YEAR ONE INTERIM REPORT

Integration of Suspended Particulate Matter and Oil Transportation Study

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES (continued)

LIST OF TABLES

OIL/SPM INTERIM REPORT

INTRODUCTION

The objective of the oil-droplet and suspended-particulate-matter interaction program is to quantify the reaction terms in the convection-diffusion equation for oil droplets and dissolved-oil species. The convective-diffusion equation is derived by writing a mass balance for the species of interest in a differential volume element. The results of writing the mass balance yield the following partial differential equation for the concentration of species i:

$$\frac{\partial C_i}{\partial t} + \frac{\partial}{\partial x}(V_x C_i) + \frac{\partial}{\partial y}(V_y C_i) + \frac{\partial}{\partial z}(V_z C_i) = \frac{\partial}{\partial x}\left(k_x \frac{\partial C_i}{\partial x}\right) + \frac{\partial}{\partial y}\left(k_y \frac{\partial C_i}{\partial y}\right) + \frac{\partial}{\partial z}\left(k_z \frac{\partial C_i}{\partial z}\right) + R_i \qquad (1)$$

This partial differential equation is a mass balance which when integrated over time and space yields the concentration of species i. This equation appears in all branches of science and engineering whenever a mass balance is written. In the above equation, the left-hand side, with the exception of $(\frac{\partial C_i}{\partial t})$, represents advection through the differential volume element (which is fixed in space) and the right-hand side, with the exception of R_i, describes horizontal and vertical dispersion.

This partial differential equation is the basis for discussing and describing oil and suspended-particulate-matter interactions in the water column. All of the "interaction" information is contained in the reaction term R_i above. This reaction term is a removal (output) or source (input) term for the species i. Thus, for oil-SPM interactions, it is necessary to describe what species are going to be identified and kept track of. It is not possible to quantify every single species in the system; there are simply too many. Instead, experience seems to indicate that simplifying assumptions can be made.

The reaction for oil droplets in the water column describes the rate of collision and sticking of an oil droplet with a suspended particulate, i.e., a loss of (free) oil droplet, and the settling (or rising) of an oil droplet. The reaction term R_i for oil droplets only then is

$$R_{op} = K_{op} C_o C_p \qquad (2)$$

where $K_{op} C_o C_p$ is the rate of collision and sticking of an oil droplet and a suspended particulate to produce an oil-particulate agglomerate. The effect of buoyancy of oil droplets or oil-SPM agglomerate appears in the vertical velocity term in the partial differential equation.

Clearly, a mass balance must also be written for unoiled sediment. The partial differential equation for suspended sediment looks exactly the same as that for C_i. Thus, in order to predict the interaction of oil and sediment for a specific location, a prediction of sediment transport is required a priori.

A complete list of the species of interest for oil-SPM interaction prediction includes: oil droplets as a function of size, sediment size and "type," and finally oil-particulate agglomerates. Oil-particulate agglomerates refer to oil-particulate species where the particulate is composed of one, two, three, ..., individual particulate(s) and the agglomerate is the result of one oil droplet scavenging more than one particulate. There are an infinite number of species when these types of agglomerates are considered. Since it is not possible to keep track of all species even on the fastest computer (nor worthwhile), some judgement based on existing results and experimentation in progress must be used to either eliminate species or lump species into pseudocomponents.

An explicit requirement for an oil-SPM interaction and concentration prediction is the velocity and dispersion vectors in the mass balance equation. It must be emphasized that these velocities and dispersion coefficients are not calculated from an oil-SPM model. An oil-SPM transport model only uses these parameters to calculate where the oil and SPM are transported. These parameters come from an ocean circulation model and if the ocean-circulation model computes salinity, then the ocean-circulation model can easily compute oil and SPM concentration in the same way (with appropriate boundary conditions).

In the discussion that follows a detailed statement of the oil and suspended-particulate-matter interaction problem is given along with the simplifying assumptions that are being pursued. A review of the literature is then given with emphasis on: particle-particle kinetics, the rate constant of these kinetics as a function of shear (and turbulence), oil droplets in water (emulsions), and the range of experimental parameters expected. Finally, a discussion of the results of the completed experiments is given along with plans for the next series of experiments. A discussion on the utilization of these results is then presented which details how the parameters are to be used.

MODEL DEVELOPMENT

Formal Description of Suspended Particulate Matter and Oil Interactions

The objective of the oil and suspended-particulate-matter interaction program is to describe the fate of oil in the water column when the presence of suspended particulate matter is considered. Oil exists in the water column as discrete droplets or (truly) dissolved oil species. The truly dissolved oil species can be either molecular specific species or pseudocomponents. The dissolved oil species interact with the suspended particulate by adsorbing onto the particle, while the oil droplets interact by colliding with and sticking to the particulate. The adsorption of dissolved oil species by particulate is thought to affect no change in the particle's hydrodynamic characteristics while the oil-droplet particle species might affect a change in hydrodynamic character relative to both parents.

An oil spill on the ocean surface moves as a function of environmental conditions such as wind speed, waves, and water currents. As the slick weathers, dissolved species and droplets of oil are fluxed into the water column. At the same time sediment transport occurs due (mainly) to a flux of sediment to or from the bottom depending on wave conditions and currents. Thus, the two species, oil and particulate, interact and are transported due to the local velocity and dispersion vectors.

The mathematics which describe the water column interactions are the continuity equations for the various species. In general, this equation is

$$\frac{\partial C_i}{\partial t} + \frac{\partial}{\partial x}(v_x C_i) + \frac{\partial}{\partial y}(v_y C_i) + \frac{\partial}{\partial z}(v_z C_i) = \frac{\partial}{\partial x}\left(k_x \frac{\partial C_i}{\partial x}\right) + \frac{\partial}{\partial y}\left(k_y \frac{\partial C_i}{\partial y}\right) + \frac{\partial}{\partial z}\left(k_z \frac{\partial C_i}{\partial z}\right) + R_i \quad (3)$$

where C_i is the concentration of the ith species of interest, t is time, v_i are the velocity components, k_is are the dispersion components, and R_i is the reaction term. This equation can only be solved if the velocity and dispersion components are known. Furthermore, when this equation applies to dilute species, it is not coupled back to the hydrodynamic equations. In other words if the presence of C_i does not affect the bulk density of the fluid, the (bulk) viscosity of the fluid, or any other physical property of interest, C_i depends on v and k while the converse is not true. For oil species, C_i, in the water column, this "not coupled" assumption is applied because the species are very dilute. This is apparently not the case for sediment at the bottom boundary. The continuity equation can be solved when v and k are given or specified as a function of x, y, z and time. If a circulation model is available which computes these vectors and also salinity, then it is straight forward to add the calculation procedure to consider other species. Actually, it is easier to add uncoupled species equations because (note that) salinity is coupled to the momentum equations through the bulk density. If the continuity equation for uncoupled species such as oil has to be integrated after a circulation model is run, then a considerable amount of work must be done to "write" an integration routine, parameterize the location of the boundary, and "plot" the results.

Consider now the reaction term for oil droplets. Oil droplets leave (change their identity) the water column by colliding with and sticking to suspended particulate. The rate expression for the "reaction" is postulated to be

$$R_{op} = K_{op}C_oC_p \tag{4}$$

where C_o is the oil-droplet concentration, C_p is the <u>total</u> particulate concentration, and K_{op} is the rate constant for this "reaction." K_{op} is a function of turbulence or energy dissipation rate and is discussed in detail in the following section.

This interaction will result in a decrease in oil droplet concentration, i.e., $\partial C_i / \partial t$ will decrease, so $K_{op}C_oC_p$ is subtracted from the right hand side of the continuity equation for oil droplets.

When oil-droplet bouyancy is considered the continuity equation is further modified by the "rising" velocity according to

$$V_y = V_y' + W_y \tag{5}$$

where V_y' is the y-component of the current velocity obtained from a (the) circulation model and W_y is the "rising" velocity. The above expression for V_y is to be used directly in the continuity equation for oil droplets.

The objective of the experimental program right now is to measure, verify, and gain insight on $K_{op}C_oC_p$. This work is being conducted in a stirred-tank "reactor."

Now consider the suspended particulate matter in the water column. There are two types (at least) to consider: unoiled particulate, C_{pu}, and oiled particulate, C_{po}. The continuity equation for unoiled particulate also contains a loss term due to collision with and adherence to oil droplets. Thus, the reaction term for unoiled particles is

$$R_{opu} = -K_{opu}C_oC_{pu} \tag{6}$$

which is to be subtracted from the right hand side of the continuity equation for unoiled particulate. The settling velocity for particulate must also be included in the V_y term for particulate only. Denoting the particle settling velocity as U_y, the y-velocity component becomes

$$V_y = V'_y - U_y \tag{7}$$

where now a minus sign is used to denote the -y direction (settling toward the bottom).

At this point in the discussion, it is becoming apparent that keeping track of all kinds of species may well be impossible, especially if particulate size fractions are to be considered. However, it is only necessary to keep track of those "things" which behave differently. An example of importance which now should be considered is oiled versus unoiled particles. If the settling velocity of these two species is not appreciably different, then there is no need to consider them as separate species. The important consideration then is "appreciably different" when considered in the ocean environment. Since settling velocity is the "comparison," information on differential settling must be obtained by examining real ocean sediment to determine how sediments are size fractionated to the bottom. If it turns out that sediments with a settling velocity range of say ±10% are uniformly deposited and experiments in the laboratory show that oiled versus unoiled particulate fall in this range, then there is no need to consider separate particle species. However, this comparison must be made. Observation appears, in a preliminary sense, to bear out the above postulate based on laboratory data only, i.e., the observed settling rates differ very little (see Section 6.1, Payne et al. 1984).

The continuity equations can be integrated only when boundary conditions are applied. For the case of oil droplets, the rate of dispersion provides a "flux" boundary condition for this species at the ocean surface. The boundary condition for this species at the bottom has not been discussed. Two possibilities are $dC_0/dy = 0$ at the bottom, i.e., no transport across the bottom; or $C_0 = 0$, i.e., the oil drops stick to the bottom. If sediment is being "lifted" from the bottom due to wave action, $dC_0/dy = 0$ would (probably) be satisfactory.

The concentration of suspended sediment in the water column can be considered as resulting from advection and mixing within the water body and resuspension from the bottom. The former is part of the full three dimensional numerical circulation model of the water body and will include source boundary conditions such as riverine input and coastal erosion. The latter involves a sub-model of the bottom boundary layer which will provide bottom boundary conditions for the suspended sediment continuity equation and bottom friction coefficients for the sea bed to the bottom boundary layer or suspended sediment concentrations in the boundary layer resulting from resuspension. The incorporation of this bottom boundary condition into the 3-D circulation model can <u>necessarily only</u> be performed by the circulation model.

The suspended sediment, bottom boundary layer sub-model will be based on Grant and Madsen (1979, 1982) and Grant and Glenn (1983). The sub-model calculates the non-linear dynamics of surface wave and current interactions in frictional boundary layers. The calculated bottom shear stress from this model (which includes moveable bed and stratification effects) is then related to sediment resuspension and transport through the Shields parameter. Inputs to this sub-model include:

1. Low frequency surface wave characteristics (amplitude, frequency and direction of the wave which most feels the bottom - that is not necessarily the most significant wave; low frequency swells resuspend sediment more easily than a steep choppy sea.)

2. Low frequency current and density profiles (from the 3-D circulation model). There is feedback from the boundary layer submodel to the current profiles and eddy viscosity parameters.

3. Bottom sediment characteristics, including size distribution and bed-form characteristics.

Detailed Discussion of Oil-SPM Kinetics

The rate of oil and SPM interaction, which appears as R_i in the continuity equations, is written as

$$R_i = K_{op}C_pC_o \tag{8}$$

This equation is based on numerous research papers that have been published on the general topic of the collision frequency of particles in a fluid medium. Therefore, in order to show why this equation can be used to describe oil-SPM interactions, an abbreviated derivation is presented which also discusses how this equation is adapted to a turbulent medium.

In order for oil droplets and SPM to interact, they must collide. Once they have collided, they can "stick" to form an oil-SPM agglomerate or rebound to remain the same as before the collision. Therefore, the first step in describing the oil-SPM interaction is to describe the collision frequency of (suspended) particles in a turbulent medium.

Consider a reference frame (x, y, z) centered on a particle which is fixed in space as shown in Figure 1. The fluid moves past the sphere in laminar flow where the velocity in the x-direction is given by $U = -Gy$. Thus, the velocity is a function only of y and the sphere is transparent with respect to the flowing fluid. If the sphere was not transparent, then the flow of fluid around (rather than through) the sphere would have to be considered.

The objective of the derivation is to calculate the number of spheres moving at the local fluid velocity that collide with the single sphere at the origin. Thus, it is necessary to calculate the product of the local fluid velocity (since the particles ride at this velocity) and the projected area of the sphere exposed to the local velocity. This concept can be visualized by examining Figure 1. Note that the velocity is zero on or near the x-axis and the projected area of the sphere in the region of the x axis is relatively large. Thus, there are relatively few collisions on the x-axis because the flow is small in this region. As the position of a flowing particle is moved off the x-axis, its fluid velocity toward the target sphere goes up and since the projected area of the target sphere is finite, collisions can occur. As the position of the moving particle changes towards y = radius of the target sphere, note that the velocity is quite high which results in more particles flowing through this position, but the projected area of the target sphere is almost zero. Thus relatively few spheres collide in this region. Mathematically, the above description is worked out as follows. A differential area of the surface of a sphere of radius "a" projected onto the y-z plane is

$$dA = \{\sin\theta\ (a\ \sin\theta\ d\phi)\}\ \{\sin\phi\ (a\ d\theta)\} \tag{9}$$

or

$$dA = a^2\ \sin^2\theta\ \sin\phi\ d\theta d\phi \tag{10}$$

any position y can be expressed as a function of a, θ and ϕ as

$$y = a\ \sin\theta\ \cos\phi \tag{11}$$

Therefore, the number of particle centers passing through a sphere of radius "a" about the origin is

$$\begin{aligned} df(\theta,\phi) &= nudA \\ &= n\{G\cdot a\cdot \sin\theta\cos\phi\}\{a^2\sin^2\theta\sin\phi d\theta d\phi\} \\ &= nGa^3\sin^3\theta\sin\phi\cos\phi d\theta d\phi \end{aligned} \tag{12}$$

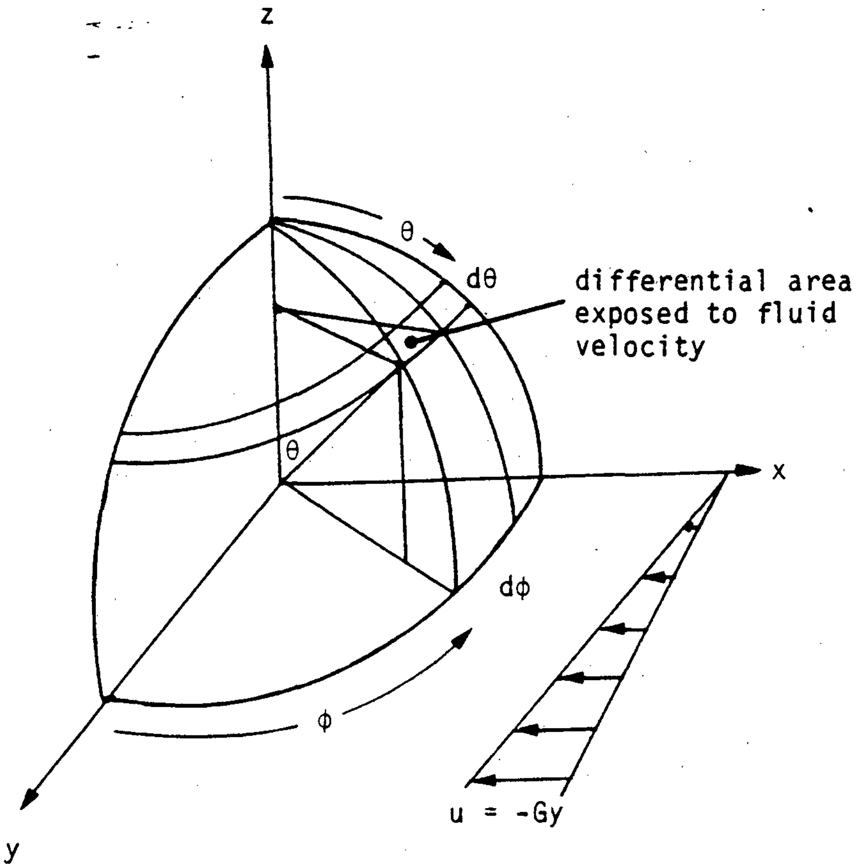


Figure 1. "Collision" Sphere of Radius a, which denotes the collision geometry for monodispersed spheres of diameter a. Note that a "collision" sphere is the center-to-center distance of approach that results in contact. The projected differential area onto the yz plane (normal) is to be integrated over the plane weighted by the local velocity.

where n is the number concentration of particles in the moving fluid. This is the differential collision frequency of the particles in the moving fluid with the single particle at the origin. Integrating θ and ϕ both through 0 to $\pi/2$ for the upper octant and multiplying by 4 to get the entire "face" exposed to the moving fluid yields

$$f = \frac{4}{3} nGa^3 \tag{13}$$

The above expression is the collision frequency for the particles in the fluid with the single particle fixed at the origin. To get the collision frequency for all the particles multiply f by n and then divide by 2. The division by 2 must be made because otherwise the collision of i onto j and j onto i would be counted twice. Therefore, the collision frequency for a fluid containing n particles with radius "a" per unit volume in laminar shear at G sec^{-1} is

$$F = \frac{2}{3} a^3 n^2 G \tag{14}$$

This equation is rearranged by taking into account of the volume concentration of solids, which is

$$c = \frac{4}{3} \pi\left(\frac{a}{2}\right)^3 n \tag{15}$$

which when substituted into the collision-frequency equation yields

$$F = \frac{4}{\pi} ncG \tag{16}$$

This is the typical equation for describing the particle-particle collision frequency for a system of monodispersed particles (Manley and Mason, 1952). Note that it is first order with respect to the particle concentration because the volume concentration of solids is constant. This equation has been tested in many experiments and shown to be valid. This equation applies to oil-oil droplet and particle-particle interactions to a first approximation.

In order to apply the collision frequency equation to oil-particle interactions, the identity of two different particles must be taken into consideration. The collision frequency of two different particles is

$$F_{ij} = \frac{4G}{3} (r_i + r_j)^3 n_i n_j \qquad (17)$$

where r_i is the radius of the i-th particle (Birkner and Morgan, 1968). Note that the shear appears in exactly the same manner as it does for the collision frequency of monodispersed particles.

The material balance, or population balance, for oil and suspended particulate can now be written using the above collision frequency equation. For oil droplets, the differential material balance is

$$\frac{dn_o}{dt} = -\alpha F = -\alpha \frac{4G}{3} (r_o + r_p)^3 n_o n_p \qquad (18)$$

where α is introduced as the "stability" constant. This constant takes into account the efficiency of oil droplet and particle adherence, i.e., sticking (Huang, 1976). If the particles collide but do not stick, $\alpha = 0$; at the other extreme is $\alpha = 1$. The above equation is applied to the (free) oil droplet concentration as

$$\frac{dn_o}{dt} = -kGn_o n_p \qquad (19)$$

where now k lumps α and the radius function. Thus, experimental measurements essentially determine a lumped reaction rate constant which is kG. Similar expressions apply to unoiled sediment and an oil-particle agglomerate which is also the rate of formation of the k-th particle composed of an i + j agglomerate. In order to apply the above equation to oil droplets, suspended particulate matter and the resulting agglomerate, at least three species are identified here. Because the material balances that are actually used in calculations involve concentrations of mass rather than populations, the differential material balances are rewritten as

$$\frac{dC_i}{dt} = -kG\ C_i C_j \tag{20}$$

where k lumps all unknowns for the reaction.

The above equation relates the collision frequency to the (laminar) shear rate. In order to apply this to the problem of interest, a turbulent shear is required. Saffman and Turner (1956) present an analysis of the collision frequency in turbulent shear which results in

$$G = \left(\frac{\varepsilon}{\nu}\right)^{1/2} \tag{21}$$

where ε is the (turbulent) energy dissipation per unit mass per unit time and ν is the kinematic viscosity.

Thus, the working equation for the rate of loss of the i-th particles due to collisions and sticking with the j-th particle is

$$\frac{dn_i}{dt} = -k\left(\frac{\varepsilon}{\nu}\right)^{1/2} n_i n_j \tag{22}$$

The assumptions involved in deriving the above equation clearly do not reflect reality exactly. The relation of laminar shear and turbulent shear that is invoked requires assumptions. Clearly the particles to which the equation is to be applied are not spheres. Furthermore, the particles are distributed over a range of sizes. However, the basic form of the above equation has been shown to be applicable in many situations and will be used and verified in the experimental program.

Dispersion of Oil Droplets

The dispersion of oil droplets from a slick into the water column is not a well understood process. The dispersion of oil droplets forms an oil-in-water emulsion, the properties of which are fairly well known. In order to provide a source of oil droplets for the oil-SPM collision process, this emulsion must be relatively stable.

As discussed in the following sections, turbulence alone cannot account for the observed oil droplet sizes. The thermodynamics of the oil-in-water interaction may be the chief driving force for the production of the majority of droplets, with turbulence and the presence of suspended particulate material affecting oil-SPM interaction rates.

Turbulence

The most common models of oil dispersion are based on the turbulent breakup of the oil where the turbulent energy is supplied by breaking waves (Raj, 1977; Milgram, 1978; Shonting, 1979). The breaking waves "beat" the oil into the water column where a fraction of the "injected" oil remains as dispersed droplets and the rest returns to the surface slick.

Models have been developed relating turbulent energy dissipation rates (ϵ) to sea state, especially wind speed. Sea state is a parameter also used to calculate the oil concentration in the water column. A review of these models is contained in the First Quarterly Report dated January 16, 1985. Difficulties encountered with this method of modelling oil droplet size and production rate using turbulence alone include the lack of data on observed energy dissipation rates and the lack of correlation of theoretical oil concentrations and droplet sizes with observed values.

Table 1 lists energy dissipation rates measured in the ocean. Emphasis has primarily been on deep ocean measurements and not at the surface (0-2 m) or ocean floor. The ocean surface has been estimated to have turbulent energy dissipation rates of 30 cm^2/sec^3 or higher in the top 6 cm with winds of 10 m/sec (Lin, 1978). Raj (1977) found that wind speeds of 12 m/s (25 knots) would be required to suspend oil to a depth of two meters using only turbulence as the dispersion process.

Table 1. Observed Energy Dissipation Rates

Depth (m)	ε(ergs/cm^3/sec)	References
1	6.4 E-2	Liu (1985)
1-2	3.0 E-2	Stewart & Grant (1962)
15	3.0 E-2	Stewart & Grant (1962)
15	2.5 E-2	Grant et al. (1968)
15	1.0 E-2	Liu (1985)
27	5.2 E-3	Grant et al. (1968)
36	1.5 E-1	Belyaev (1975)*
40	2.65 E-3	Liu (1985)
43	3.0 E-3	Grant et al. (1968)
58	4.8 E-3	Grant et al. (1968)
73	1.9 E-3	Grant et al. (1968)
89	3.4 E-4	Grant et al. (1968)
90	3.1 E-4	Grant et al. (1968)
100	6.25 E-4	Liu (1985)
140	3.7 E-2	Belyaev (1975)*

*In Raj (1977).

Unit Conversions

1 erg/cm^{3}sec = 1 cm^2/sec^3 water
= 10^{-4} watts/kg water
= 10^{-7} watts/cm^3

The air-sea boundary and sea-bottom boundary are expected to be the regions of greatest energy dissipation based on velocity profile considerations. Oil-droplet concentrations will be highest near the surface (near the slick) and sediment concentrations will be highest near the bottom (in resuspension cases). The region of greatest oil-SPM interaction may then be the middle region of lowest energy dissipation, with source terms of oil-droplet and sediment input described by the boundary regions (surface and bottom) of higher energy dissipation rates. Turbulent energy dissipation rates, when known, can be readily duplicated in the laboratory as discussed in the section on experimental procedures, though only with serious scaling uncertainties.

The prediction of oil droplet size from turbulence-only models generally uses the Weber number approach. Milgram (1978) predicted that the smallest droplet possible is approximately 50μ (while the typical droplet size is larger). Aravamuden (1981) found a similar value but found an inverse linear relationship between droplet diameter and the number of droplets. Observations around an oil spill support this inverse relationship but the minimum observed droplet size was approximately 1μ (Shaw, 1977). The use of the Weber number approach also requires the prediction of oil viscosity and oil-water interfacial surface tension over time. Neither of these physical properties is predictable strictly from oil composition.

The affect of turbulence on a coagulating suspension is complex. Hunt (1982) described this effect as two-fold. "First, it (turbulence) generates small-scale fluid shear which controls the suspended particle volume removal rate and second, disperses the discharged particle suspension which decrease the particle concentration and lowers collision and removal rates."

Emulsions

It is known from emulsion theory that without the presence of an emulsifying agent, oil-in-water emulsions (for pure compounds) are limited to a maximum concentration of about 2% and are not stable (Clayton, 1923). Liquid-liquid emulsions may be stabilized by the addition of one of three types of compounds: 1) compounds with a polar-nonpolar structure (surfactants); 2) compounds which form a protective barrier at the liquid-liquid interface (hydrophilic colloids, i.e., gelatins and gums); and 3) finely divided powders or insoluble particles (Huang and Elliot, 1977; Overbeek, 1952). The use of agitation (turbulence) alone cannot result in the formation of a stable oil-in-water emulsion but increases the interaction rate of droplets with the stabilizing compound.

Stable oil-in-water emulsions may be formed spontaneously (i.e., with no agitation) when polar compounds are present in the oil (Overbeek, 1952). Micelles are spontaneously formed by the alignment of the polar compounds into a sphere with the hydrophilic heads at the water interface and the hydrophobic tails to the center where the nonpolar oil compounds are contained. This alignment of polar-nonpolar hydrocarbons occurs in many biological systems and is the basis for the formation of cell membranes and the micelles that comprise latex and milk (Overbeek, 1952; Bretscher, 1985).

Oil-in-water emulsions formed either spontaneously or with a stabilizing agent have droplet sizes on the order of 0.1μm for pure substances with sizes increasing for nonpure compounds and in the presence of electrolytes. Oil droplets have been experimentally produced in seawater (as an unstable emulsion) with agitation in this size range as measured by filtration (Shaw, 1977).

Because oil is known to oxidize at ambient temperatures over time and its surface tension decreases, it is possible to hypothesize that polar products are formed in oil as it weathers (Baldwin and Daniel, 1953). This would lead to the increased possibility of spontaneous emulsion formation and/or stabilized emulsion formation. The exact mechanism of oil-droplet formation probably involves the combined effects of turbulence, spontaneous emulsification and increased stabilization due to polar compound production and the presence of fine particles of suspended materials.

General Discussion of Experimental Procedure

The experimental procedure for determining the oil-droplet and suspended-particulate interaction is based on the continuity equation in which the rate term is identified. This rate term for the interaction kinetics is first order with respect to oil-droplet concentration and first order with respect to suspended-particle concentration. The rate expression is proportional to the energy dissipation rate to the one-half power. In this program, the rate-determining experiments are conducted in a 28 liter stirred vessel. Thus, the conditions of the contents of the vessel must duplicate or be scaled to the ocean water column conditions. The scaling parameter for the kinetics expressions is $(\frac{\varepsilon}{\nu})^{1/2}$ which is called the turbulent shear rate. It is important to recognize that conditions in the 28 liter vessel cannot be made to match exactly the conditions in the ocean water column. The main reason for this mismatch is the fact that the walls (or boundary) of the vessel are always close to the water (movement). It has been stated that "no one has yet suggested a quantitative relationship between laboratory mixing and the mixing that occurs at sea" (Shaw, 1977). However, in order to proceed with these experiments, the energy dissipation rate, ε, is considered the major scaling parameter. Energy is put into the contents of the vessel by stirring. In order to calculate the energy dissipation rate for an experiment, the power input can be calculated from

$$P = wT$$

where w is the angular velocity of the stirrer (radians/sec) and T is the measured torque (dyne-cm) which yields the power delivered to the contents of the vessel (dyne-cm/sec). Because all of the power delivered to the stirrer is dissipated in the entire fluid mass of the vessel, the rate of energy dissipation per unit mass of fluid is

$$\varepsilon = \frac{P}{V\rho}$$

where V is the actual volume of fluid in the vessel and ρ is the fluid density. Therefore, the working equation is

$$G = \left(\frac{\varepsilon}{\nu}\right)^{½} = \left(\frac{P}{V\rho\nu}\right)^{½} \quad (23)$$

Initial experiments were conducted with oil added as a slick and the production of oil-in-water droplets allowed to proceed. This method of adding oil is somewhat difficult to quantify on this relatively small scale. Therefore, experiments were conducted to determine if oil droplets could be made by agitating an aliquot of oil in approximately one liter of water to produce a relatively stable emulsion. These experiments were successful for the purpose of producing a "charge" of oil droplets in water that can then be added to the water and SPM in the stirred vessel. The problem then is to describe mathematically the progress of the oil-droplet and SPM interaction and predict observable quantities which can be measured in the laboratory.

Consider a fluid being stirred at a rate quantified by $(\varepsilon/\nu)^{1/2}$ with a volume V and an initial SPM load of C_p^o mass per unit volume. At the beginning of the experiment an aliquot of oil droplets in water is added to the vessel that yields an oil concentration (as droplets) of C_o^o mass per unit volume. The material balance for the oil droplets is

$$V\frac{dC_o}{dt} = -Vk_o\left(\frac{\varepsilon}{\nu}\right)^{1/2} C_oC_p = k_1C_oC_pV \quad (24)$$

The reason this equation is written in this very specific manner rather than in terms of populations (i.e., N_o and N_p) is that N_o can be converted to C_o as previously described in the discussion on collision frequency. While this conversion is exact only for single-sized droplets, it is applied here to a narrow size range. The constant k_0 "lumps" not only this conversion for N_0 to C_0 but also the collision efficiency factor which denotes the formation of the oil-particle agglomerate. This differential material balance denotes the loss of oil droplets in the vessel. The constant k_1 is denoted only for the purpose of deriving a solution. Likewise, the material balance for the SPM is

$$V \frac{dC_p}{dt} = -V\, k_p \left(\frac{\varepsilon}{\nu}\right)^{1/2} C_o C_p = k_2\, C_o C_p V \tag{25}$$

In this expression, the rate constant k_p is not the same as k_o for oil droplets. The reason is that the change in mass per unit volume will not be the same for oil and particles simply because an oil drop and particle will not (almost always) have the same mass. Again, k_2 is a "lump" constant. The material balance for the oil-particle agglomerate is

$$\frac{dC_a}{dt} = k_a \frac{dC_o}{dt} \tag{26}$$

where k_a accounts for the mass per unit volume of the agglomerate relative to the oil droplet. Also, note that

$$\frac{dC_p}{dt} = \frac{k_2}{k_1} \frac{dC_o}{dt} \tag{27}$$

and α is defined as the ratio k_2/k_1. This equation states that a change (i.e., a decrease) in the oil-droplet concentration results in a proportionate change in the SPM concentration, i.e., α. In order to solve the differential equations and, hence, provide a prediction of observables in the experiment, it is necessary to write the equation for dC_o/dt in terms of C_o alone. Thus, the stoichiometry of the oil-droplet and SPM reaction must be examined.

Consider a change in the oil-droplet concentration from t = 0 as

$$\Delta_o = C_o^o - C_o(t) \tag{28}$$

where $C_o(t)$ is the concentration of oil droplets at some time t. There will also be a corresponding change in the particle (SPM) concentration

$$\Delta_p = C_p^o - C_p(t) \qquad (29)$$

The stoichiometry of the "reaction" relates the change in mass concentration of one species to the other. For this reaction, the stoichiometry is quantified as

$$C_p^o - C_p(t) = \alpha \{C_o^o - C_o(t)\} \qquad (30)$$

and this equation takes into account the changes in mass per unit volume when oil and SPM react to form the agglomerate.

Therefore, solving for $C_p(t)$ and substituting into the expression for dC_o/dt yields

$$\frac{dC_o}{dt} = C_o \, [k_1 \, (\alpha C_o^o - C_p^o) \;\; - \alpha \, k_1 C_o{}^2 \qquad (31)$$

which is Bernoulli's differential equation. Solving this equation subject to the initial condition that $C_o = C_o^o$ at $t = 0$ yields

$$\frac{1}{C_o} = - \frac{k_b}{k_a} + \left\{ \frac{1}{C_o^o} + \frac{k_a}{k_b} \right\} e^{-k_a t} \qquad (32)$$

where k_a is defined as $k_1 \, (\alpha C_o^o - C_p^o)$ and k_b is $- \alpha k_1$. Thus, three parameters are unknown: k_o, k_p, and α. The results of an experiment then provide plots of C_o and C_p versus time from which α is determined directly. The shape of the $C_o(t)$ and $C_p(t)$ curves determine k_1 and k_2 from the best fit of the data to the equation above. These parameters are then used in the continuity equations for the three species of oil droplets, SPM, and the resulting agglomerate. This derivation illustrates how "tank" data are to be analyzed to determine rate constants when a "charge" (step change) of oil droplets are put into the tank.

EXPERIMENTAL RESULTS: OIL/SPM PROGRAM

During the past year, work has been conducted on not only refinements in sample collection and processing methodology but also outdoor wave tank and laboratory stirred chamber experiments regarding interactions between oil and suspended particulate matter (SPM). Although the analyses for all of these efforts are still being completed, the following summarizes the status of the information available to date for these efforts.

Refinements in Sampling Methodology

In previous experiments in our oil/SPM program for MMS and previously, NOAA, hydrocarbon analyses have been performed on two fractions from whole water samples: 1) a "dissolved" fraction consisting of the filtrate from a whole water sample that is vacuum filtered through glass fiber filter of 1 μm nominal pore size and 2) a "particulate" fraction consisting of all material retained on the filter. Unfortunately, this "particulate" fraction consists of SPM and dispersed oil droplets because both are retained on the filter. Hence, discrete quantities of hydrocarbons in the SPM and dispersed oil fractions cannot be distinguished with this filtration approach.

Separation of SPM and dispersed oil fractions by inherent density differences.

To obtain better estimates of the discrete hydrocarbon quantities in the SPM and dispersed oil fractions, the following change in sampling methodology has been adopted. A sub-surface whole water sample is collected from an experimental chamber (i.e., outdoor wave tank or stirred reaction vessel) in a glass separatory funnel that is completely filled with solution. The sample in the separatory funnel is maintained in a stationary position for a sufficient period of time to allow for inherent density differences between dispersed oil droplets and SPM to produce a physical separation between the two fractions (i.e., oil droplets rise and SPM sinks in the separatory funnel). Losses of specific hydrocarbons due to volatilization of lighter fractions into an overlying air space are minimized because the separatory funnel is completely filled with sample. This sampling protocol subsequently allows for three reasonably discrete "phases" to be collected from the separatory funnel: 1) an "SPM phase" that is comprised of SPM accumulating at the bottom of the separatory funnel, 2) a "dissolved phase" that is comprised of the water in the separatory funnel (excluding the upper oil layer) and 3) a "dispersed oil phase" that is comprised of the oil layer at the top of the separatory funnel. The "SPM" and "dissolved phases" are extracted with methylene chloride to recover hydrocarbons. The "dispersed oil phase" is recovered with solvent rinses following removal of the "SPM" and "dissolved phases" from the separatory funnel.

Although this separatory funnel approach yields three discrete samples, a limitation in the general application of this procedure became apparent during experiments in oil-SPM-water systems. For distinctions between hydrocarbon quantities contained in the "dissolved" and "SPM phases" to be accurate, all of the SPM in a water sample must collect at the bottom of the separatory funnel. Observations during experiments indicated that a portion of the SPM often adhered to the sides of the funnel rather than sinking to the bottom. Furthermore, this trend was more pronounced when SPM particles became more "oiled". This adherence of SPM particles to the separatory funnel walls would result in the following limitations: 1) an underestimation of the total amount of hydrocarbons contained in the "SPM phase" of a sample (due to not only incomplete recovery of all of the SPM in the water phase but also the possible loss of more heavily "oiled" particles that preferentially adhere to the funnel walls) and 2) an overestimation of hydrocarbon quantities in the "dissolved phase" due to inclusion of SPM adhering to the separatory funnel walls. The latter "dissolved phase" could be further misleading since it would likely contain the relatively insoluble aliphatic compounds (specifically associated with the SPM) that would not in reality exist in the "dissolved" phase of the sample. Hence, a means needed to be developed to insure that SPM particles were not included in the "dissolved phase" of a sample.

Utilization of polyester membrane filters to separate "dissolved" and "SPM phases" of samples.

To achieve the desired separation between "dissolved" and "SPM" phases, the following general approach was adopted. After "differential phase settling" in a separatory funnel, the aqueous portion of a sample (i.e., containing both SPM and water) would be vacuum filtered through an appropriate filter. The resulting water filtrate (free of SPM) would be analyzed for the "dissolved fraction" of hydrocarbons, and the particulate matter retained on the filter would contain the "SPM fraction" of hydrocarbons. Recovery of the "SPM" hydrocarbons from the filter would be achieved by additional vacuum filtration with appropriate solvents (i.e., methanol and methylene chloride) through the filter.

Selection of the type of filter to be used for this approach was based on the following criteria: 1) the filter had to be resistant to the extraction solvents (i.e., methanol and methylene chloride), 2) the filter had to maintain its structural integrity through all manipulation steps of the filtration process (i.e., pre- and post-filtration measurements of filter weights would then allow for determination of the exact mass of SPM filtered) and 3) the filter would not require pre-wetting with an organic solvent (e.g., methanol) to facilitate passage of aqueous solutions. Filters made of teflon were excluded because they require pre-wetting with methanol. Any methanol left on the filter (or filtration apparatus) could result in an undesirable solubilitization of "SPM" hydrocarbons during the subsequent filtration of the water sample. Polycarbonate membrane filters were excluded because they were observed to disintegrate in methanol. Glass fiber filters were excluded because individual glass fibers could be lost during the filtration process, thus affecting final filter weights independent of the quantity of SPM retained on the filter. Membrane filters made of polyester were ultimately selected for testing because they appeared to satisfy all of the desired criteria (i.e., resistance to methanol and methylene chloride, maintenance of structural integrity throughout filter manipulations, and ready compatibility with aqueous solutions).

Polyester filters were obtained from Nuclepore Corporation and had the following characteristics: polyester membrane filter, 47 mm diameter, 0.4 µm pore size, Nuclepore catalog number 181107. The following tests were performed with these filters to evaluate their adequacy for use in oil-SPM-water experiments.

Measurements of hydrocarbons in the various phases of oil-SPM-water samples are routinely performed by gas chromatography with flame ionization detection (FID-GC). Consequently, initial concern centered around possible introduction of compounds from the polyester filters that would be detected by FID-GC. To test this, a filter was placed in a glass beaker with 30 mls of methanol for 30 minutes. The methanol was then decanted into a separatory funnel, and 30 mls of methylene chloride was added to the beaker with the filter for an additional 30 minutes. This methylene chloride was then decanted into the separatory funnel. The combined methanol-methylene chloride fraction was partitioned with 100 mls of hydrocarbon-free sea water. Following collection of the lower methylene chloride layer, the sea water-methanol solution was back-extracted with 30 mls of methylene chloride. The combined methylene chloride fractions were condensed to an appropriate volume and analyzed by FID-GC. A concurrent solvent blank was processed in an identical manner, except that no filter was added to the initial extraction beaker. The FID-GC chromatograms for the solvent blank and filter extractions are illustrated in Figures 2a and 2b, respectively, and appear to be identical. Consequently, solvent extraction of the polyester filter did not appear to introduce any interfering compounds for FID-GC. A filter was also placed in the filtration apparatus and vacuum filtration (30 cm Hg) performed with the following sequence of solvents: 1) 30 mls of methanol and 2) 30 mls of methylene chloride. These combined solvent filtrates were treated in an identical manner to the preceding solvent blank and filter extractions. The FID-GC chromatogram from this vacuum filtration sample is illustrated

(a)

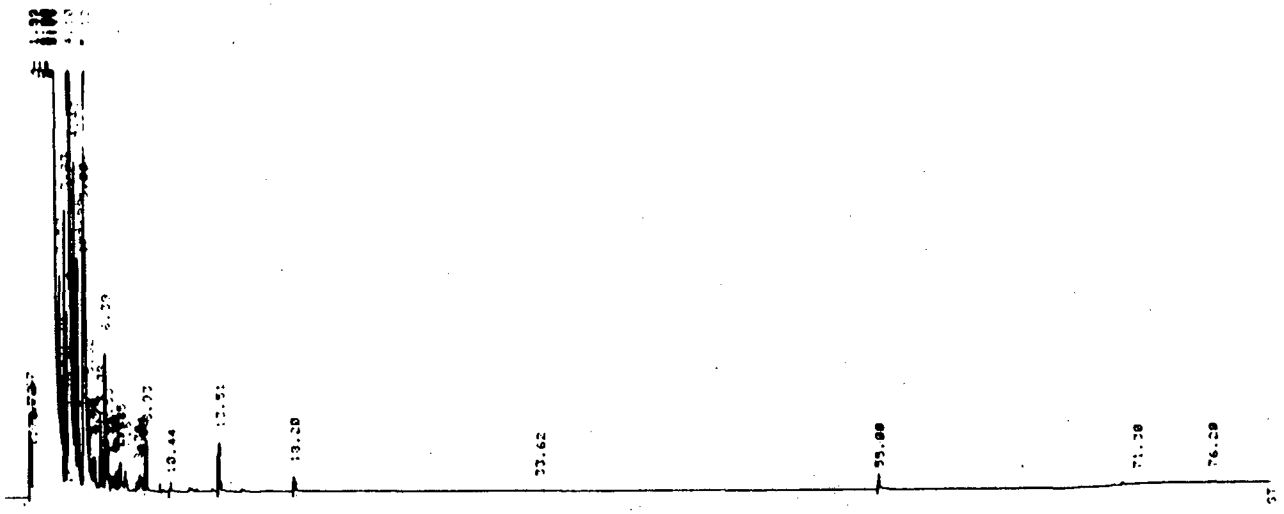
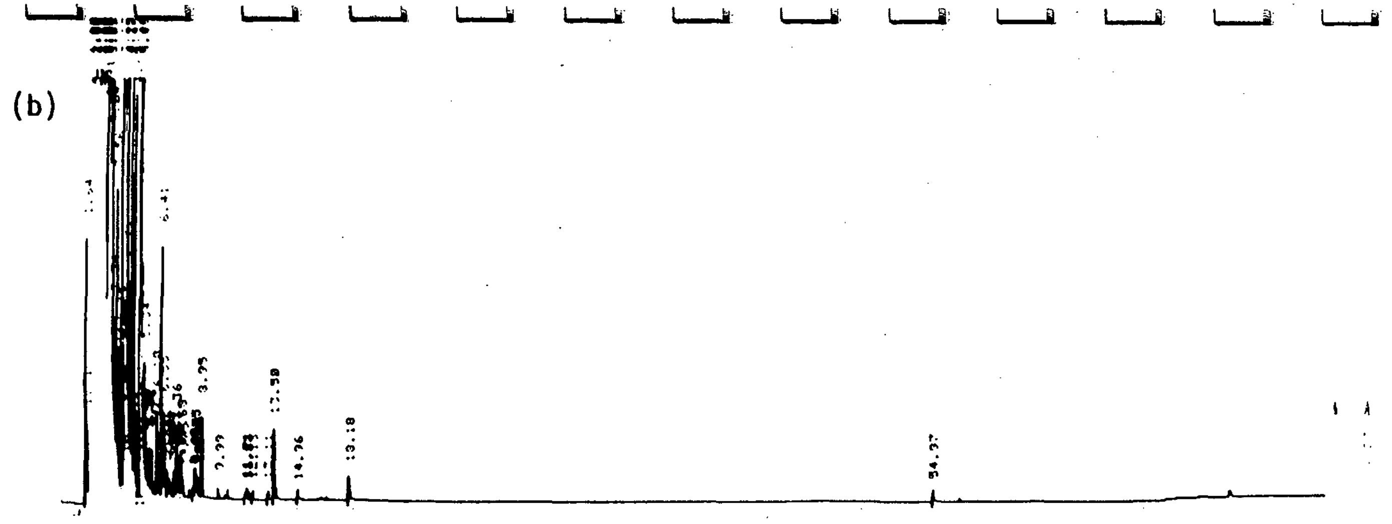


Figure 2a. Extraction solvent blank (30 mls MeOH + 30mls methylene chloride). 300 ul post-injection volume, 1 ul injected.



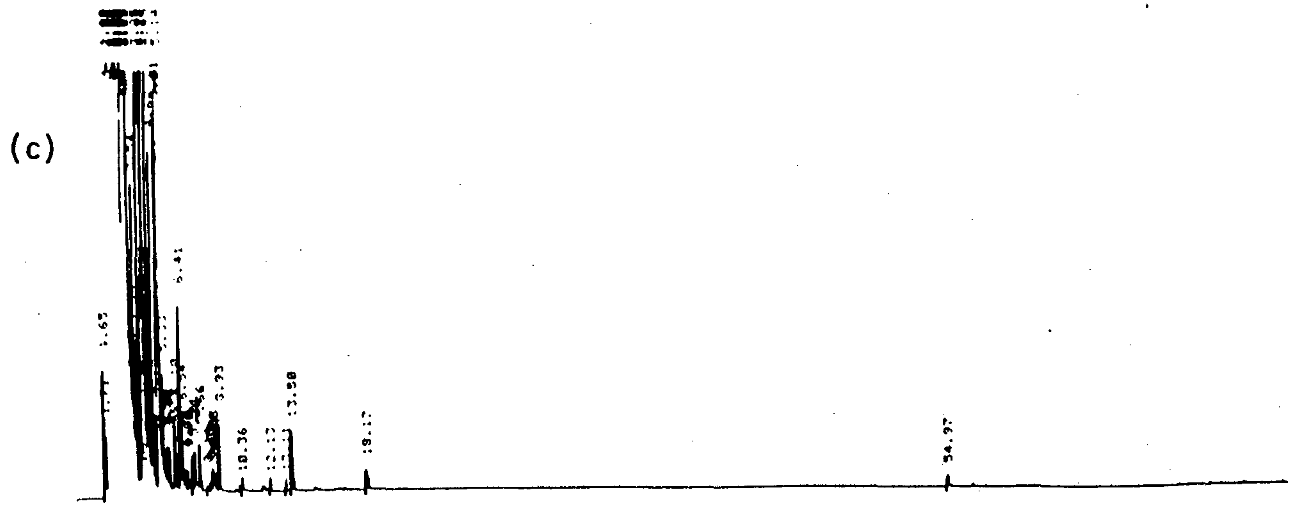


Figure 2b. Polyester filter blank (same solvents as in Figure 1a). 300 ul post-injection volume, 1 ul injected.

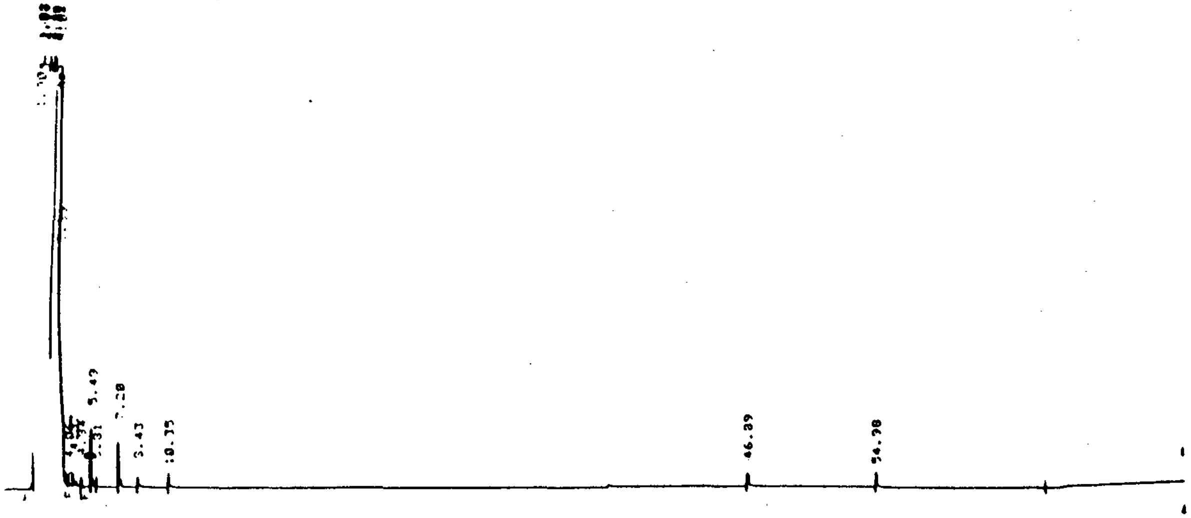
Figure 2c. Vacuum filtration blank using polyester filter (same solvents as in Figure 1a). 300 ul post-injection volume, 1 ul injected.

illustrated in Figure 2c, and is again identical to that in Figures 2a and 2b. Hence, vacuum filtration with the solvents introduced no artifact into the FID-GC chromatogram profile.

Because the sea water from an experimental oil-SPM-water sample would be passed through a filter in the normal processing sequence, one also had to consider whether some FID-GC artifact would be introduced into the water filtrate (i.e., the "dissolved phase") by the filter. To test this, 600 mls of whole sea water from the sea water pumping system at the NOAA field laboratory at Kasitsna Bay, AK was vacuum filtered (30 cm Hg) through a polyester filter. The filtrate was partitioned twice against 100 ml volumes of methylene chloride, and the combined methylene chloride fractions reduced to an appropriate volume and analyzed by FID-GC. A control consisting of 600 mls of whole sea water was processed in an identical manner, except that this sample was directly extracted without vacuum filtration. The chromatograms from these vacuum filtered sea water and sea water control samples are illustrated in Figures 3a and 3b, respectively. Their identical appearance indicates that no FID-GC artifact was introduced into the "dissolved phase" of a sample by the polyester filter.

A further test of the polyester filter procedure was performed with sediment collected from the upper intertidal zone at the head of Jakolof Bay near the NOAA field laboratory at Kasitsna Bay, AK. This sediment was first passed through a 53 µm geological sieve. The filtrate portion of this sediment was added to sea water (see Figure 2b for the FID-GC chromatogram of the latter) to a final concentration of 54.6 mg dry weight/liter and stirred for 4.5 hours with a magnetic stir bar. This SPM-sea water solution was then vacuum filtered (30 cm Hg) through polyester filters. The water filtrates were extracted with methylene chloride, and the methylene chloride then condensed and analyzed by FID-GC for a "dissolved phase" sample. Additional vacuum filtrations on the polyester filters (containing the SPM) were then performed in the following sequence to obtain an "SPM phase" sample:

(a)



(b)

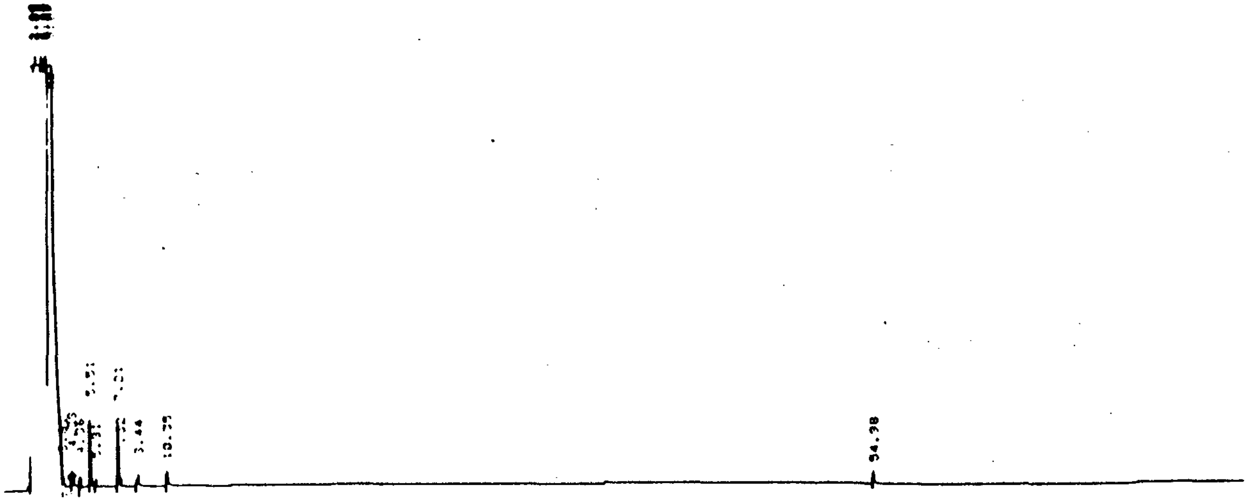
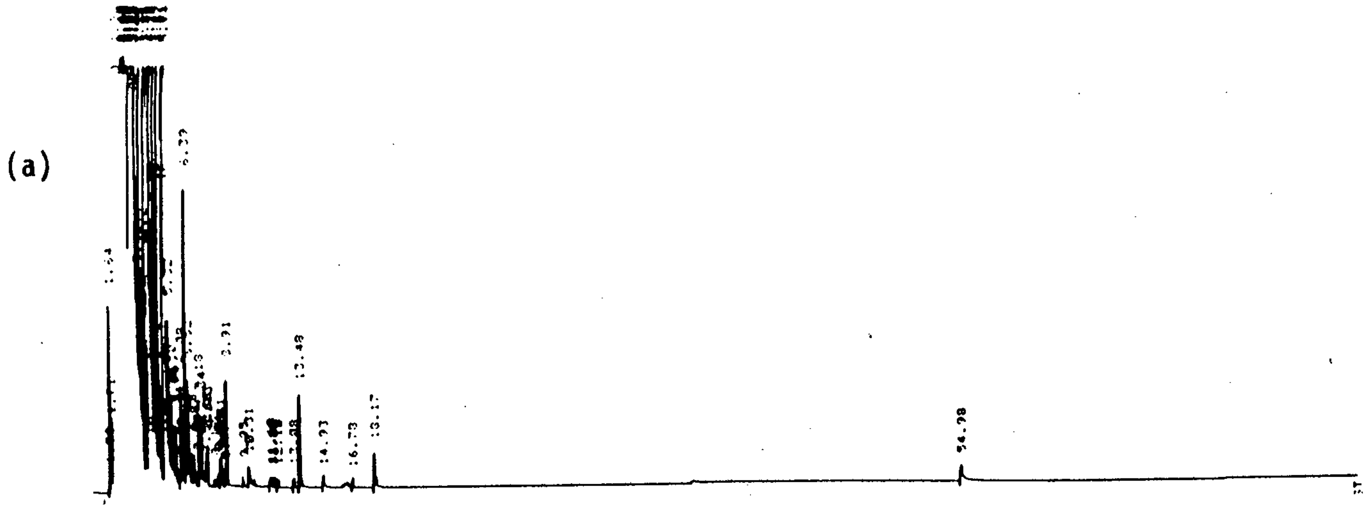


Figure 3a. Whole sea water extract. 600 mls sea water, 300 ul post-injection volume, 1 ul injected.

Figure 3b. Vacuum filtered whole sea water extract. 600 mls sea water, 300 ul post-injection volume, 1 ul injected.

1) approximately 10 mls of hydrocarbon-free distilled water (this removed residual sea water and salt and was discarded), 2) 15 mls of methanol and 3) 30 mls of methylene chloride. The combined methanol-methylene chloride filtrates were partitioned against sea water and the resulting methylene chloride fraction transferred to a collection flask. The remaining sea water-methanol solution was partitioned a second time against methylene chloride. The combined methylene chloride fractions were condensed and analyzed by FID-GC. As a control for the filtered SPM fraction, an equivalent dry weight of the Jakolof sediment was directly extracted in a beaker with comparable volumes of methanol and methylene chloride. The decanted methanol and methylene chloride fractions from the latter sample were combined and processed in an identical manner to that for the vacuum filtered SPM fraction. The FID-GC chromatograms for the vacuum filtered SPM and whole sediment extracts are illustrated in Figures 4a and 4b, respectively. The profiles are remarkably similar to each other and to the polyester filter blanks in Figures 2a through 2c. This indicated that the sediment in Figures 4a and 4b had essentially no extractable compounds detectable by FID-GC. The chromatogram from the sea water filtrate of the Jakolof SPM-sea water solution was identical to those of the sea water extracts in Figures 3a and 3b indicating that the Jakolof SPM did not introduce FID-GC detectable compounds into the "dissolved phase" of the sample.

A final test of the polyester filtration protocol was performed with an oil-SPM-water solution. The latter was prepared by making the following additions to a 1000 ml glass beaker: 1) 40.8 mg dry weight of the 53 μm sieved Jakolof sediments, 2) 600 mls of sea water and 3) 8.0 mls of unweathered Prudhoe Bay crude oil. The contents of the beaker were stirred with a magnetic stir bar for 9 hours and then transferred to a separatory funnel. The latter was allowed to sit for 3.5 hours to affect a separation of the oil and water phases. The water (and SPM) phase was then vacuum filtered (30 cm Hg) through polyester filters. The water filtrate was analyzed as the "dissolved phase" for hydrocarbons. The filters were then vacuum extracted with fresh water, methanol and methylene chloride in a manner identical to



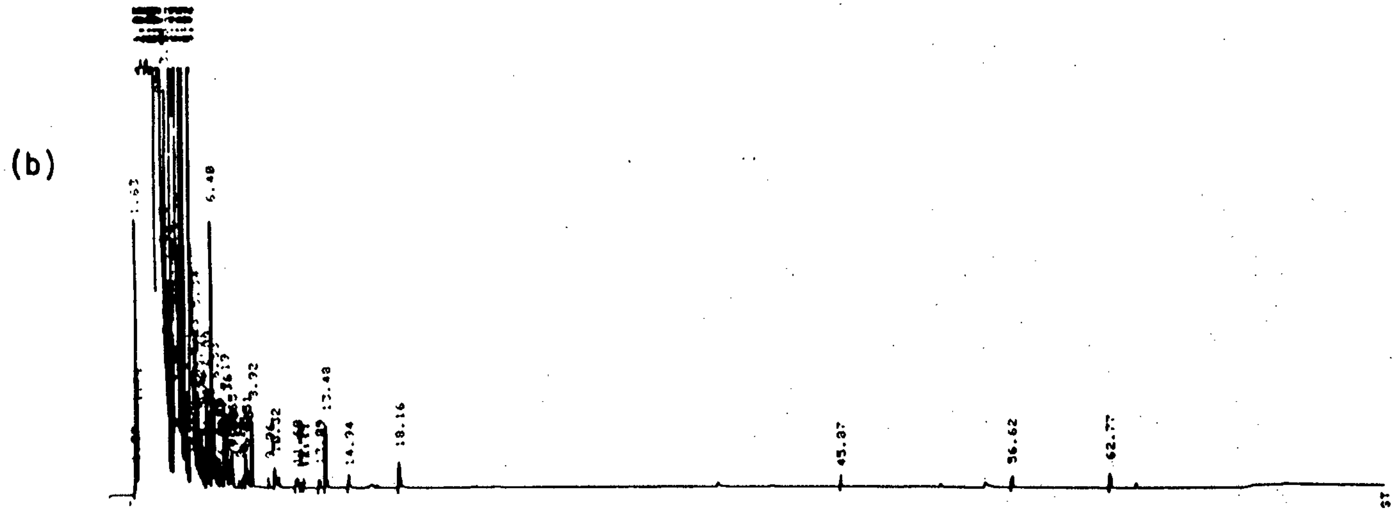


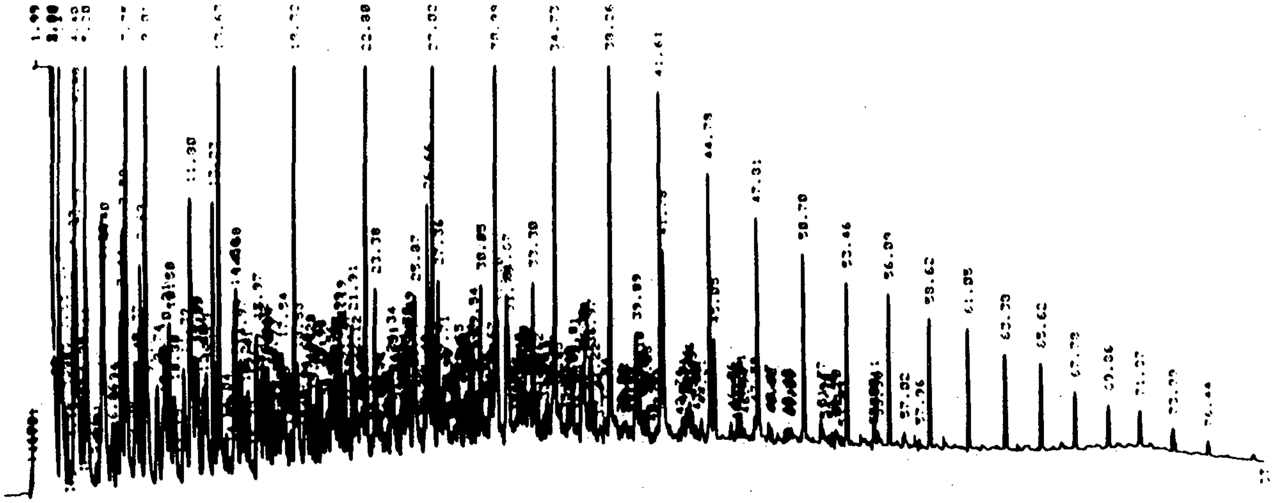
Figure 4a. Vacuum filtered extract of Jakolof Bay SPM/sea water system. 32.7 mg dry SPM in 690 mls sea water, 400 ul post-injection volume, 1 ul injected.

Figure 4b. Extract of Jakolof Bay SPM used in Figure 4a. 31.8 mg dry SPM, 400 ul post-injection volume, 1 ul injected.

that for the sample described in Figure 4a. To evaluate whether the solvent rinses (i.e., methanol and methylene chloride) of the filters were sufficient to recover all of the oil from the SPM, an additional 30 mls of methylene chloride was vacuum filtered and analyzed separately by FID-GC. A FID-GC chromatogram of the Prudhoe Bay crude oil used in this experiment is presented in Figure 5a. The FID-GC chromatogram of the sea water filtrate (i.e., "dissolved phase") is shown in Figure 5b. Comparison of the two chromatograms demonstrates that aliphatic n-alkanes so apparent in the parent crude oil do not appear in the "dissolved phase" of the sample. The peaks that are present in the "dissolved phase" correspond to aromatic hydrocarbons, which are characterized by greater water solubilities. These results agree with previous findings in our currently funded programs. The FID-GC chromatograms of the initial solvent rinse of the polyester filters (i.e., the normal "SPM phase") of the sample and the second solvent rinse of the filters are presented in Figures 5c and 5d, respectively. The normal "SPM phase" (Figure 5c) has a chromatographic profile for n-alkanes and other aliphatic compounds that is very similar to that of the parent crude oil (Figure 5a), except that the more volatile low molecular weight n-alkanes are partially missing. The latter observation reflects the selective evaporation of these compounds during the initial 9 hour stirring phase of the experiment when the oil-SPM-water system was open to the atmosphere. Because the second methylene chloride rinse of the filter (Figure 5d) yielded a chromatogram with essentially none of the oil indicated in Figure 5c, the solvent rinse sequence in the filter processing protocol (i.e., methanol followed by 30 mls of methylene chloride) appears to be nearly 100% efficient in recovering petroleum hydrocarbons from the filtered SPM.

The sum of the preceding results indicate that the combined separatory funnel/polyester filter technique will allow for oil hydrocarbon components to be identified in discrete "SPM", "dissolved" and "dispersed phases". The polyester filters also do not introduce any FID-GC detectable contamination into the various phases of a sample. It must be emphasized, however, that a complete physical separation of dispersed oil droplets from

(a)



(b)

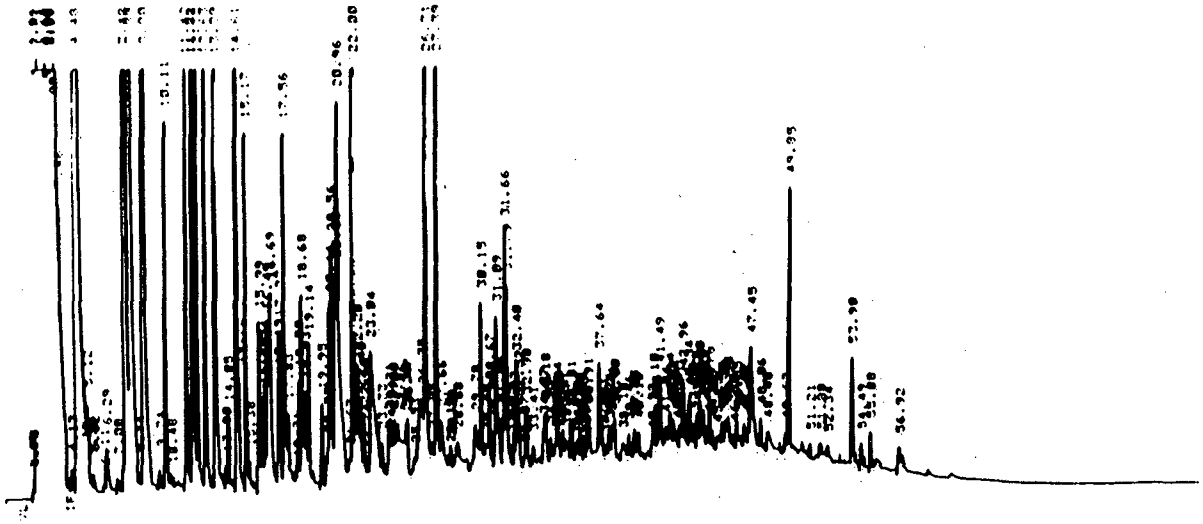
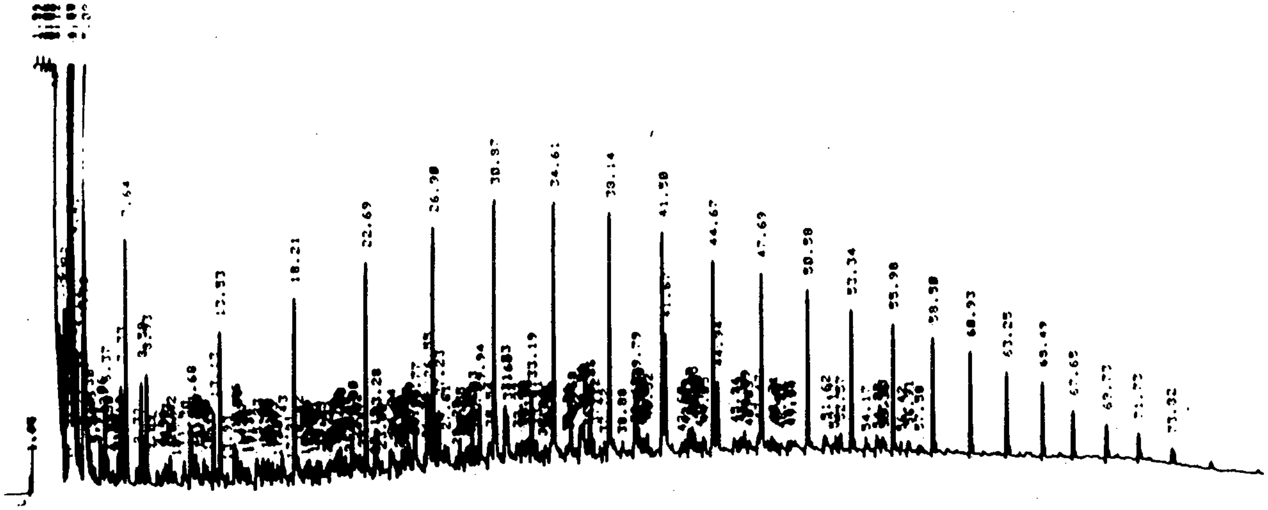


Figure 5a. Unweathered Prudhoe Bay crude oil used for experimental oil-SPM-water system. 19.2 mg oil/1800 ul methylene chloride; 1 ul injected.

Figure 5b. "Dissolved phase" from experimental oil-SPM-water system. 600 mls sea water, 400 ul post-injection volume, 1 ul injected.

(c)



(d)

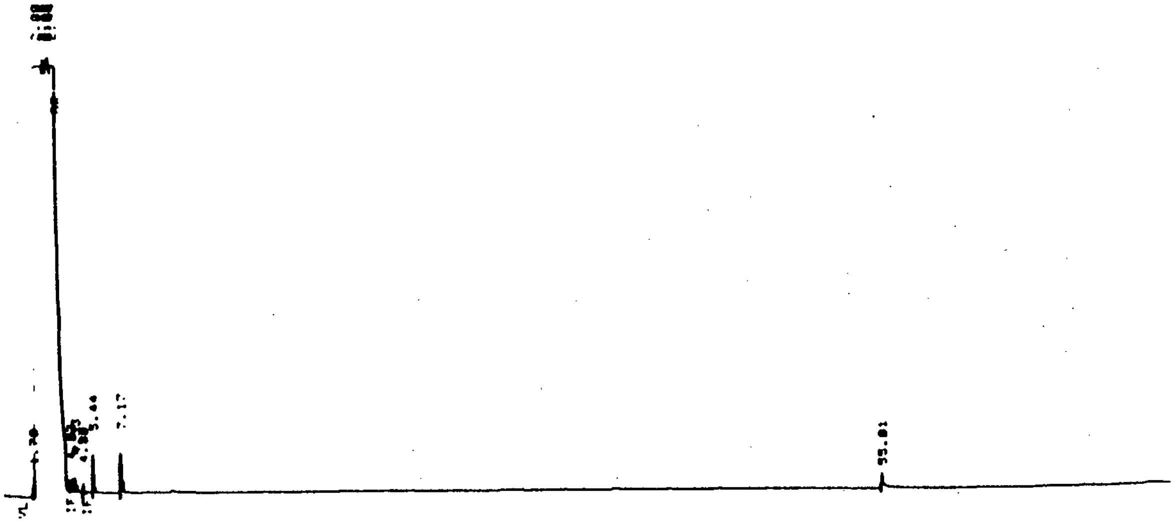


Figure 5c. "SPM phase" from experimental oil-SPM-water system. 40.8 mg dry SPM, 400 ul post-injection volume, 1 ul injected.

Figure 5d. Second methylene chloride rinse of filter from "SPM phase" in Figure 5c. 400 ul post-injection volume, 1 ul injected.

SPM in a sample (e.g., in the separatory funnel) must be achieved for this procedure to yield unambiguous results.

Experimental Results from Outdoor Wave Tank Studies

An experimental oil spill was performed in an outdoor wave tank at the NOAA field laboratory at Kasitsna Bay, AK during March 1985. At the initiation of the spill, a total of 5 gallons (18.9 liters) of fresh Prudhoe Bay crude oil was poured into the wave tank that contained approximately 2800 liters of sea water in a flow-through mode (turn over time for the water was approximately 1 tank volume every 3 hours). Wave action was generated by a rotating paddle wheel at one end of the tank. Whole sediment obtained from Jakolof Bay near the NOAA lab was periodically added to the tank in the vicinity of the paddle. A portion of this sediment was kept suspended in the water column by the wave action generated by the paddle. Whole water samples were collected in separatory funnels before the spill and at specific time intervals thereafter. These samples were subsequently analyzed by FID-GC for their hydrocarbon content and composition in the "SPM", "dissolved" and "dispersed oil phases". Processing of water samples included separation of the water/SPM and dispersed oil phases in separatory funnels, but did not include filtration of the water/SPM portion of samples through polyester filters for definitive separation of the "SPM" and "dissolved phases". The actual SPM load in the water column of the wave tank at the time of a specific sampling event was measured in a separate water sample by vacuum filtration of a known volume through a tared polycarbonate membrane filter (Millipore Type HA, 25 mm diameter, 0.45 µm pore size). The filter was then dried in a dessicator and reweighed to determine the SPM load at the time of the sample.

The results of measurements pertaining to chemical and physical properties of the oil in the surface slick of the wave tank during the initial 12 days following the spill are summarized in Table 2. The observed trends agree with our previous findings in comparable flow-through wave tank experiments. For example, the quantities of both FID-GC total resolved and unresolved compounds per gram of oil declined. This resulted from a continuing loss of

Table 2. Chemical and Physical Characteristics of Oil from Wave Tank #4 Oil/SPM Interaction Experiment

	Hydrocarbon Concentration (mg/g oil)		Interfacial Tension (dynes/cm)		Viscosity @ 38°C (centipoise)	Water Content (% by weight)
Time	Total Resolved	Unresolved Compounds	Oil/Water	Oil/Air		
ting Crude	119	229	24.6	31.8	30	.30
24 hours	87.2	204	7.0	33.2	43	.35
48 hours	63.8	145	11.1	33.0	43	.17
4 days	36.5	106	9.2	33.8	180	47.0
7 days	29.5	112	13.0	32.0	200	8.9
12 days	27.5	104	11.5	34.6	800	6.3

more water soluble and volatile compounds from the bulk oil, with a consequent enrichment in refractory compounds that were not detectable by the FID-GC procedure. Oil-water interfacial tension values declined while both the viscosity and water content of the oil increased during the course of oil weathering. In conjunction with the trends in these chemical and physical properties, visual observations over this time period indicated that the bulk surface oil became much less fluid (i.e., it took on a somewhat "congealed" appearance). This latter change was accompanied by a noticeable decrease in the tendency to form small dispersed oil droplets that were injected by wave action into the underlying water column. Although decreasing oil/water interfacial tension values will favor increasing dispersion of oil into the water, this trend does not become effective until interfacial tension values decrease to at least 5 dynes/cm (Payne and Phillips, 1985a). Since this value was not reached, the increasing viscosity of the oil was presumably responsible for the visible decline in dispersed oil droplets in the water column over time (see Table 2).

Results of the FID-GC measurements for total hydrocarbons (i.e., total resolved components plus the unresolved complex mixture) in the "dispersed oil", "dissolved" and "SPM phases" of water samples collected in separatory funnels from the wave tank are summarized in Table 3 and the temporal trends are illustrated in Figure 6. The concentrations of the "dispersed oil fraction" had their highest values (approximately 5 mg total hydrocarbons/liter) at 1 hour after the spill. The levels then declined, showing agreement with the visual observations of declining dispersed oil droplet formation noted above. This decline in total "dispersed oil" levels measured by FID-GC would have resulted from two factors: 1) the flow-through characteristic of the wave tank (i.e., the inherent turn over rate for the water in the tank tended to "flush out" dispersed oil droplets from the water column) and 2) the natural weathering of the oil (specifically, its increasing viscosity) tended to inhibit further dispersion of oil droplets into the water column. The concentrations of total hydrocarbons in the "dissolved" and "SPM phases" of the water samples achieved their maxima (0.5-0.7 mg/liter) at 1-4

Table 3. Results of Outdoor Wave Tank Oil/SPM Partitioning Experiment

	Concentration[a] (ppm)				
			Particulate Bound Oil[b]		
Sample Time	Dispersed Oil	Dissolved Oil	Relative to the SPM Load	Relative to the Water Mass	SPM Load
1 hour	5.13	.441	172	.00339	19.7
4 hours	3.13	.512	2250	.707	314
8 hours	3.62	.252	3460	.107	31.0
24 hours	.104	.0299	700	.0281	40.2
48 hours	.105	.0703	350	.0327	93.5
72 hours	.0277	--	ND[c]	ND	24.9
5 days	.0273	.0528	ND	ND	2.8 (ambient)

[a] - Concentrations shown are the sum of all resolved compounds and the unresolved mixture.

[b] - "Relative to the SPM load" is an indication of the ug of oil associated with one g of SPM, whereas "Relative to the water mass" is an indication of the mg of particle bound oil in one liter of the water column.

[c] - "ND" indicates "not detected"

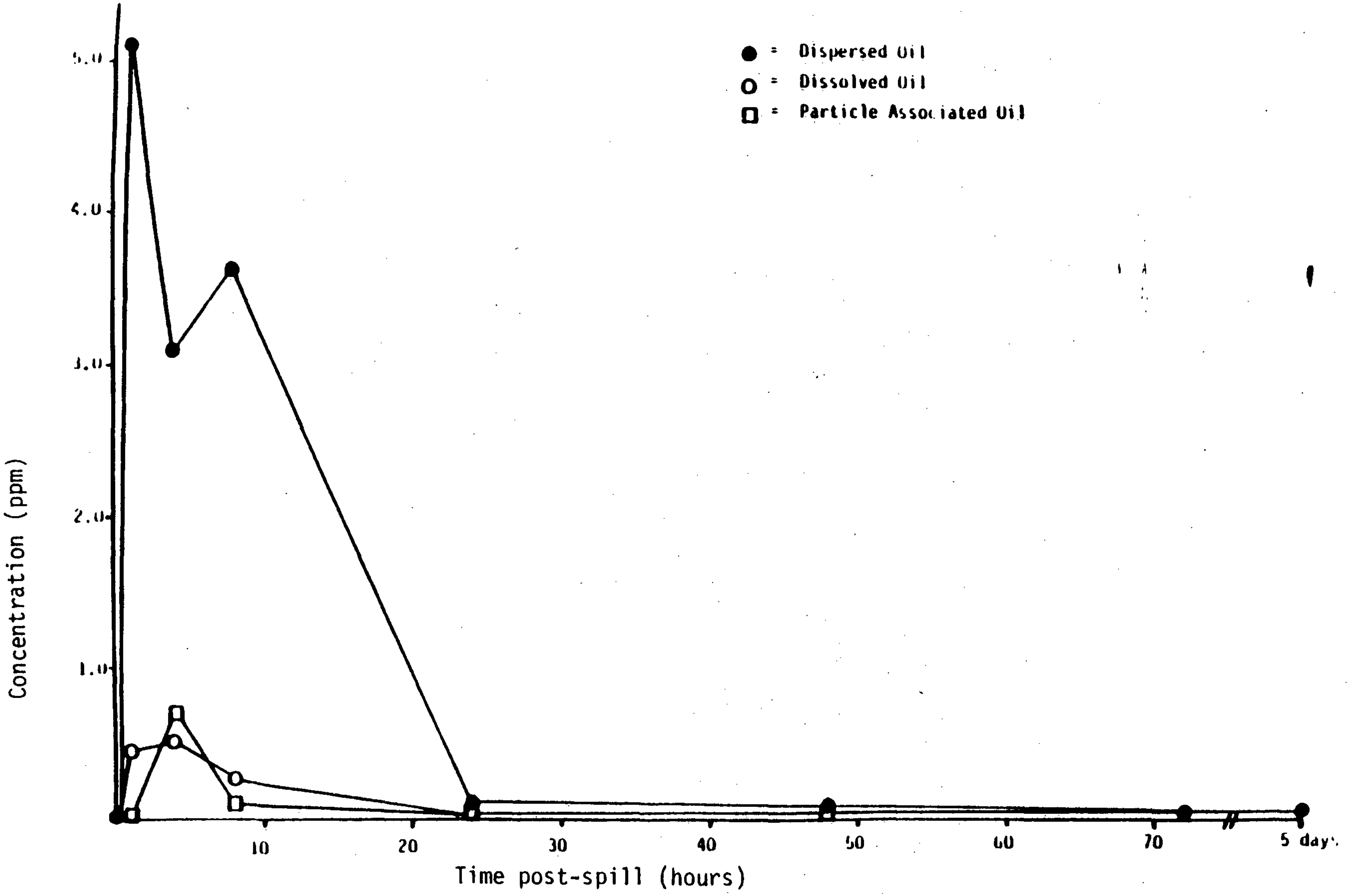


Figure 6. Results of outdoor wave tank oil/SPM partitioning experiment.

hours post-spill. Subsequent declines in the hydrocarbon concentrations in both of these sample phases resulted from the same factors influencing the "dispersed oil" concentrations: 1) the flow-through mode for the water in the wave tank and 2) the weathering of the bulk surface oil. The decline in the oil content in the "SPM phase" was also affected by lower total SPM loads in the water column after the 4 hour sampling time. This is supported by the fact that total FID-GC hydrocarbon concentrations in the "SPM phase" normalized to the mass of SPM actually achieved a maximum at 8 hours rather than 4 hours post-spill (see Table 3). Subsequently, declines in the SPM hydrocarbon levels coincided with declining "dispersed oil" levels. Consequently, in this wave tank experiment the temporal association of oil with SPM particles was a "relatively" slow process. For example, observed maxima in SPM hydrocarbon levels on a particle mass basis did not occur until 8 hours post-spill, even though substantial "dispersed oil" was available to interact with SPM by 1 hour post-spill. It should also be noted that total FID-GC hydrocarbon levels in the "SPM phase" (normalized to the volume of water sampled) were less than those in either the "dispersed oil" or "dissolved phases", except when very high SPM loads (e.g., >300 mg dry weight/liter) were present in the water column.

In addition to the preceding trends in total hydrocarbon concentrations, differences were observed in the specific compositions of the FID-GC hydrocarbons in the bulk surface oil over time. For example, Figures 7a, 7b and 7c are chromatograms of surface oil collected from the wave tank at 1, 4 and 9 days post-spill, respectively. Although n-alkanes persist as major components in the oil in these samples, compounds with shorter retention times (e.g., lower molecular weight n-alkanes and aromatic compounds) selectively disappear over time. Similar changes in the composition of surface oils as they weather by natural processes have been noted in other investigations (e.g., Boehm et al., 1982; Payne and McNabb, 1984). This trend of selective losses of lower molecular weight constituents results from the greater volatilities and water solubilities of the lower molecular weight aliphatic and aromatic compounds.

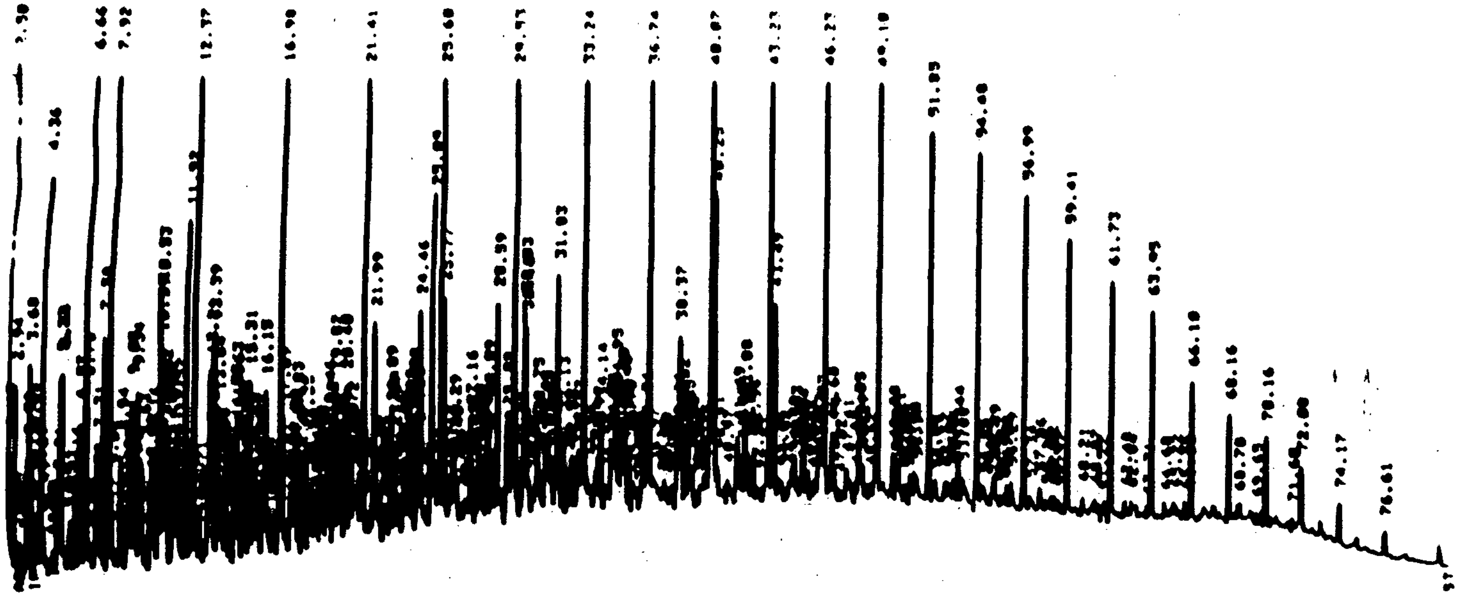


Figure 7a. Surface oil, 1 day post-spill, outdoor wave tank experiment.

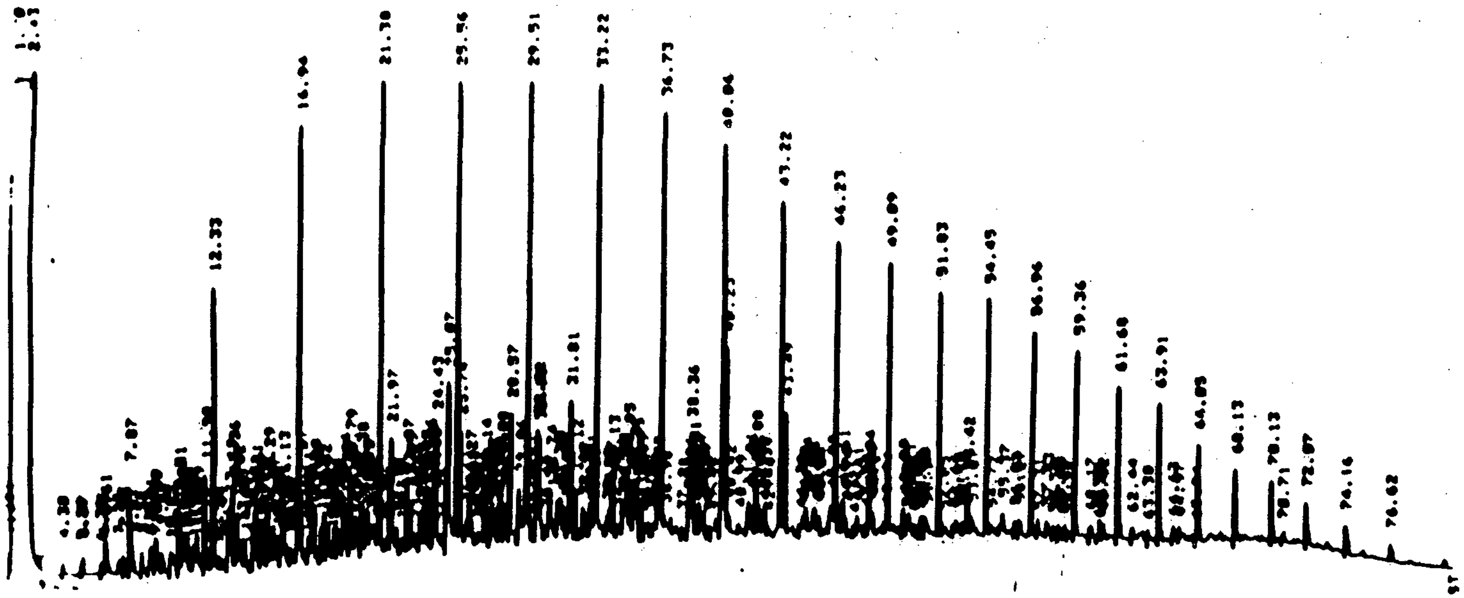


Figure 7b. Surface oil, 4 days post-spill, outdoor wave tank experiment.

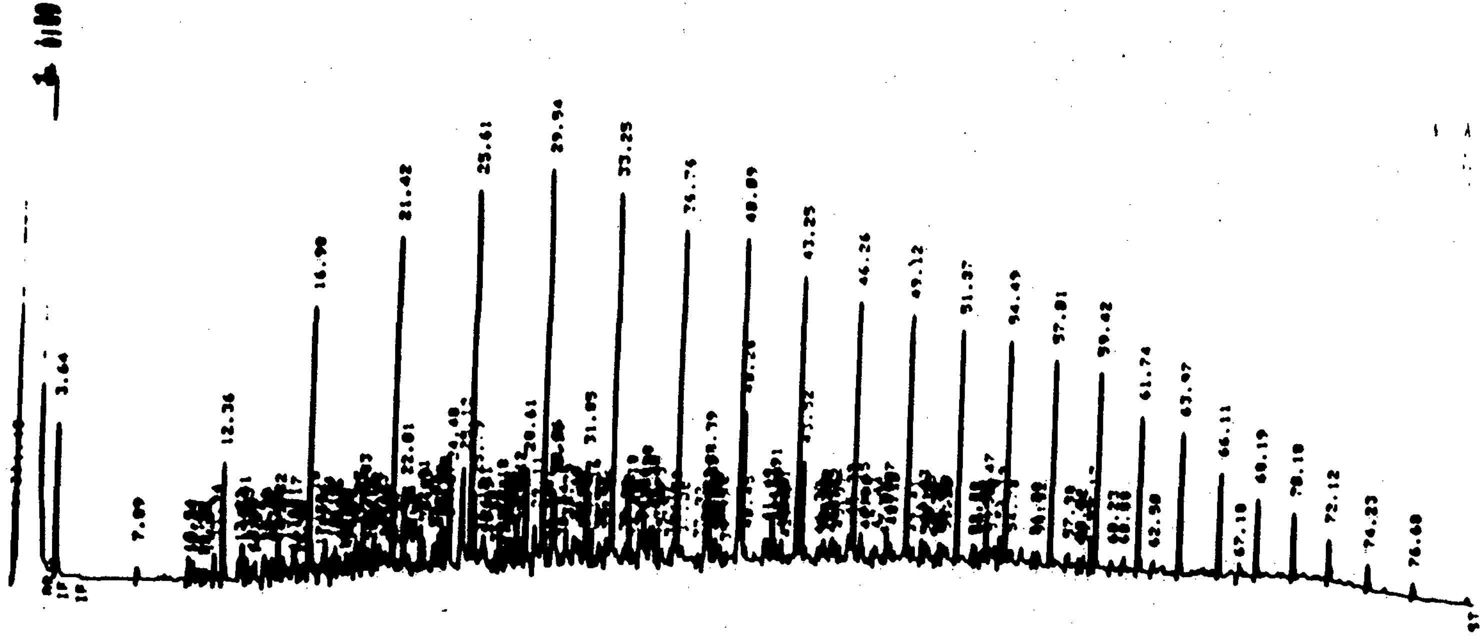


Figure 7c. Surface oil, 9 days post-spill, outdoor wave tank experiment.

Interesting compositional changes in the specific hydrocarbons in the three phases of a water sample (i.e., "dispersed oil", "SPM" and "dissolved") were also observed. Chromatograms of these fractions from the 4 hour post-spill sampling time are illustrated in Figures 8a, 8b and 8c. A very marked predominance of aliphatic compounds (particularly n-alkanes) can be noted in both the "dispersed oil" and "SPM phases". However, lower molecular weight aliphatic and aromatic compounds that were still present in the bulk surface oil (e.g., see Figure 7a for surface oil at the 24 hour post-spill time point) had either substantially declined or disappeared from these "dispersed oil" and "SPM phases" at the 4 hour post-spill time. These declines in lower molecular weight aliphatic and aromatic compounds (relative to the bulk surface oil) would be the result of the large surface areas of both the small dispersed oil droplets and the "oiled" SPM particles, allowing for selective dissolution of more soluble hydrocarbon components (e.g., lower molecular weight aliphatic and aromatic compounds) into the ambient aqueous medium. In contrast to the "dispersed oil" and "SPM phases", the "dissolved phase" of the 4 hour post-spill sample (Fig. 8c) is comprised almost exclusively of aromatic compounds, supporting the phenomenon of greater water solubilities of the aromatic hydrocarbons. Quantities of specific aromatic compounds in the "dissolved phase" of the samples from 1 hour to 7 days post-spill are summarized in Table 4. The sequence of compounds in the table are listed according to sequentially increasing retention times in the FID-GC chromatograms. This sequence also reflects a general decrease in aqueous solubilities and volatilities of individual compounds. The declines in the concentrations for all of the aromatic compounds over time is due to both the flow-through mode of the wave tank (i.e., dissolved compounds are "flushed out" of the tank) and decreasing dissolution and/or availability of individual compounds from the bulk surface oil as a result of oil weathering. At the same time, the magnitude of the declines for individual compounds (e.g., the ratios of concentrations of 7 days to those at 1 hour post-spill) were much greater for compounds with shorter retention times. This reflects the greater water solubilities and volatilities of the compounds at the shorter retention times. Hence, over

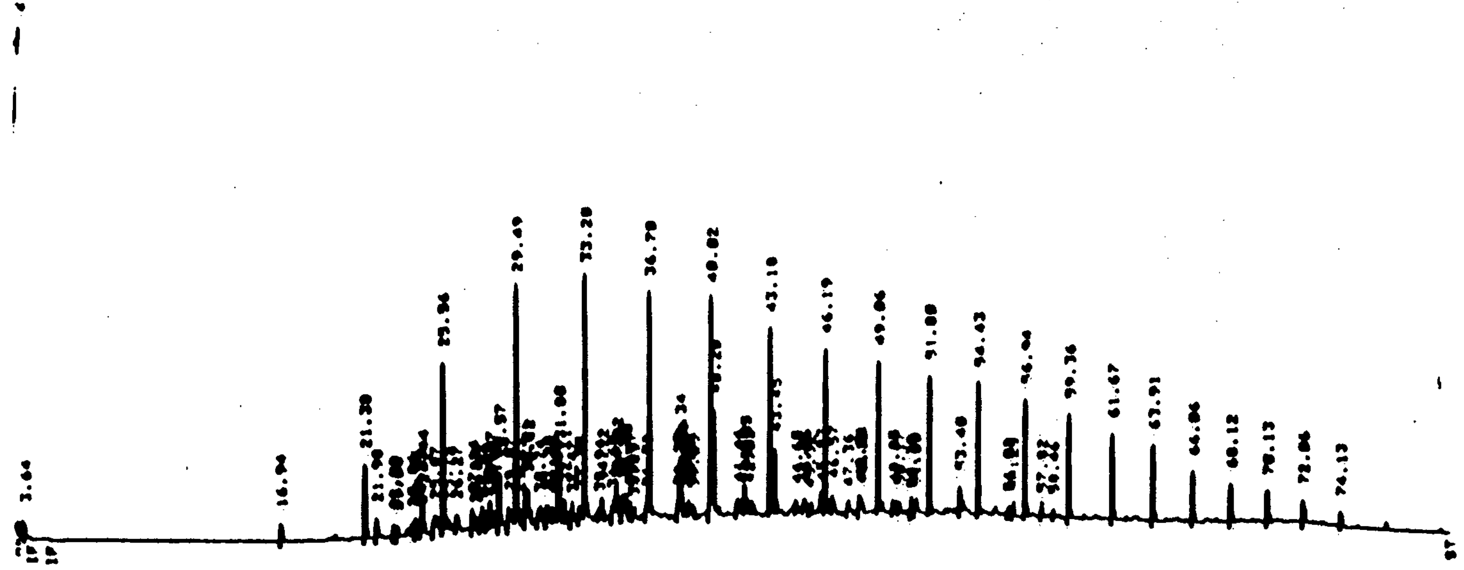


Figure 8a. "Dispersed oil" phase, 4 hours post-spill, outdoor wave tank experiment.

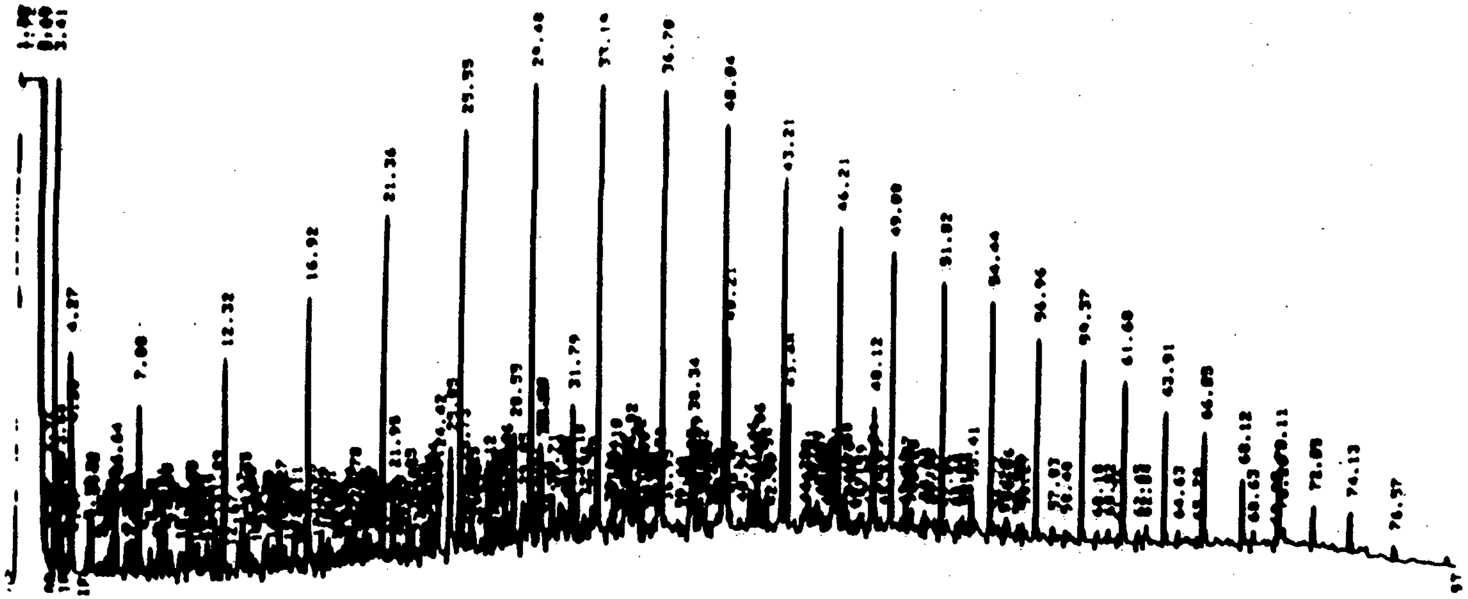


Figure 8b. "SPM" phase, 4 hours post-spill, outdoor wave tank experiment.

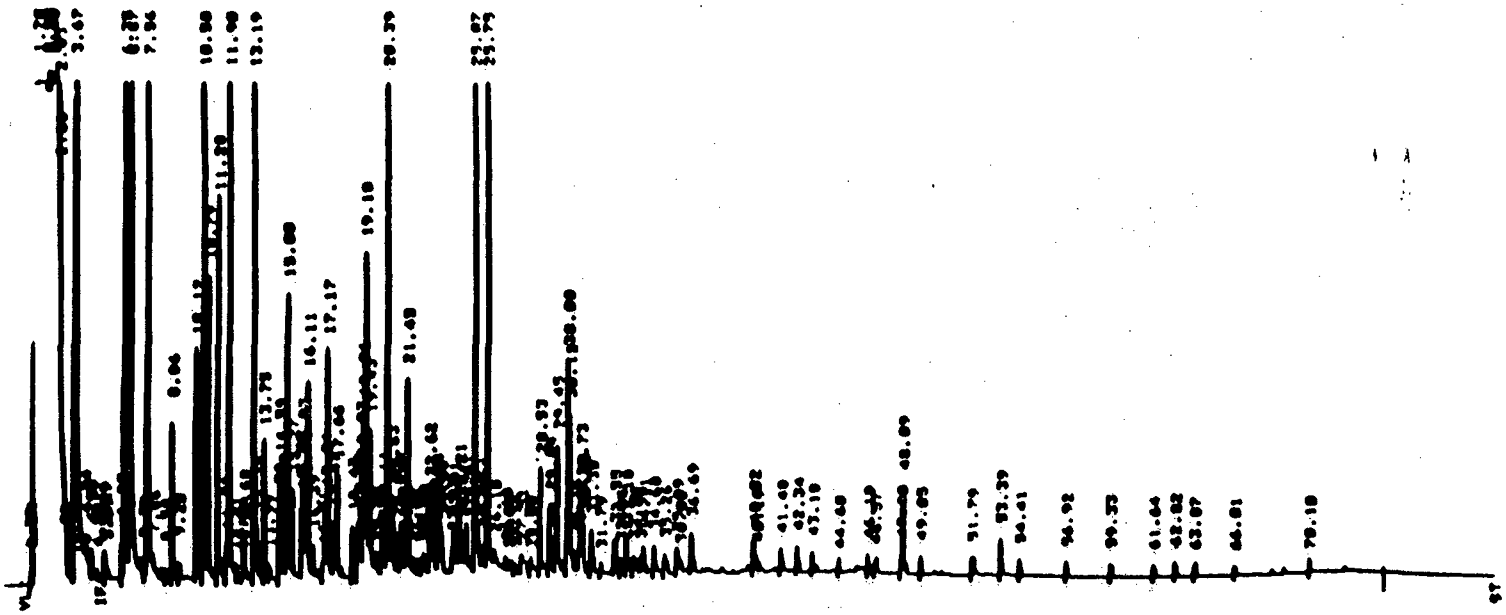


Figure 8c. "Dissolved" phase, 4 hours post-spill, outdoor wave tank experiment.

Table 4. Dissolved Compound Concentrations from the Wave Tank #4 Oil/SPM Interaction Experiment

Compound	Concentration (ug/l)					
	1 hr	4 hrs	8 hrs	24 hrs	2 days	7 days
Toluene	155	158	48.7	6.95	2.06	1.08
Ethylbenzene	17.5	19.1	7.57	1.09	1.17	ND
m & p-xylene	55.4	63.8	24.9	2.35	5.38	.378
o-xylene	25.5	30.6	12.8	2.86	3.35	.222
Isopropylbenzene	1.99	2.40	.896	ND	.235	ND
n-propylbenzene	3.27	3.47	1.47	.277	.450	ND
C_3-benzene	11.3	12.4	5.41	.574	1.87	.575
C_3-benzene	3.77	4.24	1.77	ND	.713	.274
1, 3, 5-trimethylbenzene	4.99	5.67	2.47	.424	.930	.309
C_3-benzene	13.0	14.6	6.82	.324	2.61	1.17
C_4-benzene	8.21	9.72	4.37	1.70	1.86	.972
Tetramethylbenzene	1.54	2.95	1.00	ND	ND	ND
Naphthalene	14.3	20.2	10.2	.349	3.64	2.79
2-methylnapthalene	13.5	15.0	8.65	.269	3.22	3.93
1-methylnapthalene	10.8	12.4	7.00	.305	2.53	2.93
1, 1'-biphenyl	1.71	1.82	1.12	ND	.335	.487
2, 6-dimethylnaphthalene	3.65	3.35	2.18	ND	.732	1.03
C_2-Naphthalene	4.20	3.77	1.68	ND	.622	.782
C_2-Napthalene	.790	.710	.442	ND	ND	.208
C_2-Naphthalene	1.00	.779	.385	ND	ND	.186
2, 3, 5-trimethylnapthalene	.628	.466	ND[a]	ND	ND	ND
Dibenzothiophene	.501	.395	ND	ND	ND	.152
Phenanthrene	.662	.459	.348	ND	ND	.218
Total Resolved Compounds	393	435	167	21.3	35.7	24.6
Unresolved Compounds	48.3	77.3	84.5	8.64	34.6	28.2

[a] - ND indicates 'not detected'

time the relative availability of these compounds, for dissolution from the parent surface oil declined. This explanation is also supported by the chromatograms of the surface oil (see Figures 7a, 7b, and 7c) which show a selective disappearance over time of compounds at the shorter retention times. Because the water/SPM portions of the samples from this wave tank experiment were not filtered through polyester filters, the very low quantities of n-alkanes at the longer retention times in Fig. 8c (i.e., "dissolved phase") may be indicative of inclusion of small amounts of "oiled" SPM particles in the "dissolved phase" of the sample.

Experimental Results from Stirred Chamber Studies

A total of eight experiments involving various combinations of oil, SPM and sea water in the stirred chamber have been performed in the past year. However, the first four of these did not include filtration of the aqueous portion of samples through polyester filters (i.e., to clearly distinguish "dissolved" and "SPM phases") and will, therefore, not be discussed in this progress report. Although the latter four experiments did incorporate the polyester filter technique, the final reduction of data from these experiments is still being completed. Therefore, only the information currently available at this time from these experiments (as well as the current status of the remaining samples) will be summarized below.

Three chamber experiments were performed at the NOAA field laboratory at Kasitsna Bay, AK and one at the SAIC facilities in La Jolla, CA. For the experiments at Kasitsna Bay, a 28 liter volume of sea water from the offshore pumping system at the lab was added to the chamber. Because ambient SPM loads (> 0.45 μm) in the natural sea water at Kasitsna Bay were never greater than 2.8 mg dry weight/liter during the experiments, the sea water added to the stirred chamber for these experiments was not pre-filtered. Sea water for the experiment at the SAIC facilities in La Jolla was collected from the offshore pumping system at the Scripps pier. The latter water was pre-filtered through Whatman #1 filter paper before addition to the chamber to remove ambient SPM particles. Sediment for all four chamber experiments was collected from the upper intertidal zone at the head of Jakolof Bay near the NOAA lab at Kasitsna Bay in June 1985. The parent sediment was kept frozen. For an experiment, the portion of the thawed sediment that passed through a 53)m geological sieve and subsequently sedimented out of a 12 cm deep, stationary water column in 2.5 hours was used. Sufficient quantities of the latter sediment were added to the sea water in the chamber to yield final SPM loads of approximately 50 mg dry weight/liter in the Kasitsna Bay experiments and 40 mg dry weight/liter in the La Jolla experiment. A relatively high level of turbulent energy (compared with natural open ocean levels) was maintained in the chamber throughout the experiments by a dual paddle system rotated at 89 rpm. The three experiments conducted at Kasitsna Bay (but not the La Jolla experiment) received additions of various types of oil to the SPM/sea water in the chamber. To initiate the oil experiments, the paddle system was momentarily stopped and 300 mls of a specified oil type were gently poured onto the surface of the water in the chamber. The oil to sea water ratio in these chamber experiments (i.e., 300 mls oil to 28 liters sea water = 0.0107) was approximately twice that in the outdoor wave tank experiment discussed earlier (i.e., 15.2 liters oil to 2800 liters sea water = 0.0054). The types of oil used in the Kasitsna Bay stirred chamber experiments included the following: 1) fresh Prudhoe Bay crude, 2) 2 day weathered Prudhoe Bay crude and 3) 12 day weathered Prudhoe Bay crude. The latter two oil types had been collected in March 1985 from the outdoor wave tank experiment at Kasitsna Bay discussed above. These weathered oil types were maintained in a cold room or refrigerator until the time of the stirred chamber experiments. All four chamber experiments (i.e., the three at Kasitsna Bay and one at La Jolla), were conducted at ambient room temperatures (21 - 22°C).

During a stirred chamber experiment, whole water samples were collected through a side port in the chamber (approximately 30 cm below the air-water interface) into a separatory funnel and subsequently processed with the polyester filter technique for both hydrocarbon and SPM load determinations. Since no oil was added to the chamber in the La Jolla experiment, only SPM load determinations were made in this experiment. Samples were collected at specified time intervals following either the oil spill event (Kasitsna Bay experiments) or addition of SPM to the chamber (La Jolla experiment) to allow for time course measurements of experimental variables such as SPM loads in the water column and interactions between the oil, SPM and water phases. Immediately following the collection of a water sample, an equivalent volume of sea water with the same SPM load (i.e., 50 mg dry weight/liter at Kasitsna Bay and 40 mg/liter in La Jolla) was added to the chamber to maintain a constant water volume (and, hence, vertical distance between the air-water interface and the stir paddle surfaces) in the chamber.

Information pertaining to the SPM loads in the water columns during each of the four chamber experiments is illustrated in Figure 9. In the experiment containing Jakolof sediment and fresh Prudhoe Bay crude oil ("fresh oil"), the initial SPM load of approximately 50 mg/liter began to decline after 24 hours, and by 120 hours post-spill had reached levels of only 25 mg/liter. Visible accumulation of SPM on the floor and sides of the stirred chamber was not obvious until the last sampling time (i.e., 216 hours post-spill). Consequently, the declines in the SPM levels in the water column prior to 216 hours post-spill reflected incorporation of SPM particles directly into the dispersed oil droplets and/or the surface oil slick. Throughout the experiment the number density of small dispersed oil droplets ($\leq$ 1 mm diameter) increased visibly in the water column. After the stirring paddle in the chamber was stopped at 216 hours post-spill, the dispersed oil droplets in the water column rapidly returned to the water's surface. However, many of the dispersed oil droplets remained as discrete entities (i.e., they did not recoalesce into a continuous body of oil), and the droplets appeared to be coated with small gray-brown particles (presumably SPM, although no microscope was available to confirm this). The SPM that adhered to the floor and walls of the stirred chamber at 216 hours post-spill had taken on a "sticky" consistency which frequently appeared as "finger-like" strings of SPM agglomerates. This presumably reflected substantial "oiling" of individual SPM particles that adhered to each other rather than being directly incorporated

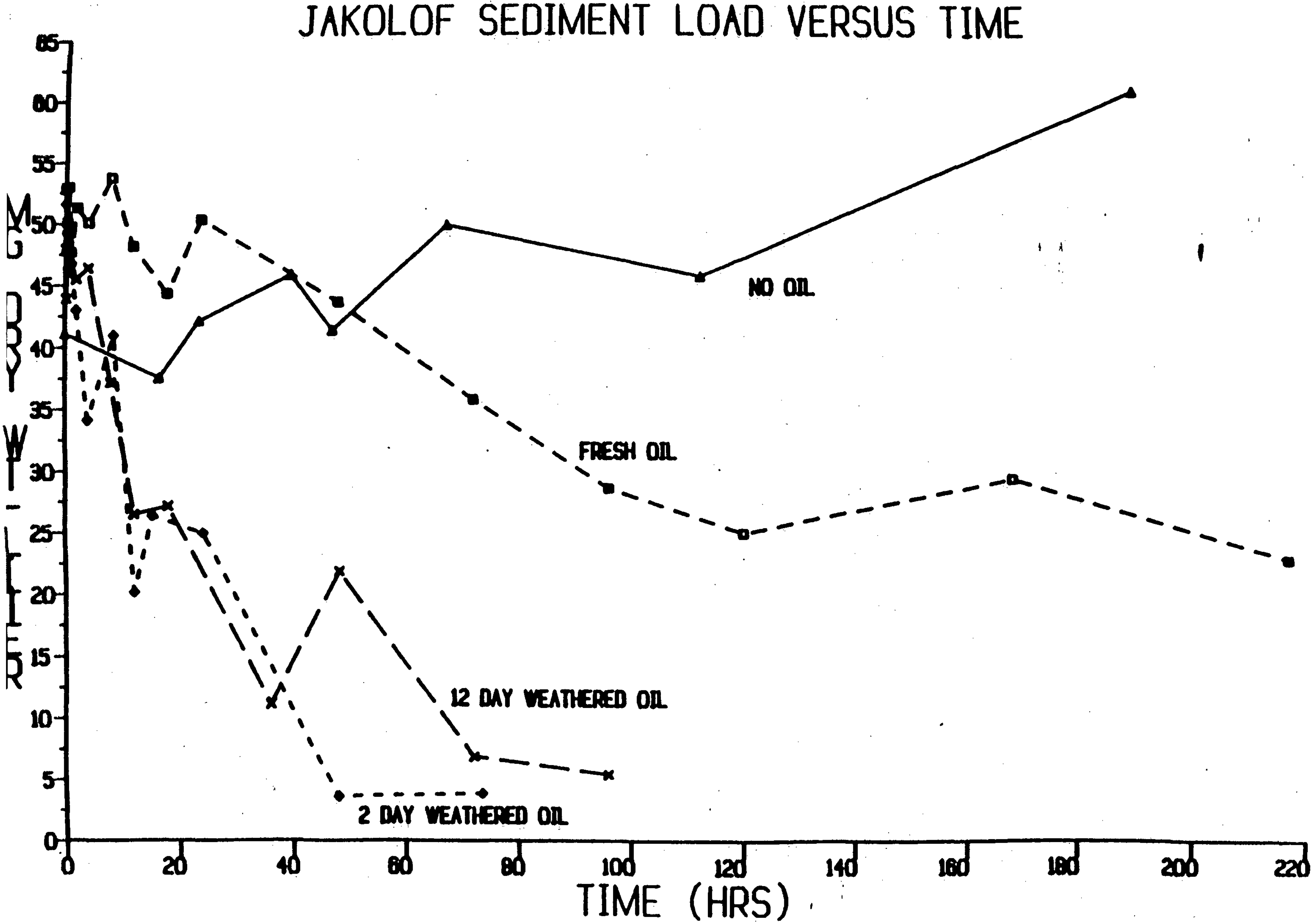


Figure 9. Temporal trends in SPM loads (mg dry weight/liter) for Jakolof Bay sediment in stirred chamber experiments with different types of Prudhoe Bay crude oil or no oil.

into either the dispersed oil droplets or the surface slick. Following contact of these "sticky" particles with either the walls of the chamber or other "sticky" particles adhering to the walls, the turbulence level in the chamber was no longer sufficient to keep these "sticky" particles in suspension. The preceding quantitative and visual behavior of SPM loads over time in stirred chamber experiments with 2 and 12 day weathered Prudhoe Bay crude oil were even more pronounced. In both of the latter experiments the initial SPM loads of approximately 50 mg dry weight/liter had declined to only 4-6 mg/ liter by 48-72 hours post-spill, and the appearance of "sticky" SPM adhering to the floor of the stirred chamber began to occur by 24-36 hours post-spill.

To confirm that the declines in SPM loads in the water columns of the preceding stirred chamber experiments were related to the presence of oil, the chamber experiment in La Jolla was conducted without any oil addition. As shown in Figure 9, the SPM load levels in the latter experiment never declined. Particle "flakes" (>53 µm) began to appear in the chamber after 16-24 hours, and the SPM load actually increased at later sampling times. Neither "flake" formation nor increasing SPM loads were observed in any of the chamber experiments that received additions of fresh or weathered crude oil. Observations of SPM samples were periodically made throughout the "no oil" experiment with a phase contrast light microscope. At the start the SPM in the chamber consisted of >50% diatom tests, with no microorganisms being "visibly" apparent. Observation of an SPM "flake" at 40 hours indicated the same general sediment composition (i.e., >50% diatoms) but a definite presence of unidentified motile microorganisms in association with the "flakes". Formation of the "flakes" from individual SPM particles was probably mediated through exudation products of the microorganisms. Microscopic observations of SPM particles and "flakes" at 190 hours indicated that the motile microorganisms were no longer apparent. However, aggregations of amorphous brown particulates were now present and presumably contributed to the increasing SPM load levels. The microorganisms previously observed in samples may have been either directly or indirectly responsible for the formation of these amorphous brown particulates. Since neither "flake" formation nor increasing SPM levels were observed in the three experiments receiving oil additions, it is likely that dissolution of toxic aromatic compounds from the oil into the water column may have inhibited the growth of microorganisms.

To summarize information related to the trends in the SPM loads in Figure 9, the declines in the levels of SPM in the presence of oil seemed to be directly related to the occurrence of oil in the stirred chamber. Furthermore, this "interaction" between the oil and SPM was more pronounced with weathered oil. In the general processes contributing to the natural weathering of oil, the abundance of polar compounds typically increases due to reactions such as photochemical and microbial oxidation (e.g., see reviews in Payne and Phillips, 1985b and Karrick, 1977). Consequently, the more rapid "interactions" between the SPM and weathered oil (i.e., more rapid declines in the aqueous SPM loads) may have resulted from enhanced reaction rates due to greater surface charge characteristics in the dispersed droplets of weathered oil.

As noted previously, the three stirred chamber experiments conducted at the NOAA lab at Kasitsna Bay, AK included collection of samples for FID-GC hydrocarbon analyses. The single variable differing between these experiments was the type of oil added to a particular chamber (i.e., fresh, 2 day weathered, or 12 day weathered Prudhoe Bay crude oil). The final processing of all of these samples for hydrocarbon measurements has not been completed at this time. The current status of all of these samples is summarized in Table 5. Although all of the samples have been extracted for hydrocarbons, a substantial number from the first experiment (i.e., fresh crude oil) and all of the samples from the second and third experiments (i.e., 2 and 12 day weathered crude oil) await final FID-GC analysis and data reduction. It is anticipated that this will occur within the next several months as appropriate time and facilities become available. However, at the time of this report, a limited suite of data from the first experiment (i.e., fresh crude oil) has been completely reduced. The following is a brief discussion of this information.

Table 5. Status of Hydrocarbon Samples from Stirred Chamber Experiments

Experiment ID	Number of Samples			
	Surface Oil	Dispersed Oil	Dissolved Fraction	SPM Fraction
1) Fresh Prudhoe Bay crude + Jakolof sediments:				
a) Total samples	4	16	16	16
b) Samples extracted	4	16	16	16
c) Samples through FID-GC	2	10	7	10
2) 2 day weathered Prudhoe Bay crude + Jakolof sediments:				
a) Total samples	2	12	12	13
b) Samples extracted	2	12	12	13
c) Samples through FID-GC	0	0	0	0
3) 12 day weathered Prudhoe Bay crude + Jakolof sediments:				
a) Total samples	2	13	13	14
b) Samples extracted	2	13	13	14
c) Samples through FID-GC	0	0	0	0
SUMS FROM THE PRECEDING EXPERIMENTS:				
a) Total samples	8	41	41	43
b) Samples extracted	8	41	41	43
c) Samples through FID-GC	2	10	7	10

The concentrations of total FID-GC resolved hydrocarbons in the "dispersed oil", "dissolved" and "SPM phases" of water samples from the chamber experiment with fresh crude oil are summarized in Table 6. Temporal trends in the concentrations on a per liter sea water basis are illustrated in Figure 10. The "dispersed oil phase" exhibited steadily increasing concentrations of hydrocarbons through the first 72 hours after the spill event. The levels of total resolved hydrocarbons in the "SPM phase" also increased over this time, and this appeared to be directly related to increases in the concentrations in the "dispersed oil phase". The latter relationship between hydrocarbon levels in "dispersed oil" and "SPM phases" was also noted in the previously discussed outdoor wave tank experiment (see Table 3 and Figure 6). Such observations support the concept that a major route for getting oil onto SPM particles in aqueous systems is through interactions with dispersed oil droplets. This coupling between hydrocarbon levels in "dispersed oil" and "SPM phases" is also supported by pronounced similarities in the FID-GC chromatograms for the two phases of a sample. For example, chromatograms for the "dispersed oil" and "SPM phases" from the 24 hour post-spill sample are illustrated in Figures 11a and 11b, respectively. Both phases have an abundance of aliphatic compounds, typified by the n-alkanes. Similar observations of a close correlation between the hydrocarbon compositions on SPM particles and a parent No. 2 fuel oil were noted by Zurcher and Thuer (1978) for a "high energy" stirred regime that promoted dispersion of oil droplets into the water column.

Certain differences between the hydrocarbon compositions of the "SPM" and "dispersed oil phases" in Figures 11a and 11b are noteworthy, however. FID-GC compounds with shorter retention times are selectively lost from the "SPM phase" due to their greater water solubilities. The relatively large surface areas that would be characteristic of oil coatings on SPM or small dispersed oil droplets associated with the SPM particles would be particularly favorable to the dissolution of the more water soluble lower molecular weight compounds.

Table 6. Available Total Resolved Hydrocarbon Concentrations from Stirred Chamber Experiment

Fresh Prudhoe Bay Crude Oil and Jakolof Bay Sediments

	Total Resolved Hydrocarbon Concentration[1]				
			SPM Fraction		
Sample Time	Dispersed Oil Fraction (µg/l)	Dissolved Fraction (µg/l)	Normalized to SPM load (µg/g)	Normalized to water vol.(µg/l)	SPM Load (mg dry wt./l)
Pre-spill	0.0	0.0	38.2	2.0	52.9
15 minutes	41.7				50.1
30 minutes	90.5	67.2	171.5	9.1	53.0
60 minutes	NA	NA	NA	NA	47.7
2 hours	270.8	407.4	167.6	8.6	51.3
4 hours	596.4	664.0	125.0	6.3	50.1
8 hours	866.6	1373.4	530.9	28.6	53.8
12 hours	1421.2	1090.5	1221.7	58.9	48.2
18 hours		1073.3	1656.5	73.6	44.4
24 hours	3343.2		3510.9	177.0	50.4
48 hours	8725.0		7216.1	316.11	43.8
72 hours	12627.4		16296.6	585.0	35.9
96 hours					28.7
120 hours					25.0
168 hours					29.5
216 hours					23.0

[1] NA = not available

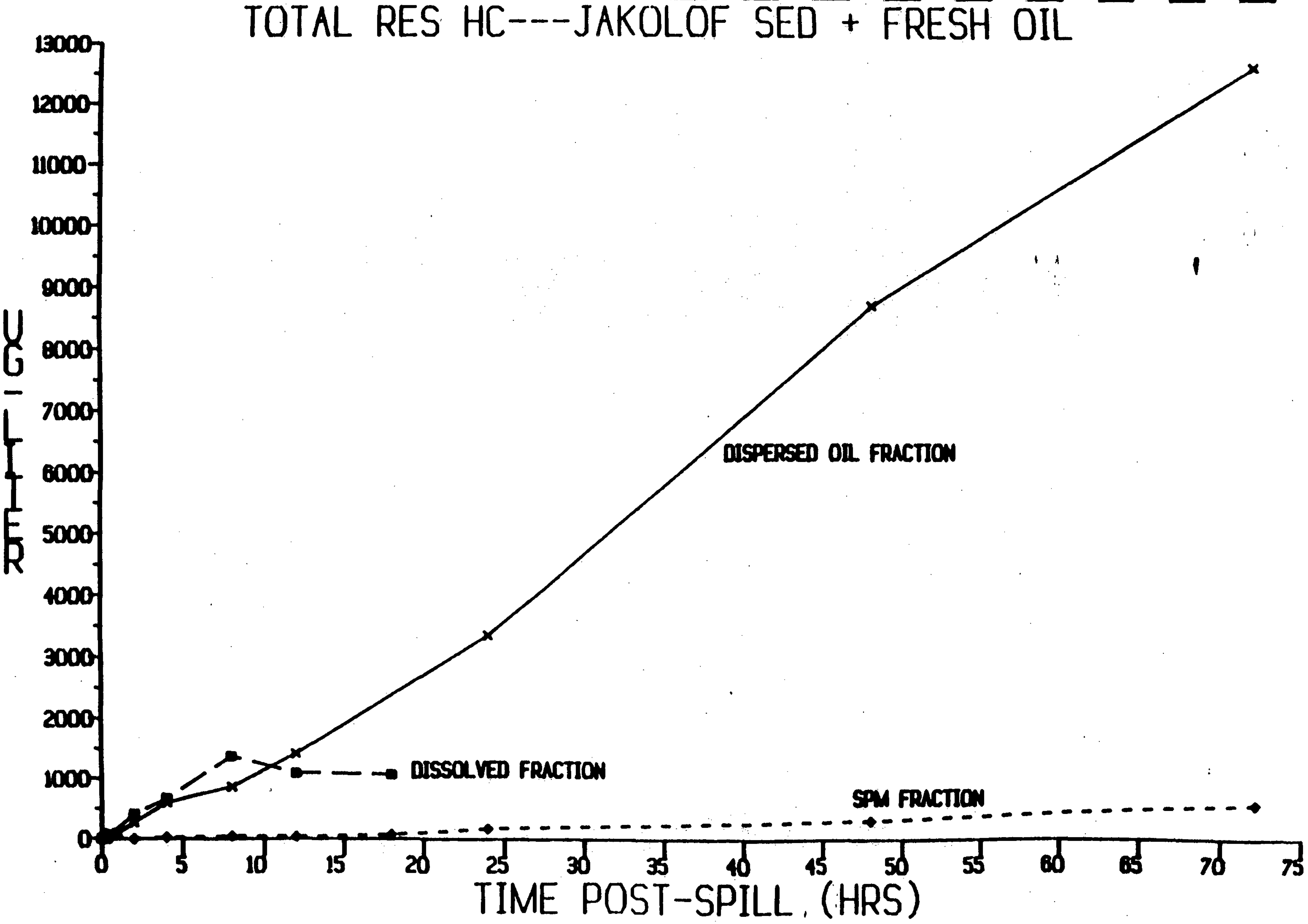


Figure 10. Temporal trends for total resolved hydrocarbons in the "dispersed oil", "SPM" and "dissolved phases" of water samples from a stirred chamber experiment using Jakolof Bay sediment and fresh Prudhoe Bay crude oil.

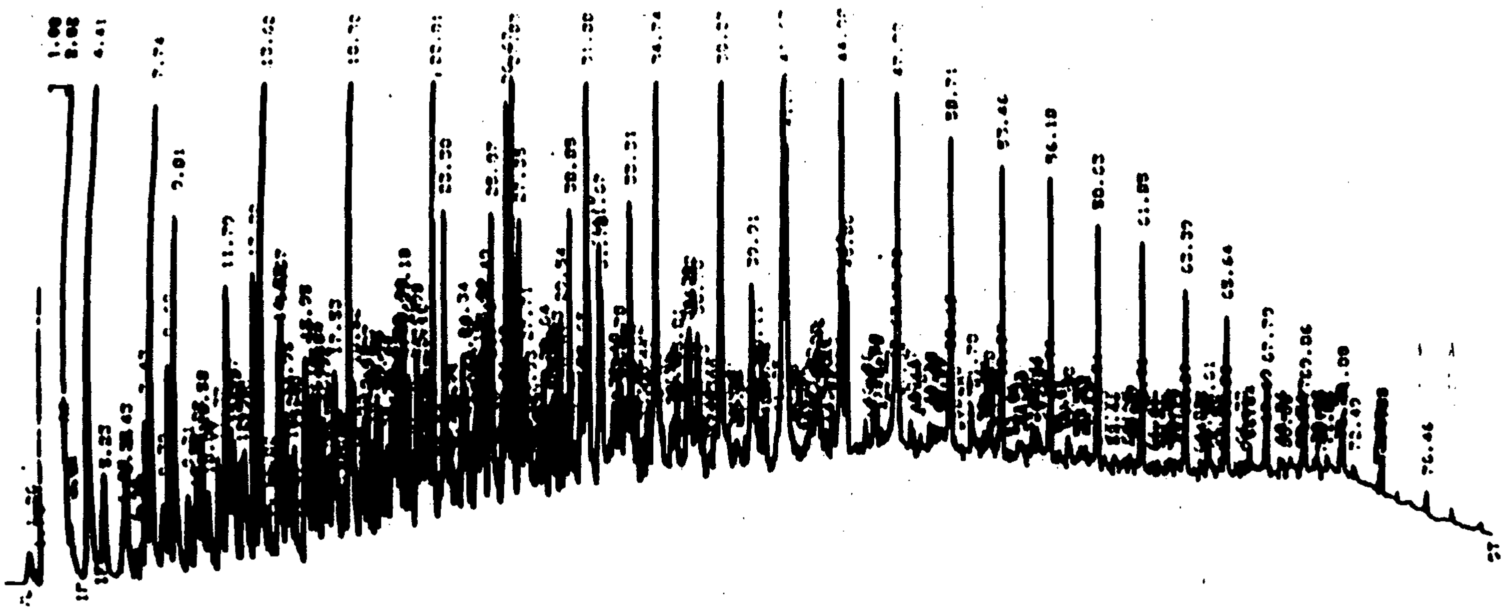


Figure 11a. "Dispersed oil phase", 24 hours post-spill, stirred chamber experiment with Jakolof Bay sediment and fresh Prudhoe Bay crude oil.

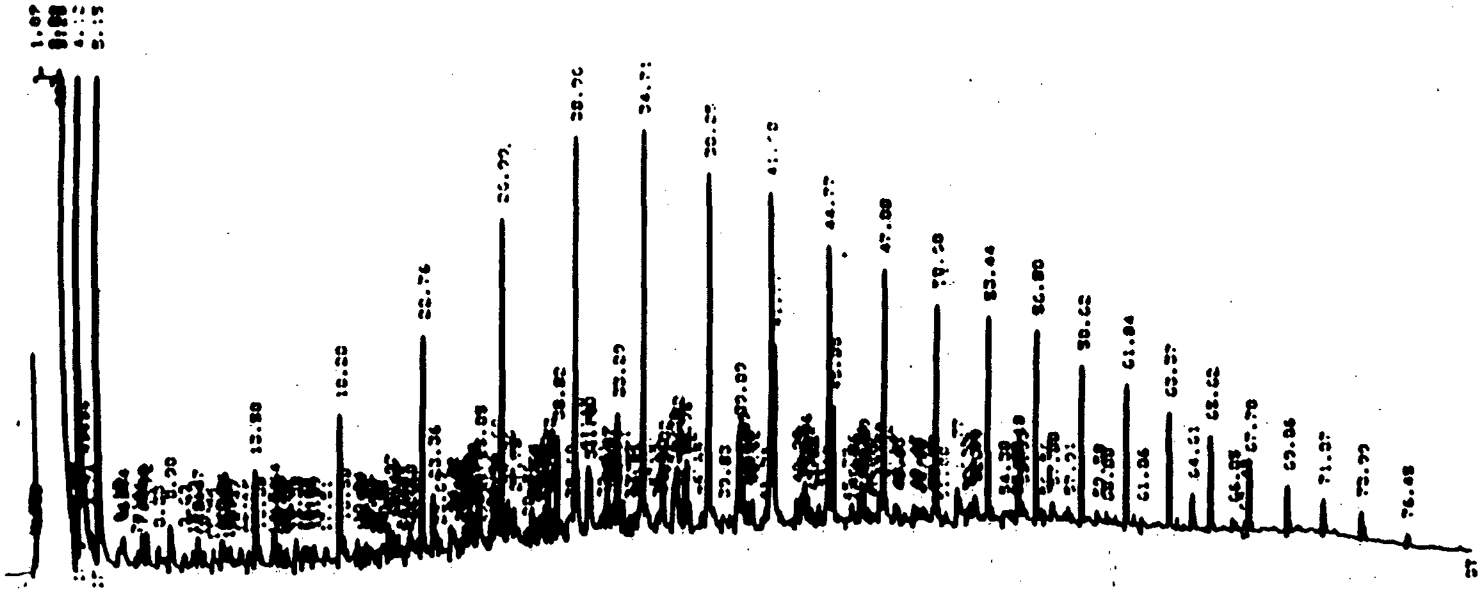


Figure 11b. "SPM phase", 24 hours post-spill, stirred chamber experiment with Jakolof Bay sediment and fresh Prudhoe Bay crude oil.

The data presented in Table 6 in the form of oil concentrations provides information about the rate of interaction of oil droplets and suspended particulate matter. The working equation for interpretating these data is

$$\frac{dN_o}{dt} = -k\left(\frac{\varepsilon}{\nu}\right)^{\frac{1}{2}} \frac{4}{3}(r_o+r_p)^3 N_o N_p \tag{33}$$

where N_o is the oil-droplet density (i.e., number of droplets per cm^3), $(\varepsilon/\nu)^{1/2}$ is the rate of shear in reciprocal seconds, N_p is the SPM particle density, r_o and r_p are the respective radii and k is a rate constant which takes into account the "sticking" factor.

The data presented in Table 6 are reworked as total masses and presented in Table 7. An approximate SPM mass of 1.35 grams total in 27 liters has been used in this table. The experimental difficulty in interpreting these data is the fact that the oil slick on the surface was "dispersing" oil droplets into the water at an unknown rate. However, this difficulty will be eliminated in future experiments by introducing oil droplets in another manner which is described at the end of this report. These data in Table 7 (and Table 6) can be used to provide "bounded" estimates of the rate of interaction of oil droplets and SPM.

In order to calculate a bounded estimate of the rate of interaction using the kinetic equation above, consider the SPM to be composed of primarily 10 micron diameter particles. Assuming a nominal wet density of 2 grams/cm^3 and a tank volume of 27 liters yields a number density, N_p, of 5×10^4 per cm^3. Voltage and amperage measurements on the stirrer motor in the chamber yielded a power input of approximately 5.8 joules/sec which results in $\varepsilon \sim 2000$ ergs/cm^3/sec. Thus, the rate expression becomes

$$\frac{dN_o}{dt} \approx -k(44\ sec^{-1})\ \frac{4}{3}\ (10^{-3}cm)^3\ N_o(5x10^{-4}cm^{-3}) \tag{34}$$

Table 7. Total Masses of Oil Droplets and SPM in Stirred Chamber Experiment (from Table 6)

Time	Oil Drops in Water, grams	Total Mass of Oil on SPM, grams	Total SPM in Water, grams
15 minutes	0.0011	0.00005	1.35
30 minutes	0.0024	0.00023	1.35
60 minutes	---	---	1.35
2 hours	0.0073	0.00026	1.35
4 hours	0.016	0.00016	1.35
8 hours	0.023	0.00071	1.35
24 hours	0.09	0.0047	1.35
48 hours	0.23	0.0097	1.35
72 hours	0.34	0.02	1.35

Since k is unitless, the units of the derivative are collisions (and sticking) per cm^3 per second. This is the working equation to calculate the mass of oil on the SPM in Table 7. The unknown in this working equation is k and the objective then is to provide a "bounded" estimate of this parameter. The oil-droplet density is approximately 400 per cm^3 based on 0.0049 grams of oil in the water when a droplet diameter of 10 microns is assumed. This is a "typical" oil concentration for the time frame of 30 minutes through 24 hours. Thus, the rate expression becomes

$$\frac{dN_o}{dt} = (-3.1\times10^4)k \quad \text{(with units of per tank per second)} \qquad (35)$$

This rate of collision represents the maximum rate of loss of oil droplets to SPM when $k \equiv 1$. A 10 micron oil droplet has a mass of approximately 4.6×10^{-10} grams; thus the maximum rate of loss of oil droplets to SPM (i.e., $k \equiv 1$) is approximately 0.052 grams/hour. However, note from Table 7 that the oil mass on SPM is significantly smaller than this number (integrated over 24 hours). This means the sticking factor is very small, i.e., the interaction is almost nil. Before firm conclusions can be drawn on this subject of interaction rates, however, it must be kept in mind that SPM particles may have been swept up in the surface slick and thereby no longer present in the water column to be measured as "oiled SPM". Only those SPM particles that have had minimal interactions with the dispersed oil will remain in the "SPM phase" that is ultimately analyzed for hydrocarbons. Since rates of interaction between dispersed oil droplets and SPM particles are determined from the measured levels of hydrocarbons in the "SPM phase", this could lead to an artificially low estimate of the rate of interaction between dispersed oil droplets and SPM particles. Based on the more rapid disappearances of SPM particles in the stirred chamber experiments employing weathered crude oil (Figure 9), this consideration may be particularly relevant to those experiments.

Clearly, the experimental difficulties involved prevent a precise interpretation (or model) of exactly the oil-SPM interaction phenomenon occurring in the tank. In this attempt to interpretate a set of data, the technical approach has been illustrated by showing what the measured parameter is (i.e., k), the required assumptions, and how the experimental difficulties interfere with data interpretation (i.e., the columns of dispersed oil and SPM numbers in Table 6 are not "smooth"). However, the modeling concepts presented above do provide a basis for planning the next set of experiments. It is still anticipated that k <<< 1, although this conclusion must await final confirmation in future experiments. How k is affected by the SPM type must also be experimentally determined.

Temporal trends in the concentrations of total resolved hydrocarbons in the "dissolved phase" of samples from the stirred chamber experiment with unweathered crude oil can be observed in Table 6 and Figure 10. These quantities increased to a maximum at 8 hours post-spill, and then appeared to begin declining. If the latter decreasing trend proves to be true (which cannot be confirmed until samples from later time points have been completely analyzed), this would likely be the result of losses of volatile compounds to the atmosphere above the surface oil slick. Hence, such volatile compounds would no longer be available for dissolution into the water column. Declines in the hydrocarbon levels in the "dissolved phase" over time in this experiment would not be expected to be as dramatic as those in Figure 6 (i.e., outdoor wave tank experiment) since the stirred chamber is not operated in a flow-through mode. Therefore, the probable source of hydrocarbon losses from the stirred chamber on the time scales incorporated into these experiments would be from volatilization into the overlying atmosphere. With regard to the specific composition of components in the "dissolved phase" of the water samples, aromatic compounds seem to account for essentially all of the resolved peaks. For example, the FID-GC chromatogram of the "dissolved phase" at 24 hours post-spill (Figure 12) has only aromatic compounds as identifiable peaks. There is no indication of obvious aliphatic compounds such as the n-alkanes, even at the longer retention times where a very smooth baseline was encountered. The identities and concentrations of individual aromatic compounds over time in the "dissolved phase" of samples from this experiment are

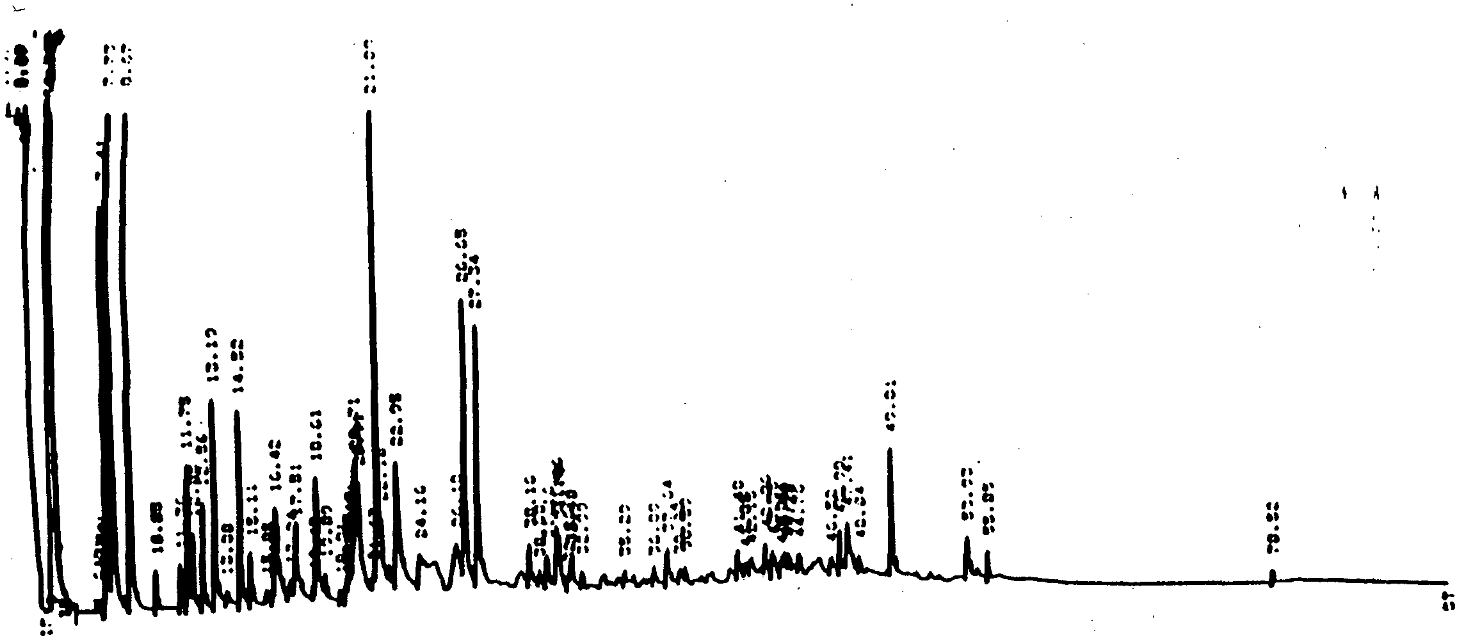


Figure 12. "Dissolved phase", 24 hours post-spill, stirred chamber experiment with Jakolof Bay sediment and fresh Prudhoe Bay crude oil. Same whole water samples as in Figures 11a and 11b.

summarized in Table 8. Conclusions regarding selective losses of lower molecular weight aromatics over time due to their greater volatilities will have to await additional data at the later sampling time points.

Technical Approach for Future Experiments with the Stirred Chamber

Methods employed in the previous stirred chamber experiments have been described above. Some of the procedural complications in applying these results to the development of a numerical dispersed oil-SPM interaction model have already been discussed. Further limitations in these previous experiments, and the proposed methodology changes to be incorporated in future experiments to minimize the uncertainties, are discussed below.

In the previously conducted stirred chamber experiments, the shear rates introduced by the stirring propellor have been high. For example, the turbulent energy dissipation rate (ε) in the experiments to date has been approximately 2000 ergs/cm^3/second. Typical ocean dissipation values are more in the range of unity. Since the square root of this parameter (divided by the kinematic viscosity) appears in the rate expression, the rate expression "moves" in time too fast by a factor of $(2000)^{1/2} = 44$. This could result in deagglomeration with the apparent result that the oil droplets and particles do not stick (but they really could at lower shears). Thus, the next set of experiments will be conducted at significantly lower energy dissipation rates (anticipated at 200 ergs/cm^3/sec) with the power input measured by torque and revolutions per minute. A torque measuring device which is to be installed in series between the stirrer motor and stirring propeller has been constructed. This device is being calibrated and the necessary hardware (motor mounting) changes are being made to install it.

As indicated in the sections of this report dealing with the modeling of dispersed oil-SPM interactions, the ideal experimental design to validate the model will also consist of a system having dispersed oil droplets and SPM particles characterized by well defined and reasonably narrow size ranges in

Table 8. Dissolved Hydrocarbon Compound Concentrations from Fresh Prudhoe Bay Crude Oil Chamber Experiment

	Concentration (µg/l)[1]									
Compound	Pre-spill	30 min	2 hrs	4 hrs	8 hrs	12 hrs	18 hrs	24 hrs	48 hrs	72 hrs
Toluene	ND	20.44	230.00	380.29	749.47	629.05	595.62	NA	NA	NA
Ethylbenzene	ND	4.62	14.86	NA	54.77	43.94	43.09	15.56	26.24	35.94
m- & p-xylene	ND	17.60	49.29	88.45	176.48	133.02	135.28	57.56	82.08	120.75
o-xylene	ND	10.02	28.22	48.51	100.30	83.28	84.82	38.11	61.02	92.46
isopropylbenzene	ND	ND	1.09	1.50	4.41	3.65	3.35	1.40	2.36	3.98
n-propylvenzene	ND	ND	1.35	2.36	5.38	4.11	3.84	1.60	2.73	4.78
C_3-benzene	ND	2.00	5.36	9.26	18.87	14.94	14.60	6.90	10.82	19.23
C_3-benzene	ND	0.61	1.42	2.38	6.03	4.79	4.50	2.07	3.26	6.03
1,3,5-trimethylbenzene	ND	0.96	2.69	5.03	10.64	8.48	8.69	3.96	6.49	12.11
C_3-benzene	ND	2.49	7.51	14.19	26.89	17.72	18.61	8.57	11.77	22.33
C_4-benzene	ND	1.66	5.39	9.57	19.29	15.45	16.21	8.59	13.68	25.09
tetramethylbenzene	ND	ND	5.65	6.67	9.77	6.59	6.69	6.16	6.60	10.12
naphthalene	ND	3.01	12.80	24.09	38.66	22.76	27.52	23.00	34.75	59.87
2-methylnaphthalene	ND	2.03	8.68	15.68	25.09	17.55	19.72	15.13	19.11	31.23
1-methylnaphthalene	ND	1.74	7.38	13.43	22.35	16.16	18.27	14.00	18.97	29.12
1,1'-biphenyl	ND	ND	0.92	1.84	2.93	2.17	2.32	1.88	2.39	2.94
2,6-dimethylnaphthalene	ND	ND	1.51	2.65	3.78	2.57	2.53	2.24	3.30	5.44
C_2-naphthalene	ND	ND	0.69	1.15	1.74	1.22	1.01	1.05	1.47	2.37
C_2-naphthalene	ND	ND	ND	1.63	2.45	1.53	1.79	ND	1.62	1.08
C_2-nathphalene	ND	ND	ND	ND	1.24	0.69	0.74	ND	0.81	1.62

ND = not detected; NA = not available.

the approximate vicinity of 10 µm diameters. In the previously conducted stirred chamber experiments, oil droplet introduction to the water has been accomplished by putting a "slick" on the water and allowing the natural action of stirring to generate the oil droplets. This method complicates the interpretation of experimental results since oil droplet introduction is erratic. For example, a slick can act as a variable source of oil droplet input to the system over time, thereby confusing measurements of the concentrations of oil droplets and SPM particles from which a rate constant is calculated. In order to minimize problems generated by surface slicks, an oil-water emulsion will be initially prepared in a mechanical blender in future experiments. Preliminary efforts have been conducted to obtain acceptable oil-water emulsions, and the resulting solutions have been evaluated by phase contrast lightr microscopy. Blending of unweathered Prudhoe Bay crude oil and sea water has produced dispersed oil droplets with well defined oil-water boundaries and diameters in the desired range of approximately 0.5-10 µm. Future experiments with this blended solution appear to be quite feasible. For a stirred chamber experiment with such a solution, the emulsion will first be transferred to a separatory funnel for a short period of time to allow any residual oil tending to form a surface slick to separate from the more "stable" dispersed oil droplets in the sea water. The oil-sea water emulsion (excluding the surface oil slick) will then be added to the stirred chamber, and an oil-SPM interaction experiment will commence. Microscopic observations will be performed on samples throughout the experiment to evaluate the behavior of both the dispersed oil droplets and SPM over time. Whole water samples will continue to be processed with the polyester filter technique to obtain estimates of both SPM loads and the FID-GC hydrocarbon concentrations in the "dispersed oil", "SPM" and "dissolved phases" of samples.

Preliminary indications for oil-sea water emulsions experiments using weathered Prudhoe Bay crude oil are less promising. Microscopy of emulsions using 12-day weathered Prudhoe Bay crude oil and sea water indicated that the oil mixtures did not have distinct oil-water interfacial boundaries (i.e., much of the oil gradually graded into the water phase at interfacial boundaries). Furthermore, the weathered oil drops (or, more appropriately, "entities") in these blended solutions were characterized by exceptionally broad size ranges (e.g., 0.5->100 µm diameters). Additional blending experiments (i.e., blending times, energy input, oil/water ratios, etc.) with weathered oil are planned to generate stable 1-10 µm weathered oil drops for future experiments.

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