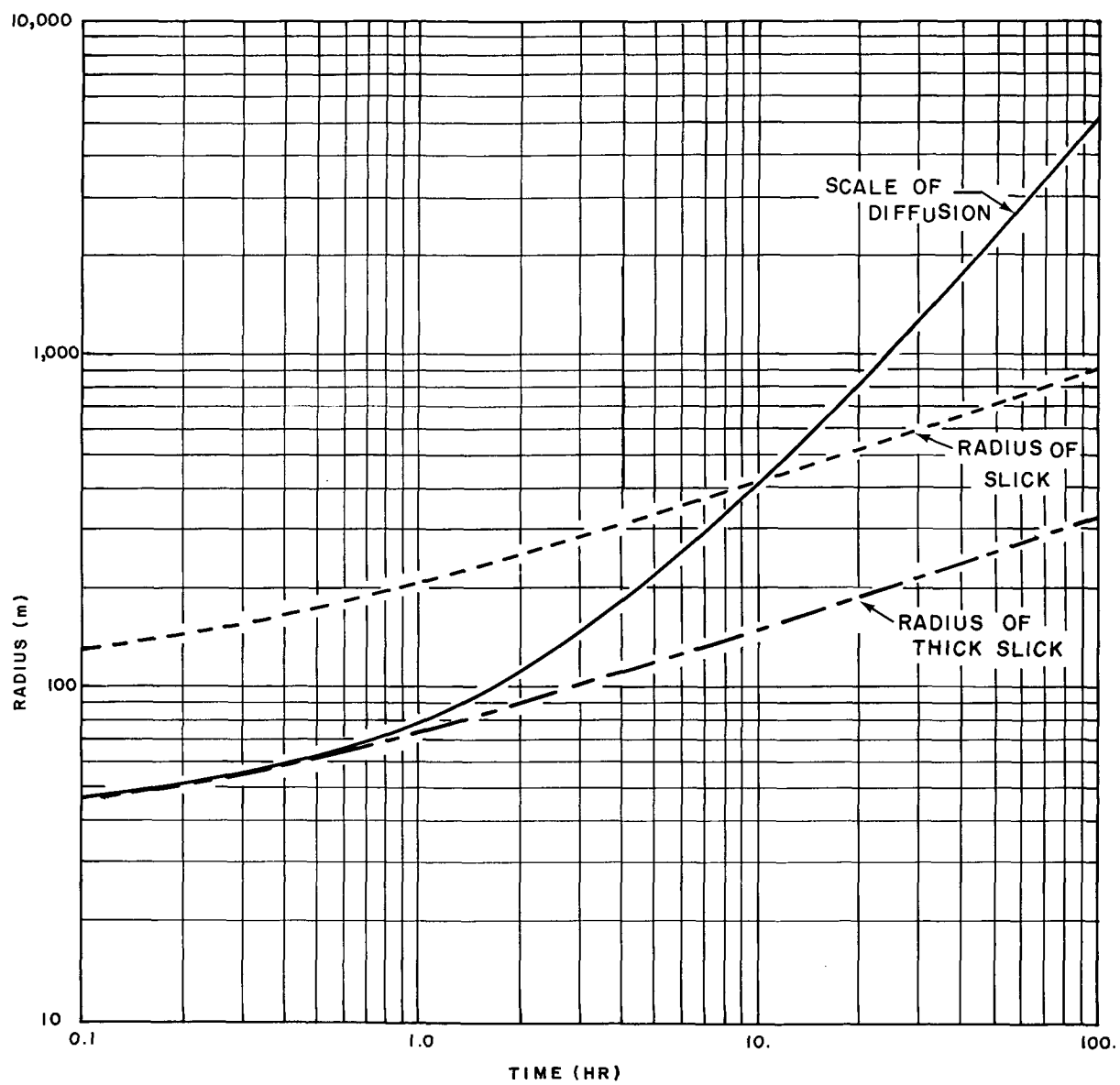


Fig. 4 Radius vs Time ($K_r=108$)

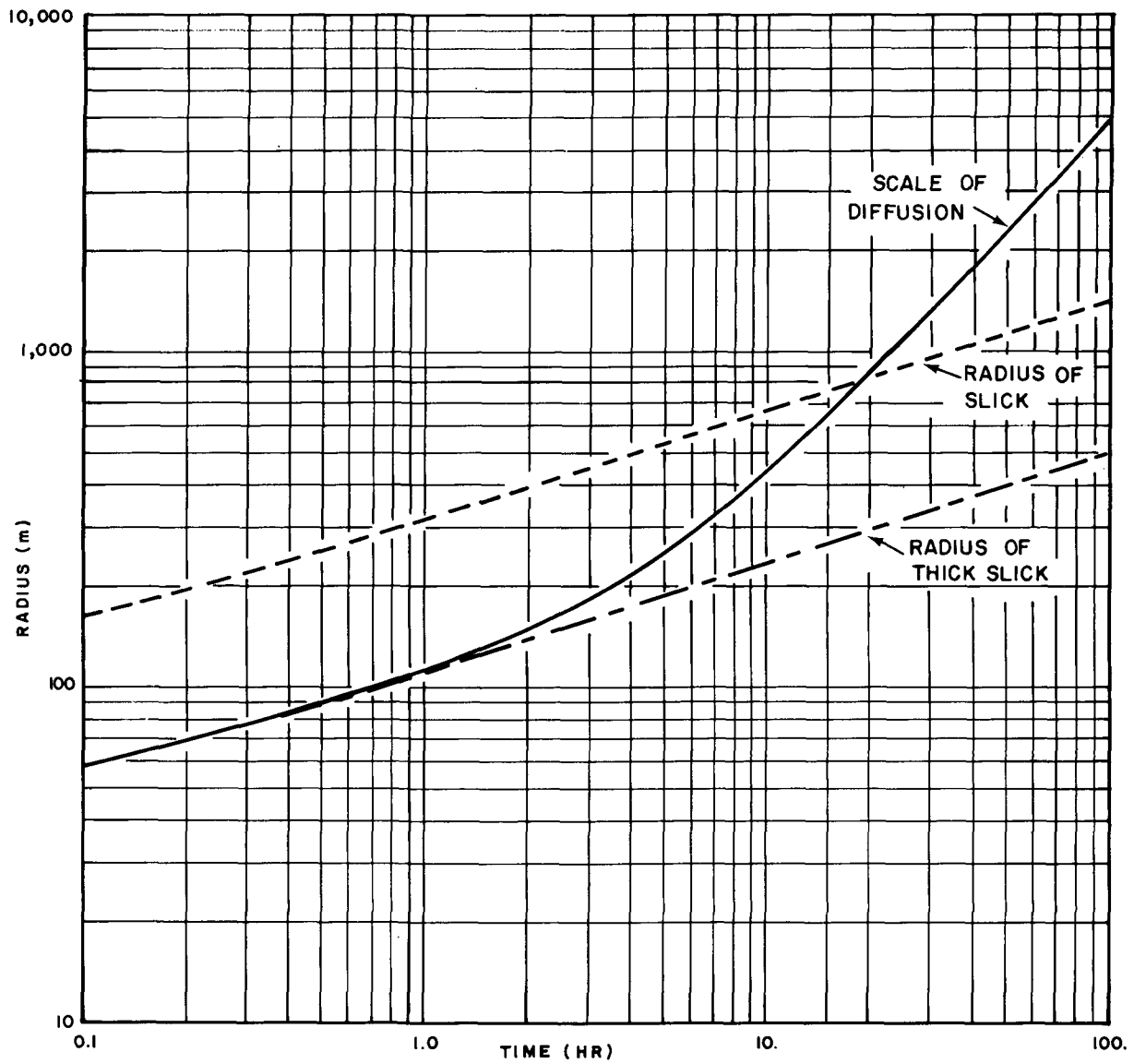


Fig.5 Radius vs Time ($K_r=432$)

Assume an oil droplet of diameter d (cm) and density ρ (g/cm³) suspended in water and dissolving slowly. Mass transfer rate measurements under such conditions suggest a Sherwood No. (Kd/D) of about 2.0, where K is the mass transfer coefficient (cm/hr); D is the continuous phase diffusivity (cm²/hr); and d is the droplet diameter (cm).

For simplicity, assume that the oil consists of two pseudo-components, a soluble hydrocarbon (mainly aromatics) and an insoluble hydrocarbon. The solubility of crude oil is about 30 mg/l and the "soluble" contents represent, say, 5% on a mass fraction basis. As the soluble material dissolves, the solubility C_s mg/l falls according to:

$$C_s = 600 x' \text{ mg/l or } 600 x' \times 10^{-6} \text{ g/cm}^3 \quad (7)$$

where x' is the mass fraction of soluble material.

Note that when $x' = 0.05$, $C_s = 30$ mg/l. Setting up the mass transfer equation for dissolution gives:

$$\frac{d(Mx')}{dt} = -K A (C_s - C_w) \quad (8)$$

where $M = \text{oil droplet mass and can be assumed constant at } \rho \pi d^3/6 \text{ (g)}$

$A = \text{droplet area, assumed constant at } \pi d^2 \text{ (cm}^2\text{)}$

$C_w = \text{concentration of dissolved hydrocarbon in the water, which is assumed for the purposes here to be much less than } C_s.$

$t = \text{time (hr)}$

Substituting for C_s gives:

$$M \frac{dx'}{dt} = -6 \times 10^{-4} K A x' / M \quad (9)$$

thus,

$$\frac{dx'}{x'} = -6 \times 10^{-4} K A dt / M \quad (10)$$

and after integration:

$$x' = x'_0 \exp (-6 \times 10^{-4} K A t / M) \quad (11)$$

The rate constant for dissolution is thus (6×10^{-4} KA/M), which is, after substitution, (7.2×10^{-3} D/ ρd^2).

Substituting $D = 10^{-5}$ cm²/s or 0.036 cm²/hr, and $\rho = 0.8$ g cm⁻³ gives ($3.24 \times 10^{-4}/d^2$) hr⁻¹. The "half life" for dissolution is then ($2.4 \times 10^3 d^2$) hr. Substituting various values of d gives:

Droplet Diameter		Rate Constant	Half life
cm	μm	hr ⁻¹	hr
0.1	1000	0.032	21
0.01	100	3.2	0.21 (12.8 min)
0.001	10	320	0.0021 (7.7 sec)
0.0001	1	32000	21×10^{-6} (0.077 sec)

It appears, therefore, that droplets of 100 μm or smaller will dissolve very quickly, or in essence, instantaneously in the time frame of these calculations. Only with droplets of oil 1 mm or larger in diameter is the dissolution time significant. It can thus be assumed, for the purposes of these calculations, that dissolution is instantaneous and that the material in the dispersed droplets consists of very low-solubility material, i.e. hydrocarbons with more than 10 carbon atoms. Therefore, it is not necessary to discriminate between dissolved material which entered the water column by dispersion and that which dissolved directly from the slick. Accordingly, total dispersed and dissolved oil is the term used in subsequent discussions.

3. RESULTS

The various parameter values used in 34 model spills are given in Table 3. The results of the computer simulations are presented in tables and graphs. Although not all information generated by the computer program is presented, that which is thought to be useful within the terms of this study is given.

Figures 6 to 13 show the calculated distribution of the oil after a spill. These graphs of four different sea states show how much oil remains in the slick, how much has evaporated and how much has dissolved and dispersed. Also shown is the distribution of the spilled oil with different water temperatures, and different Blokker constants in a medium sea.

Figure 14 illustrates the thickness of the "thick" slick as a function of time for three Blokker constants and a medium sea state.

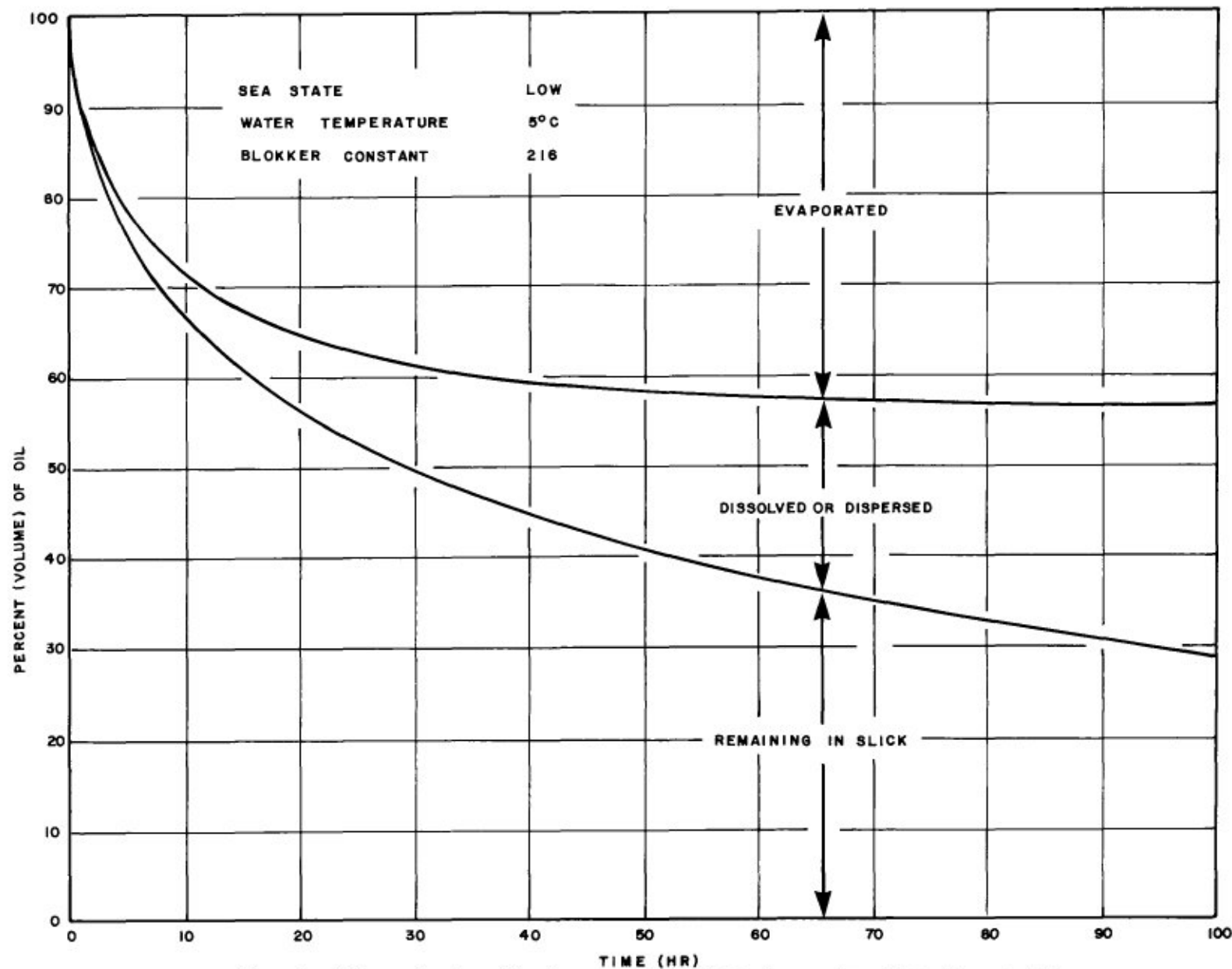


Fig.6 Fate of oil spilled on water (SS=Low, T=5°C, $K_r=216$)

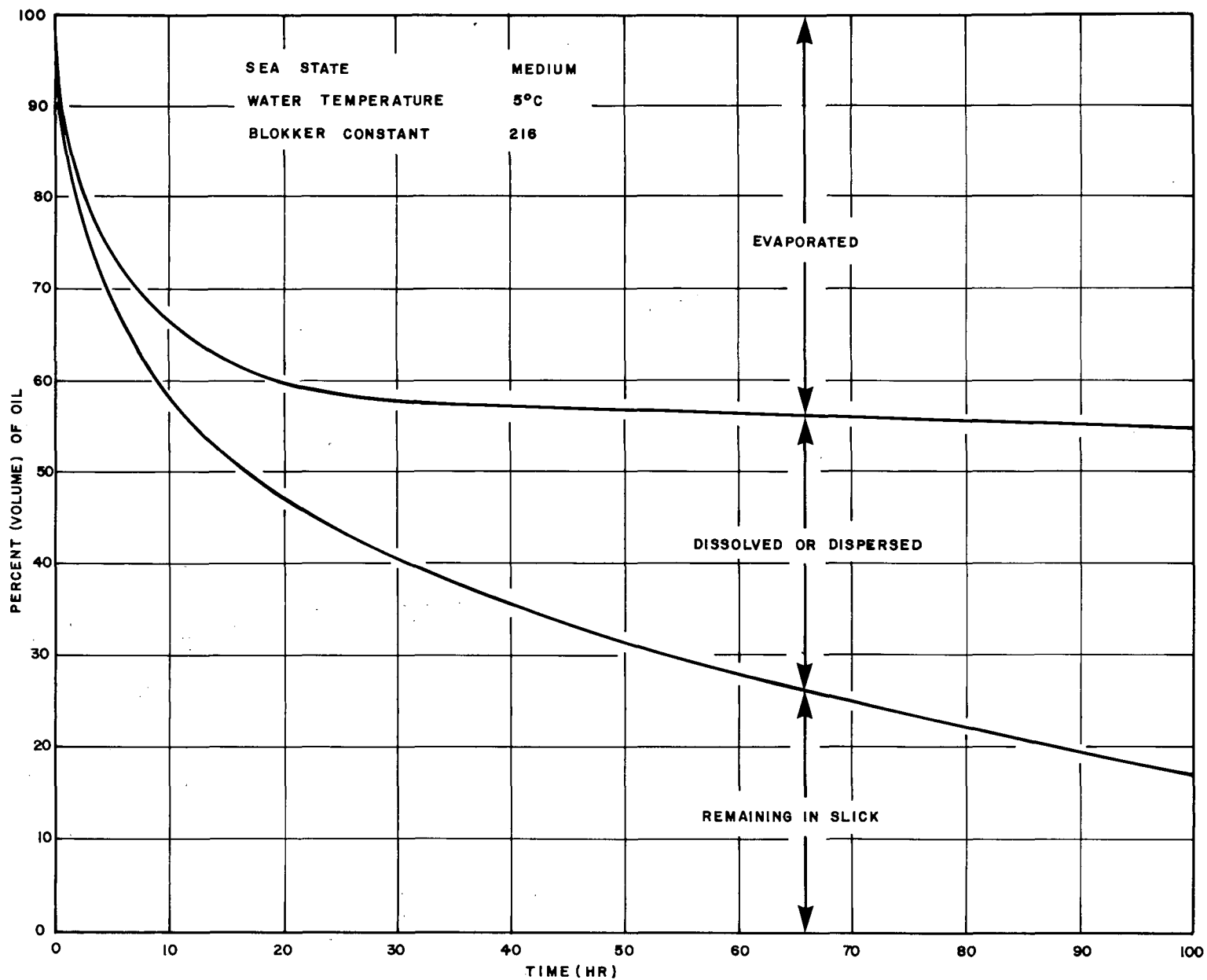


Fig.7 Fate of oil spilled on water (SS = Medium, T = 5°C, $K_r = 126$)

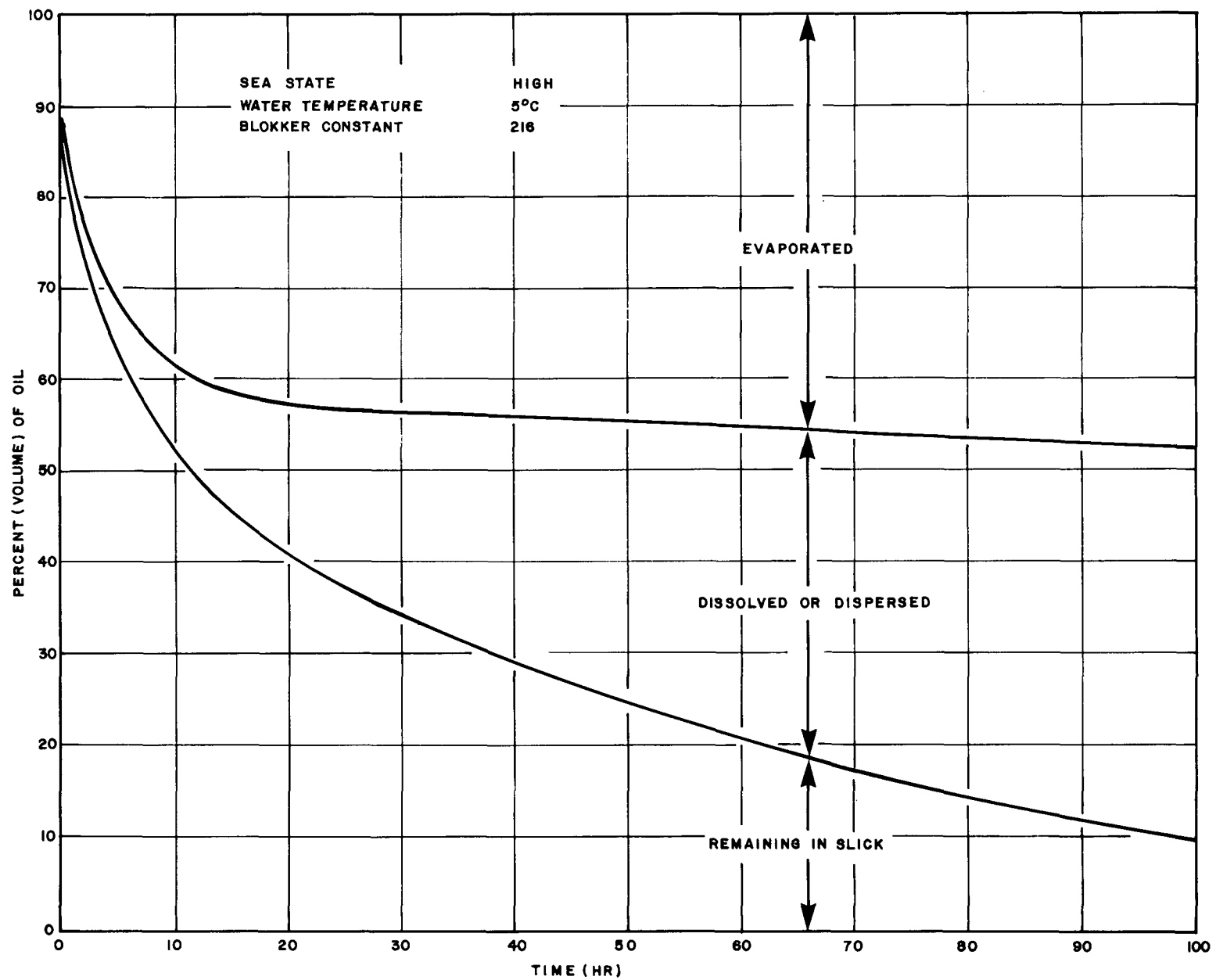


Fig. 8 Fate of oil spilled on water (SS = High, T = 5°C, $K_r = 216$)

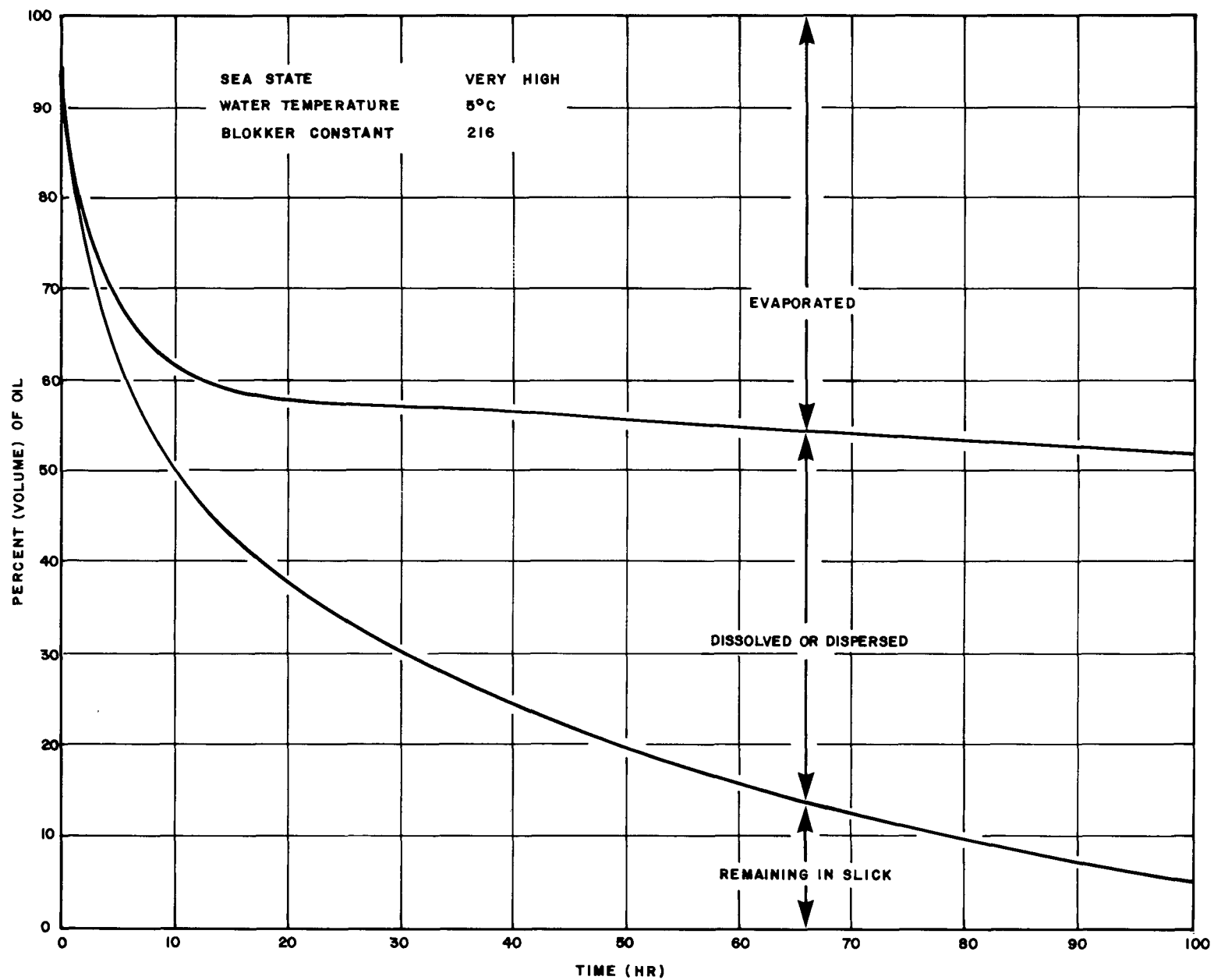


Fig. 9 Fate of oil spilled on water (SS = Very High, $T = 5^{\circ}\text{C}$, $K_f = 216$)

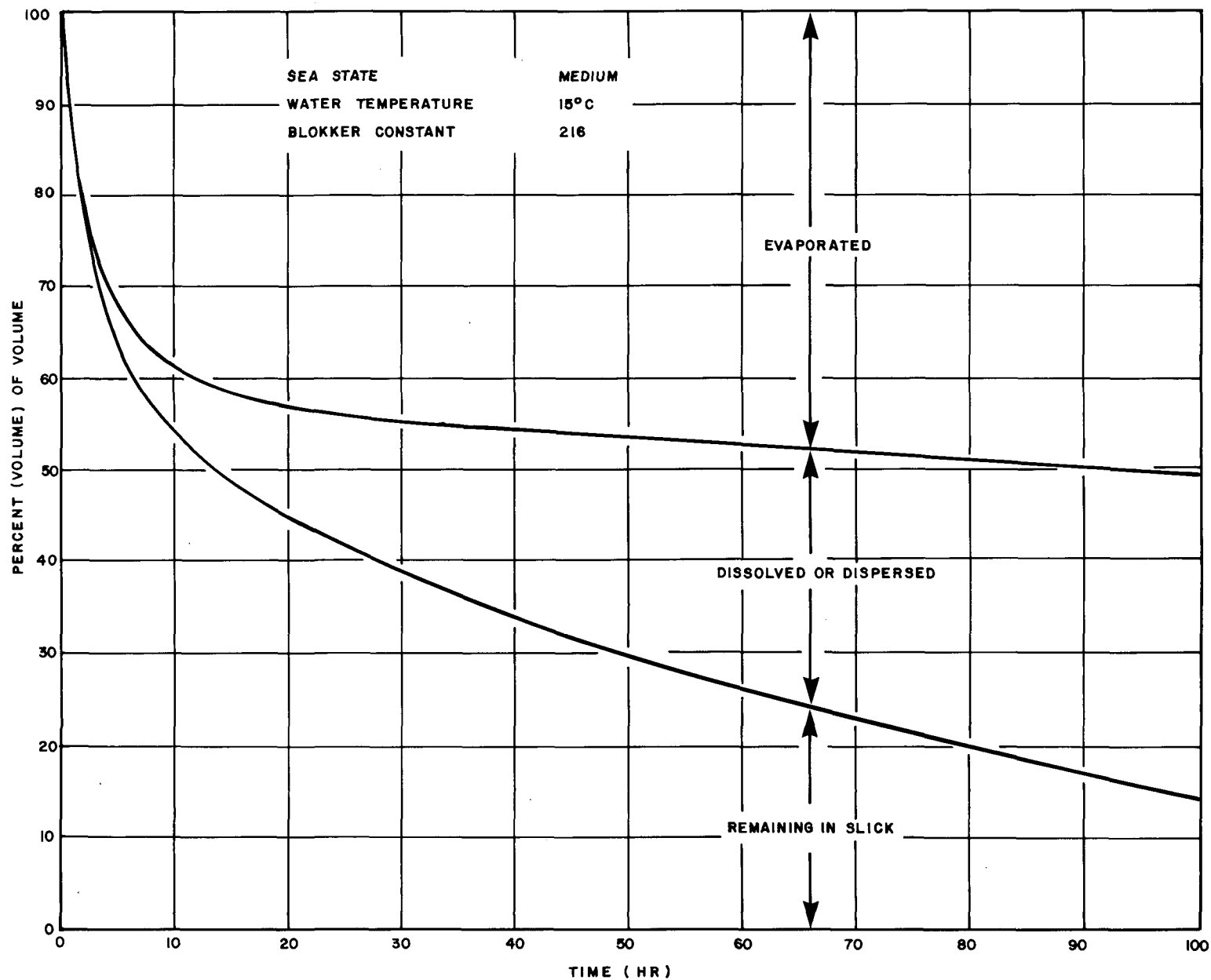


Fig.10 Fate of oil spilled on water(SS = Medium, T = 15°C, K_v = 216)

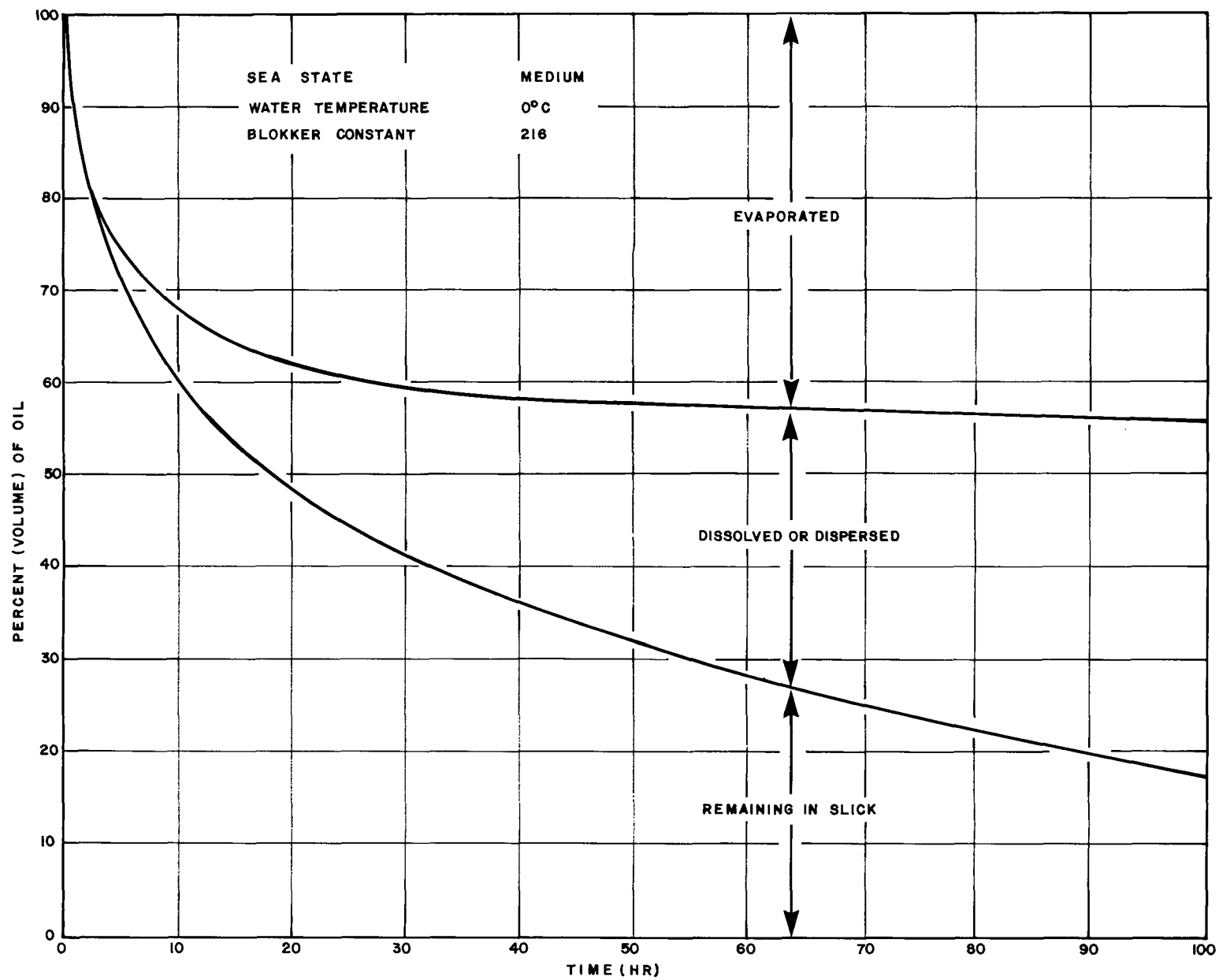


Fig.11 Fate of oil spilled on water (SS = Medium, $T = 0^{\circ}\text{C}$, $K_r = 216$)

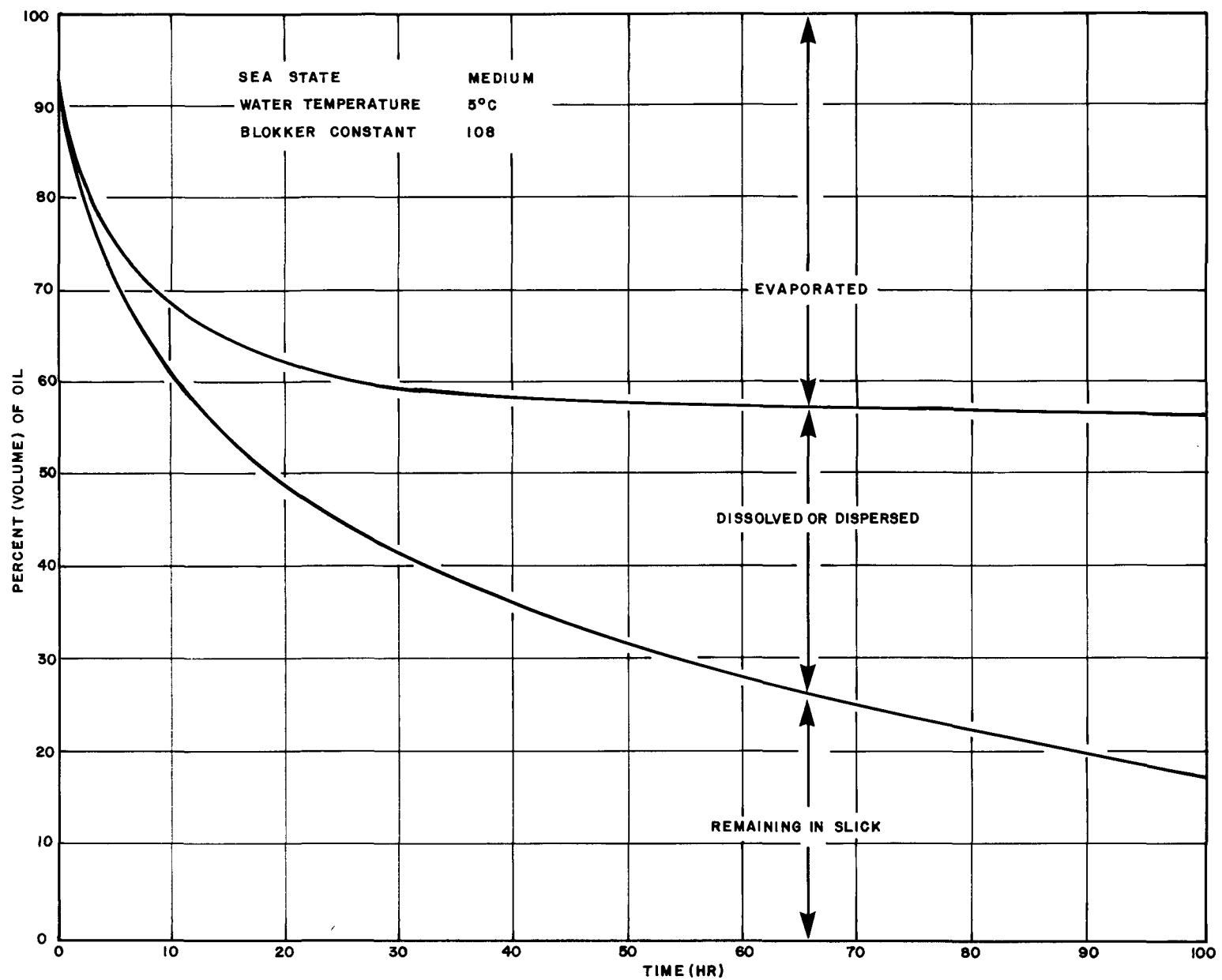


Fig. 12 Fate of oil spilled on water (SS = Medium, $T = 5^{\circ}\text{C}$, $K_r = 108$)

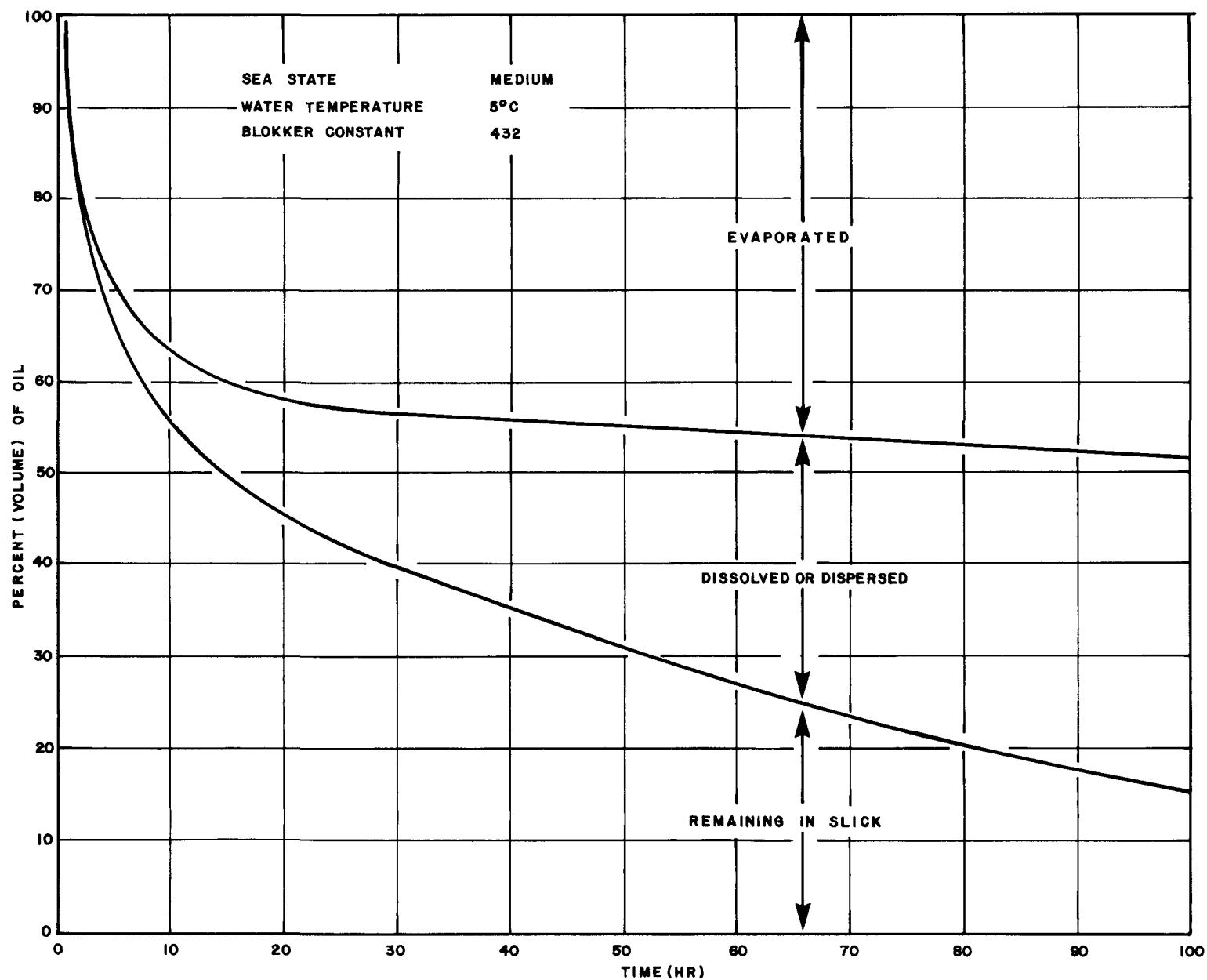


Fig. 13 Fate of oil spilled on water (SS = Medium, T=5°C, K_f= 432)

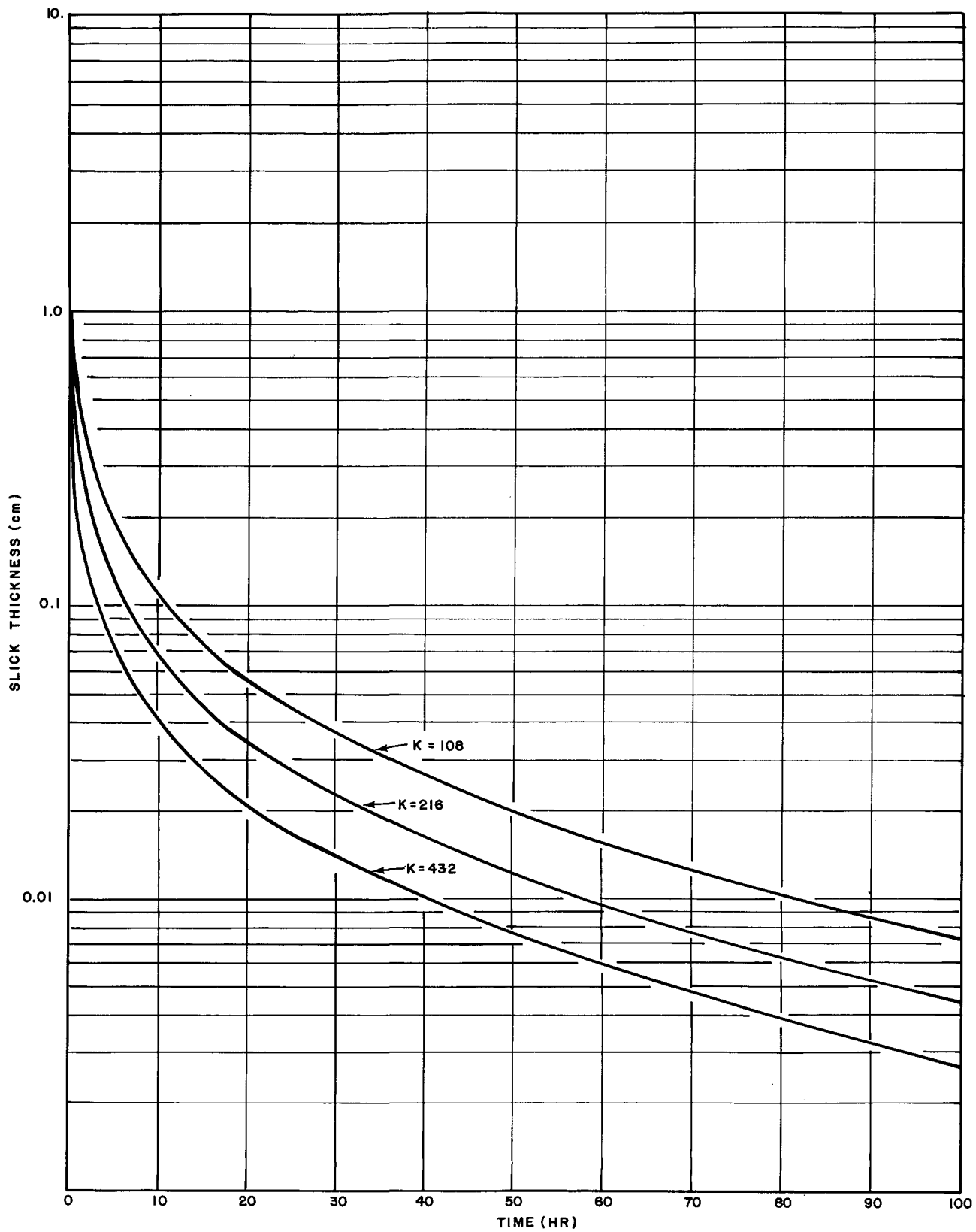


Fig.14 SLICK THICKNESS vs TIME

TABLE 3 PARAMETER VALUES - 34 MODEL SPILLS

Spill No.	Wind Beaufort No.	km/hr	knots	Seastate	K^e	K^d $\times 10^4$	K_{disp} $\times 10^6$	K_r	t_{disp}	Tw	Tair	Water Depth
1	2	10	5.5	Low (2)	0.4	2.36	1.71	216	1	5	15	10
2	↓	↓	↓	↓	↓	↓	↓	↓	3	↓	↓	↓
3	↓	↓	↓	↓	↓	↓	↓	↓	6	↓	↓	↓
4	↓	↓	↓	↓	↓	↓	↓	↓	12	↓	↓	↓
5	↓	↓	↓	↓	↓	↓	↓	↓	24	↓	↓	↓
6	↓	↓	↓	↓	↓	↓	↓	↓	48	↓	↓	↓
7	5	32	18	Medium(4)	1.0	2.36	2.89	216	1	↓	↓	↓
8	↓	↓	↓	↓	↓	↓	↓	↓	3	↓	↓	↓
9	↓	↓	↓	↓	↓	↓	↓	↓	6	↓	↓	↓
10	↓	↓	↓	↓	↓	↓	↓	↓	12	↓	↓	↓
11	↓	↓	↓	↓	↓	↓	↓	↓	24	↓	↓	↓
12	↓	↓	↓	↓	↓	↓	↓	↓	48	↓	↓	↓
13	9	77	42	High (7)	2.0	2.36	4.05	216	1	↓	↓	↓
14	↓	↓	↓	↓	↓	↓	↓	↓	3	↓	↓	↓
15	↓	↓	↓	↓	↓	↓	↓	↓	6	↓	↓	↓
16	↓	↓	↓	↓	↓	↓	↓	↓	12	↓	↓	↓
17	↓	↓	↓	↓	↓	↓	↓	↓	24	↓	↓	↓
18	↓	↓	↓	↓	↓	↓	↓	↓	48	↓	↓	↓
19	10	88	49	very high (7+)	2.2	2.36	5.21	216	1	↓	↓	↓
20	↓	↓	↓	↓	↓	↓	↓	↓	3	↓	↓	↓
21	↓	↓	↓	↓	↓	↓	↓	↓	6	↓	↓	↓
22	↓	↓	↓	↓	↓	↓	↓	↓	12	↓	↓	↓
23	↓	↓	↓	↓	↓	↓	↓	↓	24	↓	↓	↓
24	↓	↓	↓	↓	↓	↓	↓	↓	48	↓	↓	↓
25	5	32	18	Medium(4)	1.0	2.36	0	216	↓	0	15	10
26	↓	↓	↓	↓	↓	↓	0	↓	↓	5	↓	↓
27	↓	↓	↓	↓	↓	↓	0	↓	↓	15	↓	↓
28	↓	↓	↓	↓	↓	↓	2.89	↓	24	0	↓	↓
29	↓	↓	↓	↓	↓	↓	↓	↓	↓	5	↓	↓
30	↓	↓	↓	↓	↓	↓	↓	↓	↓	15	↓	↓
31	↓	↓	↓	↓	↓	↓	↓	↓	↓	5	↓	5
32	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	10
33	↓	↓	↓	↓	↓	↓	↓	108	↓	↓	↓	↓
34	↓	↓	↓	↓	↓	↓	↓	432	↓	↓	↓	↓

NOTE: Arrows indicate no change in parameters.

Figure 15 gives the concentration of dissolved and dispersed hydrocarbon in the water column as a function of time for low, medium, high and very high sea states. Also shown on this graph is the concentration in the water column after chemical dispersion at 48 hours. Figure 15 also includes the concentration which would be reached in the water column with dissolution only and not natural dispersion.

Figure 16 presents the computed concentration of dissolved and dispersed hydrocarbon as a function of time for a medium sea state and for various chemical dispersion times.

Figure 17 gives the calculated concentration of hydrocarbon which is reached in the water column immediately after dispersion as a function of time of dispersion.

Figure 18 gives the ratio of the aqueous hydrocarbon concentration immediately after chemical dispersion to the concentration immediately before and the ratio of the concentration immediately after dispersion to the concentration at 1.5 hours (i.e. maximum concentration from dissolution and natural dispersion alone) as a function of time of dispersion. All values are for a medium sea state and a water temperature of 5°C.

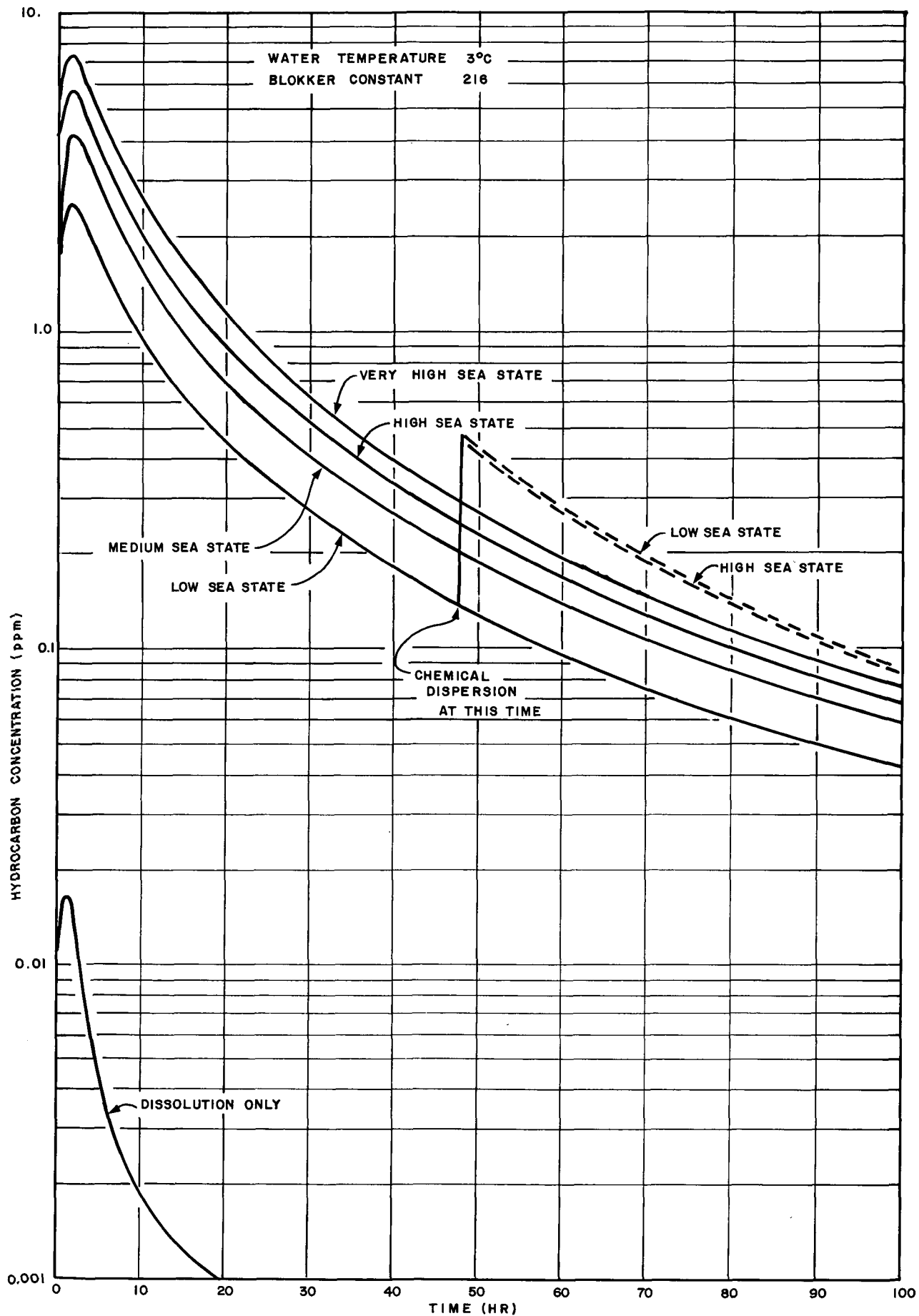


Fig.15 CONCENTRATION OF DISSOLVED AND DISPERSED
HYDROCARBONS vs TIME

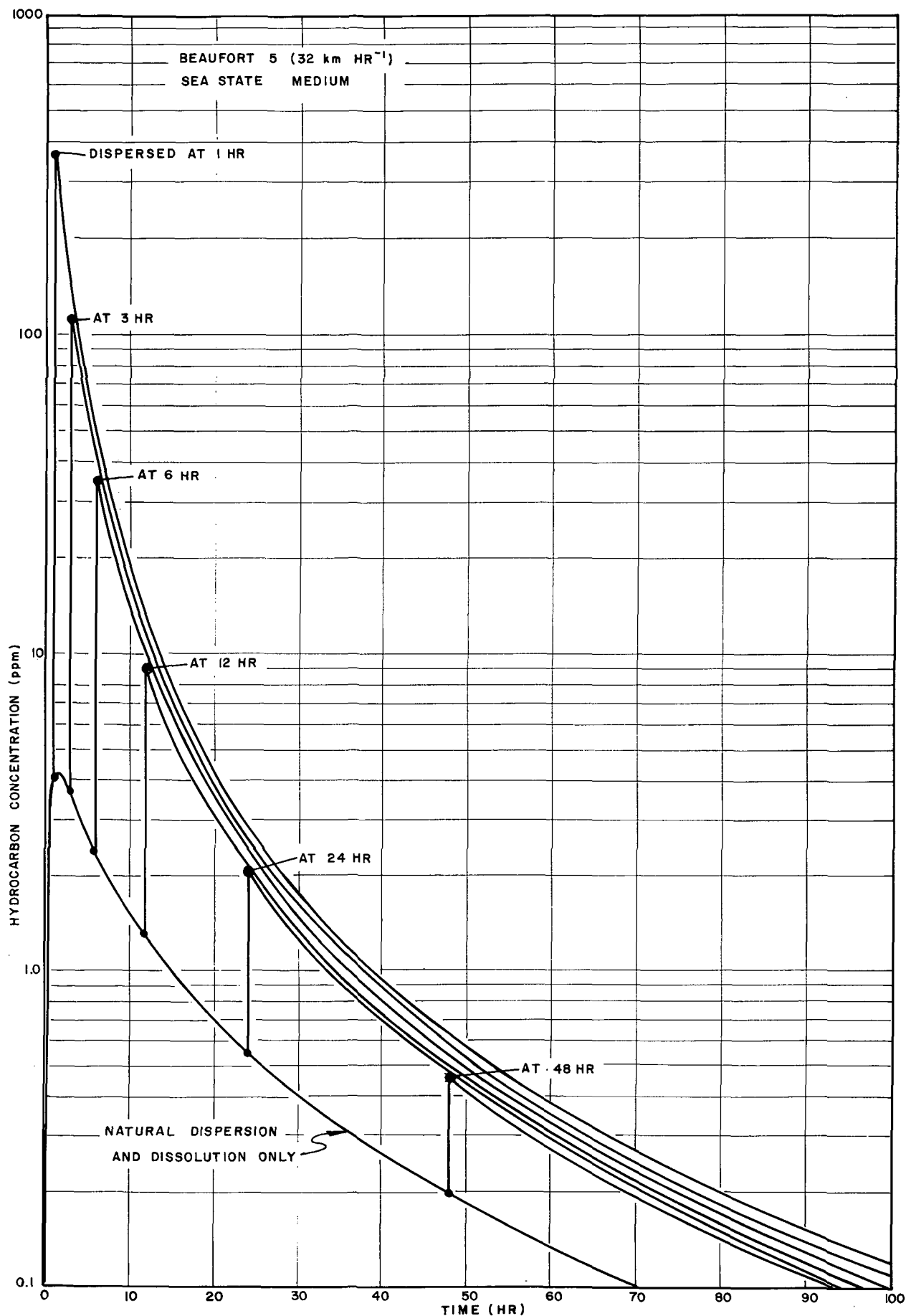


Fig.16 CONCENTRATION vs TIME

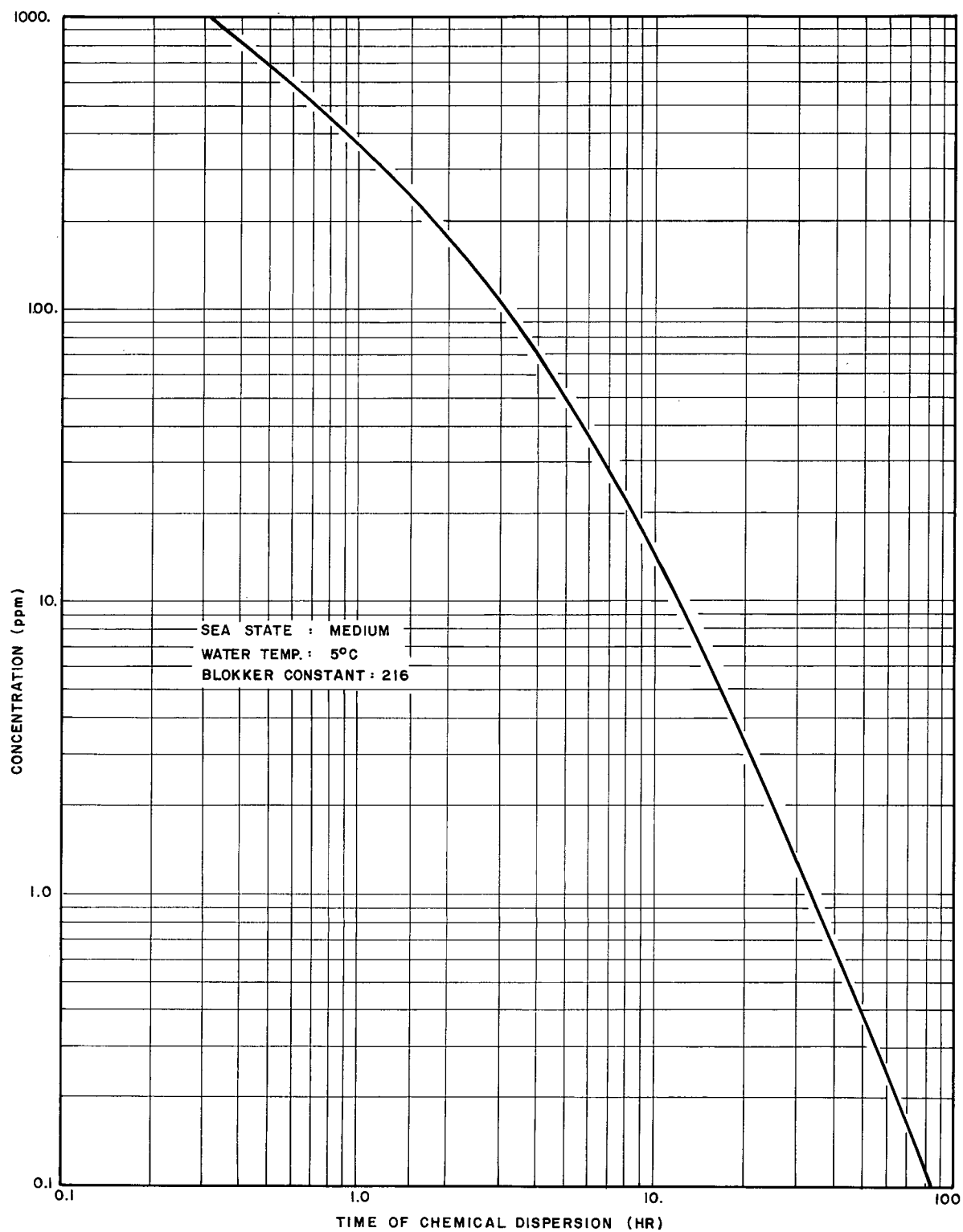


Fig. 17 CONCENTRATION IN WATER COLUMN IMMEDIATELY AFTER CHEMICAL DISPERSION vs DISPERSION TIME

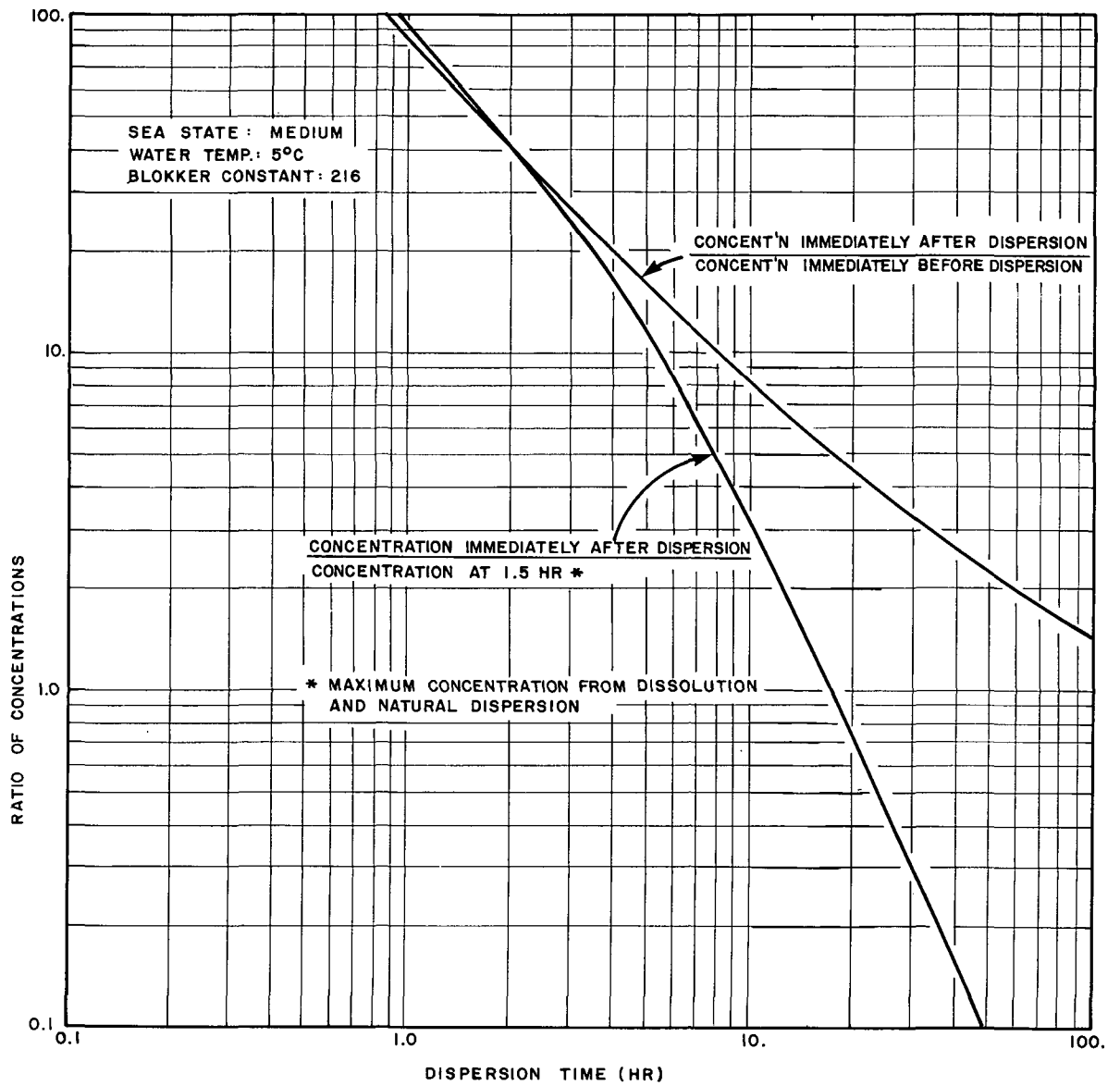


Fig. 18 Ratio of concentration after dispersion to concentration before dispersion vs dispersion time

Figures 19 gives the viscosity of the oil in the thick slick as a function of time at 0°C, 5°C, and 15°C. The viscosity is based on the correlation of the viscosity of Norman Wells Crude oil as a function of temperature and percent evaporated as developed by Mackay et al (1975). It is given below in equation (12):

$$\log \mu = (830 + 29E) (1/T) - (2.0 + 0.07E) \quad (12)$$

where μ = viscosity in centipoise

T = temperature in °K

E = percentage evaporated

Figure 20 presents the concentration profiles across the cloud of dispersed oil as a function of time-after-dispersion and radius. The curves were generated from the solution of the diffusion equation in cylindrical coordinates. The solution is given below:

$$C/C_0 = \frac{\exp(-r^2/4Dt)}{2Dt} \int_0^a \exp(-r^{*2}/4Dt) I_0 \left(\frac{rr^*}{2Dt} \right) r^* dr^* \quad (13)$$

where C_0 = concentration immediately after chemical dispersion

a = radius of the dispersed oil-contaminated water

D = eddy diffusivity (horizontal in this case)

t = time after chemical dispersion

r = radial cylindrical coordinate

r^* = dummy variable

C = concentration at time, t , and radius, r

I_0 = modified Bessel function of the first kind of order zero

The integral must be evaluated numerically, except on the axis $r=0$ where equation (13) becomes:

$$C/C_0 = 1 - \exp(-a^2/4Dt) \quad (14)$$

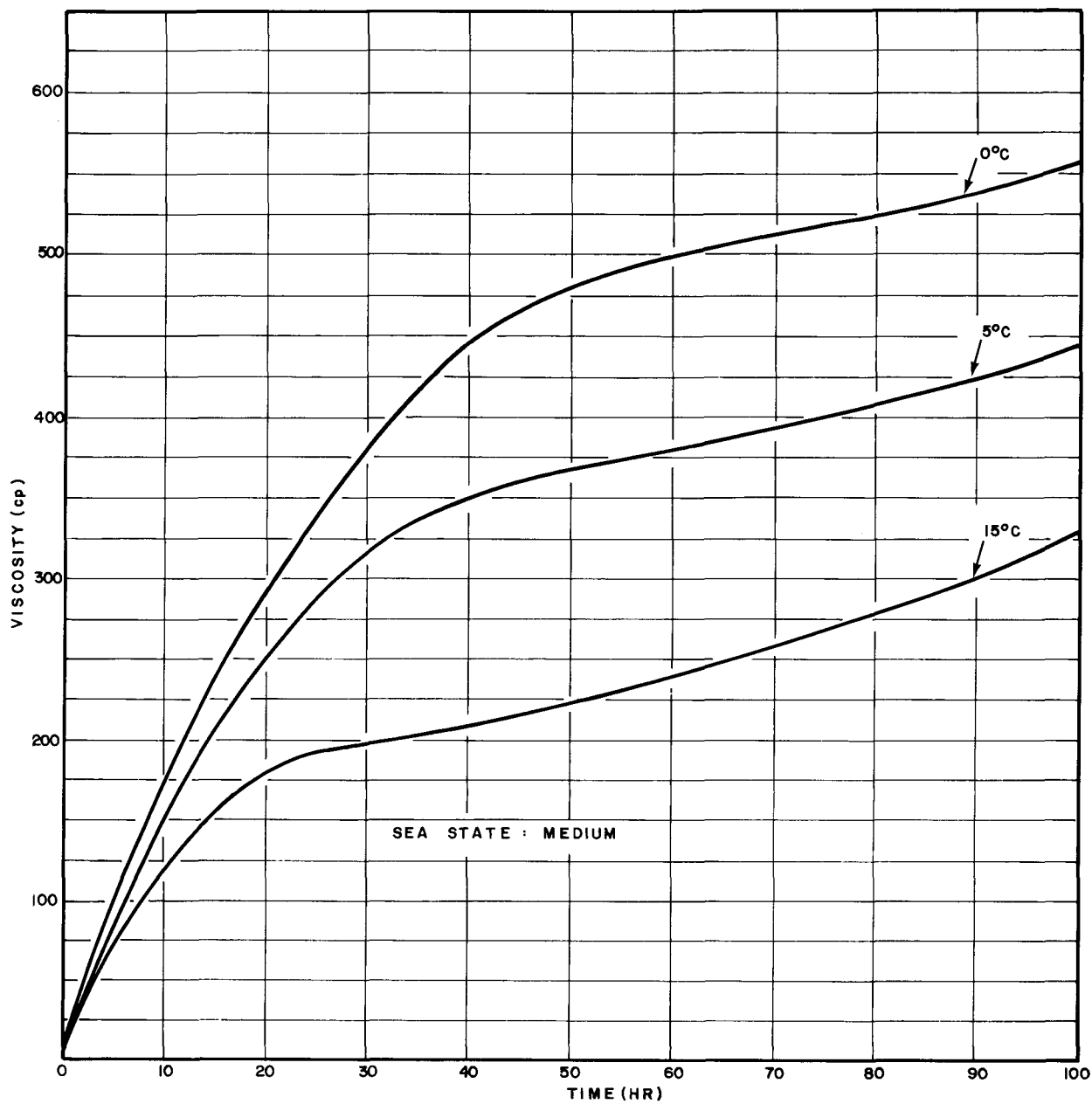


Fig. 19 Viscosity of oil (Norman Wells crude) in slick

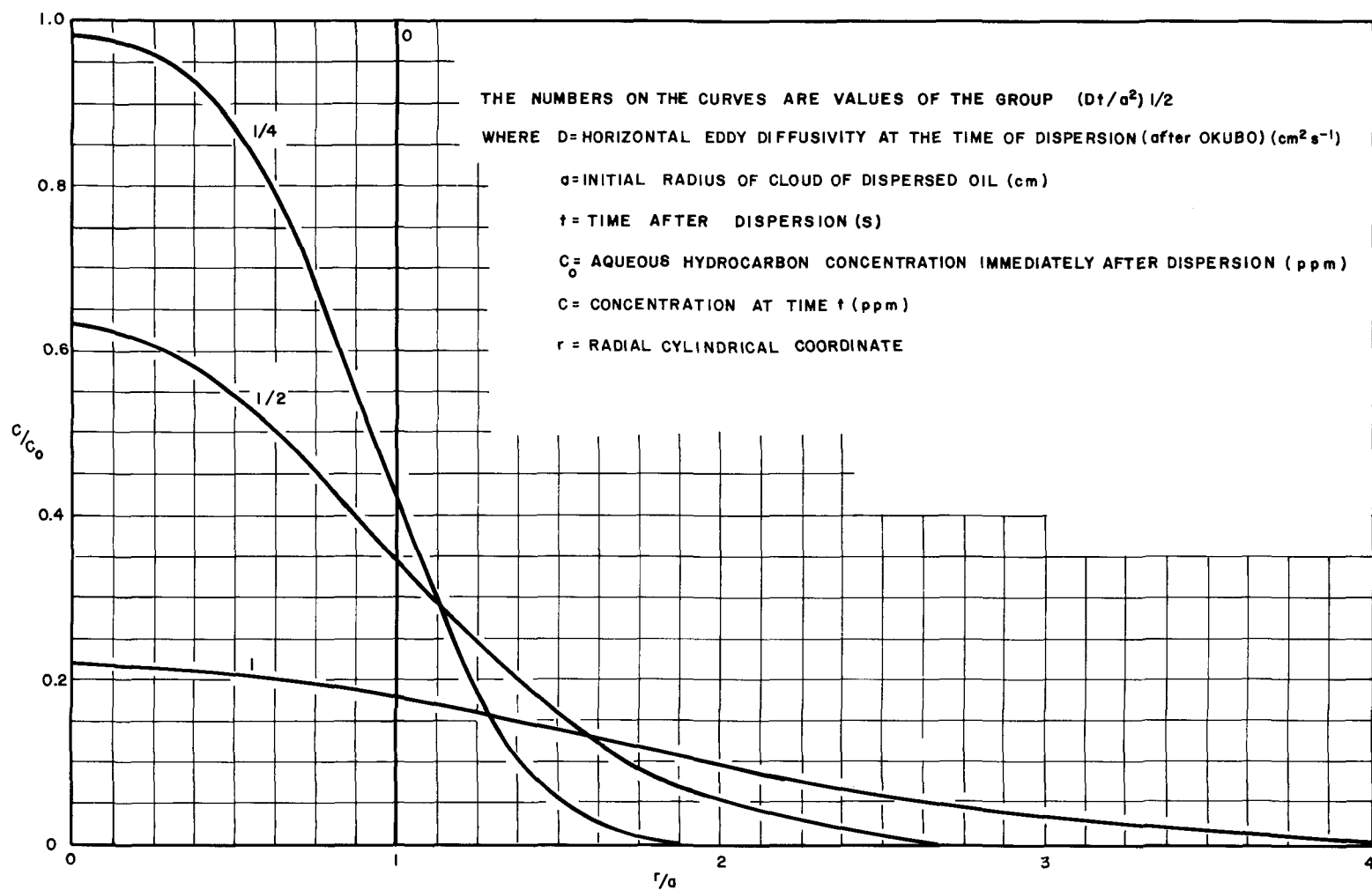


Fig.20 Concentration distributions for a cylindrical source

The various curves are labelled with a number which corresponds to a value of the group $(Dt/a^2)^{\frac{1}{2}}$. The values of the parameters for chemical dispersion times of 1, 3, 6, 12, 24 and 48 hours are given in Table 4.

Figure 20 gives concentration distributions for a cylindrical source and is applicable to each spill.

Figures 21 to 24 give concentrations of hydrocarbon in the water at three points as a function of time after dispersion. The three locations are at the centre of the dispersed slick, at the original radius of the dispersed oil cloud and at twice this radius. Figures 21-24 are applicable to chemical dispersion at 1, 12, 24 and 48 hours respectively after the spill.

Tables 5 to 11 give data from Figures 15 and 16 in tabular form, plus more complete data for low, high and very high sea states, and for different water temperatures, Blokker constants and mixed water depths.

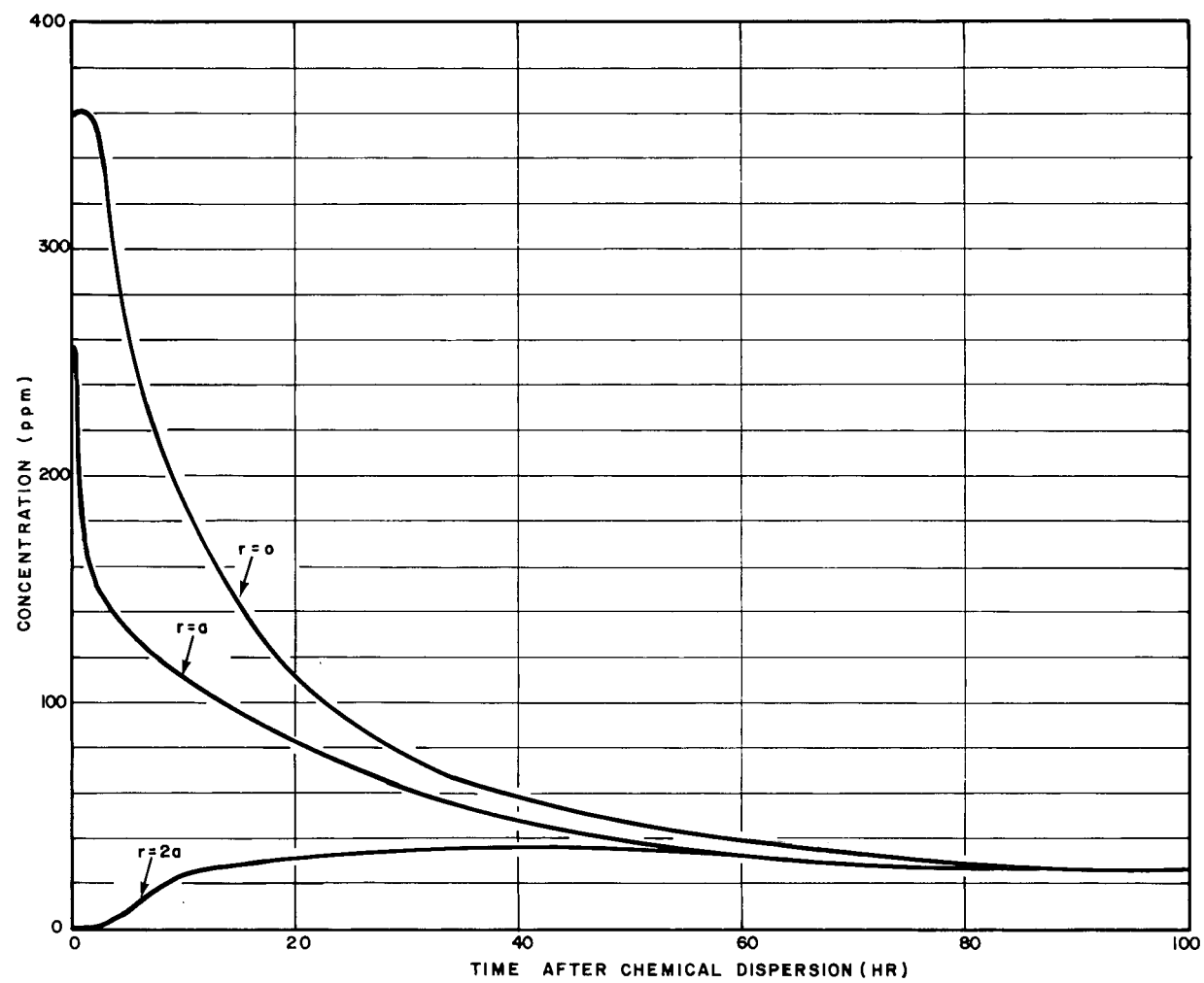


Fig. 21 Concentration vs time (1 HR) after chemical dispersion

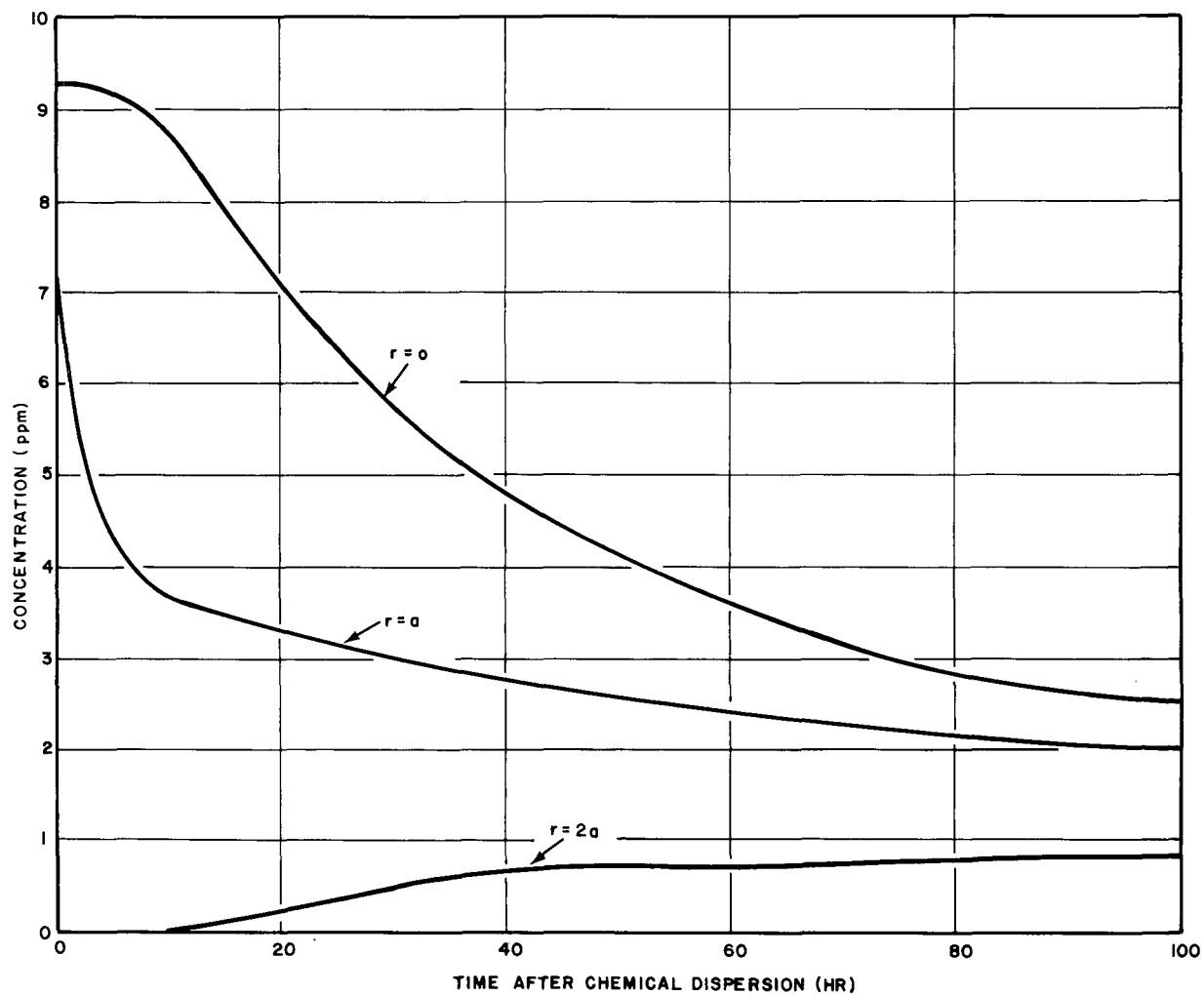


Fig.22 Concentration vs Time (12 HRS) after chemical dispersion

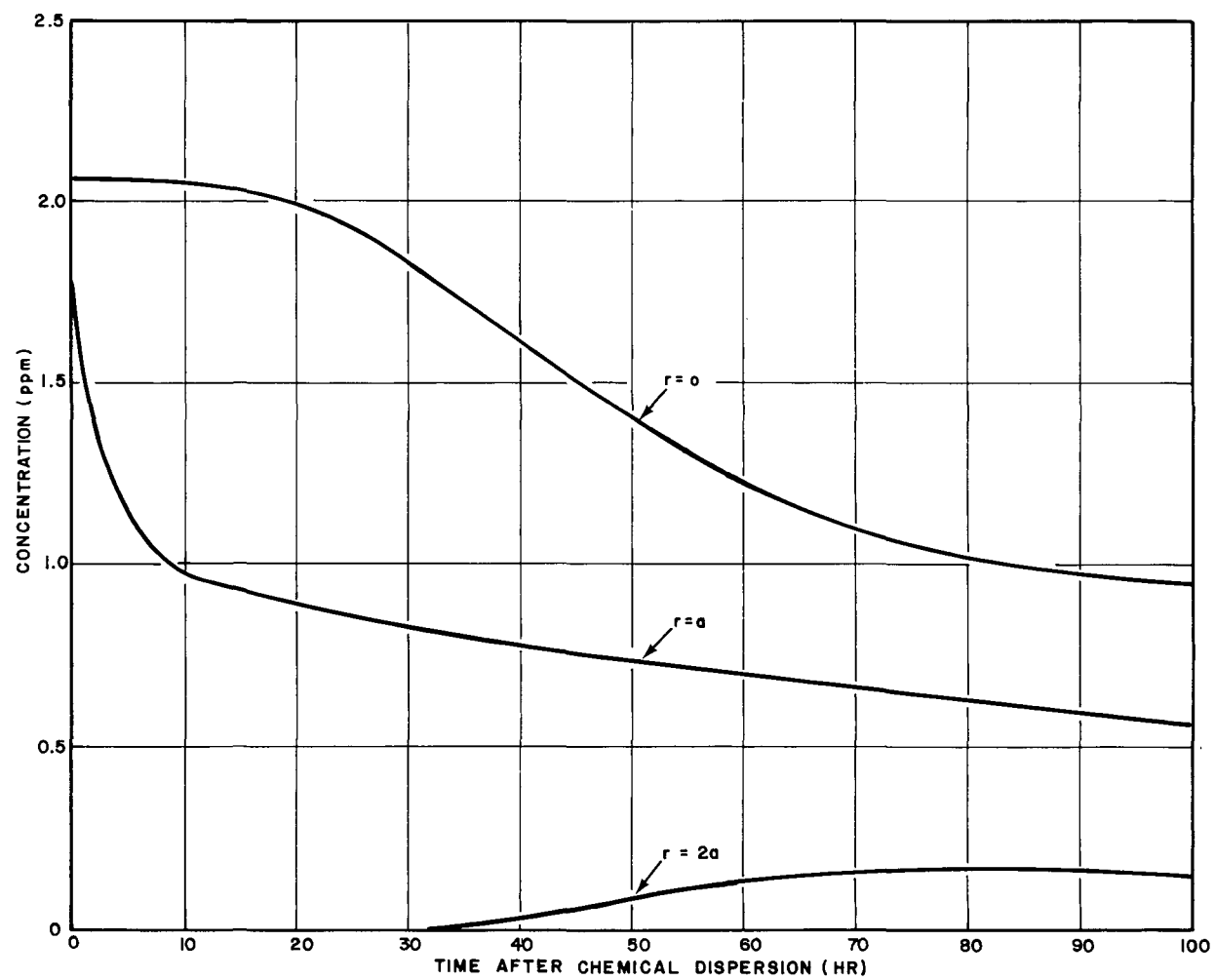


Fig. 23 Concentration vs Time (24 HRS) after chemical dispersion

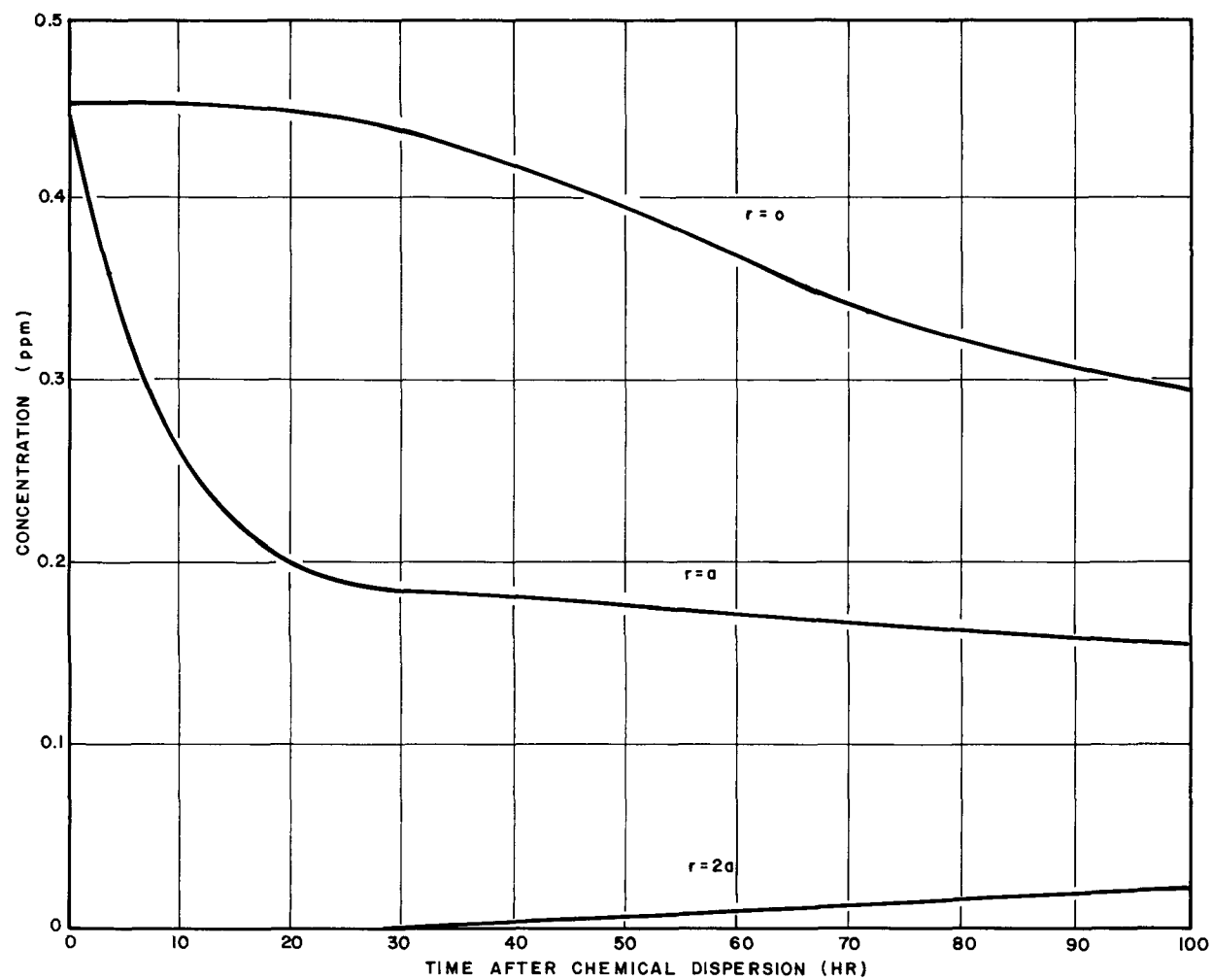


Fig.24 Concentration vs Time (24 HRS) after chemical dispersion

TABLE 4 PARAMETER VALUES - CHEMICAL DISPERSION TIMES

Time of chemical dispersion after spill, hr	Concentration immediately after dispersion (ppm) C_0	Radius of water (a) cm	contaminated		Horizontal eddy diffusivity ($\text{cm}^2\text{sec}^{-1}$) D	Time after chemical dispersion when $(Dt/a^2)^{1/2}$ is ... (hr)		
			km	km (diam)		$\frac{1}{4}$	$\frac{1}{2}$	1
1	360	9.01×10^3	0.090	0.190	8.06×10^2	1.75	7	27.9
3	110	1.57×10^4	0.157	0.315	1.53×10^3	2.8	11.2	44.75
6	36	2.66×10^4	0.266	0.533	2.81×10^3	4.4	17.5	69.9
12	9.3	5.04×10^4	0.504	1.01	5.30×10^3	7.5	30.1	120
24	2.1	1.03×10^5	1.03	2.06	1.33×10^4	13.8	55.4	220
48	0.45	2.2×10^5	2.29	4.39	3.17×10^4	26.5	106	424

TABLE 5 CONCENTRATION AT TIME t (SS=Low, $T=5^{\circ}\text{C}$, $K_d=216$)
(Concentration (ppm) of dissolved and dispersed HC at $t=\text{hr}$)

t (hr) till dispersant application

	t (hr) after spill								
	$\frac{1}{2}$	1	3	6	12	24	48	72	96
1	1.9	378.	124.	43.3	12.1	2.9	0.64	0.26	0.13
3	1.9	2.4	116.	40.6	11.3	2.7	0.60	0.24	0.12
6	1.9	2.4	2.3	38.3	10.7	2.6	0.56	0.23	0.12
12	1.9	2.4	2.3	1.5	10.0	2.4	0.53	0.21	0.11
24	1.9	2.4	2.3	1.5	0.80	2.2	0.48	0.19	0.10
48	1.9	2.4	2.3	1.5	0.80	0.36	0.46	0.18	0.095
∞	1.9	2.4	2.3	1.5	0.80	0.36	0.14	0.074	0.047

Spill: 142.5 m³ (120 tons) of crude oil $\rho=0.8575 \text{ g cm}^{-3}$
 Water Temperature (T): 5°C
 Sea State: Low (2)
 Wind at Beaufort (2): 10 km/hr
 Blokker Constant: 216
 Dispersion Constant: $1.71 \times 10^{-6} \text{ sec}^{-1}$ (15%/day)
 Evaporation MTC: 0.4 CM sec^{-1}
 Dissolution MTC: $2.36 \times 10^{-4} \text{ cm sec}^{-1}$

TABLE 6 CONCENTRATION AT TIME t (SS=Medium, T=5°C, K_d=216)
(Concentration (ppm) of dissolved and dispersed HC at t=hr)

t (hr) till dispersant application

t (hr) after spill									
	$\frac{1}{2}$	1	3	6	12	24	48	72	96
1	3.1	365.	120.	41.7	11.7	2.8	0.61	0.25	0.13
3	3.1	4.0	111.	38.7	10.8	2.6	0.57	0.23	0.12
6	3.1	4.0	3.7	36.3	10.2	2.4	0.53	0.21	0.11
12	3.1	4.0	3.7	2.4	9.3	2.2	0.49	0.20	0.1
24	3.1	4.0	3.7	2.4	1.2	2.1	0.46	0.19	0.096
48	3.1	4.0	3.7	2.4	1.2	0.5	0.45	0.18	0.094
∞	3.1	4.0	3.7	2.4	1.2	0.5	0.2	0.1	0.064

Spill: 142.5 m³ (120 tons) of crude oil $\rho=0.8575$ g cm⁻³
 Water Temperature: 5°C
 Sea State: Medium (4)
 Wind at Beaufort (5): 32 km/hr
 Blokker Constant: 216
 Dispersion Constant: 2.89×10^{-6} sec⁻¹ (25%/day)
 Evaporation MTC: 1.0 cm sec⁻¹
 Dissolution MTC: 2.36×10^{-4} cm sec⁻¹

TABLE 7 CONCENTRATION AT TIME t (SS=High, $T=5^{\circ}\text{C}$, $K_r=216$)
(Concentration (ppm) of dissolved and dispersed HC at $t=\text{hr}$)

		t (hr) after spill								
		$\frac{1}{2}$	1	3	6	12	24	48	72	96
t (hr) till dispersant application	1	4.3	356.	117.	40.8	11.4	2.7	0.60	0.24	0.12+
	3	4.3	5.4	107.	37.3	10.4	2.5	0.55	0.22	0.11+
	6	4.3	5.4	4.9	34.4	9.6	2.3	0.50+	0.20	0.11-
	12	4.3	5.4	4.9	3.2	8.9	2.1+	0.47	0.19	0.097-
	24	4.3	5.4	4.9	3.2	1.6	2.1-	0.45+	0.18	0.094
	48	4.3	5.4	4.9	3.2	1.	0.70	0.45-	0.18	0.093
	∞	4.3	5.4	4.9	3.2	1.0	0.7	0.24	0.12	0.074

Spill: 142.5 m³ (120 tons) of crude oil $\rho=0.8575$ g cm⁻³
 Water Temperature: 5°C
 Sea State: High (7)
 Wind at Beaufort (9): 77 km/hr
 Blokker Constant: 216
 Dispersion Constant: 4.05×10^{-6} sec⁻¹ (35%/day)
 Evaporation MTC: 2.0 cm sec⁻¹
 Dissolution MTC: 2.36×10^{-4} cm sec⁻¹

TABLE 8 CONCENTRATION AT TIME t (SS=Very High, T=5°C, K_r=216)
(Concentration (ppm) of dissolved and dispersed HC at t=hr)

t (hr) after spill

	$\frac{1}{2}$	1	3	6	12	24	48	72	96
1	5.5	355.	117.	40.6	11.4	2.7	0.60	0.24-	0.12+
3	5.5	7.0	106.	37.1	10.4	2.5	0.55	0.22	0.11
6	5.5	7.0	6.3	34.1	9.5	2.3	0.50	0.20	0.10
12	5.5	7.0	6.3	4.0	8.9	2.1+	0.47	0.19	0.097
24	5.5	7.0	6.3	4.0	2.0	2.1-	0.46	0.18	0.095-
48	5.5	7.0	6.3	4.0	2.0	0.86	0.45+	0.18	0.094+
∞	5.5	7.0	6.3	4.0	2.0	0.86	0.29	0.14	0.082

Spill: 142.5 m³ (120 tons) of crude oil $\rho=0.8575$ g cm⁻³

Water Temperature: 5°C

Sea State: High (7+)

Wind at Beaufort (10): 88 km/hr

Blokke Constant: 216

Dispersion Constant: 5.21×10^{-6} sec⁻¹ (45%/day)

Evaporation MTC: 2.2 cm sec⁻¹

Dissolution MTC: 2.36×10^{-4} cm sec⁻¹

t (hr) till dispersant application

TABLE 9 CONCENTRATION AT TIME t (SS=Medium, $T=5^{\circ}\text{C}$, K_d =Varying)
(Concentration (ppm) of dissolved and dispersed HC at t =hr)

t (hr) after spill

	$\frac{1}{2}$	1	3	6	12	24	48	72	96	Blokker Constant
24	4.5	5.6	4.5	2.8	1.5	2.3	0.49	0.19	0.10	108
24	3.1	4.0	3.7	2.4	1.2	2.1	0.46	0.19	0.096	216
24	2.1	2.6	2.7	2.0	1.1	1.9	0.44	0.18	0.092	432

Spill: 142.5 m³ (120 tons) of crude oil $\rho=0.8575 \text{ g cm}^{-3}$
 Water Temperature: 5°C
 Sea State: Medium (4)
 Wind at Beaufort (5): 32km/hr
 Blokker Constant: Different Blokker constants as noted
 Dispersion Constant: $2.89 \times 10^{-6} \text{ sec}^{-1}$ (25%/day)
 Evaporation MTC: 1.0 cm sec^{-1}
 Dissolution MTC: $2.36 \times 10^{-4} \text{ cm sec}^{-1}$

t (hr) till dispersant application

TABLE 10 CONCENTRATION AT TIME t (SS=Medium, $T=5^{\circ}\text{C}$, $K_r=216$)
(Concentration (ppm) of dissolved and dispersed HC at $t=\text{hr}$)

t (hr) after spill

	$\frac{1}{2}$	1	3	6	12	24	48	72	96	Mixed Depth
24	6.3	8.0	7.3	4.8	2.5	4.2	0.92	0.37	0.19	5m
24	3.1	4.0	3.7	2.4	1.2	2.1	0.46	0.19	0.096	10m
24	1.6	2.0	1.8	1.2	0.62	1.05	0.23	0.093	0.048	20m

Spill: 142.5 m³ (120 tons) of crude oil $\rho=0.8575 \text{ g cm}^{-3}$
 Water Temperature: 5°C
 Sea State: Medium (4)
 Wind at Beaufort (5): 32 km/hr
 Blokker Constant: 216
 Dispersion Constant $2.89 \times 10^{-6} \text{ sec}^{-1}$ (25%/day)
 Evaporation MTC: 1.0 cm sec^{-1}
 Dissolution MTC: $2.36 \times 10^{-4} \text{ cm sec}^{-1}$

t (hr) till dispersant application

TABLE 11 CONCENTRATION AT TIME t (SS=Medium, T=Varying, K_r 216)
(Concentration (ppm) of dissolved and dispersed HC at t=hr)

		t (hr) after spill									
t (hr) dispersant application		$\frac{1}{2}$	1	3	6	12	24	48	72	96	Water Temperature
	24	3.2	4.0	3.7	2.4+	1.3	2.2	0.47	0.19	0.099	0°C
	24	3.1	4.0	3.7	2.4	1.2	2.1	0.46	0.19	0.096	5°C
	24	3.1	3.9	3.6-	2.3	1.2	2.0	0.44	0.18	0.092	15°C
Spill:		142.5 m ³ (120 tons) of crude oil $\rho=0.8575$ g cm ⁻³									
Water Temperature:		0, 5, 10°C									
Sea State:		Medium (4)									
Wind at Beaufort (5):		32 km/hr									
Blokke Constant:		216									
Dispersion Constant:		2.89x10 ⁻⁶ sec ⁻¹ (25%/day)									
Evaporation MTC:		1.0 cm sec ⁻¹									
Dissolution MTC:		2.36x10 ⁻⁴ cm sec ⁻¹									

4. DISCUSSION

It has previously been reported that the amount of hydrocarbon which evaporates from an oil spill is many times greater than the amount which enters the water column (Harrison, 1973; Leinonen and Mackay, 1975). These workers considered only that portion of the oil which dissolves from the oil slick. Subsequent work has shown that natural dispersion of oil droplets into the water column can also be substantial. This is illustrated in Figures 6 through 13 and Figure 15.

In Figures 6 to 9 the distribution of the oil from an oil spill is illustrated for low, medium, high and very high sea states with a water temperature of 5°C. Within the first few hours after oil spillage, it is seen that in all cases the rate of evaporation is indeed very high as compared with the rate of dissolution and dispersion. During this time the volatile low-molecular weight components of the oil spill flash off. However, this rapid evaporation lasts only a short while, perhaps 12 hours for a low sea state, and only 3 or 4 hours for a very high sea state. After this, evaporation proceeds much more slowly, but dissolution and the dispersion continue at approximately the same rate. Even in a low sea state and after 24 hours, the amount of oil which is dispersed or dissolved becomes significant, e.g., in a medium sea after 6 hours, approximately 30% by volume of the oil has evaporated, but only 10% has dissolved or dispersed. In the next 90 hours only an additional 15% of the oil will evaporate, while the amount dispersed or dissolved has increased to almost 40%.

From Figure 15 it is seen that most of the hydrocarbon found in the water column results from natural dispersion. Even at its maximum, the concentration achieved by dissolution alone is at least two orders of magnitude smaller than that caused by natural dispersion. Since this is the case, the process of dissolution from the slick is probably not significant and could be neglected without seriously altering the results of the model. This will be the case only if the dissolution MTC does not greatly exceed $2.36 \times 10^{-4} \text{ cm sec}^{-1}$, which is probably the case.

Figures 7, 10 and 11 illustrate the effect of different water temperatures on the weathering of an oil slick. The temperatures studied are typical of Canadian marine situations at different times of the year, namely, 0, 5, and 15°C. For purposes of illustration, a medium sea state is assumed. It is seen that evaporation at 15°C is initially much greater than at 0°C, as can be expected. At 15°C, 30% of the oil evaporates in 4 hours, but at 0°C, it takes 8 hours to achieve 30% evaporation. After 4 days this difference is almost eliminated, with 44% having evaporated at 0°C and about 50% at 15°C. The amounts which have dissolved and dispersed, however are comparable to those at 0°C than at 15°C but with more dispersing action. This reflects the fact that since evaporation at 0°C is slower, more oil remains in the slick to be dispersed. The effect of temperature on the concentration of hydrocarbon in the water column as a result of dissolution and natural dispersion is not great.

Figures 7, 12 and 13 show the effect of different Blokker constants on the weathering of spilled oil. Blokker constants of 108, 216 and 432 are studied, and again a medium sea state is assumed.

The result of varying the Blokker constant from 108 to 432 is similar to the effect of the temperature rise from 0°C to 15°C, as discussed previously. In this case, the evaporation rate is increased because at higher Blokker constants the surface area of the slick is greater than for lower spreading velocities. Additionally, because the evaporation rate is the product of a flux times the area, increasing the area increases the rate.

Further illustrations of the effect of different Blokker constants are given in Figures 3, 5 and 14 and Table 9.

Figure 15 gives the concentration of dispersed and dissolved hydrocarbon as a function of time for four sea states and for chemical dispersion 48 hours after the spill. Also shown is the concentration of hydrocarbons in the water column. Since the natural dispersion constant is higher for higher sea states, it is to be expected that higher concentrations will be reached in rougher seas. This is seen to be the case, at least until chemical dispersion, at which time a higher concentration results for lower sea states. This occurs because in a higher sea state the evaporation rate is greater, and after a given period of time (here 48 hours) less oil remains on the surface to be dispersed. In all cases it is seen that with a Blokker constant of 216, the maximum concentration of hydrocarbon in the water column is reached in about 1.5 hours. After this, the scale of diffusion expands faster than the slick, and the concentration begins to decrease.

The effect of chemical dispersion at different times after the spill occurs is illustrated in Figure 16. For these curves, a medium sea state and the resulting dispersion constant and evaporative MTC are assumed. The bottom curve gives the concentration of the dispersed and dissolved hydrocarbon in the water column as a function of time when no chemical dispersions occurs. At given times, namely, 1, 3, 6, 12, 24 and 48 hours, it is assumed that chemical dispersion has occurred, and consequently, the concentration jumps immediately to a higher value. It is further seen that when a slick is dispersed a short time after the spill occurs, the concentration remains higher in the water column as opposed to that for later chemical dispersion. This again is a direct result of greater evaporation when the slick is allowed to weather for a longer time prior to chemical dispersion. The fact that the slick has spread over a wider area before dispersion does not enter into this calculation, because the volume of water contaminated is determined solely by the scale of diffusion, which is independent of whether or not the slick is dispersed.

Data from Figure 16 is presented in a different form in Figure 17. This curve gives the concentration reached immediately after chemical dispersion as a function of time before chemical dispersion occurs. It is seen that the maximum concentration decreases rapidly if chemical dispersion occurs at a later time.

Figure 18 shows the factor by which the hydrocarbon concentration in the water column increases as a result of chemical dispersion as a function of dispersion time. Again it is seen that when a slick is dispersed early in its history, the concentration increase is much greater than when dispersion occurs at a later time. This effect is even greater when it is remembered that the concentrations before chemical dispersion are much lower at 24 or 48 hours than at 1 or 3 hours. It is also seen from the lower curve that if chemical dispersion occurs after approximately 17 hours, the concentration obtained is still less than the maximum concentration reached by natural dispersion alone at about 1.5 hours.

Figure 19 shows the viscosity of the oil remaining in the slick as a function of time for three different water temperatures. These curves are very important because it is well known that chemical dispersants are less effective on oils of higher viscosity than on less viscous oils. It is seen that for the three temperatures involved, the greatest increase in viscosity occurs during the first 24 hours when the greatest amount of evaporation occurs. Therefore, from the standpoint of dispersant effectiveness, dispersal should be initiated as soon as possible after a spill. If dispersion has not been undertaken within 24 hours, further delays will not cause the viscosity of the oil to increase as rapidly. The slick will, of course, continue to spread, making application of dispersants more difficult.

It must be emphasized that these curves are only for Norman Wells Crude oil, which is a light (non viscous) oil. Other crude oils may have very different viscosity versus time behaviour. It should also be noted that the formation of chocolate-mousse would also increase the oil viscosity greatly, and possibly reduce dispersant effectiveness. This factor, however, is not considered here.

Figures 20 to 24 give concentration profiles across the dispersed slick as a function of time and radius. Figure 20 gives the solution of the diffusion equation in cylindrical coordinates, given in equation (13), and is applicable to all dispersed spills. Figures 21 to 24, however, are applicable only to the spill which was dispersed at the time indicated. For all these figures, time is computed from the instant of dispersion and not from the time of the spill. In these Figures, a is the initial radius of the cloud of dispersed oil and D is the horizontal eddy diffusivity for a scale diffusion equal to a . Values of a and D are given in Table 4. As seen in Figure 16, at a given time after the spill occurs, the concentration of hydrocarbon in the water column from a spill dispersed early in its history is not much higher than that resulting from a spill which is dispersed later. The difference is only that amount of oil which would have evaporated between dispersion times. Because the scale of diffusion is the same for all these spills, the amount of hydrocarbon dispersed at 1 hour is approximately the same as the amount dispersed at 48 hours. This approximation applied regardless of whether the partial differential equation is used to compute concentration profiles after dispersion or whether the scale of diffusion

approach is used. Therefore, the amount of hydrocarbon dispersed in the water column is approximately equal for all dispersion times. If the volume of water contaminated is smaller, the concentration must, of course, be higher.

It is seen from Table 4 that the horizontal eddy diffusivity E_d is much smaller for a dispersion time of 1 hour than for 12, 24 or 48 hours. Since it is assumed in the partial differential equation solution that the horizontal eddy diffusivity remains constant and does not increase, as is indicated by the Okubo correlation, the volume of water contaminated will remain smaller at all subsequent times for an early application of dispersant. This means, therefore, that according to this model, the concentration in the contaminated water will always be higher than that of a spill which is dispersed later. For dispersion at the later time, however, the volume of water contaminated is considerably larger and may affect greater numbers of organisms. Again it should be noted that this model is a "worst case" analysis and that concentrations encountered in an actual spill situation may be lower.

Tables 5 through 8 give all the data presented in Figures 15 and 16 and also data similar to Figure 16 for low, high and very high sea states. From these Tables it is very easy to determine what the concentration for various dispersion times would be at a given time after the spill.

Table 9 gives the concentrations which will be found in the water column and various times after spill for a dispersion time of 24 hours for three Blokker constants: 108, 216 and 432. It is seen that for low Blokker constants, prior to dispersion, the concentration of hydrocarbon in the water column is somewhat higher than is the case for larger Blokker constants. This reflects the fact that for low Blokker constants the volume of water contaminated is somewhat smaller, and since the amount of hydrocarbon dissolved and dispersed is approximately the same, the concentration must be higher. After dispersion the same trend is indicated, but the effect is not great.

In Table 10 the concentration of hydrocarbon in the water column is given for three different mixed depths; 5, 10 and 20 metres with a dispersion time of 24 hours after the spill. It is seen that the water column concentration is inversely proportional to mixed depth. This is expected since the amount of hydrocarbon which enters the water column is the same in all cases. If this amount of hydrocarbon is distributed in twice the volume of water, the concentration will therefore be one half.

Table 11 shows the effect of different water temperatures on the concentration of hydrocarbon in the water column. It is seen that the effect, though not great, increases the concentration at lower temperatures. This was shown in Figures 7, 10 and 11 to be the result of decreased evaporation at lower temperatures. It is quite likely that the lower water temperatures would increase the viscosity of the

oil and reduce the Blokker and dispersion constants, with the ultimate overall effect not being immediately evident.

It is evident that dissolution from an oil slick does not play a major role in transferring hydrocarbons into the water column as compared with natural dispersion or emulsification. Natural dispersion, however, is not exactly the simple process assumed here. In this study the natural dispersion constant was taken to be a function only of sea state. In fact, it is probably a complex function of temperature, viscosity, oil composition and other parameters. The nature of some of these relationships can be postulated, but quantitative estimates cannot be made. For instance, it seems reasonable that a more viscous oil would be less easily dispersed by wind and waves than a less viscous oil. It follows, therefore, that as the oil weathers through evaporation and other processes, it increases in viscosity and the dispersion constant should decrease in time. This has not been taken into consideration. If the dispersion constant did in fact decrease with time, it would decrease the concentration in the water column due to natural dispersion and dissolution. During chemical dispersion in this case, a slightly lower concentration in the water column would result because a large amount of oil has evaporated from the slick.

The Blokker constant variation with temperature has not been considered as well. It seems likely that the Blokker constant is dependent on the viscosity of the oil. Therefore, if the temperature decreases, the viscosity of the oil increases and the Blokker constant should be lowered. This was not considered in the model.

At all times in the model it has been assumed that the oil slick is perfectly mixed, i.e. no concentration gradients exist within the oil slick itself. This makes the calculation of the evaporation rate and the dissolution rate much simpler. Two cases can be envisioned where this assumption may be inadequate. The first would occur late in the spill history when the slick is very viscous. It seems unlikely that wave motion alone would cause perfect mixing in the slick, and therefore, concentration gradients may exist within it. At this time, however, evaporation is not an important factor. A second, and probably more important case, is the production of chocolate-mousse. It is well known that this water-in-oil emulsion can be very stable. In this situation, the oil is almost certainly not well mixed, and since chocolate-mousse formation can occur fairly early in a spill history, it is possible that evaporation of even high-volatility, low-molecular weight material would be seriously curtailed. It is also probable that chocolate-mousse formation would reduce oil-in-water suspension formation (natural dispersion).

Another problem area is the assumption that the dissolved and dispersed oil is of uniform concentration across the entire scale of diffusion. From Figure 3 it is seen that 24 hours after the spill, the diffusion cell is over four times as wide as the thick slick. If the oil were dispersed at this time, it may or may not be reasonable to

assume a uniform concentration across the entire diffusion cell. If the thick slick is coherent, as is assumed in the model, the concentration will not be uniform. In reality, however, the thick portion of oil spills does not stay coherent, but tends to break up into smaller patches with areas of thin slick in between. When this occurs the assumption of a constant concentration across the diffusion cell is probably more reasonable.

In contributing to the decision-making process of oil spill cleanup, one of the questions this report addresses is whether or not the utilization of chemical dispersants is advisable. Obviously it is best to minimize the concentration of hydrocarbon in the water column and thereby reduce the detrimental effects of these on aquatic biota. This being the case, the best strategy is one of mechanical skimming, or possibly even total inaction, i.e. let the oil spread, evaporate, and disperse naturally. In some cases, however, these alternatives may not be possible or advisable. For example, if the oil threatens beaches or water-fowl breeding areas, it is imperative to remove the oil from the surface of the water or at least reduce the threat of oil coating anything it contacts. The use of chemical dispersants in this situation is possible.

The decision to disperse must be made on the basis of certain factors and knowledge. From a logistics point of view, it is best to disperse as soon as possible after a spill when the oil is concentrated over as small an area as possible. This study reveals that early oil dispersal would result in an extremely high concentration of hydrocarbon in a relatively small volume of water. This concentration will almost certainly be lethal to fish and other aquatic life in the area. The effect would be quite localized, however, and it is possible that biota with some sort of mobility could avoid the spreading cloud of dispersed oil.

At later times it might become more difficult to apply the dispersant effectively. At 24 hours the diameter of the coherent thick slick is about 500 metres and when breaking up of the slick is considered, the area concerned may be much larger. The resultant concentration of hydrocarbon in the water is much lower however, and by waiting it may be possible to reduce the hydrocarbon concentration to such a level that marine organisms can survive.

In an earlier chapter it was noted that evaporation directly from water body to the atmosphere was not considered in this model. If chemical dispersion occurs much later than a few hours after the spill only a small amount of volatile, low-molecular weight hydrocarbon would remain in the slick and, therefore, evaporation of hydrocarbon from the water would not be great. It is not believed that omission of this process from the model is very critical.

The final decision as to whether or not chemical dispersants should be used to break up an oil spill must be made on the basis of the

spill in question. If chemical dispersion is considered necessary, then it is probably better to wait as long as possible, keeping the capability of applying the dispersants in mind so as to minimize the aqueous hydrocarbon concentrations. It should be noted that if a spill is dispersed early, a high concentration would result, contaminating roughly the same volume of water that would be contaminated in the case of later spill dispersal. In the meantime, a certain volume of water would be subjected to a much higher concentration than would result from dissolution and natural dispersion alone.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

1. Initially, the rate of evaporation from a spill of crude oil is very rapid, but after four days, depending on sea state, the amount of hydrocarbon in the water column as a result of dissolution and natural dispersion is comparable to the amount which has evaporated. In general, dissolution is more than two orders of magnitude slower than natural dispersion.
2. Changes in water temperature do not significantly affect the concentration of hydrocarbon in the water column, but assuming, in general, equal natural dispersion constants, slightly higher concentrations are reached in cold water than those reached in warm water because of decreased evaporation from the slick.
3. If a slick spreads faster, i.e. a higher Blokker constant applied, lower aqueous hydrocarbon concentrations result because of enhanced evaporation from the larger surface area of the slick. The effect, however, is not great.
4. The level of the concentration of hydrocarbon in the water column as a result of dissolution, natural dispersion and chemical dispersion is inversely proportional to the mixed depth of the surface water.
5. The viscosity of crude oil spilled on water increases as a result of weathering, which is, initially, evaporation for the most part. The largest proportional change in the viscosity comes in the first of 24 hours. The effect of water-in-oil emulsion formation has not been included.
6. The concentration of hydrocarbon in water column always increases as a result of chemical dispersion. If a spill is dispersed in the first few hours, hydrocarbon concentrations in the order of 100 parts per million can be expected for a short period of time. For dispersion after 24 hours, the concentration is about 2 parts per million and after 48 hours, 0.5 ppm.

7. If the spill is dispersed early in its history, a cloud of high hydrocarbon concentration is formed, which will eventually spread to a lower concentration over a wider area. Thus, the end result is similar to later slick dispersal. In the latter situation, however, the high concentrations of the early dispersion are never realized.

5.2 Recommendations

1. The rates of natural dispersion should be measured as a function of sea state, oil viscosity, temperature and time.
2. The effect on temperature and viscosity on Blokker constants should be elucidated.
3. The effectiveness of dispersants on weathered oil and chocolate-mousse should be tested.
4. The results of the model should be tested in an actual experimental oil spill of reasonable size.

NOMENCLATURE

a	initial radius of dispersed oil in water cloud, cm
C	concentration, mol/cm ³
D	amount of hydrocarbon which disperses naturally, cm ³ /sec diffusivity, cm ² /sec
e	solubility enhancement factor
E	Per cent evaporated
k	natural dispersion constant, sec ⁻¹
K	mass transfer coefficient, cm/sec
K _r	Blokker constant for slick spreading
L	scale of diffusion, cm
N	mass transfer flux, mol cm ² /sec
P	vapour pressure, torr
r	radius, cm
R	Gas constant, torr cm ³ /mol K
t	time, sec
T	temperature, K
V	volume, cm ³
x	mole fraction
μ	viscosity, centipoise
ρ	density g/cm ³

Superscripts

d	of dissolution
e	of evaporation
s	of the pure component
w	of the aqueous phase

Subscripts

- a of the air
- d of dissolution
- e of evaporation
- i of component i
- o initial, or, of the oil
- w of the water

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APPENDIX A - DISTRIBUTION OF INDIVIDUAL COMPONENTS OF SIMULATED OIL AFTER A SPILL ON WATER

Given in Tables A-1 to A-9 are data for the individual components of the simulated oil at various times after the spill; namely, 1, 3, 6, 12, 24, 48, 72 and 96 hours. For each time, the slick radius, "thick" slick radius, and diffusion cell radius are given. Also presented are data for the thick slick, per cent remaining in the slick, per cent evaporated, and per cent dissolved and dispersed; for the thin slick, per cent in slick, and per cent dissipated (by evaporation, dissolution, and natural dispersion); and for the water column, concentration (ppm).

Data for the concentration of the individual components in the water column immediately after chemical dispersion at 24 hours are also given (Table A6).

The components are numbered in the Tables according to the following scheme:

<u>Component Number</u>	<u>Compound</u>
1	n-butane
2	n-hexane
3	n-octane
4	n-decane
5	n-dodecane
6	n-hexadecane
7	benzene
8	toluene
9	naphthalene
10	phenanthrene
11	"inert"

The simulated spill conditions were as follows:

Sea State:	Medium
Windspeed:	32 km/hr
Evaporative MTC:	1.0 cm/sec
Dissolution MTC:	2.36×10^{-4} cm/sec
Natural Dispersion Constant:	2.89×10^{-6} sec ⁻¹ (25%/day)
Blokker Constant:	216
Water Temperature:	5°C
Initial Spill Radius:	112.5 m
Spill Volume:	142.5 m ³
Water Mixed Depth:	10m

TABLE A-1 SIMULATED OIL DISTRIBUTION 1 HOUR AFTER A SPILL ON WATER

<u>THICK SLICK</u>				<u>THIN SLICK</u>	
Compound	% in Slick	% Evap.	% Diss. & Disp.	% in Slick	% Dissipated
1	0	99.9	0.1	0	100
2	1.0	98.6	0.4	0	100
3	72.3	26.8	0.9	0	100
4	95.8	3.2	1.0	2.6	97.4
5	98.5	0.5	1.0	63.2	36.8
6	99.0	0	1.0	98.5	1.5
7	12.1	86.6	1.3	0	100
8	49.9	49.0	1.1	0	100
9	98.6	0.4	1.0	68.1	31.9
10	99.0	0	1.0	98.5	1.5
11	99.0	0	1.0	99.0	1.0

WATER COLUMN

Compound	Concn. (PPM)	Compound	Concn. (PPM)
1	6.02×10^{-3}	7	1.16×10^{-2}
2	1.25×10^{-1}	8	3.56×10^{-2}
3	2.47×10^{-1}	9	1.56×10^{-2}
4	5.06×10^{-1}	10	2.14×10^{-2}
5	4.08×10^{-1}	11	<u>1.80</u>
6	8.15×10^{-1}	TOTAL	3.99

Time after spill: 3600 sec; or 1 hr.

Slick Radius: 2.5×10^{-1} Km

Thick Slick Radius: 9.0×10^{-2} Km

Diffusion Cell Radius: 9.0×10^{-2} Km

TABLE A-2 SIMULATED OIL DISTRIBUTION 3 HOURS AFTER A SPILL ON WATER

<u>THICK SLICK</u>				<u>THIN SLICK</u>	
Compound	% in Slick	% Evap.	% Diss. & Disp.	% in Slick	% Dissipated
1	0	99.9	0.1	0	100
2	0	99.6	0.4	0	100
3	9.7	88.5	1.8	0	100
4	77.7	19.4	2.9	0	100
5	94.0	3.0	3.0	2.2	97.8
6	96.9	0	3.1	93.8	6.2
7	0	98.6	1.4	0	100
8	0.3	98.0	1.7	0	100
9	94.4	2.4	3.2	4.6	95.4
10	96.9	0	3.1	93.9	6.1
11	96.9	0	3.1	96.9	3.1

WATER COLUMN

Compound	Concn. (PPM)	Compound	Concn. (PPM)
1	1.98×10^{-3}	7	4.19×10^{-3}
2	4.14×10^{-2}	8	1.82×10^{-2}
3	1.53×10^{-1}	9	1.53×10^{-2}
4	4.64×10^{-1}	10	2.08×10^{-2}
5	3.94×10^{-1}	11	<u>1.76</u>
6	7.95×10^{-1}	TOTAL	3.66

Time after spill: 10,800 sec; or 3 hr.

Slick Radius: 3.6×10^{-1} Km

Thick Slick Radius: 1.3×10^{-1} Km

Diffusion Cell Radius: 1.6×10^{-1} Km

TABLE A-3 SIMULATED OIL DISTRIBUTION 6 HOURS AFTER A SPILL ON WATER

<u>THICK SLICK</u>				<u>THIN SLICK</u>	
Compound	% in Slick	% Evap.	% Diss. & Disp.	% in Slick	% Dissipated
1	0	99.9	0.1	0	100
2	0	99.6	0.4	0	100
3	0	98.2	1.8	0	100
4	42.4	52.8	4.8	0	100
5	84.0	10.1	5.9	0	100
6	93.8	0.1	6.1	84.0	16.0
7	0	98.6	1.4	0	100
8	0	98.3	1.7	0	100
9	85.6	8.2	6.2	0	100
10	93.8	0.1	6.1	84.4	15.6
11	93.9	0	6.1	93.9	6.1

WATER COLUMN

Compound	Concn. (PPM)	Compound	Concn.
1	6.90×10^{-4}	7	1.46×10^{-3}
2	1.44×10^{-2}	8	6.35×10^{-3}
3	5.56×10^{-2}	9	1.05×10^{-2}
4	2.73×10^{-1}	10	1.44×10^{-2}
5	2.64×10^{-1}	11	<u>1.22</u>
6	5.50×10^{-1}	TOTAL	2.41

Time After Spill: 21,600 sec; or 6 hr.

Slick Radius: 4.5×10^{-1} Km

Thick Slick Radius: 1.6×10^{-1} Km

Diffusion Cell Radius: 2.7×10^{-1} Km

TABLE A-4 SIMULATED OIL DISTRIBUTION 12 HOURS AFTER A SPILL ON WATER

<u>THICK SLICK</u>				<u>THIN SLICK</u>	
Compound	% in Slick	% Evap.	% Diss. & Disp.	% in Slick	% Dissipated
1	0	99.9	0.1	0	100
2	0	99.6	0.4	0	100
3	0	98.2	1.8	0	100
4	2.9	91.0	6.1	0	100
5	57.7	31.8	10.5	0	100
6	87.8	0.4	11.8	59.4	40.6
7	0	98.6	1.4	0	100
8	0	98.3	1.7	0	100
9	61.9	26.4	11.7	0	100
10	87.9	0.3	11.8	60.6	39.4
11	88.2	0	11.8	88.2	11.8

WATER COLUMN

Compound	Concn. (PPM)	Compound	Concn.
1	1.93×10^{-4}	7	4.08×10^{-4}
2	4.03×10^{-3}	8	1.77×10^{-3}
3	1.55×10^{-2}	9	5.54×10^{-3}
4	9.67×10^{-2}	10	8.01×10^{-3}
5	1.32×10^{-1}	11	<u>6.74×10^{-1}</u>
6	3.03×10^{-1}	TOTAL	1.24

Time After Spill: 43,200 sec; or 12 hr.

Slick Radius: 5.6×10^{-1} Km

Thick Slick Radius: 2.0×10^{-1} Km

Diffusion Cell Radius: 5.0×10^{-1} Km

TABLE A-5 SIMULATED OIL DISTRIBUTION 24 HOURS AFTER A SPILL ON WATER

<u>THICK SLICK</u>				<u>THIN SLICK</u>	
Compound	% in Slick	% Evap.	% Diss. & Disp.	% in Slick	% Dissipated
1	0	99.9	0.1	0	100
2	0	99.6	0.4	0	100
3	0	98.2	1.8	0	100
4	0	93.8	6.2	0	100
5	13.8	71.4	14.8	0	100
6	76.5	1.4	22.1	15.6	84.4
7	0	98.6	1.4	0	100
8	0	98.3	1.7	0	100
9	18.4	63.3	18.3	0	100
10	76.6	1.2	22.2	17.2	82.8
11	77.8	0	22.2	77.8	22.2

WATER COLUMN

Compound	Concn. (PPM)	Compound	Concn.
1	4.67×10^{-5}	7	1.03×10^{-4}
2	9.72×10^{-4}	8	4.43×10^{-4}
3	3.75×10^{-3}	9	2.14×10^{-3}
4	2.36×10^{-2}	10	3.86×10^{-3}
5	4.52×10^{-2}	11	<u>3.28×10^{-1}</u>
6	1.43×10^{-1}	TOTAL	5.51×10^{-1}

Time After Spill: 86,400 sec; or 24 hr.

Slick Radius: 7.1×10^{-1} Km

Thick Slick Radius: 2.5×10^{-1} Km

Diffusion Cell Radius: 1.0 Km

****TABLE A-6 SIMULATED OIL DISTRIBUTION 24 HOURS AFTER CHEMICAL DISPERSION**

THICK SLICK

THIN SLICK

Compound	% in Slick	% Evap.	% Diss. & Disp.	% in Slick	% Dissipated
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					

****ALL VALUES ARE ZERO SINCE NO SURFACE OIL IS PRESENT, THE OIL PREVIOUSLY ON THE SURFACE (AS INDICATED IN TABLE A5) HAVING BEEN INCORPORATED INTO THE WATER COLUMN**

WATER COLUMN

Compound	Concn. (PPM)	Compound	Concn.
1	4.67×10^{-5}	7	1.03×10^{-4}
2	9.71×10^{-4}	8	4.43×10^{-4}
3	3.75×10^{-3}	9	4.48×10^{-3}
4	2.36×10^{-2}	10	1.59×10^{-2}
5	9.33×10^{-2}	11	<u>1.36</u>
6	6.04×10^{-1}	TOTAL	2.11

Time After Spill: 86,400 sec; or 24 hr.

Slick Radius: _____ Km

Thick Slick Radius: _____ Km

Diffusion Cell Radius: _____ Km

TABLE A-7 SIMULATED OIL DISTRIBUTION 48 HOURS AFTER A SPILL ON WATER

<u>THICK SLICK</u>				<u>THIN SLICK</u>	
Compound	% in Slick	% Evap.	% Diss. & Disp.	% in Slick	% Dissipated
1	0	99.9	0.1	0	100
2	0	99.6	0.4	0	100
3	0	98.2	1.8	0	100
4	0	93.8	6.2	0	100
5	0	84.4	15.6	0	100
6	56.3	5.0	38.7	0	100
7	0	98.6	1.4	0	100
8	0	98.3	1.7	0	100
9	0.1	79.7	20.2	0	100
10	56.5	4.4	39.1	0	100
11	60.5	0	39.5	60.5	39.5

WATER COLUMN

Compound	Concn (PPM)	Compound	Concn.
1	1.02×10^{-5}	7	2.26×10^{-5}
2	2.13×10^{-4}	8	9.70×10^{-5}
3	8.21×10^{-4}	9	5.16×10^{-4}
4	5.17×10^{-3}	10	1.44×10^{-3}
5	1.04×10^{-2}	11	<u>1.28×10^{-1}</u>
6	5.34×10^{-2}	TOTAL	2.00×10^{-1}

Time After Spill: 172,800 sec; or 48 hr.

Slick Radius: 8.9×10^{-1} Km

Thick Slick Radius: 3.2×10^{-1} Km

Diffusion Cell Radius: 2.2 Km

TABLE A-8 SIMULATED OIL DISTRIBUTION 72 HOURS AFTER A SPILL ON WATER

THICK SLICK

THIN SLICK

Compound	% in Slick	% Evap.	% Diss. & Disp.	% in Slick	% Dissipated
1	0	99.9	0.1	0	100
2	0	99.6	0.4	0	100
3	0	98.2	1.8	0	100
4	0	93.8	6.2	0	100
5	0	84.4	1.6	0	100
6	39.5	9.8	50.7	0	100
7	0	98.6	1.4	0	100
8	0	98.3	1.7	0	100
9	0	79.8	20.2	0	100
10	39.8	8.6	51.6	0	100
11	47.1	0	52.9	47.1	52.9

WATER COLUMN

Compound	Concn (PPM)	Compound	Concn.
1	4.11×10^{-6}	7	9.06×10^{-6}
2	8.54×10^{-5}	8	3.89×10^{-5}
3	3.30×10^{-4}	9	2.07×10^{-4}
4	2.08×10^{-3}	10	7.51×10^{-4}
5	4.19×10^{-3}	11	<u>6.87×10^{-2}</u>
6	2.78×10^{-2}	TOTAL	1.04×10^{-1}

Time After Spill: 259,200 sec; or 72 hr.

Slick Radius: 1.0 Km

Thick Slick Radius: 3.6×10^{-1} Km

Diffusion Cell Radius: 3.5 Km

TABLE A-9 SIMULATED OIL DISTRIBUTION 96 HOURS AFTER A SPILL ON WATER

<u>THICK SLICK</u>				<u>THIN SLICK</u>	
Compound	% in Slick	% Evap.	% Diss. & Disp.	% in Slick	% Dissipated
1	0	99.9	0.1	0	100
2	0	99.6	0.4	0	100
3	0	98.2	1.8	0	100
4	0	93.8	6.2	0	100
5	0	84.4	15.6	0	100
6	28.0	14.3	57.7	0	100
7	0	98.6	1.4	0	100
8	0	98.3	1.7	0	100
9	0	79.8	20.2	0	100
10	28.3	12.5	59.2	0	100
11	38.2	0	61.8	38.2	61.8

WATER COLUMN

Compound	Concn (PPM)	Compound	Concn.
1	2.35×10^{-6}	7	5.18×10^{-6}
2	4.89×10^{-5}	8	2.23×10^{-5}
3	1.89×10^{-4}	9	1.19×10^{-4}
4	1.19×10^{-3}	10	4.90×10^{-4}
5	2.40×10^{-3}	11	<u>4.59×10^{-2}</u>
6	1.80×10^{-2}	TOTAL	6.84×10^{-2}

Time After Spill: 331,200 sec; or 96 hr.

Slick Radius: 1.1 Km

Thick Slick Radius: 3.9×10^{-1}

Diffusion Cell Radius: 4.6 Km

APPENDIX B - SCALE-UP TO 1,000-TON SPILL

This appendix gives the results of the computer simulation of a spill of 1,000 tons ($1,425 \text{ m}^3$) of the simulated oil.

Figures B-1, B-2, B-3 and B-4 are presented for comparison to Figures 3, 7, 15 and 16, and 19, respectively, to illustrate some of the differences caused by the larger spill volume and initial area. The spill volume was taken to be ten times that of the other simulations, but the initial area only five times as large. The resulting initial thick slick thickness is, therefore, twice as large, 5.16 cm.

The spill conditions are as follows:

Spill Volume:	$1.425 \times 10^3 \text{ m}^3$
Initial Slick Radius:	$2.515 \times 10^2 \text{ m}$
Sea State:	Medium
Water Temperature:	5°C
Blokker Constant:	216

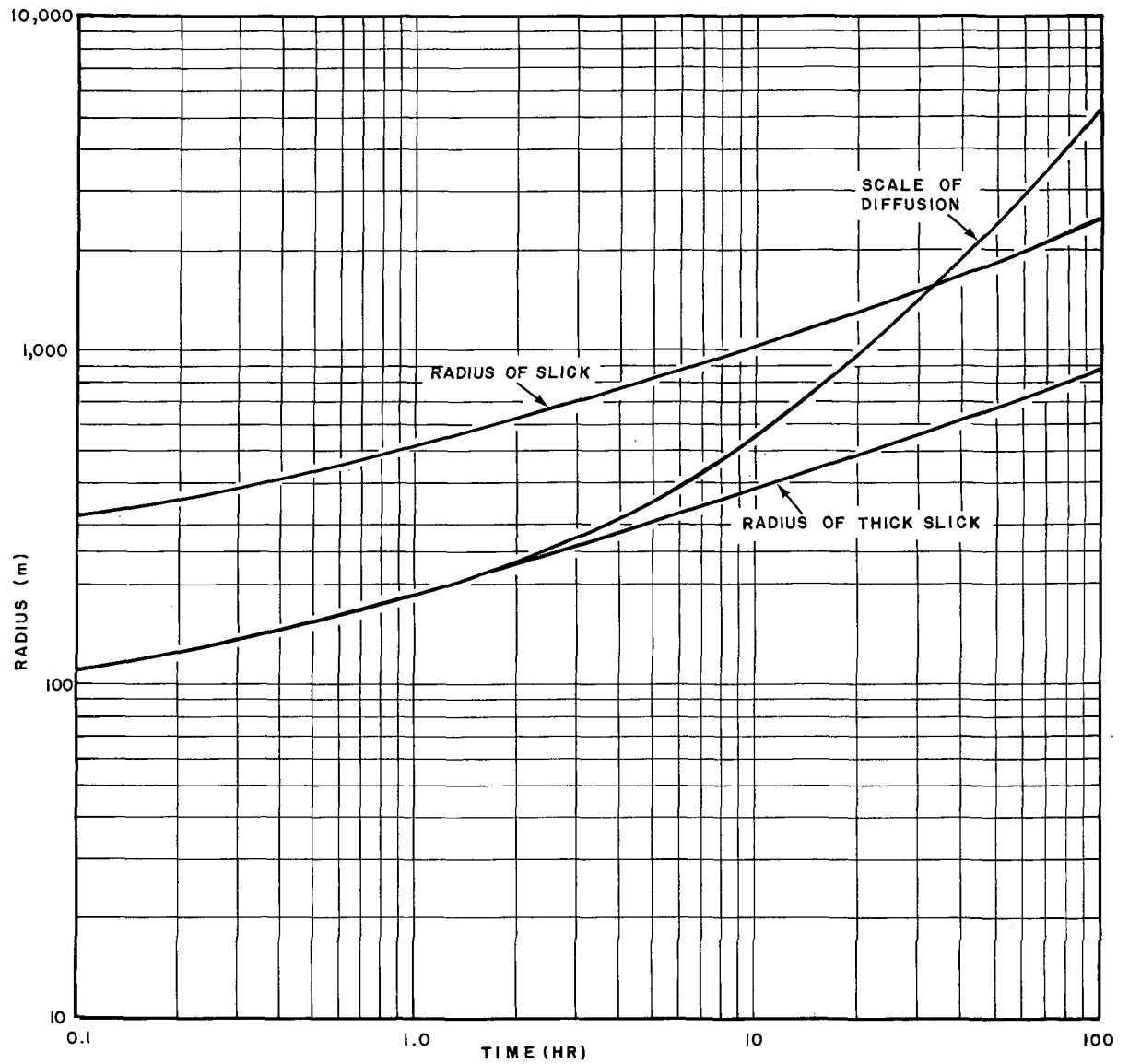


Fig. B-1 RADIUS vs TIME ($K_r=216$, $V=1,425 \text{ m}^3$)

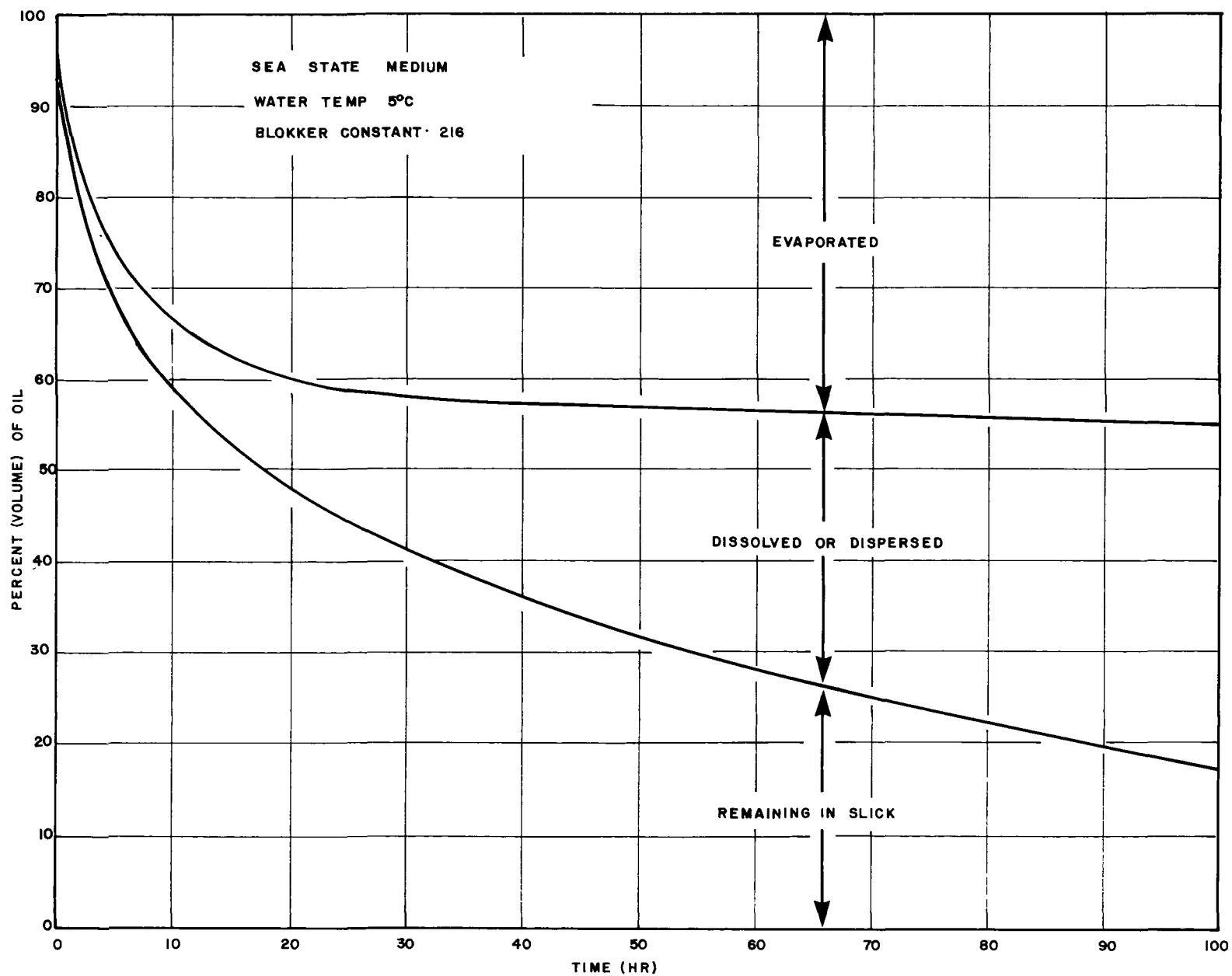


Fig. B-2 Fate of oil spilled on water (SS = Medium, $T = 5^{\circ}\text{C}$, $K_p = 126$)

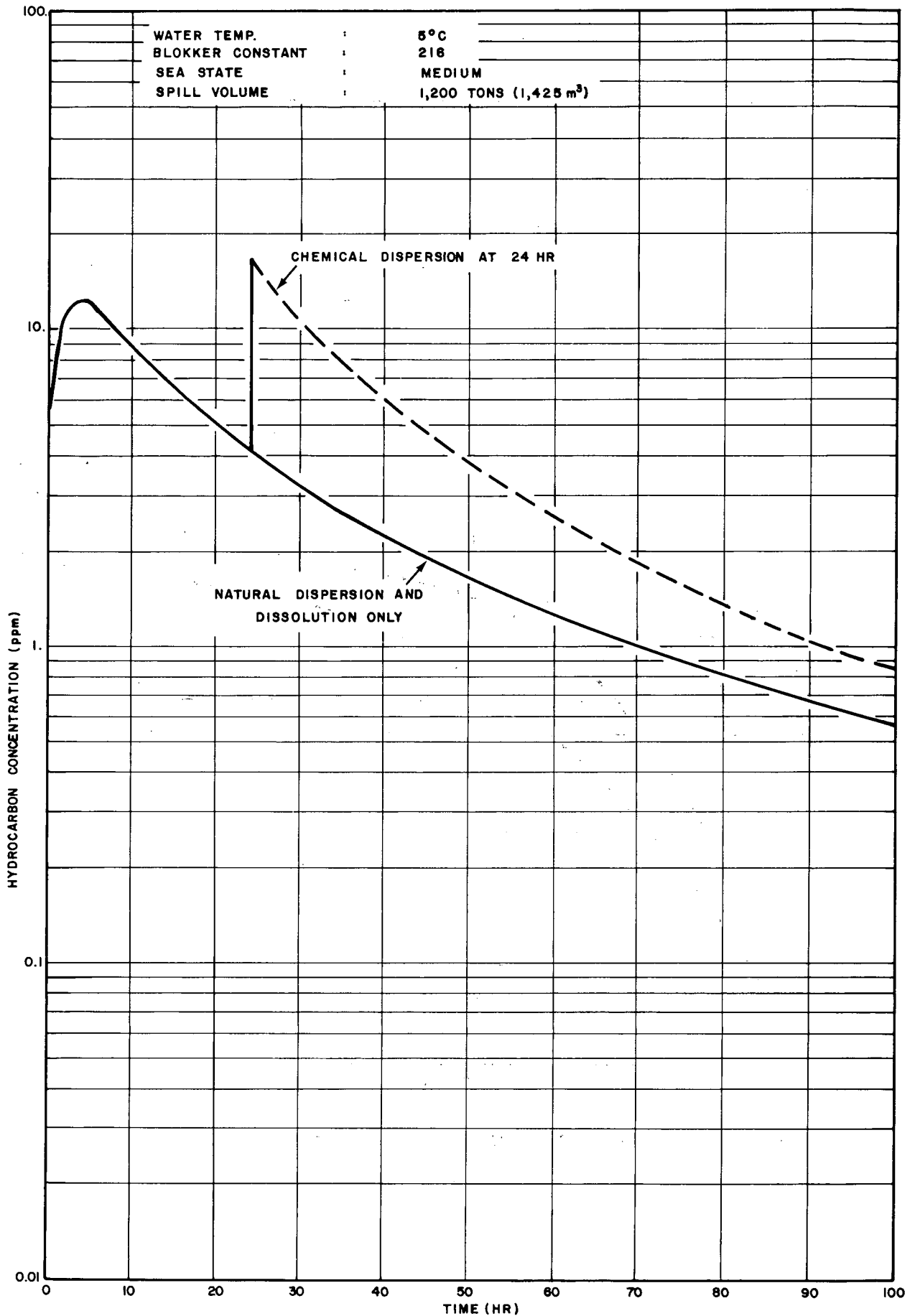


Fig. B-3 Concentration of dissolved and dispersed Hydrocarbons vs. Time

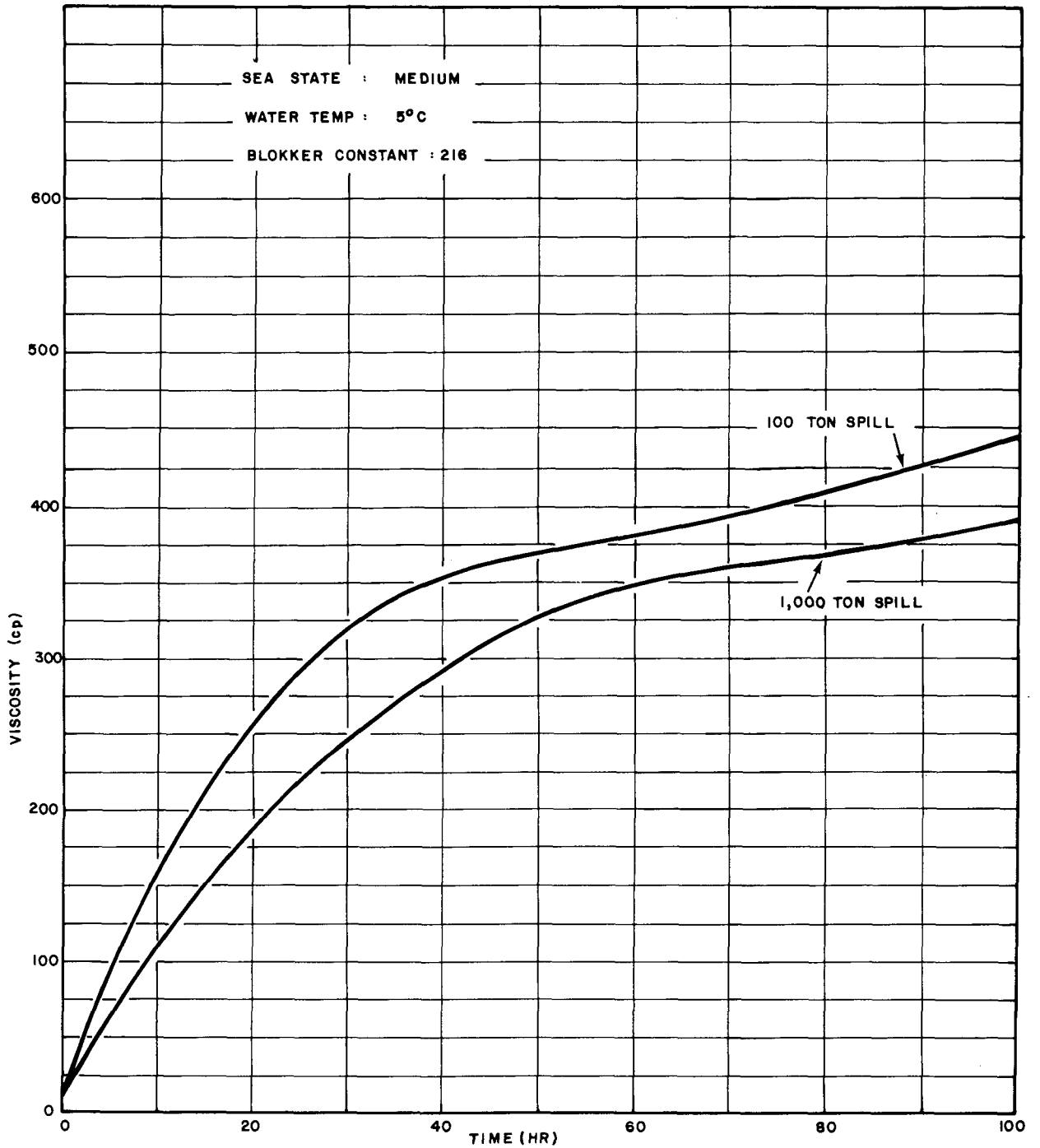


Fig. B-4 Viscosity of oil (Norman Wells Crude) remaining in slick

APPENDIX C - WIND SPEED, BEAUFORT SCALE AND SEA STATE

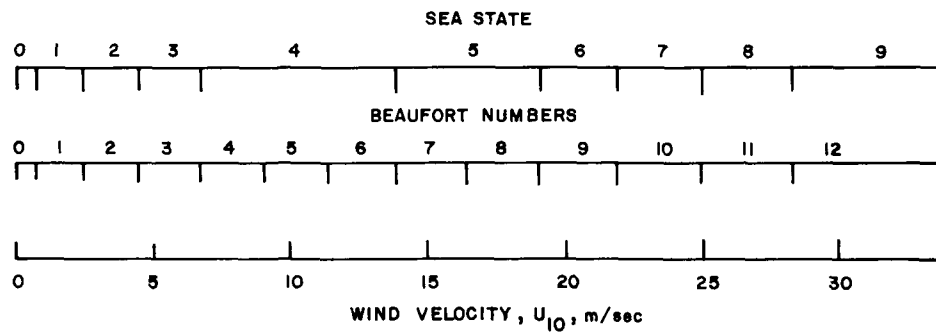


Fig. C-1 Correlation of Sea State, Beaufort Numbers and Wind Velocity

TABLE C-1 DESCRIPTION OF THE BEAUFORT SCALE

Beaufort Number	Wind		Estimating wind speed		
	Knots	mph	Seaman's Terms	Observations at sea	Observations on land
0	under 1	under 1	Calm	Sea like mirror	Calm; smoke rises vertically
1	1-3	1-3	Light air	Ripples with appearance of scales; no foam crests	Smoke drift indicates wind direction; vanes do not move
2	4-6	4-7	Light breeze	Small wavelets; crests of glassy appearance, not breaking	Wind felt on face; leaves rustle; vanes begin to move
3	7-10	8-12	Gentle breeze	Large wavelets; crests begin to break; scattered whitecaps	Leaves, small twigs in constant motion; light flags extended
4	11-16	13-18	Moderate breeze	Small waves, becoming longer; numerous whitecaps	Dust, leaves, and loose paper raised up; small branches move
5	17-21	19-24	Fresh breeze	Moderate waves, taking longer form; many whitecaps; some spray	Small trees in leaf begin to sway
6	22-27	25-31	Strong breeze	Larger waves forming; whitecaps everywhere, more spray	Larger branches of trees in motion; whistling heard in wires
7	28-33	32-38	Moderate gale	Sea heaps up; white foam from breaking waves begins to be blown in streaks	Whole trees in motion; resistance felt in walking against wind
8	34-40	39-46	Fresh gale	Moderately high waves of greater length; edges of crest begin to break into spindrift; foam is blown in well-marked streaks	Twigs and small branches broken off trees; progress generally impeded
9	41-47	47-54	Strong gale	High waves; sea begins to roll, dense streaks of foam; spray may reduce visibility	Slight structural damage occurs; slate blown from roofs
10	48-55	55-63	Whole gale	Very high waves with overhanging crests; sea takes white appearance as foam is blown in very dense streaks; rolling is heavy and visibility reduced	Seldom experienced on land; trees broken or uprooted; considerable structural damage occurs
11	56-63	64-72	Storm	Exceptionally high waves; sea covered with white foam patches; visibility still more reduced	
12	64-71	73-82	Hurricane	Air filled with foam; sea completely white with driving spray; visibility greatly reduced	Very rarely experienced on land; usually accompanied by widespread damage
13	72-80	83-92			
14	81-89	93-103			
15	90-99	104-114			
16	100-108	115-125			
17	109-118	126-136			

APPENDIX D - COMPUTER PROGRAM LISTING AND DOCUMENTATION

This appendix contains a listing of the computer program used to generate the results given in this report. Part I is a glossary of variable names used and listed in the order in which they appear in the program. Some working variables are not listed. Part II gives some documentation on the program itself and the purpose of each statement or group of statements. Part III is an actual listing of the program.

Part I: Glossary of Variable Names

<u>Variable</u>	<u>Description</u>
N	number of components in simulated oil
NSTOP	number of simulated spills per computer run
JTT	spill counter
BK1	dummy variable for comparison
WM	molecular weight
VM	molar volume
SOL	solubility of pure hydrocarbon
EF	solubility enhancement factor
ANT, BANT	constants for Antoine equation
X20	initial mole fraction
VFR	volume fraction
DA, DB, DC, DD, DE, DF	values of time increments
RO	initial radius of spill
VS	volume of oil spilled
DO, DW	density of oil, seawater
TW, TA	temperature of seawater, air
KE, KD	evaporative, dissolution MTC
DISP	natural dispersion constant
BK	Blokker constant
WDPTH	mixed depth of water
SEF	solubility X enhancement factor
NT20, NT30	initial number of moles in thick (thin) slick
PLOG	log (vapour pressure) from Antoine equation
PP	vapour pressure
KEP	modified evaporative MTC
VM2, VM3	volume of component in thick (thin slick)
ND4, ND6	number of moles under A4 (A6)
CW4, CW6	hydrocarbon concentration under A4 (A6)
TFE2, TFE3	total moles evaporated from thick (thin) slick
TFD2, TFD3	total moles dissolved and dispersed from thick (thin) slick
RD, RD3	radii of diffusion cells initially under thick (overall) slick
all variables ending in P	value of variable at time TIME + DELTA e.g. A1 → A1P
all variables ending in A	average value of variable over time increment DELTA e.g. A1A = (A1 + A1P)/2

V4, V7	volume of water in diffusion cells
TCK	working variable to determine whether TIME = TDISP
FE2, FE3	evaporative flux from thick (thin) slick
DELC	concentration difference
FD2, FD5	dissolution flux from thick (thin) slick into diffusion cell
TDISP	time after spill of chemical dispersion
JT	step counter
R	Gas constant
TIME	time
DELTA	time increment
Z1, Z2, Z3	working variables for Blokker equation
R1	radius of oil slick
A1	area of oil slick
A2	area of thick slick
A3	area of thin slick
A4	area of diffusion cell
A5	$A4 - A2$
A6	$A1 - A4$
A7	area of diffusion cell of overall slick
V20, V30	initial volume of oil in thick (thin) slick
THK2, THK3	thickness of oil in thick (thin) slick
HDF, HDD	subroutines to calculate when the scales of diffusion exceeds thick (thin) slick radius
AST, CST	time when scale of diffusion exceeds thick (thin) slick radius
BST, DST	time to be added to real time for Okubo correlation
X2, X3	mole fraction in thick (thin) slick
FDS2, FDS5	amount of hydrocarbon entering diffusion cell from thick (thin) slick as a result of natural dispersion
FE3	evaporative flux from thin slick
FD6	dissolution flux from thin slick into A7
FDS6	natural dispersion from thin slick into A7
PCT2, PCT3	percent of original oil dissipated by evaporation natural dispersion and dissolution from thick (thin) slick
PCTE, PCTD	percent of original oil evaporated (dissolved and dispersed)
VISC	viscosity of oil in thick slick

Part II: Program Documentation

This program is written in FORTRAN IV with some features from WATFIV. The most obvious WATFIV feature is that the program is partially "packed", that is, more than one statement is written on each card (line). The program was run on a WATFIV compiler which numbers the statements sequentially. These numbers appear to the left of the listing.

It will be observed that the program includes contributions to the aqueous hydrocarbon contamination from the "thin" slick. It was determined that these contributions were minor relative to those from the "thick" slick. These are not reported separately, therefore, except in Appendix III where percentages of individual components remaining in the thin slick are given.

<u>Statement number(s)</u>	<u>Description</u>
1 - 2	declaration of Double Precision
3	dimension statement
4 - 66	data input and initialization of variables
67 - 251	calculation of fluxes, concentration, etc. as a result of evaporation, dissolution and natural dispersion
114 - 179	calculation of evaporative flux and dissolution flux, and natural dispersion from thick and thin slicks and mass balance of individual components
179 - 219	calculate overall mass balances and percentage loss
220 - 234	update slick concentrations and calculate individual component percentage loss
235 - 251	check and adjust value of time increment
253 - 275	calculate and output of concentrations and areas after chemical dispersion occurs
252 - 259	individual component values at the time of dispersion
260 - 275	calculation and output of overall concentrations and areas affected from time of chemical dispersion to 96 hours after spill
276 - 279	check if another spill is to be simulated
280 - 299	format statements for input and output
300	end
301 - 342	subroutines to calculate relative spreading rates of scale of diffusion and slicks, and time when scale of diffusion begins to expand faster than slick.

```
$JOB      LEINONEN,KP=29,PAGES=300
1      IMPLICIT REAL*8 (A-H,O-Z)
2      REAL*8 KD,KEP,KE,ND6,ND4,NT2,NT20,NT3,NT30,NTT2,NTT3
3      DIMENSION WM(12),VM(12),ANT(12),BANT(12),CANT(12),SOL(12),EF(12),
1VFR(12),X2(12),X3(12),NT2(12),NT3(12),TFE2(12),TFE3(12),TFD2(12),
2TFD3(12),CW4(12),CW6(12),ND4(12),ND6(12),KEP(12),CW4A(12),CW6A(12)
3,NT30(12),NT20(12),FE2(12),FD2(12),FDS2(12),FE3(12),FD5(12),FDS5(12),FD
42),FD6(12),FDS6(12),SEF(12),VM2(12),VM3(12),X20(12)
4      READ(5,19)N ,NSTOP
5      JTT=1; BK1=0.DO
7      DO 101 I=1,N
8      READ(5,3) WM(I),VM(I),SOL(I),EF(I),ANT(I),BANT(I)
9      READ(5,4) X20(I),VFR(I)
10 101 CONTINUE
11      READ(5,5) DA,DB,DC,DD,DE,DF
12      READ(5,1) RO,VS,DO,DW,TW,TA,N
13 215 READ(5,2)KE,KD,DISP,BK,WDPTH
14      READ(5,13)TDISP
15      WRITE(6,11) TDISP
16      TDISP=TDISP*3.6D3
17      JT=1; PI=4.DO*DATAN(1.DO)
19      R=6.23D4
20      TIME=0.DO; DELTA=DA
22      CST=4.921D0*(RO**0.8547D0)
23      Z1=R0**3; Z2=BK*VS*(DW-DO)*DO/(PI*DW)
25      Z3=Z1+3.DO*TIME*Z2; R1=Z3**0.33333D0
27      A1=PI*(R1**2); A2=A1/8.DO; A3=A1-A2; A4=A2; A5=A4-A2; A6=A1-A4
33      V20=0.9D0*VS; V30=VS-V20; THK2=V20/A2; THK3=V30/A3; A7=A3
38      IF(EK.EQ.EK1) GO TO 216
39      CALL HDF(Z1,Z2,AST,BST)
40      CALL HDD(Z1,Z2,CST,DST)
41 216 BK1=EK
42      WRITE(6,20)AST,BST
43      WRITE(6,20)CST,DST
44      DO 102 I=1,N
45      X2(I)=X20(I)
46      X3(I)=X2(I); SEF(I)=SOL(I)*EF(I)
48      NT20(I)=0.9D0*VS*VFR(I)/VM(I); NT30(I)=NT20(I)/9.0D0
50      PLOG= ANT(I)-BANT(I)/TW
51      PP=10.DO**FLOG; KEP(I)=KE*PP/(R*TA)
53      VM2(I)=0.9D0*VS*VFR(I); VM3(I)=0.1D0*VS*VFR(I)
55      ND4(I)=0.DO; CW4(I)=0.DO; TFE2(I)=0.DO; TFE3(I)=0.DO
59      ND6(I)=0.DO; CW6(I)=0.DO; TFD2(I)=0.DO; TFD3(I)=0.DO
63      WRITE(6,6) I,X2(I),VFR(I),PP,SOL(I),NT20(I),NT30(I)
64 102 CONTINUE
65      WRITE(6,8)KE,KD,DISP,BK,WDPTH
66      WRITE(6,7) A1,A2,THK2,A3,THK3,VS,TW,TA,DO
67 300 TIME=TIME+DELTA
68      TD3=TIME+DST; RD3=0.155D0*(TD3**1.17D0)
70      Z3=Z1+3.DO*TIME*Z2; R1P=Z3**0.33333D0
```

```
72      A1P=PI*(R1P**2); A2P=A1P/8.DO; A3P=A1P-A2P;
75      IF(TIME.GT.AST) GO TO 201
76      A4P=A2P; A5P=A4P-A2P; A6P=A1P-A4P; GO TO 202
80 201  TIMD=TIME+EST; RD=0.155D0*(TIMD**1.17D0)
82      A4P=PI*(RD**2); A5P=A4P-A2P; A6P=A1P-A4P; IF(A6P.LT.0.DO) A6P=0.DO
86 202  AA7=PI*(RD3**2); A7P=AA7-A4P; IF(TIME.LT.CST) A7P=A6P
89      A7A=(A7+A7P)/2.DO
90      A1A=(A1+A1P)/2.DO; A2A=(A2+A2P)/2.DO; A3A=(A3+A3P)/2.DO
93      A4A=(A4+A4P)/2.DO; A5A=(A5+A5P)/2.DO; A6A=(A6+A6P)/2.DO
96      V4A=A4A*WDPHT; V7A=A7A*WDPHT
98      TCK=DAES(TDISP-TIME)/TIME; IF(TCK.LT.1.D-02) GO TO 402
100     DO 103 I=1,N
101     IF(TIME.GT.AST) GO TO 203; Z5=CW6(I)*(A2P-A2)*WDPHT
103     ND4(I)=ND4(I)+Z5; ND6(I)=ND6(I)-Z5; GO TO 204
106 203  IF(A5P.GE.A3P) GO TO 401
107     Z5=CW6(I)*(A4P-A4)*1.DO; ND4(I)=ND4(I)+Z5; ND6(I)=ND6(I)-Z5
110 204  CW4A(I)=ND4(I)/V4A; IF(A6A.LE.0.DO) GO TO 205; CW6A(I)=ND6(I)/V7A
113     GO TO 206; 205: CW6A(I)=0.DO
115 206  FE2(I)=KEP(I)*X2(I)*A2A*DELTA; DELC=X2(I)*SEF(I)-CW4A(I)
117     IF(DELC.LT.0.DO) DELC=0.DO; FD2(I)=KD*DELC*A2A*DELTA
119     FDS2(I)=(DISP*VM2(I)/VM(I))*DELTA; DELC=X3(I)*SEF(I)-CW4A(I)
121     IF(DELC.LT.0.DO) DELC=0.DO; FD5(I)=KD*DELC*A5A*DELTA
123     FDS5(I)=(DISP*VM3(I)*A5A/(A3A*VM(I)))*DELTA
124     ND4(I)=ND4(I)+FD2(I)+FDS2(I)+FD5(I)+FDS5(I)
125     CW4(I)=ND4(I)/(A4P*WDPHT); FE3(I)=KEP(I)*X3(I)*A3A*DELTA
127     DELC=X3(I)*SEF(I)-CW6A(I); IF(DELC.LT.0.DO) DELC=0.DO
129     FD6(I)=KD*DELC*A6A*DELTA; FDS6(I)=DISP*VM3(I)*A6A*DELTA/(A3A*VM(I))
131     ND6(I)=ND6(I)+FD6(I)+FDS6(I); IF(A6P.EQ.0.DO) GO TO 207;
133     CW6(I)=ND6(I)/(A7P*WDPHT); 207: TFE2(I)=TFE2(I)+FE2(I)
135     TFD2(I)=TFD2(I)+FD2(I)+FDS2(I); NT2(I)=NT20(I)-TFE2(I)-TFD2(I)
137     IF(NT2(I).LE.0.DO) NT2(I)=0.DO; VM2(I)=NT2(I)*VM(I)
139     TFE3(I)=TFE3(I)+FE3(I); TFD3(I)=TFD3(I)+FD5(I)+FDS5(I)+FD6(I)+FDS6
1(I); NT3(I)=NT30(I)-TFE3(I)-TFD3(I); IF(NT3(I).LE.0.DO) NT3(I)=0.DO
143     CHECK2=NT20(I)-TFD2(I); IF(TFE2(I).GT.CHECK2) TFE2(I)=CHECK2
145     CHECK3=NT30(I)-TFD3(I); IF(TFE3(I).GT.CHECK3) TFE3(I)=CHECK3
147     VM3(I)=NT3(I)*VM(I)
148     GO TO 103
149 401  ND4(I)=ND4(I)+ND6(I); ND6(I)=0.DO; CW4A(I)=ND4(I)/V4A
152     FE2(I)=KEP(I)*X2(I)*A2A*DELTA; DELC=X2(I)*SEF(I)-CW4A(I)
154     IF(DELC.LT.0.DO) DELC=0.DO; FD2(I)=KD*DELC*A2A*DELTA
156     FDS2(I)=(DISP*VM2(I)/VM(I))*DELTA; DELC=X3(I)*SEF(I)-CW4A(I)
158     IF(DELC.LT.0.DO) DELC=0.DO; FD5(I)=KD*DELC*A3A*DELTA
160     FDS5(I)=DISP*VM3(I)*DELTA/VM(I)
161     ND4(I)=ND4(I)+FD2(I)+FDS2(I)+FD5(I)+FDS5(I)
162     CW4(I)=ND4(I)/(A4P*WDPHT); FE3(I)=KEP(I)*X3(I)*A3A*DELTA
164     TFE2(I)=TFE2(I)+FE2(I)
165     TFD2(I)=TFD2(I)+FD2(I)+FDS2(I); NT2(I)=NT20(I)-TFE2(I)-TFD2(I)
167     IF(NT2(I).LE.0.DO) NT2(I)=0.DO; VM2(I)=NT2(I)*VM(I)
169     CHECK2=NT20(I)-TFD2(I); IF(TFE2(I).GT.CHECK2) TFE2(I)=CHECK2
171     TFE3(I)=TFE3(I)+FE3(I); TFD3(I)=TFD3(I)+FD5(I)+FDS5(I)
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173      NT3(I)=NT30(I)-TFE3(I)-TFD3(I); IF(NT3(I).LE.0.D0)NT3(I)=0.D0
175      CHECK3=NT30(I)-   TFD3(I); IF(TFE3(I).GT.CHECK3)TFE3(I)=CHECK3
177      VM3(I)=NT3(I)*VM(I); CW6(I)=OW6(I)*A7/A7P
179 103  CONTINUE
180      VET=0.D0
181      NTT2=0.D0;NTT3=0.D0; VV2=0.D0;VV3=0.D0;TCW4=0.D0;TCW6=0.D0
187      DO 104 I=1,N
188      VET=VET+TFE2(I)*VM(I)
189      NTT2=NTT2+NT2(I); VV2=VV2+VM2(I)
191      NTT3=NTT3+NT3(I); VV3=VV3+VM3(I)
193      TCW4=TCW4+CW4(I)*WM(I)*1.D6; TCW6=TCW6+CW6(I)*WM(I)*1.D6
195 104  CONTINUE
196      A1=A1P; A2=A2P; A3=A3P; A4=A4P; A5=A5P; A6=A6P; JT=JT+1
203      A7=A7P
204      THK2=VV2/A2; THK3=VV3/A3
206      PCT2=VV2*1.D2/V20 ; PCT3=VV3*1.D2/V30
208      PCT2=100.D0-PCT2; PCT3=100.D0-PCT3
210      PCTE=VET*100.D0/V20; PCTD=PCT2-PCTE
212      VLOG=(830.D0+29.D0*PCT2)*(1.D0/TW)-(2.D0+0.07D0*PCT2)
213      VISC=10.D0**VLOG
214      R2P=R1P/DSQRT(8.D0); R4P=A4P/PI;R4P=DSQRT(R4P)
217      R1P=R1P/1.D5; R2P=R2P/1.D5; R4P=R4P/1.D5
220      WRITE(6,9) TIME,A1,A2,THK2,A3,THK3,TCW4,TCW6
221      WRITE(6,12)A4,A5,A6,A7
222      WRITE(6,17)PCT2,PCTE,PCTD,VISC,PCT3
223      WRITE(6,18) R1P,R2P,R4P
224      DO 105 I=1,N
225      X2(I)=NT2(I)/NTT2; X3(I)=NT3(I)/NTT3
227      P2R=(NT2(I)/NT20(I))*100.D0
228      P2E=(TFE2(I)/NT20(I))*100.D0
229      P2D=100.D0-P2R-P2E
230      P3R=(NT3(I)/NT30(I))*100.D0
231      P3E=100.D0-P3R
232      CW4P=CW4(I)*WM(I)*1.D6
233      WRITE(6,21)I,P2R,P2E,P2D,CW4P,P3R,P3E
234 105  CONTINUE
235      IF(JT.EQ. 7)GO TO 208
236      IF(JT.EQ.11)GO TO 209
237      IF(JT.EQ.22)GO TO 210
238      IF(JT.EQ.30)GO TO 211
239      IF(JT.EQ.36)GO TO 212; IF(TIME.GT.3.46D5) GO TO 213
241      GO TO 300
242 208  DELTA=DB; GO TO 300
244 209  DELTA=DC; GO TO 300
246 210  DELTA=DD; GO TO 300
248 211  DELTA=DE; GO TO 300
250 212  DELTA=DF; GO TO 300
252 402  WRITE(6,16)
253      TCW4=0.D0
254      DO 106 I=1,N
255      ND4(I)=ND4(I)+(VM2(I)/VM(I))
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256      CW4(I)=ND4(I)/(A4P*WDPH); TCW4=TCW4+CW4(I)*WM(I)*1.D6
258      WRITE(6,14)I,ND4(I),CW4(I)
259 106   CONTINUE
260 301   WRITE(6,15)TIME,TCW4,RD
261      DDD=1.08D4;TK=DABS(TIME-3.6D3);IF(TK.LT.1.D2)GO TO 404
264      A4=A4P; TIME=TIME+DDD ; IF(TIME.GT.3.46D5) GO TO 213
267 405   TIMD=TIME+BST; RD=0.155D0*(TIMD**1.17D0); A4P=PI*(RD**2)
270      TCW4=TCW4*A4/A4P; RD=RD/1.D5; GO TO 301
273 404   A4=A4F; TIME=1.08D4; GO TO 405
276 213   JTT=JTT+1; IF(JTT.GT.NSTOP) GO TO 214; GO TO 215; 214: STOP
280      1  FORMAT(6D10.4,I2)
281      2  FORMAT(3D10.4,F4.0,F5.0)
282      3  FORMAT(2D10.4,D8.2,F3.1,F8.6,F6.1)
283      4  FORMAT(F5.3,F7.5)
284      5  FORMAT(6F5.0)
285      6  FORMAT(5X,I3,6D15.4)
286      7  FORMAT(//,12X,9D12.4)
287      8  FORMAT(//,5D12.4)
288      9  FORMAT(//,8D12.4)
289     11  FORMAT(1H1,F8.1)
290     12  FORMAT(24X,D12.4,12X,3D12.4)
291     13  FORMAT(F4.1)
292     14  FORMAT(I3,2D12.4)
293     15  FORMAT(/,3D12.4)
294     16  FORMAT(//34H  CHEMICAL DISPERSION HAS OCCURRED,/)
295     17  FORMAT(3F12.2,D12.4,F12.1)
296     18  FORMAT(3D12.4,/)
297     19  FORMAT(2I2)
298     20  FORMAT( 2D12.4)
299     21  FORMAT(I3,6D12.4)
300      END

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301      SUBROUTINE HDF(Z1,Z2,AST,BST)
302      IMPLICIT REAL*8 (A-H,O-Z); Z4=DSQRT(8.D0)
304      T=0.D0; D=1.D0; 1: TN=T+D
307      Z3=Z1+Z2*TN*3.D0; RI= Z3**0.33333D0; R=RI/Z4
310      DRDT=Z2/((RI**2)*Z4); DLDT=.2386D0*(R**1.1453D0)
312      IF(DLDT.GT.DRDT) GO TO 2; T=TN; GO TO 1
315     2  D=D/10.D0; IF(D.LT.10.D0) GO TO 3; GO TO 1
318     3  AST=TN; THD=4.921D0*(R**.8547D0);BST=THD-TN; RETURN;END

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323      SUBROUTINE HDD(Z1,Z2,CST,DST)
324      IMPLICIT REAL*8 (A-H,O-Z)
325      T=0.D0; DELTA=1.D3; 1:TN=T+DELTA
328      Z3=Z1+3.D0*TN*Z2; R=Z3**0.33333D0
330      DRDT=Z2/(R**2); DLDT=0.2386D0*(R**0.1453D0)
332      IF(DLDT.GT.DRDT) GO TO 2; T=TN; GO TO 1
335     2  DELTA=DELTA/10.D0; IF(DELTA.LT.10.D0)GO TO 3
337      GO TO 1; 3: CST=TN; THD=4.921D0*(R**.8547D0);DST=THD-TN
341      RETURN
342      END

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