BULLETIN OF MARINE SCIENCE, 32(1): 1–13, 1982

AN EXAMPLE STUDY OF THE WEATHERING OF SPILLED PETROLEUM IN A TROPICAL MARINE ENVIRONMENT: IXTOC-1

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ABSTRACT

Some initial findings that resulted from a research cruise to the site of the IXTOC-1 oil well blowout in summer 1979 are represented. The primary research effort was directed to learning more about the kinds and rates of spilled oil weathering processes in a tropical marine environment. Results showed that petroleum concentrations in the water column were as high as 10,000 ppb near the wellhead but dropped off rapidly to background values of 5 ppb. Chemical evidence for bacterial degradation of this oil was slight. However, separate microbiological experiments showed that the resident community had the capability of oxidizing the oil in the water column in 1 to 10 days. Apparently this did not occur because of nutrient limitation. During the period of observation no "mousse"-like emulsion was found on the surface at the wellhead, but, did form several kilometers down plume from it. This formation apparently occurred as sunlight and microbial activity oxidized the surface oil forming polar compounds. Separate microbiological microcosm and photo-oxidation experiments using fresh IXTOC-1 oil indicated that this oxidation did occur and that the oxidation products from the sunlight and microbial processes were very similar.

It has been shown that if all the petroleum spilled in the world oceans during any one recent year (approximately six million metric tons) were left on the ocean surface that 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 Meterological 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 study that situation, i.e., 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 in early June 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 December 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—5 December 1979, Serial No. 9666), and in a special publication of the Oil Spill Intelligence Report (OSIR, 1980, Special Report, IXTOC-1: Vol. III(1), Cahners Publishing Co., Cambridge, MA). 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 (Fig. 1). The specific mission of the cruise was to conduct research on the biogeochemistry of the spilled oil, e.g., 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. This helicopter proved to be absolutely essential to 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 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, accompanied 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 11 September. Two control stations were occupied on 14 September (stations R2 and P1 at 21°41'N, 90°24'W, see Fig. 1) and two more on 15 September (stations R4 and P2 at 19°48'N, 91°22'W) with the latter two being about 10 nm northeast of the northeast extremity of the spill plume. Subsequent to occupation of these stations, both ships operated in the vicinity of the plume and wellhead until 21 September and then sampled along the coast of the western Gulf of Mexico arriving in Galveston, Texas on 27 September. Cruise tracks for both ships are shown in Figure 1 along with the positions of the stations occupied. The general shape and position of the spill plume, at the time the RESEARCHER and PIERCE were in the vicinity, is shown by the locations of stations near the wellhead and northeast of that position to station R5.

PHYSICAL SITUATION

Effects of Gulf Circulation on IXTOC-1 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

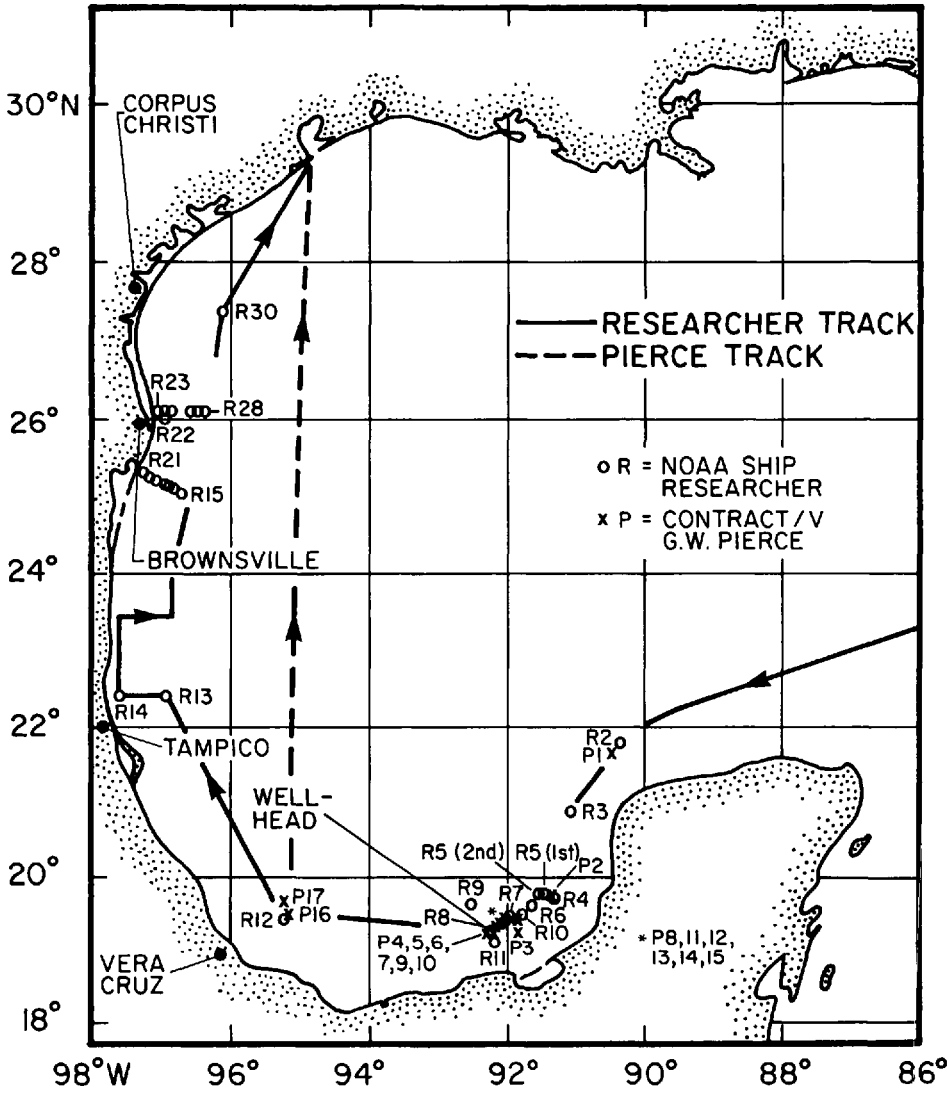

Figure 1. IXTOC-1 Campeche Bay Oil Spill Cruise, 11–27 September 1979. R refers to RESEARCHER stations and P to PIERCE stations. R2, R4, R9, P1, and P2 were control stations. R3 was an STD station only.

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 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, NOAA Pacific Marine Environmental Laboratory, Seattle, WA, 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. From early August through mid-September beaches along the south Texas coast were heavily impacted by oil that had moved considerably north of this triangle (Gundlach et al., 1981). 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.

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 13 September. During the early stages of work in the wellhead and blowout plume area (14–17 September), 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. However, all drilling rigs in the vicinity of IXTOC-1 were evacuated and any oil cleanup operations in progress were abandoned.

Wind speeds observed by RESEARCHER personnel seldom exceeded 15 kn, except for 16 September when Henri was just north of the operating area and wind speeds of 24 kn were recorded. These winds did not appear to control the direction of oil flow, as evidenced by the fact that wind direction was often 180° to the direction of the plume flow. The wind may have had effects on weathering and weathering rates, as will be discussed below.

During the time of observation, daytime dry-bulb temperatures in the southern Bay of Campeche were consistently 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 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‰ to 36.6‰ and were variable over that range throughout the water column. In general, when low (<35.0‰) salinities were observed they occurred at the surface. Below 10 m salinities were generally in excess of 35.5‰.

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 tubidity was a general coastal feature and was observed from the eastern Bay of Campeche to Veracruz. Apparently, it was related to extremely high rainfall and coastal flooding occurring at that time. 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 showed little evidence of silicious input from coastal runoff.

Location of Oil

As stated before, the extent of the oiled area throughout the period of 15–20 September is generally indicated by the locations of stations depicted in Figure 1, from the wellhead northeast to station R5. In that figure, P1, P2, R2, R3, R4, and R9 are all control-type stations outside of the plume. The rest of the stations in that area 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 21 September, 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 flakes of mousse, about 3 to 10 mm in diameter, 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 speed, and flow rate. The way in which these factors affected weathering and size of these zones is discussed below.

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 meters 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 meters down-plume from the well and extended out to a maximum of 1 or 2 nm, depending on wind speed. As wind speeds increased, zone 3 (see below) expanded to cover this area and at times zone 2 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 centimeters to a few meters, and the length varied from one to tens of meters. These dimensions depended on wind speed. 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 meters 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 (hereinafter called *mousse*) broke off. (The operational "definition" used for mousse during this cruise was surely different from that for other such events. 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 wellhead 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 speed. 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 11 helicopter flights in the vicinity of the oil plume from 15 to 21 September 1979. (2) These descriptions are operative only for that period. (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 Figure 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 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 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

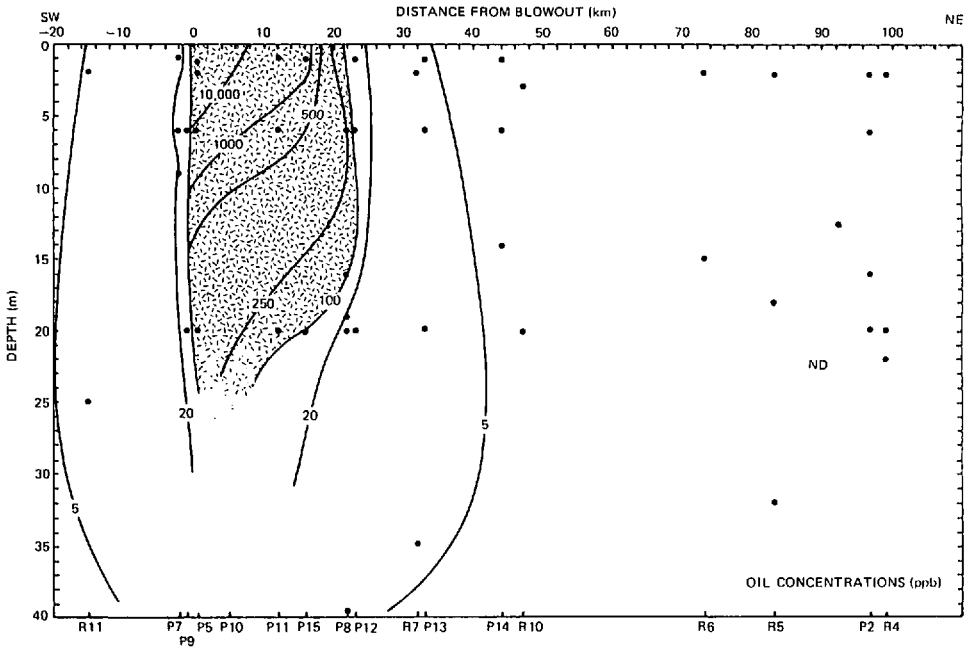

Figure 2. Concentrations of oil along a transect oriented to the northeast of the IXTOC-1 blowout, September 1979 (after Fiest and Boehm, 1980).

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_2 by the microbial community present in water samples. Biodegradation potential is that oxidation to CO_2 that occurs in 2 to 30 days. In addition, model ecosystem experiments (microcosm experiments) were conducted in which 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 latter 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 highlights of the results of the above-described efforts. Details of these results can be obtained from the papers referenced throughout the text.

Table 1. 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

D = dissolved (filterable); W = whole water.

Water Column Chemistry

Water column concentrations of petroleum hydrocarbons measured by Fiest and Boehm (1980) along the IXTOC-1 blowout plume are shown in Figure 2. These data were obtained from hexane extracts of IXTOC-1 cruise water column samples by synchronous fluorescence spectroscopy. Concentrations range from

Table 2. Hydrocarbon metabolism rates (after Pfaender et al., 1980)

Station	Site* (km)	Depth (m)	Hydrocarbon Respiration Aliphatic†	Hydrocarbon Tt (h)	Hydrocarbon Respiration Aromatic‡	μg/l/h Tt (h)
P10	0.5	1	44.30	94	1.58	1,772.0
		9	21.70§	—	9.20§	304.0
P15	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
P08	27.0	1	7.88§	35	6.44§	7.9
		3	—		2.51§	20.3
		18	0.12	216	—	
P14	37.0	1	—		0.65	70.7
		9	—		0.01§	320.0
		20	—		0.02	160.0
R02	300.0	3	0.05		0.007§	157.0
		9	0.09		0.002§	550.0
		20	0.04	30	0.037	29.7
R22	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}C-hexadecane.
‡ Calculations based on total aromatic hydrocarbon concentration and metabolism of ^{14}C-naphthalene.
§ Calculated value using hydrocarbon concentration from depth other than that from which sample was taken.

levels of less than 5 μg/l, found 80 km down the spill plume, to a value of 10,600 μg/l, found a few hundred meters from the blowout itself. Samples with oil concentrations greater than 20 μg/l, i.e., 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 μg/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 ARGO MERCHANT spill (450 μg/l). They estimate that about 20,000 gallons, or 70×10^6 g 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, i.e., 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 1.

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 2) 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. 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 2 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 NH_4NO_3 and KH_2PO_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

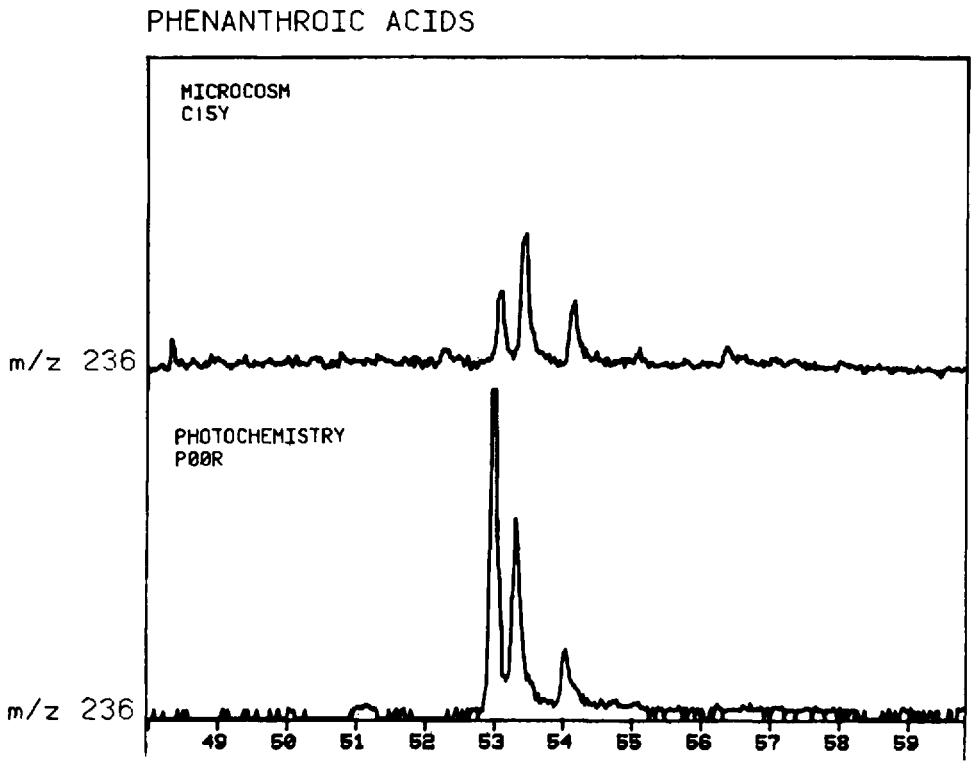

Figure 3. Selected (mass/charge, m/z, 236) ion current profiles for phenanthroic acids from the GC^2MS analyses of: top: methylated acidic extract from a microcosm experiment utilizing fresh wellhead oil after seven days of incubation; bottom: methylated acidic extract of the water column sample from a simulated environmental photooxidation experiment after exposure to 32 h of bright sunlight. Mass 232 is characteristic of the parent ions in the mass spectra of phenanthroic acids (after Overton et al., 1980).

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 increase 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. Exposure on the sea surface seemed to change the oil so that chocolate-mousse-like emulsions formed, and this ability to emulsify also seemed to be a function of time, 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

Table 3. 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_7-C_{11})	Fatty acids (n-C_{16} predominant)
Branched fatty acids (C_9-C_{12})	Phenylacetic acid
Alkyl phenols	Alkyl phenols
Alkyl benzoic acids (C_1-C_6)	Alkyl benzoic acids (C_1-C_6)
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

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 3 shows this clearly. It compares selected ion current profiles for 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 3 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 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 sedimenting oil was associated with phytoplankton material. They also showed that oil concentrations in the top 10 mm of the bottom sedi-

ments 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.

Acknowledgments

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. The helicopter used in this work, and its crew, were provided by Crescent Airways, Inc., Miami, Florida.

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DATE ACCEPTED: July 8, 1981.

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