

Subsurface Distributions of Petroleum from an Offshore Well Blowout. The Ixtoc I Blowout, Bay of Campeche

Paul D. Boehm* and David L. Flest

Energy Resources Co., Inc. (ERCO), Environmental Sciences Division, 185 Alewife Brook Parkway, Cambridge, Massachusetts 02138

■ Concentrations of oil were measured in seawater in the vicinity of the blowout of the exploratory well Ixtoc I located in the Bay of Campeche (Gulf of Mexico) during the month of September 1979. Seawater samples from more than 20 stations located within 100 km of the blowout were analyzed aboard ship for petroleum hydrocarbons by synchronous fluorescence spectroscopy. Concentrations of oil ranged from $5 \mu g/L$ at a distance of 40 km to 10600 $\mu g/L$ within several hundred meters of the blowout. A subsurface plume of oil droplets suspended in the top 20 m of the water column extended 25 km to the northeast of the blowout. The physical processes which might be controlling the behavior of the oil in the plume are discussed.

Introduction

A significant part of the oil released to the marine environment from a tanker spill or a well blowout may be retained and dispersed in the water column. The relative amount of oil which resides in the water column is a function of a number of factors including the chemical and physical nature of the oil, the point of release, the sea surface turbulence, and other hydrographic conditions. During an undersea well blowout, very favorable conditions exist for retention and transport of particulate, dispersed, and dissolved oil in the water column. For example, the turbulent subsurface release of the oil is expected to enhance the formation of small droplets of oil. These droplets can be retained in the water column for a period of time during which ocean currents can carry them away from the blowout. The formation of droplets increases the surface area of the oil, thereby increasing the rates of physical/chemical and biological processes such as dissolution and microbial attack. Measurements of the concentrations of oil in seawater are important for assessing the potential impact on marine organisms and for predicting the dispersion and weathering pattern of the oil.

Concentrations of high-molecular-weight hydrocarbons $(n-C_{10} \text{ to } n-C_{32})$ in seawater have been measured in coastal water following oil spills (1-6), in oil-spill test tanks (7), and in uncontaminated seawater (5, 8, 9, 10). Reported concentrations generally are $<1 \ \mu g/L$ for "clean" open ocean seawater, $2-100 \ \mu g/L$ for oil spills in nearshore environments, and $100-800 \ \mu/L$ in heavily polluted urban environments (e.g., Boston Harbor). Before this study of the Ixtoc I blowout, few measurements of oil concentra-

tions in the vicinity of a well blowout had been reported. The notable exceptions are those reported after the Ekofisk blowout (11, 1). Gaseous and volatile hydrocarbons in seawater have been examined after a gas well blowout in the northwestern Gulf of Mexico (12), and as part of the Ixtoc I blowout research program (13, 14).

The exploratory well Ixtoc I, located in 48 m of water and 80 km northwest of Cuidad del Carmen, Mexico, in the Bay of Campeche (Gulf of Mexico), blew out on June 3, 1979. Estimates of the rate of release of oil during the first 4 months range from 10000 to 30000 barrels per day (15). The oil slick was transported to the north and west of the well from June until early September 1979. In mid-September, a shift in prevailing currents transported the spilled oil to the east and south of the platform (14). Floating booms and chemical oil dispersants were used periodically in the vicinity of the blowout to mitigate the impact of the oil. A continuous fire covering $\sim 4000 \text{ m}^2$ at the blowout site consumed an unknown fraction of the gaseous and volatile components of the oil. The liquid portion of the oil underwent emulsification with seawater either during or subsequent to its release to the water column.

The data presented here were collected as part of a National Oceanic and Atmospheric Administration sponsored study of the Ixtoc I well blowout. Scientists aboard the ships NOAA ship R/V Researcher and contract vessel G. W. Pierce conducted a research cruise in the western Gulf of Mexico from September 11 to October 3, 1979 (14). While samples were being collected near the well, no booming or dispersant spraying operations were being conducted. Hurricane Henri passed near the well on September 15-16 and caused extensive flooding in and subsequent freshwater runoff from adjacent onshore areas. The locations of sampling stations are shown on the chart of the study area (Figure 1) and were oriented for the most part along the observed axis of the surface oil plume. The extent and location of observed surface oil and sheen emanating from the wellhead (16) varied during the September 18-21 sampling period. The surface slick was oriented to the northeast ($\sim 45-55^{\circ}$ true) through September 20 and then shifted southeasterly.

This study addresses the subsurface nature of highmolecular-weight (> C_{10}) hydrocarbon compounds observed during this period of the blowout event. The results presented consist mainly of data obtained on the oil concentrations in seawater samples. The dissolved and par-



Figure 1. Map showing locations of samples taken in wellhead region ((...) approximate extent of observed coherent surface oil slick).

ticulate fractions thereof and the weathering of the surface and subsurface petroleum hydrocarbons are presented elsewhere (17, 18).

Experimental Section

Samples from the immediate vicinity of the Ixtoc I blowout were collected between September 14 and 21. 1979. Seawater was collected with either a 10-L Teflonlined GO-FLO Sampler (General Oceanics), a 30-L glass Bodman bottle (19), a 90-L aluminum Bodega Bodman bottle (20), or a submersible pumping system (17). The pumping system consisted of a submersible pump (Cole Parmer Model 7111: nylon impeller, silicone rubber gaskets, Viton seals) and 2-m sections of stainless-steel tubing (0.5-in. o.d. type 903) connected with 0.5-m flexible stainless-steel joints and stainless-steel quick connects (Swagelock: Viton seals). Immediately following collection, a 1-L sample was drawn from each sampler, preserved with 100 mL of dichloromethane (Burdick and Jackson, UV grade), and stored at ambient temperature awaiting extraction.

Precautions were taken to ensure that the water samples were not contaminated with surface oil. The GO-FLO, Bodega Bodman, and glass Bodman samplers were deployed in the closed position in which valves or seals prevent surface oil from contaminating the inner surfaces of the sampler during deployment. The pumping system was deployed through an unoiled or lightly oiled sea surface and all tubing purged at each depth by pumping for several minutes before a sample was collected. All surfaces of the samplers which contacted the water sample were constructed of noncontaminating materials (glass, aluminum, stainless steel, Teflon, silicon rubber, and Viton rubber). Cross contamination due to carryover between samples was minimized by cleaning bottle samplers between deployments. An in-line Turner fluorimeter on the pumping system indicated that response to oil "hot spots" was rapid and that any subsequent bleed was nondetectable. Thus, oil sorption was not a significant problem. Cross calibration between bottle- and pump-obtained samples indicated good reproducibility between devices in all but the most heavy oil concentrations (17, 13), the latter situation most likely owing to heterogeneity within the water column.

All samples were collected in light seas from a stationary vessel. Surface samples (1 m) were taken during these light sea state conditions. Uncertainty as to sampling depth was on the order of $\pm 1 \text{ m}$.

The unfiltered water sample was transferred to a 1-L separatory funnel and extracted 3 times with 50 mL of dichloromethane. At a few stations, the seawater collected by the pumping system was pressure filtered through a 142-mm, 0.45- μ m, glass-fiber filter held in a stainless-steel filter holder (Millipore) prior to extraction. The solvent extract was dried over sodium sulfate, transferred to a Kuderna-Danish apparatus, and concentrated to 1 mL. The dichloromethane was displaced by repeatedly adding hexane (Burdick and Jackson, UV grade) and evaporating

under a stream of purified nitrogen.

The hexane extracts were analyzed for petroleum hydrocarbons by using a synchronous fluorescence spectroscopy technique (21, 22). In summary, a measured aliquot of the sample extract was dissolved in a known volume of hexane. The intensity of the fluorescence emission was measured from 250 to 500 nm while synchronously scanning at an excitation wavelength 25 nm shorter than the wavelength at which the emission was measured. This technique measures aromatic hydrocarbons with a two- to five-ring aromatic structure (23). The analyses were performed on board the R/V Researcher by using a Farrand Mark I spectrofluorometer equipped with corrected excitation and emission modules. The instrument conditions were as follows: excitation slit, 2.5 nm; emission slit, 5.0 nm; scan speed, 50 nm min^{-1} ; sample cell, single 10-mm nonfluorescing quartz cell. The instrument was calibrated daily by analyzing a series of dilutions of a standard solution of the API Reference No. 2 fuel oil.

The intensities of the fluorescence spectra were measured at several wavelengths which correspond to peak maxima present in an Ixtoc I reference oil sample. The fluorescence spectra were converted to relative concentration units by comparing the peak height at 312 nm to that of the appropriate No. 2 fuel oil standard curve. No. 2 fuel oil was initially used as the calibration standard as it yields a very reproducible and available standard, and due to the lack of an appropriate Ixtoc oil reference prior to the sampling effort. As many of the fluorescence measurements were made on board, and, as the two-ringed aromatic fluorescence signal was strongest in all samples encountered, a strategy was adopted to base all measurements made at sea using fuel oil as the calibration standard and after returning to the laboratory to recalibrate the method using actual microgravimetric measurements on samples. Use of a fresh Ixtoc I oil standard was deemed inappropriate because of rapid compositional changes occurring at the blowout site itself. A more accurate calibration was achieved by using a series of microgravimetric measurements on actual Ixtoc I subsurface oil samples rather than a single reference oil, as the subsurface oil collection more accurately reflects the compositional characteristics of the oil actually present in the sample collection.

The concentrations of oil in No. 2 fuel oil equivalents were converted to absolute concentrations by multiplying by a factor of 2.30. This factor was determined from a linear regression of oil concentrations in No. 2 fuel oil equivalents vs. concentrations of Ixtoc I oil in the actual samples measured by microgravimetry using a Cahn electrobalance. The samples used for this calibration had concentrations of Ixtoc I oil which ranged from 74 to 1700 $\mu g/L$ by gravimetry. The fluorescent material in samples with low concentrations (<20 $\mu g/L$) differs chemically from the material in the samples used for the regression. Although a lower conversion factor should have been used because of this discrepancy, none is available from existing data and the same conversion factor was used for all calculations.

Results

The concentrations of oil in the water column ranged from values of less than $5 \mu g/L$ at a distance of 80 km from the blowout to peak values of 10600 $\mu g/L$ within a few hundred meters of the blowout. The highest concentrations were observed within 25 km of the blowout in the top 6 m of the water column. The higher values reported here may be an underestimate since some oil was visibly adsorbed onto the walls of the bottle samplers during sampling in the plume.

The concentration data are summarized in Figure 2, which is a contoured vertical cross section of the oil concentrations along the plume axis, and in Table I. Elevated concentrations of subsurface petroleum hydrocarbons occurred from the wellhead out to 40 km to the northeast of the well. At distances greater than 40 km to the northeast and 16 km to the south and west, concentrations were less than 5 μ g/L. The northeastern orientation of the oil-contaminated seawater plume coincided with the observed direction of movement of the surface plume of oil. However, emulsified oil was observed floating on the ocean surface at distances greater than the apparent extent of the oil-contaminated seawater plume. Whereas surface oil was found 80 km or more to the northeast of the well, elevated concentrations of oil in the water column were limited to within 40 km. It is apparent that somewhat dissimilar processes are controlling the transport of surface and subsurface oil. Subsurface petroleum concentrations are heterogeneous in the vicinity of the wellhead as evidenced by the concentration contours in Figure 2. Sorption of oil onto sampling bottle walls probably caused an underestimate of petroleum concentrations at station PO5.

Several distinct spectral patterns were observed among the samples which were collected. Samples containing low concentrations (<5 μ g/L) had a spectrum with a single fluorescence peak at 308 nm (type A). This spectrum results from either background fluorescent material in seawater or low-level contaminants from the sample workup. Most samples containing Ixtoc-related petroleum hydrocarbons exhibited spectral types B and D (Figure 3). Samples with concentrations from 5 to 20 μ g/L had a unimodal spectrum with a peak maximum at 312 nm (type B). This peak results from a predominance of petroleumderived two-ring aromatics which fluoresce from 310 to 330 nm (23). As discussed below, this spectral type reflects the selective dissolution by seawater of two-ring aromatics from the whole oil released from the blowout. Spectral type D is characterized by a series of fluorescent peaks at 312, 328, 355, and 405 nm. This spectrum was predominant for samples with concentrations greater than 20 μ g/L. The series of peaks results from two-, three-, four-, five-, and larger-ring polycyclic aromatic compounds (23). Type D spectra were similar to spectra of the whole oil collected from surface mousse samples.

At a few stations, samples of both whole seawater and filtered seawater through a 0.45- μ m glass-fiber filter from the same depth were analyzed. At stations with low concentrations of oil (P1, P2, and P14), no systematic differences between the filtered and unfiltered samples were found. However, at station PIX 08, the concentrations of oil in the filtered samples were 21% and 28% of the concentrations in unfiltered samples collected at 6 and 16 m, respectively (Table II). In both cases, the spectrum of the filtered sample was depleted in the three- to five-ring region compared to the unfiltered sample.

The distinction between the three spectral types was confirmed by glass capillary gas chromatography analysis (17). The saturated and unsaturated (aromatic) fractions of samples with type D, whole oil, spectra contain petroleum hydrocarbons in a boiling range equivalent to that of $\langle n-C_{10}-n-C_{30}$. The glass capillary gas chromatogram combined with gas chromatographic mass spectrometry data (17) of the aromatic fraction confirms the presence of polycylic aromatic hydrocarbons (PAHs) with two to five rings (Figure 4). Normal alkanes from $\langle n-C_{10}$ to $n-C_{34}$ and a low-boiling unresolved complex mixture predominate

station	collection date	depth, m	wind velocity (direction), knot	sea surface condi- tion ^a	sampling device ^b	petroleum concn, $\mu g/1$	spec- tral type ^c	distance from wellhead, ^d km	sample type ^e
P 7	09/17/79	1	NM ^f	Α	Р	11	В	-2.0	W
		6	NM	Α	Р	40	B	-2.0	w
		14	NM	Α	Р	4	в	-2.0	W
		14	NM	Α	Р	10	В	-2.0	W
		20	NM	Α	Р	5	В	-2.0	W
P9	09/18/79	6	7-9 (75-90° true)	Α	\mathbf{GF}	11	В	-1.0	W
		20	7-9 (75-90° true)	Α	\mathbf{GF}	9	В	-1.0	W
P 5	09/17/79	2	NM	но	30B	2100	D	+0.5	W
		6	NM	но	30B	7000	D	+0.5	W
	\$	20	NM	HO	30B	1500	D	+0.5	W
P10	09/19/79	2	11 (295° true)	но	Р	10500	D	+0.8	W
P11	09/19/79	1	11 (295° true)	BO/S	\mathbf{GF}	300	D	+0.8	W
		1	11 (295° true)	BO/S	\mathbf{GF}	340	D	+0.8	W
		6	11 (295° true)	BO/S	\mathbf{GF}	530	D	+0.8	W
		20	11 (295° true)	BO/S	\mathbf{GF}	110	D	+0.8	W
P15	09/21/79	2	14 (300° true)	BO/S	Р	1000	D	+16.0	W
		20	14 (300° true)	BO/S	Р	50	D	+16.0	W
P 8	09/18/79	6	7-9 (75-90° true)	S/BO	Р	87	В	+22.0	\mathbf{F}
		6	7-9 (75-90° true)	S/BO	Р	416	D	+22.0	W
		6	7-9 (75-90° true)	S/BO	30B	60	D	+22.0	W
		16	7-9 (75-90° true)	S/BO	Р	37	В	+22.0	\mathbf{F}
		16	7-9 (75-90° true)	S/BO	Р	133	D	+22.0	W
		19	7-9 (75-90° true)	S/BO	Р	50	D	+22.0	W
		20	7-9 (75-90° true)	S/BO	30B	20	D	+22.0	W
		40	7-9 (75-90° true)	S/BO	30B	19	В	+22.0	W
P12	09/19/79	1	11 (295° true)	S/BO	\mathbf{GF}	71	С	+23.0	w
		1	11 (295° true)	S/BO	\mathbf{GF}	12	D	+23.0	W
		6	11 (295° true)	S/BO	\mathbf{GF}	22	С	+23.0	W
		20	11 (295° true)	S/BO	\mathbf{GF}	19	\mathbf{C}	+23.0	W
R7	09/18/79	2	7-9 (75-90° true)	S/BO	30B	3	Α	+32.0	W
		35	7-9 (75-90° true)	S/BO	30B	12	С	+32.0	W
		43	7-9 (75-90° true)	S/BO	90B	11	D	+32.0	W

 Table I.
 Sample Description and High-Molecular-Weight Petroleum Hydrocarbon Concentrations (0-30 km from the Wellhead)

^a A = absence of surface oil; HO = heavy oil/mousse coverage (>50%); BO = broken oil/mousse patches (<50%); S = sheen observed. ^b P = pump; GF = 30-L GO-FLO (Teflon-lined); 30B = 30-L glass Bodman; 90B = 90-L Bodman. ^c See text for explanation. Type C intermediate between B and D. ^d (-) = southwest of wellhead (opposite to surface oil movement); (+) = in direction of surface oil and currents. ^e W = whole (unfiltered) water; F = filtrate. ^f NM = not measured.

Table II. Concentrations of Oil in Filtered vs. Unfiltered Water Samples

		concn		
station	depth, m	unfil- tered sample	filtered sample	filtered/ unfil- tered
PIX 08	6 16	$\begin{array}{c} 416 \\ 133 \end{array}$	87 37	$\begin{array}{c} 0.21 \\ 0.28 \end{array}$

in the saturated fraction which does not account for any observed fluorescence. Samples with type B, dissolved oil, spectra contain predominantly substituted one- and tworing aromatic hydrocarbons (Figure 4). Relatively small amounts of PAHs with more than two rings and saturated hydrocarbons are present. Samples with type A spectra contained very low amounts of material.

In summary, higher concentrations (>20 μ g/L) of oil were associated with type D (whole oil) spectra and were found at shallow water depths (<20 m) within 25 km northeast of the well. Moderate concentrations of oil (5–20 μ g/L) occurred to the south and west of the well and from 25 to 40 km to the northeast of the well. Samples collected in this region were of spectral type B, which is characterized by soluble two-ring aromatics. A comparison of oil concentrations in filtered and unfiltered seawater supports the contention that oil in the water column occurred in both a whole-oil (droplet) form and in a fractioned-oil ("dissolved") form, although the operational definition of the material in the filtrate can include dissolved and colloidal oil as well as small oil droplets if the filter is overwhelmed.

Discussion

The high concentrations of oil in samples collected near the blowout probably resulted from suspension of oil droplets in the water column (spectral type D). This hypothesis is consistent with laboratory studies of the formation of oil-in-water dispersions (24-26). These studies have shown that, under vigorous mixing conditions, droplets of oil, which contain two-, three-, four-, and five-ring aromatic compounds, are entrained in the water, and a type D spectrum results. Since the high shear associated with an undersea blowout enhances the formation of oilin-water dispersions (i.e., droplets), the predominance of oil droplets in the water samples is not unexpected.

Seawater samples with less than 20 μ g/L of oil were collected farther than 25 km from the blowout and have type B spectra which are dominated by two-ring aromatic hydrocarbons. Two-ring aromatic hydrocarbons are 1–2 orders of magnitude more soluble than three- and four-ring structures (27). Laboratory studies have confirmed that, under gentle mixing conditions, two-ring aromatics in oil are selectively dissolved by seawater which would result in a type B spectrum dominated by a single peak. The same selection for two-ring aromatics occurs if the large (>1 μ m) droplets are removed from the vigorously mixed dispersion by filtration (25) or centrifugation (24). In samples with type B spectra, oil is present in a "dissolved" state. Two of the three filtered seawater samples collected



(Vertical exaggeration 5,000x; $\sqrt{2}$ = area of concentrations > 100 μ g/l) area of concentration 5–100= μ g/l).

Figure 2. Concentrations of oil along a transect oriented to the northeast of the Ixtoc I blowout, September 1979.

within the oil plume also had type B spectra. These two samples contained approximately 20–30% (37 and 87 μ g/L) of the oil in the unfiltered sample.

We postulate that, within the subsurface oil plume (within 5 km), high concentrations (>600 μ g/L) of oil droplets predominated. The diameters of the oil particles are estimated to be greater than 0.7-1.0 μ m, which has been shown to be the effective pore size of glass-fiber filters (28). Near the leading edge of the oil-contaminated plume, 25 km from the blowout, moderate concentrations (100-300 μ g/L) of oil droplets with diameters generally about 1 μ m comprised 70-80% of the oil in the water. The remaining 20-30% consisted of two-ring aromatics dissolved in the water. Droplets of whole oil with diameters less than about 1 μ m (i.e., passing through the filter) were not found near the edge of the plume, and low concentrations (<20 μ g/L) of dissolved two-ring aromatics predominated.

The absence of high concentrations of oil at depths below 20 m in the plume may have been the result of several processes. The plume of oil and water streaming from the blowout in the sea bed had a net upward velocity which probably caused it to rise quickly to the surface where it spread horizontally in response to prevailing currents. In addition, the positive buoyancy of the oil droplets within the plume may have caused them to move vertically within the plume and remain close to the surface. The possibility that droplets of oil generated by turbulence were formed at the air/oil interface and subsequently driven down into the water column has been largely ruled out through comparisons of the detailed chemistry of surface and subsurface oil (17). The synoptic 20-kHz acoustic reflectance measurements (29) obtained during chemical sampling in addition to detailed GC- and GC/ MS-based chemical measurements (17) support the facts that droplets were present in discreet subsurface plumes within the top 20 m of the water column and that significant subsurface horizontal movement (~ 20 km) of this oil occurred before buoyancy and dilution caused the droplets to rise to the surface or become nondetectable by acoustic reflectance techniques.

Laterally, the chemically detected subsurface oil plume was limited to within 25-40 km to the northeast of the blowout. Although rigorous physical oceanographic measurements were generally lacking, visual observations of surface and subsurface current velocities which were made indicated that surface and subsurface oil were both transported in the same direction (northeast) largely due to a ~ 0.5 -knot current. Movement of surface oil appeared to be more influenced by currents than by winds, the wind vector generally being perpendicular to the direction of surface and subsurface oil movement. Based on the supportable assumption that the subsurface oil was moving to the northeast at a minimum speed of 0.5 knot, it would take approximately 28 h for the oil to reach stations PIX 08 and PIX 12 at the edge of the plume. Mathematical modeling of the weathering of surface and subsurface oil supports this rate of movement (18). Since all stations were sampled 2-4 days after Hurricane Henri had left the study site, oil streaming from the blowout would have had more than ample time to travel beyond these stations and reestablish a quasi-steady-state subsurface plume. Processes other than simply the rate of advection of the oil

Table III.	Mass Balance of	of Oil in	the Top	20 m c	of Water	Column	(Wellhead to 40 km)	
------------	-----------------	-----------	---------	--------	----------	--------	---------------------	--

				-			
distance, km	approximate width of plume, m	water depth, m	mean whole water concn, µg/L	total amt oil in water, g	% of total	total amt ot oil spilled during oil transit, ^a bbl	
0-1	1000	20	1000	$20 imes 10^{6}$	23		
1-12	500	20	500	60 x 10°	69		
12 - 25	100	20	250	6.5×10^{6}	7.5		
25 - 40	100	20	10	$0.2 imes 10^6$	0.2		
				86.7 × 10 ⁶		20 000	

^a Rate of spillage = 10000 bbl/day (OSIR, 1980); at 0.5-knot current, oil travels ~22 km/day; study region (~40 km) is therefore equivalent to 2-day transit distance; hence, 20 000 bbl figure. ^b ~530 bbl.



Figure 3. Representative synchronous fluorescence spectra of seawater samples collected near the Ixtoc I blowout.

must have been responsible for the horizontal limitation $(\sim 40 \text{ km})$ of the subsurface plume.

As previously mentioned, one such process may have been a progressive agglomeration of smaller droplets to form larger droplets as oiled seawater was carried away from the blowout. According to Stokes' law, the formation of larger droplets would increase the positive buoyancy and upward velocity of the oil (30). Such a process would remove oil from the subsurface plume to the ocean surface as the oiled water moved away from the blowout.

Alternately, one of the many frontal zones observed from the air in the region may have restricted the horizontal advection or diffusion of the plume. Such fronts have been observed (31) to affect the lateral movement of surface oil slicks. A vertical cross section of $\sigma_{\rm T}$ (seawater density) along the plume axis (Figure 5) suggests the possibility of the existence of such a front through the sampling region. The profile, which was generated from STD profiles and salinity and temperature measurements of discrete water samples at stations occupied over a 5-day period, suggests the presence of a lens of less saline, less dense water to the northeast of the blowout. This lens may have resulted



Figure 4. Glass capillary gas chromatograms of aromatic fractions of water samples with types B and D fluorescence spectra (N = naphthalenes; P = phenanthrenes; DBT = dibenzothiophenes; AB = alkylated benzenes; I.S. = internal standard (deuterated anthracene); C₁, C₂, C₃, C₄, C_n = alkylated compounds with *n* carbons; UCM = unresolved complex mixture).

from freshwater runoff from the adjacent land which had experienced heavy rains and flooding both prior to and during Hurricane Henri. The extent of the lens to the southwest (i.e., toward the blowout site) occurred between 25 and 40 km from the blowout, which was the location of both the strong subsurface oil concentration gradient and the loss of definition of the surface oil plume. While the hydrographic data were collected over several days and hence are not synoptic, the constancy of aerial observations of blue water/turbid water interfaces (i.e., fronts) suggests that gross changes in the hydrographic regime probably did not occur within the 4-day sampling period. Samples were not taken on either side of the transect near the gradient which would allow the three-dimensional behavior of the oiled seawater plume to be better defined.

Low concentrations (<20 $\mu g/L$) of oil occurred to the south and west of the well (stations PIX 07, PIX 09, PIX 06, and RIX 11). The lack of significant oil at these stations indicates the strong influence of advection on the dispersion of subsurface oil from the blowout driving the oil to the northeast. During the sampling period, the subsurface plume of oiled seawater and the surface plume were similarly aligned to the northeast under the presumed influence of oceanic currents.

Based on the determined subsurface oil concentrations, a mass balance was constructed (Table III) to determine



Figure 5. σ_T along a transect oriented to the northeast of the Ixtoc I blowout, September 1979 (vertical exaggeration, 5000×).

the quantity of Ixtoc I oil present in the water column within 40 km of the wellhead at any given time during the blowout event (i.e., a "standing crop" of subsurface oil). Using the assumptions of plume width and spillage rate shown in the table which ignore oil beneath 20 m and at distances greater than 40 km from the wellhead, we calculate that at any given time $\sim 3\%$ of the oil introduced from the blowout existed in the top 20 m of the water column. Most of this 3% was located within 25 km of the wellhead. This calculation would not be significantly altered by inclusion of petroleum in the water column outside of the observed surface plume as measurements of outside plume oil concentrations were very low (generally $<1 \mu g/L$ (32)). The mass balance considers only the oil's behavior within the study region. Subsequent dispersion of surface oil by natural physical processes driving oil into the water column are not incorporated.

Conclusions

Oil released from the Ixtoc I blowout tended to form a subsurface plume of oil droplets suspended and laterally advected in the top 10–20 m of the water. The subsurface petroleum hydrocarbons, representing $\sim 3\%$ of the introduced oil, moved in a northeasterly direction in response to ocean currents rather than wind. The northeasterly horizontal advection of the oiled seawater plume may have been inhibited or deflected by a lens of less saline water situated to the northeast of the blowout.

Concentrations of oil within the plume ranged from 20 to >10000 μ g/L. The highest concentrations of oil (up to 10600 μ g/L), which may have been underestimated because of adsorption in the sampling systems, were found within the oiled seawater plume near the Ixtoc I blowout. These values were in the same range as concentrations found underneath oil slicks during experimental surface spills in the New York Bight (33). During the experimental

spills maximum concentrations within the top 3–9 m of water ranged from 950 μ g/L under an untreated slick to 17800 μ g/L under a slick treated with dispersant. Maximum concentrations of oil (300 μ g/L) measured in the vicinity of the Ekofisk blowout in the North Sea (11, 1) and in the Amoco Cadiz (350 μ g/L) and Argo Merchant (450 μ g/L) tanker spills (2, 6) were comparable to concentrations at the outside edge of the oil plume at the Ixtoc I blowout. The higher concentrations of subsurface oil found during the Ixtoc I blowout resulted from the subsurface release of oil, rather than at or above the ocean's surface as occurred during the Ekofisk blowout or during the tanker spillages.

The horizontal and vertical limitations of the size of the oiled seawater plume from the Ixtoc I blowout suggest that both the physical properties of the oil (i.e., droplet size and density) and the density and current structure of the seawater controlled the dispersal of oil from this undersea blowout. Oceanic frontal systems may act as barriers to subsurface transport of oil and may also act as conduits for subsurface movement of oil along the frontal axis.

Acknowledgments

We acknowledge the valuable assistance given by the following individuals to the intensive shipboard sampling effort: Keith Hausknecht, Jack Barbash, George Perry (ERCO); John Farrington (Woods Hole Oceanographic Institution); James Payne (Science Applications Inc.); Larry McCarthy (University of New Orleans); Donald Atwood, Chief Scientist (NOAA); and the officers and crew of the R/V Researcher and Pierce.

Literature Cited

 Grahl-Neilsen, O. In "Proceedings of the Conference on Assessment of Ecological Impacts of Oil Spills", AIBS, Keystone, CO, June 14-17, 1978.

- (2) Grose, P. L., Mattson, J. S., Eds. "The Argo Merchant Oil Spill. A Preliminary Scientific Report"; U.S. Department of Commerce, NOAA, ERL: Boulder, CO, 1977.
- (3) Levy, E. M. Water Res. 1971, 5, 723-33.
- (4) Boehm, P. D.; Perry, G.; Fiest, D. In "Proceedings of a Symposium: In the Wake of the Argo Merchant", Jan 11-13, 1978, University of Rhode Island, Kingston, RI, 1978, pp 58-64.
- (5) Boehm, P. D. Mar. Chem. 1980, 9, 225-81.
 (6) Calder, J. A.; Lake, J.; Laseter, J. "Chemical Composition" of Selected Environmental and Petroleum Samples from the Amoco Cadiz Oil Spill", NOAA/EPA Special Report, The Amoco Cadiz Oil Spill, A Preliminary Scientific Report, 1978. U.S. Department of Commerce, NOAA, Boulder, CO.
- (7) Gordon, D. C., Jr.; Keizer, P. D.; Hardstaff, W. R.; Aldous, D. G. Environ. Sci. Technol. 1976, 10, 580-5.
- (8) Gordon, D. C., Jr.; Keizer, P. D.; Dale, J. Mar. Chem. 1974, 2. 251-61.
- (9) Berryhill, H. L. "Environmental Studies. South Texas Outer Continental Shelf, 1975: An Atlas and Integrated Summary"; U.S. Bureau of Land Management: New Orleans, LA, 1977.
- (10) Brown, R. A.; Searl, T. D.; Eliot, J. J.; Phillips, B. G.; Brandon, D. E.; Monaghan, P. H. In "Proceedings, Joint Conference on Prevention and Control of Oil Spills"; API: Washington, DC, 1973; pp 505–19. (11) Mackie, P. R.; Hardy, R.; Whittle, K. J. J. Fish. Res. Board
- Can. 1977, 35, 544-51.
- (12) Brooks, J. M.; Bernard, B. B.; Sauer, T. C., Jr.; Abel-Reheim, H. Environ. Sci. Technol. 1978, 12, 695-703.
- (13) Brooks, J. M.; Wiesenberg, P. A.; Burke, R. A.; Kennicutt, M. C. Environ. Sci. Technol. 1981, 15, 951-9.
- "Proceedings of a Symposium on the Preliminary Results (14)from the September 1979 Researcher/Pierce Ixtoc-1 Cruise"; NOAA Office of Marine Pollution Assessment: Boulder, CO, 1980.
- (15) Oil Spill Intelligence Report (OSIR). "Special Report: Ixtoc I", Jan 4, 1980, Newsletter; Center for Short-Lived Phenomena: Cambridge, MA, 1980.
- (16) Payne, J. R.; Flynn, N. W.; Mackiewicz, P. J.; Smith, G. S. In "Proceedings of a Symposium on the Preliminary Results from the September 1979 Researcher/Pierce Ixtoc-1 Cruise"; NOAA Office of Marine Pollution Assessment: Boulder, CO, 1980; pp 239-67.
- (17) Boehm, P. D.; Fiest, D. L. In "Proceedings of a Symposium on the Preliminary Results from the September 1979 Researcher/Pierce Ixtoc-1 Cruise"; NOAA Office of Marine Pollution Assessment: Boulder, CO, 1980; pp 267-340.

- (18) Boehm, P. D.; Fiest, D. L.; Mackay, D.; Paterson, S. In "Proceedings 1981 Oil Spill Conference"; American Petroleum Institute: Washington, DC; 1981; pp 453-60.
- Gagosian, R. B.; Dean, J. P., Jr.; Hamblin, R.; Zafiriou, O. C. Limnol. Oceanogr. 1979, 24, 583-8.
- (20) Payne, J. R.; Clayton, J. R., Jr.; de Lappe, B. W.; Millikin, P. L.; Parkin, J. S.; Okazaki, R. K.; Letierman, E. F.; Risebrough, R. W. "Hydrocarbons in the Water Column", Southern California Baseline Study, Vol. III, Report 3.2.3, Final Report, submitted to the Bureau of Land Management, Washington, DC, 1977, pp 1-207.
- (21) Wakeham, S. G. Environ. Sci. Technol. 1977, 11, 272-6.
- (22)Gordon, D. C., Jr.; Keizer, P. D. Technical Report No. 481, Fisheries and Marine Service, Environment Canada, Dartmouth, Nova Scotia, 1974.
- (23) Lloyd, J. B. F. J., Forensic Sci. Soc. 1971, 11, 83-94.
- (24) Zurcher, F.; Thuer, M. Environ. Sci. Technol. 1978, 12, 838-43
- (25) Shaw, D. G.; Reidy, S. K. Environ. Sci. Technol. 1979, 13, 1259-63.
- (26)Prouse, N. J.; Gordon, D. C., Jr.; Keizer, P. D. J. Fish. Res. Board Can. 1976, 33, 810-8.
- Mackay, D.; Shu, W. Y. J. Chem. Eng. Data 1977, 22, 399. (27)
- Sheldon, R. W. Limnol. Oceanogr. 1972, 17, 494-8. (28)
- Walter, D. J.; Proni, J. R. In "Proceedings of a Symposium (29)on the Preliminary Results from the September 1979 Researcher/Pierce Ixtoc-I Cruise"; NOAA Office of Marine Pollution Assessment; Boulder, CO, 1980, pp 525-44.
- (30) Thuer, M.; Stumm, W. Prog. Water Technol. 1977, 9, 183-94.
- (31) Klemas, V. Int. J. Remote Sensing 1980, 1, 11-28.
- (32) Payne, J. R.; Smith, G. S.; Mankiewicz, P. J.; Shokes, R. F.; Flynn, N. W.; Moreno, V.; Altamirano, J. In "Proceedings of a Symposium in the Preliminary Results from the September 1979 Researcher/Pierce Ixtoc-I Cruise"; NOAA Office of Marine Pollution Assessment: Boulder, CO, 1980; pp 119-68.
- (33) McAuliffe, C. D.; Canevari, G. P.; Searl, T. D.; Johnson, J. C.; Greene, S. H. In "Proceedings of the International Conference of Petroleum and the Marine Environment", Monaco, May 27-30, 1980.

Received for review August 5, 1980. Revised manuscript August 26, 1981. Accepted October 12, 1981. This work was supported by a research contract from the National Oceanic and Atmospheric Administration, Office of Marine Pollution Assessment (No. NA 79 RAC 00151).