

## EFFECTS OF HYDROCARBONS ON FISHERY RESOURCES

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### **An Example Study of the Fate of Spilled Petroleum in a Tropical Environment: IXTOC-1**

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#### RESUMEN

Este trabajo es una exposición general de los resultados obtenidos durante el crucero de investigación de la NOAA en el lugar de la explosión del IXTOC-1 en Septiembre, 1979. Se describe los factores físicos, químicos y microbiológicos que afectan el intemperismo del derrame de petróleo. La luz solar fué la responsable de la producción de varios productos fotooxidantes que contribuyeron a formaciones de una espesa emulsión parecida a mousse de chocolate y semejante a la observada en derrames anteriores. Es de interés que los mismos productos oxidantes se formaron en la oscuridad por bacterias *in situ* en experimentos de microcosmos llevado a cabo a bordo del buque RESEARCHER de la NOAA durante el crucero. La misma emulsión parecida al mousse se formó en estos experimentos, iguales a las formadas en la superficie del mar. Existían poblaciones de bacterias respirantes de petróleo coincidentes con los derrames de petróleo, y eran lo suficientemente grandes para que potencialmente pudieran asimilar los componentes del derrame de petróleo disuelto en el agua en el transcurso de una a dos semanas. Sin embargo, la tasa de asimilación bacteriana en el petróleo flotante en la superficie era más lenta. Aparentemente ello es debido a la limitación de nutrientes para la población bacteriana existente en la nata de petróleo superficial.

#### INTRODUCTION

It has been shown that if all the petroleum spilled in the world oceans during any one recent year (approximately 6 million metric tons) were left on the ocean surface, it could result in a covering two molecular monolayers thick over the entire ocean surface (Garrett, 1972). This could have obvious dramatic effects on air/sea exchange processes and world climate. It is also obvious that this is not the case.

Recent calculations based on observations made during the Intergovernmental Oceanographic Commission/World Meteorological Organization (IOC/WMO) Marine Pollution (Petroleum) Monitoring Pilot Project (MAPMOPP) showed that a maximum of 0.1% of the sea surface is covered at any one time in the area where MAPMOPP data exist (areas of heavy ship traffic), and that probably less than 0.02% of the global ocean surface is covered with oil at any one time (Garrett, 1980). It is clear that a number of natural physical, chemical and biological processes affect spilled oil, and not only remove it from the sea surface, but drastically change its character and eventual fate in the marine environment. Our knowledge of these processes through late 1977 is summarized in the updated Reports and Studies Number 6 of the Group of Experts in Scientific Aspects of Marine Pollution (GESAMP) Working Group on Impacts of Oil on the Marine Environment (GESAMP, 1977).

In the summer of 1979 a major spill of petroleum into the marine environment occurred when the PEMEX/IXTOC-1 well blew out in the southern Bay of Campeche. Since this spill continued over a long time period (many months) and from a point source of fresh, crude petroleum, it provided an excellent opportunity to study those processes which control the fate of oil in a tropical marine environment. This paper describes some preliminary results of an effort to take advantage of that situation, that is, results of a multidisciplinary research cruise sponsored by the United States Department of Commerce, National Oceanic and Atmospheric Administration to the site of the IXTOC-1 spill in September 1979. The paper is only a summary of some of these results and is based on information contained in papers by individual scientists that participated in the effort. These papers are contained in the report of a symposium held on these cruise results in June 1980 (Proceedings of IXTOC-1 Symposium, 1980).

The IXTOC-1 well blew out on June 3, 1979, with an initially estimated flow of about 30,000 bbl of oil per day. Although this flow seemed to some observers to lessen during the summer, there was still a considerable discharge of oil into the Gulf of Mexico in August 1979, 3 months later. A detailed account of the blowout and subsequent events up to late November 1979 is available in testimony before the U.S. Senate (Campeche Oil Spill: Joint Hearing before the Committee on Commerce, Science & Transportation, and the Committee on Energy and Natural Resources — December 5, 1979, Serial No. 9666).

In September 1979 the NOAA ship RESEARCHER and the Tracor-Marine-owned-and-operated R/V PIERCE conducted a research cruise to the site of the IXTOC-1 blowout in the southern Bay of Campeche and then proceeded along the coast of the western Gulf of Mexico (Figs. 1 and 2). The specific mission of the cruise was to conduct research on the biogeochemistry of the spilled oil, for example, the kinds and rates of physical, chemical and microbial weathering.

The primary vessel for the cruise was the NOAA ship RESEARCHER, whose extensive laboratory space was augmented by one laboratory van and a portable freezer unit. A helicopter landing platform was placed aboard to accommodate a four-passenger helicopter, leased from Crescent Airways, Inc., along with its crew. This helicopter proved to be absolutely essential to the conduct of the research. It allowed observation of oil coverage over large areas and was consistently used to observe the position of the well discharge plume and the positions of the two ships

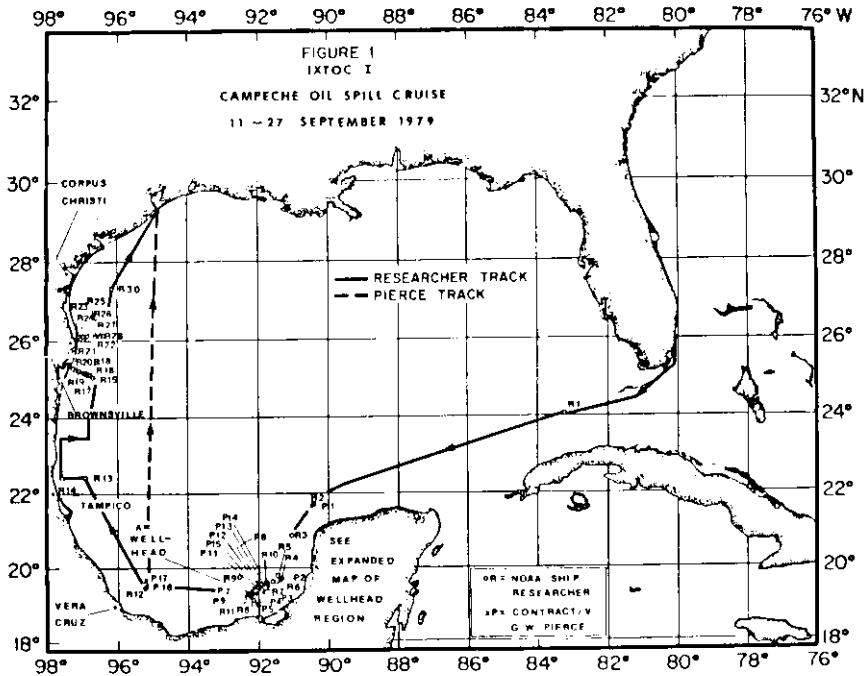


Figure 1. IXTOC-I Campeche oil spill cruise, 11-27 September 1979.

relative to it. Since the RESEARCHER's engine cooling system does not permit entry into heavily oiled waters, a second, keel-cooled vessel, the R/V PIERCE, was leased from Tracor Marine to accompany the RESEARCHER to the blowout site. This vessel's laboratory space was also augmented by two portable laboratory vans. During the cruise, the R/V PIERCE sampled in the well output plume, up to within a few hundred meters of the flame at the wellhead. At the same time, the RESEARCHER sampled along the edge of the plume and provided extensive laboratory space for sample workup and underway experiments. Sample transfer between the two vessels was accomplished using small boats and the helicopter.

Both ships staged for the cruise in Miami, Florida, and departed that port on September 11. A timetable for the cruise is given in Table 1, and the overall cruise track is shown in Figure 1. Figure 2 shows the detail of stations occupied in the immediate vicinity of the blowout and along the blowout plume.

## PHYSICAL SITUATION

### Effects of Gulf Circulation on IXTOC-I Oil

At the time of the cruise, the Gulf Loop Intrusion was at a maximum, with the northern extremity reaching very close to the Mississippi River Delta. The extent of this intrusion was maintained at least through April of 1980, with no formation of major eddies as a result of pinching off the intrusion as described by Maul (1977) and Molinari (1978). Nor was there any evidence of relic eddies in the northern or

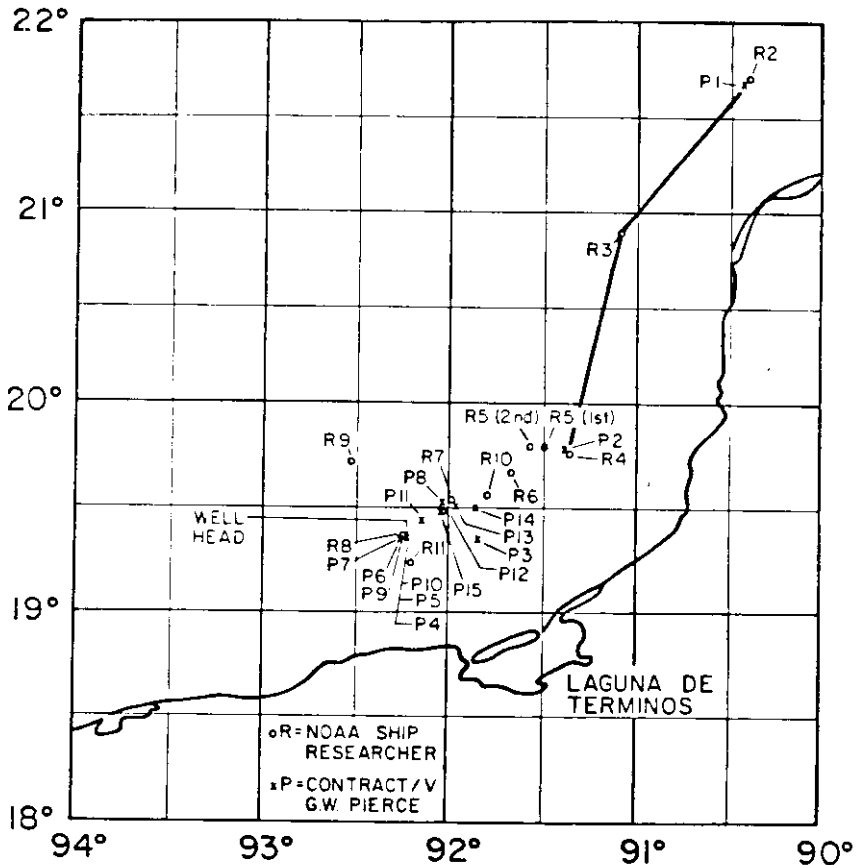


Figure 2. IXTOC-1 Campeche oil spill cruise, 11-27 September 1979, expanded wellhead region.

western Gulf. The Western Boundary Current, described by Sturges and Blaha (1976) as existing along the coasts of Mexico and Texas, was operative throughout the summer of 1979 and constituted a northerly flow (Galt, personal communication). Flow in the western Gulf of Mexico carried IXTOC oil northwesterly through June, July and August of 1979, so that major concentrations occurred mostly in a triangle with apexes at the IXTOC-1 wellhead, Veracruz, Mexico, and at Cabo Rojo, Mexico, which is just south of Tampico. In late July and early August, beaches along the south Texas coast were heavily oiled by IXTOC oil that had moved considerably north of this triangle. This was not the case in September when the RESEARCHER/PIERCE cruise was in progress. Seasonal current shifts resulted in minimal amounts of oil being found within the above-described triangle. Instead, major surface concentrations of oil were found to the northeast, east, and southeast of the well. This will be discussed further below.

Table 1. Timetable for RESEARCHER/PIERCE IXTOC-1 cruise (September 1979)

Date	Activity
11 September	Departed Miami
13 September	Commenced helicopter reconnaissance
14 September	Cleared Arrecife, Alcaran, off Yucatan; set up first control (R2, P1) station at 21°41'N, 90°24'W
15 September	Arrived at NE extremity of plume; set up second control station (R4, P2) at 19°48'N, 91°22'W
16 September	PIERCE arrived at wellhead, RESEARCHER commenced sampling plume
16-21 September	Both ships sampled in vicinity of wellhead and plume
22 September	Both ships sampled off Veracruz, Mexico (R12, P16, P17)
23 September	PIERCE departed for Galveston, Texas, RESEARCHER sampled off Tampico, Mexico
24 September	RESEARCHER sampled sediment transect south of U.S./ Mexico border
25 September	RESEARCHER sampled off Brownsville, Texas; sampled BLM sediment transect off Brownsville
26 September	RESEARCHER sampled off Corpus Christi, Texas
27 September	RESEARCHER and PIERCE tied up in Galveston, Texas

### Climatic Factors

Immediately prior to departure of the vessels from Miami, Hurricane Frederick crossed the western tip of Cuba and traversed the eastern Gulf of Mexico with a landfall at Mobile Bay on September 13. During the early stages of work in the wellhead and blowout plume area (September 14-17), Tropical Storm Henri developed off Yucatan and moved in an erratic course across the southwestern Gulf. The fringes of this storm were felt in the plume area on 16 and 17 September, resulting in seas in excess of 15 feet. Both vessels operated throughout this storm period with minimal time loss. However, all drilling rigs in the vicinity of IXTOC-1 were evacuated and any oil cleanup operations in progress were abandoned.

Wind speeds and directions observed by RESEARCHER personnel are given in Table 2 for the dates during which that vessel operated in the wellhead/plume area and off Veracruz, Tampico, Brownsville, and Corpus Christi. As can be seen, except for 16 September when Henri was just north of the operating area, wind speeds seldom exceeded 15 knots. These winds did not appear to control the direction of oil flow, as evidenced by the fact that wind direction was often 180° to direction of the plume flow. The wind may have had effects on weathering and weathering rates, as will be discussed below.

Table 3 is a listing of wet and dry bulb temperatures recorded by the RESEARCHER Quartermaster Department during the cruise. As can be seen, daytime dry bulb temperatures in the southern Bay of Campeche were consistently

Table 2. Wind speed and direction observed during the RESEARCHER/PIERCE IXTOC-1 cruise (September 1979)

Date	Time (local/ Miami)	Speed (knots)	Dir. (true)	Position	
14 September	0800	05	010	21° 42.3'N	090° 23.5'W
	1500	14	015	21° 40.2'N	090° 23.8'W
	2000	08	000	21° 24.0'N	090° 46.0'W
15 September	0800	12	010	20° 54.6'N	091° 10.8'W
	1500	12	320	19° 30.2'N	091° 29.8'W
	2000	Lt. Airs		19° 48.8'N	091° 21.7'W
16 September	0800	15	215	19° 55.8'N	091° 14.3'W
	1500	16	220	19° 49.4'N	091° 32.6'W
	2000	24	215	19° 58.8'N	091° 32.0'W
17 September	0800	10	130	19° 49.5'N	091° 33.5'W
	1500	Lt. Airs		19° 34.9'N	091° 46.7'W
	2000	08	075	18° 58.2'N	091° 54.0'W
18 September	0800	10	090	19° 32.2'N	091° 59.1'W
	1500	Lt. Airs		19° 34.7'N	091° 57.9'W
	2000	11	340	19° 21.0'N	091° 51.8'W
19 September	0800	07	030	19° 34.3'N	092° 19.8'W
	1500	12	330	19° 44.8'N	092° 30.2'W
	2000	12	000	19° 19.8'N	091° 59.0'W
20 September	0800	10	250	19° 30.6'N	091° 50.1'W
	1500	13	260	19° 19.5'N	091° 56.8'W
	2000	16	250	19° 17.5'N	092° 08.3'W
21 September	0800	12	225	19° 19.1'N	092° 13.0'W
	1500	15	300	19° 18.4'N	092° 12.8'W
	2000	13	305	19° 15.1'N	093° 11.0'W
22 September	0800	12	355	19° 15.1'N	095° 10.8'W
	1500	14	330	19° 14.2'N	094° 56.2'W
	2000	17	350	19° 56.0'N	095° 15.1'W
23 September	0800	15	350	22° 00.1'N	096° 40.6'W
	1500	16	360	22° 30.0'N	096° 58.0'W
	2000	13	035	22° 22.6'N	097° 31.7'W
24 September	0800	12	340	23° 38.6'N	097° 20.2'W
	1500	13	000	24° 09.1'N	096° 32.1'W
	2000	12	025	25° 03.2'N	096° 42.9'W
25 September	0800	16	015	25° 58.7'N	096° 48.6'W
	1500	17	005	26° 10.0'N	097° 01.0'W
	2000	18	020	26° 10.1'N	096° 20.0'W
26 September	0800	16	030	27° 17.2'N	096° 11.0'W
	1500	15	010	27° 41.7'N	095° 48.5'W
	2000	14	080	28° 20.3'N	095° 10.9'W

Table 3. Wet and dry bulb temperatures observed during the RESEARCHER/  
PIERCE IXTOC-1 cruise (September 1979)

Date	Time (local/ Miami)	Wet bulb	Dry bulb	Position	
14 September	0800	26.5	30.5	21° 42.3'N	090° 23.5'W
	1500	25.7	29.1	21° 40.2'N	090° 23.8'W
	2000	26.5	29.0	21° 24.0'N	090° 46.0'W
14 September	0800	27.0	29.5	20° 54.6'N	091° 10.8'W
	1500	26.3	28.6	19° 30.2'N	091° 29.8'W
	2000	26.0	26.5	19° 48.8'N	091° 21.7'W
16 September	0800	26.0	28.0	19° 55.8'N	091° 14.3'W
	1500	25.0	26.8	19° 49.4'N	091° 32.6'W
	2000	25.0	27.0	19° 58.8'N	091° 32.0'W
17 September	0800	24.0	27.0	19° 49.5'N	091° 33.5'W
	1500	22.1	27.4	19° 34.9'N	091° 46.7'W
	2000	23.5	27.5	18° 58.2'N	091° 54.0'W
18 September	0800	25.0	28.5	19° 32.2'N	091° 59.1'W
	1500	25.2	28.2	19° 34.7'N	091° 57.9'W
	2000	25.0	26.5	19° 21.0'N	091° 51.8'W
19 September	0800	24.5	27.5	19° 34.3'N	092° 19.8'W
	1500	23.8	26.0	19° 44.8'N	092° 30.2'W
	2000	24.5	27.0	19° 19.8'N	091° 59.0'W
20 September	0800	26.0	28.0	19° 30.6'N	091° 50.1'W
	1500	24.4	27.6	19° 19.5'N	091° 56.8'W
	2000	24.0	27.0	19° 17.5'N	092° 08.3'W
21 September	0800	25.5	28.0	19° 19.1'N	092° 13.0'W
	1500	24.5	28.0	19° 18.4'N	092° 12.8'W
	2000	24.0	26.5	19° 15.1'N	093° 11.0'W
22 September	0800	23.5	27.0	19° 15.1'N	095° 10.8'W
	1500	23.3	26.5	19° 14.2'N	094° 56.2'W
	2000	24.0	26.0	19° 56.0'N	095° 15.1'W
23 September	0800	22.5	27.5	22° 00.1'N	096° 40.6'W
	1500	22.5	26.9	22° 30.0'N	096° 58.0'W
	2000	23.5	26.5	22° 22.6'N	097° 31.7'W
24 September	0800	23.5	26.0	23° 28.6'N	097° 20.2'W
	1500	22.0	26.6	24° 09.1'N	096° 32.1'W
	2000	22.0	26.0	25° 03.2'N	096° 42.9'W
25 September	0800	20.0	26.0	25° 58.7'N	096° 48.6'W
	1500	18.1	25.4	26° 10.0'N	097° 01.0'W
	2000	20.5	25.5	26° 10.1'N	096° 20.0'W
26 September	0800	22.0	27.0	27° 17.2'N	096° 11.0'W
	1500	20.2	25.1	27° 41.7'N	095° 48.5'W
	2000	22.5	25.0	28° 20.3'N	095° 10.9'W

above 27°C, with maximum daily values ranging from 26.0°C to 30.5°C. Nighttime (2000 h) temperatures were not much lower, with a maximum difference between night and day dry-bulb values being only 2°C.

#### Water Characteristics

Water column characteristics in the vicinity of the well and plume were variable and typical of subtropical coastal environments. Surface temperatures were in excess of 28°C and the water column was isothermal to at least 10 m and often to as deep as 40 or 50 m. Water temperatures below 25°C were not observed above 50 m in the vicinity of the well.

Surface salinities in the vicinity of the well and plume varied from about 34.5 ppt to 36.6 ppt and were variable over that range throughout the water column. In general, when low (<35.0 ppt) salinities were observed they occurred at the surface. Below 10 m salinities were generally in excess of 35.5 ppt.

Water in the vicinity of the well and plume was quite turbid, with a greenish color. This color extended from the shore to 1 to 5 NM seaward of the wellhead. This turbidity apparently was a general coastal feature at that time and the interface between it and the clear, blue waters of the open Bay of Campeche was very sharp.

Dissolved oxygen concentrations measured by Winkler titrations on samples collected from throughout the water column varied from 4.20 to 5.05 ml/l in the vicinity of the well and plume, indicating that the water was fully saturated with oxygen.

Nutrient levels were low and typical for tropical nearshore waters. Nitrate values were all less than 0.5 micromolar and nitrite values below 0.1 micromolar. Ammonia values were usually below our detection limit of 0.07 micromolar and above 0.3 micromolar in only one instance. Phosphate values were slightly higher than most tropical waters, but were usually below 0.5 micromolar. Silicate values ranged from 0.5 to 4.0 micromolar, which is common for tropical surface waters, and show little evidence of silicious input from coastal runoff.

#### LOCATION OF OIL

The extent of the oiled area throughout the period of September 15-20 is generally indicated by the locations of stations depicted in Figure 2. In that figure, P1, P2, R2, R3, R4, and R9 are all control-type stations outside of the plume. The rest of the stations are either in or at the edge of the plume proper. Very little oil was noted on the surface west of the wellhead, and what was observed in that direction was assumed to be older oil moving back past the well due to changes in the circulation noted above. Throughout this period, the output plume trended northeast from the wellhead (045° to 055° true) and extended for 40 to 50 NM. At times, the plume took sharp meanders, which were generally to the south. As mentioned above, the direction of oil flow on the surface seemed independent of wind speed or direction.

On September 21, the output plume swung to a southeasterly direction over about a 12 h period. When the RESEARCHER departed, at about sunset on that date, the plume output was flowing at about 135° true.

Virtually no oil was found elsewhere during the cruise, with the exception of some surface sheen and small balls of chocolate-mousse-like emulsion (see below) at P17 off Veracruz and some small "fingernail-sized" flakes of mousse at R30 off Corpus Christi.



## PHYSICAL DESCRIPTION OF OIL

The physical state of the oil, based on visual observations during the cruise, is best described in terms of zones within the output plume. These zones are described below. Their relative size and position appeared to be a function of many factors, such as sunlight intensity, wind stress, and flow rate.

Zone 1. This zone is characterized by a continuous light-brown-colored light emulsion of water and oil on the surface. The zone existed in the immediate vicinity of the flames and extended for no more than a few hundred m down the plume.

Zone 2. This zone is characterized by a 30 to 50% coverage of the sea surface by a light brown water and oil emulsion in disoriented streaks. The zone started a few hundred m down-plume from the burn and extended out to a maximum of 1 or 2 NM, depending on wind stress. However, at times it was virtually absent.

Zone 3. This zone is characterized by a 20 to 50% coverage of the sea surface by light brown water and oil emulsion oriented in Langmuir "streaks" parallel to the wind direction. The width of these "streaks" varied from a few cm to a few m, and the length varied from one to tens of meters. These dimensions depended on wind stress. In general, these Langmuir streaks were surrounded by a light to heavy sheen of oil. This zone extended from as close as a few hundred m from the flames to several NM down the plume.

Zone 4. This zone is characterized by a darkening of the light brown water and oil emulsion until the streaks were black. This was assumed to result from oxidation of the oil, and the rate seemed to be dependent on sunlight intensity. Commonly, Langmuir streaks were blackened in the center and light brown at the edges where emulsification may have been occurring. At times, these streaks coalesced into long lines of blackened oil that extended for several kilometers. In the brown edges of these lines or streaks, small balls of chocolate-mousse-like emulsion (hereafter called *mousse*) broke off. (The operational "definition" used for mousse during this cruise was surely different from that for other such events, for example, the Amoco CADIZ spill. There is a definite need for a clearer definition of such terms in order to allow adequate comparison of data from future events. In this report, mousse is considered to be an oil and water emulsion of a very thick and viscous consistency that forms into sticky but discrete balls. These balls readily coalesce into larger balls upon contact with each other.) At other times, the wind rolled portions of a streak up onto itself; this also served as a mechanism for the formation of mousse, as did passage of a boat hull or seeding by debris such as sugar cane stalks. Varying concentrations of these balls often covered the sea surface and, like the light brown emulsion, lined up in Langmuir lines or cells. In some instances, these balls reached grapefruit size and/or coalesced into huge "rafts" of mousse up to 50 or 60 m in diameter. In one instance, one of these rafts was sampled and found to be approximately 1 m thick. This zone began from 5 to 15 NM from the burn and extended out to about 20 NM. The extent of the zone and rate of mousse formation apparently were dependent on sunlight intensity and wind stress. A light to heavy sheen of surface oil was always present in this zone.

Zone 5. This zone is 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.

This zone overlapped zones 2, 3 and 4 and extended out to the farthest extremity of the plume.

It is important to remember that: (1) The description of the zones is based on a combination of detailed observations from RESEARCHER, PIERCE, and small boats coupled with observations from eleven helicopter flights in the vicinity of the oil plume from September 15 to 21, 1979. (2) These descriptions are operative only for the period of this cruise. (3) There were no distinct boundaries between these various zones, and they tended to interweave at the transitions, more so on some days than on others.

#### SAMPLES COLLECTED AND EXPERIMENTS CONDUCTED

As indicated in Figures 1 and 2 and Table 1, sampling was concentrated in the vicinity of the wellhead and the immediate output plume; however, sampling was also conducted at uncontaminated control stations. Sampling along the Mexico and Texas coasts (off of Veracruz, Tampico, Brownsville, and Corpus Christi) constituted an effort to find evidence of spilled oil known to have been resident in these areas in July and August. The water column was characterized throughout the sampling area using XBT's and a Plessey 9040 CTD equipped with a 12-bottle sampling rosette for collecting salinity and dissolved oxygen samples. Water samples for hydrocarbon analysis were collected using large-volume steel sampling bottles (Bodega-Bodman bottles), as well as glass bottles and a Teflon-lined pumping system developed by Energy Resources Corporation in Cambridge, Massachusetts. Sediment samples were collected at RESEARCHER stations using either a Smith-McIntyre grab sampler or Shipek grab sampler. Sea surface microlayer samples were collected using both Garrett screens and a Teflon disk. Air samples were collected using a pumping system designed for this purpose by Science Applications, Inc., in La Jolla, California. Samples of surface oil were collected by neuston net tows or from small boats using stainless-steel buckets. Microbiological samples were collected using General Oceanics sterile-bag samplers. The positioning of many of these sampling devices was guided by use of 20 and 200 kHz acoustic profilers developed by the Ocean Acoustics Laboratory of NOAA/AOML in Miami, Florida.

On-board microbiological experiments were conducted to estimate *in situ* rates of microbial oxidation and biodegradation potentials for constituents of spilled oil. This was done using C-14-labeled aliphatic (hexadecane) and aromatic (naphthalene) compounds for the *in situ* oxidation studies and C-14-labeled hexadecane, pristane, 9-methyl anthracene, and benzanthracene for the biodegradation potentials. The *in situ* oxidation rate is based on short-term (6-h) oxidation of labeled hydrocarbons to CO<sub>2</sub> by the microbial community present in water samples. Biodegradation potential is that oxidation to CO<sub>2</sub> that occurs in 2 to 30 days. In addition, model ecosystem experiments (microcosm experiments) were conducted where natural Bay of Campeche populations of microbes were stressed with fresh IXTOC-1 oil, mousse resulting from spilled IXTOC-1 oil, and mousse that was collected in August off South Padre Island, Texas. The effect of the oil added to these microcosms on the natural microbial populations was studied, as well as the effects of the microbes on the oil. Laboratory photooxidation experiments were also conducted on fresh IXTOC-1 oil. Results of these

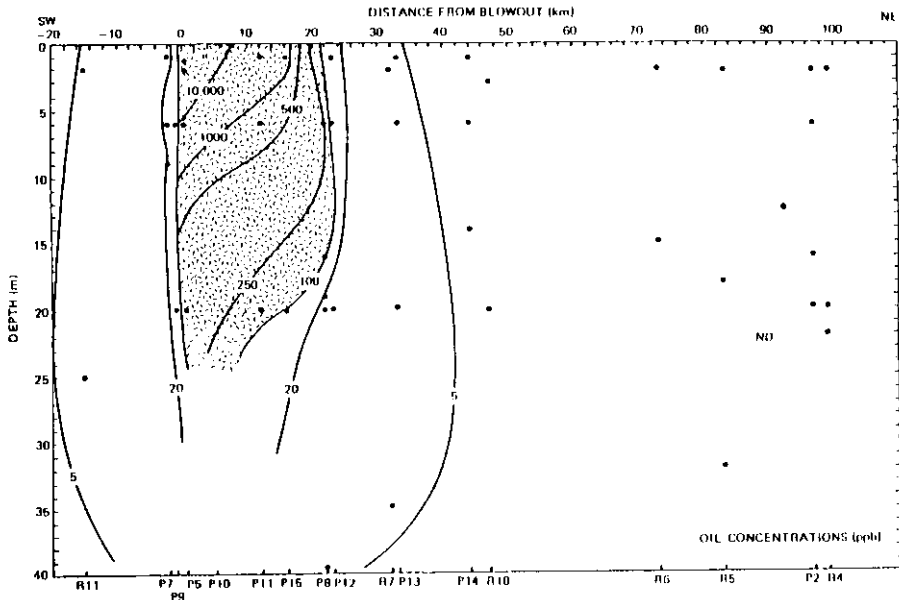


Figure 3. Concentrations of oil along a transect oriented to the northeast of the IXTOC-1 blowout, September 1979 (after Fiest and Boehm, 1980).

experiments were compared to observations of oil and mousse samples collected near the wellhead and to observations made on oil and mousse exposed to microbial activity in the dark experimental microcosm experiments.

#### SUMMARY OF RESULTS OF CHEMICAL AND MICROBIAL WEATHERING AND FATE STUDIES

The following is a summary of some of the highlights of the results of the above-described efforts. Details of these results can be obtained from the papers referenced throughout the text.

##### Water Column Chemistry

Water column concentrations measured by Feist and Boehm (1980) along the IXTOC-1 blowout plume are shown in Figure 3. These data were obtained from hexane extracts of IXTOC-1 cruise water column samples by synchronous fluorescence spectroscopy. Concentrations range from levels of less than  $5 \mu\text{g/l}$ , found 80 km down the spill plume, to a value of  $10,600 \mu\text{g/l}$ , found a few hundred meters from the blowout itself. Samples with oil concentrations greater than  $20 \mu\text{g/l}$ , that is, samples within 25 km of the well in the direction of the plume, probably contained a suspension of oil droplets. This suspension was restricted to the upper 10-20 m of the water column. The spectra of oil in these samples showed that they contained two-, three- and four-ring aromatic hydrocarbons. The samples containing less than  $20 \mu\text{g/l}$  contained a predominance of two-ring aromatic hydrocarbons which are one to two orders of magnitude more soluble than the three- and four-ring compounds. It is important to note that the Fiest and Boehm

data also show that in areas not below the spill plume, hydrocarbon concentrations rapidly dropped off to background levels (less than 5 µg/l) within a few kilometers of the blowout.

Boehm and Fiest (1980a), in a separate paper, point out that concentrations of oil in the top 20 m of the water column below the IXTOC spill plume, within 25 km of the wellhead, exceeded values observed at the EKOFISK BRAVO blowout (300 µg/l), the Amoco CADIZ spill (350 µg/l), and the ARGOMERCHANT spill (450 µg/l). They estimate that about 20,000 gallons, or  $70 \times 10^6$  grams of oil were contained in the upper water column and that this represented only 1% of that observed on the surface. Boehm and Fiest also showed that concentrations of some of the most toxic compounds, for example, alkylated benzenes, naphthalenes, and methyl naphthalene, appeared in the water column in measurable concentrations. A listing of some of these compounds, their solubilities, and the range of levels found below the plume are given in Table 4.

#### Water Column Biology

Boehm and Fiest (1980a) noted little chemical evidence that any microbial degradation of oil had occurred in the water column, or in surface oil/ mousse layers and microlayer oil. They postulated that this was due to the low level of nutrients in the water which limited microbial activity. However, Pfaender et al. (1980) showed that the aquatic microbial community was oxidizing hexadecane and naphthalene

Table 4. Observed concentrations of hydrocarbons compared with their solubilities (after Boehm and Fiest, 1980a)

Compound	Approximate solubility in seawater at 25°C (mg/l)	Observed concentration range within 20 km distance from blowout (µg/l)
Trimethyl benzenes	30-40	0.050 - 2.00 (W*) 0 - 0.60 (D†)
Tetramethyl benzenes	10-20	0 - 3.0 (W) 0 - 0.4 (D)
Naphthalene	30	0.02 - 3.0 (W) 0.06 - 0.8 (D)
Methyl naphthalene	25	0.05 - 15.0 (W) 0.01 - 2.5 (D)
Dimethyl naphthalene	2	0.04 - 38.0 (W) 0.01 - 2.6 (D)
Phenanthrene	1	0.02 - 1.6 (W) 0.01 - 0.4 (D)
Petroleum	—	100 - 10,000

\*whole water

†dissolved (filterable)

Table 5. Hydrocarbon metabolism rates (after Pfaender et al., 1980)

Station	Site* (km)	Depth (m)	Aliphatic†	Hydrocarbon Respiration - $\mu\text{g}/\text{l}/\text{h}$		
				Tt (h)	Aromatic‡	Tt (h)
PIX 10	0.5	1	44.30	94	1.58	1772.0
		9	21.70§	—	9.20§	304.0
PIX 15	17.0	1	0.36	266	2.18	34.8
		9	0.14	228	2.17§	8.85
		20	0.72	44	1.84	10.3
PIX 08	27.0	1	7.88§	35	6.44§	7.9
		3	—	—	2.51§	20.3
		18	0.12	216	—	—
PIX 14	37.0	1	—	—	0.65	70.7
		9	—	—	0.01§	320.0
		20	—	—	0.02	160.0
RIX 02	300.0	3	0.05	—	0.007§	157.0
		9	0.09	—	0.002§	550.0
		20	0.04	30	0.037	29.7
RIX 22	770.0	3	—	—	—	—
		35	0.01	200	0.03	112.0
		40	0.01	142	0.02§	170.0

\*Distance from wellhead.

†Calculations based on total aliphatic hydrocarbon concentration and metabolism of  $^{14}\text{C}$ -hexadecane.

‡Calculations based on total aromatic hydrocarbon concentration and metabolism of  $^{14}\text{C}$ -naphthalene.

§Calculated value using hydrocarbon concentration from depth other than that from which sample was taken.

(Table 5) and could account in part for the decrease in oil concentrations some distance from the spill. The rates measured indicate that substantial microbial degradation of IXTOC oil could have occurred in surface waters within 27 km of the wellhead. It is a fact that rates measured in experiments such as those described by Pfaender et al. (1980) are difficult to extrapolate to *in situ* rates, because confining the water dramatically increases the number and activity of microbes in the sample (bottle effects). However, these effects are not a significant factor in short-term experiments such as these (6 h). Thus, in the absence of a surface oil/ mousse layer, or oil microlayer, which could continually supply oil to the water column, microbial oxidation could remove the levels of oil measured in the water column between 17 and 27 km of the wellhead in 1 to 10 days. For example, the data in Table 5 indicate that the microbial degradation rate at 1 m depth 27 km from the wellhead was 3% per hour for hexadecane and 13% per hour for naphthalene. However, biodegradation potentials for oil (water column) and mousse (surface) were substantially lower than observed in previous spills (Atlas et al., 1980). Oxidation rates of confined oil/ water mixtures were about 5% per year. Interestingly, this rate increased by factors of 20 to 300 when natural samples were spiked with  $\text{NH}_4\text{NO}_3$  and  $\text{KH}_2\text{PO}_4$  to final concentrations of 1 micromolar. On this basis, it is reasonable

to assume that, as Boehm and Fiest postulated, the response of the bacterial community and the rate of bacterial weathering of the spilled oil was nutrient-limited. Thus, even though the potential for fairly rapid biodegradation of the oil existed, this degradation probably did not occur.

Pfaender et al. (1980) and Atlas et al. (1980) both showed distinct effects of spilled IXTOC-1 oil on the water column microbial community. Although little or no increases in total bacteria cell numbers resulted, there were large increases in culturable hydrocarbon-utilizing bacteria. The spilled oil also resulted in an increase in total microbial metabolic activity, but it inhibited microbial amino acid respiration. These effects were limited to areas very near floating surface oil; at distances of greater than 25 km down-plume all of these parameters were at what were perceived as natural ambient levels.

### Floating Oil

Sunlight and resulting photooxidation played a major role in weathering spilled IXTOC oil on the sea surface. The fact that this occurred is evident in the above physical description of the spilled oil. It is obvious that exposure on the sea surface changed the oil so that chocolate-mousse-like emulsions formed and that this ability to emulsify was a function of time and sunlight intensity, and possibly microbial activity. It was postulated that this occurred as a result of increasing hydrophilic content of the oil as exposure continued and that this resulted from the formation of photooxidation and microbial oxidation products. To test this hypothesis: (1) the floating oil was analyzed for these products, (2) laboratory photooxidation experiments were conducted on fresh IXTOC-1 oil, and (3) the oil placed in dark microcosm experiments was examined to see if the same type products could be formed by microbes without the aid of sunlight.

The laboratory photooxidation experiments were conducted at the Center for Bio-Organic Studies at the University of New Orleans. The results have been reported by Overton et al. (1980) and clearly show that exposure of IXTOC-1 oil to air, sunlight, and artificial seawater formed mousse which was physically and chemically the same as that found in the IXTOC-1 spill plume. Photooxidation produced oxygenated compounds including alkyl benzoic, naphthoic, and phenanthroic acids. The same compounds formed in these laboratory experiments were found in the surface mousse samples collected in the IXTOC-1 spill plume. Even more interestingly, Overton et al. found that these same compounds were formed in the dark by microbial action in the microcosm experiments conducted by Buckley et al. (1980), but with different distribution ratios. Figure 4 shows this clearly. It compares selected ion current profiles for a mass/charge ratio of 236 from a glass capillary gas chromatograph coupled to a mass spectrometer ( $GC^2MS$ ) for phenanthroic acid and its  $C_1$  and  $C_2$  homologs for extracts from a laboratory photooxidation experiment (32 h bright sunlight) and from a microcosm experiment (7 days incubation in the dark). The plots show the same homologs, but with different distributions. The different distributions apparently result from the specificity of microbial degradation, which appears to favor certain isomers. Table 6 is a summary listing of the classes of compounds observed to be formed in the photooxidation and microcosm experiments. The similarity of the listings is obvious. Buckley et al. (1980) showed that this oxidation process caused by the

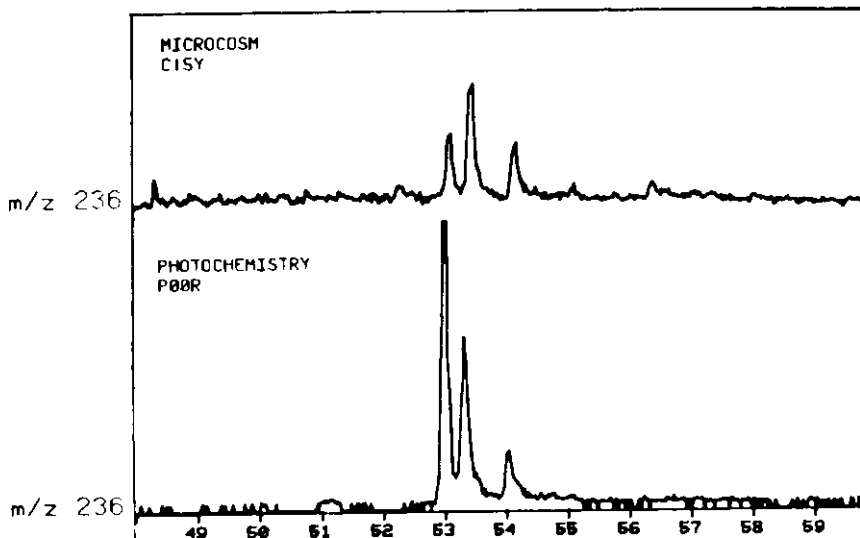


Figure 4. Selected (mass/charge,  $m/z$ , 236) ion current profiles for phenanthroic acids from the GC<sup>2</sup>MS analyses of: (TOP) methylated acidic extract from a microcosm experiment utilizing fresh wellhead oil after seven days of incubation; (BOTTOM) methylated acidic extract of the water column sample from a simulated environmental photooxidation experiment after exposure to 32 hours of bright sunlight. Mass 232 is characteristic of the parent ions in the mass spectra of phenanthroic acids (Overton et al., 1980).

Table 6. Summary listing of classes of major oxidized hydrocarbons found in laboratory photooxidation experiments and in dark microcosm incubation experiments (from Overton et al., 1980)

Photooxidation experiment	Microcosm experiment
Normal fatty acids (C <sub>7</sub> -C <sub>11</sub> )	Fatty acids (n-C <sub>16</sub> predominant)
Branched fatty acids (C <sub>9</sub> -C <sub>12</sub> )	Phenylacetic acid
Alkyl phenols	Alkyl phenols
Alkyl benzoic acids (C <sub>1</sub> -C <sub>6</sub> )	Alkyl benzoic acids (C <sub>1</sub> -C <sub>6</sub> )
Alkyl naphthols	Alkyl naphthols
Alkyl naphthoic acids	Alkyl naphthoic acids
Alkyl phenanthroic acids	Alkyl phenanthroic acids
Phenanthrol	Phenanthrol
Alkyl benzothiophenoic acids	Alkyl benzothiophenoic acids
Alkyl dibenzothiophenoic acids	Alkyl dibenzothiophenoic acids
	Alkyl methoxybenzoic acids
	Alkyl benzene diacids

microbial action in the microcosm experiments resulted in the formation of mousse just as happened in the photooxidation experiments. Clearly, these processes occur simultaneously when oil is spilled in a marine environment.

### Sediments

Boehm and Fiest (1980b) also studied the partitioning of IXTOC-1 oil to the sediments. By collecting sedimenting particles in trap arrays they showed that a significant amount of the sedimenting oil was associated with phytoplankton material. They also showed that oil concentrations in the top 10 mm of the bottom sediments were at least as high as 100 ppm and probably higher close to the well; however, in spite of these concentrations only minor quantities of the spilled oil (0.5-3%) resided in sediment layers within 50 km of the well. As was the case for surface oil and oil in the water column, this oil was only marginally degraded by marine bacteria, but showed evidence of substantial physical/chemical weathering.

### ACKNOWLEDGMENT

Our thanks to Dr. G.R. Harvey and Dr. J.W. Farrington, who provided critical comments on this manuscript. This research was sponsored by the NOAA Office of Marine Pollution Assessment.

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