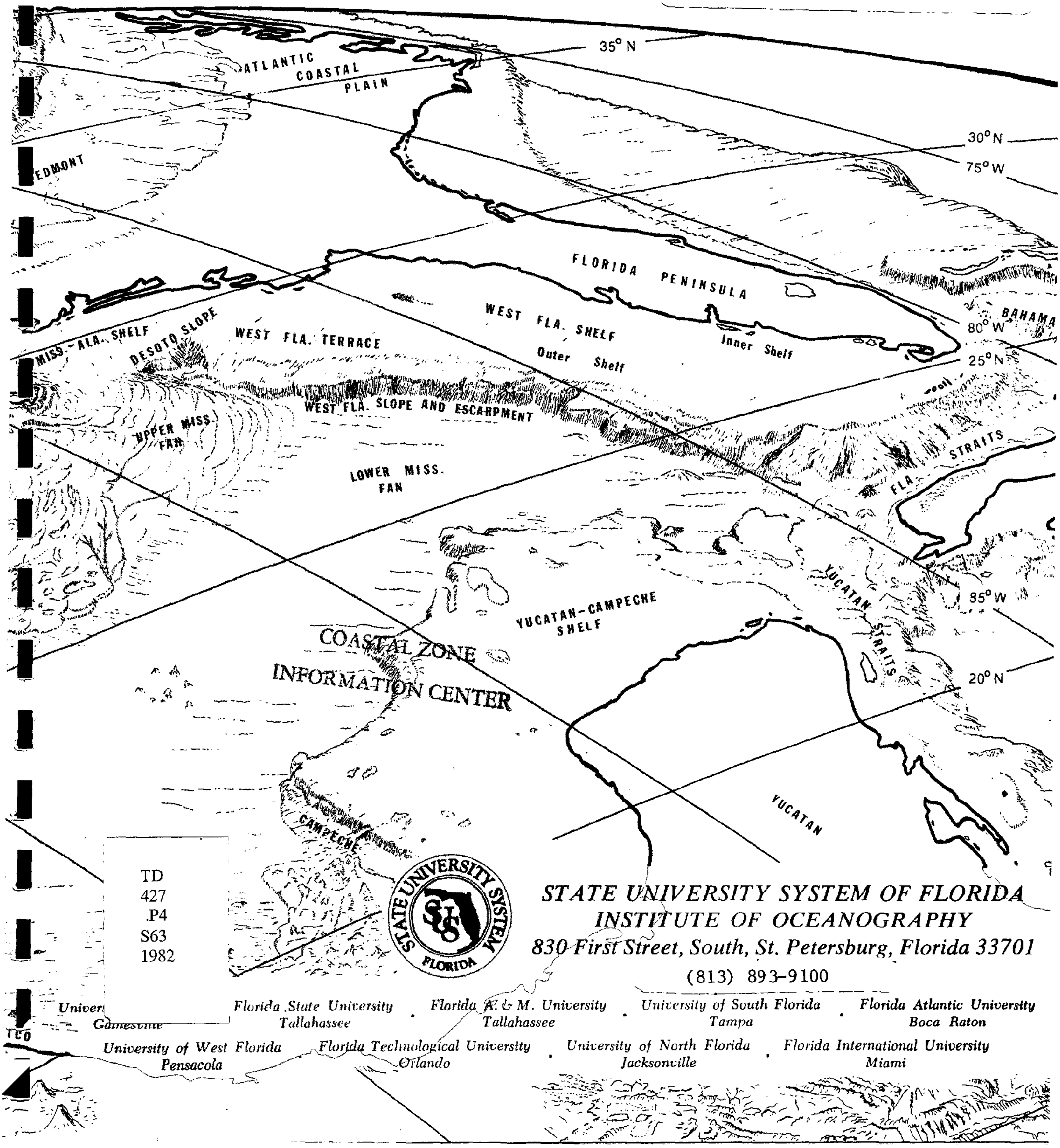
SPATIAL AND TEMPORAL VARIATION OF CRUDE OIL RESIDUES IN CONTINENTAL SHELF WATERS OFFSHORE WESTERN FLORIDA

FINAL REPORT

1981 -- 1982

Attachment 2



STATE UNIVERSITY SYSTEM OF FLORIDA
INSTITUTE OF OCEANOGRAPHY
830 First Street, South, St. Petersburg, Florida 33701
(813) 893-9100

Univer · *Florida State University* · *Florida A. & M. University* · *University of South Florida* · *Florida Atlantic University*
Gainesville · *Tallahassee* · *Tallahassee* · *Tampa* · *Boca Raton*

University of West Florida · *Florida Technological University* · *University of North Florida* · *Florida International University*
Pensacola · *Orlando* · *Jacksonville* · *Miami*

ACKNOWLEDGMENTS

The project described in this report was supported by Florida Department of Natural Resources Contract No. 34014. Additional support was provided by the Coastal Energy Impact Program (CEIP Grant #82-CE-CW-13-00-05-001), which is administered by the Office of Ocean and Coastal Resource Management, National Oceanic and Atmospheric Administration through the Florida Department of Community Affairs.

SPATIAL AND TEMPORAL VARIATION OF CRUDE OIL RESIDUES IN CONTINENTAL SHELF WATERS OFFSHORE WESTERN FLORIDA

FINAL REPORT

Year 2

(1981 - 1982)

Prepared for

Florida Department of Natural Resources
State of Florida

Florida Institute of Oceanography
and
University of South Florida
Department of Marine Science

830 First Street South
St. Petersburg, Florida 33701

October 1982

ABSTRACT

A two-year study of pelagic tar in the eastern Gulf of Mexico has been conducted. The first year was concerned with monitoring pelagic tar from the surface down to 100 m depth along standard transects intersecting the Gulf Loop Current. A major goal of the first year's study was to detect the impingement of crude oil residues from the IXTOC-I oil well blowout into Florida's coastal waters. First year results have previously been reported and are summarized in this report. During the second year of the study, pelagic tar was collected from surface waters (top 50 cm) during six monthly cruises along the same standard transects as during Year 1. The remaining six months were used to investigate possible tar sources and fluxes in surface waters as well as to examine pelagic tar in environmentally sensitive areas around coastal Florida.

In general, results obtained during Year 2 confirmed and expanded the findings of Year 1. Surface concentrations of pelagic tar (expressed as the toluene extractable lipid) ranged from 0 to 20.81 mg m^{-2} during Year 2, giving an overall two-year average of 0.78±2.66 mg m^{-2}. Pelagic tar found in the eastern Gulf of Mexico is primarily associated with the Gulf Loop Current. The overall two-year average concentration of pelagic tar found off the continental shelf (i.e. roughly correlated with the presence of the Loop Current) was 1.37 mg m^{-2} while the average on-shelf concentration (i.e. generally outside the influence of the Loop Current) was 0.10 mg m^{-2}. Thus, continental shelf areas around the eastern Gulf of Mexico appear to be quite clean with respect to pelagic tar. Although concentrations of tar found in stations off of the continental shelf are generally higher than most other areas of the world, Gulf of Mexico concentrations apparently have not increased over the past decade. Based upon gravimetric and chemical

analyses, the major single source of tar in the eastern Gulf was determined to originate from tanker operations. The Mississippi River and oil drilling platforms did not contribute substantial amounts of pelagic tar to this area. Approximately 10 to 50% of the tar observed in the eastern Gulf of Mexico appears to enter through the Yucatan Straits via the Loop Current, while the remaining oil residues appear to originate within the Gulf. The northern edges of the Florida Keys, as well as Florida Bay, are relatively unimpacted by pelagic tar. These pristine areas are located in a zone of little circulation indicating that crude oil or pelagic tar spilled into this area could remain in the environment for substantially long periods of time without being washed away. This has far reaching implications with respect to future offshore oil drilling and transportation activities off lower southwest Florida.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ACKNOWLEDGEMENTS

We are especially grateful to the Captain and crew of the R/V BELLOWS, as well as several Department of Marine Science graduate students, for their help and support during the sampling cruises. We also appreciate the efforts of Dr. Karen Steidinger and Mr. Alan Huff of the Florida Department of Natural Resources Bureau of Marine Science and Technology. Several polycyclic aromatic hydrocarbon standards were provided by the National Cancer Institute. Standard crude oils were provided by Gulf Research and Development Company. Crude oil collected form the IXTOC-I well site was provided by Drs. P.L. Parker, R.S. Scanlan, and J.K. Winters of the University of Texas Marine Science Institute. Financial support was provided by the Florida Coastal Protection Trust Fund.

INTRODUCTION

Florida's natural geography dictates that prevailing currents in the Gulf of Mexico strongly influence the ecology of its long coastline. With its large tourist industry, recreational and commercial fishing interests, and many other important economic and environmental considerations, it is imperative to have prompt warning of impending danger to Florida's valuable coastal ecosystems. Particular dangers which threaten shoreline and coastal ecosystems include a high potential of damage from oil well blowouts and from oil released from ship collisions or groundings. Offshore leasing, exploration, and oil well drilling began in 1974 off the West Florida coast, and will continue for several years. Drilling, production and marine transportation activities throughout the Gulf are expected to multiply many fold compared to today's activities. Since the frequency and magnitude of oil spillage will probably increase proportionately, maintaining the pristine nature of the eastern Gulf of Mexico will, at best, be difficult.

One of the most dramatic pathways by which oil is introduced into the marine environment is by oil tankers breaking up and spilling their cargo into surrounding coastal waters. Examples of these types of tanker accidents include the ARGO MERCHANT which ran aground on Nantucket Shoals in 1976 (NOAA, 1977; Hoffman and Quinn; 1979, 1980), the AMOCO CADIZ which grounded off the coast of France in 1978 (Chassé, 1978; Laubier, 1978; O'Sullivan, 1978), and the BURMAH AGATE which collided with the freighter, MIMOSA, in the Galveston shipping channel in 1979. As oil from these types of spills washes ashore, it coats the beaches, tidal flats, marshlands and the associated biota. In addition to physically smothering the flora and fauna, oil washing ashore contains many toxic hydrocarbon components that can have both lethal and sublethal effects on marine organisms. In addition, large numbers of birds that feed on surface-dwelling plants and animals can become coated with the oil as they dive through the surface waters. Most of these birds do not recover from the oil coating.

Direct purposeful discharge of tanker washings also introduces oil into oceanic environments. After unloading the bulk of their crude oil cargo into onshore processing or storage facilities, tankers use sea-water to wash down their holding tank walls. International agreements prohibit discharge of this water-oil mixture at sea. According to U.S. Coast Guard regulations, tankers must use the "load-on-top" (LOT) procedure for cleaning the holds. Sea water used to wash the holding tank walls must be allowed to stand in order for the oil to float to the top of the water-oil mixture. Most of the subsurface water can then be pumped out, but the remaining oil and water must remain on board until it can be discharged into a holding facility on shore. Although the LOT procedure has been a Coast Guard regulation for more than a decade, enforcement on the open seas is difficult. As a result, the discharge of oily water by tankers is still common. This practice is thought to be one of the main pathways by which oil enters the marine environment (Butler et al, 1973; NAS, 1975).

A third method by which oil enters the sea is from offshore oil well blowouts. The prime example is the IXTOC-I blowout on June 3, 1979 in the Bay of Campeche (19°24'N, 92°19'W) (NOAA, 1980). Initially, an estimated 30,000 barrels (5×10^6 liters) of crude oil were escaping daily from the well. Two months later (August 16, 1979), as the well continued to spill oil into the Bay of Campeche, oil from the blowout began to wash up on south Texas barrier islands, 800 km away. The well continued to release oil for a total of 9½ months until it was successfully capped on March 23, 1980. By that time, approximately 5.1×10^8 liters (134 million gallons) of crude oil had been released (Geo-Marine, 1980), a quantity equivalent to the combined cargoes of about two or three super-tankers. Previous studies (Haegh and Rossemyr, 1980) have indicated that approximately 65-70% of the oil released from IXTOC-I was lost due to either evaporation or dissolution. The remaining 30-35% of the discharged oil consisted of higher molecular weight, more viscous hydrocarbons that aggregated to form large, sticky masses. Continual wave action broke these floating oil residues down into smaller fragments called pelagic tar, or tarballs. Similar weathering mechanisms are responsible for tarball formation from crude oil spilled into the oceans through the other pathways.

During the past ten to fifteen years, the presence of pelagic tar in the open ocean has attracted considerable attention. Concentrations of floating tar vary widely in different parts of the world (Wong et al. 1976; Levy 1977; Jeffrey 1980). Based upon indirect evidence from the high wax composition and high iron-content of pelagic tar, as well as known tanker routes, Butler et al. (1973) and McGowan et al. (1974 a, b) have suggested that the largest single source of pelagic tar is from the discharge of tanker washings and ballast by crude-oil tankers (NAS 1975).

Two disastrous oil spills occurred in the Gulf of Mexico in 1979 and contributed to the already high background levels of pelagic tar found in the Gulf. The IXTOC-I drilling blowout and the collision involving the oil tanker, BURMAH AGATE, offshore Galveston, Texas, released more than 3,000,000 and 390,000 barrels of petroleum, respectively. These major spills are realistic examples of what the future may hold for the coastal environments of the Gulf. Florida, with the longest ocean coastline in the contiguous 48 states and its large ocean oriented tourist industry, is especially sensitive to oil pollution.

Following the IXTOC-I blowout, the Florida Department of Natural Resources became interested in determining if and when large quantities of IXTOC-I oil would foul beaches along the west Florida coastline. Although the United States Coast Guard (USCG) and the National Oceanic and Atmospheric Administration (NOAA) maintain the responsibility for cleaning up and dealing with the impact of oil spills in U.S. waters, it is the people and local governments that must deal with the economic impact resulting from a major spill. At present, there are still more than $400 million in outstanding damage suits resulting from IXTOC-I oil washing up on Texas beaches and causing serious economic damage to both tourism and commercial fishing industries. The State of Florida, to protect its own interests, sought to establish a program to compliment the efforts of the USCG and NOAA so that in the event of major environmental damage resulting from oil spills, financial restitution, based upon sound and established scientific knowledge, could be obtained.

In April, 1980, the Florida Institute of Oceanography and the University of South Florida Department of Marine Science were contracted by the Florida Department of Natural Resources to conduct a two-year survey of the eastern Gulf of Mexico to determine spatial and temporal variations of pelagic tar in this area. Year 1 of the study was directed at maintaining an attentive surveillance of offshore waters of the west Florida continental shelf. This surveillance was to be carried out by conducting a routine sampling and analysis program for pelagic crude oil residues in west Florida's coastal waters. The program was designed not only to give an advance warning of impending danger, but also to recognize and identify any polluting oil. Special emphasis was placed on the detection of oil from IXTOC-I. Year 2 studies were conducted with the following goals: (1) to firmly establish baseline data by which future spillage may be detected and assessed, (2) to investigate possible sources responsible for the presence of this oil, and (3) to investigate the pelagic tar burden of environmentally sensitive areas around the west coast of Florida. This report summarizes the Year 1 findings and reports new data and conclusions from Year 2.

SURFACE CIRCULATION IN THE GULF OF MEXICO

The distribution of pelagic tar in the eastern Gulf of Mexico is directly coupled to surface current circulation patterns. In order to fully understand the spatial and temporal variations of pelagic tar, it is therefore necessary to understand surface circulation patterns in the Gulf. In November, 1979, the State of Florida contracted Geo-Marine, Inc. (Richardson, Texas) to predict where and when oil from the IXTOC-I blowout could impact Florida's coastal waters. Based upon satellite information obtained from the National Environmental Satellite Service plus shipboard measurements and information obtained from wind vector data derived from drift cards, buoy, and oil slick observations, the following circulation information was compiled for the Gulf of Mexico by Geo-Marine, Inc. (1980).

Surface circulation in the Gulf is generally thought to be dominated by two circulation patterns. The eastern Gulf is dominated by the Loop Current, an offshoot of the Gulf Stream system which enters the Gulf of Mexico via the Yucatan Straits and exits through the Florida Straits. Circulation in the western Gulf of Mexico is less clear, and there is still controversy as to whether the circulation is dominated by wind stress or by eddies breaking off of the Loop Current, forcing a large anticyclonic gyre to exist in the western Gulf. Winds across the entire Gulf are easterly year round. Primary seasonal circulation changes are caused by the passage of cold fronts and tropical storms. These non-easterly episodes are generally of short duration and do not markedly alter the predominant yearly circulation pattern. Nonetheless, they provide an opportunity for disruption of dominant circulation patterns in the Gulf.

Data collected from wind, Loop Current, and drifter studies led Geo-Marine, Inc. to propose four zones of circulation in the Gulf of Mexico (Figure 1). The northwestern Gulf (Zone 1) is dominated by an anticyclonic gyre generated by a coupling of wind and Loop current circulation vectors. Along-shore currents and onshore-offshore water movement in the northwestern Gulf are highly variable and are not well understood. The Bay of Campeche defines the boundaries of Zone 2, containing a cyclonic gyre that expands and contracts depending upon changing wind conditions. The Loop Current in the eastern Gulf of Mexico (Zone 4) is better defined, but highly variable in lateral extent and volume flow. No consistent seasonal correlation of Loop Current intrusions into the Gulf has been discerned. It is well documented, however, that the Loop Current makes periodic intrusions northward onto the West Florida Shelf and westward of the Yucatan Straits, and can then entrain material transported from the western Gulf of Mexico. Geo-Marine (1980) estimated that the Loop Current intrudes onto the West Florida shelf approximately 20% of the time, thus making it possible for transport of material to West Florida coastal waters. Zone 3 is a transition zone between Zones 1 and 4 with no well defined circulation pattern. On an annual basis, very little exchange would be expected between adjacent zones. As mentioned above, however, short term circulation anomalies can be expected.

Sturges and Blaha (1976) reported the presence of an anticyclonic gyre in the western Gulf of Mexico similar to the Geo-Marine (1980) report, but also found evidence of a western boundary current along the Mexico-Texas

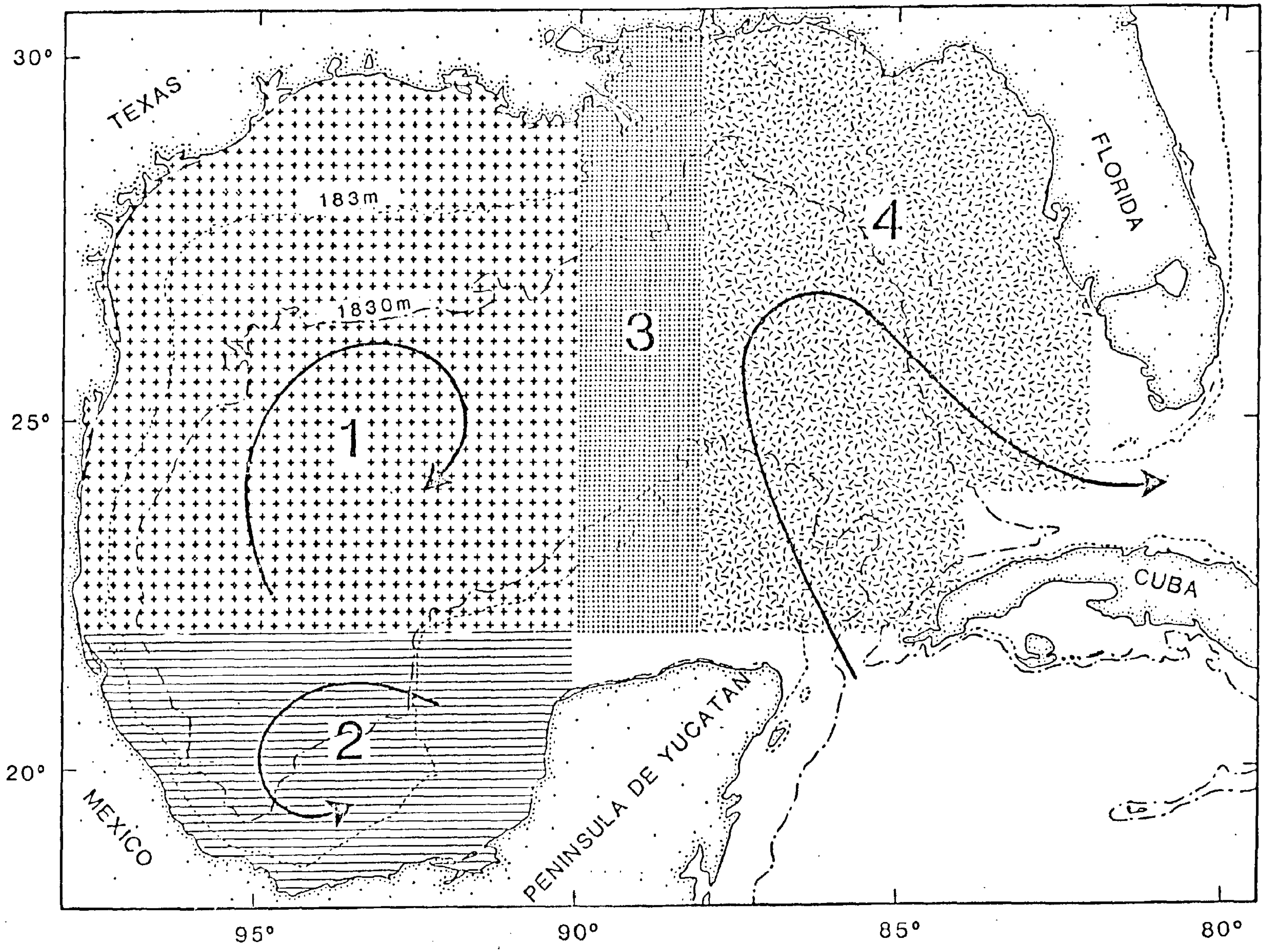


FIGURE 1. The four circulation zones of the Gulf of Mexico based on studies of wind, Loop current, and drifter data (Geo-Marine, Inc. 1980).

coastline. Merrell and Morrison (1981) report data that also supports the Geo-Marine (1980) study, i.e. the presence of an anticyclonic gyre in the central western Gulf of Mexico and the presence of a cyclonic gyre in the Bay of Campeche (Zone 2, Figure 1).

SUMMARY OF RESULTS OBTAINED DURING YEAR 1

During the first year of the study, twelve research cruises were undertaken to monitor pelagic tar residues in Florida's coastal waters. To provide for regular monitoring, the original sampling scheme called for two standard transects of seven stations each (Figure 2). These standard sampling transects were shifted throughout the year to insure maximum penetration into the Loop Current. At each station, two surface neuston tows and two oblique tows (0 to 100 m) were taken for analyses of floating and suspended tar residues. Duplicate tows were taken at each station to provide information on sampling variability. In the laboratory, each pelagic tar sample was analyzed by gravimetric analysis, gas-liquid chromatography, and isotope-ratio mass spectrometry to provide information on the quantitative, molecular, and isotopic characteristics (Tables 1 and 2).

A total of 265 tows were taken during the study. Of these tows, 109 (41%) contained pelagic tar. Size of the individual tar particles ranged from about 165 μ m to approximately 4.5 cm in diameter. Most fell in the range of 0.5 mm to 5 mm. Consistency of the tar varied from hard and crusty to soft and sticky. Colors varied between brown, grey, and black. Full details of the chemical data can be found in FIO/USF (1981).

Concentrations of pelagic tar observed in Florida's coastal waters during Year 1 ranged from 0 to 45.27 mg m^{-2} wet weight (0 - 90.54 mg m^{-3} wet weight) and 0 - 26.49 mg m^{-2} toluene extractable lipid material. The

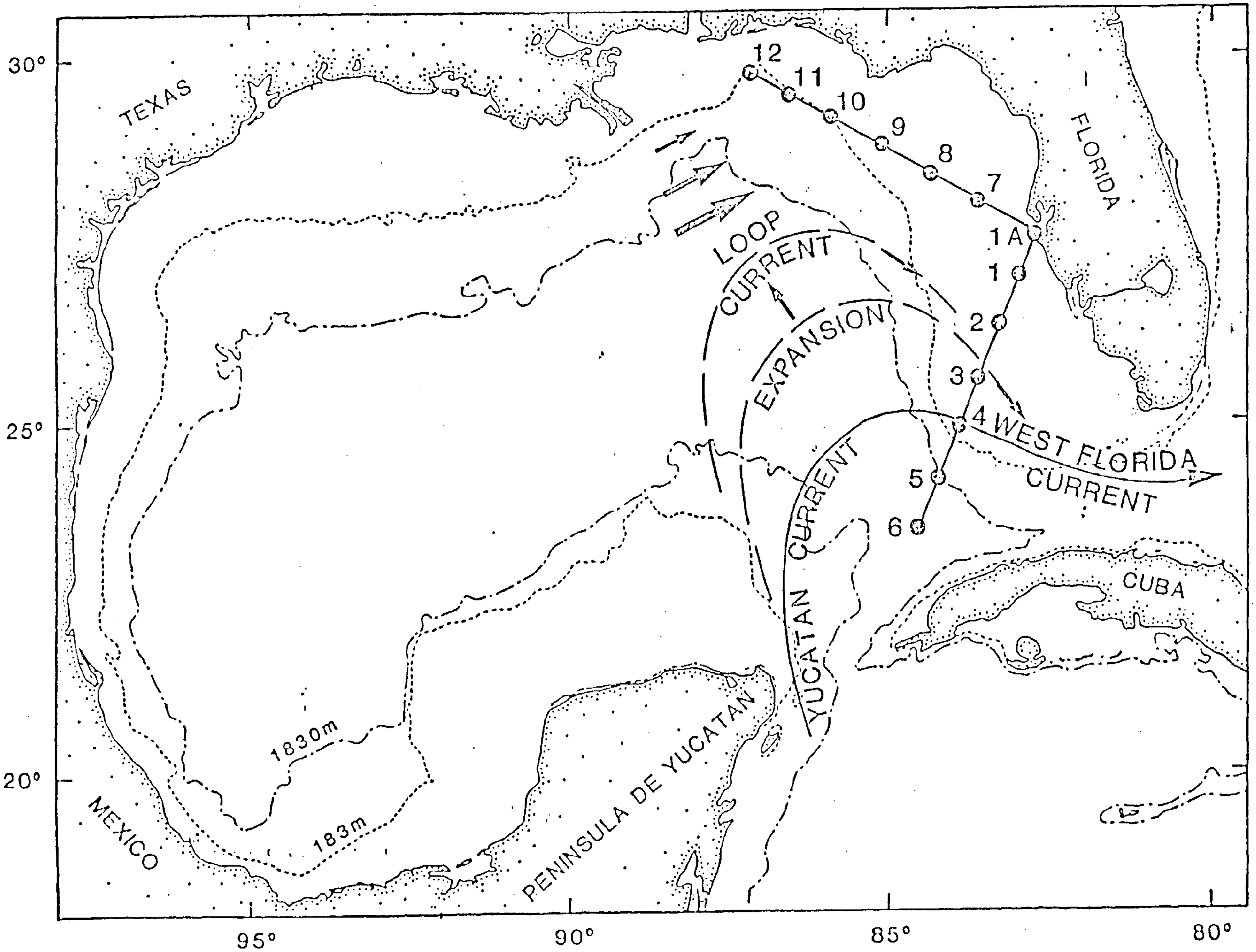


FIGURE 2. Representation of the Loop Current and positions of standard transects.

TABLE 1. Average pelagic tar concentrations (expressed in mg m^{-2} of toluene extractable lipid ± standard deviation) observed in neuston and oblique tows during Year 1 (after Van Vleet et al., 1982a).

Transect	(I) Concentration in neuston tows (all stations)	(II) Concentration in oblique tows (all stations)
Southern	1.33 ± 3.81	0.02 ± 0.01
Northern	0.13 ± 0.35	0.00 ± 0.00
Overall	1.01 ± 2.94	0.01 ± 0.01

Transect	(III) Concentration in neuston tows on west Florida shelf	(IV) Concentration in neuston tows off west Florida shelf
Southern	0.06 ± 0.08	2.07 ± 3.16
Northern	0.02 ± 0.06	0.19 ± 0.32
Overall	0.05 ± 0.08	1.60 ± 2.45

TABLE 2. Chemical parameters observed in pelagic tar collected during Year 1 (from Van Vleet *et al.*, 1982b).

PARAMETER MEASURED	RANGE	AVERAGE
$\delta^{13}C$ (total)	-26.5 - -28.0°/oo	-27.2 ± 0.8°/oo
$\delta^{13}C$ (F1)	-26.3 - -29.9°/oo	-27.5 ± 1.4°/oo
$\delta^{13}C$ (F2)	-25.4 - -29.6°/oo	-27.0 ± 1.1°/oo
aliphatics/aromatics	0.68 - 7.33	2.69 ± 1.63
nC_{17}/pristane	0.14 - 4.60	1.54 ± 0.79
nC_{18}/phytane	0.31 - 5.21	1.92 ± 0.99
pristane/phytane	0.41 - 2.79	1.00 ± 0.38
n-alkane range	C_{12} - C_{38}	C_{14} - C_{38}
n-alkane maximum	C_{18} - C_{38}	C_{19}-C_{20};$C_{29}$$C_{35}$
% resolved F1	33.4 - 94.7	40.2 ± 15.4
% unresolved F1	5.3 - 71.4	59.8 ± 15.4
% resolved F2	7.9 - 45.6	25.4 ± 13.8
% unresolved F2	55.4 - 92.1	74.6 ± 13.8

floating tar had a moisture content of approximately 59±21% (observed range = 19.2 - 97.0%) Moisture content of the tar samples was inversely related to tarball size. The remainder of the tar particles consisted of toluene extractable organic matter ($\bar{x} \cong 38.4\%$ of the wet weight; range 0 to 86%) plus inorganic detrital material.

Average pelagic tar concentrations from neuston and oblique tows observed for each cruise are shown in Table 1. Average concentrations for the neuston tows are also shown for stations taken approximately on the West Florida continental shelf versus stations taken off of the West Florida shelf. The stations sampled off of the shelf are roughly equivalent to those which are associated with the Gulf Loop Current. Concentrations of pelagic tar observed in the oblique (0 - 100 m) tows (Table 1, II) are negligible compared to the concentrations observed in the neuston tows (Table 1, I). Stations that showed significant tar in oblique tows invariably showed high surface concentrations as well. It is therefore likely that pelagic tar observed in the oblique tows consisted solely of tar collected as the nets passed through the surface layers. Thus, most of the pelagic tar is believed to have been found in the upper 0.5 m of the water column. Nets used to collect the neuston samples collected tar to a depth of 50 cm, and thus, tar that was floating directly on the surface could not be distinguished from tar at about 50 cm depth. It is quite possible that most of the tar was actually floating directly on the surface.

Pelagic tar concentrations reported for various other areas of the world are listed in Table 3. In comparing the concentrations from different areas, it should be kept in mind that tar concentrations are a function of such things as net size, length of tow, number of samples, sea state, season, and duration of study. Since these conditions were not uniform in all studies,

TABLE 3. Pelagic tar concentrations reported in various oceanic surface waters (expressed as mg m^{-2} toluene extractable lipid). Some data recalculated based on the assumptions that (1) the tar has a moisture content of 50%, and (2) the toluene extractable lipid comprises 38.4% of the tar's wet weight.

Location	Concentration Average (mg m^{-2})	Concentration Range (mg m^{-2})	Reference
North Pacific	0.03	0 - 6.26	Wong et al., 1976
North Pacific	0.05	0 - 0.48	Shaw and Mapes, 1979
Barents Sea	<0.04	0 - 6.37	Heyerdahl, 1978
North Sea	0.04	0 - 4.65	Smith, 1976
North Sea	<0.08	0 - 6.72	Heyerdahl, 1978
North Atlantic	0.16	0 ->10.0	Levy, 1977
North Atlantic	0.42	0 - 4.12	McGowan et al., 1974b
North Atlantic	0.61	0 - >1.84	Sherman et al., 1974
South Atlantic	0.67	0 - >5.15	Eagle et al., 1979
Caribbean Sea	0.74	0 - 4.5	Jeffrey et al., 1974
Western Gulf of Mexico	1.20	0 - 10.0	Jeffrey et al., 1974
Western Gulf of Mexico	1.27	0 - 8.61	Pequegnat, 1979
Sargasso Sea	2.64	0 - 8.30	McGowan et al., 1974b
Sargasso Sea	2.97	0 - > 30	Butler and Morris, 1974
Mediterranean Sea	3.03	0 - 33.27	Zsolnay et al., 1978
Gulf of Mexico Loop Current	1.60	0 - 26.49	This study (Year 1)
Eastern Gulf of Mexico (overall)	1.01	0 - 26.49	This study (Year 1)

comparison of the data from different areas is not unequivocable. Average tar concentrations in the eastern Gulf of Mexico are generally comparable to those reported in the western Gulf of Mexico, the Sargasso Sea, and the Mediterranean Sea (Tables 1(I) and 3). These areas have the highest average pelagic tar concentrations reported anywhere in the world. Concentrations found in the Gulf Loop Current are generally much higher than concentrations reported for most other areas (∿ 2 times higher than the Caribbean Sea to over 40 times higher than in the North Pacific).

A method for classifying pelagic tar concentrations has been proposed by Wong et al. (1976) based on samples collected in the Pacific Ocean. These authors arbitrarily assigned the following designations to the floating tar concentrations (wet weights):

No visible tar $\equiv$ Zero (0)
<0.1 mg m^{-2} $\equiv$ Trace (T)
$0.1 - 1$ mg m^{-2} $\equiv$ Medium (M)
$1 - 5$ mg m^{-2} $\equiv$ Heavy (H)
>5 mg m^{-2} $\equiv$ Extra Heavy (X)

This classification procedure has subsequently been used by other authors (Shaw and Mapes 1979; Eagle et al. 1979) and provides a convenient means of comparing pelagic tar data from different areas. Based upon this classification, pelagic tar distributions observed during Year I are presented in Figure 3. The distribution of pelagic tar is extremely patchy. As a result of this patchiness, there is certainly some overlap in the contours shown in Figure 3. The contours more accurately represent the probability of finding trace, medium, heavy, or extra heavy pelagic tar concentrations in various sectors of the eastern Gulf of Mexico. If the contour curves (Figure 3) are compared to the expected axis of the Loop

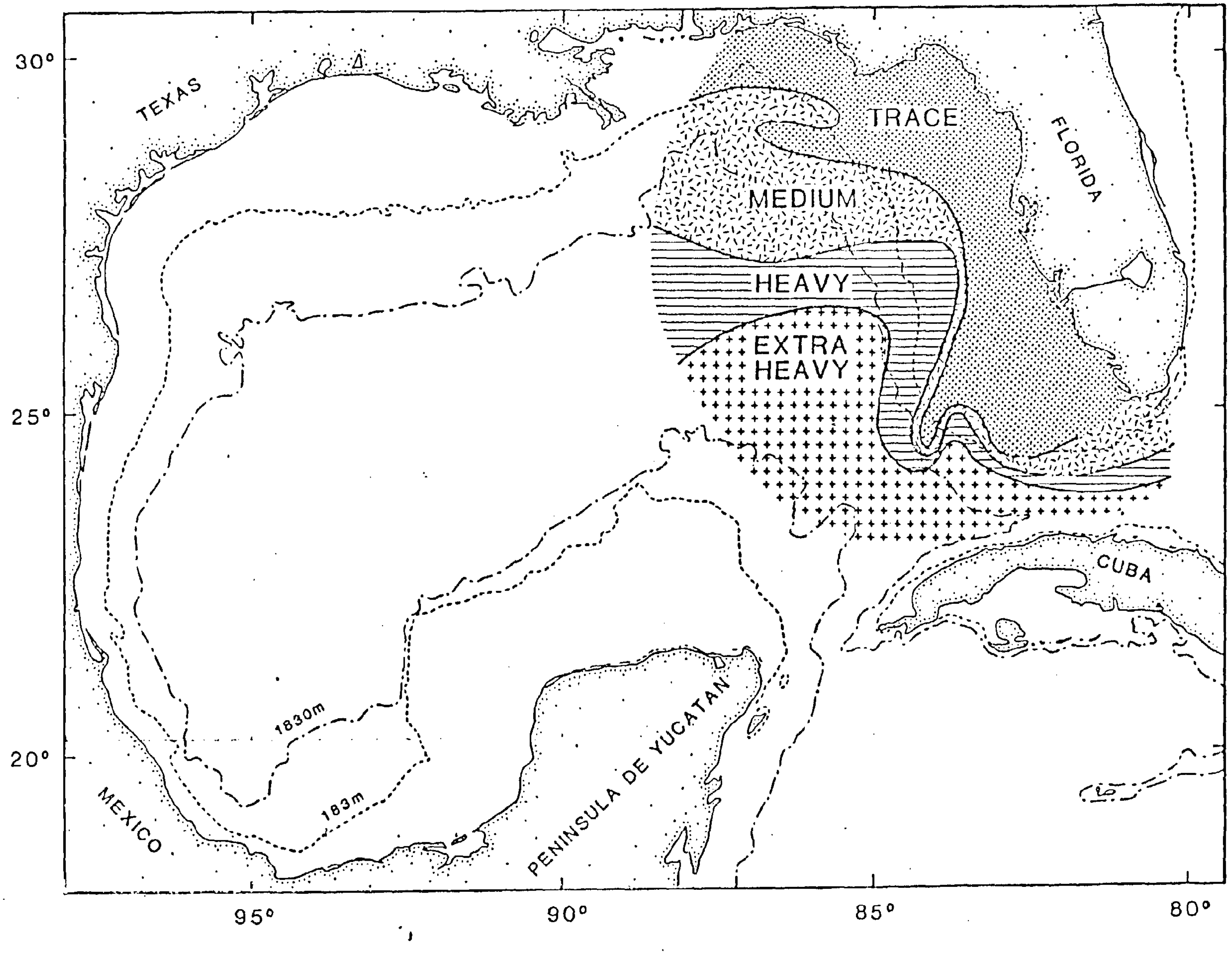


FIGURE 3. Average distribution of surface tar observed in the eastern Gulf of Mexico during Year 1.

Current (Figures 1 and 2), it can be seen that the highest tar concentrations correlate with the Loop Current while stations on the west Florida continental shelf (< 100 fathoms) generally show the lowest tar concentrations.

The distribution of pelagic tar in the eastern Gulf of Mexico is extremely patchy and highly variable. Duplicate neuston tows collected at Station 2 during cruise S580, for example varied by a factor of 30 (toluene extractable lipid concentrations: tow 1 = 26.49 mg m^{-2}, tow 2 = 0.88 mg m^{-2}). This variability is reflected in the large standard deviations reported in Table 1. The highest concentrations of pelagic tar were associated with the presence of large amounts of *Sargassum*.

Average concentrations of pelagic tar at all stations (from Table 1, I) was plotted against cruise date (Figure 4). On southern transects, the average concentration was highest during the May 1980 cruise (4.60 ± 7.34 mg m^{-2}) and decreased throughout the summer, fall, and winter months. Higher concentrations observed during the spring and summer months were probably due to both calmer sea conditions and higher shipping activities. Rougher sea conditions during the fall and winter months caused the downward mixing of tar in the surface waters which partially led to the lower observed tar concentrations. The variability in these concentrations (i.e., the standard deviations shown in Table 1) indicates that there is not a statistically significant difference between tar concentrations at any station. Overall averages, however, showed an apparent seasonal trend.

According to Butler *et al.* (1973), crude oil sludge (i.e., tanker wall washings) is characterized by a bimodal distribution in the envelope of n-paraffin peaks. One maximum occurs at approximately C_{17} while the other maximum is at approximately C_{29}. Crude oils from normal operations, tanker

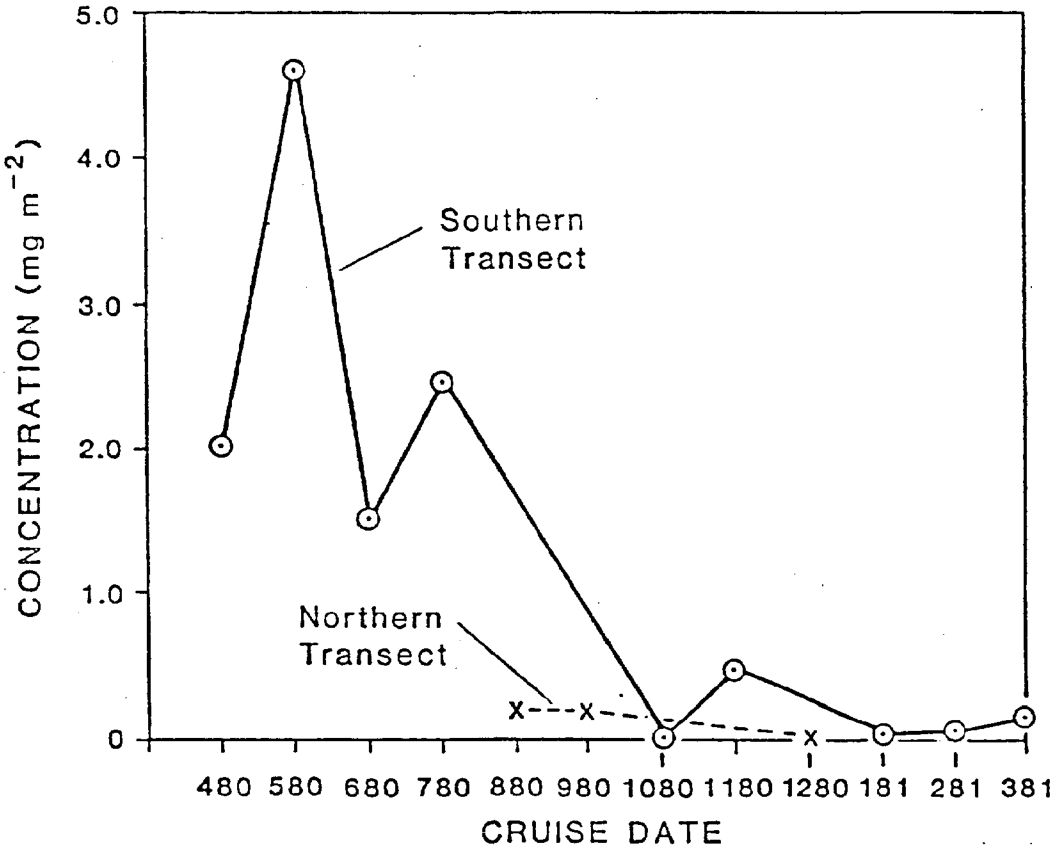


FIGURE 4. Average pelagic tar concentrations (expressed in mg m^{-2} of toluene extractable lipid) in neuston tows during Year 1 plotted versus sampling cruise.

accidents, or natural seeps do not show this bimodal n-paraffin distribution. In pelagic tar samples investigated during Year 1, approximately 40% showed a bimodal distribution with the n-alkane maxima occurring in the C_{19}-C_{20} and the C_{29}-C_{35} ranges. Approximately 60% of the samples showed a unimodal distribution of n-alkanes with the maxima varying from C_{18}-C_{38}. In addition, a few chromatograms of the tar samples appeared similar to chromatograms of refined (Bunker C) oils. These results suggested that tanker operations are a prime contributor to the pelagic tar found in the eastern Gulf of Mexico.

Molecular and isotopic characteristics of each pelagic tar sample that we collected were compared to the weathered IXTOC-I tar sample to determine their "similarity". Gas chromatographic and mass spectrometric data of the weathered IXTOC-I sample were interpreted quite liberally to allow for more or less weathering of the tar during its transport to the West Florida shelf. By taking this approach to weathered IXTOC-I tar values, we could be reasonably certain that tar samples falling outside of the similarity limits did not come from the IXTOC-I blowout. Although several pelagic tar samples showed some characteristics of IXTOC-I oil, very few could not be completely distinguished from the IXTOC-I oil. Out of 109 stations where measurable pelagic tar was collected, 15 samples ($\sim$ 14%) could not be distinguished from weathered IXTOC-I oil. Eight cruise transects contained 0, 1, or 2 samples that resembled the IXTOC-I oil. Only two of the transects had a slightly higher number of stations containing IXTOC-like tar (S680: $n = 5$; N880: $n = 4$). Thus, it does not appear that large amounts of IXTOC-I oil impinged on Florida's coastal waters, but rather that there may have been a small background of IXTOC-like oil present, over which were superimposed larger amounts of oil from different origins.

SAMPLING STRATEGY FOR YEAR 2

Based on the results of the first year of this study, in conjunction with the results of the Geo-Marine, Inc. (1980) report, an integrated, three-phase sampling program was designed for the second year of the project (Table 4). The three main objectives of this sampling program were (1) to continue monitoring oil residues in coastal waters of the West Florida continental shelf and Gulf Loop Current for indications of impending high concentrations of pelagic tar, (2) to further investigate the sources and fates of pelagic tar entering the eastern Gulf of Mexico, and (3) to focus additional investigations on specific high-risk areas of environmental concern along the Florida continental shelf.

The two standard transects from Year 1 (Figure 2) continued to be sampled during Year 2 (objective 1). The southern transect was designed to intersect the Loop Current and monitor the central West Florida continental shelf. The northern transect was designed to monitor the coastal waters adjacent to the Florida Panhandle. (According to the Geo-Marine, Inc. report, this may be an area of potential impact from oil entrained in the Gulf Loop Current). Each transect was approximately 300 miles long with seven stations equally spaced along each transect. Based upon the pelagic tar distribution observed during Year 1, most standard transect cruises were carried out on the southern transect, where most of the pelagic tar was observed. The northern transect showed much lower concentrations of pelagic tar during Year 1 and consequently was not as intensively studied during Year 2. Six cruises were conducted along standard transects. Four standard southerly cruises were carried out in September, April, June, and July. The northern standard transect was sampled twice during Year 2 -- once during summer (August) and once during winter (January). These standard transect

TABLE 4. Cruise schedule carried out during Year 2.

Sampling Location	Number of Ship Days (per cruise)	Number of Cruises	Total Ship Days
Standard Southern Transect	4	4	16
Standard Northern Transect	4	1	4
Standard Northern Transect and Mississippi Delta Region	6	1	6
Florida Straits	5	1	5
Florida Keys	5	1	5
Florida Bay	5	1	5
Yucatan Straits	5	1	7
TOTAL SHIP DAYS		10	48

sampling cruises were used to help confirm the seasonal and spatial variations in pelagic tar distributions observed during Year 1. Sampling was conducted using 165 or 280 μ m mesh neuston sampling nets. The 280 μ m nets used during the second year had a slightly larger mesh opening than the nets previously used (165 μ m). The larger mesh size was chosen to help avoid net blowout (experienced twice during Year 1) while at the same time not compromising sampling efficiency (most of the tar collected during Year 1 was greater than 280 μ m in diameter). Two surface neuston tows were taken at each of the seven stations along each sampling transect. Oblique tows from 0 to 100 m were deleted from the sampling program due to the absence of pelagic tar from these tows during Year 1. Neuston nets were equipped with flow meters in order to determine the volume and surface area covered during each tow. In addition, XBT's were used to determine if and when sampling was carried out in the Gulf Loop Current. The Gulf Loop Current was identified by the presence of the 22° isotherm at 100 m (Nowlin, 1971; Maul, 1977).

The second objective of the sampling program was to further investigate the sources and fates of pelagic tar entering the eastern Gulf of Mexico. In order to accomplish this objective, three main areas were examined: South Louisiana coastal water, the Yucatan Straits, and the Florida Straits. The first area, the Mississippi Delta and Mobile Bay region, is an area of high river discharge, high drilling, and high shipping activity. Any oil released in this area could become entrained in the Loop Current and transported to Florida coastal waters. Since this is one of the main oil producing areas on the U.S. Gulf Coast, it is critical to have an understanding of the nature of the oil being produced (and potentially released) there. South Louisiana crude oil was analyzed during Year 1 of the study. One purpose of the research cruise to South Louisiana was to collect potential weathering products of this oil that are found in the surface waters for comparison to tar collected in Florida coastal waters. The second purpose of this cruise was to collect water being discharged from the Mississippi River for pelagic tar analysis. During Year 2 we also attempted to investigate oil residues entering and leaving the eastern Gulf of Mexico by the Gulf Loop Current. A cruise was carried out to the Yucatan Straits to investigate the nature of the oil entrained in the Loop Current as it enters the eastern Gulf, and an additional cruise was carried out to the Florida Straits to examine the oil associated with the Loop Current as it leaves the eastern Gulf. Samples were also collected in the West Florida Current (Figure 2) during transit to the Yucatan Straits. Although these locations were sampled only once during the year, these results, along with other results from both years of the study, were used to get an indication of the total burden and steady state nature of pelagic tar in the eastern Gulf of Mexico.

The third objective of Year 2 sampling was to more closely examine specific areas of environmental concern along Florida's continental shelf. Oil production operations that are presently being undertaken along the West Florida shelf are located around Florida Bay. There is little transport of water into or out of Florida Bay with the circulation in the area being rather sluggish. As a result, any major oil spills occurring in this area are likely to remain in Florida Bay and will not be rapidly dispersed or removed from this area. Therefore, background levels of pelagic tar in Florida Bay were investigated during Year 2. A second environmentally sensitive area in which background data were needed is the Florida Keys. According to Geo-Marine, Inc. (1980), the area from Key West to Fort Pierce is the most likely area to be impacted by oil entrained in the Gulf Loop Current. Major oil spills could have disastrous effects on the fragile coral reef ecosystems found in the Florida Keys. Consequently, coastal waters off of the Florida Keys and the southeast Florida coastline (Miami-Ft. Lauderdale area) were sampled for pelagic tar. This information was used to help determine the transport of oil from the Gulf Loop Current to southeast Florida coastal waters as predicted by Geo-Marine, Inc. (1980).

ANALYTICAL METHODS

With the great increase in the anthropogenic oil burden in the seas over the past ten years, numerous techniques have been developed to characterize insoluble oil residues found floating on the surface, coating beaches, and contaminating organisms. These analytical procedures may be subdivided into three categories: isotopic, molecular, and elemental. Isotopic and molecular characterization were used to investigate oil residues collected in this study using "state-of-the-art" analytical equipment.

After collection, the samples were stored in glass jars at 4°C or on ice until returned to the laboratory for analysis. In the laboratory, tar particles were removed from the bulk neuston samples, and their wet weight determined. Dry weights were determined after drying each sample overnight at 40°C. Each tar sample was then dissolved in toluene to form a homogeneous sample and 1 ml aliquots taken for determination of (A) toluene extractable material, (B) molecular characterization, (C) isotopic characterization, and (D) a reserve. The toluene was evaporated from aliquot A under a stream of nitrogen and weighed on an O'Haus 300 top loading balance. Aliquots taken for molecular and isotopic characterization were charged to a 10 cm x 1 cm diameter activated silica gel column to separate the aliphatic and aromatic hydrocarbon fractions. Oil residues were separated into these fractions in order to minimize problems associated with differential weathering and solution during the days, weeks, or months of transport in the surface waters. The F1 (aliphatic hydrocarbon) fraction was eluted with two column volumes of hexane; after which, the F2 (aromatic hydrocarbon) fraction was eluted with two column volumes of toluene. Each hydrocarbon fraction was evaporated to dryness in a preweighed Teflon weighing boat and the F1 and F2 hydrocarbon weights determined on a Mettler microgram balance.

The molecular nature of the hydrocarbons was determined for each fraction by glass capillary gas-liquid chromatography (GLC) and combined high resolution gas chromatography-mass spectometry (GCMS). Hydrocarbon extracts were redissolved in 20-30 μ l of hexane and approximately 1 μ l of each fraction was injection into a Hewlett-Packard Model 5880A gas chromatograph equipped with a 12m x 0.2mm i.d. SP2100 fused silica capillary column and flame ionization detector. Running conditions were as follows: injection port temperature = 225°C, splitless injection mode, detector temperature = 250°C, column oven temperature programmed from 100-255°C at 4°C min^{-1}, carrier gas = helium, column flow = 0.78 ml min^{-1}, auxiliary make up gas flow = 30 ml min^{-1}, hydrogen flow = 30 ml min^{-1}, compressed air flow = 420 ml min^{-1}. Chromatograms were recorded and integrated using a Hewlett-Packard Level 4 data processor equipped with BASIC programming capability.

Gas-liquid chromatography (GLC) has commonly been used for the analysis of petroleum hydrocarbons. Tar residues were investigated using GLC by determining such parameters as percent aliphatics, percent aromatics, n-alkane range, n-alkane maximum, percent resolved versus unresolved components, and specific resolved component ratios (including nC_{17}/pristane, nC_{18}/phytane, and pristane/phytane). Butler et al. (1973) found that tarballs can retain certain molecular characteristics for several months, but the reliability of distinguishing between different oils decreases with time of exposure in the environment. Several authors have demonstrated that one of the most diagnostic characteristics of a petroleum sample is the molecular nature of the aromatic hydrocarbon fraction (Youngblood and Blumer, 1975; Farrington et al., 1977). Aromatic hydrocarbons in a petroleum sample cannot be adequately determined using conventional gas chromatographic techniques. The reason for this is that in addition to the many polycyclic aromatic hydrocarbon (PAH) parent compounds, there also exist C_1->C_3 alkylated homolog series for each parent PAH. In addition, each of these alkylated homologs can be present as a number of different isomers for each parent structure, resulting in several thousand aromatic hydrocarbon compounds that cannot be resolved by gas chromatography alone. Substituted versus non-substituted aromatic hydrocarbons, as well as homologs of related compounds such as the ringed organo-sulfur compound, dibenzothiophene, have been found to be characteristic of individual oils. Overton et al. (1981) demonstrated that the ratios of C_1-C_3 alkyl phenanthrenes to C_1-C_3 alkyl dibenzothiophenes are useful indicators for tracing petroleum sources in environmentally impacted samples. These ratios were found to be uniquely characteristic for several oils even after weathering processes had degraded other more commonly used molecular parameters. Similar ratios have been used to trace the fate of oil resulting from the tanker TSESIS oil spill of 1977 (NOAA, 1979). According to Giger and Schaffner (1978), only combined gas chromatography-mass spectrometry (GCMS) can identify each of the aromatic homologs.

Approximately half of the aromatic hydrocarbon fractions of the pelagic tar collected in this study were analyzed by GCMS (one sample was analyzed for each duplicate tow). Samples were analyzed on a Hewlett-Packard Model

5992B computerized GCMS system equipped with a 15m or 30m OV-101 fused silica capillary column. Running conditions were as follows: carrier gas = helium; column flow rate = 1.7 ml min^{-1}; injection port temperature = 240°C; splitless injection mode; column oven temperature programmed from 90 - 250°C at 4°C min^{-1}; electron multiplier voltage = 1200-2000 eV; GCMS run in selected ion monitoring mode; dwell time = 100 msec for each ion. A list of the compounds monitored and the characteristic mass units (ion of maximum response) used to identify each compound are listed in Table 5. A window of ±0.5 a.m.u was used for the monitored ion to insure maximum response. Response factors were determined for each compound and the quantity of each compound relative to phenanthrene was calculated. From this data, we have reported the alkylated homolog to parent compound ratios and the ratios of alkylated phenanthrenes to alkylated dibenzothiophenes as described above.

Stable carbon isotopic composition, expressed in terms of $\delta^{13}C$ where

$$\delta^{13}C \text{ (in } {}^{\circ}/_{\circ\circ}) = [({}^{13}C/{}^{12}C \text{ sample})/({}^{13}C/{}^{12}C \text{ standard})-1] \times 1000$$

was determined for the total tar (aliquot C) as well as for individual F1 and F2 hydrocarbon fractions. The residue of each sample was combusted at 500°C in the presence of CuO in a sealed ampule to convert the organic matter to CO_2. The isotopic composition of the resulting CO_2 was determined using a Varian MAT 250 isotope ratio mass spectrometer. Readout of the MAT 250 was directly in °/∘∘ vs the PDB standard (Craig, 1953).

Stable carbon isotopic compositions of naturally occurring carbonaceaus materials give information about sources, maturation processes, and pathways of carbon. Over the past few years, increasing use of this parameter is being made in characterizing natural gases, oils, and coals and using natural

TABLE 5. Compounds monitored by GCMS for each aromatic hydrocarbon fraction analyzed. The ion monitored for identification is given by the ion of maximum response. C_1, C_2, and C_3 represent the number of alkyl carbons substituted on the parent aromatic compound.

COMPOUND	MAXIMUM ION RESPONSE
Naphthalene	127.95
C_1 - Naphthalene	141.95
C_2 - Naphthalene	156.00
C_3 - Naphthalene	170.05
Phenanthrene	177.95
C_1 - Phenanthrene	192.00
C_2 - Phenanthrene	206.05
C_3 - Phenanthrene	220.10
Dibenzothiophene	183.95
C_1 - Dibenzothiophene	197.95
C_2 - Dibenzothiophene	212.00
C_3 - Dibenzothiophene	226.05

variations in exploration efforts. These uses have been reviewed in papers by Feux (1977) and Stahl (1977). As demonstrated by these papers and the references therein, this area of science is well developed and ideally suited for characterization of insoluble petroleum residues found on and in the ocean.

The detection limits for both the isotopic and gas chromatographic analyses were about 150 μg of aliphatic hydrocarbons and about 200 μg of aromatic hydrocarbons (i.e., twice the blank values). In virtually all cases these corresponded to approximately 10 mg of total tar (wet weight). This resulted in a minimum detectable floating tar concentration of approximately 0.01 mg m^{-3} (i.e., 0.01 μg l^{-1}). Dissolved hydrocarbon concentrations in the Gulf Loop Current have been reported of up to 75 μg l^{-1} (Iliffe and Calder, 1974). Hence our detection limits were well below background levels reported for the Gulf of Mexico.

RESULTS AND DISCUSSION

Spatial and Temporal Variations

During the second year of this study, a total of 151 neuston tows were made to collect pelagic tar. Ninety-one of these tows (≅60%) contained measurable quantities of tar. The size of the tar particles ranged from approximately 0.3mm to approximately 50mm with the majority falling in the range of 1 to 5mm. The shape of the tar particles varied from rough and spherical to smooth, flat, and plate-like. Much of the tar had a soft, sticky texture and adhered readily to whatever it contacted. In this regard, these tar particles can absorb particulate material from the water column and increase their density enough to allow them to sink to the bottom and become available to filter and deposit feeding organisms. The soft sticky tar is indicative of relatively unweathered material recently discharged into the Gulf waters. Conversely, some of the tar had a hard, brittle texture signifying older, more highly weathered tar. This tar could either have originated locally or could have been transported over long distances from elsewhere in the Gulf of Mexico or Caribbean.

One problem in comparing pelagic tar concentrations to previously published data is that different investigators have reported tar concentrations in a variety of different ways, including concentrations based on wet weight, dry weight, and organic solvent extractable weight. In order to make our results more easily comparable with other studies, we report the tar concentrations found in the present study by all of the above methods.

Pelagic tar concentrations found during Year 2 ranged from 0 to 35.91 mg m^{-2} wet weight (w.w.) [0 to 24.52 mg m^{-2} dry weight (d.w.); 0 to 20.81 mg m^{-2} toluene extractable lipid (t.e.l.)] with an overall average of 1.23±4.48 mg m^{-2} w.w. (0.71±2.78 mg m^{-2} d.w.; 0.53±2.36 mg m^{-2} t.e.l.) (Table 6). The overall average surface concentration observed during Year 1 was 1.71±4.98 mg m^{-2} w.w. (t.e.l. = 1.01±2.94 mg m^{-2}). Thus the concentrations observed during Year 2 appear to be slightly lower than those observed during Year 1, but due to the large variation in tar concentrations, the difference is not statistically significant for the two-years. The overall two-year average for pelagic tar concentrations was 1.48±4.74 mg m^{-2} w.w. (0.89±2.94 mg m^{-2} d.w.; 0.78±2.66 mg m^{-2} t.e.l.; Table 6).

Tar observed during the second year of the study had an average moisture content of 58±21%, which was essentially identical to that measured during Year 1 (59±21%). The observed range of moisture contents during Year 2 was from 0 to 90%. McGowan et al. (1974b) reported moisture contents of tarballs ranging from 0 to 51% with an average of 21%. Since the moisture content of

TABLE 6. Average pelagic tar concentrations observed in neuston tows during each year of study. Concentrations are given in mg m^{-2} (±standard deviation). Concentrations are also shown for stations taken on and off the continental shelf.

	YEAR 1	YEAR 2	TWO-YEAR AVERAGE
OFF SHELF			
Wet weight	2.85±3.52	2.37±6.20	2.66±4.64
Dry weight	1.68±2.22	1.35±3.85	1.55±2.90
Extractable lipid	1.60±2.45	1.00±3.30	1.37±2.80
ON SHELF			
Wet weight	0.08±0.13	0.34±0.98	0.23±0.60
Dry weight	0.05±0.08	0.21±0.69	0.14±0.42
Extractable lipid	0.05±0.08	0.14±0.50	0.10±0.31
ALL STATIONS			
Wet weight	1.71±4.98	1.23±4.48	1.48±4.74
Dry weight	1.06±3.09	0.71±2.78	0.89±2.94
Extractable lipid	1.01±2.94	0.53±2.36	0.78±2.66

our tar samples was inversely related to tarball size, the difference between our percent moisture data and McGowan's (1974b) could have been due to the analytical methods employed in the two studies. McGowan could possibly have blotted or air dried his samples initially to remove excess water. In our study, tar samples were picked from the tows and weighed directly. In addition to the water associated with the tar particles, the remaining fractions consisted of toluene extractable organic matter (x±s.d. ≅32±10% of the wet weight; range = 4-42%) plus inorganic or other insoluble organic material (average ∿ 10% of the wet weight). Thus approximately 75±25% of the dry tar particles was extractable with toluene, i.e. lipid material. The remaining ∿ 25% of the dry tar weight could have consisted largely of heavy asphaltene type material which is common to most crude oils, but insoluble in toluene.

Average pelagic tar concentrations found during individual cruises from stations taken on and off the eastern Gulf of Mexico continental shelf are reported in Tables 7 and 8. Stations taken off the continental shelf are those which are generally associated with the Gulf Loop Current. Stations taken on the continental shelf are correlated with stations generally outside the influence of the Gulf Loop Current. Stations occupied during these cruises are designated in the same manner as during Year 1, i.e. by direction of transect (S = Southern, N = Northern, FB = Florida Bay, FS = Florida Straits, SE = Southeast Florida Coast, CG = Central Gulf, YS = Yucatan Straits) plus month and year (example: N881 = Northern Transect, August 1981). Individual tows are designated by station, type of tow, and replicate 1 or 2 (example: 4N2 = station 4, Neuston tow 2; G = Grab sample). Most of the pelagic tar observed during the present study was associated with the Gulf Loop Current (Tables 6 - 8), thus confirming the trend established during

TABLE 7. Average pelagic tar concentrations (±standard deviations) observed on individual cruises taken on the continental shelf. Concentrations are reported mg m^{-2}.

CRUISE	SAMPLING AREA	WET WEIGHT	DRY WEIGHT	TOLUENE EXTRACTABLE LIPID
N881(A)	Standard Northern Transect	1.38±3.10	1.09±2.17	0.80±1.56
N881(B)	Mississippi Delta Region	0.16±0.50	0.10±0.31	0.07±0.22
S981	Standard Southern Transect	0.02±0.05	0.01±0.02	0.01±0.02
FB1081	Florida Bay and Northside of Florida Keys	0.00±0.00	0.00±0.00	0.00±0.00
FS1181	Florida Straits and Southside of Florida Keys	2.14±2.71	1.18±1.49	0.82±1.14
N182	Florida Panhandle (Northern Transect)	0.00±0.01	0.00±0.00	0.00±0.00
SE282	Southeast Florida Coast (Miami--Ft. Lauderdale)	0.30±0.28	0.14±0.15	0.13±0.13
S482	Standard Southern Transect	0.38±0.44	0.14±0.20	0.11±0.14
YS582	Yucatan Straits		(No onshore stations)	
S682	Standard Southern Transect	0.00±0.00	0.00±0.00	0.00±0.00
CG782	Central Gulf of Mexico	0.16±0.19	0.04±0.05	0.02±0.03
	OVERALL AVERAGE	0.34±0.98	0.21±0.69	0.14±0.50

TABLE 8. Average pelagic tar concentrations (±standard deviations) observed on individual cruises taken off continental shelf. Concentrations are reported mg m^{-2}.

CRUISE	SAMPLING AREA	WET WEIGHT	DRY WEIGHT	TOLUENE EXTRACTABLE LIPID
N881(A)	Standard Northern Transect	5.83±12.39	3.89±8.48	3.31±7.20
N881(B)	Mississippi Delta Region	0.00±0.00	0.00±0.00	0.00±0.00
S981	Standard Southern Transect	2.25±2.89	0.94±1.58	0.67±0.95
FB1081	Florida Bay and Northside of Florida Keys	(No offshore stations)		
FS1181	Florida Straits and Southside of Florida Keys	4.80±10.10	2.56±5.44	2.43±5.67
N182	Florida Panhandle (Northern Transect)	(No offshore stations)		
SE282	Southeast Florida Coast (Miami--Ft. Lauderdale)	1.12±2.33	0.72±1.52	0.20±0.28
S482	Standard Southern Transect	0.18±0.12	0.03±0.03	0.03±0.03
YS582	Yucatan Straits	0.57±0.52	0.24±0.37	0.18±0.24
S682	Standard Southern Transect	0.12±0.07	0.03±0.03	0.02±0.01
CG782	Central Gulf of Mexico	5.12±9.78	3.00±5.69	1.89±3.98
	OVERALL AVERAGE	2.37±6.20	1.35±3.85	1.00±3.30

Year 1. Stations sampled on the continental shelf during Year 2 showed higher average tar concentrations than on-shelf stations sampled during Year 1 (Table 6). The distribution of pelagic tar in on-shelf and off-shelf stations from each cruise was classified using the scheme of Wong et al. (1976) (Tables 9 and 10 and Figure 5). On-shelf stations were heavily skewed toward zero or trace tar concentrations. Sixty-five percent of the on-shelf stations contained no detectable pelagic tar. Only 8% of the off-shelf stations contained no measurable pelagic tar and showed a normal distribution around medium tar concentrations. Concentrations of pelagic tar were approximately log-normally distributed in the offshore stations based upon wet weights, with the largest fraction of the tar falling in the 0.1 to 1.0 mg m^{-2} w.w. range.

Each pelagic tar sample collected during Year 2 was classified according to the procedure of Wong et al. (1976) and plotted (Figure 6) Contours showing the average distribution of tar observed in neuston tows during Year 1 are also shown in Figure 6. It can be seen that the spatial distribution of tar observed during the two years generally agree quite well. Wet weight concentrations from each tow were averaged to obtain on-shelf and off-shelf concentrations for each cruise transect (Tables 7 and 8). These values were classified using the above procedure and plotted. The data was then smoothed and contoured as for the Year 1 data. The resulting distribution of pelagic tar for Year 2 is shown in Figure 7. Comparing Figure 7 with Figure 3 indicates several similarities in the two-year's data. First, the nearshore stations are quite pristine along the Gulf of Mexico continental shelf from Key West to Louisiana. Second, most of the pelagic tar is found offshore in the proximity of the Gulf Loop Current with the loading of tar apparently following the Loop Current axis in the eastern Gulf. Third, the small finger

TABLE 9. Distribution of pelagic tar in on-shelf neuston tows (using the classification procedure of Wong et al., 1976.)

	NUMBER OF STATIONS WITH FOLLOWING CLASSIFICATION				
CRUISE	O	T	M	H	X
N881(A)	3	1	2	1	0
N881(B)	9	0	0	1	0
S981	5	0	1	0	0
FB1081	17	1	0	0	0
FS1181	0	1	2	1	2
N182	12	2	0	0	0
SE282	0	0	2	0	0
S482	0	1	6	1	0
YS582			(No onshore stations)		
S682	6	0	0	0	0
CG782	3	1	4	0	0
TOTAL	55	7	17	4	2

TABLE 10. Distribution of pelagic tar in off-shelf neuston tows (using the classification procedure of Wong et al., 1976.)

	NUMBER OF STATIONS WITH FOLLOWING CLASSIFICATION				
CRUISE	O	T	M	H	X
N881(A)	2	0	0	0	0
N881(B)	2	0	1	1	2
S981	0	0	3	4	1
FB1081			(No offshore stations)		
FS1181	0	2	2	3	1
N182			(No offshore stations)		
SE282	1	6	2	2	1
S482	0	2	2	0	0
YS582	0	2	6	2	0
S682	0	3	5	0	0
CG782	0	0	4	1	1
TOTAL	5	15	25	13	6

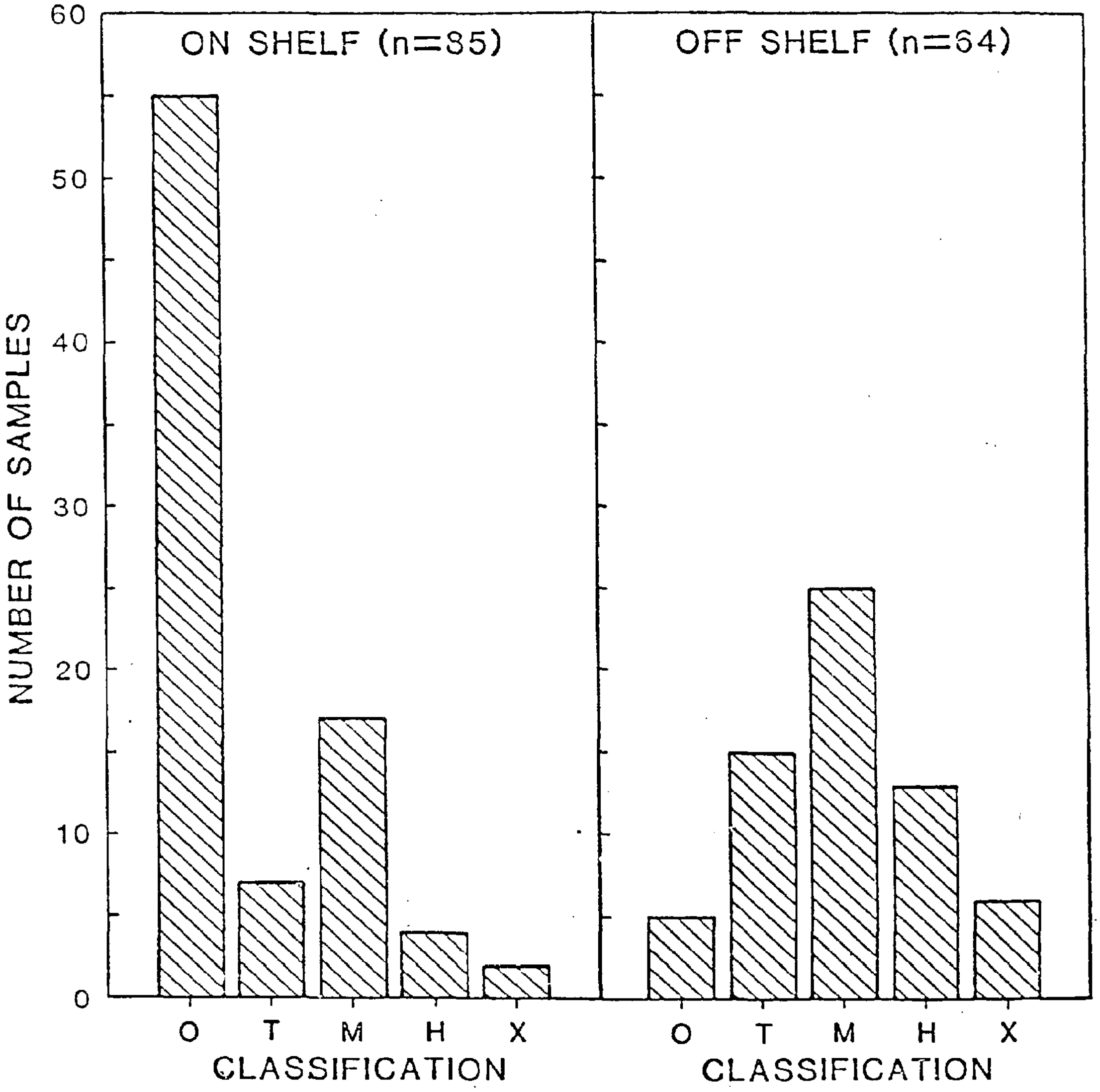


FIGURE 5. Distribution of pelagic tar in on-shelf and off-shelf neuston tows (using the classification scheme of Wong et al., 1976. (n=total number of tows).

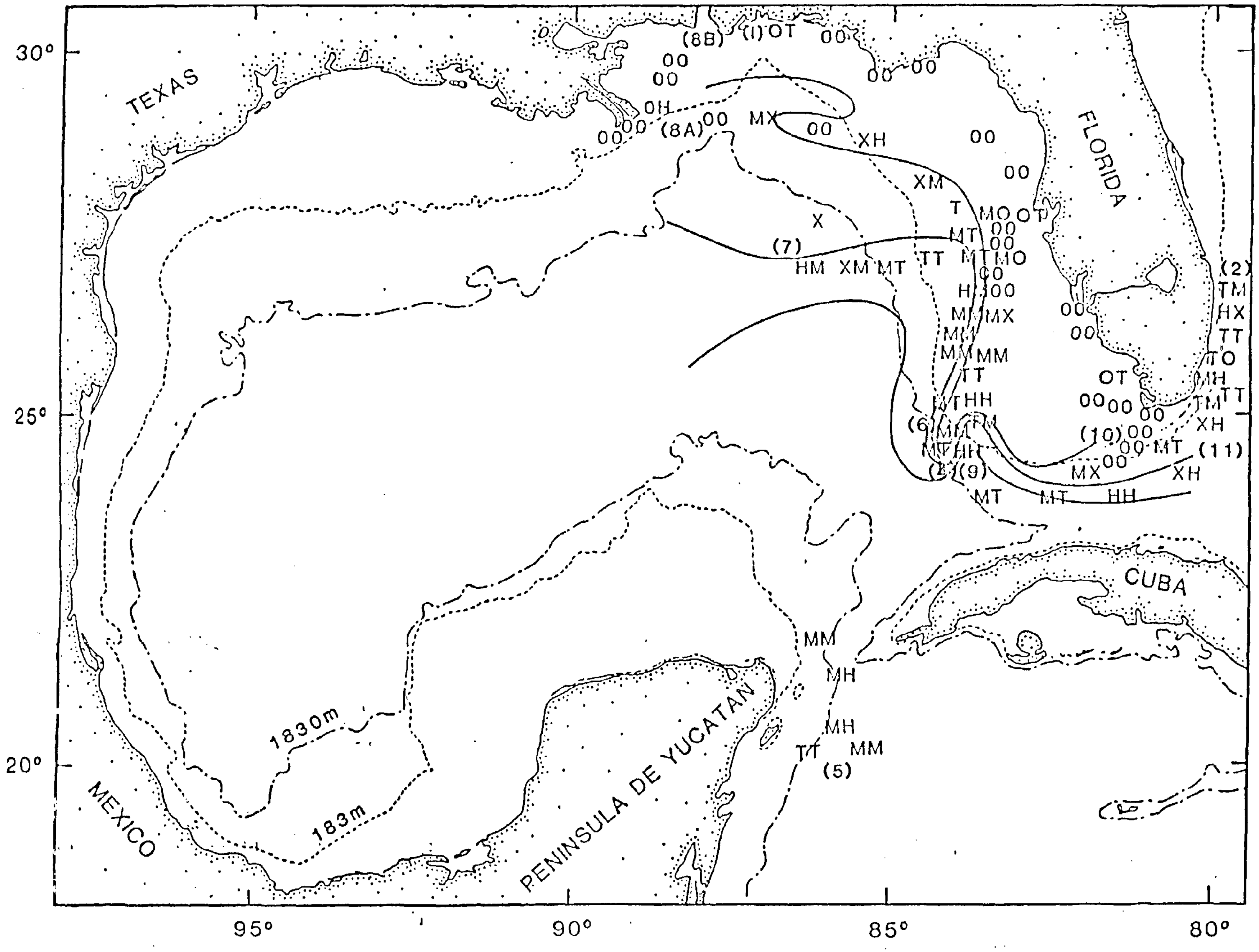


FIGURE 6. Classification of pelagic tar observed during Year 2 (After Wong et al., 1976). Contours show average distribution of tar observed in neuston tows during Year 1.

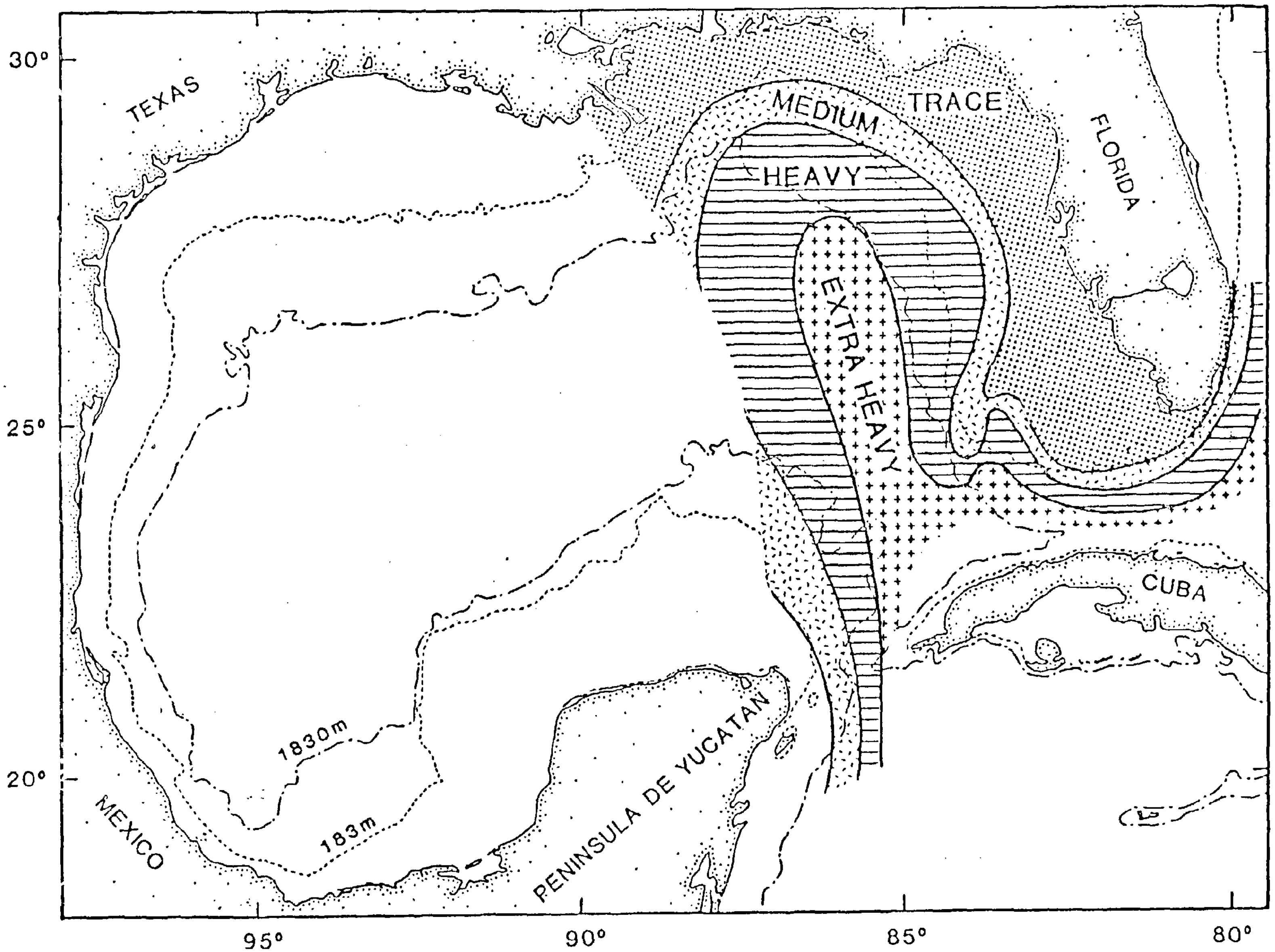


FIGURE 7. Average distribution of surface tar observed in the eastern Gulf of Mexico during Year 2.

of tar seen during Year 1 (~29°N, 86°W, Figure 3) was not seen during Year 2 and is thought to be a short term phenomenon found during Year 1. Fourth, the small finger of tar found at approximately 25°N, 84°W was observed during both years of the study and may represent a permanent feature in the Gulf Loop Current.

Pelagic tar data for Years 1 and 2 have been combined and contoured as above to represent the two-year average of pelagic tar distributions in the eastern Gulf of Mexico (Figure 8). Over the two-year study, concentrations of pelagic tar found in the off-shelf stations were approximately an order of magnitude higher, on the average, than tar concentrations found in continental shelf surface waters (Table 6). The distribution of pelagic tar seen throughout the study was extremely patchy and highly variable. Duplicate tows collected at Station 12 during Cruise N881(A) varied by two orders of magnitude (toluene extractable lipid concentrations: tow 1 = 20.81 mg m^{-2}, tow 2 = 0.16 mg m^{-2}; see Appendix I). Similar patchiness of pelagic tar has been observed in other areas of the world. As a result of this patchiness, there is certainly some overlap in the contours plotted in Figures 7 and 8. Heavy or extra heavy tar concentrations were found in six of the onshore stations during Year 2 (Table 9). The contours shown in Figures 7 and 8 more accurately represent the probability of finding trace, medium, heavy, or extra heavy pelagic tar concentrations in various sectors of the eastern Gulf of Mexico.

We reported during Year 1 that the Gulf of Mexico had approximately the third highest pelagic tar loading of any area in the world (Table 3). Only the Mediterranean Sea and the Sargasso Sea had long term pelagic tar concentrations higher than the Gulf of Mexico. Using the revised two-year average for pelagic tar concentrations in the eastern Gulf of Mexico

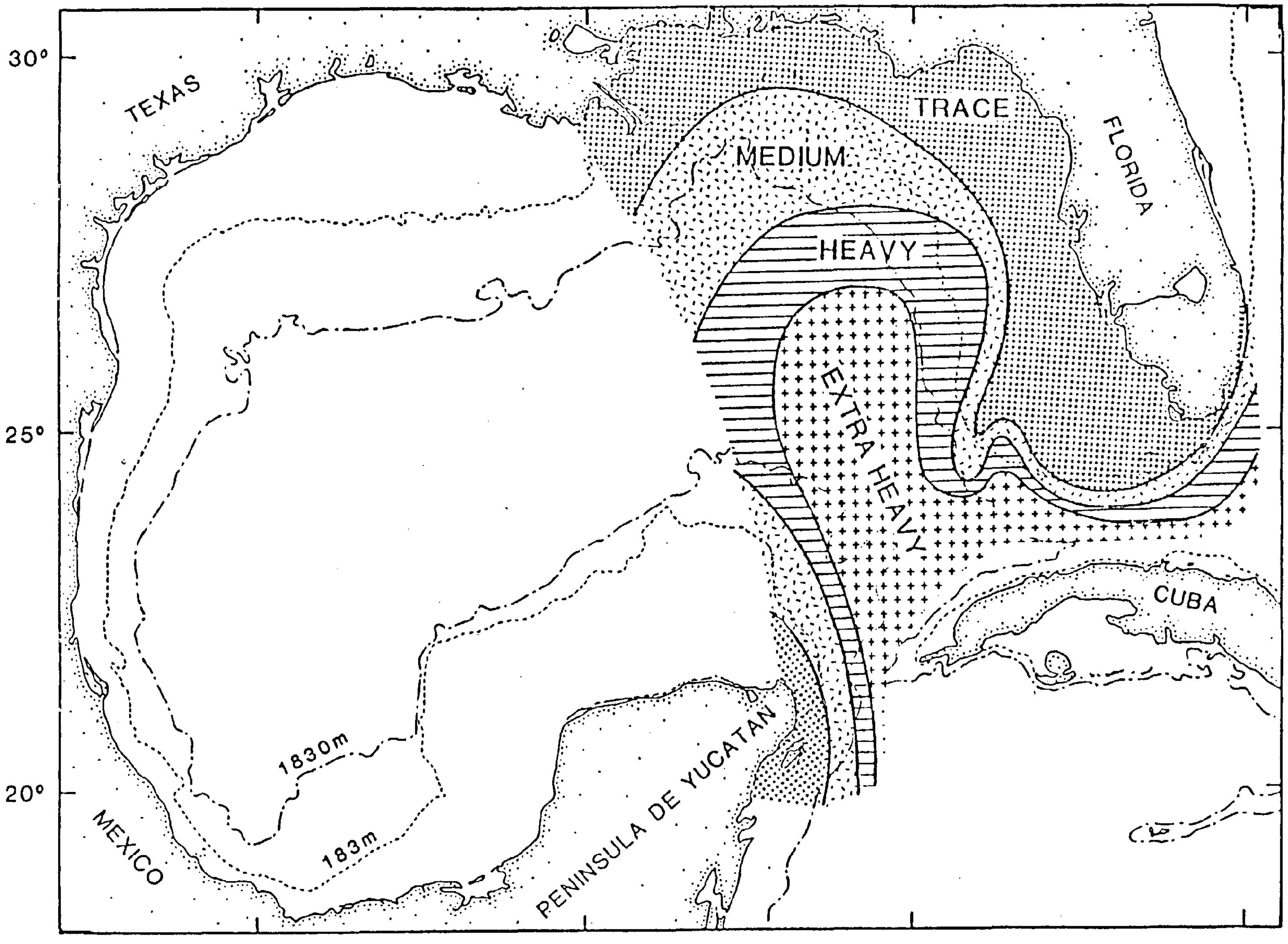


FIGURE 8. Average two-year distribution of surface tar observed in the eastern Gulf of Mexico.

(Table 7), we can see that the average offshore tar concentrations (1.37±2.80 mg m^{-2} t.e.l.) still places the Gulf of Mexico Loop Current as having the third largest loading of pelagic tar reported in long-term studies worldwide (Table 3). The overall average (including both on-shelf and off-shelf stations) tar concentration (0.78±2.66 mg m^{-2} t.e.l.) found during this study are similar to concentrations found in the Caribbean Sea and elsewhere around the Atlantic Ocean (Table 3). The distribution is not uniform in the Gulf of Mexico, however, and due to the association of the tar with the Gulf Loop Current, on the continental shelf waters are quite clean relative to the rest of the world, while off-shelf stations are considerably more contaminated.

During Year 1, we reported an apparent temporal variation in pelagic tar concentrations with the highest concentrations being found in early summer months and decreasing throughout the fall and winter months (Figure 4). This trend could not be investigated during the second summer (1981) due to a gap in project funding. The second year of the project started in August (1981) and continued through midsummer (1982). During this period, the temporal variations seen during Year 1 were not observed (Figure 9). Although the highest tar concentrations collected along the northern transects appeared in August, southern transect cruises showed a tar concentration maximum in November in the Florida Straits. It is possible that these variations are simply the difference in sampling sites and not the time of year. Thus, the temporal variations observed during Year 1 of this study cannot be confirmed, nor denied, from the second year's data.

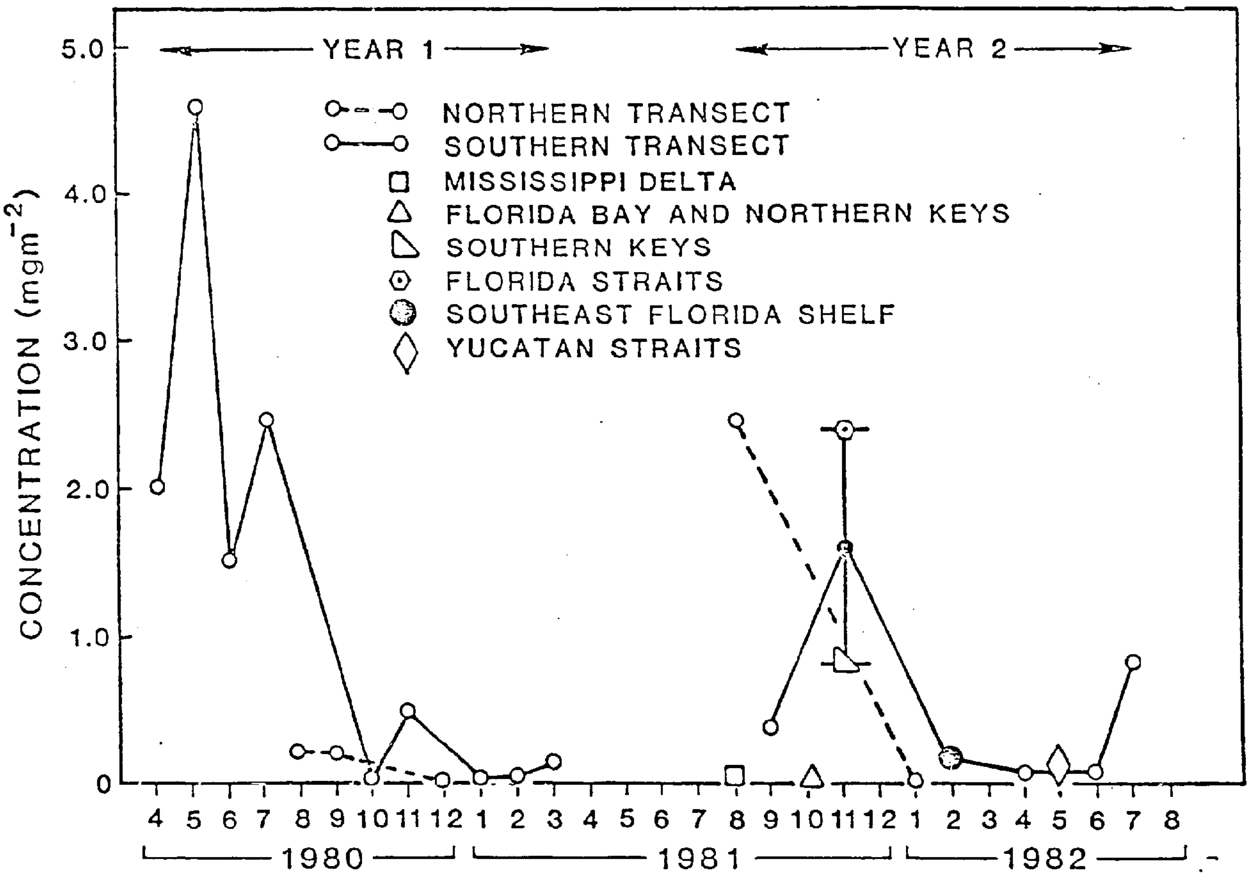


FIGURE 9. Temporal variation of pelagic tar (as to toluene extractable lipid) over two-year study.

Environmentally Sensitive Areas

One major objective of the second year's study was to investigate the pelagic tar burden of certain environmentally sensitive areas around the west coast of Florida. Four specific areas were chosen for study to meet this objective: the Florida Keys, the southeast coast of Florida (Miami-Ft. Lauderdale area), the Florida Panhandle, and Florida Bay. According to the Geo-Marine, Inc. (1980) report, the area of the Florida coastline having the highest probability of being impacted by pelagic tar entrained in the Gulf Loop Current is the southeast coast from Key West to Ft. Pierce. For this reason, pelagic tar was investigated along both sides of the Florida Keys and along the Miami- Ft. Lauderdale area. Cruise FB1081 investigated pelagic tar concentrations along the northern edge of the Florida Keys. Four stations were occupied directly along the Keys in 4 to 8 m of water. No pelagic tar was observed in any of the eight tows (see Appendix I). Cruise FS1181 investigated pelagic tar concentrations along the southern edge of the Florida Keys. Three stations (six tows) were occupied in approximately 10-11 m of water. Trace (0.03 mg m^{-2} w.w.) to extra heavy (5.93 mg m^{-2} w.w.) tar concentrations were observed at these stations. The average tar concentration (2.14±2.71 mg m^{-2} w.w.) found in these six tows represents a heavy tar loading along the southern edge of the Florida Keys. Romero et al. (1981) investigated the concentrations of tar stranded along all Florida beaches and found the heaviest concentrations between Key West and Fort Pierce with the maximum loading being found along the southern edge of the Florida Keys (Figure 10). This data along with our pelagic tar data support the Geo-Marine, Inc. (1980) prediction of pelagic tar entrained in the Loop Current being washed ashore in this area. Stations taken on the north side of the Keys are not affected by the Loop Current circulation, and as a result

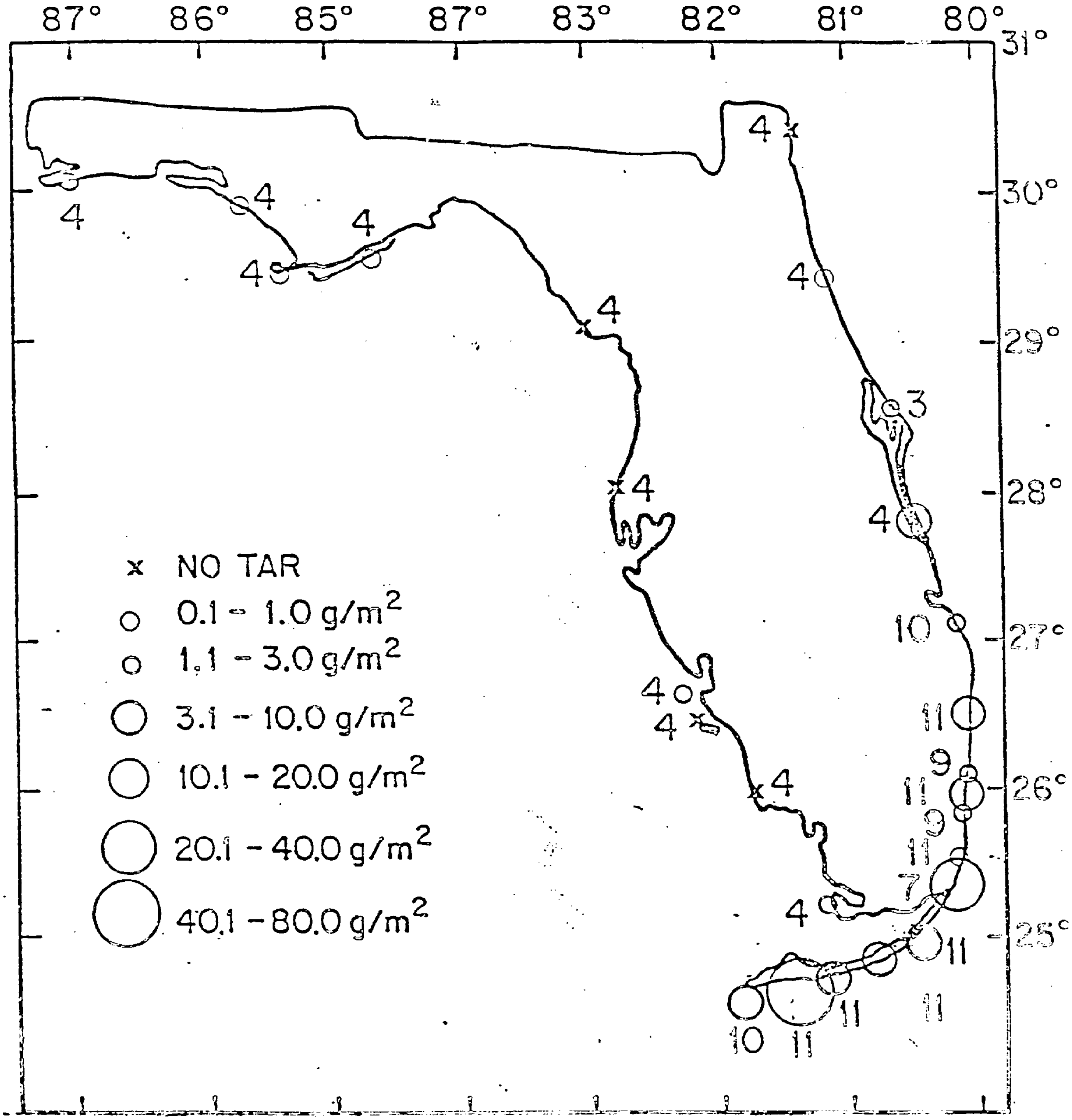


FIGURE 10. Stranded tar on Florida beaches: September 1979 - October 1980 (from Romero et al., 1981). Numbers represent the number of observations at each site.

did not show the high tar concentrations observed along the southern edge. The restricted circulation through the Florida Keys from south to north was reflected in the absence of pelagic tar along the Keys' northern edge.

To further substantiate Loop Current transport of pelagic tar to the southeast Florida coast, Cruise SE282 investigated pelagic tar in the vicinity of Miami-Ft. Lauderdale. Nearshore continental shelf stations sampled on this cruise averaged 0.30±0.28 mg m^{-2} w.w. while slightly more offshore stations averaged 1.12±2.33 mg m^{-2} w.w. (Tables 7 and 8). Although these nearshore stations were generally lower in pelagic tar concentrations than nearshore stations from the Keys' southern edge, the concentrations were higher than in most other nearshore stations located along the west Florida continental shelf. The lateral distribution of tar was also more widespread than in most other areas with pelagic tar being found in thirteen of the fourteen neuston tows. In view of these and earlier findings, it is not unlikely that pelagic tar found in this area originated in the Gulf of Mexico and was transported to the southeast Florida coastal waters by the Gulf Loop Current through the Florida Straits. The pelagic tar data obtained in this study, along with the beach tar data reported by Romero et al. (1981) and the circulation data reported by Geo-Marine, Inc. (1980) present a very complementary picture of the entrainment of pelagic tar by the Gulf Loop Current with subsequent transport to southeast Florida beaches.

Geo-Marine, Inc. (1980) also predicted that the second most likely area of possible impact of pelagic tar transported to Florida beaches by the Gulf Loop Current would be the Panhandle area. To investigate pelagic tar concentrations in this area, Cruise N182 collected samples from seven nearshore stations (fourteen tows) along the Panhandle in 11 to 34 m of water. Visible tar was observed in only two of the fourteen neuston tows. At these two stations, only trace tar concentrations (0.02 mg m^{-2} w.w.; see Appendix I) were observed. Based upon these results, the Florida Panhandle area appears to be as free of pelagic tar contamination as the other coastal waters of western Florida.

The last environmentally sensitive area around Florida's Gulf Coast which was studied during this program was Florida Bay. Florida Bay is an area proposed for future nearshore oil drilling and the need for background hydrocarbon data is essential in order to assess any future impacts due to drilling operations. In addition to the stations occupied along the northern edge of the Florida Keys, five stations (10 tows) were occupied in Florida Bay and along the southwestern Florida continental shelf during Cruise FB1081. Essentially no pelagic tar was observed at any of these stations (Table 8, Appendix I). This exemplifies the pristine nature of this area and suggests that future drilling operations can only have a negative impact on the ecology of Florida Bay with respect to pelagic tar.

Sources and Fates

Another objective of Year 2 was to investigate possible inputs and outputs of pelagic tar in the eastern Gulf of Mexico. In addition to tanker operations, possible inputs to the Gulf include discharge from the Mississippi River, drilling operations around the Gulf, and Loop Current transport of tar from the Caribbean to the Gulf through the Yucatan Straits. Each of these possibilities was investigated during the present study. Discharge of pelagic tar from the Mississippi River was investigated during Cruise N881(B). The plume of Mississippi River water was apparent by the large quantities of estuarine seagrasses which were collected in the nets.

Concentrations of pelagic tar in the Mississippi Delta Region were unexpectedly low. Only one station (16N2) contained measurable quantities of pelagic tar (concentration = 1.58 mg m^{-2} w.w. = 0.70 mg m^{-2} t.e.l.). None of the remaining tows taken in the Mississippi Delta Region contained any measurable pelagic tar.

In addition to investigating pelagic tar being discharged from the Mississippi River, Cruise N881(B) also investigated pelagic tar in the vicinity of oil rigs and drilling platforms in the Delta region. Four of the five stations sampled in this area were located in areas containing high densities of oil rigs. Three of these stations (numbers 15, 16 and 17) contained 15-30 drilling platforms within 2 to 8 miles of the ship. One station (Number 14) had 50 to 100 platforms within 2 to 6 miles of the ship. Of the eight stations sampled in the high platform density areas, only one tow (16N2) contained measurable quantities of pelagic tar (see above and Appendix I). Thus it is unlikely that oil rigs are a primary contributor of pelagic tar to the Gulf of Mexico. This does not imply that they are not discharging other forms of oil to the Gulf. Brooks et al. (1977) have shown that low-molecular-weight hydrocarbons are significantly higher in concentration near oil rigs than in the open Gulf. These volatile hydrocarbons do not form pelagic tar, but are equally hazardous. The results of Cruise N881(B) indicate that continental shelf area around the Mississippi Delta is quite clean with respect to pelagic tar and that the Mississippi River and oil drilling platforms do not appear to be primary contributors of this type of contamination to the eastern Gulf of Mexico.

Another possible source of pelagic tar to the eastern Gulf is by transport of tar from the Caribbean Sea into the Gulf by the Loop Current. Cruise YS582 was designed to investigate the input of pelagic tar to the eastern Gulf through the Yucatan Straits. Eight stations were originally scheduled for the cruise; three were cancelled due to high seas and heavy weather. A total of ten neuston tows were taken in the Yucatan Straits. Concentrations of pelagic tar collected in the Straits ranged from 0 to 0.82 mg m^{-2} t.e.l. with an average of 0.17±0.24 mg m^{-2} t.e.l. (0.57±0.52 mg m^{-2} w.w.). These pelagic tar concentrations are much lower than the values reported by Jeffrey et al. (1974) for the Caribbean (average = 0.74 mg m^{-2} t.e.l., Table 2). During Year 1, we estimated that approximately half of the pelagic tar found in the eastern Gulf of Mexico Loop Current was entering through the Yucatan Straits and about half was entering from local sources in the eastern Gulf. This was based upon the first year's average tar concentration in the Loop Current of 1.60 mg m^{-2} t.e.l. Using the two-year average pelagic tar concentration (1.37 mg m^{-2}, Table 7), the measured value of 0.17 mg m^{-2} for the minimum tar concentration coming through the Yucatan Straits, and Jeffrey et al.'s (1974) value of 0.74 mg m^{-2} for the maximum tar concentration coming through the Straits, we can reestimate the amount transported by the Loop Current as follows.

According to Leipper (1970) and Nowlin (1972), penetration of the Loop Current into the eastern Gulf varies seasonally. Average Loop Current volume through the Yucatan Channel is 25 to 30 x 10^6 m^3 s^{-1}; current velocities at the surface near the edge of the Loop reach 200 cm s^{-1} (Leipper 1970; Jones 1973). The effective depth of the Loop Current roughly coincides with the thermocline depth of 200 m. The only other principal water flow into the Gulf of Mexico is the Mississippi River, which contributes only 0.1% of the volume of the Loop Current (estimated average = 0.07 x 10^6 m^3 s^{-1}; Turekian, 1971; Jones, 1973; LaRock and Bittaker, 1973). Mississippi River water input to the Gulf is considered negligible compared to Loop Current input. Average tar concentration observed in the upper 0.5 m of the Loop Current over the two-year study period was 1.37 mg m^{-2} t.e.l., corresponding to an average surface water concentration of 2.74 mg m^{-3} for the top 50 cm. Quantities of pelagic tar occurring from 50 cm to 200 m are considered negligible based upon Year 1 results. Average surface water discharge (to 50 cm) through the Florida Straits is approximately the same as the input through the Yucatan Channel, i.e., 6.2 to 7.5×10^4 m^3 s^{-1}. Using an average tar concentration of 2.74 mg m^{-3} yields an annual discharge from the Gulf Loop Current to the North Atlantic of 5.4 to 6.5×10^3 tons (average $\cong 6.0 \times 10^3$ t) of pelagic tar. It should be emphasized that this represents a yearly average discharge and does not account for seasonal variations in tar input or Loop Current flow. If we assume that the maximum average concentration of tar coming in through the Yucatan Straits is 0.74 mg m^{-2} (Jeffrey et al. 1974) and the minimum average concentration coming in is 0.17 mg m^{-2} (this study), the average concentration found in the Loop Current during the two-year study (1.37 mg m^{-2}) is approximately 2 to 8 times the amount entering the Gulf via the Yucatan channel, e.g. the input from the Caribbean (0.6 to 2.7×10^3 t yr^{-1}) can account for roughly 10 to 50% of the pelagic tar found in the eastern Gulf of Mexico Loop Current. The remaining tar is assumed to originate from local sources in the Gulf of Mexico.

Discharge of pelagic tar from the eastern Gulf of Mexico to the Atlantic Ocean through the Florida Straits was investigated by examining the nature and distribution of tar found in the Straits during cruise FS1181. Concentrations of pelagic tar collected in the Florida Straits ranged from 0.02 to 16.38 mg m^{-2} t.e.l. with an average of 2.43±5.67 mg m^{-2} (wet weight average = 4.80± 10.10 mg m^{-2}; Table 8, Appendix I). Tar was observed in all eight of the neuston tows collected in the Florida Straits during this cruise. The tar concentrations observed in the Florida Straits was higher than the two-year average concentration (1.37 mg m^{-2} t.e.l.), but may simply reflect the spatial and temporal variation of the tar rather than a build-up of tar in this area. The abundance of tar found in the Straits supports the model of pelagic tar being transported via the Loop Current to the Southeast Florida beaches. Lee (1971) showed that eddies frequently break off of the Loop Current along the southeast Florida coast and move shoreward. An average of four eddies per week were recorded between December 1968 and September 1969, each having an estimated residence time in coastal waters of approximately one week. These eddies are one mechanism for transporting pelagic tar from the Loop Current to Florida Beaches. This transport has also been demonstrated by bottle studies along the southeast coast of Florida (Williams et al., 1977). Further lateral transport studies from the Loop current to the beaches are necessary to confirm this hypothesis.

Chemical Characteristics

In order to differentiate and identify oils of different origin in the sea, the following conditions must exist (Ehrhardt and Blumer, 1972):

(1) Characteristic compositional differences must exist between oils of different origin and/or oils resulting from different refining processes.

(2) Some of these differences must be persistent or undergo predictable changes when exposed to weathering processes in the sea.

(3) It must be possible to distinguish oil pollution from the natural hydrocarbon background.

Initially, evaluating petroleum contamination in an environmental sample, requires differentiation between recently biosynthesized (biogenic) hydrocarbons and petroleum hydrocarbons. A comparison of biogenic and petroleum hydrocarbons shows the following differences which are useful in detecting petroleum contamination in environmental samples (Farrington and Meyers, 1975):

(1) Petroleum contains a much more complex mixture of hydrocarbons with a much greater range of molecular structures and molecular weights than biogenic hydrocarbons. Analysis of marine and terrestrial organisms have shown that most species do not produce more than a few individual hydrocarbons which can easily be separated by gas chromatography.

(2) Petroleum contains many homologous series. Adjacent members of a series usually are present in nearly the same concentration. The 1:1 correspondence of even-and-odd-numbered n-alkanes is an example. In marine organisms, odd carbon-numbered n-alkanes clearly predominate.

(3) Petroleum contains numerous cycloalkanes and aromatic hydrocarbons in comparison with the small number of each class which are characteristic of marine organisms.

(4) Petroleum contains numerous naphtheno-aromatic hydrocarbons which have not been found in marine organisms.

Geochemical processes responsible for crude oil formation also lead to the production of an immense number of individual hydrocarbon types, including many isomers and many different homologous series (Ehrhardt and Blumer, 1972). The composition of each individual type of petroleum reflects the chemistry of its source material as well as time and temperature dependent geochemical subsurface processes that have led to its formation. For certain classes of organic compounds, compositional differences between crude oils are well known. For source identification and differentiation of crude and/or refined oils in the sea, it is necessary to examine these compositional differences by investigating the compounds most resistant to environmental alterations. Once released into the sea, the composition of oil is altered by several modes of degration. Since not all hydrocarbons are affected by the various modes at the same rates, differential weathering occurs for different types of oils.

Much of the early, but definitive, work on weathering of crude oils was conducted by Ehrhardt and Blumer (1972). These authors found the following trends to hold for most crude oils. Early stages of marine weathering of oil are dominated by evaporation and dissolution, resulting in a rapid loss of lower molecular weight n-alkanes, isoalkanes, cycloalkanes, and aromatics up to about C_{14}. After the initial rapid loss of lower molecular weight components, dispersion (propulsion of oil droplets into the water column by breaking waves) microbial and chemical (photo/autooxidation) degradation and sedimentation become the dominating processes in determining the fate of the residual oil. Chemical degradation is not well understood but may approach microbial degradation in importance. During microbial degradation, normal alkanes are degraded first, followed by isoalkanes, cycloalkanes and aromatics. The ratios of n-alkanes to isoprenoid compounds (i.e., nC_{17}/pristane and nC_{18}/phytane) are among the most diagnostic characteristics of microbial degradation of crude oil residues. The critical factor in applying these generalizations to the weathering of a specific oil is in understanding the rates at which these processes are occurring.

In addition to the gravimetric data discussed above, detailed analytical work was conducted on the pelagic tar samples using state-of-the-art techniques. The techniques used to investigate the chemistry of the pelagic tar included isotope-ratio mass spectrometry (IRMS), glass capillary gas-liquid chromatography (GLC) and combined high resolution gas chromatography-mass spectrometry (GCMS). Since there were likely to be several sources, as well as several transport and weathering mechanisms, for the pelagic tar, the average values found for each chemical parameter are not indicative of the wide variety of tars present (Tables 11 and 12). This is apparent from the large standard deviation for each chemical parameter.

Stable carbon isotopic composition of naturally occurring carbonaceous materials gives information about sources, maturation processes, and pathways of carbon. Over the past few years, there has been increased use of this parameter in characterizing natural gases, oils and coals. These studies have been reviewed in papers by Fuex (1977) and Stahl (1977), and demonstrate that this area of science is well developed and ideally suited for characterization of insoluble petroleum residues found on and in the ocean.

Crude oils exhibit a wide range of characteristic $\delta^{13}C_{PDB}$ values (-22°/₀₀ to -35°/₀₀) that can often be used to differentiate various crude oil types (Kvenvolden and Squires 1967; Degens 1969; Stahl 1977). Considerable background information in this area has been published by Silverman (1968)(Figure 11). This figure shows the distribution of 30 crude oils produced along the Gulf Coast, oil like material in a core taken on Challenger Knoll (about 3600 m depth) in the central Gulf of Mexico and two samples of tar collected in South Texas in 1970 and 1971. These last two samples were analyzed by one of the principal investigators (WMS) while at Texas A & M University. The latter two samples were considerably different

TABLE 11. Summary of chemical data (excluding GCMS data) for pelagic tar samples collected during Year 2 of the study.

Parameter Measured	Mean ± Standard Deviation	Range
Extractable lipid (% of dry weight)	75±25	9-100
Hydrocarbon lipid (% of dry weight)	48±29	0-100
Hydrocarbon lipid (% of extractable lipid)	63±29	0-100
$\delta^{13}C_{PDB}$ total tar (°/₀₀)	-27.1±1.0	-30.1 - -23.5
$\delta^{13}C_{PDB}$ aliphatic (F1) hydrocarbons (°/₀₀)	-27.2±1.0	-30.2 - -23.5
$\delta^{13}C_{PDB}$ aromatic (F2) hydrocarbons (°/₀₀)	-26.9±1.0	-29.3 - -23.9
Aliphatic hydrocarbons (mg m^{-2})	0.20±0.78	0-5.51
Aromatic hydrocarbons (mg m^{-2})	0.09±0.35	0-2.84
Aliphatic + aromatic hydrocarbons (mg m^{-2})	0.29±1.08	0-8.02
Aliphatic/aromatic	2.22±3.14	0-18.00
Aliphatic % resolved by GLC	51±16	9-89
Aliphatic % unresolved by GLC	49±16	11-90
Aromatic % resolved by GLC	48±21	14-89
Aromatic % unresolved by GLC	52±21	11-86
nC_{17}/pristane	1.54±0.59	0.23-3.09
nC_{18}/phytane	2.06±0.96	0.26-6.36
Pristane/phytane	1.18±0.61	0.35-3.69

TABLE 12. Summary of GCMS data for pelagic tar samples collected during Year 2 of the study. (CRTP = concentration relative to phenanthrene, N = naphthalene, P = phenanthrene, D = dibenzothiophene, C_1 = methyl, C_2 = dimethyl + ethyl, C_3 = trimethyl + (ethyl + methyl) + propyl).

Parameter Measured	Mean ± Standard Deviation	Range
Naphthalene (CRTP)	20.2±41.4	0-196.4
C_1 - Naphthalene (CRTP)	21.1±45.3	0-177.0
C_2 - Naphthalene (CRTP)	49.4±99.8	0.1-368.9
C_3 - Naphthalene (CRTP)	45.2±61.2	0.1-265.3
Phenanthrene (CRTP)	1.0±0.0	-
C_1 - Phenanthrene (CRTP)	17.3±12.1	1.6-54.7
C_2 - Phenanthrene (CRTP)	98.7±101.2	7.3-447.1
C_3 - Phenanthrene (CRTP)	58.7±81.0	4.4-469.6
Dibenzothiophene (CRTP)	0.5±0.4	0.1-1.8
C_1 - Dibenzothiophene (CRTP)	9.1±6.3	0.5-23.5
C_2 - Dibenzothiophene (CRTP)	90.0±114.4	2.2-520.6
C_3 - Dibenzothiophene (CRTP)	68.5±125.8	0.8-667.4
$(C_1P+C_2P+C_3P)/P$	174.8±174.8	13.6-898.0
$(C_1D+C_2D+C_3D)/D$	529.4±550.0	5.0-1977.0
C_1P/C_1D	3.9±5.7	0.4-30.6
C_2P/C_2D	2.2±2.5	0.1-10.1
C_3P/C_3D	2.3±3.5	0.1-18.9

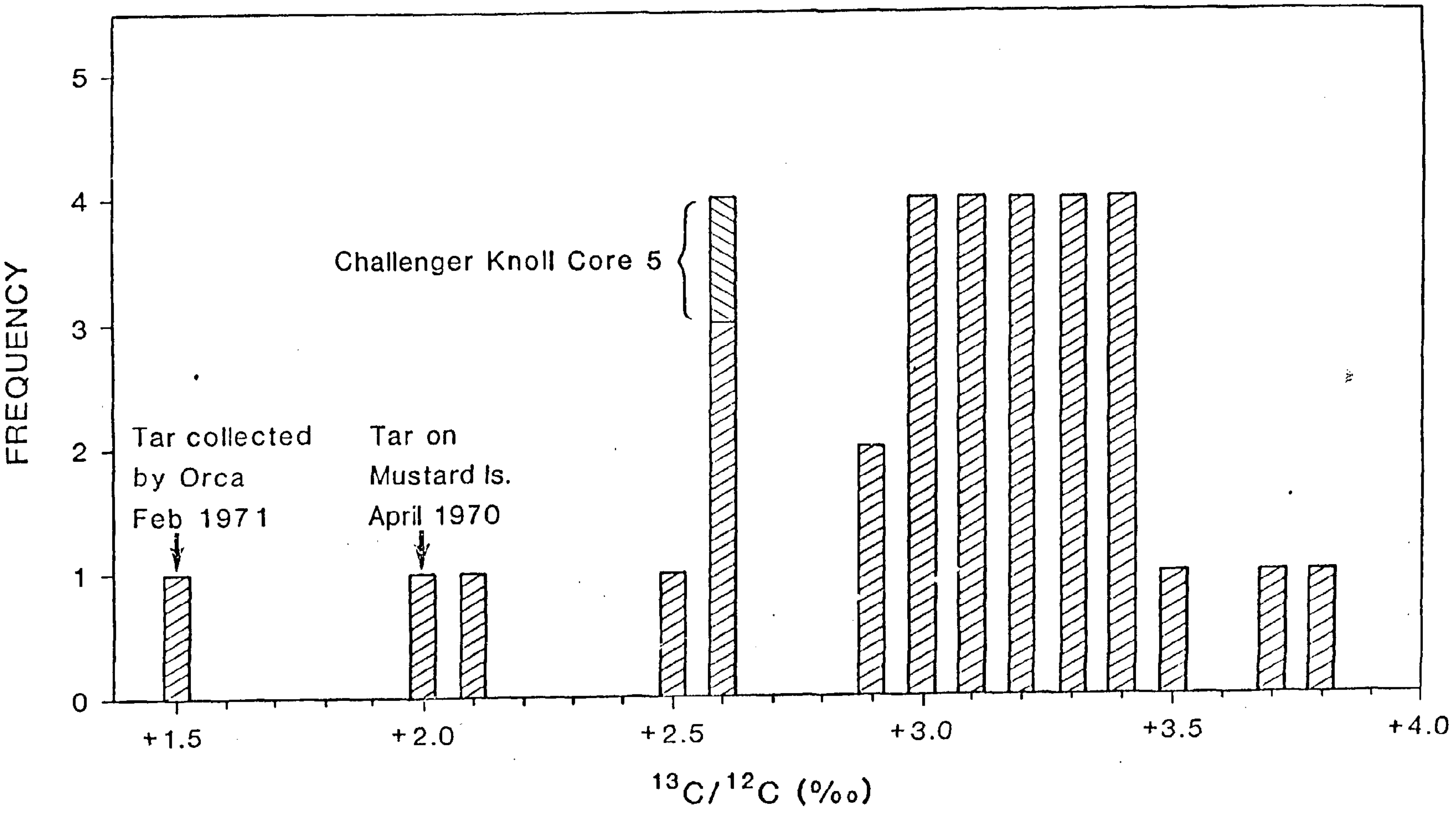


FIGURE 11. C^{13}/C^{13} ratio in organic extract from Challenger Knoll (Sigsbee) Core No. 5 and thirty other Gulf Coast crude oils (Miocene) (from Silverman, 1968).

than oils produced along the northern Gulf Coast. It was believed that they originated either from illegal tanker discharges of oil shipped in from other producing areas or more likely from oil produced along the Mexican coast near Tampico, Mexico. Thus, crude oils from different parts of the Gulf of Mexico may be differentiated based upon their isotopic carbon composition. $\delta^{13}C_{PDB}$ values of the aliphatic and aromatic fractions of crude oils also vary between oils, and can be used in conjunction with the $\delta^{13}C_{PDB}$ value for the whole oil to give a more sensitive indicator of crude oil source.

In the present study, stable carbon isotope values were measured on the total tar sample plus the aliphatic (F1) and aromatic (F2) fractions to minimize the problems associated with differential weathering and solution during transport through the eastern Gulf. Stable carbon isotopic values for the total tar samples analyzed during Year 2 averaged -27.1°/₀₀ with the F1 fractions averaging -27.2°/₀₀ and the F2 fractions averaging -26.9°/₀₀ (Table 11). For the entire two-year study, the $\delta^{13}C_{PDB}$ of the total tar averaged -27.2°/₀₀ with aliphatic fractions averaging -27.3°/₀₀ and aromatic fractions averaging -27.0°/₀₀. These values are similar to those measured during each year with the $\delta^{13}C_{PDB}$ values for the F1 fractions generally being more negative than the F2 fractions and the total tar samples having intermediate $\delta^{13}C_{PDB}$ values. Although this trend was generally observed during the study, it did not hold for all samples. These samples could easily be distinguished from the rest of the pelagic tar based upon their unusual $\delta^{13}C_{PDB}$ values.

The use of $\delta^{13}C_{PDB}$ values for distinguishing pelagic tar samples is considerably enhanced when other chemical parameters are measured and used in conjunction with the $\delta^{13}C_{PDB}$ values. The more parameters that are measured on a given sample, the more specific the "fingerprint" of that sample becomes. The molecular nature of the tar samples, as measured by GLC and GCMS, can be used with the stable carbon isotopes to provide a much more detailed set of parameters for distinguishing specific crude oil residues.

Total aliphatic (F1) hydrocarbons averaged 0.20 mg m^{-2} while the aromatic hydrocarbons averaged 0.09 mg m^{-2}. This gives a total average hydrocarbon concentration (F1 + F2) of 0.29 mg m^{-2} with an aliphatic/aromatic ratio of 2.2 (Table 11). Total hydrocarbon material (F1 + F2) comprised an average of 63% of the toluene extractable lipid and 48% of the tar's dry weight (Table 11). The roughly 27% of the lipid extract that is not pure hydrocarbon material is primarily polar pigment-type compounds that are not removed from the chromatographic column during solvent elution. These include hetero-atomic species containing nitrogen and sulfur as well as porphyrin and carotenoid-type complexes commonly found in crude oils. The remaining portion of the tar's dry weight contains toluene insoluble components such as inorganic material, asphaltenes and other insoluble organic residues.

Both the aliphatic and aromatic fractions were made up of approximately 50% resolved and 50% unresolved components as measured by GLC (Table 11). These values are not statistically different from the values measured during Year 1. Reproducibility of this parameter, however, is low and its use is not recommended for definitive classification of pelagic tar. In the case of the aliphatic (F1) fraction, the unresolved components consisted of numerous cyclic and naphthenic compounds, while the resolved components were primarily saturated alkanes (including normal, branched, and isoprenoid hydrocarbons). In the aromatic (F2) fraction, the unresolved components consisted primarily of naphtheno-aromatic compounds plus various aromatic and heterocyclic ringed structures. The resolved components in the F2 fraction consisted primarily of the parent aromatic hydrocarbons plus their numerous alkylated homologs.

One of the most diagnostic sets of molecular parameters used to differentiate crude oil sources and weathering processes at sea are the normal and isoprenoid alkane distributions. During Year 2 eight crude and refined oils were reanalyzed by GLC (Figures 12-19). These oils included South Louisiana crude, IXTOC-I crude, Kuwait crude, Alaskan crude, Leona crude, Venezuelan crude, No. 2 fuel oil and Bunker C (No. 6) fuel oil. The relationship between the resolved components of these chromatograms can be used to help differentiate crude oils and crude oil residues found at sea. Diagnostic parameters measured during the present study include n-alkane range, n-alkane maximum, nC_{17}/pristane, nC_{18}/phytane, and pristane/phytane. As can be seen from Figures 12-19, the n-alkane range for most crude oils extends from C_{11} to C_{34}. Refined oils, however, show a much narrower boiling range. No. 2 fuel oil contains n-alkanes ranging from approximately nC_{10} to nC_{22} (n-alkane maximum = nC_{14}; Figure 18) while the n-alkanes in No. 6 fuel oil range from about nC_{15} to nC_{29} (n-alkane maximum = nC_{22}; Figure 19). Given the weathering patterns discussed above, it is relatively simple to distinguish refined oils such as No. 2 or No. 6 from crude oils. No. 2 fuel oil is a mixture of light boiling components and does not readily form pelagic tar particles. No. 6 fuel oil is heavier and more viscous and is capable of forming tarballs.

Pelagic tar found at sea with a narrow boiling range and n-alkane distribution similar to No. 6 fuel oil (or similar refined oil) can be assumed to have come from tanker operations. Crude oils do not resemble refined oils chemically nor do transport paths exist for transporting large quantities of these refined oils from land to the open Gulf (since the Mississippi River did not appear to be a major transport mechanism). Tanker operations can be implicated in other ways by examining the molecular

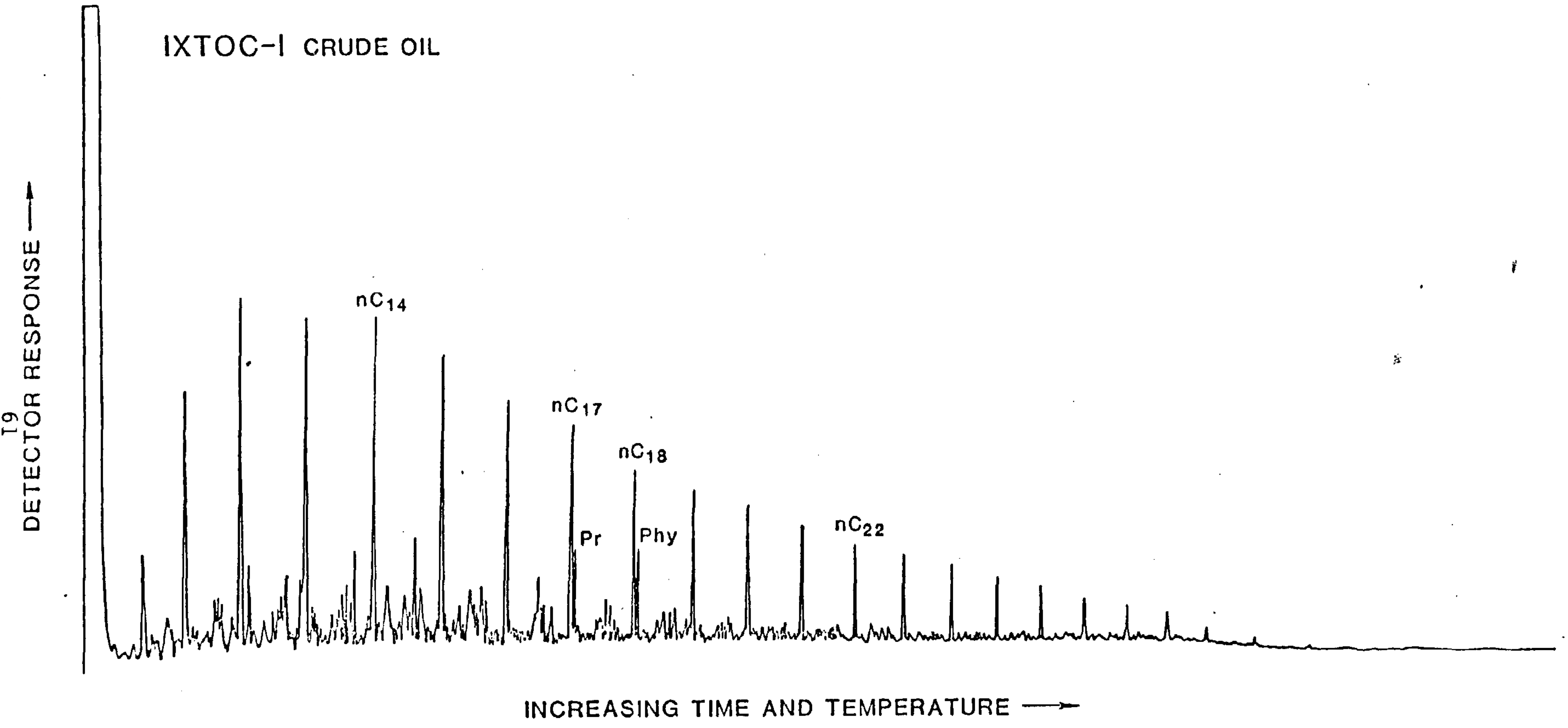


FIGURE 12. Gas chromatogram of IXTOC-I crude oil. Chromatographic conditions given in text.

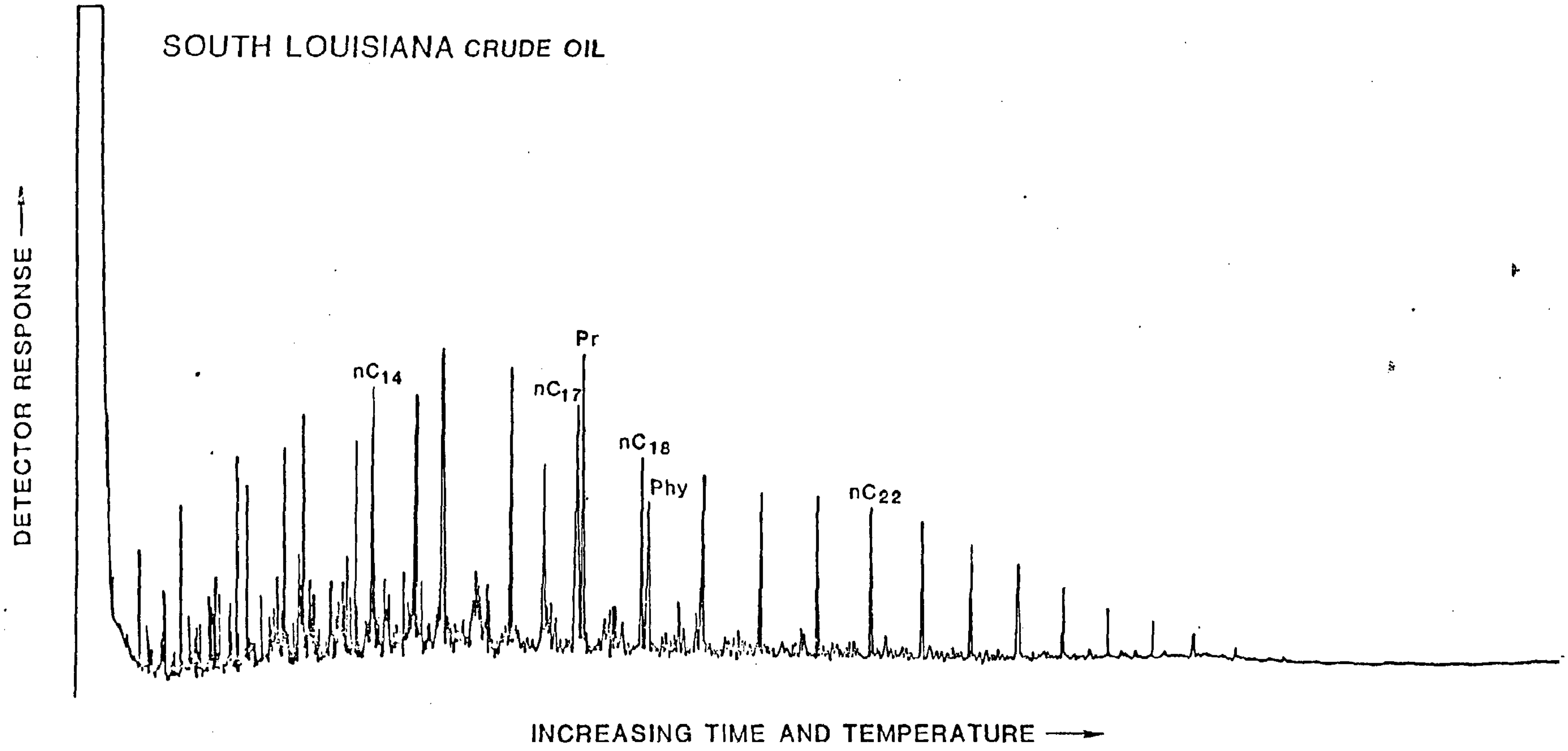


FIGURE 13. Gas chromatogram of South Louisiana crude oil. Chromatographic conditions given in text.

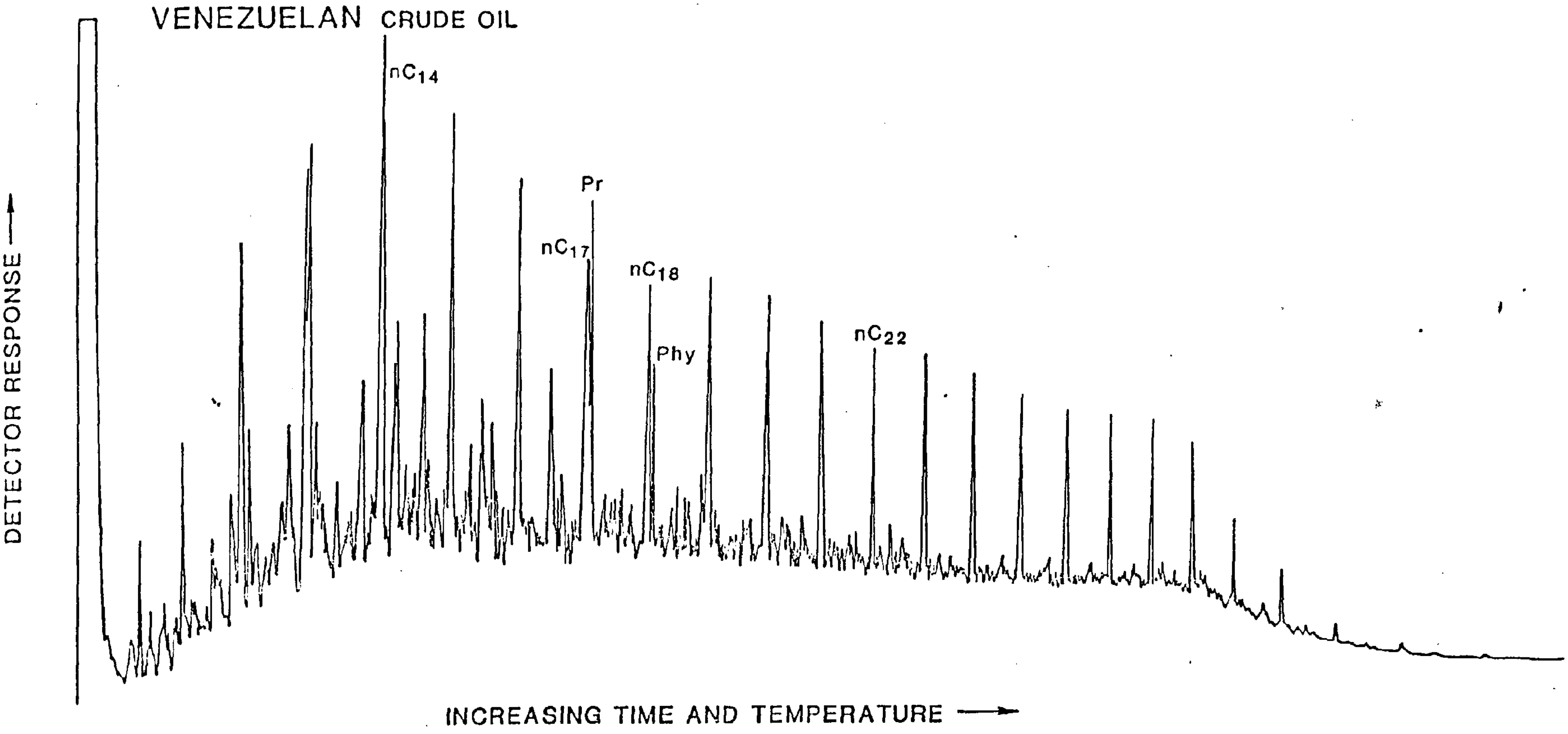


FIGURE 14. Gas chromatogram of Venezuelan crude oil. Chromatographic conditions given in text.

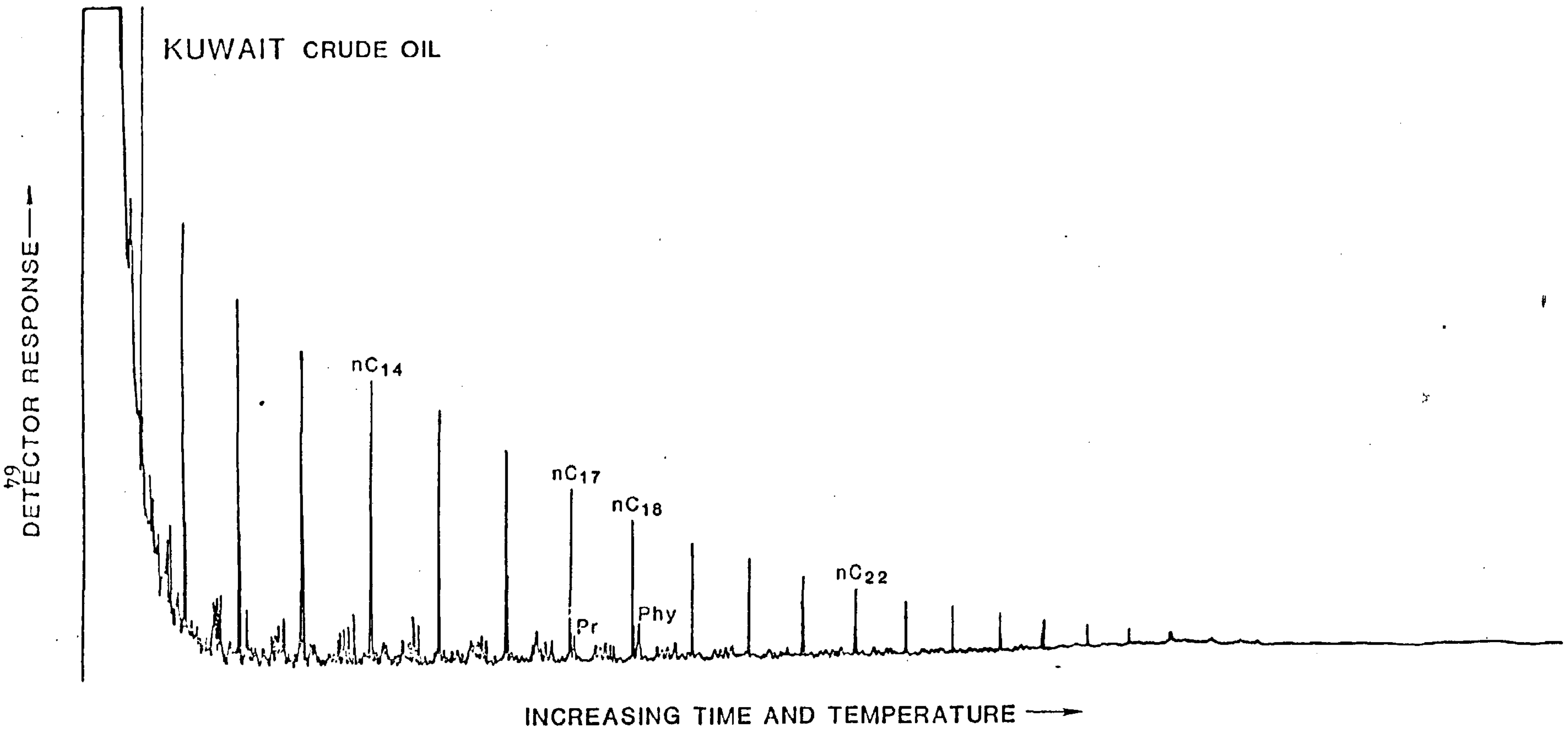


FIGURE 15. Gas chromatogram of Kuwait crude oil. Chromatographic conditions given in text.

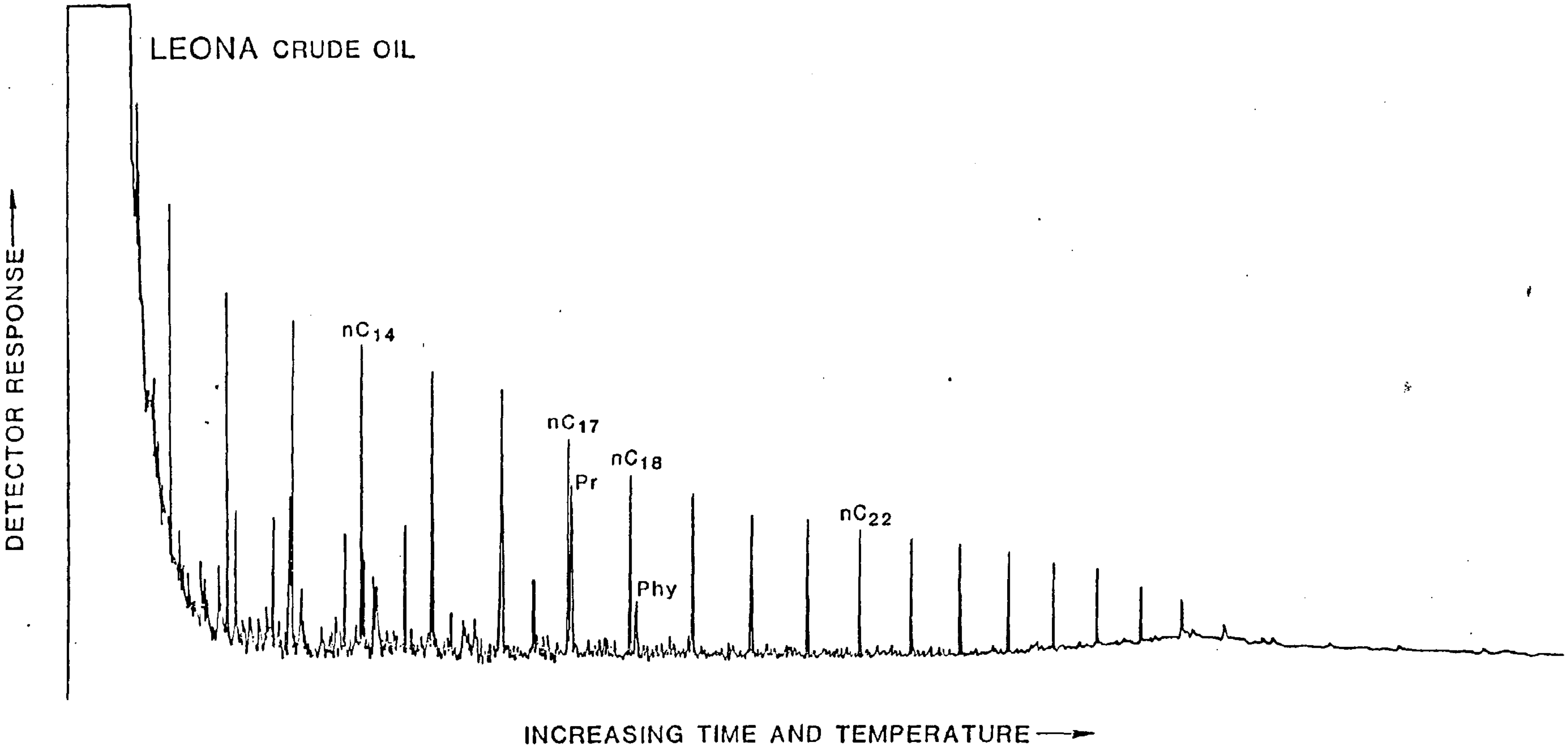


FIGURE 16. Gas chromatogram of Leona crude oil. Chromatographic conditions given in text.

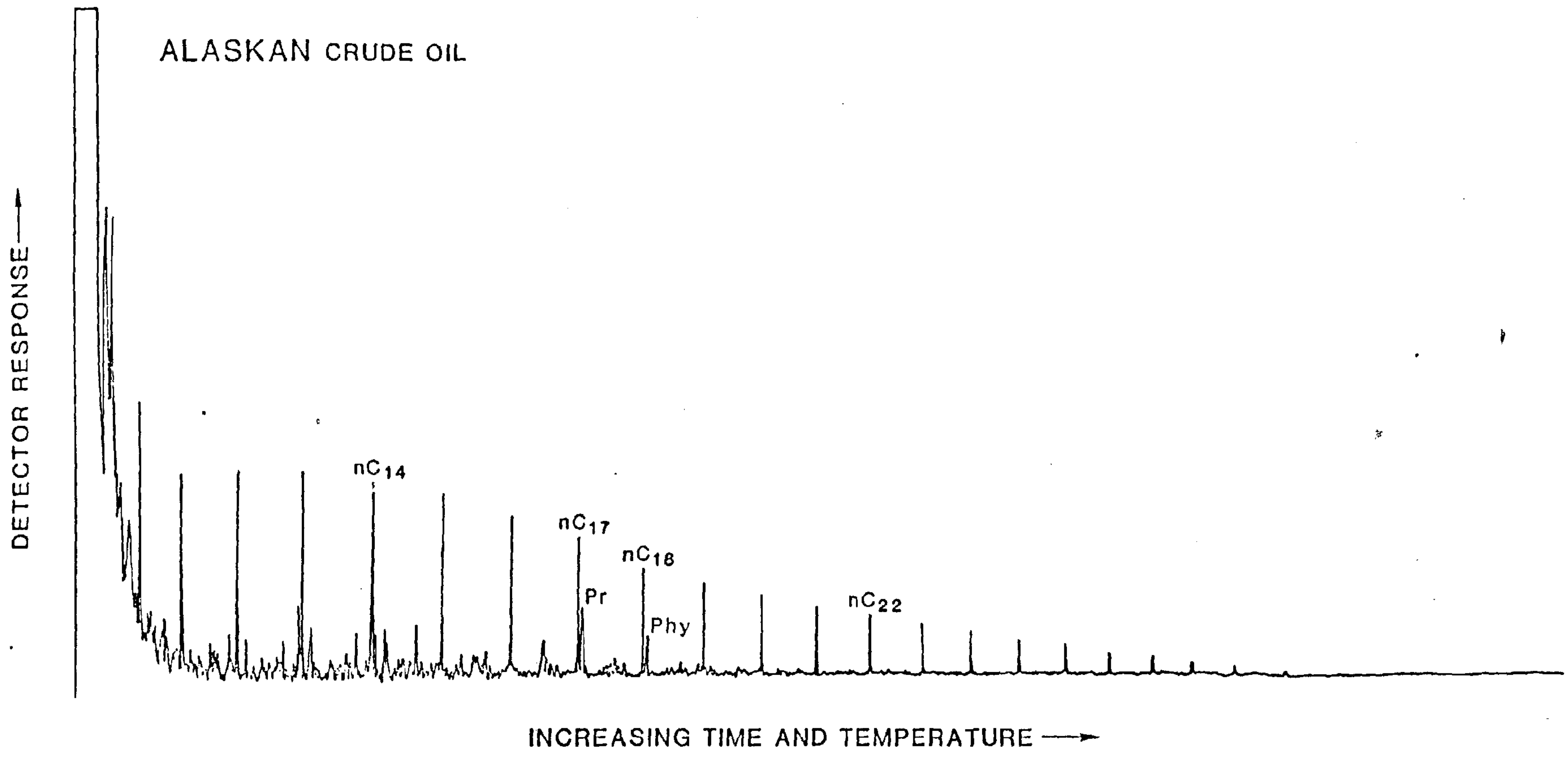


FIGURE 17. Gas chromatogram of Alaskan crude oil. Chromatographic conditions given in text.

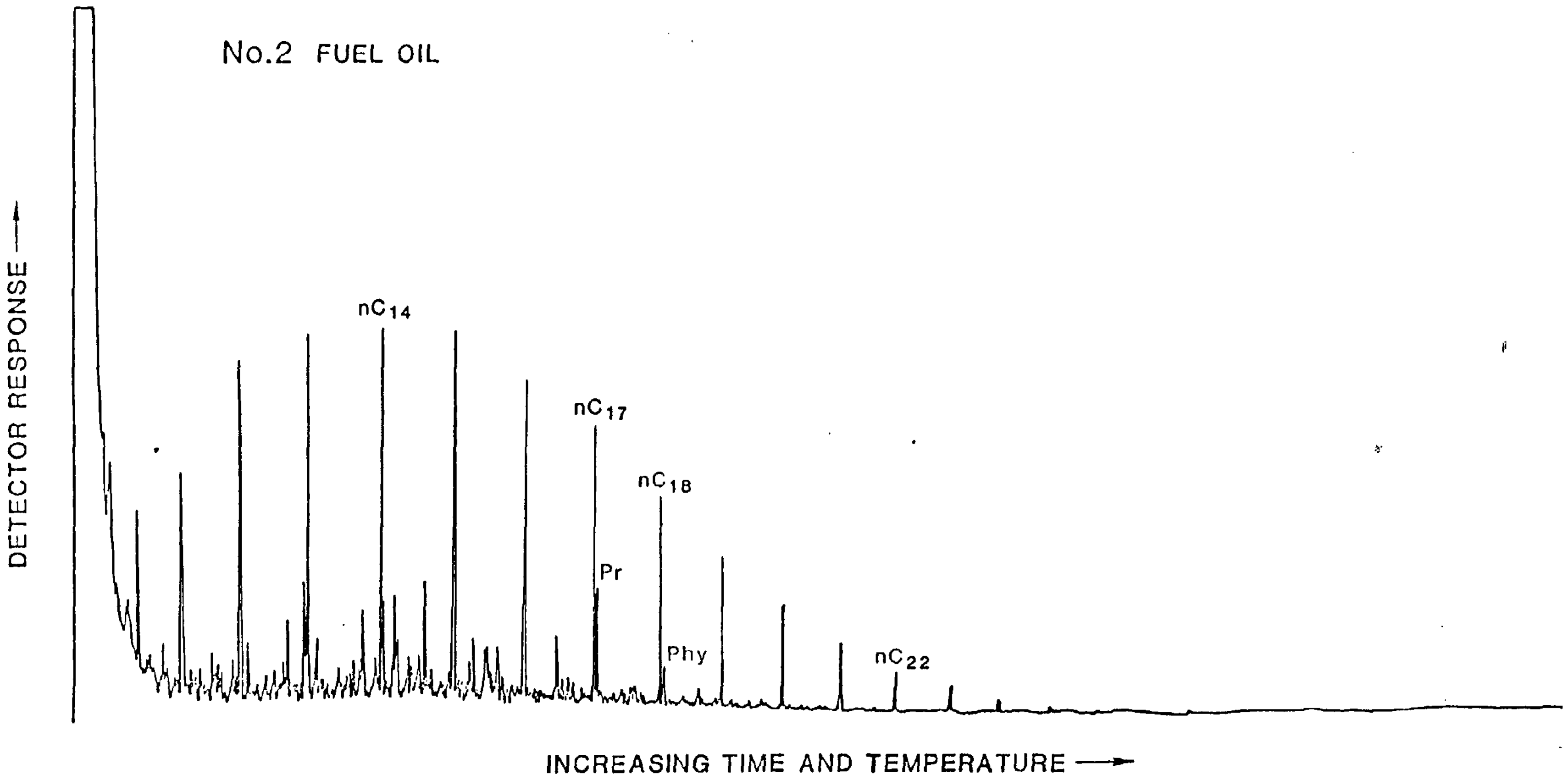


FIGURE 18. Cas chromatogram of No. 2 fuel oil. Chromatographic conditions given in text.

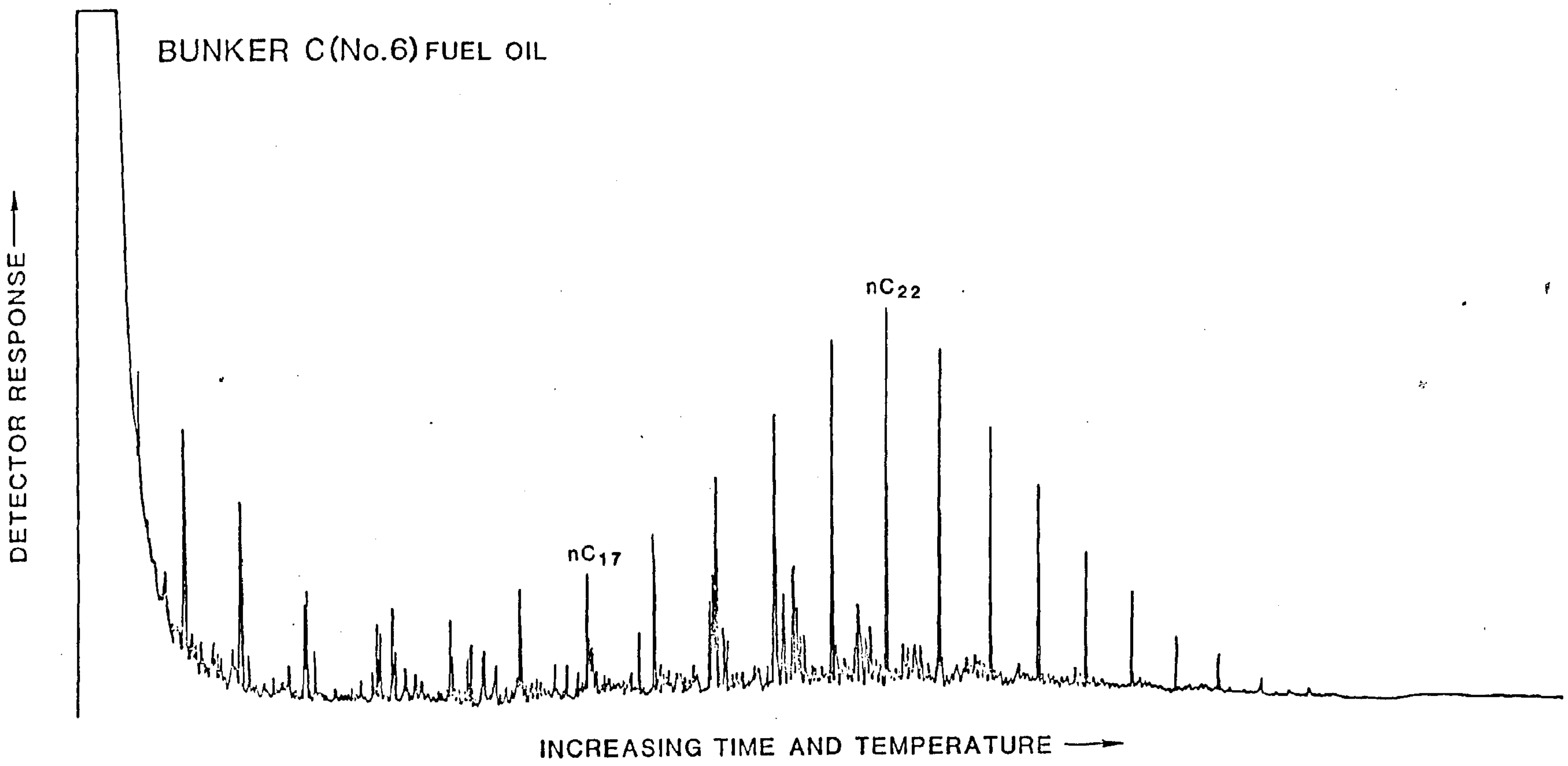


FIGURE 19. Gas chromatogram of Bunker C (No. 6) fuel oil. Chromatographic conditions given in text.

composition of pelagic tar. According to Butler et al. (1973) crude oil sludge (i.e., tanker wall washings) is characterized by a bimodal distribution in the envelope of n-paraffin peaks. The crude and refined oils shown in Figures 12-19 show a unimodal n-paraffin distribution. The bimodal distribution arising from tanker discharge results from the differential condensing of heavier n-alkanes out of the warm crude oil as it is pumped out of the drilling rigs and onto the crude oil tankers. The cold seawater surrounding the tankers causes the more viscous components of the oil to condense onto the tanker walls. This results in the enrichment of the crude oil by the heavier boiling components and leads to a bimodal n-alkane distribution. After unloading the bulk of their crude oil cargo into processing or storage facilities on shore, tankers use seawater to wash down the walls of their holding tanks. International regulations (OILPOL 54/69, MARPOL 73/78; NAS 1983) prohibit discharge of the resulting oil-water mixture at sea. According to regulations, tankers must use the "Load-on-Top" (LOT) procedure for cleaning the holds. Seawater used to wash holding tank walls must be allowed to stand in order for the water-oil mixture to separate. The oily surface mixture is then allowed to collect in overflow tanks where it must remain on board until it can be discharged into a holding facility on shore. The subsurface water can then be pumped out if the maximum amount of oil discharged is less than 1/30,000 of the total cargo carrying capacity. Although the international regulations have been in effect for more than a decade, enforcing the regulation is difficult on the open seas. As a result, the discharge of oily water by tankers is still common. According to Butler et al. (1973) the bimodal n-alkane distribution of pelagic tar resulting from these operations shows one n-alkane maximum at approximately nC_{17} and a second n-alkane maximum at approximately nC_{29}. During the present study, approximately 47% of the pelagic tar samples analyzed by gas chromatography showed either a bimodal n-alkane distribution or a unimodal n-alkane distribution with a narrow n-alkane range and an n-alkane maximum occurring above nC_{24}. Figure 20 shows an example of the bimodal n-alkane distribution characteristic of the former type of tar samples. The latter type of tar samples are similar to the heavy refined oils as discussed above (e.g. no. 6 Fuel oil). Each of these types of n-alkane distributions in pelagic tar collected in the open Gulf are indicative of tanker discharges. This data suggests that approximately half of the pelagic tar observed in the present study originated from tanker operations.

The remaining portion of the tar may or may not have originated from tanker operations. Bulk crude oil discharged directly from tanker holds would not be expected to be depleted substantially in the heavier n-alkanes since the volume of bulk oil in the holds is much greater than the volume adhering to the holding tank walls. This oil would produce a gas chromatogram with a unimodal n-alkane distribution similar to crude oils. Another possible source of this oil is from natural seeps of crude oil coming out of the bottom. There is little evidence for natural oil seeps in the eastern Gulf of Mexico (Geyer and Giammona, 1980). All natural seeps thus far reported for the Gulf are found in the western portions of the Gulf. Natural seeps have also been reported for the Caribbean sea. Therefore, this type of oil could possibly have originated in the Caribbean and then have been transported into the Gulf through the Yucatan Straits. Koons and Monaghan (1973) used gas chromatography and isotopic characterization to analyze pelagic tar collected off the coast of Texas. These authors suggest that most of the tar that they analyzed in the western Gulf was derived from natural seeps. Based upon the surface circulation patterns previously

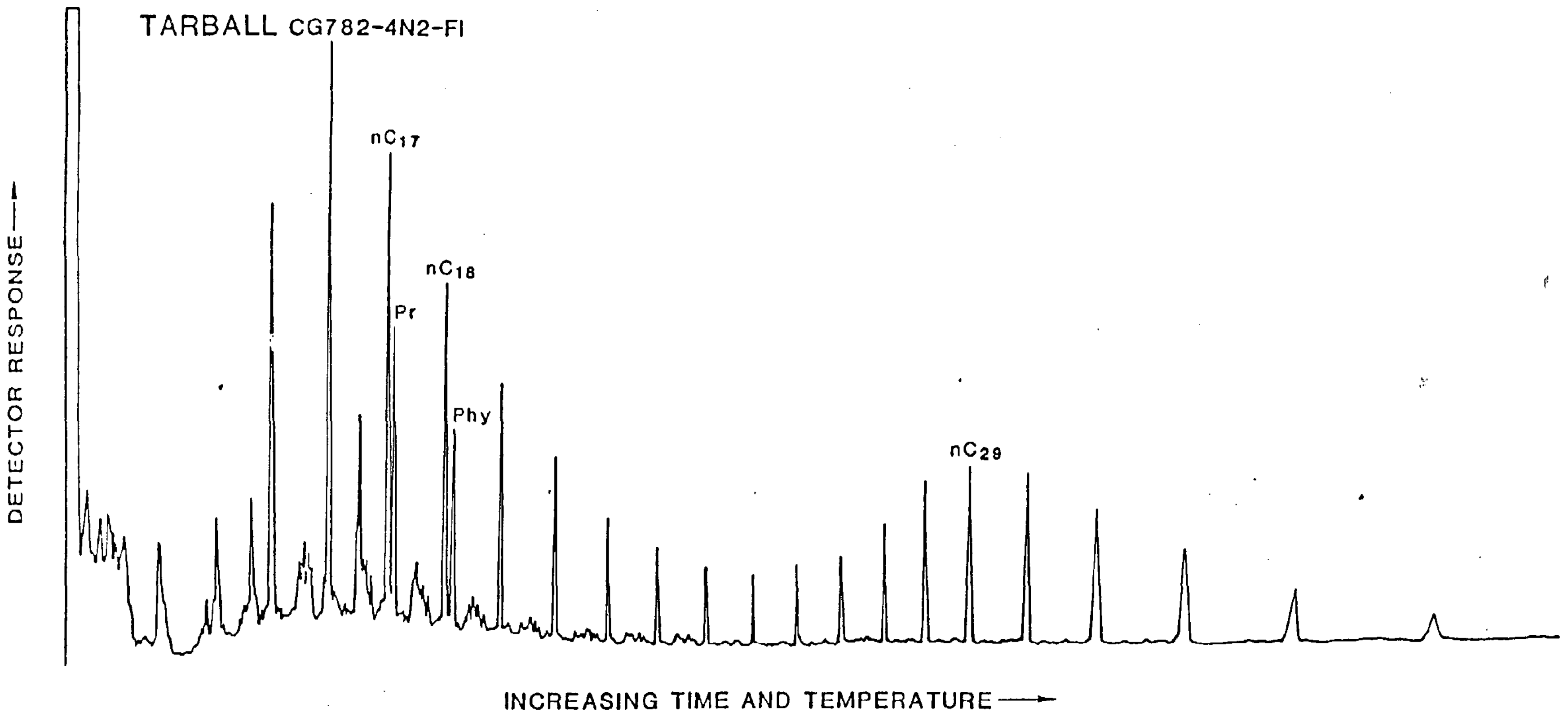


FIGURE 20. Gas chromatogram of pelagic tar sample CG782-4N2-F1 showing bimodal n-alkane distribution.

discussed, most of this tar may be restricted to the western Gulf and not entrained by the Loop Current and transported to the eastern portions of the Gulf of Mexico.

Other chemical data on the molecular composition of the tarballs has been compiled as baseline information in the event of future oil spills in the eastern Gulf. Chemical data on the nC_{17}/pristane, nC_{18}/phytane, and pristane/phytane data is summarized in Table 11. The variation in the chemical nature of the tar is evident from the large ranges and standard deviations around the means of these ratios. These values are very similar to the ratios observed during Year 1 of the study (Tables 2 and 11). Hence, an individual source of oil is not implicated in these studies. The chemical data suggests multiple sources for the tar and a wide scatter in their chemical nature.

Several authors have demonstrated that one of the most diagnostic characteristics of a petroleum sample is the molecular nature of the aromatic hydrocarbon fraction (Youngblood and Blumer, 1975; Farrington et al., 1977). Polycyclic aromatic hydrocarbons (PAH) have routinely been analyzed by combined gas chromatography-mass spectrometry to differentiate suites of compounds originating from petroleum sources from those originating from combustion processes (Youngblood and Blumer, 1975; LaFlamme and Hites, 1978; Hites et al., 1980). Youngblood and Blumer (1975) further suggest that the PAH sequences can also be used to differentiate fossil fuel combustion processes (temperature ∿ 2200°K) from natural combustion processes, such as forest fires (temperature ∿ 1600°K), based upon the different thermal effects involved in each process. This latter claim, has been disputed by LaFlamme and Hites (1980) on the basis of post-depositional alterations, and the issue is still unresolved. However, fossil fuel hydrocarbons can still be clearly distinguished from hydrocarbons originating from petroleum seeps or spillage, such as those found in the pelagic tar samples analyzed in this study. This differentiation is based upon the relationship between the parent aromatic compounds (such as phenanthrene) and the alkylated homologs such as methyl-phenanthrene, dimethyl-phenanthrene and trimethyl-phenanthrene -- designated C_1P, C_2P, and C_3P respectively. The C_2P contains not only all isomers of the dimethyl-phenanthrene, but also ethyl-phenanthrene isomers, since these are not readily distinguished by the GCMS procedures utilized. The C_3 phenanthrenes would consist of a mixture of methyl, ethyl and propyl homologs. Under conditions of relatively low temperatures and slow heating, such as in petroleum formation, the alkylated homologs are formed in the greatest abundance. Under conditions of higher temperature and more rapid heating, such as during combustion, the alkylated homologs undergo thermal cracking, resulting in a greater abundance of non-alkylated parent compounds. Petroleum compounds (Figure 21A) show a homolog maximum at C_2 or C_3. The combustion processes (Figure 21B) show a maximum at C_0 (i.e. the parent compounds). The pelagic tar samples represented in Figure 21C show the homolog maximum at C_2 or C_3 similar to the petroleum compounds as expected. None of the analyzed samples showed a C_0 maximum indicative of a combustion source. Significant variation did occur among the pelagic tar samples indicating different origins and different weathering processes. Examples of the PAH data for IXTOC-I crude oil are reported in Table 13. An example of the reconstructed ion chromatograms from the GCMS showing the specificity of the mass spectrometer detector is shown in Figures 22 and 23.

Naphthalenes are the most water soluble of the PAH's analyzed. Hence the relative amounts of naphthalenes present in pelagic tar are indicative of the freshness of the tar. Most of the tar collected during the N881 cruise

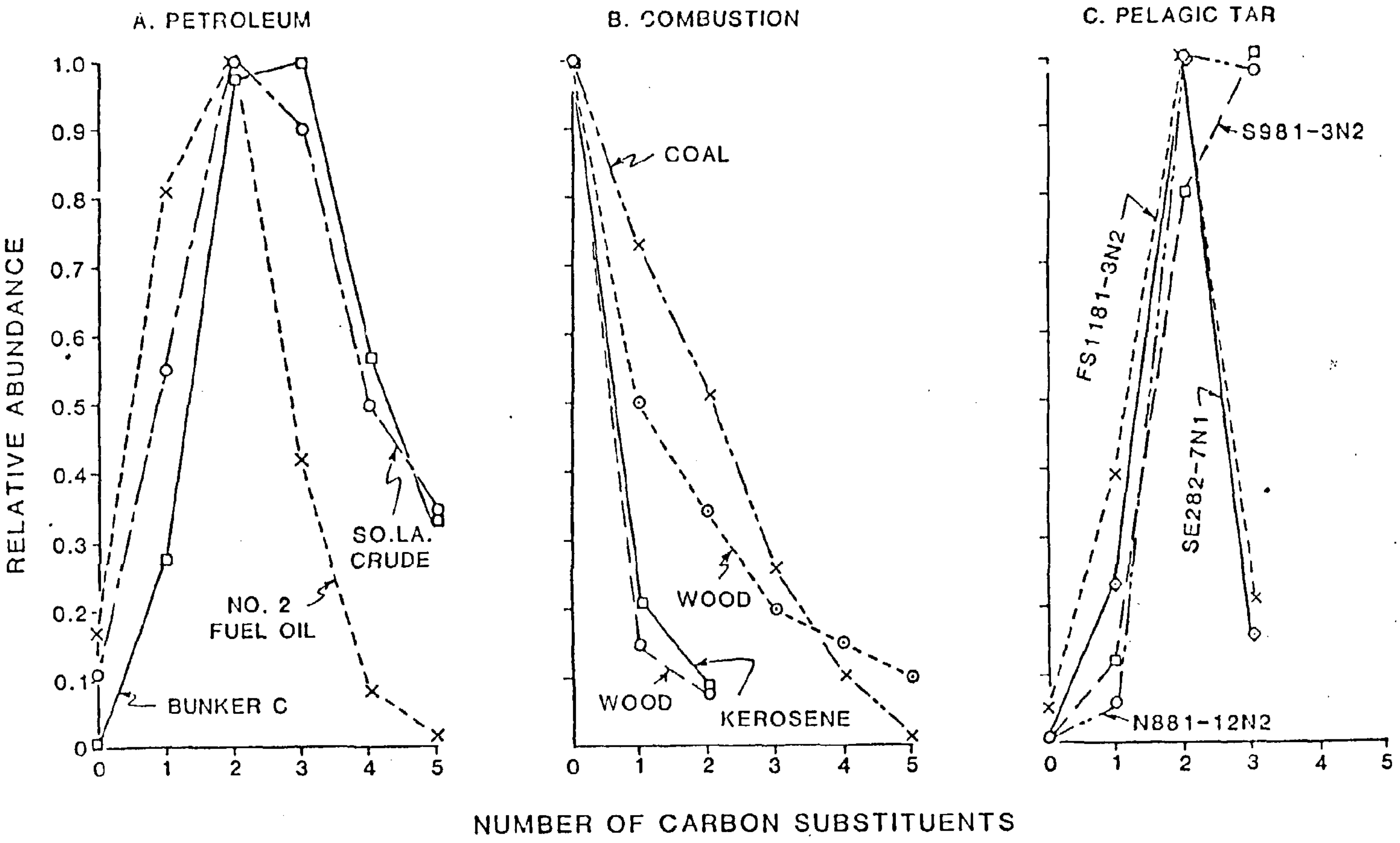


FIGURE 21. Alkyl homolog distributions for (a) petroleum (phenanthrenes), (b) combustion products (pyrenes), and (c) pelagic tar (phenanthrenes). Phenanthrene and pyrene have been shown to have similar homolog distribution patterns for the above processes (Youngblood and Blumer, 1975; LaFlamme and Hites, 1980).

TABLE 13. Aromatic Hydrocarbon Data from IXTOC-I Crude Oil

I. Concentrations relative to phenanthrene

Naphthalene = 2.62
C_1 Naph = 2.77
C_2 Naph = 27.41
C_3 Naph = 58.91

Phenanthrene = 1.00
C_1 Phen = 6.39
C_2 Phen = 16.12
C_3 Phen = 4.60

Dibenzothiophene = 1.88
C_1 DBT = 9.81
C_2 DBT = 19.57
C_3 DBT = 10.50

(Average standard error = ±10%)

II. Phenanthrene and dibenzothiophene homolog ratios

$$\frac{(C_1+C_2+C_3)\ P}{P} = 27.11$$

$$\frac{(C_1+C_2+C_3)\ DBT}{DBT} = 21.21$$

$$\frac{C_1P}{C_1DBT} = 0.65$$

$$\frac{C_2P}{C_2DBT} = 0.82$$

$$\frac{C_3P}{C_3DBT} = 0.44$$

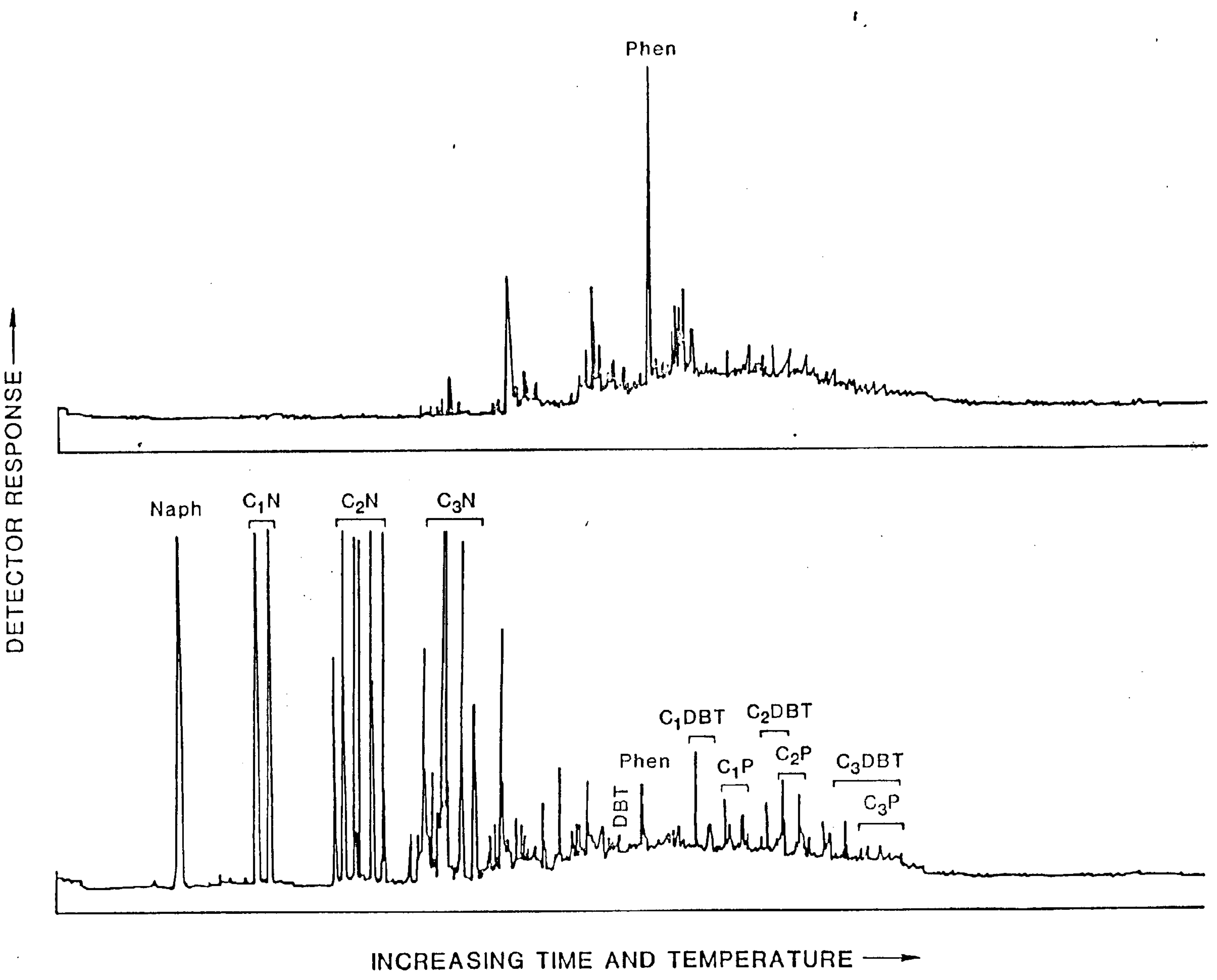


FIGURE 22. Reconstructed GCMS ion chromatogram of aromatic hydrocarbons from pelagic tar sample CG782-2N2-F2. See Table 12 for compound identifications.

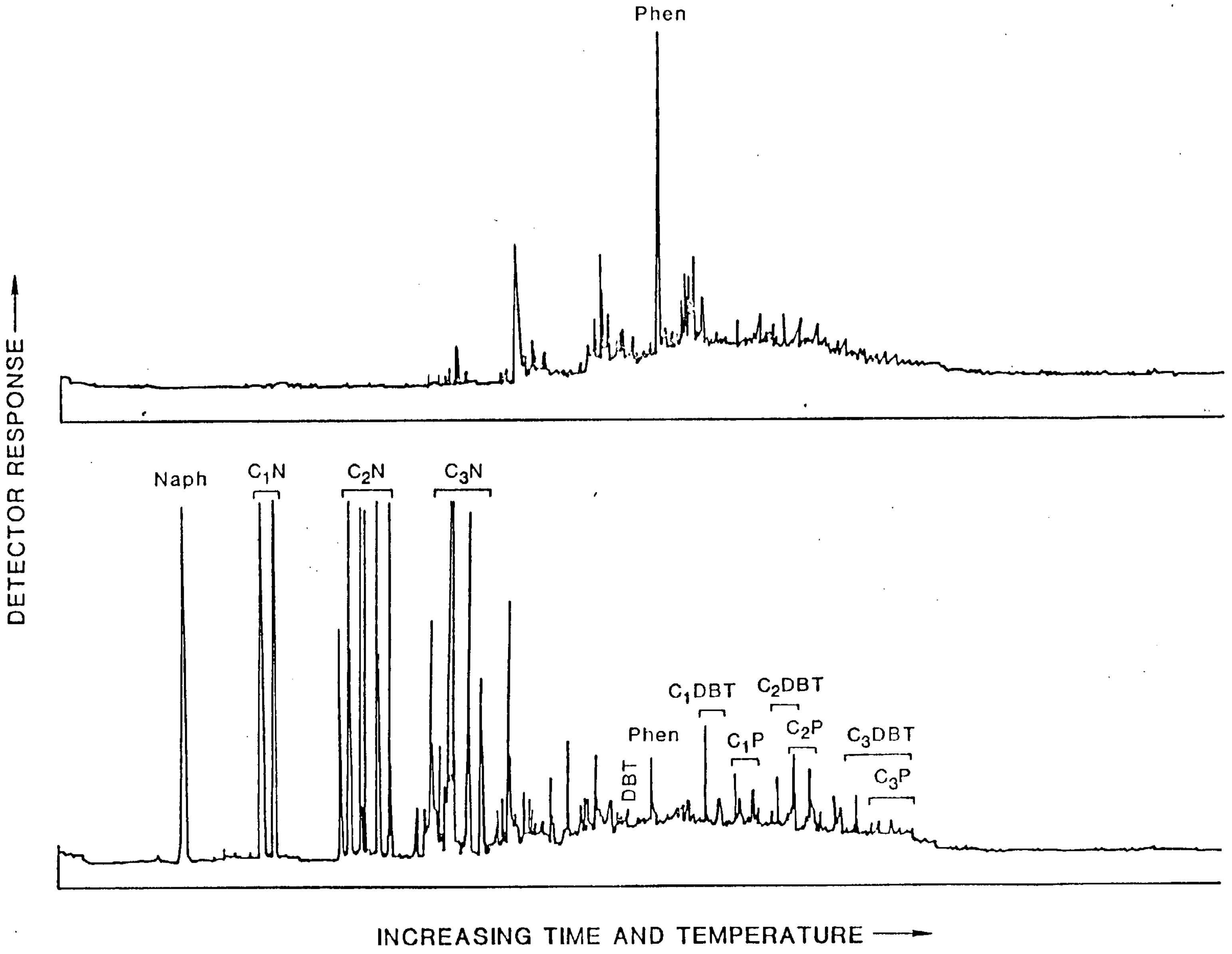


FIGURE 22. Reconstructed GCMS ion chromatogram of aromatic hydrocarbons from pelagic tar sample CG782-2N2-F2. See Table 12 for compound identifications.

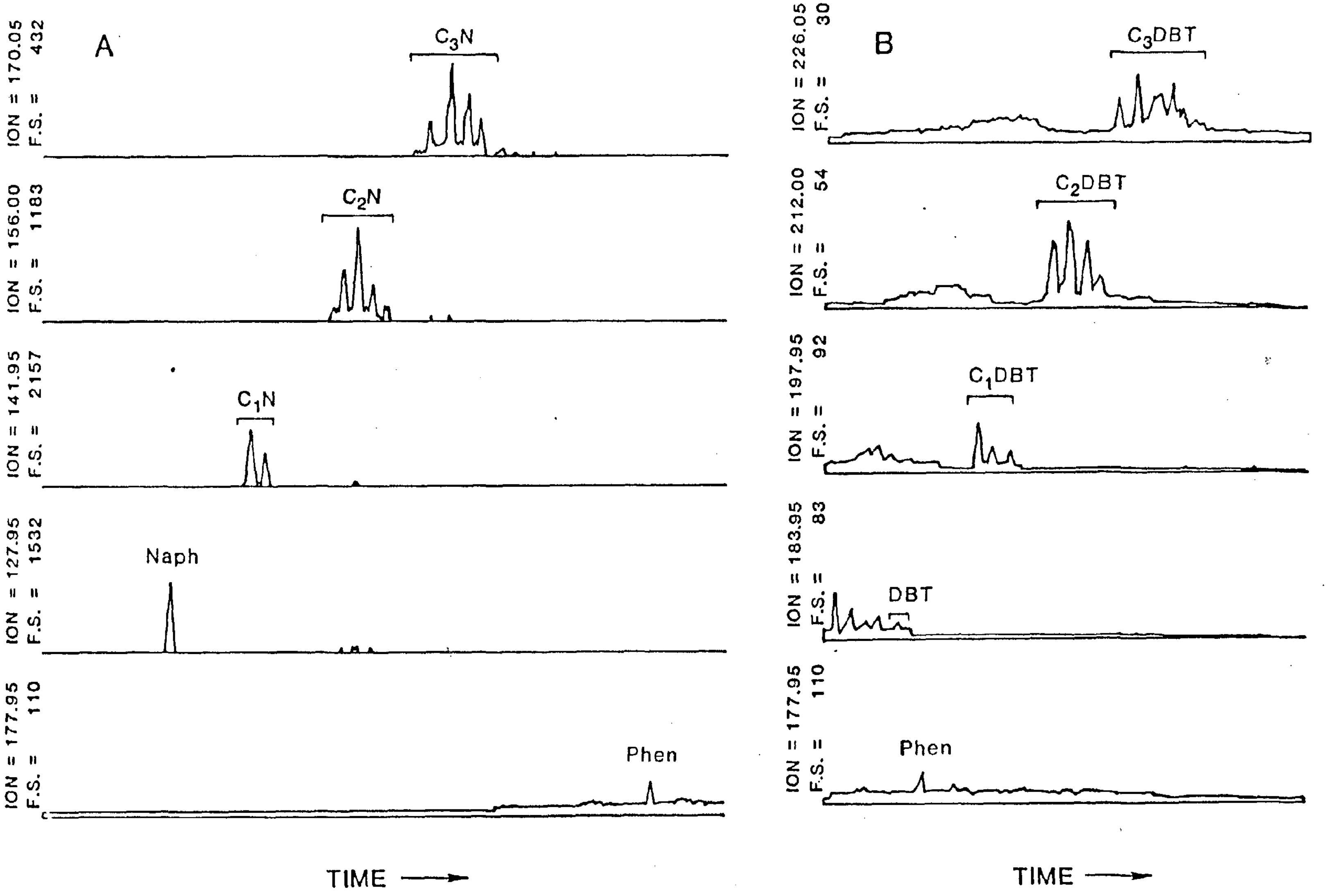


FIGURE 23. Selected ion plots of naphthalenes and dibenzothiophenes from pelagic tar sample CG782-2N2-F2. See Table 12 for compound identifications.

contained measurable quantities of C_0 to C_3 naphthalenes. By contrast, none of the tar collected during the S981 cruise contained any measurable naphthalenes. Thus samples collected on the northern coastal transect appear to have contained relatively fresh tar, while samples collected in the Loop Current on the southern transect appeared to contain more highly weathered tar particles. Samples collected in the Florida Straits (Cruise FS1181) also appeared to be fresh, while the SE282 samples collected along the coast of southeast Florida appeared more highly weathered. These variations indicate a temporal variation in the tar as well as a spatial variation.

Overton et al. (1981) has shown that the ratios of alkyl phenanthrenes to alkyl dibenzothiophenes are useful indicators for tracing petroleum hydrocarbon sources in environmentally impacted samples. The ratios of the C_1, C_2 and C_3 alkyl homologs for these PAH's have been shown to be uniquely characteristic of specific oils and are not rapidly altered by weathering processes. Each oil type can be assumed to have a unique set of these homolog ratios. Considering that there are over 2000 drilling wells in the Gulf of Mexico alone, it is impossible to pinpoint specific wells or tankers as the source of the pelagic tar until the fingerprints of the individual wells are known. If it is possible to analyze oil from a specific spill incident, the homolog data can then be used to determine if an oil under question originated from the specific spill or if the spill originated from a particular ship or well. It is in this light that the phenanthrene to dibenzothiophene homolog ratios can be most valuably utilized. All of the C_1, C_2, and C_3 ratios for the pelagic tar samples are reported in Appendix I and are summarized in Table 12. This background information is necessary for comparison in the event of a major spill in Florida coastal waters.

In addition to all of the routine samples analyzed and discussed above, one additional tar sample (CG782-7G1) was collected with a dip net in the central Gulf of Mexico (27°43'N, 86°36'W) in an area of noticeably high tar concentration. The tar had accumulated in an area characteristic of wind rows created by Langmuir circulation cells. Internal waves or frontal systems could also have resulted in similar surface water patterns. The wind row from which sample 7G1 was collected was approximately 5 m wide and several kilometers long. Tar concentrations were high in the wind row, and decreased rapidly away from its center. The tar concentration (based upon the estimated area swept by the dip net) was 44,000 mg m^{-2} toluene extractable lipid material (wet weight = 160,000 mg m^{-2}; dry weight = 60,000 mg m^{-2}). This concentration is much higher than the concentrations observed at other stations, although the high concentration may have largely been due to the collection technique. If a 30 minute neuston tow would have been made perpendicular to the wind row, the observed concentration would have been much lower. The largest tarball collected using the dip net was approximately 5 cm in diameter. Tarballs collected at the other stations were significantly smaller (average size ∿ 1 cm). It has been observed in the past that Langmuir circulation cells, and the resulting wind rows, can actively concentrate surface active material in downwelling waters. Based upon the above observations, it appears that pelagic tar can be concentrated in surface waters in a similar manner.

CONCLUSIONS

Pelagic tar was monitored over a two-year period in the eastern Gulf of Mexico. A total of 416 surface and subsurface samples were collected during monthly cruises. Eighteen cruises were conducted along standard sampling transects designed to ensure maximum intrusion into the Gulf Loop Current. In addition, six cruises were conducted to examine possible inputs and discharges of oil from the eastern Gulf, as well as environmentally sensitive areas around the Florida coastline. Among the conclusions reached during the two-year study are the following:

(1) Quantities of pelagic tar found in the eastern Gulf of Mexico are substantially higher than concentrations reported in several other coastal areas around the world. The only areas where long term studies have been conducted that show higher concentrations of tar than the eastern Gulf of Mexico are the Mediterranean Sea and the Sargasso Sea.

(2) The distribution of pelagic tar in the eastern Gulf is extremely patchy with concentrations varying by as much as two orders of magnitude over a distance of a few kilometers.

(3) Pelagic tar found in the eastern Gulf of Mexico is primarily associated with the Gulf Loop Current. The continental shelf areas around the eastern Gulf appear to be quite clean with respect to pelagic tar, with only minor concentrations being found in these areas.

(4) The concentration of pelagic tar found in the Gulf Loop Current was approximately the same as the tar concentrations reported for the Gulf of Mexico in the early 1970's. The concentration of tar does not appear to have increased substantially in the last decade.

(5) Essentially all of the pelagic tar is found in the upper 0.5 m of the water column. Very little tar was observed in oblique tows from 0-100 m.

(6) Approximately half of the pelagic tar samples collected during the study appeared to have originated from tanker operations. The remaining tar samples may or may not have come from this source. Natural seeps have not been reported in the eastern Gulf of Mexico, although natural seeps in the Caribbean may account for a portion of the tar entering the eastern Gulf via the Yucatan Straits. Neither the Mississippi River nor oil drilling platforms around the Mississippi Delta region appear to contribute a substantial portion of the pelagic tar to the eastern Gulf. Pelagic tar transported to the Gulf of Mexico from the Caribbean Sea by the Gulf Loop Current can account for approximately 10 to 50% of the tar in the eastern Gulf. The remainder appears to originate locally, primarily from tanker operations. The wide range of chemical characteristics of the pelagic tar indicate a variety of crude and refined oil sources for tar in the eastern Gulf.

(7) Most of the pelagic tar that is associated with the upper 1 m of the Loop Current and ultimately impinges upon Florida's beaches, washes ashore along the southeastern coast of Florida between Key West and Fort Pierce. Transport of surface tar from the Gulf Loop Current to beaches along the west coast of Florida or the Florida Panhandle appears to be less likely.

(8) The northern edges of the Florida Keys as well as Florida Bay appear to be unimpacted by pelagic tar. These pristine areas are located in an area of little circulation indicating that crude oil or pelagic tar spilled into this area could remain in the environment for substantially long periods of time without being washed away. This has far reaching implications with respect to

future offshore oil drilling and transportation activities in this area.

(9) No definitive seasonal trend in pelagic tar concentrations could be observed during the two-year study.

(10) No major impingement of IXTOC-I oil into Florida's coastal waters was observed during the study.

It should be stressed that this study was only concerned with particulate oil residues in the Gulf of Mexico. In this regard there does appear to be a significant amount of oil contamination in the surface waters. With respect to the rest of the Gulf ecosystems, however, this is not the case. Below the surface there is little evidence that the water, fish, bottom dwelling organisms, shellfish, or sediments contain abnormal levels of petroleum contamination. These parts of the Gulf actually appear to be quite clean compared with some other areas of the world's oceans.

RECOMMENDATIONS

Florida's economy is highly dependent on its large tourism industry as well as its recreational and commercial fishing (and shellfishing) interests. Projected dramatic increases in oil drilling and shipping operations in the Gulf of Mexico over the next decade increases the probability that accidental discharges will occur. Pelagic tar associated with the Gulf Loop Current does not appear to be having a significant effect upon the beaches or ecosystems of west Florida. The main impact that this tar is having on the State of Florida appears to be a socio-economic impact on the tourism industry due to tar washing ashore on the beaches of southeast Florida between Key West and Fort Pierce. The economic extent of this impact is uncertain. The major impact of oil on west Florida beaches is not likely to result from this pelagic tar, but would more likely result from a nearshore tanker accident or nearshore oil well blowout releasing most of its oil into semi-enclosed bays, estuaries, or nearshore waters where it can wash ashore and impact the beaches or benthic ecosystems. Since future oil development of the west Florida continental shelf may certainly lead to these types of accidents, it is imperative that the State of Florida develop as many safeguards as possible to prevent or minimize damage from these discharges. It is also imperative for the State to establish a policy by which indemnity may be recovered in the event of a major spill. In order to protect the State of Florida during litigation in the event of spill incidents, it is essential that we (1) have baseline data for comparison, (2) are able to show that the oil is from a new source, and (3) are able to attempt identification of the source. The two-year study just completed on pelagic tar has laid the foundation for addressing these goals. In order to maintain the necessary safeguards for the State of Florida and to maximize the results of this study, we recommend the following:

(1) Establish a quick response team to be prepared to act in the event of a major oil spill in Florida's coastal waters. This should include (a) a small group of scientists to collect and analyze the oil immediately after spillage, (b) the necessary analytical equipment to be maintained and available for immediate analysis, and (c) a small contingency fund set aside for the purpose of funding the necessary collection and analysis of the spilled oil.

(2) Transport studies should be conducted in order to evaluate the physical transport of pelagic tar between the Gulf Loop Current and the Florida beaches. Although indirect chemical data from tar collected in the upper 1 m of the water column suggests areas of

maximum transport, this data is not altogether consistent with biological data. Most physical transport studies have been conducted in the open Gulf and have not been concerned with onshore-offshore transport. This information is critical in understanding the impact of pelagic tar and other spilled pollutants on the beaches and ecosystems of the State of Florida.

(3) Future background pelagic tar studies should be focused on the eastern Florida continental shelf. Although some gravimetric work has been conducted along this area, very little chemical work has been attempted. In order to complete the picture of pelagic tar along the coasts of Florida, this work is necessary. This work should include samples taken in the Gulf Stream.

(4) Future efforts in studying oil pollution in Florida's coastal waters should also include sampling of beach tar along the Florida coastline, and benthic organisms and sediments in commercially important shellfishing areas.

REFERENCES

Brooks, J.M., B.B. Bernard and W.M. Sackett. 1977. Input of low-molecular-weight hydrocarbons from petroleum operations into the Gulf of Mexico. In, Fate and Effects of Petroleum Hydrocarbons in Marine Ecosystems and Organisms. D.A. Wolf, ed. Pergamon, Oxford. pp 373-384.

Butler, J.N. and B.F. Morris. 1974. Quantitative monitoring and variability of pelagic tar in the North Atlantic. In, NBS Spec. Publ. 409. Marine Pollution Monitoring (Petroleum). pp.75-78.

Butler, J.N., B.F. Morris and J. Sass. 1973. Pelagic Tar from Bermuda and the Sargasso Sea. Bermuda Biological Station. Spec. Publ. No. 10. 346p.

Chassè, C. 1978. The ecological impact on and near shores by the AMOCO CADIZ oil spill. Mar. Pollut. Bull. 9: 289-301

Craig, H. 1953. The geochemistry of the stable carbon isotopes. Geochim. Cosmochim. Acta 3: 53-92.

Degens, E.T. 1969. Biogeochemistry of stable carbon isotopes. In, Organic Geochemistry. G. Eglinton and M.T.J. Murphy, eds. Springer, Berlin. pp. 304-329.

Eagle, G.A., A. Green and J. Williams. 1979. Tar ball concentrations in the ocean around the Cape of Good Hope before and after a major oil spill. Mar. Pollut. Bull. 10: 321-325.

Ehrhardt, M. and M. Blumer. 1972. The source identification of marine hydrocarbons by gas chromatography. Environ. Pollut. 3: 179-194.

Farrington, J.W., N.M. Frew, P.M. Gschwend and B.W. Tripp. 1977. Hydrocarbons in cores of Northwest Atlantic coastal and continental margin sediments. Estuarine Coastal Mar. Sci. 5: 793-808.

Farrington, J.W. and P.A. Meyers. 1975. Hydrocarbons in the marine environment. In, Environmental Chemistry, Vol. 1. Eglinton, G., ed. pp. 109-137.

Fuex, A.N. 1977. The use of stable carbon isotopes in hydrocarbon exploration. Jour. Geochem. Explor. 7: 155-188.

FIO/USF. 1981. Spatial and Temporal Variation of Crude Oil Residues in Continental Shelf Waters Offshore Western Florida. Final Report submitted to the Florida Department of Natural Resources by the Florida Institute of Oceanography and the University of South Florida, August 1981. 87 p.

Geo-Marine, Inc. 1980. A Report on If, When, and Where Oil From the Mexican Oil Well Blowout (IXTOC-I) Could Impact Florida's Coastal Waters. Report prepared for the Florida Department of Natural Resources. 77 p.

Geyer, R.A. and C.P. Giammona. 1980. Naturally occurring hydrocarbons in the Gulf of Mexico and Caribbean Sea. In, Marine Environmental Pollution. I. Hydrocarbons. R.A. Geyer, ed. Elsevier, New York. pp. 37-106.

Giger, W. and C. Schaffner. 1978. Determination of polycyclic aromatic hydrocarbons in the environment by glass capillary gas chromatography. Anal. Chem. 50: 243-249.

Haegh, T. and L.I. Rossemyr. 1980. A comparison of weathering processes of oil from the BRAVO and the IXTOC blowouts. Proceedings of the Offshore Technology Conference 1980. pp. 237-245.

Heyerdahl, T., Jr. 1978. Resultater fra 3 års overvåking av partikulaer oljefrurensning i havet utenfor norskekysten. Fisken Hav. 2: 3-12.

Hites, R.A., R.E. LaFlamme, J.G. Windsor, Jr., J.W. Farrington and W.G. Deuser. 1980. Polycyclic aromatic hydrocarbons in an anoxic sediment core from the Pettaquamscutt River (Rhode Island, U.S.A.). Geochim. Cosmochim. Acta 44: 873-878.

Hoffman, E.J. and J.G. Quinn. 1979. Gas chromatographic analyses of ARGO MERCHANT oil and sediment hydrocarbons at the wreck site. Mar. Pollut. Bull. 10: 20-24.

Hoffman, E.J. and J.G. Quinn. 1980. The ARGO MERCHANT oil spill and the sediments of Nantucket Shoals: research, litigation and legislation. In, Contaminants and Sediments, Vol. 1. R.A. Baker, ed. Ann Arbor Science Publishers. Ann Arbor. pp. 185-218.

Iliffe, T.M. and J.A. Calder. 1974. Dissolved hydrocarbons in the eastern Gulf of Mexico Loop Current and the Caribbean Sea. Deep-Sea Res. 21: 481-488.

Jeffrey, L.M. 1980. Petroleum residues in the marine environment. In, Marine Environmental Pollution. I. Hydrocarbons. R.A. Geyer, ed. Elsevier, New York. pp. 163-179.

Jeffrey, L.M., W.E. Pequegnat, E.A. Kennedy, A. Vos. and B.M. Jarnes. 1974. Pelagic tar in the Gulf of Mexico and Caribbean Sea. In, NBS Spec. Publ. 409. Marine Pollution Monitoring (Petroleum). pp. 233-235.

Jones, J.I. 1973. Physical oceanography of the northeast Gulf of Mexico and Florida continental shelf area. pp. IIB1-11. In, Florida State Univ. Syst. Inst. Oceanogr. (coord.), A Summary of Knowledge of the Eastern Gulf of Mexico.

Koons, C.B. and P.H. Monaghan. 1973. Petroleum hydrocarbons in Gulf of Mexico waters. Trans. Gulf Coast Assoc. Geol. Soc. 23: 170-181.

Kvendolden, K.A. and R.M. Squires. 1967. Carbon isotopic composition of crude oils from Ellenburger Group (Lower Ordovician), Permian Basin, West Texas, and Eastern New Mexico. Amer. Assoc. Petrol. Geol. Bull. 51: 1293-1303.

LaFlamme, R.E. and R.A. Hites. 1978. The global distribution of polycyclic aromatic hydrocarbons in recent sediments. Geochim. Ciosmochim, Acta 42: 289-303.

LaRock, P. and H.L. Bittaker. 1973. Chemical data of the estuarine and nearshore environments in the eastern Gulf of Mexico. pp. IIIC8-86, In, Florida State Univ. Syst. Inst. Oceanogr. (coord), A Summary of Knowledge of the Eastern Gulf of Mexico.

Laubier, L. 1978. The AMOCO CADIZ oil spill -- lines of study and early observations. Mar. Pollut. Bull. 9: 285-287.

Lee, T.N. 1971. Oceanographic features of nearshore waters on a narrow continental shelf. In, Limitations and Effects of Waste Disposal on an Ocean Shelf. EPA Water Pollution Control Res. Ser. 10697EFG. pp. 105-170.

Leipper, D.F. 1970. A sequence of current patterns in the Gulf of Mexico. J. Geophys. Res. 75: 637-657.

Levy, E.M. 1977. The geographical distribution of tar in the North Atlantic. Rapp. P.-v. Reun. Cons. Int. Explor. Mer. 171: 55-60

Maul, G.A. 1977. The annual cycle of the Gulf Loop Current. Part I: Observations during a one-year time series. J. Mar. Res. 35: 29-47.

McGowan, W.E., W.A. Saner and G.L. Hufford. 1974a. Tar ball distribution in the western North Atlantic. U.S. Coast Guard Rept. CGR&D 24/74. Washington, D.C. 30 p.

McGowan, W.E., W.E. Saner and G.L. Hufford. 1974b. Tar ball sampling in the western North Atlantic. In, NBS Spec. Publ. 409. Marine Pollution Monitoring (Petroleum). pp. 83-84.

Merrell, W.J., Jr. and J.M. Morrison. 1981. On the circulation of the western Gulf of Mexico with observations from April 1978. J. Geophys. Res. 86: 4181-4185.

NAS. 1975. Petroleum in the Marine Environment. National Academy of Sciences. Washington, D.C. 107 p.

NAS. 1983. Petroleum in the Marine Environment, Second Edition. National Academy of Sciences. Washington, D.C. In Press.

NOAA. 1977. The ARGO MERCHANT Oil Spill -- A Preliminary Scientific Report. National Oceanic and Atmospheric Administration. Boulder. 327 p.

NOAA. 1979. The TSESIS Oil Spill. Kineman, J.J., R. Elmgren, and S. Hansson, eds. pp. 219-273.

NOAA, 1980. Proceedings of the Symposium on Preliminary Results from the September 1979 RESEARCHER/PIERCE IXTOC-I cruise. Key Biscayne, Florida, June 9-10, 1980.

Nowlin, W.D. 1971. Water masses and general circulation of the Gulf of Mexico. Oceanog. Internat. 6: 28-33.

Nowlin, W.D. 1972. Winter circulation patterns and property distributions. In, Contributions on the Physical Oceanography of the Gulf of Mexico, V. 2. L.R.A. Capurro and J.L. Reid, eds. Gulf Publ. Co. pp. 3-51.

O'Sullivan, A.J. 1978. The AMOCO CADIZ oil spill. Mar. Pollut. Bull. 9: 123-128.

Overton, E.B., J. McFall, S.W. Mascarella, C.F. Steel, S.A. Antoine, I.R. Politzer and J.L. Laseter. 1981. Identification of petroleum residue sources after a fire and oil spill. Proceedings of the 1981 Oil Spill Conference. American Petroleum Institute. Washington, D.C. pp. 541-546.

Pequegnat, L.H. 1979. Pelagic tar concentrations in the Gulf of Mexico over the South texas Continental Shelf. Contrib. Mar. Sci. 22: 31-39.

Romero, G.C., G.R. Harvey and D.K. Atwood. 1981. Stranded tar on Florida Beaches: September 1979 through October 1980. Mar. Pollut. Bull. 12:280-284.

Shaw,G.D. and G.A. Mapes. 1979. Surface circulation and distribution of pelagic tar and plastic. Mar. Pollut. Bull. 10: 160-162.

Sherman, K., J.B. Colton, R.L. Dryfoos, K.D. Knapp and B.S. Kinnear. 1974. Distribution of tar balls and neuston sampling in the Gulf Stream system. In, NBS Spec. Publ. 409. Marine Pollution Monitoring (Petroleum). pp. 243-245.

Silverman, S.R. 1968. Reference to $^{13}C/^{12}C$ ratio of Challenger Knoll oil. In, Initial Reports of the Deep Sea Drilling Project, Vol. 1 p. 500.

Smith, G.B. 1976. Pelagic tar in the Norwegian coastal current. Mar. Pollut. Bull. 7: 70-72.

Stahl, W.J. 1977. Carbon and nitrogen isotopes in hydrocarbon research in exploration. Chem. Geol. 20: 121-149.

Sturges, W. and J.P. Blaha. 1976. A western boundary current in the Gulf of Mexico. Science 192: 367-369.

Turekian, K.K. 1971. Rivers, tributaries, and estuaries. In, Impingement of Man on the Oceans. D.W. Hood, ed. Wiley-Interscience. New York. pp. 9-73.

Van Vleet, E.S., W.M. Sackett, F.F. Weber, Jr. and S.B. Reinhardt. 1982a. Spatial and temporal variation of pelagic tar in the eastern Gulf of Mexico. Advances in Organic Geochemistry, 1981. In Press.

Van Vleet, E.S., W.M. Sackett, F.F. Weber, Jr. and S.B. Reinhardt. 1982b. Input of pelagic tar to the Northwest Atlantic from the Gulf Loop Current: Chemical characterization and its relationship to weathered IXTOC-I oil. Can. J. Fish. Aquat. Sci. In Press.

Williams, J., W.F. Grey, E.B. Murphy and J.J. Crane. 1977. Drift bottle analyses of eastern Gulf of Mexico surface circulation. In, Memoirs of the Hourglass Cruises. Vol. IV Part III. Florida Department of Natural Resources. pp. 1-134.

Wong, C.S., D.R. Green and W.J. Cretney. 1976. Distribution and source of tar on the Pacific Ocean. Mar. Pollut. Bull. 7: 102-106.

Youngblood, W.W. and M. Blumer. 1975. Polycyclic aromatic hydrocarbons in the environment: homologous series in soils and recent marine sediments. Geochim. Cosmochim. Acta 39: 1303-1314.

Zsolnay, A., B.F. Morris and J.N. Butler. 1978. Relationship between aromatic hydrocarbons and pelagic tar in the Mediterrenean Sea, 1974-75. Environ. Conserv. 5: 295-297.

APPENDICES

APPENDIX I: Gravimetric, isotopic, gas chromatographic and GCMS data for pelagic tar samples collected during Year 2.

DNR Tar Ball Study
Cruise N881

Gravimetric and Isotopic Analyses

		Total Tar				Final Results		Aliphatic Hydrocarbons		Aromatic Hydrocarbons	
Sta. No.	Tow No.	wet wt (mg m^{-2})	dry wt (mg m^{-2})	% moisture	extractable lipid (mg m^{-2})	aliphatic + aromatic (mg m^{-2})	$\delta^{13}C$	mg m^{-2}	$\delta^{13}C$	mg m^{-2}	$\delta^{13}C$
1A	N1	0	0	-	0	0	-	0	-	0	-
	N2	0	0	-	0	0	-	0	-	0	-
7	N1	0.31	0.09	69.5	0.07	0.03	-27.1	0.02	-27.1	0.01	-26.9
	N2	0	0	-	0	0	-	0	-	0	-
8	N1	NQ‡	NQ	33.8	NQ	NQ	-28.0	NQ	-28.4	NQ	-26.6
	N2	0.03	0.01	66.7	<0.06	0.01	-26.6	<0.01	-27.0	0.01	-28.5
9	N1	8.37	5.79	30.8	4.16	5.35	-25.7	4.77	-26.0	0.58	-24.9
	N2	0.97	1.74	-	1.29	0.59	-26.7	0.42	-27.0	0.17	-25.8
10	N1	6.66	4.40	33.9	3.90	2.46	-24.6	1.40	-27.9	1.06	-26.6
	N2	3.43	2.06	39.9	1.63	1.34	-26.6	1.13	-26.6	0.21	-26.0
11	N1	0	0	-	0	0	-	0	-	0	-
	N2	0	0	-	0	0	-	0	-	0	-
12	N1	0.67	0.17	25.7	0.16	0.06	-27.1	0.04	-27.2	0.02	-26.6
	N2	35.91	24.52	31.7	20.81	7.26	-28.0	5.51	-28.4	1.75	-27.8

<β = less than twice the blank value.
NQ‡ = not quantitative. Flowmeter clogged with <u>Sargassum</u>.

DNR Tar Ball Study
Cruise N881

Gravimetric and Isotopic Analyses

		Final Results						Aliphatic Hydrocarbons		Aromatic Hydrocarbons	
		Total Tar									
Sta. No.	Tow No.	wet wt ($mg\ m^{-2}$)	dry wt ($mg\ m^{-2}$)	% moisture	extractable lipid ($mg\ m^{-2}$)	aliphatic + aromatic ($mg\ m^{-2}$)	$\delta^{13}C$	$mg\ m^{-2}$	$\delta^{13}C$	$mg\ m^{-2}$	$\delta^{13}C$
13	N1	0	0	-	0	0	-	0	-	0	-
	N2	0	0	-	0	0	-	0	-	0	-
14	N1	0	0	-	0	0	-	0	-	0	-
	N2	0	0	-	0	0	-	0	-	0	-
15	N1	0	0	-	0	0	-	0	-	0	-
	N2	0	0	-	0	0	-	0	-	0	-
16	N1	0	0	-	0	0	-	0	-	0	-
	N2	1.58	0.99	37.3	0.70	0.30	-28.2	0.26	-28.3	0.04	-27.2
17	N1	0	0	-	0	0	-	0	-	0	-
	N2	0	0	-	0	0	-	0	-	0	-
18	N1	0	0	-	0	0	-	0	-	0	-
	N2	0	0	-	0	0	-	0	-	0	-

$<\beta$ = less than twice the blank value.

DNR Tar Ball Study
Cruise N881

Aliphatic and Aromatic Hydrocarbon Data

			Aliphatics		Aromatics	
Sta. No.	Tow No.	aliphatics / aromatics	% Resolved	% Unresolved	% Resolved	% Unresolved
1A	N1	-	-	-	-	-
	N2	-	-	-	-	-
7	N1	2.00	32.3	67.7	75.6	25.4
	N2	-	-	-	-	-
8	N1	2.67	61.4	38.6	29.1	70.9
	N2	<1.00	74.1	25.9	‡	‡
9	N1	8.22	59.9	40.1	29.0	71.0
	N2	2.47	61.2	38.8	44.2	55.8
10	N1	1.32	88.8	11.2	26.8	73.2
	N2	5.38	52.9	47.1	34.2	65.8
11	N1	-	-	-	-	-
	N2	-	-	-	-	-
12	N1	2.00	46.8	53.2	63.6	36.4
	N2	3.15	54.8	45.2	15.5	84.5

(-) = concentration of tar is less than twice the blank.
‡ = Sample lost during work up.

DNR Tar Ball Study
Cruise N881

Aliphatic and Aromatic Hydrocarbon Data

			Aliphatics		Aromatics	
Sta. No.	Tow No.	aliphatics / aromatics	% Resolved	% Unresolved	% Resolved	% Unresolved
13	N1	–	–	–	–	–
	N2	–	–	–	–	–
14	N1	–	–	–	–	–
	N2	–	–	–	–	–
15	N1	–	–	–	–	–
	N2	–	–	–	–	–
16	N1	–	–	–	–	–
	N2	6.50	71.3	28.7	37.5	62.5
17	N1	–	–	–	–	–
	N2	–	–	–	–	–
18	N1	–	–	–	–	–
	N2	–	–	–	–	–

(–) = concentration of tar is less than twice the blank.

DNR Tar Ball Study
Cruise N881

Aliphatic Hydrocarbon Molecular Data

Sta. No.	Tow No.	$\frac{nC_{17}}{pristane}$	$\frac{nC_{18}}{phytane}$	$\frac{pristane}{phytane}$	n-alkane range	n-alkane maximum
1A	N1	-	-	-	-	-
	N2	-	-	-	-	-
7	N1	0.28	0.26	0.60	C_{15} - C_{38}	C_{33}
	N2	-	-	-	-	-
8	N1	1.66	2.30	1.16	C_{14} - C_{38}	C_{30}
	N2	2.09	3.74	1.13	C_{14} - C_{38}	C_{25}
9	N1	2.90	6.36	1.81	C_{14} - C_{38}	C_{31}
	N2	1.12	1.65	1.08	C_{14} - C_{38}	C_{34}
10	N1	1.48	1.92	1.01	C_{14} - C_{38}	C_{33}
	N2	2.02	2.85	1.11	C_{13} - C_{38}	C_{28}
11	N1	-	-	-	-	-
	N2	-	-	-	-	-
12	N1	1.39	1.65	0.74	C_{15} - C_{38}	C_{30}
	N2	2.05	2.32	0.88	C_{14} - C_{38}	C_{28}

(-) = concentration of tar is less than twice the blank.

DNR Tar Ball Study
Cruise N881

Aliphatic Hydrocarbon Molecular Data

Sta. No.	Tow No.	$\frac{nC_{17}}{\text{pristane}}$	$\frac{nC_{18}}{\text{phytane}}$	$\frac{\text{pristane}}{\text{phytane}}$	n-alkane range	n-alkane maximum
13	N1	-	-	-	-	-
	N2	-	-	-	-	-
14	N1	-	-	-	-	-
	N2	-	-	-	-	-
15	N1	-	-	-	-	-
	N2	-	-	-	-	-
16	N1	-	-	-	-	-
	N2	1.09	1.30	0.91	C_{15} - C_{38}	C_{36}
17	N1	-	-	-	-	-
	N2	-	-	-	-	-
18	N1	-	-	-	-	-
	N2	-	-	-	-	-

(-) = concentration of tar is less than twice the blank.

DNR Tar Ball Study
Cruise N881

COMBINED GC/MS ANALYSES OF AROMATIC HYDROCARBONS
(Relative to Phenanthrene)

Sta. No.	Tow No.	N‡	C_1N	C_2N	C_3N	P	C_1P	C_2P	C_3P	DBT	C_1DBT	C_2DBT	C_3DBT
7	N1	-	-	0.9	13.0	1.00	19.8	124.1	77.1	1.0	23.5	201.4	12.9
8	N1	0.3	0.2	1.2	14.5	1.00	27.8	138.2	83.7	0.1	3.8	17.1	10.7
9	N1	-	-	-	2.6	1.00	18.5	60.6	26.4	0.4	1.4	8.6	1.4
10	N1	0.0	0.0	1.4	41.2	1.00	8.5	104.7	64.8	0.1	22.2	75.7	41.6
11	N1/N2	-	-	-	-	-	-	-	-	-	-	-	-
12	N2	0.1	0.0	1.3	41.8	1.00	10.2	163.6	161.1	0.3	15.9	129.8	85.2
13	N1/N2	-	-	-	-	-	-	-	-	-	-	-	-
14	N1/N2	-	-	-	-	-	-	-	-	-	-	-	-
15	N1/N2	-	-	-	-	-	-	-	-	-	-	-	-
16	N2	0.1	-	0.1	5.3	1.00	32.3	108.7	23.6	0.6	12.8	84.4	56.3

‡ N = Naphthalene; P = Phenanthrene; DBT = Dibenzothiophene;

C_1 = methyl-; C_2 = dimethyl-; C_3 = trimethyl

(-) = concentration of tar is less than twice the blank value.

DNR Tar Ball Study
Cruise N881

COMBINED GC/MS ANALYSES OF AROMATIC HYDROCARBONS

Sta. No.	Tow No.	$\frac{(C_1+C_2+C_3)P}{P}$	$\frac{(C_1+C_2+C_3)DBT}{DBT}$	$\frac{C_1P}{C_1DBT}$	$\frac{C_2P}{C_2DBT}$	$\frac{C_3P}{C_3DBT}$
7	N1	221	238	0.8	0.6	6.0
8	N1	250	316	7.3	8.1	7.8
9	N1	106	28	13.2	7.0	18.9
10	N1	178	1395	0.4	1.4	1.6
11	N1/N2	-	-	-	-	-
12	N2	335	763	0.6	1.3	1.9
13	N1/N2	-	-	-	-	-
14	N1/N2	-	-	-	-	-
15	N1/N2	-	-	-	-	-
16	N2	165	256	2.5	1.3	0.4

(-) = concentration of tar is less than twice the blank value.

DNR Tar Ball Study
Cruise S981

Gravimetric and Isotopic Analyses
Final Results

		Total Tar						Aliphatic Hydrocarbons		Aromatic Hydrocarbons	
Sta. No.	Tow No.	wet wt ($mg\ m^{-2}$)	dry wt ($mg\ m^{-2}$)	% moisture	extractable lipid ($mg\ m^{-2}$)	aliphatic + aromatic ($mg\ m^{-2}$)	$\delta^{13}C$	$mg\ m^{-2}$	$\delta^{13}C$	$mg\ m^{-2}$	$\delta^{13}C$
1A	N1	0	0	–	0	0	–	0	–	0	–
	N2	0	0	–	0	0	–	0	–	0	–
1	N1	0.12	0.05	54.5	0.04	0.04	-26.6	<0.01	-27.1	0.03	27.3
	N2	0	0	–	0	0	–	0	–	0	–
2	N1	0	0	–	0	0	–	0	–	0	–
	N2	0	0	–	0	0	–	0	–	0	–
3	N1	0.26	0.09	65.9	0.07	0.04	-25.8	<0.01	-28.0	0.04	-27.5
	N2	8.50	4.75	44.5	2.89	2.89	-26.1	2.69	-26.4	0.55	-26.1
4	N1	0.35	0.07	80.6	0.05	0.05	-27.1	0.04	-27.8	0.01	-26.6
	N2	0.18	0.05	75.0	0.05	0.02	-27.3	0.01	-26.6	0.01	-28.7
5	N1	1.60	0.69	56.8	0.60	0.28	-27.0	0.22	-27.2	0.06	-26.7
	N2	4.51	1.15	75.3	0.96	>0.62	-26.2	0.62	27.3	ǂ	ǂ
6	N1	1.26	0.39	69.4	0.39	0.22	-26.6	0.19	-26.9	0.03	-25.9
	N2	1.31	0.37	71.4	0.37	0.08	-26.8	0.06	-27.1	0.02	-27.2

<β = less than twice the blank value.
ǂ = Sample lost during work up.

DNR Tar Ball Study
Cruise S981

Aliphatic and Aromatic Hydrocarbon Data

Sta. No.	Tow No.	aliphatics / aromatics	Aliphatics % Resolved	Aliphatics % Unresolved	Aromatics % Resolved	Aromatics % Unresolved
1A	N1	-	-	-	-	-
	N2	-	-	-	-	-
1	N1	0.33	60.5	39.5	82.1	17.9
	N2	-	-	-	-	-
2	N1	-	-	-	-	-
	N2	-	-	-	-	-
3	N1	<0.25	76.2	23.8	50.4	49.6
	N2	4.89	68.9	31.1	37.0	63.0
4	N1	4.00	66.4	33.6	66.7	33.3
	N2	1.00	52.5	47.5	89.4	10.6
5	N1	3.67	24.7	75.3	58.5	41.5
	N2	>0.62	42.3	57.7	57.6	42.4
6	N1	6.33	55.3	44.7	50.7	49.3
	N2	3.00	41.1	58.9	60.8	39.2

(-) = concentration of tar is less than twice the blank.

DNR Tar Ball Study
Cruise S981

Aliphatic Hydrocarbon Molecular Data

Sta. No.	Tow No.	$\frac{nC_{17}}{\text{pristane}}$	$\frac{nC_{18}}{\text{phytane}}$	$\frac{\text{pristane}}{\text{phytane}}$	n-alkane range	n-alkane maximum
1A	N1	-	-	-	-	-
	N2	-	-	-	-	-
1	N1	2.18	3.50	0.87	$C_{15}-C_{38}$	C_{22}, C_{29}
	N2	-	-	-	-	-
2	N1	-	-	-	-	-
	N2	-	-	-	-	-
3	N1	1.75	1.53	0.63	$C_{15}-C_{38}$	C_{31}
	N2	1.72	2.54	1.16	$C_{14}-C_{38}$	C_{32}
4	N1	0.98	1.19	0.60	$C_{16}-C_{38}$	C_{32}
	N2	1.57	1.77	0.48	$C_{15}-C_{38}$	C_{30}
5	N1	0.64	0.63	0.50	$C_{16}-C_{38}$	C_{20}, C_{36}
	N2	0.77	0.91	0.71	$C_{15}-C_{38}$	C_{30}
6	N1	1.03	1.51	0.82	$C_{15}-C_{38}$	C_{30}
	N2	1.91	2.18	0.58	$C_{15}-C_{38}$	C_{21}, C_{30}

(-) = concentration of tar is less than twice the blank.

DNR Tar Ball Study
Cruise S981

COMBINED GC/MS ANALYSES OF AROMATIC HYDROCARBONS
(Relative to Phenanthrene)

Sta. No.	Tow No.	N‡	C_1N	C_2N	C_3N	P	C_1P	C_2P	C_3P	DBT	C_1DBT	C_2DBT	C_3DBT
1A	N1/N2	-	-	-	-	-	-	-	-	-	-	-	-
1	N1	-	-	-	-	1.0	3.8	15.6	5.2	1.5	4.7	3.9	-
2	N1/N2	-	-	-	-	-	-	-	-	-	-	-	-
3	N2	-	-	-	-	1.0	54.7	373.6	469.6	0.3	9.1	151.9	407.8
4	N1	-	-	-	-	-	-	-	-	-	-	-	-
5	N1	-	-	-	-	1.0	37.7	161.6	87.7	0.3	6.6	55.1	11.3
6	N1	-	-	-	-	1.0	29.7	447.1	90.1	0.5	10.5	310.8	667.4

‡ N = Naphthalene; P = Phenanthrene; DBT = Dibenzothiophene;

C_1 = methyl-; C_2 = dimethyl-; C_3 = trimethyl

(-) = concentration of tar is less than twice the blank value.

DNR Tar Ball Study
Cruise S981

COMBINED GC/MS ANALYSES OF AROMATIC HYDROCARBONS

Sta. No.	Tow No.	$\frac{(C_1+C_2+C_3)P}{P}$	$\frac{(C_1+C_2+C_3)DBT}{DBT}$	$\frac{C_1P}{C_1DBT}$	$\frac{C_2P}{C_2DBT}$	$\frac{C_3P}{C_3DBT}$
1A	N1/N2	-	-	-	-	-
1	N1	25	6	0.8	4.0	-
2	N1/N2	-	-	-	-	-
3	N2	898	569	6.0	2.5	1.2
4	N1	-	-	-	-	-
5	N1	287	243	5.7	2.9	7.8
6	N1	567	1977	2.8	1.4	0.1

(-) = concentration of tar is less than twice the blank value.

DNR Tar Ball Study
Cruise FB1081*

Gravimetric and Isotopic Analyses
Final Results

		Total Tar						Aliphatic Hydrocarbons		Aromatic Hydrocarbons	
Sta. No.	Tow No.	wet wt (mg m^{-2})	dry wt (mg m^{-2})	% moisture	extractable lipid (mg m^{-2})	aliphatic + aromatic (mg m^{-2})	$\delta^{13}C$	mg m^{-2}	$\delta^{13}C$	mg m^{-2}	$\delta^{13}C$
FB1	N1	0	0	–	0	0	–	0	–	0	–
	N2	0	0	–	0	0	–	0	–	0	–
FB2	N1	0	0	–	0	0	–	0	–	0	–
	N2	0	0	–	0	0	–	0	–	0	–
FB3	N1	0	0	–	0	0	–	0	–	0	–
	N2	0	0	–	0	0	–	0	–	0	–
FB4	N1	0	0	–	0	0	–	0	–	0	–
	N2	0	0	–	0	0	–	0	–	0	–
FB5	N1	0	0	–	0	0	–	0	–	0	–
	N2	0	0	–	0	0	–	0	–	0	–
FB6	N1	0	0	–	0	0	–	0	–	0	–
	N2	0	0	–	0	0	–	0	–	0	–
FB7	N1	0	0	–	0	0	–	0	–	0	–
	N2	<0.01	<β	–	<β	<β	–	<β	–	<β	–

<β = less than twice the blank value.
*FB = Florida Bay

DNR Tar Ball Study
Cruise FB 1081*

Gravimetric and Isotopic Analyses

		Total Tar						Aliphatic Hydrocarbons		Aromatic Hydrocarbons	
Sta. No.	Tow No.	wet wt ($mg\ m^{-2}$)	dry wt ($mg\ m^{-2}$)	% moisture	extractable lipid ($mg\ m^{-2}$)	aliphatic + aromatic ($mg\ m^{-2}$)	$\delta^{13}C$	$mg\ m^{-2}$	$\delta^{13}C$	$mg\ m^{-2}$	$\delta^{13}C$
FB8	N1	0	0	–	0	0	–	0	–	0	–
	N2	0	0	–	0	0	–	0	–	0	–
FB9	N1	0	0	–	0	0	–	0	–	0	–
	N2	0	0	–	0	0	–	0	–	0	–

$<\beta$ = less than twice the blank value.

*FB = Florida Bay

DNR Tar Ball Study
Cruise FS1181

GRAVIMETRIC AND ISOTOPIC ANALYSES

Final Results

		Total Tar						Aliphatic Hydrocarbons		Aromatic Hydrocarbons	
Sta. No.	Tow No.	wet wt (mg m^{-2})	dry wt (mg m^{-2})	% moisture	extractable lipid (mg m^{-2})	aliphatic + aromatic (mg m^{-2})	$\delta^{13}C$	mg m^{-2}	$\delta^{13}C$	mg m^{-2}	$\delta^{13}C$
FS1	N1	0.23	0.06	73.9	0.03	0.02	-27.4	0.01	-27.5	0.01	-27.3
	N2	0.08	0.05	37.5	0.02	0.02	-27.6	0.02	-27.6	<0.01	-27.4
FS2	N1	0.15	0.04	73.3	0.02	0.02	-27.1	0.02	-24.2	<0.01	-26.1
	N2	0.06	0.02	66.7	0.02	0.01	-27.8	0.01	-27.8	<0.01	-27.0
FS3	N1	1.16	0.43	62.9	0.32	0.19	-26.9	0.15	-26.9	0.04	-26.6
	N2	4.23	1.98	53.2	1.60	0.92	-27.3	0.62	-27.1	0.30	<β
FS4	N1	29.51	15.86	46.3	16.38	8.02	-29.2	5.18	-29.1	2.84	-28.3
	N2	3.01	2.01	33.2	1.04	0.49	-27.5	0.34	-27.8	0.15	-27.2
FS5	N1	5.93	3.70	37.6	2.87	1.24	-27.5	0.78	-27.7	0.46	-24.7
	N2	1.32	1.04	21.2	0.50	0.27	-26.3	0.12	-26.9	0.15	-26.0
FS6	N1	0.22	0.11	50.0	0.09	0.02	-28.2	0.01	-28.5	0.01	<β
	N2	0.03	0.01	66.7	<β	<β	<β	<β	<β	<β	<β
FS7	N1	0.13	0.05	61.5	0.01	0.01	-27.7	<0.01	-28.2	<0.01	<β
	N2	5.23	2.17	58.5	1.43	0.64	-27.4	0.39	-27.4	0.25	-28.0

<β = less than twice the blank value.

DNR Tar Ball Study
Cruise FS1181

Aliphatic and Aromatic Hydrocarbon Data

Sta. No.	Tow No.	aliphatics / aromatics	Aliphatics % Resolved	Aliphatics % Unresolved	Aromatics % Resolved	Aromatics % Unresolved
FS1	N1	1.00	68.1	31.9	19.7	80.3
	N2	>0.50	43.9	56.1	13.8	86.2
FS2	N1	>0.50	35.6	64.4	73.0	27.0
	N2	>1.00	53.0	47.0	59.5	40.5
FS3	N1	3.75	24.6	75.4	33.6	66.4
	N2	2.07	37.9	62.1	21.8	78.2
FS4	N1	1.82	37.4	62.6	19.6	80.4
	N2	2.27	31.7	68.3	15.4	84.6
FS5	N1	1.70	28.5	71.5	33.7	66.3
	N2	0.80	25.3	74.7	26.9	73.1
FS6	N1	1.00	21.3	78.7	44.6	55.4
	N2	-	-	-	-	-
FS7	N1	-	46.8	53.2	83.7	16.3
	N2	1.56	23.7	76.3	29.5	70.5

(-) = concentration of tar is less than twice the blank.

DNR Tar Ball Study
Cruise FS1181

Aliphatic Hydrocarbon Molecular Data

Sta. No.	Tow No.	$\frac{nC_{17}}{\text{pristane}}$	$\frac{nC_{18}}{\text{phytane}}$	$\frac{\text{pristane}}{\text{phytane}}$	n-alkane range	n-alkane maximum
FS1	N1	2.19	3.45	0.97	C_{15}-C_{38}	C_{23},C_{26}
	N2	1.93	2.42	0.83	C_{15}-C_{38}	C29
FS2	N1	1.48	1.81	0.77	C_{16}-C_{38}	C_{29}
	N2	1.49	2.07	0.57	C_{14}-C_{38}	C_{29}
FS3	N1	1.73	1.90	0.86	C_{13}-C_{38}	C_{20},C_{26}
	N2	1.90	1.93	0.89	C_{14}-C_{38}	C_{20}
FS4	N1	2.38	2.67	3.69	C_{14}-C_{38}	C_{19}
	N2	1.58	1.33	0.80	C_{15}-C_{38}	C_{20}
FS5	N1	0.64	0.32	0.35	C_{15}-C_{38}	C_{32}
	N2	0.35	1.27	0.57	C_{15}-C_{38}	C_{25},C_{30}
FS6	N1	0.49	0.30	0.65	C_{15}-C_{38}	C_{24}
	N2	-	-	-	-	-
FS7	N1	2.22	2.43	0.82	C_{15}-C_{38}	C_{33}
	N2	0.23	0.37	0.94	C_{15}-C_{38}	C_{28}

(-) = concentration of tar is less than twice the blank.

DNR Tar Ball Study
Cruise FS1181

COMBINED GC/MS ANALYSES OF AROMATIC HYDROCARBONS
(Relative to Phenanthrene)

Sta. No.	Tow No.	N‡	C_1N	C_2N	C_3N	P	C_1P	C_2P	C_3P	DBT	C_1DBT	C_2DBT	C_3DBT
1	N1	0.1	-	0.1	2.5	1.0	19.0	96.2	98.5	0.5	15.9	38.5	29.7
2	N1	-	-	-	-	1.0	23.9	286.9	114.3	0.5	15.6	238.6	138.3
3	N2	0.1	0.6	4.9	58.2	1.0	8.2	21.0	4.4	1.5	7.3	32.7	40.2
4	N1	0.1	0.0	5.6	92.9	1.0	10.9	32.6	7.6	0.4	1.2	5.9	1.9
5	N1	2.0	0.5	-	21.0	1.0	24.3	76.2	36.2	0.4	14.3	520.6	130.2
6	N1	-	-	-	-	-	-	-	-	-	-	-	-
7	N2	3.6	0.4	2.7	5.2	1.0	19.9	159.8	57.0	0.4	9.0	401.2	57.3

---

‡ N = Naphthalene; P = Phenanthrene; DBT = Dibenzothiophene;

C_1 = methyl-; C_2 = dimethyl-; C_3 = trimethyl

(-) = concentration of tar is less than twice the blank value.

DNR Tar Ball Study
Cruise FS1181

COMBINED GC/MS ANALYSES OF AROMATIC HYDROCARBONS

Sta. No.	Tow No.	$\frac{(C_1+C_2+C_3)P}{P}$	$\frac{(C_1+C_2+C_3)DBT}{DBT}$	$\frac{C_1P}{C_1DBT}$	$\frac{C_2P}{C_2DBT}$	$\frac{C_3P}{C_3DBT}$
1	N1	214	168	1.2	2.5	3.3
2	N1	425	785	1.5	1.2	0.8
3	N2	34	53	1.1	0.6	0.1
4	N1	51	22	9.1	5.5	4.0
5	N1	137	1663	1.7	0.1	0.3
6	N1	-	-	-	-	-
7	N2	237	1169	2.2	0.4	1.0

(-) = concentration of tar is less than twice the blank value.

DNR Tar Ball Study
Cruise N182

Gravimetric and Isotopic Analyses
Final Results

Sta. No.	Tow No.	Total Tar wet wt (mg m^{-2})	dry wt (mg m^{-2})	% moisture	extractable lipid (mg m^{-2})	aliphatic + aromatic (mg m^{-2})	$\delta^{13}C$	Aliphatic Hydrocarbons mg m^{-2}	$\delta^{13}C$	Aromatic Hydrocarbons mg m^{-2}	$\delta^{13}C$
1A	N1	0.01	<β	-	<β	<β	-	<β	-	<β	-
	N2	0	0	-	0	0	-	0	-	0	-
7	N1	0	0	-	0	0	-	0	-	0	-
	N2	0	0	-	0	0	-	0	-	0	-
8	N1	0	0	-	0	0	-	0	-	0	-
	N2	0	0	-	0	0	-	0	-	0	-
9	N1	0	0	-	0	0	-	0	-	0	-
	N2	0	0	-	0	0	-	0	-	0	-
10	N1	0	0	-	0	0	-	0	-	0	-
	N2	0	0	-	0	0	-	0	-	0	-
11	N1	0	0	-	0	0	-	0	-	0	-
	N2	0	0	-	0	0	-	0	-	0	-
12	N1	0	0	-	0	0	-	0	-	0	-
	N2	0.02	<β	-	<β	<β	-	<β	-	<β	-

<β = less than twice the blank value.

DNR Tar Ball Study
Cruise SE282

GRAVIMETRIC AND ISOTOPIC ANALYSES

Final Results

	Total Tar							Aliphatic Hydrocarbons		Aromatic Hydrocarbons	
Sta. No.	Tow No.	wet wt (mg m^{-2})	dry wt (mg m^{-2})	% moisture	extractable lipid (mg m^{-2})	aliphatic + aromatic (mg m^{-2})	$\delta^{13}C$	mg m^{-2}	$\delta^{13}C$	mg m^{-2}	$\delta^{13}C$
1	N1	0.10	0.03	70.0	0.04	0.01	-26.82	0.01	-27.07	<0.01	-26.24
	N2	0.50	0.25	50.0	0.22	0.20	ǂ	0.14	-27.62	0.06	-25.30
2	N1	<0.01	<β	-	<β	<β	-	<β	-	<β	-
	N2	0.04	0.01	75.0	0.01	0.01	-27.35	0.01	-25.87	<0.01	-26.70
3	N1	2.83	1.93	31.8	0.61	0.19	-23.46	0.12	-23.47	0.07	-25.18
	N2	0.95	0.50	47.4	0.45	0.29	-26.80	0.20	-27.80	0.09	-23.94
4	N1	0.01	<β	-	<β	<β	-	<β	-	<β	-
	N2	0.00	0	-	0	0	-	0	-	0	-
5	N1	0.02	0.01	50.0	<0.01	<0.01	-26.45	<0.01	-26.42	<0.01	-25.76
	N2	0.04	0.01	75.0	0.01	0.01	-27.63	0.01	-27.10	<0.01	-27.86
6	N1	7.99	5.20	34.9	0.49	0.57	-27.17	0.28	-27.12	0.29	-26.25
	N2	1.37	0.74	46.0	0.74	0.50	-27.46	0.44	-27.78	0.06	-26.96
7	N1	0.18	0.18	0.0	0.05	0.02	-24.78	0.02	-25.14	<0.01	<β
	N2	0.01	0.01	0.0	<0.01	<0.01	-26.35	<0.01	-26.40	<0.01	-26.64

<β = less than twice the blank value.
ǂ = sample lost during work up.

DNR Tar Ball Study
Cruise SE282

ALIPHATIC AND AROMATIC HYDROCARBON DATA

Sta. No.	Tow No.	Aliphatics / Aromatics	Aliphatics % Resolved	Aliphatics % Unresolved	Aromatics % Resolved	Aromatics % Unresolved
1	N1	13.51	39.0	61.0	66.3	33.7
	N2	2.33	36.1	63.9	42.5	57.5
2	N1	-	-	-	-	-
	N2	-	54.5	45.5	29.3	70.7
3	N1	1.71	62.1	37.9	34.3	65.7
	N2	2.22	50.7	49.3	53.2	46.8
4	N1	-	-	-	-	-
	N2	-	-	-	-	-
5	N1	3.00	58.9	41.1	18.7	81.4
	N2	4.93	51.2	48.8	60.2	39.8
6	N1	0.97	41.5	58.5	45.4	54.6
	N2	7.33	49.9	50.1	71.6	28.4
7	N1	-	52.8	47.2	53.0	47.0
	N2	-	57.6	42.4	62.8	37.2

(-) = concentration of tar is less than twice the blank.

DNR Tar Ball Study
Cruise SE282

ALIPHATIC HYDROCARBON MOLECULAR DATA

Sta. No.	Tow No.	$\frac{nC_{17}}{\text{pristane}}$	$\frac{nC_{18}}{\text{phytane}}$	$\frac{\text{pristane}}{\text{phytane}}$	n-alkane range	n-alkane maximum
1	N1	1.20	1.86	0.61	$C_{14}-C_{38}$	C_{18}
	N2	0.86	2.18	2.42	$C_{14}-C_{38}$	C_{17}(Pr)
2	N1	-	-	-	-	-
	N2	1.87	1.99	0.79	$C_{15}-C_{38}$	C_{18}
3	N1	2.41	3.54	1.14	$C_{15}-C_{38}$	C_{19}
	N2	1.45	3.06	1.90	$C_{14}-C_{38}$	C_{18}
4	N1	-	-	-	-	-
	N2	-	-	-	-	-
5	N1	1.23	3.07	1.30	$C_{16}-C_{38}$	C_{19}
	N2	1.24	2.08	0.69	$C_{16}-C_{38}$	C_{18}
6	N1	1.44	2.11	0.79	$C_{16}-C_{38}$	C_{18}
	N2	0.86	2.23	3.17	$C_{14}-C_{38}$	C_{17}(Pr)
7	N1	1.83	2.92	1.37	$C_{13}-C_{38}$	C_{18}
	N2	1.19	3.23	0.87	$C_{16}-C_{38}$	C_{20}

(-) = concentration of tar is less than twice the blank.

DNR Tar Ball Study
Cruise SE282

COMBINED GC/MS ANALYSES OF AROMATIC HYDROCARBONS
(Relative to Phenanthrene)

Sta. No.	Tow No.	Nǂ	C_1N	C_2N	C_3N	P	C_1P	C_2P	C_3P	DBT	C_1DBT	C_2DBT	C_3DBT
1	N2	-	-	1.9	22.3	1.0	7.8	22.3	4.8	0.7	0.5	2.2	0.8
2	N2	-	-	-	-	-	-	-	-	-	-	-	-
3	N1	-	-	-	-	-	-	-	-	-	-	-	-
4	N1/N2	-	-	-	-	-	-	-	-	-	-	-	-
5	N1	-	-	-	-	1.0	42.8	250.0	17.3	-	1.4	71.3	21.4
6	N1	-	-	-	-	1.0	5.8	54.0	40.6	0.3	4.1	40.7	55.4
7	N1	-	-	-	-	1.0	37.1	161.9	25.3	-	9.3	111.1	14.4

ǂ N = Naphthalene; P = Phenanthrene; DBT = Dibenzothiophene;

C_1 = methyl-; C_2 = dimethyl-; C_3 = trimethyl

(-) = concentration of tar is less than twice the blank value.

DNR Tar Ball Study
Cruise SE282

COMBINED GC/MS ANALYSES OF AROMATIC HYDROCARBONS

Sta. No.	Tow No.	$\frac{(C_1+C_2+C_3)P}{P}$	$\frac{(C_1+C_2+C_3)DBT}{DBT}$	$\frac{C_1P}{C_1DBT}$	$\frac{C_2P}{C_2DBT}$	$\frac{C_3P}{C_3DBT}$
1	N2	35	5	15.8	10.1	6.0
2	N2	-	-	-	-	-
3	N1	-	-	-	-	-
4	N1/N2	-	-	-	-	-
5	N1	310	-	30.6	3.5	0.8
6	N1	100	314	1.4	1.3	0.7
7	N1	224	-	4.0	1.5	1.8

(-) = concentration of tar is less than twice the blank value.

DNR Tar Ball Study
Cruise S482

GRAVIMETRIC AND ISOTOPIC ANALYSES

		Total Tar						Aliphatic Hydrocarbons		Aromatic Hydrocarbons	
Sta. No.	Tow No.	wet wt (mg m^{-2})	dry wt (mg m^{-2})	% moisture	extractable lipid (mg m^{-2})	aliphatic + aromatic (mg m^{-2})	$\delta^{13}C$	mg m^{-2}	$\delta^{13}C$	mg m^{-2}	$\delta^{13}C$
1	N1	0.01	<B	-	<B	<B	-	<B	-	<B	-
	N2	0.15	0.09	42.1	0.06	<0.02	-27.41	0.01	-28.45	<.01	-28.09
2	N1	1.35	0.58	56.7	0.36	0.12	-29.25	0.07	-27.68	0.04	-26.99
	N2	0.14	<B	-	<B	<B	-	<B	-	<B	-
3	N1	0.25	0.05	81.0	0.10	<0.02	-26.59	0.01	-26.81	<0.01	-26.99
	N2	0.20	<B	-	<B	<B	-	<B	-	<B	-
4	N1	0.29	0.13	54.1	0.03	<0.03	-26.13	0.02	-26.30	<0.01	-25.93
	N2	0.67	0.24	63.9	0.31	0.09	-27.68	0.08	-27.84	0.01	-27.14
5	N1	0.09	<B	-	<B	<B	-	<B	-	<B	-
	N2	0.19	0.03	85.7	0.03	0.02	-26.61	0.01	-26.77	<0.01	<B
6	N1	0.08	<B	-	<B	<B	-	<B	-	<B	-
	N2	0.34	0.07	78.4	0.08	0.04	-27.40	0.03	-27.75	0.01	-26.86

<B = less than twice the blank value.

DNR Tar Ball Study
Cruise S482

ALIPHATIC AND AROMATIC HYDROCARBON DATA

Sta. No.	Tow No.	Aliphatics / Aromatics	Aliphatics % Resolved	Aliphatics % Unresolved	Aromatics % Resolved	Aromatics % Unresolved
1	N1	-	-	-	-	-
	N2	>1.00	9.6	90.4	44.2	55.8
2	N1	1.75	31.2	68.8	16.2	83.8
	N2	-	-	-	-	-
3	N1	>1.00	23.6	76.4	54.7	45.3
	N2	-	-	-	-	-
4	N1	>2.00	28.6	71.4	29.7	70.3
	N2	8.00	59.2	40.8	14.0	86.0
5	N1	-	-	-	-	-
	N2	>1.00	69.6	30.4	83.6	16.4
6	N1	-	-	-	-	-
	N2	3.00	50.0	50.0	17.9	82.1

(-) = concentration of tar is less than twice the blank.

DNR Tar Ball Study
Cruise S482

ALIPHATIC HYDROCARBON MOLECULAR DATA

Sta. No.	Tow No.	$\frac{nC_{17}}{\text{pristane}}$	$\frac{nC_{18}}{\text{phytane}}$	$\frac{\text{pristane}}{\text{phytane}}$	n-alkane range	n-alkane maximum
1	N1	-	-	-	-	-
	N2	1.8	2.8	0.8	C_{14}-C_{35}	C_{19}
2	N1	1.0	0.9	0.9	C_{14}-C_{35}	C_{19}, C_{27}
	N2	-	-	-	-	-
3	N1	1.3	1.6	0.9	C_{14}-C_{35}	C_{19}, C_{27}
	N2	-	-	-	-	-
4	N1	1.4	1.5	1.1	C_{14}-C_{34}	C_{19}, C_{29}
	N2	1.7	2.7	2.0	C_{13}-C_{34}	C_{15}
5	N1	-	-	-	-	-
	N2	2.2	2.3	0.6	C_{16}-C_{33}	C_{19}
6	N1	-	-	-	-	-
	N2	1.9	1.7	1.2	C_{14}-C_{35}	C_{16}, C_{31}

(-) = concentration of tar is less than twice the blank.

DNR Tar Ball Study
Cruise S482

COMBINED GC/MS ANALYSES OF AROMATIC HYDROCARBONS
(Relative to Phenanthrene)

Sta. No.	Tow No.	N‡	C_1N	C_2N	C_3N	P	C_1P	C_2P	C_3P	DBT	C_1DBT	C_2DBT	C_3DBT
1	N1/N2	-	-	-	-	-	-	-	-	-	-	-	-
2	N1	0.01	0.14	1.43	8.96	1.00	13.28	84.83	63.08	0.23	11.83	73.47	38.45
3	N1	0.05	0.01	-	0.19	1.00	21.37	99.02	85.54	0.04	2.86	11.95	25.32
4	N2	0.00	0.01	0.03	0.76	1.00	1.63	7.34	4.58	0.01	0.95	3.50	2.62
5	N1/N2	-	-	-	-	-	-	-	-	-	-	-	-
6	N2	0.03	0.07	0.86	11.58	1.00	12.45	44.31	17.92	0.96	12.93	61.66	24.45

---

‡ N = Naphthalene; P = Phenanthrene; DBT = Dibenzothiophene;

C_1 = methyl-; C_2 = dimethyl-; C_3 = trimethyl

(-) = concentration of tar is less than twice the blank value.

DNR Tar Ball Study
Cruise S482

COMBINED GC/MS ANALYSES OF AROMATIC HYDROCARBONS

Sta. No.	Tow No.	$\frac{(C_1+C_2+C_3)P}{P}$	$\frac{(C_1+C_2+C_3)DBT}{DBT}$	$\frac{C_1P}{C_1DBT}$	$\frac{C_2P}{C_2DBT}$	$\frac{C_3P}{C_3DBT}$
1	N1	-	-	-	-	-
2	N1	161.19	538.04	1.12	1.15	1.64
3	N1	205.93	1003.25	7.47	8.29	3.38
4	N2	13.55	707.00	1.72	2.10	1.75
5	N2	-	-	-	-	-
6	N2	74.68	103.17	0.96	0.72	0.73

(-) = concentration of tar is less than twice the blank value.

DNR Tar Ball Study
Cruise YS582

GRAVIMETRIC AND ISOTOPIC ANALYSES

		Total Tar						Aliphatic Hydrocarbons		Aromatic Hydrocarbons	
Sta. No.	Tow No.	wet wt (mg m^{-2})	dry wt (mg m^{-2})	% moisture	extractable lipid (mg m^{-2})	aliphatic + aromatic (mg m^{-2})	$\delta^{13}C$	mg m^{-2}	$\delta^{13}C$	mg m^{-2}	$\delta^{13}C$
1	N1	0.12	0.01	88.0	<B	<B	-	<B	-	<B	-
	N2	0.54	0.21	61.4	0.16	0.24	-26.63	0.18	-27.72	0.06	-26.56
2	N1	0.18	0.04	78.4	0.02	<B	-26.75	<B	-26.95	<B	-26.34
	N2	1.34	1.25	6.4	0.82	0.55	-30.10	0.35	-30.20	0.20	-29.30
3	N1	0.68	0.35	47.9	0.18	<0.19	-27.00	0.18	-27.27	<0.01	<B
	N2	1.54	0.21	86.5	0.21	0.15	-26.42	0.10	-26.58	0.05	-26.29
4	N1	0.51	0.14	71.9	0.14	0.05	-26.21	0.04	-26.50	0.01	-26.59
	N2	0.67	0.21	68.1	0.21	0.11	26.95	0.09	-27.46	0.02	-27.02
5	N1	0.09	0.02	82.4	<B	<B	-	<B	-	<B	-
	N2	0.03	<B	<B	<B	<B	-	<B	-	<B	-

<B = less than twice the blank value.

DNR Tar Ball Study
Cruise YS582

ALIPHATIC AND AROMATIC HYDROCARBON DATA

			Aliphatics		Aromatics	
Sta. No.	Tow No.	Aliphatics / Aromatics	% Resolved	% Unresolved	% Resolved	% Unresolved
1	N1	-	-	-	-	-
	N2	3.00	57.7	42.3	51.4	48.6
2	N1	-	39.4	60.6	33.7	66.3
	N2	1.75	55.4	44.6	28.4	71.6
3	N1	>18.00	71.7	28.3	61.8	38.2
	N2	2.00	47.7	52.3	31.0	69.0
4	N1	4.00	57.0	43.0	24.3	75.7
	N2	4.50	61.5	38.5	51.4	48.6
5	N1	-	-	-	-	-
	N2	-	-	-	-	-

(-) = concentration of tar is less than twice the blank.

DNR Tar Ball Study
Cruise YS582

ALIPHATIC HYDROCARBON MOLECULAR DATA

Sta. No.	Tow No.	nC_{17} / pristane	nC_{18} / phytane	pristane / phytane	n-alkane range	n-alkane maximum
1	N1	-	-	-	-	-
	N2	2.2	2.9	1.6	C_{13}-C_{35}	C_{17}, C_{27}
2	N1	1.5	2.1	1.3	C_{12}-C_{34}	C_{19}
	N2	2.1	1.6	1.2	C_{13}-C_{35}	C_{14}
3	N1	2.3	4.0	2.1	C_{13}-C_{34}	C_{17}, C_{29}
	N2	1.8	2.8	2.3	C_{12}-C_{35}	C_{15}, C_{27}
4	N1	1.3	2.8	2.4	C_{12}-C_{35}	C_{17}, C_{27}
	N2	2.2	2.5	1.2	C_{12}-C_{35}	C_{17}, C_{27}
5	N1	-	-	-	-	-
	N2	-	-	-	-	-

(-) = concentration of tar is less than twice the blank.

DNR Tar Ball Study
Cruise YS582

COMBINED GC/MS ANALYSES OF AROMATIC HYDROCARBONS
(Relative to Phenanthrene)

Sta. No.	Tow No.	N‡	C_1N	C_2N	C_3N	P	C_1P	C_2P	C_3P	DBT	C_1DBT	C_2DBT	C_3DBT
1	N2	0.03	0.05	3.55	19.32	1.00	12.91	36.25	12.18	0.48	4.36	19.10	8.11
2	N2	0.10	0.16	31.53	114.85	1.00	6.60	17.95	10.86	0.72	6.74	31.91	23.99
3	N1/N2	-	-	-	-	-	-	-	-	-	-	-	-
4	N1	-	0.08	0.37	14.07	1.00	27.65	113.75	58.73	0.62	13.59	98.52	55.98
5	N1/N2	-	-	-	-	-	-	-	-	-	-	-	-

---

‡ N = Naphthalene; P = Phenanthrene; DBT = Dibenzothiophene;

C_1 = methyl-; C_2 = dimethyl-; C_3 = trimethyl

(-) = concentration of tar is less than twice the blank value.

DNR Tar Ball Study
Cruise YS582

COMBINED GC/MS ANALYSES OF AROMATIC HYDROCARBONS

Sta. No.	Tow No.	$\frac{(C_1+C_2+C_3)P}{P}$	$\frac{(C_1+C_2+C_3)DBT}{DBT}$	$\frac{C_1P}{C_1DBT}$	$\frac{C_2P}{C_2DBT}$	$\frac{C_3P}{C_3DBT}$
1	N2	61.34	65.77	2.93	1.90	1.50
2	N2	35.41	87.00	0.98	0.56	0.45
3	N1/N2	-	-	-	-	-
4	N1	200.13	271.11	2.03	1.15	1.05
5	N1/N2	-	-	-	-	-

(-) = concentration of tar is less than twice the blank value.

DNR Tar Ball Study
Cruise S682

GRAVIMETRIC AND ISOTOPIC ANALYSES

		Total Tar						Aliphatic Hydrocarbons		Aromatic Hydrocarbons	
Sta. No.	Tow No.	wet wt ($mg\ m^{-2}$)	dry wt ($mg\ m^{-2}$)	% moisture	extractable lipid ($mg\ m^{-2}$)	aliphatic + aromatic ($mg\ m^{-2}$)	$\delta^{13}C$	$mg\ m^{-2}$	$\delta^{13}C$	$mg\ m^{-2}$	$\delta^{13}C$
1A	N1	0	0	-	0	0	-	0	-	0	-
1A	N2	0	0	-	0	0	-	0	-	0	-
1	N1	0	0	-	0	0	-	0	-	0	-
1	N2	0	0	-	0	0	-	0	-	0	-
2	N1	0	0	-	0	0	-	0	-	0	-
2	N2	0	0	-	0	0	-	0	-	0	-
3	N1	0.11	0.02	80.78	0.02	0.02	-27.0	0.01	-27.2	0.01	-27.6
3	N2	0.14	0.01	89.65	0.02	<0.02	-26.2	<0.01	-26.4	0.01	-26.8
4	N1	0.09	0.01	86.36	0.02	<0.01	-26.5	<0.01	-26.8	<0.01	-29.3
4	N2	0.09	0.01	85.01	0.02	<0.01	-26.8	<0.01	-26.8	0.00	<β
5	N1	<β	<β	-	<β	<β	-	<β	-	<β	-
5	N2	0.23	0.08	65.22	0.02	0.04	-27.5	0.02	-27.7	0.02	-27.0
6	N1	0.16	0.04	77.42	0.02	0.04	-27.1	0.02	ǂ	0.02	-26.2
6	N2	0.17	0.06	66.68	0.02	<0.03	-27.2	0.02	-27.7	<0.01	-26.7

<β = less than twice the blank value.

ǂ = sample lost during workup.

DNR Tar Ball Study
Cruise S682

ALIPHATIC AND AROMATIC HYDROCARBON DATA

Sta. No.	Tow No.	Aliphatics / Aromatics	Aliphatics % Resolved	Aliphatics % Unresolved	Aromatics % Resolved	Aromatics % Unresolved
1A	N1	-	-	-	-	-
1A	N2	-	-	-	-	-
1	N1	-	-	-	-	-
1	N2	-	-	-	-	-
2	N1	-	-	-	-	-
2	N2	-	-	-	-	-
3	N1	1.0	48.08	51.92	53.38	46.62
3	N2	0.3	37.42	62.58	41.81	58.19
4	N1	1.0	50.48	49.52	85.55	14.45
4	N2	0.0	46.69	53.31	52.83	47.17
5	N1	-	-	-	-	-
5	N2	1.0	48.49	51.51	75.38	24.62
6	N1	1.0	50.95	49.05	22.63	77.37
6	N2	5.0	55.80	44.20	42.42	57.58

(-) = concentration of tar is less than twice the blank.

DNR Tar Ball Study
Cruise S682

ALIPHATIC HYDROCARBON MOLECULAR DATA

Sta. No.	Tow No.	$\frac{nC_{17}}{pristane}$	$\frac{nC_{18}}{phytane}$	$\frac{pristane}{phytane}$	n-alkane range	n-alkane maximum
1A	N1	-	-	-	-	-
1A	N2	-	-	-	-	-
1	N1	-	-	-	-	-
1	N2	-	-	-	-	-
2	N1	-	-	-	-	-
2	N2	-	-	-	-	-
3	N1	1.60	1.62	0.78	nC16-nC28	nC18
3	N2	0.60	0.77	0.65	nC16-nC22	Phytane
4	N1	1.33	1.65	1.19	nC14-nC32	nC18
4	N2	1.23	1.35	1.02	nC15-nC35	nC18
5	N1	-	-	-	-	-
5	N2	0.92	2.05	1.51	nC14-nC35	nC16,nC35
6	N1	1.24	1.82	1.51	nC14-nC35	nC17,nC35
6	N2	1.99	1.99	1.21	nC14-nC35	nC17

(-) = concentration of tar is less than twice the blank.

DNR Tar Ball Study
Cruise S682

COMBINED GC/MS ANALYSES OF AROMATIC HYDROCARBONS
(Relative to Phenanthrene)

Sta. No.	Tow No.	N‡	C_1N	C_2N	C_3N	P	C_1P	C_2P	C_3P	DBT	C_1DBT	C_2DBT	C_3DBT
1A	N1/N2	-	-	-	-	-	-	-	-	-	-	-	-
1	N1/N2	-	-	-	-	-	-	-	-	-	-	-	-
2	N1/N2	-	-	-	-	-	-	-	-	-	-	-	-
3	N1	30.53	6.71	2.65	0.13	1.00	18.27	100.81	82.82	0.23	3.42	45.64	102.16
4	N1	49.59	9.11	4.50	3.95	1.00	12.85	43.20	36.87	0.17	7.80	67.34	64.00
5	N2	43.14	11.53	14.69	20.98	1.00	9.26	46.01	57.94	0.08	2.42	37.76	31.59
6	N2	0.84	0.33	0.40	0.36	1.00	14.71	95.27	156.33	0.43	12.95	177.18	166.44

‡ N = Naphthalene; P = Phenanthrene; DBT = Dibenzothiophene;

C_1 = methyl-; C_2 = dimethyl-; C_3 = trimethyl

(-) = concentration of tar is less than twice the blank value.

DNR Tar Ball Study
Cruise S682

COMBINED GC/MS ANALYSES OF AROMATIC HYDROCARBONS

Sta. No.	Tow No.	$\frac{(C_1+C_2+C_3)P}{P}$	$\frac{(C_1+C_2+C_3)DBT}{DBT}$	$\frac{C_1P}{C_1DBT}$	$\frac{C_2P}{C_2DBT}$	$\frac{C_3P}{C_3DBT}$
1A	N1/N2	-	-	-	-	-
1	N1/N2	-	-	-	-	-
2	N1/N2	-	-	-	-	-
3	N1	201.90	657.48	5.34	2.21	0.81
4	N1	92.92	818.47	1.65	0.64	0.58
5	N2	113.21	897.12	3.83	1.22	1.83
6	N2	266.31	829.23	1.14	0.54	0.94

(-) = concentration of tar is less than twice the blank value.

DNR Tar Ball Study
Cruise CG782

GRAVIMETRIC AND ISOTOPIC ANALYSES

		Total Tar						Aliphatic Hydrocarbons		Aromatic Hydrocarbons	
Sta. No.	Tow No.	wet wt (mg m^{-2})	dry wt (mg m^{-2})	% moisture	extractable lipid (mg m^{-2})	aliphatic + aromatic (mg m^{-2})	$\delta^{13}C$	mg m^{-2}	$\delta^{13}C$	mg m^{-2}	$\delta^{13}C$
1A	N1	0.23	0.08	65.22	<β	<β	<β	<β	<β	<β	<β
1A	N2	0	0	-	0	0	-	0	-	0	-
1	N1	0	0	-	0	0	-	0	-	0	-
1	N2	0	0	-	0	0	-	0	-	0	-
2	N1	0.15	0.03	80.00	0.03	0.01	-27.73	0.01	-27.87	0.003	-26.49
2	N2	0.45	0.13	71.11	0.08	0.02	-26.65	0.003	-27.18	0.02	-26.28
3	N1	0.42	0.04	90.48	0.02	0.01	-26.93	0.01	-26.46	0.004	-26.55
3	N2	0.03	<β	-	<β	<β	<β	<β	<β	<β	<β
4	N1	0.14	0.02	85.71	0.01	0.01	-27.21	0.01	-27.58	0.002	-29.22
4	N2	0.43	0.22	48.84	0.14	0.07	-28.79	0.04	-25.67	0.03	-28.15
5	N1	24.82	14.37	42.10	9.98	4.31	-26.99	2.03	-27.24	2.28	-28.08
5	N2	0.64	0.18	71.88	0.14	0.07	-26.95	0.04	-26.80	0.03	-27.02
6	N1	4.25	3.04ǂ	28.47ǂ	0.99ǂ	0.44ǂ	-26.94	0.20ǂ	<β	0.24ǂ	-26.96
6	N2	0.42	0.17	59.52	0.10	0.12	-29.13	0.11	-29.40	0.01	-28.23
7	*G1	1.60×10^5	0.60×10^5	62.64	0.44×10^5	0.20×10^5	-29.16	0.11×10^5	-26.46	0.09×10^5	-26.44

<β = Less than twice the blank value.
*G1 = Grab sample
ǂ = Sample partially lost during analysis, value estimated.

DNR Tar Ball Study
Cruise CG782

ALIPHATIC AND AROMATIC HYDROCARBON DATA

Sta. No.	Tow No.	Aliphatics / Aromatics	Aliphatics % Resolved	Aliphatics % Unresolved	Aromatics % Resolved	Aromatics % Unresolved
1A	N1	-	-	-	-	-
1A	N2	-	-	-	-	-
1	N1	-	-	-	-	-
1	N2	-	-	-	-	-
2	N1	3.33	54.59	45.41	59.20	40.80
2	N2	0.15	53.02	46.98	87.18	12.82
3	N1	2.50	55.28	44.72	49.01	50.99
3	N2	-	-	-	-	-
4	N1	5.00	55.88	44.12	81.40	18.60
4	N2	1.33	79.24	20.76	65.15	34.85
5	N1	0.89	77.73	22.27	86.88	13.12
5	N2	1.33	48.02	51.98	58.06	41.94
6	N1	0.83	57.33	42.67	61.00	39.00
6	N2	11.00	73.64	26.36	66.82	33.18
7	G1	1.22	82.95	17.05	56.46	43.54

(-) = concentration of tar is less than twice the blank.

DNR Tar Ball Study
Cruise CG782

ALIPHATIC HYDROCARBON MOLECULAR DATA

Sta. No.	Tow No.	$\frac{nC_{17}}{\text{pristane}}$	$\frac{nC_{18}}{\text{phytane}}$	$\frac{\text{pristane}}{\text{phytane}}$	n-alkane range	n-alkane maximum
1A	N1	-	-	-	-	-
1A	N2	-	-	-	-	-
1	N1	-	-	-	-	-
1	N2	-	-	-	-	-
2	N1	1.12	1.40	1.20	$C_{13}-C_{35}$	C_{18}, C_{32}
2	N2	2.10	1.66	1.16	$C_{13}-C_{35}$	C_{17}
3	N1	1.38	2.06	1.90	$C_{12}-C_{35}$	C_{17}, C_{31}
3	N2	-	-	-	-	-
4	N1	1.49	2.23	1.84	$C_{13}-C_{34}$	C_{17}, C_{29}
4	N2	1.78	1.73	1.66	$C_{13}-C_{34}$	C_{16}, C_{31}
5	N1	2.02	1.96	1.62	$C_{13}-C_{34}$	C_{17}
5	N2	0.62	0.76	1.15	$C_{13}-C_{35}$	Pristane
6	N1	1.85	2.19	1.88	$C_{13}-C_{35}$	C_{16}
6	N2	1.76	1.49	1.45	$C_{13}-C_{35}$	C_{16}, C_{30}
7	G1	3.09	2.81	1.69	$C_{13}-C_{35}$	C_{15}

(-) = concentration of tar is less than twice the blank.

DNR Tar Ball Study
Cruise CG782

COMBINED GC/MS ANALYSES OF AROMATIC HYDROCARBONS
(Relative to Phenanthrene)

Sta. No.	Tow No.	N[‡]	C_1N	C_2N	C_3N	P	C_1P	C_2P	C_3P	DBT	C_1DBT	C_2DBT	C_3DBT
1A	N1/N2	-	-	-	-	-	-	-	-	-	-	-	-
1	N1/N2	-	-	-	-	-	-	-	-	-	-	-	-
2	N2	43.08	58.39	180.02	108.48	1.00	4.35	9.92	6.92	0.17	6.00	21.67	19.19
3	N1	53.43	177.04	368.93	156.21	1.00	8.26	26.57	24.34	0.03	4.18	23.59	28.81
4	N2	11.20	0.13	136.61	72.92	1.00	9.52	23.11	19.18	0.72	15.93	56.52	26.45
5	N1	196.41	114.76	133.94	59.50	1.00	8.89	18.38	12.74	0.45	6.08	26.97	20.66
6	N2	43.16	91.94	318.94	265.27	1.00	8.55	15.19	16.66	0.62	12.13	34.87	25.04
7	G1	26.74	34.78	66.43	131.24	1.00	7.81	11.75	10.82	1.75	22.19	37.70	19.01

[‡] N = Naphthalene; P = Phenanthrene; DBT = Dibenzothiophene;

C_1 = methyl-; C_2 = dimethyl-; C_3 = trimethyl

(-) = concentration of tar is less than twice the blank value.

DNR Tar Ball Study
Cruise CG782

COMBINED GC/MS ANALYSES OF AROMATIC HYDROCARBONS

Sta. No.	Tow No.	$\frac{(C_1+C_2+C_3)P}{P}$	$\frac{(C_1+C_2+C_3)DBT}{DBT}$	$\frac{C_1P}{C_1DBT}$	$\frac{C_2P}{C_2DBT}$	$\frac{C_3P}{C_3DBT}$
1A	N1/N2	-	-	-	-	-
1	N1/N2	-	-	-	-	-
2	N2	21.19	275.65	0.73	0.46	0.36
3	N1	59.17	1886.00	1.98	1.13	0.84
4	N2	51.81	137.36	0.60	0.41	0.73
5	N1	40.01	119.36	1.46	0.68	0.62
6	N2	40.40	116.19	0.70	0.44	0.67
7	G1	30.38	45.09	0.35	0.31	0.57

(-) = concentration of tar is less than twice the blank value.

APPENDIX II: Personnel

Florida Institute of Oceanography

Dr. W.W. Behrens, Jr. - Project Coordinator
Mr. D.M. Milliken - Assistant Project Coordinator
Ms. B. Estes - Secretary
Ms. L. Miros - Secretary

University of South Florida, Department of Marine Science

Dr. E.S. Van Vleet - Principal Investigator
- GC and GCMS Coordinator
Dr. W.M. Sackett - Principal Investigator
- Stable Carbon Isotope Coordinator
Ms. S. Reinhardt - Graduate Student Assistant
Ms. M. Mangini - Graduate Student Assistant
Mr. B. Weigle - Graduate Student Assistant

APPENDIX III: List of publications resulting from Year 1 study.

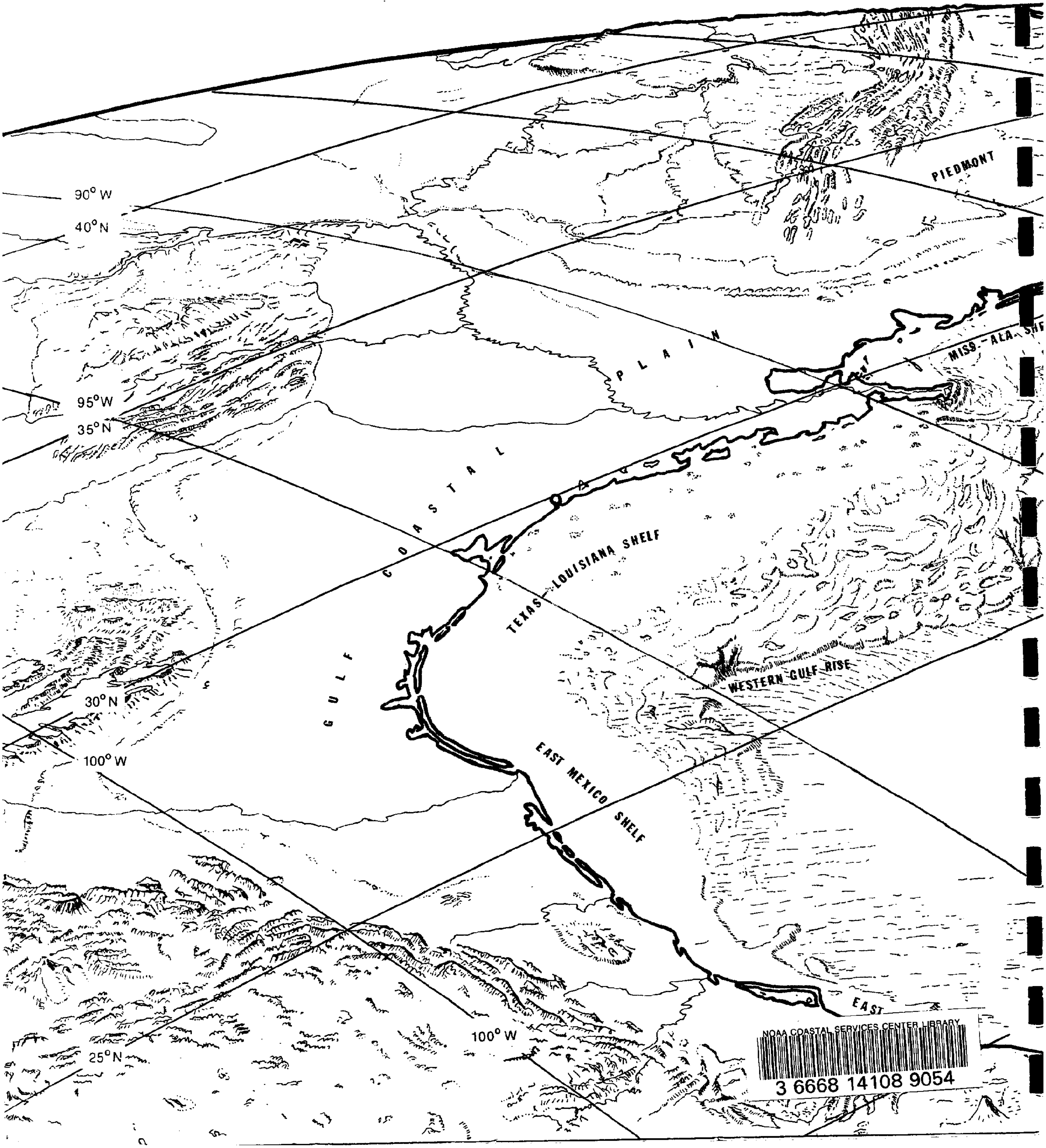
Van Vleet, E.S., W.M. Sackett and W.W. Behrens, Jr. 1981. Spatial and Temporal Variations of Crude Oil Residues in Continental Shelf Waters Offshore Western Florida. Final Report submitted to the Florida Department of Natural Resources. 87 p.

Van Vleet, E.S. and W.M. Sackett. 1981. Pelagic tar distribution in the Eastern Gulf of Mexico. Coastal Oceanography and Climatology News. 3(4): 51-52.

Van Vleet, E.S., W.M. Sackett, F.F. Weber, Jr. and S.B. Reinhardt. 1982. Spatial and temporal variation of pelagic tar in the Eastern Gulf of Mexico. In, Advances in Organic Geochemistry, 1981. M. Bjoray (ed.), In Press.

Van Vleet, E.S., W.M. Sackett, F.F. Weber, Jr. and S.B. Reinhardt. 1982. Input of pelagic tar into the northwest Atlantic from the Gulf Loop Current: Chemical characterization and its relation to weathered IXTOC-I oil. Canadian Journal of Fisheries and Aquatic Science. In Press.

Van Vleet, E.S. 1982. Oil Contamination of the Gulf of Mexico. Proceedings of the Gulf of Mexico -- Trends for the '80's Conference. July 23-25, 1982. Louisiana University Marine Science Consortium. New Orleans, Louisiana. In Press.


PIEDMONT
90° W
40° N
MISS.-ALA. SH
PLAIN
95° W
35° N
GULF COASTAL
TEXAS-LOUISIANA SHELF
WESTERN GULF RISE
30° N
100° W
EAST MEXICO SHELF
EAST
100° W
25° N