

# Marine Technology Society Journal

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Cover: A fast response unit with boom and skimmer deployed and ready for oil recovery in the Gulf of Mexico. Skimmer is attached to a workboat with one storage tank (right) to contain spilled oil once recovered. Courtesy of American Petroleum Institute.

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Editorial and executive offices: Marine Technology Society, 2000 Florida Avenue, N.W., Suite 500, Washington, D.C., 20009. Tel. (202) 462-7557.

# Weathering of Petroleum in the Marine Environment

James R. Payne and G. Daniel McNabb, Jr.

Science Applications International Corporation  
La Jolla, California

## ABSTRACT

*This paper presents a review of the more salient studies on the physical and chemical weathering of whole crude oils and petroleum products released to the marine environment. Emphasis is placed on the role that the chemical composition of the crude plays on weathering processes, and selected results from flow-through sub-arctic wave tank studies are used to illustrate the time-series changes in composition and rheological properties which occur to spilled Prudhoe Bay crude oil. Details of environmental partitioning (evaporation, dissolution, dispersion, etc.) are presented and approaches to modeling spill behavior and deriving an overall mass balance for spilled crude oils and petroleum products are discussed.*

## INTRODUCTION

**W**hen crude oil or petroleum distillate products are released to the marine environment they are immediately subject to a wide variety of weathering processes.<sup>1</sup> These processes can include: spreading, evaporation, dissolution, dispersion of whole oil droplets into the water column, photochemical oxidation, water-in-oil emulsification, microbial degradation, adsorption onto suspended particulate material (SPM), ingestion by organisms, sinking and sedimentation. To a certain degree, the relative rates of these processes are affected by the position of oil release (surface versus subsurface), and the relative magnitudes and importance of each weathering process are also controlled by, or dependent upon, the oil composition.

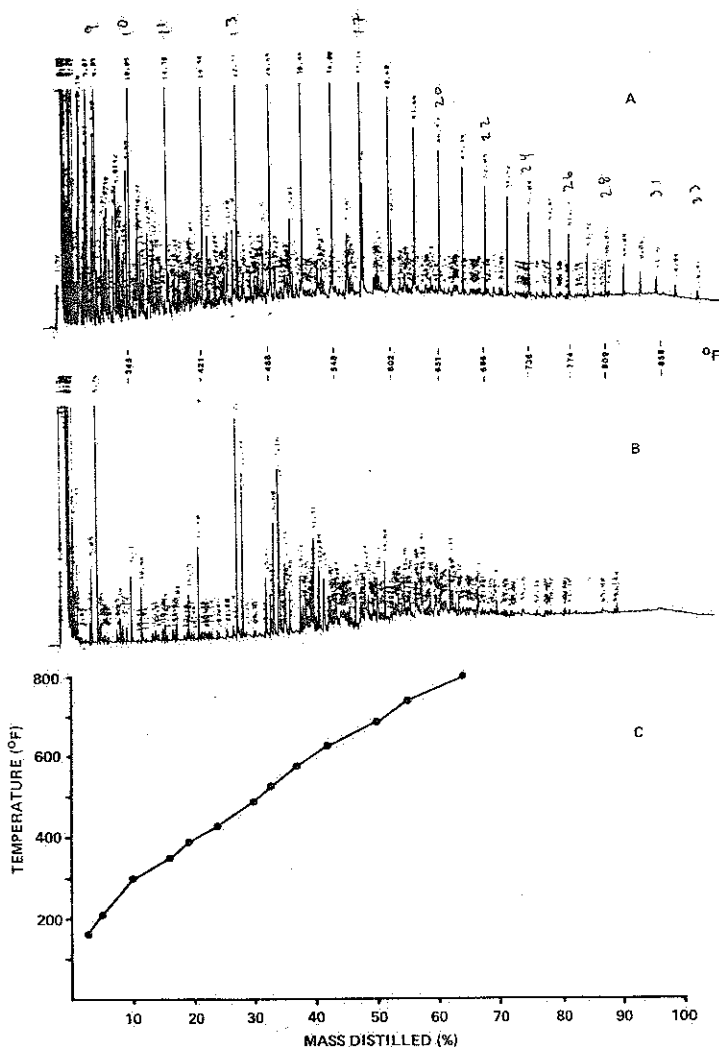
This paper addresses the changes in oil composition and associated rheological properties due to physical/chemical weathering in the sea and the role that the initial composition of the whole crude oil or refined product has on weathering behavior. The effects of ice on the weathering of petroleum products in arctic environments are briefly considered and, finally, an overview of our recent attempts to model oil weathering processes is presented.

## OIL COMPOSITION

Crude oils and refined petroleum products are often characterized by the petroleum industry by a wide variety of parameters and techniques including specific or API gravity, viscosity, pour point, boiling point range, paraffin, olefin, naphtha, and aromatic (PONA) content, and percent nondistillable residuum.<sup>2-5</sup> Among the foremost approaches for en-

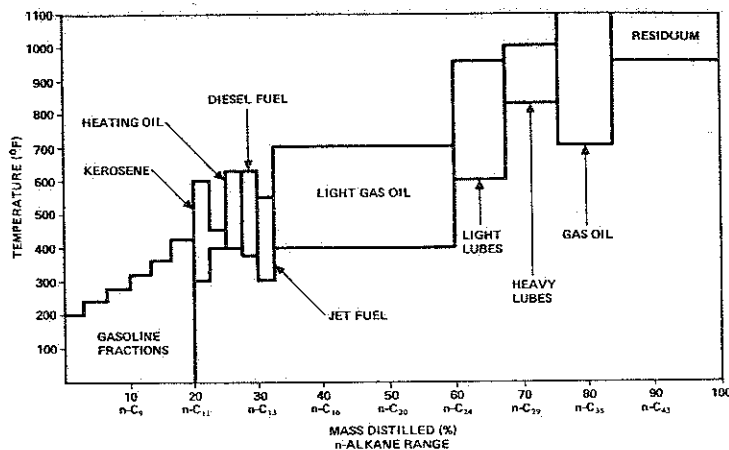
vironmental characterizations of oils and refined products are those of gas chromatography and gas chromatography/mass spectrometry. These latter techniques are useful in that compound specific data, including component identifications and concentrations (which are important for consideration of biological effects) can be obtained; however, gas chromatographic techniques do not allow for an overall accounting of the total mass of a crude because significant portions of material in whole crudes often cannot be analyzed by gas chromatograph. For example, Figure 1 presents a superposition of two gas chromatograms obtained on the aliphatic and aromatic fractions of Prudhoe Bay crude oil along with a True Boiling Point (TBP) distillation curve obtained on the whole crude mixture.<sup>6</sup> The chromatogram of the aliphatic fraction (Figure 1A) is characterized by the evenly repeating pattern of the homologous series of n-alkanes from n-C<sub>7</sub> through N-C<sub>33</sub> and the aromatic fraction chromatogram (Figure 1B) contains peaks for individual aromatics ranging from benzene and its alkyl-substituted derivatives through the di- and tri-cycle polynuclear aromatics and their alkyl-substituted homologs. The higher boiling components ( $\geq$  n-C<sub>26</sub>; bp 809°F) are only poorly represented, and yet the TBP distillation curve of a sample of Prudhoe Bay crude oil (Figure 1C) illustrates that only ~64% of the whole crude oil is capable of being distilled (even at reduced pressure). Thus, a total of 36% of the material in the crude is contained in the nondistillable residuum (bp >800°F), which is not adequately represented by most gas chromatographic techniques. Furthermore, this fraction is extremely important from the standpoint of changes in rheological properties and the behavior of the crude oil during at sea weathering.

The true boiling point characterization approach is also useful because it represents the first step in the industrial characterization of a crude to determine what distillate products may be present.<sup>6</sup> Figure 2 presents a graphical illustration of the types of refined products which may be obtained from a whole crude as characterized by the boiling point range of the different component materials. The lighter distillate cuts or products do not include the non-distilled residuum which often contains high concentrations of wax, asphaltic and polar materials discussed later in greater detail. These components are important in affecting the behavior of crude oil spilled at sea, and it has been shown that refined products do not form stable water-in-oil emulsions (or mousse) due to the absence of surface active materials contained in the higher boiling residuum.<sup>7-16</sup>



**Figure 1.** Flame ionization detector gas chromatographic profiles depicting (A) the aliphatic fraction, and (B) the aromatic fraction of Prudhoe Bay crude oil. Marked temperatures indicate the true boiling point (TBP) of compounds eluting at these retention times. The TBP distillation curve of whole Prudhoe Bay crude (C) illustrates that 36% of the mass is non-distillable as well as non-chromatographable with boiling points in excess of 800°F.

The boiling point range of the various refined products also affects their susceptibility to weathering by evaporation and dissolution processes. Compounds with boiling points below  $n\text{-C}_{14}$  (488°F) are generally the only ones subject to partitioning into the atmosphere under normal (temperate) marine conditions.<sup>1</sup> In general, aromatic hydrocarbons in this same boiling point range (175-500°F) are the only ones subject to significant dissolution. Thus, from Figure 2, it follows that certain refined products, such as gasoline, light kerosenes, aviation gas, etc., may be subject to nearly complete removal by evaporation (and limited dissolution) processes, whereas heavier distillate products such as gas oils, lube oils and Bunker C residual fuel



**Figure 2.** Distribution percent versus boiling point for most crude oils. Adapted from Clark and Brown, 1977. *Petroleum: Properties and analysis in biota and abiotic systems*. In: D.C. Malins, ed., *Effects of Petroleum on Arctic and Subarctic Marine Environments and Organisms*, Academic Press, New York.

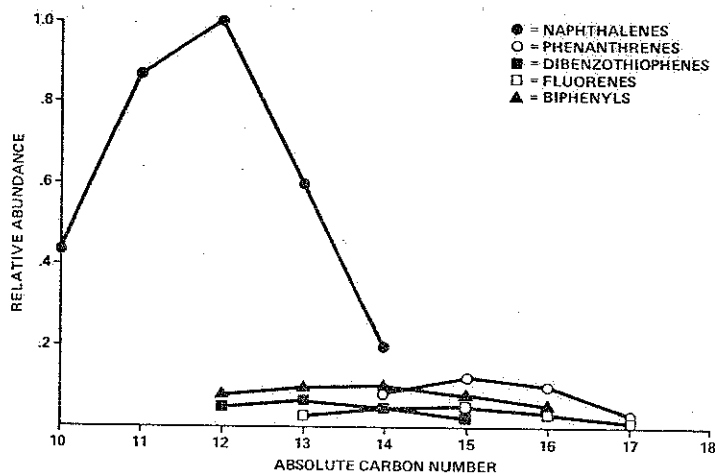
oil, etc. would not be subject to significant weathering by these mechanisms.

By virtue of the fact that most whole crude oils contain all or most of the components which constitute the refined products shown in Figure 2, they are subject to a wider variety of weathering processes. For this reason, whole crudes will be considered in the greatest detail in this review. From the standpoint of toxicity, however, it should be noted that the aromatic fractions of both whole crude oils and lighter, refined products are generally characterized by a predominance of alkyl-substituted aromatics compared to the parent aromatic compounds. For example, the relative distributions of the alkyl-substituted homologs of mono-, di- and tri-cyclic alkyl-substituted aromatics in Prudhoe Bay crude are shown in Figure 3. This distribution of alkyl-substituted products is important in that many toxicological and microbial degradation studies have been completed to date on the individual parent polynuclear aromatic hydrocarbons and not on the alkyl-substituted homologs which make up the larger fraction of the aromatic components in the bulk oil. Future biological studies should take these compositional differences into consideration. Further, the presence of the alkyl-substituents on the aromatic hydrocarbons is useful for differentiation of polynuclear aromatic hydrocarbons derived from combustion versus fossil fuel sources, when such compounds are recovered and identified in marine samples.<sup>17,18</sup>

## WEATHERING PROCESSES

### Spreading and Drift

Spreading is the first major process which affects the behavior of crude oil and refined products during the first hours after release at sea. Spreading increases the overall surface area of the slick, thus enhancing mass transfer via evaporation and dissolution processes. The spreading process has been fairly well



**Figure 3.** Relative abundance of alkyl-substituted homologs to parent aromatic compound. The parent aromatic compound for each set is represented by the point with the lowest absolute carbon number. All the values shown are relative to dimethylnaphthalene.

studied in laboratory and small scale field situations.<sup>19-21</sup> Principal forces influencing the lateral spreading of oil on a calm water surface are gravitational, inertial, frictional, and those due to surface tension;<sup>19-21</sup> however, it has been very difficult to model spreading behavior in open ocean situations due to competing sea-state effects. Furthermore a variety of oil types in accidental and test spills have been observed to spread into a random mixture of thin and thick patches at sea.<sup>22-23</sup> In these instances, the thicker patches have been observed to move down wind at a faster rate leaving a thinner trailing sheen behind. Thus, while spreading is understood in an empirical sense, it is not possible at this time to model spilled oil behavior beyond first order estimations of total area potentially covered for a defined range of slicklet thicknesses.

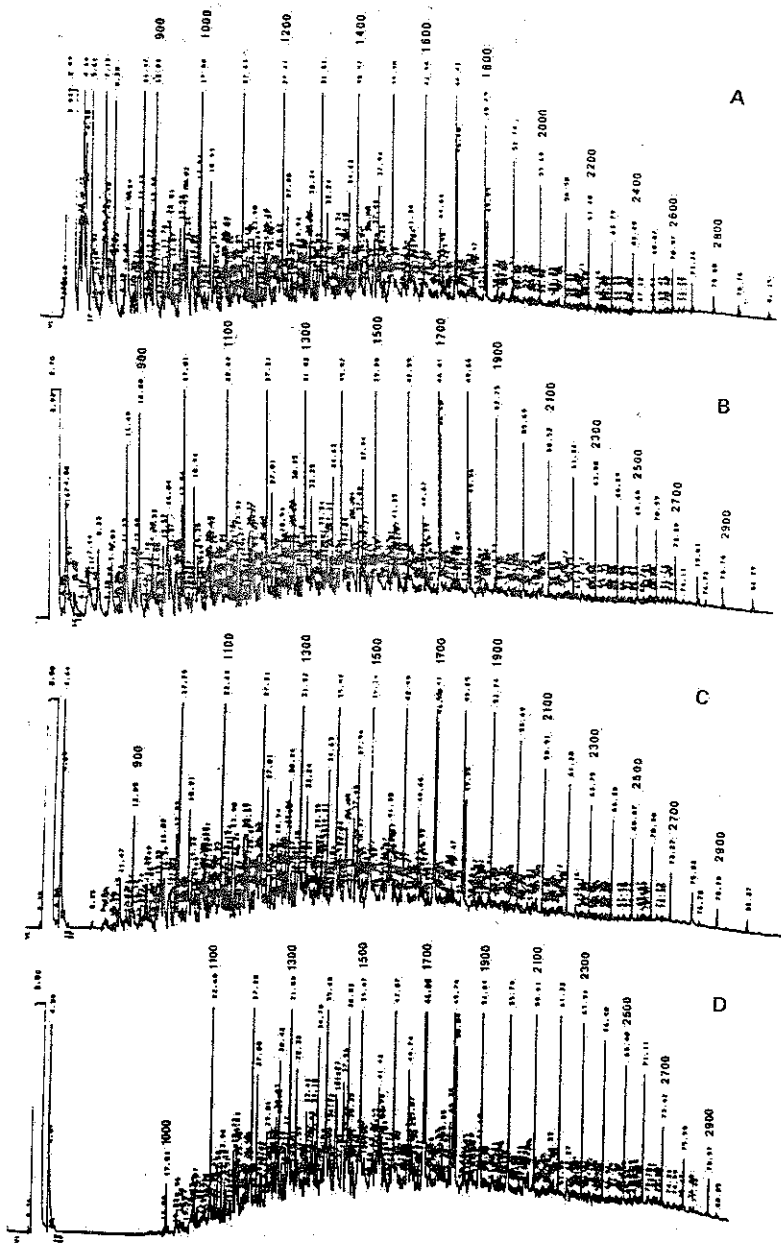
Drift is considered to be a large scale phenomenon which characterizes the movement of the center of mass of a slick. To a rough approximation, drift is independent of spreading and spill volume, and numerous investigators have found that the overall drift of the slick is primarily controlled by wind, waves, and surface currents.<sup>1-24-29</sup> The center of mass can move at approximately 3% of the wind speed with a 20-30° shift to the right, in the northern hemisphere (due to Coriolis Effect) in the absence of other perturbations affecting the overall slick travel such as residual currents or land masses.<sup>24-25</sup> Attempts to model slick drift range from simple "back-of-the-envelope" calculations to extremely sophisticated multi-layer circulation models, such as those developed by Liu and Lendertsee<sup>30</sup> for much of the outer continental shelf waters surrounding Alaska. Venkatesh et al.<sup>28</sup> have also developed open-ocean (ice free) drift models which have been partially verified by the results of simulation experiments conducted in the Bay of Fundy. In all

cases, however, better determinations of wind field vectors are critical for modeling and predicting slick advection.

### Evaporation

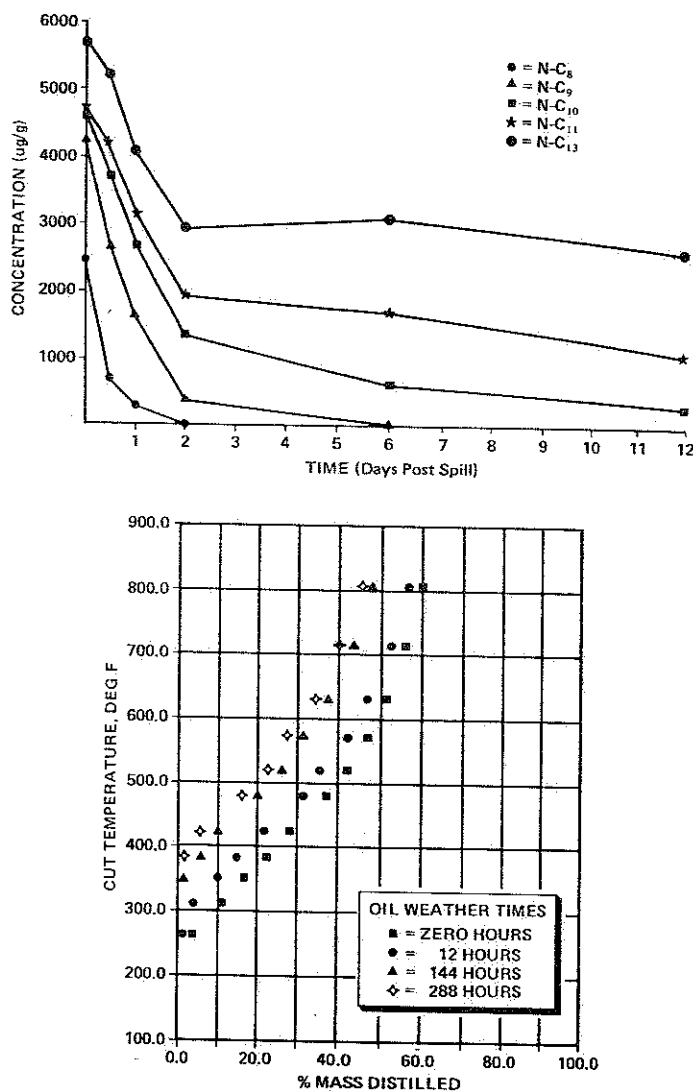
During the first 24 to 48 hours of oil spill, evaporation is the single most important weathering process from the standpoint of mass transfer (molecular partitioning) and removal of the more toxic lower molecular weight components from the slick. Evaporative loss is controlled by the composition of the oil, its surface area and physical properties, the wind velocity, air and sea temperatures, sea state, and the intensity of solar radiation.<sup>1,2,20,31-40</sup> From examination of numerous samples from spills of opportunity and test tank simulations, compounds with vapor pressures greater than that of n-C<sub>8</sub> will not persist in a slick, whereas compounds with vapor pressures less than n-C<sub>18</sub> do not evaporate appreciably under normal conditions.<sup>35</sup> The rates and magnitudes of evaporative loss are extremely dependent on the environmental conditions surrounding the spill event, and generally, compound-specific losses are difficult to predict. In attempts to model evaporative behavior it has become clear that compound specific partitioning is too complex even for sophisticated computers.<sup>2,41</sup> Henry's law constants for individual components are required, and a pseudo-Raoult's law behavior must be assumed wherein the rate of individual component loss is controlled by the mole fraction of a given component in the crude or distillate product and the pure component vapor pressure. Therefore, pseudo-components (or distillate cuts) of various boiling point ranges have been used in modeling evaporative behavior, and very good agreement between observed and predicted behavior has been obtained.<sup>2,41</sup> In these instances, the mass transfer coefficient for evaporation has been modeled as: (a) an overall mass transfer coefficient which is a correlation value (as derived by Mackay and Matsugu)<sup>42</sup> and is a function of wind speed, slick size and the Schmidt number;<sup>2</sup> or (b) individual phase, mass transfer coefficients as discussed by Liss and Slater.<sup>43</sup> Figure 4 presents four selected gas chromatograms obtained from oil samples isolated over a nine-day period from outdoor flow-through wave tank studies completed near Lower Cook Inlet, Alaska. From these chromatograms the loss of lower molecular weight components is readily apparent. Component-specific concentrations remaining in the slick (Figure 5A) show the loss of individual compounds due to evaporation (and to a lesser extent dissolution). As noted earlier, compounds below n-C<sub>14</sub> are readily removed, however, these compound-specific data alone do not allow an overall accounting of the total mass balance of the slick. For this reason, a distillation characterization of the weathered crude is required. The distillation curves in Figure 5B show an increase in initial boiling point of the weathered residual material with time, and also permit an accounting of the non-distillable residuum or asphaltic crude oil.

From the data presented in Figure 5B, an estimate



**Figure 4.** Flame ionization detector gas chromatographic profiles of Prudhoe Bay crude oil from an outdoor flow-through wave tank spill. Time series samples were obtained at (A) time zero, (B) eight hours, (C) 48 hours, and (D) nine days after the experimental spill. Evaporation can be observed by the time-dependent disappearance of lower molecular weight peaks. (KOVAT retention indices are indicated above predominant peaks.)

for the overall loss due to evaporation processes alone of 15-20% from the slick over a 288 hour period can be derived.<sup>2</sup> Note that after that time interval, the relative amount of non-distillable material has also increased from 34 to greater than 50 percent. The distillation curves also allow a characterization of the relative abundance of other pseudo-compounds or distillate cuts of the crude, from which compound-specific compositional data can be inferred, by correlating the boiling point range with component specific charac-



**Figure 5.** The effect of weathering time on individual compound concentrations in the oil phase (A). More volatile species, (i.e.,  $n-C_5$  and  $n-C_9$ ) are rapidly removed by evaporative processes while less volatile compounds are seen to persist longer. (All concentrations are corrected for water incorporation by the oil.) Figure 5B presents TBP distillate curves for Prudhoe Bay crude oil at various times during weathering. The effects of weathering time on the position of the curve is indicative of the losses due to evaporation.

terizations derived by the gas chromatographic analyses shown in Figure 1.

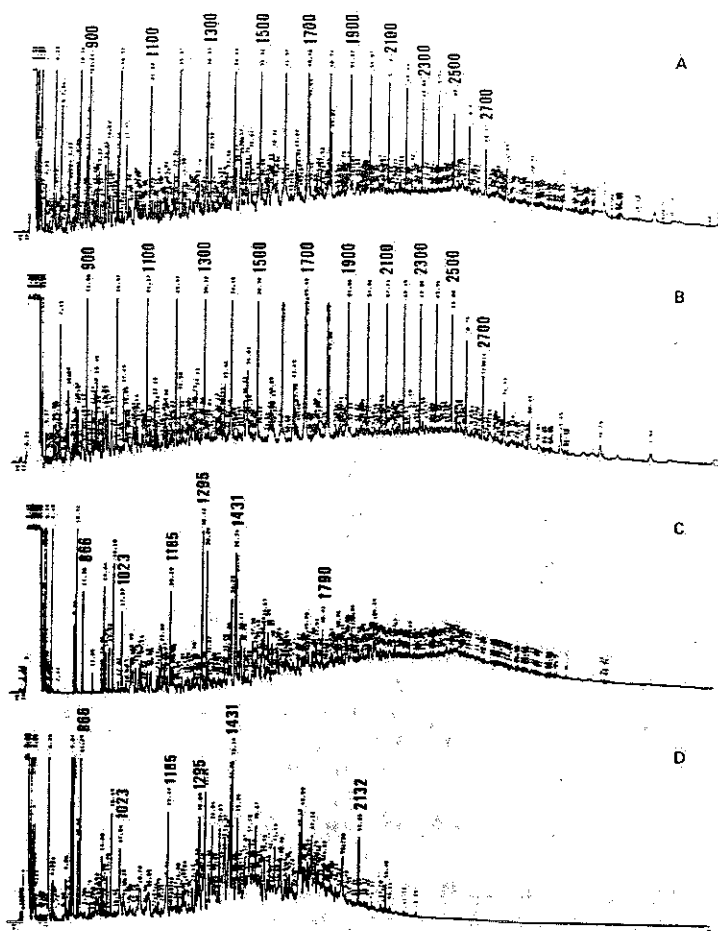
#### Dissolution

True dissolution of molecular components from an oil slick is not generally significant in terms of the overall mass balance of an oil spill,<sup>141</sup> although it may be important when considering biological impacts. The extent of dissolution can be affected by the point of oil release, with subsurface releases of whole

crude oil (such as that encountered during the *Ixtoc* / blowout) enhancing dissolution of lower molecular weight aromatic components.<sup>44,45</sup> In the *Ixtoc* event evaporation processes were slightly delayed as lower molecular weight aromatics partitioned into the water column while the oil floated upwards to the water surface. In particular, benzene was almost totally removed from the oil mass by the time it reached the surface, accounting for the elevated (greater than 100 microgram/liter) levels of benzene measured directly beneath the slick.<sup>44,46</sup> In general, however, when oil is released to the surface of the water column, evaporative processes will predominate over other simultaneous weathering processes by as much as a factor as 100 to 1.<sup>37</sup>

Dissolution of individual molecular components from the slick is controlled by partition coefficients, which are often referred to as M-values.<sup>2</sup> Figure 6 pre-

sents chromatograms obtained on whole Prudhoe Bay crude oil (6A), the aliphatic fraction of whole crude oil (6B), the aromatic fraction of whole crude oil (6C), and the dissolved *unfractionated* components which partitioned into seawater (Figure 6D). These chromatograms show that the truly dissolved components are almost exclusively lower molecular weight aromatic and alkyl-substituted aromatic components (for a general review of the numerous studies on pure components solubilities see Ref. 1). Table 1 presents partition coefficients (oil/water concentration ratios) derived from these partitioning experiments. For the purposes of modeling dissolution, however, pure component solubility data alone are not enough, and partition coefficients such as those in Table 1 must be used. Specifically, true dissolution of individual components is controlled by the mole fraction of each component in the slick, the oil/water partition coefficient, and interphase mass transfer coefficients, but not pure component solubilities.



**Figure 6.** Flame ionization detector gas chromatographic profiles obtained from oil/seawater partitioning experiments showing (A) whole Prudhoe Bay crude oil, (B) the aliphatic fraction, (C) the aromatic fraction and (D) seawater extract at concentration equilibrium. Note from Figure 6D, the preferential partitioning (dissolution) of the more water soluble aromatic compounds (KOVAT retention indices are indicated above predominant peaks).

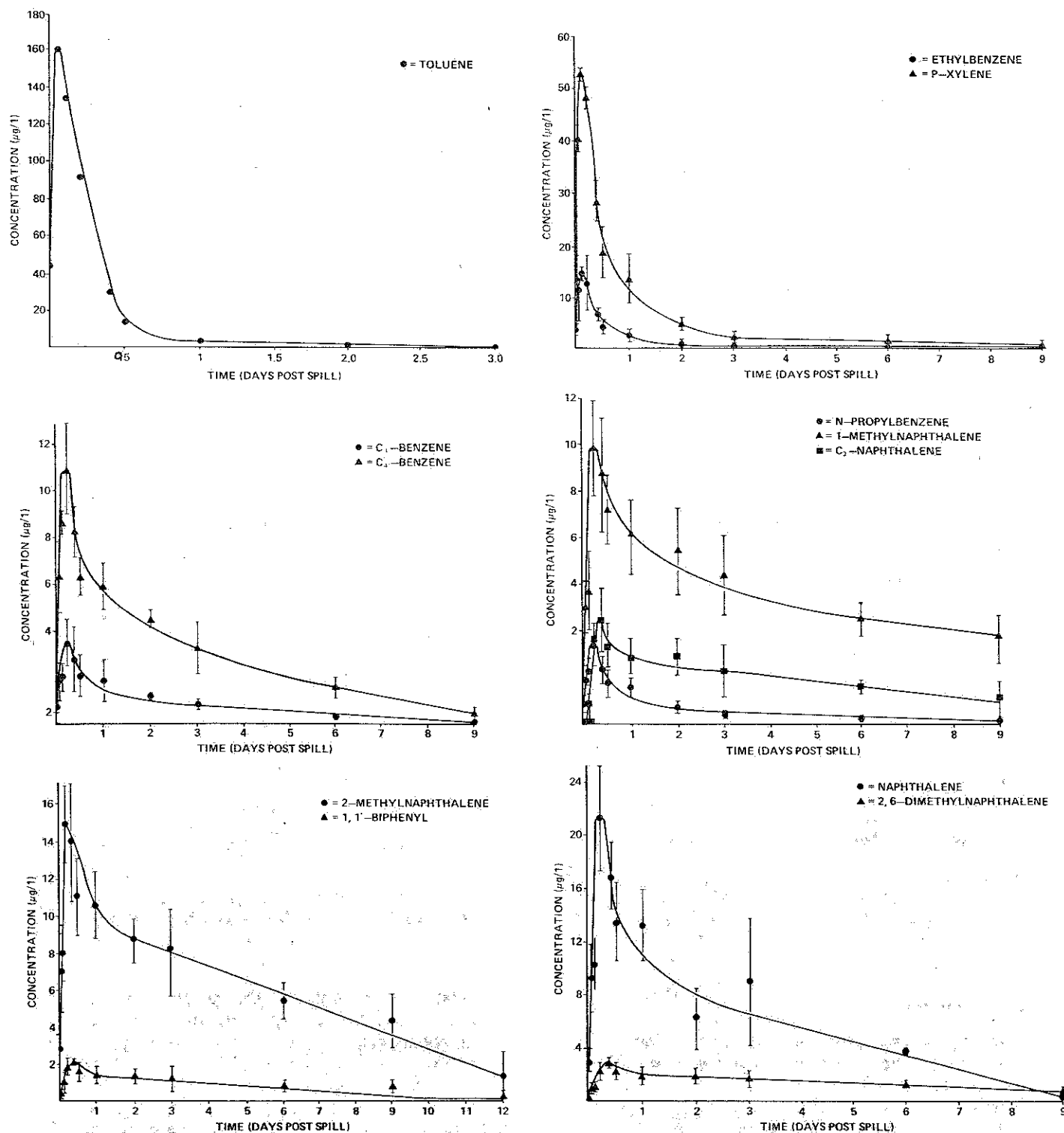
**Table 1. M-Values Determined From Stirred Chamber Experiments**

Compound Name	KOVAT	M-Value <sup>a</sup>
Ethylbenzene	765	3330
m & p-xylene	866	3600
o-xylene	892	5900
Ethylmethylbenzene	961	6800
1,3,5-trimethylbenzene	967	1900
Dimethylethylbenzene	1086	9500
Naphthalene	1185	7800
2-methylnaphthalene	1295	46400
1-methylnaphthalene	1316	35800

a—the M-Value is defined as the compound concentration in oil divided by the compound concentration in water at equilibrium.

Payne et al.<sup>2,41</sup> performed a series of flow-through wave tank experiments at Kasitsna Bay, Alaska to examine the dissolution behavior of specific components from whole crude oil, where subsurface advection or removal of dissolved components could be simulated. In these studies, wave turbulence was introduced by paddle wheels with constant water column replacement (turn-over) in the tanks to simulate an oil slick drifting or being blown over water which had not previously been exposed to oil. In this manner, more realistic measurements could be completed on time-series concentrations of dissolved components partitioning into the water column with concomitant removal by advective and evaporative processes.

Figure 7 presents time-series concentrations of selected lower molecular weight aromatics dissolved in the water column from the wave tank systems. As the data illustrate, the peak concentration of dissolved



**Figure 7.** Dissolved individual aromatic compound concentrations in the water column as a function of weathering time. Peak concentrations in the wave tanks studies occurred between eight and twelve hours after the spill, with subsequent decreases primarily due to advective removal and evaporation.

compounds occurs approximately 8-12 hours after initial release of the oil to the water surface. The concentration then drops off in an exponential fashion, reflecting the loss of these compounds by evaporation (from both the slick and water column) and the removal of the truly dissolved components by advection (water mass transport). While the early time-series

concentrations of total aromatics are in the 10 to 100 parts per billion (ppb) range, predictions of water-column concentrations resulting from advection and diffusion quickly yield values in the low parts-per-trillion level in an open ocean spill. Such predictions are in agreement with measured values in subsurface water column samples collected within 2 to 3 kilo-



meters of the slick generated during the 1979 *Ixtoc I* blowout in the Bay of Campeche, Gulf of Mexico.<sup>45,46</sup> In that instance, dissolved phase water column concentrations of total intermediate molecular weight aliphatic and aromatic hydrocarbons were generally in the low to mid parts-per-trillion range. Thus, while higher dissolved or "water accommodated" aromatic hydrocarbon levels have been observed in closed lagoon or estuarine systems, concentrations in better agreement with those reported for wave tank studies and in the *Ixtoc I* blowout might be considered in designing future experiments assessing the toxicological impacts of open ocean oil spills.

### *Dispersion*

Whole oil droplet dispersion is ultimately the most important process in the breakup and disappearance of a surface oil slick. Droplet dispersion is largely controlled by sea surface turbulence, although the processes of spontaneous emulsification or dispersion of oil droplets into the water column from calm seas can also occur. Dispersion of oil droplets increases the surface area, allowing enhanced dissolution of lower molecular weight aromatics, provides material for direct interaction of dispersed oil with suspended particulate material, and provides materials which may be ingested by organisms and ultimately desposited to the sediments in fecal pellets. In general, the larger (greater than 0.1 mm) droplets will return to the sea surface once the turbulence or surface agitation is reduced, and the smaller (less than 0.1 mm) size droplets will remain in the water column. Forester<sup>47</sup> reported that oil concentrations due to particles between 0.1 and 1.0 mm decreased with depth, whereas concentrations from particles less than 0.1 mm were constant to as deep as 80m during water column sampling to investigate the tanker *Arrow* spill in Chedabucto Bay, Nova Scotia.

Attempts to model the dispersion process usually couple the rate of dispersion with wind speed or sea surface roughness;<sup>2</sup> however, our understanding of the phenomena is largely empirical at this time and detailed models predicting slicklet breakup have not been verified under realistic open ocean or near coastal regimes.

During wave-tank simulations in outdoor flow-through experiments, Payne et al.<sup>2</sup> reported that the total concentration of dispersed hydrocarbons was approximately ten times greater than the truly dissolved lower aromatic components. However, their data suggested that with changes in slick rheological properties (viscosity and interfacial surface tension), due to water-in-oil emulsification, dispersion of smaller oil droplets becomes self-limiting within 2-3 days. Figure 8 presents time-series profiles of waterborne concentrations of dispersed/particulate bound oil droplets from the wave tank systems. After oil viscosities approached 2000 centipoise, continued dispersion of whole oil droplets into the water column was largely inhibited under the test conditions which simulated turbulence from a 3-5 knot wind. Gordon et al.<sup>48</sup> have also reported that the ratio of dispersed particulate

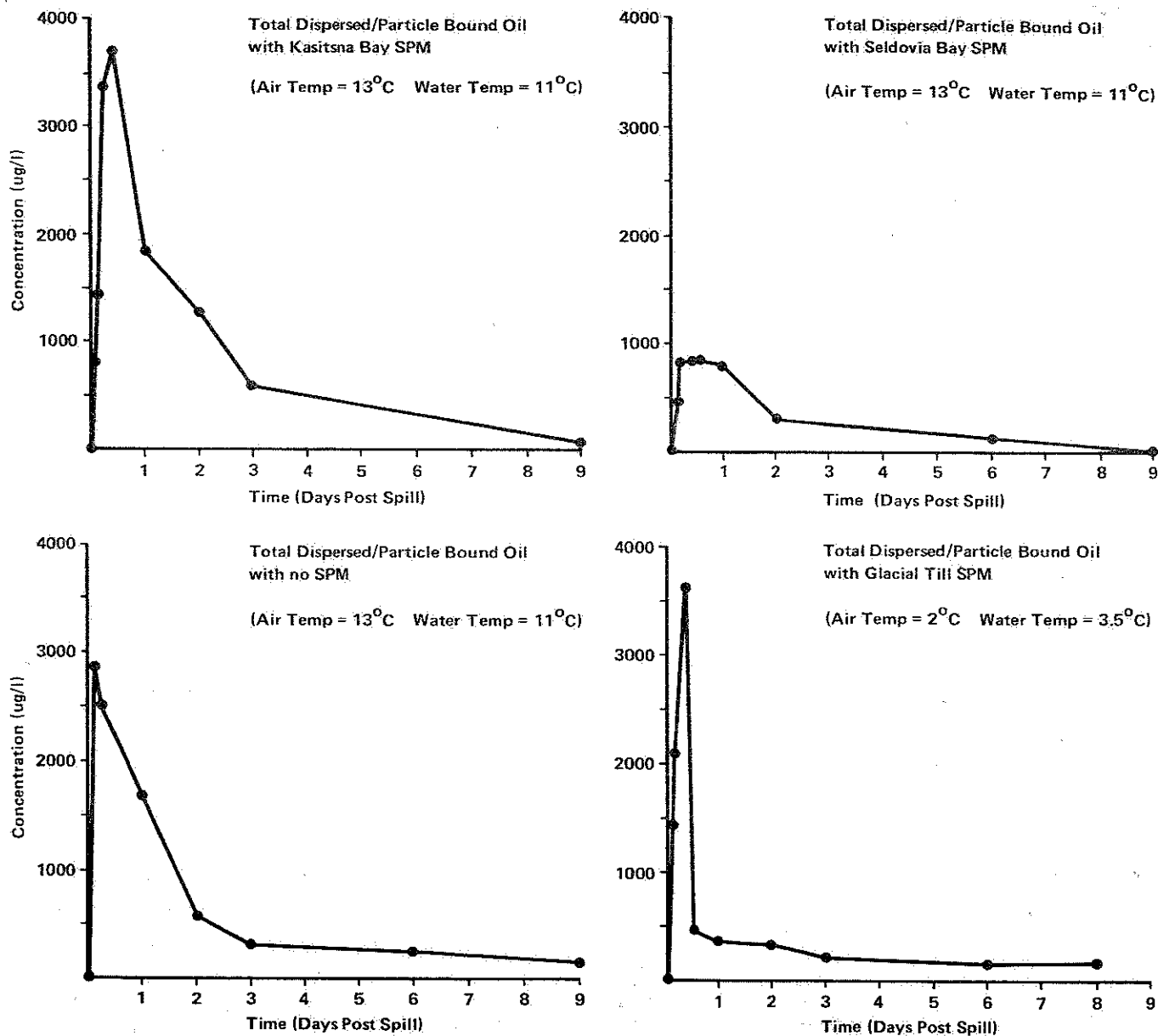
oil to dissolved (sub-0.45  $\mu$ m-particles) fractions was directly related to the viscosity of the oils tested. With increased viscosity then, breakup of a slick would be limited to higher turbulence regimes wherein 1-3 cm size oil droplets could be broken away from the main slick and dispersed into the water column. Such higher turbulence regimes were present during the NOAA Ship *Researcher* investigation of *Ixtoc I* blowout, and near complete dispersion of more heavily emulsified oil was noted after Hurricane Henri passed to the north of the wellhead during September 1979. As noted previously, however, these droplets would tend to return to the sea surface with time unless adsorbed onto suspended particulate material, ingested (whereby they could be deposited as fecal pellets), or ultimately used (as tar balls) by sessile organisms as a substrate to support growth.

### *Photochemical Oxidation*

Numerous laboratory studies have been completed on photochemical oxidation and, in general, changes in the water soluble fraction of most crude oils are readily apparent.<sup>8,49</sup> Exposure of simulated slicks and pure hydrocarbon components have shown that a variety of oxygenated products, including peroxides, aldehydes, ketones, alcohols and fatty acids, can be formed from a variety of substrates.<sup>8,50-54</sup> Formation of these products usually leads to an enhanced water solubility, and enhanced toxicity of the peroxide and other oxygenated moieties to selected test organisms has been demonstrated.<sup>55,56</sup> Other work has shown that the formation of oxidation products can significantly increase the levels of surfactant materials present in a slick which are required for the formation of stable water-in-oil emulsions.<sup>8,57</sup> In fact, several oils (Brega, Nigerian, Zarzantine and Light Arabian) have been studied wherein stable water-in-oil emulsions can only be formed after simulated photochemical or microbial oxidation.<sup>8,14,51,58-60</sup> It should be noted, however, that most of the product formation and rate estimates for photochemical processes have been derived from laboratory studies, with only limited information available on the isolation of photo-oxidation products at spills of opportunity.

Several mechanisms for the photo-oxidation of petroleum have been proposed, including: (a) free radical oxidation in the presence of oxygen; (b) singlet oxygen initiation of hydroperoxide formation; and (c) ground-state triplet oxygen combining with free radicals to form peroxides.<sup>5,52,54-56,61,62</sup> Rates of photo-oxidation are considered wavelength dependent, but rates are also affected by turbidity levels and SPM concentrations (particularly for higher molecular weight aromatics). Photosensitized reactions are described by first-order kinetics. The presence of inhibitors, such as sulfur compounds (e.g., thiocyclanes) or beta carotenes, can restrict the formation of radicals or inhibit singlet oxygen-mediated peroxide formation. Humic substances may reduce the photolysis rates of UV-sensitive compounds, but humic materials can also photo-sensitize transformations of organic compounds through an intermediate transfer of energy to molecular oxygen.





**Figure 8.** Whole dispersed oil and particle bound oil concentrations as a function of weathering time and SPM type. Because dispersion is extremely dependent on the physical state of the slick, dispersed oil concentrations become depressed with the initial formation of mousse.

The presence of several photo-oxidized products, including alkyl-substituted dibenzothiophene sulfoxides in oil samples and benzoic acids and fatty acid methyl esters in seawater extracts, have been reported in field studies at spills of opportunity.<sup>63-65</sup> Those photo-oxidized compounds had an enhanced water solubility and, consequently, were removed from surface slicks and diluted in underlying waters.

Additional data are needed to further characterize the products derived from photo-oxidation of weathered oil, as well as the eventual fate of the products and chemical transformations. Similarly, additional research on the toxicity of the photochemical products is needed to characterize the environmental impacts associated with long-term weathering. Further study to define the possible effect of photo-oxidation processes on water-in-oil emulsification is also

needed. Research in these areas will improve the predictive capabilities for future modeling of photochemical effects on oil weathering.

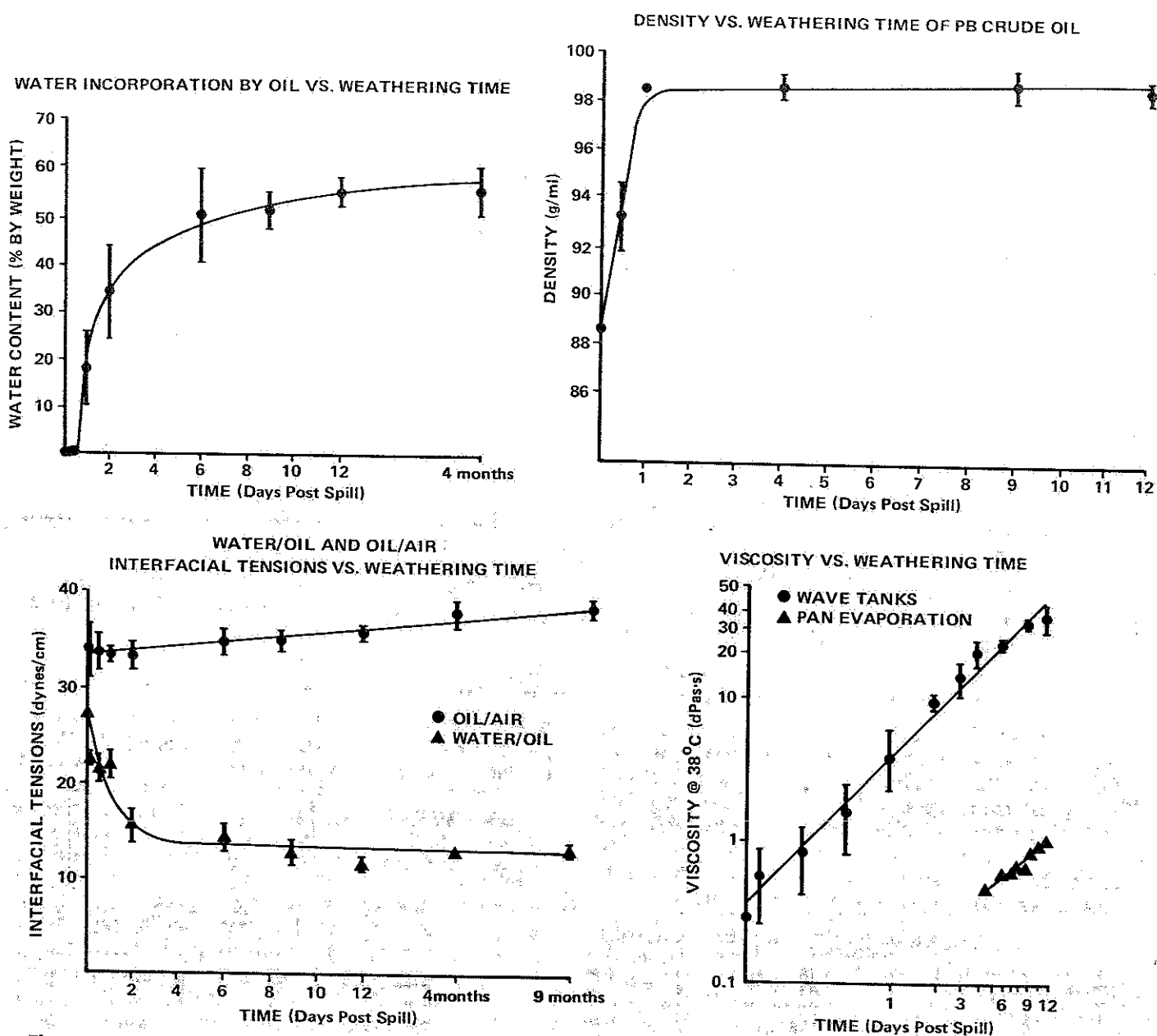
#### *Water-in-oil Emulsification*

The tendency of certain oils to form a stable water-in-oil emulsified mixture or mousse is extremely oil dependent, and appears to rely heavily on the presence of wax and asphaltic materials in the whole crude.<sup>6-16</sup> Refined petroleum products which do not contain asphalts and waxes do not form stable water-in-oil emulsions.<sup>9-13</sup> In addition to the presence of wax and asphalt, the formation of oxygenated surface active materials, due to photochemical and microbial degradation processes, also appear to be important in stabilizing water-in-oil emulsions.<sup>8,9,14,51,57-60,66</sup> Other indigenous surface active agents such as metallo-

porphyrin, organo-sulfur and oxygen compounds may also be important. Surface active compounds are believed to surround the water droplets, which usually range in size from less than one to 10 micrometers,<sup>11-12</sup> preventing water/water droplet coalescence and ultimate oil/water phase separation.<sup>67,68</sup> A much more extensive review of the water-in-oil emulsification behavior of a wide variety of crude oils is currently in preparation.<sup>7</sup>

Significant changes in the rheological properties of the slick or oil mass can be observed during the formation of water-in-oil emulsions. For example, Figure 9 presents time-series data on rheological properties obtained from wave tank experiments at Kastisna Bay,

Alaska wherein Prudhoe Bay crude oil formed a stable water-in-oil emulsion (with up to 55% water) over a period of 12 days.<sup>41</sup> During this time frame the viscosity of the mixture increased to well over 2,800 centipoise, whereas the oil/air interfacial tension changed very little and the oil/water interfacial surface tension dropped from 27 to 13 dynes/cm. Subsequent changes in oil/air and oil/water interfacial surface tension did not occur over a 12-month period. The formation of such stable water-in-oil emulsions is important, however, in that it affects clean-up, combustability and control effectiveness,<sup>7,13</sup> and severely limits additional weathering and removal of components from the emulsified mass. Under these conditions, the oil slick no longer behaves as a well-stirred phase, and



**Figure 9.** Changes in various physical properties of Prudhoe Bay crude oil as a function of weathering time. The formation of a stable water-in-oil emulsion is marked by increases in density, water content, and viscosity and a decrease in oil/water interfacial tension.

diffusion controlled weathering processes become self-limiting.<sup>2</sup> Thus, additional evaporative and dissolution weathering can be significantly reduced, and penetration of nutrients and dissolved oxygen into the interior of the emulsified mass can inhibit microbial degradation processes. Under these conditions then, additional degradation by either microbial or photochemical oxidation processes are limited to the exterior surface of the tarballs or mousse.

In the area of modeling the formation of water-in-oil emulsions, significant progress has been made in predictions of viscosity as a function of weathering conditions and input turbulent energy.<sup>2</sup> However, much of our understanding is still empirical at best, and most data used for model verification are extremely oil-specific. Additional progress in this area can be made with continued effort towards identifying the surface active materials responsible for stabilization of the water-in-oil emulsion. However, predictions as to how a *particular* oil would behave under a given spill scenario requires an *a priori* knowledge of the wax, asphaltene, and NSO resinous materials content in the oil before realistic predictions on emulsification behavior can be made.

#### *Adsorption onto Suspended Particulate Material*

Oil and SPM interactions occur through two primary mechanisms: (a) molecular sorption of dissolved species; and (b) oil droplets colliding with suspended particulate materials. The parameters and/or conditions that might influence the rate of "reaction" between dispersed oil and SPM are numerous: the concentrations, composition and density of dispersed oil and SPM; and the size distribution of the oil droplets and SPM will all have some effect on the rate of oil droplet/SPM associations. The solubility of individual hydrocarbon components in seawater influences rates of molecular sorption of dissolved species onto SPM. Data from field and laboratory studies suggest that sorption of truly dissolved components is not important to the overall *mass balance* of an oil spill,<sup>12</sup> although such adsorption may be important for the biological considerations described below.

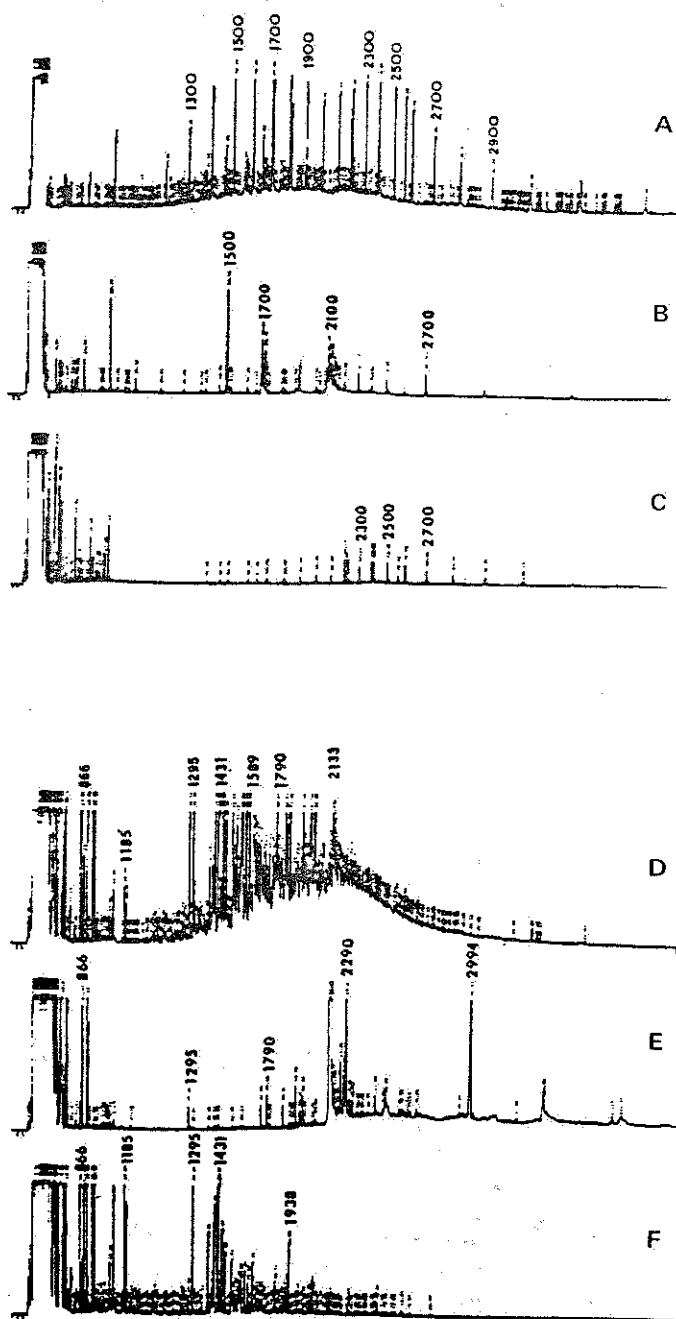
Interactions between spilled oil and suspended particulates represent an important mechanism for the rapid dispersal and removal of oil from surface waters. Rates of oil/SPM interactions and dispersal are, in turn, related to concentrations of suspended materials and fluxes of SPM into and out of an impacted area. In particular, oil spills in nearshore waters with high suspended particulate loads experience rapid dispersal and removal of the oil due to sorption onto SPM along frontal zones.<sup>47,69</sup> Boehm<sup>70</sup> characterized the SPM concentration dependence on oil/SPM fluxes as follows: At SPM concentrations from 1-10 mg/liter, no appreciable transport of particle-associated oil to the seabed occurs; at SPM loads from 10-100 mg/liter, considerable oil/SPM interactions, with subsequent transport and deposition is possible in the presence of sufficient turbulent mixing; and at concentrations >100 mg/liter massive oil transport may occur with potentials for significant adverse impacts on the benthos.

In this case, adsorption of dispersed oil onto suspended particulates may provide a relatively efficient mechanism for sedimenting significant fractions of the oil mass. For example, following the *Tsesis* oil spill in the Baltic Sea, approximately 10-15% of the 300 tons of spilled oil were removed by sedimentation of SPM-adsorbed oil. The high oil flux was due to the large SPM concentrations resulting from turbulent resuspension of bottom sediments.<sup>71</sup>

As part of an Open Ocean Oil Weathering Program,<sup>2</sup> compound-specific partition coefficients were measured for fresh Prudhoe Bay crude oil and four representative sediment types, characteristic of suspended particulate material encountered in Alaskan outer continental shelf waters. Table 2 presents the SPM/water phase concentrations obtained on specific aromatic compounds from those measurements. Figure 10 presents representative chromatograms showing the preferential partitioning of lower molecular weight aromatics into the water column and intermediate and higher molecular weight aromatic and aliphatic hydrocarbons partitioning onto the suspended particulate material.

Based on results from simulated spills in outdoor wave tanks, the following mechanism for incorporating oil into bottom sediments has been proposed. Oil droplet dispersion and oil/SPM interactions occur soon after a spill and before appreciable weathering affects oil viscosity. Oil laden particles sink and become incorporated into the bottom sediments. However, once a stable water-in-oil emulsion is formed, additional input of hydrocarbons to the water column and subsequent SPM adsorption is greatly reduced. Once assimilated into the bottom sediments (or during the particulate sinking phase), highly soluble aromatic compounds and the more volatile aliphatic compounds are partitioned into the water column, while the intermediate and higher molecular weight aliphatic compounds remain associated with the sinking or deposited particles. This preferential partitioning of higher molecular weight aliphatics into bottom sediments, with solubilization of aromatic hydrocarbons, also agrees with results from previous ecosystem studies<sup>72,73</sup> and these levels of oil adsorbed onto bottom sediments also agree with levels from smaller scale laboratory studies.<sup>74</sup>

Similar, selective partitioning of lower and higher molecular weight compounds has been observed by deLappe et al.<sup>75</sup> in a study designed to measure the partitioning of petroleum hydrocarbons among seawater, particulates, and the filter feeding *Mytilus californianus*. Payne et al.<sup>46</sup> and Boehm and Fiest<sup>76</sup> also observed a similar partitioning between lower and higher molecular weight compounds in dissolved phase and suspended particulate material samples removed by filtration of large volume water samples obtained in the vicinity of the *Ixtoc 1* blowout in the Gulf of Mexico. A more extensive review of these and other oil/SPM interactions was presented by Jordan and Payne,<sup>1</sup> and the interested reader is referred to that reference and more recent updates<sup>70</sup> for additional details.



**Figure 10.** Flame ionization detector gas chromatographic profiles of oil/SPM adsorption using Seldovia Salt Marsh sediment. (A) aliphatic hydrocarbons in oil-exposed sediment, (B) aliphatic hydrocarbons in exposed sediment, (C) aliphatic hydrocarbons in the water column, (D) aromatic hydrocarbons in an exposed sediment, (E) aromatic hydrocarbons in unexposed sediment, (F) aromatic hydrocarbons in water column. Figures 10A and 10D show that preferential oil/SPM interactions occur with intermediate and higher molecular weight aliphatic and intermediate molecular weight aromatic hydrocarbons. Lower molecular weight aromatics preferentially partition into the aqueous phase (10F).

Changes in salinity, pH, turbulence, temperature, concentrations of oil, and presence of natural surfactants (dissolved organic matter) will also influence the partitioning of oil onto SPM.<sup>70</sup> The affinity of a particular hydrocarbon component for particulate adsorption is described by the partition coefficient ( $K_d$ ) such that  $K_d = C_p/C_w$ , where  $C_p$  is the concentration of the hydrocarbon on the particles and  $C_w$  is the concentration of the hydrocarbon in the water.

#### Shoreline Interactions

The discussions thus far have focused on the weathering and interaction of dispersed whole oil droplets in the water column. Any attempt at understanding the weathering (partitioning and distribution) of hydrocarbons in a natural environment or in an enclosed coastal environment must also allow for oiling of various shoreline habitats and redistribution of oiled intertidal substrates into the near shore environment during storm events.

Conceptually, when oil is released in the nearshore environment, it can immediately undergo the previously considered weathering processes and these, along with inshore energy dynamics, will ultimately control the partitioning of hydrocarbons onto sediments and into the water column. The following discussion presents a conceptualization and overview of the more important aspects of this inshore oil/sediment interaction.

Partitioning of hydrocarbons into sediments can be broken down into subtidal and intertidal interactions.

- Subtidal partitioning includes dispersed droplet and dissolved oil interactions with suspended particulate material as well as direct contact of dispersed droplets with the shallower sediments within the surf zone.
- Intertidal interactions include the stranding and penetration of oil on and into the upper, middle, and lower intertidal zones; this behavior is largely controlled by tidal conditions and intertidal substrate type.

Studies of the long-term weathering of oil-coated subtidal sediments in Lower Cook Inlet<sup>277</sup> have shown that continued dissolution and removal of aromatics to interstitial and bottom waters can occur over time frames as short as one year. Microbial degradation of the lower and intermediate molecular weight aliphatics and aromatics associated with subtidal sediments can also occur, resulting in concentration-dependent removal of the total hydrocarbon burdens from the sedimentary regime with time.<sup>2</sup> Above certain threshold concentrations ( $\geq 10$  parts per thousand), the Cook Inlet crude oil used in that study was apparently toxic, and very little evidence of microbial degradation of the oil was noted.

Field studies have shown that fresh oil can penetrate coarse-grained intertidal sediments quite rapidly.<sup>1,2</sup> Ultimately, oil can reach depths of 1-2 ft. in gravel or coarse sand, where the depth of oil penetration is controlled by the interstitial water table. Thus, in extreme-

Table 2. Results of Equilibrium Partitioning Oil/SPM Interaction Studies (Static System, 19°C)

Selected Concentrations <sup>a</sup>	KB-1 <sup>a</sup>		KB-2A <sup>c</sup>		KB-2B <sup>d</sup>		KB-3 <sup>e</sup>		KB-4 <sup>f</sup>	
	Sediment	Aqueous	Sediment	Aqueous	Sediment	Aqueous	Sediment	Aqueous	Sediment	Aqueous
Total Resolved Aliphatic	340,000	4,760	795,000	3,380	647,000	170	85,000	5,840	253,000	0
Unresolved Aliphatic	73,000	0	18,000	0	57,000	0	10,000	0	262,000	0
Σ n-alkanes	26,000	33	16,000	11	14,000	17	5,000	8	60,000	0
Σ n-alkanes/branched ratio	0.08	0.007	0.02	0.003	0.02	0.1	0.06	0.001	0.3	—
Total Resolved Aromatic	46,000	601	385,000	1,910	9,600	2,720	12,000	512	44,000	2,180
Unresolved Aromatic	42,000	75	7,100	0	22,000	0	10,000	0	75,000	0
m & p-xylene	15.0	2.9	46.0	3.4	ND <sup>g</sup>	ND	33.0	2.0	12.0	2.9
ethylbenzene	64.0	0.56	270	1.4	ND	ND	130	0.74	200	0.46
naphthalene	40.0	1.3	90.0	3.3	ND	ND	4.0	ND	29.1	0.16
2-methylnaphthalene	630	7.4	550	7.2	ND	ND	91	0.63	48	0.49
1-methylnaphthalene	400	7.4	310	6.8	ND	ND	83	4.4	370	1.3
2-ethylnaphthalene	103	9.8	96.0	0.70	ND	ND	25	0.28	125	0.12
2,3-dimethylnaphthalene	440	3.1	240	2.2	ND	ND	89	2.3	337	2.2
1,6,7-trimethylnaphthalene	290	1.0	143	1.0	ND	ND	35	0.28	210	0.34
phenanthrene	570	0.23	200	ND	ND	ND	44	0.53	71	ND
2-methylphenanthrene	390	ND	ND	ND	ND	ND	ND	ND	ND	ND

a Sediment concentration in  $\mu\text{g/kg}$ , water concentration in  $\mu\text{g/l}$

b KB-1—Grewingk Glacier Till—fine grained terrestrial plus diatoms, many flakes  $5\ \mu\text{m}$  and less—Specific Surface Area 9.1

c KB-2A—China Poot Bay (surface 1 cm)—mostly  $>5\ \mu\text{m}$  terrestrial plus some plant material— " 8.2

d KB-2B—China Poot Bay (1-8 cm depth)—mostly material  $<5\ \mu\text{m}$  " 15.2

e KB-3—Kasitsna Bay consolidated sediment—90% diatoms  $>5\ \mu\text{m}$ , some terrestrial  $<5\ \mu\text{m}$  " 9.1

f KB-4—Seldovia River Salt Marsh—organic plus fecal pellets " "

g ND indicates "not detected"

ly steep, coarse, sandy beaches, penetration of fresh oil may be expected if the oil is deposited during a receding tide. With recurring high tides, dissolved components may be removed from the interstitial waters, but significant amounts of the higher molecular weight (greater than  $\text{n-C}_{12}$ ) aliphatic and aromatic components could remain for several years.

In most cases the degree of penetration into the sediments will be sediment-controlled, with the finer-grained sediments—silts and clays—limiting oil penetration. In the case where clays and very fine sands and silt are encountered in lower energy regimes, penetration of the oil into the intertidal sedimentary regime will be limited to holes from burrowing organisms. During real spill events, such as the *Amoco Cadiz* spill,<sup>27,78</sup> and during controlled field experiments in the Kachemak Bay, Alaska region,<sup>2</sup> the fresh oils from surface mud flat sediments were lifted off the substrate with repeating tides. Under these conditions, oil will continue to undergo increases in viscosity with evaporative/dissolution and mixing in the intertidal zone. With time, however, the weathered oil material will be encrusted with greater amounts of the finer grained sedimentary material. After several days or weeks, sufficient particulate material will be entrained in the sediment-oil mass such that an asphalt-like material may be formed. This material would no longer be resuspended with additional tidal floodings, but may be transported into upper and middle intertidal zones. With increased storm activities, the deposited oil can be scoured from the

beach surface and deposited in offshore berms, as observed off the south Texas coast during the *Ixtoc I* blowout incident in 1979 and 1980.<sup>79,80</sup>

If a higher density or more viscous oil were spilled (or a more weathered crude released from a greater distance from shore is encountered), its penetration into intertidal sediments would be limited due to the viscosity-controlled inhibition of flow into the interstitial regimes. This behavior was observed during both the *Metula* spill<sup>81,82</sup> and during controlled, small scale experiments in lower Kachemak Bay where water-in-oil emulsions containing up to 60% water were deposited within several intertidal regimes.<sup>2</sup> Under these conditions little penetration of the mousse into the intertidal regime was observed, and the mousse was primarily subject to mixing with sand and refloating with incoming tides. If a large oil mat (covering kilometers of shoreline) were present, this continued lifting and redeposition would ultimately cause accumulation of sedimentary materials into the oil, resulting in an oil/sand, asphalt-like mat. During the *Metula* spill, mousse thickness ranged from 0.5-10 cm and in some areas reached 15 cm. At one area, mousse mixed with sand was observed to a depth of 30 cm. Coating of vegetation and deposition in the upper intertidal zones (and along the storm berm with receding tides during the lunar tidal cycle) may be expected. Evaporative weathering of material deposited on the shore, and temperature controlled crust formations might yield an asphalt-like product which again would be resistant to further microbial or

chemical weathering with time. A limited dissolution of the lower molecular weight aromatics in this material could occur, affecting interstitial waters and nearshore waters for periods up to several months or years. Similar behavior was observed in oil released during the *Amoco Cadiz* spill in 1978.<sup>83</sup>

The "importance" of partitioning of the different oil components depends on the time frame and the biological and shoreline conditions. During the seasons when juvenile stages are present in estuarine areas, the dissolution-partitioning of the more toxic aromatics into backwaters might be of primary concern. Alternatively, on a rocky headland or coastal high energy regime (where the dissolved components might be rapidly advected away), oil-into-water dispersion might be a greater concern. In this latter instance, dispersed oil droplets could interact with finer suspended particulate material offshore and ultimately be susceptible to sedimentation. Most whole crude oils will not undergo weathering to the point where their density is greater than that of seawater; it is only after incorporation of detrital material or sand during deposition on shore, or through interactions with suspended particulate material in the water column and/or attachment of pelagic organisms such as barnacles, that densities can increase sufficiently to sink crude oils.

At this time, little has been done to model the transport behavior of oiled sediments in intertidal and nearshore subtidal regimes. Various types of crudes have been shown empirically to increase sediment cohesion, which may inhibit sediment transport. During the *Ixtoc 1* blowout, for example, oil impacted selected areas of the shoreline off the South Padre Island, Texas coast,<sup>79</sup> and most of the beached oil was heavily resistant to transport during storms. Oil/sediment mats were ultimately covered by clean sand deposits, although this material was re-exposed approximately one year later, during a hurricane and subsequently removed to subtidal berms in water depths up to 30 meters. At this point, the oil/sand mats were deposited and not subject to further transport. Similar behavior could be anticipated in the Alaskan shelf regions subject to high storm turbulence.

In the South Padre Island case, many of these subtidal asphalt/oil/sand mats supported algal and bacterial growth which further served to stabilize the mixtures. It is not known if similar behavior might be expected in the intertidal and subtidal regions in the arctic or sub-arctic. Certainly, any such growth would be seasonally variable, and would also depend on the point of ultimate deposition (intertidal versus subtidal). Further, the effects of ice scour in the intertidal zone may serve to resuspend and enhance the movement of larger oil/sediment mats to offshore areas (again depending on storm activities).

#### *Effects of Ice on Oil-weathering Behavior— Weathering Behavior in Arctic Environments*

The weathering of petroleum in the presence of sea ice is dependent on the point of oil release and the extent of ice cover. Specifically, if oil is spilled in open

or broken ice, the oil will tend to pool in the open leads and will not spread to the same extent of a comparable spill in open ocean conditions. The structure of the ice encountered by spilled oil may also have an effect on the subsequent weathering and partitioning of oil. Oil weathering processes specific to ice-covered waters are spreading (on ice, under ice, and within open leads) and encapsulation. Spreading in the presence of ice is an extremely important facet of weathering because this process determines the surface area of the oil spill, and thus affects the component mass transfer through the oil/air and oil/water interface. Oil spilled during winter in the presence of level ice may be deposited on the ice, underneath the ice, or in both environmental pools. A subsea pipeline rupture or oilwell blowout, for example, could result in extensive under-ice coverage.<sup>84,86</sup> Oil released into subsurface waters subsequently rises through the water column and is trapped underneath the ice; the thickness of the under-ice slick is primarily controlled by the depth of the under-ice depressions, although oil droplets have been observed to stick to the bottom of smooth first-year ice even in the presence of under-ice currents.<sup>86</sup> Within hours of release, an ice lip forms around pools of trapped oil, thus further restricting horizontal movement or transport. Depending on the seasonal conditions, an ice sheet may continue to grow around and underneath the oil and eventually completely entrap the spill.<sup>86</sup> After encapsulation, the oil is not subjected to further weathering or alteration of its physical properties until the following spring.<sup>87</sup> During spring, brine channels in first-year ice form rapidly as the ice melts. After the brine channels have penetrated to the depth of the encapsulated oil, the oil may migrate slowly upwards through the ice and eventually spread on the ice surface.<sup>88</sup> Later in the spring, as the porosity of the ice increases, oil movement through the ice is less restricted.

The weathering behavior of oil released under a solid ice sheet is appreciably different than the weathering of oil spilled in broken ice or open ocean conditions. Evaporative losses are completely inhibited and cannot occur until the oil reaches the surface. Under winter conditions, oil trapped as a lens under the ice surface can be totally encapsulated within 24-48 hours, although some dissolution of lower molecular weight aromatics can occur before that time. The absence of evaporative losses will effect the combustibility of the oil, thus burning can be an effective cleanup or disposal mechanism if the oil can be ignited immediately at the ice/water surface during ice breakup.<sup>87</sup> With regard to the breakup itself, tank and field studies have shown that the oil will tend to migrate up brine channels that are formed during ice maturation. Oil migrating to the surface will pool, causing a decreased albedo in the ice and further enhancing localized melting. This leads to further upward migration of the oil towards the surface of the ice where it ultimately will be subject to evaporation. With continued breakup of the ice, open leads form and lead matrix pumping effects<sup>88</sup> can become important for promoting increased water-in-oil emulsification and increased dispersion of oil droplets into the

water column. This dispersion process quickly becomes limited due to enhanced water-in-oil emulsification, which increases oil viscosity and inhibits small oil droplet breakup from the parent slick. Emulsified products of the whole crude ultimately will be subject to open ocean weathering processes after the complete breakup of the ice floe.

Oil released on the surface of broken ice is subjected to a variety of weathering processes including spreading between leads, evaporation, dissolution, and emulsification. Evaporation is the dominant weathering process, and can result in the removal of a considerable fraction of the spilled oil (although the specific evaporative loss is again *extremely* oil and temperature dependent). These concurrent weathering processes are responsible for the continued changes in the physical and chemical properties of the exposed oil as described for open ocean conditions. Emulsification is of particular importance because it leads to both orders-of-magnitude increases in viscosity and decreases in the fire and flash points of the resultant product.<sup>13</sup>

In a similar fashion, oil discharged onto the ice surface from an above-ice pipeline rupture or well blow-out would also spread on the ice surface. Snow cover or ice ridges would confine oil and thus limit the extent of spreading. Weathering of the spilled oil during winter is relatively slow due to the cold temperatures, reduced solar radiation, and diffusion-controlled restriction of component evaporation due to the limited surface area and greater oil layer thickness.<sup>12</sup> However, during the spring thaw, melt pools are rapidly formed in these areas due to increased absorption of solar radiation, with a subsequent thinning of the oil slick.

At the initiation of break-up (or if the spill occurs in broken ice), the oil on the ice surface enters the leads and cracks between the floes.<sup>89</sup> This oil then spreads to various equilibrium thicknesses, depending on the ice concentration and the physical properties of the oil. In this case the ice would no doubt restrict the initial spread of the oil, and the spill area would be smaller than that predicted for open water conditions. Accelerated mousse formation and sinking of the water-in-oil emulsion beneath the grease ice (but still within the leads of the ice pancakes) has been reported in ice tank studies with Prudhoe Bay crude oil.<sup>90</sup> Moreover, the combined action of lead/matrix pumping and agitation of the grease ice against the larger ice floes may result in a considerable increase of dispersed oil micelles in the water column, further enhancing immediate dissolution of aromatic hydrocarbons.

Once breakup progresses to the point where ice floes move independently under the influence of wind and currents, the effect of the ice on oil-weathering is less predictable. At this stage, the oil is subjected to open-ocean weathering conditions (primarily evaporation and additional emulsification), and further dissolution of the more water-soluble, lower-molecular weight aromatics may be limited by diffusion con-

trolled processes within the emulsified oil phase itself. In the absence of ice, a spill is subject to open-ocean weathering, including spreading to some equilibrium thickness and surface area, with concomitant evaporation, emulsification, dissolution, and dispersion processes (as in more temperate sub-arctic waters). The temperature-dependence of these physical and chemical processes indicates, however, that the rates of weathering would be significantly decreased under the colder arctic temperatures.<sup>2,90,91</sup>

If the oil persists until the following year's freeze-up (or the spill occurs at freeze-up), the oil rises to the surface of the forming grease ice or is pumped laterally onto the surface of pancake ice.<sup>88</sup> In these instances oil is confined to the surface or upper few centimeters of the young first-year ice and is again subjected to slow weathering, mixing with snow, and entrapment within the ice throughout the winter. Portions of the oil spill would undoubtedly persist until the spring thaw. This would clearly be the case for most refined products and intermediate weight fuel oils. If water-in-oil emulsification occurs (as noted for Prudhoe Bay crude oil) then this material may reside just under the grease ice at the grease ice/seawater interface.<sup>90</sup> After freeze up, additional dissolution weathering would not be expected.

There are almost no data on the fate of oil released under pack ice or multi-year ice. However, the fact that pack ice is in more or less constant motion, added to the fact that leads of open water can be expected to appear frequently with associated high lateral under-ice currents, indicate that the resulting area of contamination could be very large. The pattern of contamination, however, would be very poorly defined and some overflow to the surface could be expected where leads had opened over the release site. The opening and closing of leads and/or polynyas directly over a blowout or pipeline rupture could, by lead matrix pumping, cause much wider dispersal of oil on the ice surface and in the water column than the above description would indicate.

Significant amounts of oil released in the transitional and shear ice zones,<sup>93,94</sup> in the Arctic would flow on the water surface almost immediately. Pressure ridge formation could expose the oiled undersurface of ice slabs, thick films of oil in leads could be squeezed between converging floes and washed onto the surface of the floes, and large pieces of ice could turn over in oil-covered water. In this situation, some of the oil could also remain under the surface and be encapsulated into the ice sheet.

Ice that has survived more than one or two summers' melts (as has perhaps two-thirds of the ice in the polar pack) has fewer brine channels. For this reason, oil trapped under pack ice probably reaches the surface slowly since there are few available avenues of upward migration. Nevertheless, Ross et al.<sup>95</sup> speculated that most oil under multi-year ice would emerge at its surface by late summer. In the worst case, because pack ice melts on top and grows from beneath, the oil could remain entrapped in ice



for periods up to ten years. Oil cleanup would thus be a long and tedious process. Initially, the biggest problems would be to track the contaminated ice for long periods and to know where to look for the oil during those brief periods when cleanup operations would be feasible.

## MODELING OIL WEATHERING

Composite models, reviewed by Huang,<sup>96</sup> have recently been developed to provide more realistic predictions on the environmental fate and behavior of oil spills. In addition to slick advection, algorithms describing weathering processes such as spreading, evaporation, dispersion and emulsification, have been derived for incorporation into simulation models.<sup>2</sup> Corresponding models do not presently exist for describing sinking/sedimentation and auto-oxidation processes.

The primary objectives for a mathematical oil weathering model are to predict both the mass of oil remaining in a slick over time and the chemical composition and physical properties of the slick. Payne et al.<sup>2,41</sup> have developed predictive oil weathering models which generate material balances for both specific compounds and pseudo-compounds (true boiling point distillation cuts) in a crude oil spill. The models are also designed to predict the behavior of any specified refined distillate product (gasoline, diesel, etc.) as well. These models are applicable to open-ocean oil spills, spills in estuaries and lagoons, and spills on land. The oil weathering processes included in the model are evaporation, dispersion into the water column, dissolution, water-in-oil emulsification (mousse formation), and slick spreading. The model is based on physical properties data, such as oil/air interfacial surface tension, oil/water interfacial surface tension, and oil viscosity, as well as mass transfer (rate) coefficients which were obtained either from the open literature or from measurements made from simulated spills in outdoor wave tanks.

In general, reasonable correlations between predicted oil weathering behavior and observed chemical changes have been obtained.<sup>2,41</sup> Changes in predicted and observed chemical and physical properties of the oil slick also accompany changes in oil slick behavior, especially during the early weathering stages (from a freely flowing slick), through the mousse formation stage, to the subsequent stage of tarball formation. Models developed by Payne et al., are presently capable of predicting oil weathering behavior in real spill situations; however, it is ironic that investigations of oil weathering at spills of opportunity have measured concentrations of specific components, whereas determinations of the overall mass balance using a pseudo-component approach are needed for model verification.

At present, further work is needed to validate existing oil weathering models under higher turbulence regimes. The oil weathering models should also be expanded to predict oil/SPM interactions, the behavior of oil in various stages of ice growth and decay, and

the transport and deposition of oiled sediments from intertidal and near shore subtidal regimes. Such models could then be an extremely powerful tool in providing information for site-specific contingency planning, estimating potential damage assessments and preparing environmental impact reports for outer continental shelf drilling activities.

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