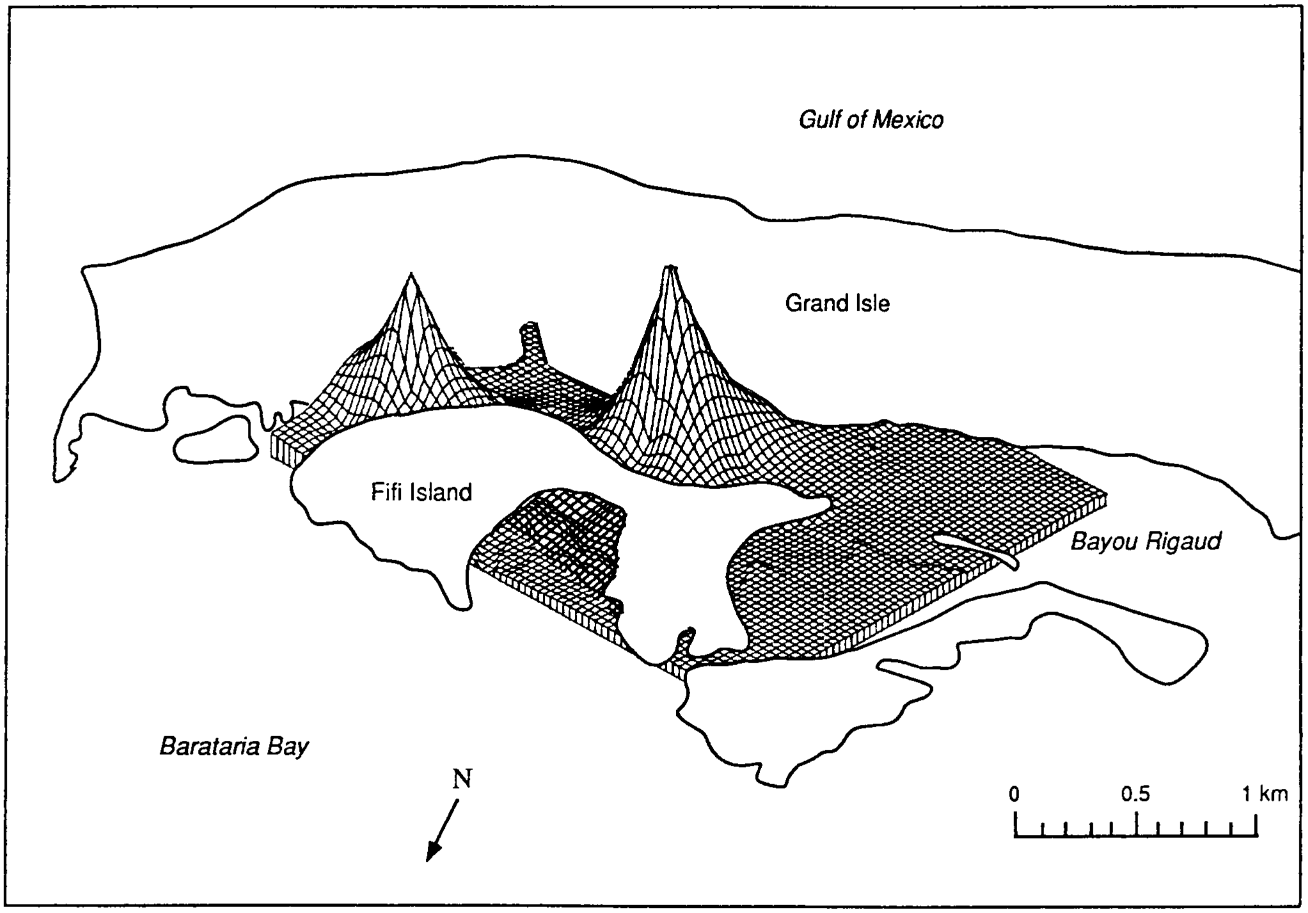
OCS Study
MMS 89-0031

An Analysis of Impacts

Produced Waters in Sensitive Coastal Habitats

Central Coastal Gulf of Mexico



U.S. Department of the Interior
Minerals Management Service
Gulf of Mexico OCS Region

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An Analysis of Impacts

Produced Waters in Sensitive Coastal Habitats

Central Coastal Gulf of Mexico

Editors

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and
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ABSTRACT

The objectives of this study were to a) quantify the location and characteristics of outer continental shelf (OCS) produced waters discharged into coastal environments of the Gulf of Mexico and b) provide an assessment of the environmental fate and effects of selected discharges. An inventory of produced water discharges based on records of regulatory agencies in Texas and Louisiana was compiled. The other Gulf states (Mississippi, Alabama, and Florida) do not permit the discharge of produced water into surface waters. A field assessment provided a general delimitation of the scope and nature of the impacts.

The total discharge of OCS-generated produced waters entering estuarine and coastal waters in the Gulf of Mexico is estimated to be approximately 435,000 barrels per day. These discharges are all in Louisiana and are located mainly along the southeastern Louisiana coast from the Atchafalaya Bay to the Mississippi River Delta. This total represents 22% of all produced waters discharged into Louisiana coastal waters, which is approximately 1,960,000 barrels per day and 13% of all produced waters discharged into all environments of the Gulf of Mexico which is estimated to be 3.4 million barrels per day.

Three sites representing large volumes of OCS-generated produced water discharges and different hydrological conditions were selected for field assessments: Bayou Rigaud, behind Grand Isle; Pass Fourchon; and the bay side of East Timbalier Island. There was no significant effect of elevated salinity resulting from the coastal discharges of OCS-generated produced waters, because the separation facilities are located close to the coast. The discharged produced water flowed to the bottom because of its high density, and the rate of its dispersion depended on tidal currents. These discharged produced waters contained elevated levels of dissolved and dispersed petroleum hydrocarbons, organic acids, and trace metals. Concentrations of the organic constituents may depend on the separation and treatment technologies employed. Substantial contamination of fine-grained bottom sediments with petroleum hydrocarbons was observed near the discharges at the three sites studied. Concentrations of polynuclear aromatic hydrocarbons in sediments exceeded apparent background levels by over an order of magnitude. Sediments that showed evidence of hydrocarbon contamination from produced water discharges extended several hundred meters to over one kilometer from the point of discharge. The effect was more extensive than reported for other produced water discharges that have been studied because of the lower physical dispersion in the bayous and canals into which the discharges take place and the larger volumes of produced water discharged. General surveys at the three sites showed evidence of biological effects in terms of reduced density and diversity of macrobenthic organisms in contaminated sediments and the accumulation of petroleum hydrocarbons in the tissues of filter-feeding bivalves proximate to the discharge sites.

ACKNOWLEDGEMENTS

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The research program, both the data compilation and field surveys, could not have proceeded without the cooperation of the oil and gas industry. Several companies provided additional information about produced water discharges that helped with our data compilation, notably Chevron Pipe Line Company, Chevron U.S.A., Exxon, Conoco, Phillips, Union, and Shell. The cooperation of Chevron Pipe Line Company, Chevron U.S.A., Exxon, and Conoco is further acknowledged for permission to study their facilities and for collection of produced water discharge samples.

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EXECUTIVE SUMMARY

INTRODUCTION

The goals of a larger study (Wicker et al. 1989) of which this report is a part were to assess the environmental impacts of outer continental shelf (OCS) oil and gas production facilities on sensitive onshore coastal habitats and to evaluate what the future impacts are likely to be in frontier areas of the Gulf of Mexico. Habitats of interest were barrier beaches and coastal wetlands (marshes and mangroves).

Approximately 95% of the oil and 98% of the gas produced from the Federally-controlled OCS comes from the central and western regions of the Gulf of Mexico. Utilization of these oil and gas fields necessitates a series of activities to explore, develop, produce and refine the petroleum products. Coastal wetlands are impacted by ancillary shore-based facilities, pipeline and navigation canals, operational spills and leaks, and operational discharges. Besides physical alterations to coastal wetlands (Turner and Cahoon 1987a,b, Wicker et al. 1989), produced water discharges occur in or near wetland areas. The results presented in this report address the impacts of OCS-generated produced waters in the developed OCS regions of the Gulf of Mexico.

During the production of oil or gas, water that is trapped within permeable sedimentary rock may also be brought to the surface. This water is called formation water, produced water or oilfield brine and may have salinity levels in excess of that of ambient sea water. In coastal Louisiana, produced waters range in salinity from 50 g/l (parts per thousand) to 150 g/l (Hanor et al. 1986) and may contain elevated levels of various inorganic (e.g. trace metals, sulfide and elemental sulfur) and organic (petroleum hydrocarbons and partially oxidized organics) substances.

The amount of produced water generated per volume of oil or gas varies greatly. In the case of new production from certain reservoirs, very little water is produced. In older fields with declining petroleum yields, the ratio of water to oil may increase dramatically to the point where many barrels of water are produced for each barrel of crude oil. Although once widespread, the discharge of produced waters into freshwater rivers and streams has now been virtually eliminated in the U.S. because of the effects of the high dissolved solids levels on those freshwater environments. The discharge of produced waters into brackish and marine waters, however, is widespread in the northwestern Gulf of Mexico region and in coastal Alaska (Neff et al. 1987). In addition, discharges of produced waters into the Mississippi and Atchafalaya Rivers and their freshwater distributaries and into some intermittent streams leading to Texas estuaries is currently allowed.

Much of the water produced in oil and gas extraction on the Federally-controlled OCS is separated and discharged from offshore production platforms. The regulation of these discharges is under the authority of the U.S. Environmental Protection Agency (EPA), National Pollutant Discharge Elimination System. However, large volumes of produced water generated in the OCS are piped ashore with the oil or gas streams and separated at shore-based or nearshore facilities. Resulting produced water is either discharged into nearshore or estuarine waters or reinjected into disposal wells. In an inventory of oil and gas drilling and production discharges in the Gulf of Mexico, Gianessi and Arnold (1982) reported that 328,470 barrels (barrel = 42 gallons or 159 liters) of produced water emanating from the OCS were discharged per day from coastal facilities. This approximated their estimate of the rate of discharge directly into OCS waters.

There have been a number of previous investigations of the effects of produced water on marine and coastal environments and organisms. These have been reviewed recently by

Middleditch (1984), Harper (1986), and Neff (1987, 1988). The environmental effects of OCS produced water discharges, and especially these large volume discharges into shallow coastal waters, however, have received little attention. The extent of the practice of onshore separation and disposal escaped recognition in the Environmental Impact Statements for OCS lease sales in the Gulf of Mexico until 1984. Based on the estimate of Gianessi and Arnold (1982), on the rationale that if produced water discharges had deleterious effects they would most likely be realized when the discharges were into shallow coastal waters with conditions of limited dilution, and on the lack of previous studies, Boesch et al. (1987) assigned a medium priority to this issue in their critical assessment of research needs related to the long-term effects of offshore oil and gas development.

The effects of the coastal disposal of OCS produced water should not be qualitatively different from those described in previous studies in coastal Texas and Louisiana (Armstrong et al. 1979, Harper 1986, Neff et al. 1989). However, because of the large volume of these discharges (tens of thousands to hundreds of thousands of barrels per day compared with thousands of barrels per day in the case of most other discharges studied) and confined waters into which the effluents are discharged, there may be quantitative differences in their effects. Concerns have been voiced about the wisdom of discharging such large volumes into confined coastal waters rather than into deeper offshore waters from which they originate.

The objectives of this study were to a) quantify the location and characteristics of OCS-generated produced waters into coastal environments of the Gulf of Mexico and b) provide an assessment of the environmental fate and effects of selected discharges. An inventory of produced water discharges based on records of regulatory agencies in Texas and Louisiana was compiled. The other Gulf states (Mississippi, Alabama and Florida) do not permit the discharge of produced water into surface waters. A field assessment provided a general delimitation of the scope and nature of the impacts.

PRODUCED WATER DISCHARGES

Although the data assembled here on the number, location and volume of produced water discharges are not necessarily exhaustive nor individually accurate, they represent the best current estimates of produced water discharges in state and OCS waters of Texas and Louisiana. Data sources were primarily the Louisiana Department of Environmental Quality (LDEQ) and the Texas Railroad Commission (TRC). Data for Louisiana were compiled from LDEQ produced water discharge permit applications. The facility name, location, oil and gas field, operator, reported volume of discharge, concentration of chloride, and wetland habitat type in which the discharge was located were compiled in a database. Vegetative habitat categories were based on the maps of Chabreck and Linscombe (1978) and Wicker (1980). The TRC data is updated monthly and provides information on the number of active or non-active disposal permits, the type of well, the operator, the disposal point, and the barrels per day water production. Discharge points were designated by major estuarine systems for both coastal Texas and Louisiana, and were identified as discharges into OCS waters or state waters. Territorial waters for Texas extend 3 leagues or about 9 miles and for Louisiana, 3 miles.

The total emissions of produced water into coastal and offshore environments in the Gulf of Mexico region is estimated at 3.4 million barrels per day, a rate considerably greater than previous estimates. Approximately 70% of these discharges enters the estuarine systems of Louisiana and Texas. The distribution of these discharges is widespread throughout the coastal zones of both states, but produced water discharges are more numerous and voluminous in southeastern Louisiana and on the upper Texas coast.

The total volume of produced waters discharged into Louisiana waters is projected to be 1,959,734 bbl/day. This includes 192,386 bbl/day discharged into the nearshore waters of the

Gulf of Mexico within the state territorial sea. The total volume of produced waters discharged into Louisiana estuarine waters is 1,767,348 bbl/d. There were 698 discharge facilities for which permit applications were received. When broken down by estuarine basin, the largest number of discharges are located in the Terrebonne and Barataria estuarine systems, with the largest aggregate volumes reportedly discharged located in the Chandeleur Sound, Mississippi River Delta and Barataria Bay estuarine systems. While the largest number and volume of coastal zone discharges in Louisiana are in the southeastern part of the state, significant produced water discharges were also reported in the Vermilion-Cote Blanche Bay systems. The majority of the produced water discharges in coastal Louisiana are small in volume. The modal class is 100 to 500 bbl/day and only 10% of the reported discharges are greater than 5,000 bbl/day. Discharges of various volumes are scattered throughout the entire Louisiana coastal zone, but obviously are clustered around major oil and gas fields.

Produced water discharges from coastal separation facilities handling oil-gas-water streams from the OCS contribute approximately 434,772 bbl/day and are located mainly along the southeastern Louisiana coast from Atchafalaya Bay to the Mississippi River Delta. The facilities discharging OCS produced water are few in number, but generally handle very large volumes because the product of numerous offshore wells is gathered and piped ashore to central treatment facilities. Several of these facilities have reported daily discharges which exceed 20,000 bbl/day and two facilities discharge in excess of 100,000 bbl/day.

The total volume of produced waters discharged into Texas waters is 823,575 bbl/day. This includes 87,721 bbl/day (11%) for those designated as "inland." The total volume of produced waters discharged into Texas coastal waters (inclusive of the 9-mile territorial limit) is 735,854 bbl/day. The total volume of produced waters discharged into Texas estuarine waters (exclusive of the offshore state waters) is 721,745 bbl/day. The totals for "estuarine" waters include some discharge points that are more inland that flow into tertiary bays or streams that empty into tertiary bays. Some of these areas are tidally influenced on meteorologically-forced, extreme high tides. During high rainfall or periodic flooding, these deposited materials in the receiving streams are flushed and enter the downstream estuaries. Because of the potential for produced waters from some of the more inland discharge points to be transported to Texas coastal waters and create water quality problems, many of the discharge points in intermittently flowing or infrequently flushed streams are being phased out.

By far, the greatest volume of produced waters is discharged into the Galveston-Trinity estuarine system. Also receiving substantial discharges is the Matagorda-Lavaca estuarine system. Most of the produced waters discharged into Gulf of Mexico waters within Texas' territorial waters is off the Sabine estuary. Lesser amounts are discharged off the Brazos, Matagorda, and San Antonio estuaries, and negligible amounts off the remaining estuaries. The total amount of produced waters discharged into Texas nearshore Gulf water, 14,109 bbl/day, is more than an order of magnitude less than that discharged into Louisiana's state Gulf of Mexico waters (192,386 bbl/day) where the state jurisdiction extends offshore only to a 3-mile limit. There are no discharges of OCS-generated produced waters in Texas state waters, i.e., within the 9-mile territorial limit.

The discharge of produced waters in estuarine and nearshore waters in the northwestern Gulf of Mexico region can be compared to those discharged into the waters of the Federally-controlled OCS. The U.S. Environmental Protection Agency grants permits for these discharges through the National Pollutant Discharge Elimination System (NPDES). Two studies, one by Gianessi and Arnold (1982) which summarized discharges in the OCS of the Gulf of Mexico as well as state waters of Texas and Louisiana prior to EPA exercising its NPDES authority and a second by Walk, Haydel and Associates (1984), both provided estimates of discharges of OCS produced waters. The estimate of OCS produced waters discharged offshore provided by Gianessi and Arnold (356,642 bbl/day) was about half of that estimated by the latter (after subtraction of the OCS produced waters discharged into coastal waters as estimated from this study). Based on estimates provided by Walk, Haydel and Associates (1984) and this study, the amount of produced waters discharged offshore and within state waters of Louisiana is 1.5 to 2 times greater than that estimated in 1982 by Gianessi and Arnold.

These higher estimates do not necessarily reflect increases in the rate of production of produced waters, although this is likely as the oil and gas fields are further depleted. Tracking of discharges by state and federal regulatory agencies was not actively pursued when Gianessi and Arnold attempted their summary and has changed little. At least there now appears to be a more complete inventory of the facilities which are operating. Based on these statistics, it appears that 37% of the produced water generated in the OCS are piped ashore for separation and disposal in Louisiana coastal waters. Furthermore, approximately 22% of the produced waters discharged into Louisiana coastal and estuarine waters emanates from the OCS. There are no discharges of OCS-generated produced waters in Texas state waters.

Offshore produced water discharges pose less serious environmental effects than disposal in estuarine systems because of the dilution potential compared to shallow, poorly flushed inshore environments. Although most discharges into estuarine environments are small in volume, several larger facilities which commingle oil from numerous wells have emission rates which are as large or larger than the largest OCS discharges. This is particularly true for coastal facilities which separate produced water from OCS product streams.

FIELD ASSESSMENTS

Three sites representing large volumes of OCS-generated produced water discharges and different hydrological conditions affecting dispersal of produced waters were selected for field assessments: Bayou Rigaud, behind Grand Isle; Pass Fourchon; and the bay side of East Timbalier Island. At each site, produced waters from the discharge point were sampled for hydrocarbon and trace metal analyses. The water column overlying the bottom and bottom sediments were sampled for similar analyses along a gradient away from the discharge point. Water column depth, temperature, and salinity were measured and benthic macroinfauna were sampled along the same gradient. Oysters (*Crassostrea virginica*) or ribbed mussels (*Geukensia demissa*) were sampled for chemical body burdens. Samples were intended to serve as a general survey of the areas, hydrologically, chemically, and biologically, rather than to provide rigorous quantification of impacts and, thus, were not replicated.

Produced water discharges from four oil-water separation facilities, Conoco at Grand Isle, Exxon at Grand Isle, Chevron at Pass Fourchon, and Chevron at East Timbalier Island, were characterized for volatile organic hydrocarbons, semivolatile organic hydrocarbons, and metals. The produced waters contained high concentrations of organic acids, phenols, volatile aromatics, saturated alkanes, low molecular weight polynuclear aromatic hydrocarbons and some trace metals. The hydrocarbon content of the produced waters analyzed here (10 to 50 ppm) is similar to that measured by Neff et al. (1989) (20-30 ppm). The concentrations of alkanes (saturated hydrocarbons) measured here (6 to 55 ppm) also encompassed the mean concentrations reported by Neff et al. (17 to 28 ppm) as did the concentrations of aromatic hydrocarbons (2.5 to 6 ppm versus 2.5 to 3.3). Although variability limits conclusions, it appears that the produced waters analyzed in this study had generally higher concentrations of naphthalene and its alkylated homologs than in other studies with the exception of the produced water from the C-2 platform in Trinity Bay, Texas, as reported by Armstrong et al. (1979). Although the limited number of samples analyzed cautions against placing too much confidence in interpreting differences between the discharges studied here, some intriguing differences bear comment. The produced water samples from the Conoco effluent collected both in October and January had higher concentrations of alkanes and volatile and polynuclear aromatic hydrocarbons than the final discharges from the other facilities. The final Exxon effluent had considerably lower concentrations of alkanes and polynuclear aromatics than the other effluents. Comparison of the final Exxon effluent with the produced water entering the open holding pond suggests that significant removal of these compounds is affected in the pond, either as a result of demulsification or oxidation. Of the produced water discharges studied, only the effluent collected from the Exxon Grand Isle facility had been processed through a holding pond system.

The concentrations of barium and zinc measured in the produced waters sampled here were similar to those reported by Neff et al. (1989); however, the concentrations of most other trace metals were much higher. Neff et al. noted that higher concentrations were also reported in several studies and attributed this to the difficulty of analysis of metals in concentrated saline brines.

Upon discharge into estuaries, produced water effluents act as a dense plume which sinks to the bottom. The rate of its dispersion depends on the receiving environment, tidal currents, and turbulence. There was no significant effect of elevated salinity resulting from coastal discharges of OCS produced waters. Elevated levels of salinity and volatile organics were found just above the bottom near discharges in Bayou Rigaud and Pass Fourchon. The probable source of the volatile organics was the effluent plume rather than the sediments, because these more soluble compounds are not concentrated in the sediments. In Bayou Rigaud, where bottom currents are swift and generate sufficient turbulence to mix the bottom plume, elevated bottom salinities and volatile organics in overlying waters were not observed beyond the immediate vicinity of the discharge. In this case, broader distribution of contaminated bottom sediments probably resulted from the resuspension and transport of sediments exposed to the near-bottom plume near the discharge points. At Pass Fourchon, on the other hand, tidal flows are much less energetic because of the dead-end nature of the closed pass. The dense plume retained its identity until mixing where the pass meets a canal and tidal energy is intensified.

Substantial contamination of fine-grained sediments with petroleum hydrocarbons was observed near the discharges at the three sites studied. Hydrocarbon contamination from produced water discharges extended several hundred meters to over one kilometer from the point of discharge. Contaminated sediments were typified by: 1) the presence of petroleum-derived PAH; 2) alkyl-substituted homologs at higher concentrations than unalkylated parents; and 3) a fossil fuel pollution index which indicated that more than one-half of the PAH were of petroleum origin (FFPI > 0.5). Sediments well removed from the discharges contained trace or non-detectable levels of petroleum-derived hydrocarbons and a FFPI < 0.3. PAH in these sediments, if detected, were usually pyrogenic in origin. Concentrations of PAH in sediments near the discharges exceeded apparent background levels by over an order of magnitude. PAH concentrations and characteristics were more useful than saturated hydrocarbons in determining the likelihood of contamination by produced water discharges. The resolved saturated hydrocarbons were usually very weathered with no homologous series of alkanes present, even in contaminated sediments.

The extent of sediment contamination was more extensive than reported for other produced water discharges which have been studied (Armstrong et al. 1979, Neff et al. 1989), because of the lower dispersion in the receiving environments and the larger volumes of produced waters discharged. The concentration of total alkanes and PAH in the most contaminated sediments sampled at Bayou Rigaud and Pass Fourchon were higher than those at the Lake Pelto discharge near Terrebonne Bay, Louisiana (Neff et al. 1989) and similar to the levels reported near a separator discharge in Trinity Bay, Texas (Armstrong et al. 1979). The fact that the overwhelmingly dominant source of petroleum into the receiving waters at the three sites is produced water, the detection of a produced water plume along the bottom, and the gradient of increased concentrations toward the produced water sources provides strong evidence of a produced water source for the observed sediment contamination.

The degree of contamination of bottom sediments by trace metals contained in the produced waters was far less than that for petroleum hydrocarbons. Because trace metals naturally occur in sediments at varying concentrations depending on grain size and associated geochemical properties, contamination must be assessed as variation from this normal relationship. Aluminum concentration is generally a strong function of clay mineral content of the sediment. Strong outliers from the normal linear relationships are thus sites of probable contamination. Sediments showing probable zinc contamination were found at stations near the produced water discharges in Bayou Rigaud and Pass Fourchon. Fewer sediment samples showed variation from the linear relationship between aluminum and lead. A sample from near the discharge at Bayou Rigaud was the greatest outlier. The picture for barium was more confused. Although several stations adjacent to the discharges had elevated concentrations of barium in surface sediments, other stations not close to the discharges did as well.

The environments which were studied and received produced water discharges are presently disturbed benthic habitats even without the effects of produced water contaminants. These environments are channels in which fine sediments accumulate, which are periodically dredged, and in which vessel traffic disturbs the bottom. Consequently, the benthic fauna is of low diversity and is composed of opportunistic species. Still, general surveys at the three sites showed evidence of biological effects in terms of reduced density and diversity of macrobenthic organisms in contaminated sediments. At locations closest to the discharge where bottom sediments were heavily contaminated, the macrobenthic fauna was essentially eliminated. Low densities of organisms and few species were found under conditions of moderate hydrocarbon contamination of sediments. Although some relatively uncontaminated sediments had a sparse benthic fauna, high PAH levels in sediments were always associated with a depauperate benthos.

Hydrocarbon concentrations and content of oysters collected near discharges at Bayou Rigaud (Exxon discharge) and East Timbalier Island were compared with those of oysters collected at a reference site near but away from the Pass Fourchon discharges. Oysters could not be found in the vicinity of the Pass Fourchon discharge. Instead ribbed mussels were collected from the marsh adjacent to the Chevron facility. Ribbed mussels from a marsh near the Louisiana Universities Marine Center in Cocodrie were analyzed for comparison. The data on contaminants in biota must be interpreted with great caution because of the limited number of samples on which the results are based. The metals results are ambiguous, and the differences in concentrations between produced water sites and control sites are not great. Results from hydrocarbon analyses, however, demonstrated the clear potential for uptake of produced water associated hydrocarbons by filter feeding molluscs in the vicinity of the discharge.

Total PAH and total saturated hydrocarbons were both at least three times more concentrated in oysters and mussels near the produced water discharges than those at reference sites. Moreover, the fossil fuel pollution index (FFPI) was greater than 0.7 in the molluscs from near discharge sites, while it was much lower or near zero at the reference sites. The oysters at the Port Fourchon Laboratory reference site actually displayed concentrations of PAH and a FFPI which suggested moderate hydrocarbon contamination. These concentrations may be related to the vessel and small boat traffic in the vicinity and were likely pyrogenic in origin. The high FFPI and PAH concentration in the Pass Fourchon mussels may be related possibly to an oil spill which took place nearby approximately one month prior to sampling.

Chapter 1

INTRODUCTION

by

Donald F. Boesch and Nancy N. Rabalais

1.1 Produced Waters

During the production of oil or gas, water that is trapped within permeable sedimentary rock may also be brought to the surface. This water is called formation water, produced water or oilfield brine. Such water is connate or fossil water that may have dissolved solids levels (salinity) in excess of that of ambient sea water, either because partially evaporated sea water was incorporated into sediments or because of leaching of salt diapirs intruding into the sedimentary strata. In coastal Louisiana, formation waters range in salinity from 50 g/l (parts per thousand) to 150 g/l depending on the depth from which they are drawn and the proximity to salt diapirs (Hanor et al. 1986). In addition, produced waters may contain elevated levels of various inorganic (e.g. trace metals, sulfide and elemental sulfur) and organic (petroleum hydrocarbons and partially oxidized organics) substances.

Water must be removed from the oil or gas as completely as possible in order to transport and use the petroleum. This is conventionally done by depressurization and gravity separation (Figure 1.1). This separation may be enhanced by the addition of demulsifiers. Following the initial separation, which is aimed at reducing the water content of the oil to acceptable levels, the produced water may be reinjected down a well, either for disposal or to enhance recovery of remaining hydrocarbons, or they may be discharged to surface waters. In the case of surface water discharge, further retention in holding tanks or ponds may be employed to reduce the oil and grease content of the effluent.

The amount of produced water generated per volume of oil or gas varies greatly. In the case of new production from certain reservoirs, very little water is produced. However, in older fields with declining petroleum yields the ratio of water to oil may increase dramatically to the point where many barrels of water are produced for each barrel of crude oil.

Although once widespread, the discharge of produced waters into freshwater rivers and streams has now been virtually eliminated in the U.S. because of the effects of the high dissolved solids levels on those freshwater environments. The discharge of produced waters into brackish and marine waters, however, is widespread in the northwestern Gulf of Mexico region and in coastal Alaska (Neff et al. 1987). In addition, discharges of produced waters into the Mississippi and Atchafalaya Rivers and their freshwater distributaries and into some intermittent streams leading to Texas estuaries is currently allowed.

1.2 Coastal Discharge of OCS Produced Waters

Approximately 95% of the oil and 98% of the gas produced from the Federally-controlled outer continental shelf (OCS) comes from the central and western regions of the Gulf of Mexico. Much of the water produced in this process is separated and discharged from offshore production platforms in the Federal OCS. The regulation of these discharges is under the authority of the U.S. Environmental Protection Agency. The EPA applies Best Practicable Treatment guidelines under National Pollutant Discharge Elimination System (NPDES) general permits for these discharges. However, large volumes of produced water generated in the Federal OCS are piped ashore with the oil or gas streams and separated at shore-based or nearshore facilities located in state waters. Resulting produced water is either discharged into

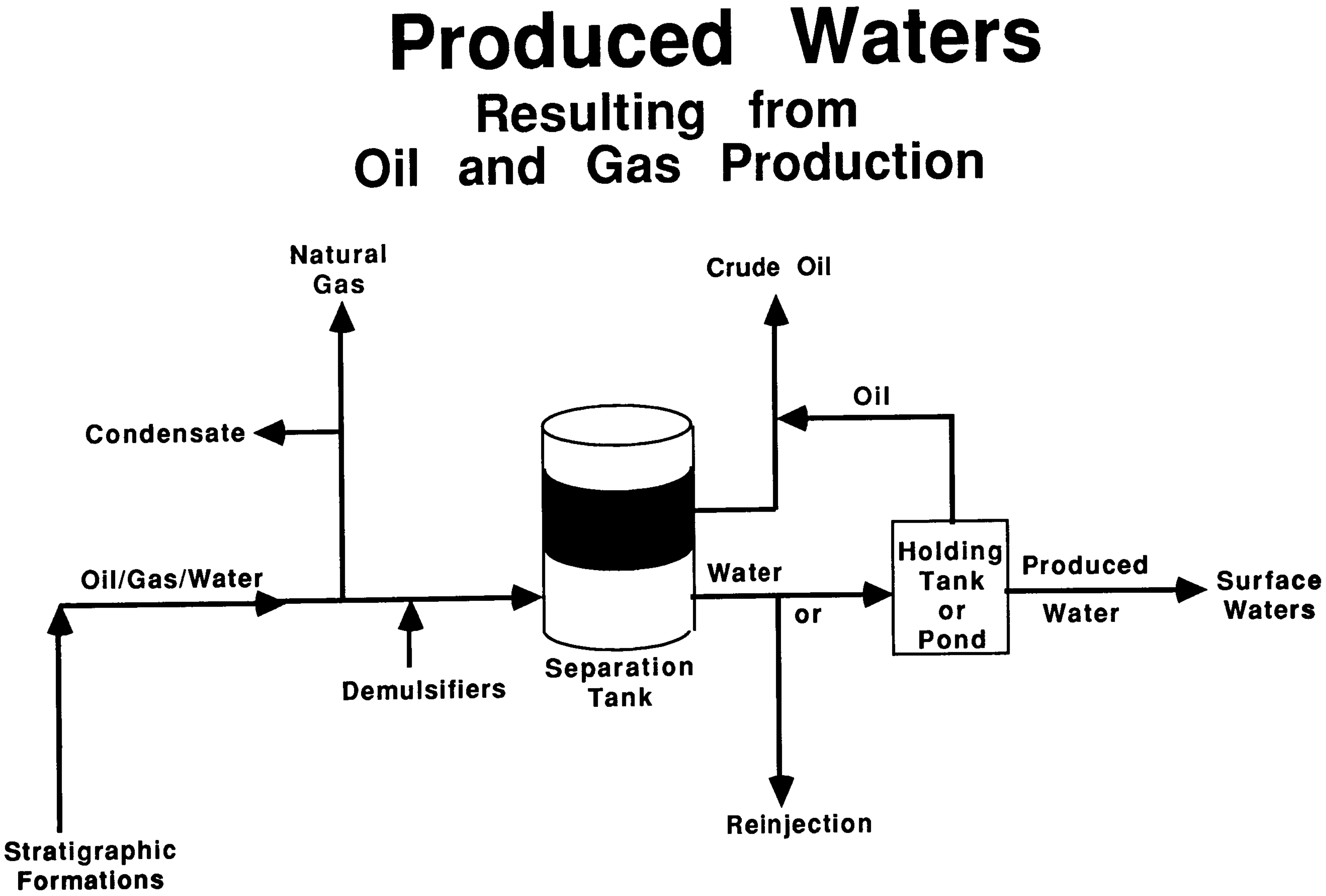

Figure 1.1. Procedures for separation, treatment, and disposal of produced waters.

nearshore continental shelf waters or estuarine waters or reinjected into disposal wells. This practice is employed for several reasons: a) large water volumes are produced from fields not far removed from shore; b) it is more cost-effective to collect production from many wells or several fields for separation; and c) it is much more costly to construct and operate large separation facilities on offshore platforms, especially in deep water.

Surprisingly, despite the controversies which have surrounded the potential environmental effects of OCS oil and gas development, the environmental effects of OCS-generated produced water discharges, and especially these large volume discharges into shallow state coastal waters, have received little attention. The extent of the practice of separation and disposal in state waters escaped recognition in the Environmental Impact Statements for OCS lease sales in the Gulf of Mexico until 1984. In an inventory of oil and gas drilling and production discharges in the Gulf of Mexico, Gianessi and Arnold (1982) reported that 305,370 barrels (barrel = 42 gallons or 159 liters) of produced water emanating from the OCS were discharged per day from coastal facilities into state offshore waters. This approximated their estimate of the rate of discharge directly into federal OCS waters. Based on this estimate, on the rationale that if produced water discharges had deleterious effects they would most likely be realized when the discharges were into shallow coastal waters with conditions of limited dilution, and on the lack of previous studies, Boesch et al. (1987) assigned a medium priority to this issue in their critical assessment of research needs related to the long-term effects of offshore oil and gas development.

1.3 Previous Studies of Effects of Produced Water Discharges

Although the environmental effects of coastal discharges of OCS produced waters have not been previously investigated, there have been a number of previous investigations of the effects of produced water on marine and coastal environments and organisms. These have been reviewed recently by Middleditch (1984), Harper (1986), and Neff (1987, 1988) and will not be reviewed in detail here. General observations from coastal Louisiana and Texas will be briefly summarized in order to set the stage for the results reported later.

In the late 1940's the effects of produced water discharges were investigated as a facet of Project 9 studies of the relationship of the then developing coastal oil industry to oyster mortality in Louisiana (Mackin and Hopkins 1961). Six oil fields located in wetland and bay environments were studied, and rapid dilution of the briny discharges was reported except where effluents were discharged into poorly flushed canals. Then, elevated salinity and stratified conditions, with the denser produced water concentrated near the bottom, were found hundreds of meters from the point of discharge. Although the chemical analytical methods then available are primitive by today's standards, Mackin and Hopkins reported that bottom sediments near produced water discharges were contaminated with "unsaponifiable hydrocarbons."

More extensive investigations of the effects of produced water discharges have been conducted in Texas estuaries, but most of these studies have not been published in the open literature. Harper (1986) reviewed this unpublished and obscure literature concerning produced water fate and effects. He concluded that the effects of produced water were heavily dependent on the volume and flow rates in receiving waters and the quantity of produced water discharged. Elevated salinity, contamination by petroleum hydrocarbons and altered biotic communities were found many kilometers downstream in coastal streams which were not tidally influenced. In tidally influenced environments, elevated salinity, sediment hydrocarbon contamination and depressed benthic biota were generally limited to within 100 to 200 m of the discharge. Armstrong et al. (1979) concluded that certain hydrocarbon fractions, particularly naphthalenes, found in sediments were responsible for depression of benthic populations. Harper (1986) pointed out that, around many discharges into tidally influenced environments, there appeared to be a "zone of stimulation" beyond the area in which depressed benthic populations were found, in which benthic standing crops were actually higher than in surrounding environments. He suggested that this resulted from the organic enrichment of sediment microbial communities beyond the area in which toxic concentrations of hydrocarbons were found.

The most recent and most detailed study of the chemical fate and biological effects of produced water discharges in the Gulf of Mexico region is that of Neff et al. (1989), who investigated discharges from two platforms in coastal Louisiana: one on the shallow continental shelf off Atchafalaya Bay and the other in Lake Pelto, an open embayment off Terrebonne Bay. Neff et al. performed extensive chemical analyses of produced waters discharged at these two sites and found that only 10 percent of the organic carbon was accounted for by hydrocarbons with the remainder consisting of uncharacterized, soluble organic matter, much of which was partially oxidized hydrocarbons. Barium, lead and zinc were present in produced water from the two platforms at concentrations more than a thousand-fold higher than those in normal sea water. At the Lake Pelto site, contamination of bottom sediments with petroleum hydrocarbons originating from produced waters was found at 20 and 100 m from the discharge, but not at 1000 m. No unambiguous evidence of sediment metals contamination was found. Effects on benthic communities were uncovered at 20 m from the discharge, but not at 100 m.

1.4 Environmental Concerns

The effects of the coastal disposal of OCS-generated produced water should not be qualitatively different from those described in previous studies. However, because of the large volume of these discharges (tens of thousands to hundreds of thousands of barrels per day compared with thousands of barrels per day in the case of most other discharges studied) and confined waters into which the effluents are discharged, there may be quantitative differences in their effects. Concerns have been voiced about the wisdom of discharging such large volumes into confined coastal waters rather than into deeper offshore waters from which they originate.

Because of increased regulatory scrutiny, it is timely to quantify the scale and nature of impacts and the chemical components most responsible for them. The Louisiana Department of Environmental Quality is evaluating permit conditions to be applied to coastal discharges of produced water, presently not subject to water quality permits. The Environmental Protection Agency is also considering whether to require permits under the National Pollutant Discharge Elimination System for coastal produced water discharges and the performance standards which it would apply in this case.

1.5 Objectives of This Study

The objectives of this study were to a) quantify the location and characteristics of discharges of OCS-generated produced waters into coastal environments of the Gulf of Mexico and b) provide an assessment of the environmental fate and effects of selected discharges. The objectives were addressed through an inventory of OCS-generated produced water discharges into coastal environments based on records of regulatory agencies and a field assessment of three sites. The field assessment component was meant to provide general delimitation of the scope and nature of impacts, and, therefore, did not include extensive replication required for statistical testing of hypotheses.

1.6 Study Organization

Principal investigator for this study was Donald F. Boesch, Louisiana Universities Marine Consortium (LUMCON), who coordinated study efforts to complete the primary objectives listed above. He also lead efforts in the compilation of discharge data for Louisiana and synthesis and interpretation of results. Co-principal investigators for the study were Nancy N. Rabalais, LUMCON, and Edward B. Overton, Institute for Environmental Studies (IES), Louisiana State University (LSU). N. N. Rabalais was responsible for compilation of discharge data for Texas, hydrography, and benthic infaunal assessments. E. B. Overton was responsible for chemical analyses; his co-investigators were Jay C. Means (IES), Charles S. Milan (IES), Charles B. Henry (IES), and Robert P. Gambrell (trace metal analyses, Center for Wetland Resources, LSU). All investigators participated in the synthesis and interpretation of results.

Chapter 2

PRODUCED WATER DISCHARGES IN THE NORTHWESTERN GULF OF MEXICO REGION

by

Donald F. Boesch and Nancy N. Rabalais

2.1 Objectives and Definitions

In order to place the discharge of OCS-generated produced waters into state waters in context with other discharges of produced waters generated by operations within state waters, a survey of all produced water discharges into the state waters of Louisiana and Texas was undertaken. The other Gulf states (Mississippi, Alabama, and Florida) do not permit the discharge of produced water into surface waters and require their reinjection or offsite disposal.

In this section, the numbers of discharges and the total volumes discharged are summarized by region and habitat and compared to the discharges of OCS-generated produced water, both that discharged in the OCS and that piped ashore for separation.

"Coastal zone" is herein defined as all state areas, both estuarine and nearshore continental shelf, within the state's territorial sea (Table 2.1). "Coastal waters" refers to those waters in the same above defined areas. In Louisiana, the state's territorial sea extends to 3 miles; in Texas, to 3 leagues or about 9 miles. Some produced water discharges are allowed in Texas waters inland of the influence of tidal exchange or the potential for contribution to a tertiary bay; these are termed "inland" waters. "State" waters include all waters that are inland, estuarine, or offshore within the territorial boundary. Federal OCS waters are those located outside the respective state's territorial sea. "Offshore" waters are continental shelf waters and will be identified as "state offshore" or federal offshore" waters depending on the location in relation to the territorial boundary. Non-OCS waters equates to "state's waters."

2.2 Data Sources

The Office of Conservation within the Louisiana Department of Natural Resources has required oil and gas well operators to report annually on the disposition of produced salt water. Although the Office of Conservation maintains no accessible database on reported discharges, Gianessi and Arnold (1982) attempted to summarize these data for several years in the late 1970's. There has been a widespread feeling that the Office of Conservation data were incomplete and underestimated the number and volume of discharges.

In 1985, the Louisiana Department of Environmental Quality (LDEQ), which was newly formed in 1983, announced its intentions to develop permits for discharges of produced waters into surface waters of the state. It required a preliminary application be completed, which included information on the location, volume and chloride concentration of all discharges. Applications were submitted by May, 1986 and, although permits have not yet been developed, the application responses constitute the most extensive and nearly complete data available. These data, however, remained stored on the permit application forms, and there had been no attempt to enter them into an automated database or otherwise summarize them.

Because the information contained in these applications was critical to the success of this project, LUMCON and LSU personnel undertook the development of a database from the applications which were stored in boxes. Information including facility name and location, the oil and gas field which it serves, the operator, and the reported volume of discharge and

Table 2.1. Delineation of water bodies as defined and used in the text of the report.

<table>
<tr><th></th><th></th><th></th><th></th><th>Texas</th><th>Louisiana</th><th></th><th></th><th></th><th></th></tr>
<tr><td rowspan="3">State = Non - OCS</td><td></td><td></td><td></td><td>Inland</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td rowspan="2">Coastal</td><td></td><td></td><td>Estuarine</td><td>Estuarine
(includes Mississippi and Atchafalaya Rivers and their freshwater distributaries)</td><td></td><td></td><td rowspan="2">Coastal</td><td rowspan="2">State = Non - OCS</td></tr>
<tr><td rowspan="2">Offshore</td><td></td><td>Nearshore
Continental Shelf
= State Offshore</td><td>Nearshore
Continental Shelf
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concentration of chloride were placed in a database on the LDEQ computer. In addition, a more convenient, microcomputer accessible version of the database was developed as a Lotus 1-2-3 file in which the estuarine basin and the estuarine habitat type in which the discharge is located were added.

The habitat types used were fresh marsh, brackish marsh, saline marsh, open bay and offshore within the state territorial sea. Habitats were differentiated based on salinity-based wetland classification because of the emerging concern that discharge of high-salinity produced waters is a contributing factor in the loss of salt-intolerant wetland vegetation. The map of Chabreck and Linscombe (1978) was used to determine the wetland habitat in which the discharge was located, except that the intermediate and brackish marsh categories used in that map were not differentiated. Sites falling in either category were simply listed as brackish in our database, because there have been changes in vegetation in these habitats resulting from a general increase in estuarine salinity since the surveys of Chabreck and Linscombe. In addition, the location of sites in fresh marsh was verified by consulting the more recent habitat maps of Wicker (1980) and the classification of habitats in these maps as palustrine (fresh) or estuarine (brackish). Only those discharges into the larger primary bays (e.g. East Cote Blanche, Timbalier and Barataria Bays and Breton Sound) were classified as Open Bay discharges. Those discharges into smaller embayments in which there may be a potential for exposure of wetlands were classified under the appropriate wetlands habitat type, i.e. fresh, brackish or saline.

In Texas, the Texas Railroad Commission (TRC) is the authority for the state that permits produced water discharges. The Texas Water Commission (TWC) manages water quality for the state and, along with the Texas Parks and Wildlife Department, monitors some produced water discharge locations. A data summary (11/23/87) was obtained from the Oil and Gas Division of the Texas Railroad Commission. Additional information was obtained in communications with Willis Steed, Director, Field Operations, TRC; Leslie Savage and Wendel Taylor, Underground Injection Control, TRC; Jim Bowman and George Guillen, TWC; and Gary Powell, Texas Water Development Board (TWDB).

The stated volume permitted for discharge in the TRC data printout is calculated from an annual well potential test. The test determines what volume of oil or gas will flow at the maximum production rate of the well and how much water will be produced by the well. According to Gary Powell, TWDB (personal communication), the actual volumes of produced water discharged may differ significantly from the permitted volumes. Although field reports are submitted to the TRC and retained in the files for five years, there is no routine tracking of actual volumes with reference to the permitted volumes.

The TRC printout (updated monthly) provided information on the number of active or non-active disposal permits, the type of well, the operator, the disposal point, and the barrels per day water production. The printout includes all disposal points for discharge of produced waters into Texas waters. This includes inland streams, inland open pits, bayous, rivers, estuaries, bays, and nearshore open Gulf waters within the 9-mile state territorial limits. Mr. Steed (TRC) stated that, to his knowledge, there are no discharges of OCS-generated produced waters in Texas waters, i.e. within the 9-mile territorial limit.

2.3 Summary Data

2.3.1 Louisiana

The total volume of produced waters discharged into Louisiana state waters was projected to be 1,959,734 bbl/day (barrel = 42 gallons or 159 liters) based on the reports in the 1986 permit applications to the LDEQ. This includes 192,386 bbl/day discharged into the state's offshore waters of the Gulf of Mexico within the 3-mile state territorial sea. The total volume of produced waters discharged into Louisiana estuarine waters is 1,767,348 bbl/day. There were 698 discharge facilities for which permit applications were received. When broken down by estuarine basin (Figure 2.1), the largest number of discharges are located in the Terrebonne and Barataria estuarine systems, while the largest aggregate volumes reportedly discharged are in the Chandeleur Sound, Mississippi River Delta and Barataria Bay estuarine systems (Table 2.2, Figure 2.2). While the largest number and volume of coastal zone discharges in Louisiana are in the southeastern part of the state, significant produced water discharges were also reported in the Vermilion-Cote Blanche Bay systems.

The majority of the produced water discharges into Louisiana waters are small in volume. The modal class is 100 to 500 bbl/day and only 10% of the reported discharges are greater than 5,000 bbl/day. However discharges of various volumes are scattered throughout the entire Louisiana coastal zone. Figures 2.3 and 2.4 represent the locations of produced waters in the Vermilion and Atchafalaya and Terrebonne and Barataria estuarine systems, respectively. Discharges are obviously clustered around major oil and gas fields.

Produced water discharges from coastal separation facilities handling oil-gas-water streams from the OCS contribute 434,772 bbl/day and are located mainly along the southeastern Louisiana coast from Atchafalaya Bay to the Mississippi River Delta (Figure 2.2, Table 2.3). The facilities discharging OCS-generated produced water are few in number, but generally handle very large volumes because the product of numerous offshore wells is gathered and piped ashore to central treatment facilities. Figure 2.5 shows the location of the coastal facilities identified which handle OCS primarily or exclusively, and Table 2.4 lists the operator, volume and exact location. Several of these facilities have reported daily discharges which exceed 20,000 bbl/day and two facilities discharge in excess of 100,000 bbl/day.

These data from the LDEQ permit applications constitute the most comprehensive representation of produced water discharges yet available, but suffer certain potential inaccuracies. They are based on a single discharge rate included on the permit application, which depending on the applicant may represent averages of recent discharge rates, estimated high rates meant to be inclusive for permitting conditions, or, on the other hand, purposeful underestimates. In addition, there are probably discharges for which permit applications were not filed, including discharges into leaking holding pits. In aggregate, however, it is felt that these discharge estimates constitute a reasonably accurate estimate of present conditions. Unfortunately, because of the variable and incomplete nature of data collected by the Office of Conservation and the LDEQ, it is impossible to conclude anything about trends in discharge volumes.

2.3.2 Texas

The total volume of produced waters discharged into Texas waters is 823,575 bbl/day (Table 2.5). This includes 87,721 bbl/day (11%) for those designated as "inland." The total volume of produced waters discharged into Texas coastal waters (inclusive of the 9-mile territorial limit) is 735,854 bbl/day. The total volume of produced waters discharged into Texas estuarine waters (exclusive of the offshore state waters) is 721,745 bbl/day. The totals for the "estuarine" waters include some discharge points that are more inland but that flow into tertiary bays or streams that empty into tertiary bays. Some of these areas are tidally influenced on meteorologically-forced, extreme high tides. During high rainfall or periodic flooding, these deposited materials in the receiving streams are flushed and enter the downstream estuaries. Because of the potential for produced waters from some of the more inland discharge points to be transported into Texas coastal waters, the volumes are included with the respective regional subtotals. Many of the discharge points in intermittently flowing or infrequently flushed streams are being phased out because of water quality problems (J. Bowman and G. Guillen, TWC, personal communications).

SABN - Sabine

CACL - Calcasieu

MERM - Mermentau

VRML - Vermilion and Cote Blanche Bays

ATCH - Atchafalaya Bay

TERR - Terrebonne and Timbalier Bays

BARA - Barataria Bay

MRD - Mississippi River Delta

CHND - Chandeleur and Breton Sounds

PONT - Lake Pontchartrain and Lake Borgne

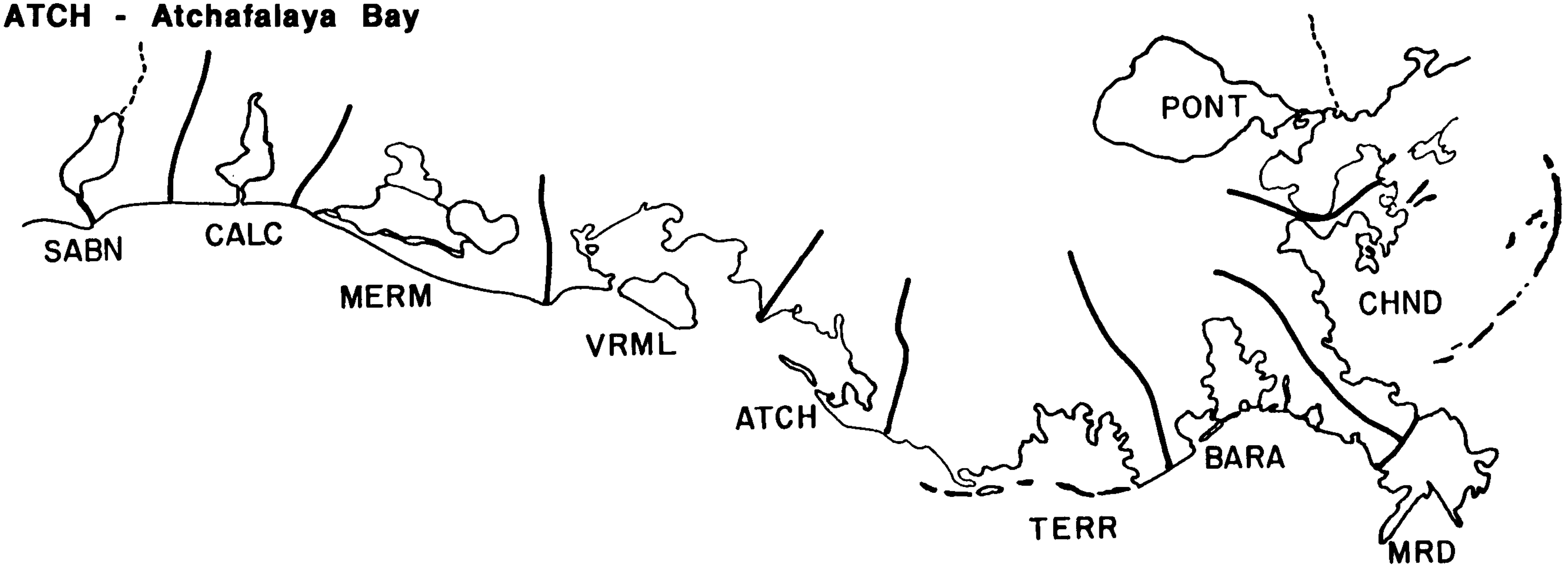

Figure 2.1. Louisiana coast showing locations of estuarine basins.

Table 2.2. Distribution of produced water discharges in Louisiana state waters by area or estuarine basin and by habitat type.

Area or Estuarine Basin	Fresh		Brackish		Saline		Open Bay		Total	
	Volume (bbl/d)	No.	Volume (bbl/d)	No.	Volume (bbl/d)	No.	Volume (bbl/d)	No.	Volume (bbl/d)	No.
Sabine	18,000	1	43,530	2	6	1	1,262	1	62,798	5
Calcasieu	7,478	10	19,470	26	6	1	1,800	2	28,754	39
Mermentau	4,000	6	4,000	1	931	2	-	-	8,931	9
Vermilion	4,000	6	134,104	21	-	-	99,172	25	237,276	52
Atchafalaya	57,614	43	2,833	8	-	-	12,810	14	73,257	65
Terrebonne	9	1	46,666	71	34,081	70	92,900	57	173,656	199
Barataria	6,940	3	118,952	66	235,185	64	1,977	3	363,054	136
Mississippi River Delta	355,381	35	42,885	27	-	-	3,986	4	402,252	66
Chandeleur	-	-	11,583	12	67,191	15	337,239	33	416,013	60
Pontchartrain	-	-	405	2	-	-	952	7	1,357	9
Total Estuarine	453,422	105	424,428	236	337,400	153	552,098	146	**1,767,348**	640
Gulf of Mexico (state offshore waters)									192,386	58
Total Louisiana									**1,959,734**	698

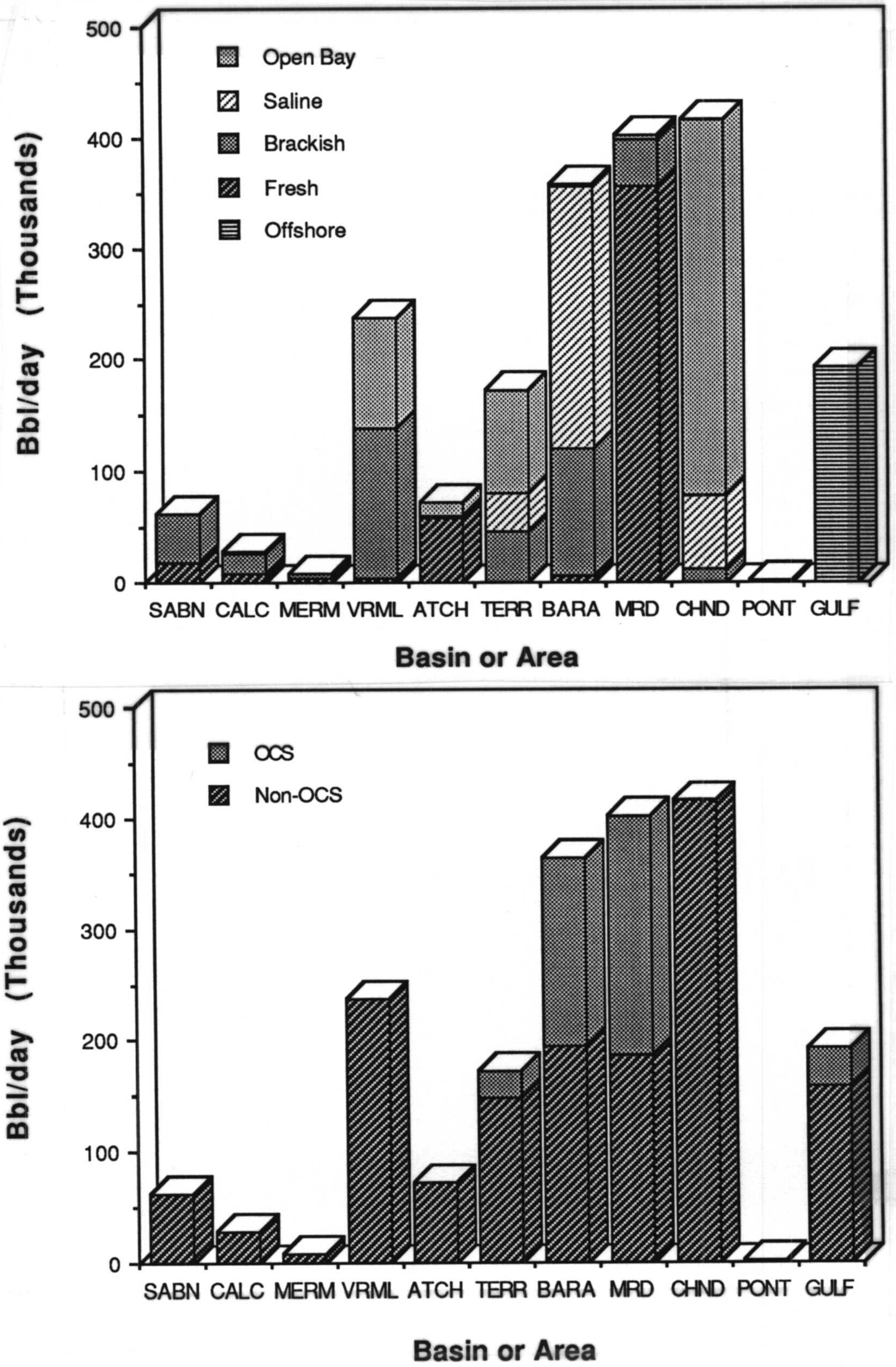

Figure 2.2. Distribution of produced water discharges in Louisiana's estuarine basins or areas by habitat type, above; and by source of discharge, either OCS-generated or not, below (Gulf = state offshore waters).

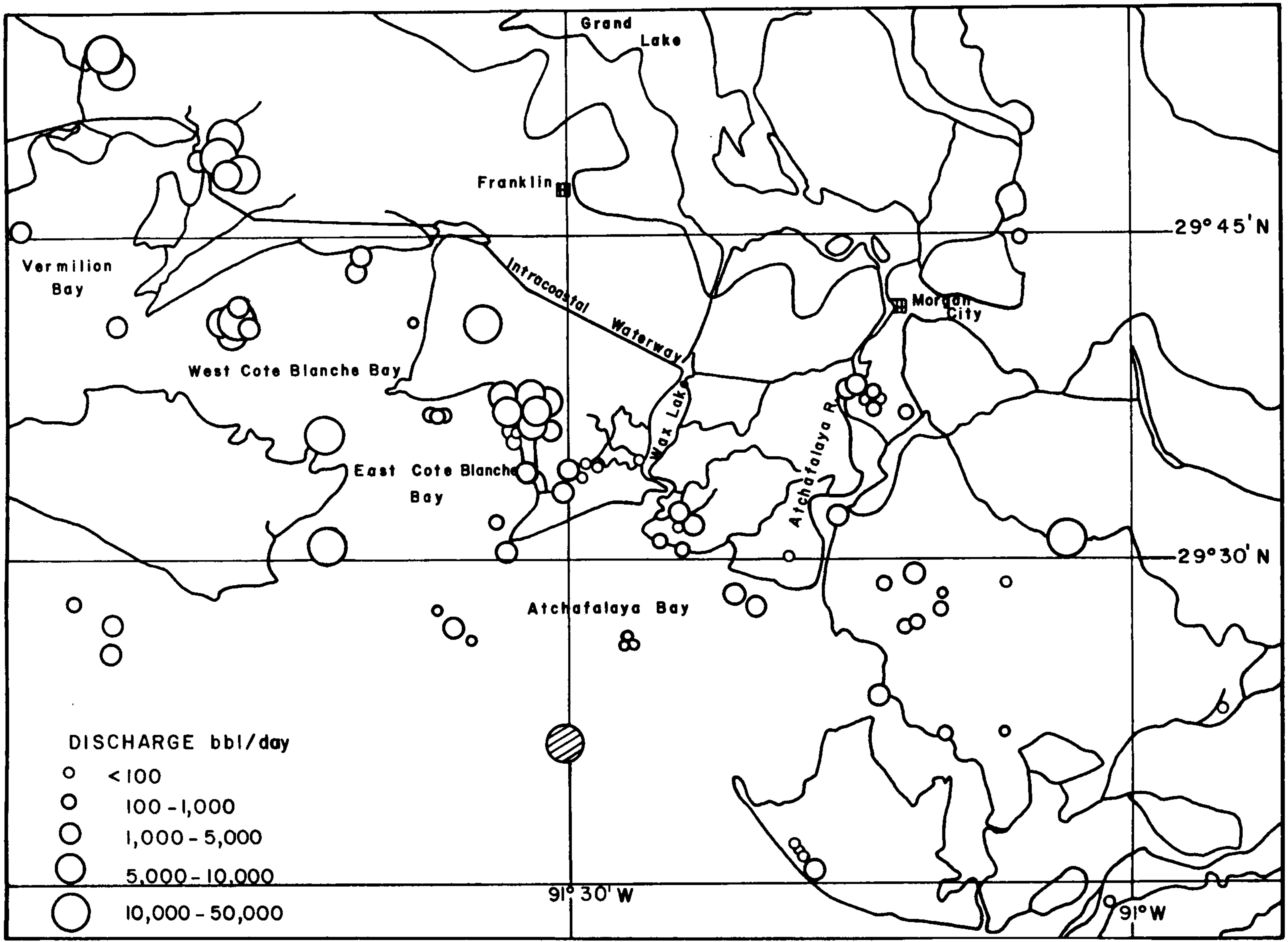

Figure 2.3. Location of produced water discharges in the Vermilion and Atchafalaya estuarine basins; hatched circles represent OCS-generated produced water.

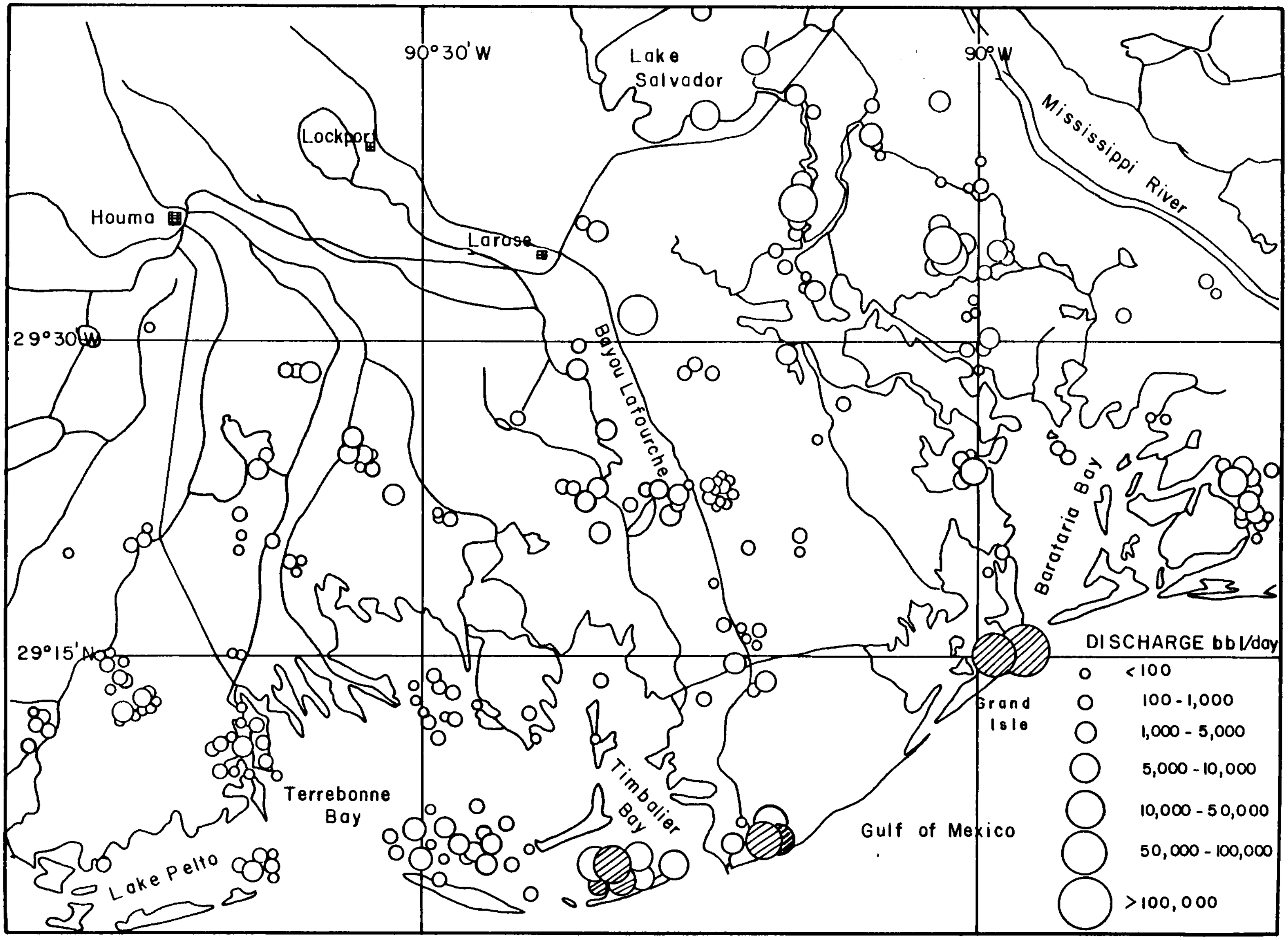

Figure 2.4. Location of produced water discharges in the Terrebonne and Barataria estuarine systems; hatched circles represent OCS-generated produced water.

Table 2.3. Distribution of Louisiana coastal produced water discharges.

Area or Estuarine Basin	Total Volume (bbl/day)	OCS Discharges (bbl/day)	Non-OCS Discharges (bbl/day)
Sabine	62,798	1,262	61,536
Calcasieu	28,754	-	28,754
Mermentau	8,931	-	8,931
Vermilion	237,276	10	237,266
Atchafalaya	73,257	-	73,257
Terrebonne	173,656	24,058	149,598
Barataria	363,054	173,000	190,054
Mississippi River Delta	402,252	203,542	198,710
Chandeleur	416,103	-	416,103
Pontchartrain	1,357	-	1,357
Gulf of Mexico (state offshore waters)	192,386	32,900	159,486
Total	**1,959,734**	**434,772**	**1,524,962**

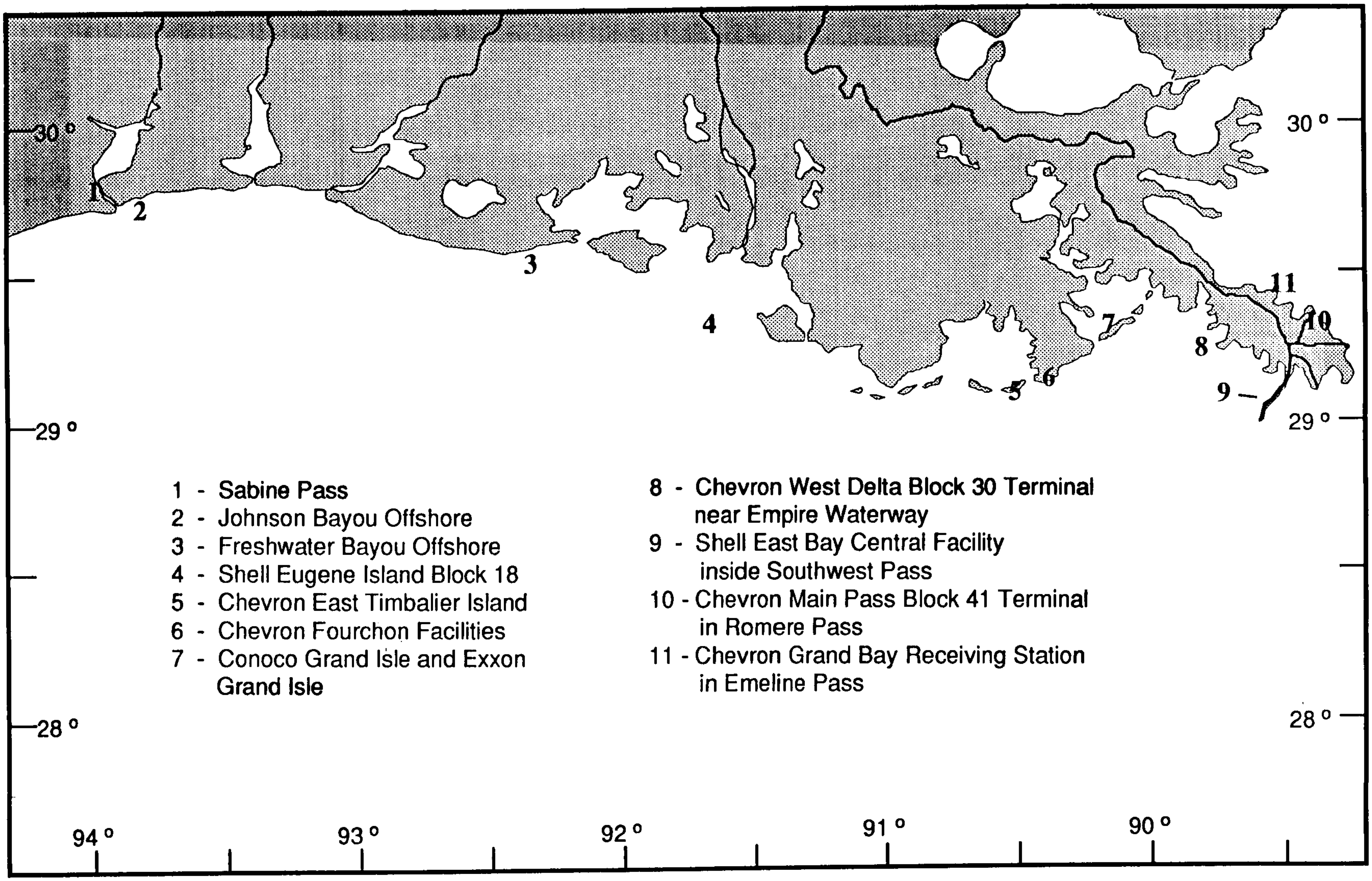

Figure 2.5. Location of OCS-generated produced water discharges in Louisiana state waters.

Table 2.4. Facilities in the Louisiana coastal zone with discharges of produced waters emanating from the Federally-controlled outer continental shelf.

	Facility	Location	Company	Discharge
1	Sabine Terminal	Sabine Pass Sec. 13, T15S, R16W	Chevron Pipe Line Co.	1,262
2	Johnson Bayou Tank Battery	Johnson Bayou Cameron Parish Sec 33, T15S, R13W	Chevron Pipe Line Co.	500
2	West Cameron Block 45	Johnson Bayou Cameron Parish	Phillips	2,400
3	Texas Gas Sales	Freshwater Bayou	Union	10
4	Eugene Island Block 18	29°21.92'N, 91°30.15'W	Shell	30,000
5	South Timbalier 21/27/28 Tank Battery	East Timbalier Island 29°04.03'N, 90°19.73'W	Chevron, U.S.A.	20,000
5	South Timbalier 36/37 Tank Battery	East Timbalier Island 29°04.22'N, 90°19.70'W	Chevron, U.S.A.	2,862
5	South Timbalier 35 Tank Battery	East Timbalier Island 29°03.95'N, 90°19.62'W	Chevron, U.S.A.	1,196
6	Fourchon Terminal	Pass Fourchon 29°06.36'N, 90°11.54'W	Chevron Pipe Line Co.	8,000
6	Bay Marchand Barge	Pass Fourchon 29°06.38'N, 90°11.80'W	Chevron, U.S.A.	18,000
7	Grand Isle Station	Bayou Rigaud 29°15.33'N, 89°58.05'W	Exxon	40,000
7	Grand Isle Shore Base	Bayou Rigaud 29°15.60'N, 89°38.00'W	Conoco	105,000
8	West Delta Block 30 Terminal	Empire Waterway 29°16.17'N, 89°36.00'W	Chevron Pipe Line Co.	2,000
9	East Bay Central Facility	Southwest Pass/ Mississippi River 29°02.93'N, 89°18.78'W	Shell	166,242
10	Main Pass Block 41 Terminal	Romere Pass/Main Pass 29°16.83'N, 89°14.67'W	Chevron Pipe Line Co. Chevron, U.S.A.	30,000
11	Grand Bay Receiving Station	Emeline Pass 29°18.63'N, 89°17.78'W	Chevron, U.S.A.	7,300

Table 2.5. Distribution of Texas produced water discharges by area (derived from data provided by the Texas Railroad Commission 11/23/87).

Area or Estuary	Code	Number of Non-Active Discharge Points	Number of Active Discharge Points	Volume Permitted (bbl/day)	% of Total Volume	% of Coastal Volume	% of Estuarine Volume
Laguna Madre	LMa	140	95	23,483	3	3	3
Corpus Christi - Nueces	CCh	84	79	70,010	8	10	10
Aransas - Copano	Ara	38	47	9,007	1	1	1
San Antonio	SAn	35	13	1,403	<1	<1	<1
Matagorda - Lavaca	Mat	92	78	209,258	25	28	29
Colorado - East Matagorda	Col	0	2	2,143	<1	<1	<1
Brazos - San Bernard	Bra	9	5	57,905	7	8	8
Galveston - Trinity	Gal	174	276	324,980	39	44	45
Sabine	Sab	10	14	23,556	3	3	3
Estuarine Subtotal				**721,745**			
Gulf of Mexico (state offshore waters	Gulf	161	66	14,109	2	2	-
Coastal Subtotal				**735,854**			
Inland	Inland	12	47	87,721	11	-	-
TOTAL				**823,575**			

The designation of the regions for Texas coastal waters follows closely that of the Texas Department of Water Resources estuarine systems given in their freshwater inflow needs studies (TDWR 1982). The regions are named, however, for the primary and/or secondary bays instead of the rivers providing the major source of freshwater inflow (Figure 2.6).

By far, the greatest volume of produced waters is discharged into the Galveston-Trinity estuarine system (Table 2.5, Figure 2.7). Within the estuary, there are 45 discharge points which deliver 137,235 bbl/day to Cow Bayou, a tributary to Clear Lake and eventually Galveston Bay, 61 discharge points which deliver 107,759 bbl/day to Trinity Bay, 72 discharge points which deliver 137,235 bbl/day to Galveston Bay proper, and 30 discharge points which deliver 17,349 bbl/day to Tabbs Bay.

Highland Bayou, a tidal estuary extending from Alta Loma to Jones Bay and discharging into West Bay of the Galveston Bay system, at one time received substantial produced water discharges. Volumes averaged 9,000 bbl/day in January-March, 1986, but decreased after April and May and ceased by August, 1986 (G. Guillen, TWC). The well ceased operations due to poor economics of secondary gas recovery. In response to reports of degraded water quality, personnel from the Texas Water Commission and Texas Parks and Wildlife Department began an intensive sampling program in the bayou (Kendall et al. 1988, Abstract, Texas Academy of Science Meeting). An area of effect (about four miles of bayou) was seen in severely impacted water quality and absence or reduction of organisms. The bayou has received little flushing since 1978-80, when 50-70% of the headwaters were diverted into a flood control diversion canal, and was a poor candidate for receipt of produced water discharges (G. Guillen, TWC). Since cessation of the discharges, an increase in the number of nektonic species, including juvenile shrimp, was observed (Kendall et al. 1988, Abstract, Texas Academy of Science Meeting; report in prep.).

The Matagorda-Lavaca estuarine system also receives substantial produced water discharges. In this system, the majority of the discharges enter the upper end of Lavaca Bay: 10 discharge points totaling 177,680 bbl/day into Venado Creek on the upper end of Lavaca Bay, 8 discharge points totaling 16,776 bbl/day into Swan Lake at the upper end of Lavaca Bay, and 14 discharge points totaling 5,996 bbl/day into Menefee Bayou and Menefee Lake which drain to the Lavaca River upstream from the head of Lavaca Bay.

In the Corpus Christi-Nueces estuarine system, most of the produced waters (54 discharge points totaling 65,650 bbl/day) are discharged into Nueces Bay or the Nueces River. The freshwater inflow models generated by the Texas Department of Water Resources for Nueces and Corpus Christi Bays consistently underestimated the observed salinities (TDWR 1981). The model was amended to include these additional source inputs, and better comparisons with the observed salinities were obtained. This estuarine system was the only one of those modelled in which the produced water discharge volumes were critical to adequately describing the salinity regime of the system.

A fairly large volume (57,905 bbl/day) of produced water discharges are shown for the Brazos-San Bernard system. These discharges are primarily those of the San Bernard River Project, San Bernard LPG Plant, and the Lone Star Salt Water Canal associated with the projects. These discharges are upstream, but the rivers flow into shallow estuaries near the mouths of the rivers before entering the Gulf of Mexico.

Produced water discharges in the Laguna Madre are primarily via tributaries to Alazan Bay, an arm of Baffin Bay. Until January, 1987 there were 12 discharge points totalling 5,770 bbl/day into Petronila Creek and 24 discharge points totaling 11,390 bbl/day into Tunas Creek. In January all discharges upstream of State Highway 70 where it crosses Petronila Creek were

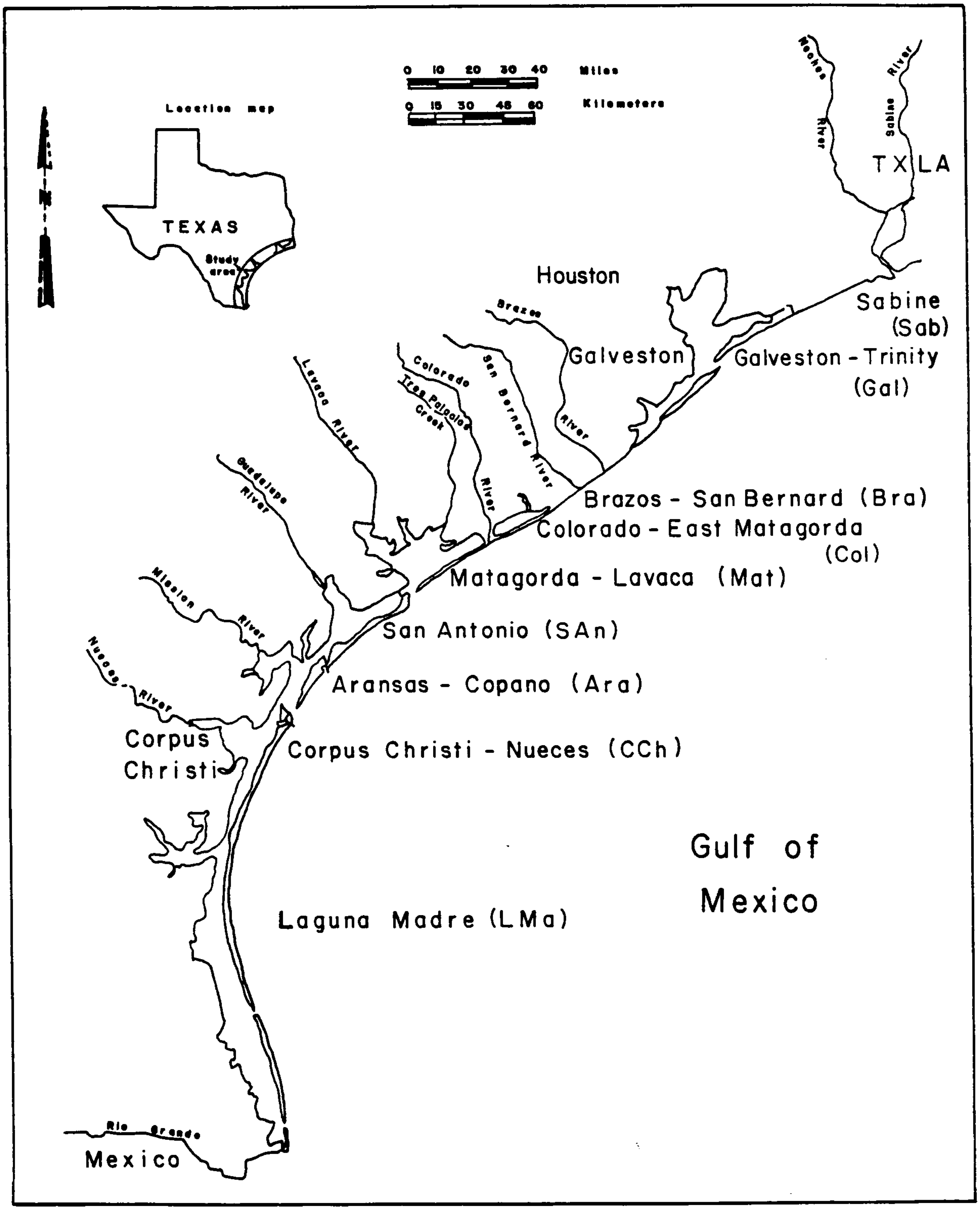

Figure 2.6. Texas coast showing locations of estuarine basins.

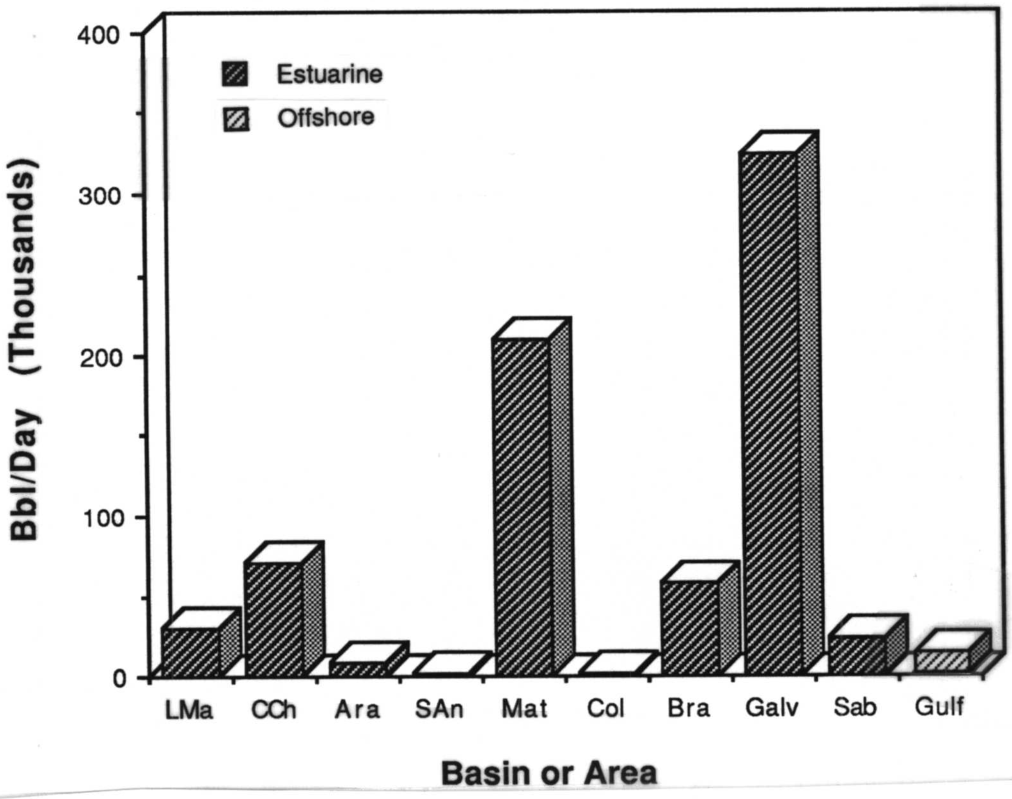

Figure 2.7. Distribution of produced water discharges in Texas coastal waters.

stopped by a cease and desist order of the Texas Water Commission (J. Bowman, TWC; W. Taylor, TRC). A single discharge remains downstream of Highway 70 in Petronila Creek. Discharges continue there and in Tunas Creek, which are considered tidally influenced portions of Alazan Bay. Discharges in intermittently flowing freshwater streams upstream from any tidal influence are being phased out (J. Bowman, TWC). F. Shipley of the Texas Water Commission (Shipley 1988, Abstract, Texas Academy of Science Meeting and manuscript in press) studied the recovery of water quality and fish communities in Petronila Creek following termination of the produced water discharges. He documented significant recovery at the uppermost brine-influenced station where fish species recolonized the creek and physiochemistry of the water improved. Two of the three brine-influenced stations, however, remained with elevated water and sediment salt concentrations and a severely reduced fish community composed mainly of characteristically tolerant cyprinodontids.

Most of the produced waters discharged into Gulf of Mexico waters within Texas' territorial waters (3 leagues, or about 9 miles) are off the Sabine estuary. Lesser amounts are discharged off the Brazos, Matagorda, and San Antonio estuaries, and negligible amounts off the remaining estuaries. The total amount of produced waters discharged into Texas nearshore Gulf waters, 14,109 bbl/day is more than an order of magnitude less than that discharged into Louisiana's state Gulf of Mexico waters (192,386 bbl/day) where the state jurisdiction extends offshore only to a 3-mile limit.

2.3.3 Outer Continental Shelf

While the focus of this report is produced water discharges into estuarine and nearshore waters, it is instructive to consider these discharges in context with the discharges of produced water into the waters of the Federally-controlled OCS. The U.S. Environmental Protection Agency grants permits for these discharges through the National Pollutant Discharge Elimination System (NPDES) authorized by the Clean Water Act.

Gianessi and Arnold (1982) summarized the regional distribution and volumes of discharges of produced waters into the OCS of the Gulf of Mexico as well as discharges into state waters of Louisiana and Texas. Their summary was based on sources concerned more with oil and gas production rather than environmental protection, thus they were in part based on extrapolation from oil and gas production. At the time of preparation of their report, the EPA had not yet exercised its NPDES authority and data from reports were filed with the Conservation Division of the U.S. Geological Survey (now an element of the Minerals Management Service). This so-called Resources for the Future (RFF) study estimated that in 1976, 356,642 bbl/day of produced waters were discharged in the OCS and that OCS operators piped an additional 328,470 bbl/day ashore for separation, treatment and discharge. Of this latter total, 23,100 bbl/day was reinjected and not discharged into surface waters. RFF further estimated that 840,800 bbl/day was discharged into Louisiana state waters and 707,744 bbl/day was discharged into Texas state waters as a result of in-state production in the late 1970's and early 1980's.

Based on the RFF data, the vast majority of produced water generated in the OCS comes from offshore southeastern Louisiana, primarily from the following OCS Areas: West Delta, Eugene Island, Ship Shoal, South Pass, Grand Isle, Main Pass, and South Timbalier. This pattern is evident in the folio sheet for oil and gas discharges of the NOAA Gulf of Mexico Atlas (NOAA 1985) which was prepared based largely on the RFF data.

Although oil and gas operators are required to submit data on volumes of discharges to the EPA Region VI as a condition of their NPDES permits, these data are not routinely accessible. Based on data submitted to the Minerals Management Service, Walk, Haydel and Associates (1984) estimated that 1,180,000 bbl/day of produced waters was generated in the

OCS. This figure includes those produced waters discharged into OCS waters and those which were piped ashore for separation and disposal. If the estimates of discharges of OCS produced waters into coastal waters (434,772 bbl/day) are subtracted from the total, this leaves approximately 745,000 bbl/day discharged into OCS waters. [Produced water discharge volumes vary monthly and annually. The Minerals Management Service maintains monthly records of produced water discharge amounts in a computer-based data system (OCSIS).]

Estimates of total produced water discharges in the Gulf of Mexico region developed from our summaries of Louisiana and Texas data together with the estimate of OCS discharges are compared with those presented in the RFF study in Table 2.6. Our present estimate based partly on Walk, Haydel and Associates (1984) is that 3.4 million barrels of produced waters are discharged daily in the northwestern Gulf region. The discharge rates are higher than those given by RFF in all categories, but are notably higher for produced waters generated in and disposed of in Louisiana state waters and those discharged in the OCS. These higher estimates do not necessarily reflect increases in the rate of production of produced waters, although this is likely as the oil and gas fields are further depleted. Tracking of discharges by state and federal regulatory agencies was not actively pursued when Gianessi and Arnold attempted their summary and has changed little. At least there now appears to be a more complete inventory of the facilities which are operating.

Based on these statistics, it appears that 37% of the produced water generated in the OCS are piped ashore for separation and disposal in Louisiana coastal waters. Furthermore, approximately 22% of the produced waters discharged into Louisiana coastal waters emanates from the OCS.

Table 2.6. **Comparison of estimates of produced water discharges (in bbl/day) from this study and that of Walk, Haydel and Associates (1984) compared with OCS discharges estimated in the Resources for the Future (RFF) study (Gianessi and Arnold 1982).**

		OCS-Generated	OCS-Generated	Louisiana State-Generated	Texas State-Generated	
		OCS Disposal	State Coastal Disposal	State Coastal Disposal	State Coastal Disposal	Total
RFF Study 1976-80	Volume	356,642	305,370	840,800	707,744	2,210,556
	Percentage	16%	14%	38%	32%	
This Study 1983-86	Volume	745,228	434,772	1,524,962	735,854	3,440,816
	Percentage	22%	13%	44%	21%	

Chapter 3

FIELD ASSESSMENTS

by

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3.1 Selection of Study Sites

Three study sites were selected for chemical and biological reconnaissance of the impacts of OCS-generated produced water discharges into coastal waters: Bayou Rigaud, behind Grand Isle; Pass Fourchon; and the bay side of East Timbalier Island. These sites were chosen because of the large volumes of produced water discharges and each represented different hydrological conditions affecting dispersal of the produced water. Other major facilities discharging OCS produced water are located mainly in the Mississippi River Delta and release effluents into one of the distributary passes of the river. Consequently, the dilution of produced waters by the river's flow is great. The dynamic sediments, the background level of contaminants and the poorly developed benthic biota in the river passes also argued against selection of a study site in the delta. The reported volumes and characteristics of produced water discharges at the three study sites are presented in Table 3.1.

3.2 Sampling and Analytical Methods

3.2.1 Field Collections

At each site, produced waters from the discharge point were sampled for hydrocarbon and trace metal analyses. The water column overlying the bottom and bottom sediments were sampled for similar analyses along a gradient away from the discharge point. Water column depth, temperature, and salinity was measured and benthic macroinfauna were sampled along the same gradient. Oysters (*Crassostrea virginica*) or ribbed mussels (*Geukensia demissa*) were sampled for chemical body burdens. Sediment cores from the marsh were collected at one of the study sites for vertical profiles of hydrocarbons and trace metals. Samples were intended to serve as a general survey of the areas, hydrologically, chemically, and biologically, rather than to provide rigorous quantification of impacts and, thus, were not replicated.

Samples were taken during October 1987 and January 1988. The October samples were collected from aboard the R/V *Acadiana* and the January samples from an outboard motorboat which allowed sampling in shallower water. Because of the two boats, some sampling devices differed between the two dates.

From the *Acadiana* sediment samples were collected with a 0.1-m^2 box corer which penetrated to a depth of 35 cm (maximally). For benthic macroinfaunal analyses, three core tubes (7.4 cm diameter) were used to remove sediment cores. The upper 10 cm of each were removed and pooled for a sample (total of 0.0129 m^2 surface area). Sediments for chemical analyses were collected from the same box core with 7.4 cm diameter core tubes, and sectioned into 0-5, 5-10, 10-15, and 15-20 cm sections. Overlying bottom waters were collected from the box corer, and other water samples with a 5-l Niskin bottle lowered to a known depth. Adequate volumes were available from a single Niskin bottle deployment for all the chemical analyses.

From the outboard boat, sediment samples were taken with a 0.0238-m^2 Petersen grab which penetrated to a depth of 10 cm (maximally). Additional grabs were taken to collect sediments for chemical analyses. Sediment samples were taken from the entire depth of

Table 3.1. General characteristics of study areas.

Site	Operator	Volume (bbl/day)	Receiving Environment	Flow Regime
Bayou Rigaud	Conoco	105,000	Into terminus of deep slip (7 m) off Bayou Rigaud (4.5 m)	Tidally energetic, swift bottom currents
	Exxon	45,000	Via holding tank and aeration system to drainage ditch (4 m) leading to Bayou Rigaud (5.5 m)	Tidally energetic, swift bottom currents
Pass Fourchon	Chevron, U.S.A.	18,000	Into dead-end dredged channel (2.5 m) near occluded end of Pass Fourchon (3 m)	Less energetic tidal flow, dead-end closed pass
	Chevron Pipe Line Co.	8,000		
	State-generated	19,000		
East Timbalier Island	Chevron, U.S.A.	70 discharges	Into dredged canals (1.5-2 m) near open bay	Dredged canals with reduced flow; open bay, shallow, well-mixed from waves and tidal currents
	Total	68,872		
	OCS	24,058		
	Largest	20,000		

penetration of the grab. Water column samples were taken with a 1-l Kemerer bottle lowered to the bottom or just below the surface. Because of the reduced volume available from a single bottle, water samples for chemical analyses were pooled from several deployments.

Marsh cores were taken with a 7.4 cm diameter core tube at two locations near Pass Fourchon in January 1988. The cores were sectioned into 0-2, 2-4, 4-6, 6-8, 8-10, 10-15, 15-20, 20-25, 25-30, and 30-35 cm sections. One sample was collected from near the Chevron Pass Fourchon facilities and the second from a reference marsh near LUMCON's Port Fourchon field laboratory.

Larger sedentary bivalves (oysters and ribbed mussels) were collected in January 1988 from areas near discharge points and comparable areas in reference sites or marshes. Suitable animals varied in occurrence between the three locations, but an attempt was made to collect similar organisms for a crude test of the bioavailability of chemical constituents of produced waters.

A Hydrolab Surveyor II CTD unit was used for all water depth, temperature, and salinity measurements. Water quality was measured just below the water surface and just above the bottom sediments at most stations. At selected stations, a profile through the water column was obtained for all parameters.

Produced water samples were collected from four separation facilities--Conoco at Grand Isle, Exxon at Grand Isle, Chevron, U.S.A. at Pass Fourchon, and Chevron, U.S.A. at East Timbalier Island. The Conoco discharge was sampled in both October 1987 and January 1988; all others were collected only in January 1988. Samples were collected at the Exxon Grand Isle facility as the water flowed from a large holding tank, which received produced water from the primary separation tank, to an open maze pond and at the point that the water flowed from the pond into a drainage ditch leading to Bayou Rigaud. Only the latter sample was used in estimates of effluent discharges.

Standard precautions were taken to prevent contamination of the chemical samples. Precleaned aluminum corers, and stainless steel grabs and box corers were used. Sediment and water samples for hydrocarbon analyses were placed in specially cleaned glass jars or bottles. Specially prepared polyethylene bottles were used to hold water samples for trace metal analyses. In the field, chemical samples and biota were placed immediately on ice in October or held at air temperature (6 to 10 °C) in January. In the laboratory, water samples were held at 4 °C until analyses. Sediment samples and biota were stored frozen.

3.2.2 Benthic Macroinfauna Analysis

Benthic macroinfaunal samples were sieved in the field through a 0.5-mm screen and preserved with 10% buffered formalin in ambient water stained with rose bengal. In the laboratory, organisms were sorted from debris and remaining sediments, counted, and identified to the lowest taxon possible. Organisms normally considered part of the meiofauna (nematodes and harpacticoid copepods), plankton (decapod megalopae) or epifauna (bryozoans) were not included in the macroinfaunal analyses. A collection of voucher specimens was retained in a reference collection.

3.2.3 Organic Analytical Methods

Volatile organic analysis

Water samples for volatile organic analysis (VOA) were stored at 4 °C. All samples were analyzed within 5 days of receipt by a purge and trap/gas chromatograph (GC) technique.

The detector used was a flame ionization detector (FID). The instrumentation used was a Tekmar LS-2 purge and trap interfaced to a Hewlett Packard 5890 GC equipped with a 30 meter J&W 624 megabore capillary column. The initial GC temperature was 30 °C for 1 min, then temperature programmed at 10 °C/min to 100 °C and held at the final temperature for 5 min. GC quantitative results were based on an external standard method using authentic standards and a 5-point standard curve. To verify method performance, an EPA QA/QC sample was analyzed. All calculated concentrations were within the 95% confidence range of the "true" values.

Additional qualitative analyses were made on selected produced water samples using the same purge and trap technique, interfaced directly to a Hewlett Packard 5970B Mass Spectrometer (MS). The column used was a 50 meter Hewlett Packard DB-5 capillary column with a 0.32 mm ID and 1.0 micron film thickness. The MS was operated in the scanning mode.

Water extraction for semivolatile organics

The samples were extracted by a liquid-liquid extraction method (EPA METHOD 625), and the extracts analyzed by GC/MS. The acid-phenol and base/neutral fractions were combined and analyzed as a single fraction. Extraction blanks were analyzed to verify adequate glassware cleanliness and solvent purity.

Sediment extraction for semivolatile neutral organics

The samples were removed from the freezer and thawed in a refrigerator at 4 °C. Approximately 25 g of wet sediment, excluding large rocks and shell fragments, was subsampled and extracted by an organic extraction method using methanol and hexane. Sodium sulfate was added in approximately equal weight with the sediment sample. The sample extracts were concentrated by rotary evaporation and a stream of purified nitrogen to a final volume of 1.0 ml before gas chromatographic (GC) analysis. Hexamethylbenzene was added to each of the samples prior to extraction as a surrogate standard. Duplicate and spiked samples were extracted to verify analytical recoveries and ensure reproducibility.

A 3-5 gram subsample of sediment was taken for dry weight determination. The wet sediment was dried in an oven at 90 °C until a constant weight was obtained. The percent moisture value calculated was used to determine the dry weight of the sample for the wet weight that was extracted.

Biota extraction method

Samples of organisms were removed from their shells, rinsed with deionized water and homogenized in a blender. The blender was washed, rinsed with water, acetone, hexane and dried in an oven at 160°C between samples. Three grams of tissue were weighed in a 50-ml beaker to ± 0.01 g and hexamethylbenzene was added to each beaker as an internal standard. The beakers were covered with clean aluminum foil and heated in an oven at 60 °C for 1 hr to digest the sample. After heating, the beakers were cooled to room temperature. Sodium sulfate (DCM-rinsed and dried at 160 °C) was added and mixed until a consistency of sand was obtained (~30 g), indicating that all water had been adsorbed. The samples were then extracted with 20 ml of dichloromethane (DCM) in a sonicator for 12 min. The DCM was withdrawn with a pipet and added to a 250-ml round bottom flask. This extraction procedure was repeated twice more and all extracts were combined in the round bottom flask. The sample extracts were reduced in volume with a rotary evaporator to ~1 ml. The extracts were then transferred to 8-ml vials, with the rinsings from the flask (~10 ml), and reduced to 1 ml under a stream of purified nitrogen. Two milliliters of hexane were added and the volume was reduced to 1 ml prior to silica gel chromatography.

Extracts were fractionated using 8 g silica gel (activated ~ 170 ^{o}C for 12 hrs) covered with 2 g alumina (activated ~ 170 ^{o}C for 12 hrs) in a column 30 cm in length x 10.5 mm i.d. Two 25-ml fractions were obtained: the F-1 fraction, containing the aliphatic hydrocarbons, was eluted with hexane and the F-2 fraction, containing the polynuclear aromatic hydrocarbons (PAH) and biogenic olefins, was eluted with DCM/hexane (1:1). The fractions were reduced under a stream of purified nitrogen to a final volume of 500 1. Both fractions were screened by FID gas chromatography. All PAH and selected aliphatic fractions were analyzed by GC/MS to confirm peak identity and quantify the PAH.

Quality control procedures were used throughout the entire analysis process. Procedural blanks were run with every 8 samples to monitor the extraction and separation procedures. Internal standards were added to each sample to correct for any losses of components during the analysis. Laboratory duplicates, labeled 'A' and 'B', were run to determine method reproducibility.

Semivolatile instrumental analysis

Many of the sample extracts were screened by GC/FID prior to qualitative and quantitative analysis by GC/MS. Quantification was based on an internal standard technique compared to authentic standards where available and corrected for recoveries by the surrogate standard. The instrument used was a Hewlett Packard 5890 GC equipped with a J&W 30 meter DB-5 capillary column, 0.25 mm ID and 0.25 micron film thickness, directly interfaced to a Hewlett Packard 5970B Mass Spectrometer.

To ensure reproducible instrument performance, the MS was tuned daily by the autotune program. Column performance was verified by the use of the Grob standard, internal standards, and standards of the analytes of interest.

Quantitative determination of the semivolatile target compounds listed in Table 3.2 was by an extraction ion/internal standard method similar to methods described in EPA Method 625. The target compounds were chosen because of: 1) their relative abundance in petroleum sources such as crude oil and production water; 2) their potential to rapidly partition into the sediment and accumulate due to their low water solubilities; and 3) their relative persistence in the environment. In addition to the petrogenic compounds, common pyrogenic compounds were qualitatively and quantitatively identified to aid in differentiating the contamination source. The surrogate standard hexamethylbenzene was used to correct for recovery in the sediment extracts. The homologous series components, C-1 through C-3, were quantitated by extracted ions using the response factor of the unalkylated parent.

An estimation of the total saturated hydrocarbons (aliphatics), total resolved saturated hydrocarbons, and total unresolved saturated hydrocarbons was determined by an extracted ion method, m/z 57, using a response factor determined from the average of nC-14 and nC-24. Total resolved hydrocarbons were determined by a valley-to-valley integration technique, total saturated hydrocarbons by integrating the entire chromatogram (including the unresolved complex as a single peak) and the total unresolved saturated hydrocarbons were determined by subtracting the resolved saturated hydrocarbons from the total. The detection limits for the saturated aliphatics are approximately 4 g/g for the total and 1 g/g for the resolved saturated hydrocarbons. Values reported as trace are detected but at less than the quantitative detection limit. In addition, pristane/nC-17, phytane/nC-18, and pristane/phytane ratios were calculated using peak ratios if the compounds were present in the sample.

Table 3.2. Semivolatile neutral target compounds (PAH).

COMPOUND	QUANT.ION (m/z)*
NAPHTHALENE	128
C-1 NAPHTHALENE	142
C-2 NAPHTHALENE	156
C-3 NAPHTHALENE	170
FLUORENE	166
DIBENZOTHIOPHENE	184
C-1 DIBENZOTHIOPHENE	198
C-2 DIBENZOTHIOPHENE	212
C-3 DIBENZOTHIOPHENE	226
PHENANTHRENE	178
C-1PHENANTHRENE	192
C-2 PHENANTHRENE	206
C-3 PHENANTHRENE	220
ANTHRACENE	178
FLUORANTHENE	202
PYRENE	202
BENZO(a)ANTHRACENE	228
CHRYSENE	228
BENZO(b)FLUORANTHENE	252
BENZO(k)FLUORANTHENE	252
BENZO(a)PYRENE	252

*Ion mass used to quantify compound.

Data presentation

Figures and tables presented give an overall view of the extent of contamination as well as the actual hydrocarbon concentrations determined. Figures consist of: 1) distribution profiles of the PAH and resolved saturated hydrocarbon concentrations in a gradient away from the closest station to the discharge; 2) location maps with bar graphs of total PAH and total saturated hydrocarbon concentrations; 3) depth profiles at selected stations to examine the quantity and quality of hydrocarbon contamination; and 4) a surface plot of PAH concentrations at the Bayou Rigaud site to provide a visual representation of contamination throughout the entire site. Resolved saturated hydrocarbon concentrations were multiplied by the value in parenthesis in order to be graphed with the PAH and average values were plotted on graphs when laboratory duplicates were analyzed. Chromatograms of produced water and sediment samples are also presented for qualitative comparisons. They consist of total ion chromatograms (TIC's) and extracted ion chromatograms (EIC's) from mass spectral data. TIC's display the detector response of all compounds in the sample, while EIC's display the response of one particular ion mass.

Tables list: 1) total concentrations of target PAH; 2) concentrations of total saturated hydrocarbons; and 3) FFPI, an index used in determining source of hydrocarbon contamination. The "fossil fuel pollution index" (FFPI) (Boehm and Farrington 1984) approximates the relative percentage of petroleum-derived hydrocarbons in the total PAH measured. This index is based on the distribution of PAH in petroleum, which contains a relative abundance of alkylated homologs of naphthalene, phenanthrene and dibenzothiophene compared to their unalkylated parent compounds. Crude oil would have a FFPI of about one (1). The FFPI is a continuum which decreases with a decrease in petroleum-derived hydrocarbons and/or an increase in petrogenic hydrocarbons. The index is a tool used in monitoring the impact of petroleum-derived PAH. The FFPI is determined by the following formula:

$$\text{FFPI} = [\Sigma\text{naphthalenes } (C_0\text{-}C_3) + \Sigma\text{dibenzothiophenes } (C_0\text{-}C_3) + 1/2\ \Sigma\text{phenanthrenes } (C_0\text{-}C_1) + \Sigma\text{phenanthrenes } (C_2\text{-}C_3)]\ /\ \Sigma\ \text{PAH},$$

C_n = number of alkyl carbons substituted.

The appendix contains tables and selected chromatograms. These tables list: 1) sample weights extracted; 2) interstitial salinities, where determined; 3) concentrations of target PAH; 4) concentrations of saturated hydrocarbons, both resolved and unresolved (UCM); and 5) ratios and indices.

3.2.4 Trace Metal Analytical Methods

Instrumentation and data tabulation

The instrument used for elemental analyses of water, tissue, and sediment samples was a Jarrell-Ash Model 855 AtomComp inductively coupled argon plasma emission spectrometer (ICP). The instrument was calibrated by a two-point calibration curve. The first point was a pure water sample (Standard 1) for the 0 µg/ml. The second calibration point was made with 10 µg/ml standards. Standard 2 contained 10.0 µg/ml of Cu, Zn, Cd, Pb, Ni, As, Fe, Mn, Ca, Mg, Mo, Al, K, and Na. Standard 3 contained 10.0 µg/ml of Cr, Si (typically not analyzed because of contamination problems with glass containers), and P. The above elements were measured by separate, fixed photomultiplier detectors operating with one fixed grating monochrometer. One additional detector was available with a variable wavelength grating for measuring elements other than those for which there were fixed detectors. This channel was used for Ba. It was calibrated with Standard 1 and Standard 4 (contained 10.0 µg/ml Ba). The linear range for the instrument was at least 100 μg/ml for all elements listed except for Zn (40 μg/ml), As (75 μg/ml), and Mg (50 μg/ml). When any element in a sample exceeded its linear range, the sample was diluted and analyzed again.

The data were entered onto a spreadsheet for tabulation where dilution factors, if any, were entered and used in calculating final concentration. For tissues and sediment samples, the sample weight was also entered onto the spreadsheet and used for calculations along with final volume of sample after acid digestion/extraction and preliminary dilution.

Water samples

Water samples were refrigerated immediately upon receipt in the laboratory. The water samples were shaken, and then a portion of each water sample filtered through a 0.45 micron filter to obtain the water soluble fraction. The remaining sample would contain the original levels of suspended particulates. Filtered and whole water samples were analyzed on the ICP. Colloidal particulates associated with the water samples were swept into the plasma along with the fine mist of the aqueous portion of samples so that a reading was obtained on the total elemental concentration of the water sample (soluble + adsorbed to colloids).

Sediment samples

Wet sediment samples containing between 1 and 3 grams of oven dry sediment were weighed into clean, acid washed 100-ml test tubes. The tubes were then placed in a forced draft oven at 105 °C for 24 hours to determine the oven dry weight of the sediment samples (calculations were based on oven dry weights). Ten ml of "Ultrex" grade concentrated nitric acid was then added to each tube and the tubes placed in an aluminum block for extracting metals with hot nitric acid. A small, clean glass funnel was placed in the top of each tube to facilitate a reflux action of the nitric acid during the hot extraction. The temperature was increased from ambient to about 120 °C over a period of 4 hours, then maintained at 120 to 130 °C for an additional 3 hours, then allowed to cool to room temperature. The acid extracts were passed through a Whatman #40 paper filter into 50 ml volumetric flasks and brought to volume with distilled, deionized water. The final nitric acid content of these prepared samples was about 5 percent. The samples were held at room temperature until analyzed on the ICP spectrometer.

Tissue samples

Tissue samples were removed from the shell where necessary, then blended on a high speed blender for about a minute. Aliquots of the blended samples were placed into 100-ml test tubes and dried at 105 °C for 24 hours to get a dry weight of the samples. From this point, the sample processing was similar to that described above for sediment samples.

3.3 Characterization of Produced Waters

Produced water discharges from four oil-water separation facilities, Conoco at Grand Isle, Exxon at Grand Isle, Chevron, U.S.A. at Pass Fourchon, and Chevron, U.S.A. at East Timbalier, were characterized for: volatile organic hydrocarbons, semivolatile organic hydrocarbons, and metals. The hydrocarbon data are presented in Tables 3.3 and 3.4.

Formation water from various fields may differ in composition. Discharges from a single field should remain relatively similar in the short term, but may change over time as the field becomes depleted. Factors that may affect the composition of discharged produced waters are efficiency and consistency of operation of the oil-water separation system, additional wastes associated with oil and gas production that may enter the produced water discharge, and the

Table 3.3. Hydrocarbon concentrations in produced water samples (October 1987).

SAMPLE	CONOCO Oct. '87	EXXON-1 Oct. '87	EXXON-2 Oct. '87
VOLATILE ORGANIC ANALYTES (detection limit 3 ng/ml)			
BENZENE	2,900	8,000	1,700
TOLUENE	1,800	1,200	640
ETHYLBENZENE	68	54	37
XYLENES	140	240	15
AROMATIC ACIDS			
PHENOL	2,800	1,200	1,200
p-CRESOL	300	110	89
m, o-CRESOL	1,400	500	440
BENZOIC ACID	2,300	220	260
POLYNUCLEAR AROMATIC HYDROCARBONS (detection limit 20 ng/ml)			
NAPHTHALENE	220	140	88
C-1 NAPHTHALENE	240	120	Tr
C-2 NAPHTHALENE	220	81	Tr
C-3 NAPHTHALENE	98	20	ND
FLUORENE	ND	ND	ND
DIBENZOTHIOPHENE	ND	ND	ND
C-1 DIBENZOTHIOPHENE	ND	ND	ND
C-2 DIBENZOTHIOPHENE	ND	ND	ND
C-3 DIBENZOTHIOPHENE	ND	ND	ND
PHENANTHRENE	Tr	120	ND
C-1 PHENANTHRENE	Tr	260	ND
C-2 PHENANTHRENE	ND	ND	ND
C-3 PHENANTHRENE	ND	ND	ND
ANTHRACENE	ND	ND	ND
FLUORANTHENE	ND	ND	ND
PYRENE	ND	ND	ND
B(a)ANTHRACENE	ND	ND	ND
CHRYSENE	ND	ND	ND
B(b)&B(k)FLUORANTHENE	ND	ND	ND
BENZO(a)PYRENE	ND	ND	ND
TOTAL PAH	780	740	88
SATURATED HYDROCARBONS			
RESOLVED	23,000	Tr	4,700
UNRESOLVED	12,000	Tr	1,700
TOTAL	35,000	Tr	6,400
PRISTANE/nC-17	0.8	N/A	1.0
PHYTANE/nC-18	0.6	N/A	0.8
PRISTANE/PHYTANE	1.4	N/A	1.6

Table 3.4. Hydrocarbon concentrations in produced water samples (January 1988).

SAMPLE	CONOCO Jan. '88	CONOCO (Dup) Jan. '88	FOURCHON Jan. '88	TIMBALIER Jan. '88
VOLATILM ORGANIC ANALYTES (detection limit 3 ng/ml)				
BENZENE (ng/ml)	2,400	N/A	2,000	1,200
TOLUENE	1,300	N/A	660	600
ETHYLBENZENE	62	N/A	24	25
XYLENES	420	N/A	180	160
AROMATIC ACIDS				
PHENOL	2,900	2,800	1,600	1,800
p-CRESOL	310	290	150	180
m, o-CRESOL	1,300	1,330	510	750
BENZOIC ACID	4,900	4,400	3,100	4,000
POLYNUCLEAR AROMATIC HYDROCARBONS (detection limit 20 ng/ml)				
NAPHTHALENE	210	260	90	190
C-1 NAPHTHALENE	250	310	170	150
C-2 NAPHTHALENE	360	410	130	180
C-3 NAPHTHALENE	270	320	54	130
FLUORENE	18	18	Tr	13
DIBENZOTHIOPHENE	Tr	7	Tr	5
C-1 DIBENZOTHIOPHENE	30	29	Tr	17
C-2 DIBENZOTHIOPHENE	45	39	11	23
C-3 DIBENZOTHIOPHENE	24	26	Tr	8
PHENANTHRENE	6	33	13	23
C-1 PHENANTHRENE	83	110	22	59
C-2 PHENANTHRENE	110	100	25	50
C-3 PHENANTHRENE	55	56	Tr	27
ANTHRACENE	Tr	Tr	ND	ND
FLUORANTHENE	Tr	ND	ND	ND
PYRENE	ND	ND	ND	ND
B(a)ANTHRACENE	ND	ND	ND	ND
CHRYSENE	ND	ND	ND	ND
B(b)&B(k)FLUORANTHENE	ND	ND	ND	ND
BENZO(a)PYRENE	ND	ND	ND	ND
TOTAL PAH	1,500	1,700	520	880
SATURATED HYDROCARBONS				
RESOLVED	25,000	26,000	5,400	8,600
UNRESOLVED	30,000	27,000	11,000	13,000
TOTAL	55,000	53,000	16,400	22,600
PRISTANE/nC-17	0.8	0.7	0.7	0.7
PHYTANE/nC-18	0.7	0.5	0.5	0.5
PRISTANE/PHYTANE	1.8	1.2	1.8	1.3

production age of the field. The large OCS separation facilities studied here each collect produced waters from numerous wells which may have different produced water characteristics.

Volatile organic composition of produced water discharges

The major volatile organic constituents found in the produced water discharges investigated were benzene and its C-1 through C-3 homologs. Figure 3.1 shows the relative comparison of the four produced water discharges investigated. The mean benzene concentration was 1900 ng/ml for the 4 stations and ranged from 1200-2900 ng/ml. Very low concentrations of various hydrocarbons, probably low molecular weight saturated hydrocarbons, cyclic hydrocarbons, ketones, and low molecular weight alcohols, were detected but not further characterized since their concentration was typically less than 0.5% of benzene. Figure 3.2 shows a chromatographic comparison of the Exxon and Conoco effluents.

The only discharge station sampled during both sampling periods was CONOCO G.I. No significant seasonal variability in the volatile organic discharge was apparent between October 1987 and January 1988. The variability in the total xylene concentrations may be due to field sampling variability or variable oil-water separator efficiency.

Semivolatile organic composition of produced water discharges

Discharged produced water was analyzed for the target PAH, phenol and its methyl homologs, and total aliphatic hydrocarbons. In addition, the January CONOCO G.I. sample was further analyzed to provide detailed characterization of the more polar, acid compounds found in produced water.

Gross comparisons of the semivolatiles in produced water

When the total ion chromatograms (TIC) of the discharge water analyses were compared, the EXXON-2 G.I. sample was markedly different (Figure 3.3). The EXXON-2 G.I. sample was practically void of the normal aliphatic hydrocarbons which were well pronounced in the other samples and had an increased amount of various acid compounds. This difference was possibly due to the chemical treatment employed at the Exxon facility or degradation in the partially aerated holding ponds, and the additional acid hydrocarbons were probably residues of the chemical agents used or partial degradation products of the aliphatic hydrocarbons.

The TIMBALIER and CONOCO G.I. samples were very similar when gross comparisons of the TIC's were made. Each had a dominant number of unresolved polar compounds eluting early in the chromatogram, an unresolved hydrocarbon complex with an apex at approximately 22 minutes, and a typical normal hydrocarbon profile from nC-11 to nC-30. The lighter normal hydrocarbons were probably lost during the extraction process. The FOURCHON sample differed only in the size and extent of the unresolved complex.

Saturated aliphatic hydrocarbons

The total saturated aliphatic hydrocarbon concentration was estimated to range from trace levels, less than 1,000 ng/ml in sample EXXON-2 G.I. to 54,000 ng/ml in the January 1988 CONOCO G.I. sample with a mean of 22,000 ng/ml for the four stations investigated. Various differences in the aliphatic hydrocarbon profiles were previously discussed.

Target PAH

Naphthalene was the most abundant PAH detected (Figure 3.4) with a mean concentration of 150 ng/ml. The highest concentration of naphthalene was in the CONOCO G.I.

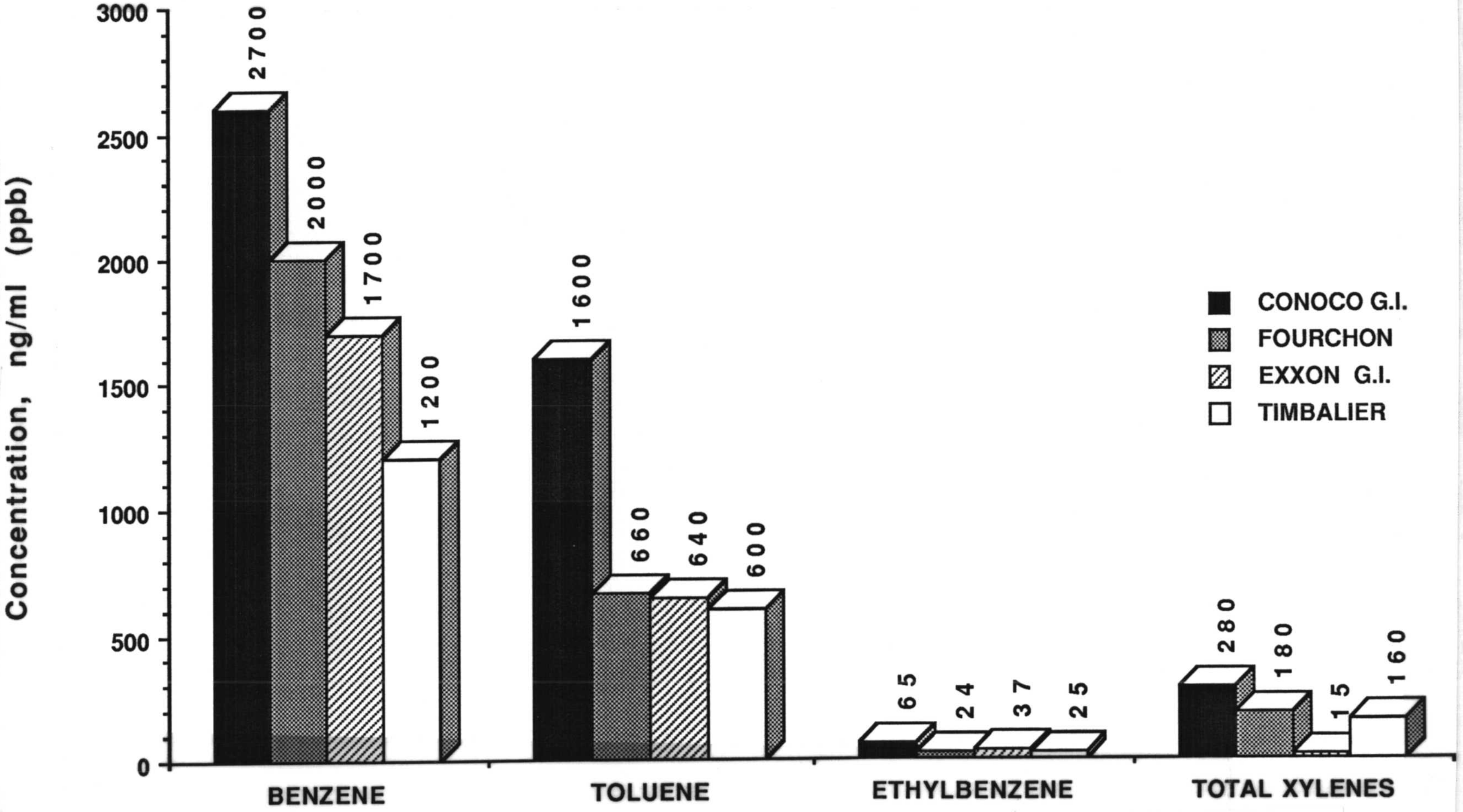


Figure 3.1. Comparison of volatile aromatics in produced water.

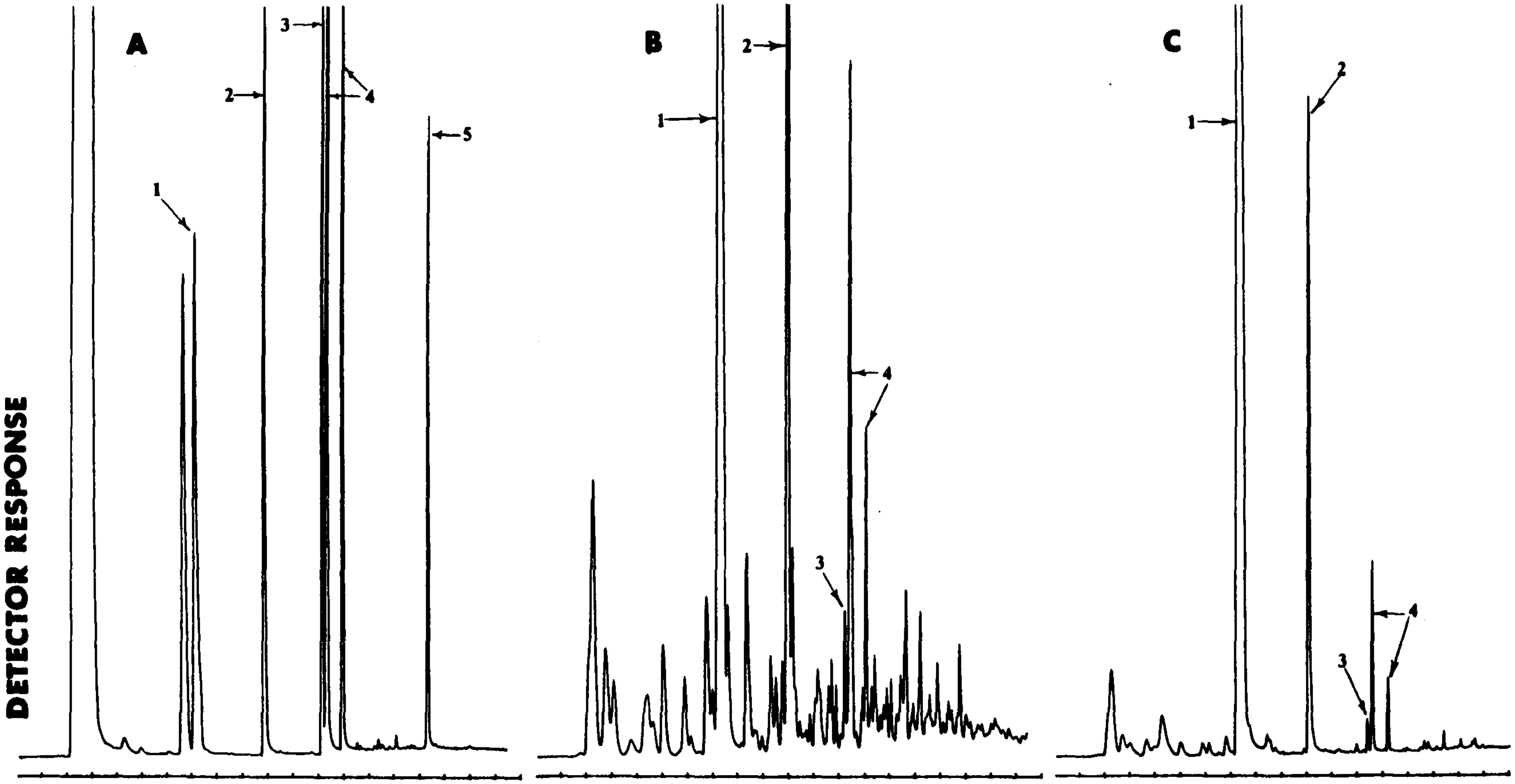


Figure 3.2. Comparison of produced water VOA: A. VOA standard, B. CONOCO G.I. (October 1987), and C. EXXON-2 G.I. Key: 1. benzene, 2. toluene, 3. ethylbenzene, 4. xylenes, and 5. dichlorobenzene.

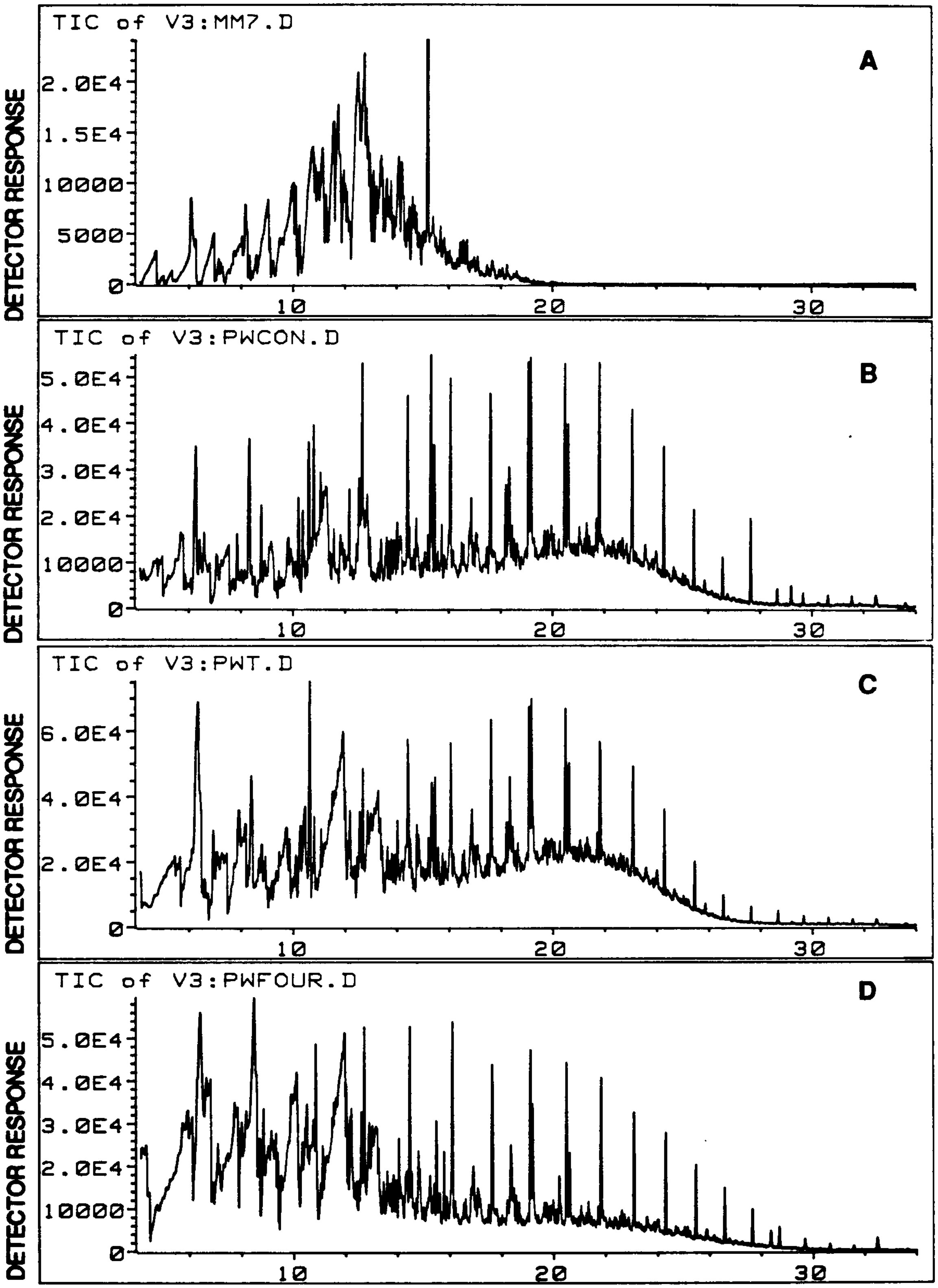


Figure 3.3. Comparison of the TIC's of four produced water samples: A. EXXON G.I. (October 1987), B. CONOCO G.I. (January 1988), C. TIMBALIER (January 1988), D. FOURCHON (January 1988).

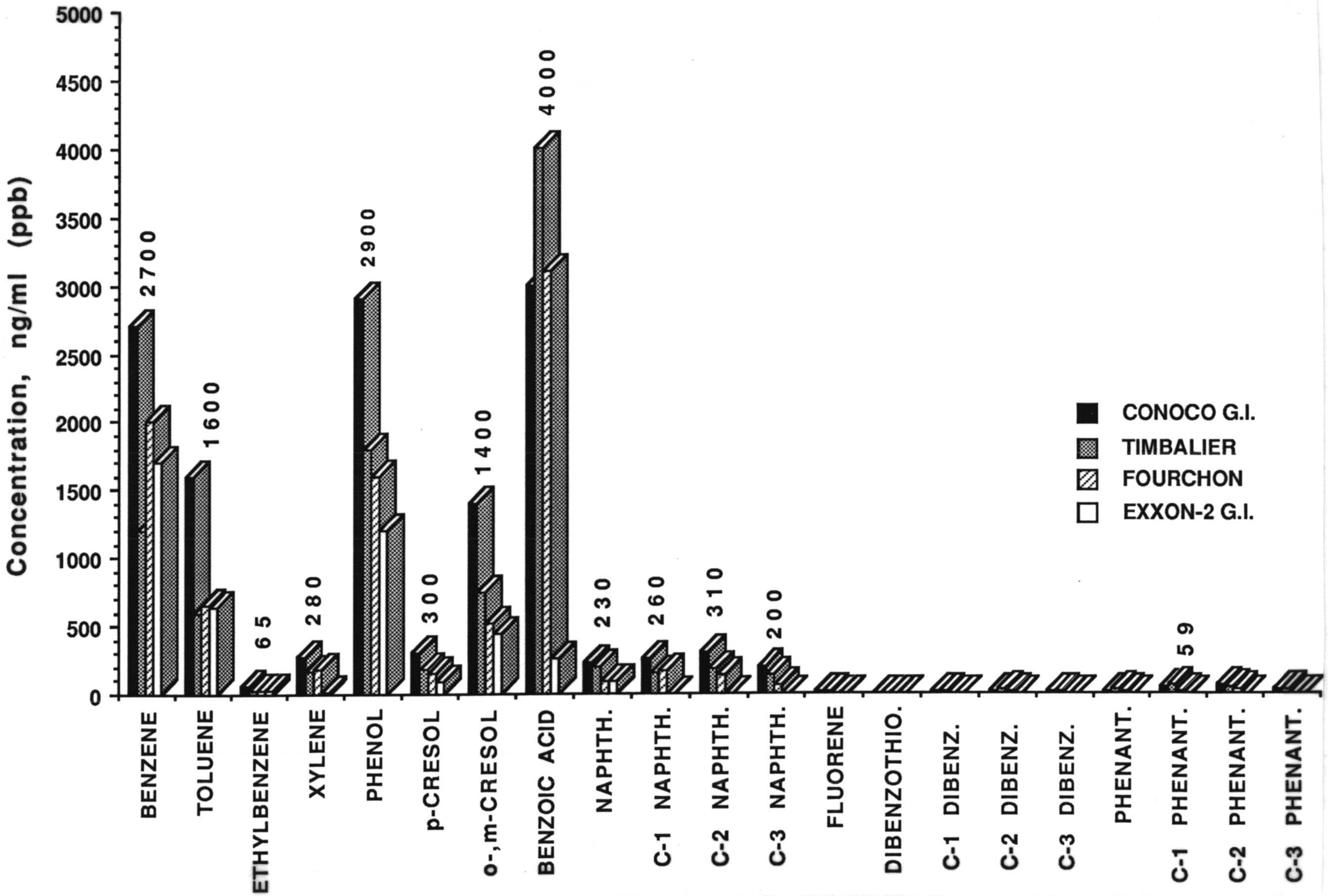


Figure 3.4. Comparison of target compounds in the produced waters investigated.

sample from January, 1988; the average of duplicate extracts was 240 ng/ml. The mean concentration for total target PAH was 690 ng/ml. The produced water discharge was enriched with naphthalene and its homologs compared to typical values for South Louisiana crude oil: an estimated 4.3-fold proportional increase in naphthalenes compared to phenanthrenes. The mean ratio of the dibenzothiophenes to the phenanthrenes was estimated at 0.32.

Acid phenols

The mean concentration of phenol was 1,900 ng/ml (Figure 3.4). The highest concentration of phenol, 2,900 ng/ml was found in the January CONOCO G.I. sample. The lowest was 1,200 ng/ml in the Exxon Grand Isle discharge. The mean concentration for the methyl phenols, or cresols, was 180 ng/ml and 780 ng/ml for p-cresol and o-,m-cresol (coeluted), respectively. The mean concentration for benzoic acid was estimated at 2,600 ng/ml. This value is semiquantitative and was determined using the response factor of the surrogate standard d5-phenol. In addition, methyl homologs of benzoic acid were detected in all samples.

Detailed evaluation of the acid constituents in CONOCO G.I. sample

The CONOCO G.I. sample was further characterized to determine the semivolatile organic acid composition of produced water. This was accomplished by liquid-solid fractionation of the sample extract and derivatization of the acid components to their methyl ester derivatives before high resolution GC/MS analysis. Both the underivatized and derivatized fractions were analyzed (Figure 3.5).

In the underivatized sample, poor chromatography of the polar components and possible absorptive losses of sensitive compounds made this analysis of little use. Phenol and its C-1 through C-2 homologs were detected and were the most abundant resolved peaks.

The derivatized sample contained the normal aliphatic acids from pentanoic acid through decanoic acid, branched aliphatic acids, cyclic carboxylic acids, benzoic acid and its methyl homologs, and various unknown acid compounds. Results are presented in Table 3.5. Further characterization of the polar organic semivolatiles was attempted by using the library search routines associated with the Hewlett Packard MS workstation and the NBS mass spectral library. Because of the lack of uniquely characteristic or molecular ions associated with most of the unknown compounds and the apparent lack of an extensive library of methyl ester derivatives in the NBS library, the library search routinely failed to identify most of the unknowns.

Figure 3.6 shows a comparison of the relative concentrations of selected compounds detected in sample CONOCO G.I. collected in January 1988. This comparison clearly illustrates the relative abundance of aliphatic acids and benzoic acids compared to the other hydrocarbon constituents.

Metals

Only the two Exxon Grand Isle produced water samples from October 1987 and the Conoco Grand Isle sample from October 1987, were analyzed for metals. Table 3.6 compares the metal concentrations found in the produced water from each plant. Results are reported for samples taken from the holding tank effluent and from the final effluent at the Exxon facility and for filtered and unfiltered samples.

The filtered and unfiltered samples demonstrated very similar results indicating that the metals detected were primarily in solution and not associated with particulates or suspended solids. Only iron showed major differences after filtration. The mean loss of iron after filtration was 96 percent.

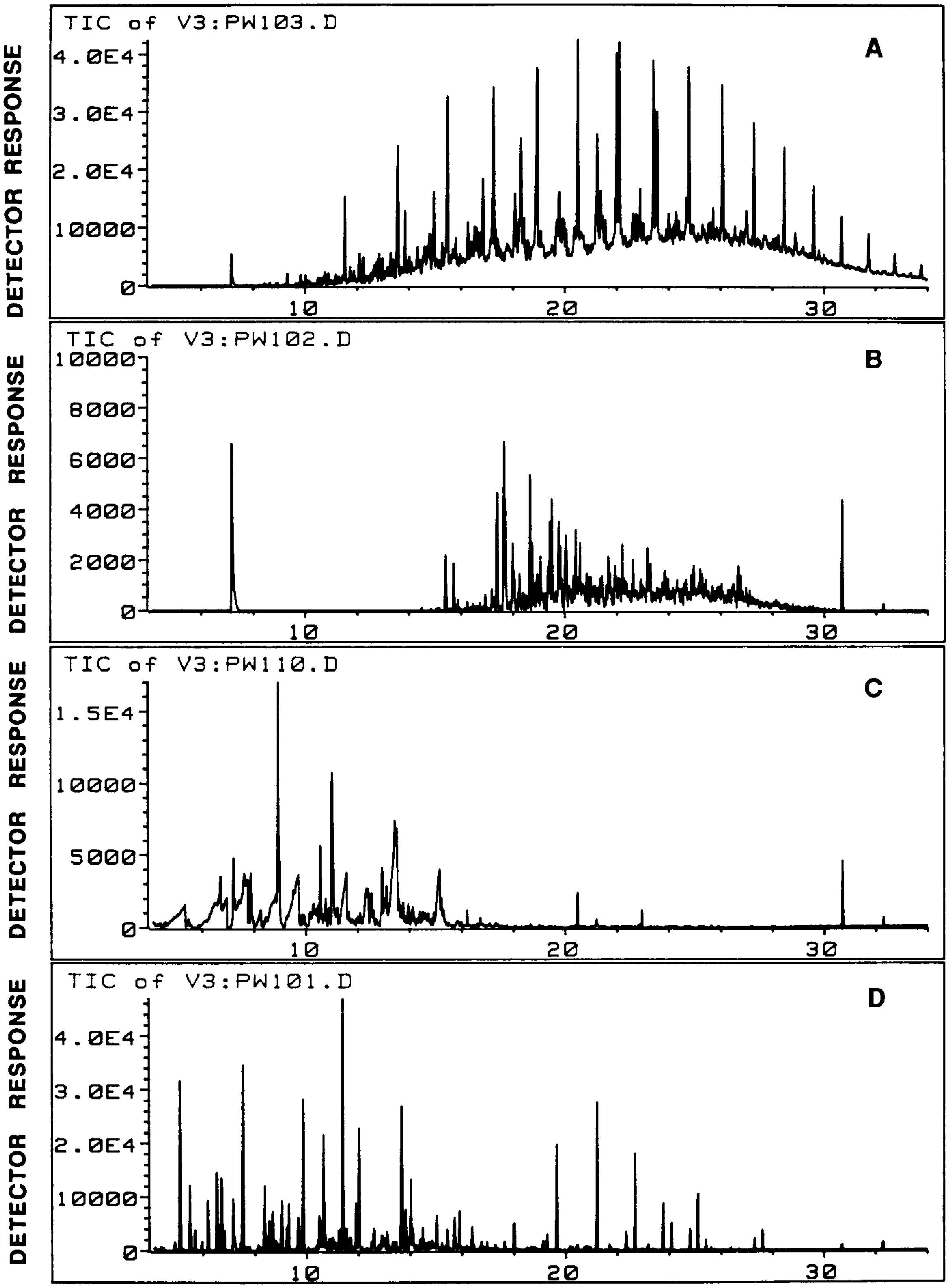


Figure 3.5. Comparison of the TIC's of the fractionated produced water sample CONOCO (January 1988): A. F-1, nonpolar saturated hydrocarbons (aliphatics); B. F-2, unsaturated hydrocarbons (PAH); C. F-3 polar hydrocarbons (phenols and acids); D. F-3 fraction after derivatization.

Table 3.5. The 24 most abundant peaks identified in the F-3 (polar) fraction of sample CONOCO G.I. (January 1988). The compound name reflects the methyl ester derivatization technique used. Concentrations are in ng/ml (ppb) and semiquantitative, SQ, concentrations are based on a response factor calculated from dodecanoic acid methyl ester. RT = retention time in minutes.

RT	ng/ml		COMPOUND
5.14	1,500		PENTANOIC ACID METHYL ESTER
5.52	680	SQ	UNKNOWN
6.21	550	SQ	UNKNOWN ALIPHATIC ACID METHY
6.56	930	SQ	UNKNOWN ALIPHATIC ACID METHYL
6.73	1,000	SQ	UNKNOWN ALIPHATIC ACID METHYL
7.57	1,500		HEXANOIC ACID METHYL ESTER
8.39	790	SQ	UNKNOWN
8.71	430	SQ	UNKNOWN ALIPHATIC ACID METHYL
9.06	610	SQ	UNKNOWN ALIPHATIC ACID METHYL
9.33	640	SQ	UNKNOWN
9.88	950		HEPTANOIC ACID METHYL ESTER
10.66	1,500	SQ	UNKNOWN
11.42	4,400	SQ	BENZOIC ACID METHYL ESTER
11.92	760	SQ	UNKNOWN CYCLIC ACID METHYL ESTER
12.04	670		OCTANOIC ACID METHYL ESTER
13.68	2,600	SQ	METHYLBENZOIC ACID METHYL ESTER
13.83	590	SQ	METHYLBENZOIC ACID METHYL ESTER
14.04	470		NONANOIC ACID METHYL ESTER
15.91	150		DECANOIC ACID METHYL ESTER
19.67	1,300	SQ	3-METHYLOCTANDIOIC DIMETHYL E.-LM
21.23	2,000	SQ	UNKNOWN
22.70	1,200	SQ	UNKNOWN
23.79	760	SQ	UNKNOWN
25.12	790	SQ	UNKNOWN ALIPHATIC ACID METHYL

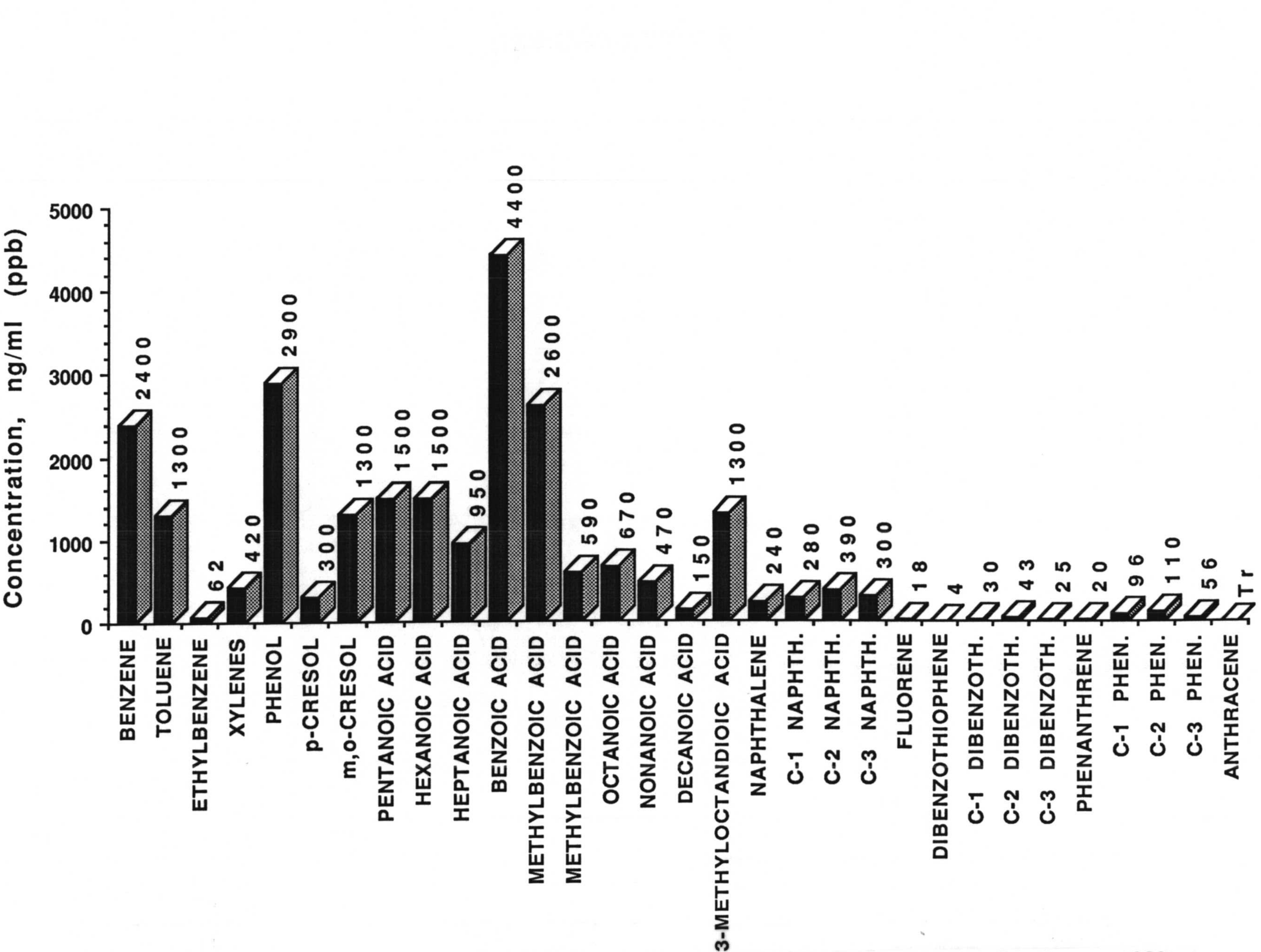


Figure 3.6. Comparison of the relative concentrations of selected compounds detected in CONOCO G.I. (January 1988).

Table 3.6. Metal concentrations in selected produced water samples.

Sample	Cu (µg/ml)	Zn (µg/ml)	Cd (µg/ml)	Pb (µg/ml)	Cr (µg/ml)	Ni (µg/ml)	Fe (µg/ml)	Mn (µg/ml)	Al (µg/ml)	Ba (µg/ml)	As (µg/ml)	Hg (µg/l)
Exxon												
Final Effluent												
filtered	0.36	0.086	0.046	0.25	0.034	0.043	0.16	0.81	0.51	20.3	0.20	<0.60
unfiltered	0.21	0.039	0.030	0.24	0.030	0.041	5.53	0.79	0.41	20.0	0.32	<0.60
Holding Tank												
filtered	0.28	0.069	0.035	0.26	0.033	0.041	0.36	0.77	0.40	20.6	0.20	<0.60
unfiltered	0.13	0.10	0.035	0.25	0.031	0.044	8.33	0.23	0.44	20.6	0.23	<0.60
Conoco												
filtered	0.32	0.053	0.043	0.17	0.024	0.036	0.11	0.62	0.27	39.9	0.27	<0.60
unfiltered	0.046	0.012	0.025	0.16	0.024	0.036	3.14	0.022	0.31	39.2	0.18	<0.60

Summary

The Exxon Grand Isle produced water discharge sample was markedly different than the other produced water discharges analyzed. The predominant components of the Exxon discharge were volatile aromatics, phenols, aliphatic acids, and various unidentified compounds which are possibly associated with the chemical treatment or partial degradation of hydrocarbons in the holding pond used at the facility. The Timbalier, Fourchon, and Conoco Grand Isle discharges contained not only the more water soluble volatile aromatics, phenols, and aliphatic acids, but also polynuclear aromatic hydrocarbons (primarily naphthalene and its alkylated homologs) and saturated aliphatic hydrocarbons up to nC-30.

3.4 Bayou Rigaud

3.4.1 Study Site

Two facilities discharge large quantities of OCS-generated produced waters into Bayou Rigaud, which constitutes the industrial harbor for Grand Isle, Louisiana (Figure 3.7). Conoco's Grand Isle Shore Base discharges approximately 105,000 bbl/day following separation in a large separation tank and temporary storage in a large holding tank. The discharge enters the terminus of a deep slip off Bayou Rigaud into the Conoco facility. The slip is dredged into a stiff clay stratum and vessel traffic in and out of the slip is apparently sufficient to keep fine sediments from depositing in the slip and its mouth. Exxon's Grand Isle Station separates approximately 45,000 bbl/day of produced water. After the separation tank, the produced water is held in a large tank with a residence time of approximately one day before discharge into a maze-structured pond which is skimmed and has a small aeration device about mid-course. From the ponds, the water flows into a drainage ditch leading to Bayou Rigaud. In comparison to the Conoco facility, the produced water in the Exxon facility receives some aeration in the pond and traverses over a sludge bed before discharge into a drainage ditch leading to Bayou Rigaud.

Bayou Rigaud is dredged to 6 m for navigational access by offshore supply vessels. Sediments on the floor of the channel are very fine, representing recently deposited material which is probably resuspended by vessel traffic and periodically removed by dredging. The bayou opposite Grand Isle is shallower and grades to the contained dredged material deposits on Fifi Island. Tidal currents through the northeastern end of Bayou Rigaud are swift, being influenced by tidal exchange through the nearby Barataria Pass. As a consequence, bottom sediments at the eastern end of the bayou grade quickly from sandy mud to hard sand with shell fragments.

Station BR-1 was in mid-channel near the Conoco discharge and BR-2 in the channel near Exxon's discharge (Figure 3.7). Stations BR-3, BR-4, and BR-5, sampled in October, were also located mid-channel, where depths ranged from 4 to 6.5 m. Additional stations were sampled in January. BR-13 and BR-14 were placed mid-channel, away from the discharge points in both directions but not as great a distance as the mid-channel stations sampled in October. A series of shallower stations (1 to 2 m) were sampled along the northern and southern shorelines of Bayou Rigaud in January (BR-7, BR-8, BR-9, BR-10, and BR-12). Station BR-11 was situated in 5 m water depth at the end of the drainage ditch receiving the Exxon discharge.

The water column in Bayou Rigaud at mid-channel was slightly stratified with regards to both temperature and salinity. Temperature differences between surface and bottom waters in both October 1987 and January 1988 were both within 2 °C. Salinity differences for the sample dates were within 2 ppt. In October 1987 salinity in the surface water was 24 to 26 ppt and near the bottom was 25 to 28 ppt. In January 1988 (Figure 3.8), salinities were about 26.5 ppt on the surface and 28.5 ppt near the bottom.

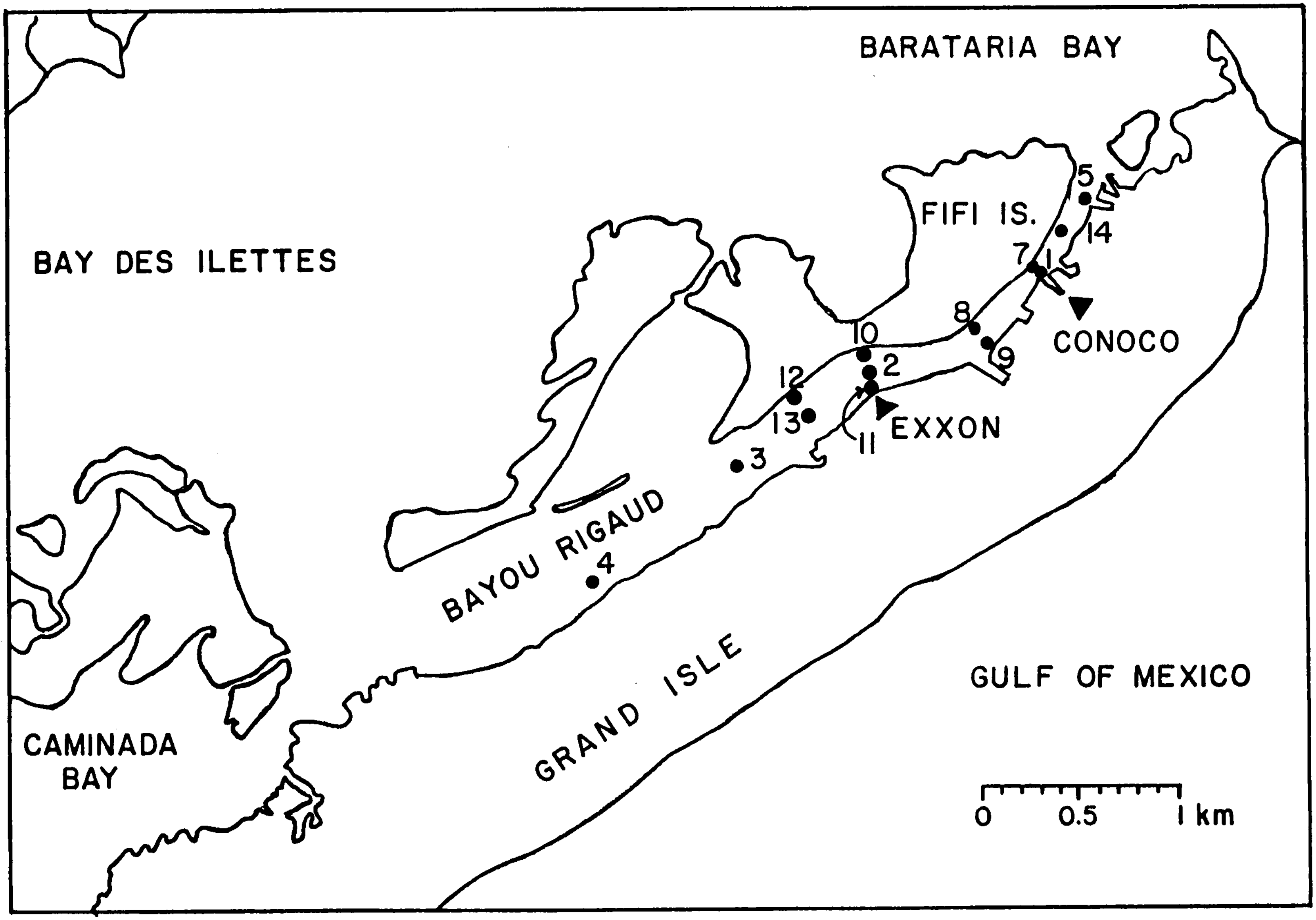


Figure 3.7. Bayou Rigaud study area; produced water discharges indicated by closed triangles.

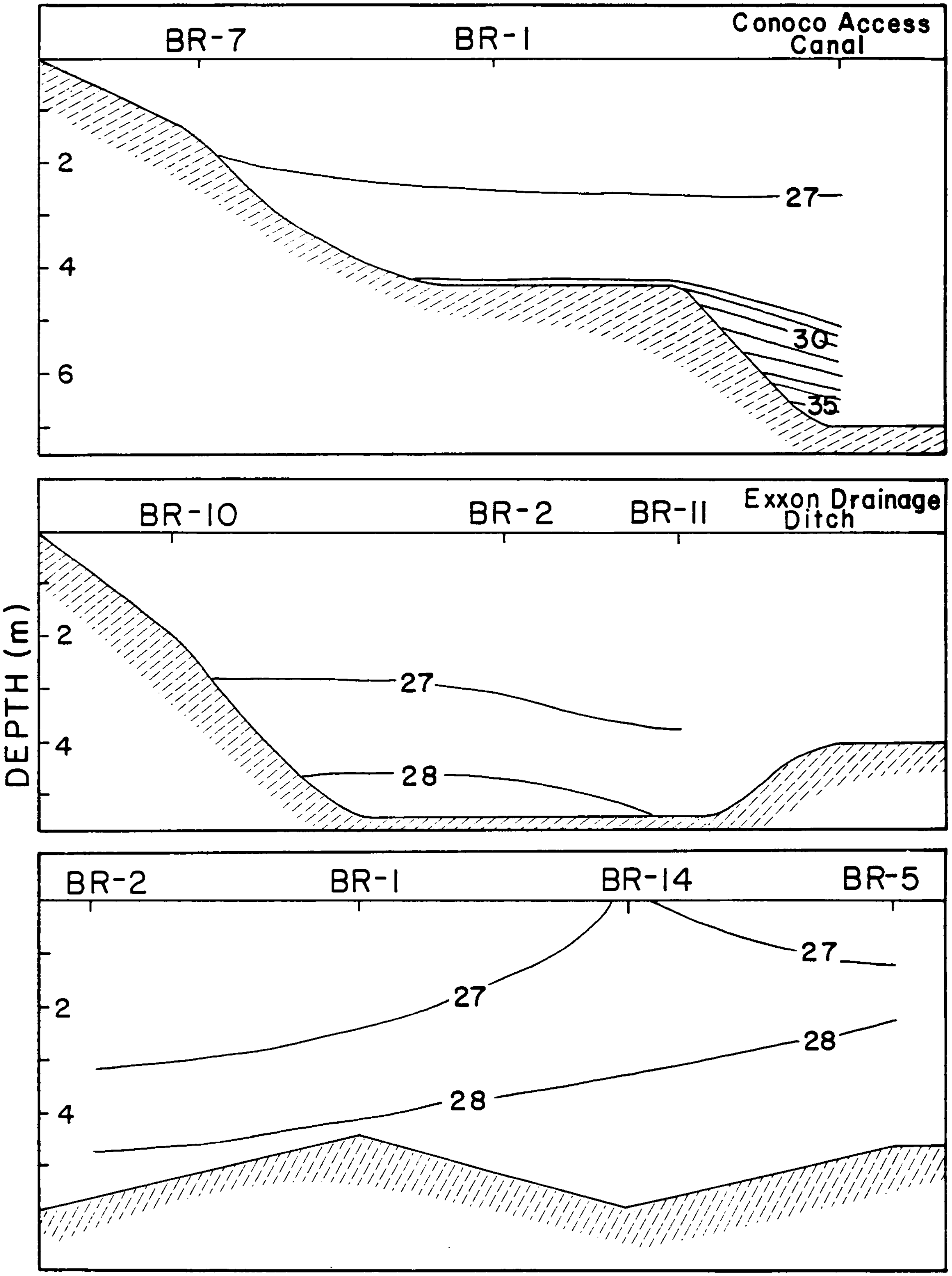


Figure 3.8. Water column salinity (ppt) profiles at two locations across Bayou Rigaud and mid-channel along the length of Bayou Rigaud in January 1988.

In January 1988, stations nearer the discharge were sampled for hydrographic profiles. At a location just inside the Conoco access canal near BR-1, near-bottom salinities were 35.3 ppt (Figure 3.8). Near bottom values at BR-1 were similar to other mid-channel stations. At BR-11, located near the Exxon discharge ditch, bottom salinities (27.9 ppt) were slightly lower than the nearby mid-channel stations (Figure 3.8). Similar near-bottom salinities were found 15 m northeast and 25 m southwest from station BR-11.

3.4.2 Organics

Sediments

The hydrocarbon data for Bayou Rigaud sediments are presented in Table 3.7 and Figures 3.9 through 3.21.

In October, the highest concentrations of petrogenic hydrocarbons were detected in the immediate vicinity of the discharges, as seen in hydrocarbon data from BR-1 and BR-2 (Table 3.7). Station BR-1 sediments contained the highest levels of PAH and saturated hydrocarbons of the five sites sampled during October. The type of hydrocarbons at BR-1 appeared primarily petrogenic in origin as evidenced by the FFPI. Station BR-2 did not appear to be as heavily impacted as BR-1, but was contaminated, primarily with petroleum-derived hydrocarbons, consisting of alkyl-substituted phenanthrenes and dibenzothiophenes.

The concentration of sediment hydrocarbons fell off toward the southwest along Bayou Rigaud (Figs. 3.9 and 3.10). Station BR-3 contained low levels of PAH, while BR-4 contained no detectable PAH, except for a trace of the pyrogenic fluoranthene. Station BR-5, 0.4 km northeast of BR-1, contained the third highest concentration of PAH and saturated hydrocarbons. The composition of these hydrocarbons indicated contamination from a petrogenic source. Because of an abrupt change to coarser sediments (sand and shell) into Barataria Pass, there was little deposition of hydrocarbon-contaminated sediments toward Barataria Pass.

At station BR-1 total PAH and saturated hydrocarbons increased with depth (Fig. 3.11). The hydrocarbon depth profile for BR-1 showed evidence of increased weathering with depth (Figs 3.12 and 3.13). The surface sediment was moderately weathered with normal alkanes up to nC-30 and an unresolved hydrocarbon complex. The ratios of the resolved branched alkanes increased compared to the normal unbranched alkanes at greater depths in the core.

Figure 3.11 shows the depth profile for the core collected at station BR-2, located near the Exxon Grand Isle discharge ditch, for both the saturated hydrocarbons and PAH. This core demonstrated a moderately weathered hydrocarbon profile on the surface with normal aliphatic hydrocarbons up to nC-26 (Figs. 3.14 and 3.15). The surface sediment was higher in aliphatic hydrocarbons compared to the discharge water sample. This apparent enrichment may be due to the partitioning of the low water soluble hydrocarbons into the sediment relative to the more water soluble hydrocarbons. A second explanation could be contamination of station BR-2 by both the Exxon discharge and the Conoco discharge located 1.1 km away. Lower in the core, there appeared to be a resistant group of compounds associated with the Exxon production water discharge. These compounds can be seen in Figure 3.15 at between 8 and 18 min.

The sediments sampled in January displayed a similar pattern of PAH and saturated hydrocarbon concentrations as in October (Figures 3.16 and 3.17). Station BR-11, located at the mouth of the drainage ditch accommodating the Exxon discharge, contained the highest concentrations of PAH and saturated hydrocarbons measured in the January sampling. The composition of PAH, based solely on the FFPI, did not indicate a pure petrogenic source as would be expected from the sample location. There was a large pyrogenic component present at

Table 3.7. Hydrocarbon concentrations (ng/g) in Bayou Rigaud sediments.

Sample	Depth	Total PAH (ppb)	FFPI	Total Saturated H.C. (ppb)
October 1987				
BR-1	0-5 cm	27,000	0.96	1,700,000
BR-1 Dup	0-5 cm	22,000	0.78	920,000
BR-1	5-10 cm	39,000	0.92	1,800,000
BR-1	10-15 cm	34,000	0.94	2,700,000
BR-1	15-18 cm	120,000	0.97	7,700,000
BR-2	0-5 cm	1,500	0.76	330,000
BR-2	5-10 cm	72	0.00	110,000
BR-2	10-15 cm	690	0.60	100,000
BR-3	0-5 cm	190	0.50	98,000
BR-4	0-5 cm	<42	N/A	38,000
BR-4	5-10 cm	<44	N/A	23,000
BR-4	10-15 cm	<34	N/A	12,000
BR-4	15-20 cm	<39	N/A	14,000
BR-5	0-5 cm	950	0.87	180,000
BR-5 Dup	0-5 cm	780	0.88	110,000
BR-5	5-10 cm	50	N/A	89,000
BR-5	10-15 cm	<81	N/A	27,000
January 1988				
BR-1	0-5 cm	4,300	0.87	72,000
BR-2	0-5 cm	1,300	0.85	58,000
BR-7	0-5 cm	3,600	0.89	73,000
BR-8	0-5 cm	1,300	0.86	34,000
BR-9	0-5 cm	890	0.69	58,000
BR-9 Dup	0-5 cm	850	0.61	49,000
BR-10	0-5 cm	570	0.84	39,000
BR-11	0-5 cm	18,000	0.49	94,000
BR-12	0-5 cm	180	0.54	14,000
BR-13	0-5 cm	630	0.67	9,000
BR-14	0-5 cm	520	0.88	38,000

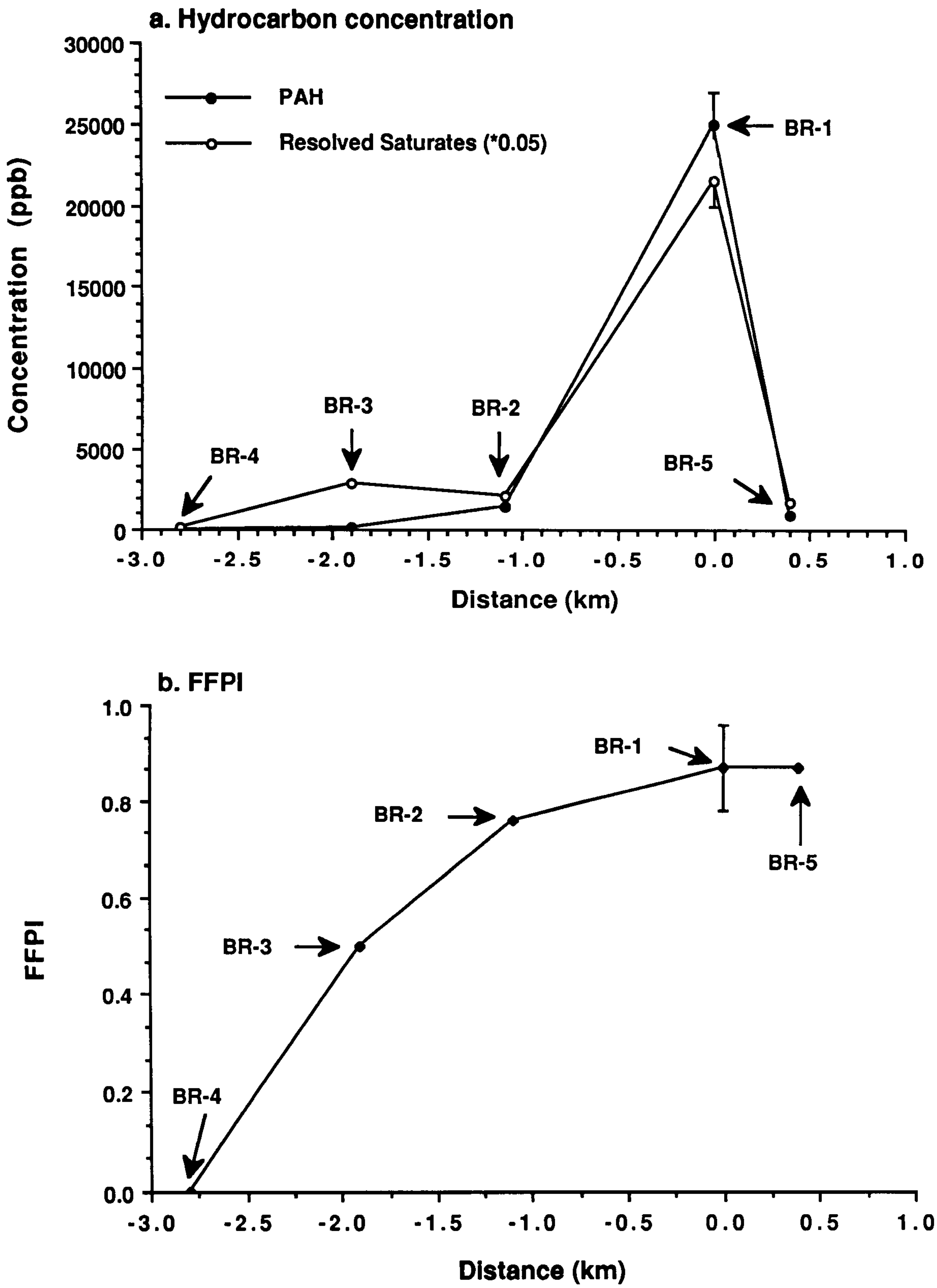


Figure 3.9. Longitudinal profiles of hydrocarbon concentrations (a.) and FFPI (b.) in sediments away from BR-1 (October 1987).

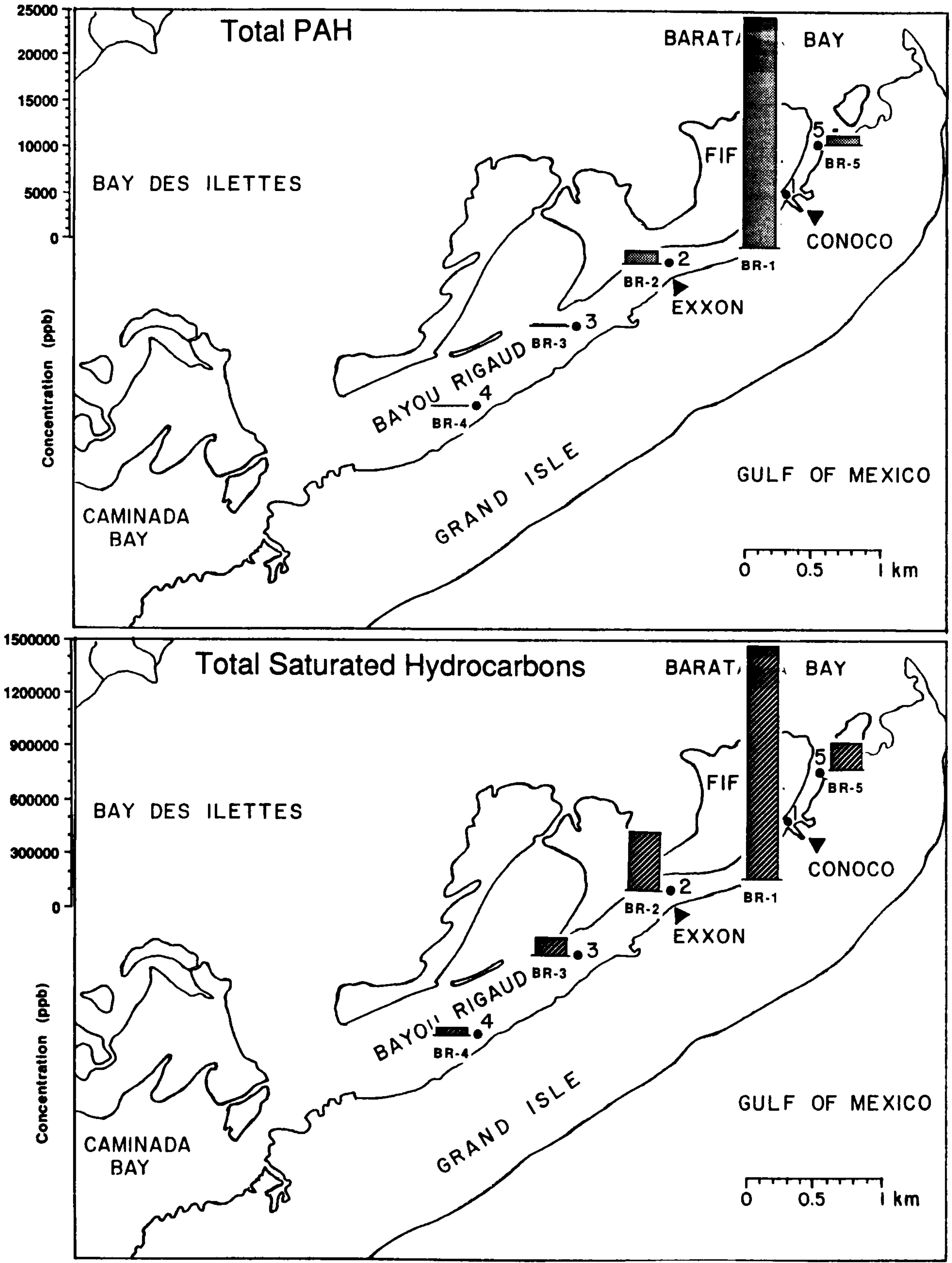
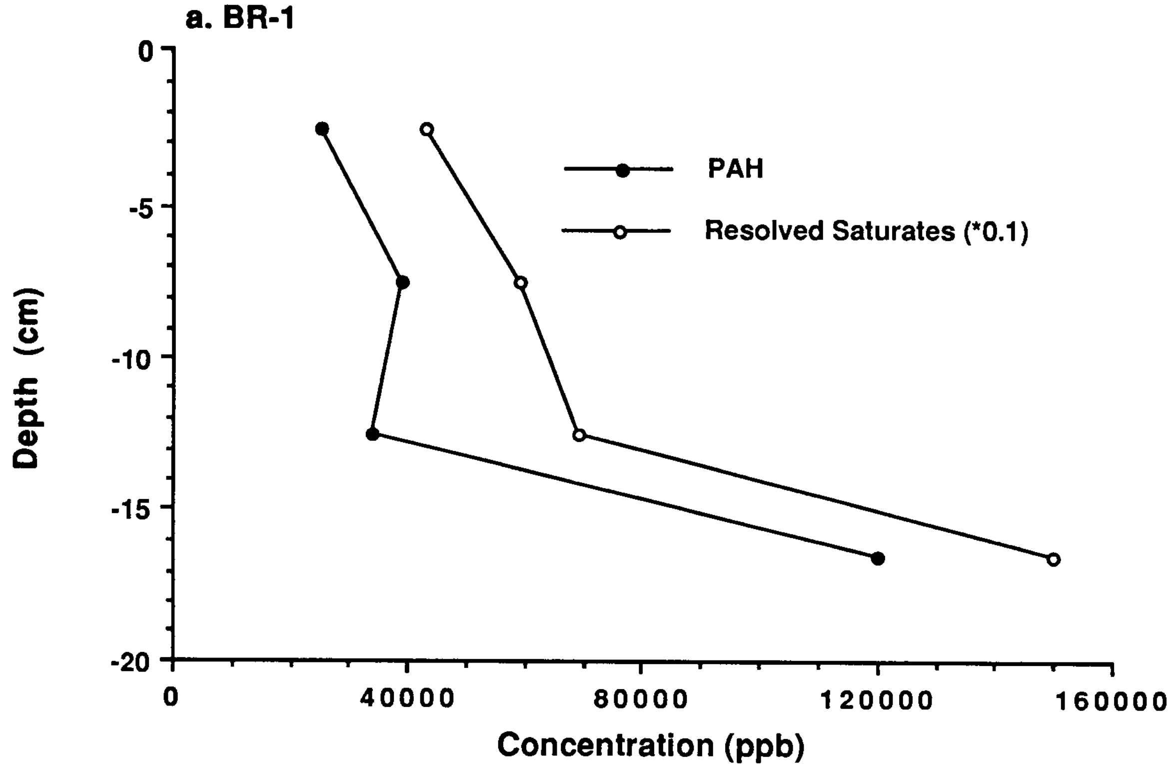


Figure 3.10. Bayou Rigaud location map with total PAH, above, and saturated hydrocarbon concentrations, below, in sediments for October 1987.



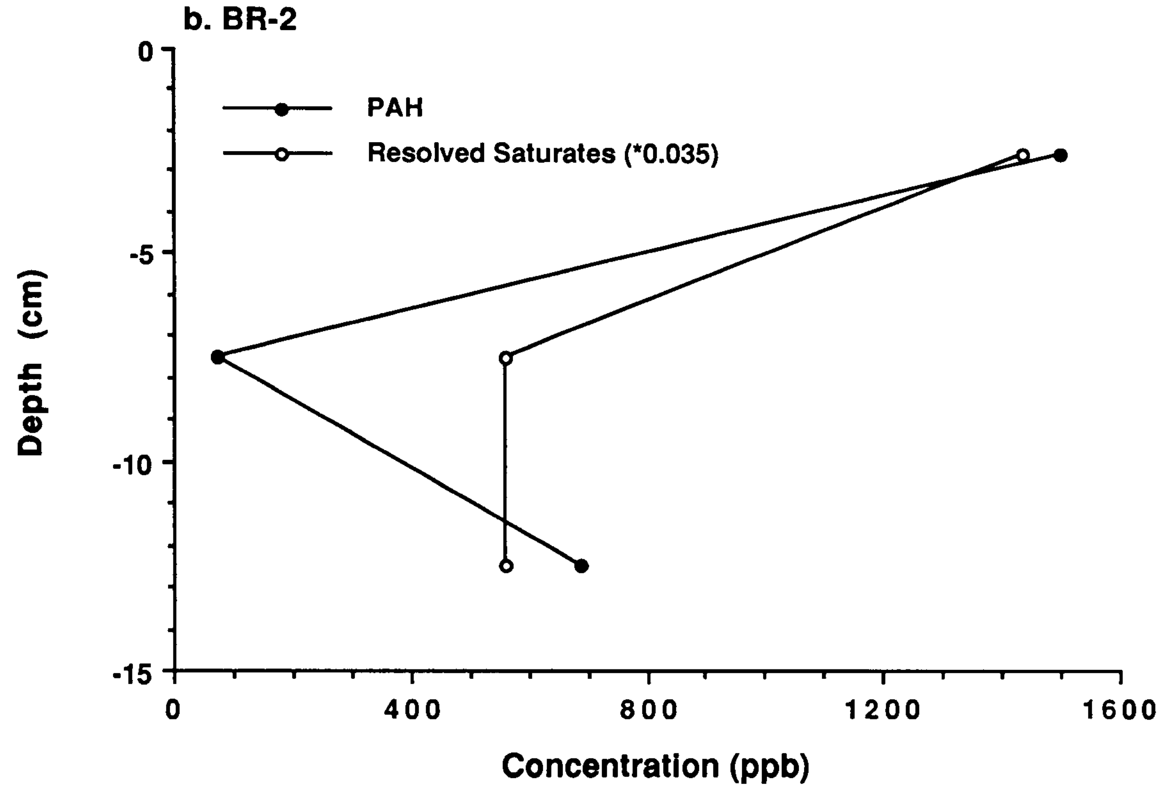


Figure 3.11. Depth profiles of hydrocarbon concentrations in sediments for two Bayou Rigaud stations (October 1987).

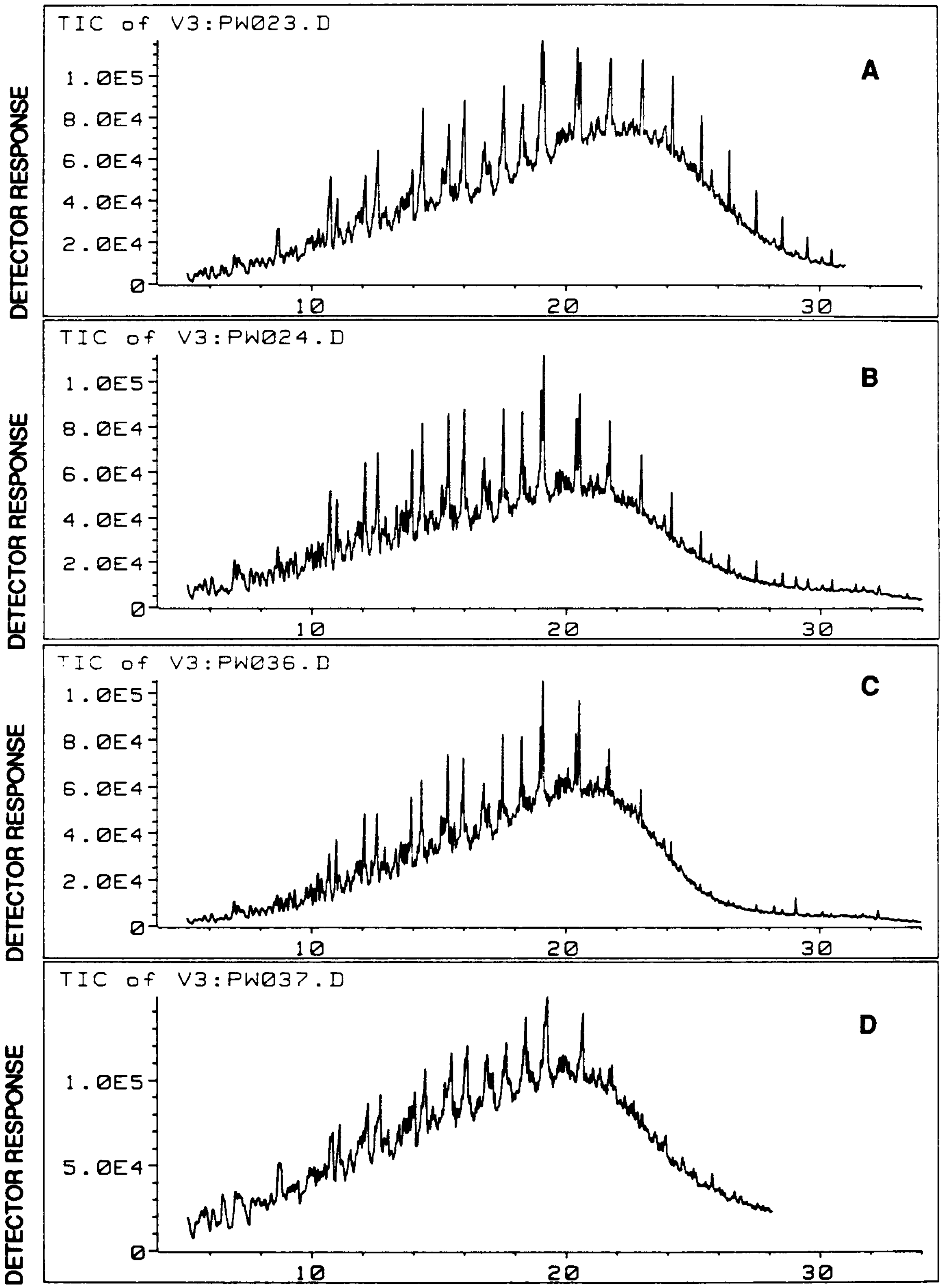


Figure 3.12. Comparison of the depth profile TIC's from core BR-1 (October 1987): A. 0-5 cm, B. 5-10 cm, C. 10-15 cm, D. 15-20 cm.

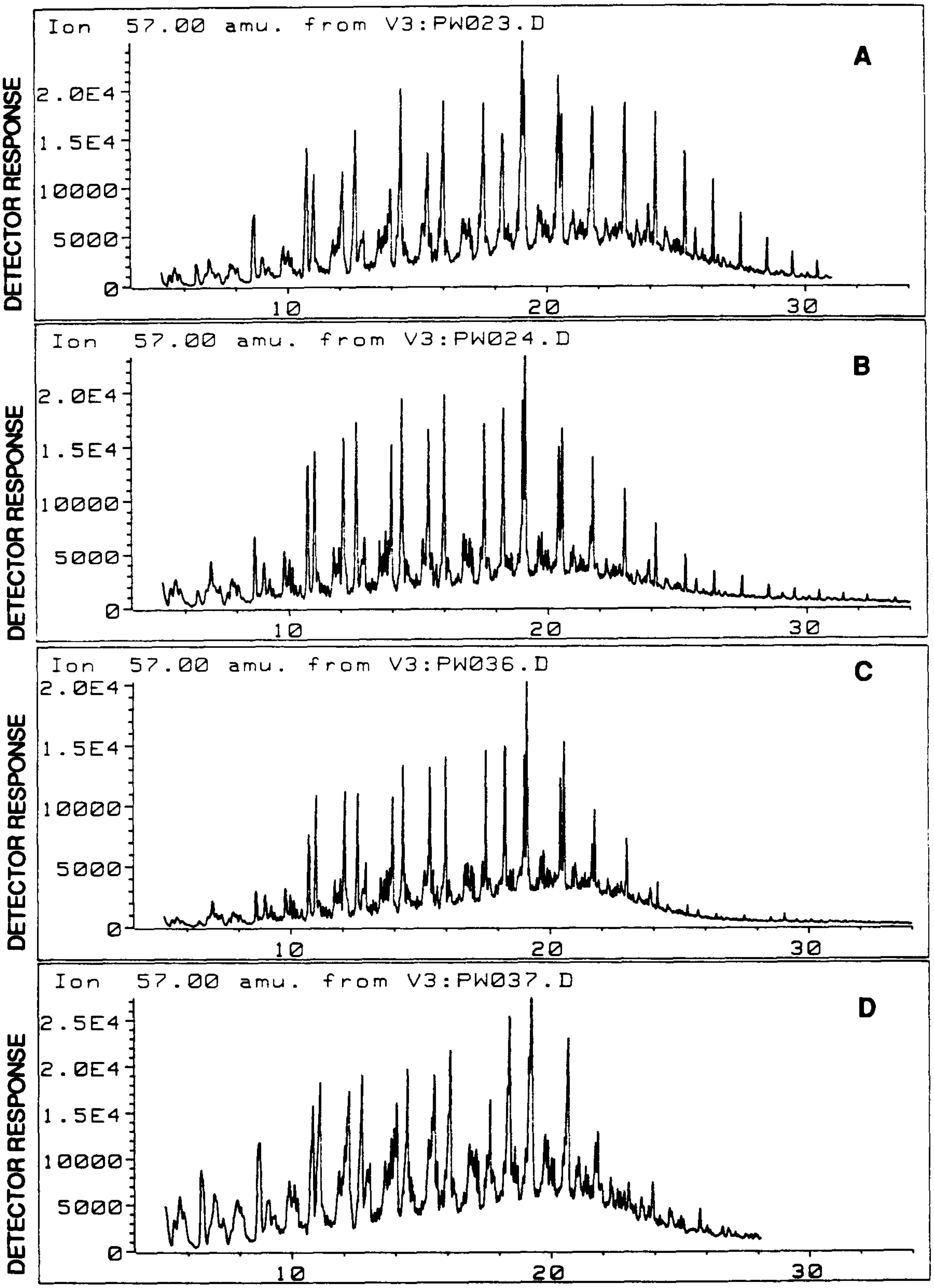


Figure 3.13. Comparison of the depth profile EIC's for m/z 57 from core BR-1 (October 1987): A. 0-5 cm, B. 5-10 cm, C. 10-15 cm, D. 15-20 cm.

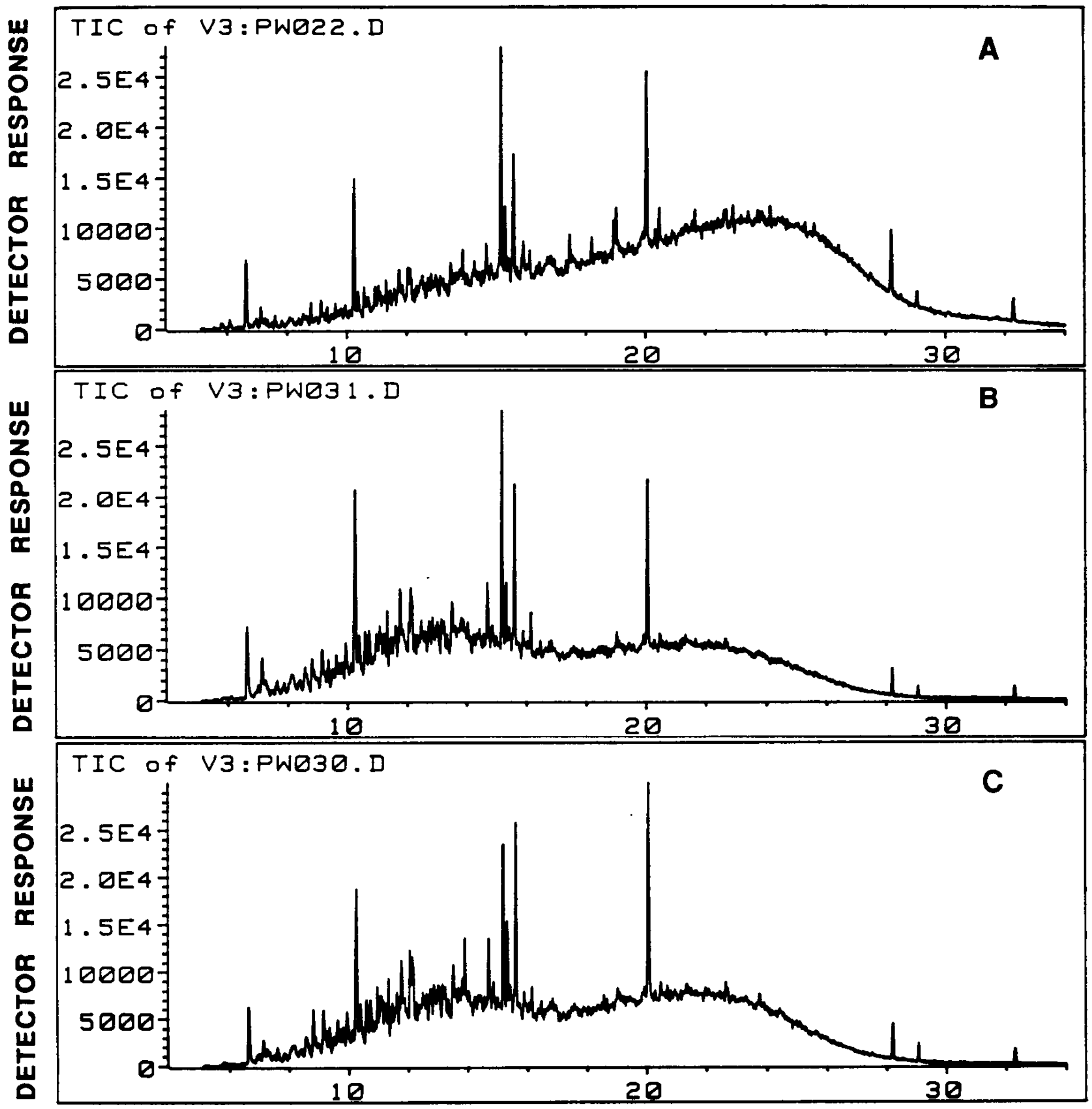


Figure 3.14. Comparison of the depth profile TIC's from core BR-2 (October 1987): A. 0-5 cm, B. 5-10 cm, and C. 10-15 cm.

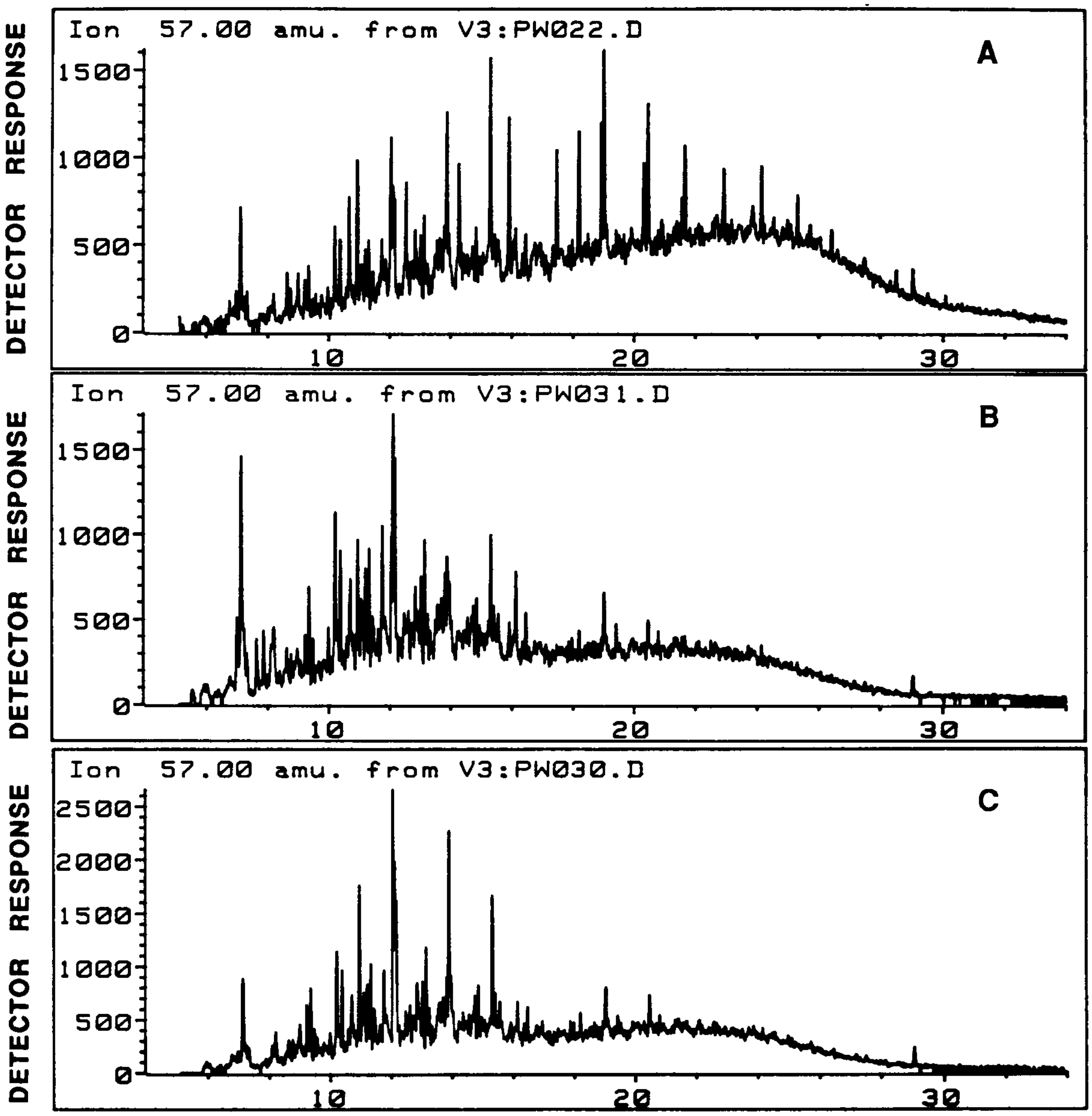


Figure 3.15. Comparison of the depth profile EIC's m/z 57 from core BR-2 (October 1987): A. 0-5 cm, B. 5-10 cm, and C. 10-15 cm.

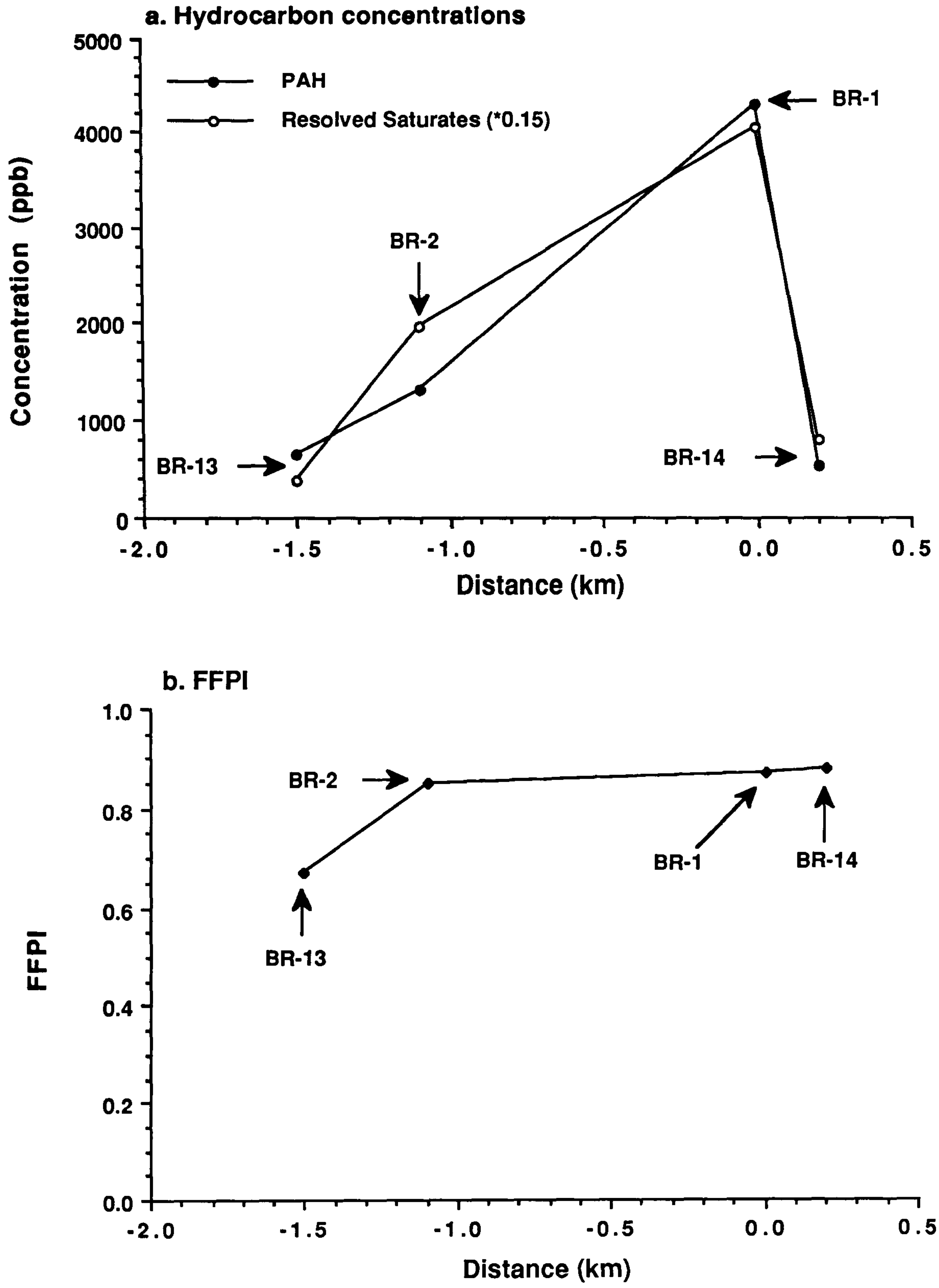


Figure 3.16. Longitudinal profiles of hydrocarbon concentrations, above, and FFPI, below, in sediments away from BR-1 (January 1988).

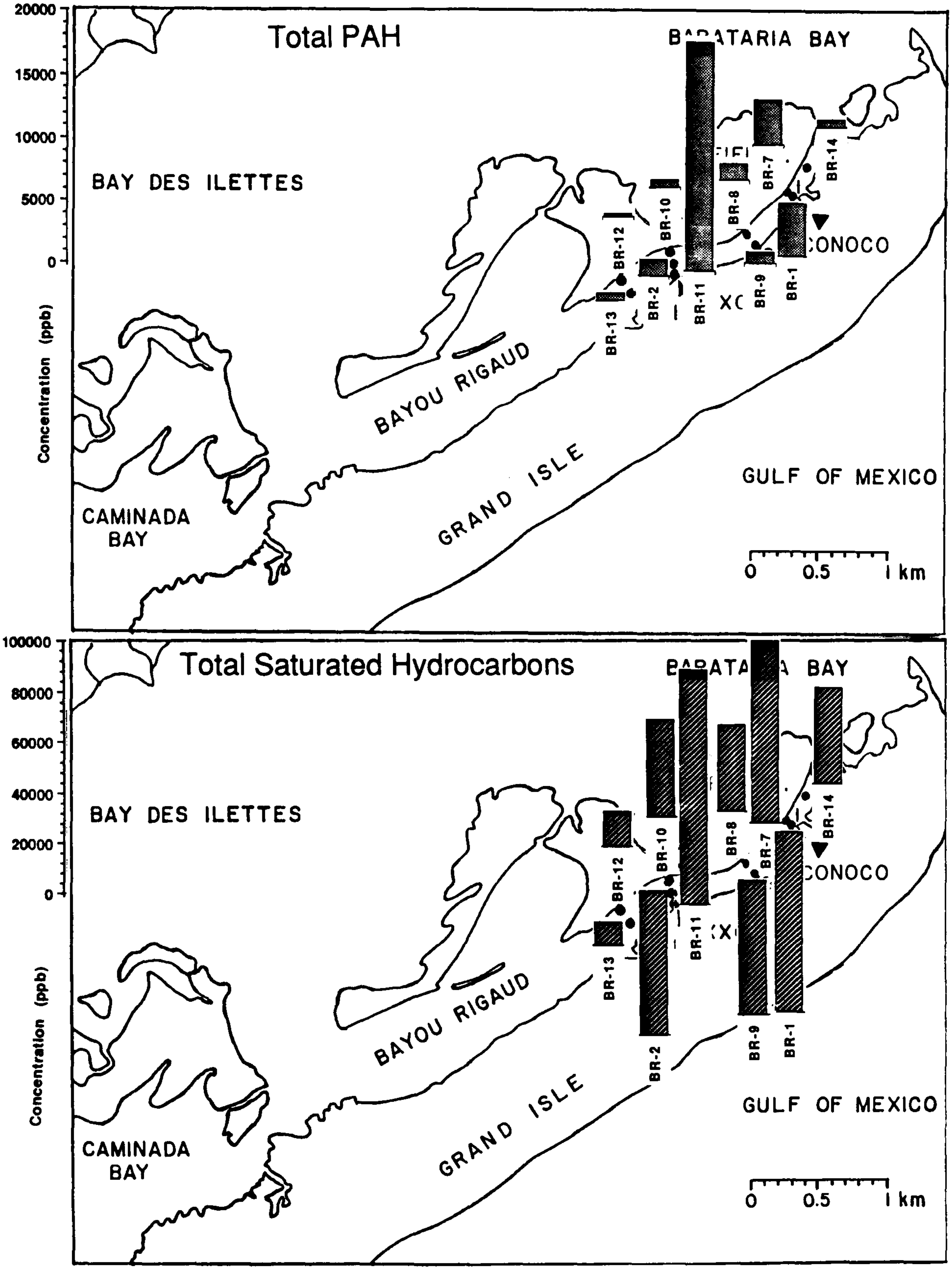


Figure 3.17. Bayou Rigaud location map with total PAH, above, and saturated hydrocarbon concentrations, below, in sediments for January 1988.

this station, the source of which is unknown. The composition of the non-pyrogenic PAH, however, is consistent with a petroleum input. The interstitial salinity was 45 ppt, which confirmed that the highly-saline produced water had impacted the sediments at this station. Figure 3.18 shows a profile north from BR-11 across the channel. Total PAH in sediment decreased drastically only 60 m from the discharge (BR-2). The interstitial salinity decreased to 26 ppt, which is in the range of ambient salinities from this area. The pyrogenic compounds that were very prominent in BR-11 were only a minor component in these sediments. This suggests that the pyrogenic hydrocarbons found in BR-11 may be a local phenomenon and not associated with the discharge. At 150 m (BR-10), there was still evidence of petroleum-derived hydrocarbons in the sediments.

Station BR-1, which is near the Conoco discharge, contained the next highest concentration of PAH, although at much lower levels than the October sampling. Qualitatively, the hydrocarbons present in each sampling period were similar, with alkyl-substituted components at much higher levels than their parent compounds. The profile of stations that were located mid-channel (Figure 3.16), showed the same pattern as in October. PAH and saturated hydrocarbon concentration dropped off drastically with distance away from BR-1. At Station BR-13, which was 1.5 km southwest of BR-1, sediment contained elevated levels of PAH but a significant portion of these were pyrogenic. At Station BR-14, which is 0.2 km northeast of BR-1, sediment contained slightly less PAH than BR-13, but compositionally they were more petrogenic.

A profile away from Station BR-7, which is opposite the Conoco discharge, of shallow stations along the north shore of Bayou Rigaud (Figure 3.19), showed the same pattern as the mid-channel profile. Station BR-7, just north of BR-1, contained the third highest concentration of PAH and was compositionally very similar to BR-1. Stations BR-8 and BR-10 both displayed decreasing levels of PAH compared to BR-7, but compositionally the PAH were still petroleum derived. Station BR-12 contained the lowest levels of PAH detected in January with the majority being pyrogenic in origin.

Station BR-9, which was 900 m from the Exxon discharge and 200 m from the Conoco discharge, contained moderately high levels of PAH. This station contained C-2 and C-3 substituted naphthalenes and phenanthrenes which indicated petroleum contamination. Along with petroleum-derived PAH, some pyrogenic PAH were detected which lowered the FFPI.

Figure 3.20 is a 3-dimensional plot of PAH concentration based on both the October and January sediment samples. The highest concentrations of PAH are readily noticeable in the vicinity of the two discharges with concentrations decreasing away from the discharges. This suggests that the impact of the produced water discharges extends across the bayou and about 1 km in either direction along the channel.

Overlying waters

Tabulated data for the overlying water samples collected in October 1987 are found in Table 3.8. The most abundant compound detected was benzene. The concentration of benzene at Station BR-1 was 930 ng/ml. Semivolatiles were also detected but at very low levels. Figure 3.21 shows a comparison of the TIC's and EIC's (m/z 57) of the Conoco discharge water and the overlying water collected at station BR-1. From the chromatographic comparison, the overlying water can be fingerprinted to the Conoco produced water discharge. The loss of the lower molecular weight aliphatics and aromatics in the overlying water is probably the result of evaporation and other weathering processes. In general, the chromatographic comparisons showed identical patterns in the relative abundance of the higher molecular weight constituents. Overlying water from station BR-2, out from the Exxon discharge, contained 800 ng/ml of benzene and 52 ng/ml of toluene. No target semivolatiles were detected.

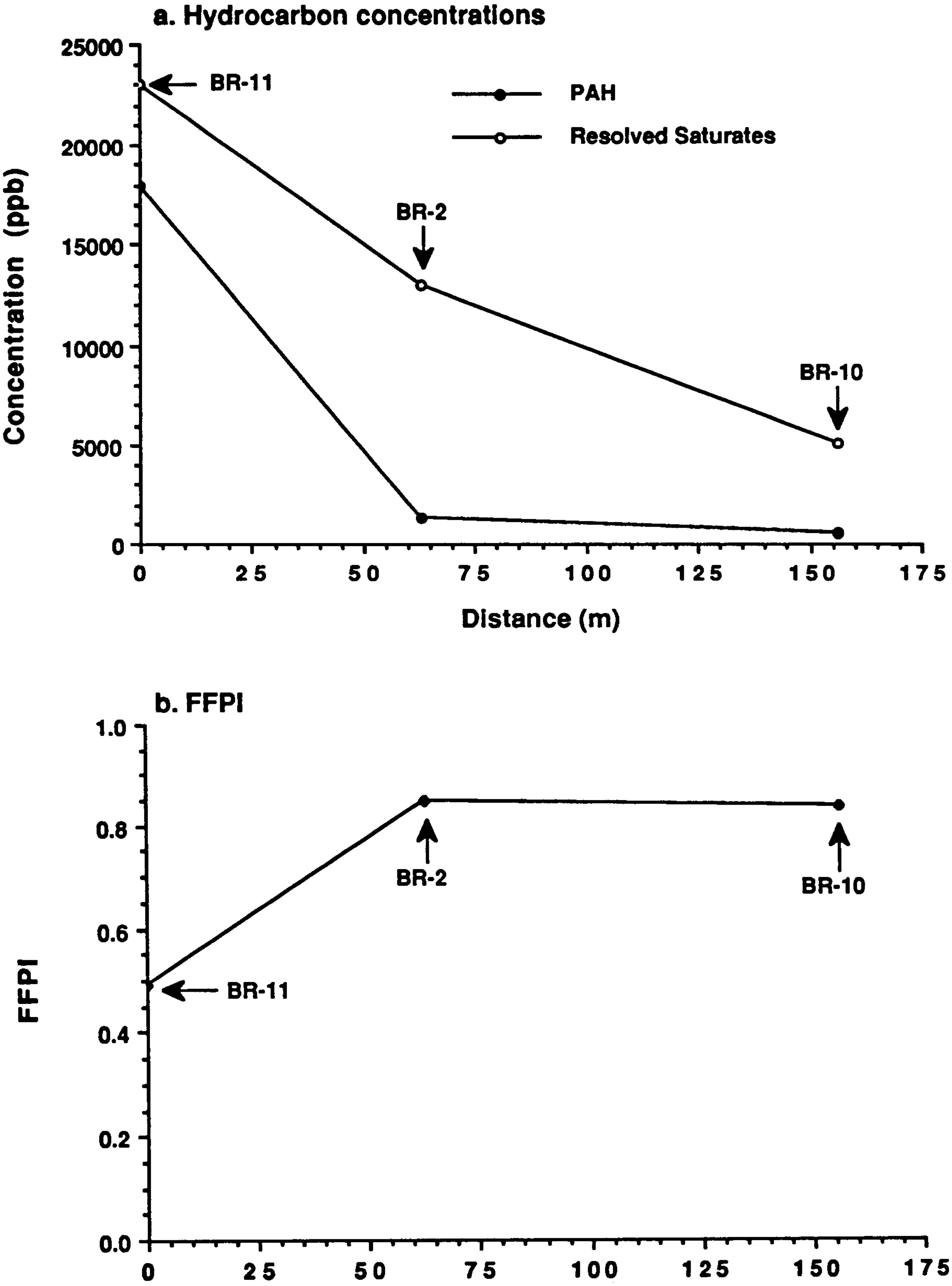
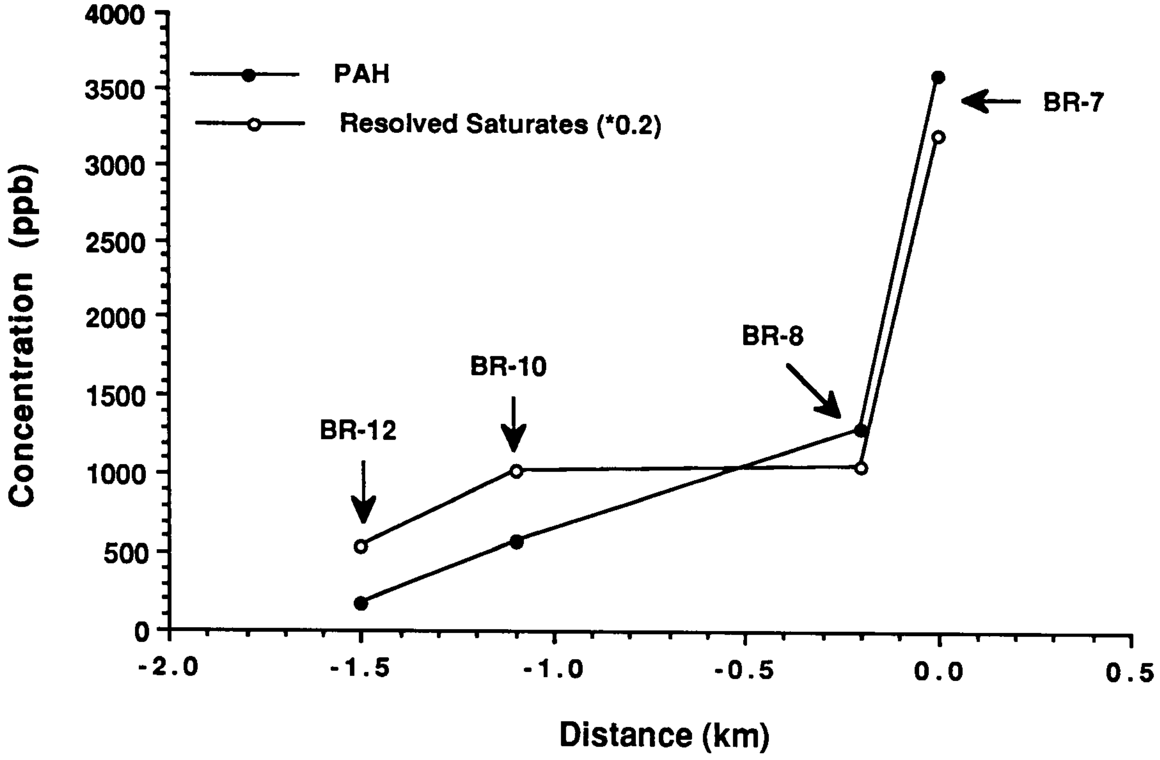


Figure 3.18. Cross-sectional profiles of hydrocarbon concentrations (a.) and FFPI (b.) in sediments away from BR-11 across the channel from the Exxon discharge, (January 1988).

a. Hydrocarbon concentrations



b. FFPI

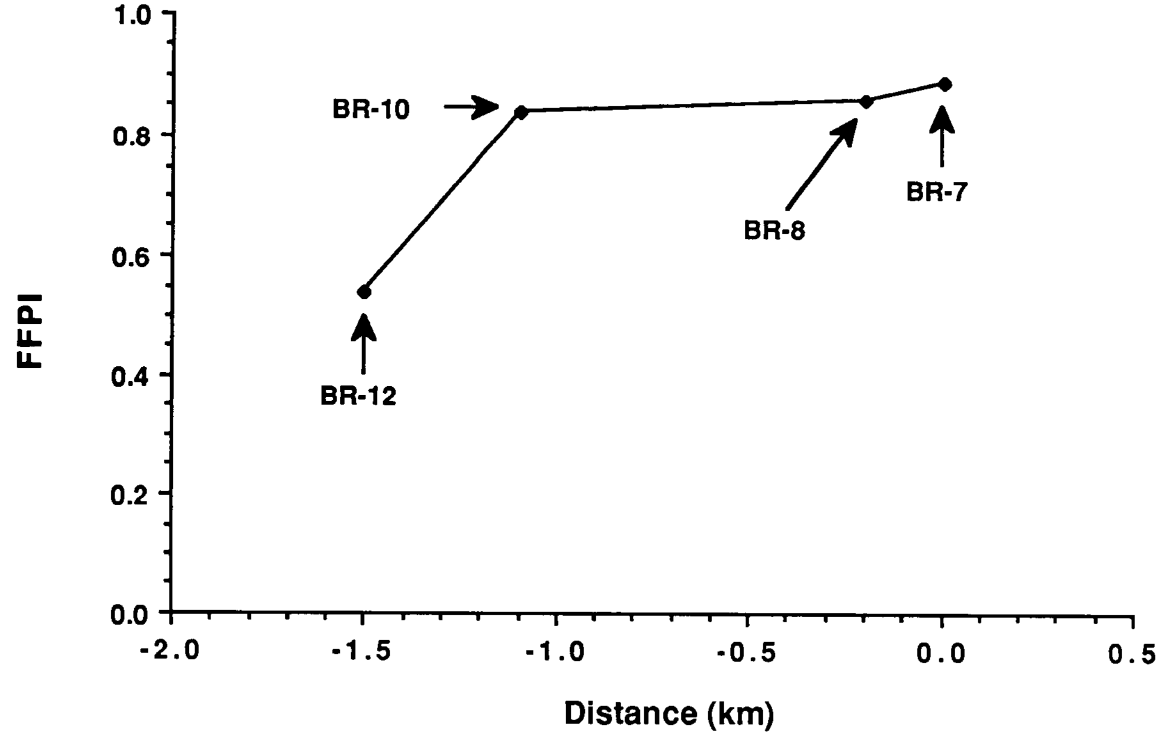


Figure 3.19. Longitudinal profiles of hydrocarbon concentrations in sediments along the northern shoreline of Bayou Rigaud away from BR-7 which is opposite the Conoco discharge (January 1988).

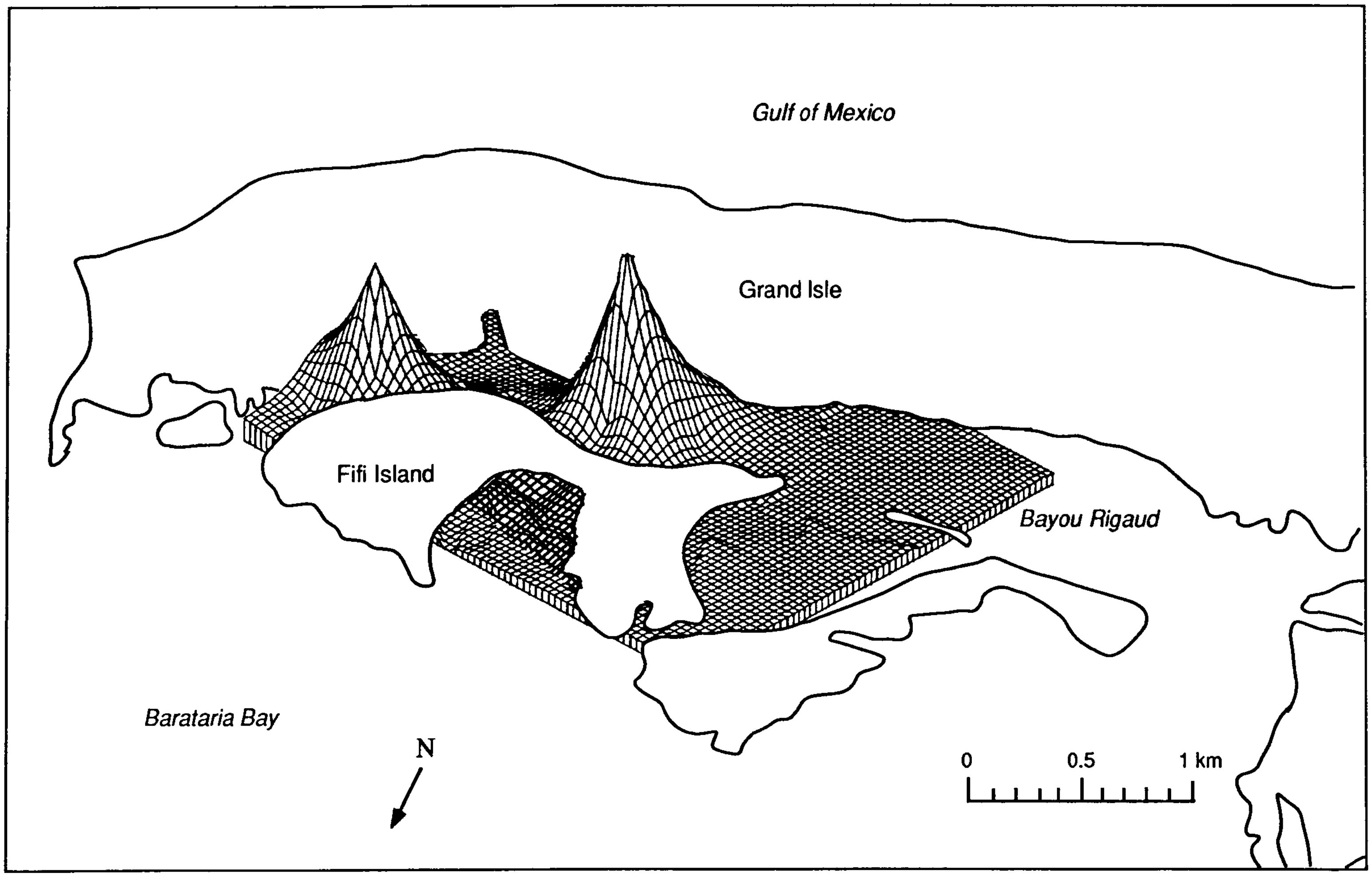


Figure 3.20. Distribution of PAH in Bayou Rigaud.

Table 3.8. Hydrocarbon concentrations in Bayou Rigaud overlying waters.

Sample	Benzene (ng/ml)	Toluene (ng/ml)	Ethylbenzene (ng/ml)	Xylenes (ng/ml)	Total PAH (ng/ml)	Total Saturated H.C. (ng/ml)
October 1987						
BR-1	930	16	ND	ND	60	570
BR-2	800	52	ND	ND	<5	ND
BR-5	ND	ND	ND	ND	<5	ND
January 1988						
BR-1	340	220	14	87	<5	ND
BR-11	120	52	3	19	<5	ND

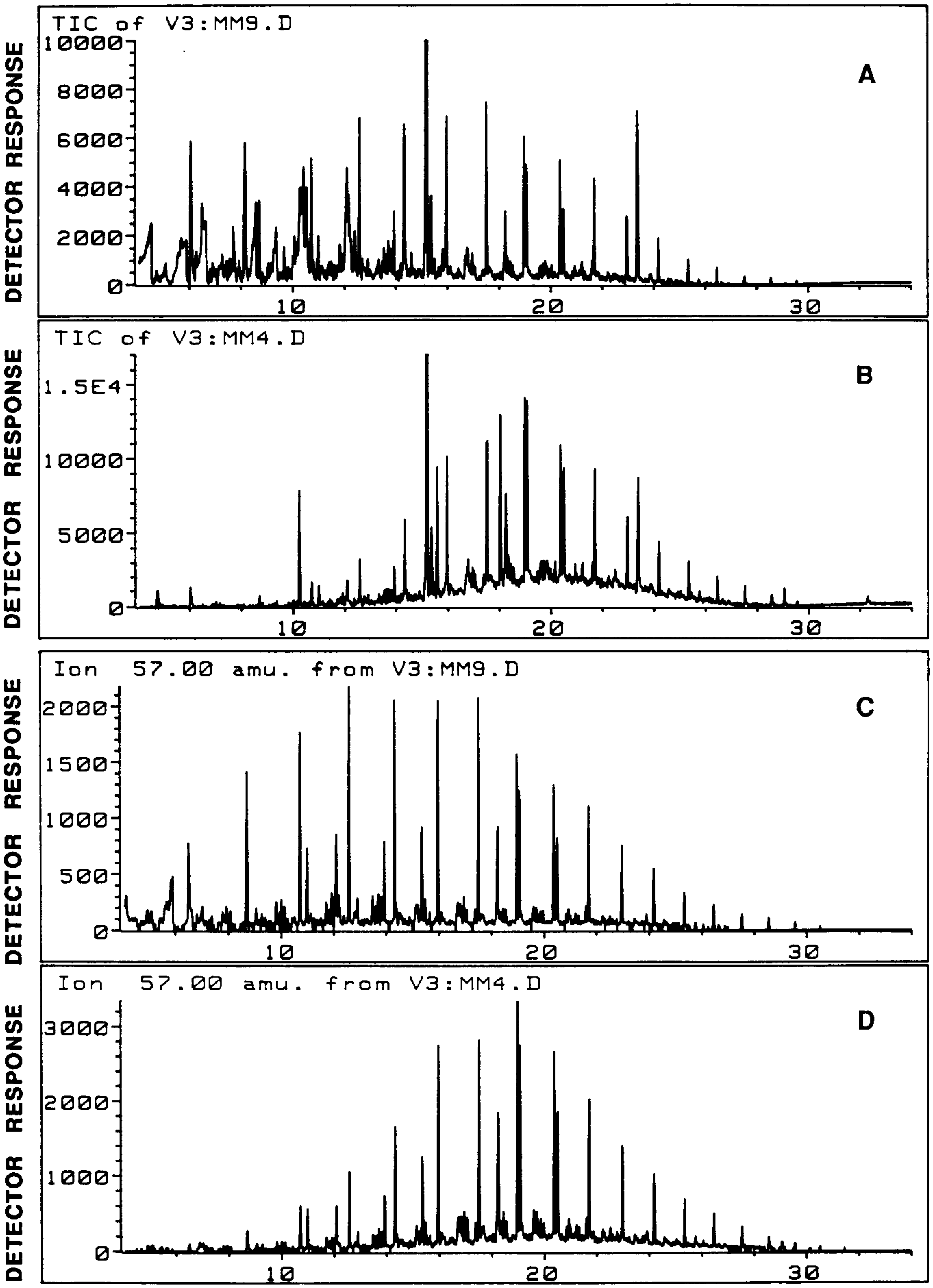


FIgure 3.21. Comparison of the Conoco discharge water and the overlying water sample collected at station BR-1 during October 1987: A. TIC of CONOCO G.I., B. TIC of BR-1, C. EIC for m/z 57 of CONOCO G.I., D. EIC for m/z 57 of BR-1.

The January 1988 overlying water analyses showed only volatile organics (Table 3.8). Station BR-1 contained 340 ng/ml of benzene, 220 ng/ml of toluene, and 87 ng/ml of xylene. Station BR-11 located near the outfall of the Exxon discharge contained 120 ng/ml of benzene, 52 ng/ml of toluene, and 19 ng/ml of xylene. Methods of overlying water collection differed between October and January (see Section 3.2.1).

3.4.3 Trace Metals

Trace metal and major element concentrations in sediments at the Bayou Rigaud stations are presented in Table 3.9. Differences in concentrations in surface sediments among the stations are not great, and there are few trends that seem to be clearly related to proximity to the major discharges of produced waters. The distribution patterns of many trace metals seems to be correlated with that of the major metals aluminum and iron (Figure 3.22), which are probably reflective of clay content (relative grain size). However, the distribution of barium in surface sediments shows a distinctly different trend with elevated concentrations near the discharges at stations BR-1 and BR-2 (Figure 3.23). Produced water discharges are a potential source of this enrichment.

There were also only small differences in the concentrations of trace metals with depth in the sediment (Table 3.9). There was a consistent pattern of subsurface maximum of lead in the cores, but the range of concentrations was not great. There appeared to be a surface enrichment of barium near the discharges (stations BR-1 and BR-2).

3.4.4 Benthos

The species richness (number of species) and number of individuals for stations in the Bayou Rigaud study area are given in Table 3.10 and Figures 3.24 and 3.25. Stations BR-1 and BR-2 were sampled in both October 1987 and January 1988. Stations BR-13 and BR-14 in January, were situated between these and stations BR-3 and BR-5, respectively, collected in October.

In October, no benthic infaunal organisms were collected at BR-1. The number of species and number of individuals were next lowest at BR-2. The community there was dominated by *Capitella capitata.* Higher species richness and number of individuals were found in both directions mid-channel from the discharge points (BR-3, BR-4, and BR-5). Individuals at these stations were primarily the capitellid polychaetes, *Capitella capitata* and *Mediomastus ambiseta* and the spionid, *Streblospio benedicti*, along with the bivalve, *Mulinia lateralis.*

Number of individuals, along with species richness, while not zero, were again lowest at BR-1 in January, 1988, and most of the individuals were *Capitella capitata.* Stations BR-7, BR-8, BR-9, and BR-14, in the vicinity of BR-1, were reduced in species numbers, and, with the exception of BR-8, which had a large population of *Streblospio benedicti*, were reduced in number of individuals. These stations, with the exception of BR-8, were dominated by *Capitella capitata.* Station BR-2 did not exhibit the same low species richness and reduced number of infaunal organisms as in October 1987. The sample contained populations of *Capitella capitata*, *Mulinia lateralis* and miscellaneous polychaetes similar to other stations located at greater distances from the discharges.

Station BR-11, at the end of the Exxon discharge ditch, while superficially appearing to be one of the more diverse stations, was, in fact, one of the most affected. The variety seen at BR-11 was a reflection of an epifaunal community associated with fouling organisms, mostly oysters, on pilings located near the entrance of the ditch into Bayou Rigaud. Many of the organisms collected in the benthic sample were "sloughed" off these pilings and had

Table 3.9. Metal concentrations in Bayou Rigaud sediments.

Sample	Depth	Cu (μg/g)	Zn (μg/g)	Cd (μg/g)	Pb (μg/g)	Cr (μg/g)	Ni (μg/g)	Fe (μg/g)	Mn (μg/g)	Al (μg/g)	Ba (μg/g)
October 1987											
BR-1A	0-5 cm	7.72	70.0	0.85	35.9	18.7	17.6	20,434	803	12,188	678
BR-1B	0-5 cm	9.43	77.5	1.09	36.9	17.6	16.7	19,276	278	12,181	512
BR-1	5-10 cm	8.56	79.4	1.10	46.2	20.1	18.8	21,254	507	13,245	567
BR-1	10-15 cm	7.52	74.5	1.12	49.0	19.0	18.1	18,925	897	11,720	335
BR-1	15-18 cm	8.55	72.9	1.19	38.0	17.2	17.9	7,990	541	4,706	269
BR-2	0-5 cm	8.66	310	1.02	39.4	17.5	17.1	21,184	389	11,754	300
BR-2	5-10 cm	10.7	113	1.23	56.0	15.3	15.7	17,549	442	9,284	168
BR-2	10-15 cm	11.6	93.8	1.25	53.4	15.7	16.2	16,801	444	9,248	143
BR-3	0-5 cm	9.74	80.0	1.26	45.7	21.7	19.6	24,880	1,379	14,522	265
BR-3	5-10 cm	12.7	81.8	1.27	47.6	22.3	19.7	22,758	799	15,000	261
BR-3	10-15 cm	10.8	67.7	1.22	40.7	17.8	16.9	18,829	752	12,182	193
BR-3	15-20 cm	13.9	73.3	1.43	44.1	20.0	18.8	20,021	1,087	12,211	214
BR-4	0-5 cm	5.72	49.8	0.77	27.6	13.9	14.1	15,054	363	8,917	196
BR-4	5-10 cm	9.64	59.3	0.93	32.7	15.8	15.3	17,310	604	10,195	263
BR-4	10-15 cm	7.58	83.4	1.22	44.6	21.6	25.9	21,689	845	11,720	249
BR-4	15-20 cm	7.96	55.1	0.95	33.4	15.5	15.9	15,069	562	8,884	165
BR-5	0-5 cm	5.53	58.6	0.76	31.1	15.0	15.3	14,293	130	9,080	226
BR-5	5-10 cm	10.5	56.4	1.10	37.2	15.0	15.7	7,767	234	4,833	171
BR-5	10-15 cm	10.7	67.1	1.16	37.1	15.4	15.7	14,497	151	10,143	140
January 1988											
BR-1A	surface	105	83.7	1.94	112	20.9	19.0	17,482	392	12,453	139
BR-1B	surface	20.1	280	2.06	56.9	19.7	18.0	18,433	382	12,907	378
BR-2A	surface	19.7	89.7	1.87	53.1	22.8	18.4	18,172	348	14,175	65.5
BR-2B	surface	19.0	88.3	1.82	51.1	22.0	18.3	17,818	339	13,891	62.9
BR-7	surface	21.6	82.8	2.22	72.0	26.8	21.3	19,419	358	16,776	277
BR-8	surface	17.5	92.5	2.06	51.5	22.8	18.3	16,990	345	13,224	326
BR-9	surface	15.7	99.9	1.65	51.3	18.1	16.9	15,474	393	9,919	177
BR-10	surface	11.3	64.1	1.30	35.7	15.1	12.6	11,170	181	8,770	243
BR-11	surface	20.7	194	1.96	54.7	24.3	21.2	20,547	463	14,637	111
BR-12	surface	19.0	85.6	1.72	52.9	22.5	19.1	16,090	355	13,493	168
BR-13A	surface	20.9	80.1	2.03	53.6	23.7	19.4	19,495	437	15,418	73.4
BR-13B	surface	21.8	80.3	2.01	54.8	23.9	19.7	19,352	447	14,522	73.0
BR-14A	surface	14.6	69.5	1.42	49.5	16.9	15.5	13,865	222	10,304	51.2
BR-14B	surface	27.2	68.3	1.41	47.7	17.2	15.4	13,826	223	10,837	50.9

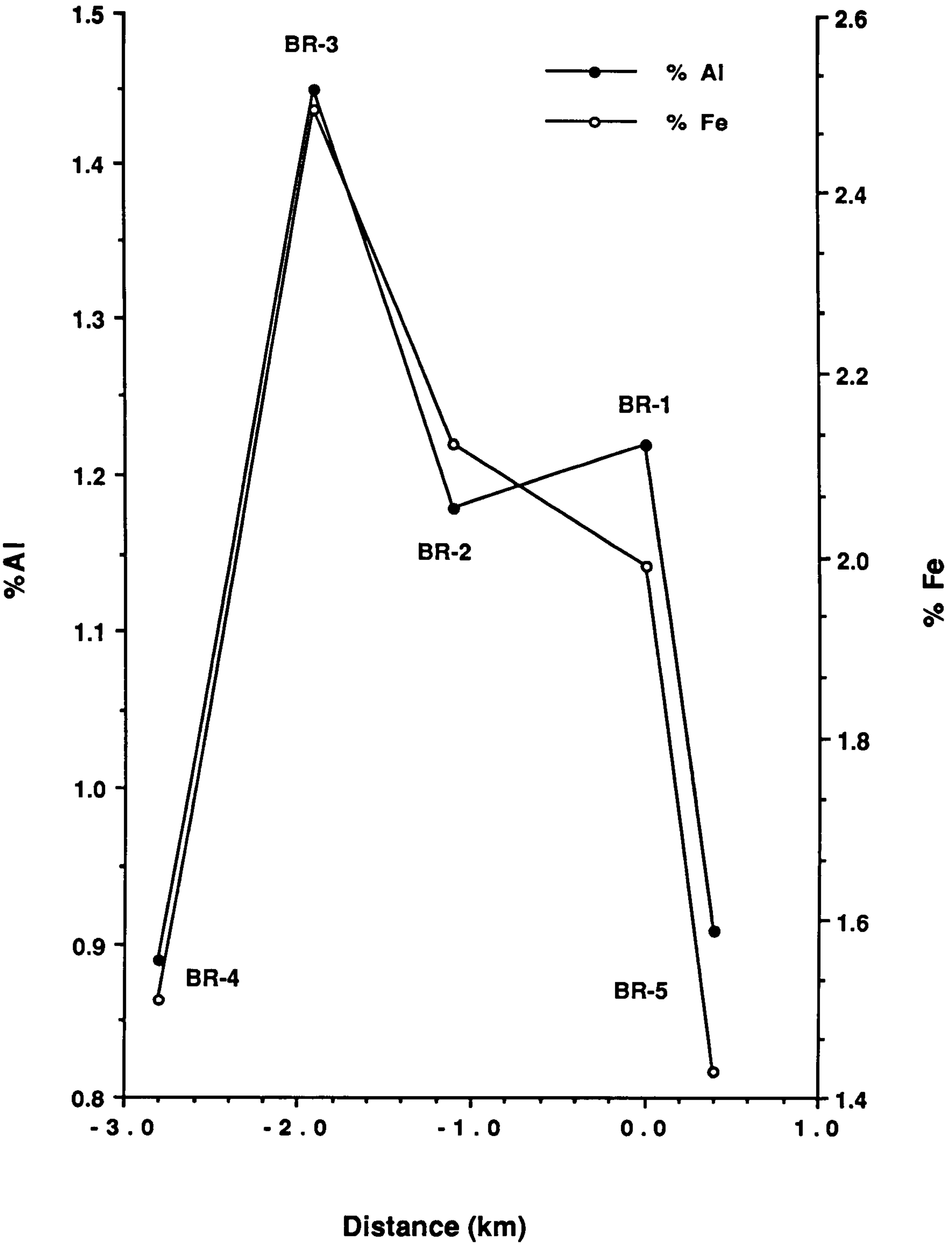


Figure 3.22. Longitudinal distribution of Al and Fe in surficial sediments at Bayou Rigaud (October 1987).

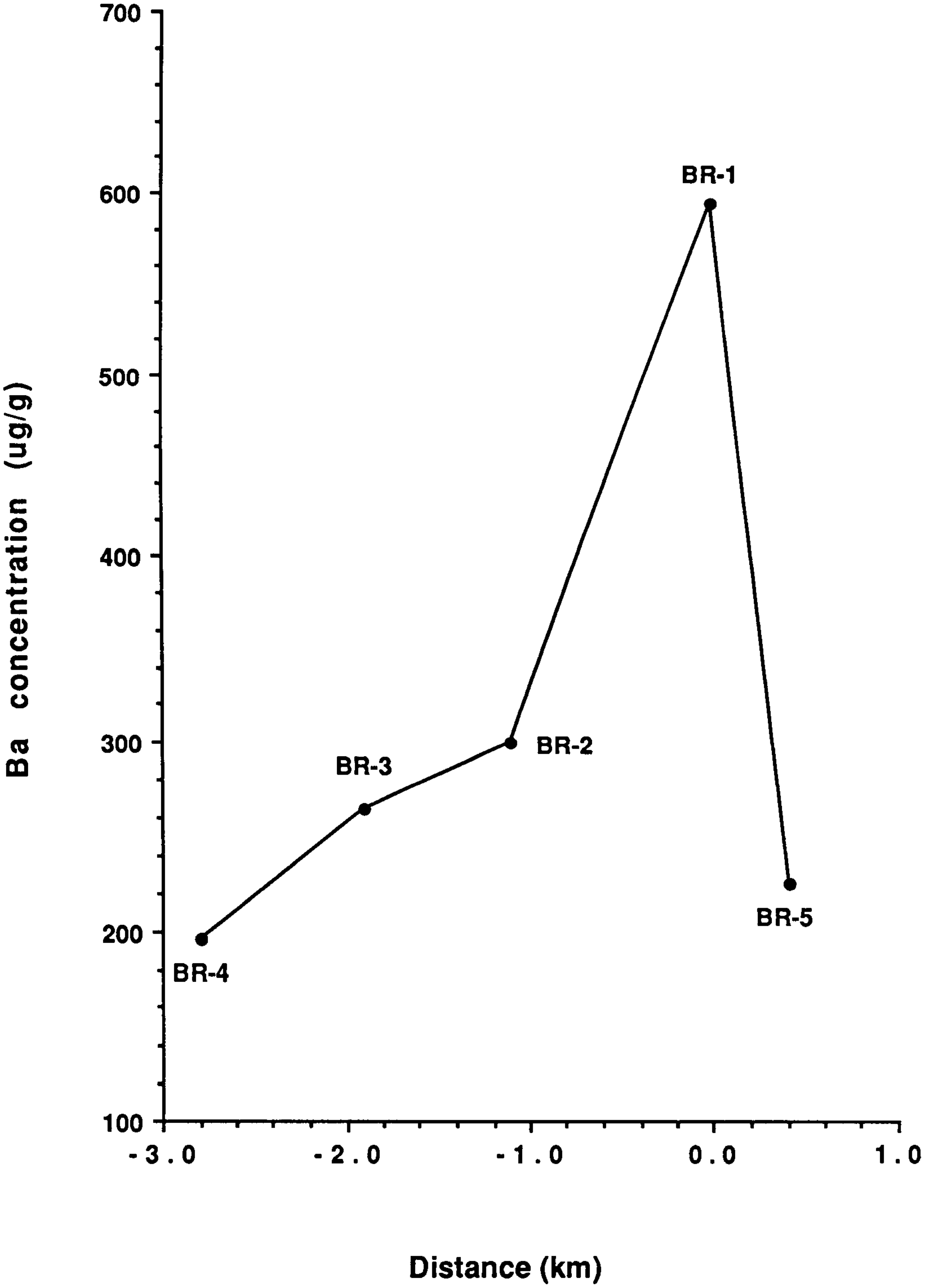


Figure 3.23. Longitudinal distribution of Ba in surficial sediments at Bayou Rigaud (October 1987).

Table 3.10. Benthic macroinfauna for Bayou Rigaud site.

Station Number	Species Richness		Number of Individuals*	
	Oct. '87	Jan. '88	Oct. '87	Jan. '88
BR-1	0	4	0	11
BR-2	5	10	20	97
BR-3	9	-	40	-
BR-4	8	-	54	-
BR-5	9	-	85	-
BR-7	-	7	-	24
BR-8	-	8	-	143
BR-9	-	8	-	40
BR-10	-	17	-	812
BR-11	-	12	-	32
BR-12	-	22	-	424
BR-13	-	10	-	56
BR-14	-	6	-	41

*Surface area of benthic sample in October 1987 = 0.0129 m^2 and in January 1988 = 0.0238 m^2, or about two times greater in January 1988 than in October 1987.

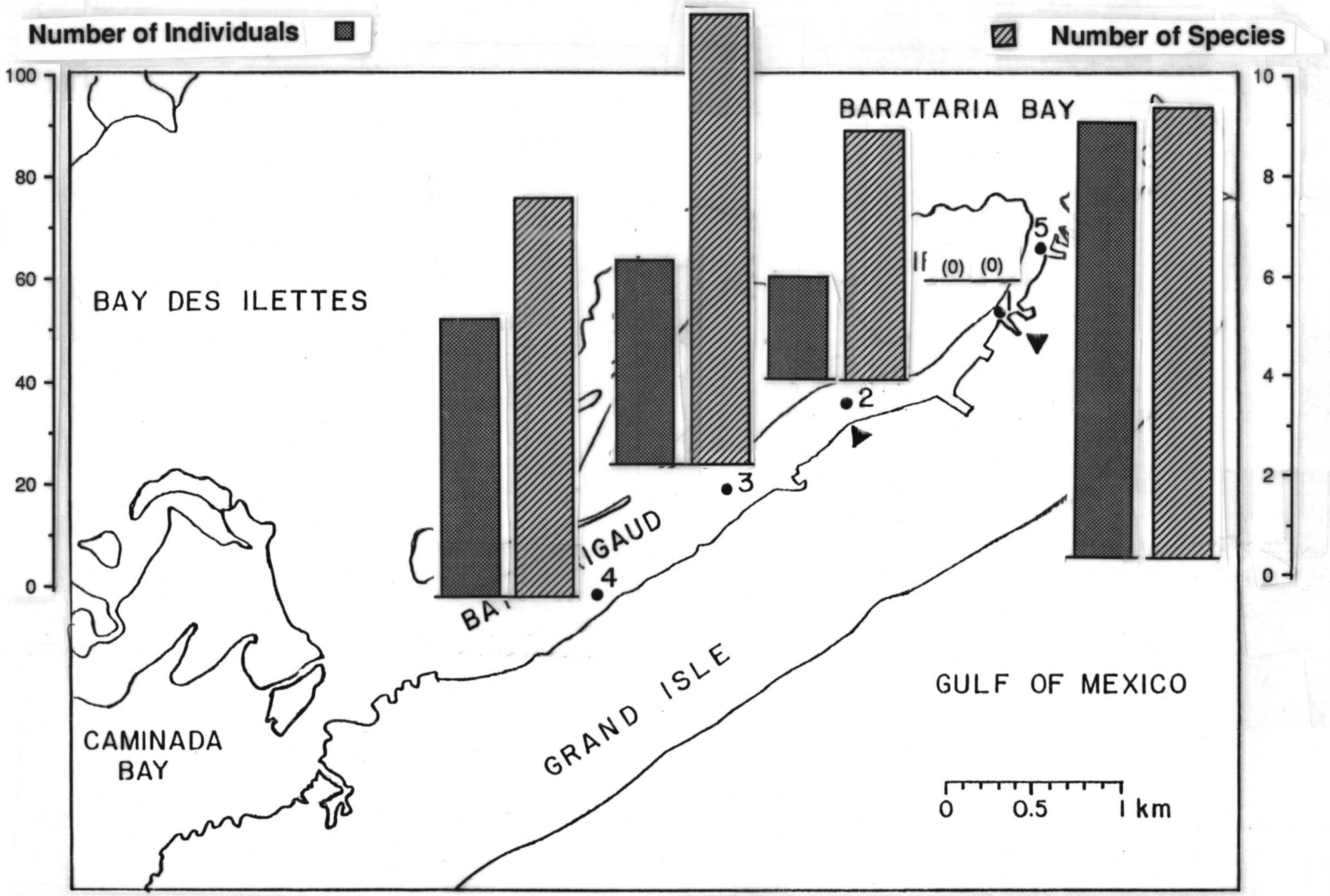


Figure 3.24. Macroinfauna data for Bayou Rigaud, October 1987.

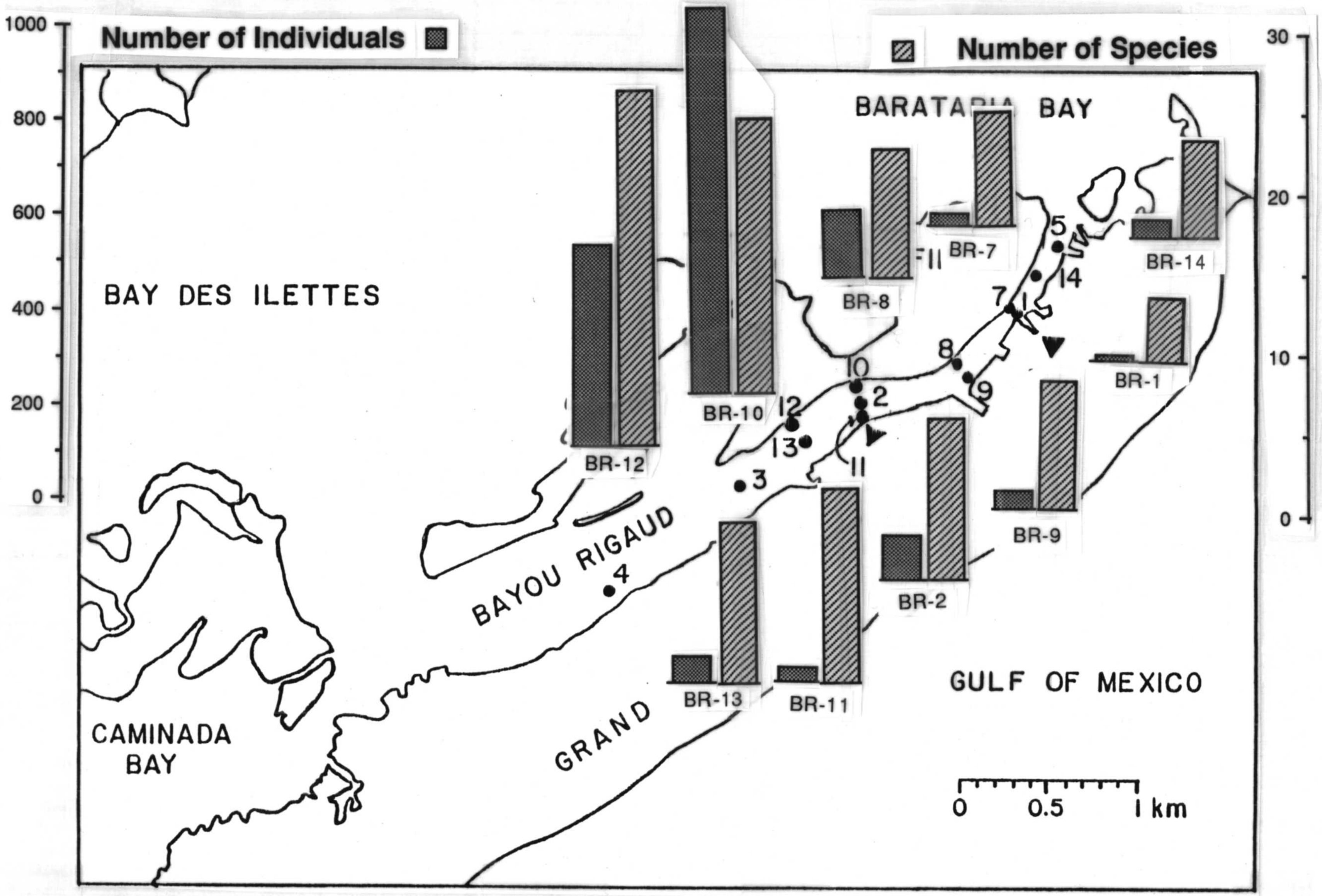


Figure 3.25. Macroinfauna data for Bayou Rigaud, January 1988.

accumulated on the bottom. In spite of the variety at BR-11, the number of individuals was low, similar to BR-7, BR-9, and BR-14 as described above. Many organisms collected in the BR-11 sample were dead and decomposed. The sediments were reduced, and the sand and shell fragments in the sample were blackened. Most organisms which fell to the bottom at this station probably did not survive. The few organisms, e.g., *Capitella capitata*, *Mulinia lateralis*, and *Tellina versicolor*, similar to those found in nearby stations, were few in number. The increased numbers of opportunistic species such as spionid and capitellid polychaetes, the bivalve *Mulinia lateralis*, and/or oligochaetes are indicative of estuarine areas with stressed or disturbed environments and/or organic pollution. Diaz (1980) noted that tubificid oligochaetes inhabiting tidal freshwater or estuarine areas respond to physical disturbance and organic pollution by increasing population size.

Stations BR-10, BR-12 and BR-13, sampled in January 1988, were the most diverse (with the exception noted above for BR-11) and had high numbers of individuals. The populations were characterized by high numbers of oligochaetes, *Mulinia lateralis*, *Streblospio benedicti*, *Mediomastus ambiseta*, *Cossura delta*, *Spiochaetopterus costarum*, *Paramphinome* sp. B, and a variety of polychaetes.

3.5 Pass Fourchon

3.5.1 Study Site

Chevron processing facilities which handle OCS produced water at Pass Fourchon include the Bay Marchand Barge and the Fourchon Terminal. The Bay Marchand Barge facility is operated by Chevron, U.S.A. and separates approximately 18,000 bbl/day of OCS-generated produced water where it is discharged into in a dead-end channel at the Chevron, U.S.A. facility (Figure 3.26). The Chevron Pipe Line facility at Fourchon Terminal is located on another arm of the dead-end canal at the Chevron facilities. Two discharges are located here: one which discharges 8,000 bbl/day of OCS-generated produced waters and one which discharges 19,000 bbl/day of non-OCS produced water. The canal leads into Pass Fourchon, which itself is occluded by a sunken barge and beach with shoreline stabilization structures. Consequently, the dead-end arm of Pass Fourchon and the Chevron canal is poorly flushed by tidal currents which are otherwise quite strong through Belle Pass and Pass Fourchon into Bayou Lafourche and the network of canals to the east of Pass Fourchon. As a consequence, bottom sediments in the passes are sandy, but abruptly become muddy into the dead-ended portion of Pass Fourchon.

Stations in October were located at the confluence of the Chevron canal which receives the discharge and Pass Fourchon (PF-2), at the southerly dead-end arm of Pass Fourchon, and other locations along Pass Fourchon (PF-4), Bayou Lafourche (PF-5), and Belle Pass (PF-6). Bottom sediments were muddy at PF-2 and -3, and sandy at the others.

Additional stations were added in January. Sandy sediments north and west of station PF-3 in Pass Fourchon could not be penetrated nor retained by the Petersen grab. Muddier sediments were sampled in the access canal to Bayou Moreau (PF-10) and sandy muds, in Bayou Moreau on the north side of Bay Champagne. All stations in the Pass Fourchon area were mid-channel (3 to 5 m water depth).

Marsh cores were collected from near the Chevron facilities (Figure 3.26) and from the marsh adjacent to LUMCON's Port Fourchon field station. The latter served as a reference station to the discharge site.

Little salinity stratification (about 0.5 ppt difference from surface to near bottom) was evident in October 1987. Salinities were between 27 and 28 ppt throughout all the stations. In January, a survey of the distribution of salinity, temperature and dissolved oxygen was

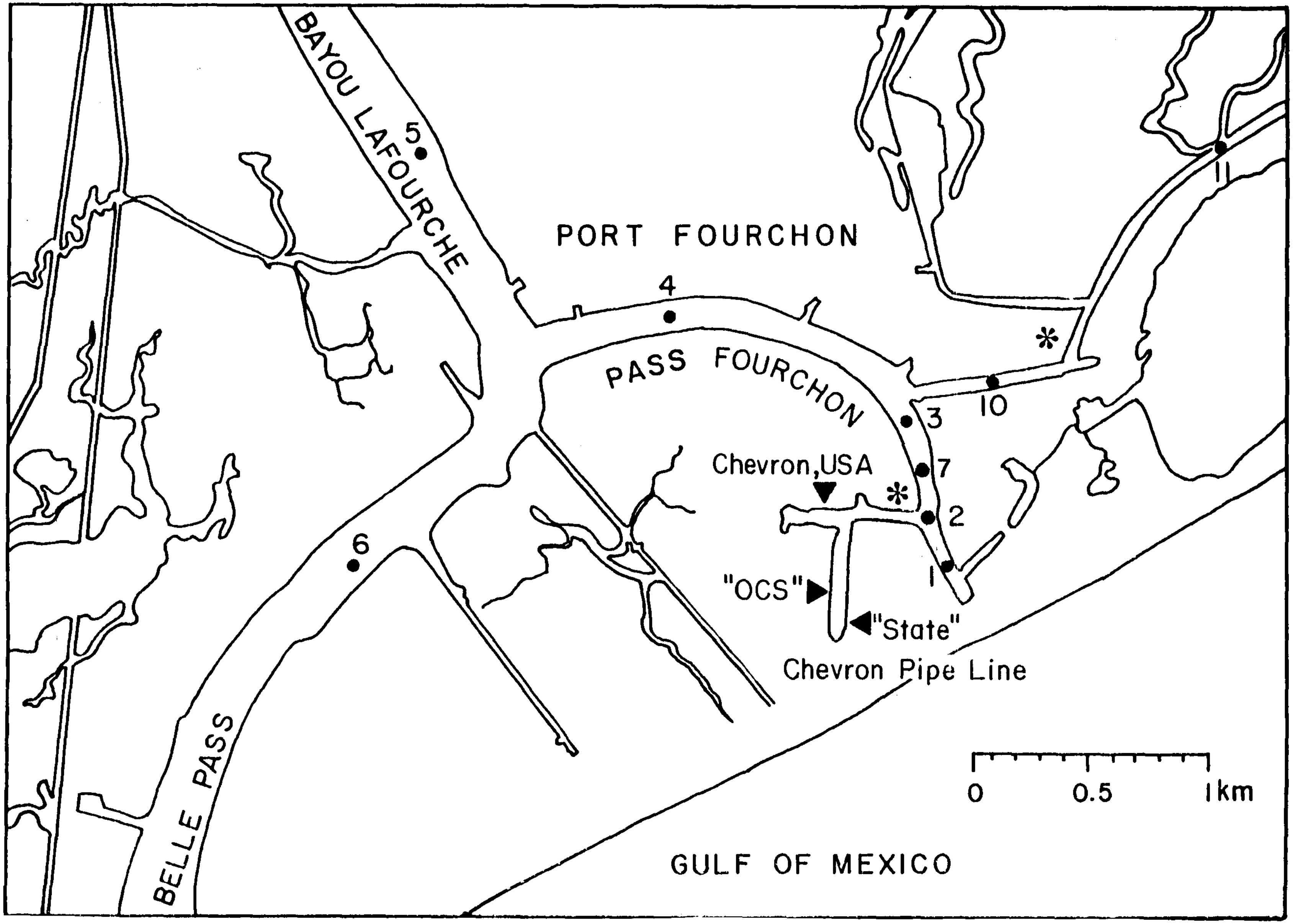


Figure 3.26. Pass Fourchon study area; produced water discharges indicated by closed triangles. Asterisks (*) indicate location of marsh cores.

undertaken within the Chevron canal and Pass Fourchon in order to assess the behavior of the high salinity produced water discharge. The profile of salinity along this gradient leading from the discharge is shown in Figure 3.27. It clearly shows a dense plume of partially mixed produced water (salinity of produced water is approximately 99 ppt compared with the ambient salinity of approximately 28 ppt) along the bottom of the channel. The identifiable plume extended approximately 1 km until it was entrained in the tidal currents moving through the canal to the east.

3.5.2 Organics

Sediments

Data for the sediment samples from the Pass Fourchon site are presented in Table 3.11 and Figures 3.28 through 3.37.

In October, Station PF-2, which is at the mouth of a canal 400 meters from the discharges, contained the highest concentration of PAH and saturated hydrocarbons (Figures 3.28 and 3.29). The composition of aromatics, based on the FFPI, was similar to the value for the produced water source and indicated a petrogenic origin. The sediments were relatively lower in concentrations of naphthalene and C-1 naphthalene, which were the PAH of greatest concentration in the produced water. The higher molecular weight (HMW) PAH tended to accumulate in sediments at greater concentrations than the lighter (LMW) PAH even though they were proportionally lower in concentration in the produced water. This is because the HMW PAH are less water soluble and, therefore, more likely to adsorb to particulate matter and deposit in the sediments. Once in the sediments, they are more resistant to microbial degradation than LMW PAH.

Station PF-1, which was 200 m from PF-2, contained the second highest concentration of PAH, but low levels of saturated hydrocarbons. The FFPI (Figure 3.28) indicated that the source of these aromatics was pyrogenic and not from the discharge. This is not surprising as this station was in the dead end arm of the closed pass and out of the flow regime that would carry hydrocarbons from the discharge. Station PF-3, 800 m from the discharge, contained only 2% of the PAH concentration of PF-2, but the composition was consistent with a petrogenic source. Stations PF-4 and PF-5 contained low levels of PAH, which were probably derived from pyrogenic sources. Station PF-6 sediment showed only traces of pyrogenic hydrocarbons. Based upon the October 1987 sampling, hydrocarbon contamination from the discharge extended about a kilometer from the source to the point where Pass Fourchon joins a deep canal to the east. Strong tidal flow from Pass Fourchon to the canal scours bottom sediments, and it is only in the dead-end portion of the pass that fine sediments accommodating hydrocarbon contaminants accumulate.

Figures 3.30 shows the PAH and saturated hydrocarbon depth profiles for stations PF-2 and PF-3. Both stations showed heavily-weathered hydrocarbon profiles. At station PF-2 there did not appear to be any compositional differences with depth. At station PF-3 there was a change in the ratio of resolved saturated hydrocarbons to PAH. This is typical of the weathering process since PAH degrade much more slowly than saturated aliphatics. It is interesting that PF-2 did not show further weathering with increasing depth. Figures 3.31 through 3.34 show the chromatographic similarities of the depth profiles of the two stations. The core depth profile data is inconclusive since the core depths were too shallow for a complete picture of the past history of this station.

Sediments at Station PF-2 in January contained six times more PAH than the October sample, however, as illustrated by the FFPI, the hydrocarbons were from the same petrogenic source (Figures 3.35 and 3.36). The differences in hydrocarbon concentrations may be the result

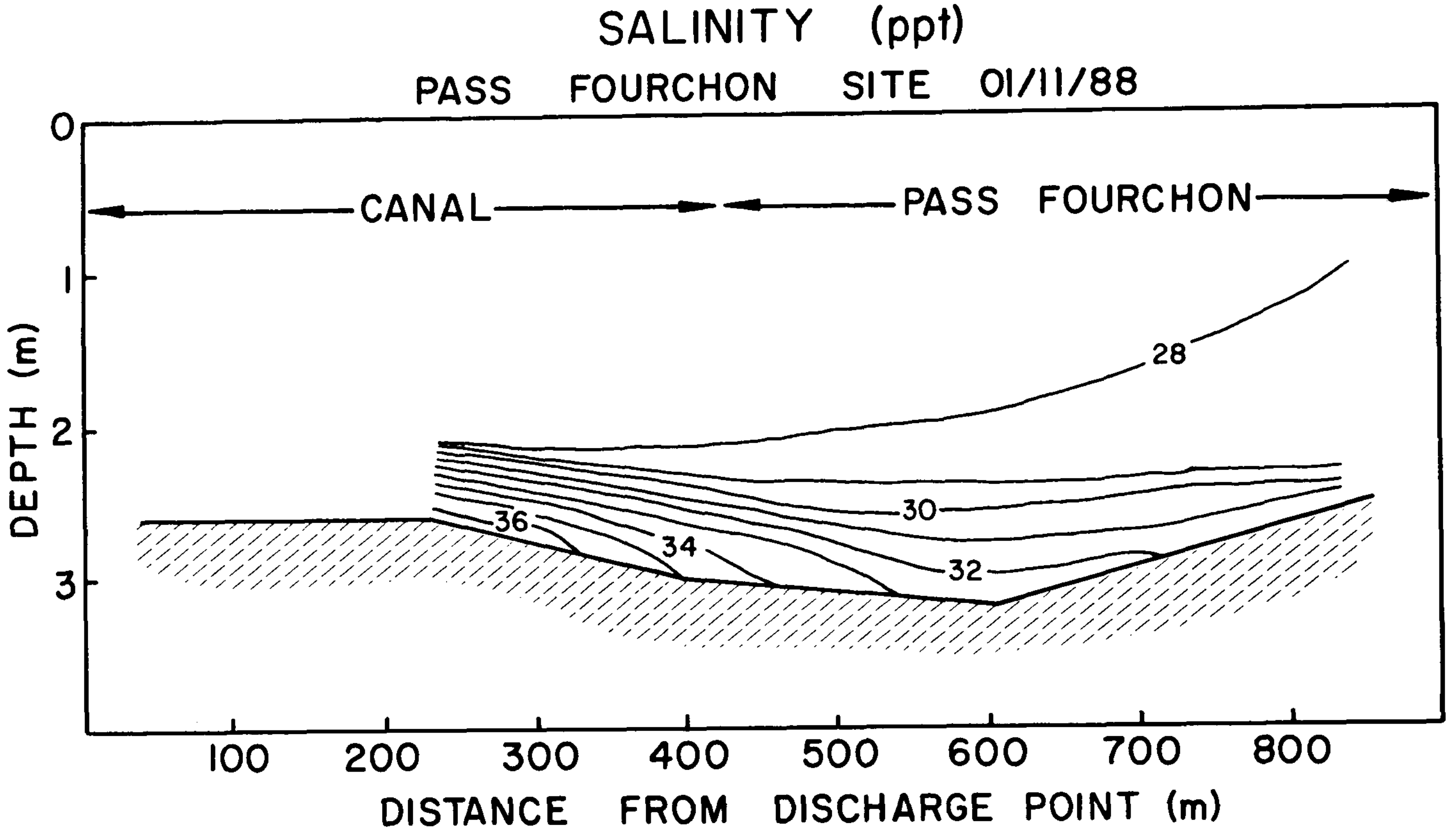
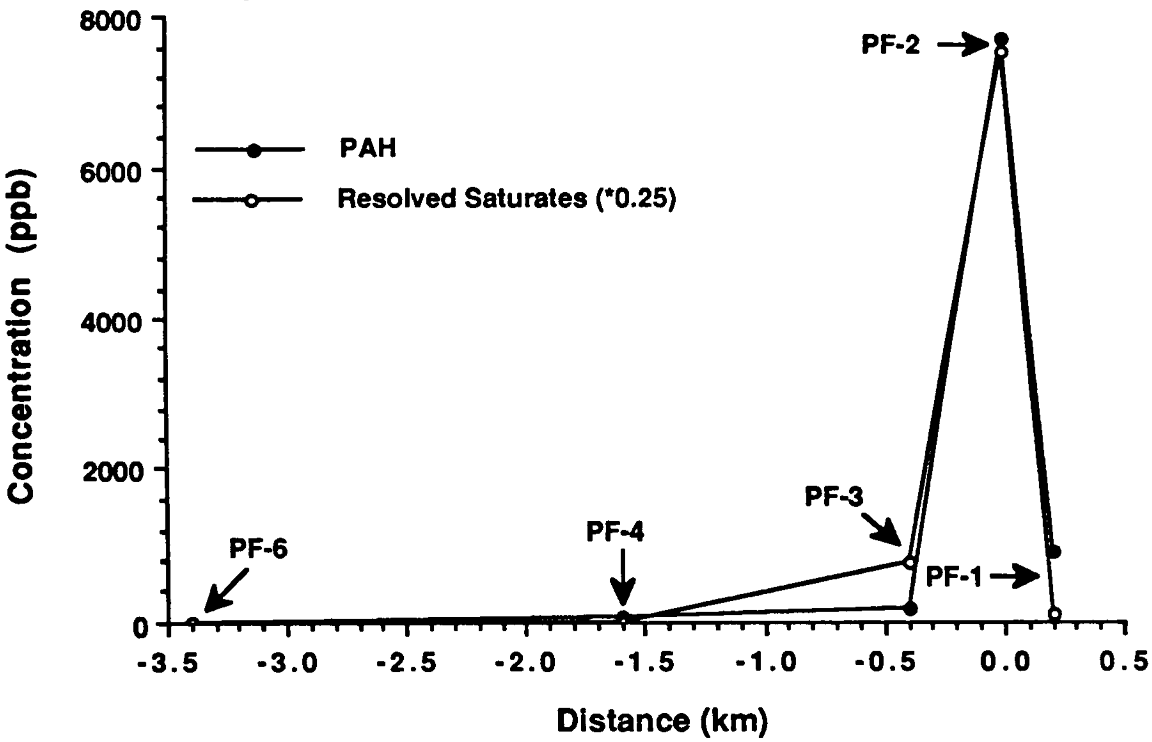


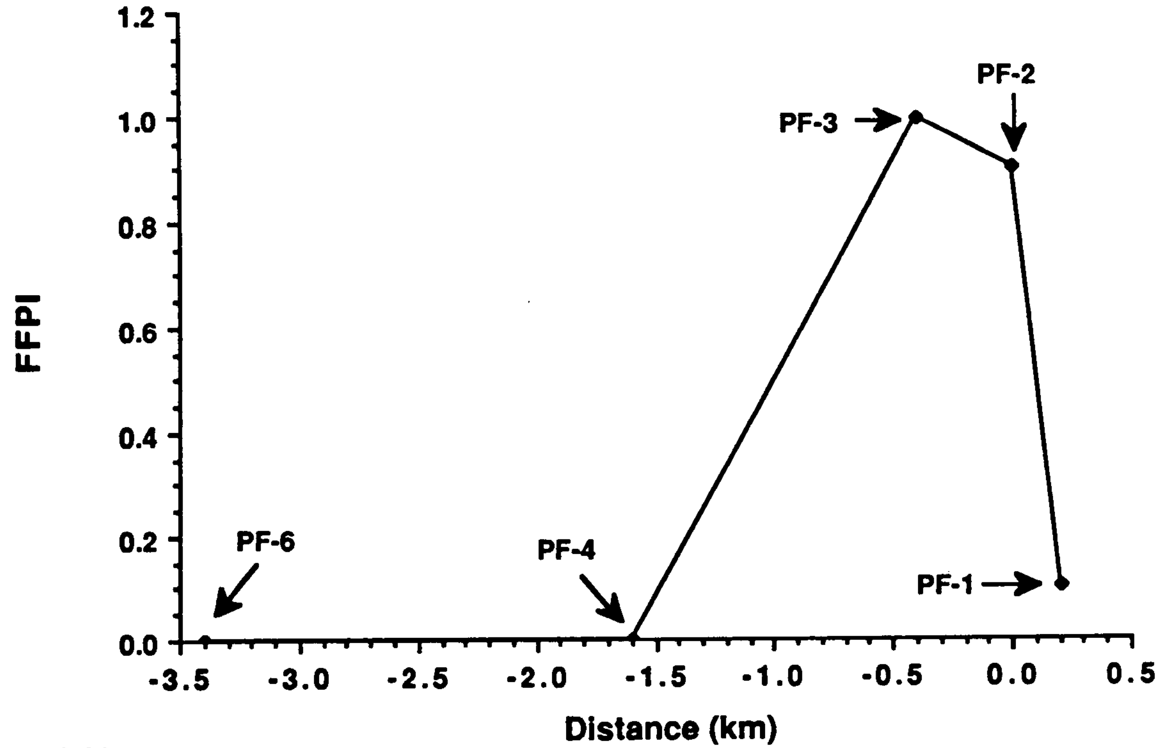
Figure 3.27. Water column salinity (ppt) profiles at mid-channel along the Chevron access canal and adjacent Pass Fourchon in January 1988.

Table 3.11. Hydrocarbon concentrations in Pass Fourchon sediments.

Sample	Depth	Total PAH (ppb)	FFPI	Total Saturated H.C. (ppb)
October 1987				
PF-1	0-5 cm	920	0.10	8,500
PF-2	0-5 cm	7,700	0.91	260,000
PF-2	5-10 cm	4,200	0.83	184,000
PF-2	10-15 cm	6,800	0.89	210,000
PF-2	15-20 cm	1,000	0.76	250,000
PF-3	0-5 cm	170	1.01	40,000
PF-3	5-10 cm	280	0.94	53,000
PF-3	10-15 cm	1,400	0.87	58,000
PF-4	0-5 cm	85	0.00	Tr
PF-5	0-5 cm	140	0.29	Tr
PF-6	0-5 cm	<30	N/A	Tr
January 1988				
PF-2	0-5 cm	43,000	0.93	650,000
PF-7	0-5 cm	180	0.67	5,200
PF-10	0-5 cm	550	0.77	5,600
PF-11	0-5 cm	2,700	0.26	43,000
PF-11 Spk Dup	0-5 cm	1,700	0.13	30,000



a. Hydrocarbon concentrations



b. FFPI

Figure 3.28. Longitudinal profiles of hydrocarbon concentrations (a.) and FFPI (b.) in sediments away from PF-2 (October 1987).

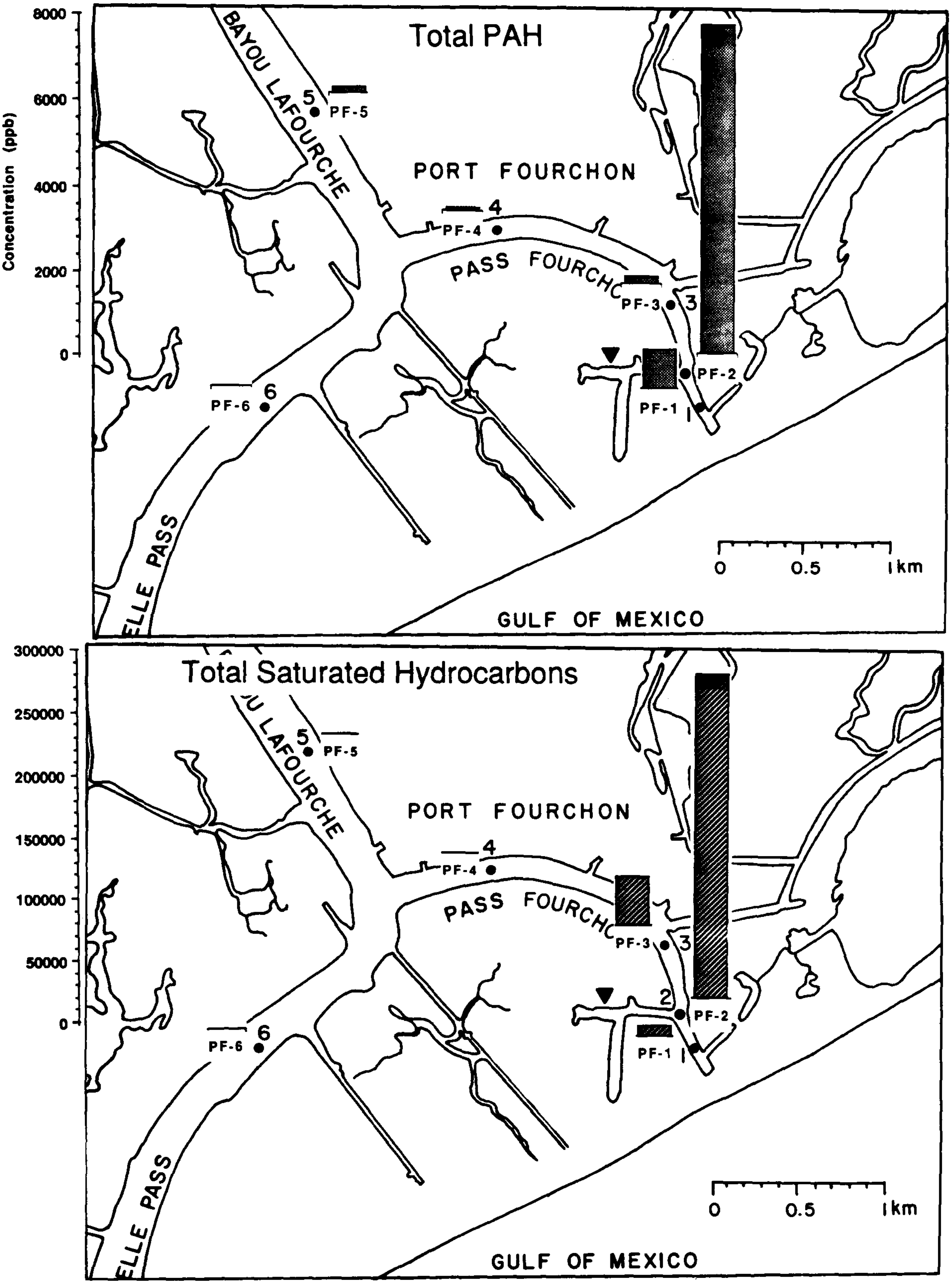


Figure 3.29. Pass Fourchon location map with total PAH, above, and saturated hydrocarbon concentrations, below, in sediments for October 1987.

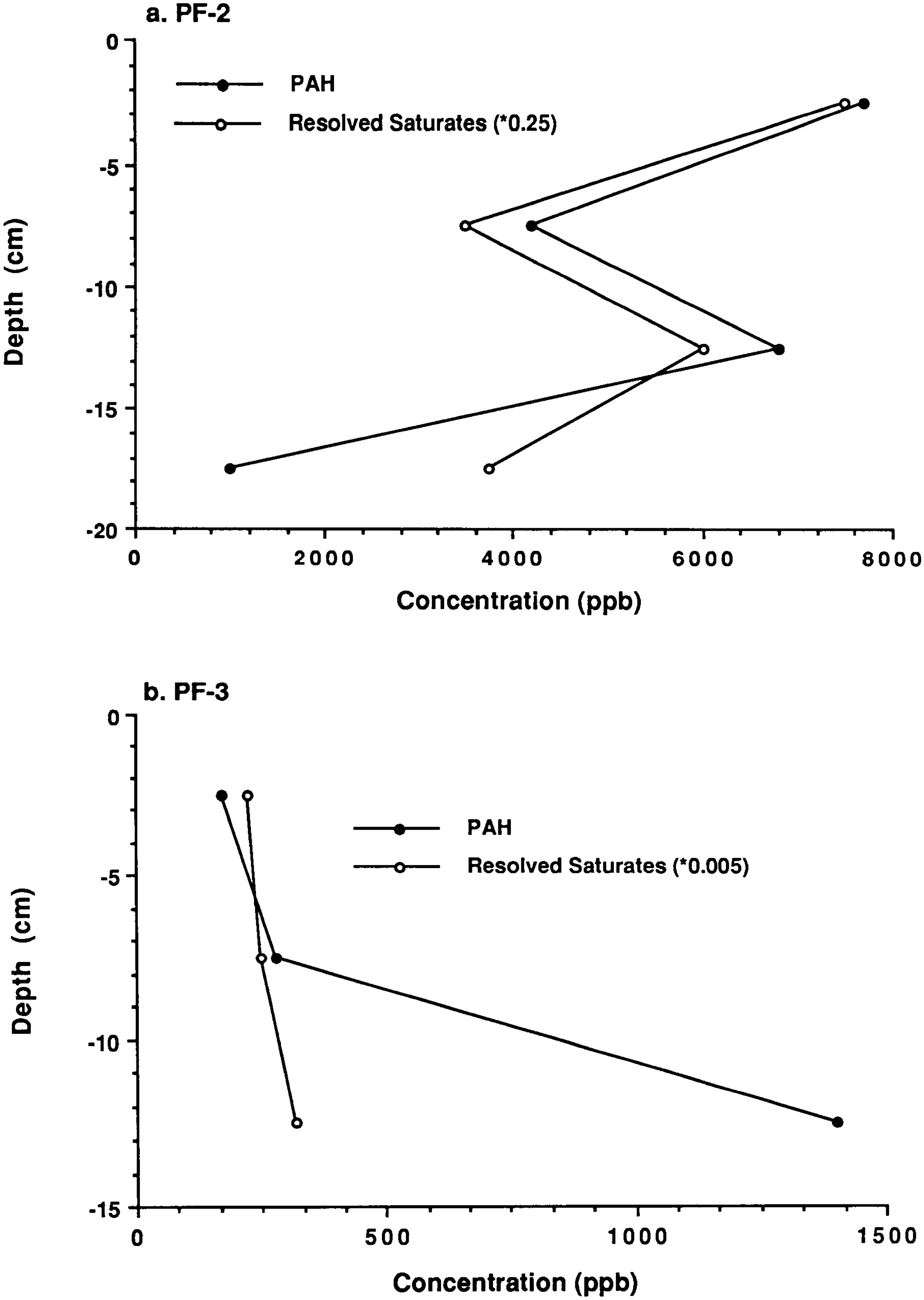


Figure 3.30. Depth profiles of hydrocarbon concentrations in sediments for two Pass Fourchon stations (October 1987).

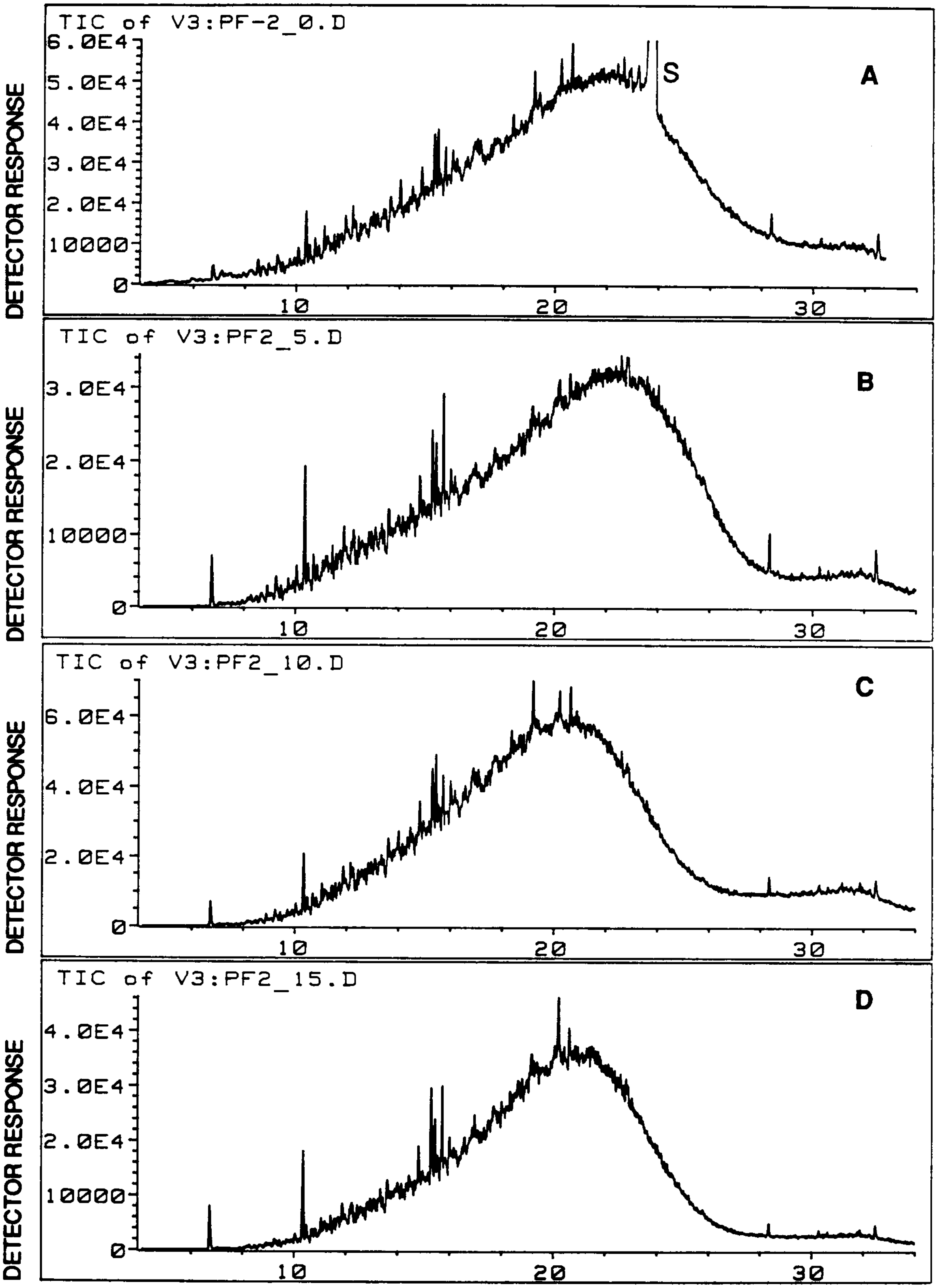


Figure 3.31. Comparison of the depth profile TIC's from core PF-2 (October 1987): A. 0-5 cm, B. 5-10 cm, C. 10-15 cm, and D. 15-20 cm.

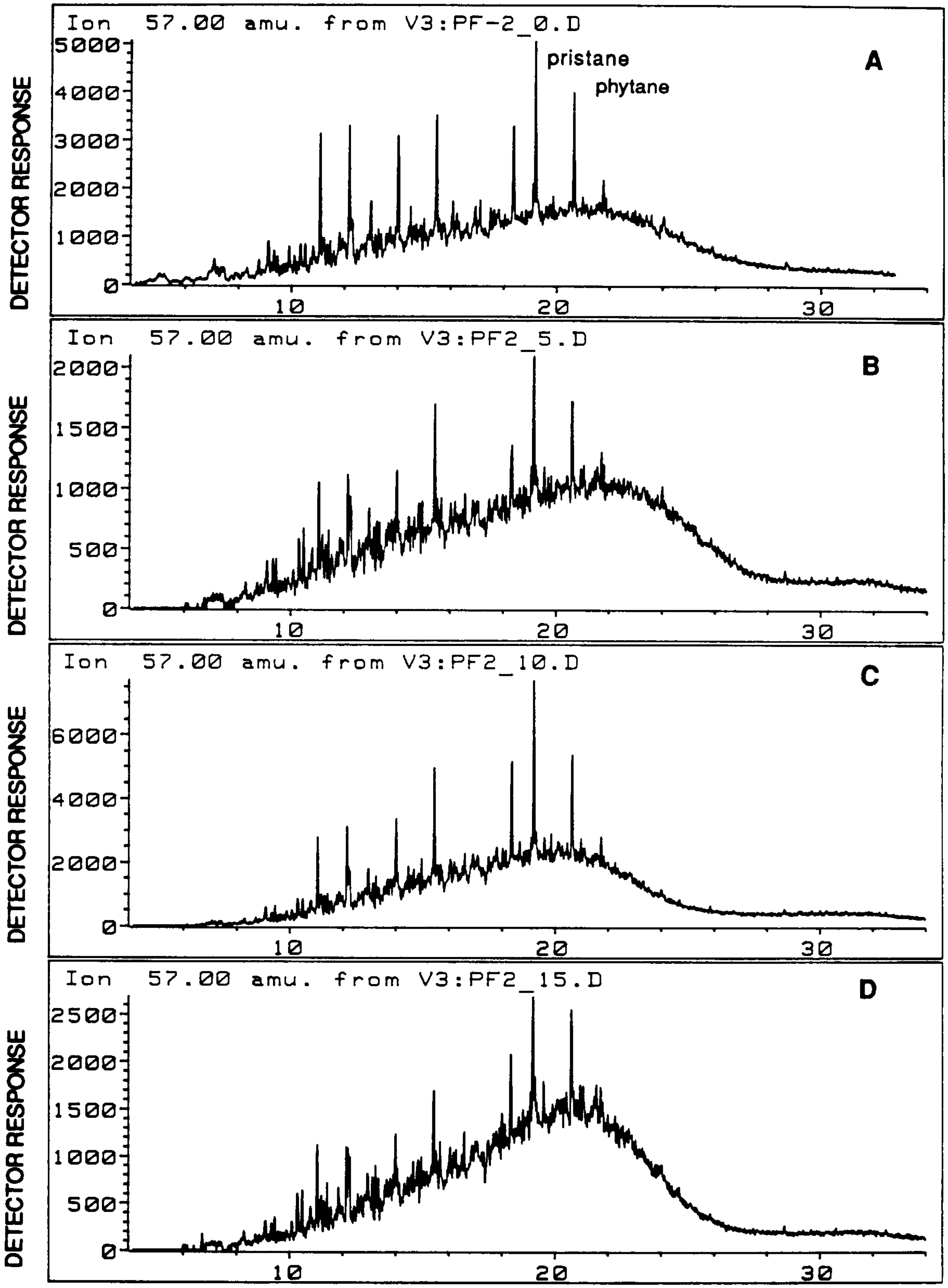


Figure 3.32. Comparison of the depth profile EIC's for m/z 57 from core PF-2 (October 1987): A. 0-5 cm, B. 5-10 cm, C. 10-15 cm, and D. 15-20 cm.

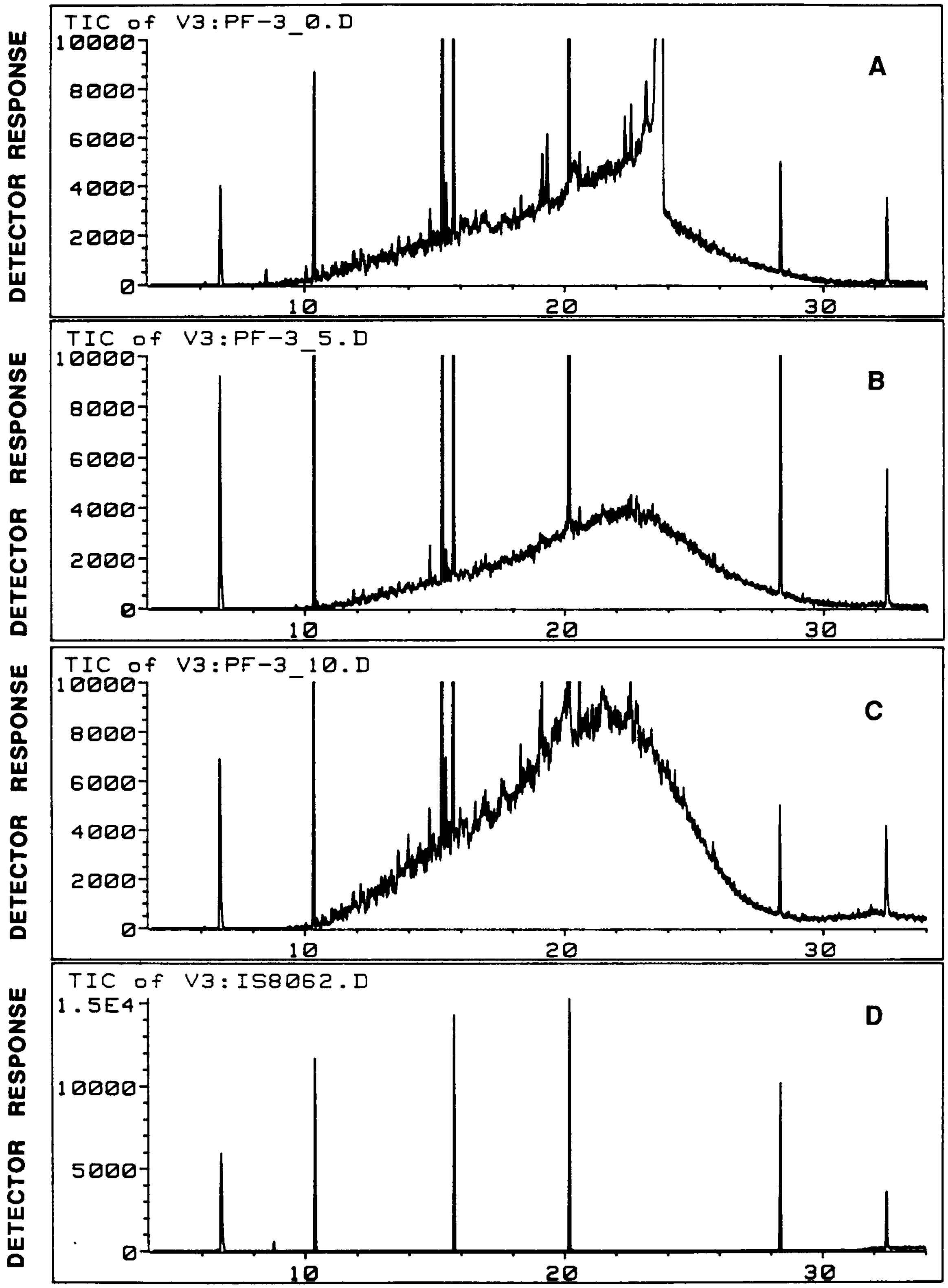


Figure 3.33. Comparison of the depth profile TIC's from core PF-3 (October 1987): A. 0-5 cm, B. 5-10 cm, C. 10-15 cm, and D. EPA internal standard mix.

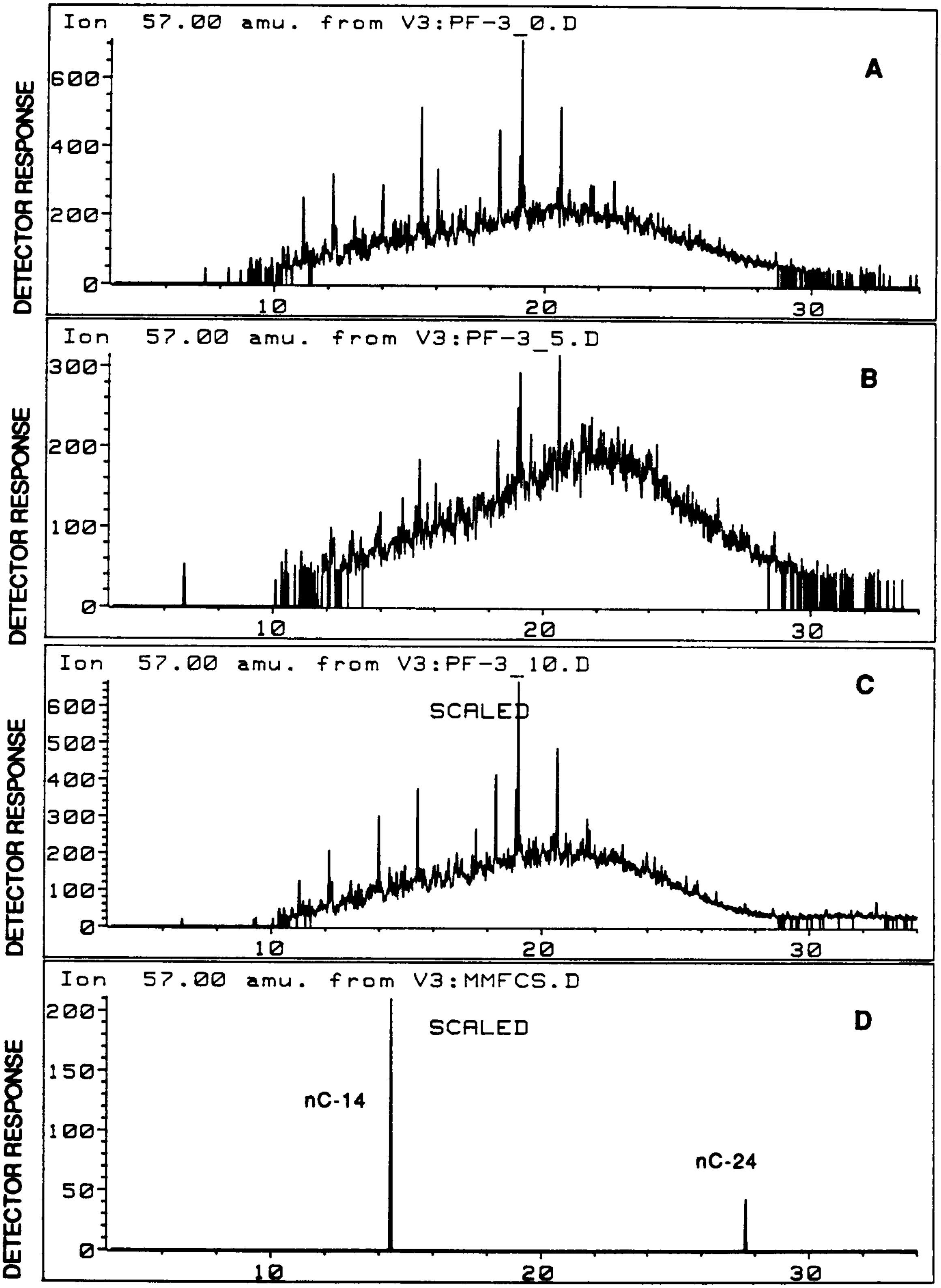


Figure 3.34. Comparison of the depth profile EIC's for m/z 57 from core PF-3 (October 1987): A. 0-5 cm, B. 5-10 cm, C. 10-15 cm, D. nC-14 and nC-24.

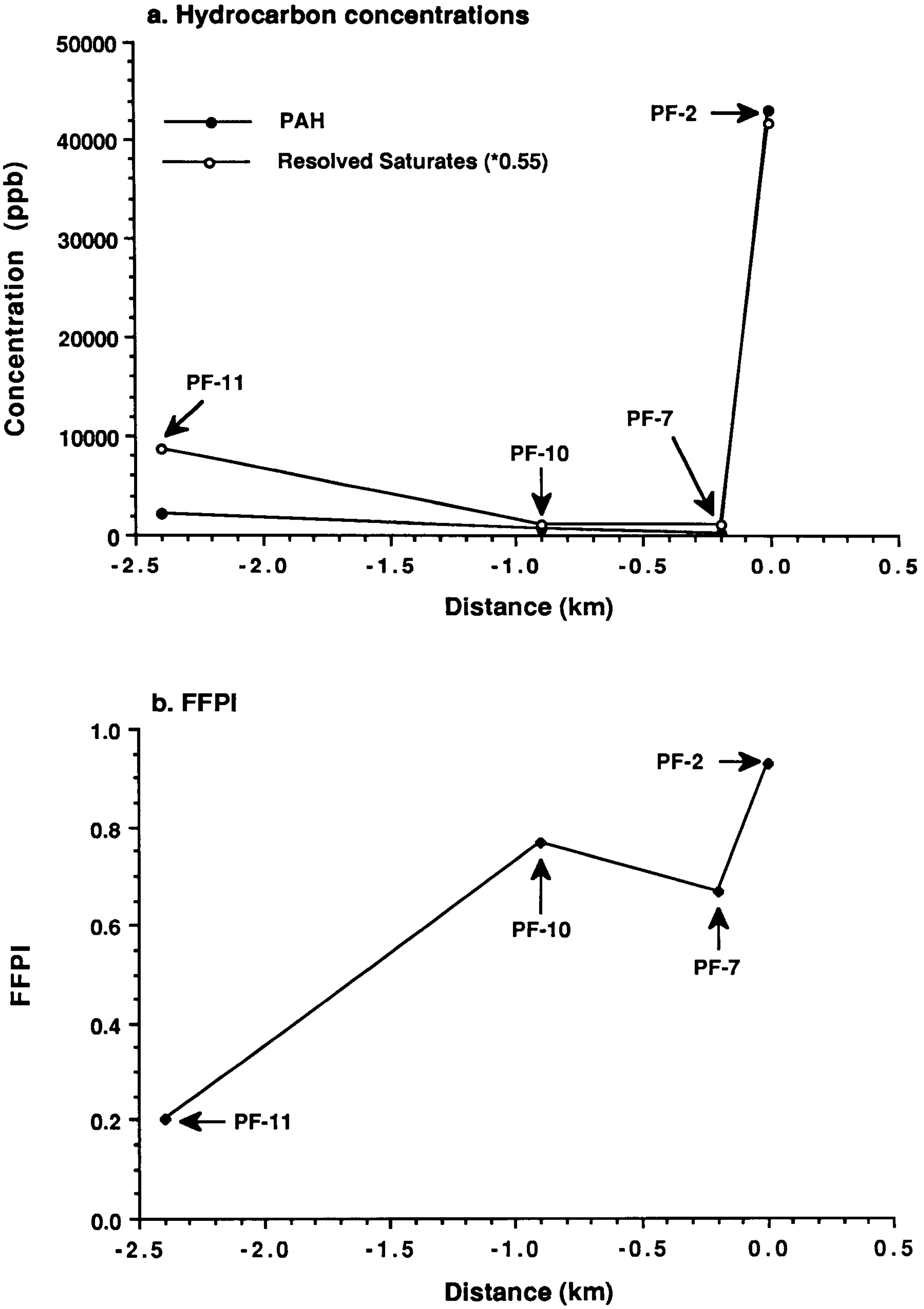


Figure 3.35. Longitudinal profiles of hydrocarbon concentrations (a.) and FFPI (b.) in sediments away out from PF-2 (January 1988).

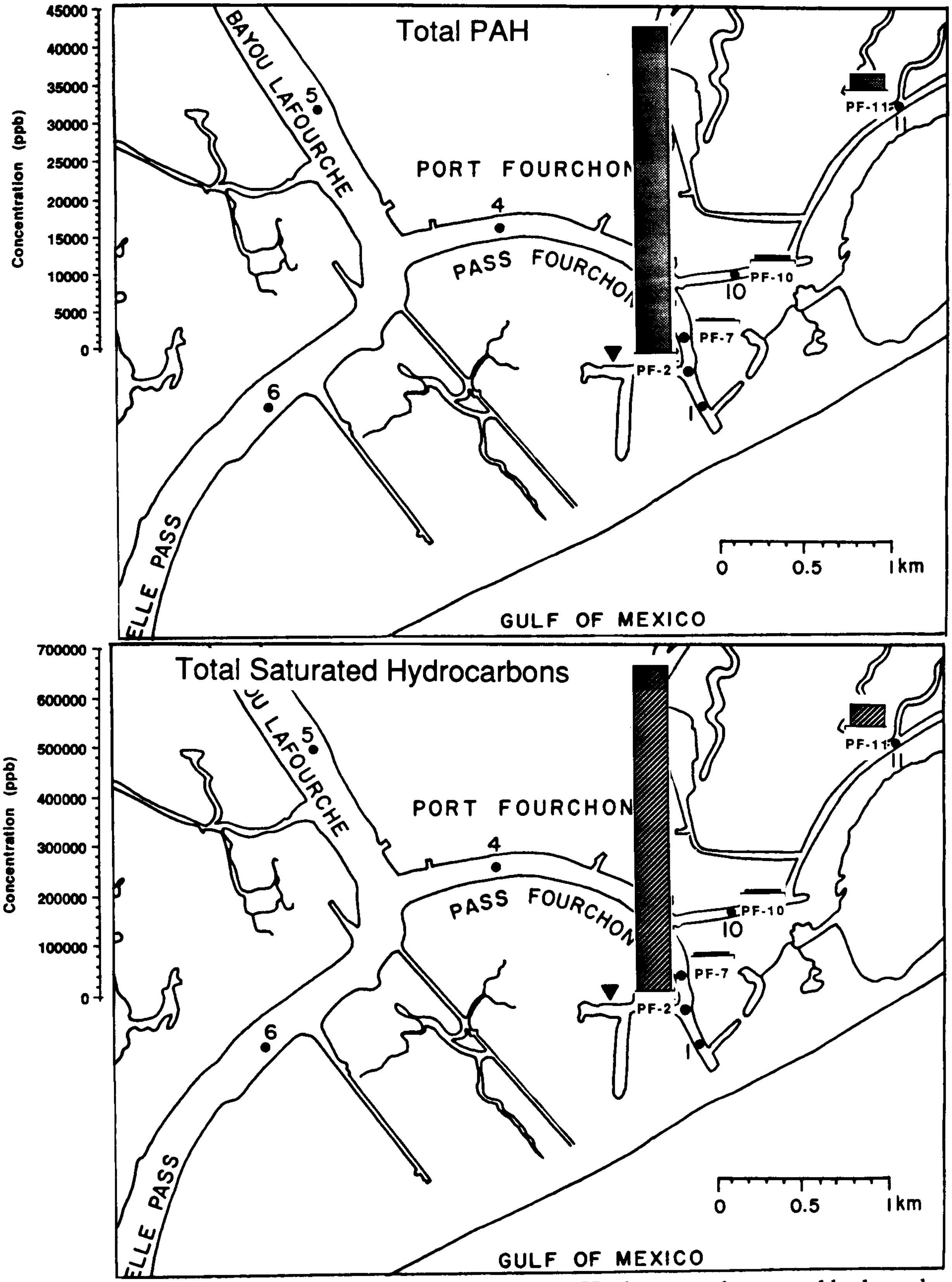


Figure 3.36. Pass Fourchon location map with total PAH, above, and saturated hydrocarbon concentrations, below, in sediments for January 1988.

of sampling variability, patchiness or patterns of deposition and erosion of sediments due to vessel traffic. The interstitial salinity was 39 ppt, and confirms contamination by the produced water discharge. Station PF-7, 200 m from PF-2, contained low levels of PAH similar to PF-3 (October 1987), but with a small pyrogenic component. A produced water source for these hydrocarbons is confirmed by the interstitial salinity which at 31 ppt was much lower than PF-2, but still higher than PF-10 (24 ppt). This suggests that the highly-saline produced water has not been totally diluted at this distance from the discharge. Station PF-10, which is in the better flushed canal to the east, contained PAH similar in composition to PF-7, but at higher levels. There is a petrogenic component which could be contamination from the discharge. Station PF-11, 3.0 km from the discharge farther up the canal and consisting of finer sediments than those at PF-10, contained significant amounts of PAH, but based upon the FFPI, the source appears pyrogenic.

Marsh cores

The marsh core collected near the Pass Fourchon Chevron facilities showed only typical background contamination of pyrogenic PAH (Table 3.12). Some saturated hydrocarbons were detected but they were primarily of a biogenic source. The reference marsh core from the LUMCON Port Fourchon Laboratory was very similar to the Pass Fourchon core. The marsh core at Pass Fourchon Chevron facilities did not display the degree of contamination from the produced water discharge that was displayed by subtidal sediments. Figure 3.37 shows a chromatographic comparison of the January 1988 PF-2 sediment sample and the marsh core collected at the same site.

3.5.3 Trace Metals

Concentrations of metals in sediments collected at the Pass Fourchon study site during October and January are presented in Table 3.13. As in the case of Bayou Rigaud sediments, there was a high level of autocorrelation in the distribution of concentrations of metals with the sediment grain size as reflected by aluminum and iron concentrations. The concentrations of zinc, barium and lead, the three trace metals found by Neff et al. (1989) to be more than a thousand-fold enriched in produced water effluent compared to sea water, are plotted versus aluminum concentrations in Figure 3.38. Good correlations are found with the exception of a few outliers which might reflect local contamination. Zinc concentrations were relatively enriched at station PF-2 during sampling periods. Barium was relatively enriched at station PF-3 and lead at station PF-5. In general, there was no strong trend apparent which suggested metals contamination consistent with produced water as a source with the possible exception of zinc at station PF-2. Comparisons of metal concentrations down core showed few interpretable patterns, except that all metals were more concentrated in surface sediments than deeper in the core at station PF-2.

Concentrations of metals measured in marsh cores taken near the Chevron produced water discharges at the Pass Fourchon Chevron facilities and at the reference station near LUMCON's Port Fourchon Laboratory are presented in Table 3.14. Concentrations of most metals were generally higher at a given depth in the core at the reference site than at the Pass Fourchon site. At Pass Fourchon, only barium showed a surface maximum, while the concentration of the trace metals showed a near-surface maximum in the reference station core.

3.5.4 Benthos

The species richness (number of species) and number of individuals for stations at the Pass Fourchon study area are given in Table 3.15. PF-2 was the only station sampled during both October 1987 and January 1988.

Table 3.12. Hydrocarbon concentrations (ng/g) in marsh cores.

Sample	Depth	Total PAH (ppb)	FFPI	Total Saturated H.C. (ppb)
Pass Fourchon Reference Marsh				
	0-2 cm	120	0.10	Tr
	2-4 cm	48	0.00	Tr
	4-6 cm	47	0.00	Tr
	6-8 cm	<19	N/A	Tr
	8-10 cm	110	0.12	Tr
	10-15 cm	120	0.00	Tr
	15-20 cm	230	0.00	Tr
	20-22 cm	<34	N/A	Tr
Pass Fourchon Chevron Facilities				
	0-2 cm	<52	N/A	24,000
	2-4 cm	<60	N/A	41,000
	4-6 cm	<58	N/A	23,000
	6-8 cm	<60	N/A	19,000
	8-10 cm	<44	N/A	11,000
	10-15 cm	<35	N/A	5,500
	15-20 cm	<49	N/A	4,300
	20-25 cm	<45	N/A	Tr
	25-30 cm	<690	N/A	Tr
	30-35 cm	<50	N/A	Tr
	30-35 cm SpkI	<50	N/A	Tr
	30-35 cm SpkII	<63	N/A	Tr

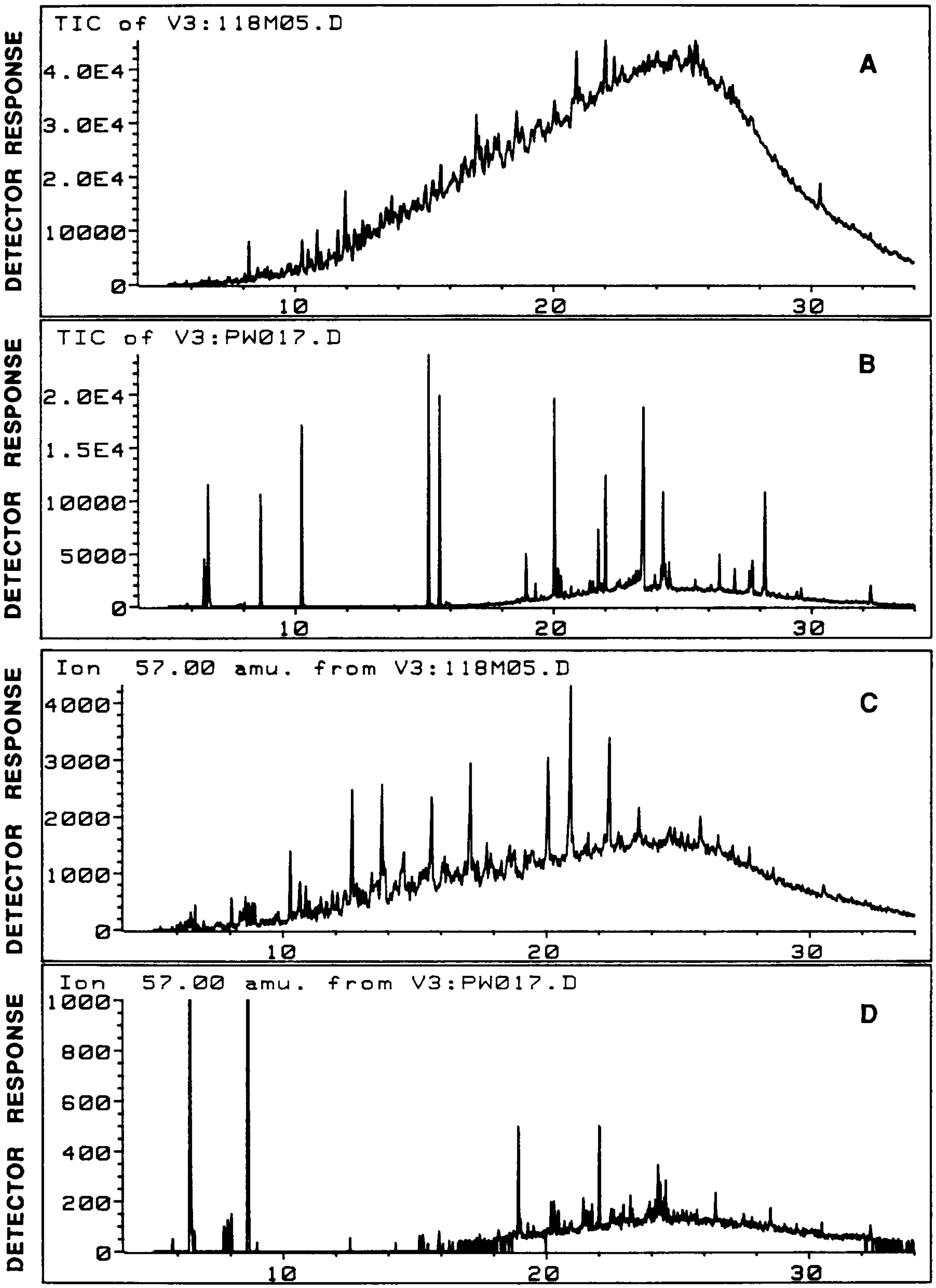


Figure 3.37. Comparison of PF-2 (January 1988) and the marsh core collected at the Pass Fourchon Chevron facilities: A. TIC of PF-2, B. TIC of marsh core, C. EIC of PF-2, and D. EIC of the marsh core.

Table 3.13. Metal concentrations in Pass Fourchon sediments.

Sample	Depth	Cu (μg/g)	Zn (μg/g)	Cd (μg/g)	Pb (μg/g)	Cr (μg/g)	Ni (μg/g)	Fe (μg/g)	Mn (μg/g)	Al (μg/g)	Ba (μg/g)
October 1987											
PF-1	0-5 cm A	13.3	46.1	1.02	25.5	11.9	14.3	14,958	263	8,046	78.3
PF-1	0-5 cm B	11.7	70.2	1.39	33.3	16.1	15.8	18,393	290	11,048	111
PF-2	0-5 cm	31.7	383	4.49	88.6	48.6	41.0	53,859	605	27,908	447
PF-2	5-10 cm	19.7	123	1.75	40.8	19.8	19.4	23,887	325	13,933	392
PF-2	10-15 cm	18.6	113	1.72	38.7	20.0	19.3	24,588	342	14,821	460
PF-2	15-20 cm	18.2	106	1.82	40.5	19.4	19.3	24,065	332	15,039	132
PF-3	0-5 cm	16.2	109	2.12	43.5	22.6	20.9	24,546	469	15,757	499
PF-3	5-10 cm A	14.9	85.1	1.68	39.1	17.2	17.1	19,367	319	12,138	212
PF-3	5-10 cm B	11.3	85.8	2.48	60.2	21.8	23.5	26,075	1,447	12,787	141
PF-3	10-15 cm	15.6	90.8	1.85	48.2	19.7	20.7	26,688	394	14,385	288
PF-4	0-5 cm	12.5	177	3.99	77.5	35.6	50.0	44,236	838	23,071	352
PF-5	0-5 cm	29.9	76.8	4.52	80.2	22.5	25.0	13,632	589	7,884	195
PF-5	10-15 cm	14.4	71.6	1.90	40.8	18.1	17.8	17,956	926	10,853	127
PF-6	0-5 cm	5.95	52.9	0.96	17.7	8.44	11.6	10,366	221	4,173	62.0
January 1988	Replicate										
PF-2	---	19.5	163	1.62	33.4	19.1	17.7	9,322	261	7,847	167
PF-7	1	24.0	130	2.09	62.3	28.4	21.2	20,852	363	17,290	77.3
PF-7	2	23.1	126	2.07	62.1	27.9	21.1	14.813	257	12,179	76.0
PF-10	1	20.3	93.8	1.88	50.7	21.9	18.7	18,751	495	14,635	99.5
PF-10	2	21.8	90.1	1.84	49.2	21.6	18.2	18,892	484	14,482	93.7
PF-11	1	18.4	81.6	1.43	45.4	20.1	15.7	16,558	238	12,615	51.8
PF-11	2	18.1	82.1	1.42	43.9	20.2	15.8	12,562	240	9,338	51.5

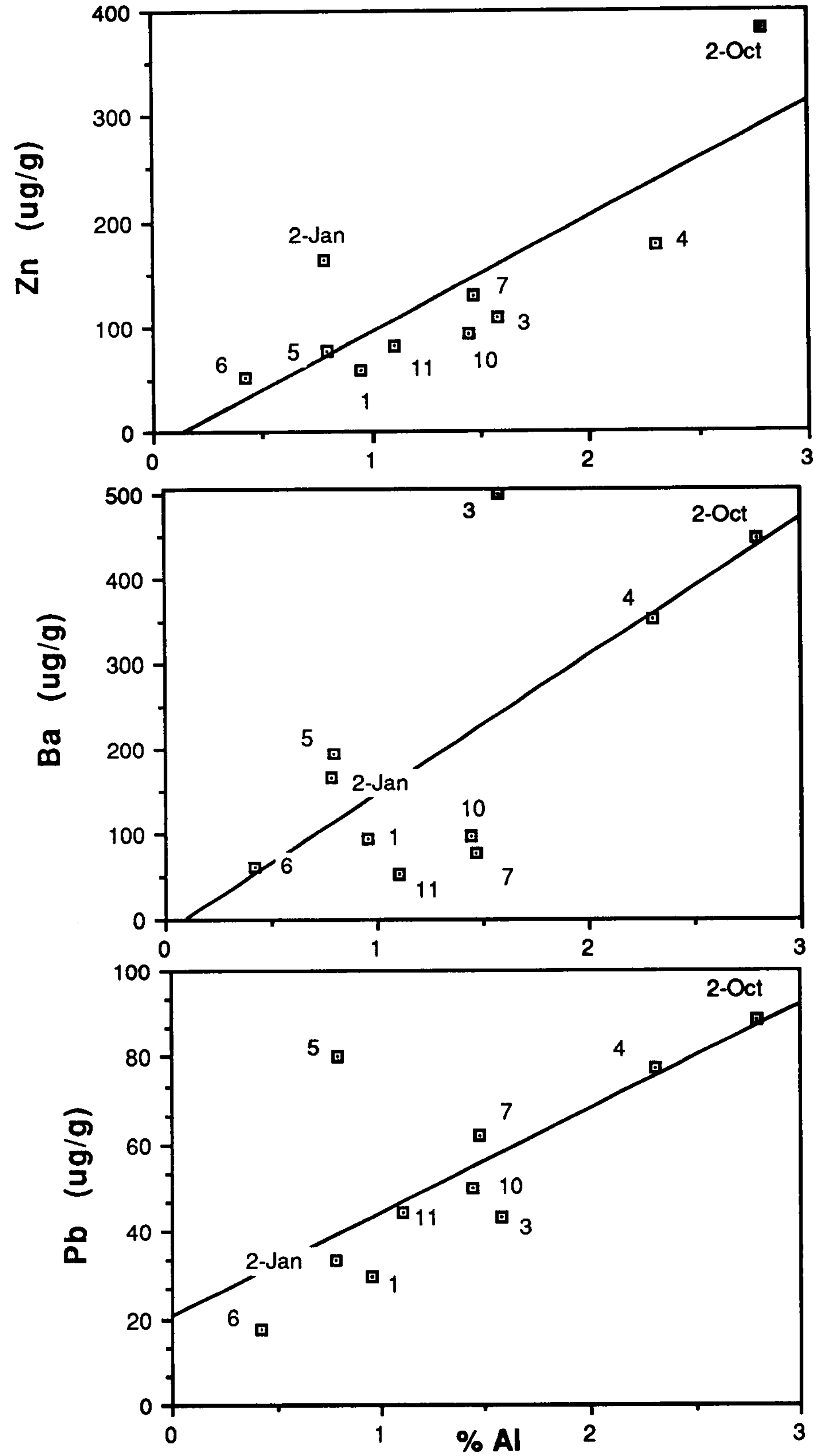


Figure 3.38. Regression of Zn, Ba, and Pb against Al in surficial sediments at the Pass Fourchon study area. Station numbers given next to data.

Table 3.14. Metal concentrations in sections of two marsh cores (January 1988).

Sample	Depth	Cu (µg/g)	Zn (µg/g)	Cd (µg/g)	Pb (µg/g)	Cr (µg/g)	Ni (µg/g)	Fe (µg/g)	Mn (µg/g)	Al (µg/g)	Ba (µg/g)
Port Fourchon Laboratory (Reference)											
	0-2 cm	22.3	93.1	1.65	53.9	23.2	18.7	19,383	408	15,990	96.1
	2-4 cm	22.8	86.7	1.63	54.9	27.5	19.0	20,107	316	16,338	118
	4-6 cm	21.2	79.7	1.63	54.2	23.5	18.5	20,433	324	16,252	124
	6-8 cm	20.2	69.1	1.37	49.7	22.2	17.0	18,819	176	16,749	104
	8-10 cm	18.2	68.2	1.31	45.1	20.6	16.6	14,939	166	14,472	51.3
	10-15 cm	22.6	81.4	1.56	54.1	24.5	19.2	17,628	147	16,592	44.4
	15-20 cm	20.7	65.2	1.37	51.0	23.4	18.6	17,197	104	17,214	42.2
	20-22 cm	11.9	33.0	0.70	33.7	16.1	12.1	10,660	75.4	10,974	22.0
Pass Fourchon											
	0-2 cm	16.6	62.2	1.01	48.2	20.3	14.3	12,983	87.8	13,428	54.3
	2-4 cm	19.9	62.2	1.02	51.3	22.9	16.2	15,058	99.6	16,192	40.5
	4-6 cm	18.3	55.6	1.05	49.4	23.0	15.7	13,554	96.4	13,755	41.1
	6-8 cm	16.1	46.1	0.73	36.0	17.1	13.7	9,268	76.0	11,628	12.9
	8-10 cm	22.3	66.6	1.09	51.9	23.3	19.3	12,513	104	16,425	18.9
	10-15 cm	24.9	70.1	1.44	58.5	25.5	20.8	16,008	139	17,652	43.4
	15-20 cm	19.2	56.7	1.05	55.2	24.6	17.2	15,500	126	18,786	13.6
	20-25 cm	18.4	49.6	0.63	48.5	24.2	15.5	9,010	113	18,506	1.26
	25-30 cm	20.7	60.6	1.33	55.3	24.5	19.1	14,617	105	16,859	45.5
	30-35 cm	20.5	54.5	1.13	52.6	23.8	16.6	12,715	101	14,174	46.6

Table 3.15. Benthic macroinfauna for Pass Fourchon site.

Station Number	Species Richness		Number of Individuals*	
	Oct. '87	Jan. '88	Oct. '87	Jan. '88
PF-1	5	-	68	-
PF-2	0	1	0	1
PF-3	0	-	0	-
PF-4	5	-	10	-
PF-5	8	-	96	-
PF-6	30	-	291	-
PF-7	-	0	-	0
PF-10	-	15	-	58
PF-11	-	18	-	437

*Surface area of benthic sample in October 1987 = 0.0129 m^2 and in January 1988 = 0.0238 m^2, or about two times greater in January 1988.

The number of species and number of individuals per station were zero or negligible at PF-2, PF-7, and PF-3 (Figures 3.39 and 3.40). The PF-2 sample in January 1988 contained a single individual; all others were zero.

In October, there were greater numbers of species and individuals in the sandier sediments along Pass Fourchon and Bayou Lafourche (PF-1, PF-4, PF-5, and PF-6) away from the Chevron discharge points. In January, the number of species and individuals increased towards Bayou Moreau (PF-10 and PF-11) away from the most severely affected stations. Collection of adequate samples in the sandier sediments of Pass Fourchon was not possible using the small grab sampler in January.

The high number of individuals at PF-1, PF-6, and PF-11 were dominated by the polychaete, *Streblospio benedicti*, an opportunistic species typically found in sandy, shallow, back-barrier habitats, the conditions at these stations. Intermediate number of species and individuals were found at PF-5 in October 1987 and PF-10 in January 1988. PF-5 was dominated by an amphinomid polychaete and oligochaetes, and PF-10 and PF-11 by spionid and capitellid polychaetes and oligochaetes. These organisms are more indicative of muddy sand sediments of saline marshes. As noted earlier, the increased numbers of opportunistic species such as the spionid and capitellid polychaetes and/or tubificid oligochaetes (Diaz 1980) are indicative of estuarine areas with stressed on disturbed environments and/or organic pollution.

3.6 East Timbalier Island

3.6.1. Study Site

Numerous discharges handling OCS-generated produced waters are located in and near the East Timbalier Island study site. These include discharges from facilities handling produced waters from state waters and those handling OCS produced waters. Those handling OCS produced waters are Chevron's South Timbalier Block 21,27,28 Tank Battery (20,000 bbl/day), South Timbalier Block 35 Tank Battery (1,196 bbl/day) and South Timbalier Block 36,37 Tank Battery (2,862 bbl/day). Stations T-1, T-2 and T-3 were located in the vicinity of the OCS produced water discharges. Sampling focused on the largest of these discharges (Station T-1) which was located in a dredged access channel leading from the otherwise shallow Timbalier Bay into East Timbalier Island (Figure 3.41). Several other produced water discharges (shown as triangles on Figure 3.41) are located in the proximity of this canal network, through which tidal currents sluggishly flow.

The stations for benthos and chemical analyses were located along an access channel to several Chevron separation facilities. Station T-1 was located mid-channel adjacent to the Chevron ST-21,27,28 discharge. Station T-2 was located mid-channel between the ST-35 and ST-36,37 discharges. Station T-3 was in a channel perpendicular to the Chevron access canal and near the ST-36,37 discharge. Stations T-4 and T-5 were located in the channel leading away from the discharge points and into Timbalier Bay. Station T-6 was at the shallow, southerly end of the Chevron access canal, and was the most distant station that could be reached by outboard in that direction from the discharges.

Sediments were muddy sands at T-1 and T-2, coarse sands at T-3, T-4 and T-5, and fine sands at T-6.

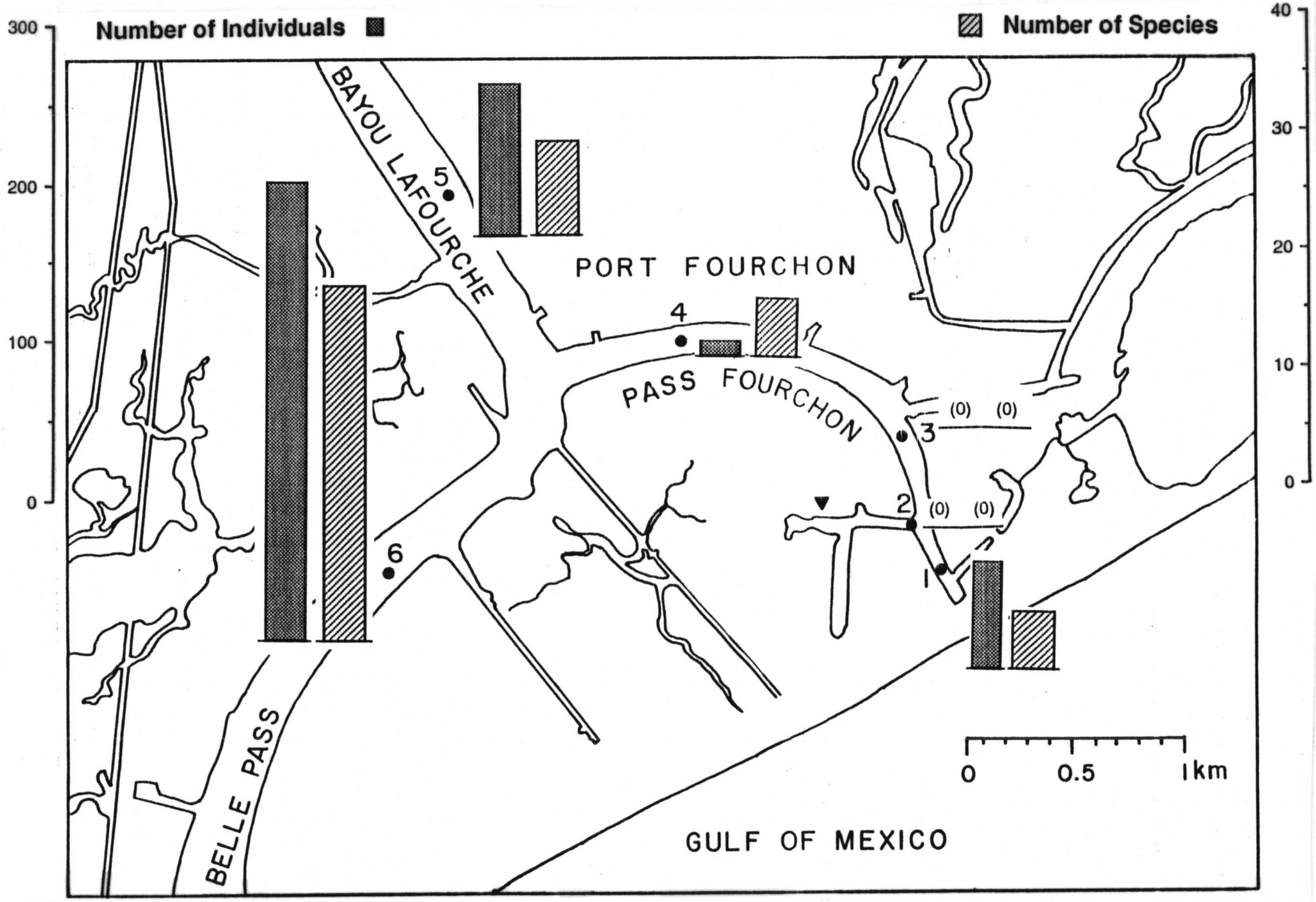


Figure 3.39. Macroinfauna data for Pass Fourchon, October 1988.

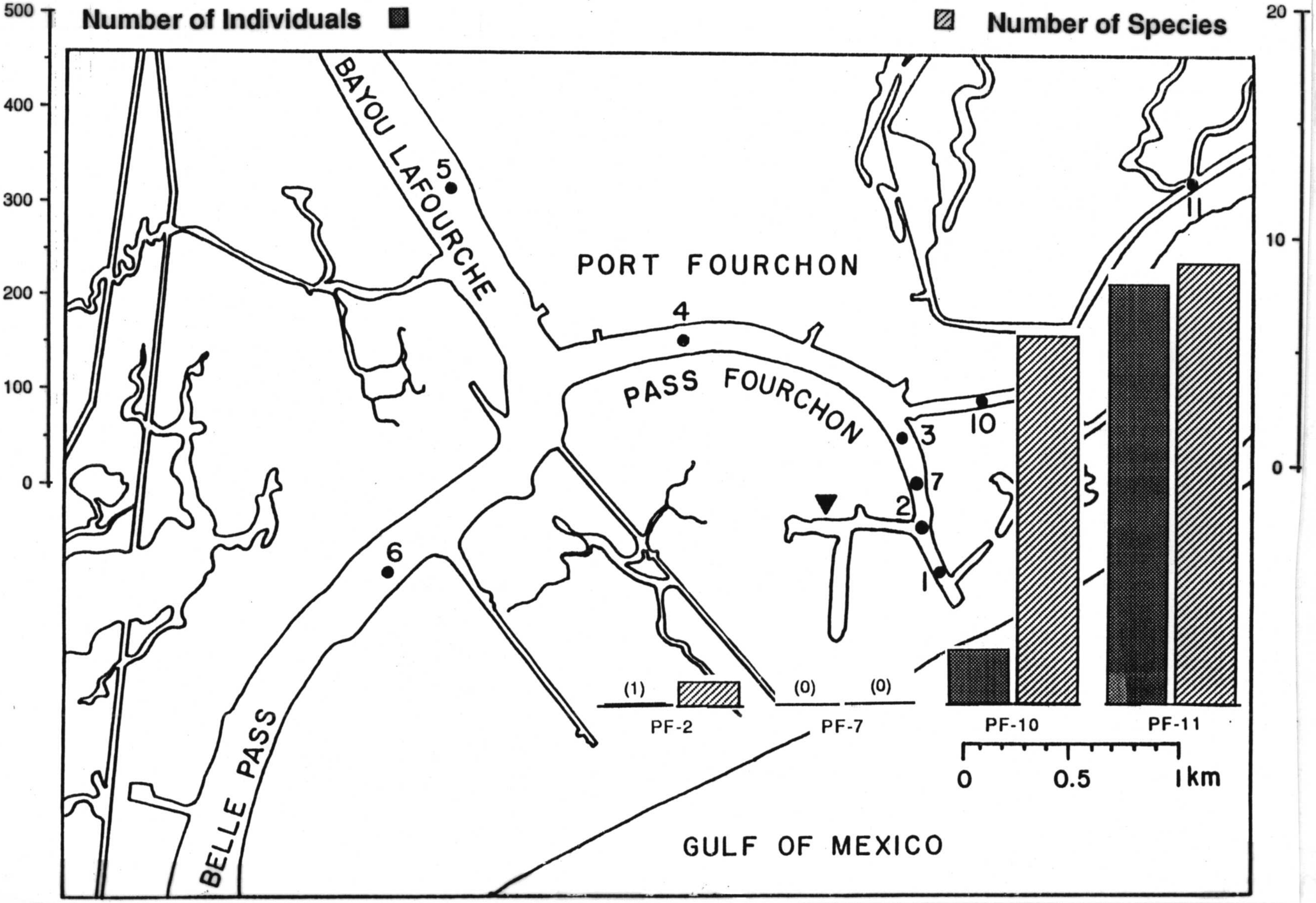


Figure 3.40. Macroinfauna data for Pass Fourchon, January 1988.

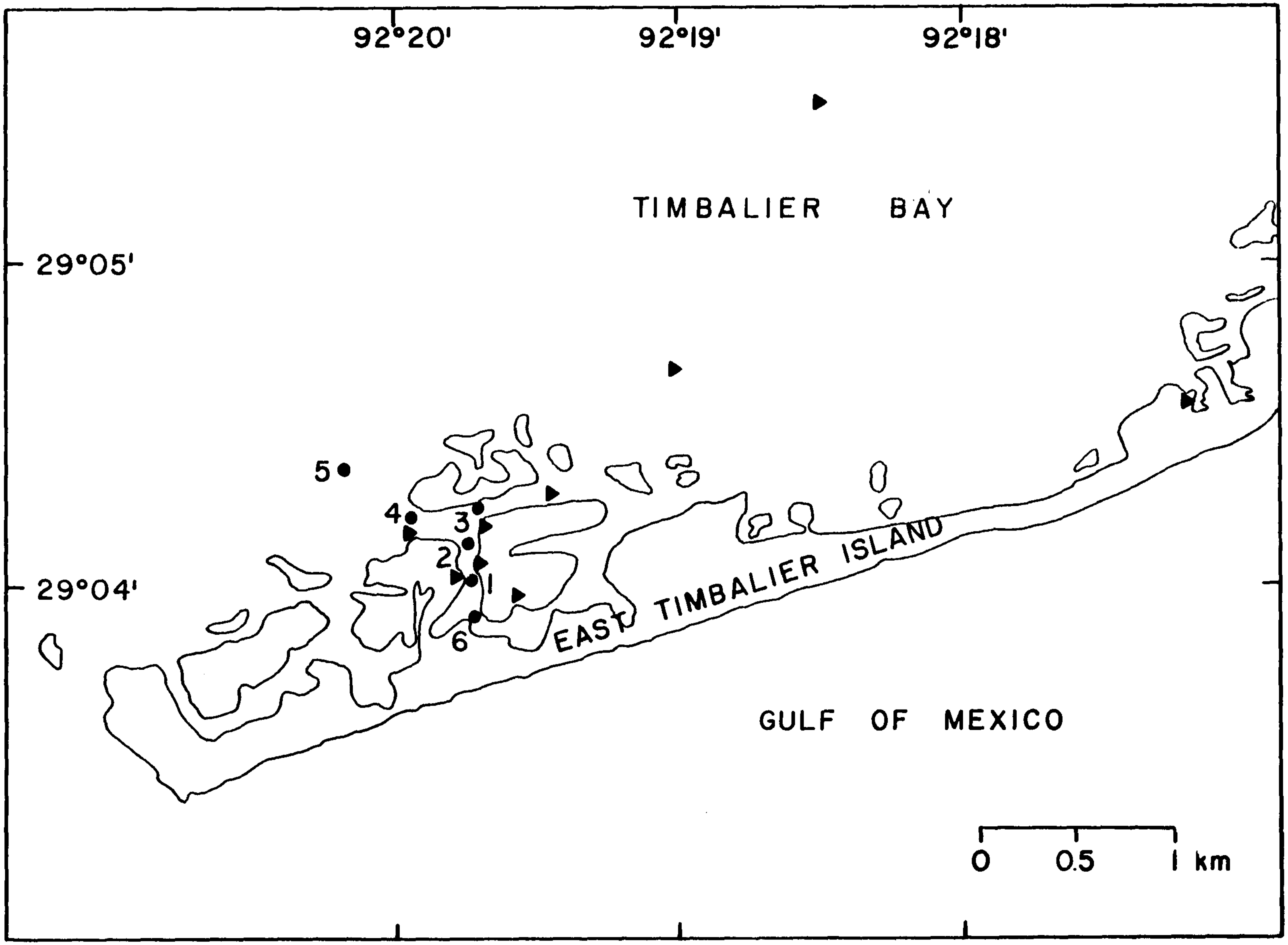


Figure 3.41. East Timbalier Island study area; produced water discharges indicated by closed triangles.

3.6.2 Organics

Sediments

Table 3.16 lists the hydrocarbon data for these samples, while Figures 3.42 and 3.43 present the areal distribution of sediment hydrocarbons.

There are several produced water discharges found in this area. Station T-1, which was located at a major discharge, contained the highest concentration of PAH and saturated hydrocarbons measured in the East Timbalier area. The FFPI indicated a petrogenic source for these hydrocarbons. The index differs slightly from the value for the produced water because of the presence of some pyrogenic PAH. The ratio of the isoprenoid hydrocarbons, pristane/phytane, in the sediments compared well with the produced water ratio. However, the ratio of isoprenoids to n-alkanes does not, with the sediments showing higher isoprenoid levels compared to n-alkanes. The isoprenoids are much more resistant to microbial degradation than the n-alkanes, which would account for the low amounts of n-alkanes relative to isoprenoids in the sediments. This resistance to degradation makes the pristane/phytane ratio a good tool in determining the source of petroleum contamination. Station T-6, 200 meters south of T-1, showed contamination from the discharge. The PAH concentration was not extremely high, but the composition suggested a petroleum-derived hydrocarbon source. Stations T-3 and T-5 contained lower levels of PAH. The composition of PAH that were detected indicated a pyrogenic source rather than one related to the produced water discharge. Station T-4 contained the second highest concentration of PAH, but the majority of the aromatics were of pyrogenic origin. T-4 also contained very low amounts of resolved saturated hydrocarbons, with the majority of saturated hydrocarbons contained in the UCM. Although T-4 was near a discharge, the PAH and saturate data indicated little contamination from petroleum-derived hydrocarbons. Based on these results it appeared that only Stations T-1 and T-6 had been directly contaminated by produced water discharges. How far the contamination extended north from T-1 is unknown, as there was no sample available for analysis at Station T-2 (broken before arrival at laboratory). Visual examination of the sediments at T-2 during collection indicated high concentration of hydrocarbons.

Overlying waters

The overlying water sample, T-1 (Table 3.17), showed only slight contamination from volatile organic hydrocarbons. Benzene was detected at 3 ng/ml and toluene at 12 ng/ml. No semivolatile target compounds were detected.

3.6.3 Trace Metals

Concentrations of metals in sediments collected at the East Timbalier study site during January are presented in Table 3.18. Concentrations of zinc, barium and lead are plotted versus aluminum concentration as was done for the Pass Fourchon stations (Figure 3.44). Correlations between zinc and lead and aluminum were good. There was a possible hint of zinc contamination at station T-1. Barium concentrations were poorly correlated with aluminum; relatively high barium concentrations were measured in the sandier sediments at stations T-5 and T-3.

3.6.4 Benthos

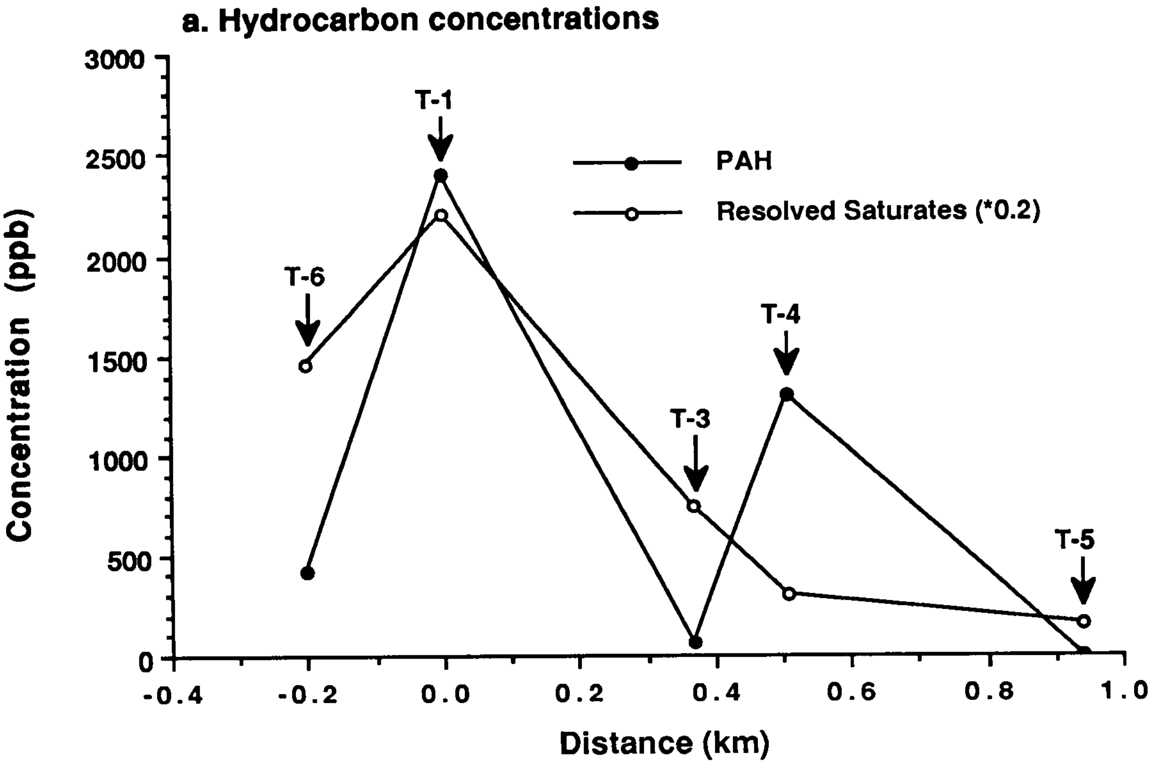
The species richness (number of species) and number of individuals for stations at the East Timbalier study site are given in Table 3.19 and Figure 3.45.

Table 3.16. Hydrocarbon concentrations in East Timbalier sediments.

Sample	Total PAH (ppb)	FFPI	Total Saturated H.C. (ppb)
T-1	2,300	0.87	57,000
T-1 Dup	2,400	0.85	63,000
T-3	<30	N/A	5,000
T-3 Spk Dup	130	0.56	18,000
T-4	1,300	0.12	16,000
T-5	<12	N/A	2,000
T-6	420	0.85	29,000

Table 3.17. Hydrocarbon concentrations in East Timbalier overlying water.

Sample	Benzene (ng/ml)	Toluene (ng/ml)	Ethylbenzene (ng/ml)	Xylenes (ng/ml)	Total PAH (ng/ml)	Total Saturated H.C. (ng/ml)
T-1	3	12	ND	ND	<5	ND



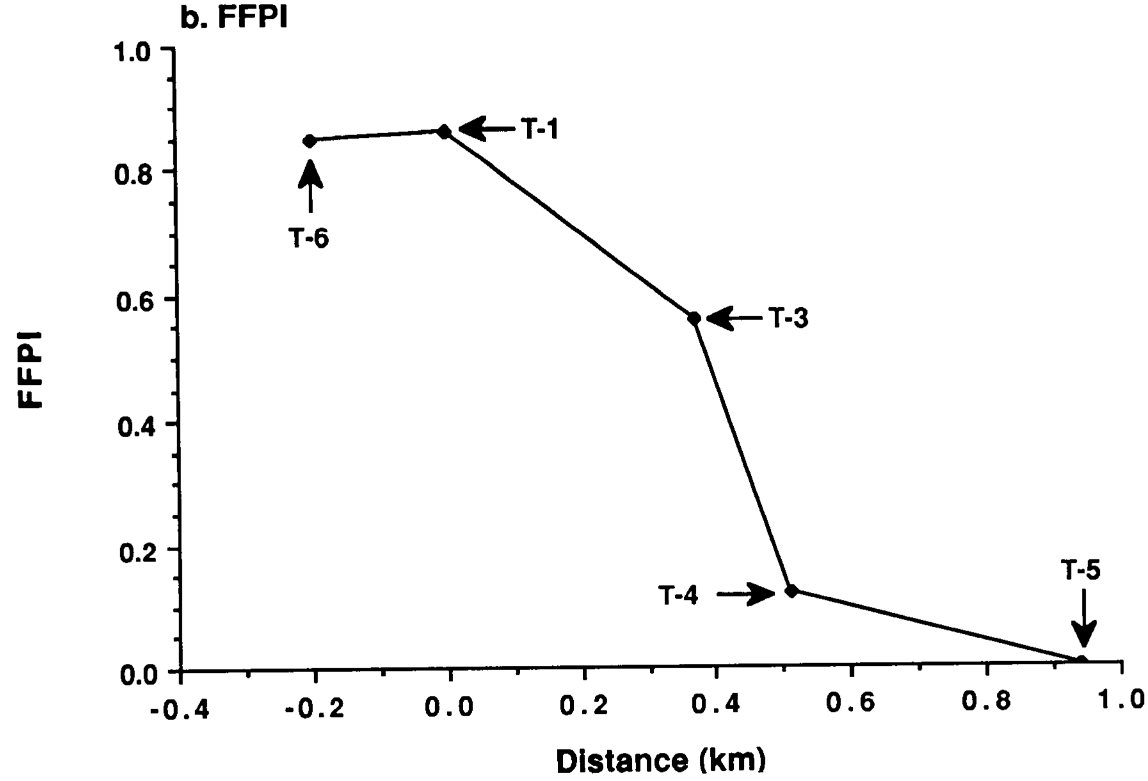


Figure 3.42. Longitudinal profiles of hydrocarbon concentrations (a.) and FFPI (b.) in sediments away from T-1 (January 1988).

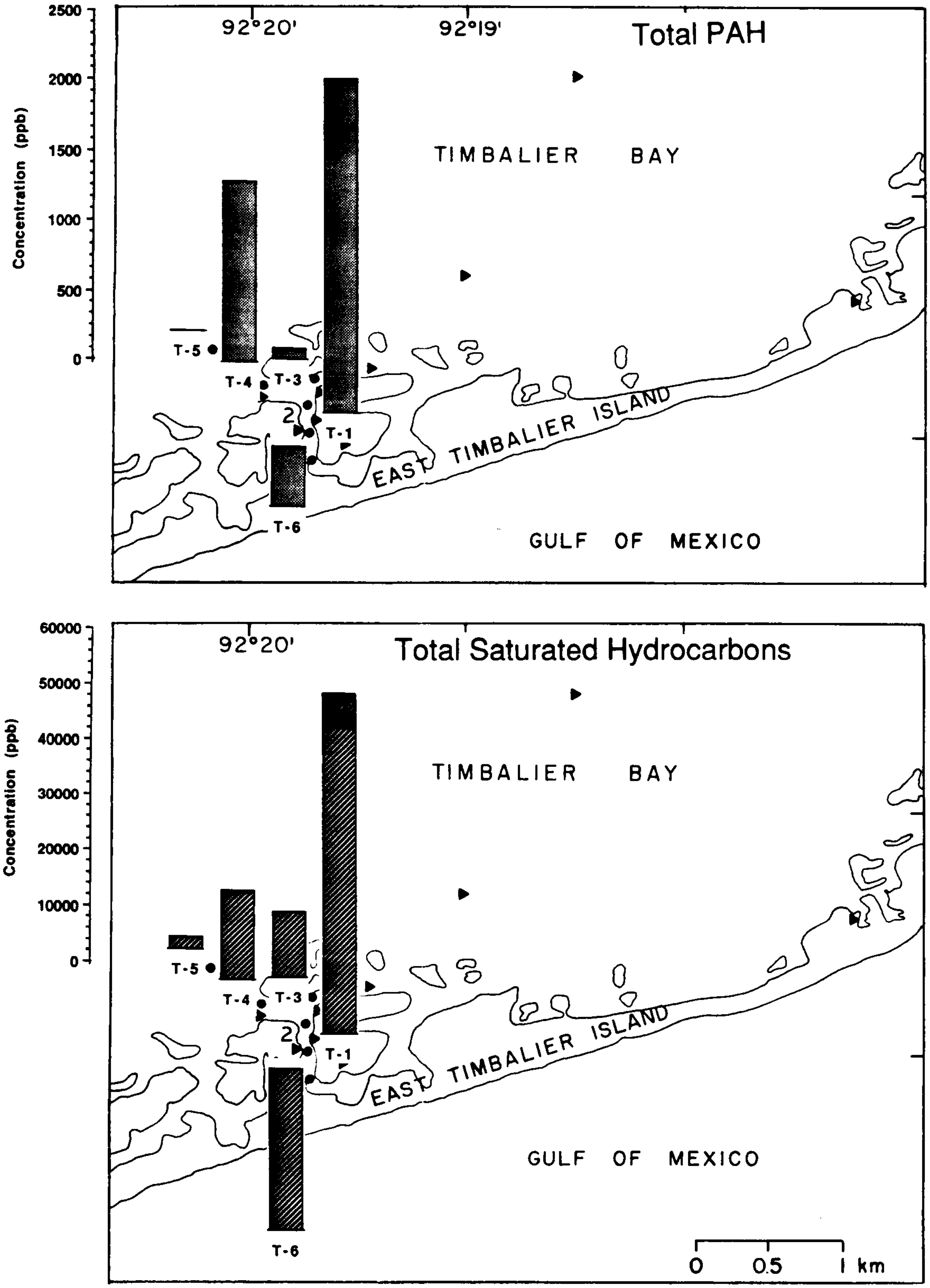


Figure 3.43. East Timbalier location map with total PAH, above, and saturated hydrocarbon concentrations, below, in sediments for January 1988.

Table 3.18. Metal concentrations in surficial sediments from East Timbalier Island site.

Sample	Replicate	Cu (μg/g)	Zn (μg/g)	Cd (μg/g)	Pb (μg/g)	Cr (μg/g)	Ni (μg/g)	Fe (μg/g)	Mn (μg/g)	Al (μg/g)	Ba (μg/g)
T-1	1	15.3	96.4	1.58	34.1	21.0	16.5	17,049	262	11,869	44.3
T-1	2	14.5	96.9	1.52	34.4	21.3	16.9	17,274	265	12,212	43.2
T-3	1	8.43	39.4	0.93	27.1	13.5	11.8	11,349	178	7,632	145
T-3	2	8.03	37.7	0.86	26.4	13.1	11.3	10,373	169	7,080	132
T-4	1	10.8	49.4	1.16	34.2	16.5	14.2	13,495	225	9,085	51.6
T-4	2	11.8	49.3	1.07	32.4	16.1	14.1	13,577	223	8,671	53.5
T-5	1	4.06	131	0.57	17.1	7.04	7.71	5,520	108	3,238	211
T-5	2	4.23	19.4	0.47	15.3	6.51	7.63	30.0	97.5	3,381	189
T-6	1	16.0	58.7	1.38	35.9	18.7	15.9	16,083	185	12,321	157
T-6	2	14.8	57.9	1.19	36.0	18.8	15.8	16,934	183	13,373	125

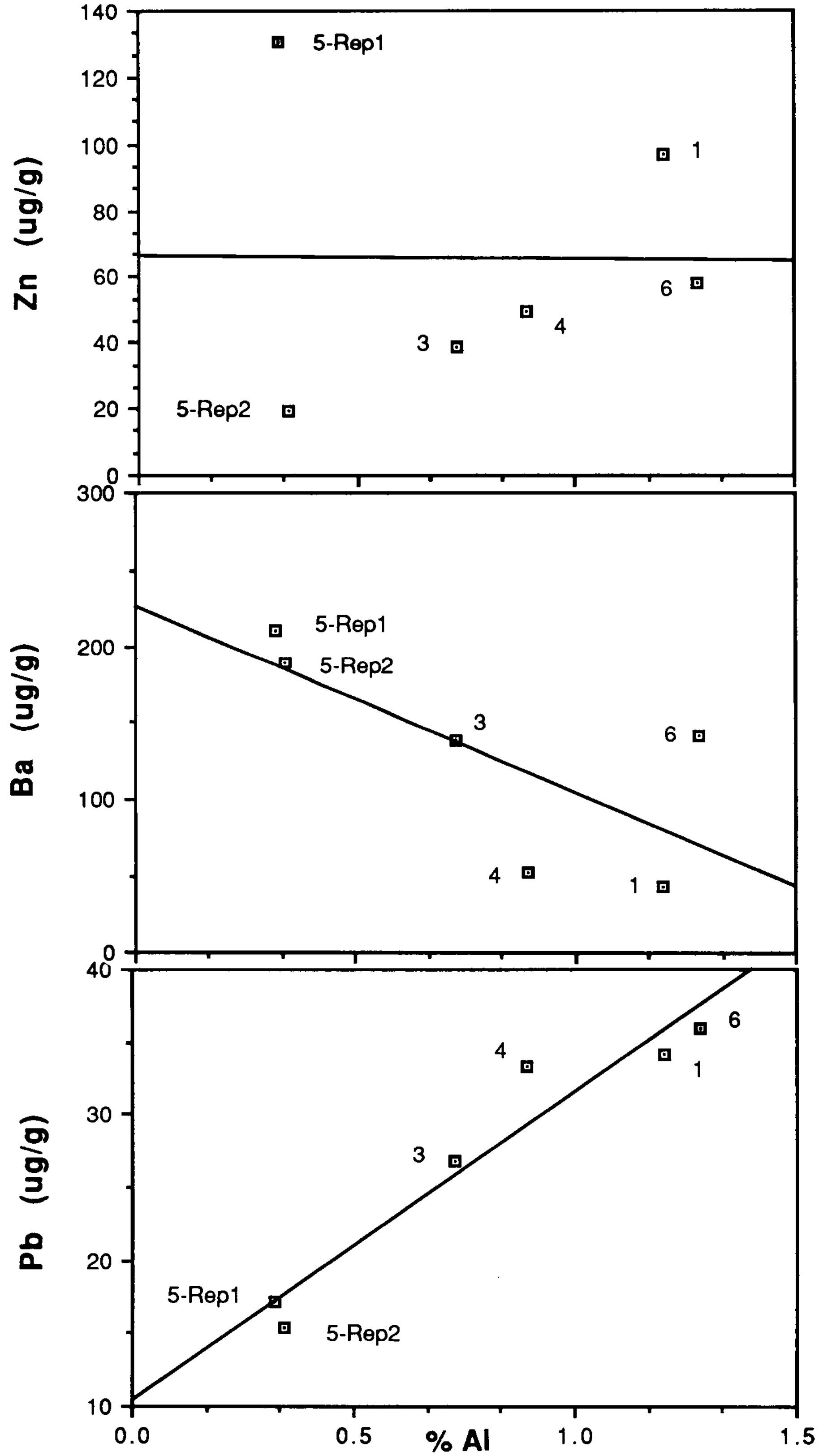


Figure 3.44. Regression of Zn, Ba, and Pb against Al in surficial sediment at the East Timbalier Island study area. Station numbers given next to data.

Table 3.19. Benthic macroinfauna for East Timbalier Island site.

Station Number	Species Richness Jan. '88	Number of Individuals* Jan. '88
T-1	2	5
T-2	0	0
T-3	18	535
T-4	13	89
T-5	11	103
T-6	11	448

*Surface area of benthic sample = 0.0238 m^2.

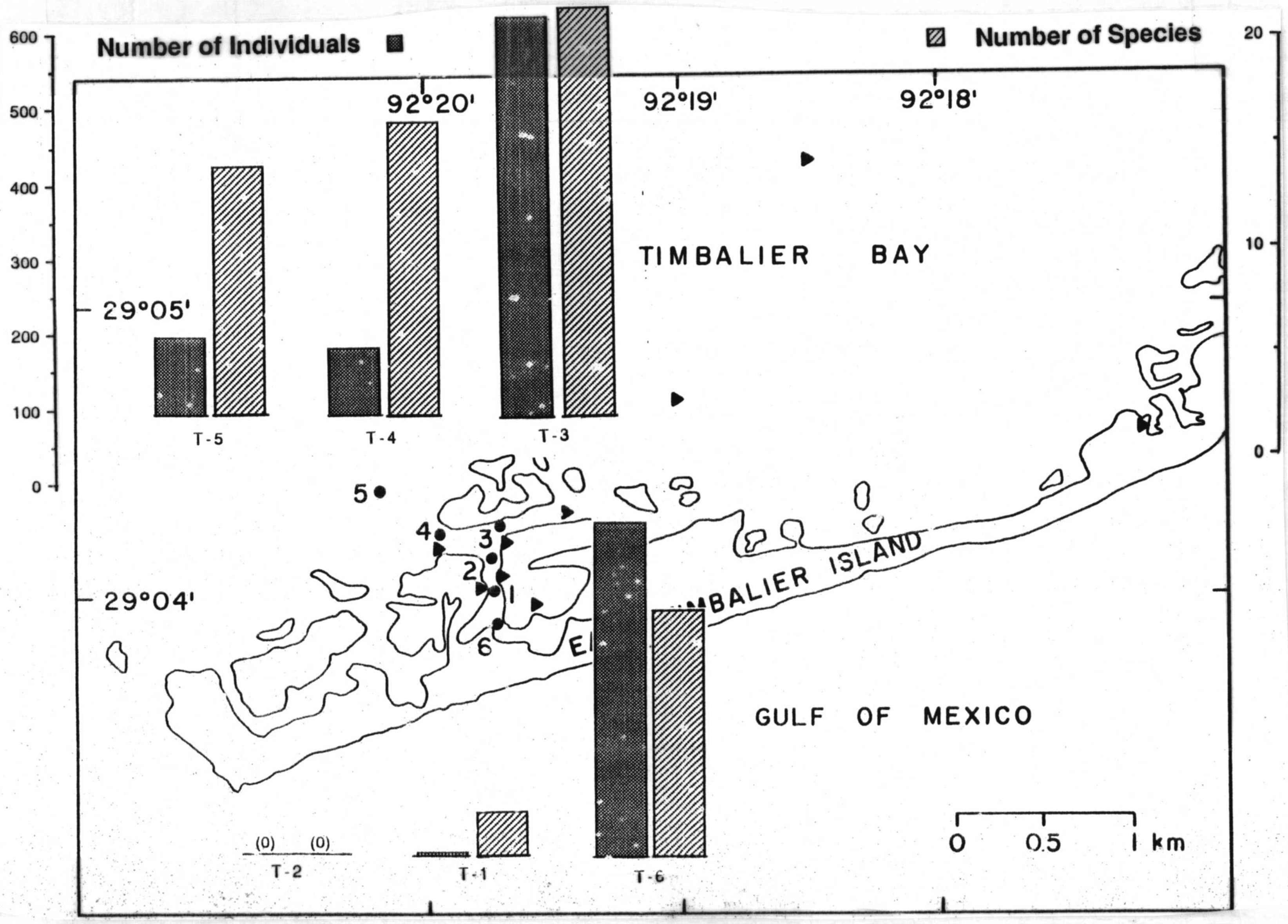


Figure 3.45. Macroinfauna data for East Timbalier Island, January 1988.

Negligible or zero number of individuals were collected at T-1 and T-2. Station T-3 was characterized by high numbers of *Streblospio benedicti* and *Mediomastus ambiseta*, indicating possible organic enrichment of the sediments and increase in populations of opportunistic species. Similar organisms were found at T-4 but in reduced numbers. The benthic macroinfaunal community at T-5 was more typical of open bay, medium salinities, and sandy sediments with numbers dominated by the bivalves, *Mulinia lateralis* and *Tellina versicolor*, and miscellaneous polychaetes.

Station T-6 was located at the shallow southerly end of the access channel to the Chevron facilities. Sediments were fine sands with the appearance of oxidized iron in the sediments. (These high Fe values were confirmed in trace metal analyses, see Table 3.18.) Numbers of individuals were high, including the opportunists, *Streblospio bendecti* and *Capitella capitata*, but also *Chaetozone* sp. which formed dense mats of mucous tubes. Tubificid oligochaetes were present at T-6 and not at any of the other East Timbalier Island stations. This community was also probably one resulting from organic enrichment of the sediments.

3.7 Contaminants in Biota

Hydrocarbon concentrations and content of oysters collected near discharges at Bayou Rigaud (from pilings near the Exxon discharge) and East Timbalier Island (from pilings near the discharge) were compared with those of oysters collected at the LUMCON Port Fourchon Laboratory in Table 3.20 and Figure 3.46. Oysters could not be found in the vicinity of the Pass Fourchon discharge. Instead ribbed mussels were collected from the marsh adjacent to the Chevron facilities. This marsh is flooded by water from the dead-ended portion of Pass Fourchon and could be influenced by the produced water discharge. Ribbed mussels from a marsh near the LUMCON Marine Center in Cocodrie were analyzed for comparison.

Total PAH and total saturated hydrocarbons were both at least three times more concentrated in oysters and mussels near the produced water discharges than those at reference sites. Moreover, the fossil fuel pollution index (FFPI) was greater than 0.7 in the molluscs from near discharge sites, while it was much lower or near zero at the reference sites. The oysters at the Port Fourchon Laboratory control site actually displayed concentrations of PAH and a FFPI which suggest moderate petroleum hydrocarbon contamination. These concentrations may possibly be related to the vessel and small boat traffic in the vicinity and were likely pyrogenic in orgin. The high FFPI and PAH concentration in the Pass Fourchon mussels (compared to the Cocodrie marsh samples) may be related to an oil spill which took place at the nearby Chevron facility approximately one month prior to sampling.

Concentrations of trace metals measured in oysters and mussels are presented in Table 3.21. Concentrations of copper and zinc were not higher at the produced water disposal sites than at the control sites for either oysters or mussels. Concentrations of cadmium and chromium were higher at both produced water sites than at the control site for both oysters and mussels (Figure 3.47). Oysters had higher concentrations of cadmium than mussels, and mussels displayed higher concentrations of chromium than oysters. Mussels from Port Fourchon had higher concentrations of lead and nickel than the mussels from Cocodrie.

Table 3.20. Hydrocarbon concentrations in study area organisms.

Organism and Location	Code*	Total PAH (ppb)	Fossil Fuel Pollution Index	Total Saturated Hydrocarbons (ppb)
Crassostrea virginica (American oyster)				
Bayou Rigaud	A	2,200	0.87	330,000
(BR)	B	3,400	0.88	330,000
LUMCON Port Fourchon Laboratory	1A	2,000	0.46	190,000
(PFL)	1B	910	0.48	150,000
	2	240	0.24	68,000
East Timbalier Island (ETI)		3,400	0.81	550,000
Geukensia demissa (ribbed mussel)				
Pass Fourchon	A	630	0.77	120,000
(PF)	B	880	0.72	180,000
LUMCON Marine Center, Cocodrie (Coco)		15	0.00	33,000

*A,B = laboratory duplicates, 1, 2 = field duplicates.

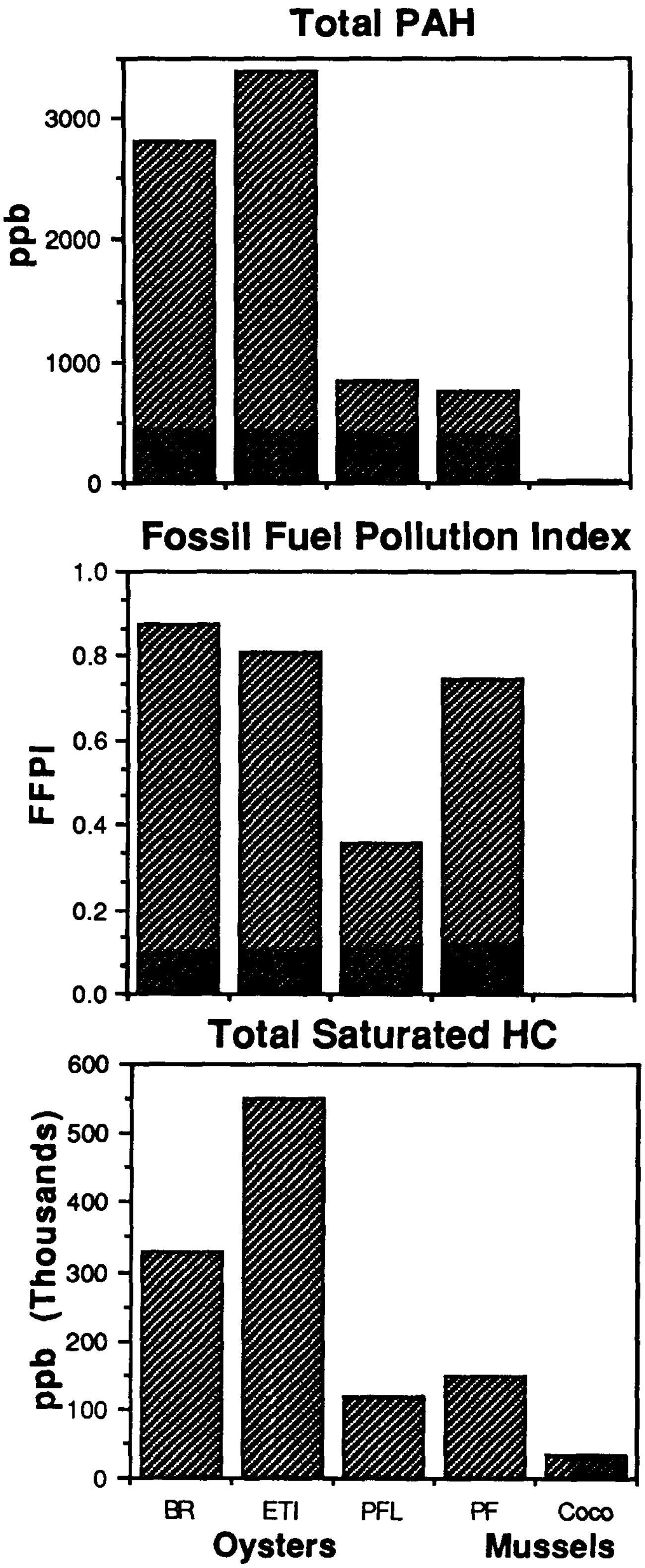


Figure 3.46. Hydrocarbon concentrations in study area oysters and mussels.

Table 3.21. Trace metal concentrations in study area organisms.

Organism and Location	Code*	Cu (µg/g)	Zn (µg/g)	Cd (µg/g)	Pb (µg/g)	CR (µg/g)	Ni (µg/g)	Fe (µg/g)	Mn (µg/g)
Crassostrea virginica (American oyster)									
Bayou Rigaud		97.5	2,142	2.18	0	1.07	1.61	172	8.18
Port Fourchon Laboratory	1	81.3	3,857	0.67	2.57	1.6	1.46	383	10.9
	2	67.3	2,479	1.73	0.17	1.65	1.73	261	15.1
East Timbalier Island	1	21	905	1.72	1.06	0.86	1.6	147	8.5
	2	19.8	906	1.71	0.84	1.16	1.85	149	8.14
Geukensia demissa (ribbed mussel)									
Pass Fourchon	A	15.1	54	1.89	3.33	5.73	3.26	411	11.5
	B	11	50	0.98	4.1	5.53	2.98	401	11
LUMCON Marine Center, Cocodrie		16.8	71	0.23	0	1.86	1.24	647	16.1

*A, B = laboratory duplicates, 1, 2 = field duplicates.

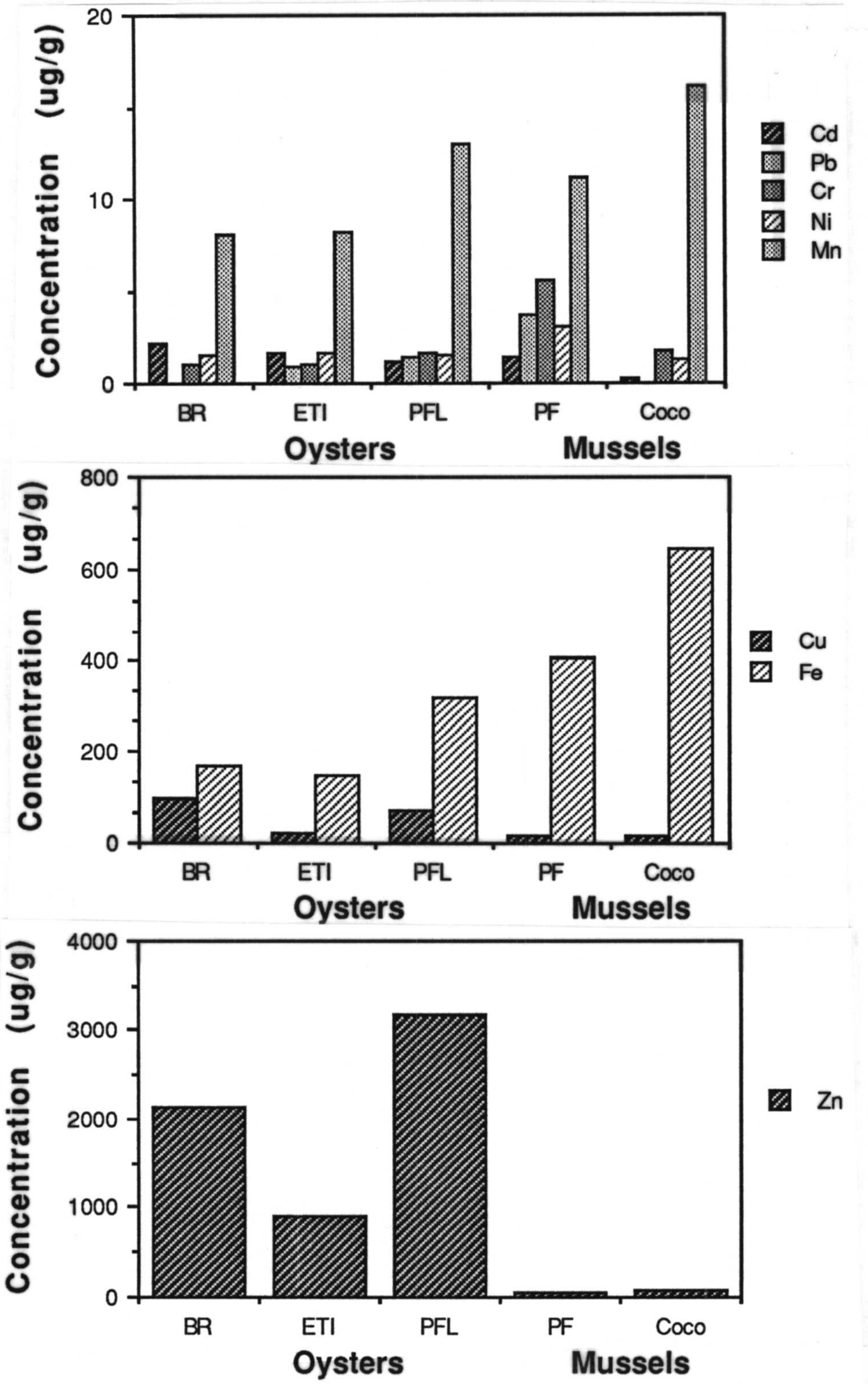


Figure 3.47. Trace metal concentrations in study area oysters and mussels.

Chapter 4

SYNTHESIS AND INTERPRETATION OF RESULTS

by

Donald F. Boesch, Nancy N. Rabalais, Charles S. Milan, Charles B. Henry, Jay C. Means, Robert P. Gambrell, and Edward B. Overton

4.1 Coastal Produced Water Discharges

Although the data assembled here on the number, location and volume of produced water discharges are not necessarily exhaustive or individually accurate, it appears that the total emissions of produced water into estuarine, coastal and continental shelf environments of the Gulf of Mexico region may be 3.4 million barrels per day (556 million l/day). This emission rate is considerably greater than previous estimates (Table 2.4).

The National Research Council (1985) estimated the release of petroleum hydrocarbons to the marine environment associated with produced water discharges to be 66,200 bbl/yr worldwide and 15,600 bbl/yr in the United States based on an assumption of a concentration of 50 mg/l of petroleum hydrocarbons in U.S. produced waters. The NRC's estimates of U.S. produced water discharges was based on a produced water to crude oil volume relationship of 0.6 and considered only OCS production. Based on our new estimates of produced water emissions, the petroleum hydrocarbon loadings from this source in the Gulf of Mexico alone would equal 64,000 bbl/yr assuming the same concentration.

Approximately 70% of the produced water discharged into Gulf environments enters the estuarine systems of Louisiana and Texas. The distribution of these discharges is widespread throughout the coastal zones of both states, but produced water discharges are more numerous and voluminous in southeastern Louisiana and the upper Texas coast. These emissions pose potentially more serious environmental effects than offshore produced water discharges because of the limited dilution potential of the shallow, poorly flushed environments which receive the effluents. Although most discharges into estuarine environments are small in volume, several larger facilities which commingle oil from numerous wells have emission rates which are as large as or larger than the largest OCS discharges. This is particularly true for coastal facilities which separate produced water from OCS product streams.

4.2 Composition of Effluents

The produced waters analyzed contained high concentrations of organic acids, phenols, volatile aromatics, saturated alkanes, low molecular weight polynuclear aromatic hydrocarbons and some trace metals. Few studies have performed detailed analyses of the organic composition of produced waters. Neff et al.'s recent study (1989) is the most complete and they also review most results reported in the literature. The hydrocarbon content of the produced waters analyzed here (10 to 50 ppm) is similar to that measured by Neff et al. (20-30 ppm). The concentrations of alkanes (saturated hydrocarbons) measured here (6 to 55 ppm) also encompassed the mean concentrations reported by Neff et al. (17 to 28 ppm) as did the concentrations of aromatic hydrocarbons (2.5 to 6 ppm versus 2.5 to 3.3). Figures 4.1 and 4.2 compare measured concentrations of specific volatile aromatic hydrocarbons and the more persistent, medium molecular weight naphthalenes, respectively, to those reported in the literature. Although variability limits conclusions, it appears that the produced waters analyzed in this study had generally higher concentrations of naphthalene and its alkylated homologs than in other studies with the exception of the produced water from the C-2 platform in Trinity Bay, Texas, as reported by Armstrong et al. (1979). Although the limited number of samples

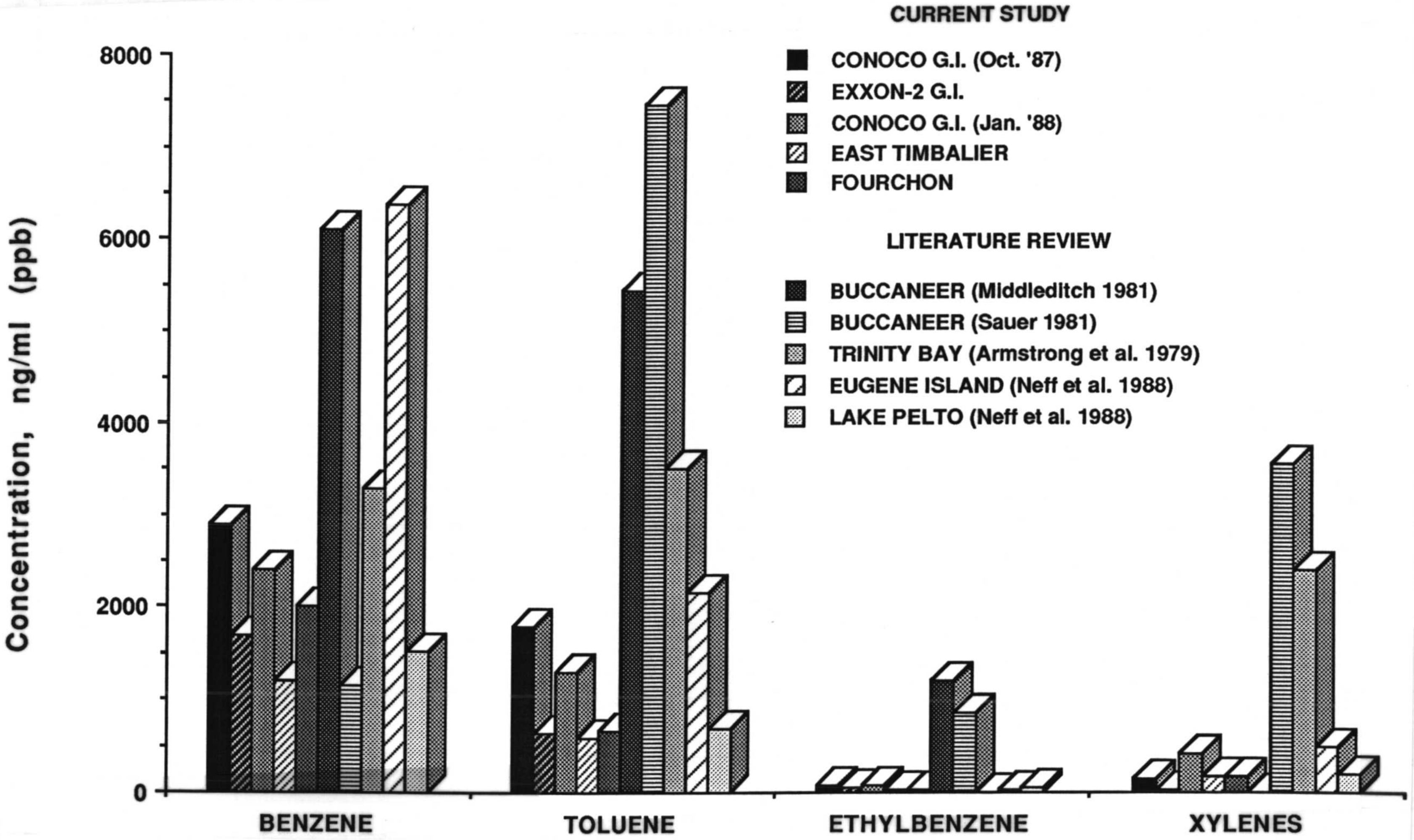


Figure 4.1. Comparison of volatile aromatics.

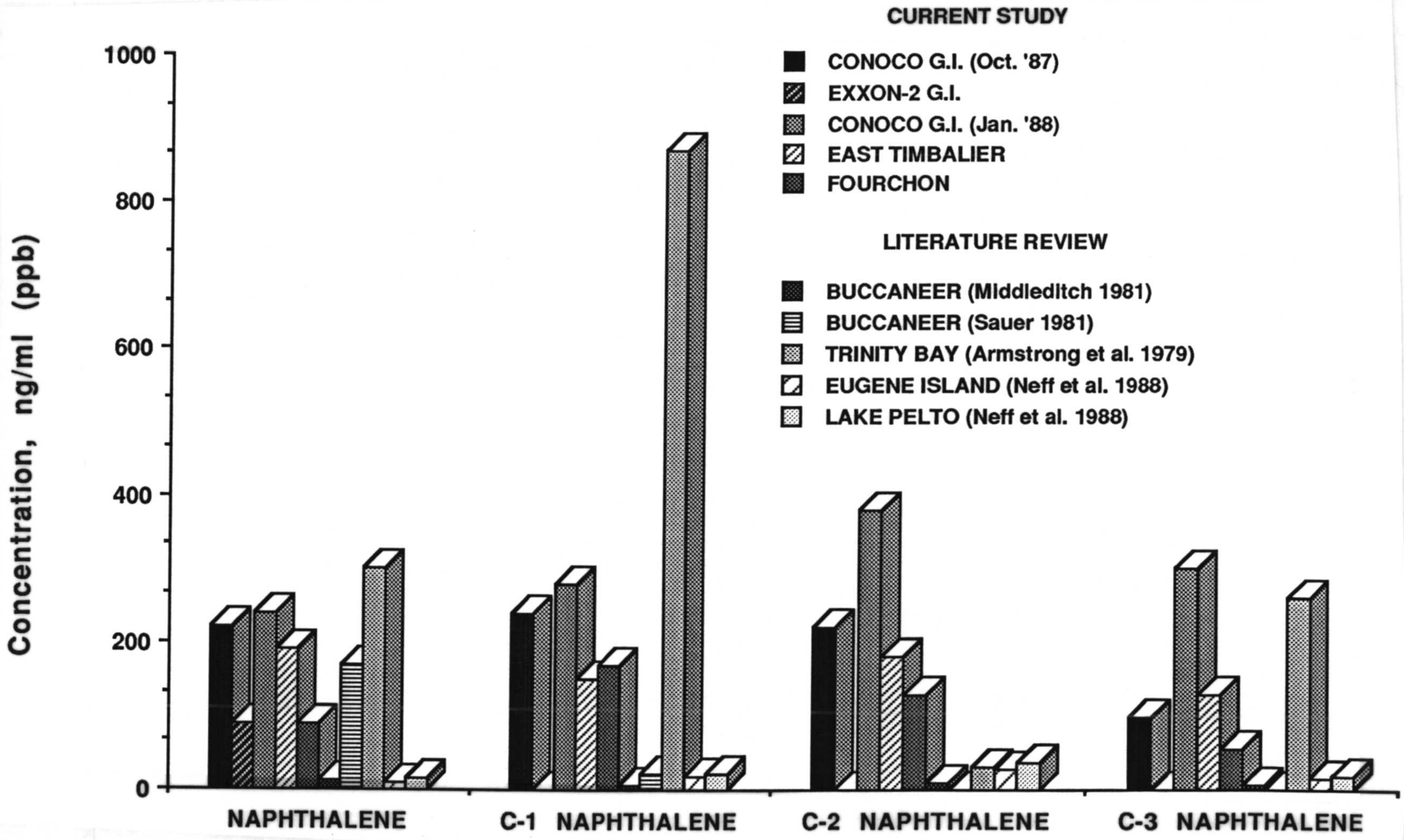


Figure 4.2. Comparison of naphthalenes.

analyzed cautions against placing too much confidence in interpreting differences between the discharges studied here, some intriguing differences bear comment. The produced water samples from the Conoco effluent collected both in October and January had higher concentrations of alkanes and volatile and polynuclear aromatic hydrocarbons than the final discharges from the other facilities. The final Exxon effluent had considerably lower concentrations of alkanes and polynuclear aromatics than the other effluents. Comparison of the final Exxon effluent with the produced water entering the open holding pond suggests that significant removal of these compounds is affected in the pond, either as a result of demulsification or oxidation. These preliminary observations must be confirmed by more extensive sampling.

The concentrations of barium and zinc measured in the produced waters sampled here were similar to those reported by Neff et al. (1989). However, the concentrations of most other trace metals were much higher than those Neff et al. found. These authors noted that higher concentrations were also reported in several studies and attributed this to the difficulty of analysis of metals in concentrated saline brines.

4.3 Mixing and Transport of Effluents

No direct measurements were made of dispersion rates of produced water effluents. Limited observations of salinity distributions made during January suggest the following:

Produced water effluents act as a dense plume upon discharge into estuarine waters. Elevated levels of salinity and volatile organics were found just above the bottom near discharges in Bayou Rigaud and Pass Fourchon. The probable source of the volatile organics was the effluent plume rather than the sediments because these more soluble compounds are not particularly concentrated in the sediments. In Bayou Rigaud, where bottom currents are swift, sufficient turbulence is generated to mix the bottom-hugging plume. Consequently, elevated bottom salinities and volatile organics in overlying waters were not observed beyond the immediate vicinity of the discharge (station BR-1, BR-2 and BR-11). In this case, the broader distribution of contaminated bottom sediments probably results from the resuspension and transport of sediments exposed to the near-bottom plume near the discharge points. At Pass Fourchon, on the other hand, tidal flows are much less energetic because of the dead-end nature of the closed pass. The dense plume retained its identity until mixing where the pass meets a canal and tidal energy is intensified. Assuming a salinity of the produced water of 99 ppt, the bottom water 800 m from the discharge was approximately 5% produced water. Not only does this prolong the contact of the hydrocarbon enriched produced water with fine-grained bottom sediments onto which the hydrocarbons might adsorb, but the limited dilution may create conditions in which the bottom waters are acutely toxic to sensitive organisms. Bioassays of produced waters have shown that most crustaceans tested had LC_{50}'s less than 10% produced water. LC_{50}'s for brown shrimp larvae were approximately 1% produced water (Rose and Ward 1981).

Comparison of interstitial salinities of surface sediments to bottom water salinity as measured by the Hydrolab is shown in Figure 4.3. Those stations which fall far above a one-to-one relationship might indicate areas where brine concentrations from produced water discharges may be reflected in elevated surface sediment interstitial salinities. Stations BR-11, PF-2, and T-1 are stations located in close proximity to discharges at the three study sites. These interstitial salinities, however, are much less than the salinities of the produced water discharges, i.e., 80 to 100 ppt. This would indicate a dilution of the dense plume prior to reaching the bottom, a dilution of salinity out of these sediments by overlying waters, or the failure of highly saline waters to be incorporated in the first place. The former two possibilities seem a more accurate assessment, since high concentrations of PAH, indicating produced water sources, have been documented in the surface sediments for these stations.

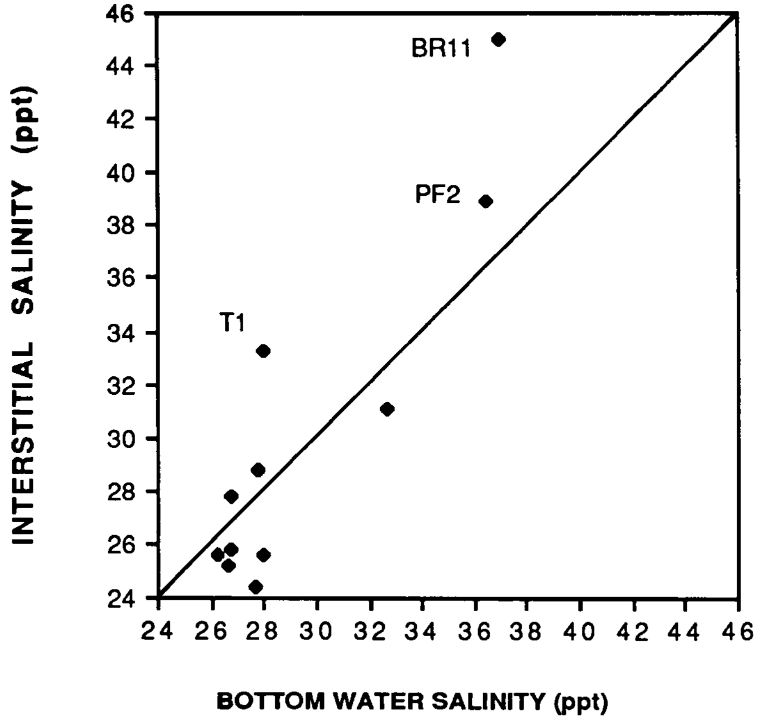


Figure 4.3. Interstitial salinity of surface sediments compared to bottom water salinities at selected stations in January 1988. Line indicates one-to-one relationship.

4.4 Bottom Sediment Contamination

4.4.1 Organic Compounds

Sediments up to one kilometer from the produced water discharges studied exhibited evidence of petroleum contamination. Contaminated sediments were typified by: 1) the presence of petroleum-derived PAH; 2) alkly-substituted homologs at higher concentrations than unalkylated parents; and 3) a fossil fuel pollution index which indicated that more than one-half of the PAH were of petroleum origin (FFPI > 0.5). Sediments well removed from the discharges contained trace or non-detectable levels of petroleum-derived hydrocarbons and a FFPI < 0.3. PAH in these sediments, if detected, were usually pyrogenic in origin. PAH concentrations and characteristics were more useful than saturated hydrocarbons in determining the likelihood of contamination by produced water discharges. The resolved saturated hydrocarbons were usually very weathered with no homologous series of alkanes present, even in contaminated sediments. This lack of alkanes made the use of indices such as odd-even preferences, pristane/nC-17, and phytane/nC-18 of little use in quantifying petroleum hydrocarbon concentration.

Few other studies have performed GC/MS analysis of sediments around produced water discharges. The most detailed and relevant study was that of Neff et al. (1989) which focused on discharges into shallow continental shelf environments and one discharge into Lake Pelto, Louisiana. An earlier study by Armstrong et al. (1979) investigated discharges from a sepatator into Trinity Bay, Texas, and performed a single GC/MS analyses of sediments collected close to the discharge. A comparison of reported concentration of total alkanes and PAH in sediments at the Lake Pelto and Trinity Bay estuarine sites and those determined at the three sites studied here is given in Table 4.1. The concentrations of PAH in the most contaminated sediments sampled at Bayou Rigaud and Pass Fourchon were higher than those at the Lake Pelto platform and similar to the levels reported from Trinity Bay. Furthermore, the distances from the actual physical location of the discharge (in both instances at the terminus of a slip or canal) to the stations displaying this level of contamination were significantly greater than at either Lake Pelto or Trinity Bay sites. The FFPI proved in our analysis to be a highly sensitive indicator of petroleum contamination. However, at the less contaminated Lake Pelto site, Neff et al. (1989) found the FFPI only modestly successful in that regard. "Background" levels of total alkanes and PAH were similar for the Lake Pelto study and the present results.

It is difficult to unequivocally tie the petroleum-derived hydrocarbons in bottom sediments to a produced water source based on a certain chemical signature or fingerprint. The hydrocarbons in the produced waters are, after all, derived from locally produced crude oils. Produced waters are also proportionally enriched in the more soluble low and medium molecular weight hydrocarbons, as are fuel oils. The fact that the overwhelmingly dominant source of petroleum into the receiving waters at the three sites is produced water, the detection of a produced water plume along the bottom, and the gradient of increased concentrations toward the produced water sources provides strong evidence of a produced water source for the observed sediment contamination.

The degree of contamination of sediments with other organic compounds found in produced water is unknown. The nature of these compounds, including naphthenic acids, in produced water is not well characterized. Furthermore, these oxidated organics are more water-soluble than hydrocarbons and less likely to absorb tightly onto sediment particles. Still, the sediments contaminated by petroleum hydrocarbons were highly organic and strongly reducing, and it is likely that the complex mixture of produced water-derived organic compounds contributes to anaerobic if not toxic conditions in sediments.

Table 4.1. Comparison of hydrocarbon levels in bottom sediments in relationship to distance from produced water sources for five estuarine discharge sites.

Location	Station	Distance from nearest discharge (m)	Total Alkanes (ppm)	PAH (ppm)	FFPI
Bayou Rigaud, Louisiana (this study)					
Proximate to Discharge	BR-1, Oct	200	1,300	27	0.96
Moderated Contamination	BR-3, Oct	800	98	0.2	0.50
Background	BR-4, Oct	1,300	38	<0.1	N/A
Pass Fourchon, Louisiana (this study)					
Proximate to Discharge	PF-2, Jan	400	650	43	0.93
Moderate Contamination	PF-7, Jan	600	5.2	0.2	0.67
Background	PF-11, Jan	2,800	37	2.2	0.20
East Timbalier Island, Louisiana (this study)					
Proximate to Discharge	T-1, Jan	10	57	2.3	0.87
Moderate Contamination	T-4, Jan	50	16	1.3	0.12
Lake Pelto, Louisiana (Neff et al. 1989)					
Proximate to Discharge	1,5,9,13	20	163	5	0.36
Moderate Contamination	2,6,10,14	100	44	4	0.24
Background	3,7,11,15	300	27	0.3	0.19
Trinity Bay, Texas (Armstrong et al. 1979)					
Proximate to Discharge	--	--	62	34	--

4.4.2 Metals

The degree of contamination of bottom sediments by trace metals contained in the produced waters is far less than that for petroleum hydrocarbons. Because trace metals naturally occur in sediments at varying concentrations depending on grain size and associated geochemical properties, contamination must be assessed as variation from this normal relationship. Figure 4.4 presents composite data on zinc, barium and lead concentrations in surface sediments from all three study sites as a function of aluminium concentration. Aluminium concentration is generally a strong function of clay mineral content of the sediment. Strong outliers from the normal linear relationship, thus sites of probable contamination, are labeled on this figure. Sediments showing probable zinc contamination were found at stations near the produced water discharges in Bayou Rigaud and Pass Fourchon (BR-1, -2 and -11 and PF-2, respectively). Fewer sediment samples showed variation from the linear relationship between aluminum and lead. A sample from BR-1 was the greatest outlier. The picture for barium was more confused. Although several stations adjacent to the discharges (BR-1 and PF-2) had elevated concentrations of barium in surface sediments, other stations not close to the discharges did as well. At both the Bayou Rigaud and the Port Fourchon area, large volumes of barite used in drilling fluids are loaded or offloaded from supply boats. Incidental loss of barite from these operations could be an additional and confounding source of barium to the sediments.

4.5 Bioavailability of Contaminants

The data on contaminants in biota must be interpreted with great caution because of the limited number of samples on which the results are based. The metals results are ambiguous, and the differences in concentrations between produced water sites and control sites are not great. Results from hydrocarbon analyses, however, demonstrate the clear potential for uptake of produced water associated hydrocarbons by filter feeding molluscs in the vicinity of the discharge.

These observations are also borne out by comparisons of tissue concentrations of substances measured in oysters with those reported from the National Status and Trends Program (NOAA 1987). Of the organic and trace metal levels measured in the Status and Trends Program, only PAH and zinc were found in levels near the produced water discharges which could be considered to be unusually high based on the national monitoring program, i.e. within the range of the highest 25 of 145 bivalve monitoring stations. Table 4.2 compares the PAH and zinc concentrations in the tissue of oysters collected at the Bayou Rigaud and East Timbalier Island discharge sites and the Port Fourchon Laboratory "reference" site with those for other northern Gulf estuarine environments. PAH levels were approximately an order of magnitude higher than "normal" and zinc levels were in the high end of the range for northern Gulf estuaries. Zinc levels higher than those measured were found in Mississippi Sound, Lake Borgne, Sabine Lake and Galveston Bay at sites removed from any direct industrial discharges.

4.6 Biological Effects

The environments which were studied and received produced water discharges are presently disturbed benthic habitats even without the effects of produced water contaminants. These environments are channels in which fine sediments accumulate, which are periodically dredged, and in which vessel traffic disturbs the bottom. Consequently, the benthic fauna is of low diversity and is composed of opportunistic species, including the polychaetes, *Streblospio benedicti*, *Mediomastus ambiseta*, and *Capitella capitata* and the bivalve, *Mulinia lateralis*. At locations closest to the discharge where bottom sediments were heavily contaminated, the macrobenthic fauna is essentially eliminated. Low densities of organisms and few species were found under conditions of moderate hydrocarbon contamination of sediments. This relationship of benthic communities and sediment contamination is depicted in Figure 4.5. Although some

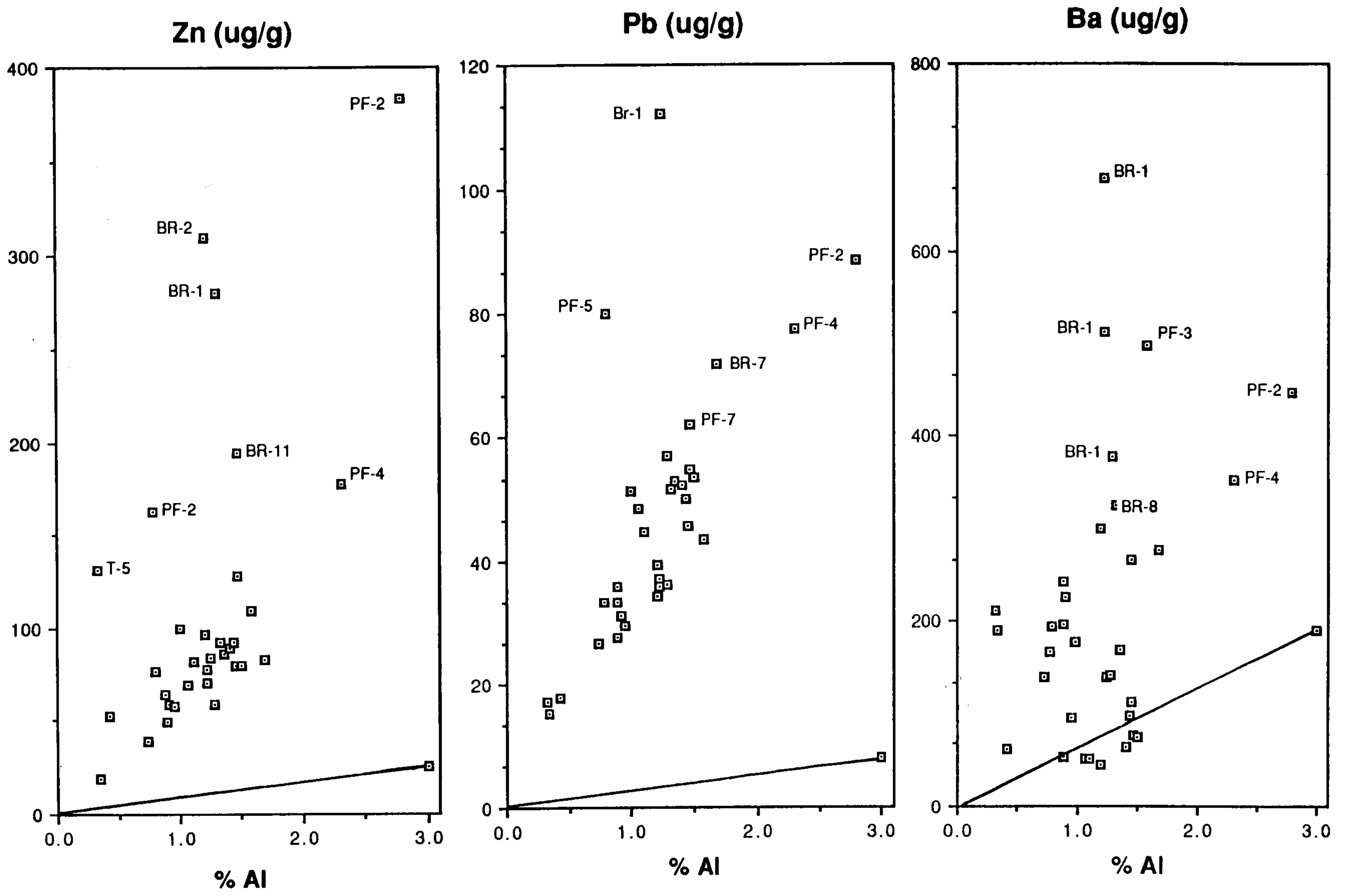


Figure 4.4. Relationship of Zn, Ba, and Pb to Al in surficial sediments at all produced water sites. Some station numbers given next to data. Lines represent the expected concentration of a metal in the sediments based on the aluminum concentration.

Table 4.2. Comparison of concentrations of polynuclear aromatic hydrocarbons (PAH) and zinc measured in oysters (*Crassostrea virginica*) collected in this study with those reported on the northern Gulf region in the National Status and Trends Program (NOAA 1987).

Location	PAH (ng/g)	Zn (µg/g)
This Study		
Bayou Rigaud	2,800	2,142
East Timbalier Island	3,400	906
Port Fourchon Laboratory	848	3,168
National Status and Trends Program		
Mobile Bay	72	916
Mississippi Sound	284-1,518	1,600-3,733
Lake Borgne	60	3,400
Barataria Bay	53-1,109	916-1,266
Terrebonne Bay	45-773	1,366-1,800
Lake Calcasieu	385	2,600
Sabine Lake	219	8,000
Galveston bay	21-1,120	1,083-4,566

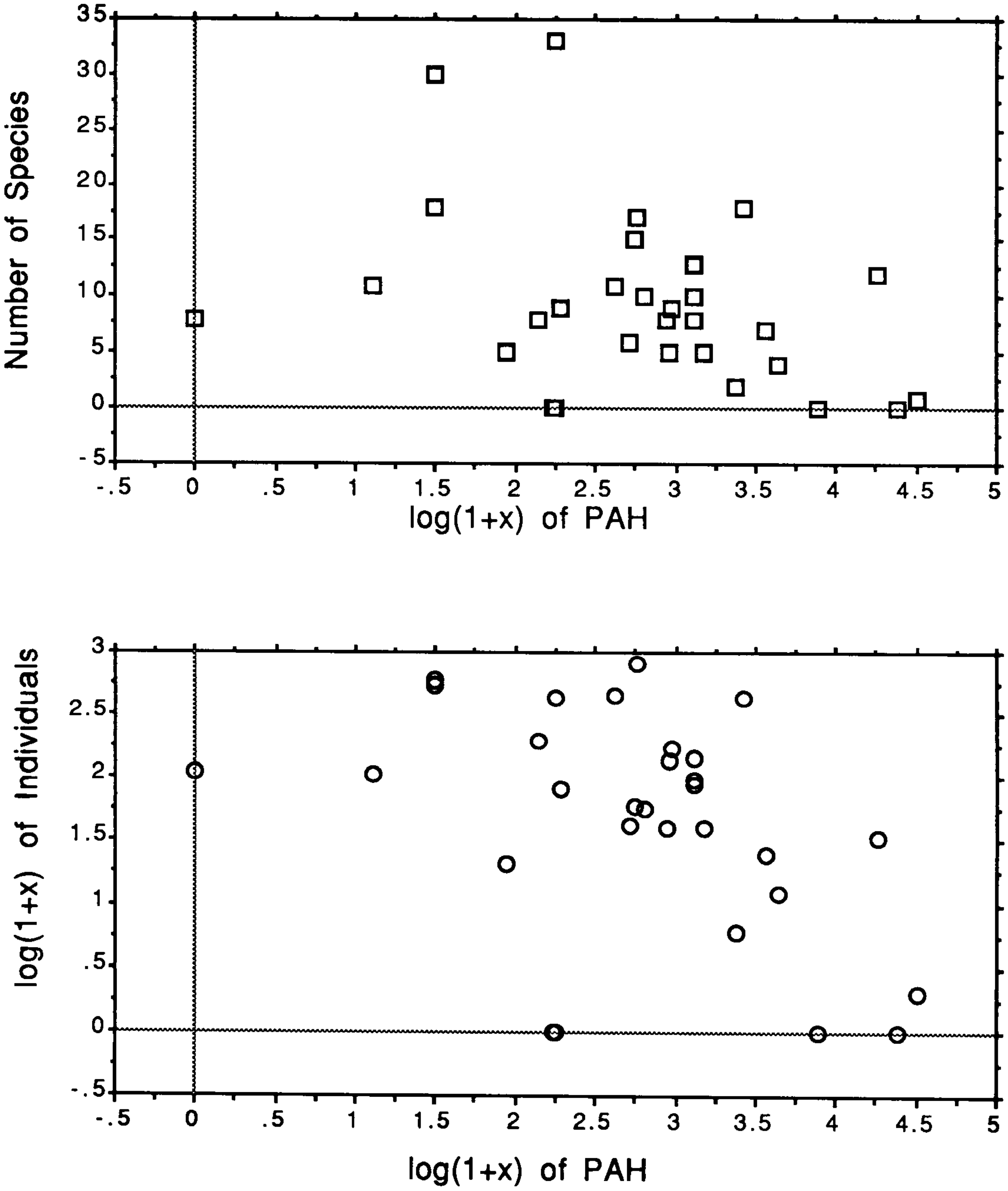


Figure 4.5. Relationship between benthic macroinfauna and hydrocarbon concentration (PAH).

relatively uncontaminated sediments had a sparse benthic fauna, high PAH levels in sediments were always associated with a depauperate benthos.

Harper (1986) noted a "zone of stimulation" beyond the heaviest hydrocarbon contamination of bottom sediments around produced water discharges in Texas estuaries. There the benthic populations were enhanced as a result of organic enrichment of the sediments. This phenomenon was not well developed in the sites studied here, but a biological indicator of organic enrichment was evident in the presence of populations of the polychaete *Capitella capitata* and tubificid oligochaetes at stations displaying intermediate contamination. The dense populations of the polychaetes *Streblospio*, *Capitella* and *Chaetozone* at station T-6 also evidenced this effect.

4.7 Factors Governing the Scale of Effects

The zone of sediment contamination and degraded benthic communities extended farther from the point of discharge of produced water at least at Bayou Rigaud and Pass Fourchon than previously reported for tidally influenced waters. As reflected in Tables 4.3 and 3.1, this is probably the result of the larger discharge volumes and the lower dispersion rates in this bayou and canal than in environments previously studied. Although dispersion rates have not been directly measured, the importance to dispersion, primarily by tidal currents and wind mixing, can be inferred from the general nature of the environments, e.g. water depth, proximity to tidal passes, and exposure to wind mixing. This is also evident from the limited observations of the plume salinity field at Bayou Rigaud and Pass Fourchon, the former being more tidally energetic and dispersive than the latter.

4.8. Conclusions and Recommendations

The discharge of produced waters into coastal and estuarine environments of Louisiana and Texas is a widespread practice, with 1,373 facilities discharging 2.7 million barrels per day. Every major estuarine system receives produced water discharges, but the largest volumes are discharged into the estuaries of southeastern Louisiana and into the Galveston Bay system. Coastal facilities which separate produced water from product streams originating in the OCS are located exclusively in Louisiana and are relatively few in number, but account for large volumes, individually and collectively. These facilities discharge into bayous and canals behind coastal barriers, distributary passess of the Mississippi River, or shallow Gulf waters.

There is no significant effect of elevated salinity resulting from the coastal discharges of OCS produced waters because the separation facilities are located close to the coast. The discharged produced water sinks to the bottom because of its high density and the rate of its dispersion depends on tidal currents. The discharged produced waters contain elevated levels of dissolved and dispersed petroleum hydrocarbons, organic acids and trace metals. Concentrations of the organic constituents may depend on the separation and treatment technologies employed. Substantial contamination of fine-grained bottom sediments with petroleum hydrocarbons was observed near the discharges at the three sites studied. Concentrations of polynuclear aromatic hydrocarbons in sediments exceeded apparent background levels by over an order of magnitude. Sediments which show evidence of hydrocarbon contamination from produced water discharges extend several hundred meters to over one kilometer from the point of the discharge. This effect is more extensive than reported for other produced water discharges which have been studied because of the lower physical dispersion in the bayous and canals into which the discharges take place and the larger volumes of produced water discharged.

General surveys at the three sites showed evidence of biological effects in terms of reduced density and diversity of macrobenthic organisms in contaminated sediments and the accumulation of petroleum hydrocarbons in the tissues of filter feeding molluscs proximate to

Table 4.3. Comparison of discharge rate, receiving environments and extent of contamination of sediments by petroleum hydrocarbons of produced water discharges in the Gulf of Mexico region.

Location	Discharge (bbl/day)	Receiving Water Depth(m)	Environment	Zone of Sediment Contaminants
Bayou Rigaud	150,000	4-5	Dredged Bayou	1.1 km
East Timbalier Island	69,000 (24,000 OCS)	1.5-2	Canals near Bay	50 m
Pass Fourchon	45,000 (26,000 OCS)	3	Canal-Dredged Bayou	600 m
Trinity Bay (Armstrong et al. 1979)	4,000-10,000	3	Open Bay	250-300 m
Lake Pelto (Neff et al. 1989)	3,700	2	Open Bay (near pass)	<300 m
Eugene Island 120 (Neff et al. 1989)	3,000	12	Shallow Shelf	100 m
Buccaneer Field (Middleditch 1981)	120-2,000	20	Shallow Shelf	200 m

the discharge sites. Quantification of these effects awaits more rigorous field and laboratory studies. To support the prudent operation and regulation of produced water discharges, more information is needed on the composition of the non-hydrocarbon organic substances in produced water, the physics of plume dispersion, the sorption and desorption of organic contaminants on fine-grained sediments, the transport of contaminated fine sediments, the biological effects of toxic organics bound to sediments and in interstitial waters on benthic organisms and sensitive larvae and postlarvae of exposed nektonic organisms, including penaeid shrimp.

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APPENDICES

Table A.1. Bayou Rigaud sediment data (October 1987).

SAMPLE I.D. DEPTH	BR-1 0-5 cm	BR-1 Dup 0-5 cm	BR-1 5-10 cm	BR-1 10-15 cm	BR-1 15-18 cm	BR-2 0-5 cm
WET WEIGHT (g)	24.9	27.6	27.6	27.8	27.4	25.4
DRY WEIGHT (g)	10.0	11.0	10.9	11.1	11.5	10.4
NAPHTHALENE (ppb)	580	530	160	170	1,800	ND
C-1 NAPHTHALENE	1,400	1,300	1,600	1,100	11,000	ND
C-2 NAPHTHALENE	6,300	4,100	8,000	6,700	35,000	92
C-3 NAPHTHALENE	9,500	6,400	13,000	12,000	40,000	180
FLUORENE	Tr	640	460	280	95	ND
DIBENZOTHIOPHENE	Tr	160	370	120	530	ND
C-1 DIBENZOTHIOPHENE	81	440	1,700	970	1,500	Tr
C-2 DIBENZOTHIOPHENE	200	530	1,800	2,200	5,500	51
C-3 DIBENZOTHIOPHENE	170	300	1,200	1,300	3,200	77
PHENANTHRENE	330	1,600	1,100	740	3,200	94
C-1 PHENANTHRENE	2,600	1,400	2,200	2,400	8,000	80
C-2 PHENANTHRENE	3,900	1,500	4,200	3,500	8,100	340
C-3 PHENANTHRENE	2,300	500	2,200	2,400	4,000	310
ANTHRACENE	77	400	120	110	490	Tr
FLUORANTHENE	Tr	890	Tr	110	140	150
PYRENE	Tr	460	ND	63	73	100
B(a)ANTHRACENE	Tr	120	ND	ND	ND	Tr
CHRYSENE	Tr	210	Tr	ND	ND	Tr
B(b)&B(k)FLUORANTHENE	ND	110	ND	ND	ND	ND
BENZO(a)PYRENE	ND	56	420	ND	ND	ND
TOTAL PAH	27,000	22,000	39,000	34,000	120,000	1,500
FFPI	0.96	0.78	0.92	0.94	0.97	0.76
DETECTION LIMIT (ppb)	50	28	46	60	44	48
TOTAL SATURATED H.C.	1,700,000	920,000	1,800,000	2,700,000	7,700,000	330,000
TOTAL RES. SATUR. H.C.	410,000	440,000	590,000	690,000	1,500,000	41,000
TOTAL UNRES. SAT. H.C.	1,300,000	920,000	1,200,000	2,000,000	6,200,000	280,000
PRISTANE/nC-17	1.0	1.1	1.1	1.6	1.1	1.8
PHYTANE/nC-18	0.7	0.8	1.2	1.5	1.8	1.8
PRISTANE/PHYTANE	2.1	1.8	1.0	1.2	0.6	1.1

Table A.1. Bayou Rigaud sediment data (October 1987) (continued).

SAMPLE I.D. DEPTH	BR-2 5-10 cm	BR-2 10-15 cm	BR-3 0-5 cm	BR-4 0-5 cm	BR-4 5-10 cm	BR-4 10-15 cm
WET WEIGHT (g)	28.8	25.4	28.0	25.0	25.7	26.1
DRY WEIGHT (g)	11.1	14.1	9.2	11.9	11.3	14.6
NAPHTHALENE (ppb)	ND	ND	ND	ND	ND	ND
C-1 NAPHTHALENE	ND	ND	ND	ND	ND	ND
C-2 NAPHTHALENE	ND	Tr	95	ND	ND	ND
C-3 NAPHTHALENE	ND	Tr	ND	ND	ND	ND
FLUORENE	ND	ND	ND	ND	ND	ND
DIBENZOTHIOPHENE	ND	Tr	ND	ND	ND	ND
C-1 DIBENZOTHIOPHENE	ND	Tr	ND	ND	ND	ND
C-2 DIBENZOTHIOPHENE	ND	47	ND	ND	ND	ND
C-3 DIBENZOTHIOPHENE	Tr	49	ND	ND	ND	ND
PHENANTHRENE	Tr	140	Tr	ND	ND	ND
C-1 PHENANTHRENE	ND	52	Tr	ND	ND	ND
C-2 PHENANTHRENE	Tr	130	Tr	ND	ND	ND
C-3 PHENANTHRENE	ND	90	ND	ND	ND	ND
ANTHRACENE	ND	38	ND	ND	ND	ND
FLUORANTHENE	72	97	90	Tr	ND	Tr
PYRENE	Tr	43	Tr	Tr	ND	ND
B(a)ANTHRACENE	ND	ND	ND	ND	ND	ND
CHRYSENE	ND	ND	ND	ND	ND	ND
B(b)&B(k)FLUORANTHENE	ND	ND	ND	ND	ND	ND
BENZO(a)PYRENE	ND	ND	ND	ND	ND	ND
TOTAL PAH	72	690	190	<42	<44	<34
FFPI	0.00	0.60	0.50	N/A	N/A	N/A
DETECTION LIMIT (ppb)	45	36	55	42	44	34
TOTAL SATURATED H.C.	110,000	100,000	98,000	38,000	23,000	12,000
TOTAL RES. SATUR. H.C.	16,000	16,000	58,000	3,800	2,600	1,900
TOTAL UNRES. SAT. H.C.	90,000	84,000	40,000	34,000	21,000	10,000
PRISTANE/nC-17	3.7	14.5	2.5	1.5	1.6	1.9
PHYTANE/nC-18	2.2	4.9	2.2	2.3	2.0	N/A
PRISTANE/PHYTANE	1.7	1.5	1.4	1.1	1.0	0.8

Table A.1. Bayou Rigaud sediment data (October 1987) (continued).

SAMPLE I.D. DEPTH	BR-4 15-20 cm	BR-5 0-5 cm	BR-5 0-5 cm Dup	BR-5 5-10 cm	BR-5 10-15 cm
WET WEIGHT (g)	25.9	25.4	25.6	26.7	24.6
DRY WEIGHT (g)	13.0	12.5	12.5	13.3	12.3
NAPHTHALENE (ppb)	ND	ND	ND	ND	ND
C-1 NAPHTHALENE	ND	ND	ND	ND	ND
C-2 NAPHTHALENE	ND	40	62	Tr	ND
C-3 NAPHTHALENE	ND	240	240	Tr	ND
FLUORENE	ND	ND	ND	ND	ND
DIBENZOTHIOPHENE	ND	Tr	ND	Tr	ND
C-1 DIBENZOTHIOPHENE	ND	25	ND	ND	ND
C-2 DIBENZOTHIOPHENE	ND	59	47	ND	ND
C-3 DIBENZOTHIOPHENE	ND	55	29	Tr	ND
PHENANTHRENE	ND	20	22	Tr	ND
C-1 PHENANTHRENE	ND	60	77	ND	ND
C-2 PHENANTHRENE	ND	210	160	50	ND
C-3 PHENANTHRENE	ND	160	99	Tr	ND
ANTHRACENE	ND	14	Tr	ND	ND
FLUORANTHENE	ND	32	27	Tr	ND
PYRENE	ND	34	13	Tr	ND
B(a)ANTHRACENE	ND	ND	ND	ND	ND
CHRYSENE	ND	ND	ND	ND	ND
B(b)&B(k)FLUORANTHENE	ND	ND	ND	ND	ND
BENZO(a)PYRENE	ND	ND	ND	ND	ND
TOTAL PAH	<39	950	780	50	<81
FFPI	N/A	0.87	0.88	N/A	N/A
DETECTION LIMIT (ppb)	39	13	10	37	81
TOTAL SATURATED H.C.	14,000	180,000	110,000	89,000	27,000
TOTAL RES. SATUR. H.C.	3,200	34,000	20,000	7,000	2,200
TOTAL UNRES. SAT. H.C.	11,000	150,000	90,000	82,000	25,000
PRISTANE/nC-17	2.0	3.2	4.6	4.1	2.4
PHYTANE/nC-18	2.6	2.4	8.7	1.5	N/A
PRISTANE/PHYTANE	1.4	1.5	1.7	1.8	N/A

Table A.2. Bayou Rigaud sediment data (January 1988).

SAMPLE I.D.	BR-1	BR-2	BR-7	BR-8	BR-9	BR-9 Dup
WET WEIGHT (g)	24.4	24.9	22.0	24.5	21.9	21.9
DRY WEIGHT (g)	10.9	12.7	10.1	12.7	9.6	9.4
INTERSTITIAL SALINITY (ppt)	25.6	25.8	25.6	26.9	26.4	26.4
NAPHTHALENE (ppb)	11	ND	ND	ND	ND	ND
C-1 NAPHTHALENE	86	ND	ND	ND	ND	ND
C-2 NAPHTHALENE	910	26	110	64	100	Tr
C-3 NAPHTHALENE	1,300	260	830	350	87	150
FLUORENE	70	Tr	20	ND	Tr	ND
DIBENZOTHIOPHENE	32	ND	ND	ND	ND	ND
C-1 DIBENZOTHIOPHENE	140	20	69	Tr	Tr	ND
C-2 DIBENZOTHIOPHENE	230	100	350	81	74	Tr
C-3 DIBENZOTHIOPHENE	140	190	220	33	Tr	Tr
PHENANTHRENE	140	24	73	22	Tr	34
C-1 PHENANTHRENE	370	58	350	170	ND	ND
C-2 PHENANTHRENE	420	240	840	320	170	210
C-3 PHENANTHRENE	230	230	570	170	180	140
ANTHRACENE	37	Tr	Tr	ND	ND	Tr
FLUORANTHENE	72	95	110	39	180	160
PYRENE	69	68	76	24	96	100
B(a)ANTHRACENE	ND	ND	ND	ND	ND	Tr
CHRYSENE	ND	ND	22	ND	ND	52
B(b)&B(k)FLUORANTHENE	ND	ND	ND	ND	ND	ND
BENZO(a)PYRENE	ND	ND	ND	ND	ND	ND
TOTAL PAH	4,300	1,300	3,600	1,300	890	850
FFPI	0.87	0.85	0.89	0.86	0.69	0.61
DETECTION LIMIT (ppb)	9	8	19	16	36	34
TOTAL SATURATED H.C.	72,000	58,000	73,000	34,000	58,000	49,000
TOTAL RES. SATUR. H.C.	27,000	13,000	16,000	5,300	6,600	9,200
TOTAL UNRES. SAT. H.C.	45,000	45,000	57,000	29,000	51,000	40,000
PRISTANE/nC-17	1.9	4.4	3.1	2.6	2.3	2.9
PHYTANE/nC-18	1.4	N/A	2.5	4.8	N/A	N/A
PRISTANE/PHYTANE	1.8	1.7	1.5	1.7	1.2	1.7

Table A.2. Bayou Rigaud sediment data (January 1988) (continued).

SAMPLE I.D.	BR-10	BR-11	BR-12	BR-13	BR-14
WET WEIGHT (g)	21.9	22.2	22.1	24.61	25.0
DRY WEIGHT (g)	10.3	9.8	9.5	10.83	14.2
INTERSTITIAL SALINITY (ppt)	27.8	45.0	26.0	25.2	28.8
NAPHTHALENE (ppb)	ND	460	ND	ND	ND
C-1 NAPHTHALENE	ND	880	ND	ND	ND
C-2 NAPHTHALENE	63	1,600	97	ND	Tr
C-3 NAPHTHALENE	Tr	2,000	ND	80	180
FLUORENE	ND	240	ND	ND	ND
DIBENZOTHIOPHENE	ND	84	ND	ND	ND
C-1 DIBENZOTHIOPHENE	ND	250	ND	Tr	ND
C-2 DIBENZOTHIOPHENE	40	360	ND	33	62
C-3 DIBENZOTHIOPHENE	44	260	ND	29	ND
PHENANTHRENE	ND	1,500	ND	36	Tr
C-1 PHENANTHRENE	ND	1,400	ND	120	Tr
C-2 PHENANTHRENE	170	1,000	ND	130	140
C-3 PHENANTHRENE	160	540	Tr	69	75
ANTHRACENE	ND	330	ND	Tr	ND
FLUORANTHENE	56	2,500	50	83	61
PYRENE	38	2,100	35	48	Tr
B(a)ANTHRACENE	ND	970	ND	ND	ND
CHRYSENE	ND	680	ND	ND	ND
B(b)&B(k)FLUORANTHENE	ND	360	ND	ND	ND
BENZO(a)PYRENE	ND	380	ND	ND	ND
TOTAL PAH	570	18,000	180	630	520
FFPI	0.84	0.49	0.54	0.67	0.88
DETECTION LIMIT (ppb)	19	16	23	13	33
TOTAL SATURATED H.C.	39,000	94,000	14,000	9,000	38,000
TOTAL RES. SATUR. H.C.	5,100	23,000	2,700	2,500	5,300
TOTAL UNRES. SAT. H.C.	34,000	71,000	11,000	6,500	33,000
PRISTANE/nC-17	3.6	2.7	2.7	3.8	1.7
PHYTANE/nC-18	2.8	1.7	N/A	2.5	N/A
PRISTANE/PHYTANE	1.2	1.2	1.4	1.3	3.7

Table A.3. Pass Fourchon sediment data (October 1987).

SAMPLE I.D. DEPTH	PF-1 0-5 cm	PF-2 0-5 cm	PF-2 5-10 cm	PF-2 10-15 cm	PF-2 15-20 cm	PF-3 0-5 cm
WET WEIGHT (g)	20.0	17.8	26.3	23.3	24.2	17.2
DRY WEIGHT (g)	14.3	12.8	20.4	18.0	18.6	11.2
NAPHTHALENE (ppb)	ND	ND	ND	ND	ND	ND
C-1 NAPHTHALENE	ND	ND	ND	ND	ND	ND
C-2 NAPHTHALENE	ND	490	49	520	40	Tr
C-3 NAPHTHALENE	ND	1,500	180	2,200	90	Tr
FLUORENE	ND	ND	ND	ND	ND	ND
DIBENZOTHIOPHENE	ND	Tr	Tr	90	Tr	ND
C-1 DIBENZOTHIOPHENE	ND	380	Tr	210	Tr	Tr
C-2 DIBENZOTHIOPHENE	ND	1,100	420	390	160	Tr
C-3 DIBENZOTHIOPHENE	ND	550	490	250	64	Tr
PHENANTHRENE	98	Tr	Tr	80	ND	ND
C-1 PHENANTHRENE	87	1,100	260	550	110	Tr
C-2 PHENANTHRENE	Tr	1,300	600	1,300	190	78
C-3 PHENANTHRENE	ND	1,100	1,600	800	160	94
ANTHRACENE	Tr	ND	ND	ND	ND	ND
FLUORANTHENE	270	100	140	73	30	Tr
PYRENE	190	110	120	60	36	Tr
B(a)ANTHRACENE	200	Tr	Tr	Tr	ND	ND
CHRYSENE	77	Tr	Tr	150	ND	ND
B(b)&B(k)FLUORANTHENE	ND	ND	Tr	67	ND	ND
BENZO(a)PYRENE	ND	ND	350	93	140	ND
TOTAL PAH	920	7,700	4,200	6,800	1,000	170
FFPI	0.10	0.91	0.83	0.89	0.76	1.01
DETECTION LIMIT (ppb)	35	40	25	28	27	44
TOTAL SATURATED H.C.	8,500	260,000	184,000	210,000	250,000	40,000
TOTAL RES. SATUR. H.C.	400	30,000	14,000	24,000	15,000	3,000
TOTAL UNRES. SAT. H.C.	8,100	230,000	170,000	180,000	230,000	37,000
PRISTANE/nC-17	1.1	3.6	3.5	7.3	3.5	2.9
PHYTANE/nC-18	1.0	2.7	6.8	4.5	N/A	3.8
PRISTANE/PHYTANE	1.1	1.6	1.2	1.4	1.4	1.2

Table A.3. Pass Fourchon sediment data (October 1987) (continued).

SAMPLE I.D. DEPTH	PF-3 5-10 cm	PF-3 10-15 cm	PF-4 0-5 cm	PF-5 0-5 cm	PF-6 0-5 cm
WET WEIGHT (g)	17.8	20.2	20.7	19.9	22.6
DRY WEIGHT (g)	12.3	15.6	16.1	14.3	16.8
NAPHTHALENE (ppb)	ND	ND	ND	ND	ND
C-1 NAPHTHALENE	ND	ND	ND	ND	ND
C-2 NAPHTHALENE	ND	Tr	ND	ND	ND
C-3 NAPHTHALENE	ND	Tr	ND	ND	ND
FLUORENE	ND	ND	ND	ND	ND
DIBENZOTHIOPHENE	ND	Tr	ND	ND	ND
C-1 DIBENZOTHIOPHENE	Tr	Tr	ND	ND	ND
C-2 DIBENZOTHIOPHENE	Tr	79	ND	ND	ND
C-3 DIBENZOTHIOPHENE	Tr	130	ND	ND	ND
PHENANTHRENE	Tr	Tr	ND	ND	ND
C-1 PHENANTHRENE	28	130	ND	ND	ND
C-2 PHENANTHRENE	110	570	ND	40	ND
C-3 PHENANTHRENE	140	370	ND	Tr	ND
ANTHRACENE	ND	ND	ND	ND	ND
FLUORANTHENE	Tr	42	48	45	Tr
PYRENE	Tr	43	37	57	Tr
B(a)ANTHRACENE	ND	ND	ND	ND	ND
CHRYSENE	ND	ND	ND	ND	ND
B(b)&B(k)FLUORANTHENE	ND	ND	ND	ND	ND
BENZO(a)PYRENE	ND	ND	ND	ND	ND
TOTAL PAH	280	1,400	85	140	<30
FFPI	0.94	0.87	0.00	0.29	N/A
DETECTION LIMIT (ppb)	41	32	30	35	30
TOTAL SATURATED H.C.	53,000	58,000	Tr	Tr	Tr
TOTAL RES. SATUR. H.C.	4,100	5,800	Tr	Tr	Tr
TOTAL UNRES. SAT. H.C.	49,000	52,000	Tr	Tr	Tr
PRISTANE/nC-17	1.4	2.4	N/A	N/A	N/A
PHYTANE/nC-18	3.6	4.5	N/A	N/A	N/A
PRISTANE/PHYTANE	0.8	1.0	N/A	N/A	N/A

Table A.4. Pass Fourchon sediment data (January 1988).

SAMPLE I.D.	PF-2	PF-7	PF-10	PF-11	PF-11 Spk Dup
WET WEIGHT (g)	24.9	24.9	24.4	24.4	24.7
DRY WEIGHT (g)	12.1	12.9	9.5	9.6	9.6
INTERSTITIAL SALINITY (ppt)	38.9	31.1	24.4	27.9	N/A
NAPHTHALENE (ppb)	ND	5	ND	ND	N/A
C-1 NAPHTHALENE	ND	Tr	ND	ND	ND
C-2 NAPHTHALENE	1,600	Tr	47	45	ND
C-3 NAPHTHALENE	4,700	14	88	ND	ND
FLUORENE	330	Tr	ND	ND	ND
DIBENZOTHIOPHENE	440	Tr	Tr	Tr	N/A
C-1 DIBENZOTHIOPHENE	2,900	Tr	20	Tr	ND
C-2 DIBENZOTHIOPHENE	5,000	Tr	27	46	ND
C-3 DIBENZOTHIOPHENE	4,900	17	16	230	Tr
PHENANTHRENE	420	32	22	230	97
C-1 PHENANTHRENE	420	20	160	240	150
C-2 PHENANTHRENE	12,000	43	96	140	100
C-3 PHENANTHRENE	7,900	15	39	Tr	Tr
ANTHRACENE	50	ND	Tr	Tr	37
FLUORANTHENE	380	18	20	870	380
PYRENE	220	13	18	590	290
B(a)ANTHRACENE	230	ND	ND	130	290
CHRYSENE	900	ND	ND	190	310
B(b)&B(k)FLUORANTHENE	ND	ND	ND	ND	ND
BENZO(a)PYRENE	130	ND	ND	ND	ND
TOTAL PAH	43,000	180	550	2,700	1,700
FFPI	0.93	0.67	0.77	0.26	0.13
DETECTION LIMIT (ppb)	20	5	10	44	24
TOTAL SATURATED H.C.	650,000	5,200	5,600	43,000	30,000
TOTAL RES. SATUR. H.C.	76,000	1,900	2,100	16,000	12,000
TOTAL UNRES. SAT. H.C.	570,000	3,300	3,500	27,000	18,000
PRISTANE/nC-17	18.0	0.7	2.7	N/A	N/A
PHYTANE/nC-18	18.0	1.2	3.8	N/A	N/A
PRISTANE/PHYTANE	3.8	0.5	1.8	N/A	N/A

Table A.5. LUMCON Port Fourchon Laboratory marsh core data.

SAMPLE I.D. DEPTH	FLC 0-2 cm	FLC 2-4 cm	FLC 4-6 cm	FLC 6-8 cm
WET WEIGHT (g)	22.0	21.9	21.8	24.8
DRY WEIGHT (g)	10.3	10.8	10.2	12.4
INTERSTITIAL SALINITY (ppt)	33.0	28.9	28.8	29.5
NAPHTHALENE (ppb)	ND	ND	ND	ND
C-1 NAPHTHALENE	ND	ND	ND	ND
C-2 NAPHTHALENE	ND	ND	ND	ND
C-3 NAPHTHALENE	ND	ND	ND	ND
FLUORENE	ND	ND	ND	ND
DIBENZOTHIOPHENE	ND	ND	ND	ND
C-1 DIBENZOTHIOPHENE	ND	ND	ND	ND
C-2 DIBENZOTHIOPHENE	ND	ND	ND	ND
C-3 DIBENZOTHIOPHENE	ND	ND	ND	ND
PHENANTHRENE	24	ND	Tr	Tr
C-1 PHENANTHRENE	ND	ND	ND	ND
C-2 PHENANTHRENE	ND	ND	ND	ND
C-3 PHENANTHRENE	ND	ND	ND	ND
ANTHRACENE	ND	ND	Tr	ND
FLUORANTHENE	61	48	29	Tr
PYRENE	39	Tr	18	Tr
B(a)ANTHRACENE	Tr	ND	Tr	ND
CHRYSENE	Tr	ND	Tr	ND
B(b)&B(k)FLUORANTHENE	ND	ND	ND	ND
BENZO(a)PYRENE	ND	ND	ND	ND
TOTAL PAH	120	48	47	<19
FFPI	0.10	0.00	0.00	N/A
DETECTION LIMIT (ppb)	21	42	10	19
TOTAL SATURATED H.C.	Tr	Tr	Tr	Tr
TOTAL RES. SATUR. H.C.	Tr	Tr	Tr	Tr
TOTAL UNRES. SAT. H.C.	Tr	Tr	Tr	Tr
PRISTANE/nC-17	N/A	N/A	N/A	N/A
PHYTANE/nC-18	N/A	N/A	N/A	N/A
PRISTANE/PHYTANE	N/A	N/A	N/A	N/A

Table A.5. LUMCON Port Fourchon Laboratory marsh core data (continued).

SAMPLE I.D. DEPTH	FLC 8-10 cm	FLC 10-15 cm	FLC 15-20 cm	FLC 20-22 cm
WET WEIGHT (g)	22.2	23.5	24.4	24.3
DRY WEIGHT (g)	10.4	10.1	9.8	11.4
INTERSTITIAL SALINITY (ppt)	28.7	28.7	28.7	29.0
NAPHTHALENE (ppb)	ND	ND	ND	ND
C-1 NAPHTHALENE	ND	ND	ND	ND
C-2 NAPHTHALENE	ND	ND	ND	ND
C-3 NAPHTHALENE	ND	ND	ND	ND
FLUORENE	ND	ND	ND	ND
DIBENZOTHIOPHENE	ND	ND	ND	ND
C-1 DIBENZOTHIOPHENE	ND	ND	ND	ND
C-2 DIBENZOTHIOPHENE	ND	ND	ND	ND
C-3 DIBENZOTHIOPHENE	ND	ND	ND	ND
PHENANTHRENE	26	Tr	ND	ND
C-1 PHENANTHRENE	ND	ND	ND	ND
C-2 PHENANTHRENE	ND	ND	ND	ND
C-3 PHENANTHRENE	ND	ND	ND	ND
ANTHRACENE	ND	ND	ND	ND
FLUORANTHENE	54	140	160	ND
PYRENE	32	82	71	ND
B(a)ANTHRACENE	Tr	ND	ND	ND
CHRYSENE	Tr	ND	ND	ND
B(b)&B(k)FLUORANTHENE	ND	ND	ND	ND
BENZO(a)PYRENE	ND	ND	ND	ND
TOTAL PAH	110	120	230	<34
FFPI	0.12	0.00	0.00	N/A
DETECTION LIMIT (ppb)	17	29	34	34
TOTAL SATURATED H.C.	Tr	Tr	Tr	Tr
TOTAL RES. SATUR. H.C.	Tr	Tr	Tr	Tr
TOTAL UNRES. SAT. H.C.	Tr	Tr	Tr	Tr
PRISTANE/nC-17	N/A	N/A	N/A	N/A
PHYTANE/nC-18	N/A	N/A	N/A	N/A
PRISTANE/PHYTANE	N/A	N/A	N/A	N/A

Table A.6. Pass Fourchon marsh core data.

SAMPLE I.D. DEPTH	PFC 0-2 cm	PFC 2-4 cm	PFC 4-6 cm	PFC 6-8 cm	PFC 8-10 cm	PFC 10-15 cm
WET WEIGHT (g)	22.1	22.1	21.7	22.2	22.5	22.5
DRY WEIGHT (g)	9.5	8.6	8.7	11.1	11.3	14.2
INTERSTITIAL SALINITY (ppt)	31.5	29.0	28.9	29.3	29.4	29.9
NAPHTHALENE (ppb)	ND	ND	ND	ND	ND	ND
C-1 NAPHTHALENE	ND	ND	ND	ND	ND	ND
C-2 NAPHTHALENE	ND	ND	ND	ND	ND	ND
C-3 NAPHTHALENE	ND	ND	ND	ND	ND	ND
FLUORENE	ND	ND	ND	ND	ND	ND
DIBENZOTHIOPHENE	ND	ND	ND	ND	ND	ND
C-1 DIBENZOTHIOPHENE	ND	ND	ND	ND	ND	ND
C-2 DIBENZOTHIOPHENE	ND	ND	ND	ND	ND	ND
C-3 DIBENZOTHIOPHENE	ND	ND	ND	ND	ND	ND
PHENANTHRENE	ND	ND	ND	ND	ND	ND
C-1 PHENANTHRENE	ND	ND	ND	ND	ND	ND
C-2 PHENANTHRENE	ND	ND	ND	ND	ND	ND
C-3 PHENANTHRENE	ND	ND	ND	ND	ND	ND
ANTHRACENE	ND	ND	ND	ND	ND	ND
FLUORANTHENE	Tr	Tr	Tr	Tr	ND	ND
PYRENE	Tr	Tr	Tr	Tr	ND	ND
B(a)ANTHRACENE	ND	ND	ND	ND	ND	ND
CHRYSENE	ND	ND	ND	ND	ND	ND
B(b)&B(k)FLUORANTHENE	ND	ND	ND	ND	ND	ND
BENZO(a)PYRENE	ND	ND	ND	ND	ND	ND
TOTAL PAH	<52	<60	<58	<60	<44	<35
DETECTION LIMIT (ppb)	52	60	58	60	44	35
TOTAL SATURATED H.C.	24,000	41,000	23,000	19,000	11,000	5,500
TOTAL RES. SATUR. H.C.	5,300	5,900	4,200	3,600	2,800	1,700
TOTAL UNRES. SAT. H.C.	19,000	35,000	19,000	15,000	8,000	3,800
PRISTANE/nC-17	N/A	N/A	N/A	N/A	N/A	N/A
PHYTANE/nC-18	N/A	N/A	N/A	N/A	N/A	N/A
PRISTANE/PHYTANE	1.7	1.6	N/A	N/A	N/A	N/A

Table A.6. Pass Fourchon marsh core data (continued).

SAMPLE I.D. DEPTH	PFC 15-20 cm	PFC 20-25 cm	PFC 25-30 cm	PFC 30-35 cm	PFC skI 30-35 cm	PFC skII 30-35 cm
WET WEIGHT (g)	21.3	25.2	22.1	22.7	22.4	25.0
DRY WEIGHT (g)	10.2	11.1	9.1	10.0	9.9	10.3
INTERSTITIAL SALINITY (ppt)	28.4	28.7	28.8	28.1	N/A	N/A
NAPHTHALENE (ppb)	ND	ND	ND	ND	ND	ND
C-1 NAPHTHALENE	ND	ND	ND	ND	ND	ND
C-2 NAPHTHALENE	ND	ND	ND	ND	ND	ND
C-3 NAPHTHALENE	ND	ND	ND	ND	ND	ND
FLUORENE	ND	ND	ND	ND	ND	ND
DIBENZOTHIOPHENE	ND	ND	ND	ND	ND	ND
C-1 DIBENZOTHIOPHENE	ND	ND	ND	ND	ND	ND
C-2 DIBENZOTHIOPHENE	ND	ND	ND	ND	ND	ND
C-3 DIBENZOTHIOPHENE	ND	ND	ND	ND	ND	ND
PHENANTHRENE	ND	ND	ND	ND	ND	ND
C-1 PHENANTHRENE	ND	ND	ND	ND	ND	ND
C-2 PHENANTHRENE	ND	ND	ND	ND	ND	ND
C-3 PHENANTHRENE	ND	ND	ND	ND	ND	ND
ANTHRACENE	ND	ND	ND	ND	ND	ND
FLUORANTHENE	ND	ND	ND	ND	ND	ND
PYRENE	ND	ND	ND	ND	ND	ND
B(a)ANTHRACENE	ND	ND	ND	ND	ND	ND
CHRYSENE	ND	ND	ND	ND	ND	ND
B(b)&B(k)FLUORANTHENE	ND	ND	ND	ND	ND	ND
BENZO(a)PYRENE	ND	ND	ND	ND	ND	ND
TOTAL PAH	<49	<45	<690	<50	<50	<63
DETECTION LIMIT (ppb)	49	45	690	50	50	63
TOTAL SATURATED H.C.	4,300	Tr	Tr	Tr	Tr	Tr
TOTAL RES. SATUR. H.C.	1,300	Tr	Tr	Tr	Tr	Tr
TOTAL UNRES. SAT. H.C.	3,000	Tr	Tr	Tr	Tr	Tr
PRISTANE/nC-17	N/A	N/A	N/A	N/A	N/A	N/A
PHYTANE/nC-18	N/A	N/A	N/A	N/A	N/A	N/A
PRISTANE/PHYTANE	N/A	N/A	N/A	N/A	N/A	N/A

Table A.7. East Timbalier Island sediment data.

SAMPLE I.D.	T-1	T-1 Dup	T-3	T-3 Spk Dup	T-4	T-5	T-6
WET WEIGHT (g)	24.4	25.0	24.7	24.9	27.3	27.8	28.6
DRY WEIGHT (g)	15.5	13.2	16.6	17.1	15.7	21.1	12.0
INTERSTITIAL SALINITY (ppt)	33.3	31.4	29.2	28.7	N/A	N/A	26.0
NAPHTHALENE (ppb)	ND	ND	ND	N/A	ND	ND	ND
C-1 NAPHTHALENE	ND	ND	ND	ND	ND	ND	ND
C-2 NAPHTHALENE	200	260	ND	Tr	ND	ND	ND
C-3 NAPHTHALENE	620	670	Tr	Tr	45	ND	31
FLUORENE	ND	ND	ND	ND	Tr	ND	ND
DIBENZOTHIOPHENE	Tr	Tr	ND	N/A	Tr	ND	Tr
C-1 DIBENZOTHIOPHENE	62	78	ND	ND	ND	ND	Tr
C-2 DIBENZOTHIOPHENE	140	140	ND	ND	ND	ND	51
C-3 DIBENZOTHIOPHENE	110	73	ND	ND	ND	ND	27
PHENANTHRENE	78	45	Tr	Tr	150	Tr	Tr
C-1 PHENANTHRENE	330	300	Tr	53	62	ND	82
C-2 PHENANTHRENE	440	440	Tr	29	Tr	ND	130
C-3 PHENANTHRENE	220	210	Tr	17	Tr	ND	76
ANTHRACENE	ND	ND	ND	Tr	38	ND	ND
FLUORANTHENE	78	87	Tr	13	330	Tr	20
PYRENE	64	60	Tr	14	240	Tr	Tr
B(a)ANTHRACENE	ND	ND	ND	ND	90	ND	ND
CHRYSENE	ND	ND	ND	ND	90	ND	ND
B(b)&B(k)FLUORANTHENE	ND	ND	ND	ND	220	ND	ND
BENZO(a)PYRENE	ND	ND	ND	ND	77	ND	ND
TOTAL PAH	2,300	2,400	<30	130	1,300	<12	420
FFPI	0.87	0.85	N/A	0.56	0.12	N/A	0.85
DETECTION LIMIT (ppb)	32	38	30	15	32	12	21
TOTAL SATURATED H.C.	57,000	63,000	5,000	18,000	16,000	2,000	29,000
TOTAL RES. SATUR. H.C.	11,000	12,000	2,900	4,500	1,500	810	7,300
TOTAL UNRES. SAT. H.C.	46,000	51,000	2,100	14,000	14,000	1,200	22,000
PRISTANE/nC-17	4.0	5.1	1.6	1.7	N/A	0.7	0.9
PHYTANE/nC-18	11.4	9.4	2.1	1.1	N/A	0.3	10.0
PRISTANE/PHYTANE	1.5	1.4	1.4	1.4	N/A	4.0	2.1

Table A.8. Hydrocarbon concentrations in organisms.

SAMPLE I.D.	FL Oysters 1A	FL Oysters 1B	FL Oysters II	Timb. Oysters	BR11 Oysters A	BR11 Oysters B
WET WEIGHT (g)	3.01	3.02	3.00	3.01	3.00	3.00
NAPHTHALENE (ppb)	Tr	14	Tr	Tr	Tr	Tr
C-1 NAPHTHALENE	ND	ND	ND	Tr	19	Tr
C-2 NAPHTHALENE	ND	ND	ND	120	140	130
C-3 NAPHTHALENE	32	Tr	ND	480	320	330
FLUORENE	ND	ND	ND	Tr	14	10
DIBENZOTHIOPHENE	Tr	31	ND	45	23	30
C-1 DIBENZOTHIOPHENE	Tr	18	ND	160	81	150
C-2 DIBENZOTHIOPHENE	99	77	ND	300	200	350
C-3 DIBENZOTHIOPHENE	88	Tr	ND	300	180	360
PHENANTHRENE	130	53	50	150	84	94
C-1 PHENANTHRENE	220	72	21	260	320	400
C-2 PHENANTHRENE	350	170	23	730	460	710
C-3 PHENANTHRENE	180	64	Tr	410	290	690
ANTHRACENE	Tr	ND	ND	ND	Tr	11
FLUORANTHENE	440	240	89	160	49	47
PYRENE	360	170	53	170	54	60
B(a)ANTHRACENE	ND	ND	ND	ND	ND	ND
CHRYSENE	88	Tr	ND	83	ND	21
B(b)&B(k)FLUORANTHENE	ND	ND	ND	ND	ND	ND
BENZO(a)PYRENE	ND	ND	ND	ND	ND	ND
TOTAL PAH	2,000	910	240	3,400	2,200	3,400
TOTAL UNSATURATED H.C.	150,000	150,000	88,000	470,000	300,000	360,000
FFPI	0.46	0.48	0.24	0.81	0.87	0.88
DETECTION LIMIT (ppb)	23	13	17	25	10	10
TOTAL SATURATED H.C.	190,000	150,000	68,000	550,000	330,000	330,000
TOTAL RES. SATUR. H.C.	12,000	13,000	5,900	41,000	28,000	36,000
TOTAL UNRES. SAT. H.C.	180,000	140,000	62,000	510,000	300,000	300,000
PRISTANE/nC17	2.4	1.9	0.5	3.2	5.0	4.6
PHYTANE/nC18	25.0	17.5	6.1	13.5	25.3	19.1
PRISTANE/PHYTANE	0.9	1.0	1.2	1.9	2.2	2.0

Table A.8. Hydrocarbon concentrations in organisms (continued).

SAMPLE I.D.	PF Mussels A	PF Mussels B	CM Mussels
WET WEIGHT (g)	3.01	3.00	3.01
NAPHTHALENE (ppb)	Tr	Tr	ND
C-1 NAPHTHALENE	14	Tr	ND
C-2 NAPHTHALENE	21	Tr	ND
C-3 NAPHTHALENE	36	31	ND
FLUORENE	ND	ND	ND
DIBENZOTHIOPHENE	Tr	Tr	ND
C-1 DIBENZOTHIOPHENE	10	18	ND
C-2 DIBENZOTHIOPHENE	27	90	ND
C-3 DIBENZOTHIOPHENE	41	51	ND
PHENANTHRENE	53	110	Tr
C-1 PHENANTHRENE	130	140	ND
C-2 PHENANTHRENE	170	260	ND
C-3 PHENANTHRENE	77	62	ND
ANTHRACENE	ND	ND	ND
FLUORANTHENE	29	67	ND
PYRENE	20	49	ND
B(a)ANTHRACENE	ND	ND	ND
CHRYSENE	ND	ND	ND
B(b)&B(k)FLUORANTHENE	ND	ND	ND
BENZO(a)PYRENE	ND	ND	ND
TOTAL PAH	630	880	<15
TOTAL UNSATURATED H.C.	100,000	160,000	34,000
FFPI	0.77	0.72	N/A
DETECTION LIMIT (ppb)	10	17	15
TOTAL SATURATED H.C.	120,000	180,000	33,000
TOTAL RES. SATUR. H.C.	20,000	31,000	6,100
TOTAL UNRES. SAT. H.C.	100,000	150,000	26,000
PRISTANE/nC17	N/A	N/A	0.8
PHYTANE/nC18	21.0	12.4	1.2
PRISTANE/PHYTANE	1.0	1.1	1.0

Table A.9. Bayou Rigaud overlying waters (October 1987).

SAMPLE I.D.	BR-1 Oct. '87	BR-2 Oct. '87	BR-5 Oct. '87
BENZENE (ng/ml)	930	800	ND
TOLUENE	16	52	ND
ETHYLBENZENE	ND	ND	ND
XYLENES	ND	ND	ND
DETECTION LIMIT VOA's (ng/ml)	3	3	3
PHENOL	ND	ND	ND
p-CRESOL	ND	ND	ND
m, o-CRESOL	ND	ND	ND
BENZOIC ACID	ND	ND	ND
NAPHTHALENE	ND	ND	ND
C-1 NAPHTHALENE	ND	ND	ND
C-2 NAPHTHALENE	ND	ND	ND
C-3 NAPHTHALENE	Tr	ND	ND
FLUORENE	ND	ND	ND
DIBENZOTHIOPHENE	Tr	ND	ND
C-1 DIBENZOTHIOPHENE	Tr	ND	ND
C-2 DIBENZOTHIOPHENE	Tr	ND	ND
C-3 DIBENZOTHIOPHENE	Tr	ND	ND
PHENANTHRENE	Tr	ND	ND
C-1 PHENANTHRENE	17	ND	ND
C-2 PHENANTHRENE	32	ND	ND
C-3 PHENANTHRENE	11	ND	ND
ANTHRACENE	ND	ND	ND
FLUORANTHENE	ND	ND	ND
PYRENE	ND	ND	ND
B(a)ANTHRACENE	ND	ND	ND
CHRYSENE	ND	ND	ND
B(b)&B(k)FLUORANTHENE	ND	ND	ND
BENZO(a)PYRENE	ND	ND	ND
TOTAL PAH	60	<5	<5
DETECTION LIMIT (ng/ml)	5	5	5
TOTAL SATURATED H.C.	570	ND	ND
TOTAL RES. SATUR. H.C.	240	ND	ND
TOTAL UNRES. SAT. H.C.	330	ND	ND
PRISTANE/nC-17	1.12	N/A	N/A
PHYTANE/nC-18	0.74	N/A	N/A
PRISTANE/PHYTANE	1.42	N/A	N/A

Table A.10. Bayou Rigaud overlying waters (January 1988).

SAMPLE I.D.	BR-1 Jan. '88	BR-11 Jan. '88
BENZENE (ng/ml)	340	120
TOLUENE	220	52
ETHYLBENZENE	14	3
XYLENES	87	19
DETECTION LIMIT VOA's (ng/ml)	3	3
PHENOL	ND	ND
p-CRESOL	ND	ND
m, o-CRESOL	ND	ND
BENZOIC ACID	Tr	ND
NAPHTHALENE	ND	ND
C-1 NAPHTHALENE	ND	ND
C-2 NAPHTHALENE	ND	ND
C-3 NAPHTHALENE	ND	ND
FLUORENE	ND	ND
DIBENZOTHIOPHENE	ND	ND
C-1 DIBENZOTHIOPHENE	ND	ND
C-2 DIBENZOTHIOPHENE	ND	ND
C-3 DIBENZOTHIOPHENE	ND	ND
PHENANTHRENE	ND	ND
C-1 PHENANTHRENE	ND	ND
C-2 PHENANTHRENE	ND	ND
C-3 PHENANTHRENE	ND	ND
ANTHRACENE	ND	ND
FLUORANTHENE	ND	ND
PYRENE	ND	ND
B(a)ANTHRACENE	ND	ND
CHRYSENE	ND	ND
B(b)&B(k)FLUORANTHENE	ND	ND
BENZO(a)PYRENE	ND	ND
TOTAL PAH	<5	<5
DETECTION LIMIT (ng/ml)	5	5
TOTAL SATURATED H.C.	ND	ND
TOTAL RES. SATUR. H.C.	ND	ND
TOTAL UNRES. SAT. H.C.	ND	ND
PRISTANE/nC-17	N/A	N/A
PHYTANE/nC-18	N/A	N/A
PRISTANE/PHYTANE	N/A	N/A

Table A.11. East Timbalier overlying waters.

SAMPLE I.D.	T-1 Jan. '88
BENZENE (ng/ml)	3
TOLUENE	12
ETHYLBENZENE	ND
XYLENES	ND
DETECTION LIMIT VOA's (ng/ml)	3
PHENOL	ND
p-CRESOL	ND
m, o-CRESOL	ND
BENZOIC ACID	ND
NAPHTHALENE	ND
C-1 NAPHTHALENE	ND
C-2 NAPHTHALENE	ND
C-3 NAPHTHALENE	ND
FLUORENE	ND
DIBENZOTHIOPHENE	ND
C-1 DIBENZOTHIOPHENE	ND
C-2 DIBENZOTHIOPHENE	ND
C-3 DIBENZOTHIOPHENE	ND
PHENANTHRENE	ND
C-1 PHENANTHRENE	ND
C-2 PHENANTHRENE	ND
C-3 PHENANTHRENE	ND
ANTHRACENE	ND
FLUORANTHENE	ND
PYRENE	ND
B(a)ANTHRACENE	ND
CHRYSENE	ND
B(b)&B(k)FLUORANTHENE	ND
BENZO(a)PYRENE	ND
TOTAL PAH	<5
DETECTION LIMIT (ng/ml)	5
TOTAL SATURATED H.C.	ND
TOTAL RES. SATUR. H.C.	ND
TOTAL UNRES. SAT. H.C.	ND
PRISTANE/nC-17	N/A
PHYTANE/nC-18	N/A
PRISTANE/PHYTANE	N/A

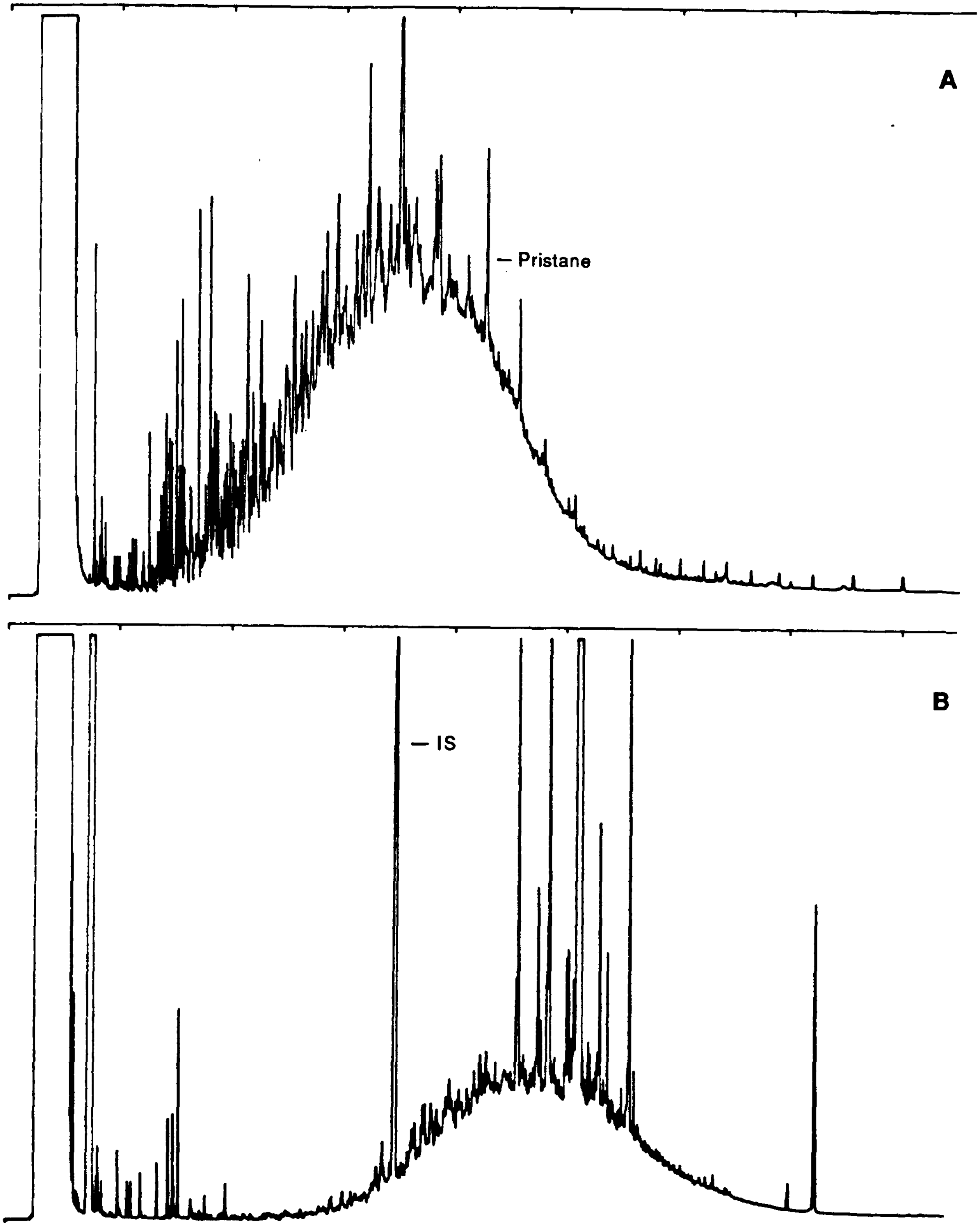

Figure A.1. Chromatograms of saturated hydrocarbon (A) and PAH (B) fractions for BR-11 Exxon outfall oysters (IS: internal standard).

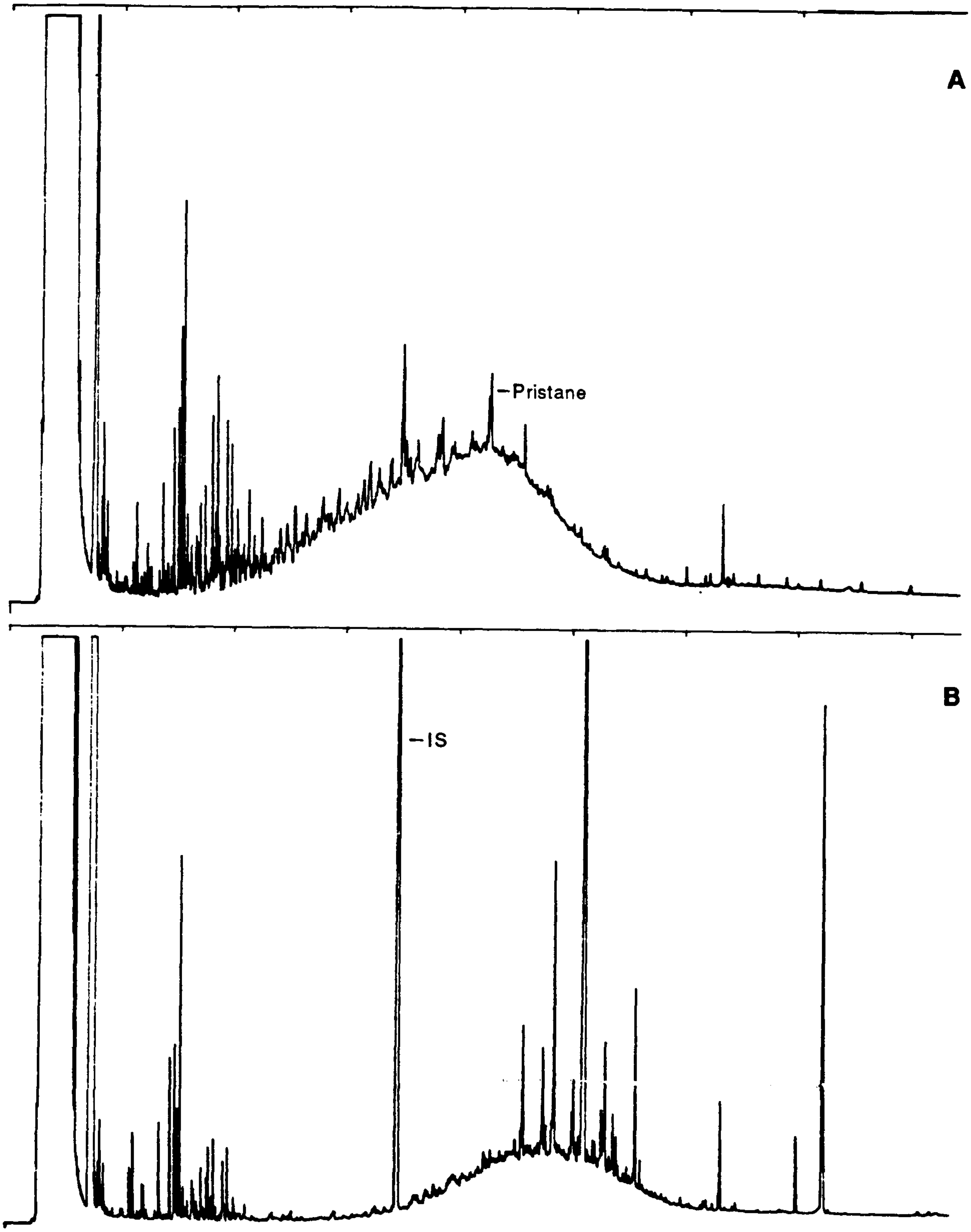

Figure A.2. Chromatograms of saturated hydrocarbon (A) and PAH (B) fractions for LUMCON Port Fourchon Laboratory oysters (IS: internal standard).

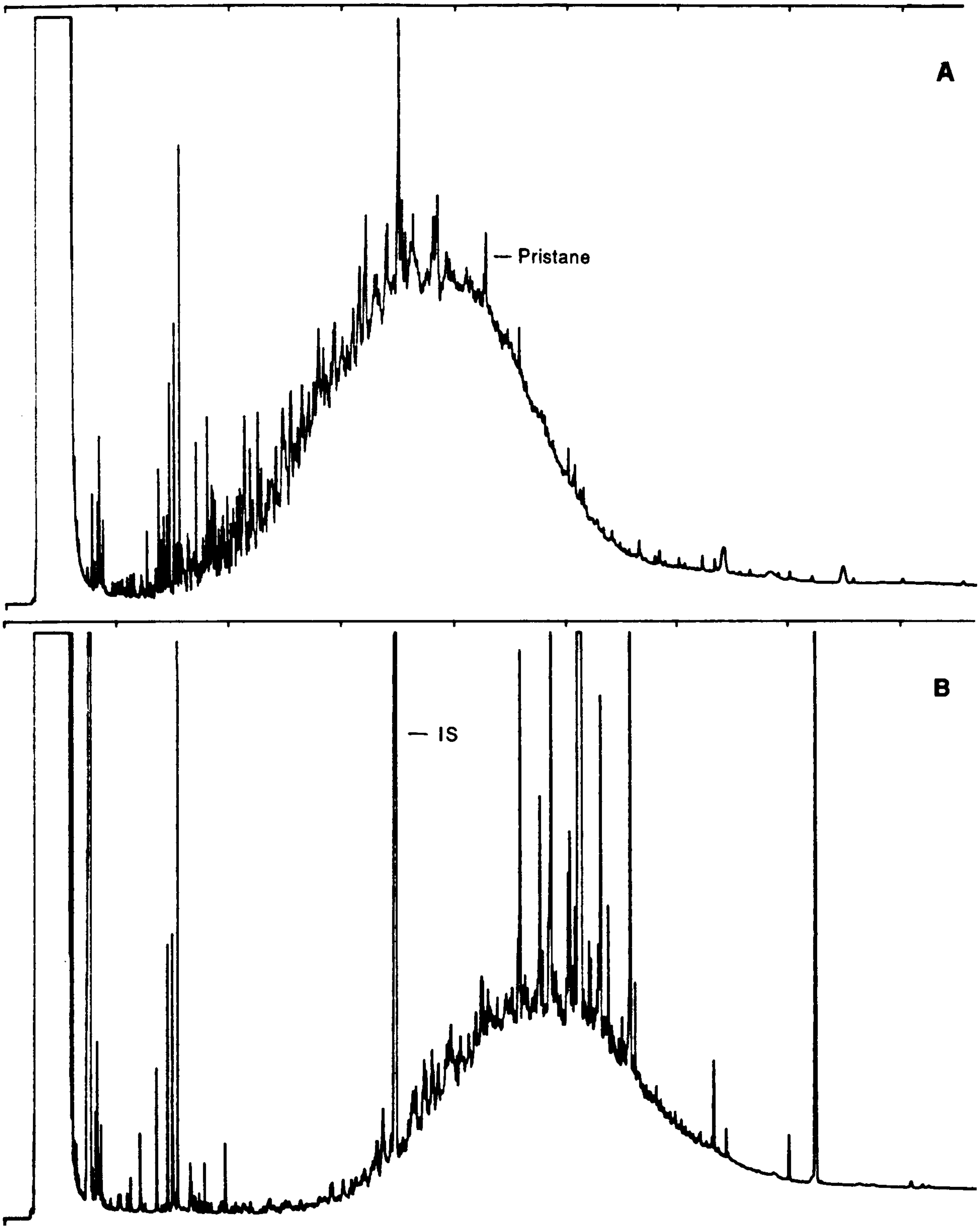

Figure A.3. Chromatograms of saturated hydrocarbon (A) and PAH (B) fractions for East Timbalier Island oysters (IS: internal standard).

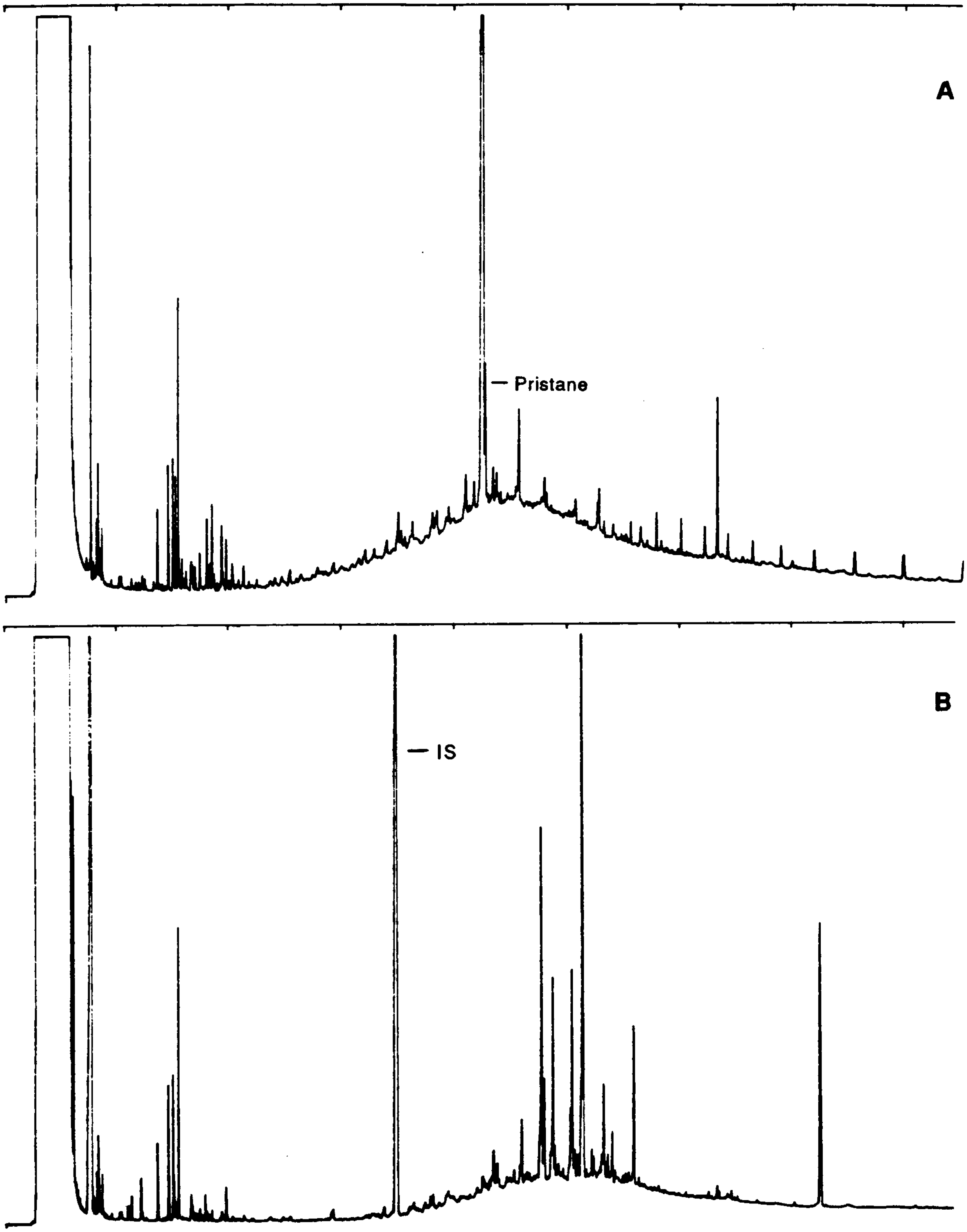

Figure A.4. Chromatograms of saturated hydrocarbon (A) and PAH (B) fractions for Pass Fourchon mussels (IS: internal standard).

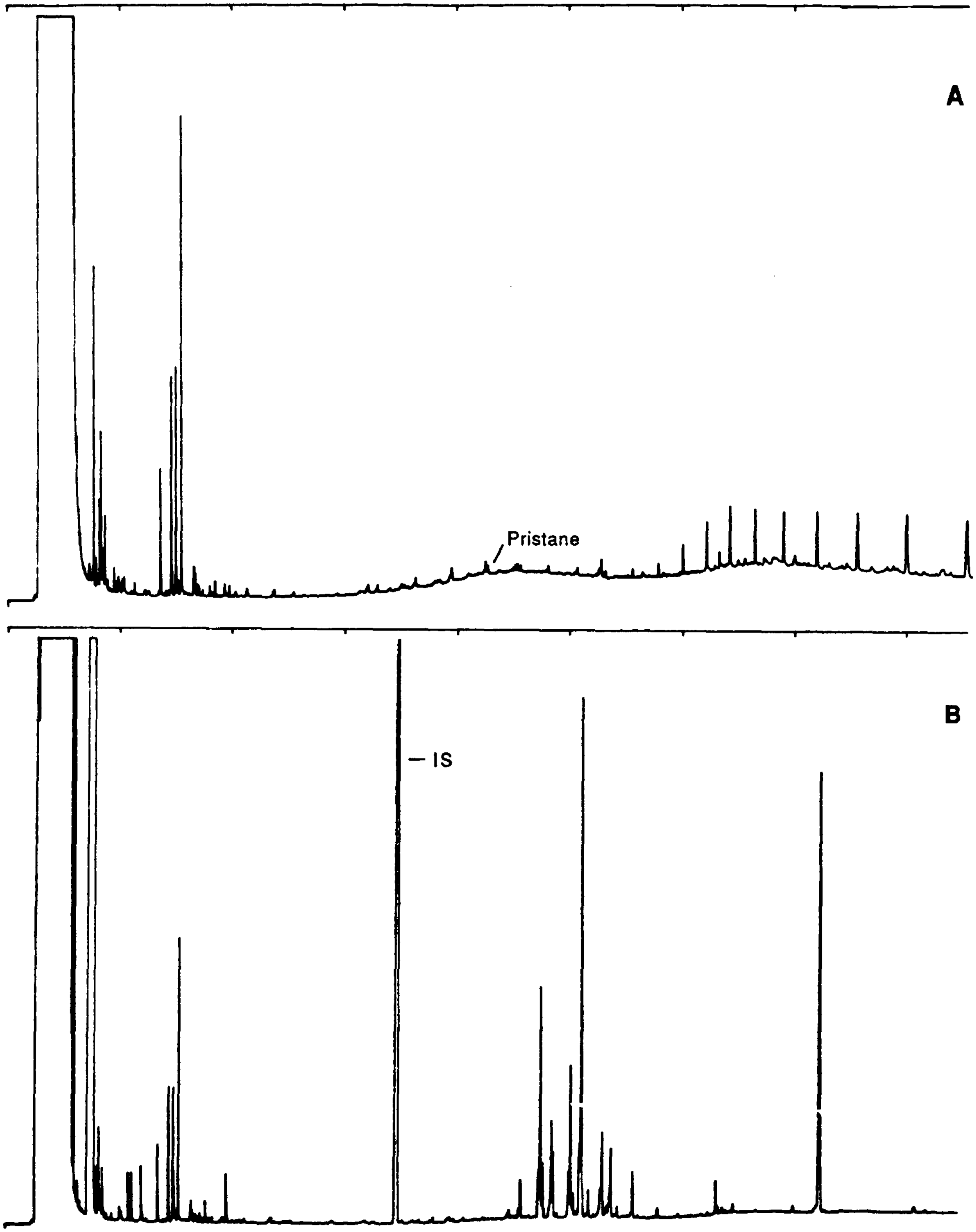

Figure A.5. Chromatograms of saturated hydrocarbon (A) and PAH (B) fractions for LUMCON Marine Center, Cocodrie, marsh mussels (IS: internal standard).

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering the wisest use of our land and water resources, protecting our fish and wildlife, preserving the environmental and cultural values of our national parks and historical places, and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to assure that their development is in the best interest of all our people. The Department also has a major responsibility for American Indian reservation communities and for people who live in Island Territories under U.S. Administration.

March 3, 1849

U.S. DEPARTMENT OF THE INTERIOR
MINERALS MANAGEMENT SERVICE