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THE CHEMISTRY AND FORMATION OF WATER-IN-OIL
EMULSIONS AND TAR BALLS FROM THE
RELEASE OF PETROLEUM IN THE MARINE ENVIRONMENT

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PREFACE

This manuscript is based **on** a review **prepared** as a contribution to the **NAS** Petroleum in the Marine Environment/Update Workshop held November **9-13**, 1981, and it may or may not reflect **the consensus** of the workshop participants or the National Academy of Sciences. A summary publication of those proceedings is anticipated in **1983**; however, there are currently no plans to publish **the** background papers per se. Thus, this text is the direct **result** of the author's desire to make its contents available to a wider audience of interested parties in the scientific and industrial community. I am grateful to a number of my **colleagues** and peers who have encouraged me over the several months which have elapsed since the NAS review to publish this material in its present form.

The original draft of the manuscript was reviewed by Dr. James N. Butler of Harvard University **and** Mr. Gerard P. **Canevari** of Exxon Research and Engineering Company. Their comments and suggestions have been incorporated throughout the text where appropriate; however, this author must assume responsibility for any omissions or errors **introduced** in reviewing the rather extensive amount of literature published on the subject.

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INTRODUCTION

The requirements for understanding and being able to predict the formation of water-in-oil emulsions, sometimes described as "chocolate **mousse**", are critical components in our ability to control and mitigate the environmental impacts of petroleum hydrocarbon spills in marine and coastal waters. Stable water-in-oil emulsions or mousse can compound clean-up strategies and logistics, as the more viscous mousses can present formidable problems in skimming, pumping and recovery operations. Mousse can take up an inordinate amount of space in transport and intermediate storage due to the often noted factor of 4 to 5 increase in volume from water incorporation, and in the final stages of disposal certain water-in-oil emulsions may resist more convenient and conventional disposal mechanisms such as burning.

When crude oil and many refined products are released at sea they are immediately subjected to a series of weathering processes including: spreading, evaporation and dissolution of selected **lower** molecular weight components, dispersion of whole oil droplets into the water column, coalescence of these droplets and return to the surface **slick** with entrapment of seawater, photo-, **microbial**- and auto-oxidation, and emulsification and **tarball** formation. The rates of these **concomitant** processes are inextractably **linked** (and in some cases compete) with one another and are dependent on the type and amount of oil spilled (component concentrations), the environmental conditions (water and air temperature, wind speed, and turbulence regime -- sea state) and man's own efforts to control or disperse the slick through the application of **dispersants** (emulsifying agents) and/or adsorbant products to enhance sinking.

Most crude oils and refined petroleum products have specific gravities less than 1 so they will not readily sink after initial release, but the combined effects of natural and enhanced weathering processes alter the density, viscosity, pour point and **volume** of these products such that ultimate cleanup and containment strategies must be designed to handle an incredible

variety of situations. During the formation of water-in-oil emulsions, products of higher density and viscosity containing up to 70-80% water (dispersed as sub-micron to 50 micrometer droplets) in the continuous oil phase can be generated, and as such, burning may become much more difficult due to the high water content, and chemical dispersion may prove to be impossible. Because of their greater density however, oil-in-water emulsions and tar balls generated from such mousse may be more susceptible to submersion, ultimately enhancing the dispersement of crude slicks. Numerous investigators have suggested that mousse formation and stability is influenced by the presence of surfactant materials such as asphaltenes, waxes, organometallics, and nitrogen, sulfur and oxygen (NSO) compounds which are important in preventing water-water coalescence within the emulsion. Turbulence has also been demonstrated to be critical in mousse formation; however, at this time no single explanation completely explains all of the observable, and not all of the mechanisms of mousse formation and stability are understood. It has been found that more viscous oils tend to form more stable emulsions and that water-in-oil emulsions are more rapidly formed under lower temperature (higher viscosity) conditions.

In this review, attempts have been made to provide a broad view of the subject. Topics range from discussions of detailed laboratory and field test-tank (wave and mixing chamber) experiments used to examine the specifics of mousse formation from the standpoint of oil composition and turbulence regimes, to studies of mousse formation and behavior in real spill situations. Several major spill incidents are considered with regard to observed and documented mousse and tarball formation, stability and fate; and when possible, correlations between real spill situations and laboratory simulations are made. The occurrence, distribution and chemistry of tarballs from other sources are then briefly considered; however, not as much emphasis has been placed on this subject due to the highly variable levels of tarballs in the world's oceans and their somewhat limited long-term environmental impact.

Finally, a brief review of recent attempts to simulate mousse formation and behavior through mathematical and computer modeling is presented. In general, these models are coupled to or based upon laboratory wave tank and mixing chamber experiments, although several attempts to model **field** observations with computer predictions (hind casting) are discussed.

LABORATORY STUDIES OF FORMATION AND STABILITY
OF WATER-IN-OIL EMULSIONS

Background

Before undertaking a discussion of water-in-oil emulsion formation and stability, it is first necessary to review several general aspects of emulsions and emulsification. A more comprehensive treatment of the subject is presented by Twardus (1980). In general, an emulsion is defined as two immiscible liquids wherein droplets of one phase (the dispersed or internal phase) are encapsulated within sheets of another phase (the continuous or external phase). When crude oil or petroleum products are spilled at sea, two basic forms of emulsions are possible. The first is an oil-in-water (O/W) emulsion in which oil droplets are dispersed and encapsulated within sheets of water. The second is a water-in-oil (W/O) emulsion in which droplets of water are dispersed and encapsulated within sheets of oil, and this is the mixture which is generally referred to in the literature as mousse. For either type of stable emulsion to form between two liquids, three basic conditions must be met. First, the two liquids must be immiscible or mutually insoluble in each other, second sufficient agitation must be applied to disperse one liquid into the other and third, an emulsifying agent or combination of emulsifiers must be present.

Following emulsification the interracial area between two liquids is increased. Because liquids tend to keep the surfaces to a minimum, however, an emulsifying agent and work (or energy) are required to allow emulsification to occur. In theory the amount of energy required to increase the surface area can be calculated (Becher, 1955) if the interracial tension between the two liquids is known. In general, in open ocean and coastal oil spills, sufficient energy is provided by wind, waves and currents to satisfy this requirement, and stable water-in-oil emulsions have been observed to form even on very calm seas. The emulsifying agent may be any surface active substance which can form a thin interracial film between the two liquids and maintain

the **emulsion** by **minimizing** the contact, **coalescence** and **aggregation** of the internal dispersed phase. For emulsions **to** be prepared in the absence of external agitation, the interracial tension between the **two** liquids should be reduced to approximately 0.5 dynes/cm, whereas this value need only be approximately 5 dynes/cm for emulsions prepared with agitation. The **surfactants** should be **able** to surround **the** dispersed droplet as a non-adhering film and should have a molecular structure in which the **polar** end is attracted to the water and the non-polar end is attracted to the oil. Surfactants should be relatively more soluble in the external phase so that it is readily available for adsorption around the internal phase. These **surfactants** also may impart an **electro-kinetic** potential, and influence the viscosity of the **emulsion** formed. Finally, the **surfactant** material must stabilize the **emulsification** process while being present in relatively small quantities.

Depending on **the** chemical composition of the **surfactant**, **emulsion** stability can either be increased or decreased. For example, materials containing **mono-valent** ions have been shown to stabilize oil-in-water emulsions while **surfactants** containing **poly-valent** ions can stabilize water-in-oil emulsions. A number of materials are present in crude oils to stabilize **water-in-oil** mixtures, and these will be discussed later in greater detail. In general, however, unrefined oils have relatively higher portions of **water-in-oil** emulsifying agents than oil-in-water emulsifying agents. Thus, while both types of emulsions can be formed in petroleum spill, the majority of the emulsion would be in the water-in-oil type. Furthermore, oil-in-water emulsions are inherently unstable, and they have been shown to invert to water-in-oil mixtures. The effects of shear rate, temperature and oil concentration on the formation of **oil-in-water** emulsions was studied using California crude (Mao and Marsden, '1977), and they noted that increases in temperature and/or oil concentration also enhanced the inversion of oil-in-water emulsions to **water-in-oil** emulsions.

In water-in-oil emulsions, **asphaltene** substances, porphyrin complexes and waxes have been shown to act as natural emulsifying agents stabilizing W/O

mixtures (Berridge et al. , 1968a, Berridge et al. , 1968b, Cairns et al. , 1974, Canevari , 1969 and Frankenfeld 1973). These agents presumably provide the required film around the water droplets which resists rupture preventing water-water coalescence. The size distribution of water droplets in W/O emulsions is also significant, and this will be discussed in greater detail later.

The stability of water-in-oil emulsions is dependent on a variety of factors, including: the presence or absence of the emulsifying agent, viscosity, specific gravity, water content, and the age of the emulsion. Essentially **the stability** of a W/O emulsion could be defined as the resistance that the dispersed water droplets have against coalescing. Such a definition is based upon the phenomenon of Brownian movement such that the emulsions having a high specific gravity and viscosity would tend to be more stable since movement of the water droplets would be theoretically reduced. As noted above, increases in temperature resulting in reduction of viscosity or increases in the water droplet concentration in the continuous petroleum phase would increase probability of collision and coalescence thus destabilizing **water-in-oil** emulsions.

Specific Studies

A number of laboratory studies have been undertaken to study the formation and behavior of mousse in mixing chambers and wave tanks, and in most cases evaporation and dissolution were allowed to occur to further simulate ambient environmental conditions. In almost **all** instances, hydrocarbons with molecular weights less than **nC-11 to nC-12** (distillation range **200-225°C**) were lost **during** the initial stages of weathering, just as has **been** noted in studies of **open** ocean and near-coastal spills. The results of these studies, the physical properties of the crude oils, and selected chemical characteristics of the crude oils and resultant water-in-oil emulsions are summarized in Table 1. Table 2 lists several additional oils **which** have demonstrated water-in-oil **emulsion** tendencies, but for which only limited data are available.

TABLE 1

Mousse Formation Experiments using a Variety of Fresh and Artificially Weathered (Topped) Crude Oils in Laboratory, Outdoor Test Tank, and Field Experimental Spills.

Product Tested	Initial Oil Properties								Water-in-Oil Emulsion (Mousse) Properties				Reference		
	Spec. Grav.	Viscosity	Pour Pt. °C	Wax % Wt.	Asphaltenes %	% Sulfur	V ppm	Ni ppm	Comments	Stable Mousse Formed/Appearance	Final % Mater Viscosity	Pour Pt. °C		Bacterial Growth Noted (6 weeks)	
Li byan (Brega)	0.829	4.13*	7.2	11.4	0.13	0.21	5		Highly paraffinic	Borderline/ Dark brown-waxy	78.3		Fairly heavy	Berridge et al., 1968a, b	
Nigerian Light	0.867	5.16*	-15.0	8.5	0.05	0.19				Borderline/Yellow Brown-granular	77.3		Heavy tnfestation	Berridge et al., 1968a, b	
Iranian Light (Agah Jari)	0.854	5.6*	-20.6	7.0	0.7	1.33	36			Rigid/foamy	79.1		Fairly heavy	Berridge et al., 1968a, b	
Iranian Heavy (Gach Saran)	0.869	8.83*	-12.2	6.7	1.9	1.58	107	37		Rigid/ml d-brown	77.3		Very few	Berridge et al., 1960a, b	
Iraq (Kirkuk)	0.845	4.75*	-34.4	6.5	1.3	1.88	25			Rigid/dark brown	78.3		Very few	Berridge et al., 1960a, b	
Kuwait	0.8369	9.6*	-31.7	5.5	1.4	2.5	21	9	Less paraffinic high Sulfur	Rigid/ml d-brown	79.1		SOME present	Berridge et al., 1968a, b	
Venezuela (Tia Juana Medium)	0.896	25.0'	-34.4	4.8	3.05	1.54	170	16		Rigid/dark oily brown	73.8		Very few	Berridge et al., 1968a, b	
Bunker C	0.990	2.8x10 ⁷ CP @ 10°C	+7							Rigid & Sticky	67	2.9x10 ⁷		Berridge et al., 1968a, b & Twardus 1900	
Light Arabian Crude	0.99**	6.04 cS @ 38°C										500-800 cS @ 20°C		Solsburg et al., 1976; Twardus 1980	
Norman Wells	0.83	8.68 cP @ 10°C	-85							Unstable	50	110 cP @ 10°C	-48	240**	Twardus, 1900 Additional data on other w/o ratios are presented in the original reference.
Sweet Blend	0.83	14.2 cP @ 10°C	-35							Unstable	60	450 cP @ 10°C	-48	520**	Twardus, 1900
Sour Blend	0.83	0.94**	-50									3000**			Twardus, 1900
Bow River	0.90	0.99**	-27									2150**			Twardus, 1980

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TABLE 1 (continued)

Mousse Formation Experiments using a Variety of Fresh and Artificially Weathered (Topped) Crude Oils in Laboratory, Outdoor Test Tank, and Field Experimental Spills.

Product Tested	Initial Oil Properties								Comments	Water-in-Oil Emulsion (Mousse) Properties				Bacterial Growth Noted (6 weeks)	Reference
	Spec. Grav.	Viscosity	Pour pt. °C	Wax % lit.	Asphaltenes	1-% Sulfur	V ppm	Ni ppm		Stable Mousse Formed/ Appearance	Final % Water	Viscosity	Pour Pt. °C		
Lloydminster	0.90	86.8 CP @ 10°	-52						Stable	60	2000 CP @ 10°			Twardus, 1980	
	0.98**		-9**								2675**				
Weyburn Midale	0.89	29 CP @ 10°	-28						Stable	60	4150 CP @ 10°	-2.5		Twardus, 1980	
	0.99**		-3**								1250**			Twardus, 1980	
				Added % wax & % asphaltenes											
				0	0				Unstable*** emulsion*** Unstable**** emulsion Stable mousse Stable mousse					Bridle et al., 1980a, b Bridle et al., 1980a, b Bridle et al., 1980a, b	
Topped 200+ Kuwait (dewaxed & deasphaltized)				5	0										
				0	1.4										
				5	1.4										
Lube Oil				5	0.14				No emulsion	<1%				Bridle et al., 1980a, b	
Lube Oil + 5% asphaltenes/wax mix									Stable emulsion	54	0.01-0.03 μm water droplet size			Bridle et al., 1980a, b	
Lube Oil + 10% asphaltenes/wax mix									Stable emulsion	67	0.01 μm water droplet size			Bridle et al., 1980a, b	
Venezuelan (Guanipa)	0.859 ²⁰			5.2	0.15	1.66	105	10	Mousse and tarballs and flakes formed after few days in wave tank at 20 C (85% water-in-oil. In first few days; dropped to 75% over 4 mos.)					MacGregor & McLean, 1977	
Li byan (Saria)	0.843 ¹⁶			20	0.15	0.14	0.5	5						MacGregor & McLean, 1977	
Algerian (Zarzitine)	0.8181 ⁴			5.3	0.08	0.09	1	1	Unstable emulsion					MacGregor & McLean, 1977	
Nigerian Medium	0.892 ¹⁶			4.6	0.1	0.25	0.8	7						MacGregor & McLean, 1977	
Alberta Crude	0.829	8.25 CP @ 20°							Stable mousse	70-80% in 30 min.	100-2CMI CP			Ma: Kay et al., 1979	
350° Topped Kuwait	0.958	208 @ 50	CS +8	2.0		7% total 3.7	50	15	Stable mousse	50% after 8-100 weeks.	2350 CS @ 50°	13-15		Davis & Gibbs 1975	
									(Polars 16%, total S 3.84; v/52 N1/17; Asphalts 8.1%)						
Gasoline									No emulsion or mousse	Nil				Berridge et al., 1968b	
Kerosine									No emulsion or mousse	Nil				Berridge et al., 1968b	

TABLE 1 (continued)

Mousse Formation Experiments using a Variety of Fresh and Artificially **Weathered** (Topped) Crude Oils in Laboratory, Outdoor Test Tank, and Field Experimental Spills.

Product Tested	Initial Oil Properties							Comments	Water-in-Oil Emulsion (Mousse) Properties			Reference		
	Spec. Grav.	Viscosity	Pour Pt. °C	Max % Mt.	Asphaltenes	% Sul fur	V ppm		Ni ppm	Stable Mousse Formed/ Appearance	Final % Water		Vi scosity	Pour Pt. °C
Auto Diesel									No emulsion or mousse	Nil				Berridge et al., 1968b
Marine Diesel	0.83	10CP @ 10°	-15						No emulsion or mousse	Nil		17**		Twardus 1980 & Berridge et al., 1968b
Lube Oil 600	9.87**		-8**						Unstable emulsion					Berridge et al., 1968b
Lube Oil 2500									Fluid emulsion but no mousse					
Heavy naph Lube									Fluid emulsion but no mousse					

*Kinematic viscosity (cS) at 100°F

**Specific grav. and pour pt. after 4 weeks pan evap. under atmospheric conditions (No water added except for occasional precipitation).

***93% of water shed after standing 15 min.

●***86% of water shed after standing 15 min.

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TABLE 2

Other Oils Which Have Demonstrated Water-in-Oil Emulsion Tendency
(from Bridie et al., 1980a)

Crude Oil	Source	Mousse Formed	Flow Properties	Spreading on Water at 10° C
Brent	N Sea GB	+	Viscous	
Ekofisk	N Sea Norway	+	Unstable	-
Auk	N Sea GB	+	viscous	
Kuwait	Kuwait	+	Paste	
Nigerian Medium	Nigeria	+	Low Visc	+
Qatar Marine	Qatar	+	viscous	
Cabimas	Venezuela			+
Iranian heavy	Iran	+	Paste	-

To study the effects of chemical composition of the starting crude, **Berridge et al.** (1968a, b) evaluated mousse formation potential and stability for seven **crudes** which were selected to give a representative sampling of oils likely to cause marine pollution. Specific gravities of the **crudes** ranged from 0.829 for Libyan (**Brega**) crude to 0.896 for the Venezuelan (**Tia Juana** medium crude). Sulfur contents for the **crudes** range from 0.2 to 2.5%, and kinematic viscosities at 100°F ranged from 4.13 to 25 centistokes. Pour points for the selected oils ranged from -34 to +7°C, and wax contents were found to vary inversely with the specific gravity ranging from a high of 11% by weight for the Libyan crude to 4.8% by weight for the **Tia Juana** crude. Additional characterization data are presented in Table 1. **Asphaltenes** were found to increase in weight percent from 0.13 to 3.5 and were roughly inversely proportional to the wax content. Vanadium content increased with the increase in specific gravity and percent **asphaltenes**. Residues with components having boiling points greater than 370°C ranged on a weight percent basis from 35-57% for the **crudes** studied, and interestingly, the residue pour points decreased from 100° to 50° going from the light to heavier **crudes**. Thus, when spilled at sea, **crudes** such as the Libyan **Zelten (Brega)** and the Nigerian **light** which have fairly low percentage ranges of residues greater than 700° will be removed relatively rapidly by evaporation. This effect is particularly significant for **Zelten** crude which contains 31% by weight of components which boil below 200°C. Heavier crudes such as the **Tia Juana** medium (78% residue boiling greater than 370°C) contain only a small fraction which distills at low temperature and thus, it will evaporate very slowly and would not be expected to weather significantly at all by evaporative processes.

The weathered residues which result from the evaporative processes acting on all the oils studied had higher specific gravities, viscosities, sulfur, metal and wax content than the original **crudes**. For example, Kuwait crude has a residue with boiling point above 1000°C which constitutes about 27% of the original material, and this residue has a specific gravity of **1.023**. Similarly, Iranian heavy crude residue has a specific gravity of 1.027, and as such, these residues have densities greater than seawater (1.025) and would be expected to sink relatively easily.

Rigid stable emulsions were formed with most of the oils tested with the exception of **Brega** and Nigerian light crude which were **classified** as borderline. Colors ranged from mid-brown to dark **oily-brown** to a yellow brown granular substance with the Nigerian light **crude**. **No** mousse could be generated using **distillants such** as gasoline, kerosene and diesel oils. Lubricating fluids did not form stable "mousse" but emulsions which were either unstable or **fluid** could be generated. Residual fuel oil (Bunker C) did form a stable mousse. In general, variation in the size of water droplets appeared to correlate with stability, and the **Brega** and Nigerian crudes which contained the relatively largest water droplets "showed the **least** stability and the greatest potential of the water to return to separate phases. The more **stable** mousses had water droplets with diameters not greater than 1 micrometer.

The effect of salinity was also investigated, and mousse type emulsions were obtained with Kuwait crude and Tia Juana crude with water contents ranging from 74 to 80% regardless of salinity. A **stable** emulsion was formed in **all** cases, but the appearance of the mousse ranged from a mid-brown for Kuwait crude with seawater to a mid-gray-brown using tap or distilled water. Tia Juana crude with seawater formed a very dark brown mousse whereas the mousse formed with tap water and distilled water was nearly black. To evaluate other factors affecting this formation, oil and water were filtered through **Whatman #1** filter paper to remove particulate above 100 microns and in several instances the water was sterilized by the addition of 500 ppm **dichlorophen**. In general, these perturbations did not affect the water content or mousse appearance.

Mousse stability was measured by placing 425 ml of mousse from the different **crudes** on glass plates and allowing them to weather naturally under environmental conditions. Identical samples were also placed in 2 gallon buckets and were then agitated with bubbles from **below**. Stable **mousse** on the glass produced an oil fringe while maintaining a rigidity overall, **while** less stable mousses deformed or slumped and flowed off the glass under the influence of wind, gravity and rain. Estimated losses due to weathering of so-

called beached mousse ranged from 10% for Kuwait crude to 80% for the **Brega** crude which was a much softer waxey mousse. Nigerian crude oil mousse was very granular on the plate and formed a waxey or **oiley** and foamy mousse. Microbial populations were observed to grow with Kuwait mousse with only very few bacteria present for Tia **Juana** crude, Iraq, **Kirkuk** and **Gatch Seran**. Heavy bacterial infestation was observed with the Nigerian **light**, the **Brega** crude, and the Iranian (Aja **Jari**) **crudes**. Bacterial infestation on samples of mousse floating on aeriated seawater was observed, but the most stable mousses again appeared **to** have the least bacterial growth. **During** experimental periods ranging **up** to 6 weeks there was little evidence to suggest that bacterial growth was sufficient to remove the mousse. In fact, with the stranded mousse **there** was slight evidence which suggested that the presence of bacteria marginally increased the stability, but the presence of particulate material had no effect. With regard to water loss on stranded mousse the two lighter crudes (**Brega** and Nigerian) showed the greatest percent water loss, **and** they also had the highest infestation of bacteria.

Of all the parameters studied, specific gravity and kinematic viscosity showed the most positive correlation with mousse stability. Interestingly, pour point showed no correlation with mousse stability. With regard to chemical composition, the percentage residue boiling above **370°C**, the asphaltene content and the vanadium content all showed a definite correlation **while** acidity, sulfur content and wax content showed little or no significant correlation with mousse stability.

The lack of bacterial activity noted with several of the mousse samples **on** the aerated seawater was attributed to the lack of phosphate and other nutrients or possibly due to toxic materials inherent to several of the **crudes**.

Davis and Gibbs (1975) used a **350°C** topped Kuwait crude (to eliminate viscosity and density changes due to evaporation losses) to study long-term **oil** and mousse behavior over a two year period in closed and flow-through

exposure tanks in Portsmouth, England. The tanks were filled with seawater and 23 liters of oil was added. The authors stated that in retrospect, however, it would have been better to add less oil and leave some of the water surface uncovered because the oil proved to be a barrier to oxygen transfer leading to oxygen depletion in the closed tanks. The initial oil thickness was about 0.7 cm, but after taking up water the "mousse" reached an ultimate thickness of about 1.4 cm. The most significant effects occurred during the first nine weeks with water content in the mousse approaching 50%. Vanadium and nickel were not lost over the 2 year period of the experiment, however, oxygen content increased in the oil from 0.2% in the crude to 3.9% and 2.8% in the mousse in the flow-through and closed tank systems, respectively. The pour point of the oil increased from 8 to 11° during the first day with the water content going from 0 to 0.8%. After one month the water content had increased to 10% and the pour point of the oil was 15°C. The final 50% water-in-oil mixture was obtained after 2 months and remained relatively stable for the 2 year period. Viscosity increases from 216 to 2350 centistokes at 50°C were noted, and the specific gravity of the residue changed from 0.9525 to 0.9825. The percent asphaltenes increased by a factor of four from 2-8%. Polar constituents also increased from 7 to 16%, presumably due to the incorporation of oxygenated products. N-alkane components decreased more rapidly in the open tank presumably due to microbial degradation, and time series graphs of water content, pour point, percent asphaltenes, specific gravity and viscosity were presented for the water-in-oil emulsion over the 2 year period. With regard to mass balance, it was observed that no net loss of the mousse occurred over this time, and the very slow rate of degradation of the water-in-oil mousse over the 2 year period was attributed to the limited diffusion of oxygen and/or minerals into the mousse. Thus, it was suggested that aside from removal of n-alkanes in the open system, microbial biodegradation was not a major process causing observed changes.

MacGregor and McLean (1977) investigated the weathering behavior of Venezuelan crude oil (Guanipa) on synthetic seawater in a fiberglass tank equipped with a wave generator and a controlled radiation system located in an

environmental chamber held at 2°C. The crude oil studied in this experiment had negligible wax content, but **asphaltenes** were measured at 5.2%, and **significant trace** metals (vanadium-105 ppm and **nickel-18ppm**) were measured in the oil. The total sulfur content was 1.6%, and the specific gravity was 0.859 grams/ml in the original oil. Evaporation removed the largest quantity of material, and the rate of evaporation was observed to vary directly with exposure time to solar radiation. After 400 hours, losses due to evaporation ceased with approximately 85% of the oil remaining. Only minimal amounts of oil were lost by sinking or solution, although these factors were observed to increase with time. The most notable change was a rapid formation of stable water-in-oil emulsions which eventually formed discreet lumps or tar balls; this occurred within a few days after the **spill**. During the four month period of the experiment, these tar balls remained very stable, and they drastically reduced weathering effects by reducing the oil contact from the air-sea interface. During the mousse and tar ball formation a rapid increase in water content to 85% occurred during the first few days, whereas this dropped off to approximately 75% at the end of the experiment. The tar balls which were observed after about 2 weeks had a flake like appearance similar to that observed in the Potomac and **IxTOC spills** (which will be discussed later under Case Histories). Water content was noted to vary with tar ball size, with the smaller lumps having lower concentrations of water than the larger ones. This was attributed to entrapment of pockets of water in **the** form of droplets inside the larger tar **balls**. During the first few days of the experiment, the specific gravity was noted to increase rapidly leveling out at approximately 1.0 compared to the seawater density at 1.027 at 2°C. When water content was taken into consideration the real increase in crude oil specific gravity (due to evaporation and dissolution alone) was from 0.85 to approximately 0.93.

Concentrations of oil dispersed in the water or in true solution increased rapidly to approximately 2 ppm and then continued to increase as time progressed. After 500 hours, the oil concentration in the water was 15 ppm, and was still increasing. Only 2-3 ppm was expected to be in true solution with the dispersed oil making up the difference. The authors analyzed

the outer surface of the tar balls compared to the inner materials, and no significant difference in the n-paraffin distributions was reported. Nickel concentrations were found to decrease approximately 30% at the end of the experiment, however, vanadium concentrations increased slightly by about 10-15%. Because of the lack of differences in external and internal alkane composition in the tar balls, the authors attributed their formation to be from mechanical break-up of the parent mousse from available wave energy rather than from additional or extended chemical weathering effects.

Nagata and Kondo (1977) studied the artificial weathering of five " crude oils in 6m x 2m x 1m deep tanks where wind , waves and rain were allowed to interact with the oil. Changes with elapsed time of physical and chemical properties were measured for Arabian light crude oil, Iranian heavy crude oil, Kuwait crude oil, an unspecified heavy oil A (50°C viscosity below 20 centi-stokes and flash point 60°C) and heavy oil B (50°C viscosity 20-50 centi-stokes, and flash point 60-70°C). Twenty-one day experiments were conducted and measurements of specific gravities, viscosities, and the amount of water incorporated were made in addition to gas chromatographic analyses of the oil. The heavy oil A showed the least change; heavy oil B and Arabian light crude oil exhibited similar and median changes and Iranian heavy and Kuwait crude showed the most significant changes, particularly during the first three days. Specific gravities for these mixtures ranged from 0.87 to 0.98 after 7 days, and constant values were approached after 21 days when an oil-in-water type emulsion was formed. The specific gravity closely paralleled the change in the amount of water in the oil, with the Iranian heavy crude and Kuwait crude showing the most significant increases which paralleled specific gravity increases. It was also stated that evaporation was found to be greatest in the cases of non-emulsified oils. Microbial degradation was reported to be approximately 30% for hydrocarbons below nC-15 after 5 days. Hydrocarbons above nC-15 remained unchanged at that time, whereas about 50% of the n-alkanes were degraded after 15 days. Photochemical decomposition studies illustrated that secondary and tertiary paraffins were more easily decomposed relative to normal n-alkanes, and this was attributed to the lower activation

tion energies encountered in breaking tertiary C-H bonds during the oxidation process. A number of aromatic compounds were also shown to be removed by photo-decomposition. These included **anthracene, phenanthrene, 1,2-benzoanthracene, chrysene, fluorene, pyrene, 3,4-benzo-a-pyrene, benzothiophenes** and dibenzothiophenes. All of the compounds **were** decomposed; however, the rates of **the** individual compounds were very different from one another. Anthracene, phenanthrene and **1,2-benzoanthracene** were rapidly decomposed in comparison with the other aromatics, and **sulfur** containing **hetero-aromatic** compounds showed the same approximate degree of decomposition as compounds with anthracene rings when pure compounds were tested. When a mixture of the hetero-atoms and aromatic compounds were examined, the aromatic **compounds** were quickly decomposed with the **sulfur** containing **hetero-aromatic** materials remaining longer.

Bocard and Gatellier (1981) generated water-in-oil emulsions with Arabian light crude oil topped at **150°C, Safanya**, and heavy **fuel** oil. Generally, viscosities greater than 10,000 centipoise were obtained with all three oils while the viscosity ranged from 10,000 to 20,000 for the Arabian light, from 20,000 to 50,000 for the **Safanya** and from 60,000 to 80,000 for the heavy fuel **oil** depending on mixing speed. All of the measurements indicated a plastic like behavior for the emulsions and the viscosities were shown to decrease as the shear rate increased. Microscopic examinations of the 75% water in Arabian light crude **oil** mixture showed that like other studies of mousse formation, most of the water droplets, were from 1-10 micrometers in diameter. These authors found that Nigerian light or **Zarzatine** (both **low asphalt content crudes**) did not form stable emulsions. They noted however, that the higher viscosity oils formed emulsions apparently independently of asphalt content.

Twardus (1980) has studied the characteristics of water-in-oil emulsions for 8 oils, and the stability of the resultant mousses vs. water content is represented in Table 1. It is interesting to note, however, that the observed increases in viscosity due to mousse formation were very similar to

viscosity increases due to simple evaporation in pan experiments completed using the same **crudes** and petroleum products (Twardus, 1980). In the evaporation experiments no seawater was added, however, the pans did accumulate some water from rain and snow **fall**. When this occurred, **the** formation of **water-in-oil** emulsions with several of the **crudes** and Bunker C fuel oil was noted. The evaporative loss of hydrocarbons (primarily within the C-4 to C-14 range) was most significant in the pan evaporation experiments during aging intervals of 6 hours, 1 day, and 2 days. **For** longer aging periods (1-4 weeks) hydrocarbon evaporation occurred at much lower rates. Evaporation of components from marine **diesel fuel oil** and Bunker C were relatively insignificant in the prevailing sub-arctic weather conditions, primarily due to the low percentage of volatile hydrocarbons in these fuel oils.

The percent water incorporated into the emulsions was significant for the stability of mousse formed with Norman Wells crude and Sweet Blend crude. With **the** first mixture, mousse which exhibited marked stability for several hours **could** only be formed with **50:50** and **40:60** water-to-oil ratios. For Sweet Blend crude, only **60:40** water-to-oil and **50:50** water-to-oil ratio produced mousse which was stable for several days. At greater water concentrations the mousse separated **following** formation. For the other oils tested, Bow River, **Lloydminster** and **Wabern-Midale**, stable mousse was formed at **water-to-oil** ratios ranging from **20%** to 60%. As in other experiments, no **stable** mousse could be formed using marine diesel fuel. The pour points for the mousses were in general higher than those of the fresh oils, but for the Norman **Wells** and Sweet **Blend** crude oil mousses, the pour point was less than that of the residue obtained by simple evaporation. For the **Wabern-Midale** Crude **oil** mousse, the pour point was very similar to that obtained from the pan evaporation experiments in the absence of added seawater.

In order to alleviate problems of density changes due to this **evaporation** behavior, Mackay et. al. (1979, 1980) used a 25% weathered Alberta crude oil and measured changes in viscosity as a function of water uptake. Their emulsion studies were conducted in wave tanks, and they have perhaps completed

the most thorough examination of the competitive processes of oil-in-water dispersions vs. water-in-oil emulsion behavior. During the first ten minutes after a spill of Alberta Crude oil (SG 0.829, viscosity 8.25 cP) the dominant process was the dispersion of oil droplets into the water column with concentrations of 20-50 mg/l being reached. It was speculated that concentrations would increase approaching limiting values at which dispersion and coalescence rates would be equal, however, this was not observed. Instead, after approximately 20 minutes, the concentrations in the water column fell and settled out at a steady 10 mg/l after 1 hour. This drop in concentration was noted to coincide with a **significant** change in oil appearance, water content, and viscosity. The water content in the **oil** increased to 70-80% volume within 30 minutes, and the viscosity correspondingly increased **to** 100-200 centipoise. The **slick** underneath the waves was noted to be thicker at wave crests and thin in the troughs, and significant formation of neutrally buoyant **water-in-oil-in-water** droplets was observed. Additional details of their studies as they relate to modeling water-in-oil emulsion formation are presented later in the discussion of modeling and computer simulations.

In several of the studies cited above, the authors also noted that mousse stability was inversely proportional to the size of the water droplet entrained in the emulsions. In general, mousses with 1-10 micrometer diameter water droplets were the most stable up to 70-80% water.

Although mousse can contain anywhere from 10-80% water, emulsions with less than **50%** water generally have characteristics which on visual **examination** suggest that the oil properties are similar to that **of** a neat **oil**. These mousses, are generally free-flowing fluids with the consistency of **industrial** fuel oils. Laboratory studies on spreading properties of several viscous oils (with viscosities greater than 40,000 centipoise at 25°) showed that viscous oils behaved differently than non-viscous slicks (viscosities less than **500** centipoise) and that spreading was significantly inhibited.

Identification of Emulsifying Agents Responsible for Mousse Formation

Berridge et al. (1968b) found some correlation between the **asphaltene** content and stability of the emulsions formed. **Mackay et al. (1973)** attempted to determine the nature of **the asphaltic** compounds responsible for the **stability** of the mousse and like **Canevari (1969)** they concluded that each water droplet was encapsulated in an envelope of **surfactant** type molecules having a plastic nature preventing coalescence of the water droplets due to altered interracial oil-water tensions.

The exact nature and identity of the **surfactants** responsible for this behavior have yet to be completely elucidated, and most laboratory studies indicate that slightly different factors are responsible for emulsion formation in different oils. In the **crudes** studied by **Berridge et al., 1968b**, the percentage of residues boiling above **370°C**, the **asphaltene** content and the vanadium content **all** showed a definite positive correlation while acidity, sulfur content and wax content showed no correlation with mousse stability. On the other hand, **Bridie et al. (1980a,b)**, in working with dewaxed and **de-asphaltenized** Kuwait crude and refined **lub oil**, found that wax content, in combination with asphaltenes, did play a significant role; these observations are discussed in detail below. **Berridge et al. (1968b)** found that **water-in-oil** emulsions generated with high **asphaltene** content crude oils were stable for many months on **exposure to the** elements on glass **plates** and on aerated seawater surfaces. These data suggested that the surface-active materials responsible for mousse formation were components of the non-volatile residues, and they were, believed to most likely be **asphaltenes** and possibly **metalloporphyrins**. **When** an artificial blend of **Tia Juana** crude was made by mixing various portions of all of the distillates except for the 30% vacuum residual, no mousse could be artificially generated, although it was stated that the metalloporphyrines were reasonably volatile enough to have been present in the distillates. Thus, it was assumed that the **asphaltenes** were primarily responsible for mousse formation. These authors also reported that the presence or absence of particulate material or bacteria did not apparently affect mousse

formation or **the** stability of the stranded mousse on land or on seawater surfaces, although some evidence suggested that under certain conditions, mousse formation can be stabilized due to the presence of bacterial slime.

Zajic et al. (1974) found that a pseudomonas growing on #6 fuel oil or on **aliphatic** hydrocarbons formed an extra-cellular emulsifying agent which appeared to be a higher molecular weight **polysaccharide**. It was found that the emulsification behavior of this extra cellular material was not affected by temperature as low as 6°C, however, when 3% sodium chloride was added to the mixture the emulsion broke up and a patch of surface oil was produced along with **oil** pellets from 1-2 mm in diameter. When Pseudomonas aeruginosa and two yeasts Candida petrophilus and C. tropicalis were grown with hexadecane as a sole carbon source, **the organisms** produced extra cellular emulsifying agents (Friede 1973 and Guire et al. 1973). These materials were believed to **also** contain **polypeptides** because they could be partially destroyed by pancreatic **lipase** suggesting some protein components.

As noted above, **Bridie et al.** (1980a ,b) have examined the emulsion forming tendency of various crude oils and found that contrary to **Berridge et al.'s** results, the presence of wax and **asphaltenes** had significant effects on emulsification. A 200° topped Kuwait **curde** oil fraction was **deasphaltized** by 30-fold dilution with pentane and then de-waxed by 6-fold dilution in methyl ethyl ketone **dichloromethane** mixture. Attempts to form a water-in-oil emulsion failed as the mixture lost 90% of its water after standing 15 minutes. The water-in-oil mixture from the treated oil **plus** the original wax exhibited a similar behavior, whereas the "mousse" from treated oil plus original **asphaltene content** showed loss of 86% of its water content after standing 15 minutes. Thus, neither the original wax or the original asphaltene content alone were responsible for stable mousse formation. When the treated oil plus original wax content and original **asphaltene** content were mixed, a stable mousse was generated, and a stable mousse was also found with the treated oil plus the original wax content and only 10% of the original **asphaltene** content. Thus, it appeared that components in the wax were important for mousse generation, although the **asphaltene** fraction played a more significant **role**. When

various lube oils were treated with 5 and 10% mixtures of the asphaltene-wax mix, stable emulsions with water content ranging from 57-67% could be formed. **Water** droplet size in these emulsions ranged from 10 to 30 micrometers. No emulsion was formed with **the lube** oil blank in the absence of the added **asphaltene/wax** mix.

Products of **photochemical** and auto-oxidation have also been implicated in mousse stability. Thus, while rigid emulsions could not be formed with fresh **Brega** and Nigerian light crude **oil** (**Berridge et al. 1968b**), stable mousse with water contents ranging **from** 67-84% were obtained using **artificially** weathered **Brega** and Nigerian **crudes**. Similarly, **Bocard** and **Gatellier** (1981) examined **the** effects of photo-oxidation on mousse stability by irradiating a thin layer of **oil** (**0.3mm**) with a fluorescent lamp emitting ultraviolet and visible light between 300 and 450 **nm** with a maximum at 365 nm. In this procedure, Arabian light crude (topped at **150°C**) produced oxygenated products corresponding to 0.08% after 132 hours. In general, it was found using Arabian crude and **Zarzatine 150°C** (a crude with very **little** asphalt), that emulsions made with unoxidized oil were very unstable whereas the emulsions made with the photo-oxidized oil were particularly stable.

Auto-oxidations resulting from free radical chain processes (with the rate of propagation being controlled by the rate of proton extraction from the hydrocarbon by **alkyl** peroxide radicals) have also been demonstrated to occur in oil-in-water mixtures. In addition to a number of oxygenated products which can be formed by these reactions, higher molecular weight polymerization products **in** the oil itself can result in enhanced mousse stability. In **gener-**al, tertiary free radicals are found to be **more** stable than those from primary or secondary hydrocarbons, such that **isoprenoids** leading to tertiary free radicals can be attacked more readily. Alkyl-substituted aromatics such as **tetralin** and **cumene** where **alkyl-radicals** can be resonance stabilized are also rapidly removed by auto-oxidation. Photo-oxidation can compete with **auto-oxidative** processes, however both processes are affected by the presence of vanadium and other metals of variable valiance which have been shown to

strongly catalyze oxidations. Sulfur compounds, on the other hand, are believed to inhibit oxidation due to terminating reactions caused by **sulfoxide** formation, so **all** of these factors **singly** and in combination can affect mousse formation and stability. The water **soluble carboxylic** acids, ketones, **aldehydes**, alcohols, **sulfoxides**, peroxides etc. which are formed by these **processes** are rapidly removed from the surface of the oil leaving a more viscous higher density residue. Once mousse formation has occurred however, **additional** photo-oxidation of the **emulsion** or resultant tarry lumps must be extremely slow because of the low surface area to volume ratio. That is, photo and auto-oxidation would tend to be limited to the external surfaces of rather viscous and diffusion controlled emulsions where oxygen and light cannot **penetrate** into the interior of the mousse. In the IXTOC spill in the Gulf of Mexico **very few oxidation** products were obtained **in** the mousse samples **collected** during the Researcher cruise, and it was concluded that most of the photo-oxidation products were presumably leached from the material near or very soon after the time of formation.

Klein and **Pilpel** (1974) reported that viscous oil slicks actually appeared to contract as photo-oxidation proceeded, and this was attributed to polymerization of the petroleum components and to the resulting increased viscosity which restricted diffusion of oxidation products to the **oil/water** interface. In this instance, then, photo-oxidation could thereby help generate intractable tarry residues and stabilize water-in-oil emulsions. **Burwood** and Spears (1974) exposed surface slicks of crude petroleum to artificial light to examine the effect of dissolution of specific petroleum hydrocarbons in seawater. They postulated **that** indigenous auto-oxidizable hydrocarbons could react **photolytically** with **thiacyclanes** to form complex water soluble mixtures of **thiocyclane** oxides. — Such compounds were detected in seawater following prolonged equilibrium with a medium sulfur content middle east crude oil, and the compounds showed up as a mixture of high boiling water soluble components reflected as an unresolved complex envelope in the **nC-15** to **nC-23** range of the water sample extracts. The area of this UCM increased significantly as the photo-degradation of the oil progressed, and **Burwood** and Spears

(1974) suggested that such a process **might** explain the loss of sulfur **materials** during weathering of crude **oils** at sea such as that which occurred in the Torrey Canyon spill. Similar loss of sulfur containing **hetero-aromatics** specifically, benzothiophene and **dibenzothiophene** were observed in the IXTOC **spill** where it was believed that formation of **sulfoxides** caused these **materials** to be preferentially leached from the bulk oil before and during mousse formation.

Physical and Behavioral Properties of Water-in-oil Emulsions

The significant increase in viscosity and specific gravity observed for many water-in-oil emulsions affect their behavior in seawater including, spreading, dispersion, interaction with suspended particulate material and presumably evaporation and dissolution. **Twardus** (1980) indicated that no quantitative data existed on mousse effects on evaporation, but that it was suspected that once mousse formation occurred evaporation would occur at reduced rates. Similar results have been suggested by **Nogata and Kondo** (1977). In our **field** programs on **sub-artic** weathering of crude oils, we have studied the quantitative loss of lower molecular weight volatile components from fresh **Prudhoe** Bay crude oil and artificially (shaker-table) generated mousse where evaporation was prevented during mousse formation in a sealed **teflon** container. Figures 1 and 2 present Flame Ionization Detector-temperature programmed gas **chromatograms** of the volatile components released from fresh **Prudhoe** Bay crude oil and freshly generated mousse, respectively, on outdoor flow-through sea water aquariums where turbulence was induced by **propellar** mixing. The **water** and air temperatures at the time of sampling were 6° and 6-12°C, respectively. The **volatiles** shown in these **chromatograms** were trapped by vacuum pumping measured volumes of air (sampled 1-2 inches above the slick) through stainless steel columns packed with **Tenax™ 1.0** and 1.5 hours after the fresh oil and mousse were spilled on the water surface of the tanks, respectively. These traps were then capped with stainless steel **Swagelok™** fittings and stored at room temperature until analysis in the laboratory. Back-up columns, in series with the front columns showed no break-through of lower

START

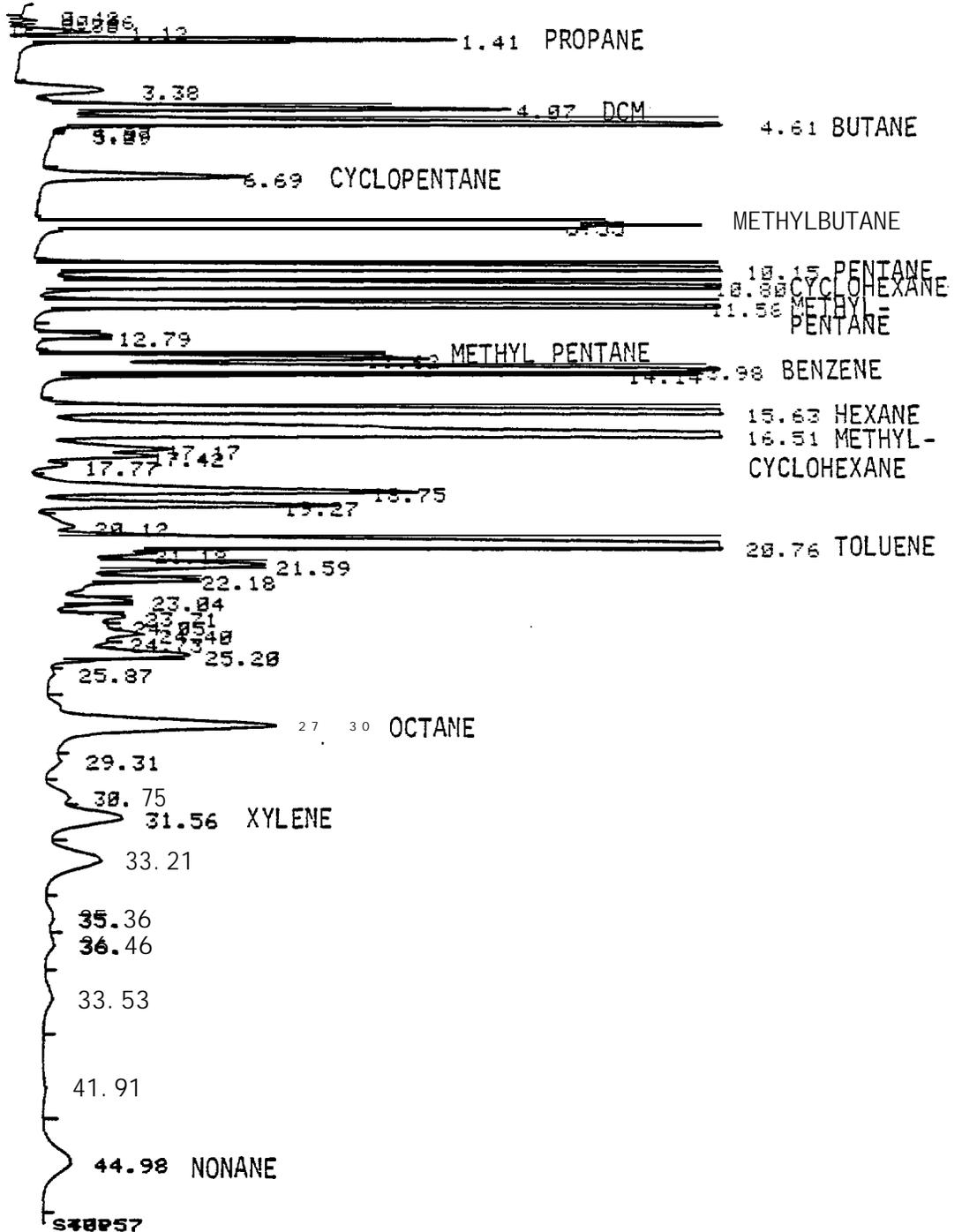


FIGURE 1. FLAME IONIZATION DETECTOR - TEMPERATURE PROGRAMMED GAS CHROMATOGRAPHIC ANALYSIS OF TENAX-TRAPPED VOLATILE COMPOUNDS LOST FROM FRESH PRUDHOE BAY CRUDE OIL AFTER 1 HOUR OF WEATHERING (WITH TURBULENCE) ON SEAWATER. WATER TEMPERATURE 6°C, AIR TEMP 6°C. (FROM PAYNE ETAL., 1981b.)

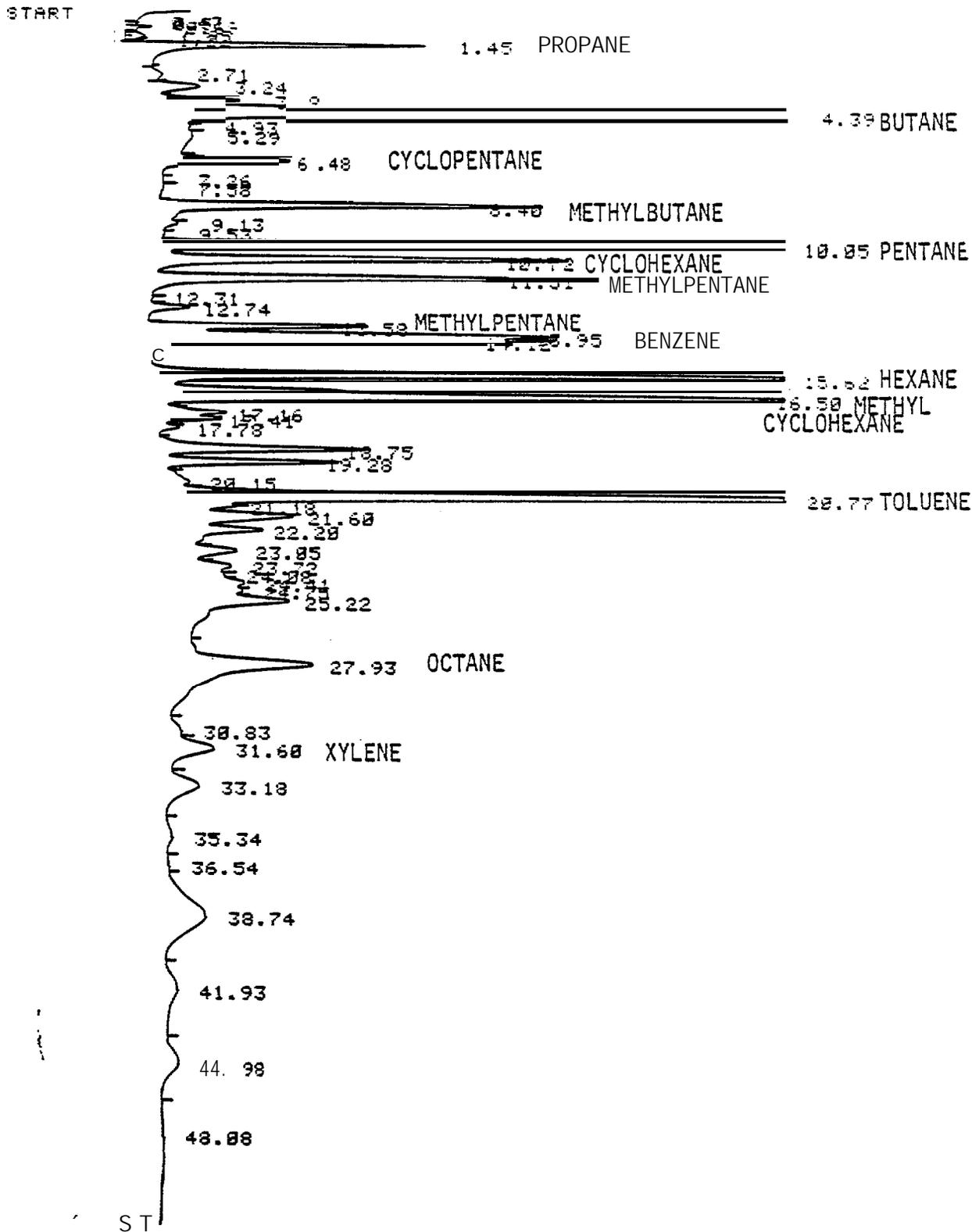


FIGURE 2. FLAME IONIZATION DETECTOR - TEMPERATURE PROGRAMMED GAS CHROMATOGRAPHIC ANALYSIS OF TENAX-TRAPPED VOLATILE COMPOUNDS LOST FROM FRESH PRUDHOE BAY MOUSSE (80% WATER) AFTER 1.5 HOURS OF WEATHERING (WITH TURBULENCE) ON SEAWATER (WATER TEMP 6°C, AIR TEMP 6°C). {FROM PAYNE ET AL., 1981b.}

molecular weight materials, indicating 95+% recovery on the front traps. Interestingly, the qualitative appearance of the **chromatograms** of the **volatiles** from both systems are remarkably similar, and the time series data **presented graphically** in Figure 3A and 3B illustrate that essentially identical losses of **lower** molecular weight compounds ranging from butane to **xylene** were obtained for both the fresh oil and fresh mousse. The data in Figure 3C and 3D, however, show longer **retention of these compounds in** mousse spread on seawater **in the absence of turbulence**. One of the static (non-mixed) **mousse** systems was treated with **Corexit 9527 immediately** after the spill (3D), but this did not apparently affect evaporative loss compared to the **non-dispersant-treated control** (3C). Figure 4 presents computer-generated time series concentration profiles from capillary **FID gas chromatographic** analyses of the intermediate and higher molecular **weight** components remaining in the **oil** and mousse from the well stirred tanks. Kovat indices for the compounds **in each plot** are identified in the figures. These data illustrate that compounds in the range of NC-9 through **nC-11** are preferentially retained in the mousse sample for longer time periods. Figure 5A and 5B show the time series concentrations of components **with kovat** indices ranging from 1300 to 2000 for the **oil** and **mousse** samples, respectively. A similar relative increase in these higher molecular **weight** compound concentrations ($\mu\text{g/g}$ oil) is noted for both the **oil** and mousse after approximately 25 hours, and this is due to the removal of significant mass of the oil from evaporation of the **lower** molecular weight components (compounds with molecular weights above **nC₁₃** are not lost during this time frame). The absolute concentrations of the individual components in **each** of the mousse sample plots (on a $\mu\text{g/g}$ of mousse basis) are lower than those of the fresh **oil** because of the additional mass of the seawater (80% by weight) in the water-in-oil emulsions. Thus, in the presence of turbulence in these studies, **the** higher viscosity of the **80%** water-in-oil mousse did not significantly affect evaporative loss of the lower molecular weight components boiling below **xylene**, but some reduction in "evaporation was noted for intermediate molecular weight compounds (**kovat** Index 800 to 1100) in the mousse. **More significant differences** were noted **in** the amounts of oil and fresh mousse that were **dissolved** and dispersed into the water **column** due to

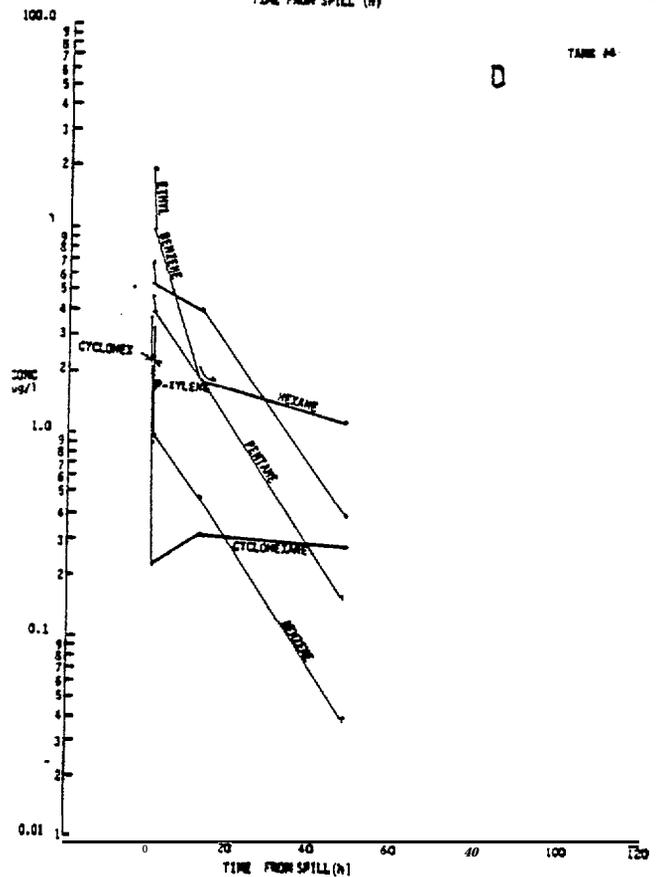
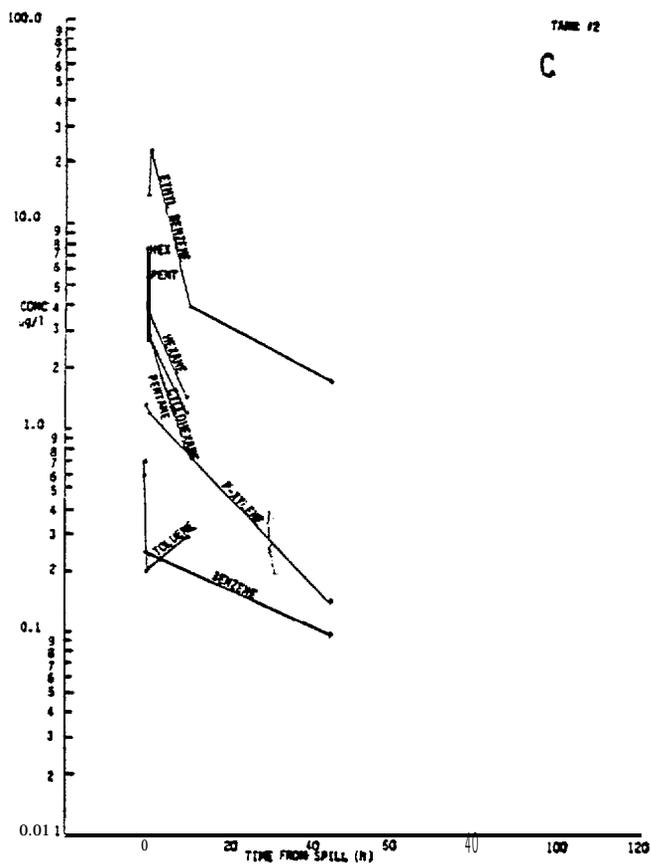
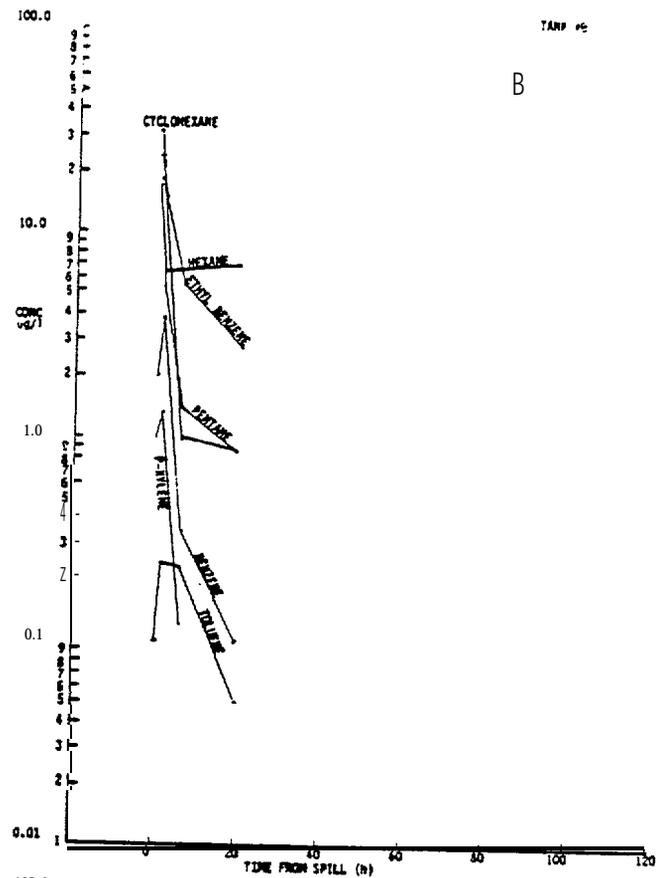
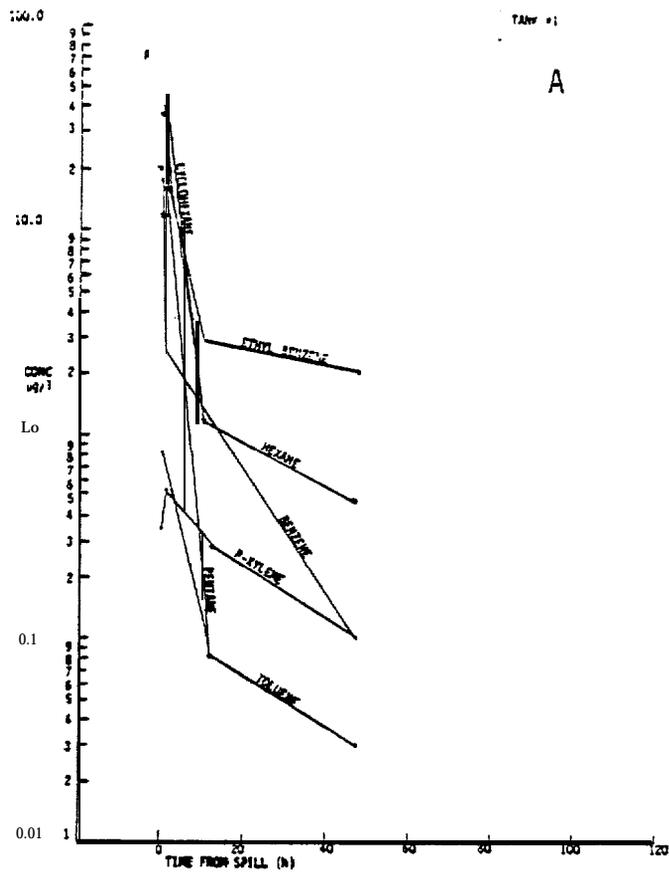


FIGURE 3. TENAX TRAP/FID GC DATA ON SUB-ARCTIC VOLATILE COMPONENT LOSS FROM PRUDHOE BAY CRUDE OIL AND MOUSSE ON FLOW-THROUGH SEAWATER ENCLOSURES IN KASITSNA BAY, ALASKA. A) FRESH OIL AND TURBULENCE; B) FRESH MOUSSE AND TURBULENCE; C) FRESH MOUSSE (NO TURBULENCE), D) FRESH MOUSSE AND COREXIT 9527 (NO TURBULENCE). WATER TEMP 6° C, AIR TEMP 6-13° C. (FROM PAYNE ET AL., 1981b.)

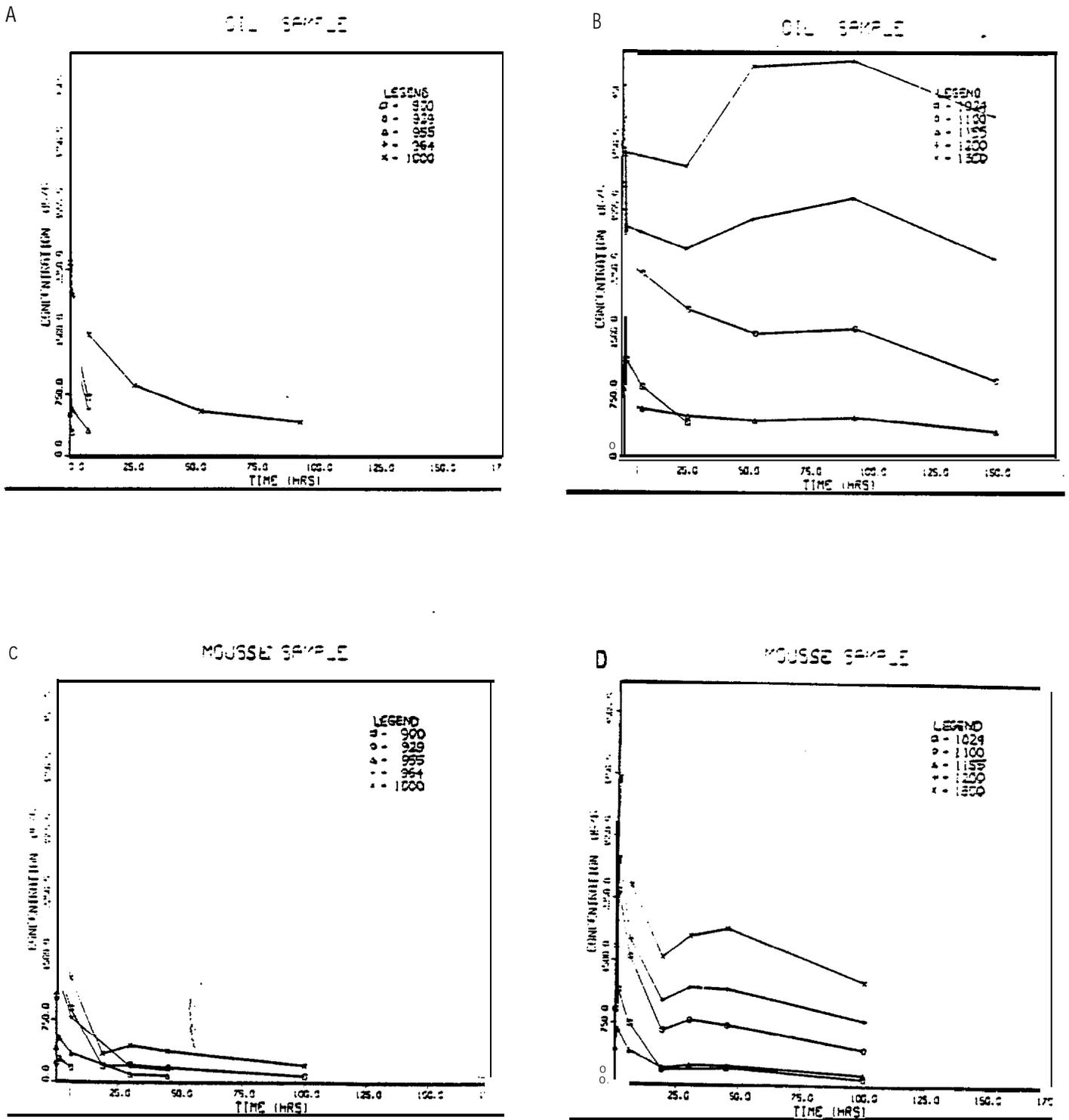


FIGURE 4. COMPUTER GENERATED PLOTS OF CAPILLARY FID-GC DATA ON INTERMEDIATE MOLECULAR WEIGHT COMPONENTS REMAINING IN PRUDHOE BAY CRUDE OIL AND MOUSSE WEATHERING UNDER SUB-ARTIC CONDITIONS ON FLOW-THROUGH SEAWATER ENCLOSURES AT KASITSNA BAY, ALASKA. KOVAT INDICES ARE IDENTIFIED ON EACH PLOT. A AND B FRESH PB CRUDE AND TURBULENCE; C AND D FRESH PB MOUSSE AND TURBULENCE. TEMPERATURE AS IN FIGURE 3. (FROM PAYNE ET AL., 1981b.)

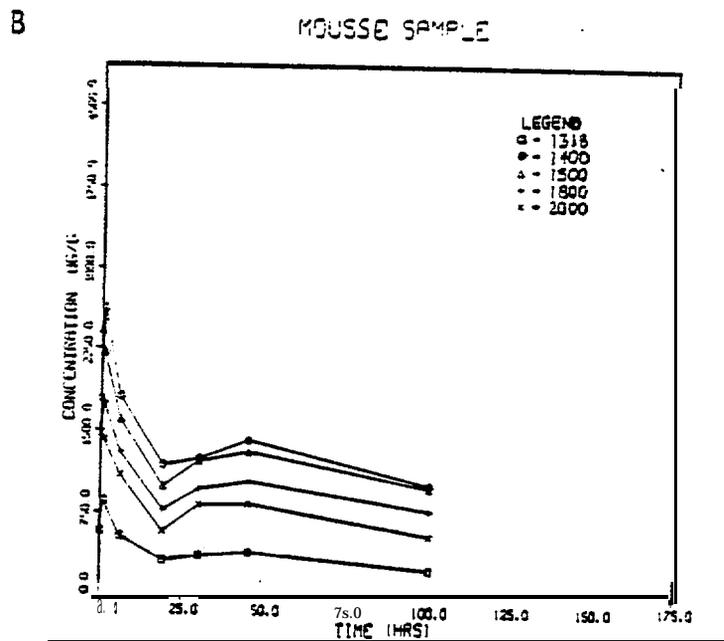
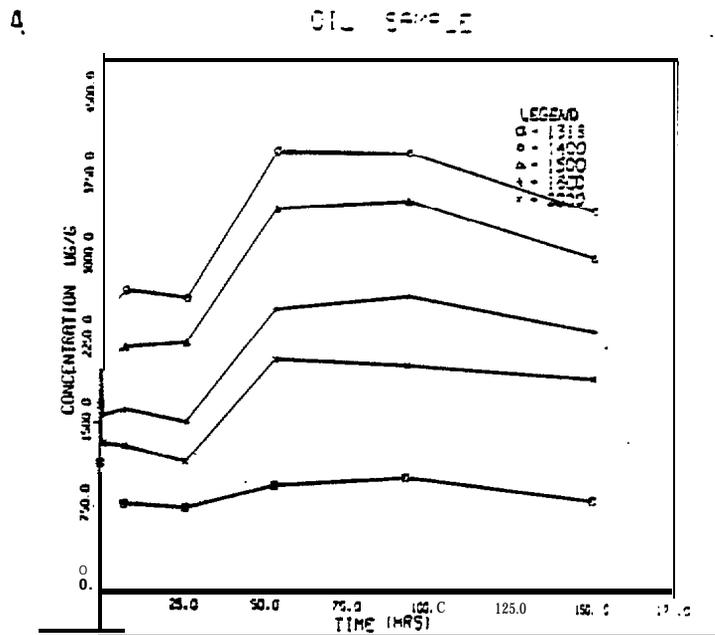


FIGURE 5. COMPUTER GENERATED PLOTS OF CAPILLARY FID-GC DATA ON HIGHER MOLECULAR WEIGHT COMPONENTS REMAINING IN PRUDHOE BAY CRUDE OIL AND MOUSSE WEATHERING UNDER SUB-ARCTIC CONDITIONS ON FLOW THROUGH SEAMATER ENCLOSURES AT KASITSNA BAY ALASKA. KOVAT INDICES ARE IDENTIFIED ON EACH PLOT. AND ENVIRONMENTAL CONDITIONS AREAS IN FIGURE 3. (FROM PAYNE ETAL., 1981b.)

the turbulence regime, and Table 3 presents the time series water column concentrations for the two systems. The three orders of magnitude difference between the fresh oil and fresh mousse systems clearly reflects the latter's resistance toward dissolution and dispersion into droplets.

Differences in the rates of volatile components from mousse and fresh oil may affect the flash point and burn point, but more significant perturbations to oil combustability probably result from simple incorporation of water. Twardus (1980) has provided the most complete characterization of the combustibility and other physical properties of aged oils and emulsions. The flash point, fire point, viscosity and pour point were all found to go up significantly as the percent of water increased. Thus, longer pre-heating and ignition times were required for water-in-oil mousse, and it was noted that since these emulsions do not spread as rapidly, evaporation and flame propagation occurred very slowly. In water-in-oil emulsions having water content approaching 20% a slight elevation in fire point was observed, and in heavier crudes where water concentrations went up above 20-30%, fire points increased dramatically. Thus, while water-in-oil emulsions formed with fresh crude oils could be burned successfully in situ (when solid fuel igniters were employed to initiate the combustion process) the maximum water content for effective burning of the emulsion layers was approximately 70% by volume for medium crudes and 30% by volume for heavy crudes. It was also noted that in emulsified crudes, separation of water and oil must occur before effective combustion could occur, and this ultimately required longer pre-heating and ignition times in the case of emulsified oils. Further, unlike the ignition of unemulsified oil slicks, the emulsified oils required a definite size flame before flame propagation over the entire oil surface could occur. Slick thickness of water-in-oil emulsions was also critical, with 10 mm thick slicks easily ignited for Norman Wells and Sweet Blend crude oils having water contents of up to 30% by volume. In fact, a 10 mm thick slick of Norman Wells crude oil emulsified with up to 70% water by volume could be easily ignited with a solid fuel ignitor. Water-in-oil emulsions of the same thickness for heavier crudes (Lloydminster and Wayburn-Midale with water contents of up to 30%) were much

TABLE 3

Time-series water column concentrations ($\mu\text{g/l}$) of dissolved and dispersed hydrocarbons from fresh Prudhoe Bay crude oil and mousse weathering on flow-through seawater enclosures (turbulent regime) at Kasitsna Bay, Alaska. (Water temperature 6°C , air temperature $6^\circ - 13^\circ\text{C}$). Concentrations determined by capillary temperature-programmed FID gas-chromatography. (from Payne et al., 1981b)

<u>Fresh Oil</u>	<u>0 hrs</u>	<u>1 hrs</u>	<u>7.5 hrs</u>	<u>26 hrs</u>	<u>53 hrs</u>		
Resolved Components	7200	4740	1400	10110⁺	659		
Unresolved Complex Mixture	3140	1460	420	447	114		
<u>Fresh Mousse*</u>	<u>0 hrs</u>	<u>1 hrs</u>	<u>6 hrs</u>	<u>19 hrs</u>	<u>30 hrs</u>	<u>45 hrs</u>	<u>100 hrs</u>
Resolved Components	23	7	29	18	10	24	34
Unresolved Complex Mixture	ND	ND	12	45	37	69	59

*Water column concentrations corrected for total oil volume added as "mousse."

ND = none detected

+Possibly due to excessive oil droplet entrainment

more difficult to ignite and often **requi**red **the** addition of fresh oil for **their ignition**. The residual oil layers remaining after combustion of **water-in-oil** emulsions ranged between 0.4 and 1.9 mm in thickness and these values were similar to residual oil layers remaining after **the** combustion of **unemulsified oil** layers of the **corresponding** crude oils.

Kolpack et al., 1977 reported that **the** residues that remained after burning "of the Bunker C cargo during the explosion and sinking of the San-sinena had densities significantly greater **than** the unburned cargo and that these rapidly sank **to** the bottom. Computer simulations of-changes in **composi-tion** of a standard Bunker C after 2 hours of evaporation at 4 different temperatures were generated using **API** standard Bunker C composition (paraffin C-12 to C-28 maximum at C-14-15; **naphthenes** C-9 to C-25, **bimodal** with maximum at **10** and 22; aromatics C-8 to C-23 with maximum from C-10 to C-17 and **as-phal**tics starting **at C-12** and increasing to 30% relative composition at C-48). In this simulation the density of Bunker C increased to that of seawater within **10** hours when the oil temperature was 75°. A specific gravity **of 1.025** was attained after 40 minutes **at 125°C** and within less than 10 minutes at **250°C**. Oil simulations for unburned spilled oil showed it to take more than 1 week for this residual -material **on the** water surface to reach a density of that approaching seawater.

Interestingly, when Dickens et al. (1981) introduced an oil -gas **mix-ture** of **Prudhoe** Bay crude oil and air under ice, no significant mousse **forma-tion** was observed. **During** spring break-up of the ice the oil was found **to** be sandwiched **among** thin **ice** sheets and brine channels, and none of the oil was in an obviously emulsified water-in-oil form. This **oil** could be removed from the scene **by** burning with burn efficiencies ranging up to 95%. Final mass balance of the **oil in** this instance was 31% burned off, **31%** evaporated, **17%** manually cleaned up and 21% naturally dispersed. **Nelson and Allen** (1981) found **little** dissolution or microbial degradation of **Prudhoe** Bay crude oil spilled under ice, and it was found that mousse formation presumably required the loss of these volatile components and **possibly** the formation of **photochem-ical** and microbial degradation **products** in addition to significant turbulent

mixing which did not occur under ice. As a result, when the oil was released in **brine** channels **during** the **spring breakup** of the ice, burning could be used as an effective clean-up/oil removal procedure. Further, the potential for mousse formation may have been attenuated by alternate freezing and thawing of the oil-water mixtures. Dickens et al. (1981) and **Twardus** (1980) reported that alternate freezing and thawing cycles of water-in-oil emulsions in pans caused the emulsions to separate **to** some extent into separate water **and** oil phases during aging. From these studies it can be seen that freezing of **water-in-oil** emulsions **will** result in a destabilization. This behavior was also **observed** in our laboratory when mousse samples were frozen.

Twardus (1980) also found that **the** clean-up of water-in-oil emulsions was more complicated as the sorption capacity (grams of emulsion/gram of dry **sorbant**) of **3M** brand oil **sorbant** was significantly reduced as the water-in-oil content increased for **Loydemister, Wayburn-Mildale, Sweet Blend** and **Norman Wells** crude oils.

Breaking and Interaction of Laboratory Mousse with Dispersants

To evaluate **the** possibility of preventing mousse formation at sea **Berridge et al.** (1968b) attempted to generate mousse in the **laboratory** with 0.1% by weight ESSO **Brexit** and varying concentrations of the **dispersant** BP1002 added to the starting oils. Results from these **and** other tests are presented in Table 4. **In** these mixtures, the crude oil was observed to take up large quantities of water ranging from 66% for the **Brega** crude to 75% for **Gatch Seran**, however, no stable mousse **could** be formed. The time required for separation **of** the oil and water layers ranged from several seconds to 2 minutes. Photo **micrographs** showed that water particles ranging in **size** from 1 to 50 micron were encapsulated **in** most of the oils however, due to the lower viscosity of the mixtures (presumably from the presence of the **dispersants**) the phases rapidly separated. The Nigerian crude used in their study appeared to contain smaller droplets and was slightly more stable. Using various ratios of from 0.1 to 1.0 weight percent BP1002, various types of mousse were

TABLE 4

Inhibition of Stable Mousse Formation by the Addition of Chemical Dispersants
(from Berridge et al., 1968b and Bridie et al., 1980a, b)

Crude	Dispersant	%	%H ₂ O	Appearance	Time to Separate into layers
Kuwait	Brexit	0.1	74.5	No stable mousse	1 minute
Tia Juana	Brexit	0.1	72.1	No stable mousse	1.5 minutes
Brega	Brexit	0.1	66	No mousse	
Iran (Agha Jari)	Brexit	0.1	71.4	No stable mousse	2 seconds
Imega (Kirkuk)	Brexit	0.1	78.1	No stable mousse	1 second
Nigerian	Brexit	0.1	70.5	No stable mousse	1 second
Gach Saran	Brexit	0.1	75.6	No stable mousse	2 minutes
Kuwait	BP 1002	0.1	81	Good mousse	Stable
	BP 1002	0.5	76	Fair mousse	2 hours
	BP 1002	0.75		No mousse	
Tia Juana	BP 1002	0.75	76	Sticky mousse	10 hours
	BP 1002	1.0	65	No mousse	
Imega (Kirkuk)	BP 1002	0.1	77	Soft mousse	12 hours
	BP 1002	0.75	67	Good mousse	10 minutes
Brent	LA 1834	0.1		No mousse	
Kuwait	LA 1834	0.1		No mousse	
Bunker C	LA 1834	0.1		No mousse	

obtained, and **their** properties ranged from stiff to sticky and soft **to** no mousse formation with increasing **dispersant** concentration. The time required for breaking of the emulsion ranged from **10** minutes to 2 hours. Less encouraging results were obtained in attempts **to** breakup previously stabilized mousse with **emulsifiers**. **Breaxit** was tested at three temperatures and BP1002 was tested at ambient temperature. In general, higher concentrations of the BP1002 were required to break the emulsion.

From these results, **Berridge** et al. suggested that to prevent mousse formation from large crude **oil** spills, the oil could be **de-asphaltized** before shipment or that emulsion breaking surface active agents could **be** added to the crude before shipment.

Bridie et al. (1980b) evaluated a **dispersant** additive (**LA1834**) in laboratory tests with artificial mousse generated with a Brent **200+** crude at 10°C and found that **the** viscosity immediately dropped significantly and that **60%** of the water separated (residual water content <50%). After the mixture stood at **30°C** for 4 hours, additional water separated and the residual water content **in the oil** was less than 10%. Similar results were obtained with Kuwait **200+** mousse, **but** its residual water content remained higher. Adding **LA1834** to either **the oil** or water prevented mousse formation (**Table 4**) at all stirring **speeds** and temperatures tested using Kuwait crude, Brent crude and **Bunker C** fuel **oil** (**LA1834** concentration, 300-1000 **mg/l**). In large scale (10 ton) tank tests, addition of 3000 **mg/l** **LA1834** caused the viscosity of the 70:30 water-in-oil emulsion to dip from 130,000 CP (18°C, shear rate $3.28 \times 10^5 \text{g/cm}^2 \text{S}^2$) to 3,800 **CP**, and the water content dropped to 25% after **10** min. and **15% after** 60 min. The additive was **also** successfully used to lower the viscosity of "recovered beached mousse from several thousand tons of **Basra** Light crude spilled from the **Irene's Serenad** after an explosion near Greece in 1980, such that the material could be pumped from oil drums and picked up by waste disposal trucks. **In** this case 200-4009 **of LA1834** was added **to** each 200 **l** drum.

In another recent study, **Bocard and Gatellier** (1981) studied the effects of **various dispersants** on water-in-oil emulsions formed from Arabian light crude topped at **150°C**, (viscosity 10,000-20,000 cP), a **Safanya** crude (viscosity 20,000 to 50,000 cP) and heavy fuel **oil** (viscosity 60,000 to 80,000 cP). To determine the effectiveness of various **dispersant** products, mixtures of the **dispersants** were **added** to the laboratory **generated** mousse with four vertical blades rotating at **500 rpm** for specific time intervals. The water released as a function of stirring time and settling time was measured in a graduate cylinder. Ratios of emulsion-breaking product to mousse ranged between 250 to **1000 ppm**; however, it was **noted** that above 500 ppm the gain in effectiveness was relatively slight. After mixing times in excess of **150 minutes**, variable results were obtained with the seven different emulsion breaking products tested. Anywhere from a **low of 18%** to a high of 56% of the water could be removed with this procedure. For **the** more viscous mousse, much greater agitation of the mousse and emulsion breaking product was necessary to effect similar separations. In all cases, injection of emulsion breaking product **did** immediately cause a significant drop in **the** viscosity before any water separation occurred. This was illustrated for **the** Arabian **light** crude **oil** mousse (75% water) treated with **1000 ppm** of product "A". In this case, the viscosity of the emulsion measured at 20" at **the** pump **outlet** of their laboratory emulsion breaker, showed that the viscosity decreased from approximately 22,000 CP to 5,400 cP at 10 **rpm** after introduction of **the dispersant**. From infrared and TOC hydrocarbon measurements, **it** was also shown that approximately 20-25% of the **deemulsified** products passed into the aqueous **phase**.

To determine the effects of emulsion breakers on stabilized mousse aged **in** a **natural** environment, the authors performed field experiments from March 1979 to February 1980 in the **oil** port terminal of **Antifer (Le Harve)**. Approximately 400 liters of Arabian light crude were poured onto a floating metal enclosure and the oil layer was measured to be about **15 mm** thick. Samples were taken periodically over time and the temperature was noted to vary from **6°C** in winter to **19°C** in **summer**. Up to 75-80% water was taken up **by** the crude **within** the first **week** and approximately 30% of the materials were

believed to have been evaporated at that time. Over the 11 month period, water content in the mousse dropped to approximately 65-75% while evaporation only increased to 44%. When dispersant tests were performed with time on the samples at 20°C (with 100 ppm of Product "A"), a progressive stabilization of the mousse on and after September 1979 was noted, and none of the products tested were able to cause the slightest phase separation. The stability of the naturally generated mousse was not apparently directly correlated to an increase in viscosity. The 12 month old weathered water-in-oil emulsion exhibited a 20°C viscosity of 24,000 cP at 10 rpm, 11,000 cP at 20 rpm and 2800 CP at 50 rpm. All of these values were considerably lower than those obtained from synthetic emulsions of Arabian light crude (topped at 150°C) with 75% water generated in the laboratory. When mixtures of the naturally generated mousse were mixed with 150" cut Arabian light crude, an emulsion was formed which had a viscosity of only 1600 CP at 10 rpm. This emulsion could not be broken up at 20°C with any of the products tested. Similar results were obtained with other artificial mixtures of Arabian crude mousse (with 70% water) and other oils. Stabilization of the emulsions by incorporation of microparticulate particles of sedimentary material was suggested as one possible hypothesis for the observed stability. It was also stated that the formation of oxygen compounds from photochemical, microbial and auto-oxidation may have acted as surfactants, thus, having a further stabilizing affect on the emulsion.

While Bocard and Gatellier (1981) suggested that viscosity did not directly affect water-in-oil emulsion stability, slightly conflicting results were reported by Lee et al. (1981). The latter authors reported that changes in water contents and viscosities for 8 crude oil mousses directly influenced dispersant efficiency. In general, it was found that dispersant efficiency was very low with mousse mixtures having viscosities greater than 10,000 cP; however, little useful dispersion could actually be achieved above 7500 CP for most crude oil emulsions studied. Lubricating oil base stocks gave an even lower viscosity limitation for effective dispersant treatment of about 2500 CP. This was attributed to a probable lack of any natural dispersants in the

lube oil stocks themselves. When a mixture of two **different** concentrations of mousse **were** spread at sea **it** was shown that the time to form a stable mousse was very short, and that within 5 hours, the viscosity had increased to a **point** where **dispersant** efficiency was significantly reduced. Different products from different manufacturers varied considerably in performance when used, however, they all performed better when used neat rather **than** diluted into seawater. Once detergents were **pre-diluted** with seawater and applied to the oil, their performance became similar and usually inferior to that observed with undiluted **dispersants**. The effect of viscosity on **dispersant** effectiveness was attributed to the fact that when the viscosity of the oil is above **the** limiting value, **the dispersant** is removed physically from **the oil** by wave action before it can diffuse into the slick and become effective. In independent investigations, MacKay et al. (1980) have stated that viscosity increases in mousse are critical in **dispersant** treatment, and that viscosity can **be** correlated mathematically with percent water uptake. In their studies they concluded that **mousse** with viscosities in excess of 4,000 centipoise **would** be **difficult** if not impossible to disperse.

Dispersants have been used with mixed results in various major **open ocean** and coastal spills, however, they will not be considered in detail in this paper. In the Amoco **Cadiz** spill when emulsion breakers were **used in** intermediate storage **tanks** and mobile van trucks, very little separation of water from the mousse occurred, however, **addition of dispersant** did speed up transfer of the mousse by reducing the viscosity of the emulsion. **It** was hypothesized (**Bocard and Gatellier, 1981**) that significant mixing energy **was** not present **in** the trucks **or** storage tanks to release a large proportion of the water. **Recommendations** were made, such that during clean-up operations, emulsion breakers be injected on-line upstream from the pump at a flow-rate that is proportional to the pumping throughput. **Also,** in field applications, when emulsion breakers were applied to slicks, the efficiency of skimmers was improved, however, preliminary tests performed in **the** laboratory with slight stirring have **shown** that the emulsion breaking **action** is very slow under these conditions.

Bacterial Utilization of Laboratory Generated Mousse

As noted earlier, **Berridge et al. (1968b)** indicated that microbial utilization of laboratory generated mousse was minimal. Likewise **only** limited evidence of bacterial degradation of 350° topped Kuwait crude oil mousse was observed by Davis and Gibbs (1975). **In** their open tank system there was some **evidence** of **n-alkane** removal (presumably due to biological activity); however, this was not observed in their closed tank system. There the rate was **believed** to be limited by significant O₂ and nutrient depletion over time. Oxygen and nutrient concentrations in the **surrounding bay waters were such** that microbial processes were not significantly affected in the bay or open tank. It was **clear** from their work, however, that truly effective degradation of the mousse **would** occur only after physical dispersal into smaller **particles**. **Nagata and Kondo (1977)** reported that limited microbial degradation occurred on laboratory generated crude-oil mousse with hydrocarbons **below nC-15 being** 20-30% **degraded after 5 days**. Hydrocarbons above **nC-15** remained unchanged at that **time whereas about 50%** of these **were** degraded after 15 days.

In open ocean oil spills, microbial degradation and utilization of components in mousse has been "variable. **In the Amoco Cadiz spill**, for example, there **was** abundant evidence that microbial degradation processes were significant and even approached rates of loss due to evaporation and dissolution. On the other hand, **in the IXTOC and Potomoc spills** there was little evidence of **microbial** degradation of the mousse or tar **flakes**, and these phenomena **will** be discussed **in** more detail in the next section on case studies of mousse **formation** from major open ocean and coastal spills and blowouts. After the **Tanyo** oil spill, mousse **samples** were collected and oxygen **consumption** was measured after adding mixed microbial cultures **to** mousse/water mixtures; however, no activity was detected during the first 200 hours. **When** the sample was first treated with a **surfactant (1% by weight)** a positive reaction was observed, and the bacterial activity was directly related to the amount of oil available (**Bocard and Gatellier, 1981**).

SELECTED CASE HISTORIES OF THE MORE DETAILED
CHEMISTRY STUDIES OF MOUSSE BEHAVIOR AND LONG TERM
FATE **IN** NEAR-COASTAL AND OPEN OCEAN OIL **SPILLS/BLOWOUTS**

A number of fairly large **oil** pollution incidents involving mousse formation have occurred over the last decade, and Table 5 presents details from several selected cases where mousse formation was noted and in some cases chemically studied. **In** the following summaries only **those** factors dealing with mousse formation were included, and by the nature of available literature, there are obviously some gaps **in** our knowledge of complete details for some of the oil spills. Because of the increased number of spills and scientific investigations during the last several years, however, it is not surprising that the most detailed chemistry data have only become available recently. Thus, most of the deficiencies in our data base are from the earlier **spills**, and there are obviously numerous other spills **which** have occurred over the last 15 years **which** are not included in this review. In many cases these other **spill** events were not studied in detail, or if they were, the data were not available at the time of this writing.

It will be noted from examination of Table 5 that most of the oils which generated mousse **in** real spill events **also** formed **stable** water-in-oil emulsions in laboratory experiments (Tables 1 and 2). Very limited data were available from other spills where mousse formation did not occur, and **as** a result, we do not have as much significant **field** data on oil spills occurring with other **crudes**. Nevertheless, it is significant that the majority of **oils** which have **been** shown to form mousse in laboratory studies were also the oils causing the **most** problems with mousse in actual oil spills as reported in the literature.

Torrey Canyon

This was the first major **spill** event where mousse formation received significant attention in terms of transport and clean-up. The Kuwait crude

TABLE 5

Chemical Studies of Oil/Mousse Behavior in Major Oceanic Spills and Blowouts

Spill/blowout incident	Location	Date	Oil Type	Volume (tons)*	Water Temp	Air Temp	Mousse Type	Fresh Oil Composition					Oil/Mousse Properties				Reference	
								S.G.	Aliphatic	Aromatic	Polar	Asphaltene	Visc./Pour Pt. (°C)	H ₂ O	Asph	Dens		100 Visc./Pour Pt. H ₂ O
Torrey Canyon W. Cornwall, England		March, 1967	Low oil crude	~100,000			Sd. w/ l of Grease-like	0.869	31.1	33.7			50-50				Theroux (1980), Berridge (1968), Mackay et al. (1973)	
Acrow	Ambeduolu m., Nova Scotia	Feb., 1979	Bunker C	12,000	0-P		Grease-like	0.940	26**	26**	29**	20**	10,600cP/-1°	40-Ad			Owen 1976, & Rashid, 1974 Mackay et al. 1973	
Netula	Strait of Magellan	Aug., 1974	Sumat Crude Bunker C	52,000 2-3,000	0-10	~8	Extremely light Brown stable / Dark Brown		(See table 8 for examples)				25-30 6-108			Stoughton, 1977; Mann, 1977		
Buerton	Brittany, France	1976	Venezuela crude	10,000				1.0	2	25			10,000cP/12°			J.L. Maurin, 1980		
Ekofisk	Brava North Sea, Norway	April, 1977	Ekofisk crude		6°		V* I (with brown unstable; after well capped, more stable brown mousse observed (more unathered)	0.814	42	21			7, 600P/6°	83 60-805	0.98	70,000cP/6°	3.5 3.5	Cornack and Nichols, 1977, Grah-Nielsen, 1977 Audumson, 1977
Potomac	Melville P., Greenland	Aug., 1977	Bunker C Pitich 55	308	3-4°	4°	Oil globs (pancakes) & 0.96 flakes; no apparent mix D emulsification	0.853	39	30	14			26			Peterson 1977	
Amco (adit)	Brittany, France	March, 1978	Arabian crude & Bunker C	230,000 4,000			Reddish-brown Quite stable	0.853	39	30	14		4-10cSt/	250-80 variable	0.98-0.98			Calder & Socha, 1981; NOAA/EPA Special Report in 1978, Mann et al 1978, p. 219
1810C	off of Campeche - Gulf of Mexico	June, 1979 March, 1980	1810C crude	476,000	25-28	20-33	Brown/stable Delayed formation until after evap & by weathering.	0.883	62	38	7-8			60-708	0.99			
Burma Agate	Galveston, TX	Nov., 1979	Nigerian crude	263,000 661		20-33	No mousse formation noted	0.828										Kelly et al. (1981)
Prudhoe Spills	East Coast	Oct/Nov, 1975 & 1978/1979 (with dispersants)	Murden crude (Middle East) to Asia crude (Venezuela)	640 gal 440 gal	11-14	12-17	Delayed formation of reddish/brown mousse No mousse noted but thicker "lenses" observed at leading edge of slick.	0.820										JBF/APL 1976 and McWhiffen et al. 1981 JBF/APL 1976 and McWhiffen et al. 1981
	West Coast	Sept., 1979 (w/ dispersants)	Prudhoe Bay (Alaska)	10-20 bbl			No mousse formation noted but thicker "lenses" observed at leading edge of slick.	0.89					10355U		0.98	121055U		McWhiffen et al., 1981

*Volume in tons except where noted

**Composition based on STD Bunker C oil

oil spilled by this vessel was reported to form a semi-solid, gel-like mousse after the spill at sea and during clean-up operations (Smith, 1968). These emulsions were fairly stable and some contained up to 80% water. In this instance, the spilled oil was fairly heavy with the composition-percent distilled at 210°C being only 21%. The oil composition consisted of 31% saturates, 33.7% aromatics and had an initial density of 0.866. There were several discussions of oil spill clean-up problems of the beached mousse along the Cornwall coast, however, most of the reports centered on the toxic effects of the dispersants used in the oil spill clean-up, and this received much greater attention in the literature immediately following the spill.

Tanker Arrow

The Liberian Tanker Arrow carrying 108,000 barrels of Bunker C crude oil was grounded off Cerberus rock in Chedabucto Bay, Nova Scotia in February 1970. It was estimated that approximately half of the cargo was spilled and driven out to sea and onto the coast contaminating approximately half of the 600 km of shoreline (Keizer et al., 1978). Mackay et al. (1973) reported that much of this oil was in the form of mousse containing up to 40% water, but it was also noted that because of the high viscosity of the cargo and the cold water temperature (0-2°C), the oil was observed (by divers) to be released as "discrete pieces, like a rope 1-3 feet long" through holes in the hull of the vessel (Barber 1970). While much of this very viscous oil and mousse eventually reached the shores of Chedabucto Bay, significant portions were also broken-up into smaller particles during the first 15 days following the spill by heavy turbulence and the addition of 10 tons of the dispersant Corexit 8666. These particles were detected at significant distances from the vessel. Forrester (1971) reported that particles of finely dispersed oil ranging from 5 mm to 10 mm were found in the water column to a depth of 80 m, and occasionally droplets as large as 2 mm were found. In general, the total oil concentration decreased with depth, however, the relative abundance of the smaller particles increased. Finely dispersed particles could be traced from the vessel to a site approximately 250 km southward from Chedabucto Bay in a

band extending up to 25 km offshore, and two weeks after the wreck, particles were still observed 70 km to the east of Nova Scotia in 10 km wide tongues along the surface. Fragmentation of large pelagic tar lumps into small particles has been studied by Wade (1974) and Wade et al. (1976), who observed that on shaking tar balls with filtered seawater for 4 weeks, micro particulate in the following size ranges are formed: 0.25 to 1 μm , 50%; 0.25-0.3 μm , 38% less than 0.3 μm , 12%. Likewise, Peak and Hodgson (1966, 1967) and Gordon et al. (1973) have mixed hydrocarbons with distilled water and found that less than 1 μm particles of oil increased the whole-water oil burden to values greatly in excess of those for saturated solutions. This excess in concentration above saturation levels was due to colloidal particles, and Gordon et al. (1973) noted that the greatest number of particles formed by mixing hydrocarbons with seawater occurred in the size range of 1-30 μm .

Conover (1971) reported that significant quantities of the finely dispersed oil from the Arrow were ingested by zooplankton, but it was believed that most of this ingested oil was eliminated in the feces which were observed to contain up to 7% oil by weight. Thus, Conover estimated that as much as 20% of the oil droplets with a diameter less than 0.1 mm could be removed from the water column, and once incorporated into the feces with a specific gravity greater than seawater, rapidly sink. In a related study, Parker (1970) found oil droplets in the gut contents and fecal pellets of copepods and barnacle larvae. In both instances, however, there was little evidence to suggest that any adverse effects to the species studied occurred as a result of the ingested oil. Parker, et al. (1971) later estimated that one copepod (Calanus finmarchicus), could conceivably ingest up to 1.5×10^{-4} grams of oil per day. Thus, a population of 2,000 individuals per cubic meter of seawater ingesting oil at this rate and covering an area of 1 sq. kilometer to a depth of 10 meters could theoretically remove as much as 3 tons of oil daily, if oil concentrations were 1.5 micrograms per liter or greater.

With regard to the stranded mousse from the Arrow spill, Thomas (1977) stated that most shoreline sampling stations showed 100% oil cover in

1970 at mean high water. Surface coverage was observed to decrease at a logarithmic rate at the lower tidal levels with shores exposed to heavy wave and ice action showing the fastest removal. By 1973, most of the oil in the lower cliff zone (lower 27-33% of the tidal range) had been removed. Above this, the percentage of surface oil increased to the mean high water mark and then rapidly declined. Slow removal was shown in higher tide levels and sheltered locations, and under the calmer conditions in the sheltered areas surface oil existed at the lower levels until 1973. By 1977, the degree of oiling was directly proportional to the wave energy and degree of sheltering of the stations, and in the more sheltered areas surface oils still persisted. Correlations of oil content with intertidal and subtidal substrates were noted, with the long-term contamination increasing from: 1) broken rock and boulder, to 2) bedrock with sand at the high water level, to 3) broken rock and gravel, to 4) muddy sand at high water, and to 5) sandy mud at low water. Toxicity to the salt marsh cord grass (S. alterniflora) was delayed for one year, and this was attributed to the fact that the spill occurred in an extremely cold regime and that at the time of the initial oiling the plants were dormant with aerial portions not being directly coated with the oil. The oil could not penetrate into the soil as the latter was frozen and the oil was extremely viscous. Thus, in the Spring of 1970, the marsh grass penetrated the oil and foliage appeared normal. During the following Summer, however, the oil was remobilized during warm periods, and living parts of the plants did contact it such that the following year the plants were reduced in number and exhibited Chlorosis. Owens (1978) also reported that the residence time of stranded oil increased as the degree of energy in the shorelines decreased, and Rashid (1974) reported on changes in viscosity as a function of weathering conditions. In a stored sample of the cargo obtained at the time of the spill, aliphatic and aromatic hydrocarbons constituted 51% of the total, asphaltenes made up 30%, and resins and NSO's contributed 29%. The viscosity of the stored cargo was 19,584 cP. The viscosity of stranded oil increased from 28,600 to 1,210,0110 to 3,640,000 CP in going from low energy to moderate energy and high energy coastlines, respectively. These samples were collected 3.5 years following the spill. At a site protected from wave action at all

times, the oil was observed to have a low viscosity and a high total hydrocarbon content (49%). Thus, oil exposed on beaches subject to continued and active wave action weathered to mixtures having higher viscosities and increased asphaltene contents.

In a concomitant study, where oil composition was considered, Vandermeulen et al. (1977) observed that 7 years after the Arrow incident, aromatic and cycloalkane components remained significantly more resistant and unaltered compared to the aliphatic components. The site studied in their article was part of a gently sloping shoreline of a large low energy lagoon system, and it was characterized by a 2-3 cm thick tar layer up to a meter wide lying along the high tide line at the top of the beach. Concentrations in the sediments ranged from 6.7 to 10 ppm at the minimum to a high of 1200 to 5500 ppm. Increasing concentrations with depth were noted in the high tide sediments, but the reverse was observed in the low tide sediments. Significant degradation of the aliphatic components was noted, in that the unweathered Bunker C contained a normal compliment of n-alkanes from nC-13 through nC-30, and the weathered samples showed almost total loss of alkanes up to nC-30. This was most pronounced in the mid- and low-tide samples, although no differences in alkane losses were noted with depth into the sediments. Large unresolved complex mixtures characterized the gas chromatograms of the unweathered Arrow Bunker C, and all of the weathered samples. Synchronous fluorescence spectra of the original oil and extracts from the high-, mid- and low-tide zones appeared to be essentially identical illustrating the extreme longevity of the polynuclear aromatic components in sediments. The loss of the alkanes and the predominance of the aromatics was generally attributed to microbial activity.

Kaizer et al. (1978) reported that an oil and sediment mixture having a "pavement like" consistency was found in the upper intertidal zones of Rabbit, Crichton and Durelle Islands 6 years after the spill. Evidence of oil contamination was also found in the intertidal sediment in many other areas of the bay; however, the pavement like material was primarily limited to the more sheltered locations. Along some of the shores of Rabbit Island and Inhabitants Bay, oil, sand and pavement mixtures up to 15 cm thick were noted in the

upper half of the intertidal zone, and this oil was observed to spread out and flow **on hot** days causing additional leached components to enter the interstitial waters. **During** their studies **there** was **also** evidence of more recent oil sedimentation on **the** beach, so they were **not** able to completely evaluate the overall extent of weathering and mobility of stranded **Bunker C** from the Arrow. Thus, while most of the oil stranded on the shores of **Chedabuctos** Bay disappeared over the 6 year period, there was persistent evidence of contamination in many locations. Specific identification of much of this **oil** was **impossible**, but a **few** isolated spots had visible **oil** contamination which could be identified as Arrow Bunker C.

Metula

The **Metula** grounded off of **Satellite** Patch just west of the first narrows in the **Straits** of **Magellan** on August 9, 1974. From that date **until** **25** Sept. **1974**, 50,000 to 56,000 tons of oil were spilled. Most of this was Kuwait **crude**, but 3,000 to 4,000 tons of **Bunker C** were also lost after the first **few days** of **the** grounding (**Straughan**, 1977). This spill occurred during the southern hemisphere winter and was augmented by extreme turbulence and very cold conditions (**water** temperatures during the surveys ranged from **8-10°C** while air temperatures averaged 8*) (**Straughan**, 1977). It is not known whether mousse was formed immediately upon release of the **oil** to the sea, but **two** distinct types of mousse were observed during **field** studies two weeks **later**. A dark brown mousse containing 5-10% water was presumably generated from the **Bunker C** fuel, while the light Arabian crude generated a light-brown mousse with 25-30% water (**Harm** 1977). A total of 25 miles of coastline, including 2 small tidal estuaries, was heavily impacted during the first **3 weeks** following this spill. **Both** types of **mousse** were deposited high on the beach front by **spring** tides and waves, and both types of mousse had incorporated seaweed, sand, and numerous **small** organisms. The darker mousse ranged from **5-10** cm thick and covered from 6-15 m of flat areas at the top of the beach. The lighter material typically covered from **15-60** m of **beach** at depths from 1-5 cm. **During** the first site visit, between 75-90% of the total oil was

washed ashore along the 40 mile stretch of Tierra del Fuego. Five months later, between 120 and 150 miles of beach was visibly impacted, and at several locations, dozens of black tar balls ranging from 3-5 cm in diameter were observed. These consisted primarily of weathered oil, shell and sand fragments. In other areas, tar balls ranging from 0.5 to 8 cm in diameter existed in beached sands. Mud flats were perhaps the most severely impacted, with mousse and sand mixtures from 15-25 m wide present. Like the mousse-sand mixtures from the Arrow incident, this material had hardened like a road or sidewalk (observed during the southern hemisphere summer). In January 1976, the lower tidal zone at Puerto Espora contained significant mousse and sand-asphalt material. At this site the intertidal zone ranges from 500 to 600 m wide and is about 3-4 km long. Of the 400 m wide lower intertidal zone, approximately 60% of the western 1/3, 95% of the middle 1/3, and 80% of the eastern 1/3 was covered with black asphalt like material. This mousse ranged from 5-10 cm thick and in some areas reached 15 cm. At one area, mousse mixed with sand was noted to a depth of 30 cm. Heavily impacted areas such as these will obviously take years to recover and will be a continuous source of contaminants to interstitial waters and the general coastal environment. Interestingly, the seaward 100 m wide stretch of the intertidal zone (exposed only at low spring tides) was not generally coated with oil, and this area did contain a rich abundance of algae and mussels (Straughan, 1977).

Ekofisk Bravo Blowout

The Ekofisk Bravo well blew-out on April 22, 1977, and was the first major blowout to occur in the North Sea area. In perhaps the fastest response time to any spill event to date, a detailed chemical, biological and physical oceanography study was initiated 36 hours following the blowout (Grahnl-Nielsen, 1978). Also, before the blowout, Cormack and Nichols (1977) had conducted a number of field tests with 0.5 ton amounts of Ekofisk oil so additional information was available on what to expect in the event of a major spill. They had shown that while emulsion formation was as rapid as for Kuwait crude oil, the resulting viscosity of the Ekofisk emulsions was low and

insufficient to **allow** interference **with** the natural spreading and dispersion rates. Evaporation was a significant removal mechanism for the **Ekofisk** oil as some 53% of the weight of the **oil** boils below **350°C**. During the test **spills** (sea temperature **11.6°C**, air temperature **18°C**, wind speed 12 knots with gusts to **18** and sea state 3-4 on **the Beaufort** scale), it was observed that up to 21% **of** the weight of the oil was lost to evaporation in 7.5 hours. After 3 hours, there was no evidence of any hydrocarbons below **nC-9**, and after 7.5 hours, hydrocarbons up to C-n **were** lost and C-12 and C-13 hydrocarbons were significantly depleted. Thus, **while** emulsification did occur in the test spills, it did not have serious effect **on** the rate of evaporative loss.

Ekofisk crude has a relatively low **asphaltene** content (0.03% by weight) when compared to other oils such as Kuwait crude (1.45% by weight), which is known to form **stable** water-in-oil emulsions, so extensive stable mousse formation was not anticipated with the **Ekofisk** Bravo oil. **Cormack** and **Nichols** did observe the **Ekofisk** crude **oil** took up water from **35%** to **72%** in a **0.5 to** 1.3 hour period following the test spills, however, the emulsion was rapidly broken up into patches of about **1-5** cm in diameter, and after approximately **21** hours, these were further broken down into small flakes with **5-10** mm diameter. **It was** also noted that the rate of water-in-oil emulsification was extremely dependent on the degree of turbulence and sea state: at wind speeds in excess of **12** knots the oil incorporated 70-80% water in **less** than 2 hours. At 2-3 knots **the** rate was 10-20 times slower. **Using** this data, **Mackay et al.** (**1980**) estimated **half**-times for emulsion formation of 2.8 hours at 3.1 knots, 16 minutes at 10 knots, and **1.6** minutes at 31 knots. Thus the oil behavior is extremely dependent on the physical oceanographic conditions, and **Mackay et al.** (**1980**) **stated** that a very real need exists to determine which of **dispersion** and emulsion formation (which are competitive processes) occurs with various oils under given temperature and sea state conditions.

In the **actual spill** situation from the **Ekofisk** Bravo rig, **Grahl-Nielsen** (**1978**) measured levels of oil-in-water at approximately 100 $\mu\text{g/l}$, to 400 $\mu\text{g/l}$ and these values clearly suggested **the** presence of oil-in-water emulsions. **Grahl-Nielsen** used **GC/MS** analyses to characterize **naphthalene**,

phenanthrene and dibenzothiophene (NPD) components in the oils, and he reported 3 basic observable phases which occurred during and after the blowout. First, during and immediately after the blowout, fresh oil appeared on the surface and at depth as a oil-in-water emulsion; second, 2 weeks after the blowout was stopped, the remaining oil was found in small lumps north of the wellhead, and third, 4-5 weeks after the blowout was capped, small oil patches on the surface of the sea were observed south of the wellhead. Although an estimated total of 20,000 tons of oil were eventually released, no detectable naphthalene, phenanthrene or dibenzothiophenes could be found in the water column under the oil patches isolated. 4-6 weeks after the blowout. At the time of the blowout, these components totalled approximately 8 µg/liter in the water near the wellhead, while their concentrations dropped to 0.1 µg/liter outside the immediate well vicinity. Two weeks after the blowout was stopped, the NPD concentration dropped to 0.4 µg/liter near the well and down to 0.05 µg/l, (the limit of detection) with increased distance from the wellhead. There was no significant depth gradient noted at that time.

Audunson (1978) also studied the fate and weathering of the surface oil from the Bravo blowout. The oil, at a temperature of 75°C, was sprayed into the air, and estimates of 35-40% of total material were given for components lost to evaporation before and after the oil hit the water surface at 6°C. The specific gravity of the crude was 0.85 to 0.87 and this increased to 0.95 after 2 days of weathering on the sea surface. The oil was observed to spread in a 1 mm thick slick, 100-200 m wide in bands up to 1 km long. At the outer edge of these bands, 1-20 mm thick water-in-oil emulsions with a yellowish-brown color and up to 70% water were noted. These proved to be very unstable, and were rapidly broken into long strips 1-20 mm thick and 10 m wide. These bands were then further broken up by turbulence. A more stable mousse was formed later, around the time the well was capped, and this had a brownish appearance and contained up to 50-60% water. This too did not have the rigid structure of a Kuwait crude oil mousse, and was broken up into smaller 2-20 mm patches and ultimately 1-3 mm droplets with time. Microscopic examinations of the 56% water-in-oil emulsion showed 1 µm sized water droplets

to be dispersed in the mixture. The slightly more stable mousse which formed after the well had been capped presumably was partially stabilized by bacterial or photo-oxidation products which were not present in starting crude. The viscosity of the oil on the sea surface increased from an initial value of approximately 1,500 cp (at 6°C) to a value of 76,000 cp (at 6°C) after 2 days. This was attributed to weathering and evaporation plus the incorporation of water (Audunson, 1978). Even this relatively more stable mousse however, was rapidly broken up into smaller patches.

To determine if this dispersed Ekofisk oil was deposited in the sediments near the well site, Johnson et al. (1978) undertook a detailed sediment sampling and analyses program. GC/MS mass fragmatograms, nC-18/nC-19 and nC-27/nC-26 ratios were used along with hopane diastereomer ratios to characterize Ekofisk Bravo crude from background pollution. Even immediately after the blowout, Ekofisk Bravo oil levels were relatively low compared to, hydrocarbons from other materials and manmade sources, and at 4-6 weeks after the spill, the hydrocarbon levels in the sediments surrounding the wellhead had returned to background levels. Of all of the sediments showing positive evidence of Bravo oil, the concentrations were less than 8 ppm, and in the majority of the samples the levels were less than 1 ppm. All the sediment samples were collected with a Smith-MacIntyre grab, however, so some problems may have been encountered due to the loss of surface flocculate material during the sampling. This phenomena will be discussed in greater detail later when considering the IXTOC spill in the Gulf of Mexico.

Addy et al. (1978) looked for changes in the biological populations occurring near the wellhead. Despite the fact that there were changes noted it was not possible to distinguish between the effects of the spill and background activities. Chronic petroleum pollution in this area and significant sediment disturbances from anchoring and pipeline installations were believed to have caused as great a perturbation to the biological species present surrounding the wells. From this study it was not possible to attribute any specific changes specifically to the Ekofisk Bravo incident. Thus, the overall impact of the Bravo spill was relatively insignificant, as no coastlines

were impacted directly, and this points out the significant differences in overall environmental impact when considering open ocean vs. coastal spills.

US/NS Potomac in Melville Bay, Greenland

On August 5, 1977 the US/NS Potomac was holed by an iceberg while being escorted by the USCGC Westwind through scattered sea ice of Melville Bay in intermittent dense fog in the northeastern part of Baffin Bay off Greenland. Approximately 380 tons of cargo (primarily Bunker C crude oil, specific gravity 0.96 containing 55% pitch, specific gravity 1.055) were lost, and Petersen (1978) studied the oil weathering behavior which occurred shortly after the spill. Evaporation and dissolution were the primary weathering mechanisms operating following the spill, however, the water temperature (3-4°C), light winds (0-7 knots) and thick oil slick (up to 0.75 cm) all lowered evaporation rates. Nevertheless, alkanes up to nC-17 and substituted naphthalenes were depleted as much as 50-100% after 15 days. Shortly after the spill the oil was seen to form small pancakes (10-20 cm in diameter and 0.5 to 0.75 cm thick). The pancakes organized in wind rows about 4 m wide, and sheen (visible thin slick) was observed to emanate from them during the first two weeks. Calm seas (waves 0-2 feet) prevented significant dispersing for the first several days, and by August 19, 14 days after the spill, pancakes ranging from 8-15 cm in diameter were still in wind rows (several hundred meters long and up to 7 m wide). By August 20, 80% of the pancakes were no longer observed to emanate a sheen, and the majority of the mass of pancakes was submerged. In addition to the pancake phenomena, corn flake like particles of tar were observed at the water surface and in the water column 10 days after the spill. These were quite possibly from submerged oil droplets which had re-surfaced after an unknown period of enhanced dissolution of water soluble components. The surface oil was spongy in texture, although it was not undergoing water-in-oil emulsification. Even after 2 weeks of weathering, less than 5% water was found in the surface collected oil.

Relative increases in methyl phenanthrenes in the " " weathered oil and sub-surface flake samples suggested that enhanced dissolution of the lower aromatics may have been occurring, however, gravimetric measurements of the asphaltenes showed no significant changes from 5-10 August. The lack of any change in nC-17/pristane, nC-18/phytane ratios over a 2 month period suggested that microbial degradation of the oil was not occurring to a significant extent, and it was estimated that most of the residues eventually sank and reached the bottom of Melville Bay in less than 50 days.

Grose (1979) used data from this spill to validate a computer model which computes slick thickness of spilled oil as a function of the physical characteristics of the oil and weathering by sheen formation and evaporation (wind speed dependent). This model will be considered in more detail in the modeling section, however, it should be noted that the model was designed to account for 3 observed phenomena: the first was that the oil did not form a single pool but rather was composed of numerous patches of thick oil surrounded by thinner sheen; the second was that the thickness of the patches was a function of the bulk physical properties of the oil and local environmental conditions including wave height, water temperature and wind speed; and the third was the weathering of individual components were dependent on the physical/chemical properties of the components in the original oil. Losses of oil dispersions into the water column were ignored in the model because they were observed to be relatively small in the field and because of a lack of parameterizations for the pertinent process. Also, there were no data available on the probability of size distribution of the patches as a function of either sea state or spill rate, although Grose did suggest that the mean size of patches will get larger as the sea state decreases and as the spill rate increases. Thus, for the model he used an equal probability for all sizes of initial oil patch volume. The model did not include parameters for emulsification or incorporation of water which would change specific densities, viscosity and the total surface area and volume of the patches, however, as noted above, significant water-in-oil emulsion formation was not observed in the field. The best fit of the data to the computer predicted outcome occurred with a 0.01 m³ patch and a wind speed of 2 m/sec. The largest

discrepancies between predicted and observed behavior occurred in the size of the patches which were reported to be an order of magnitude less (0.018 m^2) in the field vs. the modeled area of 0.4 cm^2 .

Amoco Cadiz

On March 16, 1978 the supertanker Amoco Cadiz was grounded off the coast of North Brittany, France, and its entire 220,000 ton cargo of Arabian crude oil and Bunker C fuel was released to the environment. Mousse formation was noted almost immediately after release of oil from the vessel or even prior to release because of mixing from wave and tide action in the bottom of the ruptured tanks. The oil and freshly released mousse consisted of 39% saturated hydrocarbons, 34% aromatics, 24% polar materials and 3% residual (Calder and Boehm, 1981). Significant downward mixing of the oil and mousse into the water column was caused by turbulence in the nearshore waters, and concentrations of dispersed mousse ranging from 200 to 1,000 $\mu\text{g/liter}$ were observed near the entrance of Aber Wrac'h. Concentrations in excess of 500 $\mu\text{g/liter}$ were observed in much of the waters throughout the estuary (Calder and Boehm, 1981). Additional evidence of dispersed oil or mousse in the water column can be inferred from Wolfe et al. (1981) where gas chromatograms of aromatic hydrocarbon fractions isolated from transplanted mussel samples (suspended in cages in areas of high contamination) showed high levels of dibenzothiophene, alkyl-substituted dibenzothiophenes and 3 and 4 ring aromatics, including phenanthrene, anthracene, benzo-a-anthracene, and chrysene plus their alkyl-substituted homologs. Gas chromatographic profiles from the organisms closely resembled those of background mousse samples, and these data suggested that the mussels incorporated significant quantities of either particulate oil or particulate mousse, in that other studies have indicated that these higher molecular weight components were not present in true solution in the water column.

In reference mousse samples collected with a bucket from the immediate vicinity of the broken tanker, **nC-11** was the most abundant **n-alkane** although an homologous series from **nC-8** to **nC-30** was noted. The **pristane** to **phytane** ratio was near unity, and both **nC-17** and **nC-18** were more than twice as abundant as the nearest **isoprenoids**. Numerous **alkyl**-substituted aromatics ranging from **tetramethylbenzene** to methyl **phenanthrene** were identified as were a series of **alkyl-di benzothiophenes**. The most abundant aromatic compounds in the parent mousse were **naphthalenes**, methyl **naphthalenes**, **dimethylnaphthalenes**, **C3-naphthalenes**, **fluorene** and **phenanthrene**. In a sample believed to be approximately 8 hours old, the **normal alkane** composition was significantly altered by evaporative weathering, and molecules boiling below **nC-15** showed detectable loss relative to **n-tetracosane**. The **nC-17/pristane**, **nC-18/phytane** ratios were not significantly altered, however, suggesting that microbial processes had not been active up to this time (Calder and Boehm 1981). The aromatic components in this sample were also altered by evaporation and dissolution with significant removal of the **alkyl-benzenes** and **methylnaphthalenes** relative to **dimethylnaphthalenes**. **Phenanthrene** and **dibenzothiophene** were not significantly reduced in this sample relative to the reference mousse. In other samples which may have been in the water column longer, and in numerous samples of buried or sedimented oil, microbial activity was shown to be extremely significant. In the dispersed oil-in-water samples collected near the entrance of **Aber Wrach** a large reduction in **nC-17/pristane** and **nC-18/phytane** ratios and a significant relative enrichment of branched, **cyclic** and aromatic hydrocarbons between the **n-alkanes** indicated that biodegradation was occurring at a faster rate than evaporation or dissolution. Aminot (1981) found that the lack of oxygen was one of the most critical environmental limitations to water column biodegradation of Amoco Cadiz oil. He related nutrient water chemistry to levels of persistent Amoco Cadiz oil, and deficiencies of nitrogen, phosphorous and oxygen were correlated with the presence of oil in the water column providing indirect in situ evidence of oil biodegradation. Ward (1981) stated that once the oil was deposited in the sediments, oxygen limitation again played a significant role in that both **n-alkanes** and aromatic compounds were found to have long term persistence in reducing sediments.

Following the wreck and initial dispersion of **oil** from the Amoco Cadiz (March 16-March 30, 1978) Hayes et al. (1979) undertook field studies to attempt a mass balance estimate of the total oil on the **beach** from March 19 to April 2, 1978 and again during the period of April 20 to April 28, 1978. During the first two weeks of the spill a total of 72 km of coast **was** heavily oiled. Using an estimate of 887 tons of **oil/km** of shoreline, Hayes et al. (1979) estimated that a total of 64,000 metric tons of oil were deposited along the coastal zone. This was approximately 1/3 of the total amount of oil lost from the Amoco Cadiz. The remaining 2/3 were believed to be lost by evaporative processes or represented by **oil** masses remaining on the water surface, sinking **to** the bottom and/or mixing into **the** water column. One month later a total of 10,000 metric tons of **oil** could be accounted for on the beaches, and this represented an 84% decrease in that found along the shore in the first visit. More coastline was covered at this time, however, due to wind shifts on April 2, 1978 which caused the oiling of previously clean coastal areas south of the wreck site. One month after the spill, the impacted area had increased to 213 km of lightly oiled beaches and 107 km of heavily oiled beaches. Hayes et al. (1979) reported that the **geomorphology** in the coastal zone was very significant in the distribution of the **oil** and mousse. In many areas oil/mousse **mixtures** were found to settle in **pools** around boulders, bar troughs, and marsh pools; intertidal rocks, joints and crevices were **also** covered with oil. As in other spills, the exposed rocky coastlines were cleaned more rapidly than sheltered coasts. Tidal flats and estuary marsh systems were found to be extremely vulnerable. Because of the wide variety of sediment headland and marsh types in the area affected by Amoco Cadiz oil, the authors generated an Oil Vulnerability Index correlating shoreline type with degree of oiling and estimated long-term impact **and** fate.

Numerous protracted studies of a variety of these sites have been completed in the years following **the spill**, and the following paragraphs **describe only** the most salient features with regard to the fate of stranded mousse in different intertidal regimes. In general, the degree of **oiling** and persistence of stranded oil can be directly correlated with intertidal energy and substrate type.

Calder and Boehm (1981) reported that the mousse which was deposited on sandy tidal flats at Aber Wrac'h contained a lower percentage of saturated **aliphatic** hydrocarbons compared to the aromatic components and that this presumably reflected microbial degradation of the saturated materials. During the first four months following the spill, both saturated and aromatic hydrocarbons were rapidly lost in surface sediments, however, after approximately 5 months the concentrations remained relatively constant at about 5% of their initial values for the next 8 months. During the 7 month period following the **spill**, the unresolved complex mixture observed in gas **chromatographic** profiles of sediment samples decreased from 410 ppm to 80 ppm, and the **n-alkanes** in the **nC-10 to nC-35** range decreased from 35 ppm to 1.5 ppm. During the first month, the **pristane** plus **phytane** concentration dropped from 6.5 to 3 ppm (factor of 2) and the **nC-17** plus **nC-18** concentrations dropped from 1.8 to 0.3 ppm (factor of 6). This greater loss of the straight chain **aliphatics** compared to the **isoprenoid** compounds clearly demonstrated the importance of bacterial activity in the reasonably well oxygenated sediments during the first month. After 7 months the **isoprenoid** family was dominant in the **chromatograms** of the sediment extracts, and only a few **n-alkanes** were detected across the entire boiling point range of **nC-10 to nC-34**. **Gravimetric** analyses of **aromatic** fractions showed similar losses with total aromatics dropping from 630 ppm in **April** to 90 ppm in **late** October with the sum of the identified resolved components dropping from 29 ppm to 2 ppm over the same time frame. Below 20 cm depth in the sediments, **aliphatic** and aromatic hydrocarbons represented materials of only biological origin. In March 1979, 1 year after the **spill**, **alkyl-substituted phenanthrenes** and dibenzothiophenes were still easily detectable in the sediments above 20 cm.

Boehm et al. (1981) studied compositional changes in beached or **sedimented** oil/mousse at a variety of coastal environments including rocky shores, sand flats, coastal embayments, tidal mud flats and salt marshes. The authors found that much of the oil appeared to be relatively long-lived in the **sediments**, although some fractions were rapidly weathered and removed. The most resistant compounds to chemical and biological weathering were **alkylated**

organo-sulfur compounds (dibenzothiophenes), alkylated phenanthrenes and polycyclic aliphatics (e.g., pentacyclic triterpanes and hopanes). It should be noted that the alkylated phenanthrenes and dibenzothiophenes did decrease on an absolute basis, although they were the more predominant compounds relative to the other aromatics as weathering occurred. Boehm et al. (1981) also detected a number of pyrolytic polynuclear aromatic hydrocarbons (PNAs) in the sediment samples collected from the spill area and control sites. These compounds included: fluoranthenes, pyrene, benzofluoranthenes, benzopyrenes and perylene at ppm levels. The concentrations of these PNA's were fairly uniform with the depth of the core, and these materials were attributed to background hydrocarbons presumably from combustion sources.

At Portsall (Station AMC-4) the surface sediment was comprised primarily of coarse sand, and after an initial heavy mousse coating, absolute concentrations decreased rapidly although the n-alkane to isoprenoid ratio remained relatively high until December 1978. The December 1978 aromatic data indicated that the remaining mousse/sediment mixture was quite abundant in alkylated 2 and 3 ring aromatics and dibenzothiophenes. Weathering reactions then appeared to increase between December 1978 and March 1979, presumably as a result of increased mixing and resuspension of the sediments due to winter storm activities. At El Grande salt marsh (station AMC-18) the degradation of deposited mousse appeared to be slower. At St. Michael-En-Greve (station AMC-19), a massive kill of benthic fauna was observed in the sand flat due to heavy oiling. Sediment samples collected in December 1978 and March 1979 showed aliphatic and aromatic profiles indicative of highly weathered oil. Several offshore stations were also studied adjacent to the Bay of Morlaix (stations AC-42, 138, 371 and 453). In April 1978 immediately after the spill, the sediments from these areas showed only low quantities of Amoco Cadiz oil: a mixture of chronic and background hydrocarbons and terrigenous runoff material, and perhaps small amounts of Amoco Cadiz oil were suggested by GC traces. Weathered Amoco Cadiz oil dominated the aliphatic and aromatic hydrocarbon assemblages in July 1978 presumably due to extended offshore transport. By November 1978 overall concentrations were significantly reduced and

the gas **chromatographic** profiles illustrated that the oil had approached a final weathering stage. Almost **all** of the resolved features other than hopanes were removed and **not** discernible above a large **bimodal** UCM. Amoco Cadiz oil was weathered and removed most rapidly from the sand beach at St. **Michael-En-Greve** and offshore sediments adjacent to the Bay of **Morlaix**. The composition of the oil changed rapidly, but remained quantitatively abundant in intertidal mud **flats** of Aber **Wrac'h** and at Isle St. **Grande salt** march where the oil was found to degrade slower in the fine substrates. In general, buried oil appeared to be preserved over the 15 month period of the study, and deeper buried **oils** apparently escaped significant weathering processes presumably due to **anoxic** conditions at depth in the sediments. In general, it was found that nitrogen, sulfur and oxygen, (**NSO** content) increased in the residues as hydrocarbon concentrations dropped, however the degree of **oiling** was important in this context, because at the more heavily oiled sites weathering appeared to be slower at both high and low energy shorelines. Thus, **Boehm et al.** (1981) concluded that the most important factors responsible for the observed relative weathering patterns were: extent of oiling ≈ shoreline energy > sedimentation oxidation state >> distance from the wreck site.

Vandermeulen et al. (1981) examined the high energy rocky shoreline on **Ti Saozin** Island and a lower energy tidal mud flat at Aber **Benoit** for mousse content in April 1978, June 1978 and January 1979. Self-cleaning of the mousse at the high energy shoreline of **Ti Saozin** was nearly 90% complete within 9 months after the **spill**. In April 1978, the shoreline was uniformly **oiled** and mousse was deposited along the upper beach at several stations. In June 1978, dried mousse completely covered one station while patches were found at other locations **at** an approximately **1 m** lower tidal **level**. Other areas appeared to be visually **clean** of **oil** although sheen was noted in some of the tide pools. By January 1979, only traces of mousse mixed with beached debris were found at one station while some tar **could** be seen in rocks, cracks and under boulders at another. The rest of the slope appeared to be clean of the **oil**. In analyzing the tide pool samples from this location, however, only the water soluble components of the stranded oil were examined. Thus, the

presence of highly insoluble **asphaltenes** and other residuals were not studied. They may have been present under rocks, sediments or bound-up in interstitial debris. **Vandermeulen et al. (1981)** did note that the rapid cleaning of the foreshore area of the **intertidal** zone (**with traces** of some oil remaining in the high tide zone) at **Ti Saozin** was faster than for similar shorelines in **Chedabucto** Bay after the Arrow spill. In the latter case, high energy shorelines were cleaned after approximately one year and **Vandermeulen et al. (1981)** stated that the differences between the two spill situations might lie in different **oil** viscosities and in a difference in air and water temperatures at the time of the spills (February vs. April). **The** self cleaning time for **Ti Saozin** was estimated about 2 to 4 **times** faster than for similar shorelines in **Chedabucto** Bay.

In the lower energy tidal mud flats at **Aber Benoit** large amounts of petroleum hydrocarbons were observed to remain in the sediments of the inshore mud flats and along the vegetable fringe **at** the edge of the river **Aber Benoit** 9 months after the spill. Synchronous excitation emission fluorescence scanning spectroscopy (SEES) spectra of the parent mousse and stranded tar collected in January 1979 showed that a number of 2, 3, 4 and 5 ring and larger aromatic compounds persisted at **Aber Benoit** where the tidal range was 9 m during high spring tides. Thus, in contrast to the **Ti Saozin** sites, **the** sediments at **Aber Benoit** remained heavily oiled as of 1979 with hydrocarbons from the Amoco Cadiz present at levels **well** above those found in control sediments. In the lower **energy** regimes it appears that the long term persistence of this oil may extend into 10's of years.

IXTOC I Blowout, Bay of Campeche, Gulf of Mexico

Background

On June 3, 1979 the **Petroleos Mexicanos (PEMEX)** exploratory well, **IXTOC-I**, blew out in approximately 60 m of water at a site about 80 km northwest of **Ciudad del Carmen** in the Bay of **Campeche, Gulf of Mexico**. **Within 1**

week the blowout had discharged more oil than the largest oil spill in U.S. history, and by late July the IXTOC-I had become the largest oil spill in history exceeding the 230,000 tons of oil that was lost when the Amoco Cadiz went aground off Brittany, France in 1978. The IXTOC-I blowout continued losing oil until successful drilling of a relief well and eventual capping on March 23, 1980, and at that time estimates of oil spilled over the 10 months were in excess of 476,000 tons (Gundlach et al., 1981).

Extensive areas of the Gulf of Mexico and its bordering beaches were eventually covered by oil released from the blowout. After the first 3 days, slicks 93 km long and several km wide were noted, and by June 12 the main slick measured 180 km long and up to 80 km wide and was reported to be moving in a westerly direction at a speed of about 0.5 knots. In the weeks and months after June, the spilled oil and mousse moved primarily in an east to west direction, and then turned north parallel to the coast at Veracruz. Satellite photographs of the oil slicks taken in mid-June showed 10 large patches of oil covering a total area of more than 30,000 km². The largest patch appeared triangular in shape and covered approximately 1800 km² and was surrounded by long streamers and smaller patches. Although the current carried most of the oil to the west and northwest small patches of oil released from the main body of the slick reached Laguna de Terminos about 80 km south of the well. By July 3 slicks were observed 16 km off Veracruz, and the oil in this area was reported to be a thick mousse similar to that observed following the Amoco Cadiz incident. By July 6-7, much of the oil had been entrained in northern coastal currents and it was estimated that the oil sheen would reach U.S. waters off Brownsville by July 23. By July 13, heavy concentrations of oil were detected off Veracruz and the main front of the leading slick was sited about 195 km southeast of Tampico. Patches of mousse and sheen were sited as far north as 22°58' North on July 23, 1979, and later overflights revealed that 8 patches of mousse and sheen had split off the main body of the oil at a point about 50 km off Tampico. The largest patch measured 800 m wide and 8-16 km long. Five 25 m diameter patches and 2 smaller aggregations of mousse were also reported heading north. NOAA trajectory

models indicated that much of the spilled oil reaching the branching point off of **Tampico** would turn south and likely impact Mexican coastlines. On July 20, oil was washed ashore at **Coatzacoalcos**, and by July 24 oil was washing ashore north of **Tampico**, on the beach at **Cabo Rojo** near **Tuxpan** de Rodriguez, and at **Veracruz**. By July 29, sheens and mousse were located about 180 km south of Brownsville, Texas, and large patches were observed off of **Tampico** to a point 230 km south of Brownsville. These slicks/patches were reported to be moving north at a rate of about 0.5 knots, and the mousse aggregates were measured to be 2-3 m in diameter and several cm thick forming a broken line more than 16 km long.

IXTOC-I mousse was first observed in the U.S. waters on August 6 with patches floating about 70 km off of Brownsville. By this time, oil had already washed onto Mexican coast as far north as 25°48' about 13 km south of the Rio **Grande** river. Much of this oil then stalled off the U.S. coast, although tar balls and patches of mousse had washed onto South Padre Island beaches north of Port Mansfield, and pancakes and sheen had been sited less than 2 km from Port Mansfield. NOAA divers discovered that subsurface oil in concentrations up to 3600 particles per cubic meter at depths of up to 12 meters could be observed outside **Laguna Madre**. By August 13 and 14 large concentrations of sheen were observed about 48 km offshore between Port Mansfield and Brownsville, and ribbons of mousse up to 16 km long and 85 m wide were observed 32 km offshore. By August 13 patches of mousse and sheen at varying concentrations were observed up to 530 km out to sea between **Tampico** and **Tuxpan** de Rodriguez Cane, and an 11 km stretch of heavy mousse concentrations were reported near **Tampico**. Dense oil coatings were reported on the beaches of **Tuxpan** de Rodriguez Cane, near **Veracruz** and at **Laguna Madre**. Heavy concentrations of mousse washed ashore along 80 km of Texas coast with the return of southeasterly winds on August 18, 1979, and NOAA oil spill trajectory models indicated that if the well were successfully capped by October 15, the oil would wash ashore according to the following: 3% between Brownsville and **Matagorda** Bay, Texas; 21% around **Laguna Madre**; 32% around **Tampico**, 40% north of **Veracruz** and 4% around **Campeche**, Mexico. If the well

were not capped until **early** spring **1980**, as actually occurred, the NOAA model predicted that the following distribution would be obtained: **1%** between Brownsville and **Matagorda** Bay, Texas; **10%** in **Laguna Madre** area; **24%** in the **Tampico** area; **43%** north of **Veracruz** and **22%** in the **Campeche** area.

Oil finally stopped washing **onto** Texas shores in mid-September when the seasonal change of winds and currents offshore began reversing the northward flow. Estimates in late August by Research Planning Institute staff suggested that when the oiling of the beaches had reached a maximum, up to 3,900 tons of oil covered Padre Island and Port **Aransas**, Texas, beaches (**Gundlach et al.**, 1981). Higher levels were reported by Roy Hahn of TAMU and John Robinson of NOAA who estimated that a total of 10,000 tons of oil had washed in total onto Texas shores (**OSIR**, 1980). Researchers and cleanup workers noted that in September IXTOC mousse had collected in the sand to depths of up to 30 cm along the beaches of Padre Island.

Significant **quantities** of IXTOC mousse and oil impacted many areas of **the** Mexican coastline; however, details on the extent of oiling and cleanup operations are not available. It was stated (Oil Spill Intelligence Report, 1980) that approximately 2100 gallons of oil was recovered from **Tuxpan** de Rodriguez Cane, and that at **Laguna de Terminos, Ciudad del Carmen**, the oil was unable to cross the natural barrier **at** the interface between the saltwater and fresh water of **the** lagoon. Thus at that location only minor quantities of oil entered the sensitive biological habitat during the first few months of the spill. Increased rains and heavy river flow extended the natural offshore barrier and helped protect the **lagoon** and shrimp nurseries **within** it.

In late September with the change in currents at the well-head, oil slicks in the Bay of **Campeche** were noted along the eastern coast of Mexico, and these were moving south at about 2.7 knots. Thus, the oil was flowing southeast during the third week of **September**, but by October **1**, the flow had shifted and the oil was moving primarily to "the northeast. In October large amounts of oil **were** sited between the **IXTOC-I** well and the northwestern tip of

the Yucatan Peninsula, and scattered sheen was noted up to 560 km northeast of the well. With this current shift, heavy coverings of IXTOC mousse (between 15-30 cm deep) were reported in November 1979, at several locations on the western shore of the Yucatan Peninsula between **Ciudad del Carmen** and **Progreso**, Mexico.

In response to this spill, the United States EPA and the National Oceanic and Atmospheric Administration, among others, launched a number of programs to study the weathering and fate of the released oil as it was moved by Gulf stream and localized currents throughout the Gulf of Mexico. Perhaps **the** most extensive study of weathering effects on IXTOC crude at sea occurred during the NOAA ship Researcher and GW Pierce cruises which took place at the **wellhead** and along the eastern coast of Mexico and Texas during September 1979 (Preliminary results from the September 1979 Researcher/Pierce IXTOC-I cruise, Symposium Proceedings - 1980).

Although there was much concern and comment about IXTOC mousse **dis-tribution** throughout the Gulf of Mexico and its eventual impact on U.S. and Mexican shores, the Researcher/Pierce field studies in September demonstrated that contrary to earlier reports (Ross et al., 1980), IXTOC mousse was not forming immediately after release of the oil at the **wellhead**, but was instead the product of extensive evaporation, dissolution and presumably **photochemical** weathering. According to a Canadian environmental protection service study in June (Ross et al., 1980), the IXTOC-I oil at the **well** site was reported to immediately form a viscous water-in-oil emulsion. Based on preliminary chemical analyses, the emulsion at the water surface was found to contain about 70% water and to have a viscosity of 350 CP and a specific gravity of 0.99. It was a very **stable** water-in-oil emulsion containing very fine droplets of water coated with thin viscous **layers** of oil; however, it was noted to exist as a 1-3 mm slick on the water surface as opposed to the thicker more **weath-ered** patches observed in September. Analyses of the oil collected in June indicated that almost all of the lighter fractions (boiling less than **nC-10**) were missing; having been burned, evaporated or dissolved before water-in-oil

mousse formation. One possible explanation for the differences noted in the two cruises is that the composition of the oil may have changed between the June and September studies. Specifically, as the upper levels of the IXTOC-I oil reservoir were depleted with time, the later-released oil would likely have migrated through more sediments within the formation, and as a result, might be expected to have changed chemically. Another hypothesis was that with decreased flow rates in August (as claimed by PEMEX) the accompanying decrease in mixing energy in the water column might have affected mousse formation. As will be shown below, microbial processes were not found to play a significant role in the formation of mousse from the IXTOC crude.

The original Researcher/Pierce cruise plan called for collecting oil and mousse samples and studying the weathering fate and chemical alterations along the semi-continuous slick and patches of oil and mousse which had been reported from the wellhead to the western portions of the Gulf of Mexico. Immediately before the research vessels began any extensive sampling near the well head, however, Hurricane Henri passed to the north of the Bay of Campeche and generated winds in excess of 24 knots and 6 m seas at the vicinity of the blowout. The storm then moved in an erratic course across the southwestern Gulf of Mexico and caused much of the semi-continuous slick which had been observed earlier to the west and northwest to be dispersed into the water column. After the hurricane, large patches of oil or mousse were not in general observed during helicopter overflights beyond 40-50 km from the well in any direction for the remaining 2 weeks of the cruise. Thus, the cruise plan had to be changed, and more intensive sampling of the oil in the immediate vicinity of the well was undertaken. Detailed studies of evaporation/dissolution weathering, mousse formation and subsurface oil/particulate movement were completed. It cannot be stressed enough, however, that much of the observed oil weathering behavior at the well-head was significantly affected by the intense storm activity. Extensive resuspension of the bottom sediments in the Bay of Campeche occurred, and suspended particulate loads were estimated to be as high as 100 $\mu\text{g}/\text{l}$, causing the waters to exhibit a light turquoise color as opposed to the clear open-ocean blue characteristic of much of

the **Gulf** of Mexico. This highly turbid water **was** observed from helicopter overflights to extend along much of the coastline **of** the Bay of **Campeche** area, and **the** distinct turbid/clear-water boundary appeared to be associated with oceanic fronts. At the time of the Researcher/Pierce study, **the** area immediately around the **IXTOC-I wellhead** was within the turbid, light turquoise aquamarine waters. In related mineralogy studies, Nelson (1980) reported that no mineral species occurred in the suspended particulate material (**SPM**) in the water column that did not also occur in the sediment directly below. Thus, he concluded that although significant amounts of SPM were introduced from heavy river flow from the intense rainfall associated with the storms, most of the water turbidity was the result of resuspended sediments in the vicinity of the well head. Six **terrigenous** and four carbonate minerals were identified in the SPM. The **terrigenous** suite contained quartz, **plagic** feldspar and the clay minerals chlorite, **smectite (montmorillonite)**, **illite** and **kaolinite** while the carbonate suite contained **aragonite**, calcite, **dolomite** and magnesium calcite. Many of these minerals have been shown to actively adsorb particulate and dissolved hydrocarbons from the water column (for a review see Jordan and Payne, 1980), and their presence was believed to significantly affect **oil** behavior.

Observations at the **Wellhead**

Upon arrival **at** the **wellhead** during the Researcher/Pierce cruise in September 1979, the **slick** was observed to be flowing in a northeasterly direction, 40-50 nautical miles from the **wellhead** at approximately 45-55° true. At times the plume took sharp meanders which were generally to the south, however, the direction of the oil flow on the surface was not directly correlated to wind speed or direction. Because the **oil** was being released at depth, water column currents **in** the vicinity of the well controlled the direction of oil flow, and on several occasions it was noted that the wind direction was often 180° to the direction of the plume.

Immediately over the well head, a large fire, about 50 m in diameter and 7 meters in height, was burning on the water surface. The fire was essentially yellowish-orange and generally smoke free with occasional discharges of a light gray smoke. From these observations, it appeared that the fire was consuming primarily lower molecular weight gases and liquid hydrocarbons. Much of the oil that was released from the wellhead was not exposed to the fire as it was advected or removed from the source by sub-surface currents. There appeared to be a continuous upwelling of water within and surrounding the fire diameter, and within 20 m of the burning zone smaller random surface flares appeared and disappeared periodically. These were generally extinguished by the surrounding turbulent surface waters. Tan to rust-colored oil could be observed on the surface ringing the fire and extending out about 150 m on each side of the flame. This oil in addition to the rising droplets released from the well then formed a semi-continuous slick which was observed progressing towards the northeast. The oil observed emanating from the wellhead and drifting to the northeast was definitely not emulsified into a stable mousse, although it was a light brown color and probably contained some water as reported earlier by Ross et al. (1980). Immediate formation of a stable water-in-oil emulsion or mousse was not observed. At distances of 3-50 nautical miles from the wellhead, large patches of stable water-in-oil emulsions were observed, and these had varying sizes and shapes. Because of reversing current conditions, however, it was often difficult to always tell freshly generated mousse from more weathered materials which had presumably been formed at an earlier period and then re-entrained into the slick by eddy currents near the wellhead.

In the vicinity near the wellhead the physical state of the oil could best be described in terms of five distinct zones within and without the plume. The relative size and position of the zones appeared to be a function of many factors including sunlight intensity, wind stress and flow rate (Atwood et al., 1980).

Zone 1 was characterized by the continuous light brown colored emulsion of water-in-oil on the surface, and this material existed in the immediate vicinity of the flames and **extended** for no more than a few hundred meters down plume. This zone represented 100% coverage of the water surface with an oil film ranging from **1** to 4 mm thick.

Zone 2 was characterized by a 30-50% coverage of the sea surface by a **light** brown water-in-oil emulsion **oriented streaks**. This area **started** a few hundred-meters down plume from the burn and extended out to a maximum of 1 to 2 nautical miles depending on wind stress. **At** times, however, this **phenomenon** was virtually absent and appeared to depend very critically on the environmental conditions.

Zone 3 **was** characterized by a 20-50% coverage of the sea surface by **light** brown water-in-oil emulsions oriented in **Langmuir** "streaks" parallel to the wind direction. These streaks varied **in** width from a **few** centimeters to several meters, and the length varied from 1 to 10's of meters. **These** dimensions depended on wind stress, and in general (although not always) **the** streaks were surrounded by a light to heavy sheen of oil. This zone also extended from as close as a few hundred meters from the flames to several nautical miles down plume.

Zone 4 was characterized by a darkening of the light brown **water-in-oil** mixture until the streaks were black. This was assumed to result from oxidation of the oil, and the rate appeared to be dependent on sunlight intensity. A slight color gradation was noted, with many **of** these streaks blackened in **the** center and light brown at the outer edges. At times these "streaks" coalesced into long lines of blackened oil that extended for several kilometers. Along the edges of these "**streaks,**" small balls of chocolate mousse-like emulsion were observed to break off. As will be discussed later, these balls readily coalesced into larger masses upon contact, and at other times the wind rolled portions of the slick up onto itself, and this was observed as a mechanism for mousse agglomeration. **In** some instances these

mousse balls reached grapefruit to basketball size and/or coalesced into huge "rafts" of mousse up to 50 or **60** meters in diameter. Several rafts of this type were found to be up to one meter **thick**. This zone began 5 to **15** nautical miles from the well head and extended out **to** about 20 nautical miles. Detailed observations of formation of this type of material on a micro-scale were made during a 26 mile down plume transect on the **GW Pierce**, and these observations will be discussed in detail later.

Zone 5 was characterized by **an** extensive light to heavy sheen of oil that covered >50% of the surface. Usually this sheen was in the form of **Langmuir lines**, and this zone overlapped Zones 2, 3 and 4 and extended out to the furthest extremity of the plume.

As noted in the introduction, these descriptions may have been operative only for the period of the **Researcher/Pierce** cruise, and they may have been influenced by the intense storm activity from Hurricane **Henri**. At several stations surrounding the **wellhead** there was no distinct boundary between these various zones as they often tended to interweave at the transitions.

Cantalope sized patches of mousse from several stations appeared to have had been stained with fresh oil. Sheen was observed coming from some of the mousse patches but not others. To a limited degree, the presence or absence of sheen emanating from the external surface of the mousse (or the interior portions, if the samples were broken and **re-introduced** into oil-free water) appeared to correlate with stickiness, and the lack of this sheen or "stickiness" was taken as evidence that such samples may have been more weathered before formation. The sizes and dimensions of the mousse patches varied, ranging from baseball sized balls to ellipsoidal 20-30 cm diameter patches ranging from 1/8 to 1/4 inch thick. Elsewhere, solid 1-2 m^2 patches were observed with thicknesses ranging from 2-3 inches. When 20-30 m diameter by thick "rafts" of mousse were encountered, **yellow** discolored water was often noted to float on top of the mousse (particularly in calm sea conditions). Most of the mousse balls or pancakes were a **light** chocolate brown in color and

had a cerebral (brain-like or "popcorn ball") appearance. Many of these appeared to contain large (several cm) pockets of water. Several such mousse **balls** were observed to **melt** and separate into water and oil when they were removed from the water column and exposed to sunlight. With this occurrence the color changed from a light chocolate brown to a dark brown/black or **mahogany**. Attempts to separate such mixtures by **centrifugation** and heating onboard the Researcher were unsuccessful. At other stations, mousse was observed to be associated with large quantities of marsh detritus and sugar cane stock, and it was hypothesized that these materials provided sites of nucleation upon which additional aggregation of mousse could occur.

Subsurface Transport and Weathering of IXTOC Oil

Because of the sub-surface release of the oil at 60 m, significant amounts of the particulate oil droplets were transported horizontally for 20-30 km distances before the oil surfaced and was exposed to evaporative loss. **Acoustic** profiling was completed by Walter and **Proni** (1980) and by **Macaulay et al.** (1980), and subsurface water and oil-in-water dispersions immediately beneath **the surface slick** were collected and studied by **Boehm** and **Fiest** (1980). Concentrations of particulate and/or colloidal petroleum in the top 20 m of the water column within 25 km of the **wellhead**, (beneath the surface slick), exceeded the maximum values observed in the other spills considered (**Ekofisk** Bravo blowout, 300)g/l, **Grahl-Nielsen**, 1978; **Amoco Cadiz** spill, 350)g/l, **Calder et al.** 1978; and the Argo Merchant, 450)g/l, Gross and Matson, 1977). The total amount of petroleum estimated in the top 20 m of water within 25 km of the well at the time of the sampling cruise was equal to 20,000 gallons or **70 x 10⁶** grams. This was estimated to be approximately **1%** of that observed on the surface. Therefore, **Boehm** and **Fiest** (1980a) hypothesized that for this type of sub-surface blowout, about 1% of the higher molecular weight hydrocarbons would be present in the water column for considerable distance from the **wellhead**. Of this material, about 90% was believed to be particulate and about 10% in the truly dissolved state.

Before the passage of Hurricane **Henri**, a vertically stratified water column existed, and the transport of much of this dispersed oil appeared to be associated with density gradients in the water column. **Boehm** and **Fiest** reported subsurface particulate material **at** distances up to 25-30 nautical miles from the **wellhead**, and Payne et al. (1980a) measured dissolved and particulate bound hydrocarbon loads above but not **below** significant density gradients **at** distances up to 20 nautical miles from the **wellhead**. After the passage of Hurricane **Henri**, the water **column** appeared to be nearly homogeneous from the surface to the bottom in the vicinity of the **wellhead**, and at that time higher levels of particulate bound hydrocarbons were noted in samples collected 5 m above the bottom (Payne et al., 1980a). It was not possible, however, to differentiate between the possible settling out of oil scavenged from the entire water **column** by the heavy particulate load vs. nearbottom re settling of resuspended **bottom** sediments which had **been** previously oiled. Following the storm it was noted that concentrations of dispersed or SPM **bound** oil were generally 1-2 orders of magnitude greater than concentrations of oil in the truly dissolved state (Payne et al., 1980a). The particulate phase contained primarily the higher **molecular** weight aromatics while the dissolved phases showed evidence of preferential dissolution of the lower molecular weight aromatics and **alkyl-substituted naphthalenes**. **Whole** water samples beneath the slick showed the presence of both low and high molecular weight compounds (**Boehm** and **Fiest**, 1980a).

By the time much of the subsurface oil droplets reached the surface significant weathering and removal of lower molecular weight components had, already occurred. Thus, many aromatics were lost from dissolution rather than evaporation because of the sub-surface release. Payne et al. (1980b) measured quantities (up to 100 $\mu\text{g/l}$) of benzene, **toluene**, **ortho-**, **meta-**, and **para-xylenes** and other selected **aliphatic** and aromatic compounds in the water column immediately beneath and adjacent to the surface slick, and air samples obtained on TENAX " traps immediately above the **slick** illustrated that dissolution rather than evaporation accounted for removal of many of the more water soluble components during transport through the water column. Significantly,

only traces of benzene were observed in the air (particularly in comparison with **toluene**, xylene and **aliphatic** and **cyclo-alkane compounds** with similar molecular weights and vapor pressures, but **lower water solubilities**) at distances as close as 3/4 of a mile from the **wellhead**. Using selected ion monitoring **GC/MS**, no positive identifications of benzene could be observed in the air (level of detection 1 ppb) above the **slick** even though **pre-field** studies had demonstrated the applicability of the technique for determining benzene and **alkyl-substituted** lower molecular weight aromatic and **aliphatic** compounds in a certified **Matheson** gas standard of benzene in air and in air samples collected over several test spills of gasoline and oil. Brooks et al. (1980) **also** measured significant quantities of benzene and other lower molecular weight aromatics in the water column. Their analyses also demonstrated that traces of these components were present in the oil slick as close as 1/2 mile from the **wellhead**, although they were at significantly reduced quantities compared to the higher molecular weight compounds above **nC-10**. In that these lower molecular weight aromatics generally constitute a fairly significant portion of most crude **oils**, their rapid removal during transport from the bottom to the surface was noted. Continued evaporative processes then dominated, such that by the time the surface oil had traveled several miles from the **slick**, (to where significant mousse formation was noted), most compounds with vapor pressures less than that of **nC-11** were removed (Payne et al., 1980b; Brooks et al., 1980).

Thus, while very high concentrations of oil were measured in the water column in the immediate vicinity of the **wellhead** 10,600 $\mu\text{g}/\text{l}$ within several hundred meters of **the** blowout to (5 $\mu\text{g}/\text{l}$ at a distance of 80 km) this oil was generally in the form of a sub-surface plume of oil droplets suspended in the top **20 m** of the water column (**Fiest and Boehm, 1980**). Only the more water soluble mono-cyclic aromatics appeared to be in the form of a true solution in this region, and this was attributed to enhanced dissolution from the high surface to volume ratio of sub-surface oil droplets.

At short (\leq 10 nautical mile) distances away from the **wellhead** and observed surface plume, water **column** concentrations were observed to be very low, and they approached those generally observed in more pristine environments (Payne et al., 1980a; Payne et al., 1978). As noted above, significant quantities of the oil in these outer stations were associated with suspended particulate material, and it was hypothesized that the high concentrations of **SPM** in the water column acted to scavenge the remaining dispersed and **semi-soluble** components from the water column thus, eventually leading to their removal via sedimentation processes (Payne et al., 1980a). Interestingly, significant quantities of **IxTOC** oil were not observed in sediment samples obtained near the **wellhead**, and this led **Boehm et al. (1980b)** to conclude that only 1 to perhaps 3% of the spilled oil **would** be found in the sediments. These observations may be confounded however, by the fact that the sediment samples were obtained after the passage of Hurricane **Henri** such that much of the recently deposited sediment load was resuspended in the water **column** and not amenable to collection. Secondly, **all** of the sediment samples were obtained with a Smith-McIntyre grab sampler, and with such a device the surface 1-2 cm can be disturbed and **lost** during the sampling operations (Callahan and **Soutar**, 1976). If either of these factors were in operation, then artificially low values of hydrocarbons **would** be measured in the sediments surrounding the well head.

Observations of Micro-Scale Mousse Formation

With regard to mousse formation, a 26-mile **downplume** transect was occupied on the vessel G. W. Pierce and continuous time-series observations of the surface oil behavior, the loss of volatile compounds due to evaporation and the eventual breakup of the continuous oil **slick** into 0.5 - 1 cm size flakes or droplets were made. During this transect, no significant **stable** mousse formation was observed up to a distance of 12-18 km from the well head. The estimated age **of** the oil droplets **or flakes** at this point would be anywhere from 13-19 hours. At that distance (and time), an interesting agglomeration phenomena of these small (snowflake to **cornflake** sized) heavily weathered

oil flakes was noted in a narrow 1 m band along the leeward side of the vessel. With the main engines off for a 2-3 hour period on the evening of 19 September 1979, the G. W. Pierce oriented itself perpendicular to the wind, and the combined effects of small waves from the rolling vessel and the wind (5-10 knots) which swirled over the lee side as an eddy current, caused the oil flakes to concentrate as a 1 m wide band approximately 1-2 meters from the hull. This band was observed along the entire length of the ship, and there was no such accumulation of flakes or tar lumps along the windward hull. As these well weathered flakes were agitated by the waves from the gentle rolling of the ship, they repeatedly contacted one another, and a number of the smaller flakes were noted to aggregate into larger balls. Considerable silver sheen was also present in a concentrated band, although it appeared to spread further from the hull than did the flakes and the tar/mousse balls. Internal markers were added to the flakes in the form of chips of styrofoam or pieces of paper to ensure that time series observations of these flakes would not be compounded by drifting into different oil/particulate mixtures. These markers remained with the oil droplets for 10-25 minutes before sinking and did not move more than 20-30 feet aft during observations. With time (45 minutes), the corn flake sized droplets consolidated into penny sized balls.

To determine if continued gentle agitation of these flakes would result in agglomeration of larger tar/mousse balls, a bucket cast of these flakes and tar balls was obtained. One golf ball sized mousse ball and 10-15 snowflake to cornflake sized pieces (3-12 mm) were isolated. The ball and flakes were left on the water surface in the bucket, and the side of the bucket was tapped lightly setting up a number of small (1-2 cm) standing waves. After 5 minutes, the smaller pieces began to aggregate together when they bumped, and most of them eventually adhered to the larger piece. At 5-7 minutes, there was only one large mousse ball and 2 semi-large (quarter-sized) flakes. The rest of the flakes had been observed to stick to the ball, and as it grew, approximately 50% in size with a large irregular shape, it was obvious that a similar mechanism could lead to the cerebral-like appearance of tar balls and pancakes observed at various locations around the wellhead.

That **is**, as one layer of flake adheres to the next, a popcorn ball type **matrix** with significant water entrapment is generated. Then with continued wave agitation this agglomerate **would** be compressed into the irregular shapes noted during the cruise. Thus, this formation mechanism could be used to explain the cerebral appearance of the **cantelope** size lumps located near the **wellhead**. After standing in the still water in the bucket for approximately 30 minutes, the golf **ball** sized tar ball and the two remaining flakes eventually formed one body. This was later broken up into two pieces which again came together with time. Chemical characterization **of** these flakes **later** showed the **composition** of this material to be identical to that obtained from several of the larger mousse patches and from a large beached mousse **sample** obtained at **Laguna Madre** (Payne et al., 1980a; Overton et al., 1980b).

Thus, one hypothesis for mousse formation in the **IxTOC** spill, **would** be that the breakdown of the continuous oil slick proceeds through the dissolution and evaporation of lower molecular weight components leading to a thin semi-continuous **oil film**. **Photochemical** oxidation and continued evaporation then eventually caused this slick to break up into streamers or partially submerged droplets or **flakes**. Sheen leads to the removal of many of the lower molecular weight materials and enhances dissolution and evaporation, and with this, the volatile and lower molecular weight aromatics are gradually removed. The residual surface droplets, which resembled corn flakes or snowflakes in the water column, no longer had a runny consistency and appearance to be very sticky. At this stage, surface spreading is no longer a factor and the flakes can exist as discrete particles. These tar flakes were observed **to** collect in wind rows or against the side of vessels, and under the influence of turbulence from **wave** energy they bump into each other and gradually aggregate into larger particles. With continued addition of small flakes, or **after** nucleation on drifting **detrital** materials such as sugar cane stock, these materials then formed larger oil bodies. This aggregation pattern was completely random, and thus, could help to explain the cerebral (brain-like appearance) of the larger clumps of the mousse collected earlier during the **IxTOC** cruise. This hypothesis tends to indicate that, at least in the case of this spill,

the mousse balls and tar balls are growth products from **smaller** particles in addition **to** breakdown products from the larger emulsified slicks. Such formation could occur in wind rows of oil flakes (which were an observed phenomena) or in standing wave situations.

In this instance, the formation or aggregation of mousse only appeared to occur after significant removal of lower molecular weight compounds by evaporation and dissolution and photo-oxidation of the slick to generate the appropriate surface active materials to stabilize the water-in-oil emulsion and mousse agglomeration. Overton **et al.** (1980a) identified a number of fatty acid methyl esters and normal fatty acids from C-7 to C-n and branched fatty acids from C-9 to C-12 after photo-oxidation of fresh **IIXTOC** crude oil. **Alkyl-phenols, allylic benzoicacids** with anywhere from C-1 to C-6 **alkyl-**substitutes, **alkyl-substituted naphthols, alkyl-substituted naphthanoic** acids and alkyl-substituted **phenanthroic** acids were **also** identified in addition to **alkyl benzothiophene** acids and **alkyldibenzothiophene** acids. Any number of these compounds could act **to** further stabilize water-in-oil emulsification or mousse formation.

Although many of these compounds would be expected to be leached from the **oil** surface as they are formed (or during extended weathering) they might serve to help stabilize the aggregation products of the smaller flakes. Evidence for this is suggested in that samples of beached tar from **Laguna Madre** were examined by Overton, et al. (1980b), and the outer surface of this beached mousse consisted primarily of **n-alkanes** with limited numbers of aromatics and no sulfur containing compounds detected by a Hall detector. The middle portions of the mousse had higher aromatic contents and a number of peaks that responded to the **sulfur** detector. Weathering thus appeared to remove the oxygenated products from the surface of the mousse ball but not from the interior. Figure 6 shows the relative aromatic concentrations of selected PNAs in the **IIXTOC** crude oil and in the mousse flakes obtained at station **PIX-13** (during observation of micro-scale mousse ball formation) and Figure 7 shows the relative **aliphatic** distributions for the **IIXTOC** crude, the

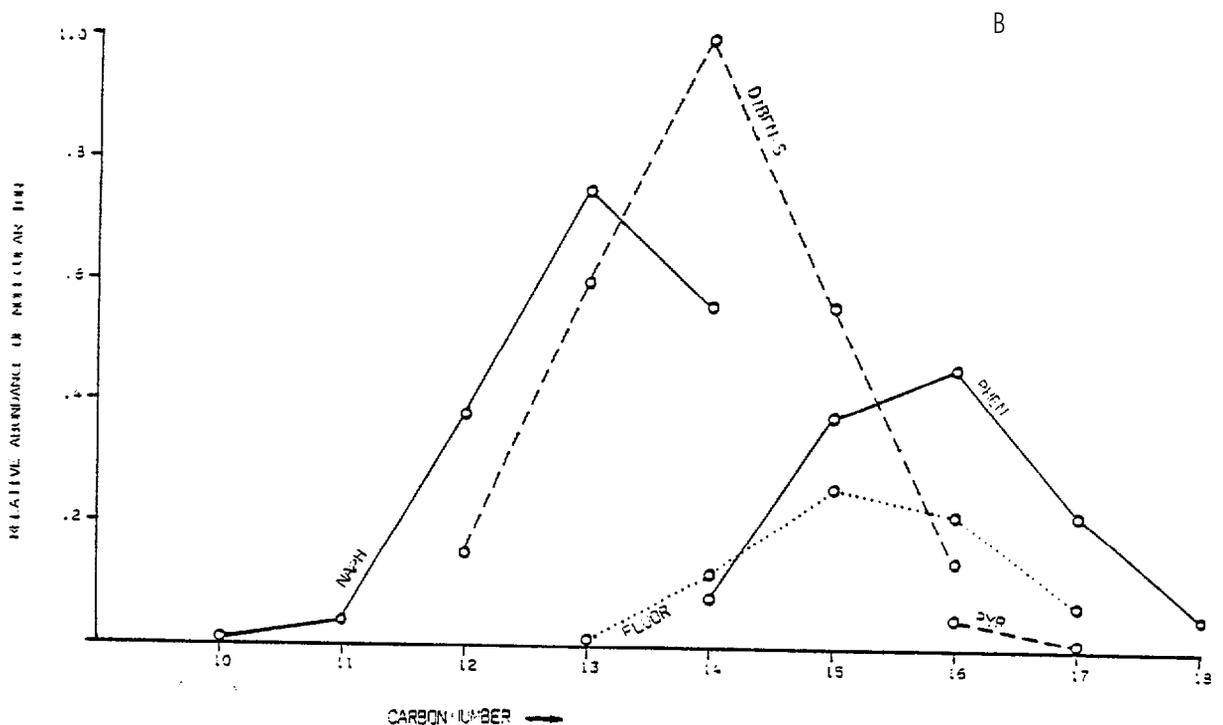
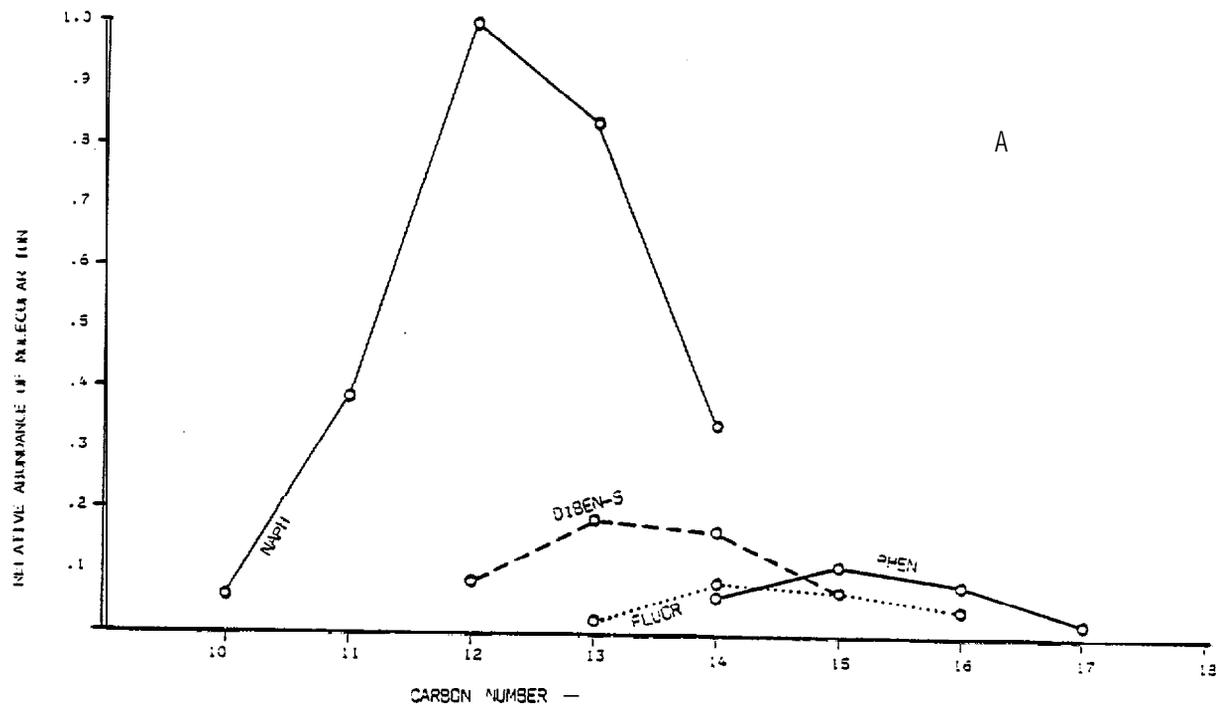


FIGURE 6. RELATIVE ABUNDANCE OF ALKYL-SUBSTITUTED POLYNUCLEAR AROMATIC HYDROCARBONS IN IXTOC CRUDE OIL COLLECTED 1/2 MILE FROM THE WELL HEAD (A) AND MOUSSE FLAKES COLLECTED 16-18 MILES FROM THE WELL HEAD (P-13) DURING THE GW PIERCE DOWN-PLUME TRANSECT. NAPH = NAPHTHALENE, DIBEN-S = DIBENZOTHIOPHENE, FLUOR = FLUORANTHENE, PHEN = PHENANTHRENE, PYR = PYRENE: CARBON NUMBER 10 = NAPHTHALENE, 11=C₁ - NAPHTHALENE, 12 = C₂ - NAPHTHALENE, ETC. (FROM PAYNE ET AL., 1980a.)

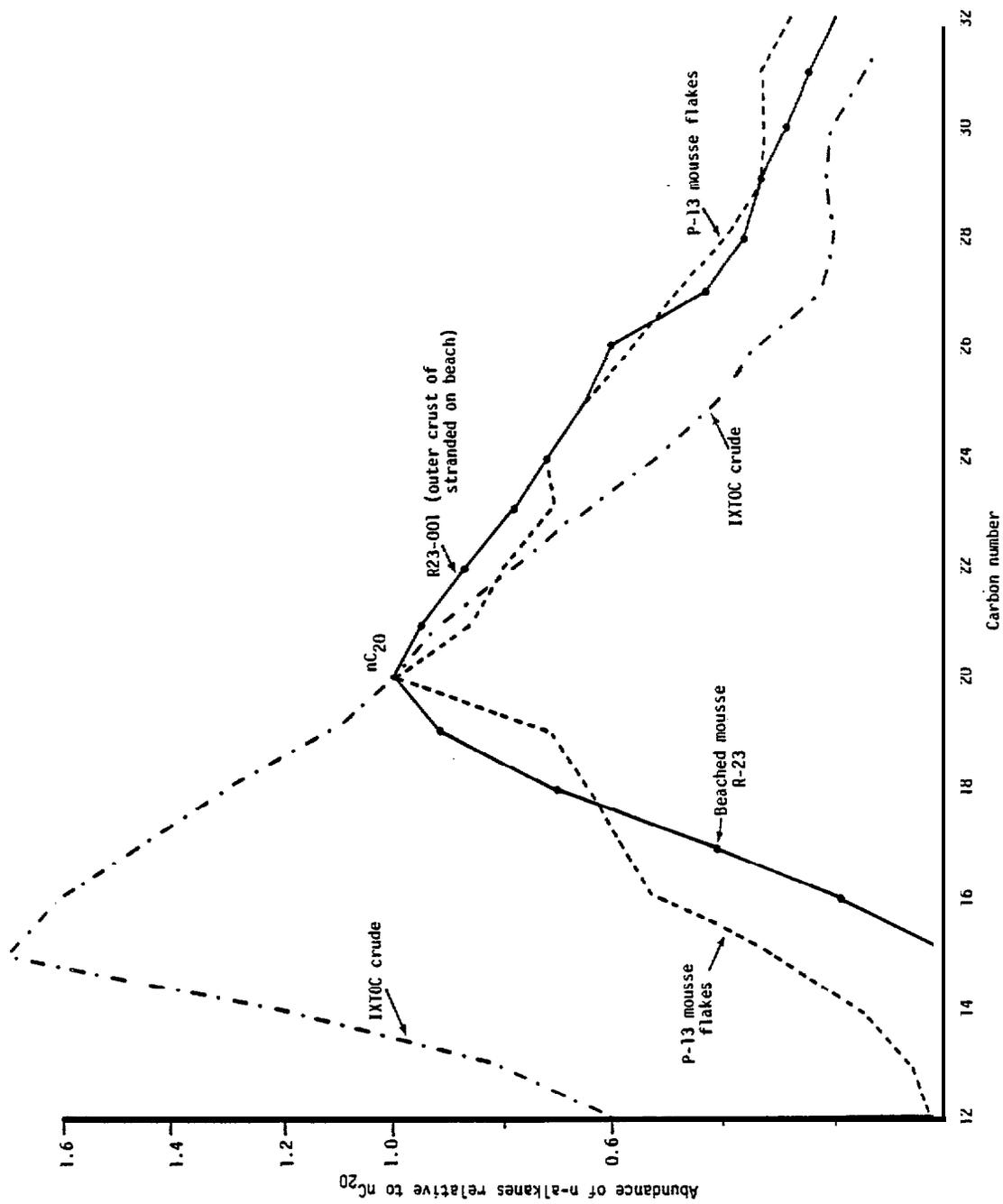


FIGURE 7. ABUNDANCE OF N-ALKANES (RELATIVE TO nC-20) IN BEACHED MOUSSE FROM LAGUNA MADRE (RIX-23), MOUSSE FLAKES COLLECTED 16-18 MILES FROM THE WELL HEAD (P-13) DURING THE GW PIERCE DOWN-PLUME TRANSECT, AND IXTOC CRUDE COLLECTED 1/2 MILE FROM THE WELL HEAD. (FROM PAYNE ET AL., 1980a.)

mousse flakes described above and the beached mousse sample obtained at **Laguna Madre** (Payne et al. , 1980a). Clearly, the alkyl-substituted **naphthalenes**, **benzothiophenes**, di benzothiophenes, **phenanthrenes**, **flourenes** and **pyrene** are present at much higher relative concentrations in the mousse than the alkyl-substituted **naphthalenes** in the starting crude. Likewise, the distribution of the **aliphatics** shows that in the flakes and beached mousse, compounds with molecular weights less than **nC-14** have been significantly removed. Based on the observations in the field, it is believed that this weathering process occurred before mousse flake or tar ball agglomeration/formation occurred. Table 6 presents **ratios of nC-25 to nC-16**, **nC-25 to nC-19** and phytane to **nC-18** with depth in the beached mousse collected at **Laguna Madre**, and these data clearly suggest the lack of any significant microbial degradation or differential weathering after formation. Again, it appears that overall chemical weathering occurred in the bulk of the oil before agglomeration into the larger 1 m² patch which was eventually stranded in the upper intertidal zone.

With regard to microbial processes relating to mousse formation, Buckley et al. (1980) reported that **Vibrio** bacteria populations were associated with the mousse, but that microcosm experiments showed little chemical evidence of microbial degradation of the **bulk** oil. This was attributed to either the large influx of oil which masked any minimal changes due to microbial activity or as Atlas postulated (1980) to the lack of nutrients in the water column in the Gulf of Mexico at the time of our observations. Another possibility was that microbial populations were inhibited by toxic effects inherent to the **IxTOC I** oil (Buckley et al., 1980; Ron Atlas, personal communication). Specifically, in the microcosm experiments, fresh oil inhibited amino acid uptake, and microbial activity could only be stimulated after 5 days, whereas mousse enhanced amino acid uptake immediately, suggesting that the removal of toxic components later allowed microbial populations to accumulate if they were capable of hydrocarbon utilization. Overton et al. (1980b), in analyzing samples from the microcosm experiments, stated that no evidence of **nC-17** or **nC-18** removal relative to **pristane** and phytane was observed in fresh oil and mousse microcosms.

TABLE 6. SELECTED COMPONENT RATIOS FOR THE DISSECTED MOUSSE SAMPLE BEACHED AT LAGUNA MADRE (STATION RIX 23). (FROM PAYNE ETAL., 1980a.)

Sample*	Depth Below Skin	nC_{25}/nC_{16}	nC_{25}/nC_{19}	Phytane/ nC_{18}
01	surface 3 mm	3.1	0.66	0.46
02	3-8 mm	4.3	1.05	0.42
03	6-13 mm	2.6	0.63	0.46
04	16-23 mm	2.3	0.61	0.44
05		---	Weeds	---
06	5-10 cm from bottom	2.4	0.69	-0.44
07	bottom 5 mm	2.9	0.79	0.46

*01 represents the sample from the air/mousse interface and 07 that from the sand/mousse interface.

During the meeting of the Researcher/Pierce cruise **synthesis** steering committee in February 1981, it was postulated that the presence of living or dead microbial biomass on the surface of mousse flakes may enhance agglomeration stability, and it was offered as one explanation for the increased **non-chromatographable** residual material noted by Boehm and Fiest (1980b) in many of the mousse samples. Atlas et al. (1980) indicated that microbes associated with the mousse could be **sluffed** off during incubations, however, he also found that microbial degradation of the mousse in the IXTOC spill was extremely slow, and that only **7%** of the mousse was actually mineralized during 180 day incubation periods. **No** changes in **nC-17/pristane** and **nC-18/phytane** ratios were observed up to 120 days in the incubations and nutrient limitations were suggested as being the biggest factor. **Only** in specialized micro-environments for example, where mousse was associated with plant material, did **microorganisms** appear to degrade mousse particles at higher rates, and this was **presumably** due to the availability of nutrients from the decaying plant material (Boehm and Fiest, 1980b). Similar observations were reported by Blumer et al. (1973) for stranded tar balls associated with decaying seaweed in the upper intertidal zone.

Fate of Stranded IXTOC Mousse along the Southeast Texas Coastline

With regard to the persistence of beached IXTOC mousse, Gundlatch et al. (1981) described several large patches of mousse observed on the south Texas coast. During August and September 1979 large patches of mousse came ashore along much of the south Texas coastline. In addition, 20 miles of north Padre Island and 4 miles of Brazes Island had heavy coverage. During this period the oil that reached the shorelines was estimated to be 3,900 tons. Due to storm activities the shoreline became noticeably cleaner due to deposition of sand over the surface oil, and the desiccation of mousse to tar caused a reduction to at least half the original volume. On September 3-6, calculations revealed that approximately 31% of the beached oil was on the surface, 53% was buried and 16% remained within the **swash** zone. Thus, even though the beach surface **appeared cleaner**, the actual mousse content stayed approximately the same.

On September 13, very high tides, strong onshore winds and 1-2 m waves were generated by tropical storms, and within 2 days, over 90% of the oil from the shoreline was removed. The authors noted a significant amount of sheen in the surface swash zone as waves reworked the sediments, however, the **small** amounts of oil that remained were found primarily high on the beach along the base of a four dune ridge. The **sample** of beached mousse **from Laguna Madre**, described above, was found in this high beach zone region, and as stated earlier, the chemical composition was remarkably similar to mousse flakes obtained only 13-16 miles from the site of the **IXTOC wellhead**. After the mid-September tropical storms, at **least** 36 "tar mats" (deposits of mousse and sediment) were discovered. It was believed that these tar mats were formed from the large oil/mousse masses which were then compressed and mixed with sediment **during** the tropical storm.

Seven months later, during mid-April 1980 only 19 of **the** tar mats were still visible, and two different types of mats could be differentiated by **color**, sediment and vegetation content (Sadd, 1980). The largest mat was 65 m long, 7.5 m wide and 20 cm thick, and it was composed of 7% oil, 14.7% water (showing significant desiccation) and 77.6% sediment yielding a specific gravity **of** 1.38. The amount of oil incorporated in the **19** measured tar mats was estimated to be 180 tons **or** less than 5% of the maximum quantity of oil found on the Texas shoreline during September 1979. A final **beach survey** was **undertaken** in August 1980, a **week** after the passage of Hurricane Allen. The tar mats remained, and in fact, because of the erosion of sand from the storm, several new tar mats (though general **ly** very **small**) became uncovered. The ability of these mats to endure Hurricane **Allen** suggests that they will persist **for** several more years.

Deposition of **oil** was found to vary with beach type such that when oil was buried along **shell** beaches, penetration as deep as 40 cm occurred whereas on **fine-grained**, sandy beaches **it** reached a depth of only 7 cm. Smaller patches of mousse were observed to be broken up into tar balls by storm activities and these were commonly found along the bottom within the shoreline

break and **swash** zone inshore **of** the first sediment sandbar. The tar **balls** rapidly decreased **in** size from 1-5 cm to less than 1 cm, and sediment laden or "armored" tar **balls** appeared to be the most common at the shorebreak **and on** the first sandbar. Seaward of **the** first sandbar tarballs became very sparse, and very little evidence was found of great quantities of nearshore bottom oil. Within the first trough, sediment laden mousse patches of **up** to 3 x 4 m and 10 cm thick were sparsely scattered. **In** conclusion of more than 476,000 tons of oil estimated **to** be released **by** IXTOC-I into the Gulf off Mexico, less than 0.8% washed ashore in Texas and after the storms one year later less than 0.04 remained as tar mats. As has been observed for other major open ocean and nearshore spills, longer term persistence in lower energy lagoons and estuaries is anticipated.

Burmah Agate

The tanker Burmah Agate and the freighter Mimosa collided near a sea buoy in the Galveston, Texas-ship channel **on** November 1, 1979. Both vessels were engulfed in flaming crude, and large quantities of a light (39.3° API gravity) Nigerian crude oil were spilled from **the** Burmah Agate. A heavier 21.9° API gravity Nigerian crude held in the Burmah Agate was not believed to be spilled. The spill was fairly continuous for the first few days, and then intermittent **flow** was noted to continue until January 8, 1980 when the fire was extinguished. Approximately 263,000 barrels of the original 400,000 barrel cargo were estimated to be ultimately spilled or burned, and an estimated 630 barrels of residue remained in the burned out tanks after the fire was extinguished. The initial **slick** was noted to move 12 miles in approximately 12 hours and approached a width of **500** ft. with thickness of 0.1 inches (Kelley et al., 1981).

This is one example of a substantial oil spill where mousse **formation** was not noted, or believed to be a significant problem. In correlation with various laboratory studies, this presumably reflects the fact that the spilled oil was a light Nigerian crude which would not be believed to form a viscous

mousse. No direct references to the presence or absence of mousse were cited in several reports on this spill, and observations of the slick behavior suggest that mousse formation was not a problem in this incident. On the third day after the spill, the **slick** was transformed into a Z formation by the influence of estuary currents, and the oil was observed to pool against the ship's hull while still being quite fluid in patches as long as the length of the vessel. On the fourth day following the spill, wind directions were noted to change and the oil moved with the wind in closer to the shore and formed wind rows parallel to the wind before impacting the shoreline at Galveston. The fluidity of the oil and the observed changes in shape of the slick as influenced by the wind and tidal currents were taken as evidence to further support the lack of any significant mousse formation problems.

Open Ocean Field Tests of Spilled Petroleum

Several controlled open ocean spills have been conducted to determine the chemical and physical behavior of crude oil in the early minutes and hours after the oil is released (JBF/API, 1976). Approximately 440 gallons of a light and heavy crude oil were spilled separately in four studies in both calm and rough seas in October and November 1975, approximately 75 miles east of Boston. A **Murban** crude (SG, 0.83; 39.0% API) and La Rosa crude (SG 0.91; 23.9% API) were used in the studies, and while the **Murban** crude appeared to initially spread faster than the La Rosa, the latter may have gained a greater total slick area because of greater surface **slick** persistence. Both oils were observed to form lenses or globs of thicker portions of the oil at the leading (down wind) edge of the slick. Evidently these thicker masses exhibited higher wind resistance and had a different frictional resistance at the oil-water interface compared to the thinner slick and sheen which trailed behind them. **Hollinger** and **Mennella** (1973) have reported that as much as 90% of the total oil may exist in such thick patches in open ocean spills. While the lenses appeared immediately after the spill, the formation of "mousse" appeared to be delayed by 60-90 minutes, and then only occurred in selected conditions. In these spill studies, mousse was reported to form with the **less**

dense Murban crude, but not with the La Rosa. Surprisingly, mousse formation was only specifically mentioned in the 1976 article for the **Murban** crude, whereas one might have a priori expected the Venezuela crude to have formed a more stable emulsion because of its higher specific gravity and several laboratory studies which have shown that Venezuelan **crudes** (in general) are capable of forming stable mousse. As in the **IxTOC** case, it appeared that mousse formation **only** occurred after sufficient time had passed to allow significant evaporation and dissolution of **lower** molecular weight components.

One of the most significant outcomes from these studies was the recommendation that time-variable factors for **the** behavior of thicker lenses and mousse be incorporated into mathematical **and** descriptive models for more accurate oil weathering and trajectory. Specifically, it was noted that the **non-homogeneity** of the oil slick must be considered when predicting oil **spill** transport, spreading and behavior. Such approaches have been undertaken by **Berridge** et al. (1968b) and more recently **Grose** (1979). Further, it was noted that **the** chemical differences in terms of composition and weathering rates between the lenses and the thinner **oil** films should be established. Approaches to studying these differences in chemistry were undertaken by Overton et al. (1980b) and **Boehm** and **Fiest** et al. (1980b) for the **IxTOC** spill.

In 1978 and 1979 four additional tests were conducted, 1 each year off of New Jersey and southern California (**McAuliffe** et al., 1981). The 1978 east coast studies consisted of 4 10-barrel spills using the same **Murban** and La Rosa **crudes**, however, in these instances the slicks were sprayed by helicopter with a self-mixed **dispersant** after 2 hours. **With** this treatment the **Murban** crude was almost **completely** dispersed, **and** the La Rosa about 1/2 dispersed. Concentrations in **the** water column up to 18 mg/l at 1 meter were found to **greatly** exceed those previously observed in the 1975 spills under natural dispersion.

In the September 1979, controlled oil spills, 10 to 20 barrels of Alaskan **Prudhoe** Bay crude oil were discharged off of **Long Beach**, California.

In this instance different approaches to **dispersant** application were incorporated into the experiments, and untreated slicks were used as controls. Three slicks were sprayed with a self-mixing **dispersant** from a DC-4 aircraft, three were sprayed with the same **dispersant** from a boat, and one was sprayed with a second **dispersant** from a boat. Chemical analysis showed that 45-80% of the oil was dispersed by aerial treatment, and the lens (thicker oil patch) phenomena noted in the 1975 spills was specifically **addressed** with regard to its behavior after treatment with **dispersants**. When the lenses of the thicker oil were treated from the surface vessel, 60% of the oil **could** be successfully dispersed whereas when the entire **slick** was uniformly treated, **dispersment** of **only** 5-10% occurred. In the southern California spills it was also noted that the chemically dispersed oil had a lower tendency to adhere to solid surfaces such as bird feathers, rocks, sand and sediment in the water column. Delayed application of **dispersant** was also incorporated into the tests to study its effect on a more dense and **viscious** weathered oil. Thus while the fresh Prudhoe Bay crude oil had an API gravity of 26.6° API (0.90 g/ml) and a viscosity of 183 **centistokes** at 15.6°O, the partially weathered crude (23% **volume nC-11** and less removed by distillation) had an API gravity of 22° (0.92 g/ml) and a viscosity of 1210 **centistokes**.

In general, it was observed that **dispersants** sprayed from the aircraft more effectively dispersed Prudhoe Bay crude oil than when applied from a spray boat. The **dispersants** worked best when applied neat, as dilution with water destroyed the "self-mix" property that caused fine oil-in-water droplet dispersion. The amount of **dispersant** applied also resulted in differences in removal of oil from the water surface. In 1978, the aerial application of 4.9% **dispersant** resulted in 78% dispersion of the oil, whereas a 3.6% **dispersant** application yielded only 60% dispersion. When the Prudhoe Bay crude oil was allowed to weather on the water surface for 2 hours (as opposed to 15 rein) before treatment, the **dispersant** efficiency decreased with only 45% of the slick vs. 60% of the slick being removed (McAuliffe et al., 1981). In all cases, the best results were obtained when the thicker portions or **lenses** of the slicks were treated directly. It was not stated in any of the articles

whether this thicker material was a true "mousse", but the data clearly **demonstrated** that **dispersants** must be applied to the heaviest part of the oil slick for the best results. **Dispersants** applied to thin **oil** patches or surface sheens, greatly overtreats them while not affecting the thicker oil. When the entire slick surface was rather uniformly sprayed, **only** 5-8% of the slick dispersed as opposed to 62% when the spray was concentrated on the thicker portions or lenses.

Smith (1977) has reported on the results obtained from several planned oil spills using #2, #4 and #6 fuel oils, light crude **oil** and heavy crude oil. All of the oils moved parallel **to** the wind direction, and a tear drop formation similar **to** that described above for the **Murban**, La Rosa and **Prudhoe** Bay crude oil spills was noted. That is, after a period of time the circular oil slick became distorted into a tear drop profile with **the** thicker portion of the oil concentrated near the down-wind leading edge of the slick with a long tail of increasingly thin oil extending towards the point of release. This was observed for **all** oil types and **all** wind conditions, but was more noticeable in the low to mid-range conditions where the thin tail was not as rapidly dispersed into the rough seas. This again documents the importance of incorporating time-variable and area-variable slick thickness parameters into algorithms for modeling oil weathering behavior. In general, the thicker **oil** slicks exhibited a greater leeway and moved faster than did the thin slicks. The apparent order of leeway arranged in decreasing magnitude (for a given wind speed) was heavy crude oil > **light** crude = #2 fuel oil > #6 fuel oil = #2 fuel oil. Interestingly, there was no apparent systematic correlation of either viscosity or density with **oil slick** leeway. That is, in terms of decreasing viscosity (and **desnity**), the oils **could** be arranged heavy crude oil > #6 fuel oil > #4 fuel oil > #2 fuel oil = light crude oil.

The chemistry of the thin vs. thick slicks appeared to be different, and evaporation of volatile constituents occurred more rapidly from the thinner slicks. Thus, in these studies, the thin films were enriched (with time) in the higher molecular weight less volatile constituents including a number

of non-volatile constituents with some surface activity. "One explanation to describe the observed behavior of the thin films following the leading edge of the slick was that they had surface active materials which tended to make them associate with the water surface and thus spread to form a mono-molecular film. The results of dye marker studies suggested that the thinner tailing portions of the film had little or no net velocity relative to the water surface because of the surface active materials. The thicker portions of the oil present a larger drag profile to the wind, and thus, exhibit a positive velocity with respect to the surface water. This **lense** was noted to fold over **on** itself because of the drag profile of the water, and as in the **IxTOC 1** case and in laboratory and field measurements using Prudhoe Bay crude oil in our own studies, this folding behavior was noted to lead to enhanced water uptake and apparent mousse formation in the absence of other more vigorous mixing regimes.

Conclusions

From the discussions of the various case histories of significant oil spill events and controlled studies, it can be seen that in general mousse formation is dependent upon the oil type and that the **field** observations from world conditions generally tend to parallel laboratory results. Exceptions to this field oil spill behavior were obtained with the loss of Bunker C from the USNS Potomac off Greenland; however, this spill occurred in extremely calm seas and demonstrated the important role played by physical oceanographic conditions. The results have **also** shown that the optimum particle size of water droplets incorporated into the more stable water-in-oil emulsions in laboratory mousse formation and field observations of stable mousse appear to be identical.

Finally, **it** is important to note the drastic differences in environmental impact in open ocean vs. coastal spills. In most of the open ocean incidence where landfalls were not directly oiled, the overall impact of even major **oil** spills such as **the Ekofisk** Bravo has been minimal or short-lived.

When direct oiling of coastlines by oil or mousse occurs, deleterious effects may last for 10-20 years or more (depending on the energy regime of the coastline). In the case of the **IXTOC** blowout, which was generally considered to be open ocean, the magnitude and time involved in the spill allow it to be classified as one exhibiting impact-effects for both open ocean and coastal situations. Thus, while the loss of hydrocarbons at the **wellhead** from dispersion, dissolution, dilution, evaporation and eventual sedimentation may tend to minimize long-term effects in that area, localized and heavy mousse contamination of impacted estuaries, lagoons and higher intertidal zones of beaches will cause extended damage which may persist for tens of years.

TAR BALL FORMATION AND DISTRIBUTION

Numerous reports have appeared in the last decade on the occurrence of tar balls in surface water samples (Horn et al., 1970; Butler et al., 1973; Morris and Butler, 1973; Wong et al., 1973; Sleeter, et al., 1974; Mommessin and Raia, 1975; Butler, 1975a, b; Sleeter, et al., 1976; Smith, 1976; Wade et al., 1976; Pequegnat, 1979; Shaw and Maples, 1979; Geyer, 1981; and van Dolah et al., 1980). Data from these and other studies were compiled by Clark and MacLeod (1977) and Table 7, adapted from Clark and MacLeod, presents an updated summary of documented tar ball measurements in the worlds oceans as of 1980. From these data it is evident, as noted by Feldman (1973), that the Mediterranean Sea is significantly more contaminated with tar balls than is the Sargasso Sea or the North Atlantic. The North Atlantic and North Pacific tar ball concentrations were estimated in 1973 to be approximately equal, but Wong et al. (1973, 1974) showed that there was a significant difference in the average levels of tar balls in the western and eastern North Pacific. Tar balls ranging in size from 0.05 to 3 cm were obtained in 30 of 37 tows in the North Pacific, and the consistency ranged from hard to soft and tacky with the majority found in the first category. A longitude center-line of 172.5° West appeared to separate the western from the eastern Pacific, with average concentrations in the western Pacific reaching 3.8 mg/m² while the eastern Pacific contained on an average 0.4 mg/m². As noted above, this range is similar to that found in the North Atlantic, and in general, it has been noted that higher levels of tar balls on the sea surface occur either along ocean routes supporting high densities of oil tanker traffic or downstream from these routes (Clark and MacLeod, 1977; NAS, 1975; Butler et al., 1973; Morris et al., 1975).

Although the distribution of sited tar balls was noted to be highly variable (variations by a factor of 10 or more found at a single station during the course of a single day and by as much as a factor of 500 in the course of a year), estimates of standing crops of tar balls have been made for several of the world's oceans: Northwest Atlantic marginal sea, 2000 metric

TABLE 7

Summary of 1971-1980 Citations of Tar Ball Distributions and Concentrations
on the World Oceans
(adapted from Clark and MacLeod, 1977)

<u>Description of Tar Samples</u>	<u>Amount of Tar Residue (mg/m²)</u>		<u>Reference</u>
	<u>Maximum</u>	<u>Mean</u>	
<u>Ocean, geographic area and time period</u>			
Atlantic Ocean			
Scotia shelf	2.4	0.9	Morris, B. F., 1971
Lat. 38° to 42° N, Long. 50° W	9.7	2.2	Morris, B. F., 1971
Virginia to Cape Cod, Coastal			
Winter	4.4	1.04	Sherman et al., 1973; Sherman et al., 1974
Summer		0.18	Sherman et al., 1973; Sherman et al., 1974
Offshore	0.2	0.04	Attaway et al., 1973
Winter		0.05	Sherman et al., 1973; Sherman et al., 1974
Summer	11	0.77	Sherman et al., 1973; Sherman et al., 1974
North Carolina to Florida		1.22	Sherman et al., 1973; Sherman et al., 1974
Winter		0.23	Sherman et al., 1973; Sherman et al., 1974
Summer	20	5.5	Attaway et al., 1973
North Antilles & Bahamas		4.8	Sherman et al., 1973; Sherman et al., 1974
Winter	87	3.9	Sherman et al., 1973; Sherman et al., 1974
Summer		1.12	Sherman et al., 1973; Sherman et al., 1974
Lesser Antilles	8.37	1.12	Sleeter et al., 1976
Ocean Station BRAVO, Labrador current	0.003	0.00	McGowan et al., 1974
Ocean Station CHARLIE, North Atlantic	1.83	0.12	McGowan et al., 1974
Ocean Station OELTA, North Atlantic	10.73	1.15	McGowan et al., 1974
Ocean Station ECHO, Sargasso Sea	21.62	2.64	McGowan et al., 1974
Off Bermuda		0.6	Morris, B. F., 1971
Northeastern North Atlantic	480		Butler et al., 1973; Horn et al., 1970
	14.2	4.8	Sleeter et al., 1974
	1	0.6	Attaway et al., 1973
Barents Sea	3.0	0.15	Smith, G. B., 1976
Norwegian Shelf	0.4	0.04	Smith, G. B., 1976
Northern North Sea	0.2	0.02	Smith, G. B., 1976
Skagerrak	12.1	0.32	Smith, G. B., 1976
Central eastern North Atlantic	22.6	9.8	Sleeter et al., 1974
Gulf Stream	0.8	0.3	Attaway et al., 1973
	6.7	3.8	Sleeter et al., 1974
Sargasso Sea	40	9.4	Morris & Butler, 1973
	1.4	0.2	Sherman et al., 1973; Sherman et al., 1974
	6	3	Attaway et al., 1973
	90.6	25	Sleeter et al., 1974
South Atlantic Bay			
Lat. 27° to 34° N, Long. 77° to 80° W			
Winter, 1973		0.31	VanDolak et al., 1980
Spring, 1973		0.46	VanDolak et al., 1980
Autumn, 1973		0.93	VanDolak et al., 1980
Spring, 1974		0.83	VanDolak et al., 1980
Summer, 1974		0.76	VanDolak et al., 1980
Winter, 1975		1.95	VanDolak et al., 1980
Central Atlantic			
Canary Current	7.69	2.02	Sleeter et al., 1976
North Equatorial Current	0.27	0.16	Sleeter et al., 1976
Equatorial Countercurrent	0.04	0.02	Sleeter et al., 1976
South Equatorial Current	0.57	0.11	Sleeter et al., 1976
Equatorial Current Region	63.6	12.7	Polikarpov et al., 1971
Caribbean Sea			
	1.5	0.4	Jeffrey, L. M., 1973
	0.9	0.2	Sherman et al., 1973; Sherman et al., 1974
	4.5	0.74	Jeffrey et al., 1974
	13.4	1.62	Sleeter et al., 1976

TABLE 7 (continued)

Summary of 1971-1980 Citations of Tar Ball Distributions and Concentrations
on the World Oceans
(adapted from Clark and MacLeod, 1977)

<u>Description of Tar Samples</u>	<u>Amount of Tar Residue (mg/m²)</u>		<u>Reference</u>
	<u>Maximum</u>	<u>Mean</u>	
<u>Ocean, geographic area and time period</u>			
Gulf of Mexico	10.0 3.5 6.0	1.2 1.1 1.12	Jeffrey et al, 1974 Jeffrey, L. M., 1973 Sleeter et al, 1976
South Texas 1976			
Winter (Jan. - Feb.)		.99	Pequegnat, 1979
March		2.25	Pequegnat, 1979
April		11.21	Pequegnat, 1979
Spring (May - June)		0.78	Pequegnat, 1979
July		0.12	Pequegnat, 1979
August		0.27	Pequegnat, 1979
Fall (Sept. - Oct.)		0.62	Pequegnat, 1979
November		0.18	Pequegnat, 1979
December		5.92	Pequegnat, 1979
South Texas 1977			
Winter (Jan. - Feb.)		1.26	Pequegnat, 1979
March		11.11	Pequegnat, 1979
April		0.41	Pequegnat, 1979
Spring (May - June)		0.93	Pequegnat, 1979
July		0.46	Pequegnat, 1979
August		0.08	Pequegnat, 1979
Fall (Sept. - Oct.)		1.38	Pequegnat, 1979
November		1.76	Pequegnat, 1979
December		0.56	Pequegnat, 1979
Overall average from 2 year study		1.66	Pequegnat, 1979
Mediterranean Sea	540	20	Horn et al, 1970; Morris, B. F., 1971
Ionian Sea	540	130	Horn et al, 1970; Morris et al, 1975
1969	110	16.0	Morris et al, 1975
1975			
Alboran Sea	10	6.5	Horn et al, 1970; Morris et al, 1975
1969	45	11.0	Morris et al, 1975
1975			
Tyrrhenian Sea	20	1.5	Horn et al, 1970; Morris et al, 1975
1969	15	3.2	Morris et al, 1975
1975			
Balearic Sea	10	2.4	Horn et al, 1970; Morris et al, 1975
1969	1	0.5	Morris et al, 1975
1975			
Central (tarballs)	6.1	-	Morris and Culkin, 1974
Eastern (tarballs)	10.0	4.1	Morris and Culkin, 1974
Central (emulsions)	0.30		Morris and Culkin, 1974
Eastern (emulsions)	0.36	0.14	Morris and Culkin, 1974
Northwest Pacific Ocean			
Lat. 35°N, Long. 140°E to 175°W	14	3.8	Wong et al, 1974
Lat. 25° to 40°N, Long. 140° to 160°W	16.3	2.1	Wong et al, 1976
Outside the Kuroshio Current		0.4	Wong et al, 1976
Northeast Pacific Ocean			
Lat. 35°N, Long. 175° to 130°W	3	0.4	Wong et al, 1974
Lat. 35°N, Long. 175° to 130°W		0.03	Wong et al, 1976
South Pacific Ocean		0.0003	Wong et al, 1976

tons, Gulf Stream 18,000 metric tons, Sargasso Sea 66,000 metric tons, total Northwest Atlantic 86,000 metric tons, Mediterranean 50,000 metric tons, total Northwest Atlantic and Mediterranean 136,000 metric tons (Morris & Butler, 1973 and Feldman 1973). The extreme variability in the data and lack of synoptic and sufficient measurements from the broad expanse of the world's oceans, make such standing crop estimates tenuous at best, and at this time it is impossible to determine whether tar ball concentrations are increasing or decreasing. Further, Wade et al. (1976) in investigating pelagic tar from the Sargasso Sea, stated that many smaller particles (ranging from 0.3 μm to 1.0 mm in diameter) are present and that previous estimates of pelagic tar may be low because they may not have included the smaller size range of these particles. Furthermore, Morris et al. (1976) measured tar like particles with diameters of 10 to 500 μm in the Sargasso Sea and estimated their total mass in the water column to a depth of 100 m to be about 4 times the standing crop of larger pelagic lumps at the ocean surface. These smaller particles would be more apt to disperse into the water column, rather than contribute to pelagic tar, however, so their inclusion in surface tar ball estimates is probably not appropriate.

Chemical Composition of Tar Balls

Butler (1973) provided a detailed summary of information on the distribution and chemical composition of tar lumps found on the surface of the ocean up to the end of 1972. Gas chromatographic profiles of a number of samples showed that in general, aliphatic and aromatic materials with molecular weights less than nC-14 to nC-17 were significantly depleted, and most of the samples showed an evenly repeating series of alkanes out to nC-45. Bimodal distributions of lower and intermediate molecular weight alkanes were observed in several instances, and unresolved complex mixtures characterized many of the samples.

Koons (1973) analyzed 34 tar balls collected from Texas beaches and the Gulf of Mexico, and the physical appearance and chemistry of the samples

was found to vary appreciably. Tar balls ranged in size from a few mm to several cm, and some samples were quite soft and appeared to flow on the beach due to heating from the sun while others were quite hard, almost brittle, and could be broken with a clean fracture. The saturated hydrocarbon composition of the tar balls ranged from 1.6 to 56.1% and the asphaltene contents from 8.8 to 54.7%. Average values of the 34 samples showed: saturated hydrocarbons, 31%; aromatic hydrocarbons, 24%; LC-elutable NSO's, 14%; non-LC-elutable NSO's, 6% and asphaltenes 25%. Evaporation and dissolution had stripped away hydrocarbons up to nC-15 to nC-17 in all of the samples, and in the fresher appearing samples, ratios of nC-17 to pristane and nC-18 to phytane did not appear significantly different from those of the seep oils from the area. The harder, brittle tar ball samples had undergone appreciable chemical and biological oxidation in addition to the physical evaporation/dissolution weathering. These latter samples, in general, contained lower amounts of saturated hydrocarbons (1.6 - 10%) and greater amounts of NSO's and asphaltenes. Further, the ratio of saturate to aromatic hydrocarbons decreased significantly (by a factor of 10) and the nC-17/pristane ratios approached zero. Both of these observations support significant biological degradation in the samples.

Mommessin and Raià (1975) presented a summary of chemical characterization data on a total of 110 tar samples collected from the northwestern Atlantic, the Sargasso Sea, along shipping routes in the vicinity of coast guard stations Echo and Delta in the Northwest Atlantic, along the Florida coast, in the vicinity of New York harbor, along the Texas coast near Galveston, and from three samples collected near coast guard station November in the Pacific ocean. The tar ball samples ranged from pea size to 1-3 inches in diameter, and in general the tars were black or brown/black and had irregular shapes. Hardness varied from very hard and dry to soft and sticky, and three of the samples examined were essentially liquid. Surface portions of a number of samples were shiny with substantial oil stain. As noted in the case history of-the IXTOC spill, researchers observed numerous large tar and mousse balls which showed evidence of accumulation of fresh oil on the surface (as demonstrated by a significant darker black oil stain).

Several of the tar balls examined in the Mommessin study were coated with tree leaves, *Sargassum*, unspecified plants, barnacles, bryozoa and other pelagic organisms. In other samples, insects and wood fragments, in addition to continental plants and leaves along with substantial quantities of quartz and carbonate sand or clay particulate, suggested that they may have been beached at one time. In the IXTOC spill, numerous large tar balls and mousse agglomerations were noted with sugar cane stock or other intertidal debris present, and these substrates were believed to act as sites for nucleation and further mousse accumulation. Mommessin also noted pieces of plastic, bits of buttons, tubing, metal fragments, synthetic fibers, fly ash and rope to be frequently abundant, illustrating industrial and commercial byproducts as a source for numerous tar samples.

In line with other observations by Blummer et al. (1973) and Butler (1973), the inside portions of the tars in the Mommessin and Raia study did not contain materials boiling below nC-12, and residues boiling above nC-34 were very high. Distinct variations were observed for the volatile materials lower than nC-34, and of the 110 samples analyzed, the median value of residual material with molecular weights greater than nC-34 was 64%. Of the samples analyzed, 90% had residues of the nC-34+ material ranging between 38-80%. In a number of the sample, large peaks were observed at nC-20 and nC-23, and unlike refined or crude petroleum products which show a smooth distribution curve throughout the distillation range, the presence of these compounds suggest biogenic material or manufactured chemicals. Most of the samples exhibiting this behavior came from New York Harbor, and were believed to be influenced by urban and/or industrial activities. Only two of the samples had appreciable lower molecular weight compounds between nC-10 and nC-30 (5 and 12%, respectively); however, the n-C34+ residue contents were the highest in these samples [70 and 80%, respectively), and the presence of the low boiling components was taken to suggest that the samples had a relatively short history in the marine environment.

The 110 samples were organized into five groups depending on the molecular weight distributions of the alkanes observed. Tar, asphaltene and resin characterizations were completed on the samples, and sulfur contents in the tar ranged from 0.1 to 2.7%. The asphaltene fractions generally had higher levels of sulfur, with most samples in the range of 1-3.5%. The resin fractions contain sulfur compounds in approximately the same range as the asphaltenes. Infrared spectra of the tar and asphaltene fractions were similar to petroleum derived waxes and oxidized petroleum products, and generally, the presence of oxygenated carbon compounds was suggested.

The authors concluded that two distinct sources for the types of tar samples were indicated. One appeared to be due to urban and industrial waste products, and the other included petroleum based materials modified by various weathering processes. High sulfur content was noted in tar samples collected from Florida, suggesting that the samples originated from sour crudes known to be transported in that area. The substantial presence of specific components at nC-20 and nC-23, and low sulfur contents with notable carbon double-bond oxygen infrared absorption suggested that most of the samples from the New York Bight were derived from waste or manufacturing processes. The higher boiling normal n-alkanes found in many of the open ocean samples were attributed to materials found in discharges from tanker washing and ballasting operations. It was interesting to note that in some instances several samples collected from the same vicinity showed similar composition values; however, many samples collected at the same locations showed no correlation of composition with location.

Wade et al. (1976) analyzed a number of smaller tar particles (0.3 μ m to 1.0 mm diameter) by gas chromatography and infrared spectrometry and found that the pelagic tar samples averaged about 32% water (with a range of 11-44%) and 68% dry weight material. Butler et al. (1973) found that tar lumps from the Atlantic ocean typically contained about 25% water by weight. An average of 53% of the wet tar was soluble in benzene (range of 31-89%) and this material counted for approximately 78% of the average dry weight of the samples.

The benzene insoluble fraction of tar **was** reported to possibly include **inorganic** salts, nonorganic debris and higher molecular weight material. The wet tar samples averaged about 16% total hydrocarbon material, and the remaining weight percentage included **non-hydrocarbon** organic material, or hydrocarbons not measured by **their** procedures (for example, hydrocarbons less than nC-14 and greater than nC-38). Jeffrey et al. (1973) found that Gulf of Mexico pelagic tar samples contained 26% **asphaltenes** on average, based on the dry weight of sample. The gas **chromatographic** analyses showed that the hydrocarbon weight percent was predominantly from components in the unresolved complex mixture (average 79% -- range of 67-97%) which would include a complex mixture of aromatic and cycle-paraffin compounds. Different degrees of resolved **alkanes** were observed in the different samples, with several showing **no** resolved peaks over the UCM, and one showing an evenly repeating series of **alkanes** from nC-15 to nC-34. A number of other samples showed **alkanes** only above nC-25, with evidence of persistent **pristane** and **phytane** suggesting microbial degradation of the lower molecular weight normal paraffins. Infrared analyses showed that of the 8 samples considered, all but 2 contained aromatic hydrocarbons.

The elevated levels of NSO compounds found in a number of tar balls are frequently higher than what might "be expected from simple evaporation and dissolution of weathered crude. This enrichment could quite easily come from the formation of NSO compounds from petroleum hydrocarbons by photo and microbial-oxidation. While these photo-oxidized NSO compounds would have enhanced water **solubilities** and might be expected to be removed from the tar mass, increased diffusion coefficients as a result of elevated viscosities and specific gravities may prevent these materials from being lost. Also, with **semi-fluid** tar masses folding over on themselves and aggregation of **small flakes** during tar ball formation, these materials can be entrained in the **interior** where ultimate loss **would** be inhibited by decreased **diffucivities** in the viscous residues. Further, bacteria have been shown to coat the surface of tar **balls** (Butler 1973), and oxidation products, cellular materials and bacterial **cell wall** components can contribute to the residual **nonchromatograph-able** materials and NSO compounds.

Sources of Pelagic Tar

It is generally accepted that waxy crude-petroleum sludge from cargo tank washings of tankers is a major source of much of the pelagic tar which has been isolated from the world's oceans (Butler, et al., 1973; Long et al., 1973; Koons, 1973; Berridge, et al., 1968a; and Blumer et al., 1973). Evidence for this source comes from the high content of ferric oxide (as high as 18% on a dry weight basis) in some residues (Attaway et al., 1973) and the predominance of paraffin-rich wax inclusions which are a common feature in open ocean tar balls (Blumer et al., 1973). The increased levels of iron are believed to originate from rust particles picked up by the oil from steel tanks or apparatus encountered during pumping, storage and transport of petroleum by ocean going tankers. The paraffin rich wax inclusions, which are found in many tar balls, are believed to result from the waxy precipitates which can form during production and transport of petroleum products. In general, normal alkanes are relatively soluble and uniformly dispersed throughout most oils. With long storage and transport at lowered temperatures, however, these materials can precipitate in a form which adheres to surfaces causing problems in pipelines and tanks (Blumer et al., 1973). This formation during transport in oil tankers is one of the reasons that necessitates "tank cleaning, and the fact that such waxy precipitates are not present in free flowing oil, in submarine seeps or oil from blowouts lead Blumer et al. (1973) to propose their presence as an unequivocal characteristics of oil from tankers either not equipped for load-on-top procedures or not following that technique. The authors also hypothesized that these waxy aggregates may play an active role in the formation of tar balls, since the higher molecular weight waxes are not readily dispersed and can provide a nucleation site around which additional floating oil may accumulate. Thus, McAuliffe (1977) stated that most of the tar balls stranded on many beaches was believed to come from tanker compartment washings, Bunker C discharges or bilge pumping, and he added that most crude oil spills probably contribute little oil appearing as tar balls. Field observations from a number of open ocean and near-coastal spills have shown that this is not necessarily the case. As described

in the previous section on Case Histories, tar balls were reported to form in significant quantities after the tanker Arrow spill, the Metula spill, Ekofisk Bravo blowout, the Potomac spill, and the IXTOC-I blowout in the Bay of Campeche. Also as Mommessin and Raia (1975) demonstrated, industrial and commercial discharges are another source of tar samples.

Fate of Pelagic Tar At Sea

Wade et al. (1976) suggested that the ultimate fate of many large tar patches would be fracturing and break-up caused by sea-surface turbulence and agitation. They approximated this behavior by shaking a 1 cm pelagic tar lump in filtered Narangansetts Bay water at room temperature for a period of 4 weeks. The mixture was filtered through a 1 mm mesh screen, and it was found that the larger particles (greater than 1 mm) still retained the basic gas chromatographic features of the original tar. The smaller particles (less than 1 mm) contained mostly unresolved hydrocarbons, and in that regard, were similar to extracts of whole-water samples collected in the Sargasso Sea at the time the larger tar balls were collected. Thus Wade et al. suggested that the major source of hydrocarbons (primarily cycle-paraffins) which were found in their unfiltered Sargasso seawater samples was from particles of weathered pelagic tar in the size range from 0.3 μm to 1 mm in diameter.

Large tar particles have also been shown to support several marine organisms (Mommessin and Raia, 1975; Horn et al., 1970), and increased colonization would be expected to eventually lead to sinking when the buoyancy of the tar ball was overcome by the weight of attached organisms. An isopod (Iodotea metacallica) 10-25 mm in length tended to stay with the tar ball it was isolated with when placed in a bucket onboard a research vessel (Horn et al., 1970), and the goose barnacle (Lepas pectinata) was frequently found attached to well weathered (firm) tarry lumps. At one location, four tar lumps had a total of 150 barnacles (2-8 mm in length) whose growth rate was measured at 1 mm per week indicating a minimum age for the tar of 2 months (Horn et al.,

1970). As noted in the IXTOC spill, and by Mommessin and Raia above, other detrital materials are also associated with tar lumps, and accumulation of these can also lead to increased density and eventual sinking. High levels of suspended particulate material have been found in tarry residues collected off of Florida (Attaway et al., 1973), and it was noted by Gundlach et al., (1981) that sand encrusted tar balls resulting from the IXTOC-I spill were rapidly removed from the mid and lower intertidal zones of several Texas beaches during storm activities. These tar balls were found along the bottom, within the shoreline break and swash zone. Seaward of the first sand bars, however, they became very sparse and were presumably dispersed by nearshore currents. Tar balls generated from heavier crudes, or some petroleum products such as Bunker C, can obtain high enough densities with the loss of volatile and soluble components to reach near bottom waters at significant rates. Following a Bunker C oil spill in San Francisco Bay in 1971, one to three cm, near buoyant oil drops were observed by remote control television moving just off the sea floor with bottom currents in 30 feet of water in Bolinas Bay (Conomos, 1975; McAuliffe, 1977). Thus, most pelagic tars are believed to eventually break up during weathering at sea. These smaller droplets are then dispersed in near-surface waters, and most are believed to remain suspended and be dispersed by water currents (Brown et al., 1973; Brown et al., 1975; Brown and Huffman, 1976).

Microbial degradation of large tar balls is believed to be only a minimal factor in their fate since oxygen and nutrient levels would not diffuse into the tar balls at sufficient rates to sustain degradative processes. Bacterial utilization of the smaller dispersed materials would be enhanced by the increased surface area-to-volume ratio, and it may play a more important role in their ultimate degradation.

Butler (1975) evoked a simple semi-quantitative model of evaporative weathering to estimate the breakup and residence time of petroleum residues at sea. This model presumed that the evaporative losses were proportional to the

components equilibrium vapor pressure and the amount remaining in the sample at a given time. It was stated that the equilibrium vapor pressure would not be precisely equal to the vapor pressure of the pure compound because petroleum is a mixture of compounds, however, large variations in the activity coefficients as weathering processes occurred were not anticipated or incorporated into the model. Although it was noted that as evaporation occurs at the surface and loss of components within the slick would become limited because of diffusion control, the prospect for diffusion control was not included in the model. To more closely approximate observed oil spill behavior, however, artificial parameters were invoked to limit compounds larger than nC-16 from diffusing into the surface sheen around the larger tar patches. On the basis of a mass balance approach (combining estimates of the standing stock of tar with estimates of the amount of oil spilled annually and the fraction of this oil which remains as pelagic tar) a residence time on the order of 1 year was obtained in earlier studies (Morris 1971; Butler et al., 1973). This was not consistent with the predicted lifetime from the evaporative weathering model, however, unless the diffusion rates were smaller than expected or the lumps collected at sea were but fragments of original lumps from which weathering began (Butler et al., 1976). Both of these hypotheses were concluded to be applicable, but they did complicate the quantitative dating of tar lumps. Estimating the lifetime of pelagic tar at sea is further complicated by the observed tendency of larger tar balls to break up into one μ m to 1 mm fragments which can be dispersed to depths more than 100 m into the water column.

As noted in the Arrow spill, ingestion of oil particles by copepods can enhance their sedimentation rates, however, it is still unclear at this time whether the ultimate fate of dispersed petroleum residues in the open ocean is biodegradation or sedimentation. From the few sediment samples which have been analyzed from the top 5 cm of the deep ocean floor in the Sargasso Sea, hydrocarbon distributions appear to be a mixture of biogenic and petroleum mixtures, and the concentrations of these materials (on the order of 50 mg/m²) are comparable to those of particulate in the water column found near

the surface (40 mg/m^2) (Barrington and Trip, 1975; Butler et al., 1976). It is not possible, however, to directly correlate these observations because of complications from horizontal **advection** and the fact that it was not clear how deeply buried the material analyzed actually was, or what the ratio of petroleum to **biogenic** hydrocarbons might be (Butler et al., 1976). Evidence from the **Ekofisk** and **IXTOC I** blowouts also suggests that **little** of the released oil from either of these **events** ended up in the sediments near the **well** sites, but as noted in the section on Case Histories, these results may have been influenced by the sampling techniques (Smith-McIntyre grab samplers) and significant **re-suspension** of the bottom due to severe storm activities prior to **sampling** the sediments in the **IXTOC spill**.

When degradation rates of known oil concentrations in **benthic sediments** have been studied, they were found to be very concentration dependent (Griffiths and Morita, 1981). Payne et al. (1981b) [cited in Griffiths and Morita (1981)] studied the chemical changes which occurred in oiled sediment **plots** in 15-30 meters of water in the sub-arctic environment of **Kasitsna Bay**, Alaska. The results of these studies showed that the most significant weathering of the oil occurred at the air/sea interface or in the water column before the oil was incorporated into **the** sedimentary regime. In an experiment where both fresh and weathered Cook **Inlet** crude oil were spiked into the sediments at one part per thousand (**ppt**), **n-alkanes** were depleted, but very little significant **loss** of higher molecular weight aromatic hydrocarbons occurred over a one year period. At spiked levels of 50 ppt (with both fresh and weathered crude oil), nearly complete inhibition of **abiotic** and microbial degradation of **aliphatic** hydrocarbons was also observed, especially for those sediments spiked with fresh crude. In the 0.1 ppt spiked samples, there was little or no evidence of either **aliphatic** or aromatic hydrocarbon contamination **after** one year. Sediment plots spiked with fresh and weathered crude oil at 50 ppt plus added nutrients (starch and Chitin) showed no evidence of enhanced biotic recovery or selective hydrocarbon utilization. It was suggested, however, that this lack of recovery may have been from the toxic aromatic compounds in the oil itself, rather than from inhibition of microbial activity by limited nutrient concentrations.

Fate of Beached or Stranded Tar Balls

The occurrence of tar ball residues on beaches have been reported on an almost **global** scale (Morris and **Culkin**, 1974; Morris and Butler, 1973; Butler et al., 1973; Saner and Curtis, 1974; **Sleeter** et al., 1976; Wong et al., 1976; **Dwivedi** and **Parulekar**, 1974; and Attaway et al., 1973). Table 8, adapted from Clark and MacLead (1977), presents the tar **ball** residues observed on beach surfaces from a variety of locations.

Because of the ease of accessibility to stranded tar **balls** on beach surfaces, their fate and weathering have been better characterized compared to tar **balls** dispersed in the water column. As was the case for major oil spills impacting intertidal zones (considered in the section on selected Case Histories), the results of the studies on isolated tar ball degradation suggest that weathering rates are also dependent upon the degree of exposure, availability of nutrients and extent of mixing into the intertidal sediments. Obviously, aside from aesthetic factors, the environmental impacts of tar ball **stranding in** intertidal zones are far less serious than those which occur from massive **oilings**.

Blumer et al. (1973) conducted a **detailed** study on the chemical changes which occurred to stranded tar in Bermuda and in **Falmouth Harbor**, near **Woods Hole**, Massachusetts. In general, evaporation processes predominated, and after 13 to 16 months the oil retained about 10% of the compounds boiling near **nC-17** to **nC-18** and 50% of those compounds boiling between **nC-19** and **nC-21**. Compounds above **nC-23** to **nC-24** were not significantly evaporated **during** the extended time spans. In contrast, oil incorporated into bottom sediments and organisms soon after a spill shows little evaporative loss even as low as **nC-12**. Climatic differences between Martha's Vineyard and Bermuda had only minimal effects on the evaporative loss. In the Bermuda station, the oil formed a crust **which** cracked after extended times exposing additional surface area, and this perhaps increased evaporative loss slightly.

TABLE 8

Summary of 1971-1976 Stranded Tar Ball Distributions
and Concentrations on Beach Surfaces
(adapted from Clark and MacLeod, 1977)

<u>Description of tar samples</u>	<u>Amount of tar residue (g/m*)^a</u>	<u>Reference</u>
<u>Geographic area</u>		
Southwest Florida coast, 1 km of shoreline	23	Saner and Curtis, 1974
Bermuda	190 (mean)	Butler et al, 1973
Barbados, Windward shore	40-62	Sleeter et al, 1976
Leeward shore	4.5	Sleeter et al, 1976
Puerto Rico, North shore	52-112	Sleeter et al, 1976
West shore	12-20	Sleeter et al, 1976
Central Caribbean island, Windward shore	13-230	Sleeter et al, 1976
Leeward shore	0-2.2	Sleeter et al, 1976
Honduras , Windward shore	90-127	Sleeter et al, 1976
Southern California		
Sunset Beach (Long Beach)	0.018-1.35	Ludwig and Carter, 1961
Torrance (Los Angeles)	0.006-0.92	Ludwig and Carter, 1961
Mussel Shoals (Sea Cliff)	0.003-0.60	Ludwig and Carter, 1961
Summerland Beach (Santa Barbara)	0.002-0.38	Ludwig and Carter, 1961
Coal Oil Point	1.22-23.9	Ludwig and Carter, 1961
Gaviota Beach	0.023-1.01	Ludwig and Carter, 1961
Beaufort Sea, Canada 264 km of shoreline (1974)	No tar residues	Wong et al, 1976
Yukon 16 km of shoreline (1974)	380 g grease	Wong et al, 1976
N.W.T. 10 km of shoreline (1974)	425 g grease	Wong et al, 1976
N.W.T. 86 km of shoreline (1974)	157 g grease & asphalt	Wong et al, 1976
West India coast	4,460 (max.)	Dwivedi and Parulekar , 1974

^a In g/m² except where otherwise indicated.

Microbial degradation of the **n-alkanes** and other components in the stranded oil depended very significantly on the presence of nutrients. Oil ed rocks placed in enclosures high in the intertidal zone showed essentially no microbial degradation. In the presence of decaying seaweed in this upper intertidal-zone enclosure, **alkanes** were depleted within 4 months. In the absence of decaying plant material in the upper intertidal splash zone of the Bermuda station, microbial degradation occurred at significantly **slower** rates than at Martha's Vineyard, but they were faster than the Martha's Vineyard rock sample that was maintained above the highest high-water line. When **microbial** degradation did occur, lower molecular weight components were utilized completely before higher molecular weight compounds above **nC-25** were degraded. Limited information on dissolution of aromatics and cyclic compounds appearing in the gas **chromatographic** unresolved complex mixtures suggested that this dissolution process was extremely slow and limited to compounds occurring in the UCM before **nC-20**. After 13 1/2 months of exposure at Bermuda the oil showed little evidence of purely chemical alteration. The initial ratio of saturate to aromatic hydrocarbons was preserved, and the **asphaltene** and **hydroxyl** content were not significantly increased. A modest increase in ester or acid content was noted; however, after 13 1/2 and 16 months at Bermuda and Martha's Vineyard, respectively, the **spill** residues were **still** far from inert asphalts. They had not been depleted of the more biologically active higher molecular weight aromatics, and the half life in terms of contamination potential for **such** beached materials was estimated to be in terms of years.

DEVELOPMENT OF ALGORITHMS AND COMPUTER PROGRAMS TO
SIMULATE THE FORMATION OF WATER IN OIL EMULSIONS

Numerous mathematical formulations have been generated to describe various individual aspects of water-in-oil emulsion behavior including: 1) the work (or mixing energy) required to generate emulsions, 2) the viscosity changes of water-in-oil emulsions as a function of water content, 3) the **competitive** process of dispersion of oil and mousse into the water column (oil-in-water dispersion), 4) the thickness and spreading of oil and mousse, and 5) the breakup or decomposition of slicks based on evaporation and dissolution weathering and creaming (mousse destabilization by separation of water and oil into distinct phases). Unfortunately, no single oil weathering model exists at this time which encompasses all of these factors, and Mackay et al. (1980) have stated that it is impossible to completely model water-in-oil emulsion formation and behavior because of the lack of a sound understanding of the physical chemistry of this system. Perhaps the most pragmatic and successful approach to **this** problem has been to postulate a realistic mechanism for the emulsification process, and relate the viscosity of the resultant mousse to the water content (Mackay et al. 1980). Algorithms for each of these various separate, but interconnected processes will be considered briefly below.

In citing work completed by **Becher** (1955), **Twardus** (1980) stated that **the** work or energy required for generation of **either** water-in-oil or oil-in-water dispersions could be theoretically calculated. Before emulsification occurs, the interracial area between two **emiscable** liquids is at a minimum and is essentially determined by the surface tension values of the two liquids. Following emulsification, it is assumed the **droplets** of the first liquid (A) are dispersed into the second (B). **If all** droplets are considered, the **inter-racial** area between liquids A and B is increased, and since liquids tend to keep their surfaces to a minimum, an emulsifying agent and work (or energy) are clearly required to allow emulsification to occur. In theory, the amount of work (ω) required to increase the surface area by an amount (S) can be given by the following formula from **Becher** (1955)

$$\omega = \gamma \Delta S$$

where γ is the interracial tension between the two liquids. An emulsifying agent, as noted in previous sections, may be any surface active substance which forms a thin interracial film between liquids A and B maintaining the emulsion by minimizing the contact and aggregation of the dispersed liquid. Additional chemical properties of this stabilizing agent are discussed by Twardus (1980) and were considered briefly in the general discussion of emulsification processes in Part 1 of this paper.

Taking advantage of the considerable literature on the rheological properties of suspensions of rigid particles, Mackay et al. (1980) have used the Mooney equations (Mooney, 1951; Mooney & Hermonat, 1955) to develop a relationship between the viscosity of mousse and its water content

$$\mu/\mu_0 = \exp(2.5W/[1-K_1W])$$

where μ is the apparent mousse viscosity, μ_0 is the apparent oil viscosity, W is the fractional water content of the emulsion and K_1 is a constant. Figure 8, from Mackey et al. (1980), shows a plot of the curves generated with this equation and the fit of experimental data obtained for six crude oils. Although there is some spread in the data, the equation gives a good average fit to the measured viscosities. It was noted by Mackay et al. (1980) that the oils usually exhibited non-Newtonian behavior, causing the viscosity ratio to depend on the shear rate as well as the water content. Similar findings have been reported by Bridie et al. (1980b). As noted by Berridge et al. (1968b), the increase in viscosity for these oils is most significant after the water content has reached 50%, and before that point many have the basic flow properties and appearance of the starting crude.

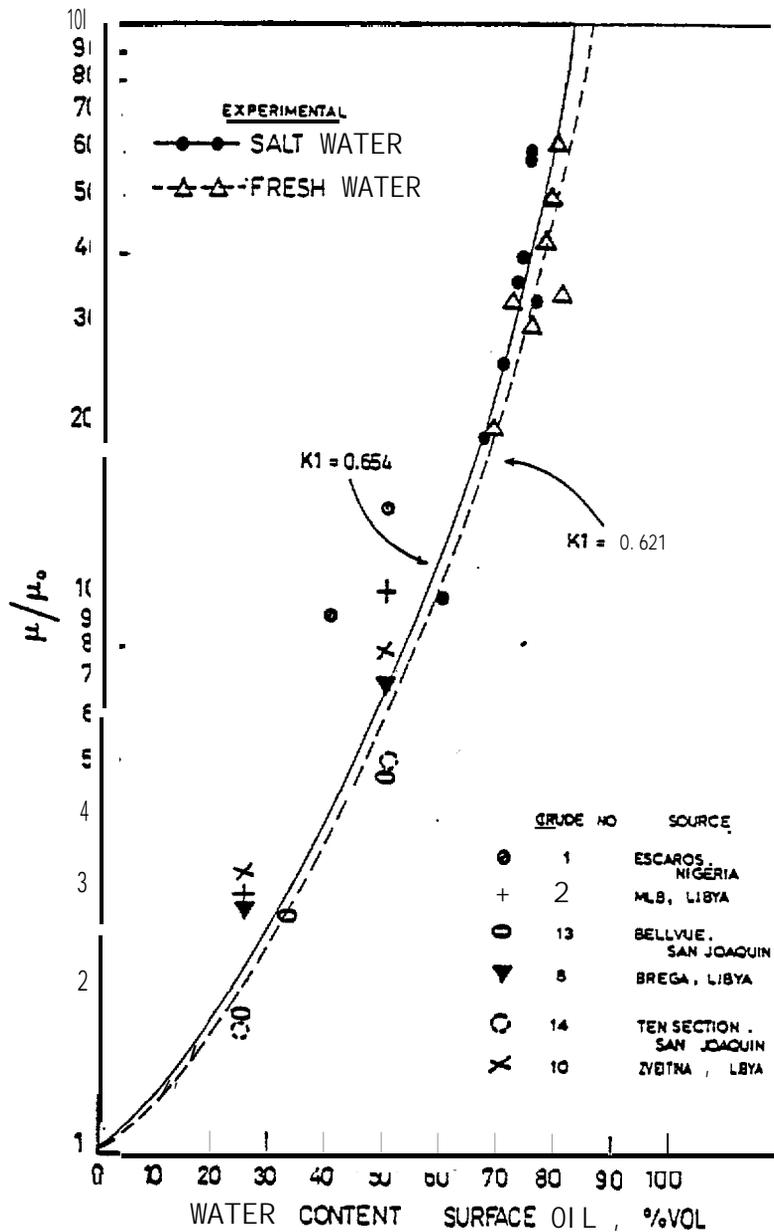


FIGURE 8. MOUSSE/OIL (μ/μ_0) RELATIVE VISCOSITY RATIO OF SIX TEST CRUDE OILS AS A FUNCTION OF WATER CONTENT. (MACKAY ET AL., 1980.) REPRODUCED BY PERMISSION OF THE AUTHOR.

Mackay et al. (1980) then used these relationships to develop a kinetic expression to describe the processes of water uptake and release. The rate of water incorporation into the oil (I) was postulated to depend on the sea state (S) and the viscosity of the oil as follows:

$$I = K_i S / \mu \quad \text{m}^3/\text{m}^2 \cdot \text{s}$$

The rate of coalescence or water removal (R) was estimated to be dependent on the oil composition, its water content, the viscosity and the slick thickness (D) as follows:

$$R = K_r W / \mu D \quad \text{m}^3/\text{m}^2 \cdot \text{s}$$

where K_r is a coalescing tendency constant.

Thus at any time the net rate of water incorporation would be:

$$d(VW)/dt = A(I-R)$$

where V is the emulsion volume and A is the area. Thus, D is V/A. Substituting yields:

$$dW/dt = (K_i S / \mu - K_r W / D^2) / \mu$$

Complete discussions of the derivation of these equations and their basis on physical properties is beyond the scope of this review, and the reader is referred to the original articles by Mackay et al. for details.

The general solutions to the differential equations generated in this paper were presented, however, explicit solutions could only be provided when the water-in-oil emulsion showed no tendency for coalescence (because of high concentrations of surfactant or coalescence preventing materials) or when the rate of water removal equalled the rate of water incorporation and the viscosity and water content stabilized at a constant value. This limitation

applies to oils which do not exhibit a mousse forming tendency. Nevertheless the equation did have predictive capabilities in generating emulsion formation rates and extents for a variety of oils ranging from heavy fuel oils, which exhibit rapid stable emulsion formation to light distillates, which reject water rapidly, and thus show little or no emulsion formation tendencies.

Data from Cormack and Nichols (1977), who reported water contents for three spills of Ekofisk oil, were fit to curves generated with the proposed equation (Figure 9), and very acceptable fits of the observed field data and predicted water uptake for varying wind speeds were obtained. Half times of emulsion formation were generated from these studies, and values of 2.8 hours at 3.1 knots, 16 minutes at 10 knots and 1.6 minutes at 31 knots were obtained (Mackay et al., 1980).

A simpler finite difference form of the equations used to describe the process of emulsion formation was also presented by Mackay et al. (1980) and this is presented below.

$$\Delta W = K_A (U+1)^2 (1-K_B W) \Delta t$$

where

W is the fractional water content

K_A is a constant

K_B is a constant with a value of approximately 1.33

U is the wind speed

t is time.

Until more experiments data are available, it was suggested that this simpler version would be adequate for describing emulsion formation.

In that Mackay et al. (1979, 1980) and others have noted that mousse formation and oil-in-water dispersion are competitive processes for any given

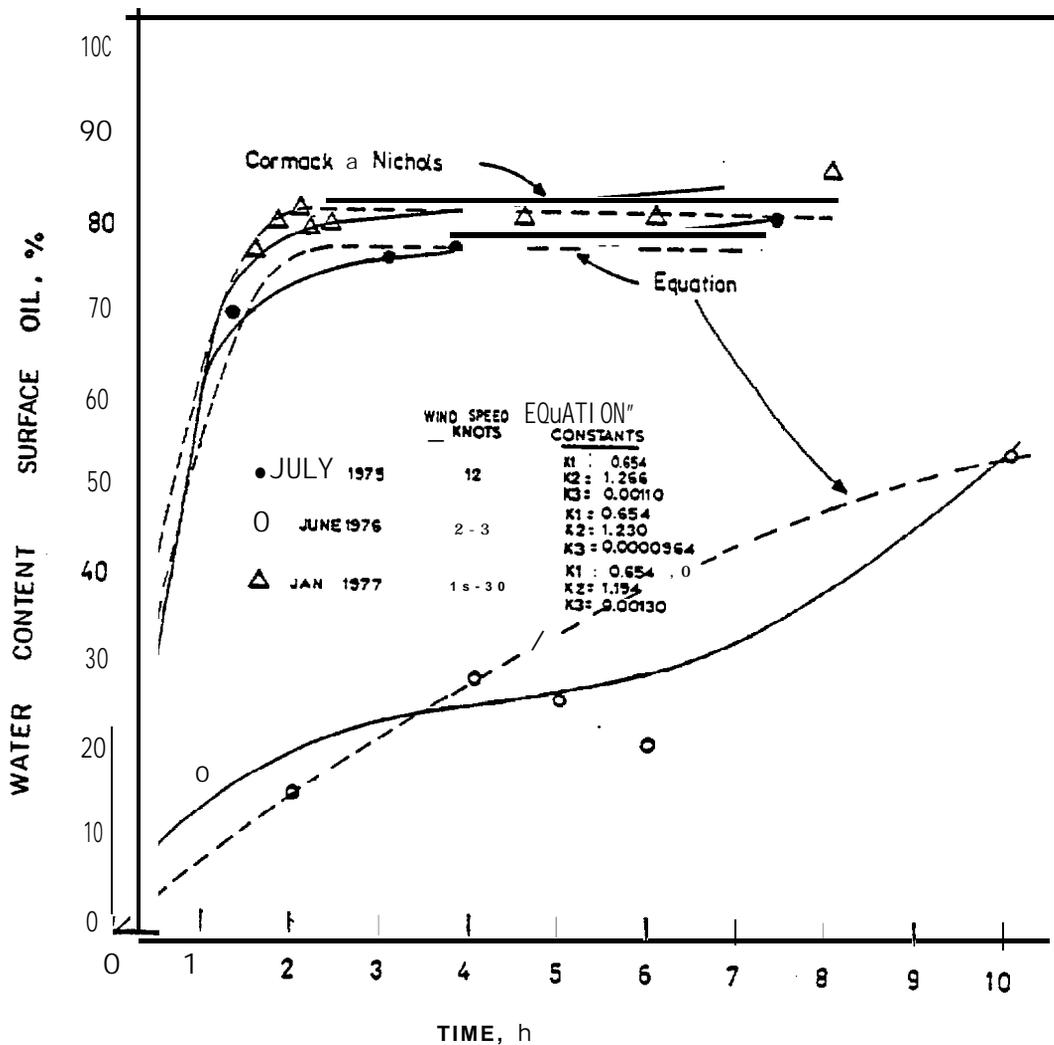


FIGURE 9. COMPUTER MODEL - PREDICTED AND OBSERVED (CORMACK AND NICHOLS, 1977) TIME-DEPENDENT UPTAKE OF WATER INTO EKOFISK OIL AS A FUNCTION OF WIND SPEED AND SEA-STATE. (FROM MACKAY ET AL., 1980.) REPRODUCED BY PERMISSION OF THE AUTHOR.

oil under certain temperatures and sea conditions, algorithms were also developed to describe the oil-in-water dispersion phenomena. Because fast dispersing slicks will yield entirely different environmental impacts than emulsified slicks, the capability of predicting which process would dominate is believed to be invaluable in spill response counter measures. Thus, in certain situations if natural oil slick dispersion into the water column could be predicted, such information would be valuable in decisions as to whether or not chemical dispersants should be applied.

As noted in many of the case histories of major oil spills and in a number of laboratory studies, oil slicks exposed to sea surface turbulence tend to break up into oil droplets, and some of these are sufficiently small that they are essentially permanently incorporated into the water column where they are later dissolved and microbially degraded. The larger drops tend to return to the surface and presumably coalesce with the slick. The mechanisms for the formation of these droplets are far from clear, and Raj (1977) has suggested that the dominant mechanism is wave breaking or white capping in which the water plunges into the oil slick driving it under the surface. It is also possible that other mechanisms are operational when oil is dispersed under calmer non-wave breaking conditions, and other factors such as rainfall, slick stretching-compression or Langmuir circulations can carry oil into the water column.

Mackay et al. (1980) have examined the dispersion process on two laboratory scales, and they have developed theoretical equations which are reasonably consistent with experimental results. Oil is believed to be dispersed from the slick by the sum of two rates, R_B by a wave breaking mechanism and R_N by non-wave breaking mechanism. The units for both processes are $g/m^2 \cdot s$. The particulate oil droplets are initially dispersed into the well mixed near surface layer to a depth U meters which is determined by the depth of the plunging wave. While in this layer, the larger drops can rise and coalesce with the slick, and thus, they are only temporarily dispersed. Smaller droplets having a lower rising velocity become permanently dispersed

and diffuse (in part) vertically down into the less well mixed layer of depth Z meters in which the vertical diffusivity (D) is m^2/s . With constant wave turbulence, the concentration of the small or potentially permanently dispersed droplets is a constant C_S in the well mixed layer and a variable C in the layer of depth Z . C increases with time at any given depth and concentrations are in g/m^3 . The rate of diffusion into the less well mixed layer R_D is the product of diffusivity D and the gradient in C at the interface between the layers where Z is equal to zero. That is,

$$R_D = D(dC/dZ)_{Z=0} = C_S K_1$$

where K_1 is the mass transfer coefficient (m/s).

Two different size classifications were considered for the model. Large drops (arbitrarily greater than 0.1 mm diameter) rise quickly at a velocity of V_L m/s and coalesce with the slick. Smaller drops (arbitrarily less than 0.1 mm diameter) have a lower rising velocity V_S m/s and may coalesce or may diffuse downwards. Their fate is thus controlled by these two competing processes. If the concentration of the large drops is C_L then the rising flux must be $V_L C_L$ $g/m^2 \cdot s$, and similarly for the small drops the rising flux is $V_S C_S$ $g/m^2 \cdot s$. Adding these two fluxes to give the total coalescence rate R $g/m^2 \cdot s$ yields:

$$R = V_L C_L + V_S C_S \text{ g/m}^2 \cdot \text{s}$$

When a differential equation is written for this upper layer, one obtains

$$R_N + R_B - R_c - R_D = U d(C_L + C_S)/dt$$

When a quasi-steady state is obtained the right hand side becomes zero.

If it is postulated that the volume fractions for the small dispersed oil drops for the two dispersion mechanisms are F_N and F_B for non-breaking and

breaking sea states, respectively, the above equation can be broken down into small and large components. For small droplets

$$F_N R_N + F_B R_B - V_S C_S - R_D = U dC_S/dt$$

Substituting $C_S K_1$ for R_D , separating variables and integrating yields

$$\ln(F_N R_N + F_B R_B - C_S [V_S + K_1]) = -t(V_S + K_1)/U + \text{constant}$$

Although the mass transfer coefficient, K_1 , is time dependent, it was taken as a constant and at the initial condition C_S was set to zero.

Thus ,

$$C_S = \frac{(F_N R_N + F_B R_B)}{(V_S + K_1)} (1 - \exp[-t(V_S + K_1)/U])$$

and at large time intervals, the quasi-steady state in C_S is reduced to

$$C_S = (F_N R_N + F_B R_B)/(V_S + K_1)$$

Likewise, for large drops after extended time, the concentration can be shown to reduce to

$$C_L = ([1-F_N]R_N + [1-F_B]R_B)/V_L$$

Details for these derivations are given in Mackay et al. (1980), and separate algorithms for non-breaking wave dispersion and breaking wave dispersion were derived. For the non-breaking wave dispersion mechanism it was suggested that the following equation applies:

$$R_N = K_2 X^n$$

where R_N is the dispersion rate ($g/m^2 \cdot s$), K_2 is a constant dependent on sea state, X is the slick thickness in meters and n is a constant. This equation had the correct properties such that when X is zero R_N is zero. Unfortunately, this equation also has the undesirable property that if n is negative R_N approaches infinity when X goes to zero. Thus, Mackay et al. suggested that a better formulation where n can be positive would be

$$R_N = K_A / (1 + K_B X^n)$$

The dependence of K_2 on sea state in the first equation above 'can only be suggested very approximately, a reasonable form of dependence being

$$K_2 = K_3 S^m$$

where K_3 is a constant, S is the sea state and m is a constant which was arbitrarily assigned a value of unity in absence of information to the contrary. From these equations it was possible to drive an algorithm for the slick life time τ

$$\tau = X_0^{1.25} \rho / (1.25 K_3 S)$$

where X_0 is the initial slick thickness and ρ is the oil density. For illustrative purposes, life times of slicks of variable thickness were then calculated. Illustrative data are presented below:

Initial Slick Thickness	τ -- Slick Lifetime
1 cm	290 days
1 mm	16 days
0.1 mm	22 hours
10 μm	75 minutes
1 μm	4.1 minutes

In summary then, it was suggested that for non-wave breaking conditions an expression for the dispersion rate into small droplets be used of the form

$$R_{NF_N} = K_3 S^m X^{-0.25} \text{ g/m}^2 \cdot \text{s}$$

where K_3 will probably have a value of approximately 10^{-4} and M a value of 1.

Similar derivations were presented for the wave-breaking dispersion model; however, the authors concluded that this mechanism like the non-breaking dispersion mode was **only** poorly understood, and that their equations could be criticized as containing an excessive number of adjustable parameters. Further, there were insufficient data to justify the equations complexities. Therefore, a simpler set of equations were derived and presented in finite difference form suitable for incorporation into oil spill models. The breaking and non-breaking dispersion algorithms were then combined in one process, the rate of which was given by

$$F = K_A (U + 1)^2$$

where

F is the fraction of sea surface subject to dispersion per second

U is the wind speed

K_A is a constant, and

$$F_B = 1 / (1 + K_B \mu^{0.5} X \cdot \gamma)$$

where

F_B is the fraction below the critical size

K_B is a constant

μ is viscosity

X is the slick thickness

Y is the oil-water interracial tension.

The rate of dispersion is then, $FX \text{ m}^2/\text{m}^3 \cdot \text{s}$, and the breakdown into large and small droplets was described as before.

With regard to modelling the thickness of oil and water-in-oil emulsions spreading at sea, Blokker has developed an equation for a circular oil spill where the slick diameter (D) in meters at a given time (t) can be determined as follows:

$$D^3 = \frac{24}{\pi} K_r (d_w - d_o) \frac{d_o}{d_w} V_o t + D_o^3$$

where

D is the slick diameter in meters

d_w and d_o are the density values for water and oil (g/cm^3)

V_o is the original oil volume, in meters^3

t is the time following the oil spill, in minutes

D_o is the immediate slick diameter at $t = 0$, and

K_r is a constant, depending on the oil type.

From spreading experiments performed with various crude oils, Berridge et al. (1968a) modified the Blokker equation to estimate the relationship between slick thickness and the time following a spill. From this work the slick thickness was calculated as follows:

$$\text{thickness} = \frac{K'}{t^{2/3}}$$

where:

t is the time, in seconds.

$$K' = \left[\frac{v}{\pi} \right]^{1/3} \left[\frac{D_w}{3D_o(D_w - D_o)K_r} \right]^{2/3}$$

v is the volume of oil, in cm³

D_o and D_w are the densities of oil and water, respectively (in g/cm³)

K_r is a constant, depending on the oil type.

Although neither of these models was designed to accommodate the emulsification process, Twardus (1980) stated that the change in spreading tendency caused by the water-in-oil emulsification could be approximated by substituting a higher value of oil density in both models. Thus, under the same conditions the equations predict that emulsified petroleum will spread less readily and will not spread as thinly over water as non-emulsified petroleum.

Grose (1979) has also reported a model which computes the thickness of bulk oil as a function of the physical characteristics of the oil and weathering parameters determined by the formation of sheen and evaporation as influenced by wind speed. The model takes into account three generally observed phenomenon:

1. Spilled oil does not form a single pool, but is rather generally composed of numerous patches of thick oil surrounded by thinner sheen;
2. The thickness of the patches is a function of the bulk physical properties of the oil and local environmental conditions including wave height, water temperature and wind speed;
3. The weathering of the individual components are dependent upon the physical-chemical properties in the original oil.

The patch thickness of the bulk oil was estimated by balancing surface tension, buoyancy and compressive forces after Grose (1978) which expanded upon the static equilibrium model derived by Langmuir (1933). The algorithm used is:

$$h = 0.01 \cdot (C_d \cdot S_w \cdot W^2) + \text{SQRT}([C_d \cdot S_w \cdot W^2]^2 - 2 \cdot FS \cdot E) / E$$

where h is the thickness in meters, Cd is the drag coefficient of the patch moving over the water surface, S_w is specific gravity of sea water, W is the relative speed of the patch through the surface water in cm/s, FS is the spreading force in dynes/cm and E is the buoyancy factor:

$$E = 980 \cdot S_o \cdot (S_w - S_o) / S_w$$

where S_o is the specific gravity of the bulk oil. The spreading forces range from +20 to -10, and are computed as the surface tension of water minus the sum of the surface tension of water and interracial tensions of the oil.

The bulk density of the patch was computed by summing masses from each fraction, and dividing by the sum of the ratios of the masses to their characteristic densities (total volume). Evaporation is computed using the bulk properties of the fractions within the patch and the vapor pressures after Mackay and Matsugu (1973). The mode? does not include parameters for emulsification or incorporation of water which would change the specific density, viscosity, total surface area and volume of the patches. Thus, some modifications would be required to predict the thickness of water-in-oil emulsions or mousse. This model was used to predict patch sizes of the Bunker C cargo lost from the Potomac off Greenland in 1977 (Petersen, 1978), and the relative agreement between predicted and observed behavior was discussed in the case history of that spill.

Several models describing the break up and dispersion of oil slicks at sea have been presented (Mackay and Matsugu, 1973; Butler, 1975a; Grose,

1979; Mackay et al. , 1979, 1980; Aravamudan et al. , 1981; Belen et al., 1981). With the exception of Butler (1975a), who used his model to predict the age of pelagic tar, most of these dispersion models do not deal directly with the ultimate weathering or fate of water-in-oil emulsions or mousse. The interested reader is, however, referred to the original articles for consideration of the oil weathering parameters which are discussed.

With regard to the destabilization of water-in-oil emulsions, Twardus (1980) stated that the separation of water from a water-in-oil emulsion could be approximated by a Stokes Law behavioral form in which the sedimentation (separation) rate (μ) of a spherical particle in a viscous liquid is given by the following equation:

$$\mu = \frac{2g r^2 (d_1 - d_2)}{9\eta}$$

where:

- g equals the acceleration due to gravity
- r equals the particle radius
- d_1 equals the density of the particle
- d_2 equals the density of the liquid, and
- η equals the viscosity of the liquid

As this equation shows, the destabilization will be faster for water droplets with a larger radius and will be inversely proportional to the viscosity of the overall fluid (a prediction in line with observed stabilities of laboratory generated emulsions).

In many of these modeling efforts, it has been stated that complete mathematical descriptions of emulsion formation (and oil weathering in general) are presently impossible because of a lack of understanding of the system's basic physical-chemical properties (Mackay et al., 1980). Thus,

although Grose (1979) had a fair agreement with the predicted patch thickness and that observed in the field after the Potomac spill of Bunker C fuel oil in Melville Bay, he too stated that the model was limited by the lack of pertinent data to determine some of the transfer rates and coefficients. This was particularly true for further parameterization of the availability of each fractional component at the air/oil interface for evaporation and the **parameterization** for sheen generation at the oil/water interface, including in particular, the availability of material for generating sheen. The availability of material for generating sheen is constrained by the total mass in the fraction and the **scale** length related to the ratio of the thickness to the diameter of the patch. **With** the Availability of Material parameter in particular, the volumetric transfer rate into sheen was assumed to be dependent only on the inverse molecular weight of fraction. The authors stated that this may not sufficiently differentiate between the more and less mobile fractions within the oil, and that it did not account for diffusion control of individual components as the viscosity of the material increased. Thus, as noted earlier, an arbitrary constant was imposed in the model to constrain the heavier fractions ($>nC_{16}$) from entering into the **sheen**.

Obviously, much more work is required before **model** simulations will be able to accurately predict slick behavior and emulsification processes, and ultimately it may be necessary to incorporate compound specific properties into such models to fully predict oil/mousse weathering for a variety of oils under different environmental **conditions**.

Research is currently **under** way in a number of laboratories, including our own to generate much of this needed compound specific data for algorithm development and model verification. Specifically, **diffusivities** of individual oil components for oils of different viscosities, and Henry's law constants for evaporation of **specific** components in different crude oils or petroleum product mixtures need to be determined. Also, the detailed and specific effects of water-in-oil emulsification on these parameters has **yet** to be elucidated.

SUMMARY

Laboratory Studies

In the laboratory studies completed to evaluate water-in-oil emulsion formation and behavior to date, it has been found that the results depend very significantly on the unique chemical compositions of the different crude oils and petroleum products tested. Heavier crudes with higher viscosities are, in general, found to form the more stable emulsions (Bocard and Gatellier, 1981), and the presence of asphaltenes and higher molecular weight waxes have been found to be positively correlated with mousse stability (Berridge et al., 1968a, b; Davis and Gibbs, 1975; MacGregor and McLean, 1977; Mackay et al., 1979; Mackay et al., 1980; Twardus, 1980; Bocard and Gatellier, 1981; Bridie et al., 1980a, b). Slightly differing results have been obtained in different investigations, but it has generally been found that these materials act together in the emulsification process, although the asphaltenes do appear to play a more significant role (Bridie et al., 1980a, b; Berridge et al., 1968b). The crystallizing properties of the component waxes (near the pour points of the oils tested) are believed to be important in affecting the internal oil/mousse structure and viscosity, and the asphaltenes are believed to act as surfactants preventing water-water coalescence in the more stable mixtures (Berridge et al., 1968b; Canevari, 1969; Mackay et al., 1973; Bridie et al., 1980a, b; Cairns et al., 1974). Other indigenous surface active agents such as metallo-porphyrin and other sulfur and oxygen compounds have been found to be equally important. The products of photo-chemical and microbial oxidation have also been identified as having an important role as stabilizing agents. In several instances, in oils where the above primary stabilizing components were not present, stable mousse could only be formed with photo-chemically or microbially weathered oils, notably Brega, Nigerian, Zarzatine and Lt. Arabian (Berridge et al., 1968b; Bocard and Gatellier, 1981; Klein and Pilpel, 1974; Burwood and Spears, 1974; Zajic et al., 1974; Friede, 1973; and Guire et al., 1973).

No stable mousses could be formed in laboratory studies at any temperatures with light petroleum distillates such as gasoline, kerosines and several diesel fuels (Berridge et al., 1968b; and Twardus, 1980). Interestingly, stable mousse formation could only be obtained with several light lube oils when they were fortified with wax and asphaltene mixtures obtained from known mousse forming oils such as Kuwait crude (Bridie et al., 1980a, b). This asphaltene mixture could also contain other high molecular weight surface active agents.

Temperature is also a factor in mousse formation, and in several instances (at lower temperatures approaching the pour point of the heavier oils), stable emulsions have been generated regardless of wax or asphaltene content. Conversely, if stable water-in-oil emulsions are repeatedly exposed to freeze-thaw cycles, some destabilization and separation of water and oil have been noted (Dickens et al., 1981, and Twardus, 1980). Similar results have been obtained when laboratory generated and real spill water-in-oil emulsions are subjected to prolonged heating on removal from the water column.

The absolute amount of water content and the size of water droplets incorporated into various mixtures of mousse also significantly affect their stability and viscosity (Berridge et al., 1968b; Mackay et al, 1980; Twardus, 1980; Bocard and Gatellier, 1981). Positive correlations of percent water versus mousse stability and viscosity have been noted for several of the crude oils studied (Mackay et al., 1979 and 1980), and, in general, the most stable emulsions from laboratory and field observations contain water droplets in the size range of from less than one to ten micrometers. Stable mousse can be formed with many oils in the range of 20 to 80% water, however, above an oil-specific critical point, significant destabilization of the emulsions occurs (Berridge et al, 1968b and Twardus, 1980). Presumably, this reflects enhanced water-water contact and coalescence resulting in ultimate phase separation.

In most of the laboratory studies, the presence and/or absence of bacteria and suspended particulate material do not appear to affect emulsion

behavior (Berridge et al., 1968a, b; Davis and Gibbs, 1975). Bacterial growth is generally limited to the surface of the mousse products tested and is believed to be inhibited by limited oxygen and nutrient diffusion into the mousse. Toxic materials inherent to the oils themselves may also be responsible for these observations, although water content (and in particular the size of the water droplets encapsulated within the mixtures) has also been correlated with bacterial infestation on the less stable emulsions (Berridge et al., 1968a, b). In several laboratory studies it has been found that significant bacterial utilization of the mousse only occurs after treatment with dispersants, resulting in the break up of the material with concomitant increased surface-to-volume ratios (Bocard and Gatellier, 1981).

Physical Properties of Water-in-Oil Emulsions

The physical properties of stable emulsions are impressively different from those of the starting crudes, and increases in specific gravity and viscosity have been observed to affect spreading, dispersion, and dissolution rates (Berridge et al., 1968b; Davis and Gibbs, 1975; MacGregor and Ncl-can, 1977; Mackay et al., 1979, 1980; Twardus, 1980; and Payne et al., 1981b). Some evidence has also suggested that evaporation of intermediate mol. wt. (C_9 to C_{12}) hydrocarbons is affected (Payne et al., 1981b; Twardus, 1980; Nagata and Kondo, 1977). In general, these effects are most significant in the emulsions containing greater than 50% water. Water-in-oil emulsions with less water usually have pour points, spreading properties and viscosities which proportionately resemble those of the starting oils (Twardus, 1980; Mackay et al., 1980).

The flash points and burn points of the water-in-oil emulsions studied have been found to vary significantly with water content, and for medium crudes, in situ combustion was inhibited when the water content reached 70% (Twardus, 1980). For heavier crudes, significant combustion inhibition occurred when the water content reached 30% (Twardus, 1980). Water dependent increases in viscosity also affect clean-up procedures as skimming, mopping,

and pumping of such mixtures becomes more difficult. The sorption capacity of various commercially available sorbent materials has also been observed to decrease as the water content in the mousse mixtures studied increases. This behavior is believed to be inherent to the hydrophobic properties of the sorbent materials examined (Twardus, 1980).

Treatment of Mousse with Dispersants

Pre-treatment of oil and/or seawater with **dispersants** or **demulsifiers** generally inhibits laboratory mousse formation with most of the oils and petroleum products tested (Berridge et al., 1968b; Bridie et al., 1980a, b). In these studies, only 0.1 to 1% **dispersant** was required, and with several of the products tested, similar results were obtained when the **dispersant** was added to either the water or oil. Previously stabilized mousse is much more difficult to break up with commercially available **dispersants**, although some success has been obtained with various products when sufficient mixing energy is utilized in the laboratory to thoroughly mix the **dispersant** into the water-in-oil mixture (Bridie et al., 1980b; Bocard and Gatellier, 1981; Lee et al., 1981). In general, however, it has been noted that with water-in-oil emulsions with viscosities greater than 4000-7000 cP, no effective break-up of stabilized mousse could be achieved (Mackay et al., 1980; Lee et al., 1981).

The ineffectiveness of several of the **dispersants** studied to break up stable mousse formations at sea has been attributed to the lack of penetration of the dispersant into the mousse and its rapid removal from the mousse surface into the water column by waves and sea-surface turbulence (Lee et al., 1981). In several planned sea tests, mousse forming **crudes** such as La Rosa, were effectively dispersed before mousse formation occurred (McAuliffe et al., 1981; JBF/API, 1976). Thicker lenses or patches of oil were observed to move along the leading (downwind) edge of these slicks, and **dispersant** effectiveness was best when the **dispersants were** applied directly to the thicker lenses or patches rather than the trailing sheen or thinner slick. Again, in the at-sea tests, mixed results have been obtained depending on the type of

dispersant/demulsifier used and the oil/mousse mixture tested. It has been noted, however, that all dispersants work better when applied to the emulsions neat, rather than when diluted with seawater.

While many of the mousse formations have not been effectively broken up by demulsifier addition in laboratory tests, significant and near immediate decreases in viscosities are often noted, and in several clean-up operations, the injection of demulsifier and dispersants into oil/mousse mixtures has greatly enhanced pumping efficiency (Bridie et al, 1980b; Bocard and Gattelier, 1981).

Case Histories of Real Spill Events

In the case histories of major open-ocean and near-coastal spills and blowouts, the occurrence of mousse formation and the subsequent fate of the mousse were found to be directly dependent upon the type of oil spilled. In general, the oils which were capable of forming a stable water-in-oil emulsion or mousse in laboratory studies were also the ones that caused the most significant problems with mousse formation in real spill situations. Thus, the Kuwait crude oil cargoes from the Torrey Canyon (Smith, 1968) and Metula (Straughn, 1977; Harm, 1977) were noted to form a very stable mousse, as would be predicted from the laboratory experiments. Likewise, the loss of the Arabian crude oil cargo and Bunker C fuel from the Amoco Cadiz resulted in stable and almost immediate water-in-oil emulsion formation (Calder and Boehm, 1981; Harm et al., 1978). Weathering of Bunker C cargoes was somewhat more variable, with significant mousse formation noted after the Arrow spill (Owens, 1978, Rashid, 1974 and Mackay et al., 1973), but no apparent water-in-oil emulsification noted for the loss of the Bunker C cargo from the Potomac (Petersen, 1977). In this latter instance, however, the cargo contained 55% pitch, and the spill occurred in very calm seas. When the Arrow went aground, intense storm activities undoubtedly contributed to the 40 to 60% water-in-oil emulsion formation. In laboratory studies using Bunker C, a rigid and sticky water-in-oil emulsion has been formed with water contents up to 60% (Berridge et al., 1968b).

in both the Arrow and Potomac spill incidents, significant break-up of the cargo into sub-micrometer to several centimeter sized oil/mousse particulates was noted, and in the Arrow spill these were observed at significant distances from the spill sight (Forrester, 1971). Ingestion of these micro-particulates by pelagic organisms was noted, and their incorporation into fecal pellets was postulated as a significant removal mechanism of such droplets from the water column (Conover, 1971).

In line with previous laboratory and field experiments using similar oils, no significant "mousse" formations were observed to occur in the Burmah Agate spill, where a light Nigerian Crude (39.3° API) was released (Kelley et al., 1981).

In the two open ocean blowouts considered in this review, significantly different results were observed. In the Ekofisk Bravo blowout, a very unstable yellowish to brown water-in-oil emulsion (35 to 72% water) was noted, but this material was rapidly broken up into smaller particles and tar patches, and was removed from the wellhead with little long-term significant environmental damage (Cormack and Nichols, 1977; Grahl-Nielsen, 1977; and Audumson, 1978). A slightly more stable mousse was observed to form with increased sea-surface weathering, but this too was unstable and disappeared after several weeks. It should be noted, however, that this crude contains very low levels of stabilizing agents (asphaltenes =0.03%). In the IXTOC I blowout in the Bay of Campeche, Gulf of Mexico, mousse formation was observed to occur only after significant evaporation, dissolution, and photochemical weathering (Atwood et al., 1980; Overton et al., 1980a). The mousse resulting from these processes was extremely stable and extensive coverage and contamination of much of the Gulf of Mexico and its adjacent shorelines was noted.

Microbial degradation of the oils released from the spills and blowouts considered was found to be extremely variable. In the Amoco Cadiz spill off of Brittany, France, microbial processes were observed to compete very

effectively with evaporation and dissolution weathering for removal of specific components in the oil while still in the water column (Calder and Boehm, 1981). In the IXTOC I blowout and the Potomac spill, on the other hand, little, if any, microbial degradation occurred to the oil or mousse in the water column over extended periods of time (IXTOC--Boehm and Fiest, 1980a; Overton et al., 1980b, Payne et al., 1980a; Buckley et al., 1980; Atlas et al., 1980; Potomac--Petersen, 1978). Long-term microbial processes were observed to be important in the fate of beached and stranded oil and mousse in the Torrey Canyon (Smith, 1968), Arrow (Vandermeulen et al., 1977), Metula (Straughn, 1977), and Amoco Cadiz (Calder and Boehm, 1981; Boehm et al., 1981; Ward 1981; Vandermeulen et al., 1981) spills, but little evidence of microbial degradation of stranded IXTOC I mousse was observed after several weeks, in samples collected up to 500 miles from the wellhead along the upper intertidal shores of Laguna Madre (Payne et al., 1980a; Overton et al., 1980b).

The long term environmental impact of oil and mousse which reaches shorelines appears to be directly correlated with the amount of coverage, the intertidal substrate type and the energy regime at the site of the oil/mousse stranding (Blumer et al., 1973). Without exception, the most significant deleterious effects have been noted in low energy lagoons, estuaries and bays, and in these instances the persistence of stranded oil may be expected to last for upwards of 10 years.

Tar Ball Distributions and Chemistry

Tar ball concentrations and compositions have been found to be variable over the world's oceans, but localized "hot spots" of significant tar ball accumulations have been noted in several areas. Quite often these higher concentrations are noted along known lines of tanker traffic or in currents downstream from these areas. In general, the Mediterranean Sea and the Sargasso Sea have similar high levels of tar balls which in turn are greater than those observed in the broader expanses of the North Atlantic and North Pacific oceans.

Chemical compositions of tar balls are extremely variable, and the physical appearance can range from brittle and hard to soft and very sticky, with sizes ranging from several mm to tens of cm (Butler, 1973, Koons, 1973, Mommessin and Raia, 1975; Wade et al., 1976; Jeffrey et al., 1974; Jordan and Payne, 1980). In general, compounds with molecular weights less than $n\text{-C}_{15}$ are not present, and most of the tar balls considered have very high residues of compounds with molecular weights greater than $n\text{-C}_{34}$. Several sources for these tar balls have been identified, and these include tanker cargo-hold washings, bilge discharges, urban/industrial wastes and residues resulting from major spills or blowouts such as the Amoco Cadiz and IXTOC I. In some instances the chemical composition of tar balls isolated from, localized areas are very similar; however, remarkably different chemical compositions of tar balls isolated in the same neuston tows have been noted (Mommessin and Raia, 1975). Because of the extreme patchiness of tar ball occurrence, and the several orders of magnitude variations in tar ball loadings in the same area over the period of a single day, standing stock estimates of tar ball pollution are tenuous at best, and it is not possible at this time to determine if tar ball occurrence is increasing or decreasing.

The ultimate fate of most of these tar balls at sea is believed to be their break up and sinking within one year (Morris, 1971; Butler et al., 1973; Butler, 1975a, b; Horn et al., 1970; Brown et al., 1973; Brown et al., 1975; Brown and Huffman, 1976; Wade, 1976), whereas beached or stranded tar balls have a fate similar to that of larger patches of mousse or oil released from major spill incidence. Tar ball siting on beaches have been reported globally; however, most evidence suggests that their levels have not changed over the last decade. The decomposition of stranded tar balls is extremely dependent on the shoreline substrate, the energy regime of the shoreline environment, the presence and absence of nutrients, and the degree of sedimentation into the intertidal zone (Blumer et al., 1973). Microbial degradation of tar balls is believed to be generally limited to the outer surfaces due to diffusion limited transport of oxygen and nutrients to the interiors. The fact that numerous tar balls have not been observed to have a significant component

concentration gradient with depth into the interior, suggests that significant evaporation, dissolution, photochemical and microbial degradation occurs to the materials before agglomeration and tar ball formation.

Mathematical and Computer Modeling of Mousse Behavior

In reviewing the status of mathematical and computer modelling of mousse formation and degradation, it was noted that numerous mathematical formulations have been generated to describe the various individual aspects of water-in-oil emulsion formation and behavior (Mackay et al., 1979, 1980; Twardus, 1980; Raj, 1977; Grose, 1979). Unfortunately, however, no single oil weathering model exists at this time which encompasses all of the variable factors, and it is impossible to completely model water-in-oil emulsion formation and behavior because of the lack of a sound understanding of all of the physical chemistry properties of the system. Significant advances have been made in modeling viscosity changes of water-in-oil emulsions as a function of water content (Mackay et al., 1979, 1980), the competitive process of dispersion of oil and mousse into the water column (Mackay et al., 1979, 1980), and the break-up or decomposition of slicks or patches of oil based on evaporation and dissolution weathering (Mackay and Matsugu, 1973; Butler, 1975a; Grose, 1979; Mackay et al., 1979, 1980; Aravamudan et al., 1981; Belen et al., 1981; and Payne et al., 1981b), but much more work will be required before model simulations will be able to accurately predict slick behavior and emulsification processes. Ultimately, it may be necessary to incorporate compound specific properties into modelling efforts to fully predict oil/mousse/tar ball weathering for a variety of oils under different environmental regimes (Payne et al., 1981b).

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