

NOAA Technical Memorandum NMFS-SEFC-41



NOAA/NMFS ANNUAL REPORT TO EPA

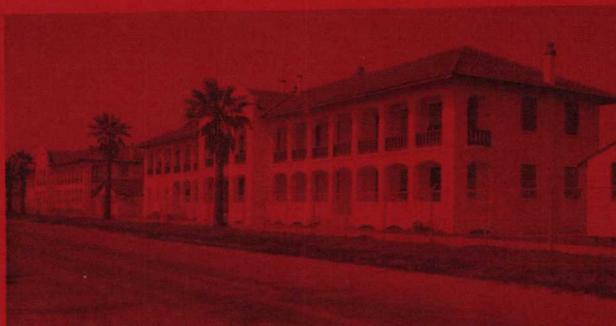
Environmental Assessment of Buccaneer Gas and Oil Field in the Northwestern Gulf of Mexico, 1978 - 1979

A report to the Environmental Protection Agency on work conducted under provisions of Interagency Agreement EPA-IAG-D5-E693-E0 during 1978 - 1979.

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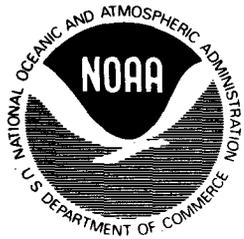
Volume VII

HYDROCARBONS



DECEMBER 1980

U.S. DEPARTMENT OF COMMERCE
National Oceanic and Atmospheric Administration
National Marine Fisheries Service
Southeast Fisheries Center
Galveston Laboratory
Galveston, Texas 77550



NOAA Technical Memorandum NMFS-SEFC-41

**Environmental Assessment of Buccaneer
Gas and Oil Field In the Northwestern
Gulf of Mexico, 1978-1979**

**VOL. VII - HYDROCARBONS, BIOCIDES, AND
SULFUR**

BY

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**A report to the Environmental Protection Agency on work conducted under
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Volume VII - HYDROCARBONS

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II. Principal Investigators' Section

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LIST OF VOLUMES

This Annual Report is printed in ten separate volumes:

Volume I - SYNOPSIS/DATA MANAGEMENT

- Work Unit 2.6.1 Synopsis
NMFS/SEFC Galveston Laboratory
Principal Investigators
- Work Unit 2.2.3 Implement, Monitor, and Modify Data
Management System
NMFS/SEFC National Fisheries
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Volume II - SEDIMENTS AND PARTICULATES

- Work Unit 2.3.2 Investigations of Surficial Sediments
and Suspended Particulates at Buccaneer
Field
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Volume III - FISHES AND MACROCRUSTACEANS

- Work Unit 2.3.5 Effect of Gas and Oil Field Structures
and Effluents on Pelagic and Reef Fishes,
Demersal Fishes, and Macrocrustaceans
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Volume IV - BACTERIA

Work Unit 2.3.7 Bacterial Communities
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Volume V - FOULING COMMUNITY

Work Unit 2.3.8 Effects of Gas and Oil Field Structures
and Effluents on Fouling Community
Production and Function
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Volume VI - CURRENTS AND HYDROGRAPHY

Work Unit 2.3.9 Currents and Hydrography of the Buccaneer
Field and Adjacent Waters
Hazleton Environmental Sciences
Corporation
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Volume VII - HYDROCARBONS

Work Unit 2.4.1 Hydrocarbons, Biocides, and Sulfur
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Volume VIII - TRACE METALS

Work Unit 2.4.2

Trace Metals

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Volume IX - FATE AND EFFECTS MODELING

Work Unit 2.5.1

Sources, Fate and Effects Modeling

Science Applications, Inc.

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Volume X - HYDRODYNAMIC MODELING

Work Unit 2.5.2

Hydrodynamic Modeling

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GUIDE TO USERS OF THE ANNUAL REPORT

Volume I (SYNOPSIS/DATA MANAGEMENT) of the Annual Report is designed to be used as a briefing document and as a key to more detailed scientific and technical information contained in Volumes II through X. Objectives, methods and results for each work unit are summarized in greatly abbreviated form within Volume I to facilitate dissemination of information. Thus, Volume I can be used alone or as a reference to companion Volumes II through X. Complete citations for literature cited in Volume I can be found in the Volumes II through X in which the detailed work unit reports are presented.

It is hoped that such an approach to environmental impact information dissemination will make the Annual Report a more useful and widely read document.

FOREWORD

Increased petroleum development of the outer continental shelf (OCS) of the United States is anticipated as the U.S. attempts to reduce its dependency on foreign petroleum supplies. To obtain information concerning the environmental consequences of such development, the Federal Government has supported major research efforts on the OCS to document environmental conditions before, during, and after oil and gas exploration, production, and transmission. Among these efforts is the Environmental Assessment of Buccaneer Gas and Oil Field in the Northwestern Gulf of Mexico, a project funded by the Environmental Protection Agency (EPA) through interagency agreement with the National Oceanic and Atmospheric Administration (NOAA) and managed by the National Marine Fisheries Service (NMFS), Southeast Fisheries Center (SEFC), Galveston Laboratory, in Galveston, Texas. Initiated in the autumn of 1975, the study is now in its last year. Its major products have been annual reports disseminated by the National Technical Information Service, data files archived and disseminated by NOAA's Environmental Data and Information Service, and research papers written by participating investigators and published in scientific or technical journals. Results have also been made available through EPA/NOAA/NMFS project reviews and workshops attended by project participants, and various governmental (Federal and State), private, and public user groups. The final products will be milestone reports summarizing the findings of the major investigative components of the study.

Objectives of the project are (1) to identify and document the types and extent of biological, chemical and physical alterations of the marine ecosystem associated with Buccaneer Gas and Oil Field, (2) to determine specific pollutants, their quantity and effects, and (3) to develop the capability to describe and predict fate and effects of Buccaneer Gas and Oil Field contaminants. The project uses historical and new data and includes investigations both in the field and in the laboratory. A brief Pilot Study was conducted in the autumn and winter of 1975-76, followed by an extensive biological/chemical/physical survey in 1976-77 comparing the Buccaneer Gas and Oil Field area with adjacent undeveloped or control areas. In 1977-78, investigations were intensified within Buccaneer Gas and Oil Field, comparing conditions around production platforms, which release various effluents including produced brine, with those around satellite structures (well jackets) which release no effluents. In 1978-79, studies around Buccaneer Gas and Oil Field structures focused on (1) concentrations and effects of pollutants in major components of

the marine ecosystem, including seawater, surficial sediments, suspended particulate matter, fouling community, bacterial community, and fishes and macro-crustaceans, (2) effects of circulation dynamics and hydrography on distribution of pollutants, and (3) mathematical modeling to describe and predict sources, fate and effects of pollutants. The final year, 1979-80, of study is continuing to focus on items (1) and (2) and on preparation of the milestone reports which will represent the final products of this study.

This project has provided a unique opportunity for a multi-year investigation of effects of chronic, low-level contamination of a marine ecosystem associated with gas and oil production in a long-established field. In many respects, it represents a pioneering effort. It has been made possible through the cooperation of government agencies, Shell Oil Company (which owns and operates the field) and various contractors including universities and private companies. It is anticipated that the results of this project will impact in a significant way on future decisions regarding operations of gas and oil fields on the OCS.

Charles W. Caillouet, Project Manager
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and

William B. Jackson and E. Peter Wilkens,
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LIST OF REPORTS AND PUBLICATIONS

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INTRODUCTION

Location of Study Area

The area selected for study is the operational Buccaneer Gas and Oil Field located approximately 49.6 kilometers (26.8 nautical miles) south southeast of the Galveston Sea Buoy off Galveston, Texas (Figure 1). This field was selected in 1975 as the study area because: (a) the field had been in production for about 15 years, which time had allowed full development of the associated marine communities; (b) it was isolated from other fields which facilitated the selection of an unaltered area (for comparison) within a reasonable distance of the field; (c) it produced both gas and oil that represented sources of pollutants from marine petroleum extraction; (d) its location simplified logistics and reduced the cost of the research; and (e) the Texas offshore area had not been fully developed for gas and oil production but was expected to experience accelerated exploitation in the future.

Operation History of Buccaneer Field

Buccaneer Field was developed by Shell Oil Company in four offshore blocks leased in 1960 and 1968 as follows:

<u>Year</u>	<u>Lease Number</u>	<u>Block Number</u>	<u>Acreage</u>	<u>Hectares</u>
1960	G0709	288	2,790	1,129
1960	G0713	295	4,770	1,930
1960	G0714	296	4,501	1,821
1968	G1783	289	2,610	1,056

In development of the field, 17 structures were built; two are production platforms, two are quarters platforms, and 13 are satellite structures surrounding well jackets. Initial exploratory drilling began about mid-summer of 1960 with mobile drilling rigs. When (as the result of the exploratory drilling) proper locations for platforms were selected, the permanent production platforms were constructed.

There have been no reports of major oil spills from this field. There have been some reported losses of oil due to occasional mechanical failure of various pieces of equipment. The largest reported spill was three barrels in 1973. The reported oil spill chronology and quantity for Buccaneer Field is as follows:

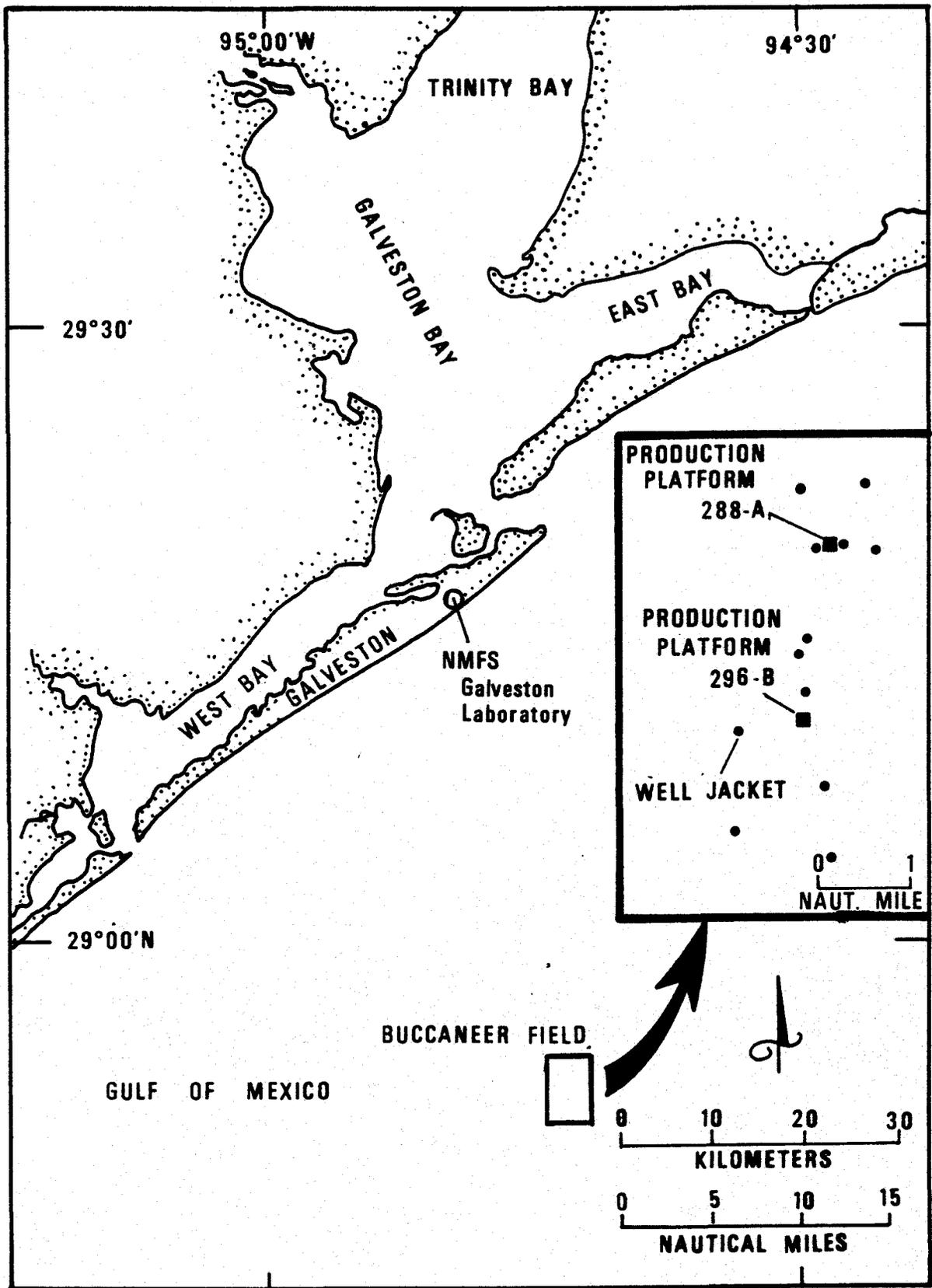


FIGURE 1. LOCATION OF BUCCANEER FIELD

<u>Date</u>	<u>Source</u>	<u>Amount</u>	
		<u>Barrels</u>	<u>Liters</u>
September 1973	Platform 296-B	0.5	79
November 1973	Unknown	3.0	477
July 1974	Platform 296-B	0.5	79
August 1974	Platform 296-B	1.7	265
September 1975	Platform 288-A	<u>0.2-0.4</u>	<u>38-56</u>
Totals		5.9-6.1	938-956

Buccaneer Field first began operations with the production of oil. Later, when significant quantities of gas were found, the field began producing both oil and gas and has continued to do so to date.

The production platforms and satellites (well jackets) are connected by a number of pipelines with a 50.8 centimeters (20-inch) diameter main pipeline connecting the field to shore. All of the pipelines that are 25.4 centimeters (10 inches) or greater in diameter are buried. The Blue Dolphin Pipeline Company was granted a pipeline permit (No. G1381, Blocks 288 and 296) in 1965 and has operated the pipeline since its construction.

Buccaneer Field occupies a limited area (about 59.3 km²; 22.9 sq. statute miles) leased in the northwestern Gulf of Mexico. Four types of structures are located in Buccaneer Field: production platforms, quarters platforms, satellites (well jackets), and flare stacks. These are shown in Figure 2, which is an oblique aerial photograph of production platform 288-A and vicinity within Buccaneer Field. A map of Buccaneer Field, (Figure 3) depicts the locations of platforms and satellites within the field.

**SATELLITE
WELL JACKET**

**PRODUCTION
PLATFORM**

**QUARTERS
PLATFORM**

FLARE STACK

FIGURE 2. BUCCANEER FIELD STRUCTURES

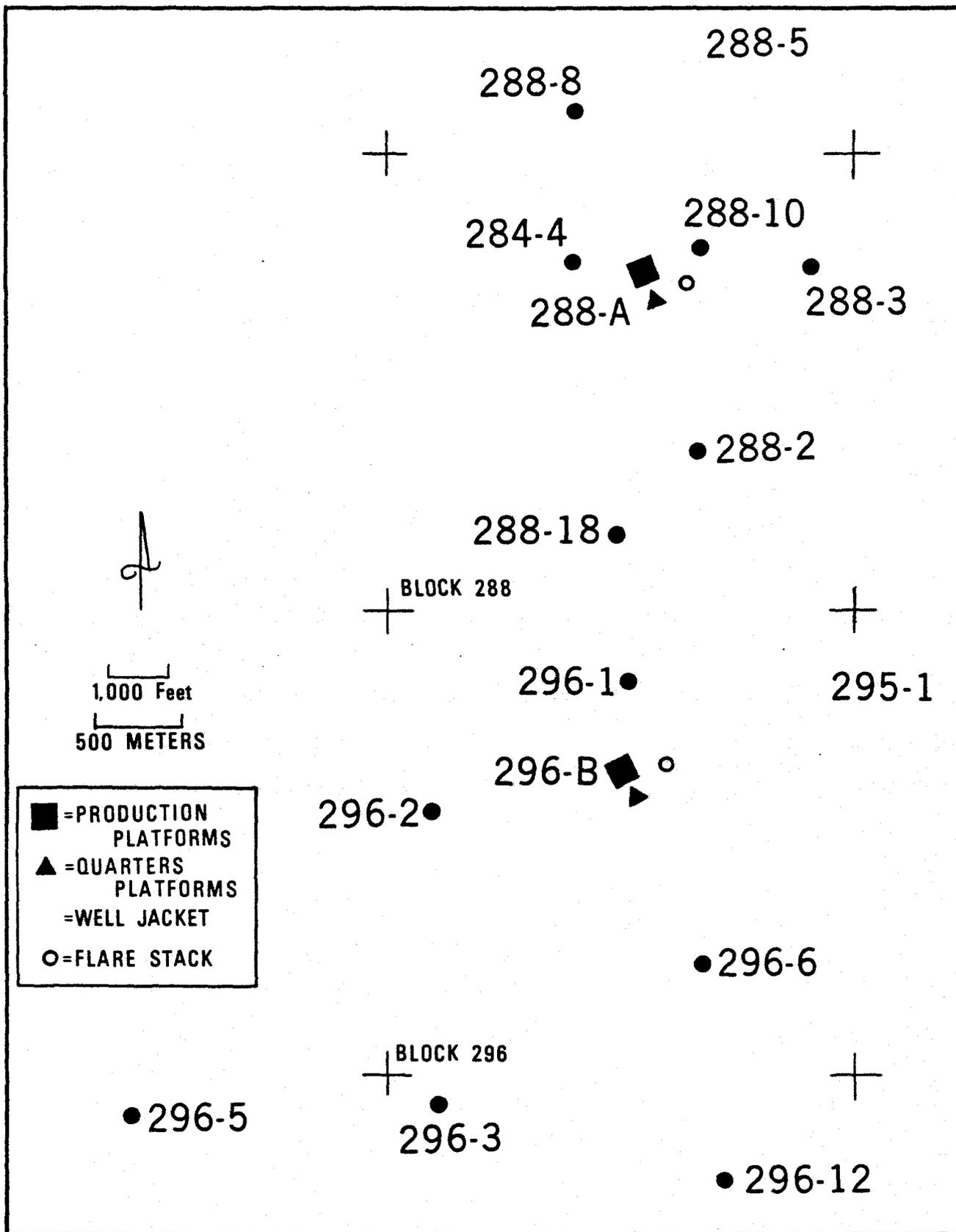


FIGURE 3. SHELL OIL COMPANY'S ALPHANUMERICAL IDENTIFICATION OF BUCCANEER GAS AND OIL FIELD STRUCTURES

WORK UNIT 2.4.1 - HYDROCARBONS, BIOCIDES, AND SULFUR

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EXECUTIVE SUMMARY

Additional data are reported for platform discharges in the Buccaneer Field and for the distribution of their components in the surrounding area. Produced water discharge from platform 288-A is now only sporadic, with routine discharge taking place only from platform 296-B. Acrolein is now used as a biocide in place of the previously employed formulations. No acrolein is detected in the formation water at a concentration greater than 1 ppm. Sulfur continues to be the major oil-field contaminant: its specific gravity is sufficiently high that it moves through the water column to the sediments.

Fouling mat on the platform legs contains a low concentration of oil near the air/sea interface (where periodic exposure to sunlight and air apparently promotes evaporation and degradation), but there are high concentrations of fresh oil at a depth of three meters.

The barnacles contain weathered oil. This implies that, in contrast to the fouling mat, the barnacles' major exposure to oil is indirect: possibly by filter-feeding on particulates in the water column (which would include resuspended contaminated sediments).

All blennies contain fresh oil, whereas the sheepshead contain weathered oil. This difference is not unexpected since the blennies feed on the small organisms of the fouling mat and the sheepshead eat barnacles.

Spadefish contain lower concentrations of weathered oil than the blennies and sheepshead. This is probably because the spadefish feed mainly in the water column and are not constantly exposed to any major pool of petroleum constituents.

The longspine porgy contains weathered oil in concentrations intermediate between those of the sheepshead and spadefish. We have no reliable information on the feeding habits of the longspine porgy.

There is a wide dispersion of oil concentrations in the red snapper. Some specimens contain no oil, while the mean concentration of oil for all specimens examined is higher than that of the spadefish. One possible explanation for this observation relates to the fact that the red snapper are recruited to the Buccaneer Field from a wide area of the Gulf. Those containing no oil are probably recent arrivals in the region of the field, whereas those which have resided longer in the area have ingested sufficient quantities of contaminated prey to accumulate high concentrations of oil.

For all of the fish species which are large enough for separate analysis of liver and muscle tissues (sheepshead, spadefish, and red snapper), oil concentrations are higher in the livers.

The major pool of hydrocarbon contaminants is in the surficial sediments. Concentration gradients around platform 296-B are always observed, but there is considerable day-to-day flux in these concentrations. This is attributable to periodic resuspension and deposition of surficial sediments.

More than 100 individual compounds have now been detected in formation water. Almost all are of petroleum origin, but 2-butanone and 2-pentanone apparently derive from a solvent used in large quantities by painters on the platform. Butylated hydroxytoluene (an antioxidant food additive) found in a spadefish may be accumulated from food scraps thrown overboard.

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1. INTRODUCTION

1.1 BACKGROUND

In a decade of oil crises, embargoes, production cutbacks, and shortages, production of domestic petroleum assumes new importance in meeting our insatiable demand for energy. While many terrestrial oil and gas reserves in North America have either been uneconomical to produce or exhausted over the years, offshore sources are now being explored and produced at an ever increasing rate.

Acquisition of oil from the continental shelf is complicated by several difficult technical problems. Recent advances in deep-water drilling techniques, however, have made possible the location and extraction of long inaccessible or unknown submarine oil reservoirs.

Coincident with the recent proliferation of offshore oil and gas production facilities around the world is growing concern for the effects of this activity on the marine environment. The impetus for this concern no doubt arises from recent catastrophic oil well blowouts such as Union Oil well A-21 off Santa Barbara California, 1969, and Chevron Oil's "Platform C" off Louisiana in 1970. As of this writing, herculean efforts are being made to cap the blown IXTOC-1 oil well, spilling an estimated 30,000 bbl of light crude per day, in the Bay of Campeche, Mexico in the Gulf of Mexico. First reported on June 3, 1979, the eruption of oil and gas was ignited, thus greatly decreasing the amount of oil actually contacting the marine environment (Weeden, 1979). Careful studies of the effects of the Santa Barbara spill (Straughan, 1971) and many tanker spills have been conducted, and much valuable information on the immediate damage and ecological changes due to huge spills has been accumulated.

1.1.1. Some Major Spills

Perhaps one of the first major oil spills to receive world-wide attention from the press and scientific community alike, was the stranding of the "Torrey Canyon" in the western approach to the English Channel on March 18, 1967. During March and April her 117,000 ton load of Kuwait crude was released, soon to pile up on the beaches of England and France. Unfortunately, conclusions from the biological effects of this well documented spill remain somewhat confused since large quantities of toxic dispersants were added to the spill during the clean-up process (Nelson-Smith, 1973).

When the oil barge "Florida" ran aground in Buzzards Bay, West Falmouth, Massachusetts in 1969, approximately 175,000 gallons of No. 2 fuel oil leaked out into the bay and marsh area. In the most highly contaminated portions of the bay and marsh, massive kills of marine and marsh life were observed. Scallops and oysters were found to be contaminated by fuel oil (Blumer et al., 1970), as were all exposed marsh organisms (Burns and Teal, 1971). Deep penetration of oil into marsh muds will probably be persistent due to anoxic conditions there. In fact, two years later these sediments were shown to have high concentrations of fuel oil hydrocarbons (Blumer and Sass, 1972).

In the largest and most recent tanker disaster recorded, the "Amoco Cadiz" released 65 million gallons of crude oil and bunker fuel just 1.5 km from the northwest coast of France on March 16, 1978. During the 15 days following the wreck, 140 km of the Brittany coast was heavily impacted by oil. Heavy mortalities of some intertidal organisms, birds and other marine organisms were observed as well as incorporation of oil in sediments up to 70 cm. in depth (Hess, 1978). Just one year after the wreck, however, a

return survey of the area by biologists from the U.S. and France reported a substantial increase in Odum's diversity index and attendant recolonization of coastal areas (Cross, 1979), thus indicating movement toward ecological recovery of the damaged area.

The estimated total volume of oil spilt from the blow-out of Union oil well A-21 in the Santa Barbara Channel was in excess of 3.25 million gallons. While the volume is certainly comparable to that spilt by tankers, it appears that the ecological effects were not as substantial. Phytoplankton productivity (essential to any marine ecosystem) after the blow-out was well within the established pattern observed under normal conditions of nutrient availability. Breeding among the copepod Labidocera trispinosa was successful, thus giving indication of minimal ecological stress (McGinnis, 1971). "Blooms" of a tunicate copepod were also observed as well as a normal variety and abundance of fish eggs and larvae (Straughan, 1971). It has been argued that, had the sophisticated analytical chemical techniques used in evaluating other spills been applied to the Santa Barbara spill, a more serious picture of the ecological damage may have been obtained (Easton, 1972).

While the literature on oil spills and related topics is voluminous, it has been criticized along two major lines (National Academy of Sciences, 1975). To accurately assess the ecology of an area not only requires a great deal of funding for a short-term intensive study, but also requires information gained from long-term investigation of several facets of that system. To date, perhaps three or four oil spills have had substantial attention from the scientific community. Some of these might include the "Torrey Canyon", Santa Barbara, West Falmouth, and "Amoco Cadiz" incidents. In all of these

and other cases, funding has limited the scope and nature of the work (Micheal, 1977). It is probable too that long-term studies may uncover minor alterations which may seem insignificant in the short-term but may be cumulative and drastic over a long period of time.

1.1.2. Biological Effects of Petroleum

The complexity of crude oil, being a mixture of hydrocarbons, non-hydrocarbon compounds containing oxygen, sulfur and nitrogen and many trace metals, in large part complicates the assessment of its effects on marine organisms. In addition, oils from different geographic locations can be very different in composition and therefore in toxicity. The deleterious effects of crude oil on living organisms may be generalized into five main categories:

1. acute toxicity;
2. direct coating and asphyxiation;
3. disruption of behavioral activities;
4. changes in biological habitat; and
5. carcinogenicity.

Laboratory bioassays have been used to quantitate the toxicity of crude and refined oils to marine life. Recently, two objectives in this type of testing have emerged. One is the use of toxicity data to determine and compare toxicity of individual components of a certain oil (e.g., naphthalenes vs. cycloalkanes) or relative toxicity of various oils (e.g., Kuwait vs. South Louisiana crude). The second is the use of acute toxicity data to compare the sensitivity of different species or life stages of that species to the individual components of specific oils (Rice et al., 1977). It should be noted that the origin of the test organism, its past history, time of year, temperature and water quality, the precise nature of the bioassay used and many other variables have such an influence on the response of the organism to the

substance under investigation, that toxicity data have, at best, comparative value, no matter how precisely the results are given (Nelson-Smith, 1973). Problems of comparing and interpreting different laboratory studies arise due to dissimilarity in experimental conditions and the lack of measurement of hydrocarbon concentrations (Moore and Dwyer, 1974).

Using bioassays, investigators have shown a high correlation between toxicity of specific oils and dispersants and the quantity of light aromatics which that substance may impart to the test medium (Nelson-Smith, 1970; Moore and Dwyer, 1974). The most prominent low-boiling aromatics found in oiled test waters are the methylnaphthalenes, presumably due to the relatively high water solubility of the diaromatics.

In an attempt to normalize reported toxicity data, Moore and Dwyer (1974) have estimated the composition of various test oils reporting soluble aromatic derivatives (SAD) as a basis for comparison. In addition, they have proposed grouping of organisms on the basis of life style to further simplify data comparison.

The second general category, direct coating and asphyxiation, demonstrates the harmful effects oil may have on living organisms due to its viscous and hydrophobic physical properties. The oiling of birds' feathers as well as consumption of oiled food accounts for mortality among these exposed animals. Fish coming into direct contact with oil may likewise be asphyxiated due to coating of gill tissue, thus preventing gas exchange.

Sublethal behavioral changes have been observed among many animals. One report (Blumer et al., 1973) points out subtle modifications in the feeding habits and behavior of the lobster Homarus americanus at oil concentrations as little as 10 ppm, while another suggests interferences with chemotactic feeding and mating responses in many organisms (Takashi and Kittredge, 1973).

Oil affects various biological habitats differently. Open ocean habitats covered by a surface slick probably are least affected due to the mobility of the slick and extensive dissolution and evaporation related to water depth, currents, and prevailing winds. Intertidal areas impacted by oil generally suffer tarry surface coatings due to loss of lighter hydrocarbons. This loss, accelerated by intermittent immersion and exposure, has the net effect of reduced toxicity. However, since the lighter aromatics are easily evaporated under these conditions (National Academy of Sciences, 1975) estuaries, bays and marshlands may suffer the most extensive damage from spilt oil. The sheltered nature of these habitats means a drastic reduction in energy available for certain physical processes: dissolution, evaporation, emulsification and sediment interaction, resulting in longer exposure of the ecosystem to the oil.

In addition to the toxic light aromatics, high-boiling polycyclic aromatic hydrocarbons are found in crude and refined oils. These compounds have long been known to induce formation of neoplasms in test animals. Certain histopathologic findings in bottom-feeding fishes and eels thought to be a result of exposure to refinery effluent and oiled sediments, respectively (Russel and Kotin, 1956), were probably due to exposure to oil-derived carcinogens. Since these compounds have been shown to be accumulated (Scaccini et al., 1970) and to cause disease in marine organisms, the possibility of human exposure to oil-derived carcinogens from commercial fish consumption is a justifiable concern.

It is now obvious that the diversity of biological effects from exposure to oil and refined products owes much to the chemical and physical complexity of these substances. The consequences of exposure may be both acute and long-term for the individual as well as the population and community, but are

inevitably the product of a multitude of variables such as individual, species, or larval sensitivity; time of year; position and importance of affected organism in marine food web; etc.

1.1.3. Petroleum Input into the Sea

Contamination by petroleum is not a new marine phenomenon. Natural oil seeps are common geological occurrences worldwide, with perhaps Coal Oil Point in the Santa Barbara Channel being the most thoroughly studied area. Two interesting findings from that research are (Straughan, 1976):

1. animals are naturally inhabiting areas of high level petroleum contamination (up to 9% in sediments), and
2. certain marine animals indigenous to the area are more tolerant to Santa Barbara crude than animals from control locations.

While it has been estimated that the petroleum contribution of natural seeps is 0.6 million tons annually (Wilson et. al., 1973), petroleum geologists generally agree that an accurate figure is extremely difficult to obtain.

The Massachusetts Institute of Technology Study Group on Critical Environmental Problems reported that, along with ocean shipping and accidents, offshore drilling may have accounted for a significant portion of about 2 million tons of oil introduced into the oceans annually (Wilson, 1970). A more quantitative and recent approximation of the loss of oil into the sea from normal drilling and production operations was from 0.08 to 0.15 million tons annually (National Academy of Sciences, 1975). From a 1971 U.S. Department of the Interior survey of operations in the Gulf of Mexico, a total of 836 barrels of oil were lost from minor spills. Assuming these figures are representative of U.S. offshore production, the total loss in U.S. waters due to minor spills is about 1,500 barrels per year

(McCaslin, 1972). Extrapolating from this, world wide yearly losses were estimated at 0.01 million metric tons. Adding to this 0.01 million metric tons of oil associated with discharge of produced brines (discussed later) and 0.06 million metric tons attributed to episodic major spills (McCaslin, 1972), the grand total accepted by the National Academy of Sciences is 0.08 million metric tons annually, circa. 1973 (Wilson et. al., 1973).

As can be seen in the summary of major petroleum inputs to the sea (Table 1), offshore production actually accounts for only a very small portion of discharged oil. Non-marine sources (e.g., urban runoff, municipal wastes, river runoff) together with transportation losses are by far the major sources of oil input into the marine environment.

TABLE 1

Summary of Petroleum Inputs Into the Sea (Adapted from Farrington, 1980)

Source	Input rate ^a	Percentage
Marine transportation	2.133	34.9%
Offshore oil production	0.08	1.3%
Coastal oil refineries	0.2	3.3%
Industrial waste	0.3	4.9%
Municipal waste	0.3	4.9%
Urban runoff	0.3	4.9%
River runoff	1.6	26.2%
Natural seeps	0.6	9.8%
Atmospheric precipitation	0.6	9.8%
TOTAL	6.113	100.0%

^aMillions of tons per annum.

1.1.4. Offshore Oil Production: Previous Environmental Studies

The ecological effects of many major oil spills have been studied intensively by groups of scientists from various disciplines and the literature generated has been incisive, informative and extensive. Unfortunately, the same cannot be said of studies of the ecological impact of offshore drilling and

production activities. Most of the literature to date has been fragmentary in that individual studies have focussed narrowly on one biological, chemical, physical or geological facet of the total ecosystem possibly affected by petroleum activities. In fact, isolated studies of the effects of oil on a single component of an ecosystem which do not have the benefit of comparison with changes in parameters of other components of the ecosystem (e.g., water column hydrocarbon content, sediment characteristics, wind and current variation, seasonal planktonic variation) approach irrelevance with respect to a comprehensive assessment.

In 1974, the Gulf Universities Research Consortium (GURC) reported its Offshore Ecology Investigation's assessment of the ecological effects of offshore oil drilling and production in Timbalier Bay off Louisiana in the Gulf of Mexico (Morgan et al., 1974). Notable of this study, and possibly the first for an environmental project, was the synoptic multidisciplinary data acquisition and synthesis. This type of approach has been called for by various commentators (National Academy of Sciences, 1975; Farrington et al., 1976) and is demanded by the complexity of environmental problems. While baseline data were not available for the area under investigation prior to the GURC study, a "suitable" control site within the same ecologically contiguous area was selected for comparison with sites in close proximity to oil field structures.

The conclusions drawn from this study show that concentrations of hydrocarbons and trace metals were low enough to pose no known biological hazard and were of the same order of magnitude as concentrations for open ocean areas. Compared to other areas of the Gulf of Mexico, sampling sites had higher biological productivity and were described as being in good ecological health. Moreover, Timbalier Bay has not experienced significant

ecological change due to drilling or production activities. Lastly, in terms of impact, natural phenomena such as seasonality, floods, upwelling and turbid layers were found to have a much greater effect on the ecosystem than production and drilling activities (Morgan *et al.*, 1974).

1.2 THE BUCCANEER FIELD

A detailed description of the Buccaneer Field is given elsewhere in this report. A map of the field showing locations of production platforms and well jackets is given in Fig. 1. Reported oil spills during the operation of the field are listed in Table 2.

TABLE 2
Reported Oil Spills in the Buccaneer Field

Amount (bbl)	Source	Date
0.2-0.4	Platform 288-A	Fall 1975
0.5	Platform 296-B	Fall 1973
0.5	Platform 296-B	Summer 1974
1.7	Platform 296-B	Summer 1974
3.0	Unknown	Winter 1973

1.3 ANALYTICAL TECHNIQUES

Many analytical methods are now being used in industry to characterize petroleum. However, the conventional methods such as viscosity, boiling range and flashpoint are of severely limited utility in determining the origin of oil introduced into the marine environment. Elemental analysis for sulfur, nickel, nitrogen, and vanadium as well as infrared, fluorescence, and UV spectroscopy have been used to identify oil (Bentz, 1976), but these suffer from similiar disadvantages, *i.e.*, lack of sensitivity and lack of specificity.

Of the common analytical tools available today for petroleum, refined products, and residues analysis, gas chromatography (GC) has been shown to be powerful indeed. With this technique, crudes have been characterized

2.4.1-20

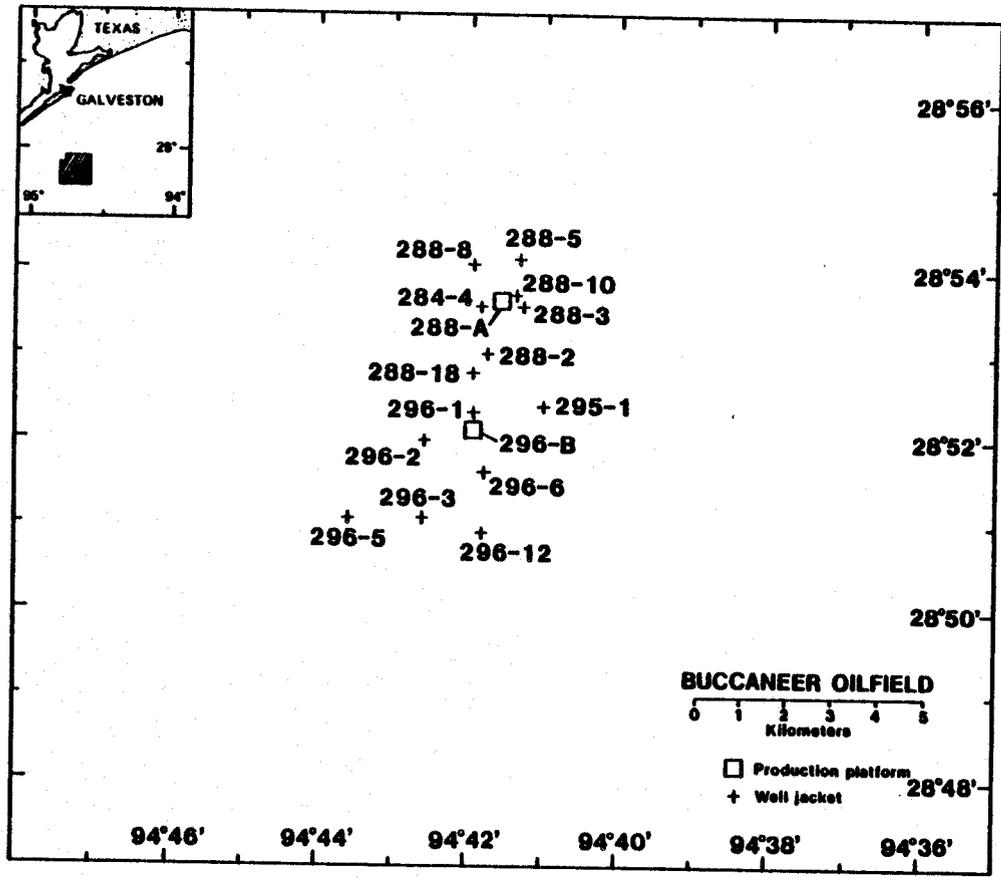


Fig 1. Map showing locations of production platforms and well jackets in the Buccaneer Field

primarily on the basis of n-alkane/isoprenoid ratios and alkane profiles (Ehrhardt and Blumer, 1972; Jackson, et al., 1975). The analysis of environmental samples via gas chromatography has gained almost universal acceptance in recent years. (Adlard et al., 1972; Ehrhardt and Blumer, 1975; Garza and Muth, 1974; Dell'Acqua et al., 1975).

Specialized detectors (e.g., nitrogen-phosphorous, and flame photometric) have been used to visualize certain classes of compounds in crude oil. The mass spectrometer, however, allows the ultimate structural determination as well as the great sensitivity which overcomes the lack of conclusive component identification inherent in gas chromatography.

2. MATERIALS AND METHODS

2.1 MATERIALS

All organic solvents (cyclohexane, benzene, methanol, and chloroform) were Mallinckrodt (St. Louis, Mo.) "Nanograde" quality, meaning distilled in glass. Alumina gel (chromatographic, neutral) for column chromatography was from Sigma (St. Louis, Mo.). Hydrocarbon standards were purchased from Applied Science Labs. (State College, Pa.) and deuterated hydrocarbons were from Merck (Elmsford, N.Y.). Bicyclohexyl was obtained from Aldrich (Milwaukee, Wis.).

2.2 SAMPLE COLLECTION AND STORAGE

2.2.1. Discharged Brine

Samples of discharged brine were collected from the sampling spigot of the 296-B discharge pipe in 1 liter narrow-mouth glass bottles with Teflon-lined screw caps and frozen immediately after collection. Brines collected on some monthly visits were drawn into 15 ml conical centrifuge tubes for volatiles analysis. The latter samples were frozen on return to the laboratory and maintained at -20°C to minimize bacterial growth as well as loss of volatile components.

2.2.2. Seawater

Water samples were collected by divers using 1 liter screw cap bottles. Surface samples were collected at less than 1 m from the air-sea interface. All samples were frozen in glass bottles and were maintained at -20°C until analysis.

2.2.3. Sediments

Sediments were collected by divers in 1 liter or 250 ml wide-mouth glass bottles fitted with ground glass stoppers. Being surficial sediments they were scooped directly from the bottom by the divers, then stoppered and later frozen and maintained at -20°C to minimize microbial activity.

2.2.4. Sediment Traps

A sediment trap is a device for collecting suspended particulate matter over a period of weeks. The traps employed consisted of acrylic tubes about 5 cm x 30 cm with a screened opening at one end to which a funnel was attached. The traps were placed at certain depths off the side of one of the structures. Collection was simply a matter of hoisting the traps up and capping the trap tubes, followed by refrigeration at -20°C.

2.2.5. Fish

Samples were obtained either by trawling with a 12 m nylon mesh semi-balloon shrimp trawl, by casting line, or by spear gun. Samples were wrapped in aluminum foil and then frozen and maintained at -20°C.

2.2.6. Shrimp

Shrimp samples were collected using a 12 m nylon mesh semiballoon shrimp trawl. Shrimp were sorted by species and were wrapped in aluminum foil. Samples were maintained at -20°C to minimize contamination.

2.2.7. Barnacles and Fouling Mat

Barnacles were removed from the structures by divers. The fouling community was left attached to the barnacle shells, and both were wrapped in aluminum foil and maintained at -20°C until analysis.

2.2.8. Other Platform Samples

Sewage was collected at the outfall in 1 liter wide-mouth glass bottles with ground glass stoppers. Fire-fighting water was collected from quarters platform 296-B after purging the hose for 2 minutes. Separator tank water and separator tank oil were collected from their respective sampling spigots. Seawater was collected either from the lower deck of the quarters platform 296-B or next to brine discharge outfall on the production platform by lowering a 1 liter wide-mouth glass bottle into the water followed by capping with a ground glass stopper. All of the above samples were frozen upon return to the laboratory and maintained at -20°C until analysis.

2.3. EXTRACTION PROCEDURES

2.3.1. Discharged Brine

Samples were acidified to pH 2 and n -[$^2\text{H}_{42}$]eicosane, [$^2\text{H}_{10}$]-2-methyl-naphthalene and [$^2\text{H}_{12}$]benzo[a]pyrene (internal standards) were added to the discharged brines. One hundred ml of cyclohexane was added to the sample and then tumbled on a modified rock polisher for at least 6 hr. The cyclohexane was concentrated using a Büchi/Brinkmann Rotavapor R rotating evaporator before column chromatography. Following extraction, sulfur in the brine sample was vacuum filtered and weighed after drying.

2.3.2. Seawater

Water samples were extracted using the same procedure as the discharged brine samples (section 2.3.1).

2.3.3. Sediments

Approximately 100 g of sediment was transferred to a 300 ml lyophilization flask (Virtis F-121), standards were added, and the sample was freeze-dried (Labconco Freeze Dryer). The dried sample was then placed in a 500 ml Erlenmeyer flask. The lyophilization flask was rinsed with 150 ml of cyclohexane and the rinse was added to the sample. The sample flask was then capped with aluminum foil and shaken (Burrell Wrist-Action Shaker) for at least 6 hr. Cyclohexane was then decanted and reduced in volume before column chromatography.

2.3.4. Sediment Traps

The total solid content of the sediment trap (30-150 g) was transferred to a 1 liter narrow-mouth screw cap bottle. Standards and cyclohexane (100 ml) were added, and this was followed by tumbling for 24 hr on a modified rock polisher.

2.3.5. Other Platform Samples

Sewage, separator tank water, and fire-fighting water were extracted using the same procedure outlined for the discharged brine (section 2.3.1). Separator tank oil was dissolved in cyclohexane, standards added, and the mixture was applied directly to the liquid chromatography column. Seawater was prepared as stated in section 2.3.2.

2.3.6. Fish

In the laboratory, a sample of dorsal flesh (including subcutaneous fat) was removed from each specimen using a degreased scalpel and forceps. With the exception of the very small specimens, livers were also removed and analyzed. Whole animal analysis was performed on Hypleurochilus geminatus, Stenotomus caprinus, and specimens too small to obtain a liver sample. Muscle (5-10 g) and liver (1-5 g) were homogenized using a Brinkman PT1035

Polytron power unit equipped with a PT20ST generator. The homogenate was transferred to a 50 ml centrifuge tube spiked with the internal standard. A sodium hydroxide solution (4 ml, 4M) was added and the homogenate saponified for 2 hr at 110°. Saponified material was allowed to cool and was extracted with 2 x 15 ml of cyclohexane. Each time, the organic layer was drawn off after centrifugation at 2000 r.p.m. for 10 min. The combined extracts were then reduced in volume and fractionated by column chromatography.

2.3.7. Shrimp

Entire shrimp (including shell) were analyzed using the same extraction procedure as used for fish (section 2.3.6.).

2.3.8. Barnacles and Fouling Mat

Scutum, tergum, and outer shell were removed from the barnacle flesh using degreased pliers and forceps. Approximately 7 g was extracted in the same manner as the fish (2.3.6.). Fouling mat was scraped from barnacle shells using a degreased scoopula and forceps. Fouling material was also homogenized and extracted the same as for fish (section 2.3.6.).

2.4 LIQUID COLUMN CHROMATOGRAPHY

Tissue samples (fish, shrimp, barnacles, and fouling mat) were fractionated on a 1 x 10 cm column of alumina. Alumina was washed with cyclohexane (20 ml), and the sample applied. "Alkanes" and "aromatics" were eluted in cyclohexane (40 ml). All other samples (sediment, discharged brine, sediment traps, and platform samples) were fractionated on a 1 x 10 cm alumina column but were eluted with 20 ml of cyclohexane. Eluates were reduced to 100 µl, first by the rotating evaporator and then under a stream of nitrogen on a hot plate, before gas chromatography or combined gas chromatography - mass spectrometry.

2.5 GAS CHROMATOGRAPHY

2.5.1. Use of Internal Standards

Deuterated hydrocarbons were added to all samples prior to analysis so that variations in sample recovery, GC injection volume, and instrument parameters would not impair the accuracy of the quantitative data. In general, differentiation between labelled and unlabelled species requires the use of a mass spectrometer as the gas chromatographic detector (Sweeley et al., 1966). Fortunately, this situation is obviated by the use of perdeuterated eicosane ($n\text{-C}_{20}\text{D}_{42}$). The deuterated analog is sufficiently resolved from the unlabelled C_{20} such that the flame ionization detector suffices for detection.

The various compounds used for quantitation were $n\text{-}[^2\text{H}_{42}]$ eicosane, $[^2\text{H}_{10}]$ -2-methylnaphthalene, and $[^2\text{H}_{12}]$ benzo[a]pyrene. An appropriate quantity of the deuterated hydrocarbons was added to the sample before analysis. For example, 10 μl of a 0.1% solution added to 1 liter of seawater afforded a concentration of 10 ppb.

2.5.2 Instrument Conditions

Gas chromatography was performed on a Hewlett-Packard 5840A instrument equipped with flame ionization detectors, a temperature programmer, and a peak integrator. Samples were examined using a 10 m glass capillary column coated with OV-101, programmed from 90° to 270°C at 4° per minute. The injector and detector temperatures were 250° and 300°C, respectively, for all analyses.

2.6 GAS CHROMATOGRAPHY - MASS SPECTROMETRY

2.6.1 Identification and confirmation

Representative samples were examined with a Hewlett-Packard 5992A GC-MS instrument to verify the identities of compounds characterized by GC. The interface for this system is a single stage glass jet separator, while

columns used were: a 1 m x 2 mm I.D. silanized glass column containing 3% OV-1 on GasChrom Q (100-120 mesh) programmed from 100-270°C at 4° per minute, and a 30 m glass capillary column coated with OV-101 programmed from 80-270°C at 4° per minute. Spectra were acquired every 2 seconds, but only those from the apices of the total ion current peaks were stored on floppy disks (Hewlett-Packard 9885M disk drive). Total ion as well as selected ion chromatograms were obtained in real time and spectra were available for a full range of data manipulation procedures.

Unknown spectra were compared to spectra of known compounds via telecommunication link with facilities at Cornell University.

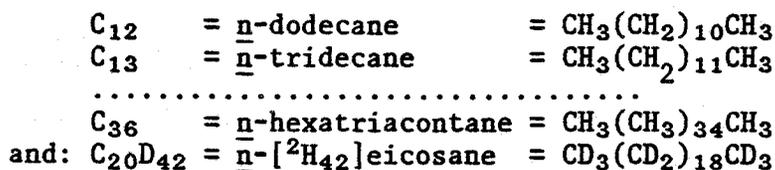
2.6.2. Volatile Analysis

Volatile organic compounds in discharged brine were examined using a purge-and-trap sampler (Hewlett-Packard 7675A). Volatile organics were purged from the sample for 15 minutes with nitrogen and simultaneously concentrated on a cooled adsorbent (Tenax-GC). The adsorbent was then heated and the volatiles were thermally desorbed and back-flushed onto the GC column of the GC-MS instrument. The 2 m x 2 mm I.D. stainless steel column containing 0.2% Carbowax 1500 on Carbopak C (80-100 mesh) was programmed from 30-150°C at 4° per minute. Spectra were acquired every two seconds, but only those from the apices of the GC peaks were stored on the floppy disk. Total ion as well as selected ion chromatograms were obtained in real time, and programs were available for a full range of data manipulation procedures.

3. RESULTS AND DISCUSSIONS

Analytical data are given for the n-alkanes from dodecane (C₁₂H₂₆) to hexatriacontane (C₃₆H₇₄) and for the branched alkanes pristane (2,6,10,14-tetramethylpentadecane) and phytane (2,6,10,14-tetramethylhexadecane).

Those of molecular weight lower than dodecane were not recovered quantitatively while those of molecular weight greater than hexatriacontane were not detected. Reference to alkanes in this report will have the following nomenclature:



Odd/even preference (OEP) was calculated for most samples. This may be regarded as a numerical indicator of continuity in alkane profiles, and is obtained:

$$OEP = \frac{\Sigma(\underline{n}-C_{2n+1})}{\Sigma(\underline{n}-C_{2n})}$$

The term "total alkanes" refers only to those compounds mentioned in this paragraph.

3.1 PLATFORM SAMPLES

3.1.1. Oil

Oil was obtained from the separator tank on production platform 296-B. The alkane composition of the oil was consistent with reports on the composition of other crudes (Smith, 1968). Alkanes from C₁₂ to C₃₆ account for about 18% of crude oil by weight but can show much variation (McDill, 1979). Alkane profiles (Figure 2) showed a gradual and continuous decrease in concentration with increasing chain length and a mean OEP of 0.86. The mean n-heptadecane/pristane and n-octadecane/phytane ratios, often used in source identification of crudes, were 1.20 and 4.46, respectively.

A detailed GC-MS analysis of the "aromatic" fraction of oil was performed using a glass capillary column. Several of the peaks were tentatively identified and listed in Table 3 showing order of elution, Kováts' retention index

2.4.1-29

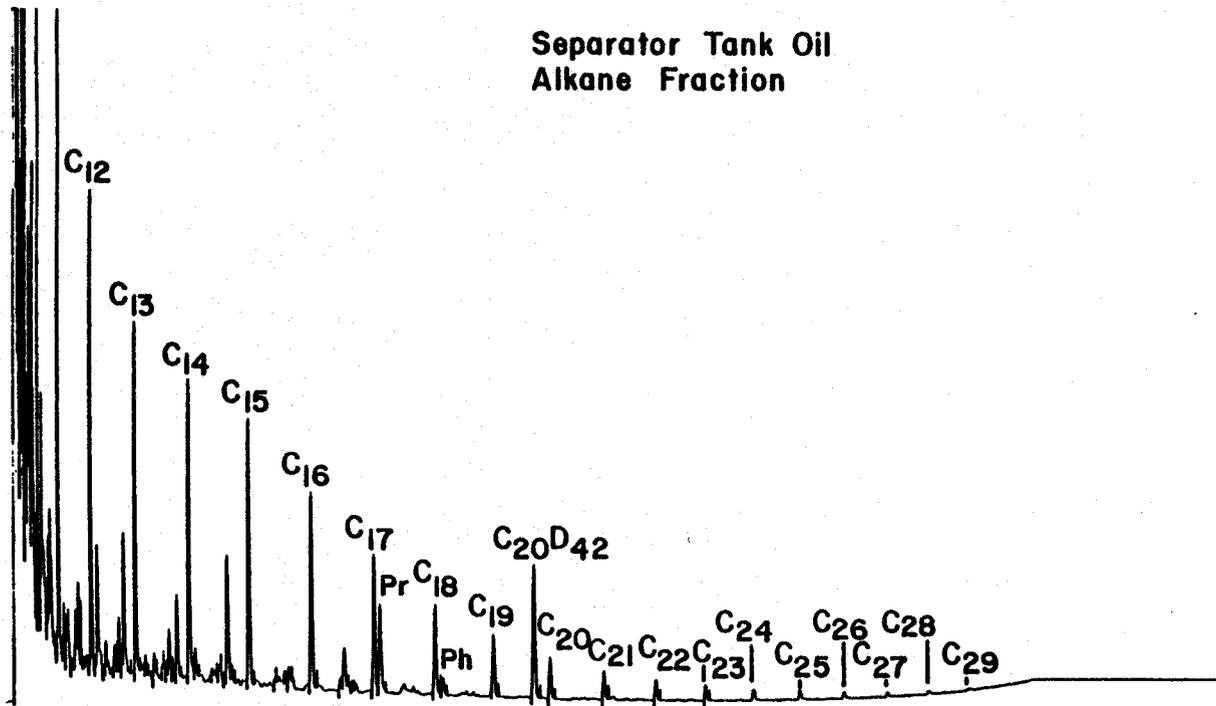


Fig. 2 Gas chromatogram of alkane fraction of separator tank oil

TABLE 3

Separator Tank Oil Aromatic Fraction: June 24, 1979

Peak	I	Component	ppm
1	1100	n-Undecane	5,840
2	1105	C ₄ -Benzene	57
3	1133	C ₄ -Benzene	216
4	1156	Naphthalene	537
5	1200	n-Dodecane, C ₅ -Benzene	8,790
6	1214	Branched tridecane	2,400
7	1262	[² H ₁₀]-2-Methylnaphthalene (IS)	[500]
8	1267	2-Methylnaphthalene	519
9	1277	Branched tetradecane	3,250
10	1281	1-Methylnaphthalene	486
11	1300	n-Tridecane	10,890
12	1317	C ₇ -Benzene	40
13	1347	Acenaphthene or Biphenyl	162
14	1363	C ₂ -Naphthalene	94
15	1374	C ₂ -Naphthalene	203
16	1387	C ₂ -Naphthalene	400
17	1390	C ₂ -Naphthalene	61
18	1400	n-Tetradecane	13,850
19	1405	C ₂ -Naphthalene	193
20	1417	C ₂ -Naphthalene	81
21	1441	?	45
22	1450	Methylbiphenyl	245
23	1463	Branched pentadecane	6,220
24	1469	?	41
25	1492	C ₂ -Naphthalene	114
26	1500	n-Pentadecane	13,750
27	1513	C ₃ -Naphthalene	164
28	1530	C ₃ -Naphthalene	234
29	1543	C ₂ -Biphenyl	44
30	1550	C ₃ -Naphthalene	178
31	1557	C ₂ -Biphenyl	1,970
32	1563	Branched alkane	75
33	1565	?	41
34	1582	?	41
35	1600	n-Hexadecane	11,690
36	1618	C ₄ -Naphthalene	45
37	1638	C ₄ -Naphthalene	57
38	1644	?	55
39	1651	C ₄ -Naphthalene Branched alkane	3,310
40	1671	?	61
41	1694	C ₄ -Naphthalene	111
42	1700	n-Heptadecane	11,260
43	1709	Pristane	6,630

TABLE 3 (Cont'd)

Peak	I	Component	ppm
44	1763	?	1,090
45	1800	<u>n</u> -Octadecane	8,720
46	1811	Phytane	1,290
47	1900	<u>n</u> -Nonadecane	6,500
48	1970	<u>n</u> -[² H ₄₂]Eicosane (IS)	[5,000]
49	2000	<u>n</u> -Eicosane	3,850
50	2100	<u>n</u> -Heneicosane	2,850
51	2200	<u>n</u> -Docosane	2,700
52	2300	<u>n</u> -Tricosane	2,420
53	2400	<u>n</u> -Tetracosane	
54	2500	<u>n</u> -Pentacosane	
55	2600	<u>n</u> -Hexacosane	
56	2700	<u>n</u> -Heptacosane	
57	2800	<u>n</u> -Octacosane	
58	2900	<u>n</u> -Nonacosane	
TOTAL			
	C ₄ -Benzenes	(2)	273
	C ₅ -Benzenes	(1)	*
	C ₇ -Benzenes	(1)	40
	Naphthalene	(1)	537
	Me-Naphthalenes	(2)	1,005
	C ₂ -Naphthalenes	(6)	1,032
	C ₂ -Naphthalenes	(4)	690
	C ₄ -Naphthalenes	(4)	213
	Biphenyl	(1)	162
	Me-Biphenyl	(1)	245
	C ₂ -Biphenyls	(2)	118
TOTAL AROMATICS		(25)	4,315 (0.4%)
TOTAL <u>n</u> -ALKANES		(13)	103,000 (10.3%)
TOTAL ISOPRENOIDS		(2)	7,920 (0.8%)
TOTAL BRANCHED ALKANES		(6)	18,240 (1.8%)
TOTAL UNKNOWNNS		(6)	318 (0.0%)
TOTAL C ₁₁ TO C ₂₃ HYDROCARBONS		(46)	133,800 (13.4%)

(I) and concentration for each peak. Of the aromatics identified, naphthalene and the alkylnaphthalenes, known for their toxicity to marine organisms (section 1.1.2), comprise 80% of the total aromatics or about 2.6% of the total hydrocarbons measured. This might indicate that Buccaneer crude has the potential to contribute a moderate quantity of soluble aromatics to water.

Also observed was a homologous series of branched alkanes having Kováts' retention indices of 1463, 1563, and 1763. It was not determined, however, whether these were isoprenoid hydrocarbons.

3.1.2. Discharged Brine

In addition to single samples collected on monthly visits to the platform, brines were collected in four series of 10, each over a two day period. Brine series were collected in September and December of 1978, and April and May of 1979. Since discharged brine is the major platform effluent, information on types and levels of hydrocarbons, trace amounts of biocide (if any) and quantity of sulfur discharged into the environment is an essential starting point in the overall chemical investigation. Other samples from the separator tank (water) were also examined for alkane content.

3.1.2.a Alkanes

The alkane profiles (Figure 3) in discharged brine are generally similar to profiles for crude oil or separator tank water (Figure 4). Concentration maxima for oil and separator tank water were usually the same and ranged from C₁₂ to C₁₅. Maxima in discharged brines collected on the same day as oil and separator tank water were similar and within the same range. Depending on the temperature at which the brine is discharged, a selective reduction in the concentration of the lighter components (C₁₂-C₁₆) is possible since their vapor pressure and subsequent rate of loss would increase with temperature (Regnier and Scott, 1975). The largest detectable alkanes in discharged brines were usually C₂₂ to C₂₄ while alkanes as large as C₂₉ and C₃₀ were often measured in oil. This feature probably owes to the decrease in water solubility with increasing carbon number of alkanes (McAuliffe, 1966).

The range of mean concentrations for all four series of 10 brines fell between 1 and 3 ppm. However, a significant hourly variation in alkane content was observed. Even brines collected one hour apart (Figures 5 and 6) showed a difference in total alkane concentration of as much as 2.3

2.4.1-33

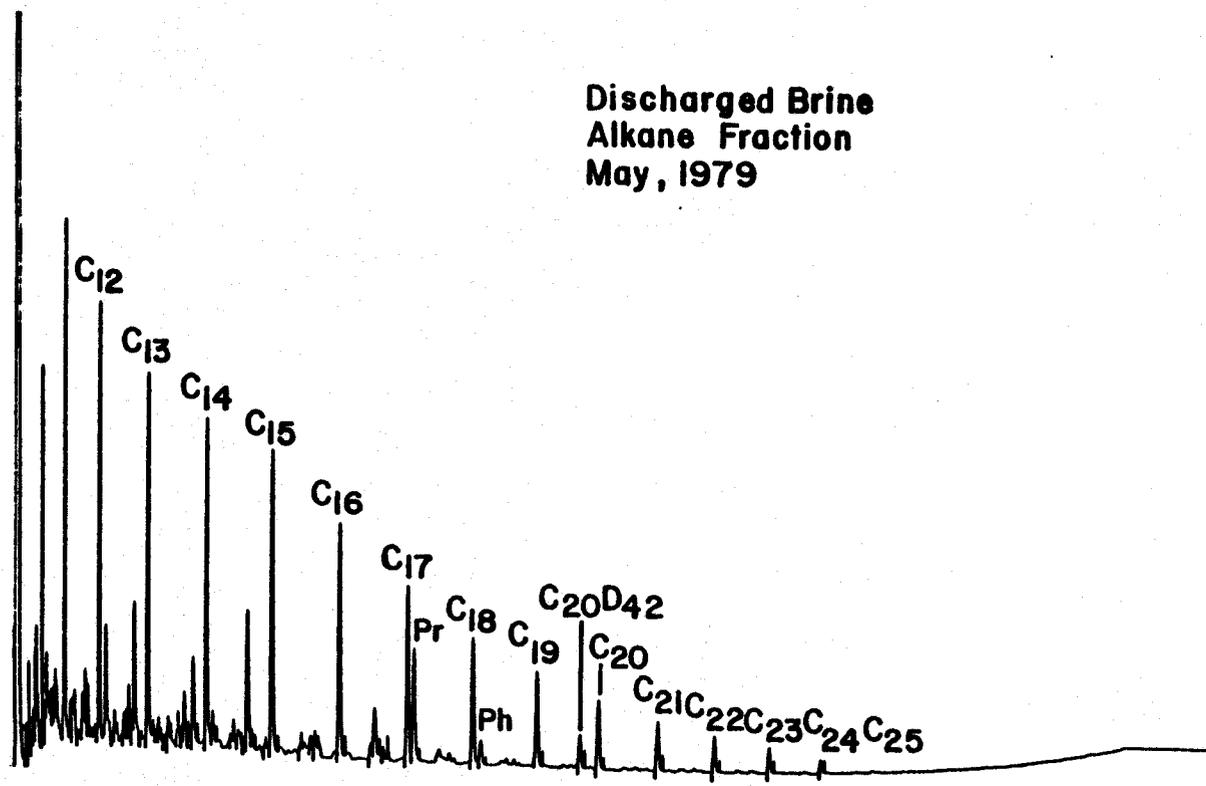


Fig. 3 Gas chromatogram of alkane fraction of discharged brine collected in May, 1979

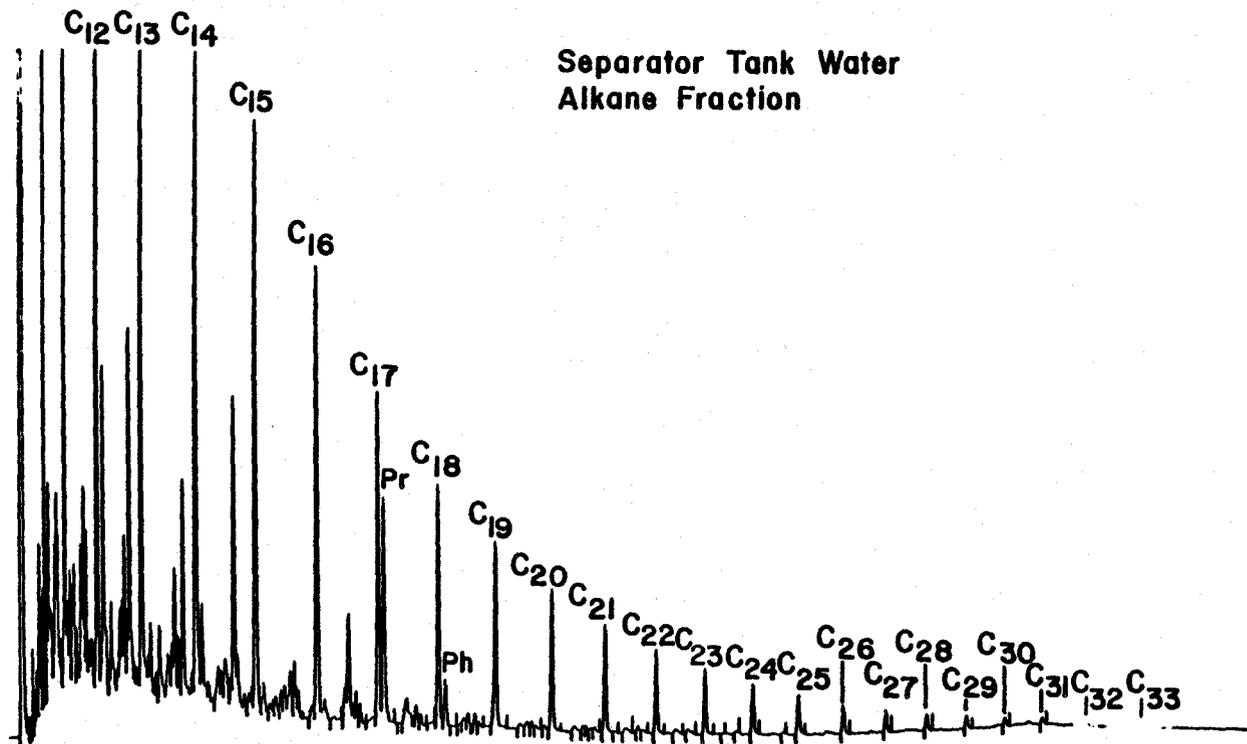


Fig. 4 Gas chromatogram of alkane fraction of separator tank water

2.4.1-35

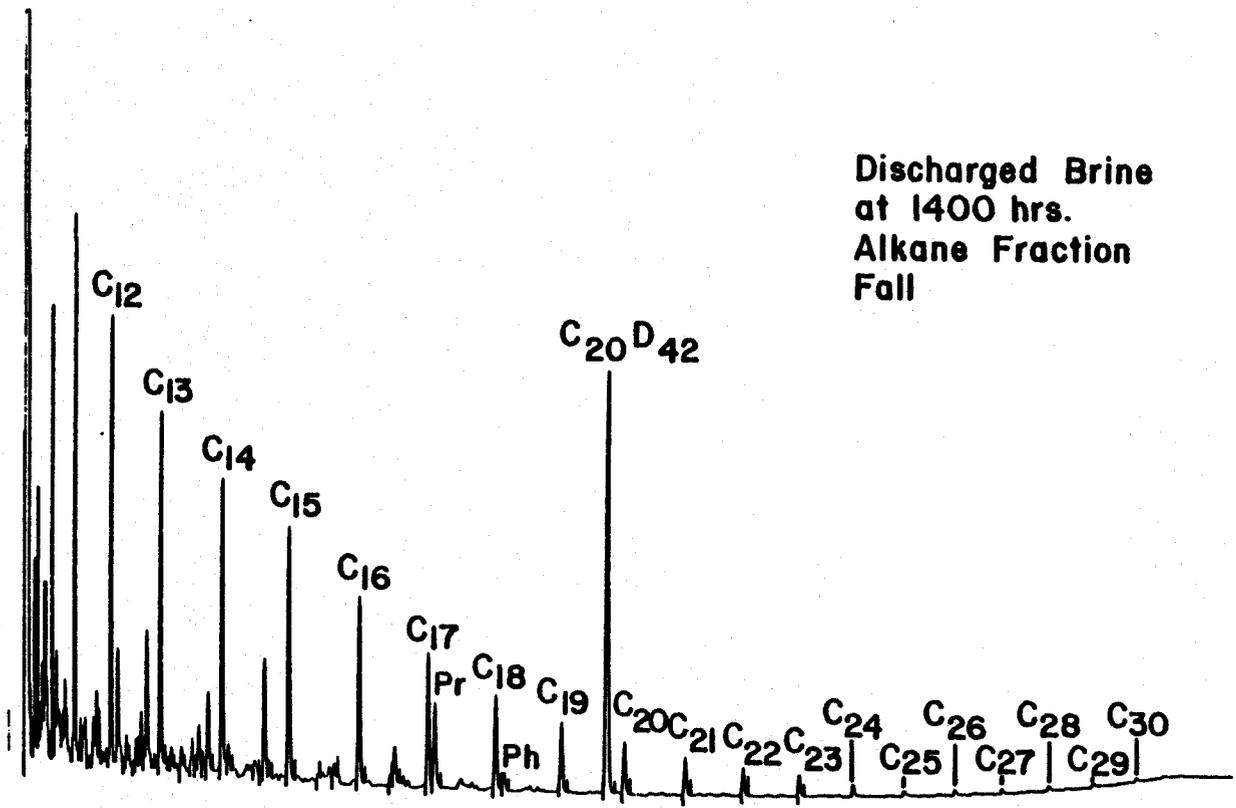


Fig. 5 Gas chromatogram of alkane fraction of discharged brine collected at 1400 hrs. December 19, 1978

2.4.1-36

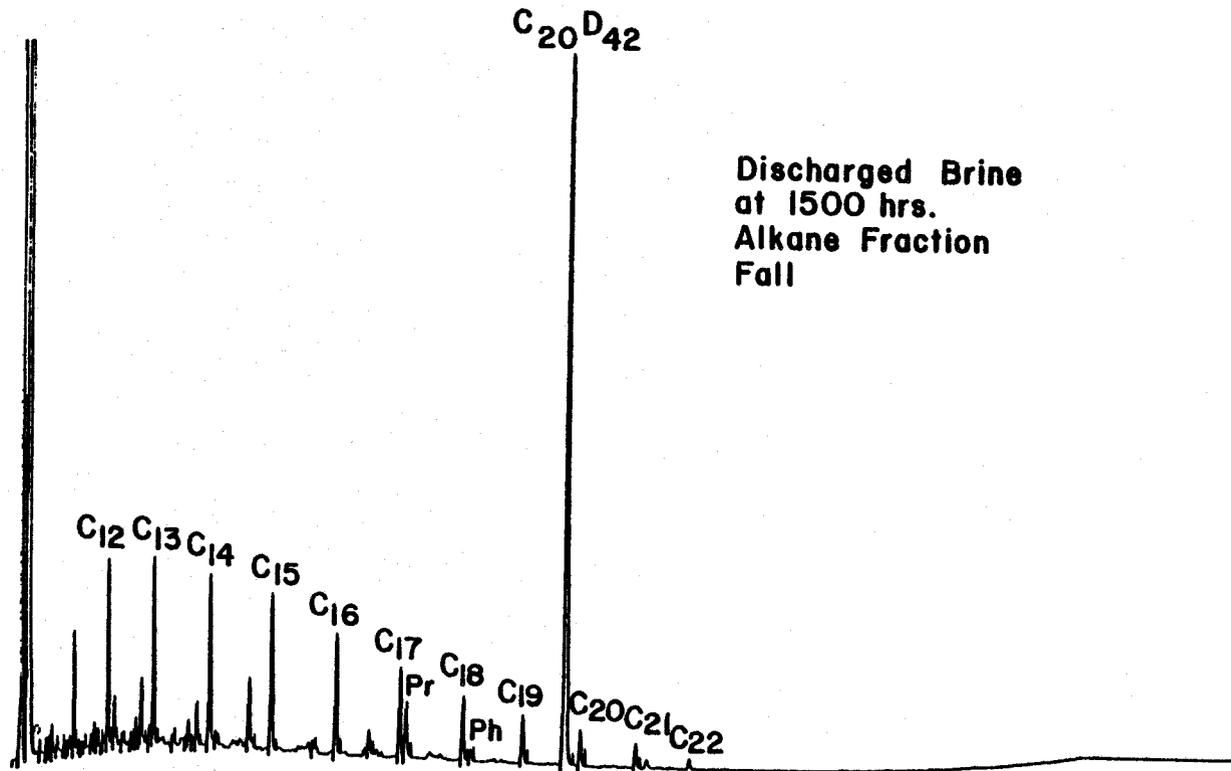


Fig. 6 Gas chromatogram of alkane fraction of discharged brine collected at 1500 hrs. December 19, 1978

ppm. Sequent brine (40 samples) ranged in concentration from 0.15 to 8.9 ppm with a mean of 2.4 ppm. This corresponds to a range of 0.83 to 49.4 ppm (mean 13.3 ppm) of total oil discharged, well within criteria specified by various environmental concerns. Since the "average" rate of brine discharge is on the order of 1,000 bbl (159,000 liters) per day (Boyd, 1979), the mean daily rate of discharge of alkanes into the environment is 382 g.

Alkanes have been reported to be only sparingly soluble in water, usually less than 3 ppb (Sutton and Calder, 1974). However, many brine samples show concentrations of individual alkanes which exceed the 3 ppb level by as much as 3 orders of magnitude. This discrepancy is best explained by the likely presence of micellar droplets of oil in brine. Although microscopic examination would confirm this, it has been demonstrated that water may accommodate significant quantities of higher molecular weight alkanes as colloids (Peake and Hodgson, 1966).

3.1.2.b. "Aromatic" Fraction

In addition to alkanes, several aromatic compounds have been identified in discharged brine (Table 4). Thirty-six different mono- and poly-alkylbenzenes, 17 naphthalenes, and 4 biphenyls were detected. Sixty-eight aromatics were separated and detected in discharged brine, and 25 in separator tank oil.

3.1.2.c. Volatiles

Several volatile hydrocarbons with a molecular weight of 72 a.m.u. and greater were separated and characterized in discharged brine samples. Compounds are tabulated (Table 5) with relative concentrations, Kováts' retention indices, and orders of elution from the GC column. Chloroform has been a frequent contaminant of analyses due to amounts normally found in air

TABLE 4

Discharged Brine Aromatic Fraction: June 24, 1979

Peak	I	Component	ppb
1	1018	C ₃ -Benzene	12.5
2	1039	C ₃ -Benzene	11.7
3	1062	C ₄ -Benzene	1.7
4	1065	C ₄ -Benzene	0.4
5	1068	C ₄ -Benzene	1.8
6	1073	C ₄ -Benzene	1.5
7	1084	C ₄ -Benzene	3.6
8	1088	C ₄ -Benzene	2.4
9	1092	C ₄ -Benzene	2.4
10	1102	C ₄ -Benzene	1.7
11	1113	C ₅ -Benzene	1.8
12	1118	C ₄ -Benzene	3.2
13	1133	C _{5:1} -Benzene] C ₅ -Benzene	0.4
14	1130	C ₄ -Benzene	5.2
15	1148	C ₅ -Benzene	0.4
16	1156	Naphthalene	11.1
17		C _{5:1} -Benzene	0.5
18		C ₅ -Benzene	0.6
19		C ₅ -Benzene	0.8
20	1162	C ₆ -Benzene] C _{6:1} -Benzene	0.7
21	1172	C ₆ -Benzene	1.3
22	1186	C ₆ -Benzene	0.3
23	1193	?	0.5
24	1243	C ₆ -Benzene	0.4
25	1249	C ₆ -Benzene	0.5
26	1255	?	0.7
27	1262	[² H ₁₀]-2-Methylnaphthalene (IS)	[6.5]
28	1281	1-Methylnaphthalene	7.2
29	1307	?	0.5
30	1320	C ₇ -Benzene	0.9
31	1338	?	0.3
32	1348	Biphenyl or Acenaphthene	2.8
33	1364	C ₂ -Naphthalene	1.0
34	1376	C ₂ -Naphthalene	1.8
35	1390	C ₂ -Naphthalene	4.0
36	1393	C ₂ -Naphthalene	1.0
37	1398	C ₈ -Benzene	0.5
38	1400	n-Tetradecane	22.5
39	1403	C ₂ -Naphthalene	1.7
40	1418	C ₂ -Naphthalene	0.9
41	1424	C ₈ -Benzene	0.4
42	1442	C ₈ -Benzene	0.7
43	1452	Methylbiphenyl	2.3
44	1458	?	0.5
45	1476	C ₃ -Naphthalene	0.6

TABLE 4 (Cont'd)

Peak	I	Component	ppb
46	1488	C _{8:1} -Benzene	0.5
47	1494	C ₂ -Biphenyl	0.6
48	1500	C ₃ -Naphthalene]	*
		n-Pentadecane]	
49	1516	C ₃ -Naphthalene]	1.1
		C ₃ -Naphthalene]	
50	1526	?	0.4
51	1523	C ₃ -Naphthalene	1.2
52	1535	C ₉ -Benzene	1.0
53	1542	C ₉ -Benzene	0.5
54	1552	C ₃ -Naphthalene	1.4
55	1558	C ₂ -Biphenyl	0.4
56	1584	C ₁₀ -Benzene	0.5
57	1600	n-Hexadecane	35.7
58	1641	C ₄ -Naphthalene]	0.5
		C ₁₀ -Benzene]	
59	1662	C ₄ -Naphthalene]	0.5
		C ₁₀ -Benzene]	
60	1697	C ₄ -Naphthalene]	0.4
		C ₅ -Naphthalene]	
61	1700	n-Heptadecane	29.6
62	1764	C ₁₁ -Benzene	0.3
63	1800	n-Octadecane	31.0
64	1868	?	0.5
65	1900	n-Nonadecane	35.4
66	1972	n-[² H ₄₂]Eicosane (IS)	[65.4]
67	2000	n-Eicosane	32.7
68	2100	n-Heneicosane	50.0
69	2200	n-Docosane	77.4
70	2300	n-Tricosane	197.1
71	2400	n-Tetracosane	248.0
72	2500	n-Pentacosane	208.6
73	2600	n-Hexacosane	170.7
74	2700	n-Heptacosane	128.5
75	2800	n-Octacosane	103.2
76	2900	n-Octacosane	105.1
TOTAL		Benzenes	62.1
		C ₃ -Benzenes (2)	24.2
		C ₄ -Benzenes (10)	23.9
		C ₅ -Benzenes (5)	
		C _{5:1} -Benzenes (2)	4.5
		C _{6:1} -Benzenes (5)	3.2
		C _{6:1} -Benzenes (1)	
		C ₇ -Benzenes (1)	0.9
		C ₈ -Benzenes (3)	2.1
		C _{8:1} -Benzenes (1)	
		C ₉ -Benzenes (2)	1.5

TABLE 4 (Cont'd)

		ppb
	C ₁₀ -Benzenes	(3) 1.5
	C ₁₁ -Benzenes	(1) 0.3
	Naphthalene	11.7
	Methylnaphthalenes	(1) 7.2
	C ₂ -Naphthalene	(6) 10.4
	C ₃ -Naphthalene	(6) 4.9
	C ₄ -Naphthalene	(3) 1.4
	C ₅ -Naphthalene	(1) 0.4
	Biphenyl	2.8
	Methylbiphenyls	(1) 2.3
	C ₂ -Biphenyls	(2) 1.0
	C ₃ -Biphenyls	(1) --
TOTAL AROMATICS	(68)	104.2 ppb
TOTAL n-ALKANES	(16)	1475.5 ppb
TOTAL UNKNOWN	(7)	3.4 ppb
TOTAL HYDROCARBONS MEASURED		(84) 1583.1 ppb

TABLE 5

Discharged Brine Volatiles: January 14, 1979

Peak	I	Component	ppb
1		2-Methylbutane	4.8
2		Chlorform (artifact)	0.5
3		2-Butanone	1.5
4	500	n-Pentane	3.6
5	509	n-Pentane	2.6
6		?	3.3
7	528	Methylcyclopentane	2.3
8	551	3-Methylpentane	0.4
9		?	0.4
10	568	Benzene	30.5
11		?	0.3
12	582	2-Pentanone	0.8
13	592	Heptane	0.4
14	600	n-Hexane	2.3
15		1,3-Dimethylcyclopentane	1.2
16		Methylcyclohexane	5.4
17		Octadiene	0.2
18		Heptane	0.4
19		Heptane	0.5
20		Heptane	0.4

Table 5 (Cont'd)

			ppb
21	Octene		1.9
22	3-Methylhexane		1.0
23	Heptane		1.2
24	Octane		0.4
25	Toluene		27.3
26	2,2-Dimethyl-3-hexene		0.8
27	Dimethylcyclohexane		0.6
28	Octane		0.2
29	Dimethylcyclohexane		0.4
30	Trimethylcyclohexane		0.4
31	Ethylbenzene		6.0
TOTAL	C ₅ -Hydrocarbons	(2)	8.4
	C ₆ -Hydrocarbons	(2)	2.7
	C _{6:1} -Hydrocarbons	(2)	4.9
	C ₇ -Hydrocarbons	(6)	3.9
	C _{7:1} -Hydrocarbons	(2)	6.6
	C ₈ -Hydrocarbons	(2)	0.6
	C _{8:1} -Hydrocarbons	(4)	3.7
	C _{8:2} -Hydrocarbons	(1)	0.2
	C _{9:1} -Hydrocarbons	(1)	0.4
	Benzene		30.5
	Toluene		27.3
	Ethylbenzene		6.0
	Ketones	(2)	2.3
	Unknowns	(3)	4.0
	Artifact	(1)	0.5
TOTAL VOLATILES			100.0%

and in tap and deionized water. Compounds identified represent best "fit" with published spectra (Heller, 1979).

While on a monthly sampling visit to the oil field in July, a 55 gallon drum of methyl ethyl ketone (McKesson Chemical Company) used by painters on the platform as a solvent, was noticed. It is highly probable that since production platform runoff is channelled into the "skim tank," paint or paint solvents may have been washed into it. This would account for the presence of quantities of 2-butanone and 2-pentanone (a contaminant in technical methyl ethyl ketone) in the discharged brine volatiles since this chemical is not intentionally added at any point in the oil-brine separation process.

Benzene, toluene, and ethylbenzene were found in relatively large quantities (30.5%, 27.3%, and 6%, respectively, of the volatiles) compared to concentrations of alkanes in the brine, which may be explained by their much greater solubility in water. Decreasing relative concentrations for benzene, toluene and ethylbenzene correlate well with their decreasing solubilities in water: 1780, 515, and 152 g/10 g of water, respectively (McAuliffe, 1966).

The probability of these compounds remaining in seawater for any length of time is minimized because of their volatility and mode of entry into the sea. The brine discharge stream impacts the seawater with such momentum and churning, that many small bubbles are released. These bubbles probably release some of the light hydrocarbons to the atmosphere thus substantially depleting concentrations near the discharge pipe.

3.1.2.d. Sulfur

All brine samples had visible degrees of turbidity due to suspended elemental sulfur particles. Sulfur concentrations in sequent brines collected September 2 and 3 (55-105 ppm) and May 17 and 18 (1100-2300 ppm) showed more variation with time of day, than those collected April 24 and 25 (1100-1700 ppm) which showed the smallest variation. There was no correlation ($p < 0.05$) between the amount of alkanes and the amount of sulfur discharged in brine. This indicates that alkanes and sulfur have a different origin, rather than the two substances being in the same subterranean location.

The sulfur content of discharged brines ranged from 0.06% to 0.42% with a mean concentration of 0.13% for the year. This is about 3 times the amount of discharged sulfur reported between 1976 and 1978 (Middleditch *et al.*, 1979). Since the mean volume of brine discharged per day is approximately 1000 bbl (159,000 liters), then about 207 kg of the sulfur is being discharged

into the environment daily, making it the major pollutant (compared with 382 g of alkanes discharged per day).

If hydrocarbons can be adsorbed onto sulfur particles, then it is reasonable that the sulfur may serve as a transport vehicle for oil through the water column and into sediments, since solid sulfur has a specific gravity of about 2 and is insoluble in water.

Once sulfur is in the sediment it may serve as an essential nutrient for sulfur-utilizing bacteria, thus enhancing the biomass of the base of the food web. Evidence for this lies in the observation in sediments of odd-preference biogenic alkanes known to be a product of bacteria which can utilize sulfur compounds (Davis, 1968).

3.1.2.e. Biocides

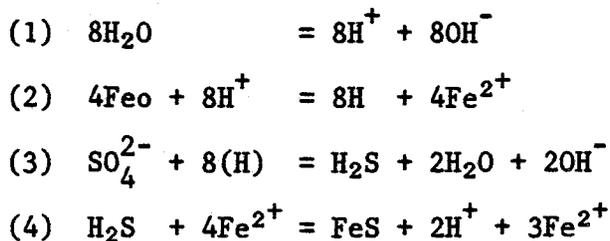
Continuous, uninterrupted flow in the brine disposal system is essential to clean production operations in the Buccaneer Field. Solid materials in the water, a result of chemical and microbiological factors, invariably build up in flow pipe bores and reduce the flow rate. A number of proprietary treatments are available to prevent or reduce chemical corrosive processes, but restriction caused by microorganisms has been more difficult to prevent.

Microorganisms exist in varying numbers naturally in subsurface brines. With man's endeavor to obtain petroleum, he invariably causes some degree of mixing within the oil reservoir thus mobilizing nutrients which stimulate the growth of these microbes (Bennett, 1979). These same bacteria, predominantly the anaerobic sulfate-reducing Desulfovibrio spp., are primarily responsible for problems created within the (closed) water disposal system in this oil field.

Previously, oil production research workers had tended to view anaerobic corrosion as a largely abiotic process, using a corrosion inhibitor and micro-

biocide to prevent problems. Recently, the focus has shifted to the by-products of microbial metabolism which may cause destruction in an otherwise corrosion-free water system. The metabolite of greatest interest, a product of the sulfate-reducers, is hydrogen sulfide.

Hydrogen sulfide has the following involvement in a localized electrolytic cell produced inside metal (iron containing) flow pipes and tanks by the sulfate-reducing bacteria:



Equation (1) is simply the ionization of water, (2) is the initial corrosion reaction, (3) describes the essence of the metabolic reduction of sulfate by bacteria yielding hydrogen sulfide, and (4) shows the formation of the insoluble, black, iron sulfide which is an excellent plugging agent (Bennett, 1979).

Biocides used formerly in the Buccaneer Field were K-31 (glutaraldelyde) and KC-14 (alkyldimethyl benzyl chloride), both manufactured by Champion Chemical Company. The weekly alternation in application of these two biocides was only partially successful in reducing the numbers of Desulfovibrio so, in April, 1978, Shell switched to the acrolein biocide, "Magnacide B" (Magna Corporation).

"Magnacide B" is a formulation of acrolein (2-propenal) of approximately 90-94% purity, depending on the source. The acrolein is not manufactured by Magna (it is obtained from several different sources) but is distributed and applied by this EPA licensed applicator. Acrolein is a highly volatile, toxic, and reactive substance.

Acrolein is toxic to higher organisms as well as bacteria. Table 6 lists representative toxicity data for some marine organisms.

TABLE 6

Acrolein Toxicity in Some Marine Organisms (adapted from Palmer, 1977)

Organism	Type of Test	Time	LC ₅₀ (ppm)	Reference
Oyster (<u>Crassostrea virginica</u>)	Chronic	96 hr.	0.05	Butler, 1965
Brown shrimp (<u>Penaeus aztecus</u>)	Acute	48 hr.	0.10	Butler, 1965
Mosquito fish (<u>Gambusia affinis</u>)	Acute	48 hr.	0.06	Louder and McCoy, 1965
Bowfin, fry (<u>Amia calva</u>)	Acute	24 hr.	0.06	Louder and McCoy, 1965
Largemouth Bass (<u>Micropterus salmoides</u>)	Acute	24 hr.	0.18	Louder and McCoy, 1965
Bluegill (<u>Eupomotis macrochirus</u>)	Acute	24 hr.	0.14	Louder and McCoy, 1965

In order to neutralize acrolein, a solution of ammonium or sodium bisulfite is used. Sodium bisulfite reacts with acrolein in the following way:



Although sodium bisulfite reacts in a 2 to 1 mole ratio with acrolein, Magna Corporation recommends and applies a 10 to 1 mole ratio of "Magnatreat OS- L" (sodium bisulfite solution) to scavenge any remaining acrolein before discharge of brine.

Acrolein has not been detected in discharged brine using the GC-MS for volatiles. Residual amounts of acrolein (1-3 ppm) have been reported (Burgbacher, 1978) but these data were obtained immediately after the installation of the injection system and sufficient time had probably not

elapsed for equilibration of acrolein usage concentration, bacterial counts and scavenger usage concentrations. Once this had been done, no residual was detected until pump failure and replacement when 2 ppm was reported. After three days, again, residual acrolein was below detection limits.

Given the high reactivity and low half-life of acrolein in the water disposal system and more than adequate means of neutralizing any possible residual, it is strongly suspected that little, if any, is even reaching the ocean. Even if trace amounts should enter the environment they would not be expected to be persistent, but easily and quickly dispersed and inactivated by environmental factors, i.e., dissolution, capillary bubble evaporation at the discharge point, photochemical deactivation, reaction with ions and organics in seawater, etc.

3.1.3. Other Platform Samples

Samples collected on monthly visits to the field included separator tank water, seawater, fire fighting water and sewage, in addition to oil and brine.

Separator tank water collected on all occasions had a small amount of finely divided dark particles which imparted a faint darkness to the solution and usually settled out before extraction. These particles are thought to be either a subterranean sand brought up with oil and water and accumulating in the separator tank, and/or iron sulfide particles, a consequence of bacterial activity. The alkane composition of this "oily" water is very similar to oil collected from the same vessel, showing identical concentration maxima and very similar alkane/isoprenoid ratios and odd-even preferences (Figure 4). The similarity between alkanes in separator tank water and oil itself is again probably a result of micellar accomodation of alkanes dispersed in the water. In addition, adsorption of oil to particulates may be responsible for the entrainment of higher alkanes found in these samples. Total alkanes measured between 5.11 and 29.05 ppm with a mean concentration of 19.62

ppm. Brines have been shown to contain an average of 2.4 ppm alkanes (see section 3.1.2.a.). Thus, the secondary oil recovery system shows an 87.8% efficiency in removing measurable hydrocarbons from formation water before disposal.

Seawater collected on monthly visits was taken from two locations. Until May, seawaters were collected from the quarters platform (296-B). Later they were taken from within 3 m of the discharge pipe on 296-B. All waters were taken from the surface and contain a portion of any surface film at that location. Waters from both locations showed little (less than 5 ppb) or no alkanes detected (Figure 7).

Fire-fighting water was generally unremarkable, usually showing levels of alkanes at only 1-5 ppb (Figure 8). A sample collected in November 1978 showed 44 ppb, however, distributed among C_{13} , C_{16} , C_{18} , and C_{20} . This was possibly a contribution from the rubber in the fire hose. A February sample showed a 0.8 ppb concentration (44% of total alkanes) of a compound within the retention window for C_{28} . This is most likely squalene which coelutes with C_{28} and could be evidence of microbial activity in the water system.

The rate of treated sewage discharged from 296-B is about 30 liters per hour but flows on an intermittent basis. Alkane concentrations in sewage were as high as 797 ppb but the alkane/isoprenoid ratios were not typical of petroleum with C_{17} , C_{18} and C_{20} alkanes predominating. Also, most samples showed a strong odd-carbon preference, indicating biogenic alkanes. Characteristic of municipal wastewater effluents is a complex unresolved "hump" in the GC trace starting at about C_{20} (Farrington and Quinn, 1973). This profile was observed in a sewage sample collected in April, but since the total alkane concentration was at most 1.0 ppm and average flow rate low,

2.4.1-48

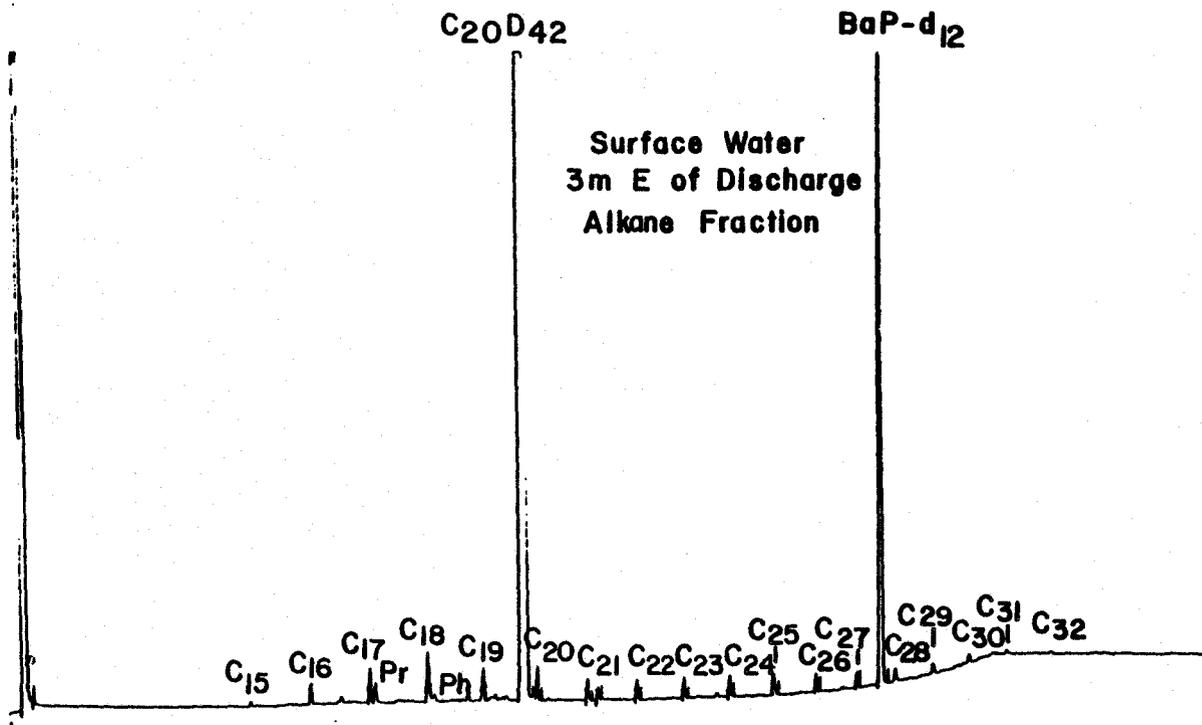


Fig 7. Gas Chromatogram of alkane fraction of surface water collected 3 m east of brine discharge

2.4.1-49

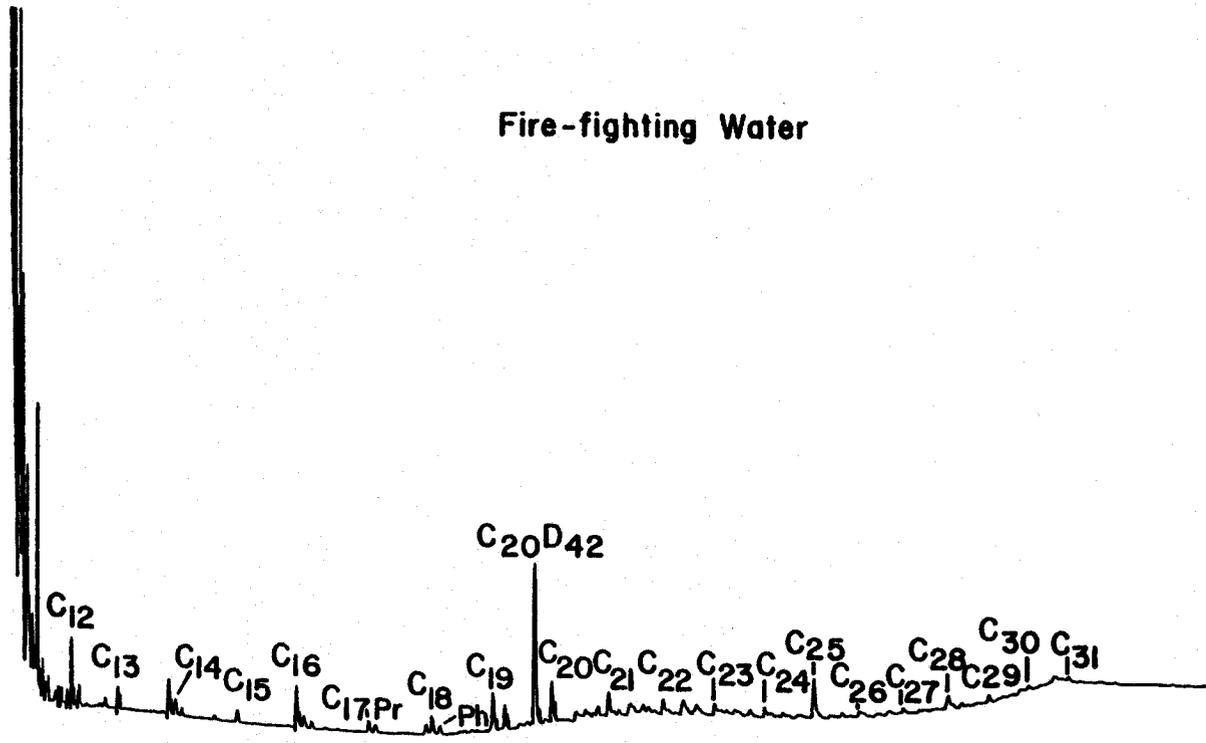


Fig. 8 Gas chromatogram of alkane fraction of water obtained from fire-fighting system

2.4.1-50

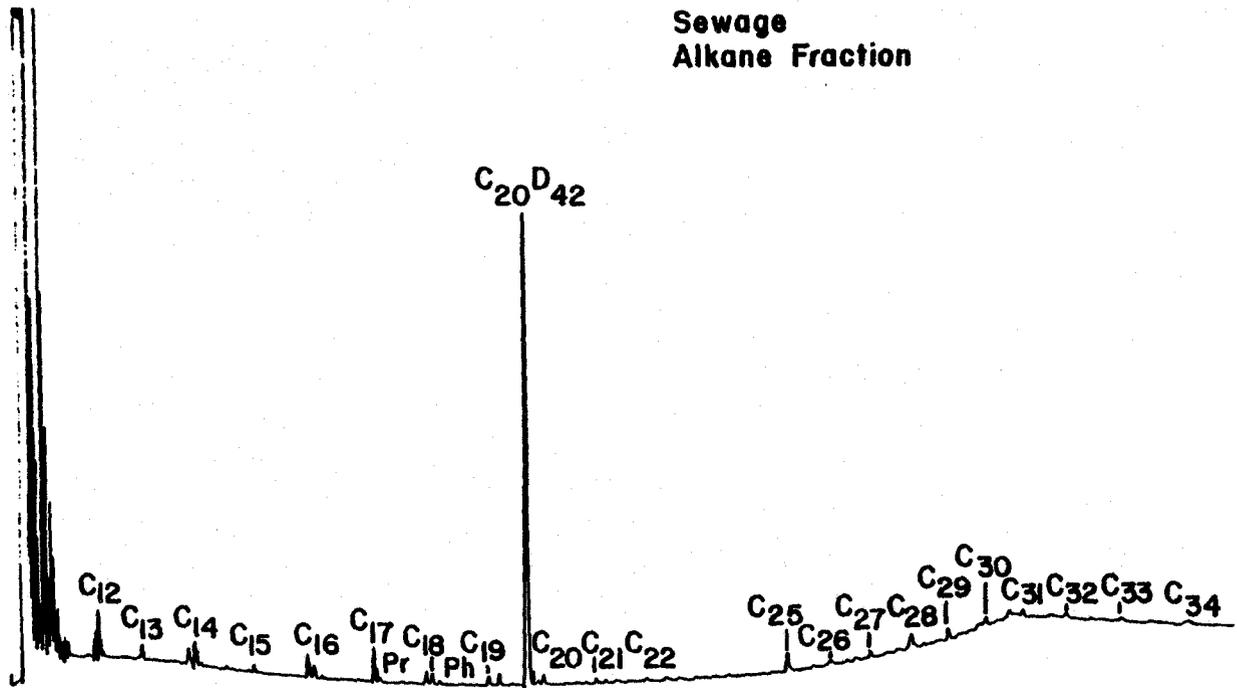


Fig. 9 Gas chromatogram of alkane fraction of sewage collected at discharge point

input is probably insignificant. It is also likely that alkanes in sewage represent biogenic input from bacteria or feces (Figure 9).

3.1.4. Miscellaneous Discharges

Other discharges from the quarters platforms include approximately 1 kg of food scraps daily and deck runoff from occasional washing with a firehose. In November, food scraps were observed to be attacked by a school of fish immediately after being tossed overboard. This discharge appears to be well accepted by the fish in the area. Identification of a common food preservative, butylated hydroxytoluene (BHT) (Figure 10), in the alkane fraction of a sheephead muscle sample suggests consumption of food scraps. This is probably of no adverse consequence to the fish, and this phenolic antioxidant preservative has been reported to inhibit formation of neoplasms in rats (Wattenberg, et al., 1978).

3.1.5. Summary

Alkane profiles in discharged brine are similar (with respect to alkane/isoprenoid ratios, OEP and concentration maxima) to profiles obtained from crude oil, but total alkane concentrations in oil may be as much as four orders of magnitude greater than in the brine.

An average of 13.3 ppm of total oil is being discharged into the sea daily, of which total alkanes account for 2.4 ppm or approximately 18%. Sixty-eight different light aromatic compounds (104.2 ppb) have been identified in discharged brine and 25 (0.4%) in separator tank oil. The greater number of aromatics in discharged brine is attributed to an enrichment phenomenon associated with increased water solubility of these compounds.

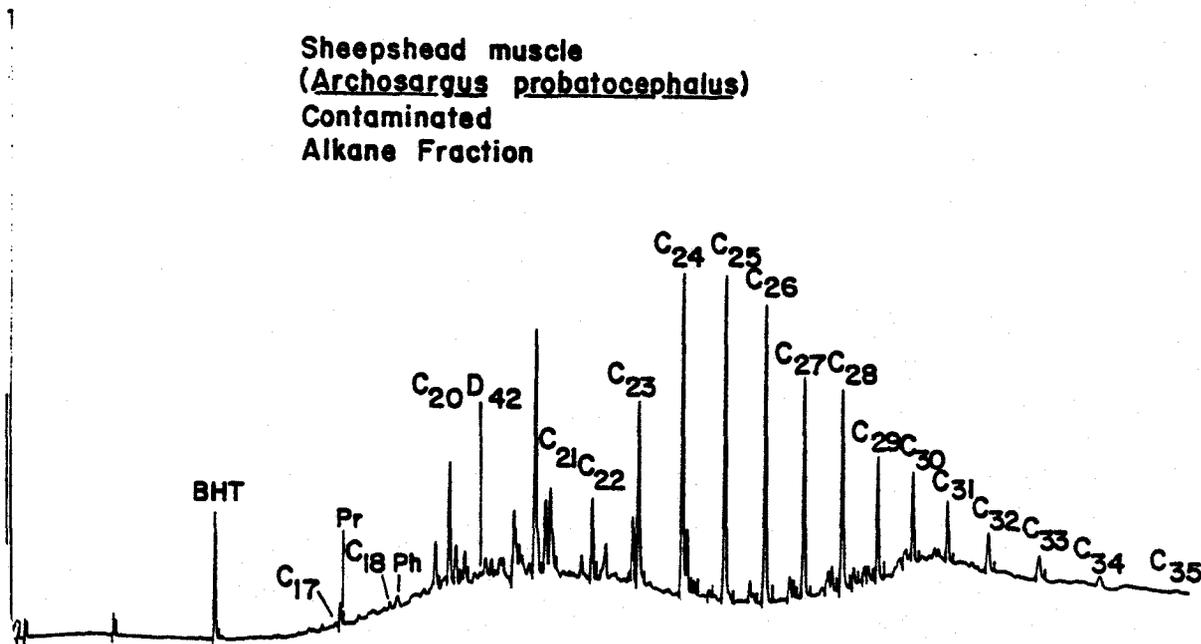


Fig. 10 (upper) Gas chromatogram of alkane fraction of sheepshead (A. probatocephalus) muscle containing BHT. (lower) Mass spectrum of BHT in sheepshead (A. probatocephalus) muscle

Twelve normal, branched, and cyclic alkanes were characterized in the analysis of volatiles in discharged brines. Three aromatics, comprising 64% of the volatile components measured, were identified as benzene, toluene and ethylbenzene. 2-Butanone and 2-pentanone were also identified.

Approximately 207 kg of sulfur is discharged daily compared to 382 g of alkanes. Sulfur may serve as an essential nutrient for bacteria, thus enhancing biomass at the base of the marine food web.

The acrolein biocide used to control microbially aggravated corrosion of pipes and vessels has yet to be detected in discharged brines. It is not expected that such a toxic yet labile compound will pose any threat to the environment as long as proper application and disposal procedures are followed.

Sewage appears to be contributing an insignificant amount of alkanes (less than 10 ppb) to the marine environment. Alkanes in sewage are probably biogenic as opposed to being derived from petroleum.

3.2 SEAWATER

In keeping with the goal of ascertaining any distribution patterns or gradients of hydrocarbon contaminants present in seawater of the near-study area, a bullseye array sampling scheme was designed. The scheme called for collection of sea water at the surface, 3 m, 5 m, and 8 m depths, and at the bottom, along 4 transects originating at the brine discharge outfall. These transects were aligned with magnetic north, south, east, and west. Horizontal sampling stations in each direction were located 0, 3, 8, and 50 m from the origin. Forty water samples each were collected and analyzed for the summer (September 3, 1978), fall (December 19, 1978), winter (April 25, 1979), and spring (May 18, 1979) seasons.

3.2.1. Summer Samples

Seawater data have been plotted in Figure 11 in accordance with the bullseye arrays. Total alkane concentrations are located near sampling stations (black dots) to which they correspond.

Surface as well as 5 m, 8 m, and bottom samples showed a distribution pattern aligned principally along the west and east transects with a high total alkane concentration of 1309 ppb at a location 3 m west of the discharge pipe at the surface. A smooth (OEP = 1.01) petroleum "hump" with concentration maxima at C₂₀ was observed (Figure 12). While hydrographic and meteorologic data were not collected on the same day as these seawater samples, recent general trends may be of some value in correlating observed alkane concentrations with physical parameters. In data collected (Danek, 1979) up until 1400 hrs. August 30, 1978, the surface current direction showed a strong stable tendency to the west-southwest and it is assumed that this tendency was maintained for the interim 4 days until these water samples were collected. In addition, a change in wind direction blowing to the north gradually moving toward the Northwest as late as August 26, would be sufficient to explain the appearance of "weathered" petroleum, possibly from 296-B, along the west transect. Difficulty, however, was encountered when an attempt was made to correlate recent wind and/or current data with the presence of relatively large quantities of alkanes at the surface, 8 and 50 m to the east of the discharge pipe.

Curiously, no "fresh" oil was encountered in any of the summer seawaters. Even the sample collected at a depth of 3 m below the discharge pipe (505.9 ppb alkanes) contained no alkanes below C₂₀. Samples containing significant amounts of alkanes generally showed concentration maxima toward the longer alkanes. No alkane profiles from bottom water (50W, 50E, and

SUMMER SEAWATERS

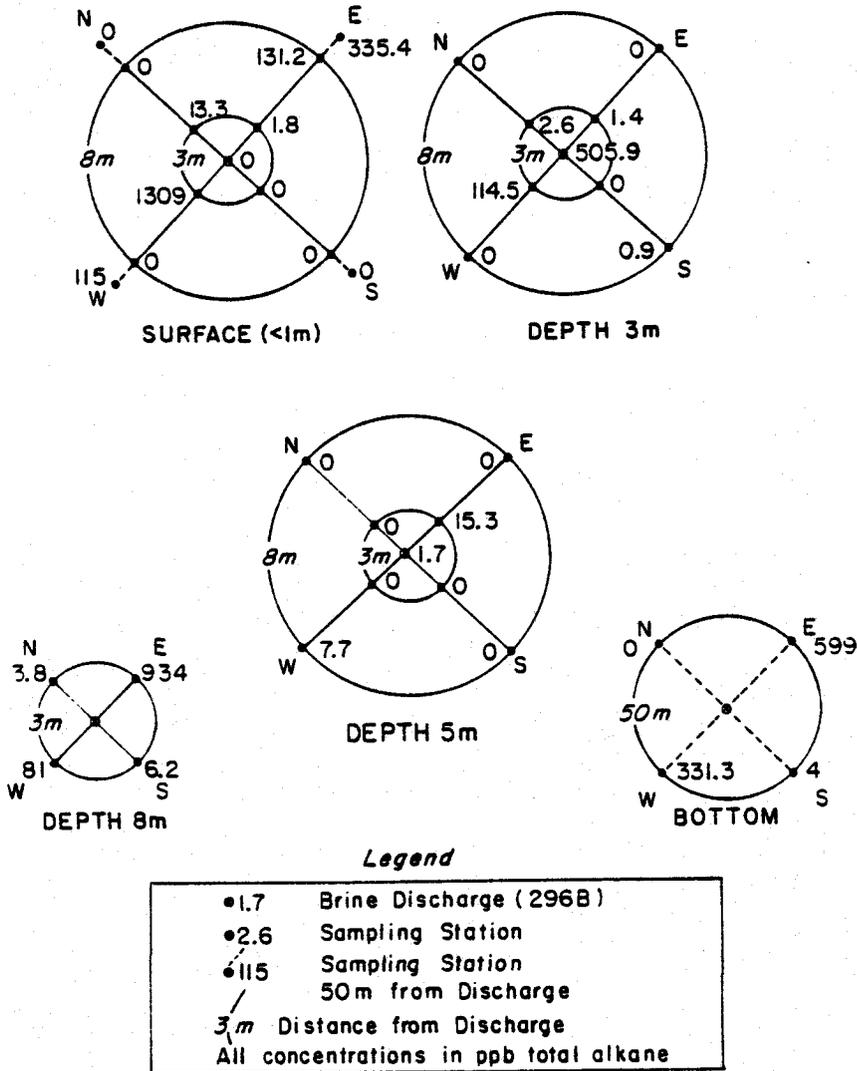


Fig. 11 Alkane concentrations in summer seawaters collected on bullseye array September 3, 1978

2.4.1-56

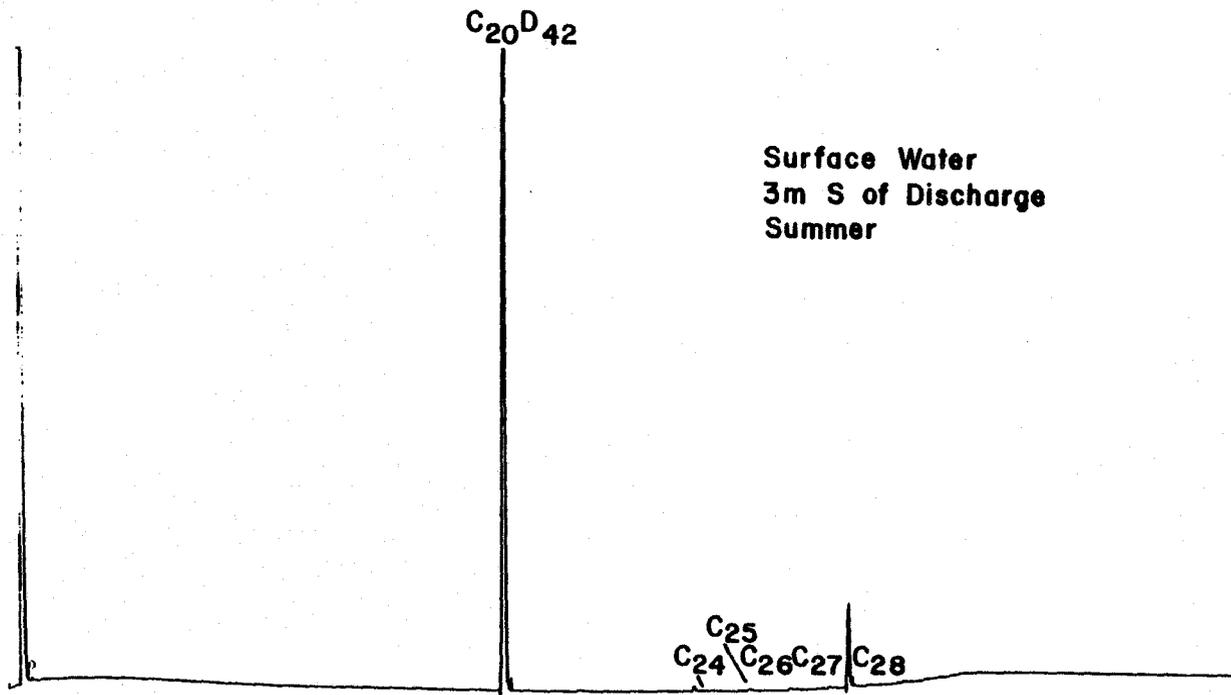


Fig 12. Gas Chromatogram of alkane fraction of summer seawater collected at the surface 3 m south of discharge, September 3, 1978

50S) could be attributed to biogenic input; in fact they showed a typical petroleum distribution and OEP of 1 or 1.01.

Since alkane/isoprenoid ratios could not be calculated for any of these seawater samples (there was no pristane or phytane detected), there was no direct evidence that contaminants originated from Buccaneer crude.

Of the total alkanes measured, 66% were found at stations below the discharge and at 3 m distant, and 34% were found in samples collected further out at 8 m and 50 m. This may give some indication of the role that current and wind activity may play in dispersing contaminants from a localized area around the brine discharge point.

3.2.2. Fall Samples

Fall seawaters were collected in the same fashion as summer samples. Surface samples showed high alkane concentrations below the discharge pipe (57 ppb), as expected, and also at a point 3 m to the north (870 ppb). The latter sample had a bimodal alkane distribution with a concentration maximum at C₂₀, indicating fresh oil, and another maximum at C₂₇, the apex of a smooth "hump".

What appeared to be a gradient of decreasing concentration extending along the east transect also showed evidence of being "fresh" under the brine outfall and becoming progressively more "weathered" as distance increased. Table 7 illustrates concentration decrease, C₁₇/pristane ratio decrease, and increasing concentration maxima.

TABLE 7

Summary of Fall Seawater Data, East Transect

Station	BD	3E<1	8E<1	50E<1
Total alkanes	57.3	2.8	1.7	1.1
n-C ₁₇ /Pr	1.12	1	1	0
Conc. max.	C ₁₅	C ₁₆	C ₂₈	C ₂₆

This gradient may be followed down to the next depth of 3 m where the sample 3 m east of the discharge pipe showed a concentration of 37.8 ppb with a maximum at C₂₂. At lower depths, however, this possible gradient became less well defined.

Bottom water samples, 50 m to the east and west of the discharge pipe, possibly contain biogenic alkanes due to discontinuity in their alkane profiles, but evidence was somewhat tenuous. Alkanes appear to be distributed only along the west and east transect at depth of 3 m, as was seen at all depths in the summer samples. A continuous, "weathered" alkane profile and a relatively high alkane concentration (93 ppb) was seen 3 m east of the discharge pipe at a depth of 8 m.

Unlike the summer samples, fall samples show much higher total alkane concentrations within 3 m at depths of 1, 3, 5, and 8 m. Generally, samples collected at a distance greater than 3 m contain only 1.4% of the alkanes measured whereas those collected at 3 m and below the discharge pipe contained 98.5% of the alkanes. This may be due to current stagnation or turnaround, but there are no synoptic hydrographic data near the collection date to verify this possibility. Hydrographic data collected in December of 1975 and 1976 show prevailing currents to be west-southwestly in direction and very erratic with respect to velocity and transient turnarounds (Armstrong and Hamilton, 1979).

3.2.3. Winter Samples

The highest concentrations of alkanes were found in the samples collected at the air/sea interface. Immediately below the discharge, a concentration of 433 ppb was observed, and a concentration maximum at C₁₅ was indicative of fresh oil. At 3 and 8 m to the east, concentrations of 41 and 53 ppb, respectively, were found. The concentration maxima were at

C₂₀ (3 m east) and C₂₅ (8 m east), attesting to a relatively rapid loss of the lighter components. A moderate concentration (30 ppb, concentration maximum at C₂₈) of alkanes was measured 3 m west of the discharge point, but no other surface water sample contained more than 10 ppb of alkanes.

At depths of 3, 5, and 8 m, samples collected 3 m east of the discharge pipe contained the highest concentrations of alkanes (8, 17, and 17 ppm, respectively), and the concentration maximum in each case was at C₂₈.

Of the samples collected near the sediment/water interface, only the one which was obtained from a location 50 m to the east of the discharge pipe contained significant amounts of alkanes (42 ppb, concentration maximum at C₂₈).

It was found that 73% of the total alkanes detected were within 3 m of the discharge point, and 27% were from more distant locations. Again, most of the alkanes were localized near the discharge point, but the distribution was skewed to the east. During April, the currents generally flow to the east or northeast (Armstrong and Hamilton, 1979).

3.2.4. Spring Samples

At the surface below the discharge, 52 ppb of fresh petroleum alkanes (concentration maximum at C₁₄) were found. Lower concentrations of weathered petroleum alkanes were found 3 m west (7 ppb) and 3 m south (6 ppb) of the discharge point and also at a depth of 3 m immediately below the discharge pipe (10 ppb).

The presence of the biogenic hydrocarbon squalene in moderately high concentrations (up to 23 ppb at a depth of 5 m) indicated the probable presence of a phytoplankton bloom at this time.

The gas chromatographic data indicated that high concentrations of C₁₃ (153 and 95 ppb) were present in two of the bottom water samples. GC-MS

data, however, demonstrated that this was due to bicyclohexyl, an impurity in the cyclohexane employed for these analyses.

3.2.5. Summary

Winds and currents obviously play an important role in the distribution and dispersion of pollutants in the water column. Unfortunately, samples collected without the benefit of concurrent wind and current information render somewhat vague conclusions concerning the effects of physical parameters on the distribution and movement of oil. All samples collected on summer transects showed a "weathered" alkane profile (Figure 13) and no discernible concentration gradient horizontally or vertically. The predominance of alkanes (2/3) were found within 3 m of the brine discharge point with a large minority (1/3) being measured in samples 8 m and beyond. By contrast, fall samples collected along the east transect displayed a definite gradient with respect to concentration (decreasing with distance) and degree of "weathering" which increased with distance from brine outfall. A similar trend, although less pronounced, was observed for the winter samples. During the spring, appreciable amounts of petroleum alkanes were again found only in close proximity to the discharge point.

Not surprisingly, the greatest concentration of petroleum alkanes was usually encountered at the air/sea interface either directly below the discharge pipe or within 3 m of that location. On the days when samples were collected, our data did not indicate any clearly-defined "plume" of contaminants in the region of the mixing zone. Such a plume would be predicted if there were a steady discharge of contaminants into receiving water which were either static (affording a circular plume) or moving with a constant speed (so that the plume would extend away from the platform in the direction of current flow). However, the discharge is not continuous, but

2.4.1-61

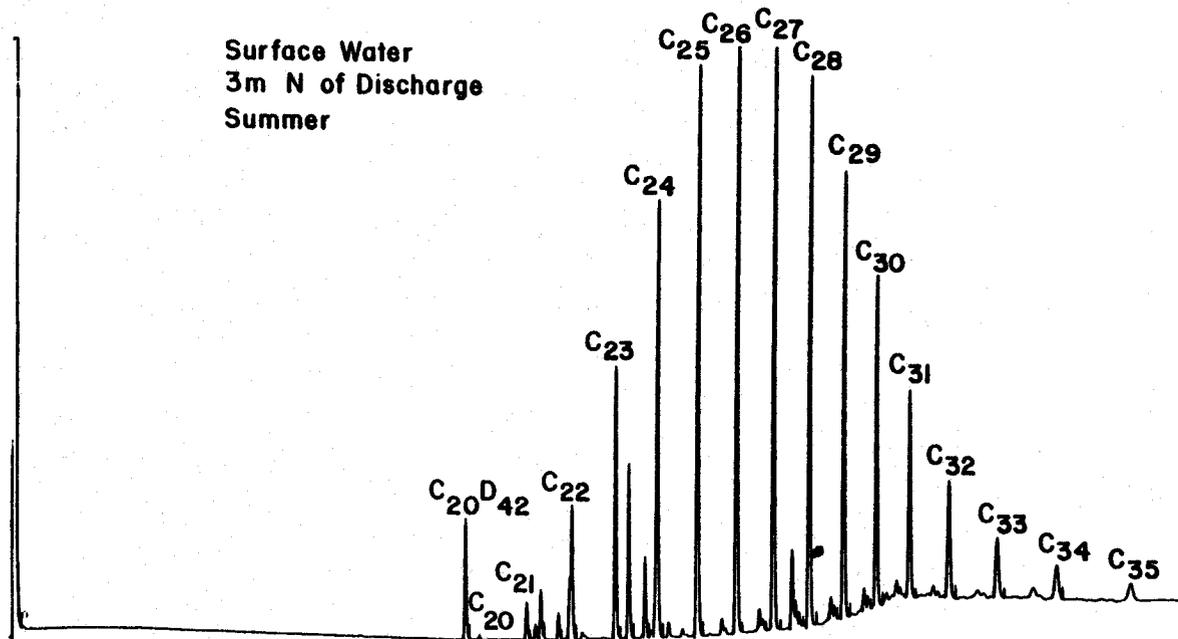


Fig. 13 Gas chromatogram of alkane fraction of summer seawater collected at the surface 3 m north of discharge, September 3, 1978

intermittent. Also, the vertical movement of the water (wave action) is comparable to the horizontal extent of the mixing zone. Moreover, samples were collected over a period of several hours and do not reflect the instantaneous concentrations of contaminants at the various locations at any particular point in time.

It was consistently found (as illustrated in Table 7) that the lighter contaminants were present only within a few meters of the discharge pipe, and that they had been dissipated (presumably by evaporation) by the time that the heavier contaminants had travelled as little as 8 m from the discharge point.

3.3 SEDIMENTS

Surficial sediments were collected on bullseye arrays along transects aligned to magnetic north, northeast, east, southeast, south, southwest, west, and northwest with sampling stations at 10, 25, and 50 m from the brine discharge pipe. In addition, five replicate samples were collected at the bases of 4 structures: production platform 296-B, production platform 288-A, flare stack 296-F, and well jacket 288-5 (see Figure 1 for locations) for summer, fall, winter, and spring.

3.3.1. Summer Transects

Summer sediments were collected on two different days, with average concentrations for each the two days varying by one or more orders of magnitude. This led to the decision to plot concentration values separately for each day. The results were two patterns of distribution and concentration variation distinctly different from one another.

North, south, east, and west transects collected together on September 1 showed a general gradient of decreasing concentration as distance from discharge increased (Figure 14). Stations with values not typical of this pattern

Summer Sediments Collected
September 1, 1978

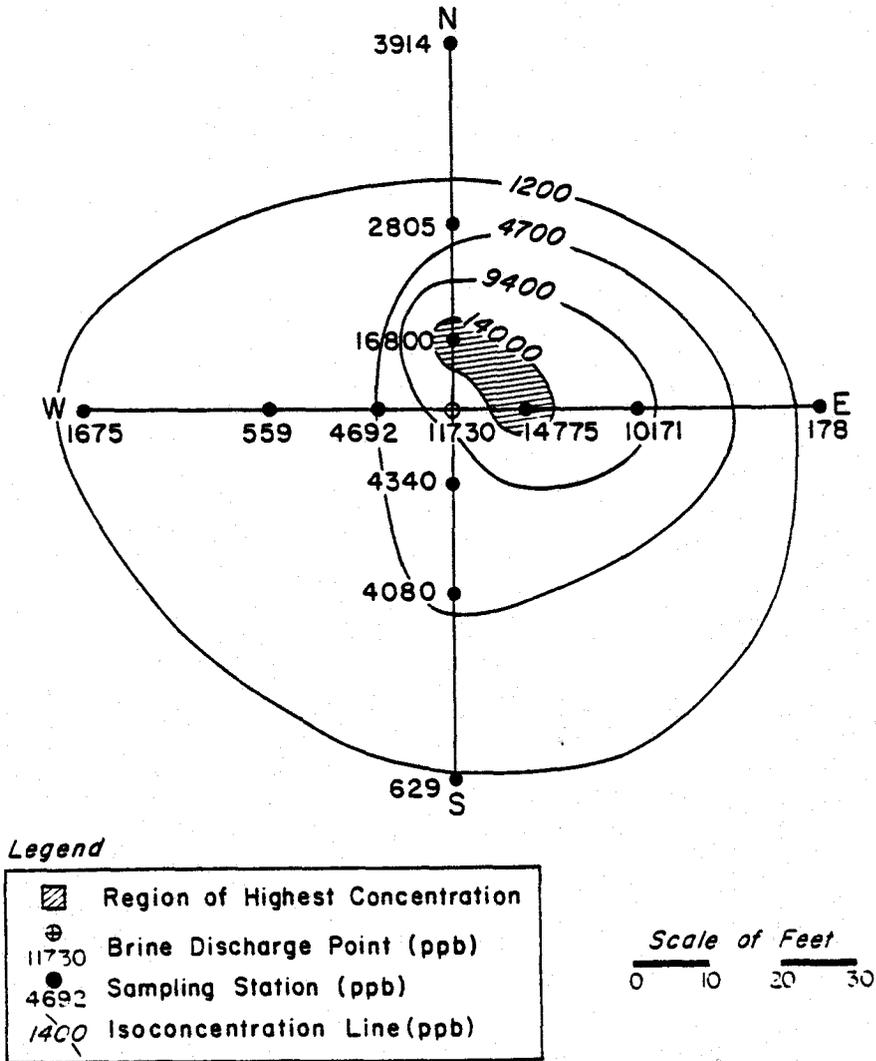


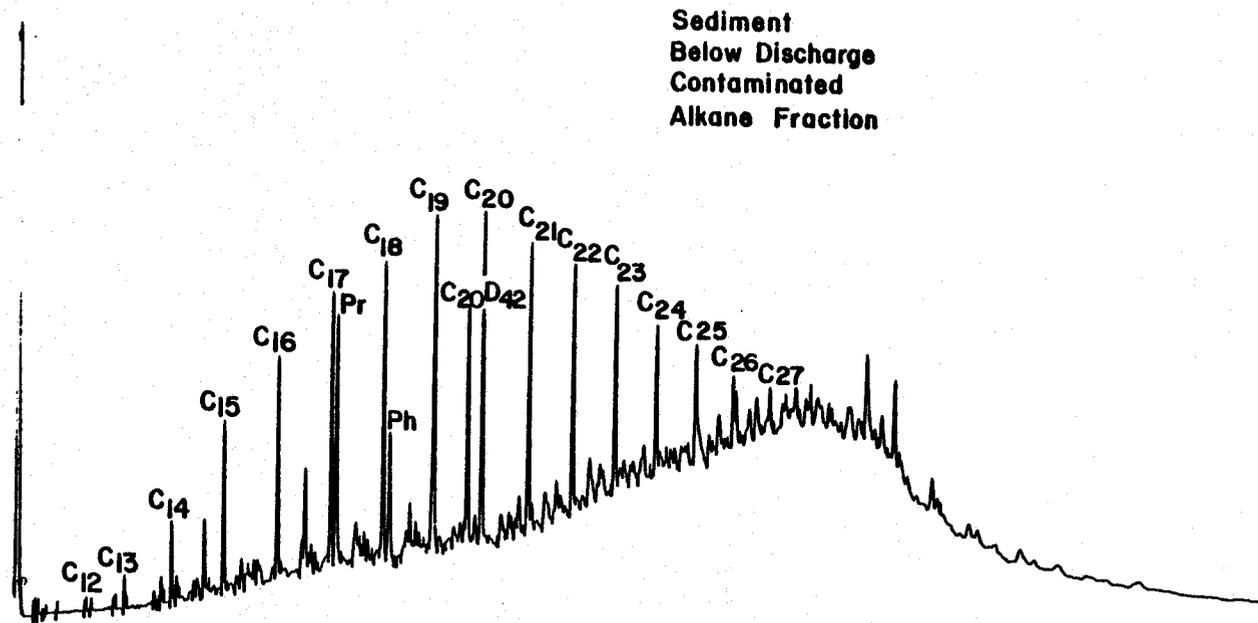
Fig. 14 Alkane concentrations in summer sediments collected on bullseye array September 1, 1978

but within the range of concentrations were two of the outermost samples on the north and west transects. A region of highest concentration (greater than 14,000 ppb) was off-center and skewed to the east-northeast. Samples collected along the east transect showed a consistent decrease in concentration from 10 to 25 m and then dropped by 2 orders of magnitude 50 m to the east. To the north, the station at 10 m was observed to have the highest concentration (16,800 ppb) and was contained within the region of highest concentration. The concentration at the center represented the mean concentration for replicate samples collected under the discharge pipe of platform 296-B.

Sediments generally showed concentration maxima between C_{15} and C_{17} , with four showing maxima at C_{19} or C_{20} (Figure 15). Usually, alkanes beyond C_{27} were not seen due to the presence of an unresolved complex envelope characteristic of sediments (Figure 16). Bacterial metabolites from the degradation of petroleum hydrocarbons, particularly alkanes, were the major contributors to the unresolved complex mixture (Walker and Colwell, 1977).

Summer sediments collected the next day, September 2, showed a similar concentration gradient as a function of distance from the discharge (Figure 17). Concentration decreases were somewhat more continuous than those observed the previous day, enhancing confidence in placement of isoconcentration contours. While the largest amounts of alkanes were measured to the northeast and southeast, the region of highest concentration appeared to be skewed slightly more to the southeast.

While sediments collected on September 1 showed a tendency for concentration maxima between C_{15} and C_{17} , those collected on September 2, almost without exception, had maxima at either C_{19} or C_{20} . It is reasonable to conclude that the more freshly oiled sediments were swept away or



2.4.1-65

Fig. 15 Gas chromatogram of alkane fraction of contaminated sediment collected below brine discharge

2.4.1-66

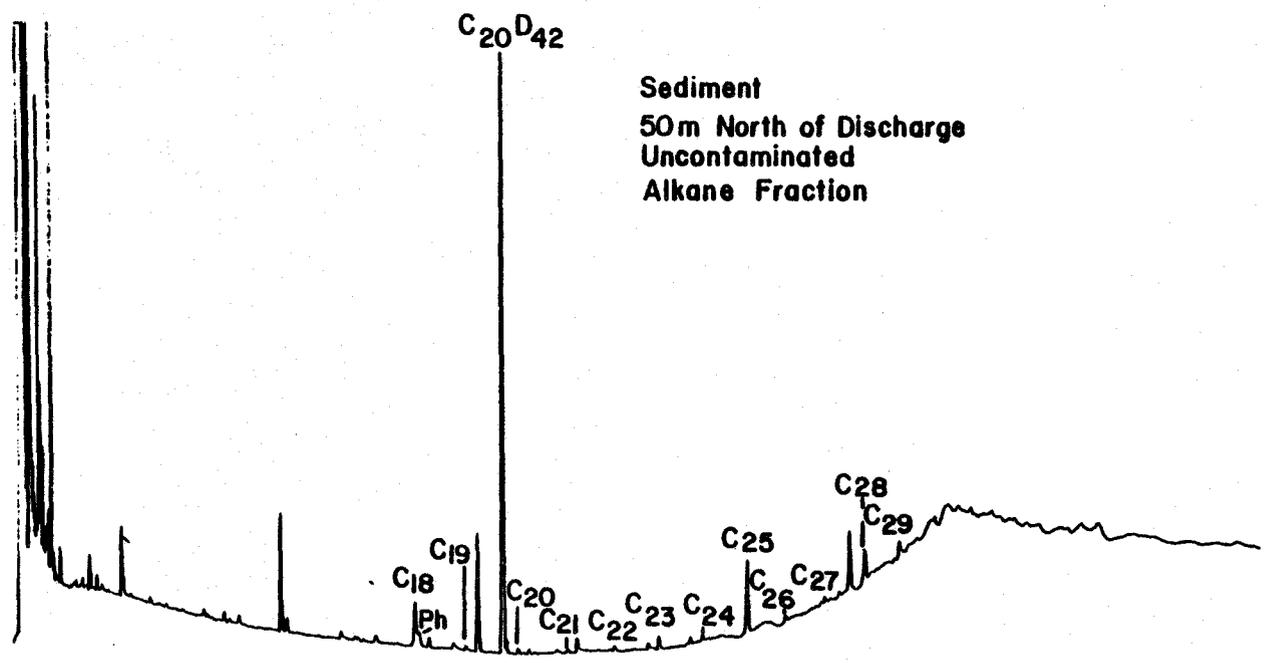
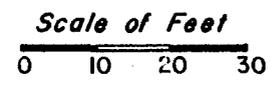
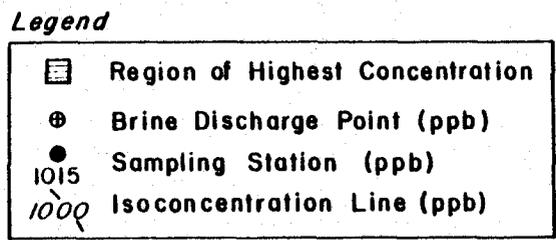
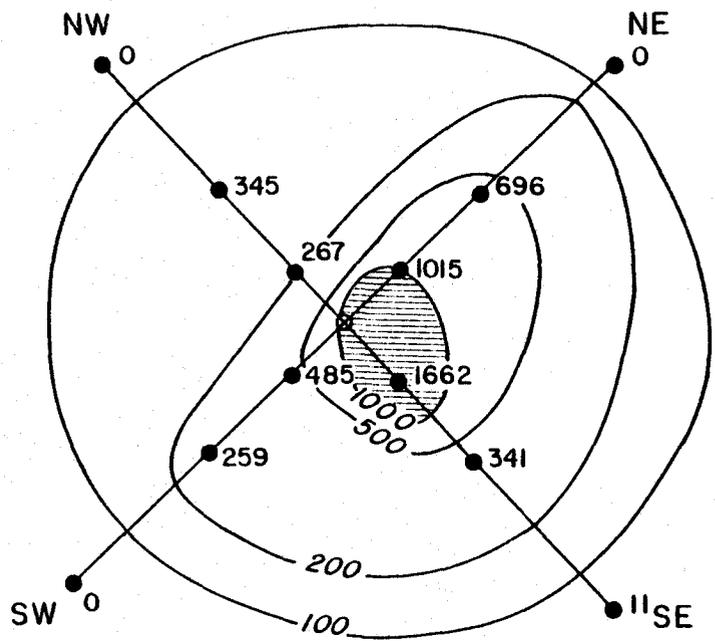


Fig 16 Gas chromatogram of alkane fraction of sediment collected 50 m north of brine discharge

September 2, 1978



2.4.1-67

Fig. 17 Alkane concentrations in summer sediments collected on bullseye array September 2, 1978

suspended in the water column during the night, exposing sediments showing a slightly more weathered condition. Evidence for this was found in the marked decrease in total alkane concentrations among all samples as compared to samples collected the day before.

Overlay of the two diagrams demonstrates an overlap of highest concentration regions to the east-northeast from 7 to 13 m out. While no information about bottom current direction or velocity was obtained during the same time period as collection of these sediments, historical trends indicate a strong probability of bottom flow to the east-northeast for late August and early September (Harper et al., 1976; Armstrong and Hamilton, 1979).

3.3.2. Winter Transects

As with the summer transects, winter samples were collected on two consecutive days. Samples to the north, west, southwest, and south were collected April 24, while northwest, northeast, east, and southeast samples were collected on April 25, 1979. There was greater similarity between concentrations of samples collected on the separate days but, in keeping with the findings for summer transects (rapid scouring), winter transects were plotted separately. Also, while concentration gradients were observed in winter samples, they were not quite as definitive as summer gradients.

A zone of highest concentration was centered to the northeast for April 24, and to the east-northeast for April 25. High concentrations at 10 m north, northeast, east, and southeast (13.8, 19.6, 21.1, and 22.9 ppm, respectively) indicated a blanket deposition of oiled sediment in these directions compared to all other 10 m stations.

The historical trend in bottom currents for this time of year, in fact, shows a distinct transition from west and west-southwest in March and April changing to east and east-northeast in late April (Armstrong and Hamilton,

1979). This fits the eccentricity observed for the region of highest concentration, bearing in mind that the bottom currents were probably in a state of directional transition on the sampling dates and had not become unidirectionally stabilized.

3.3.3. Summary

Hydrographic information indicated that, under normal conditions, there was sufficient wave energy to readily penetrate to the bottom, thereby resuspending bottom, surficial sediments (Danek, 1979). This information, in connection with past observations of a "scouring" of sediments (Anderson et al., 1979; Machemehl and Abad, 1975) indicated that sediments may be in a high flux condition at any given time.

This situation was demonstrated in summer transects. On September 1 a total of 64.6 ppm total alkanes were measured in sediments from stations on north, south, east, and west transects (excluding sediments under platform 296-B). The next day, sediments from stations on the diagonal transects showed a total alkane content of 7.08 ppm, or an overnight reduction of 89% in the amount of alkanes in area sediments.

Distribution of oil in sediments seems to follow prevailing currents with generally higher concentrations in sectors 10 to 25 m down-current from the discharge pipe.

Resuspension of oiled sediments is of some importance to biota in the area since this increases the oil concentration in the water column. An increase of this type would result in greater availability of petroleum hydrocarbons to free-swimming marine animals which may be ingested and accumulated by them. This would be particularly true for such fish as spadefish (Chaetodipterus faber) which are primarily zooplankton-particulate feeders (Gallaway and Martin, 1980).

3.3.4. Substructure Sediments

Surficial sediments were collected below four structures.

For September samples, sediments collected below platform 296-B showed the highest mean concentration (11.73 ppm) while the mean concentration at platform 288-A was 9.78 ppm. Mean concentrations for flare stack 296-F and well jacket 288-5, were 1.75 and 7.34 ppm, respectively.

In December, the mean concentration for sediments at platform 296-B was 30.1 ppm, and at platform 288-A it was 13.2 ppm. Concentrations below other structures were also proportionally higher. Since the higher values in December could not be ascribed to an increase in oil content of the brine (it was actually lower by about 1.5 ppm) it is possible that prevailing bottom currents from May through August may have carried contaminated sediments to the northeast and east-northeast. With the 180° current change occurring during September, contaminated sediments may have been re-deposited in the study area along with more recently oiled sediments.

In April, alkane concentrations below platform 296-B and well jacket 288-5 were 22.0 and 10.7 ppm, respectively. Platform 288-A sediments, on the other hand, contained 60.8 ppm of alkanes. Three of these samples proved to be heavily oiled, containing 223.6, 20.2, and 44.6 ppm of petroleum alkanes. Two of the samples showed a concentration maximum of C₂₆ and OEP \cong 1, indicating weathered petroleum, whereas another two of the samples had concentration maxima at C₁₉, and the fifth sample at C₂₂, indicating relatively fresh oil for these three samples. Although platform 288-A was reported not to be discharging brine, it was suspected that some discharge activity was responsible for the great increase in sediment concentrations of oil for April.

One month later in May, sediments collected below platform 288-A showed a decrease in oil concentration to 17.04 ppm. Flare stack 296-F and platform

296-B concentrations varied only slightly from April values, while the well jacket 288-5 sediment alkane concentration increased to 4.3 ppm. Under probable bottom current conditions for May (northeasterly), it is thought that oiled sediments from the area of platform 288-A may have been carried and deposited in the area of well jacket 288-5 which lies 300 m to the northeast.

3.3.5 Summary

Oil concentrations in sediments collected below structures varied considerably for platforms 296-B and 288-A, with 288-A showing the greatest variation in mean concentration, from 9.78 to 60.8 ppm. Change in concentrations below flare stack 296-F and well jacket 288-5 was not as radical, but may have been influenced by deposition of oiled sediments from highly contaminated areas such as platforms 288-A and 296-B.

The great increase in alkane concentration below platform 288-A seen in April may have been due to a sporadic discharge activity which may be evidenced in oil build-up in the sediment.

3.4. SEDIMENT TRAPS

Sediment traps were designed to trap and accumulate suspended particulates in the water at various locations. Locations were at 3 depths (designated top, middle, and bottom) on platform 296-B and well jacket 288-3. Suspended particulates (e.g., sediment particles, sulfur, and fecal pellets) may contain petroleum hydrocarbons which can be ingested by marine organisms or serve as a transport mechanism for hydrocarbons into the sediment. Traps were collected during July, August, and December, 1978 and April, 1979.

3.4.1. Platform 296-B Traps

Traps collected in July showed an increasing hydrocarbon concentration (from 1.98 ppm to 11.8 ppm) as depth increased. The n-C₁₇/pristane ratio

in the top trap showed evidence of Buccaneer oil as did the $n\text{-C}_{18}$ /phytane ratio (1.13 and 2.37, respectively). The OEP, however, was 1.61, indicating significant biogenic input of odd-carbon alkanes. OEP ratios of greater than 1 generally characterized most sediment trap samples. It is probable that biogenic alkanes from fecal pellets and microbial activity in this richly organic sample were present in addition to petroleum alkanes, but much more the former. A prominent unresolved complex envelope, characteristic of bacterial activity, was also seen. The bottom trap showed the same biogenic input, but the middle trap had a more petroleum-like profile with concentration maximum at C_{17} .

Platform traps from August 22 contained much fewer total alkanes (top, missing; middle, 0.8 ppb; bottom, 1.3 ppm), but again there was strong evidence of biogenic input mentioned above. In December, total alkane concentrations ranged from 7.3 ppm in the top trap to 1.9 ppm in the middle trap and, again, were mostly biogenic alkanes.

The top and middle sediment traps retrieved from platform 296-B during April, 1979 contained no alkanes, and the bottom trap contained only biogenic hydrocarbons (169 ppb).

3.4.2. Well Jacket Traps

Traps collected during July from well jacket 288-3 had large quantities of alkanes, ranging from 34.4 ppm in the top trap (Figure 18) to 4.9 ppm in the bottom trap. While the $n\text{-C}_{17}$ /pristane ratio was 0.79, indicating a larger amount of pristane than in Buccaneer oil, the profile was smooth with an OEP = 1.08. The significance of this enrichment with pristane is that zooplankton and/or their fecal pellets might have been trapped. Since a large proportion of zooplankton is made up of Calanoid copepods known to convert phytol to

2.4.1-73

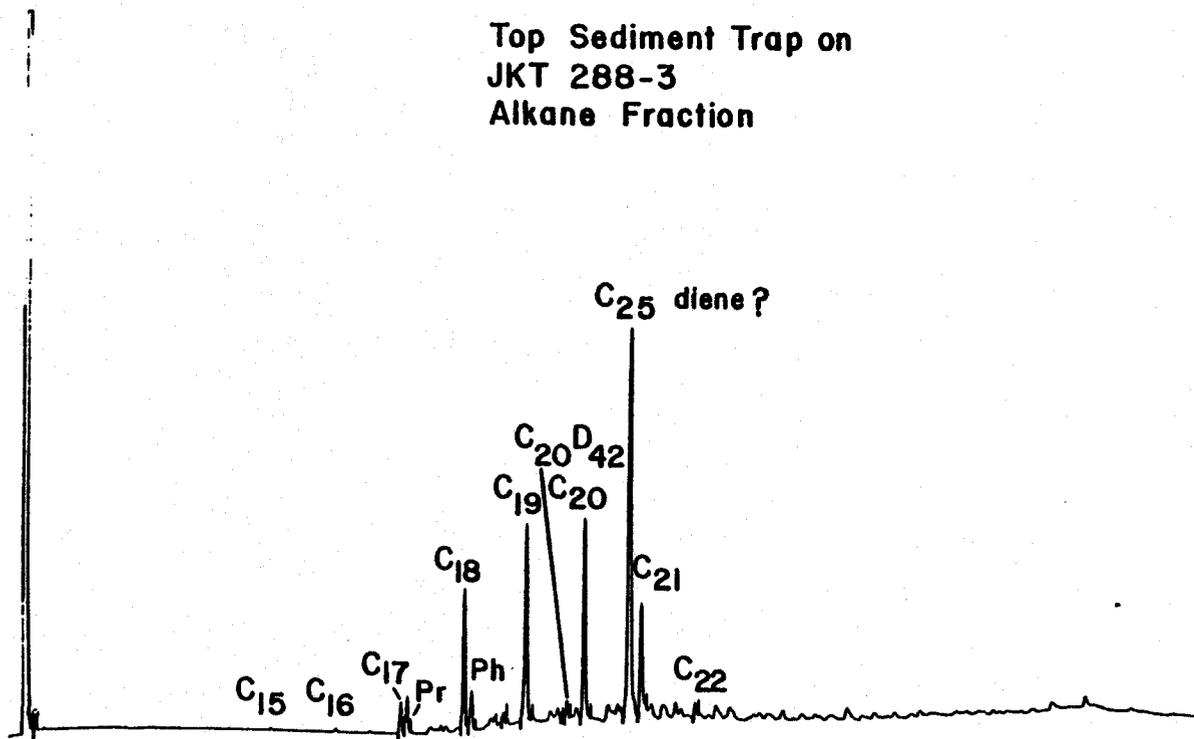


Fig. 18 Gas chromatogram of alkane fraction of top sediment trap on well jacket 288-3 showing suspected C₂₅ diolefin peak

pristane, this would be a likely source of the pristane (Blumer and Avigan, 1968). Also of note in this sample was the presence of a hydrocarbon (Kováts' retention index 2075-80) of unknown identity. After mass spectral analysis (Figure 19) it was determined to be a C₂₅ branched diolefin of molecular wt. 348. This is most likely a biogenic hydrocarbon but its immediate source is not known.

Showing much lower total alkane concentrations were traps collected in August. The top trap had a strong odd-carbon preference, with profiles in middle and bottom traps also suggesting biogenic input.

December traps again showed strong evidence of biogenic input with high OEP's and larger quantities of pristane and phytane than would be found in oil alone. These samples appeared to be relatively free of petroleum alkanes based on low total alkane concentrations and biogenic evidence.

Of the traps retrieved during April, 1979, the top one contained no alkanes and the other two contained only biogenic hydrocarbons (middle, 802 ppb; bottom, 709 ppb).

3.4.3 Summary

Sediment trap contents, being rich in organic and presumably inorganic nutrients (from feces), are a hotbed of microbial activity. This explains the significant input of biogenic alkanes, sometimes obscuring petroleum alkanes. Sediment traps may also be representative of processes occurring in surficial sediments, whereby even-carbon alkanes are preferentially degraded and metabolized by bacteria.

3.5 FISH

Three species of fish were analyzed for hydrocarbon content in liver and muscle samples while two smaller species were analyzed whole. Large fish included sheepshead (Archosargus probatocephalus), spadefish (Chaetodipterus

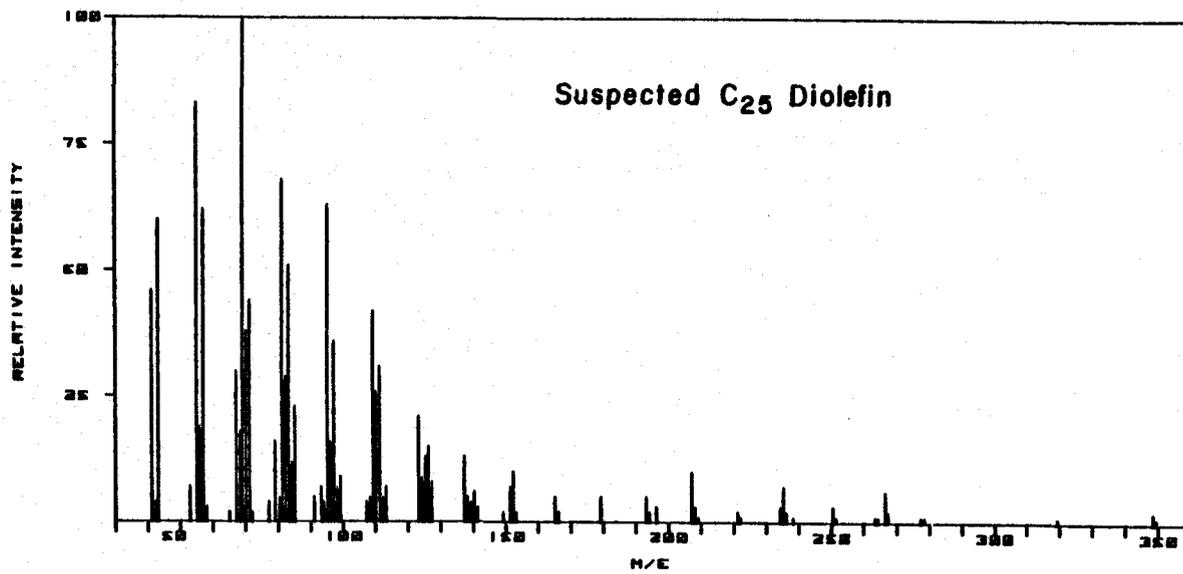


Fig. 19 Mass spectrum of suspected C₂₅ diolefin found in sediment trap sample

faber), and red snapper (Lutjanus campechanus). The small fish were longspine porgy (Stenotomus caprinus) and crested blenny (Hypleurochilus geminatus).

Fish were selected on the basis of their habitats and feeding habits. All fish chosen were known to spend their entire lives at the Buccaneer Field (Gallaway and Martin, 1980) except for red snapper (Lutjanus campechanus), which is recruited from a wide area of the Gulf and which was selected primarily because of its commercial importance.

3.5.1. Sheepshead (Archosargus probatocephalus)

Fifty specimens were analyzed, 25 each in the summer and winter.

Distinctive petroleum alkane profiles were observed in 11 muscle samples (Figure 20) and in 5 livers (Figure 21) from the fish collected in the summer. The predominant n-alkane among the contaminated livers was C₂₆, and squalene was seen coeluting with C₂₈ in many samples. Contaminating alkanes usually ranged from C₂₀ to C₃₆ with a maximum at C₂₅ or C₂₈ in muscle and liver. The mean total alkane concentration in livers was 6.08 ppm, and it was 4.57 ppm in muscle samples.

Petroleum alkanes were not detected in either liver or muscle samples of any of the specimens collected during the winter. The mean concentration of biogenic alkenes in livers was 11.6 ppm, and it was 9.24 ppm in muscle samples.

Sheepshead feed primarily on fouling biota, but consume mainly swimming crabs during the summer months (Gallaway and Martin, 1980). This difference in diet may be sufficient to account for the seasonal difference between contaminant levels in the spadefish. However, we are reluctant to draw such a conclusion based upon the limited measurements performed to date.

2.4.1-77

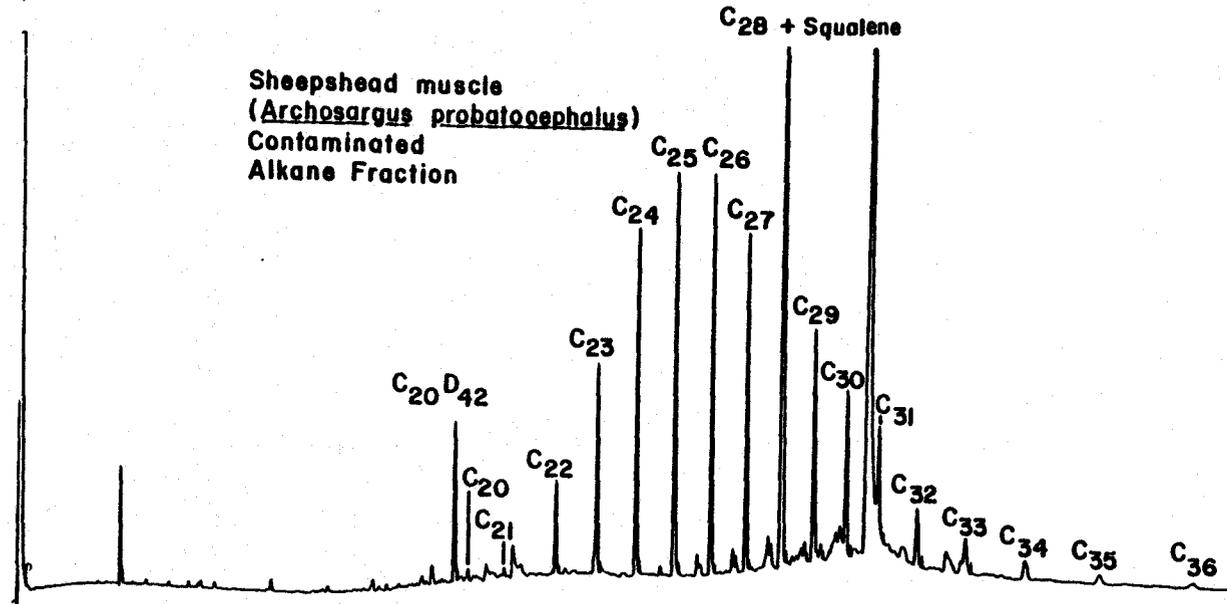


Fig. 20 Gas chromatogram of alkane fraction of contaminated sheephead (A. probatocephalus) muscle sample

2.4.1-78

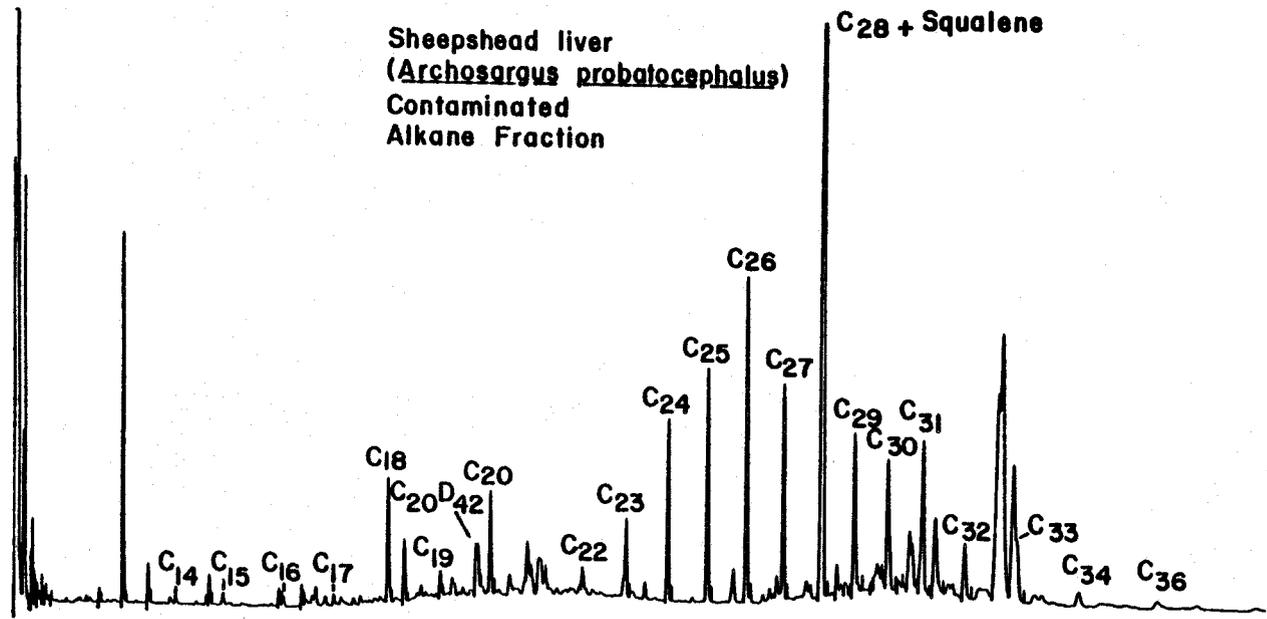


Fig. 21 Gas chromatogram of alkane fraction of contaminated sheepshead liver

3.5.2. Spadefish (*Chaetodipterus faber*)

A gill sample analyzed showed a small quantity of n-alkanes from C₁₂ to C₂₅ with C₁₅ predominating (Figure 22). A large amount of pristane (1.6 ppm) was also observed. It is probable that there were plankton associated with the gill and may account for the high pristane content.

Livers, like the gill, tended to have higher concentrations of C₁₅, C₁₇, and pristane than other alkanes (Figure 23). This may be due to consumption or ingestion of organisms which biosynthesize odd-carbon alkanes and produce pristane. The mean alkane concentration in livers was 1.96 ppm, and it was 0.55 ppm in muscle (Figure 24).

Spadefish feed primarily on particulates in the water column and are probably ingesting many of the entities responsible for biogenic alkanes in the sediment traps. Compared to sheepshead, spadefish showed a much lower mean concentration of alkanes by about 4 ppm in each tissue.

3.5.3. Red Snapper (*Lutjanus campechanus*)

We had planned to analyze liver and muscle samples from 25 fish collected in the summer and 25 collected in the winter. However, we were provided with only 24 specimens in the summer, one of which had a liver which was too small for analysis.

From the fish collected in the summer, 5 out of 23 livers were found to have distinctive petroleum alkane profiles (Figure 25) while the same type of profile was observed in 6 of 24 muscle samples (Figure 27). Uncontaminated liver and muscle specimens are shown in Figures 26 and 28 for comparison. Squalene was the most prominent hydrocarbon in both muscle and liver but more so in the liver (Figure 26). The mean alkane concentration for livers was 12.7 ppm. Disproportionate amounts of odd-carbon alkanes, C₁₇, C₁₉, and C₂₁ were seen in many liver and muscle samples. Again this may be a

2.4.1-80

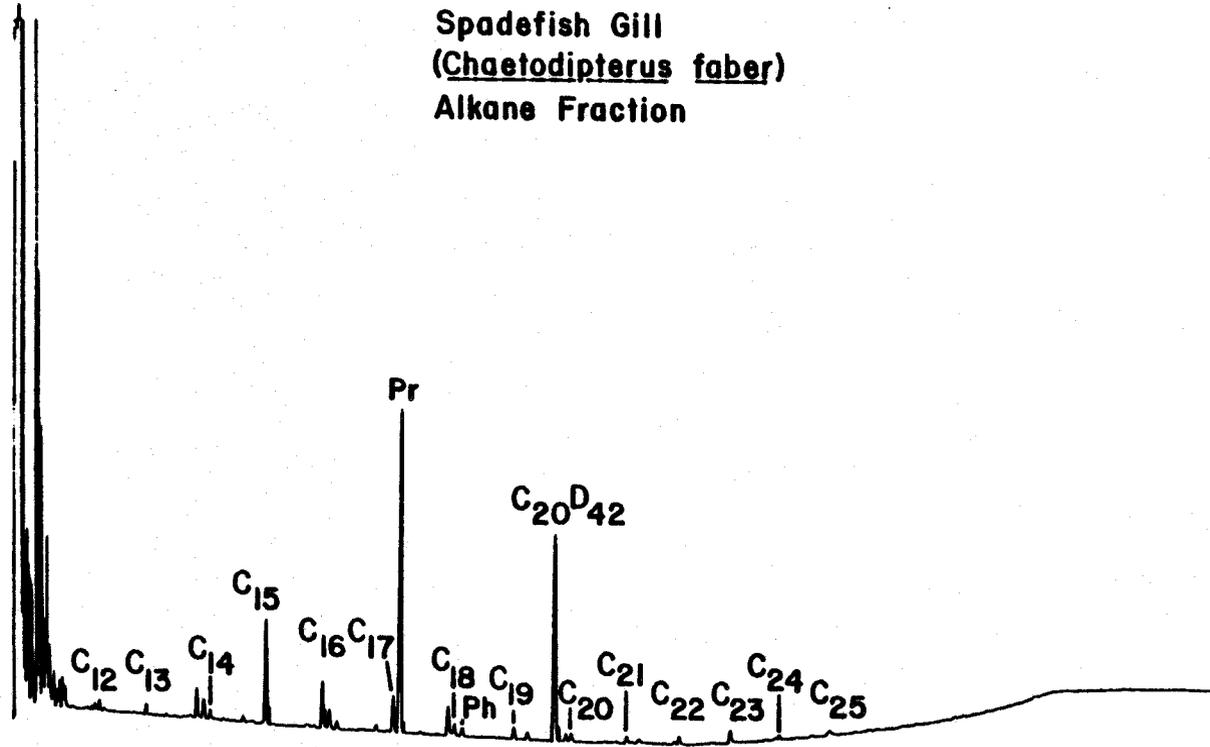


Fig 22. Gas Chromatogram of alkane fraction of spadefish (*C. faber*) gill

2.4.1-81

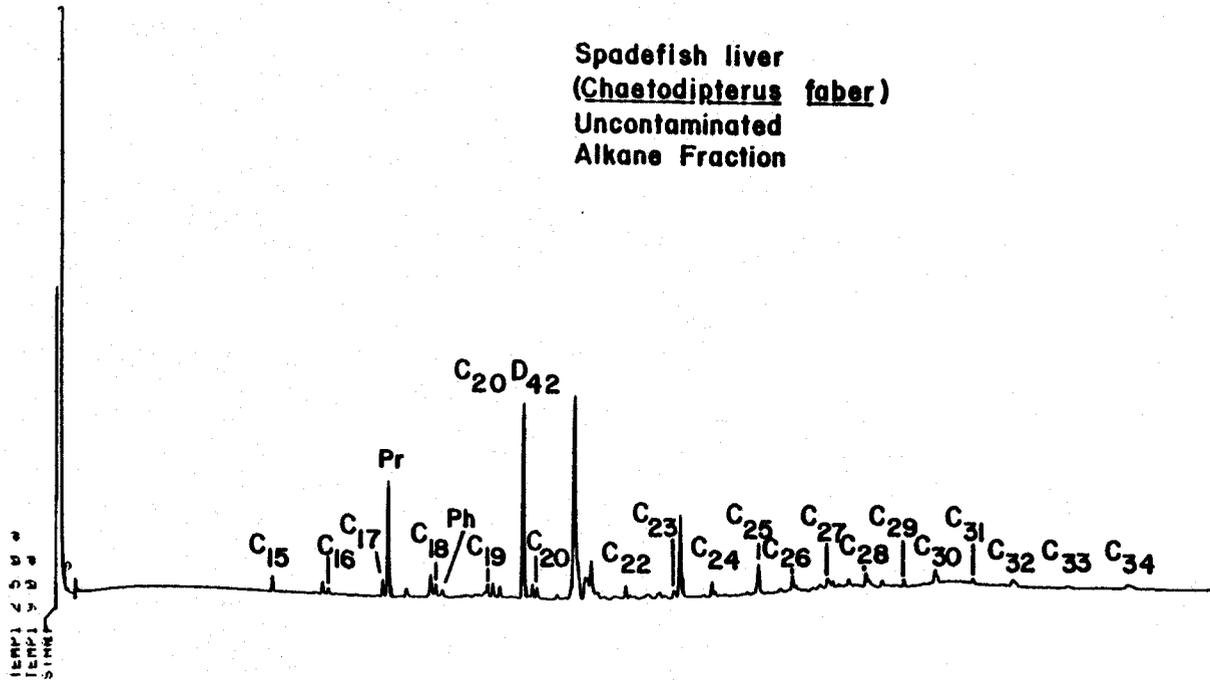


Fig. 23 Gas chromatogram of alkane fraction of spadefish liver

2.4.1-82

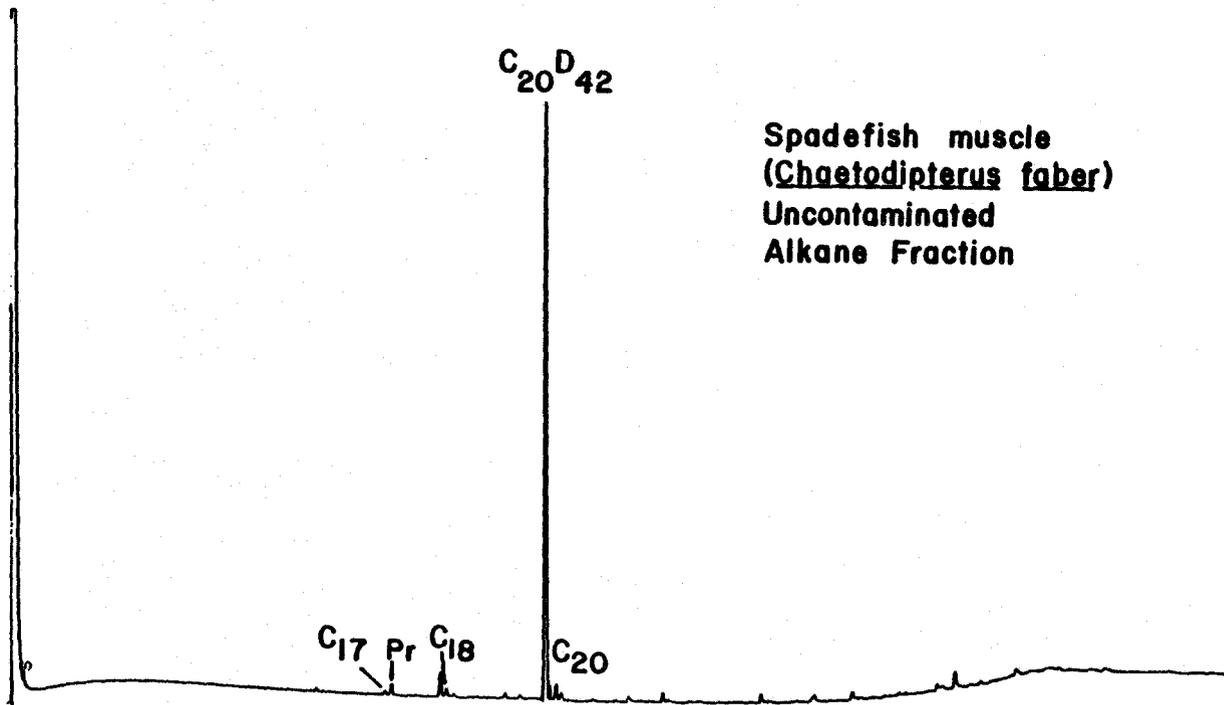


Fig. 24 Gas chromatogram of alkane fraction of spadefish muscle

2.4.1-83

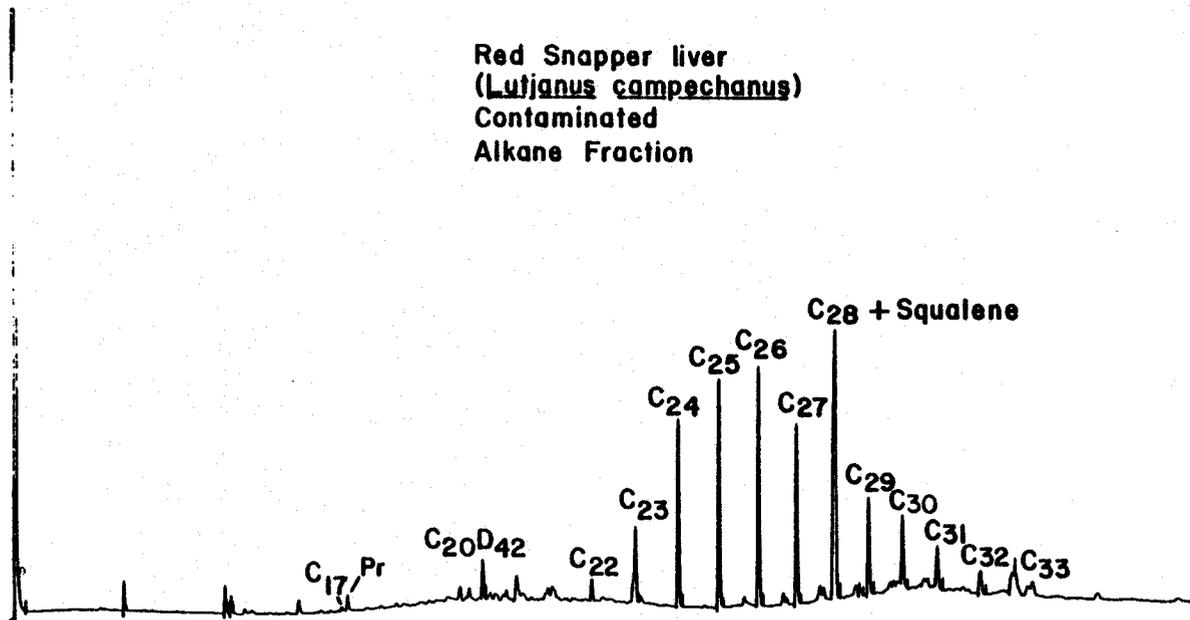
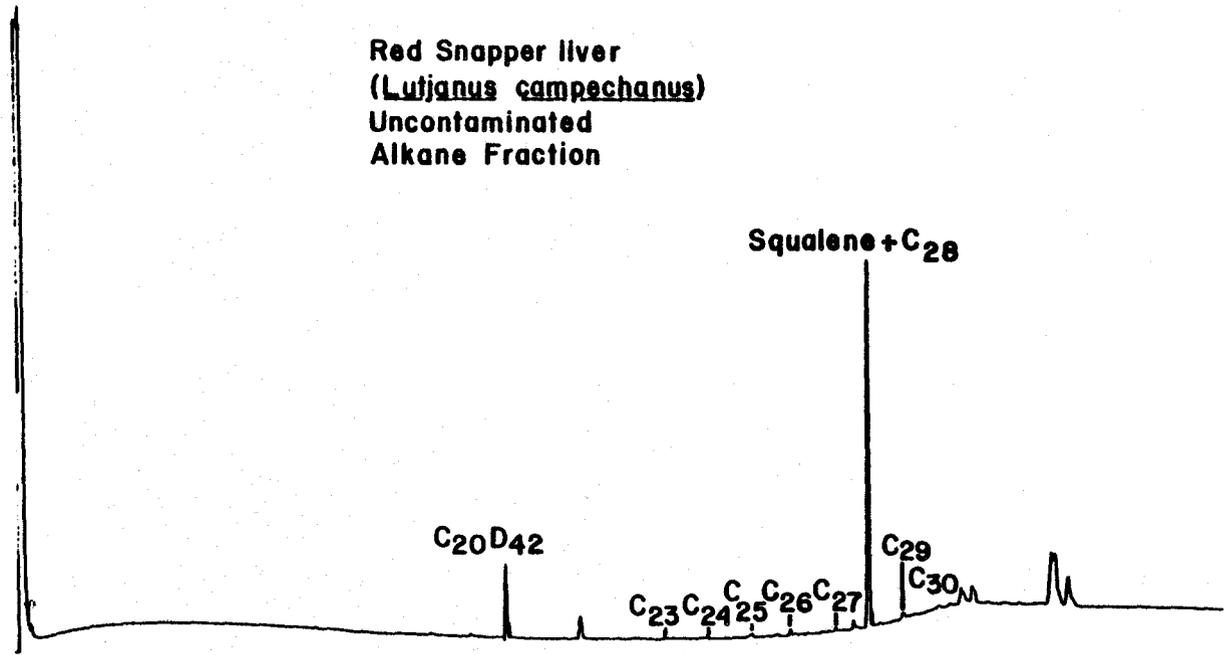


Fig. 25 Gas chromatogram of alkane fraction of contaminated red snapper (L. campechanus) liver



2.4.1-84

Fig. 26 Gas chromatogram of alkane fraction of red snapper liver

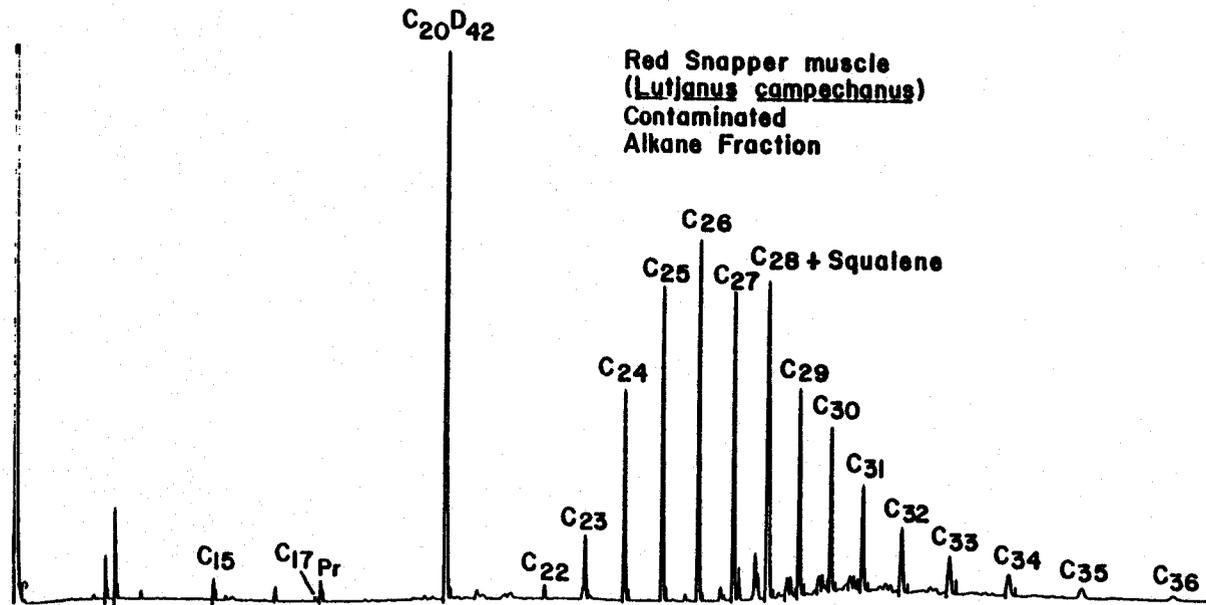


Fig. 27 Gas chromatogram of alkane fraction of contaminated red snapper muscle

2.4.1-86

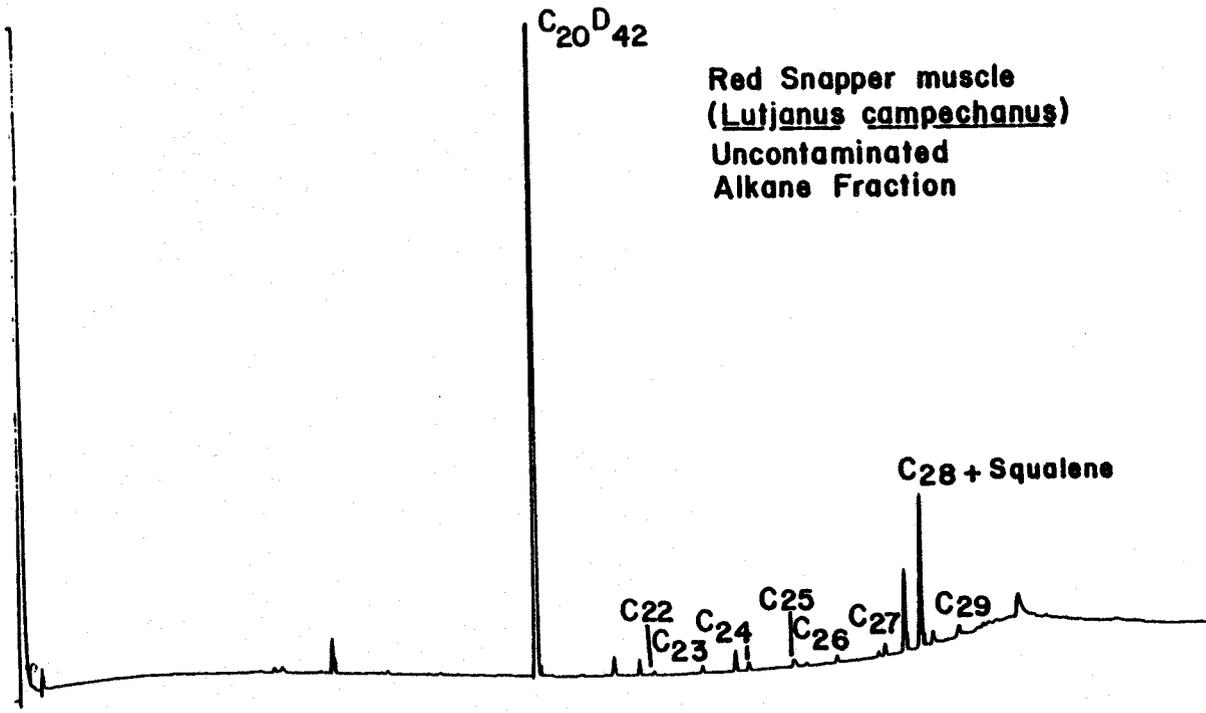


Fig. 28 Gas chromatogram of alkane fraction of red snapper muscle

consequence of dietary intake of plants and animals with odd-preference alkanes.

Of the specimens collected during the winter, only one exhibited any evidence of contamination by oil. The muscle sample analyzed contained a very high concentration (68.6 ppm) of petroleum-like C₁₉ to C₂₂ alkanes. Curiously, the liver contained no petroleum-like alkanes, suggesting that the petroleum contaminants of the muscle were topical. The mean concentrations of biogenic alkanes in liver and muscle samples were, respectively, 83.5 and 19.5 ppm.

3.5.4. Longspine Porgy (*Stenotomus caprinus*)

Twenty-five animals collected during the summer were analyzed for hydrocarbons. Most profiles showed some evidence of oil contamination, with smooth petroleum profiles and concentration maxima between C₂₀ and C₃₀ (Figure 29), while the remainder did not (Figure 30). As with the other fish, there was evidence of biogenic alkanes as seen by an odd-carbon preference early in the chromatogram and predominance of pristane and phytane over C₁₇ and C₁₈. In spite of petroleum contamination in many samples, this species showed a much lower mean alkane concentration (1.37 ppm) than crested blennies (*Hypleurochilus geminatus*; section 3.5.5.) collected at the same time (mean = 6.79). Both of these fish inhabit empty barnacle shells and are generally closely associated with the platform, feeding on algal mat attached to barnacle shells. The porgy feeds on invertebrates, also, since it is an omnivore.

3.5.5. Crested Blenny (*Hypleurochilus geminatus*)

Virtually all of the 25 animals collected during the summer showed contamination with petroleum alkanes (Figure 31). Concentration maxima were usually C₂₀ to C₂₉, with some profiles having a maximum at C₃₁. Blennies,

2.4.1-88

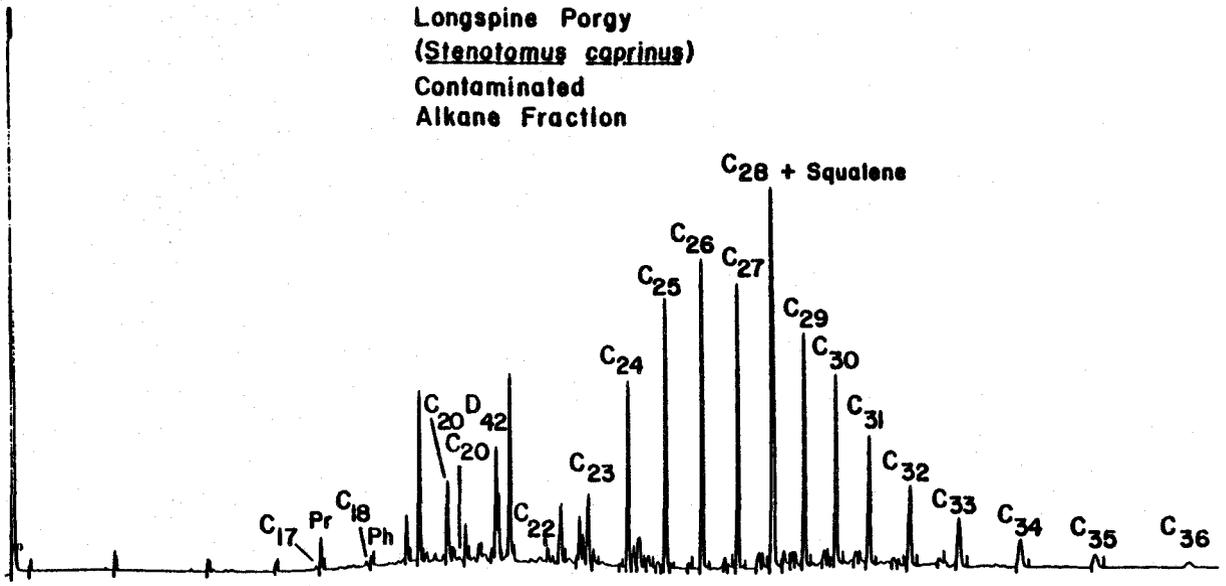


Fig 29. Gas Chromatogram of alkane fraction of contaminated longspine porgy (*S. caprinus*)

2.4.1-89

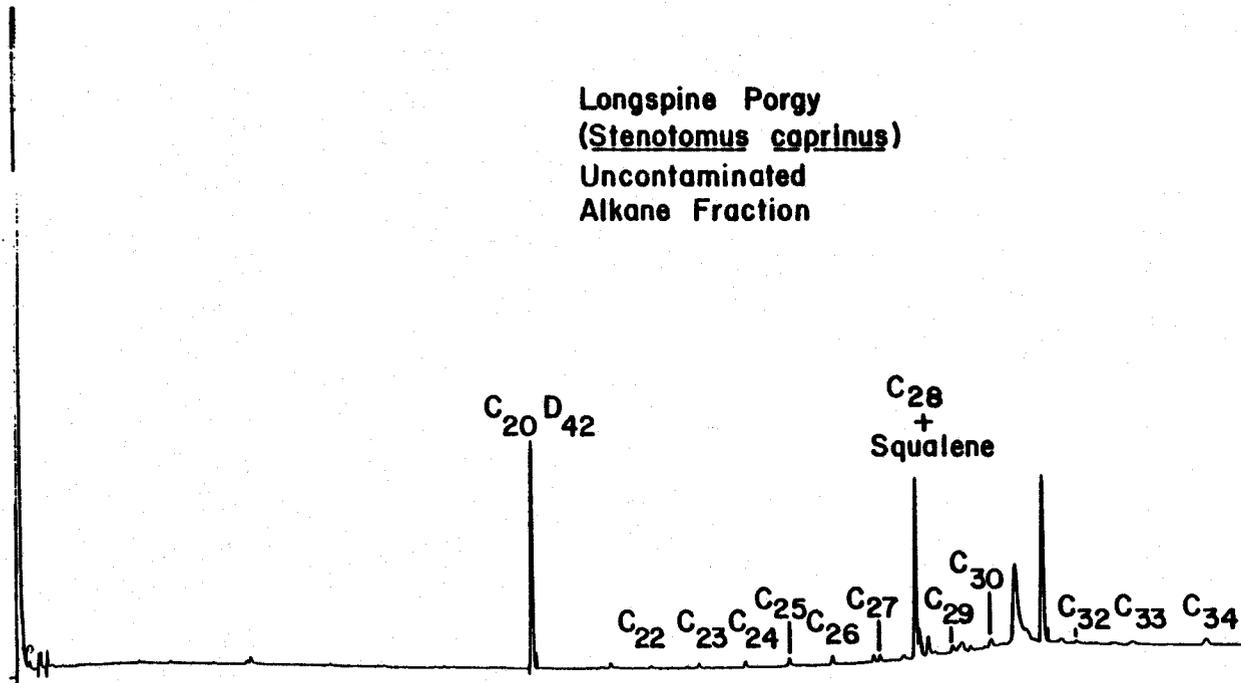


Fig. 30 Gas chromatogram of alkane fraction of longspine porgy

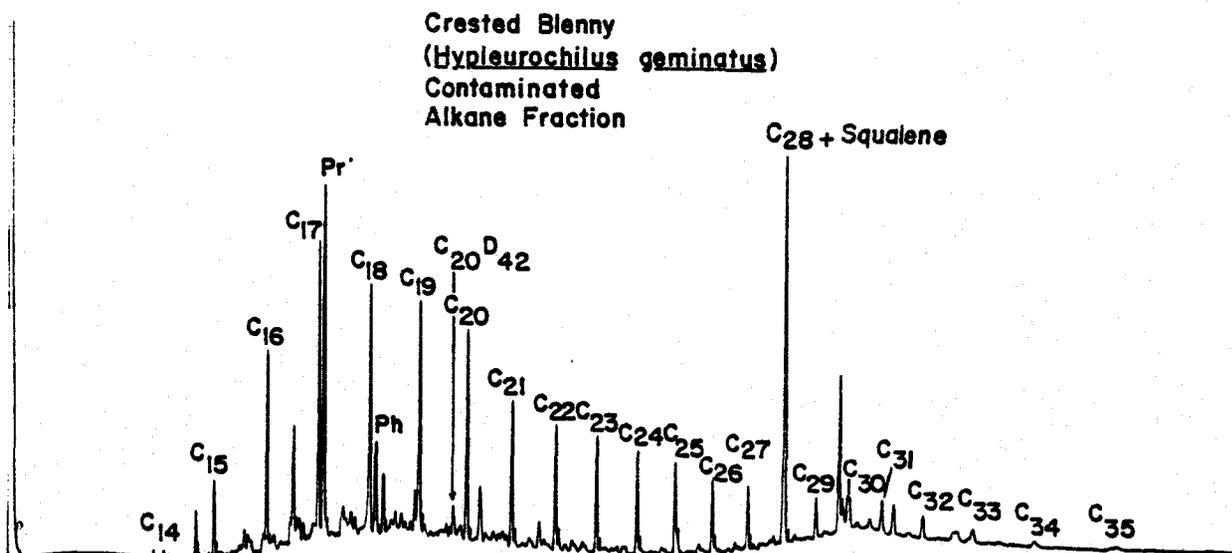
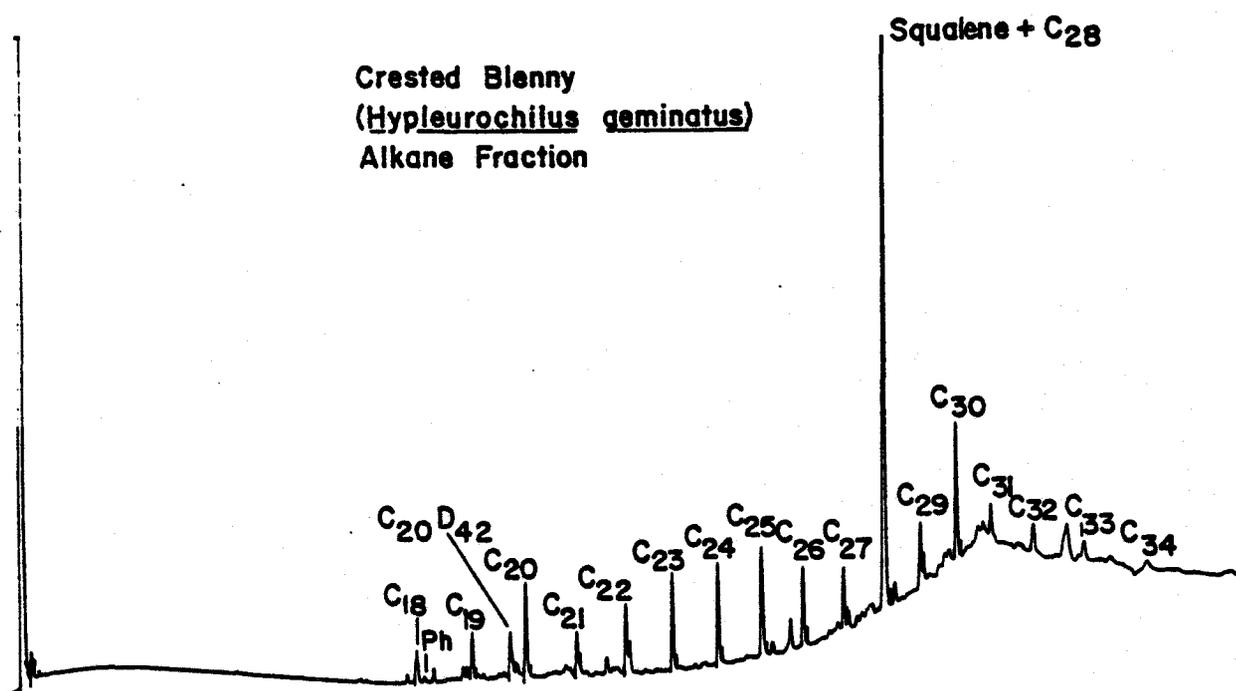


Fig. 31 (upper) Gas chromatogram of alkane fraction of least contaminated crested blenny. (lower) Gas chromatogram of alkane fraction of freshly contaminated crested blenny

unlike other fish examined, tended to have more of the lighter n-alkanes (from C₂₀ to C₂₅) than the heavier ones. This is probably a result of exposure to fresh oil since they are closely associated with the production platforms and rarely leave the area. The mean alkane concentration in this species (6.79 ppm) was considerably higher than mean alkane concentrations in other fish.

The situation was somewhat different in the winter, when only 15 of the 25 blennies analyzed contained petroleum alkanes. The mean concentration (2.33 ppm) in the contaminated fish was lower than in the summer. However, the alkanes encountered were relatively fresh and unweathered. Ten of the contaminated fish had alkane concentration maxima at C₁₇, and the other five had maxima in the region C₁₅ to C₁₈.

3.5.6. Summary

Crested blennies were generally the most highly contaminated fish, and the petroleum alkanes that they contained were always fresh and relatively unweathered. The alkane profiles to these fish (Figure 31) were very similar to those of the fouling mat (Figure 34) which provides a major component of their diet.

Of the larger fish, sheepshead were usually the most heavily contaminated and spadefish the least contaminated, with red snapper and longspine porgy intermediate in degree of contamination.

It appears that livers serve as a repository for alkanes, as evidenced by the higher concentrations of these compounds in livers than in muscle samples. This is not unexpected since the liver has a high lipid content and serves as a center for metabolism of many compounds, including chemical pollutants.

Concentrations of petroleum alkanes in fish tissues were generally higher in the summer than in the winter. This observation is discussed in more detail below (Section 4).

Alkane concentrations in red snapper (L. campechanus) were measured over a range of 4 orders of magnitude for liver and muscle samples. Mean alkane concentrations, however, fell within the same order of magnitude as sheephead. Many liver and muscle alkanes were of biogenic origin as evidenced by disproportionate amounts of C₁₅, C₁₇ and C₂₁.

Mean alkane concentrations in longspine porgy (S. caprinus) were close to those for red snapper and sheephead, but profiles showed evidence for petroleum contamination in most of the animals.

Alkane levels in crested blenny (H. geminatus) were generally higher than those in other fish with a mean alkane concentration 2 to 3 ppm above sheephead and longspine porgy, and more than 4 ppm higher than spadefish. Blennies generally showed an accumulation of fresh oil evidenced by maximum concentrations of light alkanes in most samples.

It appears that livers may in fact serve as a repository for alkanes as evidenced by higher mean alkane concentrations than in muscle. This is reasonable since the liver serves as a center for metabolism of many compounds, including chemical pollutants, and is high in lipid content.

3.6. SHRIMP

Whole shrimp were analyzed for hydrocarbon content. They were obtained from a March 8, 1979 trawl in close proximity to production platform 296-B.

3.6.1. Sugar Shrimp (Trachypenaeus similis)

Most profiles from shrimp showed low levels of hydrocarbons (0.26 to 0.66 ppm) with the exception of one specimen with a total alkane content of 9.7 ppm. The mean alkane concentration was 2.3 ppm. Most samples showed a C₁₇/pristane ratio much lower than 1, indicating substantial quantities of pristane in the animal. An odd-carbon preference was always observed.

3.6.2. Summary

While shrimp are of great commercial importance, especially on the upper Texas Gulf Coast, past studies, as well as this one, have not indicated significant contamination by hydrocarbons from offshore facilities. Shrimp are normally highly mobile in shelf waters affording them ample opportunity for depuration of ingested hydrocarbons (Neff et al., 1976). Since they are only found occasionally in the area under study, it would be difficult to attribute hydrocarbon contamination (if any) to Buccaneer oil.

3.7. Barnacles

Barnacles (Balanus tintinnabulum) were collected during each of the four seasons from four structures: production platform 296-B, production platform 288-A, flare stack 296-F, and well jacket 288-5. All were collected at the level of the air/sea interface, at a depth of less than 1 m. The flesh from 3-10 animals was pooled for each analysis, with five analyses being performed for each structure and in each season.

Only one analysis of barnacles collected at platform 296-B during the summer revealed any semblance of petroleum contamination, and the specimens collected from this location during the other seasons were devoid of contamination.

All five analyses performed on specimens collected from platform 288-A during the summer indicated various degrees of contamination, but the presence of large amounts of the biogenic alkanes C_{15} , C_{17} , C_{21} , C_{27} , and pristane made the precise quantitation of petroleum alkanes impossible. No petroleum alkanes were encountered in barnacles from platform 288-A in the other three seasons.

Petroleum alkanes were clearly present in all five analyses of barnacles collected from flare stack 296-F during the summer (Figure 33). One

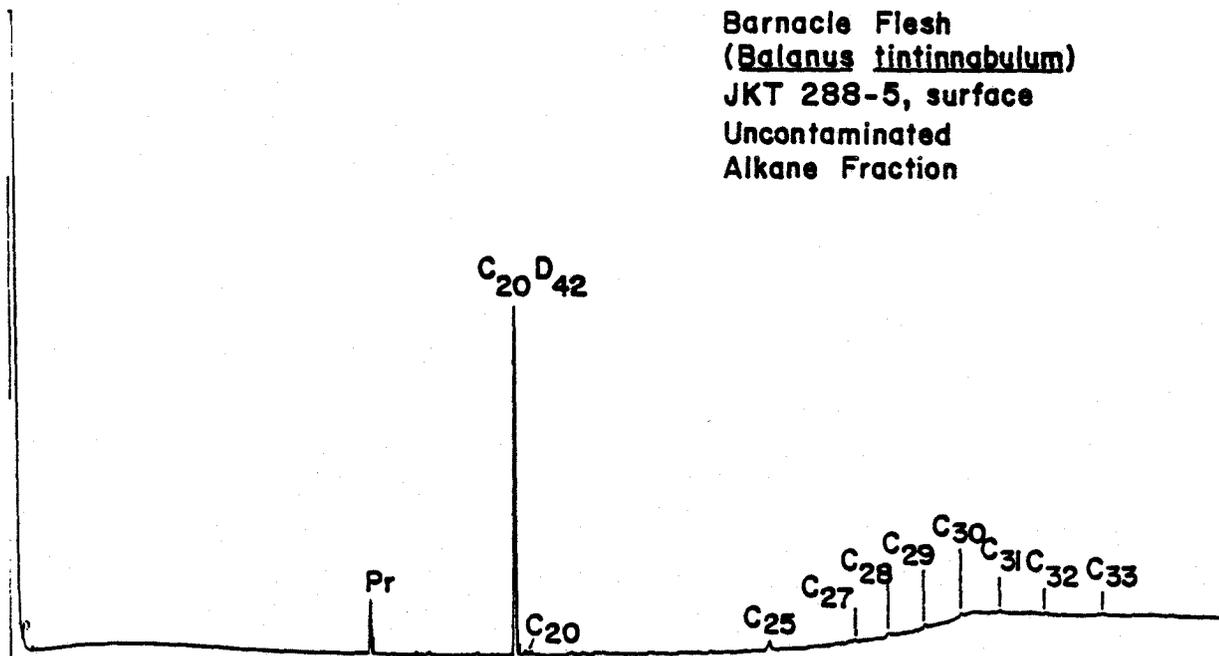


Fig. 32 Gas chromatogram of alkane fraction of barnacle (B. tintinnabulum) collected from well jacket 288-5 at the surface

barnacle sample contained 16 ppm of petroleum alkanes, while the mean concentration in the other four was only 1.02 ppm. Petroleum alkanes were not found in barnacles from this location during the other three seasons.

No petroleum alkanes were found in barnacles from well jacket 288-5 during the summer, fall, and winter. During the spring, however, four of the five samples analyzed were contaminated (mean, 3.15 ppm; range, 2.19-3.74 ppm). The alkanes were extensively weathered, with a concentration maximum at C₂₉ in each case, and it was not possible to determine whether they derived from Buccaneer oil.

In summary, the barnacles from all four structures, with few exceptions, did not contain measurable amounts of petroleum alkanes. They did contain the biogenic alkanes C₁₅, C₁₇, C₂₁, and C₂₇, as well as large amounts of pristane, typical of animals filter-feeding on phytoplankton and detritus. Even animals from the discharge leg of the brine-discharging platform 296-B showed little petroleum contamination.

3.8 FOULING MAT

Fouling mat was scraped from barnacle shells attached to the discharge leg and east leg (about 10 m from discharge) of production platform 296-B. While fouling mat represents no one species of plant or animal, it is ecologically important since many other organisms feed on it (e.g., sheepshead, section 3.5.1).

Mat samples typically showed smooth alkane profiles with occasional odd-carbon alkanes C₁₅, C₁₇, C₁₉, and C₂₁ interrupting continuity. The highest concentration of alkanes was observed in mat samples from the discharge leg but at a depth of 3 m. The mean concentration for these samples was a very high 122 ppm. Obviously, these samples were contaminated with oil directly and all showed signs of fresh oiling with

Barnacle Flesh
(*Balanus tintinnabulum*)
Flare Stack 296, surface
Contaminated
Alkane Fraction

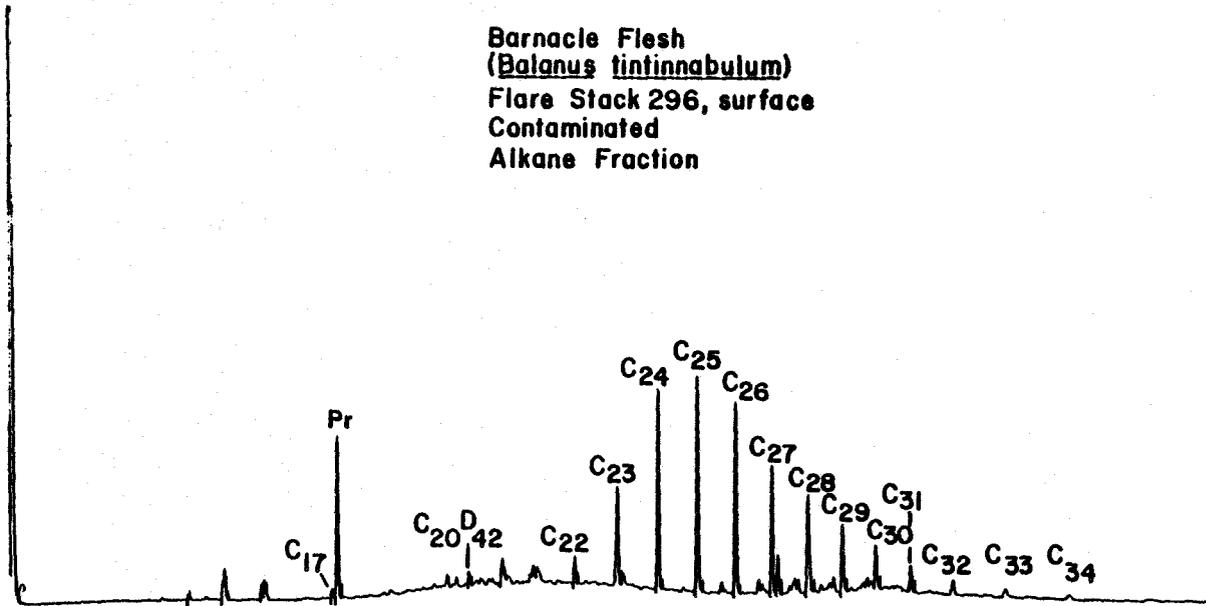


Fig 33. Gas Chromatogram of alkane fraction of contaminated barnacles collected from flare stack 296 at the surface

2.4.1-96

profiles having concentration maxima at C₁₅. These samples did not show the biogenic odd-carbon preference since the petroleum alkanes predominated (Figure 34).

At the surface, mat samples on the discharge leg showed some amount of petroleum alkanes but quantities of odd-carbon alkanes were prominent in the profile. The mean was 1.1 ppm compared to 220 ppm at a depth of 3 m.

On the east leg, mat samples collected at the surface and at a depth of 3 m were similar, with the exception of a sample from the 3 m depth showing background petroleum alkanes. Again, matters were confused by the presence of prominent odd-carbon alkanes. The mean alkane concentration for the east leg at the surface was 6.8 ppm, and at 3 m depth was 12 ppm. Typical of the east leg fouling mat alkane profiles is Figure 35.

Since some fouling mat samples were contaminated with large quantities of petroleum alkanes and sheepshead feed on fouling community, it is highly probable that the higher levels of alkanes found in these fish are due to ingestion of contaminated mat. Also it is probable that, since mat at a depth of 3 m is not exposed to the same wave "scrubbing" experienced by intertidal mat at the surface, this could account for the much higher concentrations at the 3 m depth.

4. SUMMARY

4.1. EFFLUENTS

The major source of petroleum and sulfur contamination in the Buccaneer Field is the discharged brine. The sulfur is mainly deposited in the surficial sediments while petroleum hydrocarbons are distributed throughout the ecosystem.

2.4.1-98

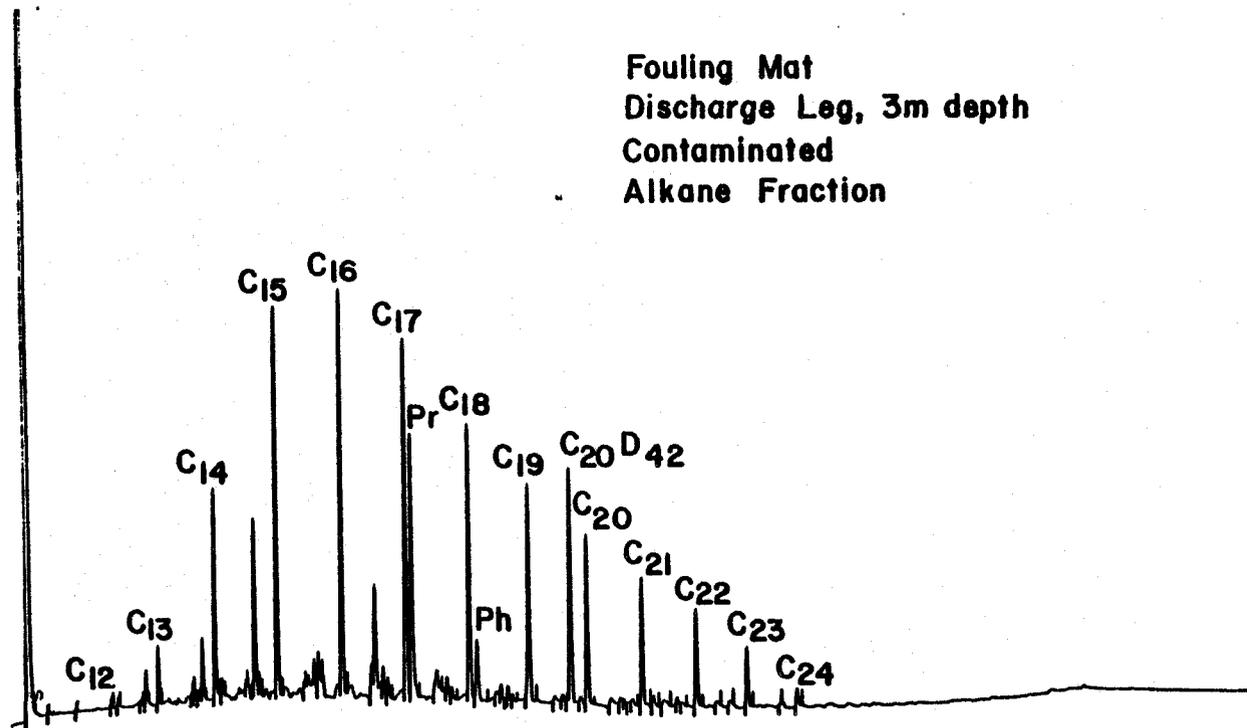


Fig 34. Gas Chromatogram of alkane fraction of freshly contaminated fouling mat from brine discharge leg at a depth of 3 m

2.4.1-99

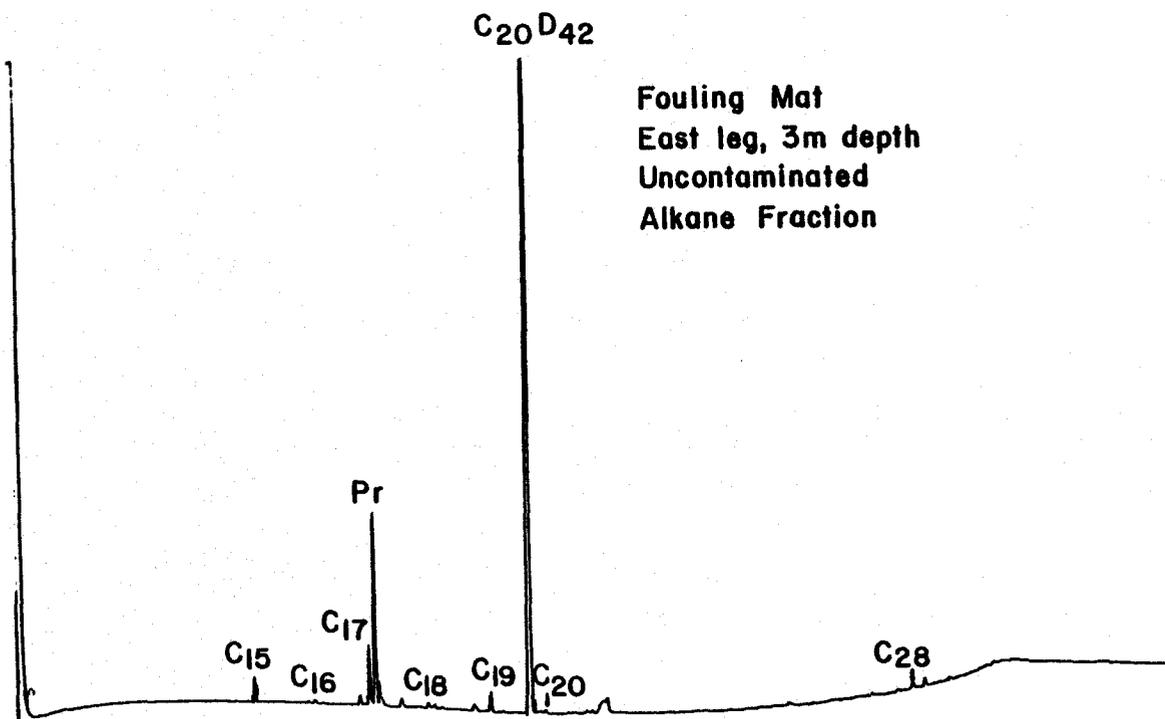


Fig. 35 Gas chromatogram of alkane fraction of fouling mat from east leg at 3 m depth

The hydrocarbon components of the discharged brine are similar to those of crude oil but are found in much lower concentrations. The organic compounds detected and identified ranged from 5 to 29 carbon atoms and included alkanes, aromatic hydrocarbons, and ketones. Dodecane to pentadecane were usually in highest concentration in the alkane fractions while C₃- and C₄-benzenes were highest in the aromatic fractions. Benzene was the major volatile hydrocarbon identified in the brine.

Elemental sulfur is by far the major contaminant discharged, but its effects on the ecology of the study area, if any, are not known with certainty. Circumstantial evidence points to sulfur serving as an essential nutrient for bacteria, thus enhancing biomass at the base of the marine food web.

The potentially hazardous acrolein biocide used in production operations has not been detected in the brine. Approximately one quart (0.946 liter) of acrolein is injected into the flow stream daily. Since acrolein has a specific gravity of 0.8410, this corresponds to an acrolein concentration of 5.3 ppm in freshly treated brine at the average brine flow of 1000 bbl/day. This is the maximum concentration of acrolein that could be present in brine treated at the rate of one quart per thousand barrels. Acrolein is reactive to many chemicals (including water) and is highly volatile so it is not unreasonable to assume that its concentration will be substantially lower prior to scavenging. The quantity of scavenger employed is more than ten times that required to remove all of the acrolein originally added, so the actual concentration of acrolein remaining in the discharged brine would be very low indeed. We did not detect any. Thus, acrolein is not expected to pose a threat to the environment if handled in this manner.

Other platform effluents have been observed to carry insignificant concentrations of contaminants measured, and appear to have no deleterious effects on the environment.

4.2. THE WATER COLUMN

When contaminants from the discharged brine first enter the environment, they do so at the air/sea interface. Most models of contaminant dispersion would assume either that the receiving water is static or that it is flowing past the discharge point at a constant speed. In the former case, the contaminants would spread in all directions and their concentrations would decrease with increasing distance from the discharge point. In the latter case, a contaminant "plume" would develop down-current from the discharge point. The models could then be used to determine the contaminant concentration at any location, if the current speed is specified, and environmental impact could be deduced.

Dye studies have tended to confirm the validity of this approach. When a steady stream of dye (Rhodamine G) was poured into the sea at the discharge point under conditions of relatively high current flow, a long, narrow plume did indeed extend down-current and, under relatively calm conditions on another occasion, the dye spread out around the platform and down into the water column (Armstrong and Hamilton, 1979).

Our water samples were all collected under relatively calm conditions since the divers could not work during conditions of strong current flow. Under model conditions, we should have been able to discern concentration gradients of contaminants, yet we did not. There were several possible reasons for this. First, the brine discharge is not continuous, but intermittent, so the contaminant concentrations would be expected to vary accordingly. Second, the concentration of contaminants in the brine is not

constant (the alkane concentration ranged from 0.9 to 4.7 ppm in ten samples collected during a 36-hour period in September, 1978, for example), further diminishing the possibility of finding any static concentration gradient. Third, the seawater samples were not collected simultaneously, but over a period of several hours. If the contaminant concentrations were changing as a consequence of intermittent discharges of effluent with varying concentration, concentration gradients would be confounded further. Fourth, the concentration gradients would be perturbed by wave action and turbulent flow around the legs of the platform. In summary the mixing zone is a highly unstable component of the Buccaneer Field ecosystem.

In light of the foregoing observations, it is not surprising that we were unable to discover any clearly-defined, stable concentration gradients of contaminants in the water column. However, we usually found moderately high concentrations of contaminants (up to 1.3 ppm alkanes) either below the discharge pipe or within 3 m of it, while contaminant concentrations were much lower at greater distances from the mixing zone.

One additional observation concerning our data on contaminants in the water column relates to their composition. We were able to detect the lighter components of the brine in the mixing zone but, even at a distance of 8 m from the discharge pipe, they had become dissipated and only the heavier components remained. While the lighter components are more soluble in water, it seems unlikely that they could be dispersed preferentially by diffusion through the water column. It is also unlikely that they would be preferentially degraded chemically or metabolically at a sufficiently high rate to account for the observed distributions. Rather, it seems likely that preferential evaporation of the lighter components takes place very rapidly. Since the lighter components are the most toxic, this observation should not be ignored when assessing the potential ecological impact of the discharge.

We also wish to indicate one further disparity between the models, the dye studies, and the "real world." Contaminants in the brine are lighter than water and, in the absence of turbulence, would tend to float at the air/sea interface. Indeed, we rarely found significant concentrations of contaminants in samples from sub-surface locations. However, the dye used to delineate the discharge plume is water-soluble and diffused down into the water column. If the data from dye studies are used to calculate contaminant concentrations, estimates for the air/sea interface will be too low, and for the water column will be too high. Moreover, any model which assumes complete vertical mixing of contaminants in the water column is clearly inappropriate and could also lead to erroneous conclusions.

In summary, we would be reluctant to place much reliance on the results of dye studies or on predictions generated by inappropriate models. We feel that it is more reasonable to employ actual experimental observations during assessments of environmental impact.

4.3. SURFICIAL SEDIMENTS

Sediments can be resuspended and transported by wave action and currents. However, this component of the ecosystem is much more stable than the water column. Thus, concentration gradients of contaminants were not difficult to find in the vicinity of the production platforms. We did observe that absolute concentrations of contaminants in the sediments could change by as much as an order of magnitude from day to day, whereas the relative concentrations reflecting concentration gradients were maintained.

The presence of such static "pools" of contaminants below the production platforms might generate concern, but for the fact that they are rather small. We were unable to detect significant amounts of contaminants in benthic organisms. Resuspension of sediment contaminants into the water column also appeared to be of no major consequence.

Our curiosity was aroused concerning the mode of transport of contaminants to the sediments since, under ideal conditions, they would float at the air/sea interface. Sediment traps collected both petroleum alkanes and biogenic alkanes and the most likely route through the water column seems to be via incorporation into fecal pellets.

4.4. FISH

Among the fish examined, crested blenny (Hypleurochilus geminatus) had a higher level of oil contamination than all others. Since blennies (like longspine porgy, Stenotomus caprinus) are in close association with the production platform, this was expected.

Alkane levels in sheepshead (Archosargus probatocephalus) were lower than in the crested blenny but somewhat higher than in the other fish examined. Higher concentrations of alkanes in the sheepshead may have reflected an accumulation from oiled fouling mat, which makes up a large portion of the sheepshead diet.

Red snapper (Lutjanus campechanus) showed the greatest diversity in alkane concentrations for both liver and muscle with the mean below the mean alkane concentration in sheepshead and above that for spadefish (Chaetodipterus faber). Characteristically, many alkane profiles from muscle and liver showed disproportionate amounts of the biogenic hydrocarbons C₁₅, C₁₇, and C₂₁.

Spadefish (Chaetodipterus faber) contained the lowest amounts of alkanes. This observation may be due to the spadefishes' reliance on suspended particulates instead of other large organisms for sustenance. This would obviate a bioaccumulation phenomenon possible in animals which feed on contaminated organisms, as in sheepsheads' consumption of contaminated fouling mat, for example.

Longspine porgy (Stenotomus caprinus) showed a similar mean alkane concentration to those for red snapper and sheepshead, but most of the animals were observed to have distinct petroleum alkane profiles.

4.5. SEASONAL VARIATIONS

Concentrations of contaminants in the discharges and in the water column were relatively constant throughout the year. Changes in contaminant levels in surficial sediments were quite small, and probably reflect the periodic resuspension and deposition of this material. In contrast, there were marked changes in the degree of contamination of fish.

The "winter" samples were collected during March, 1979, and contaminant levels in these fish were very much lower than in samples collected previously.

Crested blennies were found for the first time that did not contain petroleum alkanes: 40% of them were uncontaminated, and the remaining 60% contained somewhat lower contaminant concentrations than we had found before. Only 4% of the red snappers were contaminated, compared with 22% in the summer. Almost half of the sheepshead collected during the summer were contaminated, but no contaminated sheepshead were found in the winter.

It is, perhaps, possible that the difference in contaminant levels in sheepshead could be attributed to a change in diet. These fish consume swimming crabs during the summer, but graze on the fouling community during the remainder of the year.

We are unaware of any analogous seasonal change in the diet of the red snapper.

The data obtained for the crested blennies provide a possible clue to the elucidation of this phenomenon. The appearance of the petroleum alkane profiles in these fish was similar in the two seasons, yet the concentrations

were lower in the winter. This suggests that the nature of the diet was similar throughout the year, but that it was less contaminated in the winter: it appears that blennies feed on the smaller components of the fouling mat that contain relatively fresh oil. Since the discharge of contaminants from the platforms was not diminished during the winter, it seems likely that contaminants were being removed from the study area more effectively.

The winter of 1978-79 was not as cold as the winter of the first full year of the study (1976-1977), but it was characterized by recurrent strong winds and, consequently, heavy seas and strong currents. This was the main reason why the "winter" samples were not collected until March, 1979. It is tempting to speculate that this severe weather resulted in greater dispersion of contaminants than had hitherto been normal. Any decrease in contaminant levels near the base of the food web (fouling fauna, blennies) would also be reflected in the larger fish (sheepshead, red snapper).

If this explanation were valid, one might suspect that the contaminant load in the surficial sediments would also be diminished. However, the relatively fresh nature of these contaminants is indicative of an efficient transport mechanism through the water column so they could, presumably, be replenished quite rapidly when meteorological conditions improve.

4.6. CONCLUSIONS

A clearer picture is emerging of the size and variability of the several pools of contaminants in the Buccaneer Field region. There appears to be a transient pool of contaminants in the mixing zone below the discharge pipe and a larger, but still unstable, pool of contaminants in the surficial sediments.

The degree of weathering of contaminants provides a clue to their origin. Evaporation of lighter alkanes takes place very rapidly as

contaminants drift away from the mixing zone, yet fresh oil is found in the surficial sediments. This is indicative of an efficient transfer of contaminants from the mixing zone through the water column. The fouling mat and the blennies which feed upon it contain relatively fresh oil, whereas fish higher in the food web contain oil which is more weathered.

Hydrocarbons are not found in concentrations high enough to elicit concern for the ecological health of the area, and discharged sulfur may act as a nutrient. The use of acrolein as a biocide appears also to be an ecologically sound practice.

It is possible that environmental parameters associated with other oil fields might lead to differences in dispersion of contaminants and, consequently, the sizes of contaminant pools. A better understanding of transport phenomena is the major goal for the fourth year (1979-1980) of this study.

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