MODELING OF OIL EVAPORATION IN AQUEOUS ENVIRONMENT

Ъу

Wei C. Yang and Hsiang Wang

Ocean Engineering Report No. 7

Department of Civil Engineering
University of Delaware
Newark, Delaware

Sponsored by the U. S. National Science Foundation, Research Applied to National Needs Program under Contract Number ENV 76-10618.

June 1976

¥ .							
			100				
	1						
		4					
	*						
			X.				
			*				
	.ft						
					9		
V .							
			20				
				V V			
*				. *		*	
				,* 			
*							
		14)					
		4					
		4					
		4					
		4					

LIST OF FIGURES

Figure 1 Mass Flux of Oil Slick Due to Evaporation and Dissolution Figure 2 Match Criteria for Different Oil Spilling Mechanisms (From Waldman, et al., 1973) Figure 3 Flow Chart Describing the Main Function of Numerical Model Figure 4 Photographic View of Circulation Tank Figure 5 Major Dimensions of Circulation Tank Figure 6 Laboratory Results of Wind Profiles Water Surface Currents With and Without Oil Slick Figure 7 Figure 8 Specific Gravity Change of No. 2 Fuel Oil With Fixed Wind Speed as Air Temperature Varies and Fixed Air Temperature as Wind Speed Varies Specific Gravity Change of Nigerian Crude With Fixed Wind Speed as Figure 9 Air Temperature Varies and Fixed Air Temperature as Wind Speed Varies Specific Gravity Change of Venezuelan Crude With Constant Wind Speed and Air Temperature Figure 11 Comparison of Numerical Results and Frankenfeld's Laboratory and Field Data Figure 12 Percent Weight Changes of Individual Fractions of No. 2 Fuel Oil With Constant Wind Speed and Air Temperature Figure 13 Percent Volume Remain of Weathered No. 2 Fuel Oil With Constant Wind Speed and Three Different Air Temperatures

Figure 14 Percent Weight Remain of Weathered No. 2 Fuel Oil With

Constant Air Temperature and Three Different Wind Speeds

LIST OF TABLES

- Table 1 Basic Data for Oil Spill Weathering Model
- Table 2 Samples Selected and Their Characteristics
- Table 3 Basic Numerical Input Data

* *	
· · · · · · · · · · · · · · · · · · ·	
*	

MODELING OF OIL EVAPORATION IN AQUEOUS ENVIRONMENT

Abstract

A numerical model is developed to predict the changes of oil characteristics, specific gravity, percentage weight remain and percentage volume remain of oil on water through evaporation known to dominate the early stage of weathering. This model is based on the assumption that oil, though complex, can be considered as a chemical compound composed of individual fractions of distinguishable chemical and physical characteristics. The major driving forces for evaporation being considered here include air temperature, wind speed and size of slick.

Laboratory experiments were conducted using No. 2 fuel oil, Nigerian Crude and Venezuelan Crude to calibrate the numerical model and to gain physical insight of the oil evaporation process. Based on the laboratory results, empirical relationships are proposed for determining the diffusion coefficient described in the first-order decay formula. Laboratory results also revealed that the first-order decay law of single slope cannot adequately cover the total range of decay.

Both numerical and laboratory results seemed to indicate that the effect of temperature on oil weathering is significant in the very early stage of weathering, but diminishes at a later time. The effect of wind speed is more uniform throughout the time duration being tested.

MODELING OF OIL EVAPORATION IN AQUEOUS ENVIRONMENT

Wei C. Yang and Hsiang Wang* Leichtweiss-Institut für Wasserbau Technische Universität Braunschweig, Germany

INTRODUCTION

During the weathering process of oil spilled in an aqueous environment, the greatest change in its property occurs within the first few days and is known to be caused by evaporation. A knowledge in this early stage of weathering is essential to assess the initial impact on the marine environment and to deploy effective cleaning operations.

In a descriptive fashion, Berridge, et al., (1968), presented the phenomenon of evaporation of oil spill and the factors that affect this process. It was pointed out by them and other investigators that the rate of evaporation of a given oil spill is a function of temperature, wind speed, solar radiation and size of spill, as well as the characteristics of oil itself. A number of parametric studies have been conducted that provide some fundamental understanding on the mechanism of oil evaporation. For instance, McKay and Matsugu (1973) studied the effect of wind speed and pool size on the evaporation rate and proposed certain functional relationships among them. Regnier and Scott (1975), on the other hand, investigated the evaporation rate as a function of temperature. Frankenfeld (1973) conducted laboratory experiments on oil weathering using six different types of oils to determine the more important

^{*} Permanent Address: Dept. of Civil Engrg., Univ. of Delaware, Newark, DE 19711

variables governing the physical and chemical changes and concluded that the most important variables were the chemical characteristics of the petroleum products themselves.

When it comes to the problem of predicting the evaporation rate of oil spill or of providing a quick assessment of the initial oil weathering after a spill occurs, very little information can be found. Blokker (1964) has proposed an evaporation model that relates the evaporation rate to wind speed and geometrical shape of the slick. A constant coefficient of evaporation is proposed in his formula. Thus, the formula disallows the change in chemical composition during weathering. Also, in light of Frankenfeld's conclusion that the actual composition of the oil slick is the most important variable, the applicability of Blokker's formula to the actual oil spill is immediately open to question even if the functional relationship as proposed were correct. Moore (1972) proposed a general scheme to model oil weathering, using a mass balance accounting for mass fluxes of each oil component. Owing to the large number of individual components in crude or refined oils, he also suggested a way of grouping them according to the number of carbon and hydrocarbon types. He used a first-order decay law to illustrate the scheme.

The present work utilizes Moore's basic model by considering the total evaporation rate as the summation of each individual component. The individual evaporation rate was established on the basis of Fick's diffusion law and the consideration of interfacial mass and heat transfer. The effect of oil slick size and its rate of change on evaporation is also included. A numerical scheme is developed to facilitate fast computations of time-dependent results.

Laboratory experiments were conducted in a continuous-circulation tank to investigate a number of coefficients appearing in the basic equations for three different types of oil. Finally, numerical computations are compared with

field and laboratory data as well as those obtained in the present experiment.

PROBLEM FORMULATION

Basic Equation. Although ultimately the accustomed first-order decay equation is used here to determine the rate of weathering of oil spill, it is essential to present here a brief derivation of this equation and to clearly identify various simplified assumptions specifically related to the present application. Up to date, many investigators have adopted the first-order decay law for oil evaporation and dissolution, the validity of this law has not been evident.

Assuming that, for any specific oil, the constituents can be grouped into individual compounds (perhaps in accordance with the number of carbons and hydrocarbon types) and that the evaporation process is a uniform one within the group, but independent to each other among groups, then from conservation of mass, we have

$$\int_{\Psi} \left(\frac{\partial C_{\underline{1}}}{\partial t} + \nabla \cdot J_{\underline{1}} \right) d\Psi = 0 \tag{1}$$

where C_i is percent weight of fraction i; J_i , the mass flux; t, the time, \forall , an arbitrary control volume and ∇ , the vector operator.

Referring to Figure 1, since the oil slick is a thin layer, the flux in the transverse directions (x and y, in this case) can be neglected in comparison with that in the vertical direction (z-axis), the above equation can be written as

$$\int_{-H/2}^{H/2} \frac{\partial C_{i}}{\partial t} dz + J_{i}|_{H/2} + (-J_{i})|_{-H/2} = 0$$
 (2)

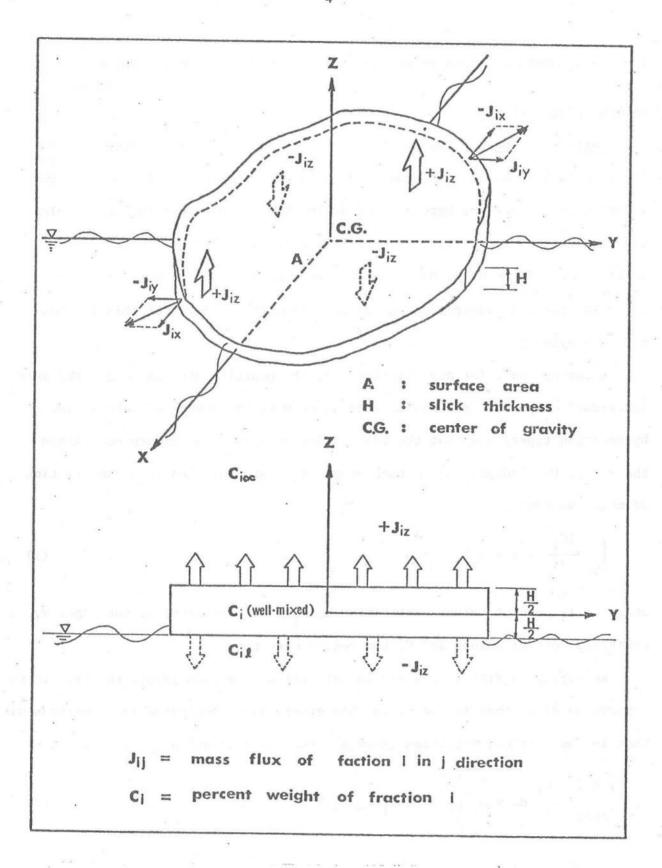


Figure 1 Mass Flux of Oil Slick Due to Evaporation and Dissolution

Here the origin of the coordinate system is taken to coincide with the centroid of the slick and H is the total thickness of the slick.

When the differentiation sign is moved out of the integral, the first term of the L.H.S. Becomes

L.H.S. =
$$\frac{\partial}{\partial t}$$

$$\int_{-H/2}^{H/2} c_{i} dz - (c_{i}|_{H/2} + c_{i}|_{-H/2}) \frac{\partial}{\partial t} (\frac{H}{2})$$

as the limits of integration are also functions of time. If the oil is well mixed within the thin film, the above expression can be approximated by

$$\frac{\partial}{\partial t} (H\hat{C}_1) - \hat{C}_1 \frac{\partial H}{\partial t}$$

which is simply H $\frac{\partial \widehat{C_i}}{\partial t}$ where $\widehat{C_i}$ is defined as

$$\widehat{C}_{\underline{i}} = \frac{1}{H} \int_{-H/2}^{H/2} C_{\underline{i}} dZ$$

the mean value of the percent weight of fraction i. This result is true if $\mathbf{C_i}$ is uniform across the thin film or H is independent of time. Fortunately, these conditions are roughly fulfilled by oil slicks as one can reasonably expect that in the early stage of a spill $\mathbf{C_i}$ is nearly uniform, while at the latter stage, H does not vary significantly. Equation (2) can be reduced to

$$H \frac{\partial \hat{C}_{1}}{\partial t} + J_{1}|_{H/2} + (-J_{1})|_{-H/2} = 0$$
(3)

The second and third terms represent mass flux due to evaporation and dissolution, respectively. According to Ficke's diffusion law, the mass flux is proportional to the gradient of concentration, i.e.,

$$J_{i} \alpha - \nabla C_{i}$$
 (4)

Since, in Equation (3), the mass fluxes are to be evaluated across the interface, the above proportionality can be approximated by:

$$J_{i}|_{H/2} \alpha \widehat{C}_{i} - C_{i\infty}$$

$$J_{i}|_{-H/2} \alpha \widehat{C}_{i} - C_{i}$$
(5)

where $C_{i\infty}$ and $C_{i\ell}$ are the percentage weight of fraction, i, in the air and water respectively. Since both the air mass and the water mass in contact with the oil slick can be looked upon as reservoirs of infinite capacity, it is not unreasonable to treat both $C_{i\infty}$ and $C_{i\ell}$ as constants of small magnitudes. Therefore, it seems appropriate to rewrite the above relations in the following equation form:

$$J_{i}|_{H/2} = D_{ie} \cdot \widehat{C}_{i}$$
and
$$J_{i}|_{-H/2} = D_{id} \cdot \widehat{C}_{i}$$
(6)

where D and D are constants of proportionality known as the diffusion coefficients of evaporation and dissolution, respectively. When Equation (6) is introduced into Equation (3), the first-order decay equation is obtained:

$$H \frac{\partial \widehat{C}_{i}}{\partial t} = -(D_{ie}' + D_{id}') \widehat{C}_{i}$$
(7)

This is the basic equation that describes the short-term weathering process. It differs from the accustomed first-order decay law in that L.H.S. consists of the

product of H and $\frac{\partial \widehat{C_i}}{\partial t}$ rather than $\frac{\partial \widehat{C_i}}{\partial t}$ alone. Only when H can be treated as a constant can Equation (7) be reduced to the conventional first-order decay equation:

$$\frac{\partial \widehat{C}_{i}}{\partial t} = -(D_{ie} + D_{id}) \widehat{C}_{i}$$
 (8)

where D_{ie} and D_{id} are defined as being equal to $D_{ie}'/_{H}$ and $D_{id}'/_{H}$ respectively.

Since the main purpose of the present study is to develop a quick scheme to estimate oil weathering, Equation (8) has been used as the base for the numerical scheme. One should bear in mind the various assumptions and simplifications that are being employed so that future refinement can be made towards the right direction.

<u>Evaporation Rate</u>. Like most problems concerning diffusion processes the task of solving Equation (8) depends heavily upon the correct estimation of the diffusion coefficients.

The mass transfer process from the oil slick to the atmosphere can be conveniently divided into liquid phase transfer and vapor phase transfer. The liquid phase transfer consists of mass transfer from the interior of the oil slick to the interface. For a thin slick of roughly uniform $\widehat{C}_{\mathbf{i}}$, the work required to perform this process is considered negligible. The vapor phase resistance which controls the rate of mass transfer across the interface is of major concern.

In analogy to the molecular diffusion process, the vapor phase mass transfer process can be expressed by (MacKay and Matsugu, 1973):

$$D_{ie} = k_{m} (p_{i} - p_{i\infty})/[RT_{s}]$$
(9)

where p_i is the hydrocarbon vapor pressure of fraction, i, at the interface; $p_{i\infty}$ is the hydrocarbon vapor pressure of fraction, i, at infinite altitude of the

atmosphere; R is the gas constant; and $T_{\rm S}$ is the absolute temperature of the oil slick.

In this equation, k is a coefficient that lumps into it all the unknown factors that affect the value of D and is likely to depend upon the transport conditions at the atmosphere immediately above the spill. In oceanic environments with spill of finite size, the following functional relationship is proposed here:

$$k_{m} = aA^{\gamma} e^{qU}$$
 (10)

where A is the slick area; U is the overwater wind speed; a, q and γ are empirical coefficients to be determined experimentally. This functional relationship is based on the results of past investigations, including, for instance, those of MacKay and Matsugu (1973) and Moore (1973). Based on field investigation, MacKay and Matsugu suggested the value of γ to be in the range from -0.025 to -0.055. By plotting existing oil weathering data, Moore came up with the value of q in the order of 0.39. Further experiments were performed here to determine the values of a and q. The results were described in later sections.

To evaluate the area of spreading in Equation (10), Fay's model (1971) as modified by Wang, et al. (1975) was used. In essence, the spreading is broken down artificially into three stages, namely the gravity-inertial, the gravity-viscous and the diffusion stages. The equations for the respective stage are as follows.

Gravity-Inertial Stage:

$$R(t) = 1.14(\Psi)^{1/3} \left[\frac{g\Delta\rho}{\rho_{\Psi}^{1/3}} \right]^{1/4} t^{1/2}$$
 (11)

Gravity-Viscous Stage:

$$R(t) = 0.98 \text{ (V)}^{1/3} \left(\frac{g\rho_o^{\Delta\rho}}{\rho_w}\right)^{1/6} \left(\rho_w^{\mu}_w\right)^{-1/12} t^{1/4}$$
 (12)

Diffusion Stage:

$$R(t) = 2[2 E_r(t-t_{gv}) + (R_{gv/2})^2]^{1/2}$$
(13)

where R is the radius of spreading; Ψ is the volume of the spill; g is the gravitational acceleration; $\Delta\rho$ is the density difference between water and oil; ρ_{o} is the density of the water; μ_{w} is the viscosity of the water; E_{r} is the turbulent diffusion coefficient. The criteria on matching are based on the size of the spill as delineated in Figure 2.

Strictly speaking, the dissolution rate should also be included in the consideration. At present, the functional relationship is difficult to arrive at, even on a speculation basis. However, Moore (1972) has shown that, at least, at the early stage of weather, the rate of dissolution is considerably smaller than evaporation. Therefore, the dissolution process is not included in the subsequent computations.

Numerical Computations. The functional relationships of the oil weathering process so far developed are relatively simple. The actual computation, on the other hand, is quite involved as the weathering process interacts with the spreading process and the number of fractions in any type of oil is quite large. A computer program is, therefore, developed here to facilitate rapid computations.

Based on Moore's suggestion (1973) eight fractions are selected, in accordance with the carbon number and hydrocarbon type, to provide adequate flexibility

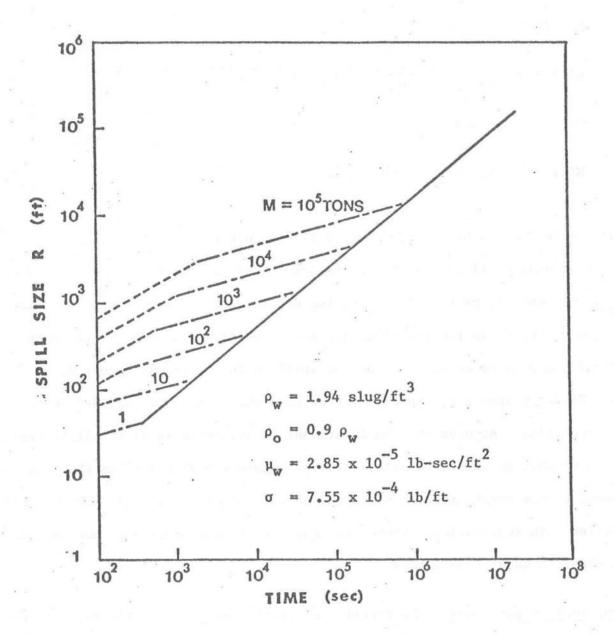


Figure 2 Match Criteria for Different Oil Spilling Mechanisms (From Waldman, et al., 1973)

in characterizing oil of various origins. The range of physical and chemical contains for each fraction is summarized in Table 1. The equations for estimating vapor pressure are also listed on the last column in the same table.

Fourth-Order Range-Kutta method was used to perform the numerical integration. A flow chart describing the major functions of the numerical model is delineated in Figure 3. It computes as a function of time the percentage change of weight of each fraction, the changes of volume, specific weight and the total weight loss.

LABORATORY EXPERIMENTS

To aid in the determination of evaporation constants and to obtain better insight of the chemical and physical weathering processes, laboratory experiments were performed in a circulation tank specially designed for this purpose.

Figure 4 is a photographic view of the tank and Figure 5 shows the major dimensions of the tank which consists of two 5-foot straight sections connected by two semi-circular sections. The cross-section is 2.5 feet high and 1 foot wide. The channel is completely covered with a plastic top.

All the tests were performed with the tank filled to 1.5 feet of water. overwater wind is provided by a 12-inch two-speed exhaust fan driven by a 1/4 hp motor. A mean air speed up to 3.2 m/sec can be obtained. A divider is installed as shown in Figure 5, extending to and above the waterline so that it will guide the fresh air into the circulation channel and force the mixture of air and oil vapor into the exhaust channel. This arrangement permits unobstructed continuous water flow but disallows oil-contaminated air flow recirculating in the channel. Exhaust air, which at times is quite heavily contaminated, is discharged outside the laboratory to prevent possible re-entering the channel.

TABLE 1 BASIC DATA FOR OIL SPILL WEATHERING MODEL

.6677 .1n .7778 2 .1n .759 .1n .9-1. 2 .9-1. 2 .1y11-1.2 2	Description	*Density (gm/ml)	*Boiling Point (°C)	*Molecular Weight	*Solubility $(gm/10^6gm)$ Distilled H_20)	**Vapor Pressure (P ₁) (mmHg)
Cycloparaffin Aromatic (Mono-and di-Cyclic) Cyclic) Cyclic) Cyclic) Cyclic)	Paraffin	jerta.	datas			
Paraffin $c_{13}-c_{25} \qquad .7778$ $cycloparaffin$ $c_{6}-c_{12} \qquad .759$ $cycloparaffin$ $c_{13}-c_{23} \qquad .9-1.$ Aromatic (Monoand di-Cyclic) $c_{6}-c_{11} \qquad .88-1.1$ Aromatic (Poly-Cyclic) $c_{12}-c_{18} \qquad 1.1-1.2$	C6-C12	. 6677	69-230	86-170	9.501	$log P_1 = 6.94-1417.61/(202.17+Ts)$
Cycloparaffin C_{6} - C_{12} .759 C_{13} - C_{23} .9-1. C_{13} - C_{23} .9-1. C_{13} - C_{23} .88-1.1 C_{6} - C_{11} .88-1.1 C_{6} - C_{11} C_{12} - C_{12} C_{12} - C_{13} 1.1-1.2 C_{12} - C_{13}	Paraffin C ₁₃ -C ₂₅	.7778	230-405	184-352	.01004	log P ₂ = 7.01-1825.04/(149.76+Ts)
Cycloparaffin $c_{13}-c_{23}$.9-1. Aromatic (Monoand di-Cyclic) c_6-c_{11} .88-1.1 Aromatic (Polycyclic) $c_{12}-c_{18}$ 1.1-1.2	Sycloparaffin C6-C12	.759	70-230	84-164	55-1.	$log P_3 = 6.91-1441.79/(204.70+Ts)$
Aromatic (Mono- and di-Cyclic) C_6-C_{11} .88-1.1 Aromatic (Poly- Gyclic) 1.1-1.2	Sycloparaffin C ₁₃ -C ₂₃	.9-1.	230-405	156-318	10	$\log P_4 = 6.99-1893.78/(151.82+Ts)$
Aromatic (Poly-Cyclic) C_{12} - C_{18} 1.1-1.2	comatic (Mono- id di-Cyclic) C ₆ -C ₁₁	.88-1.1	80-240	78-143	17800	$log P_5 = 6.91-1407.34/(208.48+Ts)$
) {	cyclic) Cyclic) Cl2-Cl8	1.1-1.2	240-400	128-234	12.5-0	$log P_6 = 6.97-1801.00/(162.77+Ts)$
7 Naphtheno-Aromatic $^{\circ}_{9}$ -C $^{\circ}_{25}$ $^{\circ}_{9}$ -1.2 180-40	theno-Aromatic C_9 - C_{25}	.97-1.2	180-400	116-300	10	$log P_7 = 6.97-1789.85/(164.56+Ts)$
8 Residual (including heterocycles) 11.1 40	dual (including terocycles)		400	300-900	0	$P_8 = 0$

^{*} Data From Moore (1973) ** Estimated From "Handbook of Hydrocarbons," Ferris, et al., (1955); Ts in °c.

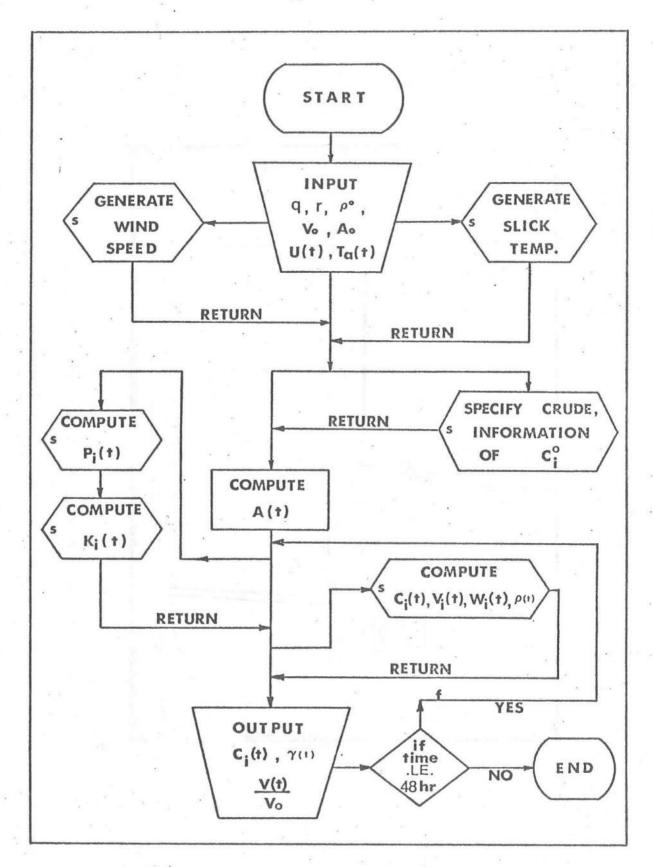


Figure 3 Flow Chart Describing the Main Function of Numerical Model

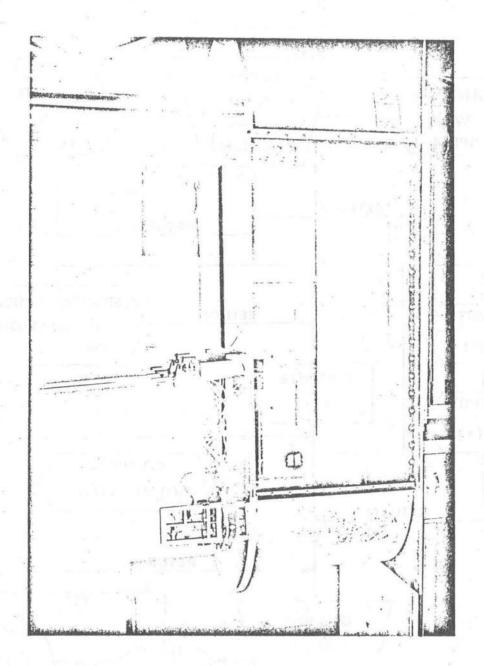


Figure 4 Photographic View of Circulation Tank

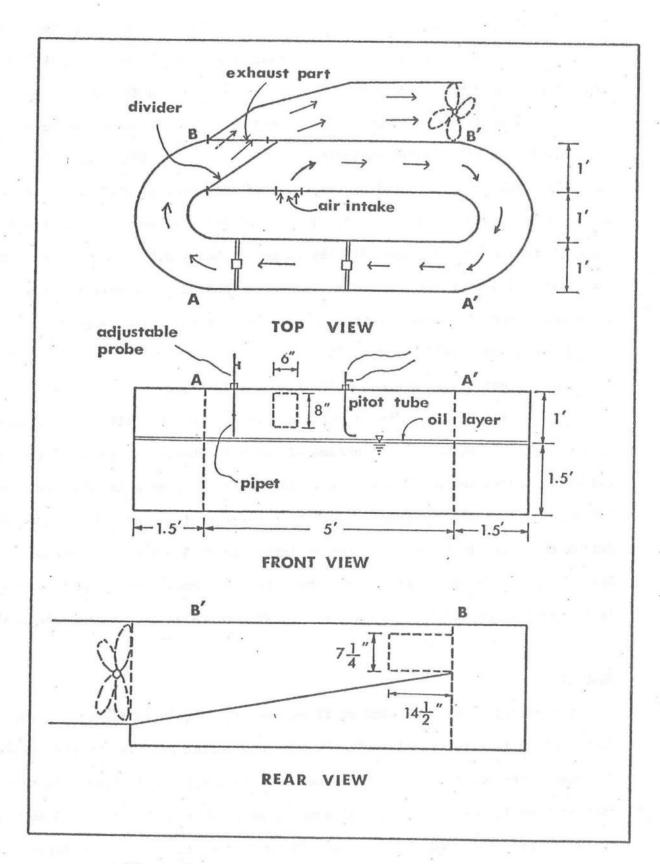


Figure 5 Major Dimensions of Circulation Tank

Overwater wind speed and profile are measured by conventional Pitot tubes in conjunction with a precision differential manometer manufactured by the Iowa Institute of Hydraulic Research. Pipet samplers are used for oil samplings.

A total of 11 short-duration (48 hours) weathering experiments were conducted using different oil samples including Venezuelan Crude, Nigerian Crude and #2 Fuel Oil. They were selected on the basis of (1) these products are fairly well characterized and documented, (2) they afford a range of physical and chemical characteristics and (3) they represent heavy U.S. consumptions. The characteristics of these samples are shown in Table 2. The effects of air temperature and wind speed are tested covering the following ranges:

Temperature: 14°C, 21°C, 26°C

Wind Speed: 0.71 m/sec., 1.54 m/sec., 3.20 m/sec.

The experiments began by circulating air over water until the temperatures of air and water equalized. A volume of about 1,500 c.c oil samples were then carefully poured on top of the water. This will cover an area of approximately $1.5 \, \mathrm{m}^2$ of $0.1 \, \mathrm{cm}$ thick. Samples were then taken at intervals of 1-2 hours during the first 10 to 12 hours and at intervals of 5-8 hours afterwards. Specific gravities were determined immediately by pycnometers. Data presented in the subsequent section represented the average value of three sample analyses.

RESULTS

Laboratory results of wind profiles are illustrated in Figure 6. The vertical distribution is surprisingly uniform. The horizontal profile, on the other hand, is skewed; the velocity along the inner wall is considerably less than that along the outer wall. Since all the oil samples were taken at location, 10 cm from the wall, the reference velocity used in the subsequent data presentations is based on the average of the hatched area shown in Figure 6. The region along the

TABLE 2
SAMPLES SELECTED AND THEIR CHARACTERISTICS

Oil Sample	Specific Gravity (78°F)	General Characteristics
Venezuelan		Medium, Aromatic,
Crude	.8769	High Volume of
		Transport
Nigerian		Light, Paraffinic,
Crude	.8446	Low in Metals
#2 Fuel Oil	.8472	Light Fuel Oil, Olefinic, Refined

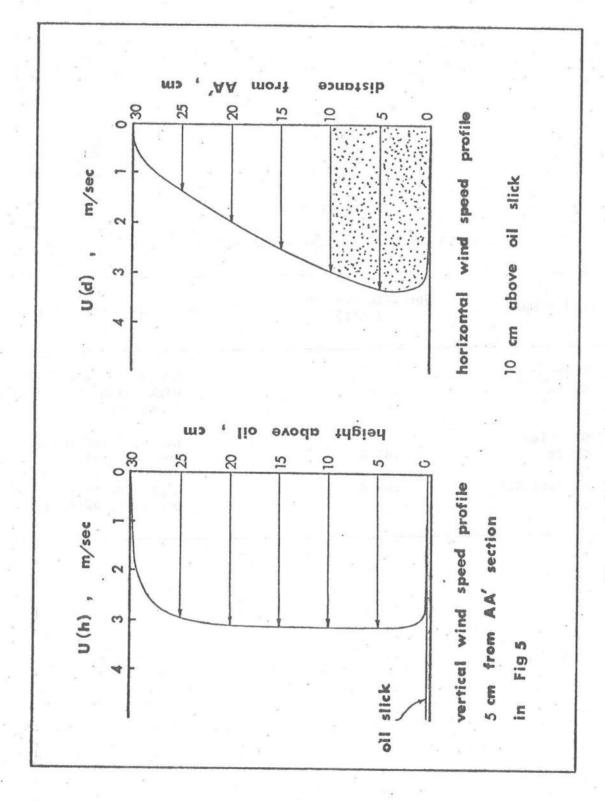


Figure 6 Laboratory Results of Wind Profiles

inner wall of low velocity but high velocity gradient is excluded. The water surface currents with and without oil slick were also measured. Figure 7 is an example for both cases. From this figure, it is evident that oil drift is considerably faster than water mass movement at the surface (approximately by 45%). The average oil drift velocity is approximately 6.2% of the average wind velocity which is, of course, considerably higher than the commonly accepted value of about 3.5%. Since only a limited number of measurements have been made, the results should not be viewed as conclusive.

One of the important observations from the laboratory experiments is that after 3 to 5 hours of weathering, a thin film formed on the surface. Subsequent samplings seem to reveal that the evaporation rate is retarded considerably. This surface resistance, not being considered in Equation (10), significantly changes the value of km. This effect should be thoroughly investigated in the future.

Based on the best-fit of the data, the following explicit relationships of km are suggested here in the interim:

Before Surface Film Being Developed $(\rho_t/\rho_o \le 1.0078)$

$$k_{\rm mb} = 69A^{-0.055} e^{0.42U}$$
 (14)

After Surface Film Being Developed $(\rho_t/\rho_o > 1.0078)$

$$k_{\text{ma}} = \frac{1}{5} k_{\text{mb}} \tag{15}$$

where ρ_0 is initial oil density and ρ_t is weathered oil density at time, t. It is evident that the change of the evaporation rate is quite drastic after the formation of the surface film although the herein proposed demarcation is an artificial one. At present, one can only conclude that k_m is a function of

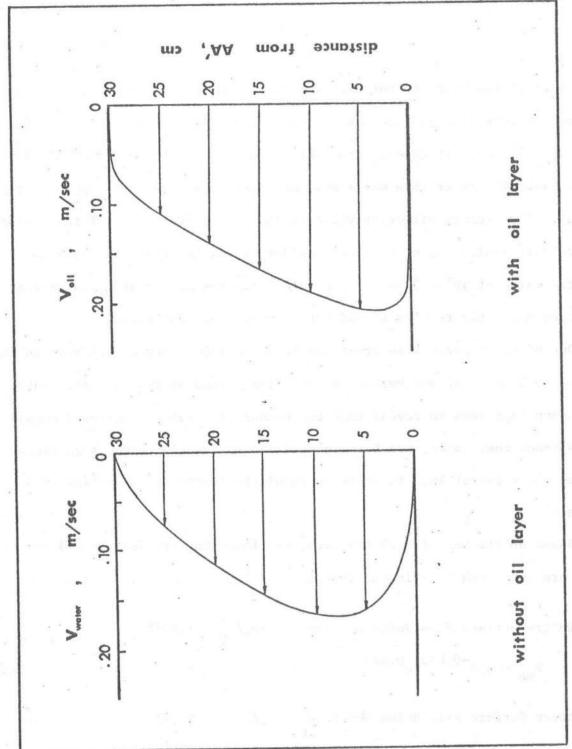


Figure 7 Water Surface Currents With and Without Oil Slick

not only surface area and wind velocity but other factors such as, we believe, the change of viscosity during weathering. The value of q = 0.42, on the other hand, seems to agree well with the existing information and to that suggested by Moore.

With the numerical values of a and q in hand, we are now in a position of performing numerical computations. Computed results of specific gravity change of No. 2 Fuel; Nigerian Crude and Venezuelan Crude are shown, respectively, in Figures 8, 9 and 10. The percentage contents of the eight fractions used as inputs to the numerical model for the three different kinds of oils and Frankenfeld's oil sample are listed in Table 3.

A comparison of numerical results of Frankenfeld's laboratory and field data (1973) is provided in Figure 11. The numerical results are consistently higher than Frankenfeld's laboratory data in the early stage of evaporation. This is likely due to the fact that Frankenfeld used the jet velocity at the exit of the fan as the reference velocity which was undoubtedly higher than the average wind velocity used in the numerical model.

Other numerical outputs including weight changes of individual fractions, total volume change and total weight change are illustrated in Figures 12, 13 and 14, respectively.

CONCLUSIONS

As part of an integrated research project dealing with the fate of oil spills in oceanic environments, the present work represents an initial effort of providing predictive capabilities on short-term oil weathering while the evaporation process dominates. The numerical model developed here is easy to use and is quite versatile in accepting various types of oils and weather conditions as inputs. To an extent, the model has been calibrated with laboratory

TABLE 3 BASIC NUMERICAL INPUT DATA

					*Estimated	*Estimated Percent Weight In:	ght In:	
b	q Fraction	lon	Description	*Average Density(Kg/m³)	Venezuelan	Nigerian Crude	#2 Fuel Oil	Frankenfeld's' Oil Sample
	1		Paraffin (C ₆ -C ₁₂)	710	10	15	10	10
	2		Paraffin (C ₁₃ -C ₂₅)	770	00	15	25	25
	3		Cycloparaffin (C ₆ -C ₁₃)	810	15	20	1.5	10
	4		Cycloparaffin (C ₁₃ -C ₂₃)	006	20	20	15	12
	2	Aı	Aromatic (Mono- and D1-Cyclic) (C_6-C_{11})	940	5	5	15	15
	9		Aromatic (Poly-Cyclic) (C ₁₂ -C ₁₈)	1000	2	٣	2	œ
	7	-53	Naphtheno-Aromatic (C_9-C_{25})	980	15	7	15	20
	90		Residual (including hetero- cyclos)	1010	25	15	0	0

* Estimated from:

Handbook of Hydrocarbons, Ferris, Seymour Washington, New York, Academic Press, 1955. Data Book on Hydrocarbons, J. B. Maxwell, D. Van Norstrand Co., 1950. The Petroleum Chemicals Industry, Richard, Frank, Goldstein, John Wiley & Sons, Inc., 1958.

^{**} Estimated from Frankenfeld(1973), Appendix A and B

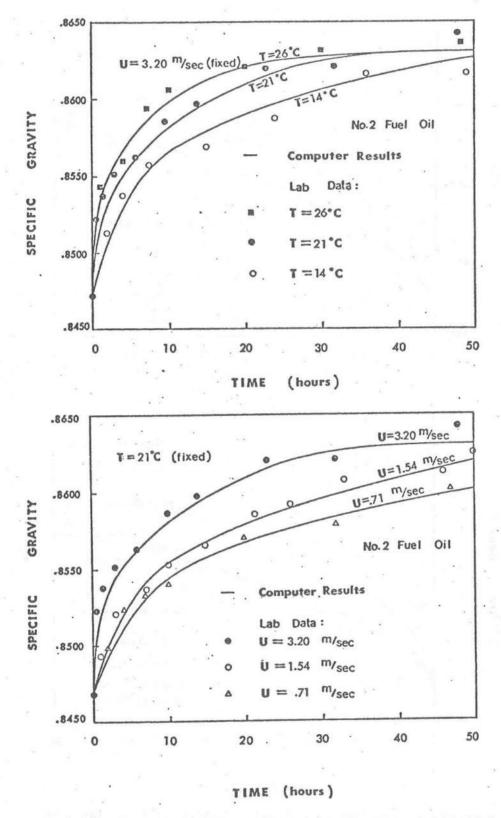


Figure 8 Specific Gravity Change of No. 2 Fuel Oil With Fixed Wind Speed as Air Temperature Varies and Fixed Air Temperature as Wind Speed Varies

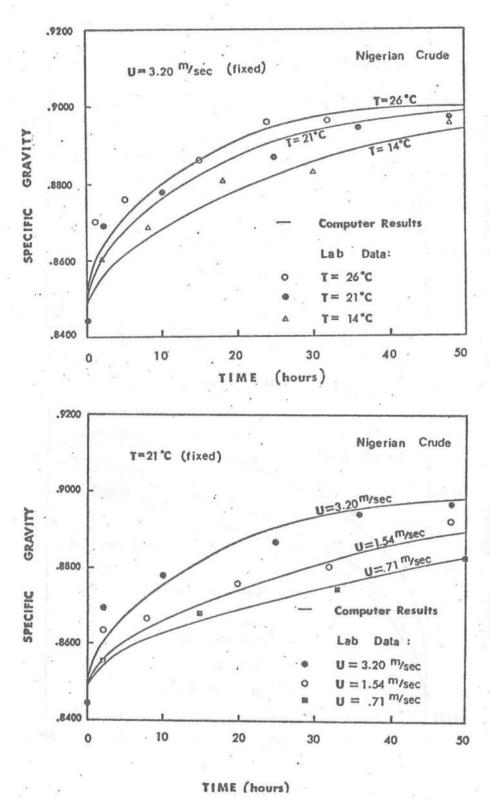
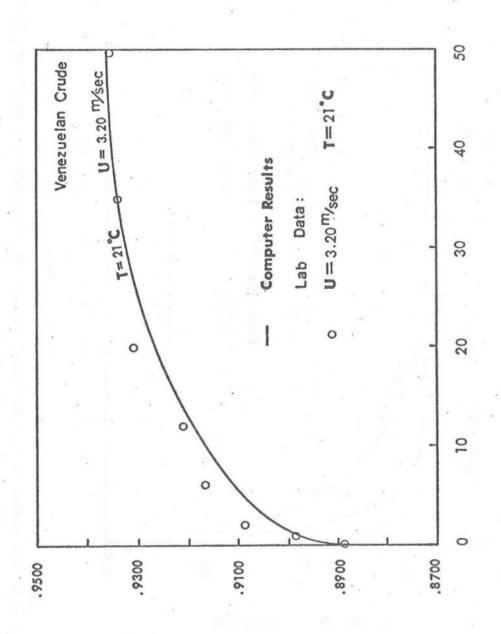


Figure 9 Specific Gravity Change of Nigerian Crude
With Fixed Wind Speed as Air Temperature
Varies and Fixed Air Temperature as Wind
Speed Varies

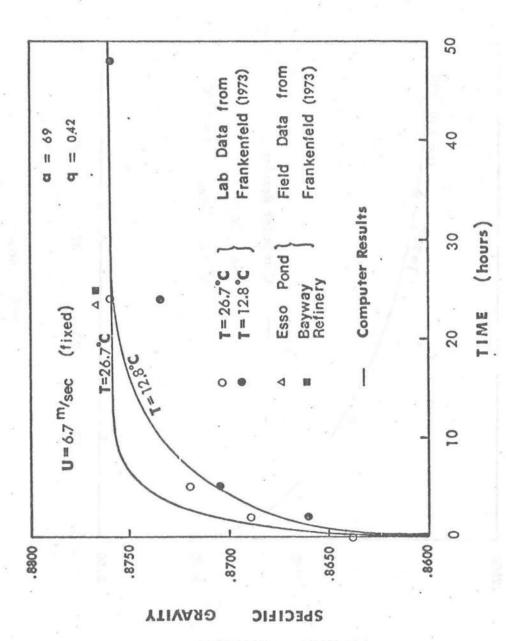


YTIVARD

SPECIFIC

Specific Gravity Change of Venezuelan Crude With Constant Wind Speed and Air Temperature Figure 10

TIME hours



Comparison of Numerical Results and Frankenfeld's Laboratory and Field Data Figure 11

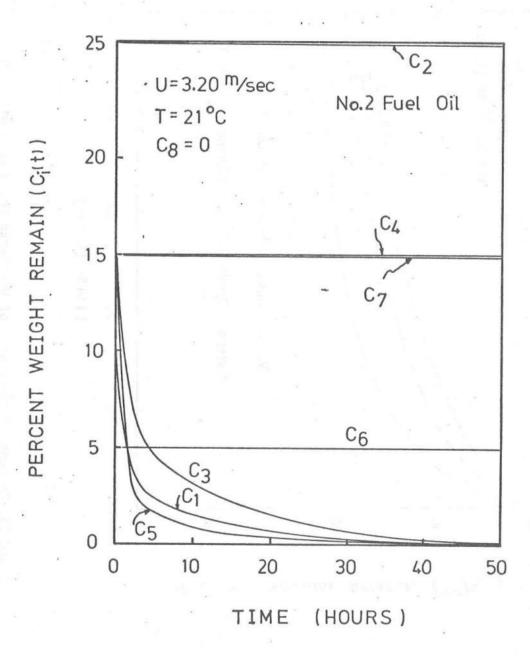
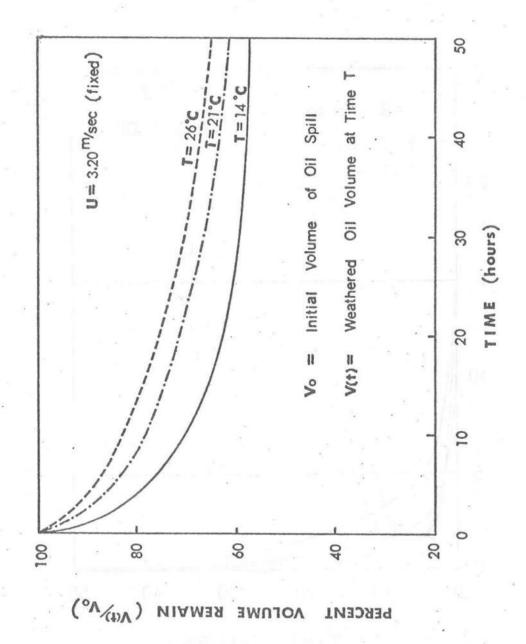
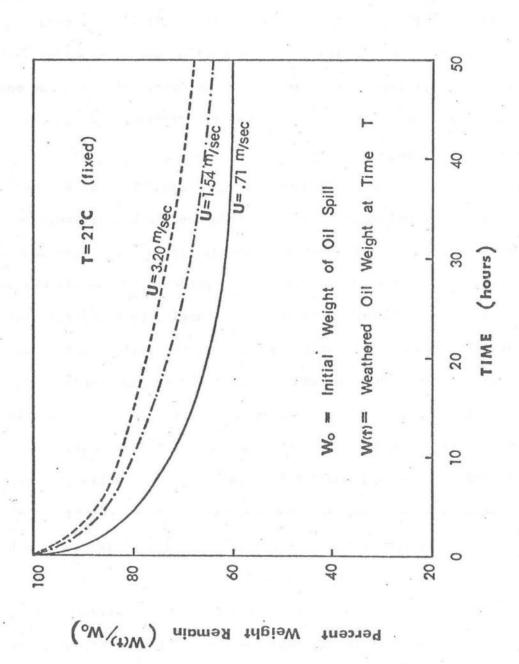


Figure 12 Percent Weight Changes of Individual Fractions of No. 2 Fuel Oil With Constant Wind Speed and Air Temperature



Constant Wind Speed and Three Different Air Temperatures Percent Volume Remain of Weathered No. 2 Fuel Oil With Figure 13



Percent Weight Remain of Weathered No. 2 Fuel Oil With Constant Air Temperature and Three Different Wind Speeds Figure 14

experiments and existing field data. The scheme is considered to be adequately predicting the trend of short-term weathering and represents the utilization of the present state-of-the art on the subject.

It is pointed out here that the validity of the first-order decay law at the very early stage of weathering is open to question as the thickness of the oil film may change significantly within the first few hours after the spill occurred. For the simplicity of computation, the first-order decay law has been adopted throughout the whole range. However, this might be one of the reasons that we are eventually forced to use two different slopes for the earlier and later stages of decay.

Once one has accepted the first-order decay law, the task becomes the correct estimation of the diffusion coefficient. This coefficient is known to be a function of, among others, temperature, wind speed, size of spill and most importantly, the characteristics of the oil itself. The dependency on the oil characteristics is treated here, and believed to be quite adequately, by characterizing the compound in terms of fractions of groups containing similar numbers of carbons and hydrocarbon types. Judging from the results, one also tends to conclude the commonly accepted functional relationship between the diffusion coefficient and the temperature (i.e., analogous to the ideal gas law) is a valid one. The effects of wind speed on this coefficient is not well established. Empirical functional relationships have been proposed based upon forced-fit to the experimental results. However, the resultant coefficient is found to be quite close to those stipulated by other investigators.

One of the important laboratory observations is the development of an apparent surface film after initial weathering, which significantly retards the rate of evaporation. This phenomenon is particularly evident for heavy crudes. Whether such a condition will develop in the actual oceanic environment is

remains unanswered at this stage.

Based upon numerical and laboratory results, one can safely conclude that temperature is of paramount importance in the early stage of evaporation up to say 50 hours for Fuel Oil No. 2 and to 20 - 30 hours for heavier crudes. The temperature effect diminishes afterward. The wind speed seems to affect the oil evaporation evenly throughout the range of test.

It is also worthwhile to note here our laboratory results yield much higher wind-induced oil drift velocity (approximately 6.2%) than commonly experienced. In addition, under similar conditions, wind-induced water surface current is considerably less than the oil drift velocity.

As was mentioned earlier, the work is part of a larger research program.

Work is now being continued to investigate the effect of waves on oil

weathering as well as an attempt to extend the model for longer term prediction

when water-oil emulsification and dissolution become important.

ACKNOWLEDGMENTS

The work is supported by the U.S. National Science Foundation/RANN. The manuscript was prepared while the authors were at the Technische Universitat of Braunschweig under the sponsorship of the Minna-James Heineman Stiftung, Hanover, Germany.

All of the second

REFERENCES

- Berridge, S. A., Dean, R. A., Fallows, R. G., and Fish, A. (1968), "The Properties of Persistent Oils at Sea," J. Inst. Petrol., V. 54, 300.
- Blokker, P. C., "Spreading and Evaporation of Petroleum Products on Water," pp. 911-919, Proc. of 4th Inter. Harbour Conf., Antwerp, June, 1964.
- 3. Fay, J. A. (1971), "Physical Processes in the Spread of Oil on a Water Surface," American Petrol. Inst., Proc. of Joint Conf. on Prevention and Control of Oil Spills, Washington, D.C., June 15-17, pp. 463-467.
- 4. Ferris, S.W., (1955), "Handbook of Hydrocarbons," New York, Academic Press.
- 5. Frankenfeld, J. W. (1973), "Weathering of Oil at Sea," Esso Research and Engineering Company, Distributed by National Technical Information Service, U.S. Department of Commerce.
- 6. McKay, D. and Matsugu, R. S. (1973), "Evaporation Rates of Liquid Hydrocarbon Spills on Land and Water," The Canadian Journal of Chemical Engrg., V. 51, August, pp. 434-439.
- 7. Moore, S. F. (1972), "Some Aspects of Deepwater Terminal Site Selection in Northern New England Coastal Areas," Proc. of 5th National Sea Grant Conf., Texas A&M Univ., pp. 107-124.
- 8. Moore, S. F., Dwyer, R. L. and Datz, A. M. (1973), "A Preliminary Assessment of the Environmental Vulnerability of Machias Bay, Main to Oil Supertankers," Rept. No. 162, Dept. of Civil Engrg., M.I.T., January.
- Regnier, Z. R. and Scott, B. F. (1975), "Evaporation Rates of Oil Components," Environmental Science & Technology, Canada, May, V. 9, No. 5, pp. 469-472.
- 10. Wang, H., Campbell, J. R. and Ditmars, J. D., (1975), "Computer Modeling of Oil Drift and Spreading in Delaware Bay," Ocean Engrg. Rept. No. 5, Dec., Dept. of Civil Engrg., Univ. of Delaware.