NOAA Ship RESEARCHER/Contract Vessel PIERCE Cruise to IXTOC-1 Oil Spill:

Overview and Integrative Data Assessment and Interpretation

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#### Abstract

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#### John W. Farrington

An overview and summary of data and major interpretations of a research cruise to the IXTOC-I oil spill during September, 1979 are presented. Over 1,000 samples for biogeochemical and microbiology studies were taken inside and outside the slick within 40 km of the well site. Hydrographic sections are presented and describe the surface and subsurface distribution of methane and oil components. Measurements of weathering parameters are summarized.

The gas and oil entered the water column at the sediment/water interface forming a vertical plume near the well site. A horizontal plume developed down current under a slick due to the advective influence of water circulation on the vertical plume. The extent of the horizontal plume seemed to be controlled by hydrographic features. Despite the subsurface injection and mixing into the water column the vast majority of the oil was in a surface slick of oil and oil-water "mousse" mixture.

Microbial populations were modified by the presence of the oil and populations capable of degrading oil were present. However, amounts of nutrients were insufficient to support extensive microbial degradation. Chemical analyses confirm that there was little microbial degradation and the fate of the oil was primarily controlled by physical and physical-chemical processes.

A separate section of the report addresses some of the sociological, political and logistical aspects of a research response to an oil spill of this type.

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#### Preface

I regret the delay in issuing this report which was caused in part by unavoidable illness, and in part by my participation in a National Academy of Sciences study of Petroleum in the Marine Environment. In view of the fact that publication of a report of preliminary findings from the cruise and several publications in conference proceedings and the scientific literature derived from cruise data were available, I placed a priority on the unexpectedly lengthy (four years) and complicated tasks of the National Academy of Sciences Steering Committee on Petroleum in the Marine Environment and a few other tasks.

My apologies to those who have been inconvenienced. My appreciation is extended to the N.O.A.A. Office of Marine Pollution Assessment - especially Capt. Larry Swanson, Dr. Lou Butler and Dr. John Calder who were patient and understanding in regard to this delay.

#### Acknowledgements

The acknowledgements in regard to this report could extend to as many pages as the report itself if proper credit were to be given to the many people I have discussed this topic with or to those active in the planning, execution of the RESEARCHER/PIERCE cruise and subsequent data interpretation. If I miss a group I hope that they accept my apologies for any inadvertent omission.

Foremost are acknowledgement of the efforts of fellow scientists and crew of the NOAA Ship RESEARCHER and the Tracor Marine Ship PIERCE. For prepara-

tion of this report, I thank Mr. Bruce W. Tripp for his valuable assistance and an advisory committee of Drs. Randolph Ferguson, Paul Boehm, James Payne, Ed Overton and Ron Atlas who guided the initial stages of this report preparation. Numerous scientists and engineers in NOAA's Hazardous Materials Response Team provided personal observations which provided a framework of reference for data interpretation: these included Dr. Peter Grose, Dr. Jerry Galt, Mr. John Robinson and colleagues.

Capt. Larry Swanson, Dr. Lou Butler and Dr. John Calder provided administrative and logistics support and assistance as did Ms. Judith Roales at the initiation of this contract.

I am greatful to the Office of Naval Research for support of my participation in the RESEARCHER/PIERCE Cruise.

#### Objectives of this Report

This report has two main objectives:

- 1) An overall integration and interpretation of some of the results of the scientific investigations of the September, 1979 NOAA Ship RESEARCHER, Contract Vessel PIERCE Cruise to the IXTOC-I Oil Well Blowout (Section I).
- 2) An examination of the socio-political planning and logistics efforts associated with the cruise and recommendations for future oil spill research response efforts for this type of spill (Section II) which has been published separately with a focus on Georges Bank as an example (Farrington, 1983).

A general summary of the results and findings of the cruise for the lay person has been prepared separately.

#### General Background

Oil spills are among the more visually dramatic aspects of modern society's intentional and accidental releases of materials to the ocean.

Thus, they attract wide publicity — at least during the stages where visual impacts can be reported. During the late 1960's and throughout the decade of the 1970's, scientific studies of several oil spills documented that spills could have effects on marine organisms and thereby directly or indirectly adversely impact economically valuable marine resources. After a few years of studies of selected oil spills and oil seep areas it became apparent that the adverse impact of oil in terms of geographic limits, severity of impact within a given area, and duration of impact in terms of days to years depended on a complex interaction of many factors. For example, the type of chemical composition of the spilled oil, the exposure dose in pelagic and benthic habitats, the oceanographic and meteorological conditions, seasonality of life cycles of biota in the area and ecosystem type were among these interacting

factors (Straughan, 1974; N.A.S., 1975). More recent reviews after several more years of oil spill studies have strengthened this conclusion (e.g. Connel and Gilbert, 1980; Vandermeulen, 1982). It is important to understand that we are investigating the fate and effects of a mixture of up to ten thousand or more chemicals released to the environment which is already a complex chemical soup. Then physical, chemical, and biological factors alter the composition of the oil and we are searching for a range of effects from the subcellular to ecosystems and on time scales from hours to years (e.g. see Farrington, 1975; Vandermeulen, 1982, among several others).

If the situation was less complex or if the net results of the interactions were more readily apparent; for example, either extensive and dramatic long-term wastage of a economically valuable fishery or if only a few dead organisms resulted from spills, then there would be very little controversy. Unfortunately, as with numerous environmental concerns, there is controversy because the situation is so complicated. Scientists with experience and reputations founded in both field observations and experimentation often publicly disagree with assessments by each other. A recent critique of an article on "Petroleum and Marine Fishes: A Review of Uptake Disposition and Effects" (Malins and Hodgins, 1981) by J. F. Payne (1982) and an earlier controversy about the Offshore Ecology Investigation of the Gulf Universities Research Consortium (Sanders and Jones, 1981) illustrate this point.

Although some of the controversy might be ascribed to differing degrees of research and scholarly excellence, if the evidence were more extensive, rigorous, and subject to less extrapolation in both time and space then we could confidently expect less legitimate disagreement.

The potential for adverse impact on valuable living resources and economically valuable coastal recreation area is entered on the decision-making balance opposite to the need for petroleum exploration, production, transportation and use to satisfy a substantial portion of society's energy needs. Thus, scientific controversies surrounding oil pollution problems are directly injected into the arena of important policy decisions involving billions of dollars of mineral resources and food resources from the sea. This has led to the study of the fate and effects of selected oil spills to provide a firmer scientific basis for unravelling the complexities of the problems and to provide insight and practical information to those attempting to contain and clean up spilled oil.

#### IXTOC-I Background

The IXTOC-I well of the national oil company of Mexico, PEMEX, blew out on June 3, 1979 in the southern Bay of Campeche in the Gulf of Mexico at approximately 80 km NW of Ciudad del Carmen position location 19°24'29.418"N, 92°19'36.640"W. Although, as previously discussed in this report, each oil spill has unique aspects, the IXTOC-I had some special aspects.

- 1) It was a sub-sea blowout as contrasted to the Bravo platform blowout in the North Sea and the Chevron spill in the Gulf of Mexico near the U.S. coast which discharged oil at or above the sea surface.
- 2) It was a continental shelf oil spill in a new exploration area; a situation much feared by environmental conservation groups concerned with several U. S. Department of the Interior outer continental shelf lease areas and similar lease areas elsewhere in the world.
- 3) The spill continued for a long period of time with oil being transported long distances to the coast of the United States.

- 4) The spill eventually became the largest up to that time. Although as will be discussed later, estimates of the input have a large uncertainty.
- 5) The fact that oil from an accident on the Mexican continental shelf entered U. S. waters provided the potential for international legal problems complicated by interactions of state and local agencies in Texas. Thus, there were international, national, and local political requirements for a response of some type to study the fate and effects of the spilled oil.

#### U. S. Scientific Response to IXTOC-I 0il Spill

The U. S. scientific resonse to the IXTOC-I oil spill can usefully be divided into three categories.

- 1) Response in Support of Protection and Clean-up. This response has been described in a separate report (N.O.A.A., 1981). The scientific inputs to this response were:
  - a) Collection, collation, and assessment of oceanographic and meteorological data relating to the probable pathways of movement of oil towards the U. S. coast and predictions of areas where oil would come ashore.
  - b) Assessment of areas of greatest potential ecological or biological impact.

These investigations were needed to provide input to the On Scene Coordinator (OSC) for deployment of protective booms, and other protective and clean-up measures.

#### 2) Damage Assessment. There was the need:

a) To provide data on the extent to which IXTOC-I oil had entered the ecosystems of the U.S. Gulf Coast continental margin and coastal areas.

- b) To assess what biological, ecological damage had occurred or might occur in the future as a result of the IXTOC-I oil and what this damage might mean in terms of economic losses.
- c) To assess economic damage resulting from loss of recreational value of oiled beaches and oiled coastal areas used for hunting and fishing.

This response has been described in a report by Energy Resources Company (ERCO, 1982).

3. Research into the General Aspects of Fate and Effects of Spilled Oil. This effort evolved with the realization early in the spill that the spill had several especially unique characteristics. The N.O.A.A. Ship RESEARCHER and Contract Vessel PIERCE cruise to the spill site was one of the largest of these efforts within this general category, although many of the activities in 1) and 2) were of a research nature.

#### SECTION I:

# Integration and Interpretation of Some Important Results from the NOAA Ship RESEARCHER and Contract Vessel PIERCE Cruise.

#### A. General Cruise Information

This section contains some paraphrasing or verbatim subsections from the paper by Atwood, Benjamin and Farrington in the Symposium on Preliminary Results from the cruise (NOAA, 1980) as well as new information. It presents information important to set the scene for later sections.

The primary vessel for the cruise was the NOAA Ship RESEARCHER, with its extensive laboratory space. A helicopter landing platform was placed aboard for a four-passenger helicopter, leased from Crescent Airways, Inc., along with its crew. This helicopter proved to be absolutely essential to operating the vessels and to 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, was leased from Tracor Marine to accompany the RESEARCHER to the blowout site. This vessel's laboratory space also was 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 sophisticated sample workup and underway experiments. Sample transfer between the two vessels was accomplished using small boats and the helicopter.

Both ships staged up for the cruise in Miami, Florida, and departed that port on September 11. A timetable for the cruise is given in Table 1a, 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. Table 1b lists science personnel participating in the cruise and Table 1c lists participating groups and their function.

#### 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 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-I 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.

#### 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

the 16th and 17th of September, resulting in seas in excess of fifteen feet.

Both vessels operated throughout this storm period with minimal time loss.

However, all drilling rigs in the vicinity of IXTOC I 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 the 16th of 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 significant effects on weathering and weathering rates, as will be discussed below.

#### Water Characteristics

Water column characteristics in the vicinity of the well and plume were variable and typical of subtropical coastal environments. Surface tempera-

tures 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  $34.5^{\circ}/_{\circ\circ}$  to  $36.6^{\circ}/_{\circ\circ}$  and were variable over that range throughout the water column. In general, when low (<  $35.0^{\circ}/_{\circ\circ}$ ) salinities were observed they occurred at the surface. Below 10 m salinities were generally in excess of  $35.5^{\circ}/_{\circ\circ}$ .

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. This will be discussed in more detail in a later section. 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, Pl, 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-hour 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.

A series of sketches of the plume based on the observations during helicopter flights are given in Figure 3. Table 3 lists the helicopter flights and observers. Table 4 presents a brief summary of pertinent observations from the C/V PIERCE.

#### 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. Chemical and physical characteristics of the oil types mentioned are discussed in more detail in papers in NOAA (1980).

#### 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 vi-

cinity 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 burn and extended out to a maximum of one to three km, 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 meters, 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 meters from the flames to several km 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 spheroids 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, e.g., 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 also forms into sticky but discrete spheroids. These spheroids (commonly referred to as balls) readily coalesce into larger masses 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 spheroids often covered the sea surface and, like the light brown emulsion, lined up in Langmuir lines or cells. In some instances, these spheroids 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 8 to 24 km from the burn and extended out to about 35 km. The extent of the zone and rate of mousse formation apparently were dependent on sunlight intensity and wind stress based on observations from helicopter flights and observations from the PIERCE. A light to heavy sheen of surface oil was always present in this zone. This will be discussed in more detail in a later section.

#### 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.

#### SAMPLING STRATEGY

The initial sampling strategy for the cruise was developed in August and called for the following sequence:

- 1) Sampling of fresh oil and "mousse" in its early stages of formation would be done near the well site. This would be accompanied by air, water, and slick sampling near the well site.
- 2) The two ships would proceed along the western Gulf of Mexico about 300 to 450 km offshore, sampling mousse of progressively older age as the coast of Texas was approached. Water and surface sheen in contact with this older mousse would also have been sampled.

The sampling strategy had to be extensively modified once it was clear that the circulation of the Gulf had changed by the time the ship arrived. This was apparent after the first helicopter flight to the well site area as the RESEARCHER and PIERCE approached. As a result, it was decided to focus more of the cruise effort at the well site area, sampling intensively at the edges of the plume and in the plume itself. One goal of this strategy was to provide some broad coverage of sampling stations for general investigation of

processes active in controlling the fate of the discharge oil and gas near the well site, and progressively farther away in the area of the visually recognizable slick. This included air sampling for  $\mathbf{C}_5$  and higher-molecular-weight compounds; surface slick sampling for heavier-molecular-weight compounds; water sampling for gases, volatile compounds in the range of  $\mathbf{C}_7$  to  $\mathbf{C}_{17}$  hydrocarbons, and higher-molecular-weight particulate and dissolved compounds; surface sediment sampling; and a few sediment trap samples. The water column was sampled in most of the same locations for microbiological studies. Plankton tows were obtained under the slick from the PIERCE, and neuston tows were obtained from the RESEARCHER. A listing of the sample type collected and the number of each is given in Table 5. Table 6 contains the sample code designations used during the cruise.

Two different acoustic arrays, 20 kHz and 200 kHz, were operated on the PIERCE to guide the sampling under the slick.

A second goal was the intensive sampling of mousse in an attempt to gain further insight into the relationship between physical form, chemical composition, and microbial processes. It was hypothesized that the chemical analyses and microbial studies would provide clues as to how the mousse formed, what its fate would be, and the extent to which toxic compounds were incorporated in the mousse or produced during mousse formation. This was, and is, an important area of investigation because "rafts" of mousse were transported across the Gulf of Mexico to distances of over 800 km to the coast of Mexico near Tampico and on up to the U.S. coast near Brownsville and Port Aransas,

A third goal was the sampling of surface sediments on two transects in the area off the coast near the U.S. Department of Interior, Bureau of Land Manage-

ment Outer Continental Shelf Environmental Studies. There had been earlier reports of slicks and mousse in the waters in this general area. If this had resulted in extensive contamination of surface sediments, analyses of these sediment samples could provide definitive data. If the analyses showed no detectable IXTOC-I oil, then these samples would provide a set of clean sediment analyses for the area in case of further incursions of IXTOC-I oil.

A total of 1,671 samples of various types were obtained during the cruise. After the cruise, time and funds placed constraints on the number of samples that could be analyzed. Two analytical strategy meetings after the cruise provided guidance to all involved as to priorities of analyses and specific sample sets and types to be analyzed in the laboratory. The general approach was again to focus on (1) the samples close to the well site and near the slick, to gain information about the immediate fate of the oil over days to weeks; (2) samples of mousse collected throughout the cruise. Table 7 summarizes the set of samples analyzed.

Table 1a. Timetable for RESEARCHER/PIERCE IXTOC-I 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 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

# Table 1b. RESEARCHER/PIERCE IXTOC-I Cruise Science Personnel NOAA/National Ocean Survey

#### NATIONAL OCEAN SURVEY PERSONNEL

Capt. Ronald L. Newson, Commanding Officer, RESEARCHER Lt. Cdr. Richard L. Permenter, Operations Officer, RESEARCHER Lt. Cdr. H. Bruce Arnold, Operations Officer assigned to G. W. PIERCE Chief Robert L. Hopkins, Chief Survey Technician, RESEARCHER

#### SCIENTIFIC PERSONNEL - RESEARCHER

Dr. Donald Atwood	NOAA/AOML, Chief Scientist
Dr. John Farrington	Woods Hole Oceanographic Institution, Senior
	Chemist
Dr. Randy Ferguson	NOAA/NMFS, Beaufort, North Carolina, Senior
	Biologist
Dr. James Payne	SAI (Science Applications, Inc.), La Jolla,
	California
Dr. Fred Pfaender	University of North Carolina
Mr. Earle Buckley	University of North Carolina
Mr. David Fiest	ERCO (Energy Resources Co., Inc.), Cambridge,
	Massachusetts
Mr. George Perry	ERCO (Energy Resources Co., Inc.)
Ms. Dale Finch	NOAA/AOML
Mr. Ricardo Klimek	Mexican Scientist
Mr. Victor Moreno	Mexican Scientist
Mr. Jose Altamirano	Mexican Scientist
Mr. Michel Marchand	French Scientist/Observer
Mr. Glen Aurelius	Helicopter Pilot
Mr. Gary Freeman	Helicopter Mechanic

#### SCIENTIFIC PERSONNEL - G. W. PIERCE

Mr. Donald Walter	NOAA/AOML, Senior Scientist
Mr. Mahlon Kennicutt	Texas A & M University
Mr. Keith Hausknecht	ERCO (Energy Resources Co., Inc.)
Mr. Jack Barbash	ERCO (Energy Resources Co., Inc.)
Ms. Kendra Daly	University of Washington
Ms. Anne Bronner	University of Louisville (Kentucky)
Mr. George Roubel	University of Louisville (Kentucky)
Mr. Antonio Puig	NOAA/AOML
Mr. Paul Dammon	NOAA/AOML
Mr. Lawrence Guest	NOAA/AOML

# Table 1c. RESEARCHER/PIERCE IXTOC-I Cruise Participating Groups and their Functions

NOAA/Office of Marine Pollution Assessment

Funding logistics

NOAA/ERL Atlantic Oceanographic and Meteorological Laboratories

Cruise logistics and procurement Science coordination Chemistry contract monitoring

NOAA/National Marine Fisheries Service, Southeast Fisheries Center

Microbiology contract monitoring Coordination of cruise biology efforts

NOAA/National Marine Fisheries Service, National Analytical Facility

Intercalibration on hydrocarbons and NSO polar compounds

NOAA/National Ocean Survey

RESEARCHER

Procurement and contract monitoring for R/V PIERCE

Woods Hole Oceanographic Institution

Organic geochemistry Coordination of cruise chemistry efforts

Texas A & M University

Sampling and analysis of  $C_1\text{--}C_4$  gases and volatile organic compounds

University of Washington

Zooplankton distributions

Energy Resources Co., Inc.

Organic geochemistry

Science Applications, Inc.

Organic geochemistry

Table 1c. - (cont.)

Global Geochemistry Corporation

Isotopic ratios in spilled IXTOC-I crude oil

Center for Bio-Organic Studies, University of New Orleans

Photooxidation of IXTOC-I crude oil Chemical analysis of microcosm experiments

University of North Carolina

Microcosm experiments on microbial degradation of IXTOC-I crude oil
University of Louisville

 $\underline{\text{In-situ}}$  studies of microbial degradation of IXTOC-I crude oil Tracor Marine, Inc.

R/V PIERCE

Crescent Airways

Helicopter and crew

Table 2. Wind Speed and Direction Observed During the RESEARCHER/PIERCE IXTOC-I 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	80	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	80	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
1	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	3000	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
Jop compor	1500	16	360	22°30.0'N 096°58.0'W
	2000	13	035	22°22.6'N 097°31.7'W

Table 2. (Cont.)

Date	Time (Local/Miami)	Speed (Knots)	Dir. (True)	Position
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
Zo september	1500	15	010	27°41.7'N 095°48.5'W
	2000	14	080	28°20.3'N 095°10.9'W

Table 3. IXTOC-I RESEARCHER/PIERCE Cruise, September 1979
List of Helicopter Flights in Vicinity of IXTOC-I Output Plume

Date	Time	Observers
9-15-79	1731 - 1921	Farrington, Atwood
9-16-79	1053 - 1248	Farrington, Moreno
9-16-79	1430 - 1645	"Mousse" pick up
9-17-79	1510 - 1900	Newsome
9-18-79	0911 - 1115	Atwood, Payne
9-18-79	1409 - 1605	Atwood, Fiest
(N.W. & S.W.	transects)	
9-19-79	0914 - 1050	Atwood, McCarthy
9-19-79	1411 - 1536	Atwood, Farrington
9-20-79	1224 - 1400	Farrington, Atwood
9-21-79	0930 - 1100	Farrington, Ferguson
9-21-79	1630 - 1800	Farrington, Buckley

Table 4. Brief Summary of Pertinent Visual Observations from C/V PIERCE (Note all times are GMT).

PIX 03		
9/16/79	1435 1503 1515	Sheen area w/many surface tarballs
PIX 04 9/16/79	1705 1800	
PIX 10 9/19/79	1343	Into heavy sheen
PIX 13 19/19/79	2306	Small flakes of oil on surface tend to collect on lee side of vessel and form balls
	2359	Passing through patches of oil which follow windrows
9/20/79	0019	19 nm from well o/c 045° going through heavy conc. of brown oil on surface
	0046	
PIX 14	3 7 5 /	
9/20/79	1540	Mousse balls floating beside ship (approx. 6 to 8" or 15 to 20 m in diameter)  Mousse forms in rolls evenly spaced about the length of surface waves
PIX 15		
19/21/79	1200 1705	Patchy mousse on surface Two nights ago as winds were picking up the heavier surface oil at the 24 mile station formed into windrows parallel to the wind. The ship was moving perpendicular to them. Last night in this same area the oil was not in this form but seemed to be formed into mousse rolls which were rolled and formed in the direction of the wind. The long axis of the rolls were perpendicular to the wind. This makes one think that after the windrows had formed on the previous night the wind caused them to roll on each other (like rolling a carpet), and thus the mousse rolls are formed perpendicular to the wind.
9/22/79	0027	Passed across boundary of sheen. Appears all water south of this boundary is covered w/light sheen. All water north has less or no sheen. Boundary is distinct and runs approximately east to west w/no visible end.

Table 5. Kinds and Numbers of Samples Collected.

Sample Type	Number of Samples
Air Sample	37
Ammonia - NH <sub>4</sub>	22
Microbiology, Acridine Orange Direct Counts of Bacteria	69
Bottom Sediment	98
Chlorophy11	82
Control H <sub>2</sub> O	19
Control H <sub>2</sub> O, Chlorophyll	18
Control H <sub>2</sub> O, Extracted	3
Control H <sub>2</sub> O, Low Molecular Weight Hydrocarbons	21
Control H <sub>2</sub> O Particulates	6
Dead Fish	1
Hydrocarbon Biodegradation	19
Kjeldahl Analysis	2
Large Scale Hydrocarbon Biodegradation	4
Long Term Microcosm Study	12
Low Molecular Weight Hydrocarbon, H <sub>2</sub> O	130
Microbiology	34
Microbiology - C <sup>14</sup> , Amino Acid	15
Microbiology - C <sup>14</sup> , Hexadecane	15
Microbiology - C <sup>14</sup> , Naphthalene	15
Microbiology - H <sup>3</sup> , Amino Acid	15
Microbiology - Plate Counts	32

Table 5. (cont.)

Sample Type	Number of Samples
Mousse	93
Nutrients	100
Oil Covered Shell	1
Oil Patch	1
Oil/Water Emulsion	2
Dissolved Oxygen	100
Particulates	31
Plankton	67
Purge Trap - Extracted - Filtered	7
Salinities	63
Sand, Beach	3
Sheen	112
Spanish Mackeral - Liver and Muscle	1
Surface Matter	10
[ar	26
Trace Metals (For Mexican Scientists)	1
Trace Organics	1
Volatile Hydrocarbons	68
Weed (Possibly Sugar Cane)	. 1
Thole H <sub>2</sub> O	303

#### Table 6. Explanation of Sample Code

An example and explanation of the Sample Code is as follows:

Example: RIXO4A005

The first letter designates the ship from which the sample was taken; 'R' designates RESEARCHER and 'P' PIERCE.

The second and third letters designates the cruise; thus, IX designates the IXTOC cruise.

The next two numbers of the Code designates the Station number; thus, '04' indicates Station number 4.

The sixth character indicates who took the sample; thus, 'A' indicates the sample was taken by someone from AOML.

The other codes and their meaning are listed below:

A = AOML

B = Texas A & M University

E = Energy Resources Company, Inc.

F = Woods Hole Oceanographic Institution

K = Global Geochemistry Corporation

L = University of Louisville

M = Mexico

N = University of North Carolina

O = University of New Orleans

R = NOAA/NMFS/SEFC, Beaufort, N.C.

S = Science Applications, Inc.

W = University of Washington

The last three numbers indicate the sequential sample #; thus, '005' indicates the fifth sample taken by that "group."

In summary the Sample Code Numbers indicate the following:

'R' or 'P'

IX

04

Α

005

Ship

Cruise

Station #

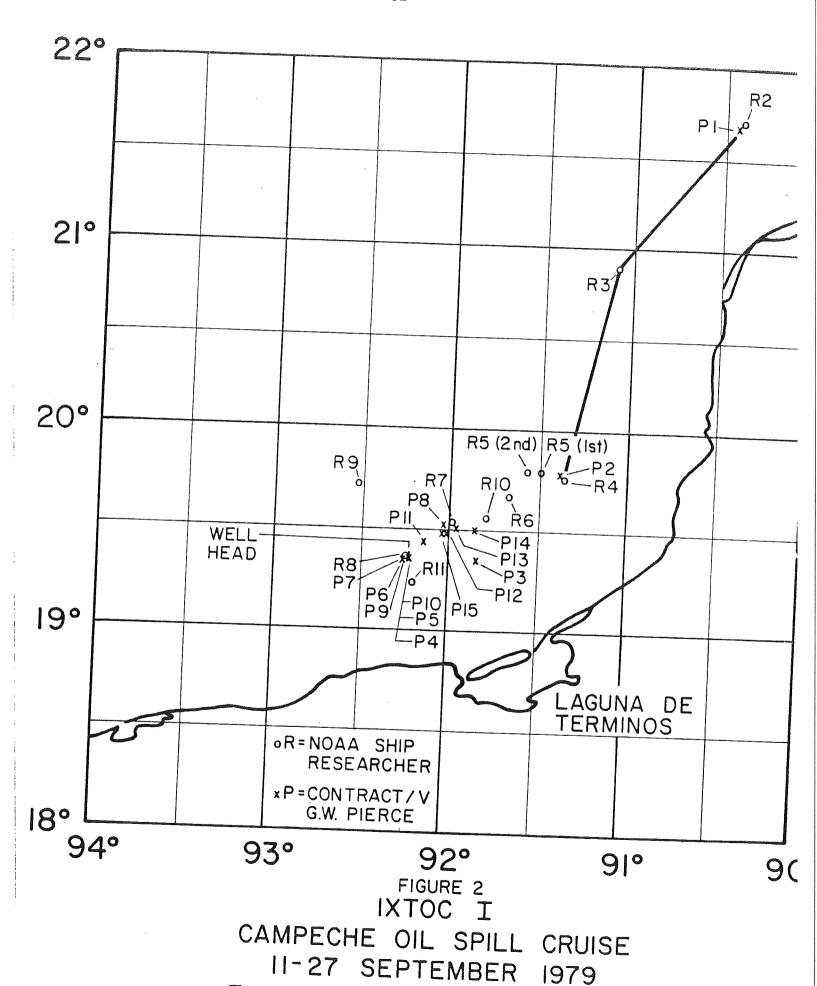
Sampler's Code

Sample #

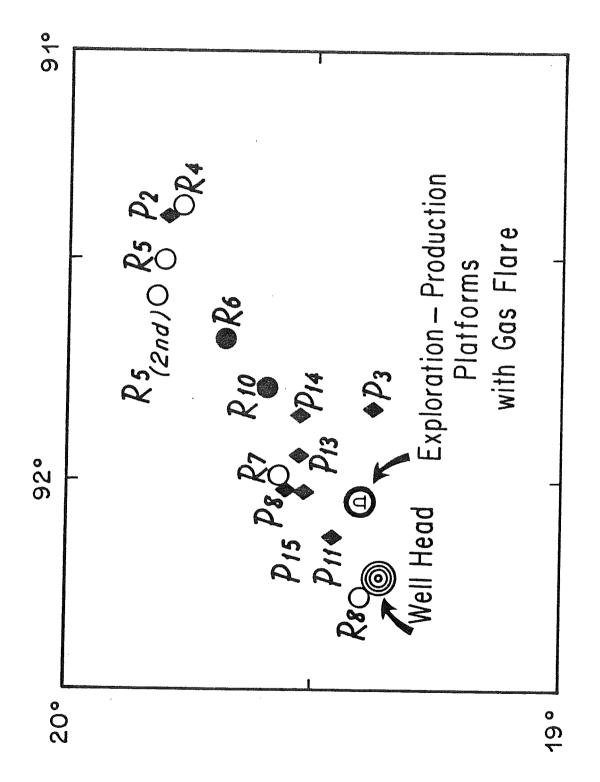
				Sample Types	•		
Investigators	Comments	Air	Screen or Slick	Water	Sediment	Oil Droplets; "Mousse"; Neuston	
U.N.O. Laseter et al.	Detailed analyses: focus on polar com- pounds where appropriate.	9 GC & GC-MS	10-12 Disc. + 3 screen	10	10	20 (focus on polar compounds).	
S.A.I. Payne et al.	Focus on alkanes, cycloalkanes, aromatics, polar compounds in "f1",	25 by GC + GC-MS	None	1. Volatiles (PIERCE collection) RESEARCHER - Bodega Bodmans by GC + GC-MS.	None	A "few" samples selected from "PIERCE/Plume Suite".	
				<ol> <li>Particulates + dis- solved phase Bodega Bodmans.</li> </ol>		-	
E.R.C.O. Boehm, Fiest	Focus on alkanes, cycloalkanes, aromatics, polar compounds in "f1", "f2".	None	9 Screen samples.	GC/GC-MS of selected particulates and dissolved phase samples from PIERCE collection.	42 Samples screened by GC; 1/3 GC-MS.	Selected samples pertinent to mousse - oil particulate phase; also sediment trap analyses.	
Global Geochem. Kaplan et al.	Isotope measurements C-13/C-12; N-15/N-14; S-32/S-34.	None	None	None	None	Maximum of 60 samples, including beach tar.	
Texas A & M Brooks et al.	GC measurements, gases + volatiles, C-13/C-12 of gases.	None	None	Gases + volatiles, PIERCE suite.	None	Those collected by Texas A & M on PIERCE.	

Additional Samples

Laseter, U.N.O. - U.N.C. (Pfaender et al.) microcosm samples by detailed GC-MS; and photochemistry experiments.



FYDANIDED



Station Locations for Comparison With Oil Slick Plume Sketches Figures 3b,c,d. Figure 3a.

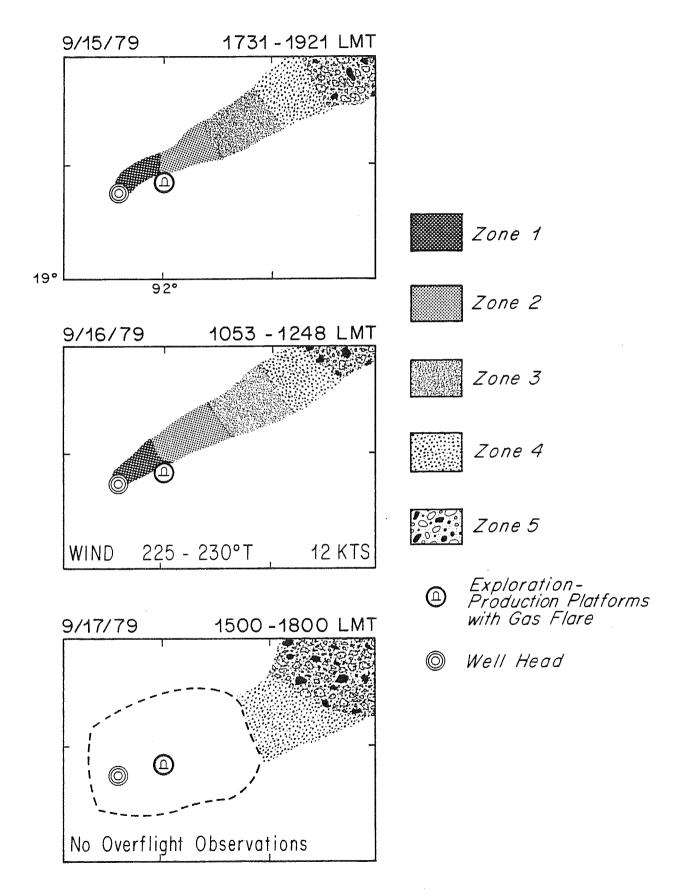


Figure 3b. Oil Slick Plume Sketches from Helicopter Overflight Observations.

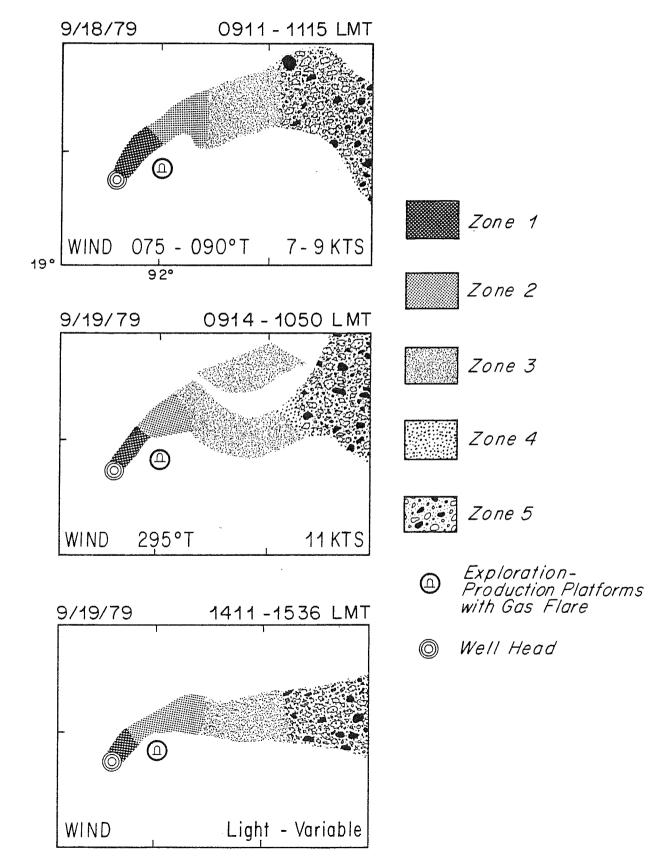


Figure 3c. Oil Slick Plume Sketches from Helicopter Overflight Observations.

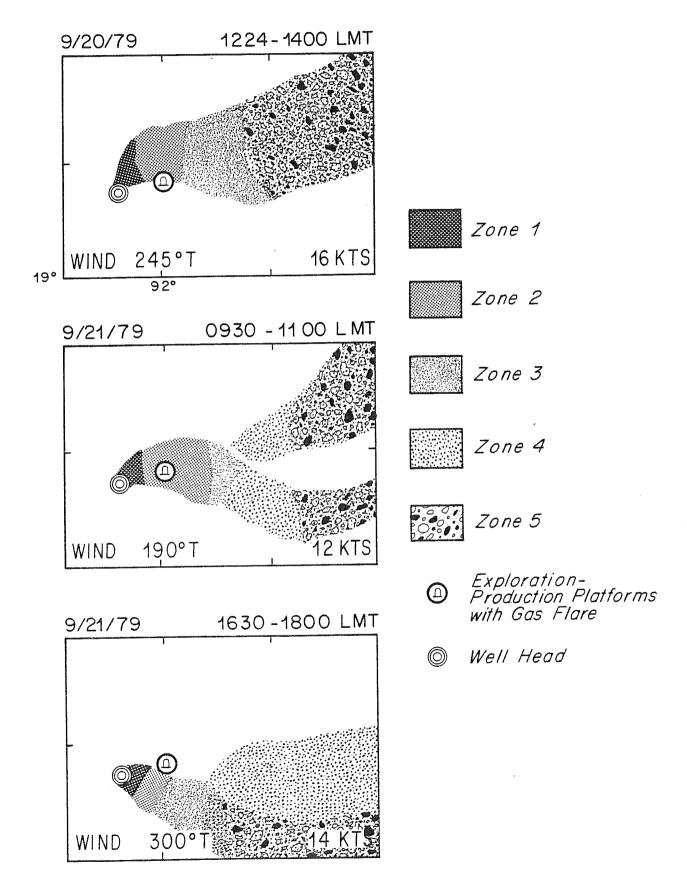


Figure 3d. Oil Slick Plume Sketches from Helicopter Overflight Observations.

# B. <u>Methodology and Intercomparison of Results of Analyses in Different</u> Laboratories

The details of sampling procedures and analytical methods are presented in the report of the symposium on preliminary results of the cruise (NOAA, 1980) and are not repeated here. Some discussion of methods will be presented in later sections.

Standard reference samples of the type needed to provide the best calibration of analytical methods for measurement of petroleum compounds in environmental samples were not available at the time of the analyses of samples during and after the cruise. Only one type of standard reference material is of use to evaluating the analyses in question and that is a shale sample certified for several aromatic hydrocarbons by the U.S. National Bureau of Standards and this can be only marginally applicable to one type of analyses - sediment analyses.

Thus, interim reference samples had to be used for purposes of quality control - intercomparison between laboratories (MacLeod and Fischer, 1980). The sediment used was obtained from an area of Puget Sound, Washington and had been previously analyzed by all laboratories participating in the analyses of higher molecular weight, greater than 15 carbon atom compounds for the cruise samples. The results of the comparison of data for nineteen n-alkanes from  $C_{14}$  to  $C_{30}$  and nine aromatic hydrocarbons showed that the majority of the results for all laboratories were within  $\pm 2~\sigma$  of the values obtained by NOAA's National Analytical Facility (MacLeod and Fischer, 1980). More details of intercomparison exercises for analyses of hydrocarbons in sediments have recently been presented by MacLeod et al. (1982).

A weathered mousse sample was distributed to the NOAA National Analytical Facility, and Science Applications Inc., by the University of New Orleans Center for Bio-Organic Chemistry and analyzed by all three laboratories. Results are given in Table 8 as taken from MacLeod and Fischer, 1980.

In general, the intercomparison analyses of split samples or subsamples of a larger sample gave encouraging results for a limited suite of compounds especially when considering the order of magnitude or more differences between stations or between selected samples needed to answer several questions of importance to further elucidating the fate of oil discharged to the sea.

However, there are serious concerns that we need to improve the precision and the numbers of molecular components in intercomparison exercises using several different sample types and ranges of concentrations if we are to make substantial progress in field studies of the type of the IXTOC-I RESEARCHER/PIERCE Cruise, or even on much smaller scales.

The complexity of the composition of petroleum and the complexity of the marine environment interact to make field sampling efforts to document the fate and effects of spilled oil a difficult sampling and analysis task. The extreme complexity of the chemical mixture of petroleum makes it impossible with present analytical methods to provide "one measure" of petroleum. Thus, several different measurements were made using a range of analytical methods in an attempt to both cover several possibilities for estimating petroleum content and to provide a real world comparison of results of these different methods. Three examples from the IXTOC-I cruise data set illustrate this point. Both Brooks et al. (1980) and Payne et al. (1980a) measured volatile

Table 8. Parts-per-thousand( $^{\circ}/^{\circ\circ}$ ) of individual alkanes found in surface portion of weathered mousse (sample (RIX23S001) by NAF and UNO.

A1kane	NAF °/。。	UNO °/	SAI* °/。。
<u>n</u> -C <sub>15</sub>	0.01		0.02
<u>n</u> -C <sub>16</sub>	0.01		0.05
$\frac{n-C_{17}}{17}$	0.11	0.11	0.20
<u>p</u> ristane	0.04	0.04	0.05
<u>n-C</u> 18	0.20	0.18	0.21
phytane	0.10	0.10	0.10
<u>n</u> -c <sub>19</sub>	0.25	0.23	0.25
<u>n</u> -C <sub>20</sub>	0.27	0.26	0.28
<u>n</u> -C <sub>21</sub>	0.27	0.24	0.26
<u>n</u> -C <sub>22</sub>	0.25		0.24
$\frac{n-C}{23}$	0.23		0.22
<u>n</u> -C <sub>24</sub>	0.20	-	0.20
<u>n</u> -C <sub>25</sub>	0.18	0.15	0.16
n-C <sub>26</sub>	0.17	0.13	0.17
<u>n</u> -C <sub>27</sub>	0.13		0.12
<u>n</u> -C <sub>28</sub>	0.12	0.09	0.10
<u>n</u> -C <sub>29</sub>	0.08		0.09
$\frac{n-C}{30}$	0.10		0.08
<u>n</u> -C <sub>31</sub>	0.10		0.07
$\frac{n-C}{32}$	0.08		

<sup>\*</sup>Added during proof.

hydrocarbons in the molecular weight range of benzene to xylenes and  $\mathrm{C}_5$  to  $C_{10}$  alkanes for samples taken from C/V PIERCE in the water column under the Samples were taken from the same depth at three stations and a comslick. parison of reported data is presented in Table 9. There are differences in data of as much as an order of magnitude for benzene and toluene. laboratories used different isolation and analysis techniques and it is tempting to explain discrepancies on that basis. However, subsampling may have been the important factor. There is nothing to be gained in speculating further as to the cause of the differences. This was presented to illustrate the problems that might be encountered in future field expeditions of this type. Since the benzenes, toluene, and xylenes are known to be toxic in elevated concentrations, it will be important to assess their distribution in the water column and compare these distributions with experimental toxicity data. An order of magnitude agreement probably will not suffice for those types of considerations. In our later discussions of volatile liquid hydrocarbons (VLHs), only data from within the set from each laboratory will be compared to avoid problems of cross comparison. Prior to the IXTOC-I cruise sample analyses, laboratory intercomparison exercises for volatile liquid hydrocarbons had not been performed. Indeed, VLH analyses in seawater are a few in number compared to higher molecular weight hydrocarbon measurements and very, very few in number compared to measurements of methane, ethane, propane and other gases. Thus, the laboratories involved (Payne et al., 1980a; Brooks et al., 1980) are not to be faulted in this discrepancy as it is not unexpected given the stateof-the-art for that type of measurement.

The second example illustrates the problem of establishing a control or background data set against which the influence of elevated petroleum compo-

nents in the water column as a result of a spill can be assessed. Table 10 presents data from Boehm and Fiest (1980a)-ERCO and Payne et al. (1980b)-SAI for dissolved and particulate hydrocarbon concentrations at stations located in close proximity to each other, RIXO4 and PIXO2 (Figure 2). The sampling gear was of different size - 90 liter aluminum Bodmans for RIXO4 and 30 liter Bodmans for PIXO2. The filtration methods were also slightly different. However, the main difference is in the method of measuring the hydrocarbons. In this case, ERCO reported concentrations on the basis of gravimetric measurements of amounts in column chromatography fractions while SAI reported concentrations as the sum of gas chromatography measurements.

The substantial differences in data for background concentrations at two control stations are not surprising to those familiar with the bias of each of the measurement methods (e.g. see Farrington et al., 1976) but could cause considerable confusion for colleagues in other scientific disciplines and for non-scientists involved with oil spill problems.

The third example involves comparison of data obtained by application of two different measurement methods by a single laboratory to estimate oil concentrations in water samples. ERCO used U.V.-fluorescence of methylene chloride ( $\mathrm{CH_2Cl_2}$ ) extracts of 1 liter water samples with the intensity of fluorescence at 312 nm and converted to relative concentration units via a calibration curve for fluorescence versus concentration of No. 2 fuel oil onboard ship and converted to oil concentration using a fluorescence to gravimetric conversion factor for No. 2 fuel oil obtained in the shore-based laboratory. ERCO also gravimetrically measured hydrocarbons in column chromatography fractions of  $\mathrm{CH_2Cl_2}$  extracts of 4 to 18 liters of water obtained at

the same time as the water for the U.V.-fluorescence measurements in 30 liter glass Bodman bottles or via a submersible pump line (Fiest and Boehm, 1980). The comparison of data from the two different methods is given in Table 11. The differences noted are probably due to the fact that the U.V.-fluorescence method is calibrated against two ring aromatic hydrocarbons while the gravimetric procedure measures all hydrocarbons in a sample - including biogenic hydrocarbons. A variety of physical-chemical processes could cause a change in the ratio of the two ring aromatic hydrocarbons to total oil present in a given sample. In addition, as will be discussed later, droplets of oil finely dispersed in samples with higher concentration may not be evenly distributed causing inhomogeneity during subsampling of the water sample. Given all these potential problems, the agreement between the two methods of estimation are not as bad as might be expected given the state-of-the-art at the time of the cruise.

These preceding three comparisons of data illustrate the problems future programs should attempt to resolve prior to field operations. The comparisons in Tables 9-11 also provide constraints on interpretations of combined subsets of data from different laboratories.

Most of the discrepancies or differences in data were suspected prior to the analyses of samples from this cruise. However, for many of the methods, intercomparison was not feasible prior to the cruise and financial constraints prevented post cruise intercomparisons because it was apparent that several major interpretations based on a subset of data from one laboratory using a single method would be possible.

Table 9. Comparisons of Reported Concentrations of Low Molecular Weight Aromatic Hydrocarbons.

Station	Benzene	Toluene	Xylenes
	(10 g/L)	(10 <sup>-9</sup> g/L)	(10 <sup>-9</sup> g/L)
PIX 11 1 M SAI T. A&N	49 1 5.8	97 1.2	1.7 1.0
PIX 12 1 M SAI T. A&M	1.2 1 .33	0.9 .19	N.R. .48
PIX 16 1 M SAI T. A&M	3.3	3.1	0.2
	1 .027	.023	.055

Table 10. Comparison of SAI and ERCO Data for Stations Outside Main Slick.

Depth	Dis		g/L <b>–</b> I Particulate	Note Depth	<b></b>	$_{ m 10^{-6}}$ Dissolved	g/L Particulate
Sta	tion RI	X04		Sta	tion H	PIX02	
1-3 m	f <sub>1</sub>	30	15	2 m	f <sub>1</sub>	11.1	3.0
	f <sub>2</sub>	0	10		f <sub>2</sub>	5.0	3.0
	Total	30	25		-	16.1	6.0
22 m	f <sub>1</sub>	N.D.	100	6 m	f <sub>1</sub>	16.0	1.0
		N.D.	_30	6 m 6 m	$\mathbf{f}_{2}^{1}$	5.0	1.0
	Total	N.D.	130		2	21.0	2.0
				16 m	f,	N.D.	1.0
					$f_2$	N.D.	1.0
					_	N.D.	2.0

RIX04 analyzed by Science Applications, Inc. (SAI) - gas chromatography determined concentrations.

PIX04 analyzed by Energy Resources Company, Inc. - gravimetric determination.

Table 11. Comparison of Estimates of Oil Concentrations in Water by Two Different Methods.

Station	Water Depth (Meters)	Oil Estimate U.VFluorescence (10 <sup>-9</sup> g/L)	Oil Estimate Column Chromatography- Gravimetry (10 <sup>-9</sup> g/L)
Stations Wit	th Oil		
PIXO5	2	10,000	1,800
	6	8,000	2,600
	20	400	619
PIXO8	6	250	329
	16	100	313
	19	20	60
PIX15	2	1,000	172
	20	100	51
Control Stat	tion		
PIXO2	2	None Detected	16
	5	None Detected	21
	16	None Detected	N.D.

# C. <u>Distribution of Petroleum Compounds in the Water Column in the Bay of Campeche Near the IXTOC-I Blowout</u>

The visual observations, as previously described, recorded substantial quantities of oil on the sea surface extending approximately 80 km down-current. These observations obtained once or twice a day from helicopter overflights and from the RESEARCHER and PIERCE provided input to the water column sampling station locations. The sampling strategy followed was:

- a) The PIERCE would occupy a transect of stations from near the well site and down-current to obtain depth profiles of petroleum components under the slick. A control station up-current from the blowout would also be occupied to provide an up-current control in addition to the control, PIXO2, far from the spill area.
- b) The RESEARCHER would operate external to the main slick and provide samples for comparison with samples taken beneath the slick. The RESEARCHER would also obtain CTD profiles to provide hydrographic data in support of the petroleum chemistry and microbiology efforts.

#### i. Gases: Lower Molecular Weight Hydrocarbons (LMWH)

Depth profiles of the gases methane, ethane, and usually other gases such as propane and butane were correlated for samples under the slick as would be expected with a fossil gas input (Brooks et al., 1980). No samples were obtained from the RESEARCHER outside the slick due to limited availability of gear and containers suitable for these types of samples. However, a few control station samples outside the slick were obtained from the PIERCE.

The range of methane concentrations were 50 nL/L at the control station PIX01 to 500,000 nL/L at stations near the well site. The concentrations of methane, ethane, and propane observed at PIX01 were typical of open ocean

concentrations influenced by air-sea exchange processes and "in situ" biological processes. All other stations sampled during the cruise had LMWH concentrations and compositions indicative of anthropogenic input (Brooks et al., 1980) or perhaps some natural seep inputs.

The high LMWH concentrations in the immediate slick area and near the well site are undoubtably due to the well blowout. The LMWH in the water column at stations outside the immediate vicinity of the well (PIXO2 and PIX16) may have been influenced by natural seeps or by activities associated with exploration and production platforms in this general area other than the IXTOC-I well. Brooks et al. (1980) measured the  $\Delta$ C-13 values for methane, ethane, and propane and found values typical of gas related to the petroleum formation and not biogenic gas.

### ii. Volatile Liquid Hydrocarbons (VLH)

The compounds considered in this category are defined in part by a molecular weight range between that of n-pentane  $(n-C_5)$  and n-pentadecane  $(n-C_{15})$ , and include benzene, toluene, xylenes, and several cyctoalkanes, e.g., alkyl-substituted one-ring cycloalkanes (Brooks et al., 1980; Gschwend et al., 1982; Wakeham et al., 1982, 1983).

VLH concentrations in the immediate vicinity of the well site were approximately  $400 \times 10^{-6}$  g/L. Visual observations of these samples indicated that these samples contained dispersed oil droplets. Changes in the ratio of aromatic hydrocarbons to alkanes and cycloalkanes down-plume indicated that much less dispersed oil was present in samples 10 to 20 km from the well site. A large fraction of the VLH in the volatility range between n-C<sub>6</sub> and n-C<sub>9</sub> were alkyl-substituted one-ring cycloalkanes; compounds which constitute the naphtha fraction of many oils.

The more soluble VLH are the aromatic hydrocarbons benzene, toluene, and xylene. Thus, it is interesting to compare concentrations of these VLH with concentrations of a representative LMWH, e.g., methane, to search for correlations. This has been investigated previously by Brooks et al. (1977), Sackett and Brooks (1975), and Sauer (1978), who demonstrated that LMWH could be used as tracers of more soluble VLH under certain conditions. Brooks et al. (1980) applied regression analysis to all data from stations PIX01 to PIX16 and obtained an equation:

$$\Delta CH_{\Lambda} = -3.17 + 0.0077$$
 VLH aromatics

[where  $\Delta \text{CH}_4$  is the difference between open ocean  $\text{CH}_4$  (background) and  $\Delta \text{CH}_4$  concentrations at the stations being investigated.] with a coefficient of variation of 0.92.

### iii) Higher Molecular Weight Hydrocarbons (HMWH) $C_{15}^+$

The totals of individual HMWH in dissolved and particulate phases as stations outside of the main slick are presented in Table 2 as taken from Payne et al. (1980). The total HMWH concentrations found in these samples are generally similar to concentrations reported for waters removed from obvious inputs of substantial amounts of petroleum (e.g., Payne et al., 1978); de Lappe et al, 1979; Brown and Huffman, 1976). Several of the most abundant HMWH had a biogenic source, e.g., n-C<sub>15</sub>, presumably from plankton or benthic algae (Payne et al., 1980b).

There were a few samples where slightly elevated concentrations of HMWH were found, e.g., RIXO5 1-3 m sample (Table 2). In those samples where elevated concentrations were found, the composition of the HMWH with complex composition and wide molecular range indicated the presence of petroleum. It is

not possible to assign the origin of these petroleum hydrocarbons to IXTOC-I blowout oil. The possibility of inputs of particulates associated and dissolved petroleum from the exploration and production activities in the area, as well as from natural seeps in this area of the Gulf, cannot be discounted. Nor can we discount the possibility of tar particles present in oceanic waters (Levy et al., 1981) contributing to the low concentrations of petroleum observed.

The concentrations of oil in water samples taken under the plume of surface oil were estimated by measuring U.V.-fluorescence with both fixed wavelength excitation emission and synchronous scanning U.V.-fluorescence spectrometry. Oil concentrations of less than  $5 \times 10^{-6}$  g/L were found in water samples taken outside the slick and at distances down-plume of 30 km or more. Highest concentrations were under the surface slick a few hundred meters away from the well site, and were up to  $10,600 \times 10^{-6}$  g/L. However, this is probably an underestimate due to adsorption of some oil dispersed in the water to sides of sampling gear and sample storage containers. The higher concentrations of oil were within the upper 20 meters of the water column.

The general characteristics of the synchronous scan U.V.-fluorescence spectra, as summarized from Fiest and Boehm (1980), were as follows:

- i) Low concentrations of  $5 \times 10^{-6}$  g/L samples with a single fluorescence peak at 308 nm resulting from background fluorescence of natural material or low levels of background petroleum (e.g. see I.O.C., 1981).
- ii) Moderate concentrations of 5 to  $20 \times 10^{-6}$  g/L with a single fluorescence peak at 312 nm as a result of a predominance of two ring aromatics (e.g. naphthalenes). This may reflect selective dissolution of two ring aromatics from oil to the water. Laboratory experiments (Shaw and Reidy,

1979; Zurcher and Thuer, 1978) have shown that selection for two ring aromatics in oil and water mixture occurs if gentle mixing conditions are employed or if vigorously mixed oil-water dispersions are filtered or centrifuged to remove the dispersed oil. This U.V.-fluorescence spectral type was characteristic of water samples taken under the slick but more than 20 km from the well site.

iii) High concentrations, >  $20 \times 10^{-6}$  g/L with a series of fluorescence peaks at 312 nm, 328 nm, 355 nm, and 405 nm resulted from two-, three-, four-, five- and larger fused ring polynuclear aromatic compounds. These spectra were similar to whole oil and mousse sample spectra. These spectra were characteristic of samples taken under the slick between the well site and 20 km down plume.

Filtration of several water samples taken under the slick demonstrated that much of the oil could be removed by 0.45  $\mu m$  filters. For example, at PIX08 at 6 and 16 m depth 70 to 80 percent of the oil was removed by filtration through 0.45  $\mu m$  filters. The 2 m water sample at PIX10, 0.8 km from the well site, contained 7,010 x 10  $^{-6}$  g/L of oil of which only 117 x 10  $^{-6}$  g/L passed through at 0.45  $\mu m$  filter. In all cases of filtration a small portion of hydrocarbons will be adsorbed by the filter. However, it is safe to conclude that a large proportion of the oil was in a form susceptible to removal by filtration. Candidate physical chemical forms are dispersed oil droplets and petroleum compounds adsorbed to particulate material.

Further details of the molecular composition of the hydrocarbons in water and suspended particulates are presented in Boehm and Feist (1980a,b); Boehm et al. (1982).

#### D. Composite Hydrographic Sections of Petroleum Components

Hydrographic section plots have been constructed for methane as a representative of LMWH, benzene as a representative of VLH, and U.V.-fluorescence measured petroleum as representative of HMWH and are presented in Figures 4, 5, and 6 respectively. The sections are oriented to the northeast away from the well head (Figure 2).

The fact that these sections are not synoptic and are composited from data for stations occupied over a period of six days should be explicitly stated — and is so stated. During this period of time hurricane Henri passed to the north of the study area. Also, there were some meanders of the surface slick as indicated in Figure 3 which could be a combined feature of wind and current effect. These may account in part for some of the features in Figures 4-6. However, as previously discussed, the positioning of the stations and sampling were designed based on once or twice daily helicopter observations to ensure placement of PIERCE stations within the slick at locations where the slick had been located for at least one day based on visual observations. Thus, there is a reasonable expectation that the sections shown in Figures 4-6 are useful for elucidating processes controlling the fate of the oil entering the sea from this spill.

The general features of the distribution of methane, benzene, and oil are similar (Figures 4-6) and can be summarized as follows:

i) Concentrations are two or more orders of magnitude higher than background concentrations for the general Bay of Campeche area at distances downplume within 1-5 km of the well head.

- ii) There are strong indications of a subsurface plume of water with elevated concentrations of methane, benzene and oil extending 20 to 30 km downplume from the well head from approximately 20 meters depth to the surface.
- iii) Concentrations of methane, benzene, and oil are very low at the stations immediately upcurrent of the well head when compared to the downplume concentrations within 20 km of the well head. This indicates the strong influence of the current estimated from drift observations at 0.5 knots (24 cm/sec) in controlling the immediate fate of the escaping oil and gas.

The extreme turbulence in the immediate vicinity of the well head and the concern about fouling gear in the platform wreakage on the bottom prevented sampling at near bottom depths in the immediate vicinity of the well head.

The general shape of the hydrographic sections in Figures 4-6 indicate substantial horizontal advection of the plume of oil and gas mixed in the water away from the well site. The concentrations of methane, benzene and oil approach the background values at a distance of approximately 40 to 50 km downplume. It is interesting that this distance corresponds to a hydrographic feature in the sigma T and salinity sections from composites of water column data at stations both in and out of the surface slick (Figures 7 and 8). This distance of 40 to 50 km is also the distance at which the slick began to lose its plume-like character and disperse into intermittent slicks, spread considerably and meander.

The temperature and salinity sections also indicate that there is halocline and thermocline at several stations at 15 to 20 meters water depth. This was also apparent in several of the CTD casts from the RESEARCHER. This depth corresponds to the depth interval at which there was a rapid decrease in methane, benzene and oil concentrations (Figures 4-6). A hydrographic section for dissolved O<sub>2</sub> for the same stations as the other sections (Figures 4-8) is presented in Figure 9. The combined temperature, salinity, and oxygen data clearly indicates a change in water mass characteristics at between 40 to 50 km and again at approximately 90 km along the section. The cause of this or the origin of this water with the main differentiating factor of lower salinity is not known. However, the lower salinity indicates an influence by fresh water from land. Several rivers and streams discharge at the coast in this area and there were several weeks of intensive periods of rain in the coastal area with flooding reported along the coast prior to and during the cruise. Although the data are sparse, a contouring of salinities for the upper 1-6 meters for stations where this data was available is consistent with this interpretation (Figure 10).

Helicopter overflights in the area provided definite and consistent observations of a feature of a distinct water coloration change of the type associated with coastal fronts. Clearer, blue water was observed offshore as indicated in Figure 10. This boundary extended along the coast north to at least the area off Tampico (Figure 1). Stations RIX13 and RIX14 were specifically taken on either side of this boundary which was clearly discernible from helicopter observations in this area for as far as could be seen by eye on a clear day from an altitude of 500 ft. Based on data from CTD casts at RIX09, RIX11, RIX12, RIX13, and RIX14, the greenish turbid water had a salinity of 34.90 to  $35.70^{\circ}/_{\circ \circ}$  with a halocline at 15 to 20 meters where salinity increased to

35.8 to 36.2°/oo. Shipboard (RESEARCHER) computer reconstructed CTD profiles are given in Figures 11a-e. Although the number of stations are limited, the available data suggests that the halocline-thermocline at 15 to 20 meters was a general feature of nearshore water mass in the area at the time of the cruise.

Acoustic surveys of the water column using 20 and 200 kHz showed features within the slick area similar to those seen in acoustic surveys of chemical wastes dumped at sea (Walter and Proni, 1980). The acoustic records corresponded with the hydrographic features of the area with a signal return indicating a definite change in acoustic properties within the top 10-20 meters within the slick area. However, it must be recognized that these acoustic measurements are the first of this type in an oil spill situation. Thus, interpretations are tentative, but the data show that this type of acoustic survey tool should be useful for detecting subsurface oil. Presumably as discussed by Walter and Proni, (1980) the survey is detecting oil droplets or oil-water emulsion droplets. Near the well site the survey also would detect gas bubbles.

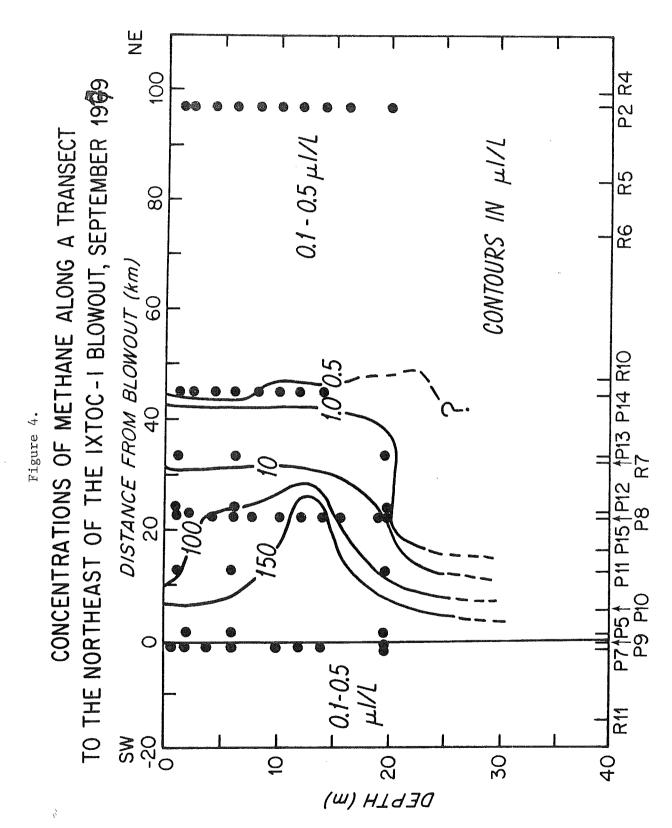
In summary, the hydrographic data, water column measurements of gases, volatile hydrocarbons, and higher molecular weight hydrocarbons and acoustic surveys provide a coherent set of data. The initial oil reservoir pressure driven upward velocity of gas and oil from the blowout injected oil and gas into the water column. There was sufficient upward velocity to maintain a coherent plume which reached the surface. However, during upward movement through the water column, the plume components were influenced by horizontal advective currents and turbulence which initiated a horizontal advective feature as indicated in Figures 4 to 6.

The exact interactions of processes controlling the shape of the advective feature are not known. However, the following seems to be a reasonable hypothesis. The vertical velocity component with turbulence associated with the escape of oil and gas under high pressure maintained a vertical plume of oil, gas and admixed water. Near the surface of the 50 meter water column the horizontal advection of the 0.5 to 1.0 knot (24-48 cm/sec) current influenced some of the plume components and advected them downstream. The density gradient in the water column with the halocline and thermocline at 10-20 meters depth maintained the oil and gas components mainly within the upper 20 meters of the water column.

The extent of horizontal spread of the subsurface plume appeared to be blocked by the lense of less saline water at 25 to 40 km from the well site. This distance had a general correspondence to the distance from the well site where the heavy surface slick changed to light sheen or broken patches of oil slicks (Figure 3). There may have been mixing between the water masses reducing the oil concentration but the sampling was insufficient on a spatial scale to define this process.

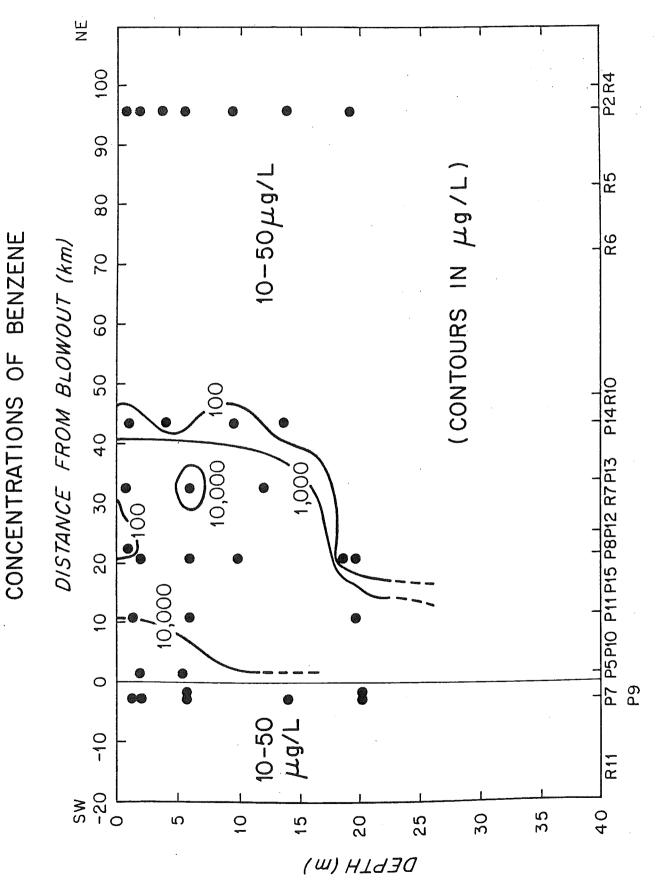
Oil sheen and patches of mousse were clearly identified further "down-stream" or further away from the well site. Thus, some components of the surface slick were apparently decoupled from the subsurface plume at distances greater than 40 km from the well site.

Although much of the preceding might have been expected given existing knowledge of physical chemical properties of oil and gas, and physical oceanographic knowledge, the combined water column hydrographic sections for a wide range of molecular weights of oil and gas components had not been attempted at previous spills. Financial and logistical constraints coupled with state-of-the-art methodology at the time of previous spills had not allowed this more

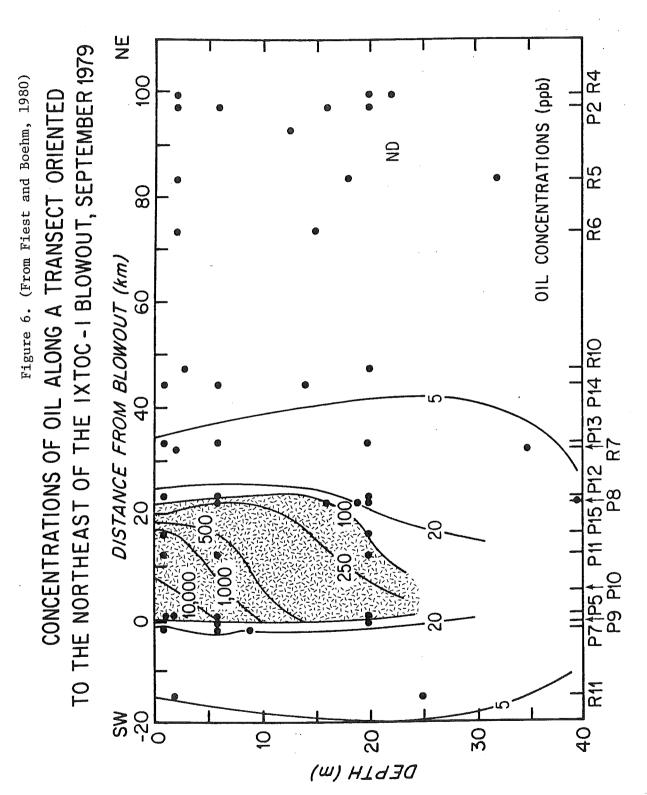


Station Designations and Positions on Transect.

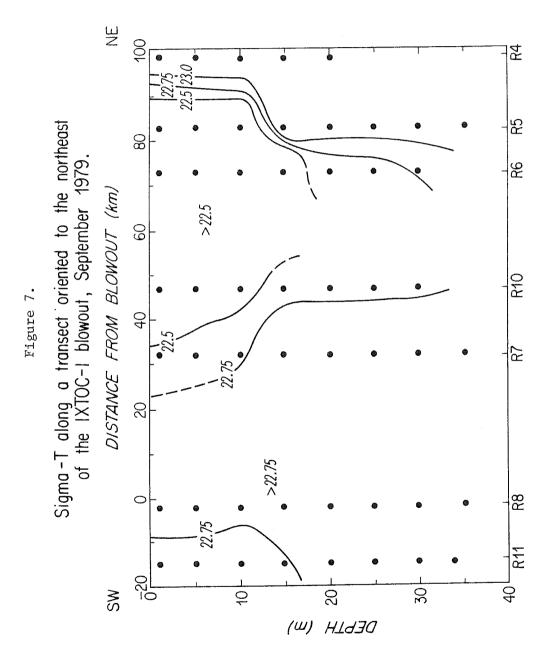




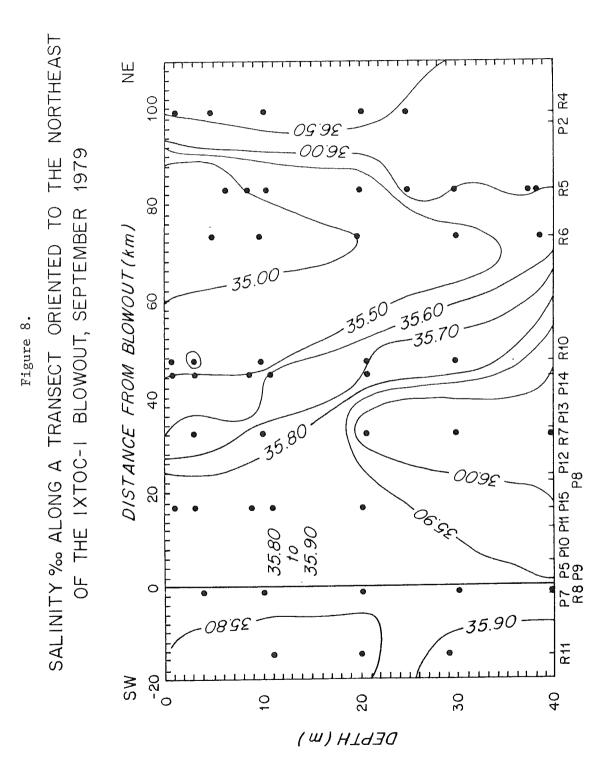
Station Designations and Positions on Transect.



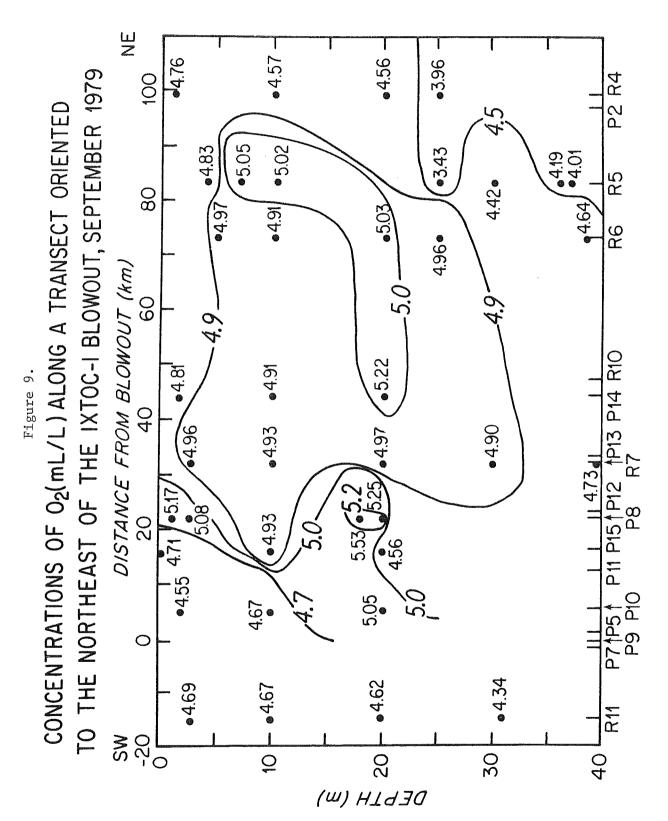
Station Designations and Positions on Transect.



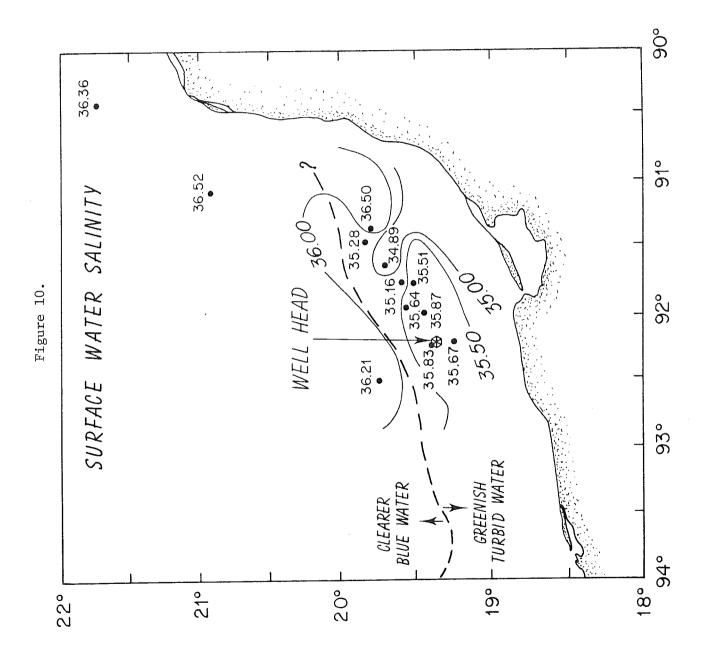
Station Designation and Position on Transect.

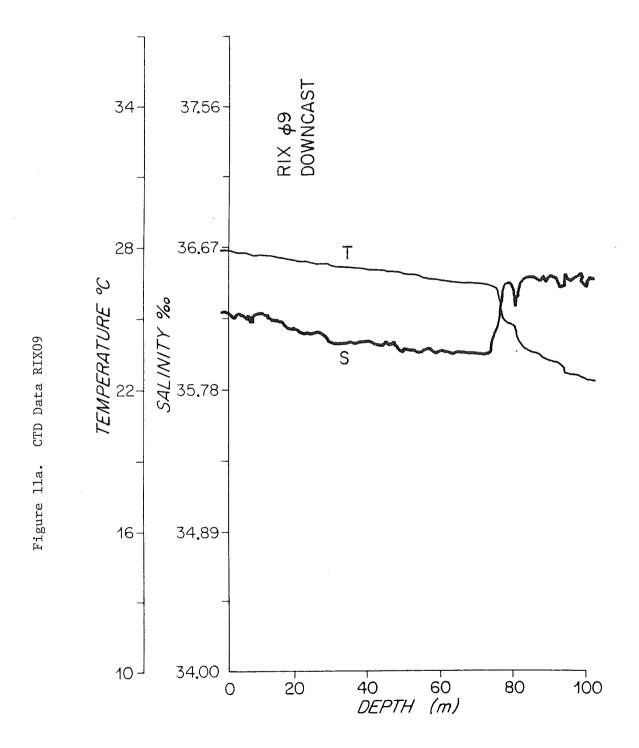


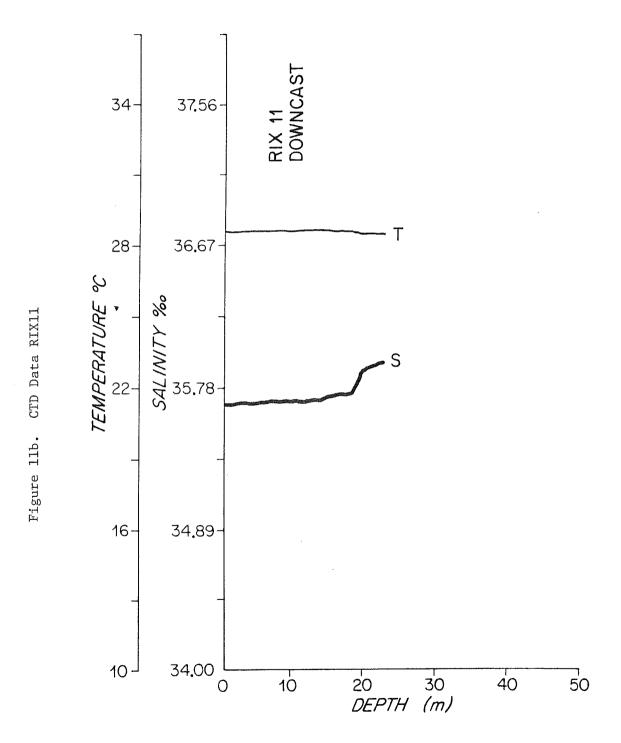
Station Designation and Position on Transect.

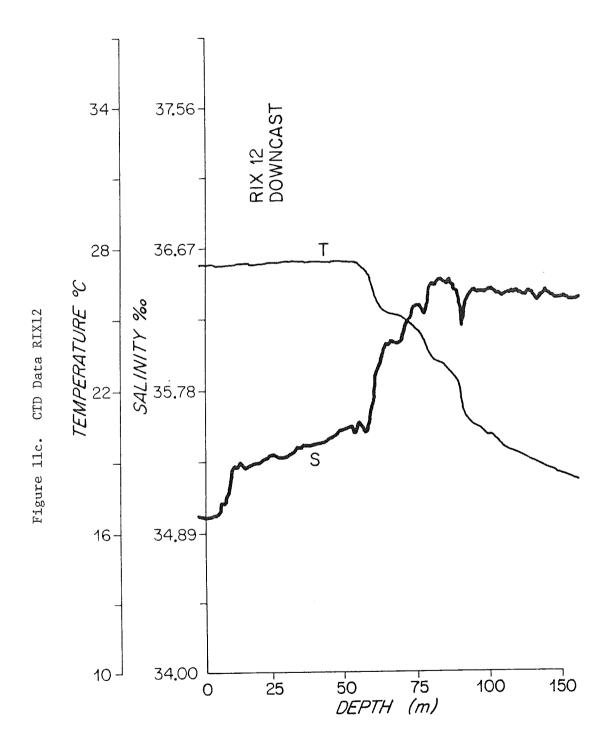


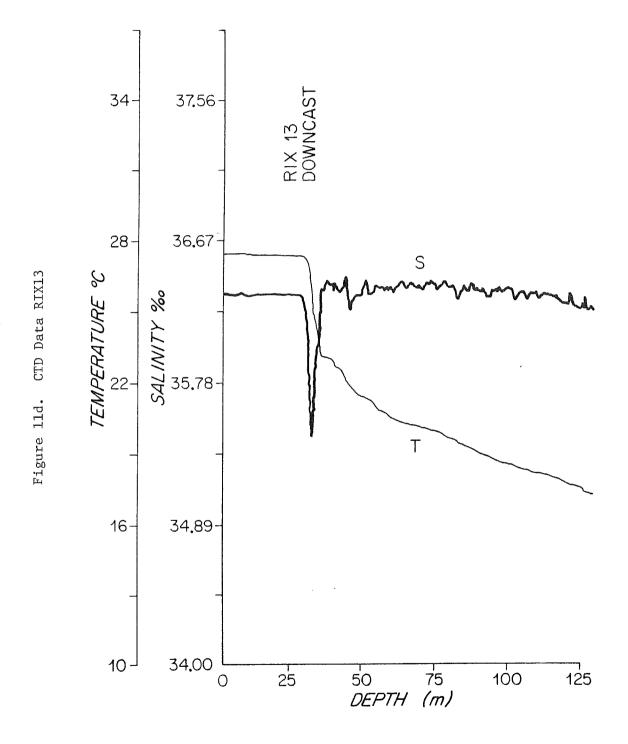
Station Designations and Positions on Transect.

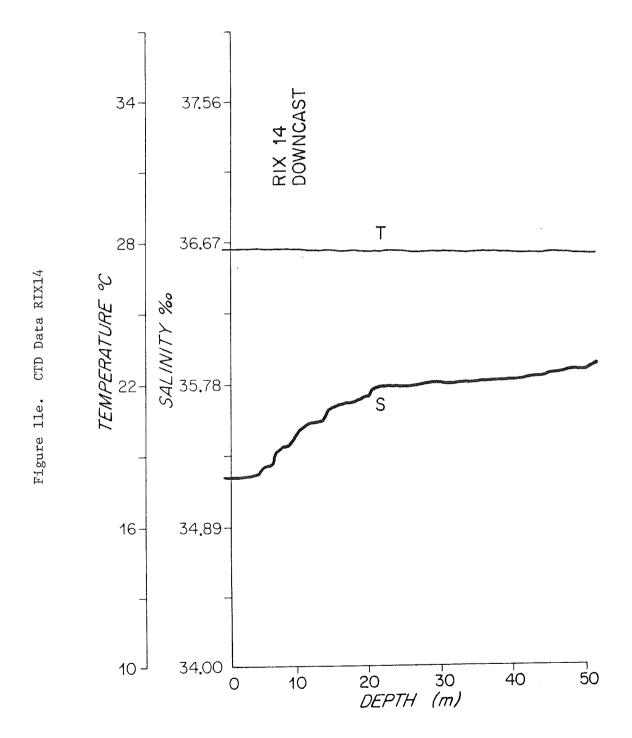












extensive investigation of the distribution of oil and gas in the water column. Certainly future efforts could be more comprehensive if warranted by a need to investigate a specific spill.

While there may be some common features among subsurface blowouts and the fate of oil and gas in the water column, it would be a mistake to generalize too much from the IXTOC-I RESEARCHER/PIERCE cruise data. The interplay of depth of release of oil and gas to the water column, reservoir pressure providing the force for vertical velocity, hydrographic features in the water column such as currents, halo- and thermoclines at different depths will most probably be different for future accidents. The value of the IXTOC-I RESEARCHER/PIERCE cruise data is to document one set of circumstances and demonstrate that data of this general type can be obtained and usefully interpreted.

# Air-Sea Exchange and Dissolution

Measurements obtained at several stations provide data for the volatile hydrocarbons given in Figure 12 adapted from Payne et al. (1980a). Concentrations in the atmosphere were definitely much greater near the spill site as compared to control areas.

A comparison of air sample data with water sample data for the same volatile compounds is given in Figure 12. A striking feature in the reduced abundance of benzene in the atmosphere (not detected) relative to cyclohexane was surprising. The explanation which seems most reasonable is that injection of benzene, cyclohexane, and other volatile components into the water column subsurface enhances the influence of relative solubility properties of these compounds in controlling relative distributions in the water column and atmos-

phere. A limited set of laboratory beaker studies by Payne et al. (1980a) provides additional data to make this suggestion a viable hypothesis.

The limited data and a dynamic air-water mass movement in the area places further discussion of comparisons of air and surface water distributions beyond the realm of reasonable speculation. The capability of making such measurements and their potential utility to documenting and modeling the fate of volatile compounds injected into the environment under oil spill conditions has been documented.

The data for volatile hydrocarbons in mousse in the slick (Brooks et al., 1980) and the data for heavier molecular weight hydrocarbons in surface slick samples (Boehm and Fiest, 1980c) show that there are evaporative losses from the slick/mousse but little indication of solution from the slick/mousse to the underlying water column.

It appears that most of the petroleum compounds in the subsurface plume were introduced into the water in the turbulent mixing at the site of the blowout and then advected away.

### Incorporation of IXTOC-I Oil into Sediments

The investigation of the deposition to and incorporation of IXTOC-I oil compounds into surface sediments in the area was hampered by several factors:

- 1) Sampling from within the slick could not be accomplished due to limitations of equipment on the PIERCE and problems of lowering and recovering sediment sampling gear through the slick without significant contamination.
- 2) Lack of adequate means to insure an undisturbed surface floc sample.

  A box corer was deployed on a few occasions but did not obtain a viable sample due to sand and coarser material present at several stations. The time ele-

ment involved in using the box core was excessive given the available station time. Thus, we opted for the less satisfactory Smith-MacIntyre grab sampler. This device almost certainly disturbed the upper few millimeters of sediment which probably contained the most recently deposited particulate matter with associated oil compounds (Gearing et al., 1979).

3) The previous petroleum exploration activities in the area had probably released tailings of ancient sediments containing petroleum compounds. Also small amounts of petroleum were probably released directly from the platform during the drilling operations.

Despite these factors, an estimate of the minimal amount of the petroleum incorporated into sediments of the area can be obtained and a comparison of the composition of sediment hydrocarbons with other samples from the area is possible.

Table 12 is taken from Boehm and Fiest (1980b) and presents the data on concentrations of hydrocarbons in the surface sediments (top 3-4 cm). The indications of the sources contributing to the hydrocarbons in each sample are also indicated in Table 13 and are from the gas chromatographic and GC/MS analyses of the composition of the hydrocarbons (Boehm and Fiest, 1980b). There is no evidence of an overwhelming input of IXTOC-I oil such that biogenic markers are overwhelmed by the IXTOC-I oil as has been the situation for nearshore sediments in some other oil spills, e.g. Amoco Cadiz (Gundlach et al., 1983); West Falmouth, Massachusetts (Blumer and Sass, 1972).

Boehm and Fiest (1980b) attempted to use pentacyclic triterpanes as source molecular markers for IXTOC-I oil in sediments. However, they report that the low concentrations of pentacyclic triterpanes such as hopanes in the IXTOC-I

oil coupled with probable chronic petroleum inputs to area, as discussed previously, precluded this molecular marker approach. GC/MS analyses revealed low concentrations of phenanthrene, alkylated phenanthrenes, dibenzothiophenes, and alkylated dibenzothiophenes in the sediments where GC analyses of alkanes and cycloalkanes indicated the probable presence of IXTOC-I oil incorporation into the sediments. Concentrations were in the range of less than  $1 \times 10^{-9}$  g/g to  $36 \times 10^{-9}$  g/g total phenanthrenes or total dibenzothiophenes.

Boehm and Fiest (1980b) made a rough calculation of the total amount of IXTOC-I oil which could be present in the sediments using several assumptions:

- 1) Maximum of a 30 km impact radius around well site.
- 2) IXTOC-I oil present to depth of 0.5 cm.
- 3) Maximum concentration of IXTOC-I oil at 150 x  $10^{-6}$  g/g dry weight.

They calculated that under those assumptions  $9 \times 10^9$  g oil were in the sediments compared to the  $550 \times 10^9$  g oil released up to that point from the well site. Thus, about 2% of the released oil could be present in the upper 0.5 cm of sediment.

However, these types of calculations are speculative as indicated by Boehm and Fiest. The sediment-water interface area can be very dynamic, especially in shallower areas of the continental shelf when intense storm conditions can induce extensive water column turbulence and resuspend sediments. The 2% amount of spilled oil in sediment could be increased to 8% if concentrations of  $150 \times 10^{-6}$  g/g dry weight were present in the upper 2 cm of sediment. Likewise, if we assume some amount of the oil and gas input burned - e.g. 30% - then we can increase the percentage amount in the water column which is incorporated into the sediments. In addition, the number of surface sediment sam-

ples analyzed (Table 12) due to financial constraints were limited given the large area in question. Few samples were obtained and analyzed for areas to the north and west of the well site where substantial flow of oil had been noted before the cruise.

All of this leads to the important point to be explicitly stated that the data are insufficient to allow a reasonable estimate of petroleum input to the surface sediments. This is explicitly stated because the issue of incorporation of petroleum into surface sediments and the issue of subsequent impact or non-impact on the benthos is a controversial question in many assessments of the possible environmental effects of release of oil to the marine environment from a variety of sources including OCS exploration and production.

Boehm and Fiest (1980b) report on an interesting effort to deploy rapidly constructed (of necessity) sediment traps using wide mouth jars. Several samples had to be composited to obtain sufficient sample for analyses. The sediment traps probably intercepted rapidly settling particles and also some smaller suspended particles. Trapping efficiencies for various particle sizes are difficult to estimate given the uncertainties in how traps of this design would operate in the hydrographic regime of the area (Staresinic et al., 1978). Unfortunately insufficient material could be obtained for aromatic hydrocarbon analyses. However, GC analyses for alkanes and cycloalkanes revealed the presence of petroleum in particulates caught in the traps at PIXO8, PIX14 and PIX15.

There were n-alkanes of biogenic - presumably planktonic - origin in the sediment trap material. Boehm and Fiest (1980b) note the particulate matter in the traps might contain as much as 1 to 25 mg hydrocarbons/g dry weight.

That concentration is much higher than the assumed  $150 \times 10^{-6}$  g hydrocarbons/g dry weight for the upper 0.5 cm of sediment. This is not unexpected and might be representative of freshly deposited material at the sediment water interface prior to incorporation into the upper 0.5 cm of sediment. The associated planktonic material indicated by the biogenic alkanes may promote microbial degradation of the petroleum hydrocarbons after deposition thereby lowering the concentration to a value closer to the maximum measured sediment concentration. Indeed, Boehm and Fiest (1980b) suggest that the sediment trap petroleum hydrocarbon mixtures appear to be less microbially altered than the sediment hydrocarbon mixtures.

Another set of calculations can be performed substituting the very few sediment trap data for the few sediment data in order to estimate the flux of petroleum hydrocarbons to the sediments. The flux of petroleum hydrocarbons was estimated from the trap data to be  $1-5~\mu g/cm^2/day$ . A 30 km radius area of  $28~x~10^{12}~cm^2~x~98$  days since the blowout (June 3, 1979 to September 15, 1979) =  $3~x~10^9~g$  petroleum. This compares favorably with the  $9~x~10^9~g$  calculated from the sediment data. However, for reasons stated previously in discussing the sediment data, it would be unwise to rely too heavily on such a limited set of data even though the agreement between two methods of estimation seem to converge.

In summary, there is evidence of IXTOC-I oil being incorporated into surface sediments although it is difficult to quantify given the presence of chronic petroleum hydrocarbon inputs from other sources. Procedures for estimating the amount of oil deposited to sediments have been tested or are now clearly described, but meaningful application to the IXTOC-I spill are limited by the limited data set.

# Weathering of IXTOC-I Oil Near the Well Site

The definition of weathering within the context of this report means the effect of physical-chemical processes, e.g. evaporation, solution, particle-solution interactions, and emulsion formation. The special investigations focused on photochemistry will be described in a later section.

Several papers by Payne et al. (1980a,b), Boehm and Fiest (1980a,b), Fiest and Boehm (1980), Boehm et al. (1982), Patton et al. (1981), Botello and Castro-Gessner (1980), Overton et al. (1980a), provide a detailed description of methodology, data, and details of interpretations which will not be repeated here. Rather, the major conclusions of those papers will be integrated and presented with a few key examples of data.

#### i) Mousse:

The most dominant form of spilled oil at the well site area during the cruise was a water-in-oil emulsion designated "mousse" because of its similarity in appearance to the chocolate mousse of French cuisine. This emulsion has been cited at other crude oil spills - most notably the Amoco Cadiz (NOAA, 1979). In fact, comparison of the surface slick appearance near the well site with color photographs in the Amoco Cadiz report (NOAA, 1979) during helicopter flights from the RESEARCHER showed a remarkable resemblance between the visual appearances of mousse in surface slicks at both spills.

There was, and still is, some controversy surrounding how and where the mousse was actually formed. Ross et al. (1980) visited the well site before September and based on their observations and accounts from others described the mousse formation as follows.

"The oil was heavily emulsified with water. It was thought that the oil from the blowout, in close association with the emerging gas, was quickly ris-

ing to the churning boil water of the plume and was mixing and frothing with seawater; this resulted in a fine emulsion of water droplets in the oil. At the same time the heat from the fire was evaporating and burning the light fractions of the oil. The heavily mixed water-in-oil emulsion in the boil area eventually was swept out of the turbulent plume area and rose to the surface of the calmer waters surrounding the fire. Based on preliminary chemical analyses, the emulsion on the water surface was found to contain about 70% water and 30% oil and to be viscous (350 cp) and heavy (SG 0.99). It is a very stable water-in-oil emulsion containing fine droplets of water with a thin viscous layer of oil." (Underlining for purposes of this report.)

In contrast, during our cruise, a sample of the surface water taken at PIXO5 at 0.4 km from the well site, was observed to separate within an hour (or less as the observation was fortuitous) with oil clinging to the surface of the sample jar and floating on top of the separated water. This and observations from the PIERCE led us to suggest that in the immediate vicinity of the well that a substantial amount of the oil was present as drops or drop-lets of oil in a fine suspension in water. Beyond 0.2 to 0.4 km, there was a transition to the more stable mousse as described by Ross et al. (1980).

We do not know the mechanism of transition. However, it may be that the fine suspension of oil droplets in water dominates over the mousse form of water-in-oil emulsion near the well site. As the plume containing both forms moves away from the well, the oil droplets might coalesce and rise to the surface or simply rise to the surface where they form the slick component found in conjunction with the mousse. As distance increases from the well site, the slick component may be more susceptible to evaporation and also to slow incorporation into the existing mousse.

This is of course only a hypothesis but it is consistent with the observations of oil droplets in the water near the well site, stable mousse formation, visual observations of slicks or streaks of oil on the surface first appearing at about 0.2 to 0.5 km away from the well site.

Boehm and Fiest (1980a) report on the GC and GC/MS analyses of the fresh emulsion of oil droplets, several mousse samples and a mousse "flake," a skin-like material thought to be more extensively weathered. The chemical composition of almost all of the samples collected within 80 km of the well site was very similar as indicated in Table 13. The major differences were in lower molecular weight n-alkanes and aromatic compounds (< n-C $_{14}$ , < C $_{3}$ -naphthalene). This is probably due to the greater susceptibility of these compounds to evaporation and dissolution.

Boehm and Fiest (1980a) and Boehm et al. (1982) have set forth three parameters calculated from GC and GC/MS analyses which facilitate comparison of hydrocarbon compositions of samples for purposes discerning the relative influences of evaporation, dissolution and microbial degradation. These are:

(1) ALK/ISO  $_{14-18}$  - alkane/isoprenoid ratio.

$$ALK/ISO_{14-18} = \frac{(1400) + (1500) + (1600) + (1700) + (1800)}{(1380) + (1470) + (1650) + (1708) + (1810)}$$

where  $(1400) + \dots$  refer to concentrations or relative amounts of  $n-C_{14}$ ,  $n-C_{15}$ ...; and (1380)... refer to concentrations of isoprenoid alkanes with retention indices 1380, 1470, ... 1708 (pristane), 1810 (phytane).

As n-alkanes are depleted relative to isoalkanes by microbial degradation the ALK/ISO  $${\rm parameter}$$  approaches 0.

(2) SHWR - saturated hydrocarbon weathering ratio.

SHWR = 
$$\frac{\text{(sum of n-alkanes from n-C}_{10} \text{ to n-C}_{25}}{\text{(sum of n-alkanes from n-C}_{17} \text{ to n-C}_{25}})$$

SHWR approaches 1.0 as evaporation removes n-C to n-C hydrocarbons.

(3) AWR - aromatic weathering ratio.

AWR approaches 1.0 as low boiling aromatics are lost by evaporation and/or dissolution.

The ALK/ISO, SHWR, and AWR for the mousse samples are presented in Table 13 taken from Boehm and Fiest (1980a) and provide more evidence of a reasonable consistency of composition for the mousse samples near the well site. There are no consistent trends of the ratios with distance from the well site. In part this could be due to older mousse being transported back through the slick area as currents and winds changed periodically over several weeks and months. For example, based on visual experience, sample PIXO5-B116 was thought to be an "older" sample of mousse carried back to the well site by currents. The tarball RIX13 E602 was thought either to be unrelated to the IXTOC event

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# iii) Seawater/Particulates

The whole water samples taken beneath the surface slick inside the plume had more lower molecular weight aromatic hydrocarbons such as alkylbenzenes and naphthalenes,, relative to higher molecular weight aromatics compared to the surface oil/mousse, i.e. the AWR was greater for the whole water compared to the mousse.

Particulate matter (filtered) had a distinctively different composition compared to dissolved samples (filtrate). As expected from the solubility properties, particulates were depleted of lower molecular weight aromatics relative to mousse samples, while the dissolved samples are enriched in lower molecular weight aromatics and depleted in alkanes.

#### iv) Summary

The higher resolution analysis of the various sample types by glass capillary gas chromatography and GC/MS provided a unique set of data. Interpretation of that data using parameters such as the AWR, SHWR, ALK/ISO within the context of knowledge of physical-chemistry provide a consistent picture of processes acting on the oil. Sufficient data has been accumulated to warrant mathematical modelling and this has been presented by Boehm et al., 1982. These modelling concepts can now be tested at other spills or under simulated field conditions.

A summary plot (Figure 13) of the AWR and SHWR data from Boehm and Fiest (1980a) and Boehm et al. (1982) show the relative relationships of mousse, water column and surface microlayer samples. Boehm and Fiest (1980) noted that, in general, concentrations of total hydrocarbons and lower molecular weight, more soluble aromatic hydrocarbons decreased along the axis of move-

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and Ferguson and co-workers examined the effect of IXTOC oil on the composition of pelagic microbial communities and their activity as a function of distance from the source of oil. They also investigated "in situ" rates of hydrocarbon degradation and employed microcosm studies to examine the response of microbial community characteristics to exposure to petroleum subjected to differing degrees of weathering (Pfaender et al., 1980; Buckley et al., 1980).

Atlas and co-workers (1980; 1981) investigated the specific, important problem of biodegradation of hydrocarbons associated with the mousse form of oil.

The details of these investigations have been presented in the cited papers. The experimental protocols made use of <sup>14</sup>C labelled hydrocarbon substrates, most probable number (MPN) techniques for enumerating petroleum degrading bacteria, <sup>3</sup>H-amino acid uptake, <sup>14</sup>C-amino acid uptake, <sup>14</sup>C-amino acid uptake, <sup>14</sup>C-amino acid respiration, acridine orange counts of total cell numbers:

i) Biodegradation of Hydrocarbons in Mousse (Atlas et al., 1980; Atlas, 1981).

There was no significant difference between the total microbial biomass by direct counts between samples from control sites and those with visible oil or mousse. Table 15 presents the data. In some instances there were elevated counts at stations with mousse (e.g. PIXO8, 14) but at other stations with mousse present there was no increase in counts (PIXO9, 13, 17). This contrasts with most probable number of hydrocarbon-utilizing microorganisms for which there was a positive correlation with the presence of mousse (Table 14).

Hydrocarbon biodegradation did not appear to proceed at appreciable rates as tested with  $^{14}\mathrm{C}$  labelled compounds. Less than 1% of hexadecane, and a maximum of 0.2% of 9 methylanthracene or benzanthracene was mineralized to  $\mathrm{CO}_{2}$  after 30 days incubation of natural water samples. However, when water

Table 12. Surface Sediment Data Summary. (From Boehm and Fiest (1980b)

	((	arbon Conte Gravimetric		
Station	f <sub>1</sub>	f <sub>2</sub>	Total	Composition
RIX 04	5.4	19.2	25.1	В
RIX 07-1	11.4	18.8	30.2	I/B
RIX 07-2	26.3	54.0	80.3	I/B
RIX 10-1	33.6	110.0	143.6	I/B
RIX 10-2	23.5	38.0	61.5	I/B
RIX 12	8.3	16.4	24.7	${f T}$
	9.6	17.3	28.9	${f T}$
RIX 14-1	6.7	12.3	19.0	T/C
RIX 14-2	5.1	10.0	15.1	T/C
RIX 22	17.9	20.5	38.4	C/T
RIX 30	16.8	30.0	46.8	T/B/C/I
Blank	2.0	2.0	4.0	

#### KEY:

- I = predominantly IXTOC-I oil in  $f_1$ ; weathered aromatics and biogenics (olefins, sterenes) in  $f_2$ .
- B = biogenic inputs in f<sub>1</sub> and f<sub>2</sub>.
- T = terrigenous biogenous biogenic inputs (i.e.  $n-C_{23}$ ,  $n-C_{25}$ ,  $n-C_{27}$ ,  $n-C_{29}$ ,  $n-C_{31}$ , n-alkanes = vascular plant waxes).
- C = chronic pollution; unresolved hump in f1; pyrogenic polynuclear aromatic hydrocarbon inputs in f2.

Summary of Petroleum Hydrocarbon Composition of Mousse Samples (From Boehm and Fiest, 1980b). Table 13.

Dia fr	Distance from well (km)	Date	Sample	Visual Observations	Total f <sub>1</sub> mg/g	Total f <sub>2</sub> mg/g	Total f <sub>3</sub> mg/g	Residual mg/g	ALK/ ISO	SHWR	AWR
1	0.4	9/17/79	B116 E050	Fresh emulsion	414	186 407	144	256 45	3.75	1.13	1.19
	0.5	9/19/79	B258	Fresh mousse	564	337	52	47	3.78	2.66	2.46
	2.8	9/11//9	B068		403	216	89	292	3.32	1.10	1.16
• •	14.8	9/21/79	E582 E585 E588 E589	Mousse chunk Black flake Pancakes Mousse chunk	399 385 393 412	171 234 232 215	137 111 140 128	293 270 235 245	3.27 2.91 3.14 3.08	1.09 1.08 1.09 1.07	1.19 1.26 1.13
	21.8	9/18/19	B184		423	239	116	222	3.38	1.11	1.21
	32.0	9/18/79	E544 E542	Mousse in plume Mousse out of plume	427 399	194 239	124 146	255 216	3.40 3.22	1.06 1.04	1.19
	34.6	9/16/79	B114		404	181	109	306	3.39	1.11	1.18
	43.8	9/20/79	E154 E155	Mousse Mousse	468 413	312 259	123 90	97 238	4.10	1.34	1.59
	46.6	9/20/79	E566 E567 E571	Top of mousse Crust of mousse Bottom of mousse Chunks of mousse	425 439 455 386	287 195 255 174	94 88 113 151	284 278 177 289	4.08 3.35 3.85 3.50	1.29 1.24 1.31 1.01	1.51
	72.9	9/11/79	E525 E523	Mousse chunk Mousse chunk	409 368	248 212	123 149	220 271	3.80 3.20	1.13	1.37
	314.0	9/22/79	E186	Mousse	391	288	112	209	3,38	1.13	1.22
	0.009	9/23/79	E602	Tar ball	274	178	133	415	0.19 alkanes	no	
	0.009	8/79	Flake 1 Flake 2	Flake Flake	464 142	150	316 83	70	2.51 2.31	1.01	! 

samples were supplemented with 1 mM  $^{\rm NH}_4^{\rm NO}$ , and 1 mM  $^{\rm KH}_2^{\rm PO}_4^{\rm O}$ , the extent of degradation of  $^{14}{\rm C}$ -labelled hexadecane was 10 to 100 times greater (Table 15) after 10 days incubation.

Long-term incubation of mousse samples over 180 days showed a gradual evolution of CO<sub>2</sub>. However, analyses of the mousse in the incubation samples indicated that changes in chemical composition of the mousse were not apparent until 120 days (Atlas et al., 1980). Some preferential degradation of n-alkanes relative to isoprenoid alkanes was noted at this time.

Calculations of mineralization rates from these long-term mousse incubations indicate approximately 1 to 2.5 mg hydrocarbons converted to  $^{\rm CO}_2$  per liter per day. This is of the same order of magnitude as the rates estimated from incubation of natural water samples with  $^{\rm 14}$ C labelled substrates. However, the rates for the mousse incubation represent that a maximum of 0.7% of the added mousse was mineralized.

These data point to a severe nutrient limitation for microbial degradation of IXTOC oil in the waters of the area sampled and also limitation on biodegradation within the mousse. Unfortunately, extensive nutrient profiles are not available for the transect of stations. However, the few data available are given in Table 16 and indicate some nutrient depletion in the area. Certainly oxygen data (Figure 9) suggest that oxygen was not limiting as far as microbial degradation is concerned although most of the samples by necessity came from hydrocasts on the periphery of the slick.

The acridine orange direct counts also show very little difference between control sites, sites near the oil slick, and between sites with visible oil present as opposed to no visible oil or mousse present on the surface (Table 17).

However, colony forming units (CFU) did show differences at some stations (Figure 14). This indicated a change in the microbial community which was substantiated by changes in bacterial isolates (Pfaender et al., 1980). The metabolic activity investigation using amino acid turnover as an indicator, suggested that there was inhibition of microbial respiration immediately adjacent to the well site. Samples from the intermediate station at PIX10 showed dramatic increases in respiration but other stations showed ambient-control station levels of activity.

The data for hydrocarbon metabolism collected by Pfaender et al. (1980) (Table 18) showed that microbial populations in the water had the capability for significant metabolism of hydrocarbons at stations near the well site and in the main plume.

Buckley et al. (1980) conducted microcosm experiments using water from a station well removed from the slick area, RIXO9, and incubations in this water using three different mousse and oil samples: IXTOC-mousse from a Texas beach; the oil droplets collected near the well site from the PIERCE and flown to RESEARCHER (RIXO7); and mousse collected from RIXO6). A variety of microbial community parameters and degradation rates of hexadecane and naphthalene were periodically determined for subsamples from these microcosms over the sevenday time period of the experiment.

There were differences in how the microbial populations in the microcosms responded to the different oil and mousse samples. Buckley et al. (1980) report:

- i) increased total bacterial cell density,
- ii) shifts in the generic composition and cell type distribution,
- iii) increased heterotrophic activity in terms of amino acid uptake and respiration,

(iv) increased mineralization of n-hexadecane and naphthalene. The results also suggested that bacteria populations capable of degrading oil were more numerous in the mousse near the well site than in the relatively fresh well site oil (Figure 15). It is interesting that Buckley and Pfaender report that at the end of the microcosm experiment the well site oil had an appearance similar to the mousse. This suggests a role for microorganisms in the conversion of oil to mousse (Buckely et al., 1980). However, even though the bulk of the added oil or mousse was always at the surface of the microcosms, there was turbulence induced in the water by a stirring bar which might have influenced mousse formation over a seven-day period.

# Summary

The relative brevity of this section on microbiology in comparison to the section on chemistry is not a reflection of the relative importance of the studies. Rather, the microbiology studies did not involve as many different facets and samples and are easier to explain. Many of the results and interpretations were unexpected at the initiation of the cruise and constitute important new information about the interaction of oil and microorganisms in a spill of the type of the IXTOC-I spill.

The microbial community in the waters of the spill site showed changes in community structure and parameters of community function such as amino acid uptake and respiration compared to control sites. The numbers of hydrocarbon degrading bacteria increased in the oiled areas but the total microbial biomass was not a simple function of the presence or absence of oil.

Sufficient oxygen was present to support microbial degradation of oil but it appears that there was a nutrient limitation. This hypothesis is based on the laboratory experiments which clearly documented increased microbial activity for degrading hydrocarbons when nutrients were added.

The cause of the nutrient limitation is not known but may be related to the prevailing hydrographic conditions in the area at the time of the RESEARCHER/PIERCE cruise. For this reason, the hypothesis of the nutrient limitation could be confusing to some readers since Ross et al. (1980) in their paper state "the normally clear turquoise water of the Bay of Campeche is nutrient-rich due to the upwelling at the nearby edge of the continental shelf."

Certainly nutrient limitation can be and probably was a major factor in regard to mousse biodegradation. Microbial communities capable of significant biodegradation of hydrocarbons were associated with the mousse but the physical-chemical form of mousse probably prevents the ready mixture of hydrocarbons, nutrients and microorganisms in the correct proportions.

Table 14. Enumeration of Microbial Populations.

(Table 1 of Atlas et al. 1980)

	Direct Count	MPN-Hydrocarbor
Site	$_{ ext{x}}$ 105 $_{ ext{mL}}$ -1	<sub>mL</sub> -1
?1	1.5	0.3
?2	3.4	0.3
23***	4.5	24
25*	1.8	4
27	2.8	4
28	2.3	9
8***	7.0	2400
9***	2.2	2400
211	2.5	4
213***	1.7	24
214	3.6	1
214***	6.2	12000
215**	4.2	46
?16	2.0	1
217***	1.1	2400

<sup>\*</sup> = 0il but no mousse present in sample

<sup>\*\* =</sup> Mousse-tar particles in sample

<sup>\*\*\* =</sup> Heavy mousse water mixture

Table 15. Natural and Non-nutrient Limited Biodegradation Potentials for Hexadecane During 10-Day Incubation.

(Table 3 of Atlas et al., 1980)

Site	Nutrient Limited (Natural) % Mineralization	Non-nutrient Limited (N, P-Supplemented) % Mineralization
5116	% Hilleralization	
P1	0.2	9
P2	0.3	9
P5*	0.1	17
P7	0.3	15
P8	0.5	17
P8***	1.1	23
P9***	0.5	15
P11	0.5	18
P13**	0.2	26
P14	0.2	13
P14***	0.2	27
P15**	0.1	23
P16	0.2	13
P17***	0.3	28

<sup>\* =</sup> Oil only no mousse present

<sup>\*\* =</sup> Mousse-tar particles in sample

<sup>\*\*\* =</sup> Heavy mousse water mixture

Table 16. Filtered Nutrient Samples -- NOAA-AOML, Miami. (Provided by G. Berberian)

Vesse1	Depth (meter)	Sample No.	Station No.	Nitrate µgr-at/l	Nitrite µgr-at/l	Phosphate µgr-at/l	Silicate µgr-at/l
RIX	300 m	RF - 1	01	< 0.5*	< 0.1*	3.48*	< 0.5*
**	60 m	RF - 2	01	Ħ	••	.88	1.77
**	40 m	RF - 3	01	n	**	.73	1.59
**	5 m	RF - 4	01	Ħ	11	.36	1.42
11	20 m	RF <b>-</b> 5	02	11	11	.36	1.42
**	10 m	RF - 6	02	11	11	.18	1.42
**	1 m	RF - 7	02	**	11	.22	1.60
	20 m	RF - 8	04	**	11	.27	1.81
**	10 m	RF <b>-</b> 9	04	н	11	.36	2.18
11	1 m	RF - 10	04	11	11	.18	2.94
PIX	2 m	RF - 11(L015)	10	11	H	.36	< 0.5
••	10 m	RF - 13(L016)	10	11	11	.50	2.39
**	20 m	RF - 12(L017)	10	н	11	1.09	3.96
RIX	10 m	RF - 14 Bodman	09-030	11	11	.50	4.16
PIX	2 m	RF - 15(L027)	14/2	n	**	.55	3.96
**	10 m	RF - 16(L028)	14/2	11	**	.32	3.60
**	20 m	RF - 17(L029)	14/2	н	**	.60	3.20
11	2 m	RF - 18(L038)	15	H	•	.50	2.61
11	10 m	RF - 19(L039)	15	**	**	.18	2.42
	20 m	RF - 20(L040)	15	rr .	**	.46	2.45

<sup>\*</sup>Detection limit for Nitrate is 0.5  $\mu gr-at/$  &

<sup>\* &</sup>quot; Nitrite is 0.1  $\mu$ gr-at/ $\ell$ 

<sup>\* &</sup>quot; Phosphate is 0.05  $\mu$ gr-at/  $\ell$ 

<sup>\* &</sup>quot; " Silicate is 0.5 μgr-at/ ℓ

Table 17. Microbial Numbers in Gulf of Mexico. (Pfaender et al., 1980)

Station	Site (km from well head)	Depth (m)	Colony-Forming Units (per ml)	Acridine Orange Direct Count (x 10 <sup>6</sup> /m1)
PIX 10	0.5	2	773	1.01
	- '	10	141	.88
		20	147	•93
PIX 15	27.4	2	38 <b>,</b> 665	.82
	•	10	34,500	.79
		20	16,230	.98
PIX 08	27.0	2	283	.73
		20	250	.71
PIX 14	37.0	2	78	1.14
		10	43	.78
		20	63	.92
RIX 02	300.0	2	151	.46
<del>-</del>		10	123	.67
		20	231	.63
RIX 22	770.0	4	42	1.19
		20	37	.92
		40	102	1.03

Table 18. Hydrocarbon Metabolism rates. (Pfaender et al., 1980)

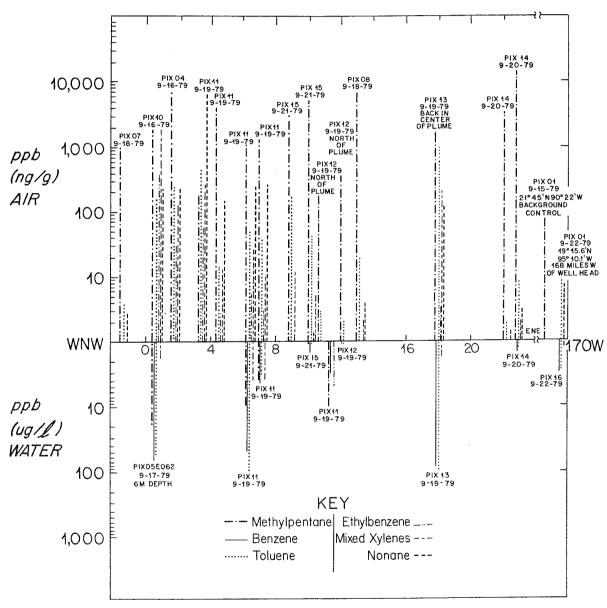
			Hydrocarbon Respiration - $\mu g/1/hr$					
Station	Site <sup>1</sup> (km)	Depth (m)	Aliphatic <sup>2</sup>	Tt(HR)	Aromatic <sup>3</sup>	Tt(HR)		
PIX 10	0.5	1 9	44.30	94	1.58	1772.0		
		9	21.70*		9.20*	304.0		
PIX 15	17.0	1	0.36	266	2.18	34.8		
		9	0.14	228	2.17*	8.85		
		20	0.72	44	1.84	10.3		
PIX 08	27.0	1	7.88*	35	6.44*	7.9		
		3			2.51*	20.3		
		18	.12	216				
PIX 14	37.0	1	<del></del>		0.65	70.7		
		9			0.01*	320.0		
		20			0.02	160.0		
RIX 02	300.0	3	.05		.007*	157.0		
		9	.09		.002*	550.0		
		20	.04	30	.037	29.7		
RIX 22	770.0	3			Over some			
		35	.01	200	.03	112.0		
		40	.01	142	.02*	170.0		

 $<sup>1</sup>_{\mathrm{Distance}}$  from well head.

 $<sup>^2\</sup>mbox{Calculations}$  based on total aliphatic hydrocarbon concentration and metabolism of  $^{14}\mbox{C-hexadecane.}$ 

 $<sup>^3\</sup>mbox{Calculations}$  based on total aromatic hydrocarbon concentrations and metabolism of  $^{14}\mbox{C-naphthalene.}$ 

<sup>\*</sup>Calculated value using hydrocarbon concentration from depth other than that from which sample was taken.



Concentrations of Selected Volatile Compounds
In Water and Air

Figure 12. (From Payne et al., 1980a).

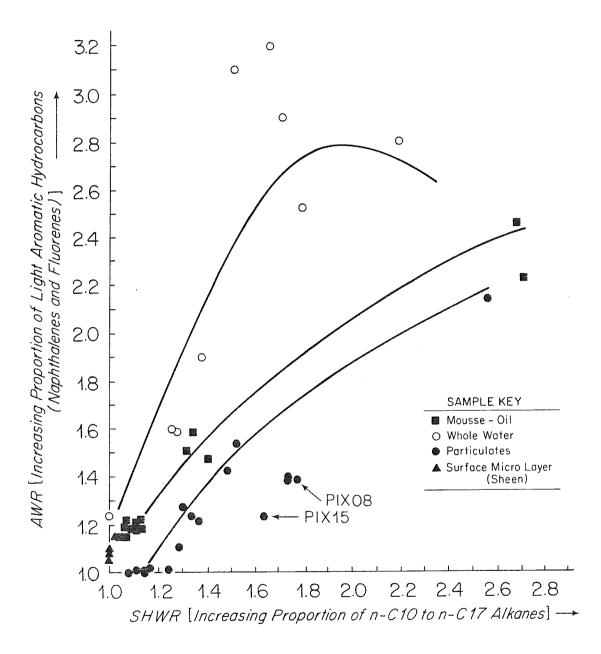
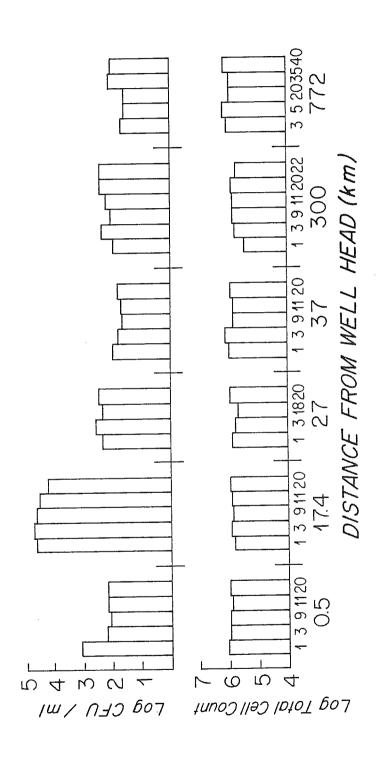


Figure 13. Oil Weathering Data (from Boehm and Fiest, 1980a; Boehm et al., 1982).



Total Cell Counts and Colony Forming Units - Microbiology Studies (from Phaender et al., 1980). Figure 14.

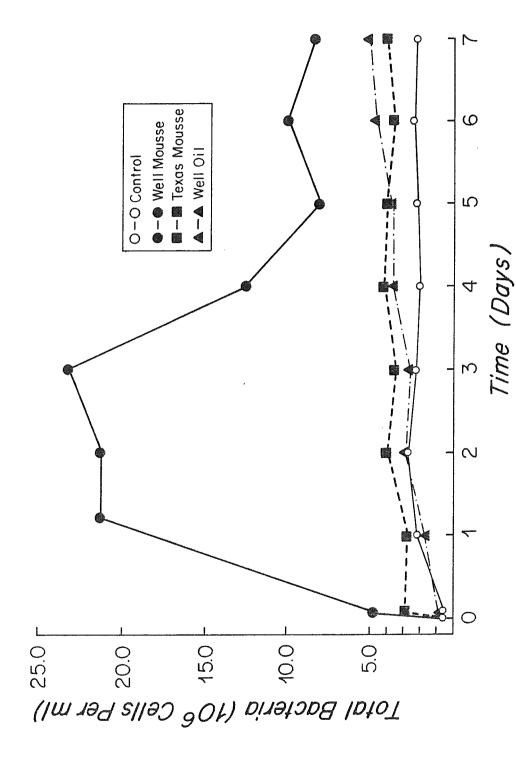


Figure 15. Bacteria Populations in Microcosm Experiments Containing Different Oils and Mousse (from Buckley et al., 1982).

# F. Photochemistry and Microbial Microcosm Experiments

The potential importance of photochemical reactions of spilled oil in terms of fate and effects of petroleum had been set forth in a few papers at the time of the IXTOC oil spill. Overton et al. (1980) reviewed these and among those relevant to the IXTOC study were papers by Burwood and Speers (1974), Patel et al. (1978), Freegarde et al. (1971), Pilpel (1973), Larsen et al. (1976). The analyses of mousse samples collected during studies of the Amoco Cadiz oil spill had yielded data on alkyl-substituted dibenzothiophene-5-oxides which were most likely the result of photochemical reactions of the alkyl-substituted dibenzothiophenes (Overton et al., 1979).

The helicopter overflight observations provided information suggestive — only suggestive — of photochemical alteration of the oil. During the early few flights in the area 15-19 September the sky was mainly overcast with some squalls and wider-spread rains. On 20 September there were clear skies with intense sunlight. The observations from the helicopter flights (personal observations of the author) recorded a marked change in the physical appearance of the oil as well as color changes close to the well site in Zones 1 and 2 (Figure 3). Mousse formation seemed to be present much closer to the well site and more intense in other areas. These observations plus the results in the literature led to analyses of selected samples to search for photochemical reaction products.

A small scale simulation of photochemical action on the IXTOC oil was carried out at the Center for Bioorganic Studies at the University of New Orleans (Overton et al., 1980b). Oil-water mixtures obtained at PIX-05 were extracted and the isolated oil was used in the experiment. This sample was

chosen as the best available sample with minimum contact time with the environment after discharge from the well. The oil was exposed to sunlight as a layer on artificial seawater in Pyrex dishes. Details are given in Overton et al. (1980b).

The main results, without belaboring the details, showed similarities in the changes in oil appearance (color and form) in this very small scale experiment and the changes in oil after discharge at the well site. However, these observations are by no means definitive proof of a major role of photochemical transformation and more rigorously defined experiments are required to investigate this phenomena.

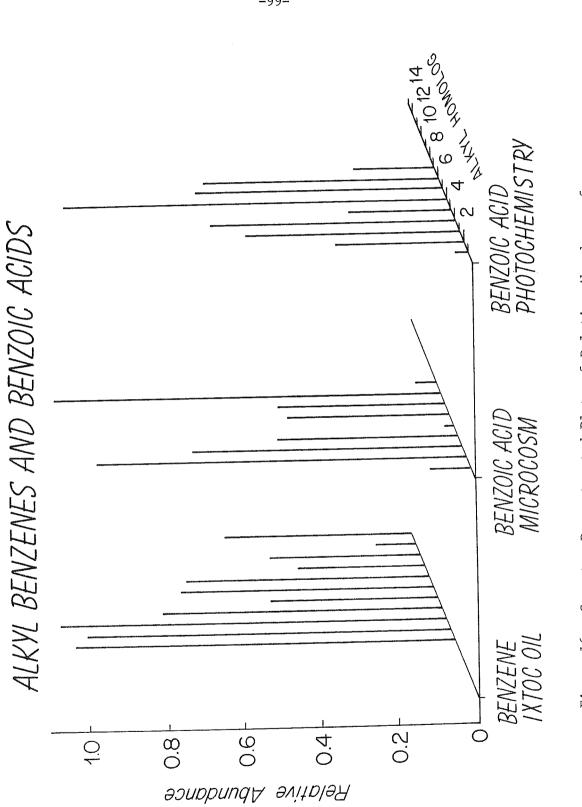
HPLC and GC/MS analyses of samples from the Pyrex dish experiment detected the presence of numerous oxygenated hydrocarbon products: alkylated naphthols, alkyl benzoic acids, naphthoic, phenanthroic, benzothiophenoic, and dibenzothiophenoic acids, phenanthrol,  $n^{-C}_{7}^{-C}_{11}$  fatty acids and branched  $^{C}_{9}^{-C}_{12}$  fatty acids. The latter compounds, the fatty acids, would most likely require reaction of n-alkanes in the spilled oil with an intermediated photochemically generated product rather than direct photochemical oxidation (Overton et al., 1980b).

Analysis of samples from microbial microcosm experiments conducted by Buckley et al. (1980) onboard the RESEARCHER using IXTOC-I samples indicate that many oxidized reaction products can also be produced and detected by HPLC and GC/MS analyses. However, there are differences in the relative abundancies between and within families of oxidation products when comparing the photochemical "microcosm" Pyrex dish experiments with the microbial microcosm experiments. For example, the relative abundancies of  $C_3$  to  $C_6$  alkyl benzoic

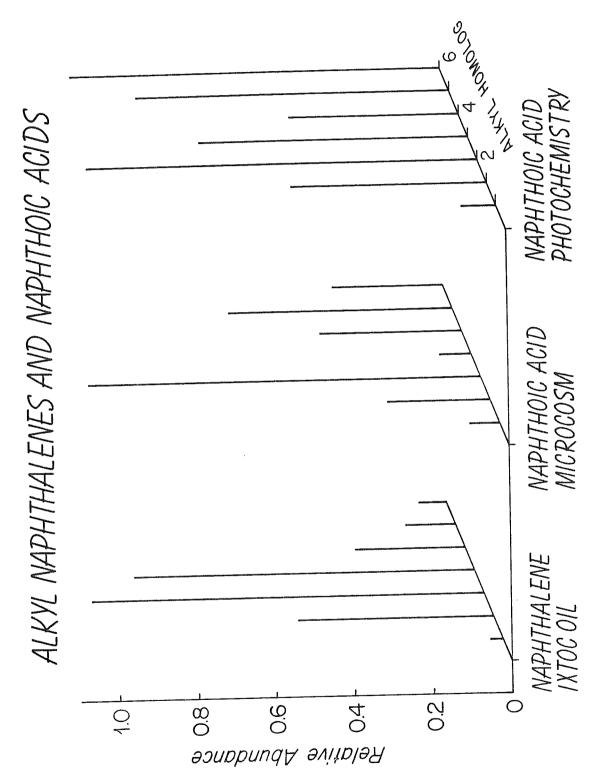
acids show marked differences while the  ${\rm C_1^{-C}_2}$  alkyl benzoic acids are quite similar in relative abundance (Figure 16). The  ${\rm C_1}$  and  ${\rm C_2}$  naphthoic acids show significant differences (Figure 17). The identification of these compounds is by interpretation of mass spectra without the benefit in most cases of standard spectra. Thus, identifications are not confirmed but are highly probable given preparative separation chemistry procedures prior to GC/MS analyses.

The search for clear evidence of photochemical oxidation products in water column samples from the collections at the spill site were disappointing. Several oxygenated compounds were identified but these were generally those found in Gulf of Mexico and other oceanic waters (Giam, 1977). If photochemical oxygenated products were formed it is likely their concentrations were below detection limits due to small sample size and either rapid dispersion/dilution in the water column or the lability of these compounds to further chemical or biologically-mediated reactions. It is also important to note that relatively few samples were analyzed because of the difficulty of these types of analyses and limited available funds.

In summary, the role of photochemical reaction of spilled oil is suspected of being an important process based on visual observations in the field and a brief small-scale laboratory experiment. Extensive, detailed physical-chemical and chemical evidence from the field samples is lacking. No definitive conclusions can be set forth except that comparison of microbial microcosm and photochemical "microcosm" reaction products indicate that analyses of certain groups of reaction products could provide a means of qualitatively detecting the action of microbial degradation or photochemical reaction in the presence of action of both processes.



Microcosm Oil, and Photochemistry Experiment Oil (from Computer Reconstructed Plots of Relative Abundance of Alkyl Benzenes and Alkyl Benzoic Acids in IXTOC 0il, Overton et al., 1980b). Figure 16.



Oil, and Photochemistry Experiment Oil (from Overton et al., 1980b). Naphthalenes, and Alkyl Naphthoic Acids in IXTOC 0il, Microcosm Computer Reconstructed Plots of Relative Abundance of Alkyl Figure 17.

An interesting speculation to keep in mind during future studies of oxygenated reaction products concerns the presence of naturally-occurring oxygenated compounds in the marine environment. There is no reason to doubt that an oil slick, and masses of mousse could function as extractants of less soluble naturally-occurring material from seawater. This would increase the concentrations of naturally-occurring oxygenated products in slicks and mousse causing more difficulties via interference signals in analysis for photochemical or microbial oxidation products from the oil.

## G. General Discussion

The importance of combined research efforts in microbiology and chemistry in understanding the fate of spilled petroleum in marine ecosystems has been clearly demonstrated by the results of the RESEARCHER/PIERCE cruise. A microbial community capable of degrading alkanes and aromatic hydrocarbons was present in the spill area several months after the spill began. It is likely that this community evolved from the indigenous population of microorganisms because of the introduction of spilled oil into the region. This latter point is supported by data from control stations.

Despite the presence of this active microbial community, the chemical analysis data for water column samples showed little, if any, evidence of microbial degradation of oil using parameters of changing chemical composition developed in other oil spill situations and laboratory experiments. The lack of more evident microbial degradation of the oil was shown by experimentation to be a nutrient limitation. Unfortunately, more extensive nutrient data were not available from more hydrographic casts to establish a clearer picture of nutrient distributions in the area at the time of the spill.

There was a clear indication in some of the chemistry data for surface sediments that microbially altered oil was present. However, it is difficult to separate the petroleum hydrocarbon input from the spilled oil from petroleum hydrocarbon input to sediments by discharge of exploration and production cuttings from the well and other wells in the region.

The hydrography of the spill area and the effects of currents and turbulence on transport and dispersal of the spilled oil were not documented due to
the lack of physical oceanographic instrumentation and physical oceanographers
onboard the ships. As will be discussed in Part II of this report, this was a
handicap recognized and reluctantly accepted in final cruise planning. Thus,
the calculations of water mass and oil movement are crude to the point of
guesstimates but are worth attempting as a guide for future endeavors of this
sort.

Estimates of the amount of oil in the water under the slick to a depth of 20 M are given in Table 19. The 20 M depth was chosen because of the shape of the hydrographic section (Figure 6). There is no way we can estimate the plume deeper than 20 M near the well site because of lack of samples due to problems in sampling in this region as explained earlier in this report. An estimate of the amount of oil in the slick to 20 KM is given in Table 20. A comparison of data in Tables 19 and 20 is presented in Table 21. This comparison shows that despite the subsea injection of the oil into the water column, most of the oil in the region is present in the slick at the surface. If we take into account the discontinuous, patchy slick extending beyond 20 KM, then even more the oil is in the surface slick.

Estimates of the amount of oil and gas spilled varied but were generally thought to be approximately 30,000 barrels per day. This converts to approxi-

mately 5 x 10<sup>9</sup> g/day. It is of interest to compare with the amount in the slick and water column -- .7 to 20 x 10<sup>9</sup> (Table 21). If we assume that the slick moved roughly at the same speed as the current speed of approximately 0.5 to 1 knot (estimated from observations) in the area, then we would expect to find one day's output to a distance of 21 to 42 KM from the well site. This is approximately what is found as stated above. For comparisons of current speed, Haegh and Rossenye (1980) report measurements of current on June 15 and July 8 in the range of 15-40 cm/sec in the upper 5 M and 25-36 cm/sec at 20 M near the well.

However, the basis for estimates of output from the well has never been firmly stated. In fact, there may be circular reasoning involved. Ross et al. (1980) state "Estimates of the amount of oil have varied. Originally PEMEX indicated the flow was 30,000 barrels of oil per day, but later appraisals put the flow at 5,000 to 10,000 barrels per day. Calculations based on inexact measurements of the oil slick flowing on the water surface place the flow rate in the 20,000 - 30,000 band-per-day range." Thus, there is no calculation of input available which estimates the input at the seafloor and from which a biogeochemical mass balance can be attempted to arrive at rates of loss to the atmosphere, to burning in the fire, and to other outputs.

It is interesting, but probably fortuitious, that Ross et al. (1980) report on their visit in June, 1979, approximately the same amount of oil in the surface slick as was present in September during the IXTOC cruise.

There is little doubt that concentrations of petroleum compounds in the subsurface plume particularly aromatic hydrocarbons such as benzene, xylene, toluene, and naphthalenes exceed concentrations known to have lethal and sub-

lethal effects on certain species of marine organisms (Neff, 1979; Vandermeulen, 1982; Grassle et al., 1981). However, with one exception to the best of my knowledge, other than the microbiology research previously discussed, no direct biological effects research, or systematic scientific survey to detect biological effects near the oil spill site were conducted, or at least have been published in the open scientific literature. The exception is the effort by Macaulay et al., 1980, to couple net tows outside the plume with acoustic observations of biological volume scattering to document correlations between populations of organisms giving an acoustic target and oil concentrations. However, this effort was frustrated to a large extent by lack of adequate sampling time, lack of adequate nets, and perhaps more importantly the probable interference of acoustic scattering from oil droplets or gas bubbles (Macaulay et al., 1980).

Effects of IXTOC oil on marine organisms along the coast of Texas are the subject of the report by ERCO (1982). Benthic communities of the South Texas Continental Shelf area were investigated by obtaining 72 grab samples in 1980 and comparing data on benthic ecology with earlier studies in 1976 and 1977 (Lewbell et al. in ERCO, 1982). There were reductions in numbers of taxa and numbers of individuals and twelve stations. However, because of gaps in sampling in 1978 and 1979 and lack of adequate life histories, descriptions, and knowledge of normal cycles of abundance, no quantitative cause and effect relationship can be inferred with respect to IXTOC oil.

Thus, while data at the organismal and mesocosm level of scientific experiments indicates that concentrations of petroleum compounds present in the plume have a significant probability of affecting organisms and ecosystems in the

Table 19. Estimate of Amounts of Oil in Plume Under Slick at the Time of the RESEARCHER/PIERCE Cruise.

Oil from U.V.-fluorescence analyses estimates (see text and Figure 6)

	Trapezoid Pyramid Parameters						
Slick Section	₩ <sub>1</sub> 	W <sub>2</sub> KM	1	d M	Volume*	Conc. g/M <sup>3</sup>	Amount
0-10 KM	.4	1	10	20	1.4	1	1.4
10-20 KM	1	2.5	10	20	2	0.5	1
20-40 KM	2.5	12	20	20	20	0.01	3
						Total	3

<sup>\*</sup>Volume = area of trapezoid  $\cdot$ depth = 1/2 (W<sub>1</sub> + W<sub>2</sub>) 1  $\cdot$  depth

Table 20. Calculation of Oil in Surface Layer Film (Slick) at Time of RESEARCHER/PIERCE Cruise.

. Slick almost continuous and as estimated 1-3 mm thick to a distance of  $20\ \mathrm{KM}$ .

Area = 
$$2.7 \times 10^7 \text{ M}^2$$
  
=  $2.7 \times 10^{11} \text{ cm}^2$ 

for 1 mm or 0.1 cm thickness

Volume = 
$$0.1 \cdot 2.7 \times 10^{11} \text{ cm}^2$$
  
=  $2.7 \times 10^{11} \text{ cm}^3$ 

assume density 1

$$2.7 \times 10^{10} \text{ g}$$

measured 30% oil

 $7 \times 109 g$ 

Similarly for 0.3 cm thick slick:  $2 \times 10^{10}$  g

Slick contained between .7 x  $10^{10}$  and 2 x  $10^{10}$  g oil

Table 21. Comparisons of Amounts of Oil in Water Under Slick and in Slick.

Oil under Slick =  $.04 \times 10^{10}$  g

Oil in Slick =  $.7 - 2 \times 10^{10} \text{ g}$ 

area, field verification or refutation in a quantitative, scientific manner was frustrated by lack of biological effects studies. The complexity and costs of such studies are great but the questions they could have answered in part are still bedevilling potential environment impact assessment reviews for continental shelf and slope oil and gas development and questions of effects of oil on marine ecosystems (Vandermeulen, 1982; Teal and Howarth, 1984).

The RESEARCHER/PIERCE cruise and subsequent sample analyses and data interpretation provided verification of some aspects of biogeochemical processes acting on oil in marine systems and contributed new knowledge about several other processes as previously discussed. A post mortem of cruise preparations and activities also provides guidance as to scientific responses to similar events in the future. This is the subject of Part II of this report; addressed specifically to the Georges Bank region but of generic value for all large oil spill studies.

#### References

- Atlas, R. M., G. Roubal, A. Bronner and J. Haines (1980). Microbial degradation of hydrocarbons in mousse from IXTOC-I. In: N.O.A.A. (1980) cited herein, pp. 411-435.
- Atlas, R. M. (1981). Microbial degradation of petroleum hydrocarbons: An environmental perspective. Microbiol. Rev., 45(1): 180-209.
- Atwood, D. K., J. A. Benjamin and J. W. Farrington (1980). The mission of the September 1979 RESEARCHER/PIERCE IXTOC-I Cruise and the physical situation encountered. In: N.O.A.A. (1980) cited herein, pp. 1-16.
- Berridge, S. A., R. A. Dean, R. G. Fallows and R. Fish (1968). The properties of persistent oils at sea. J. Inst. Petrol., 54.
- Blumer, M. and J. Sass (1972). Oil pollution: persistence and degradation of spilled fuel oil. Science, 1976: 1120-1122.
- Boehm, P. D. and D. L. Fiest (1980a). Surface water column transport and weathering of petroleum hydrocarbons during the IXTOC-I Blowout in the Bay of Campeche and their relation to surface oil and microlayer compositions. In: N.O.A.A. (1980) cited herein, pp. 267-338.
- Boehm, P. D. and D. L. Fiest (1980b). Aspects of the transport of petroleum hydrocarbons to the offshore benthos during the IXTOC-I Blowout in the Bay of Campeche. In: N.O.A.A. (1980) cited herein, pp. 207-236.
- Boehm, P. D., D. L. Fiest, K. Hausknecht, J. Barbash and G. Perry (1982).

  Investigation of the transport and fate of petroleum hydrocarbons from the IXTOC-I Blowout in the Bay of Campeche sampling and analytical approaches, Chapter 7. In: Energy and Environmental Chemistry, Vol. 1,

  Fossil Fuels (L. H. Kieth, ed.). Ann Arbor Science Publishers, Ann Arbor,

  Michigan 48106, USA, pp. 129-159.
- Botello, A. V. and S. Castro-Gessner (1980). Chemistry and natural weathering of various crude oil fractions from the IXTOC-I oil spill. In: N.O.A.A. (1980) cited herein, pp. 387-407.
- Brooks, J. M., D. A. Wiesenburg, R. A. Burke, M. C. Kennicutt and B. B. Bernard (1980). Gaseous and volatile hydrocarbons in the Gulf of Mexico following the IXTOC-I Blowout. In: N.O.A.A. (1980) cited herein, pp. 53-115.
- Brown, R. A. and H. L. Huffman, Jr. (1976). Hydrocarbons in open ocean waters. Science, 191: 847-849.
- Buckley, E. N., F. K. Pfaender, K. L. Kylberg and R. L. Ferguson (1980). Response of the pelagic community to oil from the IXTOC-I Blowout. II. Model ecosystem studies. In: N.O.A.A. (1980) cited herein, pp. 563-586.

- Burwood, R. and G. C. Speers (1974). Photooxidation as a factor in the environmental dispersal of crude oil. Estuar. Coastal Mar. Sci., 2: 117-135.
- Connel, D. W. and G. J. Miller (1980). Petroleum hydrocarbons in aquatic ecosystems behavior and effects of sublethal concentrations. <u>Critical</u> Review in Environmental Control (CRC Press), Volume II: 37-162.
- deLappe, B. W., R. W. Risebrough, J. C. Shropshire, E. F. Letterman, W. R. Sistek and W. Walker, II (1979). Hydrocarbons in the waters of the Southern California Bight in 1977. Submitted to U.S. Department of Interior, Bureau of Land Management, as Science Applications, Inc., Report No. SAI-77-917-LJ, 50 p.
- ERCO (1982). IXTOC Oil Spill Assessment Final Report. Prepared for Bureau of Land Management, U.S. Dept. of Interior under Contract No. AA851-CTO-71. Submitted by Energy Resources Company, Inc., Environmental Sciences Division, One Alewife Place, Cambridge, MA 02138, USA, 327 pp.
- Farrington, J. W. (1975). Oil pollution in the environment. In: Proceedings of the Conference: Estuarine Pollution Control and Assessment, Vol. II.

  U.S. Environmental Protection Agency, Washington, D. C., pp. 385-400.
- Farrington, J. W., J. M. Teal and P. L. Parker (1976). Petroleum hydrocarbons, Chapter 1. In: Strategies for Marine Pollution Monitoring (E. D. Goldberg, ed.). Wiley Interscience, New York.
- Farrington, J. W. (1983). Scientific Research and Monitoring Response to Offshore Oil Spills: The Example of the IXTOC-I Blowout Cruise. In:

  Proceedings of the Conference: <a href="https://Hydrocarbon.exploration">Hydrocarbon Exploration</a> and Development on Georges Bank An Environmental Examination (W. W. Tiffney, Jr. and R. F. Hill, eds.). The American Society for Environmental Education, Hanover, New Hampshire 03755, pp. 122-152.
- Fiest, D. L. and P. D. Boehm (1980). Subsurface distributions of petroleum from an offshore well blowout the IXTOC-I Blowout, Bay of Campeche. In: N.O.A.A. (1980) cited herein, pp. 169-185.
- Gearing, J. N., P. J. Gearing, T. L. Wade, J. G. Quinn, H. B. McCarty, J. W. Farrington and R. F. Lee (1979). The rates of transport and fates of petroleum hydrocarbons in a controlled marine ecosystem and a note on analytical variability. Proceedings 1979 Oil Spill Conference, American Petroleum Institute, Washington, D. C., pp. 555-564.
- Giam, C. S. (ed.) (1977). <u>Pollutant Effects on Marine Organisms</u>. Lexington Books, Massachusetts, Toronto, pp. 32-33.
- Gschwend, P. M., O. C. Zafiriou, R.F.C. Mantoura, R. P. Schwarzenbach and R. B. Gagosian (1982). Volatile organic compounds at a coastal site 1. Seasonal variations. <u>Environ. Sci. and Technol.</u>, <u>16</u>: 31-38.

- Gundlach, E., P. D. Boehm, M. Marchand, R. M. Atlas, D. M. Ward and D. A. Wolfe (1983). The fate of Amoco Cadiz oil. Science, 221: 122-129.
- Haegh, T. and L. I. Rossenye (1980). A comparison of weathering processes of oil from the Bravo and the IXTOC Blowouts. Paper presented to 12th Offshore Technology Conference (OTC 3702), Houston, Texas, USA, pp. 237-244.
- Larson, R. A., L. L. Hunt and D. W. Blankenship (1976). Toxic hydroperoxides: Photochemical formation from petroleum constituents. AIBS Symp. on Sinks of Hydrocarbons in the Aquatic Environment, Washington, D. C.
- Levy, E. M., M. Ehrhardt, D. Kohnke, E. Sobtchenko, T. Suzuoki and A. Tokuhiro (1981). Global Oil Pollution. Results of MAPMOPP, the IGOSS Pilot Project on Marine Pollution (Petroleum) Monitoring. Intergovernmental Oceanographic Commission, UNESCO, Paris, France, 35 pp.
- Macaulay, M. C., K. Daly and T. S. English (1980). Acoustic observations of biological volume scattering in the vicinity of the IXTOC-I Blowout. In: N.O.A.A. (1980) cited herein, pp. 499-521.
- MacLeod, W. D., Jr. and J. R. Fischer (1980). Intercalibration of analytical laboratories. In: N.O.A.A (1980) cited herein, pp. 41-49.
- MacLeod, W. D., Jr., P. G. Prohaska, D. D. Gennero and D. W. Brown (1982). Interlaboratory comparisons of selected trace hydrocarbons from marine sediments. Anal. Chem., 54: 386-392.
- Malins, D. C. and Hodgins, H. O. (1981). Petroleum and marine fishes: A review of uptake, disposition, and effects. Environmental Science and Technology, 15: 1272-1278.
- Maul, G. A. (1977). The annual cycle of the Gulf Loop Current Part I:

  Observations during a one year time series. J. Mar. Res., 35: 29-47.
- Molinari, R. L. (1978). Current variability and its relation to sea-surface topography in the Caribbean Sea and Gulf of Mexico. Mar. Geodesy, 3: 149-419.
- N.A.S. (1975). Petroleum in the Marine Environment. National Academy of Sciences, Washington, D. C., USA.
- Neff, J. (1979). Polycyclic Aromatic Hydrocarbons in the Aquatic Environment. Applied Science Publishers, Ltd., London, 262 pp.
- N.O.A.A. (1978). The Amoco Cadiz Oil Spill: A Preliminary Scientific Report. U.S. Dept. of Commerce, NOAA, U.S. EPA, August, 1978. Superintendent of Documents, U.S. Government Printing Office, Washington, D. C.

- N.O.A.A. (1980). Proceedings of a Symposium on Preliminary Results from the September, 1979 RESEARCHER/PIERCE IXTOC-I Cruise, Key Biscayne, Florida, June 9-10, 1980. Publications Office, NOAA/RD/MP3, Office of Marine Pollution Assessment, N.O.A.A., U.S. Dept. of Commerce, 325 Broadway, Boulder, CO 80303, USA.
- N.O.A.A. (1981). The IXTOC-I Oil Spill. The Federal Scientific Response NOAA Hazardous Materials Response Project (C. Hooper, ed.). N.O.A.A., U.S. Dept. of Commerce, Washington, D. C., USA, 202 pp.
- Overton, E. B., J. R. patel and J. L. Laseter (1979). Chemical characterization of samples from the Amoco Cadiz oil spill. 1979 Oil Spill Conference (Prevention, Behavior, Control, Clean-up).
- Overton, E. B., L. V. McCarthy, S. W. Mascarella, M. A. Maberry, S. R. Antoine, J. L. Laseter and J. W. Farrington (1980a). Detailed chemical analysis of IXTOC-I crude oil and selected environmental samples from the RESEARCHER and PIERCE cruises. In: N.O.A.A. (1980) cited herein, pp. 439-495.
- Overton, E. B., J. L. Laseter, W. Mascarella, C. Raschke, I. Nuiry and J. W. Farrington (1980b). Photo-chemical oxidation of IXTOC-I oil. In: N.O.A.A. (1980) cited herein, pp. 341-383.
- Patel, J. R., J. McFall, G. W. Griffin and J. L. Laseter (1978). Toxic photogenated products generated under environmental conditions from phenanthrene. EPA Symp. on Carcinogenic Polynuclear Aromatic Hydrocarbons in the Marine Environment, Pensacola Beach, Florida, August 14-18, 1978.
- Patton, J. S., M. W. Rigler, P. D. Boehm and D. L. Fiest (1981). IXTOC-I Oil Spill: flaking of surface mousse in the Gulf of Mexico. Nature, 290: 235-238.
- Payne, J. R., J. R. Clayton, Jr., B. W. deLappe, P. L. Millikan, J. S Parkin, R. K. Okazaki, E. F. Letterman and R. W. Risebrough (1978). Hydrocarbons in the water column, Southern California Baseline Study. Submitted to U.S. Department of Interior, Bureau of Land Management as Science Applications, Inc. Report No. SAI-76-809-LJ, 149 pp.
- Payne, J. R., N. W. Flynn, P. J. Mankiewicz and G. S. Smith (1980a). Surface evaporation/dissolution partitioning of lower-molecular-weight aromatic hydrocarbons in a down-plume transect from the IXTOC-I wellhead. In: N.O.A.A. (1980) cited herein, pp. 239-263.
- Payne, J. R. G. S. Smith, P. J. Mankiewicz, R. F. Shokes, N. W. Flynn, V. Moreno and J. Altamirano (1980b). Horizontal and vertical transport of dissolved and particulate-bound higher-molecular-weight hydrocarbons from the IXTOC-I Blowout. In: N.O.A.A. (1980) cited herein, pp. 119-166.

- Payne, J. F. (1982). Critique of petroleum and marine fishes: A review of uptake, disposition and effects. Environmental Science and Technology, 16: 370-372.
- Pfaender, F. K., E. N. Buckley and R. Ferguson (1980). Response of the pelagic microbial community to oil from the IXTOC-I Blowout. I. <u>In situ</u> studies. In: N.O.A.A. (1980) cited herein, pp. 545-560.
- Pilpel, N. (1973). Sunshine on a sea of oil. New Scientist, 59: 636-644.
- Ross, S. L., C. W. Ross, F. Lepine and R. K. Langtry (1980). IXTOC-I Oil Blowout. In: N.O.A.A. (1980) cited herein, pp. 25-38.
- Sanders, H. L. and C. Jones (1981). Oil, Science and Public Policy in Coast Alert (T. C. Jackson and D. Reische, eds.). Published for the Coast Alliance by Friends of the Earth, San Francisco, CA, pp. 73-94.
- Shaw, D. G. and S. K. Reidy (1979). Chemical and size fractionalization of aqueous petroleum dispersions. Environ. Sci. Technol., 13: 1259-1263.
- Staresinic, N., G. T. Rowe, D. Shaughnessy and A. J. Williams, III (1978). Measurements of the vertical flux of particulate organic matter with a free-drifting sediment trap. Limnol. Oceanogr., 23: 559-563.
- Straughan, D. (1974). Factors causing environmental changes after an oil spill. J. Pet. Technol., 24: 250-254.
- Sturges, W. and J. P. Blaha (1976). A western boundary current in the Gulf of Mexico. Science, 192: 367-369.
- Sweeney, R. E., R. I. Haddad and I. R. Kaplan (1980). Tracing the dispersal of the IXTOC-I oil using C, H, S, and N stable isotope ratios. In: N.O.A.A. (1980) cited herein, pp. 89-115.
- Teal, J. M. and R. W. Howarth (1984). Oil spill studies: A review of ecological effects. Environmental Management, 8: 27-44.
- Vandermeulen, J. H. (1982). Some conclusions regarding long-term biological effects of some major oil spills. Phil. Trans. R. Soc. Lond., B297: 335-351.
- Wakeham, S. G., A. C. Davis, and J. T. Goodwin (1982). Volatile organic compounds in marine experimental ecosystems and the estuarine environment initial results. In: Marine Mesocosms: Biological and Chemical Research in Experimental Ecosystems (G. D. Grice and M. R. Reeve, eds.). Springer-Verlag, New York, N.Y., pp. 137-151.
- Wakeham, S. G., J. T. Goodwin and A. C. Davis (1983). Distribution and fate of volatile organic compounds in Narragansett Bay, Rhode Island. Can. J. Fish. Aquat. Sci., 40(Suppl. 2): 304-321.

- Walter, D. J. and J. R. Proni (1980). Acoustic observations of subsurface scattering during a cruise at the IXTOC-I Blowout in the Bay of Campeche, Gulf of Mexico. In: N.O.A.A. (1980) cited herein, pp. 525-541.
- Zurcher, F. and M. Thuer (1978). Rapid weathering processes of fuel oil in natural waters analysis and interpretations. Environ. Sci. and Technol., 12: 838-843.

#### SECTION II:

### Scientific Research and Monitoring Response to Offshore Oil Spill:

### The Example of the IXTOC-I Blowout

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### SCIENTIFIC RESEARCH AND MONITORING RESPONSE TO OFFSHORE OIL SPILLS: THE EXAMPLE OF THE IXTOC-I BLOWOUT

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### ABSTRACT

The blowout of the IXTOC-I oil well in the Gulf of Mexico in June 1979 and the resulting large discharge of oil to the continental shelf area off the Mexican coast near the Bay of Campeche tested the ability of the scientific community to provide research, monitoring, and damage assessment capabilities for offshore oil spills. The experiences of the combined cruise of the NOAA Ship Researcher and the contract vessel Pierce to the spill site in September 1979 provide an example of the types of problems which might be encountered in U.S. OCS areas such as the Georges Bank in the event of an oil spill associated with exploration or production.

Ship scheduling, sampling and analytical equipment availability, diverse sampling strategies, multiple-ship and helicopter operations, communications and control problems, weather contingencies, compatibility of multidisciplinary research, mixed authority and responsibilities within and between U.S. government agencies, and chain of command leadership within a mixed group of government, contracting company and academic scientists were all major hurdles to the execution of the cruise. These are discussed within the context of scientific research, monitoring, and damage assessment for Georges Bank oil spills.

A much stronger planning effort with periodic updating is needed once the general goals of such studies have been set by policy decisions. The lack of policy decisions regarding oil spill studies, or the lack of communication of these decisions to the scientific community to be involved in such studies, needs to be rectified.

#### INTRODUCTION

Many times during the 1970's and 1980's, the scientific and engineering community has been asked to respond to accidental oil spills to provide advice on clean-ups, prediction of spilled oil movement through particular ecosystems, and ecological damage assessment. An assessment of the literature over the past ten years suggests that the scientists and engineers of academia, government agencies, the oil industry, and environmental consulting companies have learned important information about spilled oil behavior and interaction with various ecosystems (A.P.I., 1969-1981; N.A.S., 1975; Bates, 1978; Pollack and Stolzenbach, 1978). However, early in the history of these studies, it became apparent that, despite some factors common to many spills, large (> 100,000 gallons, ~ 360,000 liters) oil spills usually produce individual characteristic problems serious enough to require independent investigation and evaluation (N.A.S., 1975). This will probably be true for large spills on Georges Bank. Given the obvious importance of Georges Bank for fisheries and the importance of nearby coastal areas for tourism, recreation, and commercial and recreational fishing, there will be compelling reasons for a scientific response to a large oil spill on Georges Bank. As an example, there certainly were considerable pressures from various sectors of society to respond to the Argo Merchant oil spill on the Nantucket Shoals area of Georges Bank (Pollack and Stolzenbach, 1978; C.O.M.S., 1978).

The preparation for, execution of, and follow-up on the cruise of the NOAA ship Researcher and contract vessel Pierce to the IXTOC-I blowout oil spill in 1979 should provide us with some guidance on how to respond to a large oil spill in the Georges Bank area. In this paper, I will also present my opinion regarding lessons to be learned from this cruise.

The preliminary scientific results from the cruise were presented in a symposium volume (N.O.A.A., 1980), and readers are referred to this volume for details of the various components of the cruise.

#### IXTOC-I BLOWOUT - ORGANIZATION OF THE CRUISE

The IXTOC-I oil well is situated off the coast of Mexico in the area generally known as the Bay of Campeche (Figures 1 and 2). On June 9, 1979, the well blew out. An account of the events of the blowout and discussion of some of the engineering aspects are provided conveniently for this audience in hearings before the U. S. Senate which cover events up to November, 1979 (U.S. Senate, 1979).

Discharges of oil and gas from the well continued from June 9, 1979 throughout the summer of 1979. In late July-early August, 1979, it became apparent that this spilled oil had entered U.S. waters and was coming ashore in Texas. Understandably, this became a matter of concern for both the governments of Mexico and the United States, as well as the state government of Texas and local

governments. The interplay between local and state governments, state and national governments, and international political interactions generated the desire to know more about the fate and effects of this spilled oil.

The situation on Georges Bank will have similar political interactions; e.g., local public officials in Cape Cod, Nantucket, Martha's Vineyard, the Commonwealth of Massachusetts; U.S. government, Canadian government, Provincial Government of Nova Scotia, local officials in, for example, Yarmouth, Nova Scotia.

I do not know for certain the origin of the initial impetus for the Researcher/Pierce IXTOC-I cruise since I was not involved in the mid-August discussions. There have been many different versions of meetings recounted to me by individuals from government agencies, academia, and private consulting companies. The exact reasons for having the cruise are not germane to my points here and, regardless of the initial intent, all I have talked to who attended the late July to mid-August meetings agree that there was considerable confusion over several weeks as to which U.S. government agency or agencies were in charge of the projected cruise and, within a given agency, which group or individual had the lead role. The responsibilities for several key aspects of the various scenarios for cruises (e.g., chemistry, physical oceanography) were not well defined. There were competing components within federal agencies, each with their entourage of academic researchers and environmental consulting companies.

### Factors Causing Confusion

Confusion at the time of the response to an oil spill can be attributed to several obvious factors, some which should be obvious but are often ignored because they reflect on the human nature of the people involved.

### Limited Predictability

There is a finite limit to the ability to predict an accidental spill. Some may argue that spills are unpredictable. However, in the case of IXTOC-I, there certainly was a greater probability of an accidental blowout after the initiation of exploration and production than before commencement of these activities, as far as the Bay of Campeche is concerned. The same reasoning obviously applies to Georges Bank. There are constraints placed on the time element, and the place element is controlled by location of the various drilling and production activities. There are limits to prediction of the type and severity of the accident and the environmental conditions at the time of the accident.

### Overlapping Mandates and the Human Factors

The overlapping responsibilities, real or perceived, of the various federal and state agencies are a two-edged sword in that the combined resources can be brought to bear on the problem, but, considering the number of people involved, time is required to organize and sort out responsibilities. I will not cite code and section or bill and section of the various federal and state legislative acts and executive branch rulings which could apply to an accidental oil spill. They are extensive (N.O.A.A., 1981), and beyond the scope of this paper.

Table 1 is a list of some of the agencies I suspect will have some role in an accidental spill on Georges Bank. Table 2 is a list of some of the various sources of scientific advice which might be brought to bear on the scientific aspects of the problem. Within this context, we must explicitly recognize the fact that a large accidental oil spill receives substantial publicity and political attention. When congressional committees responsible for oversight and budgets of one or more federal agencies become interested in the response of the agency, the administrators and scientists of that agency understandably become very much interested in demonstrating that their agency, or group within an agency, have a key role in the response activities. Environmental consulting companies want to be involved because of the prospect of large contracts or the publicity they can glean from their participation (e.g., key laboratory in response to IXTOC-I oil spill), which provides them with a claim to experience relevant to a large number of other potential contracts. Last, but not least, are the motivations of academic scientists. Marine scientists and others at state universities are usually under some subtle or direct pressure to demonstrate that their research, which is supported in part or entirety by state funds, can provide guidance in a crisis situation or has prepared them for direct involvement. The same pressures are experienced by academic scientists at private universities and institutions vis a vis federal research funding. In summary, the advancement or enhancement of professional careers of several scientists in government agencies, academia, and consulting companies could evolve from the response to a large accidental oil spill.

A very important motivating factor which influences most of the participants is a genuine desire to serve the public need. For research scientists who specialize in oil pollution problems, a large spill such as IXTOC-I is seen as a rare opportunity to gain valuable data needed in their area of research. While they do not wish for such a spill, just as volcanologists do not wish for a Mount St. Helen's eruption, they feel obligated to take advantage of the situation to gain new knowledge which can be of public use in the future. It is my belief that the vast majority of participants in the planning and execution of the Researcher/Pierce IXTOC-I cruise had the public need foremost in mind. However, even when ones intentions as a scientist are good, they are often misunderstood by others, including other scientists. This can create tension, confrontation and confusion. The federal agencies with prime responsibility for clean-up of the oil spill want to conduct research applicable to the situation immediately at hand. Some scientists may want to conduct work applicable to the longterm questions of oil pollution in the marine environment. Even when the objectives of several different groups of people are the same, they may have different priorities, thereby causing misunderstandings.

To illustrate this point, I can draw on my own experience with the Argo Merchant oil spill on Georges Bank. Several of the scientists at the Woods Hole Oceanographic Institution participated in emergency response cruises to provide initial observations and samples during the early days of the Argo Merchant oil spill. Our choice of sampling locations and sampling strategy was dictated by our collective opinion of the most important samples to obtain in terms of the study of the spill. Despite this, a frustrated federal agency scientist and two academic researchers assessing our response to the spill suggested other contributing motives, e.g., that our activities "reflected the interests and capabilities of the chief investigators — Farrington, John Teal and Howard Sanders." (Pollack and Stolzenbach, 1978, p. 85), or "the researchers did not care where the oil was going and merely wanted to sample their favorite areas." (Pollack and Stolzenbach, 1978, p. 89).

#### Weather

The violent winter storms during the first weeks of the Argo Merchant oil spill (Pollack and Stolzenbach, 1978) and three hurricanes during the Researcher/Pierce IXTOC-I cruise (NOAA, 1980) caused three main problems: (1) limitations of shipborne sampling and research activity; (2) limitations of airborne and satellite surveillance of the spill and associated slicks; (3) changes in the circulation and turbulence transporting and mixing oil into the marine ecosystem in question.

#### Funding Priorities

The best scientific plans are captive to available funds. Uncertainty as to available funds causes reluctance to spend a large effort in planning. The confusion and frustration in this category can be described in a few cryptic phrases characterizing the conversations of scientists and those with responsibility for funding during the late August planning stages of the IXTOC-I cruise. Scientist: "We need to have three large research vessels in the area for at least a month, and a commitment of one or two years follow-on funding." Agency official: "How much do you estimate this will cost?" Scientist: "Approximately two million dollars." Agency official: "You're kidding! That's our whole budget for this year! You will have to give me a list of priorities and a plan for only one ship and the initial sampling and on-board measurements." Scientist: "Who decides the priorities?" Agency official: "We will do it together, but the final decision is out of our hands." Scientist: "Who makes the final decision?" Agency official: "We are checking on that issue but we have to get feedback from OMB (Office of Management and Budget) on reallocation of some of our funds."

I distinctly remember thinking during such a conversation that the more funding that went to the cruise efforts, the less funds would be available to fund other research, and I had plans to submit a large joint proposal with several other colleagues to this same agency for longer term research into other marine environmental quality problems. I put this out of my mind as I concentrated with others, many with proposals also of the same status, on producing the list of priorities and deciding on a one ship operation — at least I think it did not influence my decision as to how much we should attempt to accomplish.

The question of inherent conflict of interest in deciding what to do in a scientific response to an oil spill has been present in every scientific response to a major oil spill. Given finite resources of funds, equipment, people, and laboratory space, how much do you commit to the immediate response to the oil spill and how much do you leave with the longer-term, carefully planned research activities? This was a very important contributing factor to some of the initial confusion in the IXTOC-I spill cruise. For example, the scientists of NOAA's Atlantic Oceanographic and Meteorology Laboratory in Miami had to postpone a carefully planned cruise focusing on long term basic research needs in regard to environmental quality research in the Gulf of Mexico in order to release the Researcher for the IXTOC-I oil spill cruise. This same problem existed at the time of the Argo Merchant oil spill. How much effort should be diverted from the longer-term, carefully planned research activities in order to study the fate and effects of an oil spill?

### Initial Cruise Plans

Early in the discussions of the research to be conducted, it was decided to send a ship to the well site for research if the Mexican government gave permission. The reasons for going to the well site and nearby area were as follows: (1) this was a seabed blowout in contrast to other recently studied blowouts at or near the sea surface, e.g., the Bravo blowout (Audunson, 1978), and therefore much could be learned about the behavior of oil interjected into the marine environment in this manner; (2) the spill was in a continental shelf location and by that time, oil had been transported long distances to the coast of Texas near the border between the United States and Mexico; (3) this was a large spill in warmer waters, whereas most other major oil spill studies had been in northern temperate areas; e.g., Argo Merchant (C.O.M.S., 1978), Amoco Cadiz (N.O.A.A., 1978; Marchand, 1981), Arrow (Connover, 1971), Bravo (Audunson, 1978).

There were several discussions about the relative merits of sending a ship to the well site as compared with an intensive study along the U.S. coast where the floating oil mats and slicks were coming ashore or were just offshore. Since I was not present at most of these discussions, I can only report my impressions based on conversations with others. There were mainly three lines of

reasoning against expending the bulk of the cruise effort along the U.S. coast: (1) there were already several cruises in progress with smaller research vessels, and thus some information was being obtained along the coast; (2) in order to understand the processes controlling the toxicity of the oil then coming into U.S. waters, it was necessary to study early weathering and biodegradation of the oil near the well site; (3) there were very good indications that there might be lawsuits filed regarding damages from the oil coming into U.S. waters and subsequent effects on fisheries, fouling of beaches, shoreline facilities, and small craft. Experience in the past demonstrated that, in order to have a hope of providing chemical analyses linking oiled areas of the Texas coast with the oil from the well blowout, samples of the fresh oil, and a better understanding of subsequent weathering processes were needed.

The final cruise combined studies near the well site with studies on the continental shelf off Texas. This, in part, satisfied the need for studies along the U.S. coast.

Three main areas of research were initially contemplated for the cruise which was to be a multiple ship operation.

- (1) Physical oceanographic studies and the movement of oil through the Gulf ecosystems. In particular, there was a need to better understand the interaction of the initial plume of oil and gas with wind and currents in the area and the subsequent behavior of rafts of emulsified oil and slicks.
- (2) Impact of the oil on the various components of the ecosystem, e.g., shrimp and fish.
- (3) Biogeochemistry of the oil; e.g., microbial and photochemical effects on the oil, dissolution/dispersion, and absorption/desorption interactions with particulate matter in the water and sediment.

The last activity, (3) Biogeochemistry, was the only major activity of the cruise. There are several different versions as to why the other two studies were not undertaken. My assessment has led me to put forth the following as the main reasons for the absence of more intensive physical oceanographic and biological effects studies. Limitations on ship time and laboratory space dictated by limitations of funds meant that not all objectives set forth by scientists planning for physical oceanographic studies and biogeochemistry studies could not be accommodated. Apparently, after somewhat acrimonious debate, the initial planning group for \_physical oceanographic studies decided that compromise plans were not worth the effort compared to the information to be gained from studies already ongoing along the coast of Texas and from remote sensing from aircraft and satellites. A second limitation to physical oceanographic studies was equipment availability, as will be discussed below, which contributed to this decision.

The ecological effects studies near the well site apparently did not take place for two reasons. First, there may have been reluctance on the part of the Mexican government to give permission for research into ecological effects in their own waters by U.S. scientists. This might have resulted from reasoning that Mexican fisheries scientists were capable of conducting these types of studies and, if adverse effects demonstrating the toxicity of oil were found, then this could be used as evidence in any international lawsuits which might be filed. Second, it was difficult to assemble the needed scientists and equipment for the studies of sublethal effects of the oil on various marine organisms and the available ship laboratory space was marginal, according to scientists who would be involved in these studies. Nevertheless, when the Researcher and Pierce left port in Miami for the cruise, I was under the impression that we would meet the Delaware II, a NMFS vessel, near the well site at a time and place to be radioed to us. Evidently, the decision was made to cancel this effort after Researcher left port.

### Final Plans for the Cruise

The western boundary current in the Gulf of Mexico had carried oil from the well site northwesterly through June, July and August, so that major concentrations occurred mostly in a triangle with apexes at the IXTOC-I well head, Veracruz, Mexico, and Cabo Nojo, Mexico, which is just south of Tampico (Figure 1). In late July and early August, beaches along the south Texas coast were heavily oiled by IXTOC oil which had moved north of the area.

The strategy of the cruise was to proceed to the well site and sample for biogeochemical and microbial studies within the fresh oil, and then move along the track of the slicks and particles of oil to the Texas coast in order to document the changes in and effects of microbial degradation processes and geochemical processes important to understanding the fate and effects of the oil.

### Research Vessel Selection

The NOAA ship Researcher was used for the cruise because it was the only relatively readily available research vessel with extensive laboratory space and the capability for helicopter operations. The helicopter operations capability was considered essential since the cruise would operate at a considerable distance from the U.S. coast, where U.S. Coast Guard and NOAA fixed-wing aircraft would have to originate. These aircraft were the only other available source of the needed overflight reconnaissance for finalizing sampling plans. The experience at other oil spills, particularly the Argo Merchant spill, had established the necessity of such a capability and, as will be discussed later in this paper, the helicopter flights proved to be essential to the research efforts.

The IXTOC-I spill demonstrated by several examples that vessels with engine cooling systems requiring pumped-through seawater cannot

operate in heavily-oiled waters -- especially in thick slicks and mousse mixed into the water. Thus, the <u>G.W. Pierce</u>, which is a keel-cooled vessel, was leased from Tracor Marine for participation in the cruise to sample in slicks.

This is a very important constraint to keep in mind when planning for cruises of this type. Aside from the very real potential problem of having to clean a ship's hull after oiling, there is the problem of the probability of a ship's engines being disabled by failure of the cooling system. In a difficult navigation area such as Georges Bank, this could be very dangerous and costly. In the well site area, we observed ships being towed by tugs because they could not chance operation of their engines in a portion of the area. These observations confirmed earlier reports and made the presence of the <u>Pierce</u> essential for the success of the cruise plan.

### Equipment

There are some types of standard oceanographic research equipment which will not operate in heavy oil slicks. For example, current meter rotors and plankton nets become fouled. Many pieces of equipment are not readily available and have to be borrowed from other research programs. Understandably, many investigators in those programs do not wish to have their equipment damaged by fouling with oil and require extensive cleaning, or be ruined. For example, standard CTD-rosettes of high quality could be rendered inoperative after passing through a heavy slick, even if you could use them.

Often, when equipment was available, it had to be shipped long distances. The large volume water samplers used on the cruise were air freighted from California to Miami. Other water samplers were air freighted from Woods Hole, Massachusetts, and a box coring device was air freighted from Yale University. Smaller pieces of equipment came from the laboratories of scientists participating in the cruise. Locating enough clean sample storage containers for sediments and water samples, and clean solvents for extraction of samples on board and cleaning of sampling gear was difficult.

There were numerous telephone conversations and a few small meetings in a three-week period after the decision on the rough outline of the cruise plan and the cruise itself. Communicating with all the scientists involved was a large task which cannot be ignored in oil spill response plans.

### Personnel

The list of participants in the cruise is given in Table 3 and the number of organizations participating in the cruise are given in Table 4. These are given to illustrate the number of communications links involved in this type of response. They also illustrate the mix of government agency scientists, academic scientists, and environmental consulting scientists who participated in this cruise and would probably be involved in a scientific response to a spill on Georges Bank.

### Health Considerations

We were concerned that the massive amount of spilled oil in the area would result in high concentrations of noxious and/or toxic volatile components of the oil in the atmosphere in the spill area. In fact, breathing masks were worn by some of the crew and scientists working on the <u>G.W. Pierce</u>, which was in the middle of the slick for several days.

Planning for a major spill response should include considerations for the health of people involved in the research.

One unexpected potential health problem evolved on the  $\frac{\text{Re-searcher}}{\text{searcher}}$ . After several days operations at the edge of the heavy slick area but in light oil sheen, the fresh drinking water acquired an oily taste and an occasional sheen. Analysis by U.V. fluorescence spectrometry on board provided an estimate of 50-80 x  $10^{-6}$  ug/kg water (ppb). Presumably, the oil components were carried over by co-distillation during the preparation of drinking water from seawater.

### THE CRUISE ACTIVITIES

### Helicopter Reconnaissance

The importance of helicopter flights in providing an overall assessment of the location of the main slick, rafts of mousse and small patches of oil, and direction of movement cannot be overstated. Surveys of this type by research vessels would have suffered from the rapidly changing situation relative to the time required to complete a survey by ship.

The most striking illustration of the importance of the helicopter operations was provided when we discovered that the slick was coming directly at us as we approached from the northeast. The slick was not being transported west-northwest along the coast to Texas as our last overflight information had indicated (Figure 1). Evidently, the hurricanes traversing the Gulf of Mexico had changed the circulation near the blowout site. The helicopter flights also allowed us to position the G.W. Pierce, Researcher and small boats from the Researcher in optimal sampling locations.

In the Georges Bank area, fixed wing aircraft and helicopter flights from land could probably accomplish much of this essential role. The major drawback I foresee to this mode of operation will be getting accurate information to the chief scientist and principal cruise scientists. During the Researcher cruise, this was accomplished by having these individuals fly in the helicopter and then return to the Researcher for final planning and execution. I emphasize this as a problem area with helicopters and aircraft operated from land because we had considerable difficulty communicating between the Chief Scientist, Senior Chemist, and Senior Biologist on board Researcher and scientists on the G.W. Pierce as to what were the immediate and long-range plans, as these

people were often in three or four different locations, e.g., helicopter, Researcher, Pierce, or small boats. Perhaps this could be overcome with more sophisticated communications.

Sampling from the helicopter was limited to landings on beaches and collection of beach samples. The dangers associated with sampling from helicopters while hovering, and special equipment needs negated use of the helicopter for sampling. I suspect that will be true for other spill responses except in extreme and unusual circumstances.

In hindsight, we had very primitive photography gear, and we would have been able to obtain much more useful information if we had had video-tape cameras and special films such as U.V. and I.R. sensitive films. This is recommended for future studies in order to obtain a more permanent record of the spatial extent of the various forms of oil on the sea surface; e.g., thick slicks, mousse, oil droplets.

The key role of overflight reconnaissance in the Argo Merchant oil spill provides additional evidence of the importance of this activity to oil spill response. Obviously, adverse weather can interfere with this activity, as was the experience at the Argo Merchant spill (Pollack and Stolzenbach, 1978; COMS, 1978).

### Communications

The simultaneous operation of two large research vessels, helicopter, and two smaller boats from the <u>Researcher</u> required careful planning and almost constant communication. This is a familiar problem for U.S. Navy and U.S. Coast Guard operations. However, the oceanographic research community has only limited experience in this type of cruise operation. The main communications problems were allocation of sufficient personnel and time of personnel to this task.

### Sample Logs, Identification, Logistics

Once we were in the spill area and for two weeks after, maintaining and updating a master sample log was the full-time assignment of a chief survey technician on the Researcher. Codes unique to each group taking samples and each sample type and location had to be devised. Each scientist carried a small pocket notebook for primary record-keeping. Each day, or sometimes more frequently, sample data from these notebooks were transcribed to the master log. There is a distinct advantage to this type of system. Mistakes can be rapidly recognized and rectified before hundreds of samples have been tagged incorrectly.

Table 5 gives the type of sample code and information which was used. This was by no means a perfect system. However, I caution against the adoption of rigid requirements of letter and number codes for different sample types to be placed immediately on

samples. It is extremely tiring and timeconsuming to look up numerous different number codes for different sample types. My opinion is that it would be better to apply the NODC (National Oceanographic Data Center) codes during the first few weeks immediately following the cruise. By this means, a computer coding could be assigned by transcription while simultaneously obtaining a post-cruise sample inventory.

The large number of samples obtained (1,671) and variety of sample types are listed in Table 6. Storing many of these samples and keeping a record of sub-sampling and custody has to be considered when budgeting for personnel and cruise expenses.

### The Flexibility Factor

The original sampling strategy of the Researcher/Pierce IXTOC-I cruise had to be altered once the observations from the first helicopter flight revealed that the change in the circulation of the western Gulf of Mexico was moving the oil 045° to 055° true with the plume extending 40 to 50 nm. There was very little oil on the surface west and northwest of the well.

The sampling strategy was changed to provide broad coverage of sampling stations for investigation of the fate of oil and gas near the well site and the major processes acting on the oil and gas in the immediate vicinity of the well site. A second goal was intensive sampling of mousse in order to gain a better understanding of its formation and fate. "Rafts" of mousse had come ashore near Brownsville and Port Aransas, Texas after crossing 500 nm of the Gulf. The mousse that came ashore contained toxic compounds of low molecular weight which generally were considered to be lost from slicks and oil spill areas during the first days to weeks unless incorporated into sediments. Thus, it was important to understand how toxic compounds were incorporated into mousse and transferred long distances.

The variability of oil slick movement and variable movement of different forms of spilled oil were also observed during the Argo Merchant oil spill.

### Some Important Measurements and Sampling Gear Considerations

### CTD Rosette Profiles and Samples

The ability to have a look at the temperature and salinity profiles prior to sampling with large bottles for petroleum compound measurements and microbiology studies was a distinct advantage. This allowed sampling of distinct areas in the water column without requiring extensive profiles with numerous samples: a real problem with the 20 and 90 liter sampling bottles needed for some measurements of hydrocarbons in the water.

Unfortunately, we could not obtain a nephelometer or transmissometer for the cruise. It may not have worked properly after passing through light oil slicks, but it would have been worthwhile for the sampling at the edge of the slick.

### Acoustics Measurements

Two types of acoustic arrays were used during the cruise. Both were deployed from the <u>G.W. Pierce</u> in the slick area, and they provided valuable information about particles, density surfaces, and depth distributions of organisms under the slick.

- (1) A 205 kHz source was deployed to guide biological sampling and to provide quantitative measurements of volume scattering strength at several stations.
- (2) A 20 kHz system was towed from the <u>G.W. Pierce</u> to test the feasibility of tracking sub-surface oil droplets and particles. The same system had proven to be useful in tracking of sewage sludge and chemical waste dumps (Walter and Proni, 1980). This acoustic information, when combined with CTD data and chemical measurements, yielded useful insights about the extent of subsurface plume and strong density interfaces which were important to overall interpretation of chemical and biological discrete sample data.

### U.V. Fluorescence Data

The IXTOC-I cruise plan provided for a test of U.V.-fluorescence measurements by pump systems and screening of discrete samples from large volume water samples. The turnaround time was relatively rapid when required, i.e., 30 minutes to a few hours. Figure 3, taken from Fiest and Boehm (1980), shows a composite transect section of all concentrations determined by U.V. fluorescence measurements. This demonstrates the value of having this type of measurement to ascertain where the oil was dispersed in the water column.

A combination of towed underway U.V.-fluorescence data or pumped-through on-deck U.V.-fluorescence data (NAE, 1980), coupled with acoustic data as previously described CTD data and nephelometry or transmissometer data, is recommended for any major spill response.

#### Gas Measurements

Gases such as methane and ethane were measured on discrete samples, as were volatile hydrocarbons (NOAA, 1980). We did not have an underway gas sniffer device available, but such devices have been routinely operated at sea (NAE, 1980) and would provide valuable information in the event that significant amounts of gas accompanied a well blowout.

### Special Sampling Devices

The Niskin baggie samplers for microbiology studies worked very well. The 20 liter and 90 liter special sampling bottles (NOAA, 1980) which entered the water closed and then were opened below the slick worked very well and provided good samples.

We had difficulty in obtaining good samples of the sedimentwater interface during the cruise because of the coarse-grained nature of sediments in some locations. In other locations, the long time involved in obtaining a useful box core precluded many samples by that means. More rapid sampling methods which obtain the surface sediment floc important for analyses to determine if oil has reached the sediment water interface are needed. The recovery of good benthic ecosystem samples is important, but it is time-consuming and personnel-intensive work. More thought needs to be given to innovative solutions to this problem.

During operations of sampling gear from the <u>G.W. Pierce</u> in the slick, there were frequent episodes of thick oil coating on gear lowered over the side. This is another topic for innovation in operations.

### Sampling for Physical-Chemical Forms of Oil in the Water Column

One area of research where we failed almost totally in precruise planning was provisions for obtaining physical-chemical measurements of the oil, e.g. viscosity, oil slick temperature. However, once we were at the spill site and tried to obtain samples of mousse, oil-in-water, or water-in-oil dispersions, it became obvious that the critical problem was to obtain a sample in a manner which did not alter its form. Oil-in-water or water-in-oil dispersions quickly separated during and immediately after sampling. Presumably, contributing factors to this phenomena were a change in turbulence once the sample was contained and the presence of the sampling container surfaces.

Since the physical-chemical form of the oil dispersed in the water is of critical importance to fine tuning modeling of oil dispersion in the ecosystem in question, some means of sampling or "in situ" measurements needs to be devised for these types of measurements, e.g., viscosity, droplet size, percent of oil-in-water or water-in-oil.

The above are some of the more important lessons for sampling and measurement in the area of studying the biogeochemistry of the spilled oil at IXTOC-I. They illustrate the need for special equipment not routinely available at all marine laboratories, and the need for some innovative thinking about sampling and measurement problems before the next spill.

### ARE WE READY TO RESPOND TO AN OIL SPILL ON GEORGES BANK?

The preceding have led to my asking this question: Are we ready to respond to an oil spill on Georges Bank? My answer is that the scientific community is better prepared now in terms of experience than we were at the time of the Argo Merchant spill. However, we are still not as prepared as we should be. After the Argo Merchant spill and the subsequent "crisis science" studies of the spill with their attendant criticisms, a series of workshops were held around the United States (EPA, 1978). One for the northeast region was convened and the results are available in a 1978 report. Four years have elapsed since that workshop and, as far as I can determine, the report has not been updated despite the fact that we have had active exploratory drilling in the Georges Bank area in addition to the tanker and barge traffic.

There are much more comprehensive data bases on previous and current levels of petroleum compounds now present in the Georges Bank ecosystem. Biological studies, in addition to the fisheries research effort, are in progress. The Bureau of Land Management and U. S. Geological Survey physical oceanographic and sediment dynamics program have made substantial progress in understanding the sediment transport and physical circulation of the Georges Bank area. All of this information is of value to predictions of where oil might go and, in the case of the biological research, provides a start towards ecological damage assessment. All of this information, if applied, could lead to a better oil spill response plan, not only in a scientific response and ecological damage assessment situation, but also for contaminant and clean-up efforts and efforts to protect valuable natural resources.

I am not advocating week-long meetings and extensive detailed multiple contingency plans. Rather, I advocate the establishment of a small core group of scientists/administrators representing the major federal and state agencies involved with advice from academic, oil industry, and Georges Bank environmental studies program contractors. This group could address such questions as:

- (1) What is the policy with regard to oil spill response for ecological damage assessment, advice to the on-scene coordinator (OSC), and scientific research?
- (2) What are the available resources and how would they be funded?(a) Personnel,(b) Equipment,(c) Ships,(d) Aircraft.
- (3) What are the best mechanisms for a response?

We should keep foremost the realization that, with the Amoco Cadiz and the IXTOC-I spills, the U.S. scientific community had much more time, post-spill, to plan and respond. The example of the IXTOC-I cruise response discussed in earlier sections of this paper demonstrates that, despite the longer lead time, considerable

confusion and lost opportunity still occurs.

The key to an effective response is to have a policy which is clearly stated and then a response plan consistent with this policy.

It may be that there are good reasons for having a minimal response. The collective wisdom, coupled with available funds, may recommend that course of action. Not all oil spills can be studied in great detail because there are not enough funds nor is there a compelling reason for such studies. However, a large spill on Georges Bank will require some study and ecological damage assessment because of international, national, regional, and local political and socio-economic pressures. The scientific community with research experience and interests in the Georges bank area will be asked to become involved and should be better prepared to fulfill its public responsibility in this endeavor.

### ACKNOWLEDGEMENTS

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### LIST OF FIGURES AND LEGENDS

- 1. Gulf of Mexico Chart Showing Researcher/Pierce Cruise Track.
- 2. Expanded Chart of Sampling Stations in Well Blowout Area.
- 3. Concentrations of oil as determined by U.V. fluorescence measurements along a transect to the northeast of the IXTOC-I blowout, September 1979. From Feist and Boehm (in N.O.A.A., 1980).

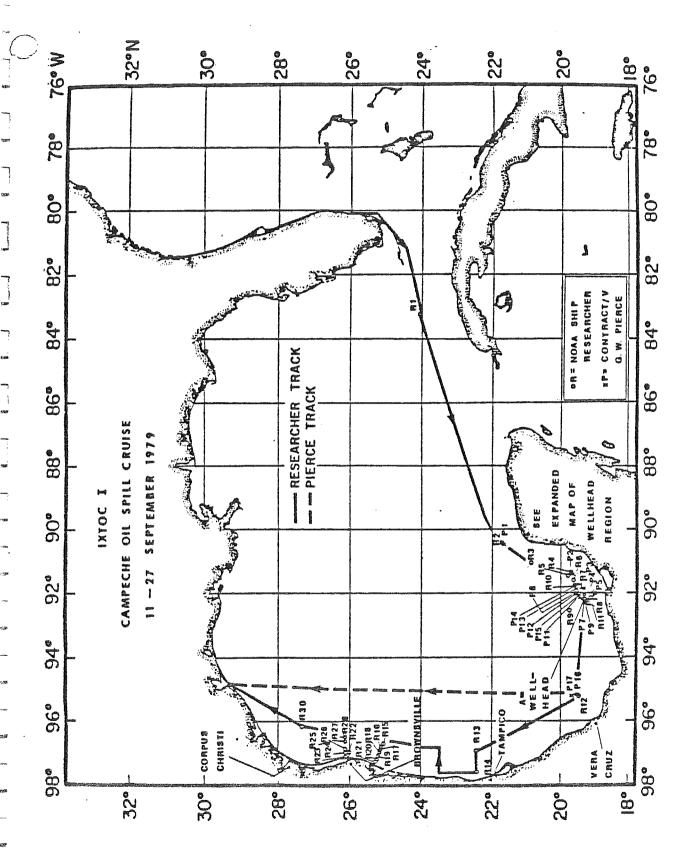


Figure 1. IXTOC-I Campeche oil spill cruise, 11-27 September 1979.

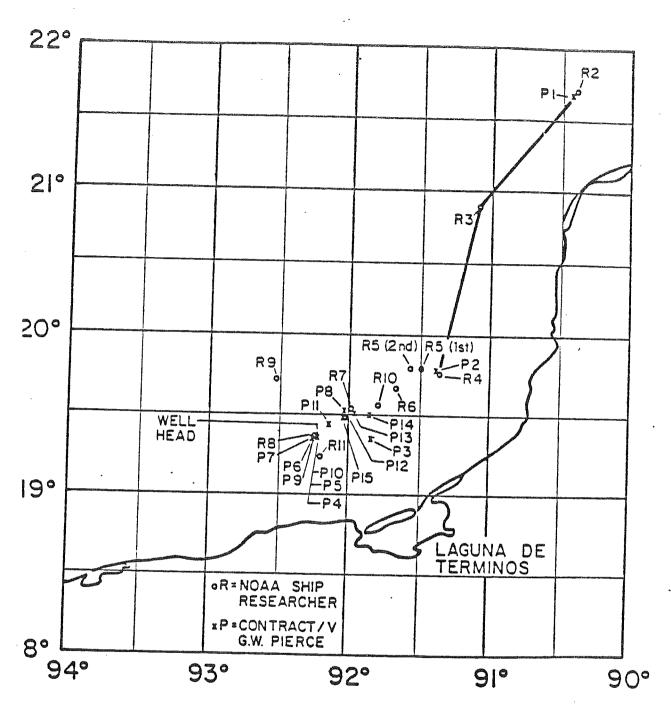


Figure 2. IXTOC-I Campeche oil spill cruise, 11-27 September 1979, expanded wellhead region.

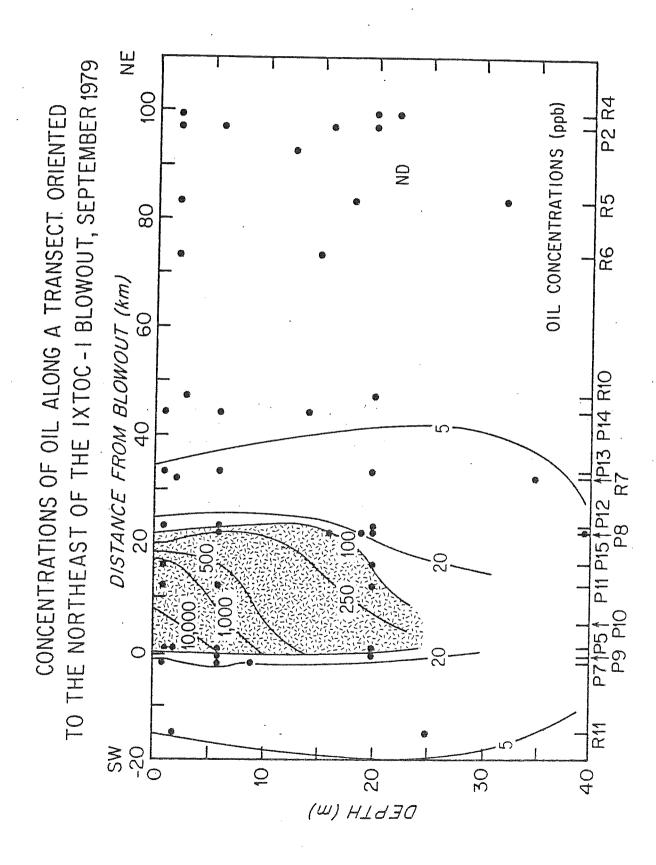


Table 1. Agencies Projected to be Involved in a Georges Bank Oil Spill.

### U. S. GOVERNMENT AGENCIES

Department of Interior

- . Minerals Management Service
- . U. S. Geological Survey
- . Fish and Wildlife Service

Department of Transportation

. U.S. Coast Guard

Environmental Protection Agency

- . Region 1
- . Environmental Research Laboratory, Narragansett, Rhode Island

Department of Commerce

National Oceanic & Atmospheric Administration

- . National Marine Fisheries Service
- . National Ocean Survey
- . Office of Marine Pollution Assessment
- . Environmental Data Service

National Aeronautics and Space Administration

Department of Defense

- . U. S. Navy, Office of Naval Research
- . U. S. Army, Army Corps of Engineers

National Science Foundation

Brookhaven National Laboratory

Department of Health and Human Services

. Food and Drug Administration

Department of State

### CANADIAN GOVERNMENT AGENCIES

External Affairs
Environmental Protection Service

### Table 1. (cont.)

### CANADIAN GOVERNMENT AGENCIES (cont).

Department of Fisheries and Oceans Coast Guard Canadian Forces

### STATE AGENCIES IN THE U. S.

Massachusetts Rhode Island Connecticut Maine New York

### PROVINCIAL GOVERNMENTS IN CANADA

New Brunswick Nova Scotia

### TOWN GOVERNMENTS IN THE U. S.

e.g., Nantucket, MA Block Island, R.I.

### ACADEMIC

University of Maine
University of New Hampshire
Bigelow Laboratories, Maine
Bowdoin College
Boston University Marine Program
Massachusetts Institute of Technology
Harvard University
Marine Biological Laboratory
Woods Hole Oceanographic Institution
University of Massachusetts
University of Rhode Island
University of Connecticut
State University of New York, Stony Brook
Lamont-Doherty Laboratories, Columbia University

#### U. S. GOVERNMENT

Brookhaven National Laboratory
National Marine Fisheries Service, Northeast Fisheries
Center Laboratories - 5 locations
U. S. Geological Survey, Woods Hole
Minerals Management Service
U. S. Coast Guard R&D Center, Groton, Connecticut

# BLM CONTRACTED ENVIRONMENTAL CONSULTING COMPANIES (PAST AND PRESENT - Example Only)

EG&G ERCO Battelle-Clapp Laboratories Science Applications, Inc.

# Table 3 RESEARCHER/PIERCE IXTOC-I Cruise Science Personnel NOAA/National Ocean Survey

### NATIONAL OCEAN SURVEY PERSONNEL

Capt. Ronald L. Newson, Commanding Officer, RESEARCHER Lt. Cdr. Richard L. Permenter, Operations Officer,

RESEARCHER

Lt. Cdr. H. Bruce Arnold, Operations Officer assigned to G. W. PIERCE

Chief Robert L. Hopkins, Chief Survey Technician, RESEARCHER

#### SCIENTIFIC PERSONNEL - RESEARCHER

Dr. Donald Atwood NOAA/AOML, Chief Scientist
Dr. John Farrington Woods Hole Oceanographic

Institution, Senior Chemist

Dr. Randy Ferguson NOAA/NMFS, Beaufort, North Carolina, Senior Biologist

Dr. James Payne SAI (Science Applications, Inc.),

La Jolla, California

Dr. Fred Pfaender University of North Carolina

Mr. Earle Buckley University of North Carolina

Mr. David Fiest ERCO (Energy Resources Co., Inc.), Cambridge, Massachusetts

Mr. George Perry ERCO (Energy Resources Co., Inc.)

Ms. Dale Finch NOAA/AOML

Mr. Ricardo Klimek Mexican Scientist

Mr. Victor Moreno Mexican Scientist
Mr. Jose Altamirano Mexican Scientist

Mr. Michel Marchand French Scientist/Observer

Mr. Glen Aurelius Helicopter Pilot Mr. Gary Freeman Helicopter Mechanic

### SCIENTIFIC PERSONNEL - G. W. PIERCE

Mr. Donald Walter NOAA/AOML, Senior Scientist

Mr. Mahlon Kennicutt Texas A & M University

Mr. Keith Hausknecht ERCO (Energy Resources Co., Inc.)

Mr. Jack Barbash ERCO (Energy Resources Co., Inc.)

Ms. Kendra Daly University of Washington

Ms. Anne Bronner University of Louisville (Kentucky)

Mr. George Roubel University of Louisville (Kentucky)

Mr. Antonio Puig NOAA/AOML

Mr. Paul Dammon NOAA/AOML

Mr. Lawrence Guest NOAA/AOML

# Table 4 RESEARCHER/PIERCE IXTOG-I Cruise Participating Groups and their Functions

### NOAA/Office of Marine Pollution Assessment

Funding logistics

### NOAA/ERL Atlantic Oceanographic and Meteorological Laboratories

Cruise logistics and procurement Science coordination Chemistry contract monitoring

## NOAA/National Marine Fisheries Service, Southeast Fisheries Center

Microbiology contract monitoring Coordination of cruise biology efforts

# NOAA/National Marine Fisheries Service, National Analytical Facility

Intercalibration on hydrocarbons and NSO polar compounds

### NOAA/National Ocean Survey

RESEARCHER

Procurement and contract monitoring for R/V PIERCE

### Woods Hole Oceanographic Institution

Organic geochemistry Coordination of cruise chemistry efforts

### Texas A & M University

Sampling and analysis of  $C_1-C_4$  gases and volatile organic compounds

### University of Washington

Zooplankton distributions

### ERCO (Energy Resources Co., Inc.)

Organic geochemistry

### SAI (Science Applications, Inc.)

Organic geochemistry

### Table 4 (cont.)

### Global Geochemistry Corporation

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Isotopic ratios in spilled IXTOC-I crude oil

### Center for Bio-Organic Studies, University of New Orleans

Photooxidation of IXTOC-I crude oil Chemical analysis of microcosm experiments

### University of North Carolina

Microcosm experiments on microbial degradation of IXTOC-I crude oil

### University of Louisville

In-situ studies of microbial degradation of IXTOC-I crude

### Tracor Marine, Inc.

R/V PIERCE

### Crescent Airways

Helicopter and crew

### Table 5. Explanation of Sample Code

An example and explanation of the Sample Code is as follows:

Example: RIX04A005

The first letter designates the ship from which the sample was taken; 'R' designates RESEARCHER and 'P' PIERCE.

The second and third letters designates the cruise; thus, IX designates the IXTOC cruise.

The next two numbers of the Code designate the Station number; thus, '04' indicates Station number 4.

The sixth character indicates who took the sample; thus, 'A' indicates the sample was taken by someone from AOML.

The other codes and their meaning are listed below:

A = AOML

B = Texas A & M University

E = Energy Resources Company, Inc.

F = Woods Hole Oceanographic Institution

K = Global Geochemistry Corporation

L = University of Louisville

M = Mexico

N = University of North Carolina

0 = University of New Orleans

R = NOAA/NMFS/SEFC, Beaufort, N.C.

S = Science Applications, Inc.

W = University of Washington

The last three numbers indicate the sequential sample #; thus, '005' indicates the fifth sample taken by that "group."

In summary the Sample Code Numbers indicate the following:

'R' or 'P' IX

04

A

005

Ship

Cruise

Station #

Sampler's Code

Sample #

Table 6. Kinds and Numbers of Samples Collected.

Sample Type	Number of Samples
Air Sample	37
Ammonia - NH <sub>4</sub> <sup>+</sup>	22
Microbiology, Acridine Orange Direct Counts of	
Bacteria	69
Bottom Sediment	98
Chlorophyll	82
Control H <sub>2</sub> O	19
Control H <sub>2</sub> O, Chlorophyll	18
Control H <sub>2</sub> O, Extracted	3
Control H <sub>2</sub> O, Low Molecular Weight Hydrocarbons	21
Control H <sub>2</sub> O Particulates	6
Dead Fish	1
Hydrocarbon Biodegradation	19
Kjeldahl Analysis	2
Large Scale Hydrocarbon Biodegradation	4
Long Term Microcosm Study	12
Low Molecular Weight Hydrocarbon, H <sub>2</sub> O	130
Microbiology	34
Microbiology - C <sup>14</sup> , Amino Acid	15
Microbiology - C <sup>14</sup> , Hexadecane	15
Microbiology - C <sup>14</sup> , Naphthalene	15
Microbiology - H <sup>3</sup> , Amino Acid	15
Microbiology - Plate Counts	32
ousse fousse	93
Nutrients	100
Dil Covered Shell	1
Oil Patch	1
oil/Water Emulsion	2
Dissolved Oxygen	100
articulates	31
lankton	67

Table 6. (cont.)

Sample Type	Number of Samples
Purge Trap - Extracted - Filtered	7
Salinities	63
Sand, Beach	3
Sheen	112
Spanish Mackeral - Liver and Muscle	1
Surface Matter	10
Tar	26
Trace Metals (For Mexican Scientists)	1
Trace Organics	1
Volatile Hydrocarbons	68
Weed (Possibly Sugar Cane)	1
Whole H <sub>2</sub> O	303

#### REFERENCES

- API (1979-1981) Proceedings of Oil Pollution Conferences, API, U.S. EPA, U.S. Coast Guard, 1969, 1971, 1973, 1975, 1977, 1979, 1981. American Petroleum Institute, Washington, DC, USA.
- Audunson, T. (1978) The Fate and Weathering of Surface Oil from the Bravo Blowout, in Bates (1978), pp. 466-475.
- Bates, C. C., Chairman (1978) Proceedings of the Conference on Assessment of Ecological Impacts of Oil Spills 14-17 June, 1978, Keystone, Colorado, American Institute of Biological Sciences, 1401 Wilson Boulevard, Arlington, VA 22209.
- Boehm, P. and Fiest D. (1980), in NOAA (1980).
- COMS (1978) In the Wake of the Argo Merchant, Proceedings of a Symposium Held January 11-13, 1978, Center for Ocean Management Studies, University of Rhode Island, Kingston, RI, USA.
- Connover, R. J. (1971) Some relations between zooplankton and Bunker C oil in Chedabucto Bay following the wreck of the tanker Arrow, J. Fish. Res. Bd. Can., 28, 1303-1307.
- EPA (1978) Proceedings of the National Response Team Oil Spill Scientific Response Workshop, New England, Interagency Energy/ Environment R&D Program Report, U.S. EPA, Washington, DC, USA.
- Marchand, M. (1981) Amoco Cadiz, Bilan du Colloque sur les consequences d'une pollution accidentelle par hydrocarbons, Brest, Novembre, 1979, Centre Oceanologique de Bretagne, Publications du CNEXO Rapports Scientifiques et Techniques No. 44, Centre National pour L'Exploitation des Oceans, Paris, France.
- NAE (1980) Underway Sampling A Workshop Report of the Marine Board, National Academy of Engineering, Washington, DC, USA.
- NAS (1975) Petroleum in the Marine Environment, U.S. National Academy of Sciences, Washington, DC, USA.
- NOAA (1978) The Amoco Cadiz Oil Spill. A Preliminary Scientific Report, U.S. Department of Commerce, NOAA, U.S. EPA, August, 1978, Superintendent of Documents, U.S. Government Printing Office, Washington, DC, USA.
- NOAA (1980) Proceedings of a Symposium on Preliminary Results from the September, 1979 Researcher/Pierce IXTOC-I Cruise, U.S. Department of Commerce, National Oceanic and Atmospheric Administration, Office of Marine Pollution Assessment, Washington, DC, USA.

- NOAA (1981) National Marine Pollution Program Plan, September, 1981, NOAA, U.S. Department of Commerce, Washington, DC, USA.
- Pollack, A. M. and Stolzenbach, K. D. (1978) Crisis Science: Investigations in Response to the Argo Merchant Oil Spill, MIT Sea Grant Program Report No. MIT SG 78-8, Massachusetts Institute of Technology, Cambridge, MA, USA.
- U. S. Senate (1979) Campeche Oil Spill: Joint Hearings Before the Committee on Commerce, Science and Transportation, and the Committee on Energy and Natural Resources, December 5, 1979, U.S. Senate Serial No. 9666.
- Walter, D. J. and Proni, J. R. (1980), in NOAA (1980).