NOAA/University of Miami Joint Publication
NOAA Technical Memorandum NOS NCCOS 9
University of Miami RSMAS TR 2005-01

Coastal and Estuarine Data Archaeology and Rescue Program

1983
BISCAYNE BAY HYDROCARBON STUDY

University of Miami
Rosenstiel School of Marine and Atmospheric Science
Miami, FL

February 2005

US Department of Commerce
National Oceanic and Atmospheric Administration
Silver Spring, MD

Miami-Dade County
Department of Environmental Resources Management
Miami, FL

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BISCAYNE BAY HYDROCARBON STUDY

FINAL REPORT

by

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February 2005

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PREFACE

This final report is the culmination of a two-year project designed to establish background levels of hydrocarbons to support oil spill impact assessment and determine possible sources of petroleum contamination in Biscayne Bay. The first year of the study supplied information on the distribution of hydrocarbons in the surface sediments and selected biota. The second year study used the previously developed database to select areas which indicated petroleum contamination. These areas were further evaluated by collecting and analyzing additional surface and subsurface sediments, biota and water.

This report contains all information collected during the two year project period. The information contained in this final report supersedes all other materials in previous quarterly and annual reports.

ABSTRACT

A two year, comprehensive, quantitative investigation was conducted to analyze and identify the spatial distribution of petrogenic and biogenic hydrocarbons in sediments, surface waters, fish and shellfish of Biscayne Bay, Florida.

The goal for the first year of the project was to establish baseline information to support oil spill impact assessment and clean-up. One hundred fifty-five sediment and eleven biota samples were collected. The areas sampled included the Miami River, Intracoastal Waterway, tidal flats, access canals and environmentally sensitive shorelines.

The second year of the study centered on areas exhibiting petroleum contamination. These areas included the Miami River, Little River, Goulds Canal, Black Creek and Military Canal. Surface and subsurface sediment, biota and surface water were collected.

Sample collection, analyses, and data handling for the two year project were conducted so that all information was court-competent and scientifically accurate. Chain of custody was maintained for all samples.

Total hydrocarbon content of surface sediments ranged from below detection limits to a high of 2663.44 pg/g. Several sample stations contained petroleum contamination. The majority of biota samples exhibited hydrocarbon concentrations and characteristics that indicated little, if any, petroleum contamination. Surface water samples ranged from 0.78 to 64.47 μg/L and several samples contained petroleum hydrocarbons.

Our results indicate several areas of petroleum contamination. These areas are characterized by industrial complexes, port facilities, marinas, major boating routes and many of the major tributaries emptying into Biscayne Bay.

EXECUTIVE SUMMARY

Location of study area

Biscayne Bay is a large lagoonal system located along the southeast coast of Florida. The Bay extends from 25° 58' N to 25° 24' N latitude, covers approximately 573 km^2, and is almost entirely contained within Dade County. The Bay is unique in many ways. It offers a large, year-round protected body of water, with a great diversity of natural resources close to a major metropolitan area (Miami) and has retained to a large degree, in its southern extremities, a character of undisturbed tropical naturalness. The local economy is tourism based and dependent on climate and esthetics. The Bay plays a very important role in the economy by supplying esthetics and extensive recreational and commercial activities. The Bay contains within its boundaries the largest port (dollar value of imports and exports) in Florida and the Biscayne National Park.

The south Florida area is dominated by major vessel traffic routes which encompass both offshore corridors and the Intracoastal Waterway. During the late seventies a US Coast Guard survey revealed that in excess of one million tons of crude oil per day passed within 25 miles or less of the southern Florida coastline. In addition, over three million tons of cargo are shipped via the Intracoastal Waterway through Biscayne Bay. Fuel oil leads all of the commodities shipped by this route in volume.

The planned exploration for offshore oil and its increased production in the Gulf of Mexico, Caribbean Sea and Mexico, the continuous growth of the Dade County economy and its rapid movement towards becoming a major trade center has increased substantially the probability of collisions and groundings resulting in oil spills and inputs of urban petroleum compounds. The prospect of a major oil spill occurring in the southern Florida/Biscayne Bay area is so prominent that during 1981-82 the South Florida Regional Planning Council produced three documents to assist in response and clean-up. These are the "South Florida Oil Spill Response Handbook", "The Sensitivity of Coastal Environments and Wildlife to Spilled Oil in South Florida" and the "South Florida Oil Spill Sensitivity Atlas."

Purpose

The purpose of the two-year study was to supply the State of Florida Department of Natural Resources with a quantitative, court-competent database of the distribution of petroleum and naturally occurring hydrocarbons in the Biscayne Bay lagoonal system. This data will supply the needed background information to support oil spill clean-up and evaluation. The first year study was designed to provide information about the spatial distribution of hydrocarbons in the surface sediments and marine organisms of commercial and recreational value. These data were to be used to establish the present background levels and distribution of petroleum and naturally occurring hydrocarbons within the Bay and to assess any future contamination. In the event of an oil spill these data can supply the necessary information needed to determine its present and potential damage. The goal of the second year of the study was to investigate and further quantify those areas where petroleum contamination was found and to determine its possible sources. In addition to surface sediment, subsurface sediment, surface water and marine organisms were analyzed to accomplish this goal.

Results

During the two year duration of the study, 205 surface sediments, 27 surface water samples and 21 marine organisms were collected and analyzed for hydrocarbons. Sediment collection sites for the Year 01 study were selected by incorporating criteria relating to the physical, chemical, and biological processes and man's historical, present and future usage of the Bay. The second year study focused on areas where high concentrations of petroleum contaminated sediment were detected.

The total hydrocarbon content in the surface sediments ranged from below detection limits to 2663.4 μg/g, surface waters ranged from 0.8 to 64.5 μg/L and organism samples ranged from 0.3 to 600.8 μg/g. Only one organism sample collected during the two year project showed any petroleum contamination. These were flat tree oysters collected from a marina. Several of the surface water samples collected showed indications of petroleum contamination. These samples were always associated with canal systems. The sample containing the highest concentration was collected in the Miami River and the lowest came from Black Creek. The sediments were the best indicator of contamination since they are the ultimate sink for this pollutant. A review of the hydrocarbon content and indices for the sediment collected during the first year indicated that 52 samples showed characteristics of petroleum contamination. These areas were associated with two main usage patterns. 1) Areas associated with boats and ships, e.g. major transportation routes, moorings, cargo handling, and construction and maintenance. 2) Areas which receive runoff and other inputs from the highly urbanized regions of Dade County.

Four major study areas which showed high concentrations of petroleum hydrocarbons were investigated during the second year of the study. These included the Little River, Miami River, Black Creek/Goulds Canal, and Military Canal. Surface water, marine organisms and additional sediment samples were collected from these areas to assist in further characterizing the magnitude of pollution and determine its sources.

The Miami River sediment had the highest concentrations of hydrocarbons detected during the two year project. The River falls under both usage patterns referenced above. It is a major complex for handling cargo, ship maintenance and repair and also receives runoff from the highly urbanized downtown Miami area. In contrast to the Miami River would be the Little River experiences only minimal boat traffic but receives high inputs of runoff from urbanized Miami. This area also showed elevated levels of hydrocarbons of petroleum origin. Military Canal, which for all practical purposes receives no boat traffic, indicated elevated concentrations of hydrocarbons. This canal, located in the southern portion of Biscayne Bay, drains a major military establishment. The Black Creek/Goulds Canal area is characterized by two canals which converge before emptying into Biscayne Bay. During the Year 01 study, the sediment sample collected at the intersection of the two canals indicated petroleum contamination, after further investigation during Year 02 it was determined that the majority of the contaminants were coming from Goulds Canal. This canal receives the majority of the small boat traffic and contains two marinas.

The information gathered during the two-year study has established a baseline for the distribution of hydrocarbons in Biscayne Bay. This database will be most useful in future studies and for establishing levels of contamination from oil spills or other sources of petroleum contaminants. It has also established a benchmark from which future changes in the concentration and distribution of hydrocarbons can be compared.

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1. Introduction

1.1. Purpose

The purpose of this two-year study was to supply the State of Florida Department of Natural Resources with a quantitative, court-competent database of the distribution of petrogenic and biogenic hydrocarbons in the Biscayne Bay lagoonal system. This data was to supply the needed background information to support oil spill clean-up and evaluation. The first year study provided information about the spatial distribution of hydrocarbons in the surface sediments. In addition selected biota of commercial and recreational value were collected and analyzed. These data were used to establish the present background levels and distribution of petrogenic hydrocarbons within the Bay and can be used to assess future contamination. In the event of an oil spill, these data can supply the necessary information needed to determine its present and potential damage. The goal of the second year of the study was to investigate and further quantify those areas where petroleum contamination was found during the first year study and to determine their possible sources. Sediment, water and biota were collected and analyzed using gas chromatography and gas chromatography /mass spectroscopy.

1.2. History of Study Area

1.2.1. Background Information

Biscayne Bay is a large lagoonal system located on the southeast coast of Florida. The Bay is unique in many ways. It offers a large, year-round protected body of water, with a great diversity of natural resources, close to a major metropolitan area and has retained to a large degree, in its southern extremities, a character of undisturbed tropical naturalness. Economically the surrounding areas are dependent on the Bay. The local economy is tourism based and dependent on climate and esthetics (Thorhaug, 1977). The Bay plays a very important role in this economy by supplying esthetics and both extensive recreational and commercial activities. The Bay is unique in another very important area best defined as user awareness and concern. This is exemplified by the establishment of the Biscayne Bay Management Plan.

Since the founding of the City of Miami in 1896, the northern and central portions of the Bay have undergone extensive physical, biological and chemical alterations. These alterations are the direct result of unmanaged and inadequately planned urbanization, dredge and fill activities, channelization, water management techniques and changes in the natural shoreline. During the mid to late seventies, great concern arose as to the future of Biscayne Bay. Past uses of the shoreline had resulted in habitat destruction, water pollution and lack of public access. To rectify these problems and abate many of the future problems caused by the increasing use pressure of the Bay the Board of County Commissioners, in 1978, declared Biscayne Bay an "Aquatic Park and Conservation Area". In conjunction with the declaration, monies were appropriated to develop a management plan to guide the Bay's future and clarify and consolidate the jurisdictional controls over the Bay and its shorelines. Since the completion of the management plan in March of 1981, the local county government has actively pursued establishing baseline data and the development and refinement of management protocols for the Bay.

The increasing growth of Dade County, the expansion of the Port of Miami for the purpose of handling more and larger shipping traffic, and increasing use of the port facilities of the Miami River have caused a constant increase in the input of anthropogenic petroleum products to the Bay and has substantially raised the possibilities of a major oil spill within the Bay proper.

A vessel traffic study conducted in 1976 by the U.S. Coast Guard showed an average of 38 oil-carrying tanker vessels per day transported over a million tons of crude oil per day within 5 to 25 miles of the southern Florida coastline.

The study also identified the major vessel traffic lanes. There are three crossing and merging areas located near southern Florida. The approximate location of these areas are: 13 miles south-southeast of Miami; 14 miles south of the Dry Tortugas; and 13 miles south-southeast of West Palm Beach. These areas, where major traffic lanes cross and merge, increase the possibility of collisions and spills.

Many vessels stay within coastal waters and utilize the Intracoastal Waterway (ICW) to avoid Gulf Stream currents and rough waters. Wilson (1975) estimated that 3 million tons of cargo were shipped via the ICW and Biscayne Bay. Fuel oil leads all of those commodities shipped in volume.

The recent planned exploration for offshore oil and the increased production in the Gulf of Mexico, Caribbean Sea and Mexico, the continuous growth of the Dade County economy and its rapid movement towards becoming a major trade center has unquestionably caused an increase in the tanker traffic off the southern Florida coast and within the coastal zone during the last several years. This substantially increases the probability of collisions, groundings and oil spills within southern Florida and the Biscayne Bay area.

1.2.2. Geography

Biscayne Bay is classified as a shallow, semi-tropical lagoon (Roessler and Beardsley, 1975). The Bay covers 573 km^2 (W. Campos, per. com.), is north-south tending, approximately 56 km in length and averages 8 km in width with a maximum width of about 16 km. The average depth is approximately 1.8 m with a maximum depth of 4 m (Roessler and Beardsley, 1975) except in dredged areas where depths are reported to exceed 12 m. The major tributaries are Arch Canal, Biscayne Canal, Little River, Miami River, Coral Gables Waterway, Snapper Creek, Black Creek, Goulds Canal, North Canal, Florida City Canal, and the Model Land Canal. The Miami River has the largest input into the Bay and averages 18 m^3/sec (Wilson, 1975).

The Bay is bound on the north by Dumfoundling Bay, which was historically a shallow water marsh, and on the south by Card Sound. The western side includes the mainland (Miami and suburbs) and to the southwest the Everglades. The eastern border is formed by sedimentary barrier islands (Miami Beach) to the north, and to the south a tidal bar belt (Safety Valve) and a continuous line of bedrock islands (Florida Keys) (Wanless, 1976).

The system was originally a freshwater basin until about 4,000 years ago, when the gradual rise in sea level inundated the area. The majority of the freshwater input during this time was by overland flow and groundwater seepage from adjacent uplands. As recently as the 19th century, freshwater marshes bordered the western side and freshwater springs flowed within the Bay. The input of freshwater declined as upland areas were drained and overland flow was altered by urban and agricultural development (Thorhaug, 1977). Accompanying this decrease in freshwater was an increase in saline water input caused by openings cut in the barrier islands to facilitate access to the Bay by ships. This resulted in an increase in the salinity of the Bay and a change from a typical bar-built estuary with a shoreline dominated by freshwater marshes to a subtropical lagoon with mangrove fringed shorelines.

For descriptive purposes the Bay is divided into three basins separated by both natural and man-made structures (Wilson, 1975). The north basin extends from Dumfoundling Bay south to the Rickenbacker Causeway; central basin from the Rickenbacker Causeway south to Featherbed Bank; the southern basin extends from Featherbed Bank to the Arsenicker Keys.

The north basin has been, for all practical purposes, totally developed. The area is bordered on the east by the barrier islands of Miami Beach and Virginia Key, and on the west by developed shorelines. In excess of 40% of this area has been either dredged or filled (Biscayne Bay Management Plan, 1981) and the shoreline is almost completely seawalled (Roessler and Beardsley, 1975). Located within this area is the Port of Miami and the Miami River where on and off loading of cargo, ship building and repair take place and many industrial complexes are located.

The central basin is commonly considered a transition zone between the heavily urbanized areas of the north basin and the relatively undeveloped southern portions of the Bay. This area contains several large marinas and is used for commercial and recreational purposes.

The southern basin is relatively pristine although several canal systems draining urban and agricultural areas empty into it. This area contains the Biscayne National Park. The Park was originally established in 1968 as the Biscayne National Monument and covers 390 km^2. Most of the mangrove shoreline is still relatively intact. The only prominent man-made structures visible from this area are the Cutler and Turkey Point power plants.

1.2.3. Climatic Conditions

The low latitude of southeastern Florida, and its proximity to the Atlantic Ocean and Gulf Stream, produce a subtropical marine climate characterized by very mild winters and warm summers. The mean annual air temperature for Miami is 24 °C (Veri *et al.*, 1975) and ranges from a low of 18 °C in January to a high of 32 °C in August. The average annual precipitation is 1524 mm (Buston, 1962) of which 73% falls during the summer months (May to October). Prevailing moderate winds are easterly and southeasterly and approach the mainland from over the water. These sea breezes help to temper the climate.

1.2.4. Ecology

Biscayne Bay is shallow throughout, vertical stratification is rare and circulation is predominantly one layer (Lee, 1975). The tides are semidiurnal and have a mean tidal range of 0.76 m at the Port of Miami entrance. This tidal amplitude decreases to the south reaching 0.22 m in Card Sound (Schneider, 1969). Input of coastal waters to the Bay occur through tidal channels (Baker's Haulover, Government Cut, Norris Cut, Bear Cut, The Safety Valve, Sands Cut, Caesar's Creek, Broad Creek and Angelfish Creek) along its eastern edge. The freshwater inputs are introduced via small mainland rivers, creeks, canals, groundwater percolation and rainfall.

Water temperatures average approximately 17 °C during the winter and 31 °C in the summer. Extremes measured during a 5 year study were 9 °C to 35 °C at shallow water stations (Roessler and Beardsley, 1975).

Salinity of the Bay is influenced by rainfall, although this relationship is modified when the flood gates of the numerous drainage canals are opened. During the wet season the salinity gradient of the Bay increases from west to east. This situation can be reversed though during periods of drought.

The bottom communities of the Bay have recently been surveyed extensively and mapped by the Dade County Department of Environmental Resources Management (G. Milano, pers. com.). This information reveals that the majority of the bay bottom consists of mixed seagrasses (*Thalassia testudinum, Syringodium filiforme* and *Halodule wrightii*). Other large areas of the bay bottom consist of a mixture of seagrasses and hard bottom communities (soft corals and/or sponges).

The Bay is populated with 468 species of fishes representing 71 families. Ninety species are of commercial importance, 89 are considered to be sport fishes, and 128 are important forage fishes. The commercial species are predominantly invertebrates, and include shrimp, spiny lobster, stone crab, and blue crab. Sport fishing consists mainly of the Spanish mackerel, grunts, crevalle jack, snappers, king mackerel, bluefish, sea trout, snook, tarpon and bonefish (de Sylva, 1970).

1.2.5. Economy

It was estimated in 1975 that the local marine industry, which includes shipping, cruise lines, boat manufacture, sales and service, shipyards, marinas, bait and tackle shops, etc., contribute 20% to the Dade County economy. This ranks it third in economic importance preceded by tourism and the airlines. Dade County's main harbor facilities are the Port of Miami and the Miami River. The Port of Miami leads all Florida ports in dollar value of imports and exports. In 1973, the combined ports handled in excess of 8 million tons of freight. Incoming cargo consists mainly of fuel oil and gasoline, foodstuffs and raw materials while outgoing cargo consists of manufactured goods, locally produced agricultural products and foodstuffs bound for Caribbean islands and Latin America. Approximately 3 million tons of freight is shipped between Jacksonville, Miami, and Key West via Biscayne Bay and the Intracoastal Waterway. Fuel oil leads all other commodities shipped via this route in volume.

The commercial fisheries of the Bay are dominated by the live bait shrimp industry which in 1975 had a wholesale value of $640,000 followed by dead shrimp ($23,700) (Wilson, 1975). Large quantities of shellfish are also landed in Dade County but the majority of these are caught in areas other than Biscayne Bay.

2. Methods

2.1. Study Area Location

Biscayne Bay is located along the southeast coast of Florida (Figure 1). The study area extended from Dumfoundling Bay (lat. 25° 58' N; long. 80° 15' W.) to Card Sound (lat. 25° 24' N; long. 80° 17' W). The study area is contained almost entirely within Dade County. Only its most northerly and southerly extremities extend into Broward and Monroe Counties, respectively.

2.1.1. Sample Station Locations

One hundred fifty-five stations were sampled for bottom sediments in Biscayne Bay during the first year of the study. Figure 1 presents their location and Appendix A gives the latitude, longitude and coring method used. The location of each sampling station was chosen by assessing multiple criteria relating to its usage by man and other biotic and abiotic parameters. A detailed description of the selection criteria used is presented in the following section.

Sampling stations for the second year of the study were located in the Little River, Miami River, Snapper Creek, Goulds Canal, Black Creek and Military Canal. These areas are outlined on Figure 2 and the sampling stations occupied for water and sediment collections are indicated. Appendix B lists the latitude, longitude, type of sample (water and/or sediment) and method of coring used. [FIGURE 2 IS MISSING IN THE ORIGINAL.]

2.1.2. Criteria for Station Selection

The sediment collection sites for the first year of the study were selected by incorporating criteria relating to the physical, chemical, and biological processes and man's historical, present and future usage of the Bay. The second year study focused on areas where petroleum contaminants had been identified during the first year of research.

The selection criteria for sample stations for the first year involved a review of the available scientific literature concerning hydrocarbons in general and Biscayne Bay in particular (see Appendix C). In addition, consultations with research faculty, local, county, state and federal agencies were conducted. These tasks produced a great deal of useful information which was synthesized into a set of selection criteria. These criteria are discussed below and summarized as to their relationship to the sample collection stations in Table 1.

2.1.2.1. Previous Studies and Dade County Water Quality Monitoring Stations

Previous studies of the pollution problems of Biscayne Bay have been centered within the confines of the northern basin (Hela *et al.*, 1957; McNulty, 1961, 1970; Austin, 1971; D'Amato, 1973; Buck, 1976; Sigel *et al.*, 1976; Voss, 1976; Thorhaug *et al.*, 1976; Waite, 1976). Although most of these studies are well documented this area has been extensively dredged and many of the sampling stations used in previous studies are no longer there. The areas not effected by dredging or other activities were incorporated within the sampling program.

In 1978, the Dade County Department of Environmental Resources Management began monitoring the water quality at 48 stations positioned throughout Biscayne Bay. To augment this database sample stations for this project were positioned on or near pre-existing county stations.

2.1.2.2. Oil Sensitivity Index

The distribution of oil-sensitive coastal resources in south Florida has been determined by the South Florida Regional Planning Council (1981) using a mapping system incorporating an Environmental Sensitivity Index (ESI) developed by Gundlack and Hayes (1978). The ESI integrates natural and man-made geomorphic features with biological and living resources (e.g., nesting sites, rookeries) information to rank environments by their sensitivity. The ranking ranges from I to 10, with 1 being the least sensitive (exposed vertical rocky shores and seawalls) and 10 (mangroves) being the most sensitive. Sampling stations have been established along shorelines with an ESI of 8 or higher (8 = sheltered rocky shores and seawalls, 9 = sheltered tidal flats, 10a = mangroves, 10b = sheltered mangroves).

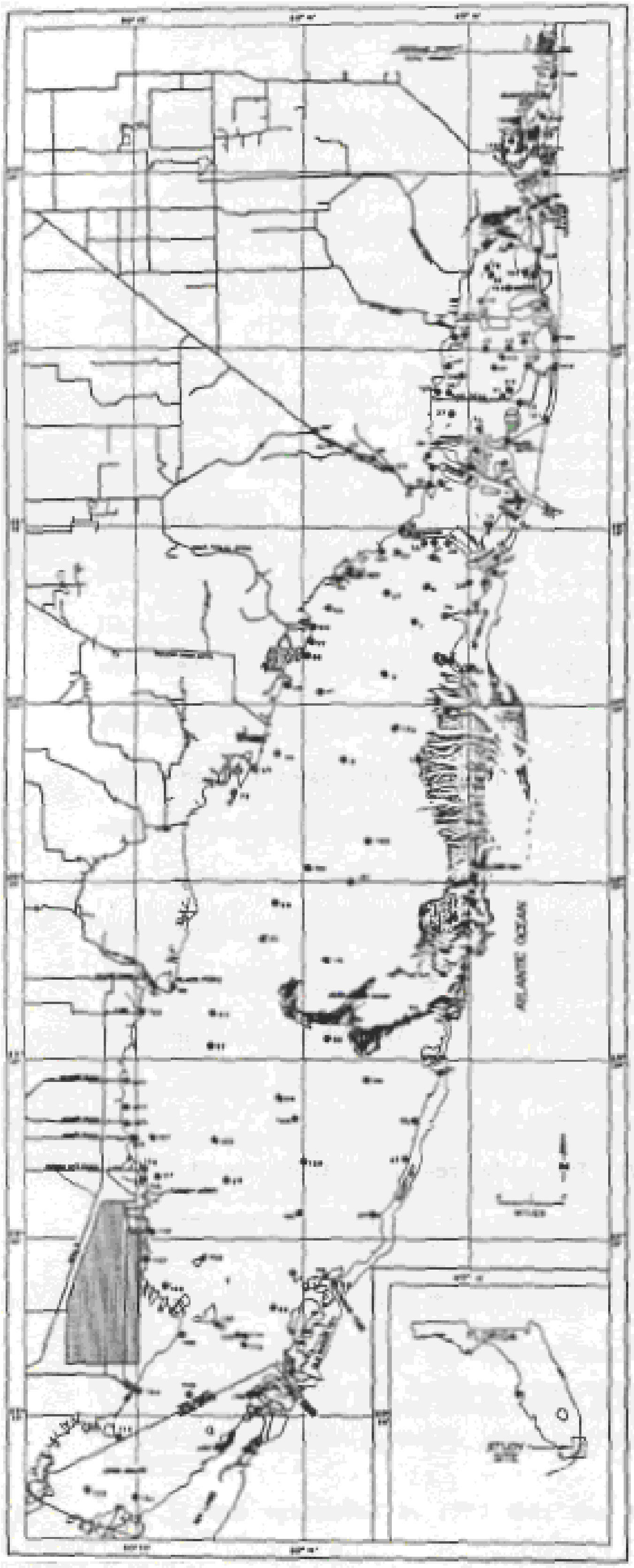

Figure 1. Biscayne Bay study area and sampling station locations for the Year 01 study.

Table 1. Criteria used in selecting the first year's sediment sampling stations.

PS = previous studies; CS = Dade County water quality station; 0SI = oil sensitivity index; ST = sediment type; VT = vegetation type; C = circulation; SI = supra and intertidal areas; BF = boating facilities; PBF = proposed boating facilities; DDR = boating departure and destination routes; PA = preferred anchorage; DED = dredge, spoil, erosional or depositional area; LU = land usage.

SELECTION CRITERIA

Sample #	PS	CS	SO	ST	VT	C	IS	BF	PBF	DDR	PA	DED	LU
1				X	X	X							
2				X	X	X							
3								X					X
4								X			X		
5		X		X	X					X			
6				X	X					X			
7				X	X					X			
8				X	X					X			
9				X	X					X			
10				X	X								
11				X	X								
12				X	X	X							
13			X	X	X	X							
14				X		X	X						
15				X	X	X							
16			X	X		X	X						
17	X	X								X		X	
18				X			X					X	
19										X			
20		X		X	X								
21				X	X								
22				X									
23										X			
24					X		X						
25						X				X			
26						X							
27						X				X		X	
28						X							
29				X	X								
30			X	X			X						
31				X									
32		X											X
33						X							X
34						X							X
35		X											X
36						X						X	
37				X			X					X	
38		X								X			
39				X		X	X						
40					X	X							

Table 1. Criteria used in selecting the first year's sediment sampling stations (cont).

PS = previous studies; CS = Dade County water quality station; 0SI = oil sensitivity index; ST = sediment type; VT = vegetation type; C = circulation; SI = supra and intertidal areas; BF = boating facilities; PBF = proposed boating facilities; DDR = boating departure and destination routes; PA = preferred anchorage; DED = dredge, spoil, erosional or depositional area; LU = land usage.

SELECTION CRITERIA

Sample #	PS	CS	SO	ST	VT	C	IS	BF	PBF	DDR	PA	DED	LU
41	X				X	X							
42						X							
43				X		X	X						
44		X		X			X			X		X	X
45				X		X	X					X	
46		X		X						X			
47		X								X		X	
48				X			X					X	
49												X	
50		X				X							
51		X						X	X				X
52		X								X		X	
53						X				X			
54						X		X					X
55		X								X		X	
56	X										X		X
57	X										X		X
58	X										X		X
59	X										X		X
60	X										X		X
61	X										X		X
62		X										X	X
63								X		X	X		X
64								X	X	X	X	X	
65										X		X	
66		X						X	X	X			X
67			X				X						
68										X			X
69			X		X								
70	X			X									
71				X		X							
72	X						X			X		X	X
73							X	X	X	X			X
74	X			X	X								
75													X
76	X												
77	X					X	X					X	
78	X			X								X	
79	X			X								X	
80					X	X							

Table 1. Criteria used in selecting the first year's sediment sampling stations (cont).

PS = previous studies; CS = Dade County water quality station; 0SI = oil sensitivity index; ST = sediment type; VT = vegetation type; C = circulation; SI = supra and intertidal areas; BF = boating facilities; PBF = proposed boating facilities; DDR = boating departure and destination routes; PA = preferred anchorage; DED = dredge, spoil, erosional or depositional area; LU = land usage.

	SELECTION CRITERIA												
Sample #	PS	CS	SO	ST	VT	C	IS	BF	PBF	DDR	PA	DED	LU
81				X	X	X							
82					X		X						
83	X												
84				X		X							
85				X	X								
86										X			
87				X		X							
88				X	X								
89				X	X					X			
90	X												
91			X			X				X			
92			X				X				X		
93		X	X					X		X			
94	X		X				X				X	X	
95		X		X	X	X	X			X			
96		X			X	X				X			
97										X			
98		X								X			
99			X	X	X		X						
100			X				X						
101		X						X	X	X			X
102													X
103		X											X
104			X				X						X
105													X
106													X
107			X				X						X
108			X				X						
109	X		X									X	X
110	X												
111										X			
112							X	X	X				X
113		X		X	X								
114		X		X	X					X			
115		X		X	X					X			
116			X			X							
117			X			X				X			
118	X		X				X						
119	X					X				X			
120				X	X								

Table 1. Criteria used in selecting the first year's sediment sampling stations (cont).

PS = previous studies; CS = Dade County water quality station; 0SI = oil sensitivity index; ST = sediment type; VT = vegetation type; C = circulation; SI = supra and intertidal areas; BF = boating facilities; PBF = proposed boating facilities; DDR = boating departure and destination routes; PA = preferred anchorage; DED = dredge, spoil, erosional or depositional area; LU = land usage.

	SELECTION CRITERIA												
Sample #	PS	CS	SO	ST	VT	C	IS	BF	PBF	DDR	PA	DED	LU
121				X	X								
122										X			
123			X		X		X						
124													X
125			X	X	X		X						
126				X	X					X			
127							X			X			
128										X		X	
129				X	X					X			
130				X	X					X			
131										X			
132										X			
133	X	X		X						X			
134	X			X	X								
135						X						X	
136									X	X		X	X
137									X	X		X	X
138						X							X
139				X		X							X
140				X		X							X
141						X							X
142						X							X
143						X							X
144						X							X
145						X				X			X
146						X		X	X	X			
147		X								X			
148								X		X			X
149						X							X
150						X							X
151	X			X		X							
152	X			X								X	
153						X							X
154													X
155	X					X							X
156					X	X							

2.1.2.3. Sediment Type

Areas of the Bay exhibiting different sediment types were evaluated for sampling using three criteria. These were: thickness of substrate, amount of organic material, and particle size distribution.

The sediment depth in Biscayne Bay is highly variable and in many areas less than 1 m (Wanless, 1976). Sediment build-ups, which are present, form distinct patch-like accumulations and are controlled by several factors (i.e., wind, dredging, currents and storm events). Six major recent sediment regimes have been recognized by Wanless (1976) based on sediment type, body geometry and depositional controls. Areas representative of these regimes as well as transitional areas were sampled.

The deposition and incorporation of petroleum hydrocarbons into marine sediments is well established in the literature (Blumer and Sass, 1972; Clark, 1966; Farrington, 1980; LaFlamme and Hites, 1978; National Academy of Sciences, 1975; Zafiriou, 1973). The amount of *n*-alkanes sorbed by marine sediments has been shown by Meyers (1975) to be dependent on sediment particle size. The smaller the particle size the greater the sorption of hydrocarbons. Samples were collected which incorporated sediments of different particle sizes.

The affinity of petroleum hydrocarbons for organic compounds has been investigated by Meyers and Quinn (1973) who suggest that organic matter may mask sorption sites in sediment, thereby reducing the available surface area for sorption of petroleum components. Suess (1968) states that an organic material coating on particles will enhance the sorption process by providing a lipophilic layer. Thus the organic content of the sediment has an important effect on its uptake of petroleum. Sediment samples were collected from environments which contained variable concentrations of organic matter. These ranged from relatively organic-free quartz sands to highly organic peat substrates.

2.1.2.4. Vegetation Type

Forty-three percent of the Bay bottom is covered with seagrasses (Snedaker and Brook, 1976). The majority of the seagrasses are *Thalassia testudinum* (turtle grass), *Halodule wrightii* (Cuban shoal grass) and *Syringodium filiforme* (manatee grass). The primary functions of these plants are: 1) food source; 2) shelter and protection; 3) sediment stabilizer; and 4) a chemical sink in terms of nutrient cycling (Thorhaug *et al.*, 1976). The environmental health of Biscayne Bay is linked directly to these seagrass communities which are relatively sensitive to pollution. The effect of pollutants on seagrass often results in mortality, thus causing the whole community dependent on them to disappear (Thorhaug *et al.*, 1976). A representative number of samples incorporating different types to vegetation were included in the sampling program.

2.1.2.5. Circulation

The dominant exchange mechanisms within the Bay are wind and the semidiurnal tides (Lee and Rooth, 1973). Tidal current velocities through passes along the eastern side of Biscayne Bay average 25 to 100 cm/sec (Hela *et al.* 1957). Within the Bay, tidal currents are less than 50 cm/sec while portions of the southwestern margin appear isolated from tidal circulation (Weiss, 1948). Several nodal points of tidal convergence are recognized within North Bay, between 49th Street and 79th Street Causeways (Lee and Rooth, 1973). Samples from areas of maximum and minimum exchange were collected.

2.1.2.6. Supratidal and Intertidal Areas

The stranding of pelagic and coastal oil slicks and tar balls is generally restricted to supratidal and intertidal environments. Oil coverage in these environments is controlled by the slope of the exposed area, with maximum amount accumulating on gently sloping or flat surfaces. Sediment samples representative of major intertidal environments such as the Safety Valve, Featherbed Banks, Arsenicker Keys, Middle Ground Shoals and mangrove shorelines were collected.

2.1.2.7. Boating Facilities

A unique combination of climate, urban and physical geographic features permit year round public access to all types of boating related activities within Biscayne Bay. In 1975-1976, there were over 250,000 recreational boating trips made from Dade County, approximately 187,500 were made within the Bay (Austin, 1971). Support facilities such as marinas and launching ramps are an integral part of recreational as well as commercial activities. In 1981, there were 78 marinas and 5 ramps marginal to Biscayne Bay (Biscayne Bay Management Plan, 1981). In many instances, boat maintenance and repair operations release paint, oil and grease into bay waters. Boyd (1976) estimates that 1% of all coastal oil pollution results from the activity of marina facilities. Marinas, harbor facilities, and other marine related industries were sampled.

2.1.2.8. Proposed Boating Facilities

Dade County Department of Environmental Resources Management estimates that 42 additional support facilities and 42 additional marinas with wet berths for recreational and commercial boaters are planned for construction in Biscayne Bay. Seven are presently under construction. The location of existing and planned boating facilities were incorporated in sample site selection.

2.1.2.9. Boating Departure Routes and Destinations

The Intracoastal Waterway and privately dredged channels are major thoroughfares for industrial, commercial and recreational transport throughout Biscayne Bay. As stated earlier, 3 million tons of cargo were transported in this manner, with the majority of it being fuel oil (Wilson, 1975). Channel sediments, resuspended by boat wakes, prop wash and hull scrapes may incorporate surface oil slicks into bottom deposits. This mechanism may result in elevated concentrations of petroleum hydrocarbons between commonly traveled departure and destination routes. Sampling stations were established along all major marine routes.

2.1.2.10. Preferred Anchorage

The recreational features of Biscayne Bay accessible by boat are numerous. Most of these are located along the southern boundaries of the Bay. The preferred anchorages at these sites are of interest for monitoring the effects of recreational boating on petroleum hydrocarbon distribution.

2.1.2.11. Dredging, Spoil, Erosional and Depositional Areas

Man-made holes and canals marginal to Biscayne Bay appear to contain complete sequences of layered sediment that have accumulated since their construction (Harlem, 1979). Once sediments are deposited in the patchwork of deep dredge holes they are less susceptible to resuspension. It is likely these areas may be prominent sinks for pollutants in particulate form. Several of these areas were incorporated into the sampling program.

The scouring and redistribution of contaminated sediments is an important mechanism of pollutant transport. Dredging, winter cold fronts, and hurricanes are the principal agents of sediment transport within the Bay. The strong northerly winds of cold fronts cause the redistribution of fine sediments and the southward transport of unstabilized sands on the Bay bottom (Warzeski, 1976). The sedimentary effects of hurricanes are more pronounced due to the far greater energy of hurricane winds. These storms can remove or deposit centuries of sediment accumulations in one single event thus, the classification of environments as erosional or depositional is necessary to accurately interpret the spatial distribution of the sediment analysis. Samples from both erosional and depositional environments were collected.

2.1.2.12. Land Use

Between the years 1896 to 1950, the process of urban settlement about Biscayne Bay was rapid and often unplanned (Prestamo and Greenan, 1976). During these 54 years, the conversion of agricultural land to residential use established the present urban distribution pattern. Within the past 30 years the urban process has become the development of open land with very few cases of redevelopment. The effects of urbanization on surface hydrology have been two fold (Delleur, 1981). The first factor is the covering of parts of the catchment (substrate) with impervious surfaces such as roofs, streets, sidewalks and parking lots. Dust, dirt, sediments and pollutants of various kinds, settled from the atmosphere and generated by the urban activities, accumulate on these impervious areas between storm events and are eventually washed into the Bay by runoff during rains and storm events.

The second factor effecting the urban runoff process is a result of the improvement of the hydraulic efficiency of the drainage network through the straightening and lining of channels, construction of sewers and culverts. The increased flow velocities enhance the transport of suspended solids and pollutants. The pollutant loading at the downstream end (the Bay) of the urban runoff conveyance is thus increased. To assess the impact of urbanization, stations were located within and around urban developments and their drainage areas.

2.1.3. Collections

In the two-year program, sediment samples were collected by three different coring techniques: vibra, remote and push. During first year, in order to obtain a good spatial coverage of the Biscayne Bay lagoonal systems, a total of 156 cores were collected, this included 15 vibra cores, 47 remote cores, 62 short push cores, and 32 long push cores. In the second year, the goal was to investigate and to quantify the areas of high petroleum contamination found during the first year. Thus, 22 cores in three selected areas were obtained, 19 remote cores and 3 short push cores. Replicate cores within a square meter of each other were collected at every station during the first year study. The sediment samples for intercalibration were grab samples collected outside Biscayne Bay in deep water southeast of Miami. Except for intercalibration samples, Figure 3 indicates the steps followed for each core from collection to analysis. The intercalibration samples which were collected with a Peterson dredge, were placed in jars, covered with aluminum foil, capped, labeled and carried on ice from ship to freezer.

Biological samples were collected in cooperation with the Fisheries and Habitat Management of Biscayne Bay study conducted by the Rosenstiel School of Marine and Atmospheric Science and funded by the Dade County Department of Environmental Resources Management. All samples, after collection, were stored under lock and key, subsampled and analyzed using procedures, methodologies and quality assurance programs which guaranteed court competence and minimized contamination.

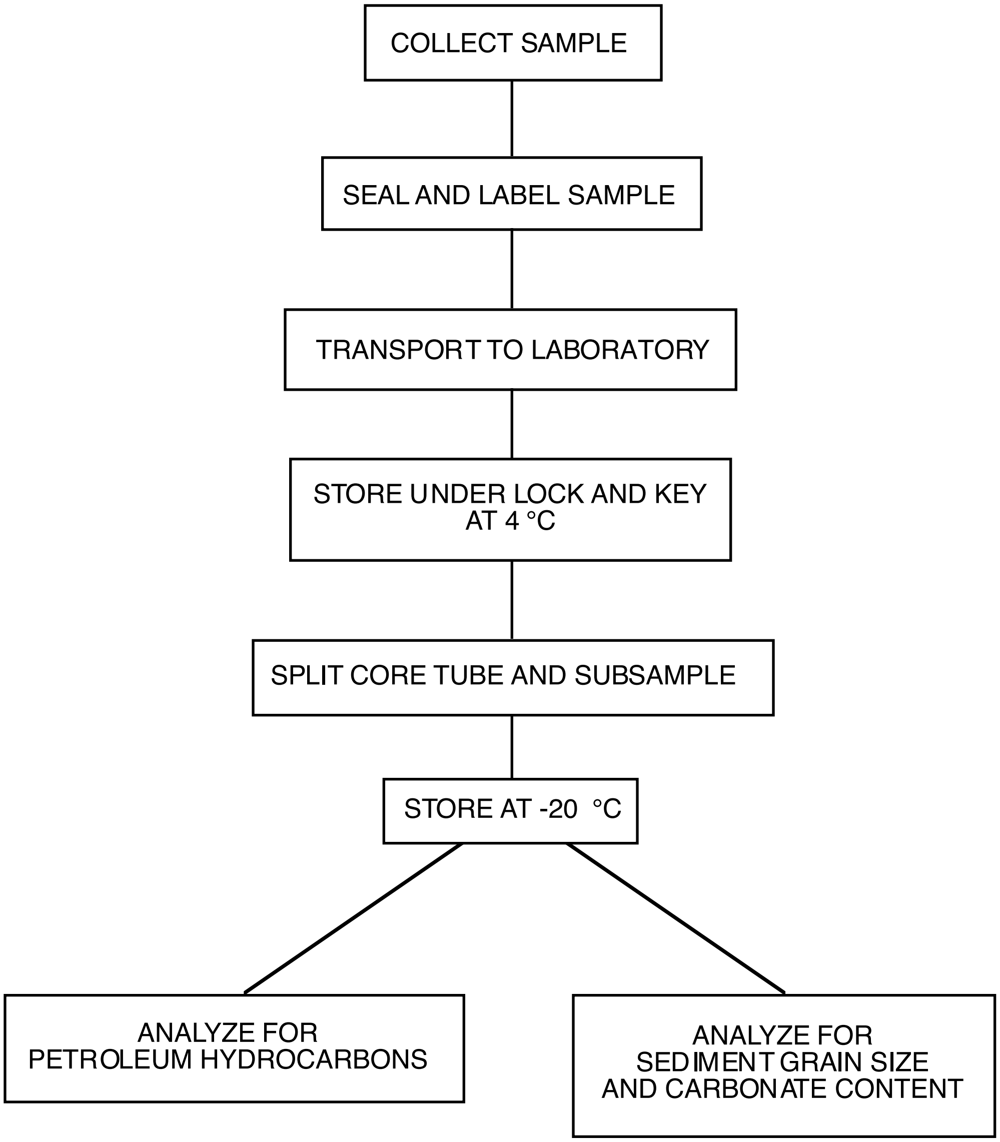

Figure 3. Flow diagram of sample collection and storage procedures.

The core tube assembly, used for all sediment collections, consisted of 7.6-cm diameter aluminum irrigation tubing, 7.8 cm diameter circular, aluminum liner plates, and 7.5-cm plastic core caps. Prior to use, all core tubes, after being cut to the appropriate length, and liner plates were washed with Alconox, rinsed with tap water and burned at 500 °C in a kiln to remove all organic contaminants. When cooled, the tubing was sealed by securing aluminum foil over both ends of the core tube. The circular liner plates were fitted into the caps and then secured to both ends of the core tube.

Short cores were obtained when sediment thickness was less than 20 cm. The tube was submerged and the core caps were removed. The short tubes were inserted by hand to bedrock, capped, withdrawn from the sediment and transported to the surface in an upright position.

Long 1.3-m push cores were collected by securing a pair of adjustable "T" handles near the top of the capped core tubes. The core caps were removed only when the apparatus was submerged below the surface (micro) layer. The tube was pushed into the sediment, the aluminum lined caps were placed over the top of the core tube prior to, and under the core tube bottom after removal from the sediment.

Areas that represented possible health hazards to divers were sampled by remote coring. This process involved the use of 1.3 m length of aluminum core tubing connected to a reusable extender, equipped with a one-way valve. The sampling device was pushed into no more than I m of sediment and the valve was closed by inserting a hexane-rinsed stainless steel sphere (7 cm diameter) into the extension tube. During the extraction of the core tube from the sediment the sphere created a vacuum which retained the sediment in the tube until capped at the surface. The remote coring method was preferred to Box coring and Grab sampling because, 1) possible sample exposure to contaminants emanating from the sampling vessel were eliminated; 2) possible sample exposure to surface films and water-borne pollutants that may be present at sample locations were eliminated; 3) the sample does not contact any lubricated moving parts; 4) undisturbed surface samples are easily and quantitatively obtained.

Sediment samples that required penetration to intercept deeper depositional layers predating anthropogenic impacts were attained by using a portable vibra core system (Lanesky, 1979). The system consisted of a vibrating head, mounted perpendicular to the top of a cleaned aluminum core tube, that initiated a low amplitude standing wave. This standing wave fluidized and displaced the sediments adjacent to the core tube and allowed it to pass through the sediment with minimal resistance. Core recovery averaged between 90 and 100%. Actual coring time ranged from 0.5 to 5 minutes. Preservation of fine laminations and cross stratification in x-ray radiographs and slabbed, impregnated cores showed that this technique gave minimal distortion along the core tube walls (Lanesky, 1979).

After collection the core tubes and caps were coded, sealed with tape, signed and dated. Any undue disturbance during this process necessitated repeating the procedure until intact samples were obtained.

At each station the latitude and longitude in degrees, minutes and seconds as well as the proximity of navigational and prominent landmarks, were recorded in permanently bound, waterproof field notebooks. Station number, sample number, date, time, water and air temperature, bottom type, salinity, water depth and coring method were also recorded. Prior to station departure, the supervising individual checked the log book and the sample to verify that they had been collected, identified and sealed correctly. At the end of each day's notes the page was signed and dated by the person who performed the work. The team leader checked all notes for accuracy, correct transfer of data, completeness, legibility and neatness.

Upon arrival at the laboratory the sealed and coded samples were transferred by project personnel to a core locker maintained at 4 °C, secured in an upright position and kept under lock and key.

Within 48 hours of collection the water above the sediment in the core tubes was removed with a large clean pipette. Once the water had been removed the core tubes were split by making two shallow longitudinal slices with an electrical circular saw. Samples for petroleum hydrocarbon analyses were collected by sub sampling from only the center of the core. This was done by removing a 5 cm long cylinder shaped subsample, with hexane rinsed stainless steel spatulas, and placing it on clean aluminum foil. An inner 2 cm diameter plug was removed by inserting a cleaned, organic-free 50 mL glass beaker through the center of the subsample. The sample was placed in a organic-free glass jar and covered with a foil lined screw top. It was then transferred to a locked freezer maintained at - 20 °C until extracted.

The thin layer from the outside of the remaining sediment was shaved away and the remains were placed in a similar glass container for sediment grain size and organic analysis. These samples were also stored at -20 °C in a locked freezer.

Biological samples for the duration of the two year project were collected in cooperation with Mr. Steve Berkeley, Principal Investigator for the Fisheries and Habitat Management of Biscayne Bay study. Samples were collected by trawl and traps in northern, central and southern areas of the Bay. In addition, during the second year study, samples were collected when available from the five study areas. Immediately upon collection samples were wrapped in aluminum foil, labeled (species, number, time, date, collection area and method), sealed in a plastic bag and placed on ice. After returning to the laboratory the samples were placed under lock and key in a freezer maintained at -20 °C until analysis could be completed.

The water samples, that were examined for hydrocarbons during the second year program, were collected in 19-liter glass bottles. To obtain these samples, the glass bottles were placed in a wooden frame, covered with a fitted wooden cover secured into place with eye bolts and stoppered with an aluminum covered stopper fitted with an eye-bolt. Before lowering this sampler into the sea, a lanyard was run through the eye bolts and secured to the winch cable, a long cord was fastened to the eye-bolt in the stopper and a lead weight was attached to the bottom of the frame. With the winch the BC (Brown-Corcoran) sampler was lowered into the sea to the desired depth, and the stopper was removed by pulling the cord. When the bottle was filled with water, the sampler was raised to just below the surface stoppered with an aluminum covered stopper, and then brought aboard. Here it was labeled, sealed and set aside for later analysis in the laboratory.

2.1.4. Quality Assurance

Great care was taken during the sampling and subsampling process to insure that contamination was kept to a minimum and chain of custody was maintained. This was accomplished by adhering to strict clean procedures, keeping all samples under lock and key and maintaining detailed field and laboratory records.

The core tubes were washed, rinsed in tap water and burned at 500 °C in a kiln to remove any sources of organic contamination. Immediately after being removed from the kiln the core tubes were sealed with clean aluminum foil. The foil was secured in place with plastic core caps lined with aluminum discs that had been cleaned using the same procedure as the core tubes. This insured a contaminant free container for sample collection.

During collection of the sediment samples the core tubes were kept sealed until they were fully submerged, this minimized any contamination by the water column and/or surface micro layer.

The collected cores were resealed with the foil and aluminum disc lined plastic core caps immediately after collection. Care was taken to keep the collected samples in a vertical position at all times to maintain its internal integrity. Immediately after being brought on board the support vessel the plastic caps were secured with tape to the core tube. This prevented the sample from falling out of the collection tube and also secured the sample against tampering. The core was labeled as to station number, top and bottom. Replicate cores were taken at each station within one meter of each other. This supplied a complete set of replicate cores from all the sampling stations should they be needed. The collected cores were under the direct responsibility and supervision of the field supervisor during collection and storage.

The samples were returned to the laboratory and transferred directly to a locked, refrigerated core locker. The samples were stored in an upright position until they could be subsampled. All materials coming into contact with the samples during subsampling were either hexane rinsed or burned at 500 °C to remove organic contaminants. The subsample fractions (for hydrocarbon, grain size and organic analysis) were stored in burned, glass screw top jars with aluminum foil liners. The jars were stored in a locked freezer at -20 °C until analysis could be performed.

Biota samples were collected using both trawl and traps. Immediately after removing the specimen from the collection device it was wrapped in clean aluminum foil and labeled as to time, date, method and location. The specimen was then placed in a plastic bag which was sealed with tape. This secured and the sample from any contamination and tampering. The sample was then placed on ice until transported to the laboratory. On arrival at the laboratory the samples were stored in a locked freezer maintained at -20 °C.

The water samples were brought to the laboratory and extracted immediately if possible. If there were more samples than could be extracted at once, they were kept sealed and stored in a cold room at 4 °C. Holding time was not more than 48 hours.

2.2. Sediment Grain Size Analysis

A representative subsample of the collected surface sediments was analyzed for grain-size fractions and distribution. The samples were freeze-dried in a Virtis Model No. 10-146-MB-BA freeze dryer. A representative subsample was obtained by recovering 35 ± 5 g from a Jones-type, H. W. Curtin sediment splitter. The samples were fractionated into three size classes, >2000 *µ* (gravel), 2000 to >63 *µ* (sand), and <63 *µ* (silt-clay) by mechanically dry sieving for 15 mins. through 2000-*µ* and 63-*µ* sieves.

The >2000 *µ* fraction (gravel) was dried at 105 °C to a constant weight, cooled to room temperature in a desiccator, weighed and archived. The <63 *µ* fraction was transferred into a labeled one-liter cylinder. The 2000 *µ* to >63 *µ* fraction was mixed with a 4% (w/v) solution of sodium hexametaphospate and placed in a Bransonic 12 sonic bath for 15 mins. After sonification this fraction was rinsed onto a 63-*µ* sieve with one liter of distilled water. The particles which passed through the 63-*µ* sieve were combined with the <63 *µ* previously stored in the labeled, one liter cylinder. The <63 *µ* fraction was transferred to a labeled aluminum weighing dish, dried to a constant weight at 105 °C, cooled to room temperature in a desiccator, and weighed.

The weight of the <63 *µ* fraction was calculated by subtracting the sum of the >2000 *µ* and the 2000 *µ* - >63 *µ* fraction weights from the total sample weight. From this data, dry weight percentages for gravel (>2000 *µ*), sand (2000 to >63 *µ*), and silt-clay (<63 *µ*p) fractions were calculated.

2.3. Organic and Carbonate Content Analysis

The determination of the total organic matter and carbonate content of the sediments was performed by using a modified version of Galle and Runnel's (1960) weight loss on ignition process. The procedure uses a high temperature muffle furnace to oxidize both organic matter and carbonate. This method has been proven to be 100% efficient for the recovery of total organic matter and carbonate bearing minerals in modern marine sediments (Byers *et al.*, 1978; Dean, 1974). However, this analysis does not distinguish between magnesium (Mg), strontium (Sr) and calcium (Ca) bearing carbonate minerals. It has been reported (Wanless, 1976) that of the carbonate bearing minerals in Biscayne Bay, calcium carbonate ($CaC0_3$) is significantly more abundant. Therefore, all carbonate values are reported as percent calcium carbonate.

Freeze dried, representative quantitative subsamples were obtained by using a Jones-type, H. W. Curtin sediment splitter. The split samples were stored in clean 25 mL Erlenmeyer flasks, oven dried at 105 °C to a constant weight and cooled to room temperature in a desiccator. A sample of approximately 10 g was transferred into a ceramic crucible of known weight. The combined crucible and sediment was then weighed, and placed in a rack for ignition.

The samples were placed in a muffle furnace and ignited for 2 hours at 500 °C. They were then cooled in a desiccator to room temperature and weighed. The difference (i.e. weight loss) between this weight (minus the crucible weight) and the initial dry weight was the quantity of total organic matter (TOM) in the sediment (Equation 1).

$$\text{dry wt. sample - wt. after ignition at 500 °C = wt. total organic matter (TOM)} \qquad (1)$$

The percent by weight of TOM in the sediment was calculated using Equation (2).

$$\frac{\text{wt. TOM}}{\text{dry wt.}}\ 100 = \text{\% dry weight TOM} \qquad (2)$$

The samples were then returned to the muffle furnace, ignited for one hour at 1000 °C, cooled in a desiccator to room temperature and weighed. The weight loss between 500 °C and 1000 °C was the amount of carbon dioxide ($C0_2$) evolved from the carbonate minerals in the samples. The weight of CO_2 evolved was converted to percent carbonate material by the following equations (3 - 5):

$$\text{wt. after 500 °C - wt. after 1000 °C = wt. } CO_2 \text{ evolved} \qquad (3)$$

$$\frac{\text{wt. } C0_2}{0.44} = \text{wt. carbonate material} \qquad (4)$$

where 0.44 is the atomic ratio of CO_2 in $CaCO_3$.

$$\frac{\text{wt. } CaC0_3}{\text{dry wt. sample}}\ 100 = \text{\% dry wt. } CaCO_3 \qquad (5)$$

Ten percent of each sample run were full procedural blanks. The blanks showed no weight changes during either the organic or the carbonate ignition procedure.

Twelve percent of the samples were run as replicates, to establish the precision of the method. The replicates were chosen to include samples of high and low percentages of both organic matter and carbonate content. The organic matter ignitions had a mean variation of 0.3 percent with a standard deviation of 0.48. The carbonate ignitions had a mean variation of 2.1 percent and a standard deviation of 2.1.

Hirota and Szyper (1975) have shown that sediments with high (>50%) percentage of calcium carbonate can interfere with the accuracy of the organic measurements. The interference results from carbonate CO_2 evolution during the organic ignition (500 °C). For this reason a sample of pure $CaC0_3$ was run with every set of samples to determine the maximum limits of influence of $CaC0_3$ on organic matter (as Hirota and Szyper suggest).

Only 0.03 percent of the $CaCO_3$ standard was measured as organic carbon. However, no sample containing greater than 50% $CaC0_3$ had an organic content less than 1%; most containing greater than 2% TOM. Thus, the natural proportions of TOM and carbonate found in the sediments analyzed reduce the significance of this problem.

2.4. Hydrocarbon Analysis

2.4.1. Sediment

The methods used for the extraction of hydrocarbons were similar to those previously described (Blumer *et al.*, 1969; Farrington *et al.*, 1972; and Sleeter *et al.* 1974). Wet sediment (25 - 75 g) was weighed into cellulose thimble pre extracted with 1:1 benzene 0.5 N methanolic KOH solution. Five grams of sample were weighed onto a watch glass and placed in an oven at 105 °C for 3 hours for dry weight determination. Sediments were extracted and saponified by refluxing for 48 hours with the 1:1 benzene:0.5 N methanolic KOH solution. A plug of clean, light copper turnings was placed beneath the cellulose thimble to remove the elemental sulfur from the sample. A 0.5 mL volume of androstane and *o*-terphenyl (1 mg/mL) was added to each sample as an internal standard. Blanks were run with each set of 6 samples.

After 48 hours, the solution containing the extracted hydrocarbons was removed from the Soxhlet and poured into a 500 mL separatory funnel. Any residue left in the round bottom flask was washed with three small aliquots of hexane and these washings were added to the extract.

Three successive 50-mL volumes of hexane were shaken vigorously with the extracted methanol:benzene mixture, separating the aqueous and organic layer, the three successive hexane:benzene mixtures were then combined and the methanol aqueous phase was discarded.

The hexane-benzene mixture was washed first with organic free water (prepared by passing distilled water through a large XAD-2 resin column) and then with a saturated sodium chloride solution to remove trace amounts of methanolic KOH. The combined extracts were dried over 1 g of anhydrous sodium sulfate to remove residual water. The methanol and water was discarded. The extract was concentrated to 5 mL in a Kuderna-Danish apparatus using a water bath. The benzene-hexane concentrate was transferred into a 12-mL evaporator tube, then the concentrate was dried in a block heater under a stream of pure nitrogen gas. The dry sample was then diluted to 1 mL with hexane, placed in a 5 mL vial with a foil-lined screw top and stored under refrigeration at 4 °C.

An alumina-silica gel column was pre-wet with 12 mL of hexane and the sample was transferred onto a (10 x 1 cm) column packed with 1.25 cm of alumina over 2.5 cm of silica gel. Both the alumina and silica gels had been partially deactivated with 2% organic free water prior to packing. The aliphatic fraction (f_1) was eluted with 12 mL of hexane and a similar volume of benzene was used to remove the aromatic fraction from the column. Care was taken not to allow the hexane level to go below the alumina layer during aliphatic elution. The aliphatic fraction was reduced to 1 mL on a block heater under stream of pure nitrogen gas, while the aromatic fraction (f_2) was brought to almost dryness and then diluted to 1 mL. The resultant samples were then stored in a refrigerator at 4 °C until they were analyzed by gas chromatography.

2.4.2. Tissue

The procedure for tissue analysis was similar to those described for the sediment and consisted essentially of saponification, separation into aliphatic and aromatic fractions and quantitative determination. However, in the case of tissue there was a slight change in the procedure for Soxhlet extraction as ethanolic KOH was used instead of 1:1 benzene: methanolic KOH. This reduced the possibility of ester formation.

The above procedure was used for tissue extraction during the first year study, however, it was found that more complete and faster extraction could be attained by placing the homogenized tissue in a round bottom flask, adding 150 mL of ethanolic KOH and extracting it for four hours under a reflux condenser. Thus, this procedure was used in the second year study. After the extraction, the mixture was poured into a separatory funnel and was extracted three times successively with 100 mL and two 50 mL portions of hexane. The alcoholic phase was then discarded, and the combined hexane extracts were washed free of caustic with organic free water and finally with saturated sodium chloride solution. The hexane extract was then poured from the separatory into an Erlenmeyer flask containing anhydrous sodium sulfate.

After drying the hexane extract was concentrated, separated into aliphatic (f_1) and aromatic (f_2) fractions on an alumina-silica gel column and again concentrated for gas chromatographic analysis as described previously.

The tissue sample was homogenized prior to extraction and copper was not necessary to remove sulfur from the tissue sample.

2.4.3. Water

In the laboratory, the 19-liter water samples were placed in a wooden frame over a large magnetic stirrer. The water sample was unsealed and the volume of each was adjusted to exactly 18 liters by siphoning down to the mark. The 100 μL volume of androstane and *o*-terphenyl (1 mg/mL) was added to each water sample as an internal standard. Then a large egg-shaped spin bar and 500 mL of methylene chloride was added to each sample; the magnetic stirrer was turned on and the speed adjusted to give a deep vortex for good mixing.

After extracting in this manner for 24 hours, a glass siphon was inserted in each sample and the methylene chloride extract was drawn from the bottom of the water bottle into a separatory funnel. Then the siphon was raised and the water was drawn down. The siphon was then removed and the remaining water and methylene chloride poured into the separatory funnel.

The methylene chloride extract was separated from the water, dried over anhydrous sodium sulfate, and evaporated down in a Kuderna-Danish concentrator. The sample was picked up in hexane, separated from aliphatic (f_1) and aromatic (f_2) fractions on an alumina-silica gel column, concentrated on a block heater, and placed in vials by the same procedure as used for sediments.

2.4.4. Gas Chromatographic Analysis

A 1.0 to 2.0 μL volume of the concentrate was injected into a Tracor model 563 gas chromatograph. This gas chromatograph was equipped with dual flame ionization detectors and two fused quartz capillary columns. In the first year's program, a 15-m SE 54 and a 25-m SE 30 column were used for the determination of the aromatic and aliphatic compounds respectively. These columns were replaced with two 30-m J & W columns coated with SE 30 for better resolution in the second year's work. Hydrogen was used as the carrier gas and a flow of 30 mL/min. was maintained. For the first year's study, the chromatograph was set to maintain the injector and detector temperatures at 280 °C and the oven temperature was programmed from 60 °C to 300 °C at a rate of 10 °C/min after an initial hold of 2 minutes and a final hold of 300 °C for 10 minutes. The temperature programming was changed slightly for the second year's study and, in general, the injector and detector temperatures were maintained at 300 °C and the chromatograph was programmed for oven temperatures of 100 °C to 300 °C at 8 °C/min with no initial hold and a final hold of 5 minutes. A full description of conditions is shown in Table 2. All samples were injected in the splitless mode. Two Hewlett-Packard integrators model 3390A were programmed to record the retention time, areas under the peaks and to calculate the amounts of hydrocarbons from C_{12}-C_{30}. The integrators were calibrated with a standard mixture. The aliphatic mixture contained hydrocarbons from C_{12} through C_{30} including phytane, pristane and androstane. The calibration mixture used for the aromatics had naphthalene, phenanthrene, dibenzothiophene and pyrene as well as the internal standards *o*-terphenyl, 1-methylphenanthrene was added in the second year's study. The standard mixtures were run daily and the integrators were re calibrated as necessary.

The quantification of the chromatograms involved evaluating the known and unknown peaks, the internal standards and the unresolved complex mixture for their retention times and areas. Calibration mixtures were run to determine response factors (concentration injected divided by the area of peak). The integrators were programmed with time windows to detect all reference peaks in the C_{12} to C_{30} range and label them. In addition, it determined the area for all other peaks. The response factors for the internal standards, androstane for the aliphatics and *o*-terphenyl for the aromatics, were used to quantify the concentration of all unknown peaks and the unresolved complex mixture.

The intergrators were capable of integrating under only one set of parameters, therefore the unresolved complex mixture was quantified separately. This involved tracing the unresolved area on a sheet of paper, cutting it out, determining its area and correcting to units which were comparable to the other data generated by the integrator. The areas of the unresolved tracings were determined by a Hayashi Denko, Type AAM-5 Automatic Area Meter. This unit is a photoelectronic apparatus that automatically determines the area of any opaque or semitransparent material by the amount of light it reflects. The area was reported in cm^2 by the area meter, and converted to integrator units by a conversion factor. This information, the areas for the known and unknown peaks, the response factors, sample number, dry weight, volume injected, and final dilution volume were all entered into a computer program written to calculate and quantify this data. The program calculated the μg/g concentration for all of the reference peaks, resolved (includes reference peaks and resolved unknown peaks), and unresolved (unresolved complex mixture) areas, total hydrocarbons, the carbon preference index (CPI), the percent recovery, and the following ratios; resolved/unresolved, pristane/phytane, C_{17}/pristane, and C_{18}/phytane. In the year-one program those samples that did not contain the internal standards were corrected to a standardized recovery.

Table 2. Gas chromatograph operating conditions for the second year study.

Descriptor	Column 1	Column 2
Column Type	SE-30	SE-30
Column length (m)	30	30
Column velocity (cm/sec)	41.7	41.4
Detector gases		
H_2 (cc/min)	30	30
Air (SCHF)	1.0	1.0
Injection timer (sec)	30.5	30.5
Detector temperature (°C)	300	300
Injection port temperature (°C)	300	300
Temperature Program		
Initial temperature 100 °C Final temperature 300 °C Program rate 8 °C/min Initial hold 0 min Final hold 5 min		

2.5. Radiocarbon Dating

To ensure the absence of any contamination during collection, transportation, subsampling, storage and analysis, sediment collected at a depth of 2 to 4 m were analyzed for hydrocarbons and ^{14}C dated to ensure that they were pre anthropogenic. Ten samples representing both peat and shell substrates were collected. The samples were dated by the University of Miami, Beta Analytic, Inc. Sampling, storage, subsampling, and analysis followed the same procedures as all other sediment samples.

2.6. Computer Mapping

A computer program was used to graphically depict the spatially distributed information generated by this project and assist in its interpretation. The program, titled SYMAP, was developed by the laboratory for Computer Graphics and Spatial Analysis, Harvard Center for Environmental Design Studies, Graduate School of Design, Harvard University, Cambridge, MA. The package assigns values to the coordinate locations of data points or data zones, and can generate three basic types of maps; contour, proximal and conformant. For this study only the contour program was used. This program uses values assigned to a set of coordinate locations and interpolates between data points assuming a continuous variation exists between these points.

3. Intercalibration

Interlaboratory calibration exercises were carried out in the three laboratories (Mote Marine Laboratory, Jacksonville University and University of Miami) involved in hydrocarbon analysis during both years of the study. These exercises were undertaken to ensure the compatibility of results from all laboratories. Table 3 lists the samples exchanged during the two-year study.

Only the results from the offshore sediment samples are reported since all other intercalibration exercises have been completed and reviewed. Tables 4 and 5 presents the concentrations of the aliphatic and aromatic hydrocarbons and their key characteristics. Appendix F and G contains a more detailed report of the analyses. Figures 4, 5 and 6 show the chromatograms for the aliphatic fraction. As can be seen from the tables all of the samples contained very small amounts of hydrocarbons. This is what would be expected from a sample collected in non contaminated offshore environment. The only sample which showed any unusual characteristics was the Jetties sample collected by Jacksonville University. This sample contained a small UCM and had a homologous series from C_{15}-C_{30}.

4. Results and Discussion

4.1. Grain Size Analysis

Table 6 presents the distribution of grain sizes for the surface sediments. The data is reported on a percent dry weight basis for three size classes; gravel (>2000 μ), sand 2000 μ - >63 μ) and silt-clay (<63 μ).

The distribution of the gravel fraction ranged from 0 to 66 percent. The mean was 7.9 percent with a standard deviation of 11.19. Figure 7 is a histogram showing the distribution of samples analyzed. Sixty-eight percent of the samples were composed of 10 percent or less of gravel. The samples which contained high quantities of gravel were almost always associated with areas where spoil had been deposited or dredging had taken place. The percentage of sand in the sediments ranged from 1.3 percent to 98.4 percent. The mean value for the samples collected was 62.9 percent and the standard deviation was 25.00. Figure 8 is a histogram of the distribution of sand in the surface sediments. The majority of the samples contained in excess of 20 percent sand. The quantity of sand in the samples collected from the northern areas of the Bay showed a large variation which is most likely due to extensive dredging activities. The silt-clay fraction ranged from 0.6 to 98.7 percent. The mean was 29.18 percent and the standard deviation was 25.70. The silt-clay fraction accounted for less than 40 percent in most of the samples. The distribution for the silt-clay fraction is shown in Figure 9. There were 9 samples in which the silt-clay fraction exceeded 80 percent. These samples were distributed throughout the Bay. Several were associated with canal bottoms and dredge holes and two of the samples were collected from Featherbed Bank.

4.2. Organic and Carbonate Content

Table 7 presents the results of the organic matter and carbonate analyses of the surface sediments. Figures 10 and 11 are histograms of the organic matter and carbonate content of the sediments, respectively. The organic matter ranged from 0.17 percent to 33.22 percent. The mean value was 5.1 percent and the standard deviation was 5.10. The majority of the samples had organic contents of less than 8 percent. The samples with high organic matter content (>10%) were predominantly located in the southern areas of the Bay and usually associated with canal bottoms. Canals sampled in the northern areas of the Bay contained high

Table 3. Summary of intercalibration samples for the two-year study.

Originator	Sample
First Year	
Mote Marine Laboratory	South Louisiana Crude Oil Sediment spiked with Kuwait Crude Oil Tissue spiked with Kuwait Crude Oil Oyster Trout Mullet
Jacksonville University	Oyster Crab Sea Trout
University of Miami	Mullet spiked with #2 Fuel Oil
Second Year	
NOAA	Duwamish Sediment
Mote Marine Laboratory	D-1 D-2 D-3
Jacksonville University	Jetties Atlantic Beach
University of Miami	N6A 201 202 203

Table 4. Aliphatic hydrocarbon characterization of interlaboratory sediment samples collected during Year 02. All values are corrected for percent recovery and expressed on a dry weight bases.

		RATIOS					KEY HYDROCARBONS (µg/g)				n-ALKANES	
Laboratory/ Sample	Total* f_1 (µg/g)	f_1/ f_2	Resol. Unres	Prist./ Phyt.	C_{17}/ Prist.	C_{18}/ Phyt.	1500	1700	2085	2900	Homol. Ser.	CPI
University of Miami												
201	1.08 (0.76)	2.6	ND	0.28	0.66	0.53	TD	0.02	0.09	ND	C_{17}-C_{28}	2.53
202	0.83 (0.90)	0.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
203	3.94 (0.02)	7.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.7
Mote Marine Laboratory												
D-1	3.19 (0.44)	2.2	ND	0.23	1.77	0.18	ND	0.03	1.44	0.12	C_{17}-C_{29}	1.35
D-2	2.57 (0.35)	1.9	ND	ND	0.34	0.73	TD	0.02	1.52	ND	C_{12}-C_{25}	1.30
D-3	2.50 (0.90)	2.0	ND	0.85	1.27	0.23	ND	0.01	1.22	ND	C_{17}-C_{30}	0.61
Jacksonville University												
Jetties	5.40 (0.45)	3.3	1.65	1.63	0.91	0.59	0.01	0.02	0.12	0.77	C_{15}-C_{30}	3.49
Atlantic Beach	6.30 (4.06)	8.3	ND	ND	ND	1.33	0.08	ND	0.07	ND	C_{15}-C_{27}	2.07
N6A	0.72 (0.50)	0.3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

* Mean and standard deviation of three replicates.
ND = None Detected
TD - Trace Detected

Table 5. Aromatic hydrocarbon characterization of interlaboratory sediment samples collected during year 02. All values corrected for percent recovery and expressed on a dry weight bases.

Laboratory/ Sample	Total f_2 (μg/g)	Naphthalene	Dibenzo-thiophene	Phenan-threne	1-Methyl-phenanthrene	Pyrene
University of Miami						
202	1.05 (1.01)	ND	ND	0.01	0.04	ND
203	0.55 (0.43)	ND	0.07	ND	ND	0.03
Mote Marine Laboratory						
D-1	1.42 (1.42)	ND	0.04	0.04	0.03	0.04
D-2	1.35 (0.91)	ND	0.03	0.03	0.05	0.02
D-3	1.22 (1.35)	ND	0.02	0.04	0.05	0.06
Jacksonville University						
Jetties	1.65 (1.10)	ND	0.09	0.02	0.08	0.26
Atlantic Beach	0.76	ND	ND	ND	ND	ND
N6G	2.47 (2.08)	ND	ND	0.03	0.04	0.06

* Mean and standard deviation of three replicates.
ND - None Detected

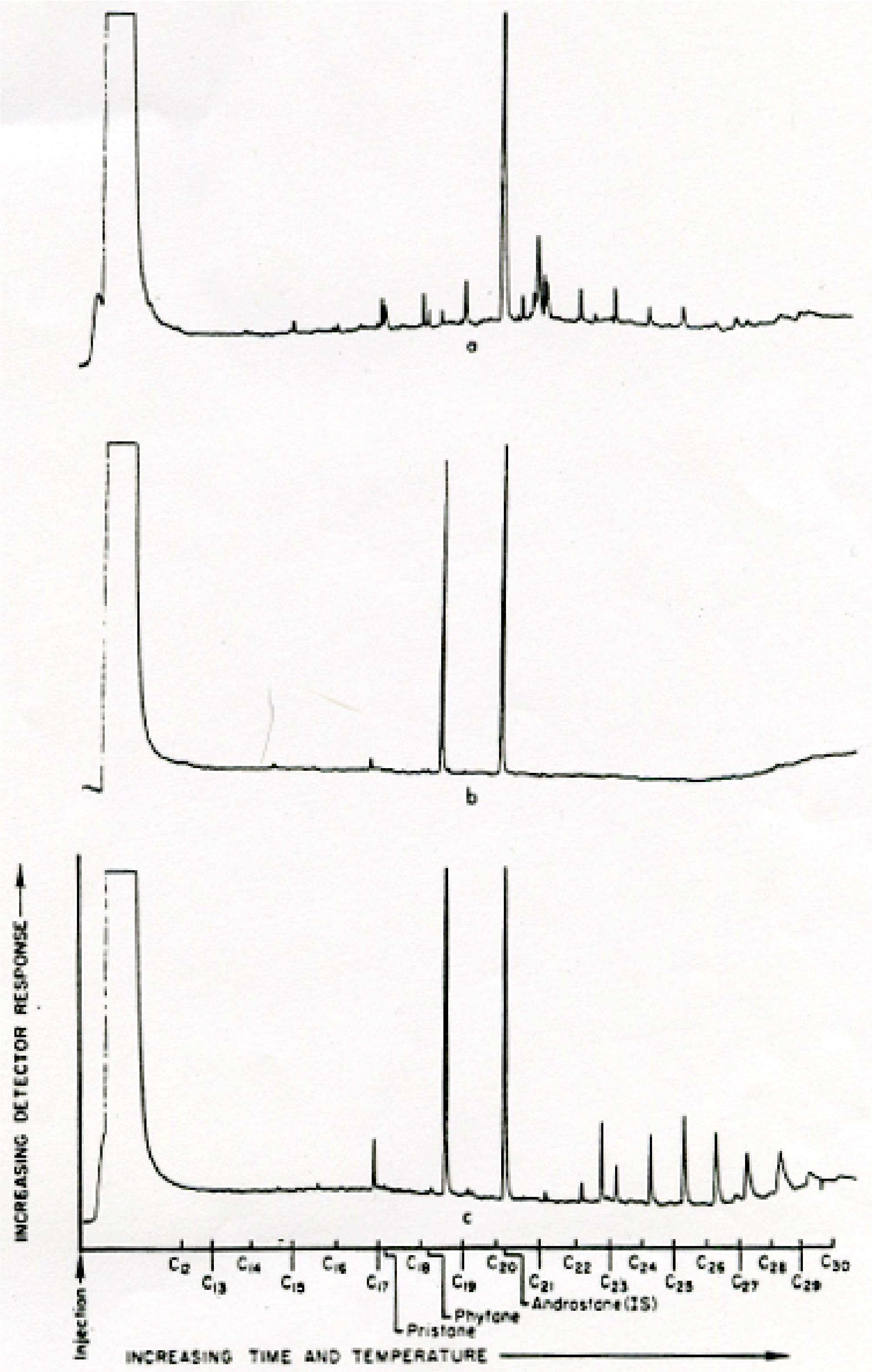

Figure 4. Chromatograms of aliphatic (f_1) fraction. Interlaboratory calibration - offshore sediment samples - University of Miami.

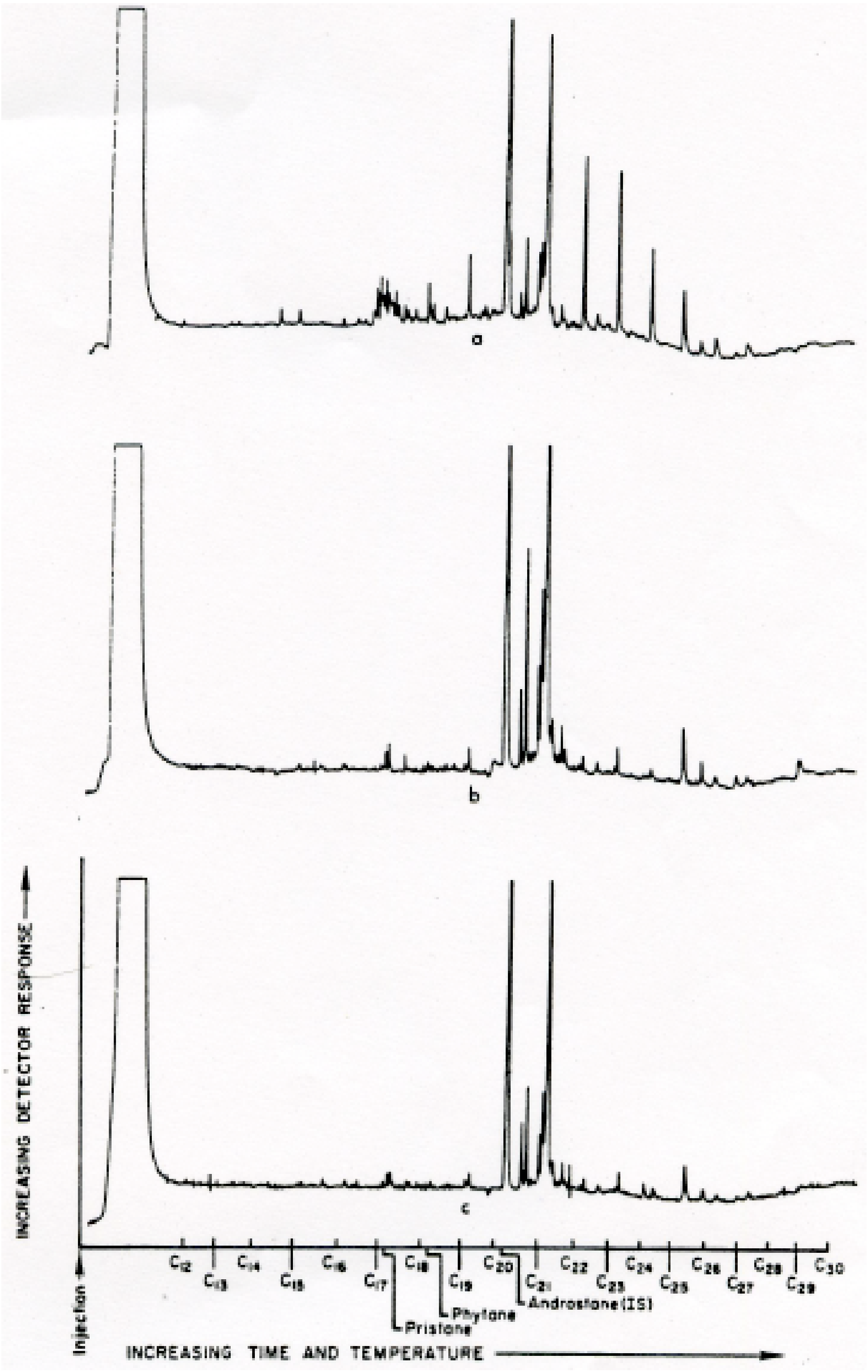

Figure 5. Chromatograms of aliphatic (f_1) fraction. Interlaboratory calibration - offshore sediment samples - Mote Marine Laboratory.

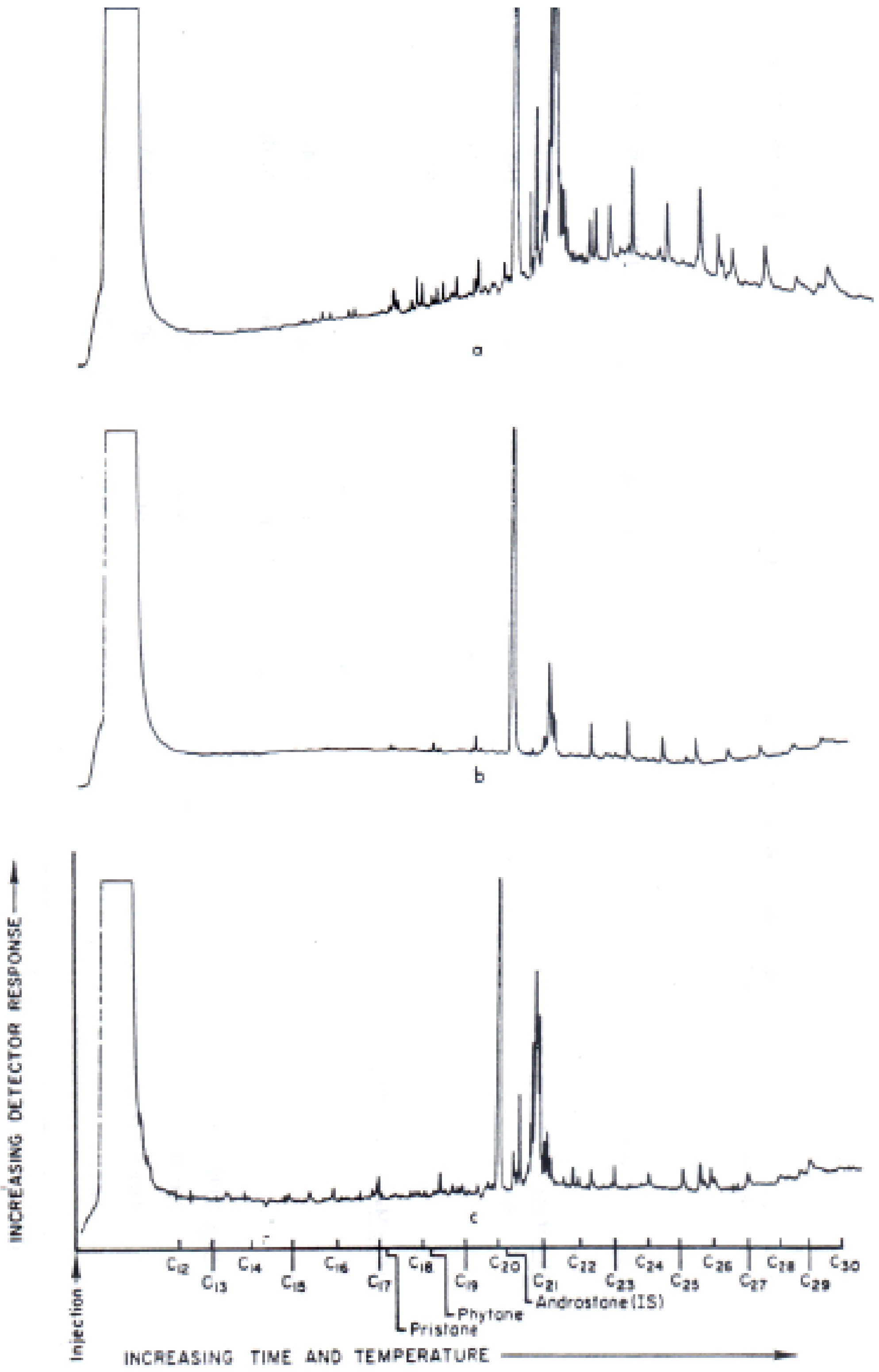

Figure 6. Chromatograms of aliphatic (f_1) fraction. Interlaboratory calibration - offshore sediment samples - Jacksonville University. a) Jetties samples, b) Atlantic Beach sample, c) sample N6A.

Table 6. Summary of surface sediment (0-5 cm depth) grain size analysis. All values are percent dry weight.

Sample #	Gravel (>2000 μ)	Sand (2000 - 63 μ)	SiltClay (<63 μ)
1	4.0	88.9	7.1
2	20.4	68.8	10.8
3	8.4	46.3	45.3
4	9.1	62.1	28.8
5	4.7	77.9	17.4
6	7.5	44.5	48.0
7	2.8	25.3	71.9
8	1.6	86.8	11.6
9	1.1	69.6	29.3
10	4.5	86.8	8.7
11	0.4	96.5	3.1
12	1.6	56.4	42.0
13	7.7	83.3	9.0
14	28.0	42.9	29.1
15	7.2	60.4	32.4
16	12.2	43.3	44.5
17	0.2	19.1	80.7
18	6.9	41.0	52.1
19	0.8	9.5	89.7
20	10.6	72.8	16.6
21	2.8	37.0	60.2
22	0.6	98.4	1.0
23	2.7	93.2	4.1
24	0.0	98.3	1.7
25	34.2	61.3	4.5
26	0.0	84.2	15.8
27	22.0	74.3	3.7
28	7.4	83.8	8.8
29	0.3	77.7	22.0
30	2.4	94.5	3.1
31	24.2	73.2	2.6
32	9.4	47.3	43.3
33	0.0	4.8	95.2
34	0.8	51.0	48.2
36	1.6	83.4	15.0
37	1.2	97.6	1.2
38	1.8	75.5	22.7
39	7.0	90.5	2.5
40	44.5	30.5	25.0
41	15.1	78.5	6.4
42	10.4	34.1	55.5
43	10.9	26.9	62.2
44	1.5	89.7	8.8
45	3.8	88.5	7.7

Table 6. Summary of surface sediment (0-5 cm depth) grain size analysis. All values are percent dry weight (cont.).

Sample #	Gravel (>2000 μ)	Sand (2000 - 63 μ)	SiltClay (<63 μ)
46	34.0	55.8	10.2
47	1.0	85.7	13.3
48	0.4	98.0	1.6
49	0.0	11.1	98.9
50	0.6	38.0	61.4
51	0.0	28.7	71.3
52	0.5	10.9	88.6
53	8.7	71.2	20.1
54	15.2	79.7	5.1
57	0.2	31.0	68.8
58	0.6	38.5	60.9
59	13.1	57.2	29.7
60	0.8	29.4	69.8
61	0.0	36.6	63.4
62	0.0	47.5	52.5
63	0.5	92.6	6.9
64	11.0	77.2	11.8
65	0.5	89.0	10.5
66	0.0	41.6	58.4
67	0.0	88.2	11.8
68	0.7	49.4	49.9
69	1.8	96.5	1.7
70	16.2	90.0	3.8
71	13.2	73.2	13.6
72	33.2	60.5	6.3
73	0.2	96.1	3.7
74	1.9	92.5	5.6
75	15.3	71.4	13.3
76	2.1	82.1	15.8
77	16.1	74.4	9.5
78	56.0	40.2	3.8
79	66.2	25.1	8.7
80	0.7	47.3	52.0
81	23.2	40.1	36.7
82	0.3	69.4	30.3
83	12.1	28.7	59.2
84	8.9	83.3	7.8
85	2.6	67.4	30.0
86	6.9	62.0	31.1
87	2.5	85.5	12.0
88	4.1	91.0	4.9
89	1.3	73.9	24.8
90	1.7	85.2	13.1
91	3.1	85.9	11.0
92	40.2	56.2	3.6

Table 6. Summary of surface sediment (0-5 cm depth) grain size analysis. All values are percent dry weight (cont.).

Sample #	Gravel (>2000 μ)	Sand (2000 - 63 μ)	SiltClay (<63 μ)
93	20.5	75.4	4.1
95	9.3	49.9	40.8
96	15.6	28.0	56.4
97	1.5	77.2	21.3
98	0.7	85.0	14.3
99	4.7	84.5	10.8
100	21.5	74.5	4.0
101	0.0	18.3	81.7
102	0.3	80.7	19.0
103	12.2	76.2	11.6
104	8.5	49.5	42.0
105	0.4	65.7	33.9
106	38.8	41.8	19.4
107	7.8	56.3	35.9
108	5.7	78.1	16.2
109	2.8	83.5	13.7
110	2.6	28.0	69.4
111	3.1	87.2	9.7
112	3.6	86.7	9.7
113	4.8	62.3	32.9
114	6.3	87.6	6.1
115	1.2	47.7	51.1
116	4.6	52.5	42.9
117	8.9	47.7	43.4
118	4.2	42.3	53.5
119	1.9	84.7	13.4
120	12.2	26.6	61.2
121	5.2	28.9	65.9
122	3.0	26.2	70.8
123	0.3	93.7	6.0
124	3.4	73.1	23.5
125	9.9	62.1	28.0
126	7.3	69.5	23.2
127	19.8	76.6	3.6
128	20.5	78.9	0.6
129	1.2	92.0	6.8
130	0.8	94.9	4.3
131	9.3	43.6	47.1
132	11.7	51.7	36.6
133	43.5	50.3	6.2
134	0.0	59.1	40.9
135	0.0	1.3	98.7
136	0.0	5.0	95.0
137	0.4	65.3	34.3
138	0.6	72.5	26.9

Table 6. Summary of surface sediment (0-5 cm depth) grain size analysis. All values are percent dry weight (cont.).

Sample #	Gravel (>2000 μ)	Sand (2000 - 63 μ)	SiltClay (<63 μ)
139	3.4	88.0	8.6
140	0.7	91.7	7.6
141	9.8	86.7	3.5
142	0.8	31.2	68.0
143	0.5	91.7	7.8
144	1.9	78.7	19.4
145	23.3	64.5	12.2
146	11.0	37.0	52.0
147	1.2	34.3	64.5
148	0.7	78.5	20.8
149	4.0	27.1	68.9
150	2.5	5.2	92.3
151	4.3	82.4	13.3
152	0.0	88.3	11.7
153	0.6	76.1	23.3
154	0.3	61.3	38.4
155	14.4	51.1	34.5
156	13.4	84.0	2.6

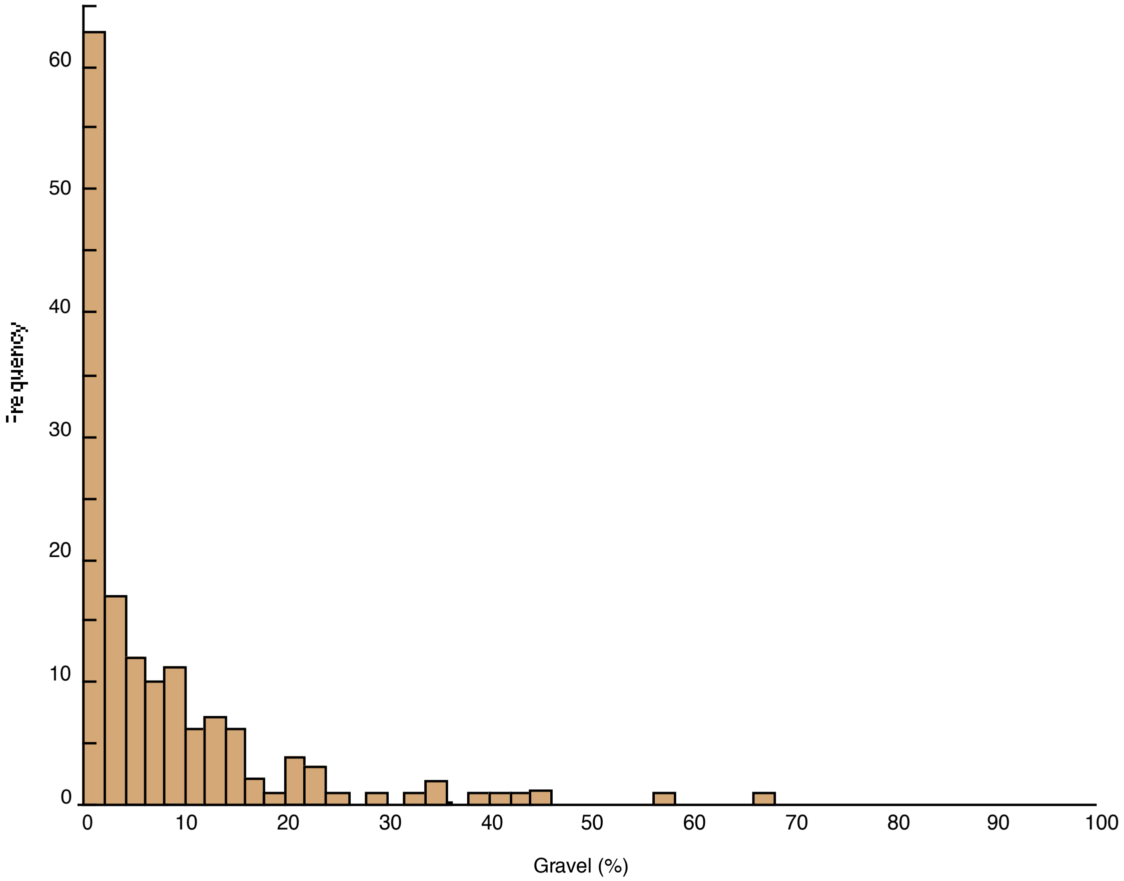

Figure 7. Histogram of percent gravel in surface sediments (0-5 cm).

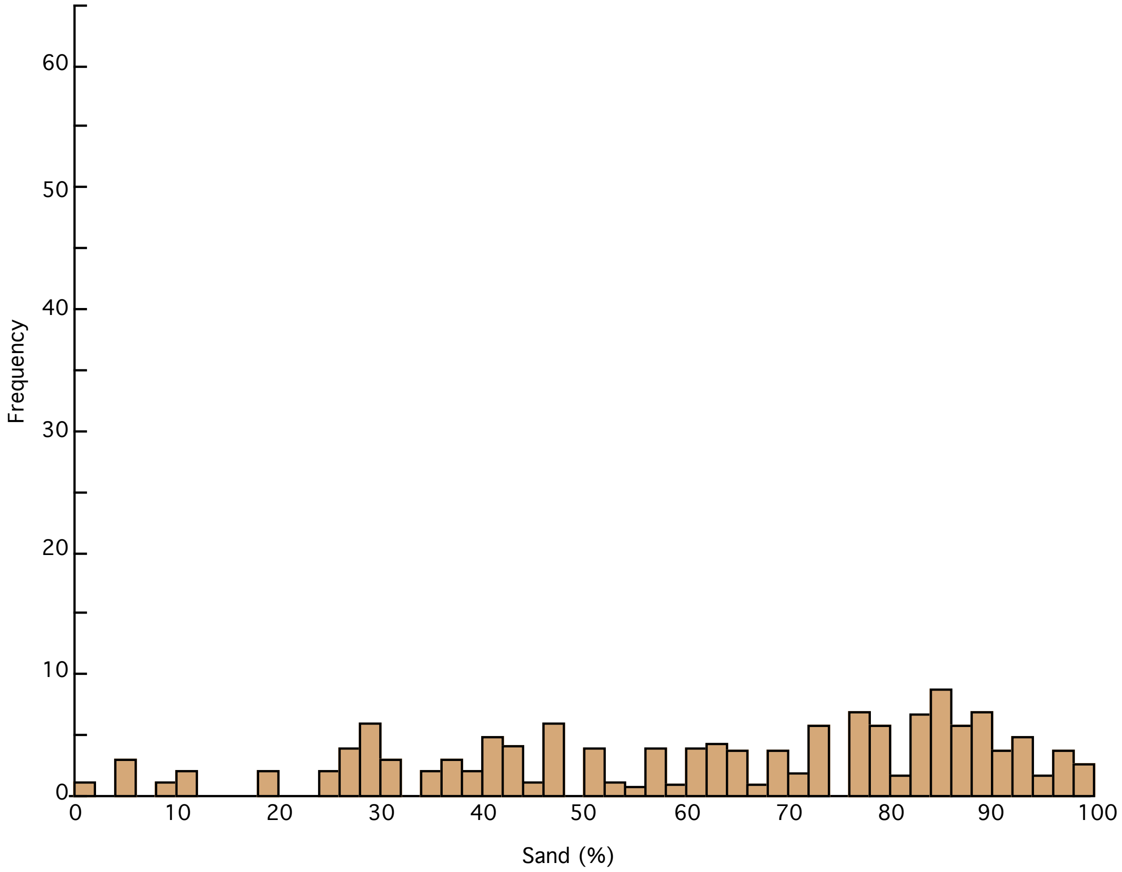

Figure 8. Histogram of percent sand in surface sediments (0-5 cm).

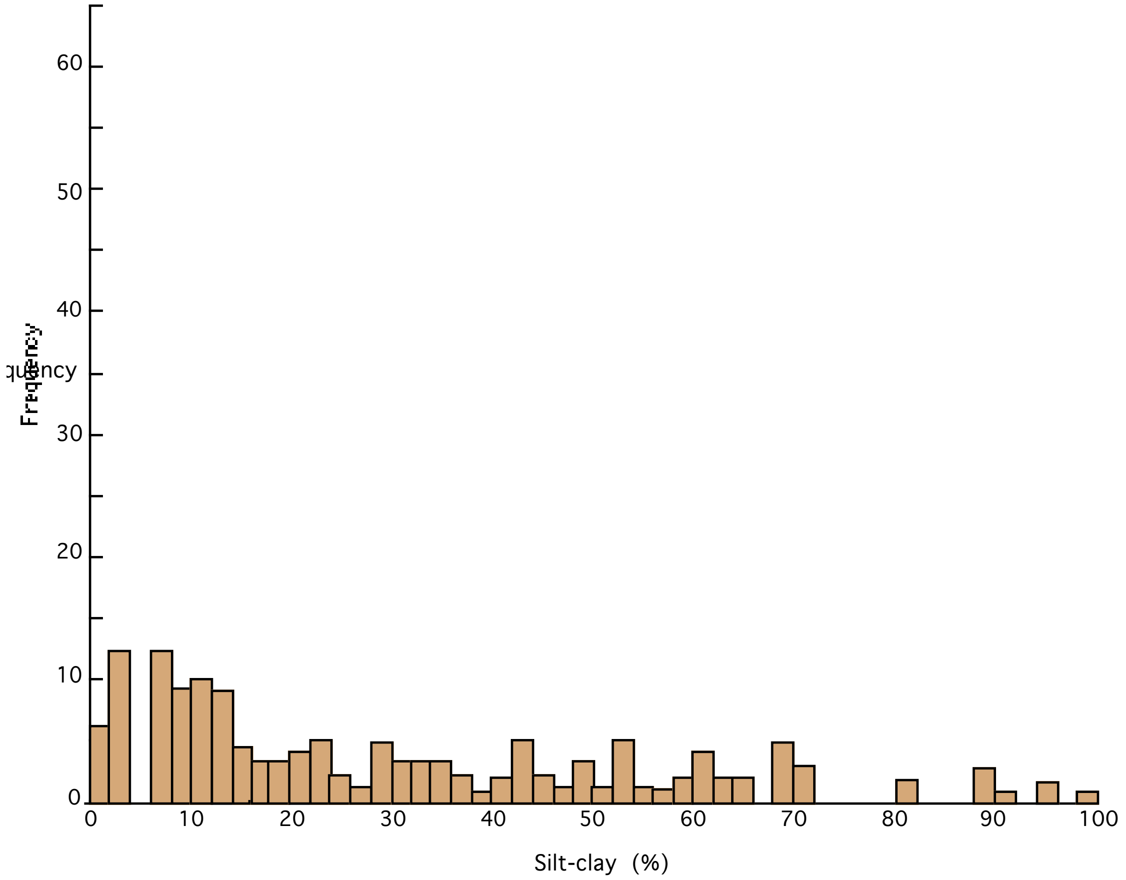

Figure 9. Histogram of percent silt-clay in surface sediments (0-5 cm).

Table 7. Summary of total organic matter and carbonate content of surface sediments (0-5 cm depth).

Sample	Organic Matter (% Dry Weight)	Carbonate ($CaCO_3$) (% Dry Weight)
1	3.00	91.69
2	3.79	87.16
3	6.00	74.57
4	1.35	56.79
5	1.69	39.24
6	4.70	75.94
7	6.30	79.90
8	1.04	15.27
9	2.78	33.70
10	1.49	22.37
11	0.60	10.75
12	4.17	85.48
13	2.34	55.99
14	3.77	91.88
15	4.60	82.53
16	7.90	80.42
17	4.99	90.46
18	3.78	79.46
19	7.58	88.10
20	4.50	75.65
21	5.26	74.21
22	0.25	4.59
23	0.58	6.35
24	0.17	0.55
25	2.76	68.68
26	1.65	12.53
27	0.52	24.46
28	1.35	43.58
29	2.78	67.79
30	1.01	43.81
31	1.50	53.71
32	5.20	52.61
33	7.07	77.36
34	8.10	77.34
35	2.52	73.93
36	0.68	10.42
37	0.30	5.87
38	0.44	13.10
39	0.48	29.41
40	5.25	92.75
41	1.46	62.87
42	7.31	73.93
43	5.71	76.97
44	1.07	45.03
45	1.32	29.22

Table 7. Summary of total organic matter and carbonate content of surface sediments (0-5 cm depth) (cont.).

Sample	Organic Matter (% Dry Weight)	Carbonate ($CaCO_3$) (% Dry Weight)
46	1.84	86.94
47	2.54	38.73
48	2.92	68.51
49	4.10	68.66
50	11.56	37.72
51	7.32	73.12
52	2.79	70.85
53	2.37	70.46
54	1.24	46.32
55	MD	MD
56	MD	MD
57	10.82	44.47
58	9.05	45.68
59	3.94	53.92
60	MD	MD
61	9.50	47.18
62	7.47	56.61
63	1.70	11.74
64	3.13	12.92
65	1.70	5.47
66	13.45	45.37
67	0.34	1.95
68	12.66	41.30
69	0.86	7.68
70	0.98	30.04
71	2.35	93.80
72	2.61	44.31
73	0.68	1.87
74	0.77	12.99
75	11.54	18.73
76	2.06	54.39
77	1.43	52.35
78	1.15	87.67
79	1.59	89.88
80	4.35	69.50
81	4.37	81.80
82	13.94	5.32
83	7.36	87.01
84	2.41	77.72
85	3.43	39.75
86	3.75	70.20
87	3.83	80.03
88	2.74	85.72
89	2.11	32.23
90	1.27	20.27

Table 7. Summary of total organic matter and carbonate content of surface sediments (0-5 cm depth) (cont.).

Sample	Organic Matter (% Dry Weight)	Carbonate ($CaCO_3$) (% Dry Weight)
91	2.12	46.80
92	23.06	48.13
93	2.89	54.16
94	MD	MD
95	5.69	87.55
96	5.79	91.95
97	2.21	30.28
98	0.49	9.86
99	1.74	31.83
100	15.76	77.56
101	MD	MD
102	15.93	66.01
103	17.49	67.77
104	7.12	80.14
105	7.60	86.91
106	7.69	88.20
107	17.56	71.48
108	1.98	40.39
109	2.39	28.95
110	11.20	77.09
111	2.39	57.01
112	14.47	68.06
113	4.54	44.51
114	2.30	59.30
115	6.95	58.32
116	5.54	90.67
117	5.51	87.24
118	15.16	78.97
119	1.42	13.62
120	MD	MD
121	7.97	69.08
122	8.10	75.30
123	2.99	92.43
124	33.22	44.33
125	MD	MD
126	5.58	53.06
127	MD	MD
128	3.34	72.34
129	1.09	27.64
130	0.86	26.32
131	2.48	41.60
132	4.39	51.93
133	4.50	60.97
134	13.97	3.66
135	12.84	66.23

Table 7. Summary of total organic matter and carbonate content of surface sediments (0-5 cm depth) (cont.).

Sample	Organic Matter (% Dry Weight)	Carbonate ($CaCO_3$) (% Dry Weight)
136	11.85	62.90
137	12.52	60.56
138	4.04	57.13
139	MD	MD
140	2.59	47.03
141	1.45	44.70
142	9.92	68.20
143	1.75	53.80
144	2.93	57.36
145	3.12	53.60
146	21.29	41.95
147	6.72	63.77
148	3.53	20.08
149	7.80	52.79
150	MD	MD
151	1.86	46.77
152	2.67	67.90
153	2.39	49.50
154	3.56	62.95
155	2.90	78.78
156	1.74	37.10

* MD - Missing Data

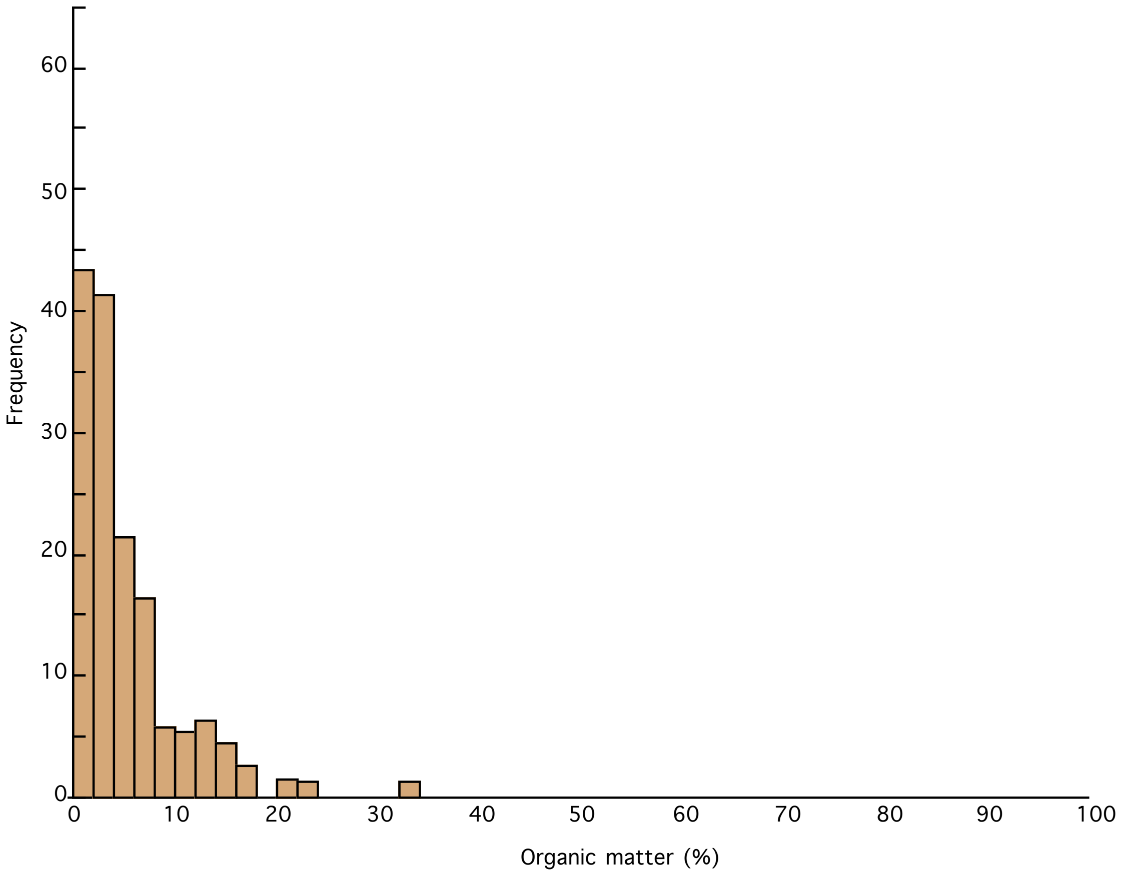

Figure 10. Histogram of percent organic matter in surface sediments (0-5 cm).

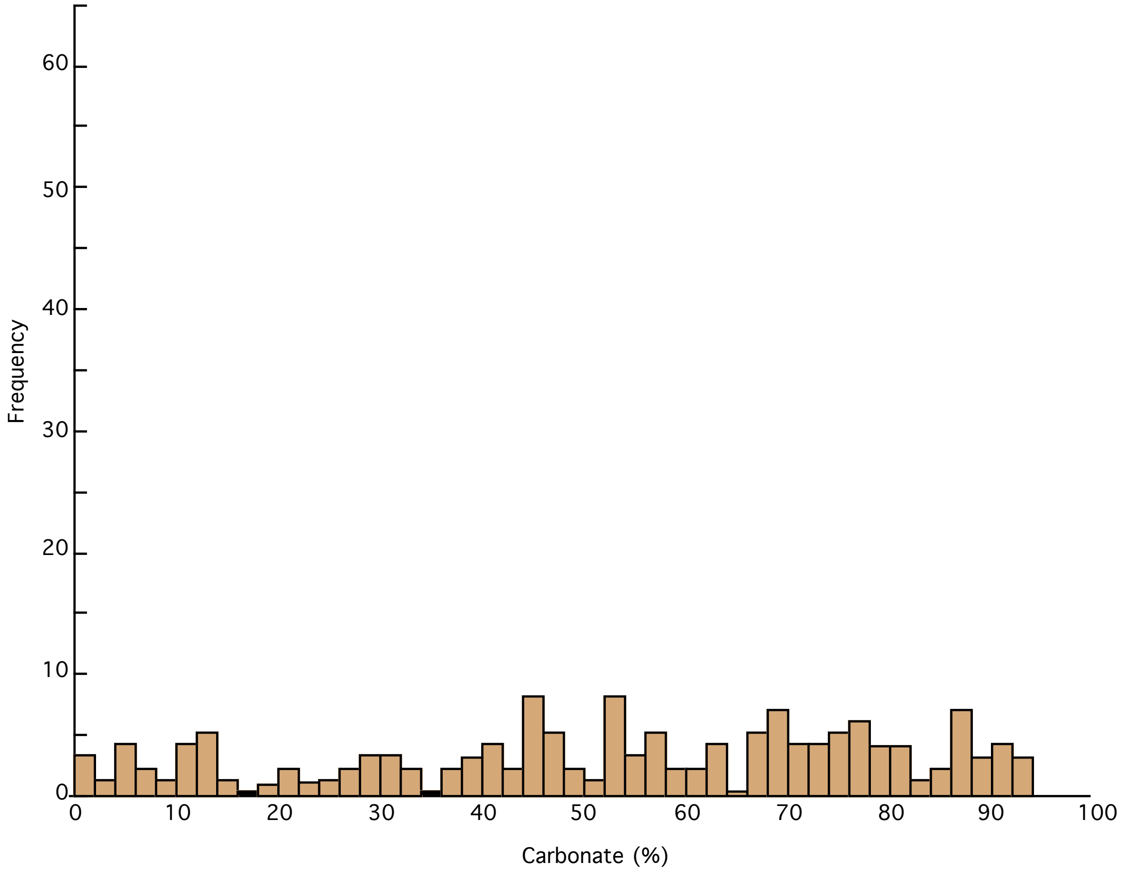

Figure 11. Histogram of percent carbonate material in surface sediments (0-5 cm).

concentrations of organic matter also. The other samples which indicated high organic content were collected from intertidal areas consisting of a mangrove peat substrate. Carbonate content ranged from 0.6 to 93.8 percent. The mean of the samples collected was 53.3 percent with a standard deviation of 26.12. Figure 11 shows that carbonate was relatively evenly distributed throughout the samples collected. The areas which exhibited the higher concentrations were distributed south of Key Biscayne along the west side of the Bay.

4.3. Radiocarbon Dating

Figure 12 is a descriptive profile of the collected cores showing the locations of the dated subsamples. Table 8 lists the location, sample number, depth of subsample and age in ^{14}C years. Table 9 and 10 lists the aliphatic and aromatic hydrocarbon values and indices for the dated samples. The dated material from cores 74, 78 and 152 showed that the oldest material was in the surface layers. This would be expected since all three of these cores were taken from spoil islands. The aliphatic hydrocarbons concentrations were all low except for sample 152-p2.

4.4. GC-MS Analyses

Gas chromatography-mass spectroscopy (GC-MS) analyses was performed by Dr. Edward S. Van Vleet, Associate Professor of Oceanography, Department of Marine Science, University of South Florida. Samples were analyzed using a Hewlett-Packard 5992B computerized GC-MS system equipped with a 30-m DB-5 fused silica capillary column. GC-MS system equipped with a 30-m DB-5 fused silica capillary column. GC-MS operating conditions were as follows:

Carrier gas: helium
Column flow rate: 2 mL/min
Injection port temperature: 240 °C
Spitless injection mode
Temperature program: 90-250 °C at 4 °C/min
Electron multiplier voltage: 1200 or 1400 eV
GC-MS run in selected ion monitoring mode
Dwell time: 100 msec/ion

Specific ions monitored included C_0-C_3 naphthalenes, C_0-C_3 phenanthrenes (plus anthracenes), C_0-C_3 pyrenes, C_0-C_2 benz[*a*]anthracenes and dibenzothiophene. Standard polycyclic aromatic hydrocarbons (PAH) mixtures were run each day for calculation of response factors. Analytical uncertainty in the quantitative GC-MS determinations was approximately ±30%. Interpretation relative to petrogenic versus pyrogenic inputs was obtained by plotting the absolute abundance of the PAH homologs. Fifteen samples, collected during the second year of the study, were analyzed by GC-.MS. These included seven sediments, six surface waters and two tissue samples. Table 11 lists the sample numbers, type, location and results of the GC-MS analyses.

The water samples were essentially free of the aromatic hydrocarbons that were monitored. Sample 227 contained peaks for C_2-phenanthrene although they were at the limits of sensitivity for the instrumentation and are therefore questionable.

The two tissue samples did not show the normal range of PAHs expected from simple petrogenic or pyrogenic inputs. These samples show only one or two PAH components (C_2- and/or C_3-phenanthrenes in each case). The PAH homologs in the oyster tissue are believed to be of petrogenic origin. The catfish contained only one PAH component therefore its source was uncertain.

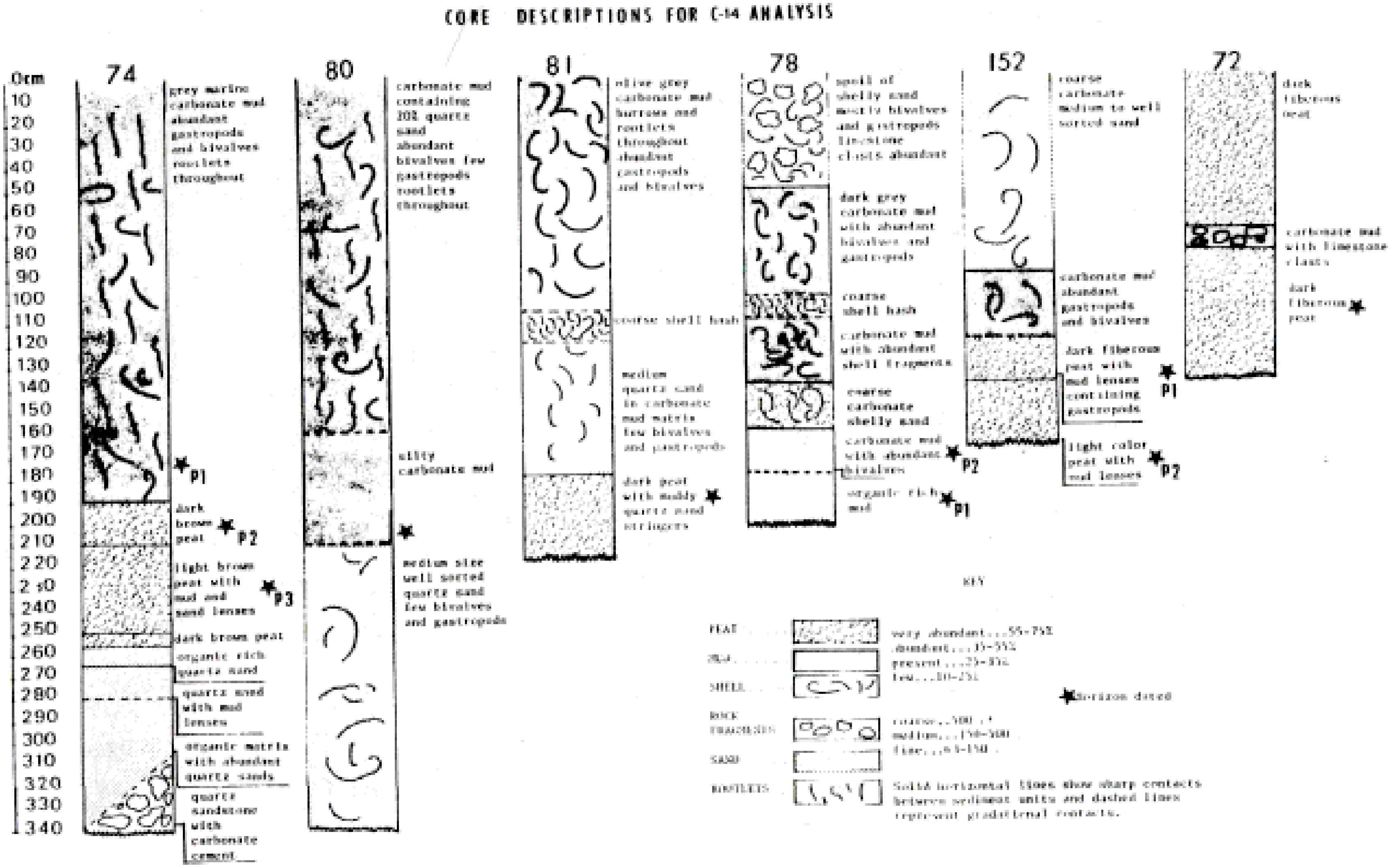

Figure 12a. Profile description of cores used in ^{14}C dating.

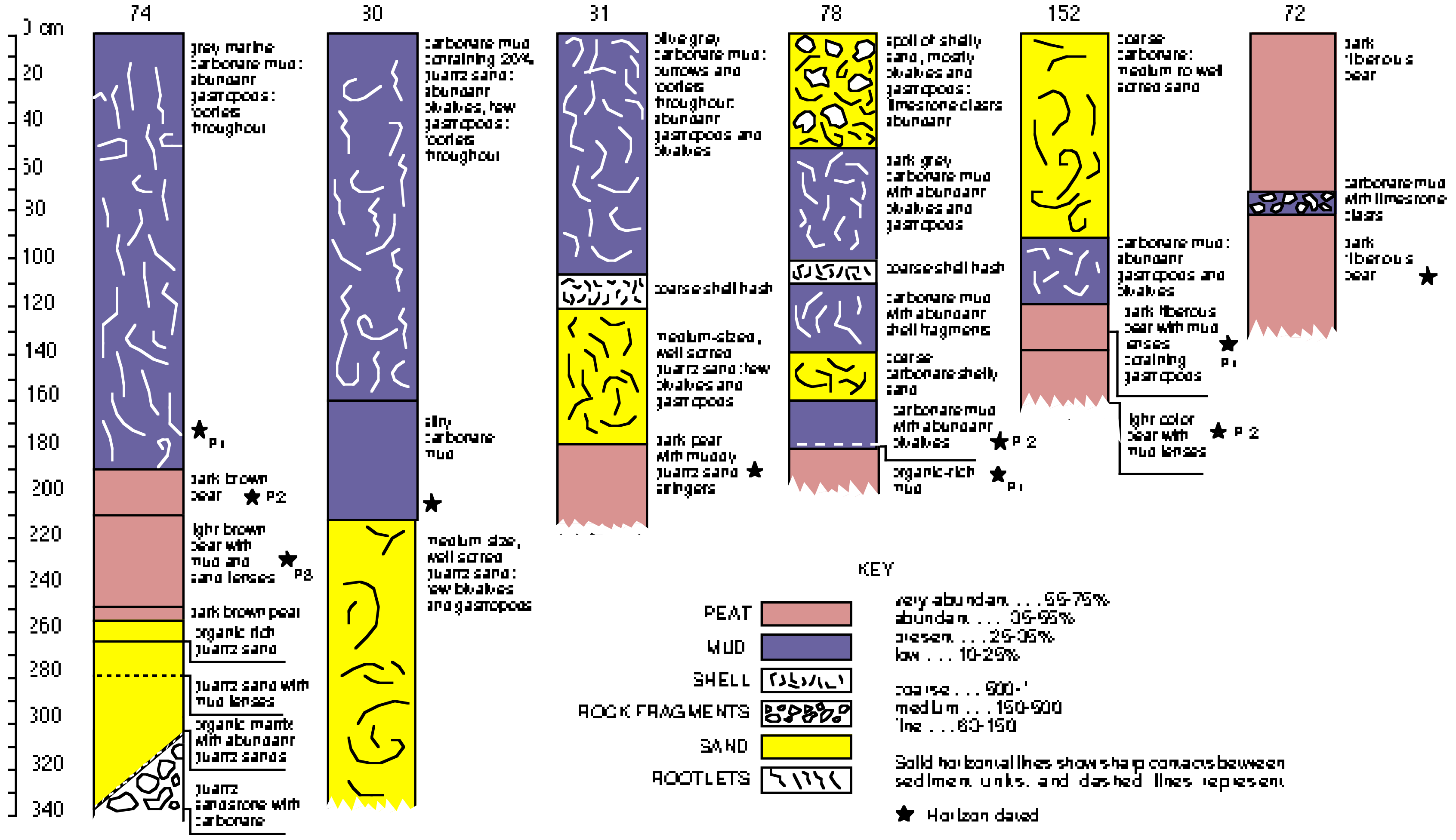

Figure 12b. Profile desription of cores used for ^{14}C dating.
[RECONSTRUCTION.]

Table 8. Summary information for ^{14}C dated sediment.

Core no.	University of Miami Laboratory Sample no.	Collection Location	Material dated	Midpoint of dated interval below sediment surface	Depth of sediment surface below mean sea level	Radiocarbon age ^{14}C years
72	UM-2670	North side of Chicken Key Channel	peat	2.36 m	1.5 m	3370 ± 80
74-p1	UM-2693	Spoil Bank 0.2 km ESE from the mouth of the Miami River	shell	3.40 m	1.1 m	4820 ± 90
74-p2	UM-2672		peat	3.70 m	1.1 m	4870 ± 90
74-p3	UM-2667		peat	4.00 m	1.1 m	3030 ± 120
78-p1	UM-2695	Spoil Island 0.7 km E of Biscayne Canal	shell	2.10 m	0.8 m	4550 + 110
78-p2	UM-2696		shell	2.30 m	0.8 m	1950 ± 60
80	UM-2694	2 km N from the NE corner of the Julia Tuttle Cswy.	shell	3.40 m	1.8 m	3240 ± 125
81	UM-2668	Central portion of the *Halimeda* flat between 79th St. and Julia Tuttle Cswy.	peat	2.95 m	1.6 m	5145 ± 110
152-p1	UM-2671	NE corner of Spoil Island 1.3 km east of Bakers Haulover Inlet	peat	2.10 m	1.5 m	4120 ± 80
152-p2	UM-2669		peat	2.50 m	1.5 m	3630 ± 80

Table 9. Aliphatic hydrocarbon characterization of ^{14}C dated sediment samples. All values are corrected for percent recovery and expressed on a dry weight bases.

		RATIOS					KEY HYDROCARBONS ($\mu g/g$)				n-ALKANES	
Laboratory/ Sample	Total* f_1 ($\mu g/g$)	f_1/f_2	Resol. Unres	Prist./ Phyt.	C_{17}/ Prist.	C_{18}/ Phyt.	1500	1700	2085	2900	Homol. Ser.	CPI
72 (302)	20.32	0.06	ND	ND	ND	4.77	ND	0.88	0.56	ND	C_{17}-C_{25}	2.24
74-p1 (310)	3.92	0.04	ND	ND	ND	ND	ND	ND	0.64	ND	C_{17}-C_{25}	0.97
74-p2 (308)	7.12	0.04	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
74-p3 (305)	ND	ND	ND	ND	ND	NI)	ND	ND	ND	ND	ND	ND
78-p1 (311)	12.90	0.01	ND	ND	ND	ND	ND	ND	ND	ND	C_{16}-C_{22}	0.12
78-p2 (312)	3.21	0.15	ND	ND	ND	ND	ND	ND	0.25	ND	C_{12}-C_{23}	1.82
80 (307)	ND	ND	ND	ND	ND	ND	ND	NI)	ND	ND	ND	ND
81 (306)	4.03	0.07	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
152-p1 (309)	1.85	0.04	ND	ND	ND	ND	ND	NI)	0.19	ND	C_{18}-C_{29}	0.63
152-p2 (301)	216.84	6.51	0.08	0.23	ND	1.37	0.26	ND	0.58	ND	C_{12}-C_{23}	0.89

ND - Not detected.

Table 10. Aromatic hydrocarbon characterization of ^{14}C dated sediment samples. Values are corrected for percent recovery and expressed on a dry weight bases (μg/g).

Sample	Total f_2	Napththalene	Phenanthrene	Dibenzothiophene	Pyrene
72 (302)	35.01	ND	0.06	2.65	1.13
74-p1 (310)	8.67	ND	1.54	0.30	1.76
74-p2 (308)	19.31	ND	0.53	1.24	4.16
74-p3 (305)	0.83	ND	ND	ND	ND
78-p1 (311)	10.80	ND	0.64	0.23	0.99
73-p2 (312)	2.08	ND	0.25	ND	ND
80 (307)	0.59	ND	ND	ND	ND
81 (306)	5.96	ND	ND	ND	ND
152-p1 (309)	4.05	ND	0.35	0.11	1.17
152-p2 (301)	3.33	ND	ND	0.12	0.82

* ND = None Detected

Table 11. Summary of GC-MS characterization of PAH homologs.

Sample type and number	Location	Total GC-MS Aromatics (μg/g)	Major Peaks*	Probable Major Source
Water				
208	Miami River	0.00	None	None
210	Miami River	0.00	None	None
227	Little River	0.11	C_2P	Uncertain
232	Goulds Canal	0.00	None	None
238	Military Canal	0.00	None	None
246	Black Creek	0.00	None	None
Tissue				
Catfish (*Arius felis*)	North Bay	0.4	C_3P	Uncertain
Flat tree oyster (*Isognomon alatus*)	Marina	3.0	C_3P, C_2P	Petrogenic
Sediment				
214 (0-5)	Miami River	13.5	Py, C_3Py	Pyrogenic
214 (20-25)	Miami River	3.9	Py, C_3Py	Mixed
225 (0-5)	Little River	0.2	Py, P, C_{3P}	Pyrogenic
225 (55-60)	Little River	0.2	C_3P, C_2P	Petrogenic
232 (0-5)	Goulds Canal	5.0	C_3N, C_3P	Petrogenic
232 (55-60)	Goulds Canal	13.2	C_3N, C_3P, Py	Mixed
240 (0-5)	Military Canal	0.5	C_2P, C_1P	Petrogenic

* N = Naphthalene; P = Phenanthrene; Py = Pyrene; C_1, C_2, C_3 = homolog number.

Sediments showed the best correlations of the three groups of samples analyzed. Generally there was good agreement between the total PAHs measured by GC and the PAHs measured by GC-MS. Figure 13 is a scattergram of this data including the regression line. The correlation coefficient (r) of this data is 0.87. This indicates that where high concentrations of total aromatics were found by GC high concentrations of the selected PAHs were also found by GC-MS. This is a good indication that the aromatic fractions are derived from petrogenic or pyrogenic sources. Sample 240 (0-5) appears to be anomalous. The GC-MS analysis of this sample indicated values much lower than those obtained by GC. This would indicate that most of the compounds in this sample are not PAHs.

In general, the correlation between the GC data and the GC-MS data was good for total aromatics. The correlations for individual compounds was poor. This poor correlation maybe explained by the misidentification by GC of the selected compounds, naphthalene, dibenzothiophene, phenanthrene, 1-methylphenanthrene and pyrene. GC-MS is generally considered to be a more selective detector for these compounds. The peaks identified by GC were either compounds that co-eluted or had very similar retention times. These compounds are believed to be complex pigments.

4.5. Hydrocarbon analysis and Distribution

Hydrocarbons in the marine environment are derived from three major sources. These are biogenic, naturally occurring hydrocarbons produced by terrestrial and marine organisms; pyrogenic, hydrocarbons generated by forest fires and industrial combustion; and petrogenic, hydrocarbons caused by petroleum contamination. These groups exhibit characteristic patterns which make their identification possible. Although when in combination these characteristics are diluted and positive quantification becomes much more difficult.

A great deal of work has been devoted to the development of the criteria for identification and separation of biogenic and petrogenic hydrocarbons. One of the most widely used and accepted is to separate the total extractable hydrocarbons into aliphatic (non-cyclic) and aromatic (unsaturated) fractions. The methodology for this was discussed previously. These fractions are then analyzed by GC-FID in conjunction with packed and/or capillary columns. The use of GC- MS for the quantification of the aromatic/olefinic fraction is of use in further establishing the sources of the hydrocarbons.

Although both fractions are useful for the identification of petroleum hydrocarbons the aliphatic has historically been used to a greater extent. The indices developed for this fraction are numerous. Table 12 lists those characteristics used by this project for the interpretation of the aliphatic chromatograms. These indices become somewhat ambiguous when the sample contains both hydrocarbons of biogenic and petrogenic origin. These mixtures obviously distort many of the indices.

The most reliable indicators found during this project were the Unresolved Complex Mixture (UCM) and the HCC/TOM ratio. Biogenic hydrocarbons in most sediments are few in number and simple in structure, whereas for petroleum the opposite is true. Petroleum compounds contain thousands of components, the majority of which are not easily resolved by capillary column gas chromatography. These unresolved compounds, when injected into a gas chromatograph, exhibit an inverted saucer effect. This has been accepted by many as a vital characteristic for the interpretation of gas chromatograms (NAS, 1975; Zafiriou, 1973; Zafiriou *et al.*, 1972; Farrington and Medeiros, 1975). The other index that proved very useful was the HCC/TOM ratio. This ratio is the total hydrocarbons as carbon divided by the organic content of the sample. The ratio was developed by Matsumoto (1982) for waters and modified by Baddour

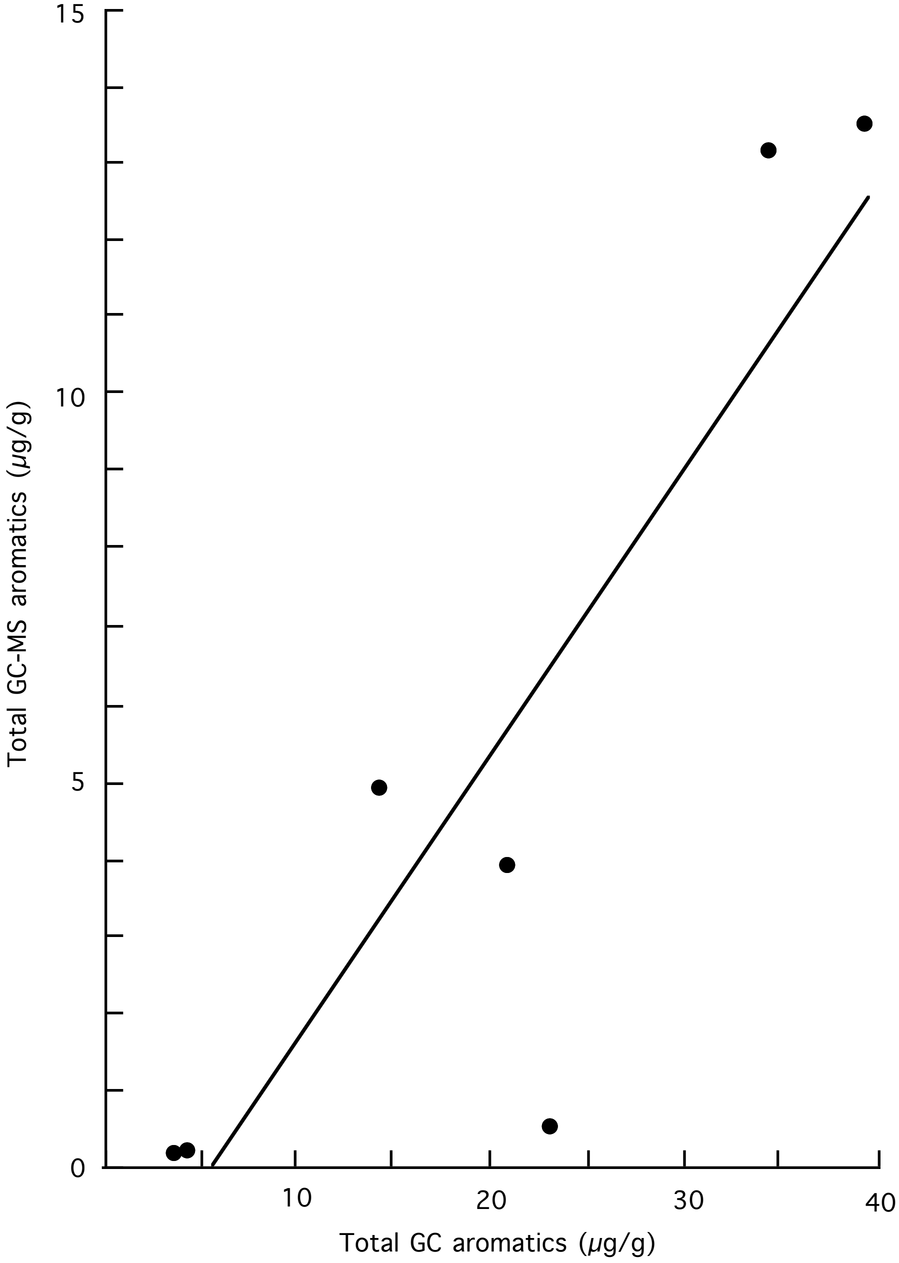

Figure 13. Scattergram of total PAHs (f2) measured by GC vs. PAHs measured by GC-MS.

Table 12. Criteria for distinguishing petrogenic from biogenic hydrocarbons.

CRITERION	PETROGENIC	BIOGENIC
1) Homologous Series	Wide boiling range (C_1 to C_{60}) Several series	Narrow boiling range (C_{15} to C_{35}) Few series (2 or 3)
2) Odd-carbon predominance	Absent (CPI $\simeq$ 1)	Usually present over a narrow range (C_{15}, C_{17} and/or C_{19} often prominent)
3) Unresolved Complex Mixture (UCM)	Present, often dominant	Absent or barely detectable
4) Isoprenoid distribution	Appreciable pristane (C_{19}), phytane (C_{20}), C_{16}, C_{18}	Pristane often abundant, no others detected
5) Pristane/Phytane ratio	1.5 to 2.5	100 or greater
6) Resolved/Unresolved Complex Mixture (Res/UCM)	1 but not zero	Infinite
7) Total hydrocarbon as carbon/total organic matter (HCC/TOM)	Larger ratio	Smaller ratio

(1983) and used for sediments. The original ratio HCC/TOC compared the total hydrocarbon as carbon (total hydrocarbon content x 0.851, as $C_{20}H_{42}$) to the total organic carbon content of the sample. Matsumoto (1982) states that usually hydrocarbons are minor constituents in living organisms, thus material contaminated with artificial hydrocarbons (e.g. petroleum products) would have a much higher ratio than those containing only natural hydrocarbons. Baddour modified the ratio by substituting total organic matter for total organic carbon. His results show that this ratio was quite reliable for the study of fuel spills around the Miami International Airport.

Tables 13 and 14 present a summary of the aliphatic and aromatic hydrocarbon content of the surface sediments collected during the first year of the project. The hydrocarbon concentrations presented in these tables have been corrected for percent recovery. Although only 22 percent of the samples analyzed during the first year contained internal standards for calculation of percent recovery, a mean value of 28.3 percent with a standard deviation of 8.60 was obtained from these data and used to correct all analyses. A more detailed listing of each sample analysis is given in Appendices D and E.

Table 13. Aliphatic hydrocarbon characterization of surface sediments collected during Year 01. All values are corrected for percent recovery and are expressed on a dry weight basis.

		RATIOS					KEY HYDROCARBONS (μg/g)				n-ALKANES	
Laboratory	Total* f_1 (μg/g)	f_1/ f_2	Resol. Unres	Prist./ Phyt.	C_{17}/ Prist.	C_{18}/ Phyt.	1500	1700	2085	2900	Homol. Ser.	CPI
1	0.77	MD	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2	2.41	0.5	ND	ND	0.22	ND	0.16	0.01	1.18	ND	C_{15}-C_{25}	ND
5	1.67	0.2	ND	2.97	0.07	0.57	0.04	0.02	0.06	ND	C_{15}-C_{25}	2.33
6	22.53	1.0	0.37	0.51	2.33	2.43	0.08	0.20	1.23	ND	C_{15}-C_{25}	1.58
7	33.23	6.1	0.45	0.67	0.21	0.51	0.34	0.01	0.13	ND	C_{12}-C_{25}	1.74
8	1.77	0.1	ND	0.94	0.33	0.57	ND	0.01	0.94	ND	C_{17}-C_{25}	9.98
9	0.05	0.1	ND	ND	ND	ND	ND	ND	0.05	ND	ND	ND
10	1.76	0.5	ND	ND	ND	ND	ND	ND	0.11	ND	C15-C_{26}	1.57
11	46.11	12.6	ND	73.39	ND	0.94	ND	ND	3.84	ND	C_{16}-C_{25}	2.57
12	71.99	23.9	0.36	6.28	1.06	3.42	ND	0.05	1.21	3.97	C_{17}-C_{29}	18.33
13	74.84	23.2	0.04	ND	ND	0.70	0.08	0.40	ND	ND	C_{14}-C_{23}	ND
14	1.33	0.3	ND	ND	ND	ND	ND	ND	0.14	ND	ND	ND
15	1.83	0.4	ND	ND	0.55	ND	0.15	0.04	0.02	ND	C_{15}-C_{25}	3.61
16	0.59	0.3	ND	ND	ND	ND	ND	0.26	ND	ND	ND	5.13
17	1.20	0.1	ND	ND	ND	ND	ND	ND	0.02	ND	C_{19}-C_{25}	1.68
18	0.09	0.9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
19	12.80	58.9	ND	3.02	0.02	3.90	0.14	0.01	1.19	ND	C_{15}-C_{25}	0.99
20	6.35	2.4	ND	ND	ND	ND	ND	ND	0.56	ND	C_{21}-C_{28}	12.06
21	67.00	34.6	0.14	50.38	ND	0.81	0.06	ND	0.43	ND	C_{15}-C_{23}	3.33
22	8.74	2.4	0.01	ND	ND	ND	ND	ND	ND	ND	ND	ND
23	70.22	8.8	0.02	2.68	ND	0.04	0.11	ND	ND	ND	C_{15}-C_{23}	2.82
24	47.96	1.3	0.16	1.29	18.55	1.42	0.03	0.69	0.15	ND	C_{15}-C_{23}	8.50
25	33.37	0.2	0.09	5.48	ND	1.12	0.03	ND	0.32	ND	C_{14}-C_{25}	2.27
26	23.22	6.1	0.09	5.49	ND	1.12	0.03	ND	0.22	ND	C_{12}-C_{23}	2.28
27	1.06	1.8	ND	5.54	ND	1.30	ND	ND	0.14	ND	C_{18}-C_{22}	2.16
28	0.12	0.2	ND	ND	ND	ND	ND	ND	0.01	ND	C_{21}-C_{23}	1.84
29	6.11	2.4	ND	0.21	3.22	2.35	ND	0.04	0.30	ND	C_{17}-C_{26}	1.25
30	0.03	4.6	ND	ND	ND	ND	ND	0.03	ND	ND	ND	ND
31	15.36	1.0	ND	ND	ND	ND	ND	0.03	0.06	ND	C_{12}-C_{25}	0.76
32	102.45	21.3	0.50	1.73	0.32	1.35	0.07	0.03	0.25	12.21	C_{12}-C_{29}	4.30
33	10.88	1.1	ND	ND	ND	0.19	ND	0.89	2.30	ND	C_{16}-C_{26}	4.96
34	31.60	21.3	0.02	ND	ND	1.84	ND	ND	0.17	ND	C_{18}-C_{23}	2.46
35	0.42	0.2	ND	7.21	ND	ND	ND	ND	ND	ND	ND	ND
36	11.24	2.5	0.03	ND	ND	ND	ND	ND	0.08	ND	ND	ND
38	2.83	2.2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
40	0.29	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 13. Aliphatic hydrocarbon characterization of surface sediments collected during Year 01. All values are corrected for percent recovery and are expressed on a dry weight basis. (cont.)

Laboratory	Total* f_1 (μg/g)	RATIOS f_1/ f_2	Resol. Unres	Prist./ Phyt.	C_{17}/ Prist.	C_{18}/ Phyt.	KEY HYDROCARBONS (μg/g) 1500	1700	2085	2900	n-ALKANES Homol. Ser.	CPI
41	17.01	6.1	0.04	ND	ND	ND	ND	ND	ND	ND	ND	ND
42	4.49	9.1	ND	ND	ND	ND	0.19	0.49	0.74	ND	C_{12}-C_{25}	13.30
43	15.55	2.4	ND	8.25	0.41	ND	ND	0.08	0.07	ND	C_{14}-C_{26}	0.13
44	2.01	0.8	ND	ND	ND	ND	ND	ND	0.04	ND	C_{21}-C_{23}	15.36
45	33.13	7.4	0.11	0.34	5.47	0.26	0.01	0.08	0.16	ND	C_{12}-C_{25}	1.87
46	4.51	4.0	ND	0.60	0.16	ND	ND	0.02	0.09	ND	C_{14}-C_{21}	0.77
47	58.92	52.8	0.06	0.97	0.18	ND	ND	0.01	ND	ND	C_{17}-C_{22}	0.01
48	29.44	2.3	0.04	0.55	0.88	ND	ND	0.01	0.08	ND	C_{17}-C_{22}	1.48
49	24.13	4.7	ND	0.60	ND	ND	ND	ND	0.05	ND	C_{19}-C_{26}	1.92
51	53.46	2.7	0.08	16.60	ND	ND	0.12	ND	0.21	ND	C_{12}-C_{24}	2.21
52	14.74	3.8	0.08	ND	ND	ND	ND	ND	0.08	ND	C_{21}-C_{23}	3.64
53	7.38	2.9	1.24	ND	6.53	ND	ND	0.07	0.41	ND	C_{17}-C_{23}	12.77
54	1.34	0.2	ND	2.74	1.27	2.75	ND	0.04	0.08	ND	C_{17}-C_{23}	1.82
55	0.25	1.1	ND	ND	ND	ND	ND	ND	0.13	ND	ND	ND
56	280.82	0.6	0.04	0.01	153.98	0.43	0.10	1.44	0.05	ND	C_{13}-C_{24}	2.68
57	669.96	7.9	0.03	0.06	5.93	0.54	0.02	0.27	0.19	ND	C_{12}-C_{24}	1.07
58	187.43	0.4	0.04	6.33	0.14	0.51	0.14	0.07	ND	ND	C_{14}-C_{21}	1.58
59	913.55	8.1	0.04	1.47	0.13	0.66	0.27	0.17	2.82	ND	C_{15}-C_{24}	1.77
60	1028.79	2.4	0.03	1.92	0.08	0.83	1.11	0.10	0.47	ND	C_{12}-C_{22}	1.74
61	2449.60	11.4	0.02	9.93	ND	ND	0.22	ND	ND	ND	ND	0.21
62	185.54	3.4	0.01	ND	ND	ND	0.03	ND	ND	ND	ND	2.36
63	0.39	0.2	ND	ND	ND	ND	ND	ND	0.08	ND	ND	ND
64	76.98	63.3	ND	0.18	1.46	ND	0.09	0.01	0.10	ND	C_{15}-C_{27}	7.12
65	0.52	3.9	ND	0.22	0.93	ND	ND	0.01	0.06	ND	C_{17}-C_{21}	ND
66	89.18	5.3	0.13	ND	ND	ND	0.25	ND	0.75	ND	C_{15}-C_{25}	2.60
67	0.65	1.2	ND	1.04	ND	0.57	0.06	ND	ND	ND	C_{15}-C_{20}	1.39
68	19.64	5.7	0.52	2.09	0.97	3.41	0.21	0.12	0.55	ND	C_{15}-C_{25}	1.79
69	13.47	2.1	0.04	ND	ND	ND	0.01	ND	0.08	ND	C_{15}-C_{23}	2.93
70	2.12	4.5	ND	0.97	0.18	0.18	0.14	0.02	0.04	ND	C_{12}-C_{23}	1.39
71	5.21	MD	ND	ND	ND	ND	0.24	0.03	ND	ND	C_{12}-C_{22}	1.76
72	100.98	13.2	ND	ND	0.27	ND	ND	0.04	0.10	ND	C_{17}-C_{28}	5.49
73	0.33	0.5	ND	ND	2.43	ND	0.03	0.07	0.02	ND	C_{15}-C_{24}	5.23
74	1.08	1.2	ND	ND	ND	ND	ND	ND	0.08	ND	ND	ND
75	333.86	4.5	0.01	38.40	ND	ND	0.30	ND	ND	ND	ND	6.79
76	4.69	9.6	ND	ND	ND	ND	0.18	ND	0.27	ND	C_{15}-C_{27}	ND
77	74.70	0.1	0.09	0.57	1.22	0.85	0.10	0.39	0.10	0.39	C_{12}-C_{29}	4.84
78	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
79	2.27	1.2	ND	ND	0.53	ND	0.04	0.24	0.09	ND	C_{15}-C_{21}	1.72
80	149.67	25.0	0.25	ND	ND	0.83	ND	0.22	0.53	ND	C_{17}-C_{28}	3.57

Table 13. Aliphatic hydrocarbon characterization of surface sediments collected during Year 01. All values are corrected for percent recovery and are expressed on a dry weight basis. (cont.)

	Total*	RATIOS					KEY HYDROCARBONS (µg/g)				n-ALKANES	
Laboratory	f_1 (µg/g)	f_1/ f_2	Resol. Unres	Prist./ Phyt.	C_{17}/ Prist.	C_{18}/ Phyt.	1500	1700	2085	2900	Homol. Ser.	CPI
81	7.01	3.4	ND	ND	ND	ND	ND	ND	0.12	ND	C_{21}-C_{25}	3.18
82	52.17	3.4	ND	ND	ND	ND	0.19	ND	0.56	11.19	C_{15}-C_{29}	7.12
83	5.03	2.1	ND	1.31	ND	0.95	ND	ND	0.16	ND	C_{12}-C_{25}	1.30
84	103.30	22.4	0.20	2.64	ND	ND	0.60	ND	1.18	ND	C_{12}-C_{24}	1.93
86	4.45	3.8	ND	0.35	1.40	1.86	0.22	0.01	0.37	ND	C_{12}-C_{25}	1.61
87	175.16	162.0	0.07	3.81	ND	0.61	ND	ND	ND	ND	C_{18}-C_{26}	2.16
88	0.76	0.1	ND	ND	ND	ND	ND	ND	0.04	ND	ND	0.62
89	0.22	1.7	ND	ND	ND	ND	0.05	0.00	0.01	ND	C_{12}-C_{22}	1.64
90	3.52	1.2	ND	34.12	ND	1.66	0.11	ND	0.48	ND	C_{12}-C_{25}	4.03
92	1.47	9.2	ND	ND	ND	ND	ND	ND	0.37	ND	C_{21}-C_{23}	2.91
93	14.68	3.2	ND	ND	1.56	ND	0.57	0.40	0.03	ND	C_{12}-C_{26}	1.33
94	1.55	0.8	ND	ND	ND	ND	ND	0.01	ND	ND	C_{12}-C_{20}	1.05
95	5.82	0.4	ND	ND	1.28	ND	0.17	0.13	0.18	ND	C_{12}-C_{21}	1.50
96	55.11	1.9	0.15	0.54	ND	1.61	0.34	ND	0.47	ND	C_{12}-C_{25}	1.54
97	5.18	0.2	ND	ND	ND	ND	0.16	ND	0.21	ND	C_{12}-C_{21}	4.23
99	13.03	592.8	ND	ND	ND	ND	0.11	ND	ND	ND	C_{12}-C_{21}	ND
100	5.82	0.2	ND	ND	11.82	ND	0.07	1.33	0.73	ND	C_{14}-C_{25}	7.39
101	204.53	19.0	0.12	0.14	88.40	1.07	0.04	3.59	0.40	ND	C_{12}-C_{27}	3.28
102	98.30	18.5	0.22	54.43	ND	0.53	ND	ND	0.32	ND	C_{12}-C_{25}	2.90
103	777.12	121.9	0.10	3.38	2.57	0.12	0.34	6.40	1.41	ND	C_{15}-C_{25}	9.79
104	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
105	50.50	18.4	ND	75.69	ND	0.60	0.07	ND	0.25	ND	C_{12}-C_{28}	1.64
106	1.07	0.2	ND	ND	0.15	ND	0.08	0.01	0.01	ND	C_{12}-C_{24}	0.93
107	6.38	6.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
108	2.96	0.1	ND	ND	ND	ND	ND	ND	ND	1.47	C_{19}-C_{24}	ND
109	8.03	2.6	ND	13.60	0.12	5.64	0.06	0.13	0.11	ND	C_{12}-C_{25}	0.86
110	5.01	0.4	ND	ND	ND	ND	ND	2.38	0.58	ND	ND	ND
111	4.45	23.3	ND	ND	0.09	ND	0.25	0.04	0.58	ND	C_{15}-C_{21}	ND
112	4.57	3.0	ND	ND	1.16	ND	ND	0.76	0.22	ND	C_{12}-C_{23}	5.73
113	1.71	0.3	ND	ND	ND	ND	ND	0.11	0.18	ND	C_{17}-C_{25}	12.10
114	0.75	0.2	ND	ND	1.72	ND	0.07	0.08	ND	ND	C_{15}-C_{19}	1.95
115	2.63	2.8	ND	ND	ND	ND	ND	ND	0.21	ND	ND	0.41
116	4.34	0.7	ND	ND	ND	ND	0.20	ND	ND	ND	C_{12}-C_{22}	0.62
117	2.58	0.4	ND	ND	ND	ND	ND	ND	0.02	ND	ND	0.42
118	37.86	MD	ND	5.31	ND	ND	ND	ND	0.40	ND	C_{19}-C_{23}	2.47
119	4.36	2.5	ND	2.15	23.09	ND	ND	0.70	1.48	ND	C_{17}-C_{23}	29.32
120	19.29	1.9	ND	ND	ND	1.76	0.04	7.25	0.86	ND	C_{13}-C_{25}	8.44

Table 13. Aliphatic hydrocarbon characterization of surface sediments collected during Year 01. All values are corrected for percent recovery and are expressed on a dry weight basis. (cont.)

		RATIOS					KEY HYDROCARBONS (μg/g)				n- ALKANES	
Laboratory	Total* f_1 (μg/g)	f_1/ f_2	Resol. Unres	Prist./ Phyt.	C_{17}/ Prist.	C_{18}/ Phyt.	1500	1700	2085	2900	Homol. Ser.	CPI
121	52.00	11.4	ND	274.03	ND	3.29	0.54	ND	0.15	13.06	C_{12}-C_{29}	2.42
122	62.94	MD	ND	12.95	0.02	ND	0.02	0.02	0.37	22.19	C_{12}-C_{29}	3.92
123	0.73	0.1	ND	ND	ND	ND	0.06	0.05	0.02	ND	C_{15}-C_{24}	1.31
124	12.61	1.5	ND	ND	3.95	ND	ND	0.70	0.03	ND	C_{17}- C_{27}	0.76
125	49.57	21.4	0.22	0.17	15.49	1.71	0.10	0.38	0.04	ND	C_{12}-C_{26}	0.90
126	0.92	0.3	ND	ND	ND	ND	ND	ND	0.39	ND	ND	ND
127	1.16	0.2	ND	11.73	ND	2.26	0.09	ND	0.10	ND	C_{15}-C_{23}	2.46
128	34.90	260.6	0.34	ND	ND	2.15	0.03	2.67	1.32	ND	C_{15}-C_{25}	13.02
129	0.01	0.1	ND	ND	ND	ND	ND	ND	0.01	ND	ND	ND
130	0.23	1.2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
132	4.66	0.2	ND	0.97	9.43	0.57	ND	0.77	0.45	1.42	C_{12}-C_{29}	4.24
134	43.16	2.5	0.30	ND	ND	ND	0.13	4.44	0.96	ND	C_{12}-C_{25}	3.40
135	237.45	35.4	0.03	0.85	18.80	1.39	ND	0.96	0.70	ND	C_{17}-C_{25}	9.92
136	484.47	31.3	0.03	ND	ND	1.95	0.47	ND	0.66	ND	C_{12}-C_{25}	2.64
137	28.79	5.4	0.01	ND	ND	ND	ND	ND	0.08	ND	ND	2.21
138	24.50	ND	0.11	0.44	3.70	3.16	0.11	0.04	0.20	ND	C_{15}-C_{25}	1.59
139	21.26	12.5	0.02	ND	ND	ND	0.03	ND	0.07	ND	C_{15}-C_{24}	2.79
140	27.90	1.4	0.04	ND	ND	ND	ND	ND	0.31	ND	C_{18}-C_{23}	5.01
142	308.74	54.4	0.04	ND	ND	ND	0.40	0.44	2.53	ND	C_{15}-C_{23}	ND
143	1.09	0.3	ND	ND	3.01	ND	TD	0.01	0.03	ND	C_{12}-C_{23}	0.97
144	73.07	15.6	0.03	1.03	0.31	7.97	ND	0.01	0.85	ND	C_{17}-C_{23}	10.73
145	2.01	0.2	ND	ND	5.43	ND	0.16	0.15	0.63	ND	C_{12}-C_{23}	4.42
146	4.29	ND	ND	ND	ND	ND	ND	ND	0.23	ND	C_{21}-C_{26}	0.57
147	216.69	43.3	0.08	ND	ND	ND	ND	ND	6.70	ND	C_{18}-C_{25}	8.23
148	86.58	0.3	0.05	8.28	ND	0.38	0.02	ND	0.29	ND	C_{15}-C_{27}	1.79
149	188.41	92.0	0.14	6.50	ND	1.16	0.26	ND	7.10	ND	C_{12}-C_{26}	9.07
150	1.81	1.6	ND	ND	ND	ND	N	ND	0.69	ND	C_{18}-C_{22}	5.53
151	23.84	6.0	ND	ND	ND	ND	0.01	0.05	1.04	ND	C_{12}-C_{23}	1.36
152	81.21	102.3	0.08	ND	ND	ND	0.10	0.05	0.51	ND	C_{15}-C_{25}	1.36
153	42.84	8.6	0.13	ND	ND	10.01	0.13	ND	0.40	ND	C_{14}-C_{22}	1.15
154	0.65	1.3	ND	ND	ND	ND	ND	0.19	0.17	ND	C_{17}-C_{21}	12.91
155	86.19	MD	0.19	0.76	3.35	2.10	0.13	0.38	0.87	ND	C_{12}-C_{24}	1.20

MD - Missing Data
ND - None Detected.
TD - Trace Detected

Table 14. Aromatic hydrocarbon characterization of surface sediments collected during Year 01. Values are corrected for percent recovery and are expressed on a dry weight basis.

Sample	Total f_2	Napththalene	Phenanthrene	Dibenzothiophene	Pyrene
1	MD				
2	4.48	ND	0.03	0.17	0.27
5	8.92	ND	0.82	0.30	0.17
6	23.65	ND	0.02	0.09	0.06
7	5.42	ND	0.19	0.11	0.28
8	13.15	ND	TD	0.17	0.04
9	2.45	ND	0.09	0.02	0.07
10	3.79	TD	0.04	0.13	0.07
11	3.67	ND	0.13	0.20	0.17
12	3.01	ND	0.11	0.19	0.01
13	3.21	ND	0.56	0.14	0.25
14	5.04	ND	0.10	0.23	0.63
15	4.10	ND	0.38	0.29	0.09
16	1.78	ND	ND	ND	0.36
17	24.94	0.07	1.00	0.18	6.30
18	5.62	0.06	1.21	0.07	0.01
19	14.29	ND	0.13	0.09	0.07
20	0.99	ND	ND	0.05	ND
21	1.12	ND	ND	ND	TD
22	3.58	ND	0.36	0.04	0.06
23	2.03	ND	0.40	0.10	0.10
24	MD				
25	MD				
26	3.81	ND	0.38	0.05	0.59
27	0.84	ND	ND	ND	0.10
28	0.71	ND	ND	ND	ND
29	3.37	ND	0.33	0.06	0.76
30	0.67	ND	0.05	ND	ND
31	6.28	ND	0.04	0.03	0.56
32	22.06	ND	0.02	0.46	0.73
33	10.46	0.14	0.05	0.32	0.78
34	1.48	ND	0.08	0.10	0.11
35	2.40	ND	0.24	0.18	0.37
36	4.51	0.26	0.08	ND	0.86
38	1.31	ND	0.03	0.06	0.23
40	22.98	0.08	0.12	2.05	ND
41	2.77	ND	0.02	0.40	0.03
42	0.49	0.06	ND	ND	0.09
43	6.78	ND	0.08	0.05	0.28
44	2.44	ND	ND	ND	0.86
45	4.48	ND	ND	ND	1.47
46	1.71	ND	0.18	ND	0.14
47	1.12	ND	0.04	0.07	0.10
48	12.90	ND	0.07	ND	0.20
49	5.15	ND	0.62	ND	0.36

Table 14. Aromatic hydrocarbon characterization of surface sediments collected during Year 01. Values are corrected for percent recovery and are expressed on a dry weight basis. (cont).

Sample	Total f_2	Napththalene	Phenanthrene	Dibenzothiophene	Pyrene
51	19.72	ND	3.13	0.86	5.82
52	3.88	0.03	0.70	1.20	2.00
53	2.54	ND	0.73	0.23	0.08
54	5.67	ND	0.51	1.21	1.69
55	2.32	ND	0.02	0.02	0.80
56	459.15	ND	0.08	0.63	12.20
57	84.43	ND	0.14	0.35	3.15
58	420.84	ND	2.82	0.60	12.35
59	112.62	ND	0.26	0.63	ND
60	446.80	ND	1.26	4.51	33.73
61	213.85	ND	11.70	6.11	3.22
62	54.46	ND	0.14	1.34	7.32
63	20.87	ND	0.07	TD	0.83
64	1.22	ND	0.04	ND	0.44
65	0.13	ND	ND	ND	ND
66	16.88	ND	0.18	0.56	5.73
67	0.57	ND	ND	0.03	0.15
68	3.44	ND	ND	ND	0.16
69	6.40	ND	0.11	0.33	2.29
70	0.46	ND	ND	ND	ND
71	MD				
72	7.65	ND	0.28	ND	0.22
73	0.72	ND	ND	ND	ND
74	0.87	ND	0.15	ND	ND
75	43.54	ND	0.04	0.04	1.01
76	0.49	ND	ND	ND	ND
77	10.06	0.03	0.65	0.06	3.73
78	9.49	ND	0.09	0.01	0.33
79	1.91	ND	0.18	ND	0.71
80	5.97	ND	0.04	ND	0.23
81	12.05	ND	0.05	0.12	2.90
82	15.20	0.10	0.18	0.73	4.42
83	2.40	ND	ND	0.17	0.27
84	4.60	ND	TD	0.44	0.60
86	1.16	ND	ND	ND	ND
87	1.08	ND	0.06	ND	0.19
88	17.47	ND	TD	0.51	0.79
89	0.13	ND	ND	ND	ND
90	2.85	ND	0.01	ND	0.33
92	0.16	ND	ND	ND	ND
93	4.63	ND	0.03	0.17	0.46
94	1.85	ND	ND	0.02	0.21
95	13.14	ND	3.94	1.03	1.53
96	28.91	1.52	0.11	0.67	1.86
97	8.75	ND	0.10	0.02	0.27

Table 14. Aromatic hydrocarbon characterization of surface sediments collected during Year 01. Values are corrected for percent recovery and are expressed on a dry weight basis. (cont).

Sample	Total f_2	Napththalene	Phenanthrene	Dibenzothiophene	Pyrene
99	0.02	ND	ND	ND	ND
100	24.29	ND	0.30	2.73	1.54
101	10.78	0.04	0.05	0.10	0.41
102	5.31	ND	1.04	0.53	0.28
103	6.37	ND	0.23	0.10	0.17
104	9.77	ND	0.03	0.10	0.28
105	2.74	ND	ND	1.92	ND
106	4.99	ND	0.10	0.29	0.26
107	1.06	ND	ND	ND	ND
108	245.33	ND	0.20	ND	0.25
109	3.41	ND	0.23	ND	0.62
110	12.75	0.20	0.04	0.22	0.83
111	0.19	ND	ND	ND	ND
112	1.52	ND	0.04	0.14	0.13
113	5.63	ND	0.04	ND	0.10
114	4.26	ND	0.03	0.52	3.96
115	0.95	ND	ND	0.03	ND
116	6.47	ND	0.02	0.16	1.81
117	7.33	ND	0.13	ND	1.69
118	MD				
119	1.71	ND	0.09	1.01	ND
120	10.29	ND	0.28	0.61	ND
121	4.55	ND	0.08	0.24	0.62
122	MD				
123	6.36	ND	0.07	0.13	0.60
124	8.50	ND	0.13	0.36	1.19
125	2.32	ND	0.22	ND	0.46
126	2.67	ND	ND	ND	0.08
127	5.11	ND	0.03	0.41	0.48
128	0.13	ND	ND	ND	ND
129	0.23	ND	ND	ND	ND
130	0.20	ND	ND	ND	ND
132	18.93	ND	0.24	0.87	1.21
134	17.16	ND	0.06	0.22	0.26
135	6.70	0.08	0.17	0.18	1.04
136	15.48	0.33	0.21	0.21	0.89
137	5.34	ND	0.11	0.46	0.35
138	MD				
139	1.70	0.04	0.04	0.05	0.16
140	20.05	ND	0.10	0.22	1.93
142	5.68	ND	0.22	0.26	0.94
143	4.09	ND	0.02	0.73	0.16
144	4.64	ND	0.41	0.04	0.66
145	9.42	ND	1.51	0.18	2.81

Table 14. Aromatic hydrocarbon characterization of surface sediments collected during Year 01. Values are corrected for percent recovery and are expressed on a dry weight basis. (cont).

Sample	Total f_2	Napththalene	Phenanthrene	Dibenzothiophene	Pyrene
147	5.00	ND	0.07	0.08	1.21
148	242.85	0.29	7.68	47.92	22.91
149	2.05	ND	ND	ND	ND
150	1.15	ND	ND	ND	0.26
151	3.95	ND	ND	0.10	1.72
152	0.79	ND	ND	ND	ND
153	5.06	ND	0.04	0.03	0.05
154	0.50	ND	ND	ND	0.04
155	MD				

MD - Missing Data
TD - Trace Detected
ND - None Detected

Figures 14 and 15 show the distribution of aliphatic hydrocarbons and the aromatic hydrocarbons. Several of the other indices were mapped (CPI, C_{17}/pristane, C_{18}/phytane and the resolved/unresolved). The mapping of these indices were of minimal use, added little to the interpretation of the distribution of hydrocarbons, and because of the high costs of reproducing them, are not presented.

To supplement the contour maps several of the indices were used to separate those samples containing only biogenic material form samples with petroleum contamination. It was found that the most useful index for this was the HCC/TOM ratio in conjunction with the resolved/unresolved (identifiable peaks/UCM) ratio. The HCC/TOM ratios were ranked in ascending order and using the resolved /unresolved and other indices (CPI, Pristane/Phytane, etc.) were separated into two groups, those that showed indications of petrogenic hydrocarbons and those that did not. Table 15 lists those samples, as per their location and concentrations, containing petroleum contamination.

The data collected from these stations was then compared for correlations using several regression equations. These included linear, exponential, logarithmic and power law. Total, aliphatic and aromatic hydrocarbons were compared to the three sediment grain sizes, organic and carbonate content, water salinity and temperature. This exercise showed no strong correlation between concentration of hydrocarbons and any of the other parameters. The strongest correlation existed between salinity and total hydrocarbons (correlation coefficient -0.54). Figure 16 presents a scattergram of the data and the regression line. Obviously salinity has no effect on the distribution of hydrocarbons. This relationship is a function of location to freshwater input.

Figures 14 and 15, and Table 15 indicate in general that many of the samples which contained petroleum contamination were associated with canals which receive runoff from large urbanized areas. This is further supported by the inverse relationship of salinity (freshwater input) to hydrocarbon content (the lower the salinity the higher the hydrocarbon concentration) shown in Figure 16.

The highest concentrations of hydrocarbons were found in the sediments of the Miami River. The highest concentration of aliphatics (2449.60 μg/g) was found at station 61, while the highest aromatic concentrations (459.15 μg/g) were at station 56, near the railroad bridge located at the most westerly point sampled.

Organisms were collected from several areas of the Bay and analyzed for petroleum contamination. Table 16 and 17 lists these results. There were no strong indication of contamination in any of the samples. Although this maybe an artifact of the small sample size extracted.

The main purpose of the second year of the study was to investigate areas where analyses indicated the presence of petroleum contamination. Four primary and one secondary study areas were chosen. The primary areas were: 1) the Little River; 2) the Miami River; 3) Black Creek-Goulds Canal area; 4) Military Canal. The secondary area was Snapper Creek. These areas were sampled for additional sediments, surface water and biota if available.

The Little River and the Miami River are located in the northern part of the Bay. The Little River is characterized by a residential community near its mouth while its upper areas receive runoff from city streets. The area is best characterized by inputs from urban runoff and a minimal input from boat traffic. The projected changes within this area will probably be minimal over the next several years. The Miami River receives a great deal of boat and ship

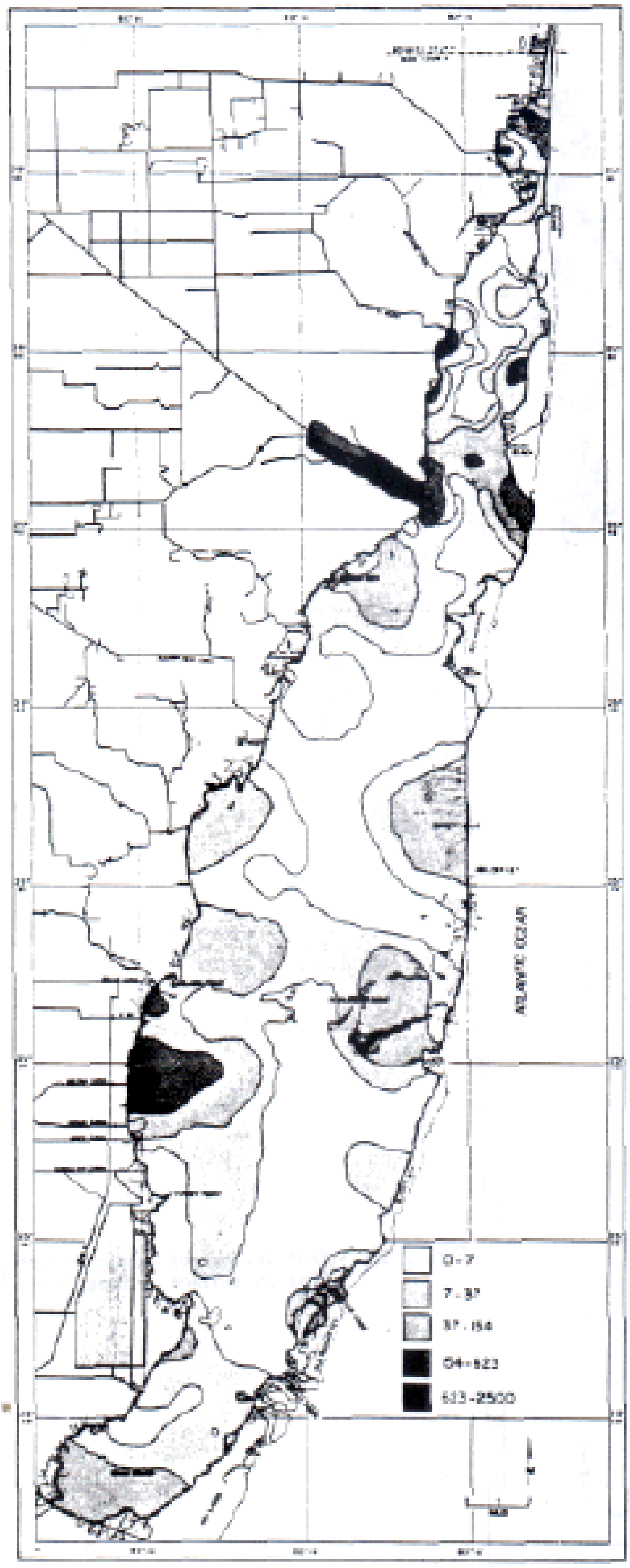

Figure 14a. Distribution of aliphatic hydrocarbons (f_1) in surface sediments of Biscayne Bay. [ORIGINAL]

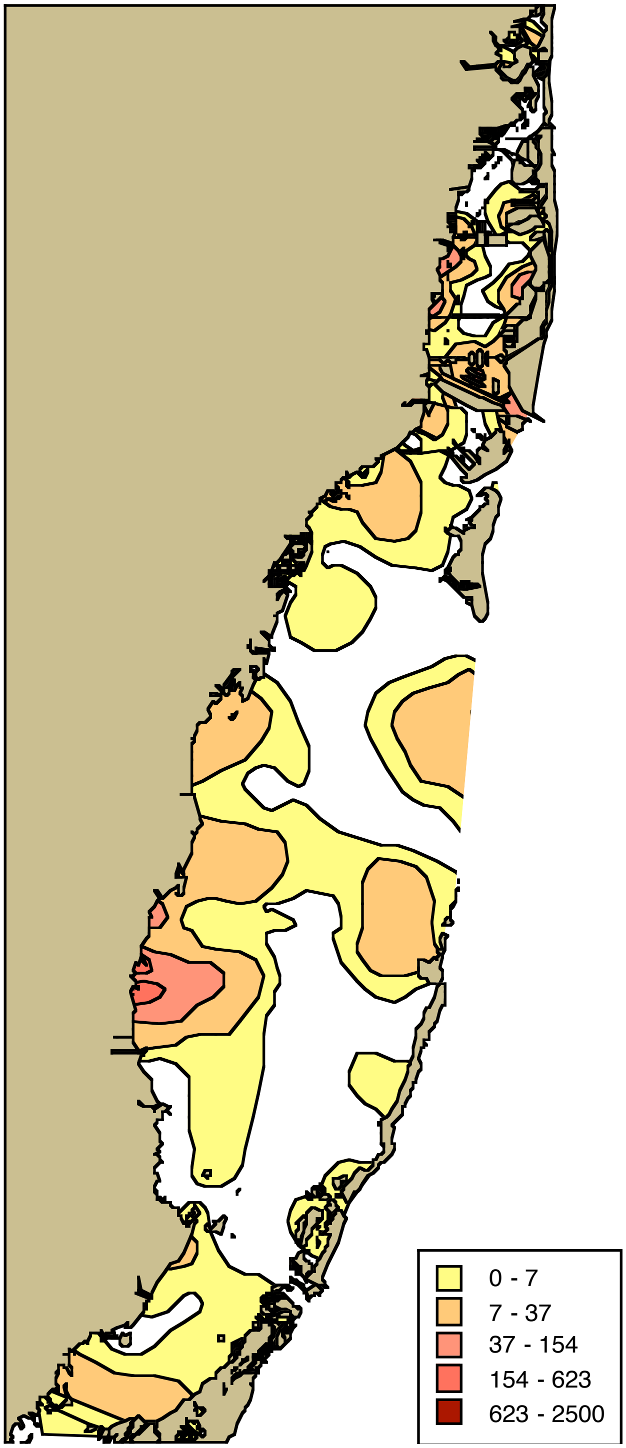

Figure 14b. Distribution of aliphatic hydrocarbons (f_1) in surface sediments of Biscayne Bay. [RECONSTRUCTION. HIGH VALUES UPSTREAM IN THE MIAMI RIVER ARE NOT SHOWN. LOCATION OF LAND MASSES RELATIVE TO HYDROCARBON DISTRIBUTIONS NOT CLEAR IN ORIGINAL.

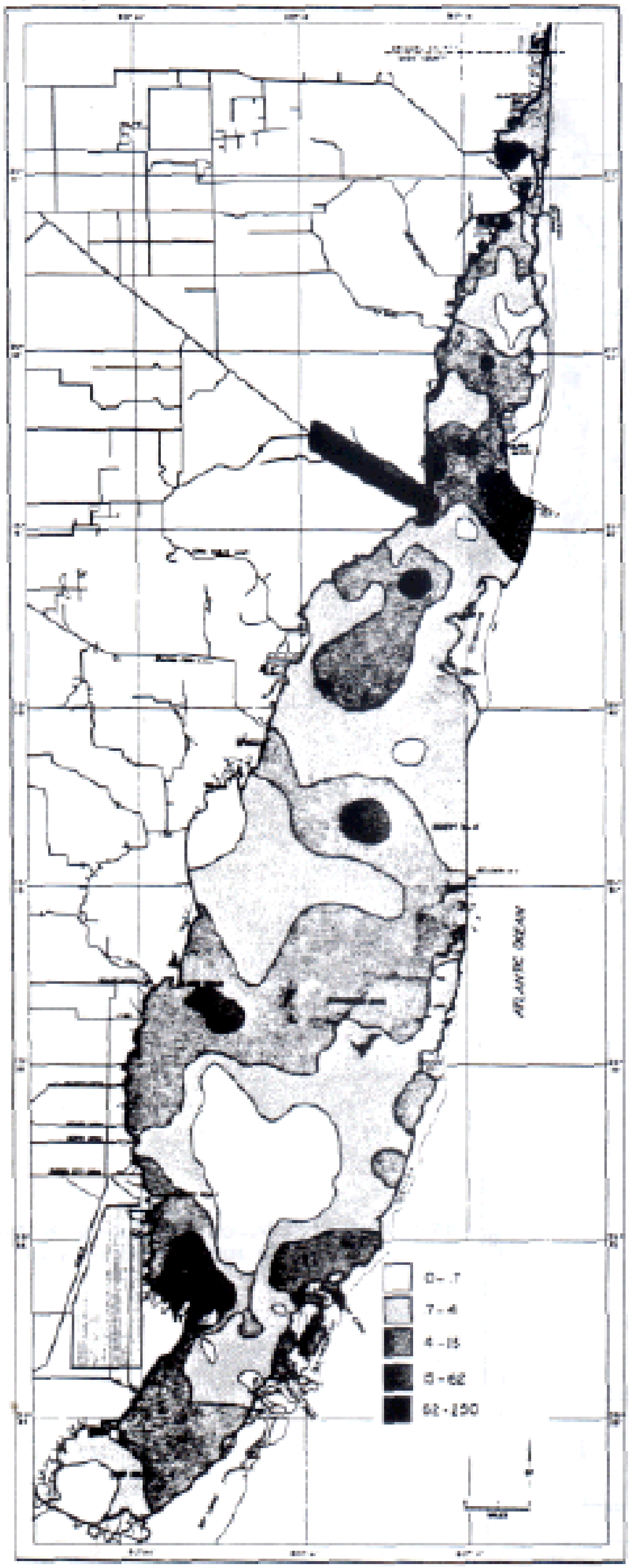

Figure 15a. Distribution of aromatic hydrocarbons (f_2) in surface sediments of Biscayne Bay. [ORIGINAL]

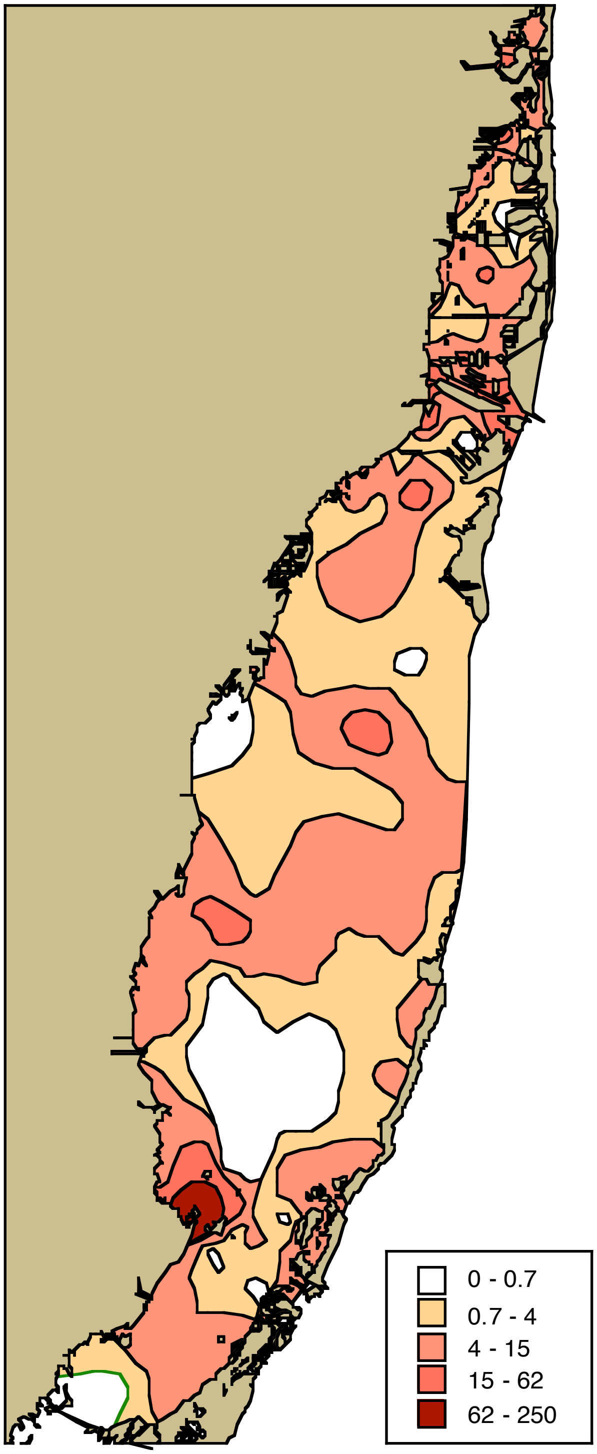

Figure 15b. Distribution of aromatic hydrocarbons (f_2) in surface sediments of Biscayne Bay. [RECONSTRUCTION. HIGH VALUES UPSTREAM IN THE MIAMI RIVER ARE NOT SHOWN. LOCATION OF LAND MASSES RELATIVE TO HYDROCARBON DISTRIBUTIONS NOT CLEAR IN ORIGINAL.]

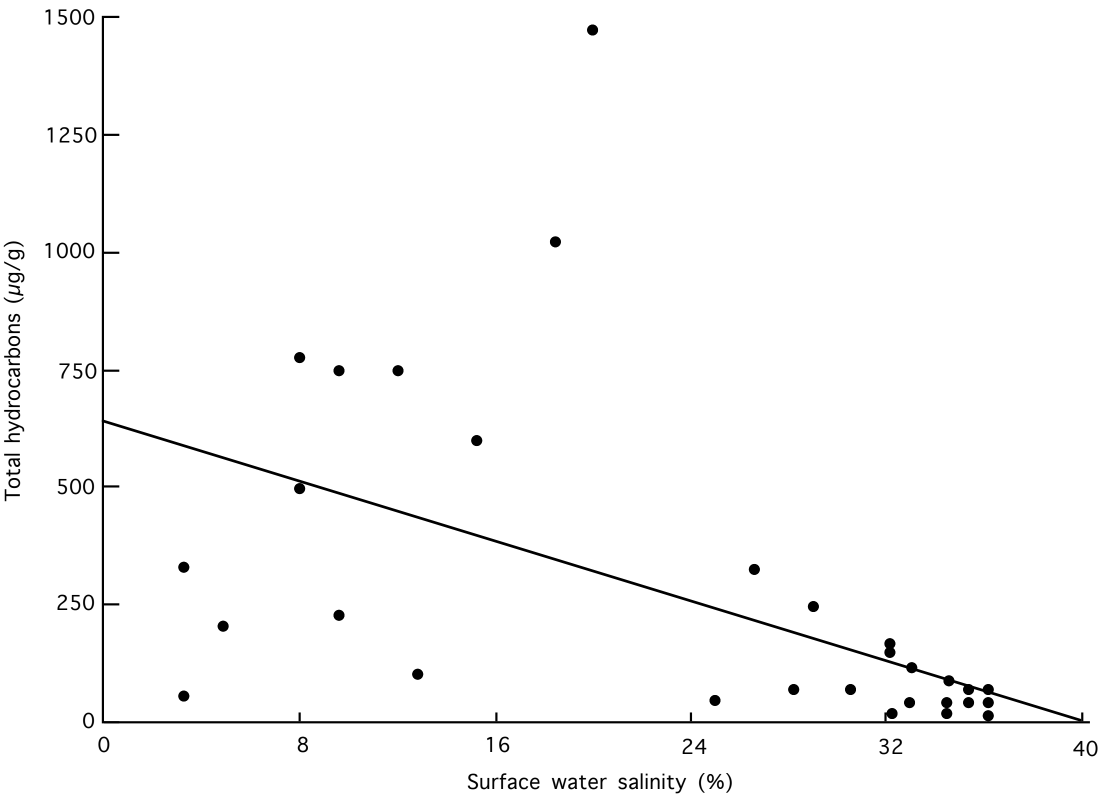

Figure 16. Scattergram of salinity vs. total hydrocarbons (aliphatic + aromatic).

Table 15. Surface sediment containing petroleum hydrocarbons collected during the first year of the study.

Sample	HCC/TOM	Resolved/ (x 10^{-2})	Total Hydrocarbons Unresolved	Location (μg/g)
Samples located north of Rickenbacker Causeway				
32	1.06	0.50	124.51	Between San Marino and Hibiscus Islands
34	0.28	0.02	33.08	Belle Isle
36	0.13	0.03	15.75	Westend Venetian Causeway
45	0.32	0.11	37.62	Spoil Island
47	0.51	0.06	60.04	Intracoastal Waterway
48	0.36	0.04	42.34	Spoil Area
49	0.24	ND	29.28	Intracoastal Waterway
51	0.62	0.08	73.18	Canal mouth
56	MD	0.04	739.97	Miami River
57	6.42	0.03	754.39	Miami River
58	5.18	0.04	608.27	Miami River
59	8.73	0.04	1026.17	Miami River
60	MD	0.03	1465.60	Miami River
61	22.67	0.02	2663.45	Miami River
62	2.04	0.01	240.00	Miami River
75	3.21	0.01	377.41	Loading area - Belcher Oil
77	0.72	0.09	84.76	Canal mouth
80	1.32	ND	155.64	West end of Julia Tuttle Causeway
135	2.08	0.03	244.15	Dredged hole
136	4.25	0.03	499.95	Little River
137	0.29	0.01	34.14	Little River
138	MD	0.11	MD	Normandy Waterway
142	2.67	0.04	314.42	Surprise Lake
144	0.66	0.03	77.71	Collins Canal
148	2.80	0.05	329.43	Junction of Royal Glades Canal and Oleta River
149	1.62	0.14	190.46	Maul Lake
153	0.41	0.13	47.90	Indian Creek
155	MD	0.19	MD	Biscayne Point

Table 15. Surface sediment containing petroleum hydrocarbons collected during the first year of the study (cont.).

Sample	HCC/TOM	Resolved/ (x 10^{-2})	Total Hydrocarbons Unresolved	Location (μg/g)
Samples Located South of Rickenbacker Causeway				
6	0.39	0.37	46.18	Intracoastal Waterway
7	0.33	0.45	38.65	Intracoastal Waterway
11	0.40	ND	47.78	East of Matheson Hammock
12	0.63	0.36	75.00	Safety Valve
13	0.67	0.04	78.06	Soldier Key
21	0.58	0.14	68.12	Northwest of Featherbed Bank - Black Ledge
22	0.10	0.01	12.32	North of Featherbed Bank - Black Ledge
23	0.61	0.02	72.25	Intracoastal Waterway
24	MD	0.16	MD	Shoal Area
25	MD	0.09	MD	Rickenbacker Causeway
64	0.66	ND	78.20	Dinner Key
66	0.90	0.13	106.06	Coral Gables Canal
68	0.20	0.52	23.08	Coral Gables Canal
84	0.92	0.20	107.90	Featherbed Bank
87	1.50	0.07	176.24	Southeast of Black Point
96	0.72	0.15	84.02	Caesar Creek
101	MD	0.12	215.32	Goulds Canal and Black Creek
102	0.88	0.22	108.61	C-102 Canal
103	6.67	0.10	783.49	Military Canal
105	0.45	ND	53.25	Mowry Canal
120	MD	ND	29.57	Key Largo
122	MD	ND	MD	Intracoastal Waterway
125	MD	0.22	51.89	South of Turkey Point
128	0.30	0.34	35.03	Turkey Point Power Plant Barge Canal

Table 16. Aliphatic hydrocarbon characterization of tissue samples collected during Year 01. All values are corrected for percent recovery and expressed on a dry weight bases.

		RATIOS					KEY HYDROCARBONS (µg/g)				n-ALKANES	
Laboratory/ Sample	Total* f_1 (µg/g)	f_1/ f_2	Resol. Unres	Prist./ Phyt.	C_{17}/ Prist.	C_{18}/ Phyt.	1500	1700	2085	2900	Homol. Ser.	CPI
Sea Trout #1 (*Cynoscion arenarius*)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sea Trout #2 (*Cynoscion arenarius*)	10.68	1.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Pinfish (*Lagodon rhomboides*)	3.66	23.0	ND	ND	ND	ND	0.73	ND	ND	ND	C_{12}-C_{15}	0.64
Grey Snapper (*Lutjanus griseus*)	36.49	11.8	ND	ND	ND	ND	1.22	ND	ND	ND	ND	ND
Scallops (*Argopecten* spp.)	589.83	53.7	ND	ND	ND	ND	0.71	ND	2.82	ND	ND	ND
Toadfish (*Opsanus beta*)	22.40	6.7	ND	ND	ND	ND	1.07	ND	ND	ND	ND	ND
Shrimp (*Penaeus* spp.)	12.05	1.4	ND	ND	ND	ND	1.13	ND	ND	ND	C_{12}-C_{15}	1.19
Grunt (*Haemulon* sp.)	16.04	2.5	ND	ND	ND	ND	0.76	ND	ND	ND	C_{12}-C_{16}	1.83
Stone Crab (*Menippe mercenaria*)												
Hepatopancreas	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Claw muscle	19.90	0.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Blue Crab (*Callinectes sapidus*)												
Hepatopancreas	0.21	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Claw muscle	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
School Master (*Lutjanus apodus*)	1.68	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 17. Aromatic hydrocarbon characterization of tissue samples collected during Year 01. All values are corrected for percent recovery and expressed on a dry weight basis.

Sample	Total f_2	Napththalene	Phenanthrene	Dibenzothiophene	Pyrene
Sea Trout #t (*Cynoscion arenarius*)	36.77	ND	ND	ND	ND
Sea Trout #2 (*Cynoscion arenarius*)	6.48	ND	ND	ND	ND
Pinfish (*Lagodon rhomboides)*	0.16	ND	ND	ND	ND
Grey Snapper (*Lutjanus griseus*)	3.08	0.63	ND	ND	ND
Scallops (*Argopecten* spp.)	10.99	ND	ND	ND	ND
Toadfsh (*Opsanus beta*)	3.39	ND	ND	ND	ND
Shrimp (*Penaeus* spp.)	85.66	ND	ND	ND	ND
Grunt (*Haemulon* sp.)	6.32	2.63	1.49	ND	2.27
Stone Crab (*Menippe mercenaria*)					
Hepatopancreas	5.55	ND	ND	ND	ND
Claw muscle	32.47	ND	ND	ND	ND
Blue Crab (*Callinectes sapidus*)					
Hepatopancreas	91.47	ND	0.05	0.62	5.75
Claw muscle	29.27	5.81	ND	ND	2.90
School Master (*Lutjanus apodus*)	65.09	ND	ND	6.78	14.32

traffic and is a major area for on and off loading cargo, ship building, repair and refurbishing. The River was dredged in and widened 1933 (Austin, 1971) thus the accumulation of hydrocarbons in the sediment has been during a 50-year time span. This area was chosen because of its use as a port facility and intensive industrialization. In addition with the growing economy of Miami this area will receive greater pressure from ship traffic in the future.

The areas located in the southern area of the Bay are Snapper Creek, Black Creek - Goulds Canal, and Military Canal. Black Creek and Goulds Canal are both water-control canals which intersect before emptying into the Bay. The sample collected during the first year study was at this intersection and indicated petroleum contamination. The landward portion of Goulds Canal runs parallel to an abandoned landfill, and the Black Creek area is under development by Dade County. A proposed public park and marina are to be built there. Military Canal also showed elevated concentrations of hydrocarbons with indices characteristic of petroleum. This canal is also a water-control structure and receives no boat traffic. The canal drains from the Homestead Air Force Base and the surrounding communities. Snapper Creek was chosen because of its location in a predominantly residential area.

Nine areas were sampled for surface water in the Bay. Six of these areas were canals, one was the Port of Miami, and the other two were in open water located in northern and southern areas of the Bay. Five of these areas contained petroleum contamination in their surface waters. The areas were as follows: the Miami River, Little River, Goulds Canal, Military Canal, and Government Cut (Port of Miami). Tables 18 and 19 present the results of the hydrocarbon analysis of the surface waters. A detailed description of the analyses are presented in Appendices F and G.

The Miami River was sampled for surface waters during an ebbing tide. Samples were collected while progressively moving inland. This insured that different water masses were sampled. Samples 205, 206 and 221 were all taken in the mouth of the Miami River and show no indications of petroleum contamination. Sample 211 which was collected in the upper most reaches of the river (the railroad bridge) accessible by the collection vessel also showed no indication of contamination. Samples 207 to 210 and 212 all indicate petroleum contamination. Figure 17 shows the chromatograms of the aliphatic fraction for surface water samples 207 and 208.

The samples collected from the Little River showed basically the same pattern as those sampled from the Miami River. The samples collected in the north and south forks of the River (224 and 222, respectively) just before it enters the Bay show no indication of petroleum hydrocarbons. Although samples 226 and 227 collected landward contained petroleum hydrocarbons.

Samples collected from Goulds Canal and Military Canal showed the same trend as the other canals sampled. The concentration of petroleum in the surface waters increase as one moves inland. Figure 18 shows the chromatograms for the aliphatic fraction of the three samples collected in Goulds Canal, 232, 233, and 234. Figure 19 shows the chromatogram of the aliphatic fraction for sample 238 which was collected from Military Canal.

Table 20 and 21 presents the hydrocarbon characterization for the sediment samples. Six areas were sampled (Miami River, Little River, Goulds Canal, Black Creek, Military Canal, and Snapper Creek), and all contained petroleum contaminants except the Snapper Creek sample. The Miami River contained the highest concentrations of total hydrocarbons 1833.46 μg/g.

Table 18. Aliphatic hydrocarbon characterization of water samples collected during Year 02. All values are corrected for percent recovery.

Laboratory/ Sample	Total* f_1 (μg/g)	RATIOS f_1/ f_2	Resol. Unres	Prist./ Phyt.	C_{17}/ Prist.	C_{18}/ Phyt.	KEY HYDROCARBONS (μg/g) 1500	1700	2085	2900	n-ALKANES Homol. Ser.	CPI
Miami River												
205	0.66	0.14	ND	ND	ND	0.08	0.01	ND	ND	ND	C_{14}-C_{28}	0.37
206	0.46	0.04	ND	ND	ND	ND	ND	ND	ND	ND	C_{18}-C_{25}	1.86
207	5.27	11.46	0.27	1.05	1.96	1.60	0.03	0.12	0.06	ND	C_{14}-C_{27}	1.27
208	14.07	54.11	0.94	0.48	2.27	2.10	ND	0.04	0.09	0.31	C_{17}-C_{30}	0.23
209	3.46	17.30	0.30	1.23	ND	0.96	ND	ND	0.03	ND	C_{16}-C_{26}	3.28
210	4.42	0.07	0.23	0.37	22.10	1.01	0.01	0.17	0.05	ND	C_{15}-C_{26}	3.28
211	2.13	0.11	ND	0.75	ND	0.58	ND	ND	0.01	ND	C_{18}-C_{26}	22.88
212	3.33	0.06	0.22	2.25	2.31	2.12	ND	0.05	0.02	ND	C_{16}-C_{25}	5.82
221	1.92	0.30	ND	ND	0.62	ND	ND	0.03	0.03	ND	C_{17}-C_{30}	0.63
Little River												
222	2.79	0.32	ND	ND	ND	ND	ND	ND	0.04	ND	C_{21}-C_{30}	1.14
224	0.27	0.14	ND	1.70	2.65	ND	0.01	0.03	TD	ND	C_{15}-C_{25}	1.75
226	0.98	0.44	0.42	3.33	0.42	1.36	0.01	0.01	TD	ND	C_{15}-C_{30}	0.45
227	8.82	4.12	0.08	0.39	5.14	0.98	ND	0.04	0.04	ND	C_{16}-C_{28}	0.94
Goulds Canal												
232	25.36	9.57	0.38	1.03	1.16	1.44	0.16	0.36	0.21	ND	C_{14}-C_{30}	0.54
233	4.24	5.89	ND	1.31	1.46	1.71	0.04	0.21	0.09	ND	C_{15}-C_{28}	1.07
234	2.69	44.83	ND	ND	ND	ND	0.17	ND	ND	0.26	C_{16}-C_{29}	0.43
Black Creek												
241	2.00	16.67	ND	ND	ND	ND	0.07	0.04	0.03	ND	C_{14}-C_{28}	0.49
242	1.07	9.73	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
246	0.41	1.11	ND	ND	ND	ND	ND	ND	0.02	ND	C_{12}-C_{27}	4.65
Military Canal												
238	6.17	10.28	0.11	ND	ND	ND	ND	0.03	0.01	ND	C_{17}-C_{27}	1.58
240	2.16	8.31	ND	ND	ND	ND	ND	ND	ND	ND	C_{16}-C_{28}	0.62
Snapper Creek												
247	0.81	5.4	ND	ND	ND	ND	ND	ND	ND	ND	C_{22}-C_{28}	0.15
Government Cut												
231	3.13	3.44	1.46	2.56	0.25	1.02	ND	0.01	0.01	ND	C_{16}-C_{28}	1.95

Table 18. Aliphatic hydrocarbon characterization of water samples collected during Year 02. All values are corrected for percent recovery (cont.).

		RATIOS					KEY HYDROCARBONS (μg/g)				n-ALKANES	
Laboratory/ Sample	Total* f_1 (μg/g)	f_1/ f_2	Resol. Unres	Prist./ Phyt.	C_{17}/ Prist.	C_{18}/ Phyt.	1500	1700	2085	2900	Homol. Ser.	CPI
Open Water-Northern Bay												
230	0.40	0.29	ND	ND	0.89	ND	0.08	0.02	ND	ND	C_{15}-C_{25}	32.97
Open Water-Southern Bay												
235	3.95	16.46	ND	ND	ND	ND	ND	ND	0.06	Nd	C_{19}-C_{26}	1.39
236	10.18	42.42	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.26
237	0.95	1.30	ND	ND	ND	1.26	ND	0.01	0.04	ND	C_{17}-C_{28}	1.11

ND = None Detected
TD = Trace Detected

Table 19. Aromatic hydrocarbon characterization for water samples collected during Year 02. All values are corrected for percent.

Sample	Total f_2	Napththalene	Dibenzo= thiophene	Phenanthrene (μg/L)	1-Methyl= phenanthrene	Pyrene
Miami River						
205	4.57	ND	ND	ND	ND	ND
206	10.61	ND	ND	ND	ND	ND
207	0.46	ND	ND	ND	ND	0.01
208	0.26	ND	ND	ND	ND	ND
209	0.20	ND	0.01	ND	ND	0.01
210	60.05	ND	0.05	0.03	0.14	0.42
211	19.59	ND	0.02	ND	ND	ND
212	50.75	ND	0.61	ND	ND	ND
221	6.48	ND	ND	ND	ND	0.03
Little River						
222	8.68	ND	ND	ND	ND	0.03
224	1.97	ND	ND	ND	ND	ND
226	2.21	ND	ND	ND	ND	0.01
227	2.14	ND	0.08	0.04	ND	ND
Goulds Canal						
232	2.65	ND	0.01	0.01	0.02	ND
233	0.72	ND	ND	N 0	ND	0.69
234	0.06	ND	ND	ND	ND	ND
Black Creek						
241	0.12	ND	0.01	ND	ND	ND
242	0.11	ND	ND	ND	ND	ND
246	0.37	ND	0.04	0.03	ND	ND
Military Canal						
238	0.60	ND	ND	ND	ND	ND
240	0.26	ND	ND	ND	ND	ND
Snapper Creek						
247	0.15	ND	ND	ND	ND	ND
Government Cut						
231	0.91	ND	ND	ND	ND	ND

Table 19. Aromatic hydrocarbon characterization for water samples collected during Year 02. All values are corrected for percent (cont.).

Sample	Total f_2	Napththalene	Dibenzo= thiophene	Phenanthrene (μg/L)	1-Methyl= phenanthrene	Pyrene
Open water-Northern Bay						
230	1.39	ND	ND	ND	ND	ND
Open Water-Southern Bay						
235	0.24	ND	ND	ND	ND	ND
236	0.24	ND	ND	ND	ND	ND
237	0.73	ND	ND	ND	ND	ND

ND = None detected.

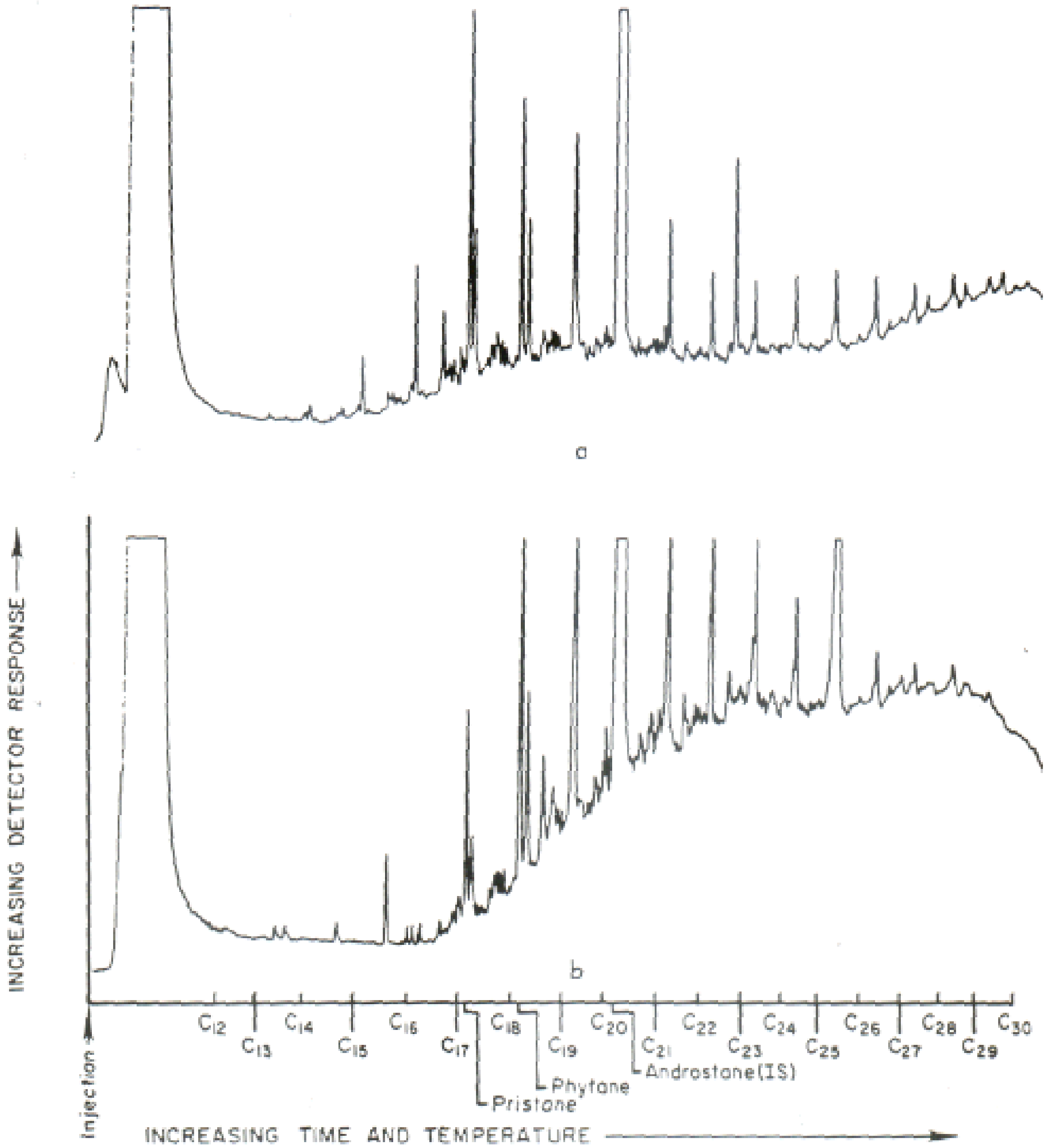

Figure 17. Chromatograms of aliphatic (f1) fraction. Surface water samples collected in the Miami River. a) sample #207, b) sample #208.

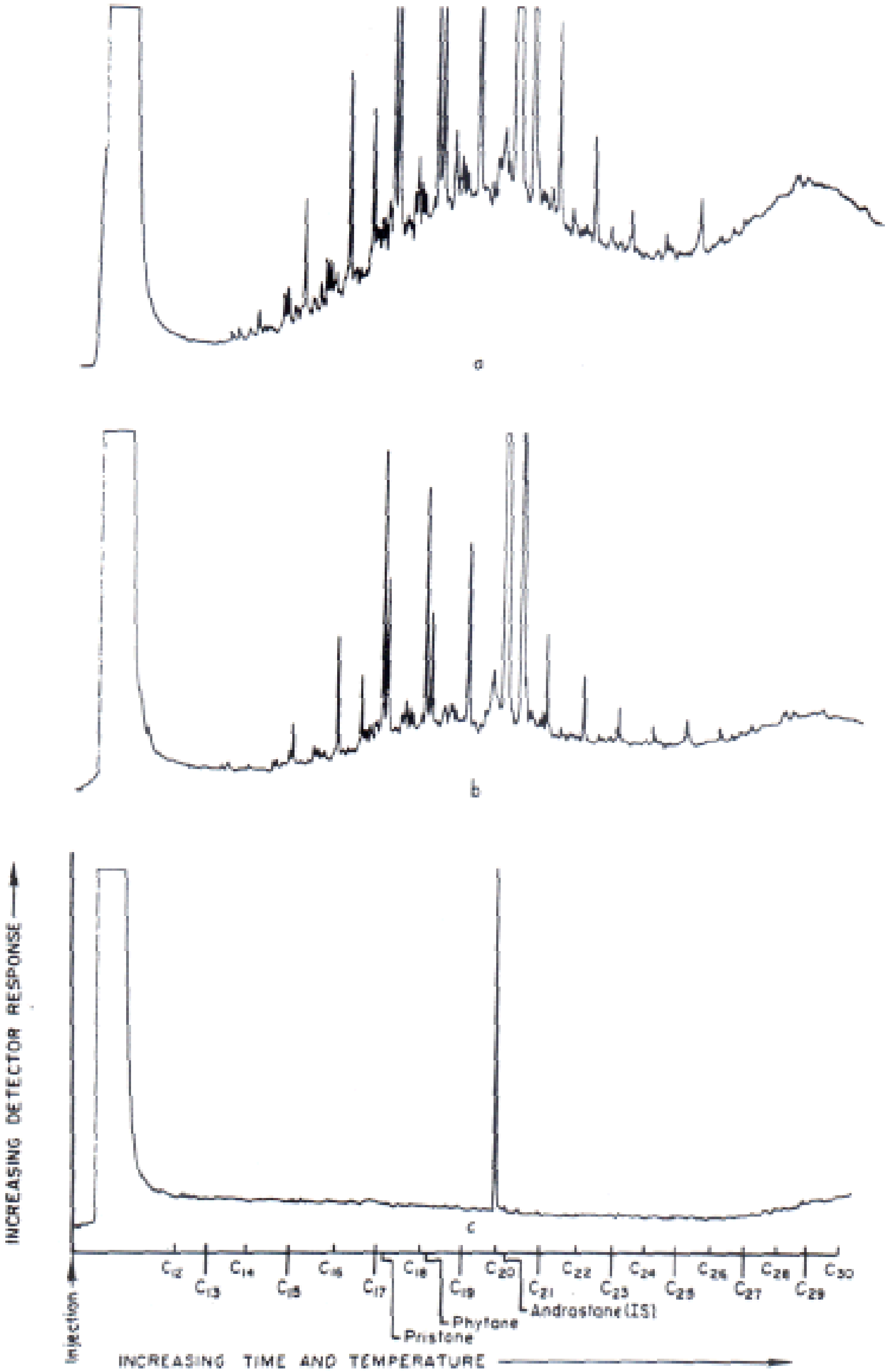

Figure 18. Chromatograms of aliphatic (f_1) fraction. Surface water samples collected in Goulds Canal.

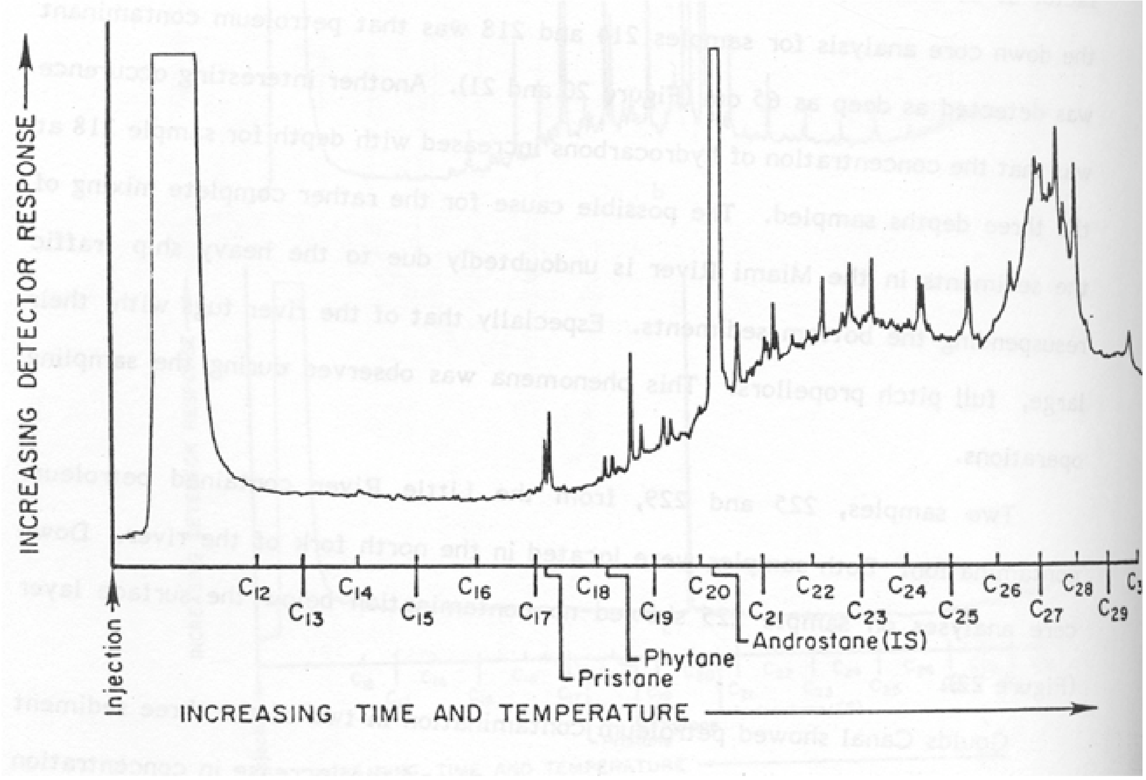

Figure 19. Chromatograms of aliphatic (f_1) fraction. Surface water sample #238 collected in Military Canal.

Table 20. Aliphatic hydrocarbon characterization of sediment samples collected during Year 02. All values are corrected for recovery and expressed on a dry weight basis.

Laboratory	Total* f_1 (µg/g)	RATIOS f_1/ f_2					KEY HYDROCARBONS (µg/g)				n- ALKANES	
		f_1/ f_2	Resol. Unres	Prist./ Phyt.	C_{17}/ Prist.	C_{18}/ Phyt.	1500	1700	2085	2900	Homol. Ser.	CPI
Miami River												
213												
(0-5)	26.40	2.3	ND	0.38	2.38	1.54	ND	0.40	ND	ND	C_{16}-C_{28}	0.06
214												
(0.-5)	531.13	13.5	0.16	2.74	0.27	0.59	1.01	1.46	0.69	3.91	C_{12}-C_{29}	2.22
(20-25)	322.50	15.4	0.16	2.70	0.10	0.91	0.39	0.21	ND	ND	C_{14}-C_{19}	0.65
215												
(0-5)	456.98	14.5	0.12	0.15	0.79	1.16	0.13	0.20	2.25	ND	C_{15}-C_{21}	0.77
216												
(0-5)	1662.40	9.7	0.21	1.11	0.29	0.25	3.46	4.62	ND	ND	C_{14}-C_{20}	1.94
217												
(0-5)	342.68	24.7	0.14	0.24	0.37	0.66	0.15	0.13	ND	ND	C_{14}-C_{20}	0.83
218												
(0-5)	55.99	12.4	0.11	0..67	1.06	0.61	0.10	0.21	ND	ND	C_{15}-C_{19}	0.97
(20-25)	169.52	20.6	0.17	0.22	0.49	0.64	0.09	0.03	ND	ND	C_{15}-C_{28}	0.15
(60-65)	1462.15	26.8	0.43	1.97	0.18	1.24	1.10	2.35	ND	ND	C_{12}-C_{20}	0.64
219												
(0-5)	534.37	9.3	0.13	4.93	0	0.87	0.43	ND	ND	ND	C_{14}-C_{18}	0.31
220												
(0-5)	206.15	11.1	0.16	1.99	0.06	0.57	0.27	0.11	0.61	ND	C_{14}-C_{25}	2.09
Little River												
223												
(0-5)	0.90	14.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
225												
(0-5)	13.99	3.6	1.25	5.78	0.05	1.85	0.02	0.01	0.44	0.36	C_{12}-C_{30}	1.67
(25-30)	7.12	24.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
(55-60)	4.07	1.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
228												
(0-5)	2.65	1.2	ND	ND	0.40	ND	ND	0.06	ND	1.34	ND	ND
229												
(0-5)	39.09	4.6	0.06	ND	ND	ND	ND	0.42	ND	ND	ND	1.37
Goulds Canal												
232												
(0-5)	227.68	15.8	0.13	0.84	0.25	0.12	0.11	0.42	ND	ND	C_{15}-C_{19}	4.00
(55-60)	413.08	9.9	0.16	7.84	0.09	0.15	0.29	0.41	ND	ND	C_{15}-C_{20}	3.36
233												
(0-5)	165.99	2.0	0.03	1.33	ND	ND	ND	ND	ND	ND	ND	ND
234												
(0-5)	14.69	1.11	ND	5.28	0.12	0.41	ND	0.12	0.47	ND	C_{17}-C_{27}	20.43

Table 20. Aliphatic hydrocarbon characterization of sediment samples collected during Year 02. All values are corrected for recovery and expressed on a dry weight basis (cont.).

	Total*	RATIOS					KEY HYDROCARBONS (μg/g)				n-ALKANES	
Laboratory	f_1 (μg/g)	f_1/ f_2	Resol. Unres	Prist./ Phyt.	C_{17}/ Prist.	C_{18}/ Phyt.	1500	1700	2085	2900	Homol. Ser.	CPI
Black Creek												
241												
(0-5)	16.25	1.7	0.68	7.41	ND	0.44	0.03	ND	0.44	ND	C_{12}-C_{28}	0.55
242												
(0-5)	3.03	1.1	ND	ND	ND	ND	ND	0.59	ND	ND	ND	ND
243												
(0-5)	1.99	0.3	ND	ND	ND	ND	0.86	ND	ND	ND	ND	ND
244												
(0-5)	37.18	0.6	ND	11.45	ND	ND	ND	ND	1.95	ND	C_{16}-C_{21}	0.76
245												
(0-5)	23.57	7.6	0.99	14.18	ND	0.38	ND	ND	1.06	4.65	C_{18}-C_{29}	10.42
246												
(0-5)	0.35	0.2	ND	ND	ND	ND	N 0	ND	ND	ND	ND	ND
Military Canal												
239												
(3-5)	29.50	3.7	1.20	2.41	0.26	ND	ND	0.07	0.91	ND	C_{17}-C_{24}	0.09
239												
(0-5)	4.84	0.8	ND	ND	ND	ND	ND	0.16	ND	ND	C_{17}-C_{19}	3.7S
240												
(0-5)	269.31	8.0	0.24	14.12	0.11	3.23	0.22	0.32	1.88	ND	ND	ND
(60-65)	3.45	0.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
(120-125)	6.29	5.2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Snapper Creek												
247												
(0-5)	0.22	0.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND = None Detected

Table 21. Aromatic hydrocarbon characterization of sediment samples collected during Year 02. All values corrected for percent recovery.

Sample		Total f_2	Napththalene	Dibenzo= thiophene	Phenanthrene (μg/L)	1-Methyl= phenanthrene	Pyrene
Miami River							
213	(0-5)	11.38	ND	0.11	2.84	0.84	4.03
214	(0-5)	39.39	ND	0.12	1.22	0.26	3.10
	(20-25)	20.96	ND	0.31	0.13	0.11	9.55
215	(0-5)	31.53	ND	0.34	ND	0.24	ND
216	(0-5)	171.06	1.74	3.69	0.90	0.50	2.46
217	(0-5)	13.86	ND	0.07	0.29	0.29	0.14
218	(0-5)	4.52	ND	0.06	0.41	0.05	0.60
	(20-25)	8.21	ND	0.15	0.62	0.10	1.25
	(60-65)	54.62	ND	1.05	1.16	0.51	1.65
219	(0-5)	57.30	0.18	0.55	0.28	0.60	2.06
220	(0-5)	18.62	ND	0.16	1.16	0.13	1.50
Little River							
223	(0-5)	16.20	ND	0.08	0.87	0.17	2. 50
225	(0-5)	3.91	ND	0.03	0.15	0.07	0.48
	(25-30)	0.29	ND	0.12	ND	ND	ND
	(55-60)	4.24	ND	0.18	ND	0.05	ND
228	(0-5)	2.13	ND	0.05	0.08	ND	0.35
229	(0-5)	8.44	ND	0.48	0.17	0.36	ND
Goulds Canal							
232	(0-5)	14.40	ND	0.50	TD	0.09	0.08
	(55-60)	41.97	ND	0.32	0.06	0.32	0.91
233	(0-5)	84.98	ND	4.05	ND	1.19	1.72
234	(0-5)	13.23	ND	0.42	ND	0.62	ND
Black Creek							
241	(0-5)	9.55	0.04	0.05	0.18	0.36	0.32
242	(0-5)	2.90	ND	0.05	0.13	0.10	0.18
243	(0-5)	6.74	ND	ND	0.11	0.33	0.52
244	(0-5)	66.79	ND	0.14	1.64	2.91	2.89
245	(0-5)	3.73	ND	0.15	ND	0.10	0.02
246	(0-5)	4.54	ND	ND	0.08	0.23	ND
Military Canal							
238	(0-5)	7.74	ND	0.14	ND	0.16	ND
239	(0-5)	6.42	ND	ND	0.09	0.02	0.34
240	(0-5)	22.86	ND	0.21	1.15	0.02	0.82
	(60-65)	5.51	ND	ND	ND	ND	ND
	(120-125)	1.22	ND	0.03	0.04	ND	0.10
Snapper Creek							
247	(0-5)	1.51	ND	0.07	ND	0.09	ND

TD - None Detected.
TM - Trace Detected.

All of the sediments collected from the Miami River contained petroleum hydrocarbons except sample 213 which was collected in the Tamiami Canal at the 37 Avenue bridge. The River had the highest concentrations of hydrocarbons by a factor of 10 than any other sampling sites. One of the very interesting results of the down core analysis for samples 214 and 218 was that petroleum contaminant was detected as deep as 65 cm (Figure 20 and 21). Another interesting occurrence was that the concentration of hydrocarbons increased with depth for sample 218 at the three depths sampled. The possible cause for the rather complete mixing of the sediments in the three depths sampled. The possible cause for the rather complete mixing of the sediments in the Miami River is undoubtedly due to the heavy ship traffic re suspending the bottom sediments. Especially that of the river tugs with their large, full pitch propellers. This phenomena was observed during the sampling operations.

Two samples, 225 and 229, from the Little River contained petroleum contamination. Both samples were located in the north fork of the river. Down core analyses on sample 225 showed no contamination below the surface layer (Figure 22).

Goulds Canal showed petroleum contamination in two of the three sediment samples collected. The contamination at depth and the increase in concentration with depth is also present in sample 232. The chromatograms for the aliphatic fraction, for both depths are presented in Figure 23. The same explanation for mixing applied to the Miami River cannot be used to explain the high concentrations of hydrocarbons at the greater depths in Goulds Canal. Sample 232 was obtained at the end of the Canal next to an earthen dike. A possible explanation for this is that the stagnation of the water caused by the dike had created a sink or that down canal sediment had been used as fill.

Only two samples collected from Black Creek showed any petroleum contamination. Sample 241 was located inland from the intersection of Black Creek and Goulds Canal and sample 245 was located in a large open basin used for boat launchings.

Two of the three samples collected from Military Canal contained petroleum contamination. Sample 240 which was subjected to down core analysis exhibited contamination only in the surface layer (Figure 24).

Biota analyses consisted of fish, shrimp, crabs, rays, bivalves and oysters. Tables 22 and 23 presents the aliphatic and aromatic data, respectively. The bivalves and oysters were collected from Black Creek, the flat tree oysters were collected from a marina located on Virginia Key, the other samples were collected from open areas of the Bay. The flat tree oyster was the only organism containing petroleum contamination. Figure 25 is the chromatogram of the aliphatic fraction for this sample.

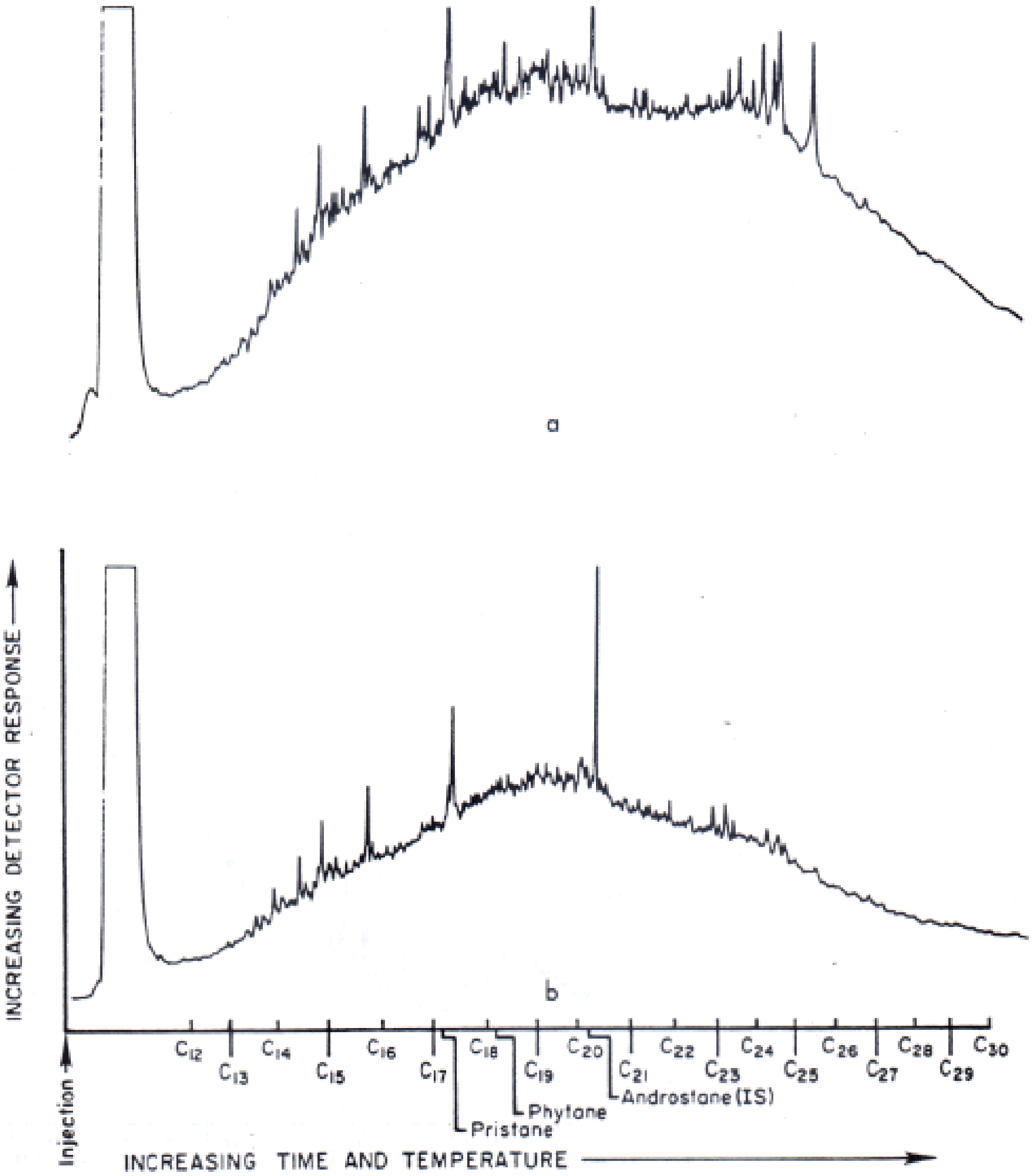

Figure 20. Chromatograms of aliphatic (f_1) fraction. Miami River sediment sample #214.

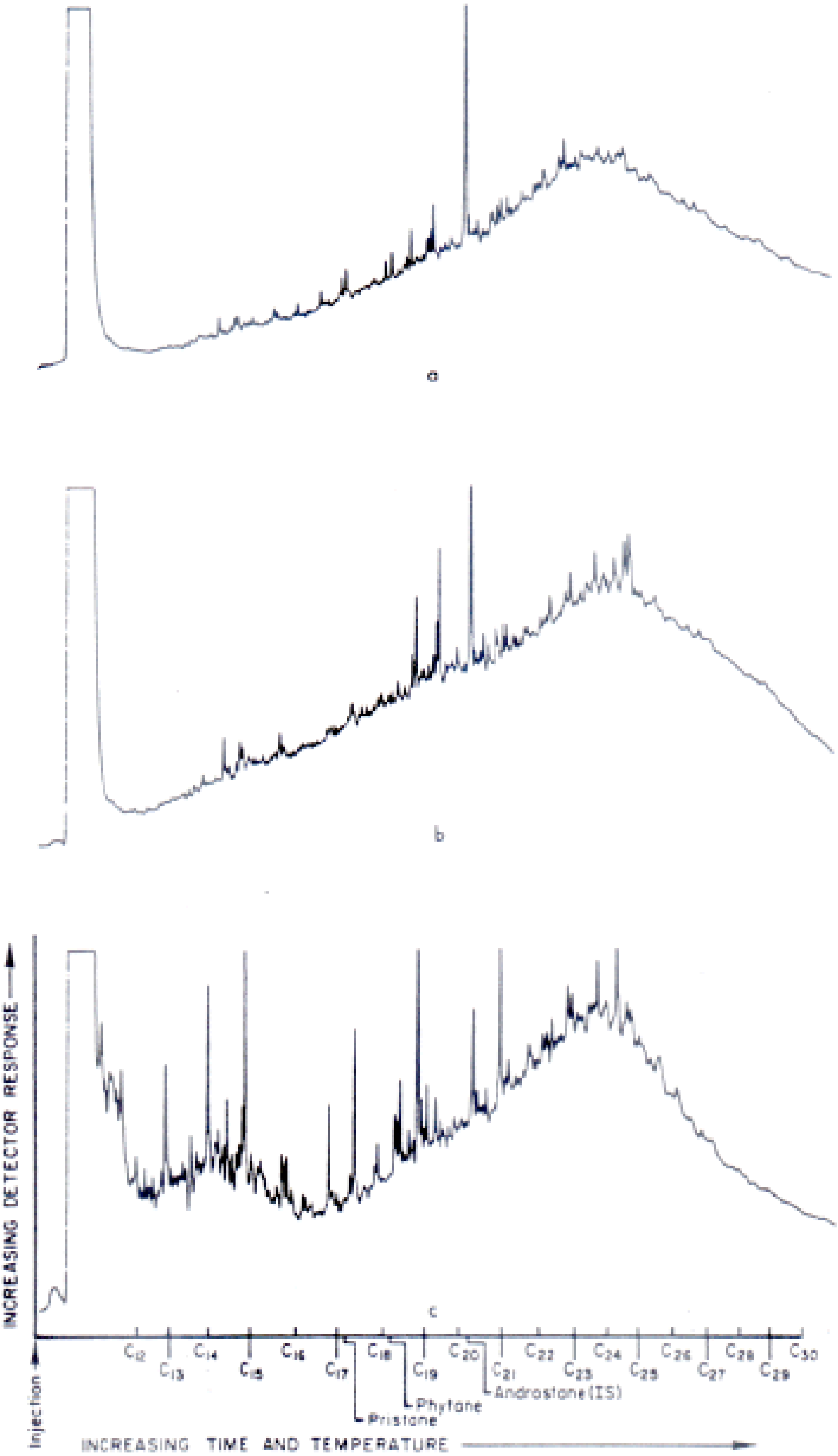
a
b
INCREASING DETECTOR RESPONSE
c
C_{12}
C_{13}
C_{14}
C_{15}
C_{16}
C_{17}
C_{18}
C_{19}
C_{20}
C_{21}
C_{22}
C_{23}
C_{24}
C_{25}
C_{26}
C_{27}
C_{28}
C_{29}
C_{30}
Androstane (IS)
Phytane
Pristane
Injection
INCREASING TIME AND TEMPERATURE

Figure 21. Chromatograms of aliphatic (f_1) fraction. Miami River sediment sample #218.

Figure 22. Chromatograms of aliphatic (f_1) fraction. Little River sediment sample #225.

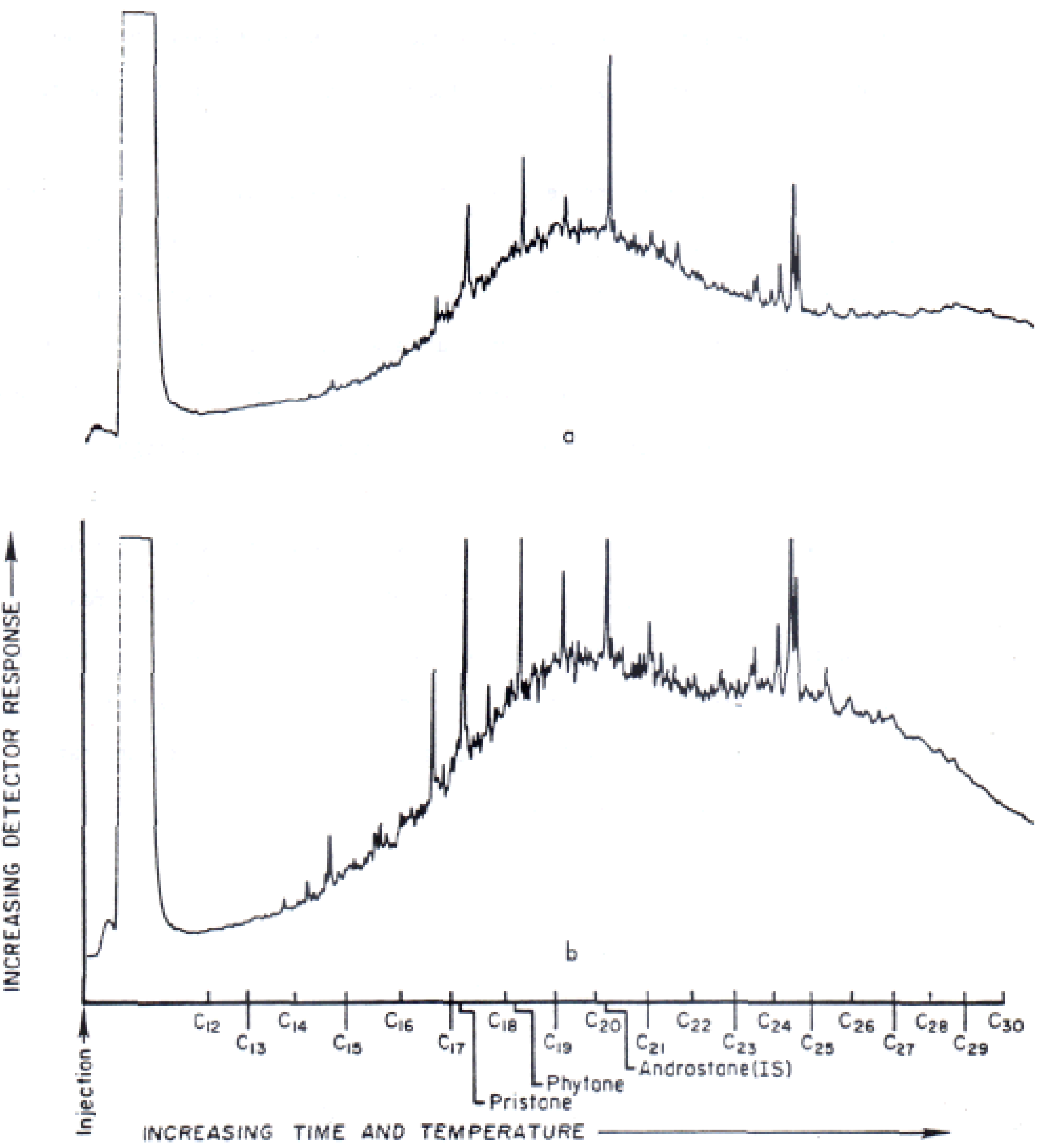

Figure 23. Chromatograms of aliphatic (f_1) fraction. Goulds Canal sediment sample #232.

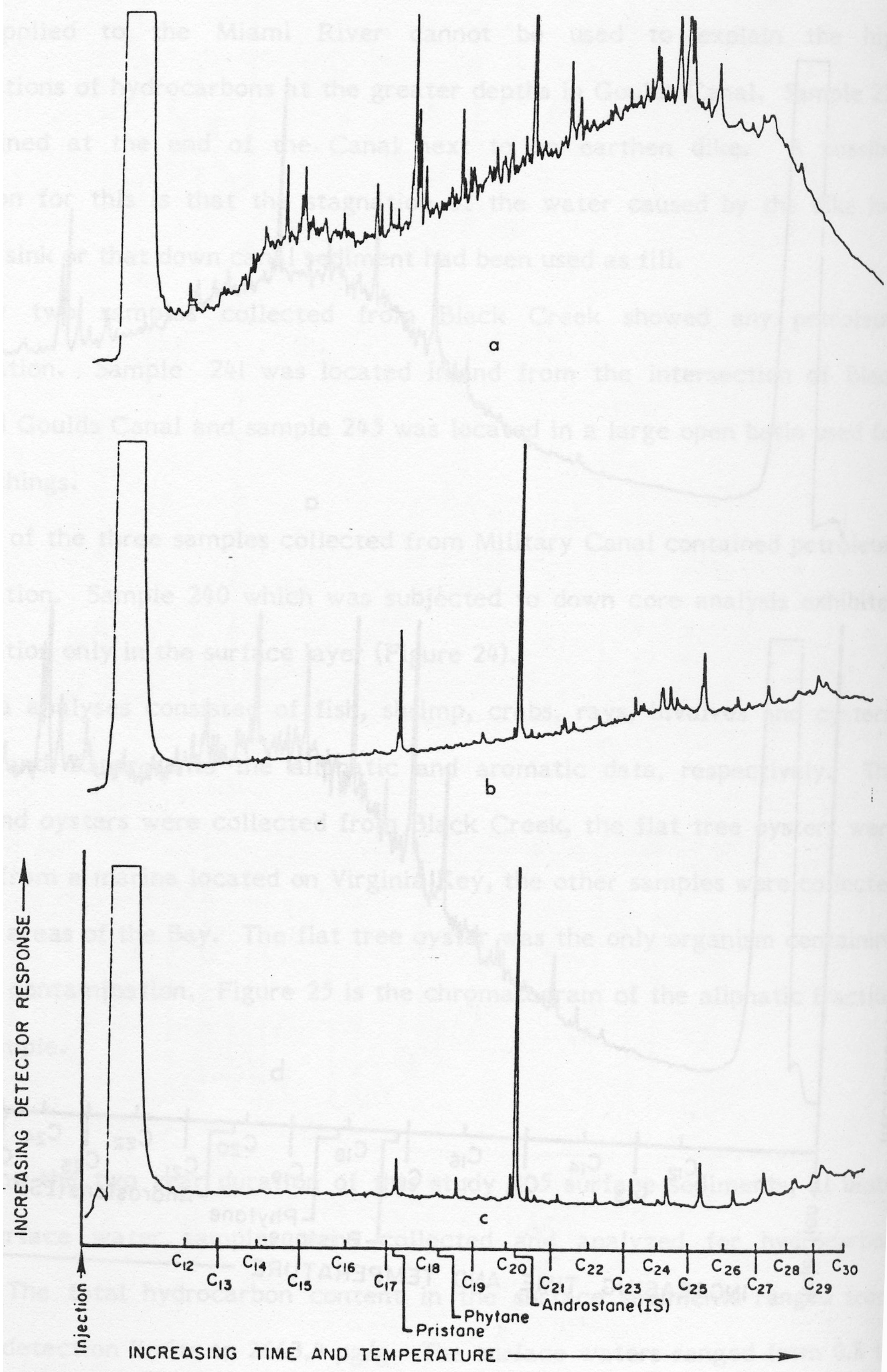

Figure 24. Chromatograms of aliphatic (f_1) fraction. Military Canal sediment sample #240. a) 0-5 cm depth, b) 60-65 cm depth, c) 120-125 cm.

Table 22. Aliphatic hydrocarbon characterization of tissue samples collected during Year 02. All values are corrected for percent recovery and expressed on a dry weight bases.

	Total*	RATIOS					KEY HYDROCARBONS (μg/g)				n-ALKANES	
Laboratory/ Sample	f_1 (μg/g)	f_1/ f_2	Resol. Unres	Prist./ Phyt.	C_{17}/ Prist.	C_{18}/ Phyt.	1500	1700	2085	2900	Homol. Ser.	CPI
Butterfly Ray (*Gymnura micrura*)	159.33	43.7	ND	ND	ND	ND	0.05	ND	0.19	ND	C_{15}-C_{28}	0.01
Catfish (*Arius felis*)	108.44	13.5	7.74	ND	ND	ND	0.10	ND	5.37	ND	C_{15}-C_{28}	0.22
Grunt (*Haemulon scrurus*)	70.64	29.9	ND	ND	ND	ND	ND	ND	ND	ND	C_{24}-C_{28}	0.29
Pigfish (*Orthopristis chrysopterus*)	62.93	2.4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Shrimp (*Penaeus* sp.)	0.33	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Crab (*Callinectes ornatus*)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Blue Crab (*Callinectes sapiches*)	24.45	0.1	ND	ND	ND	ND	ND	0.76	ND	ND	C_{20}-C_{23}	0.21
Mixed bivalves (*Mytilopsis leucophacata* and *Brachidontes exustus*)	16.61	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Oyster (*Crassostrea virginica*)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Flat Tree Oyster (*Isognomon alatus*)	125.20	2.8	0.41	0.60	0.04	0.11	ND	0.08	2.65	8.92	C_{17}-C_{30}	0.22

ND = None Detected

Table 23. Aromatic hydrocarbon characterization of tissue samples collected during Year 02. All values are corrected for percent recovery and expressed on a dry weight bases.

Sample	Total f_2 (μg/g)	Naphthalene	Dibenzo-thiophene	Phenan-threne	1-Methyl-phenanthrene	Pyrene
Butterfly Ray (*Gymnura micrura*)	3.65	ND	ND	ND	0.03	ND
Catfish (*Arius felis*)	8.02	0.54	0.15	0.11	0.40	ND
Grunt (*Haemulon scrurus*)	2.36	ND	ND	ND	ND	ND
Pigfish (*Orthopristis chrysopterus*)	26.52	ND	ND	ND	1.19	ND
Shrimp (*Penaeus* sp.)	ND	ND	ND	ND	ND	ND
Crab (*Callinectes ornatus*)	53.99	ND	ND	ND	4.89	11.05
Blue Crab (*Callinectes sapiches*)	192.09	ND	ND	ND	4.05	30.58
Mixed bivalves (*Mytilopsis leucophacata* and *Brachidontes exustus*)	ND	ND	ND	ND	ND	ND
Oyster (*Crassostrea virginica*)	138.16	ND	ND	ND	ND	132.66
Flat Tree Oyster (*Isognomon alatus*)	57.51	ND	ND	ND	6.00	14.50

ND - None Detected

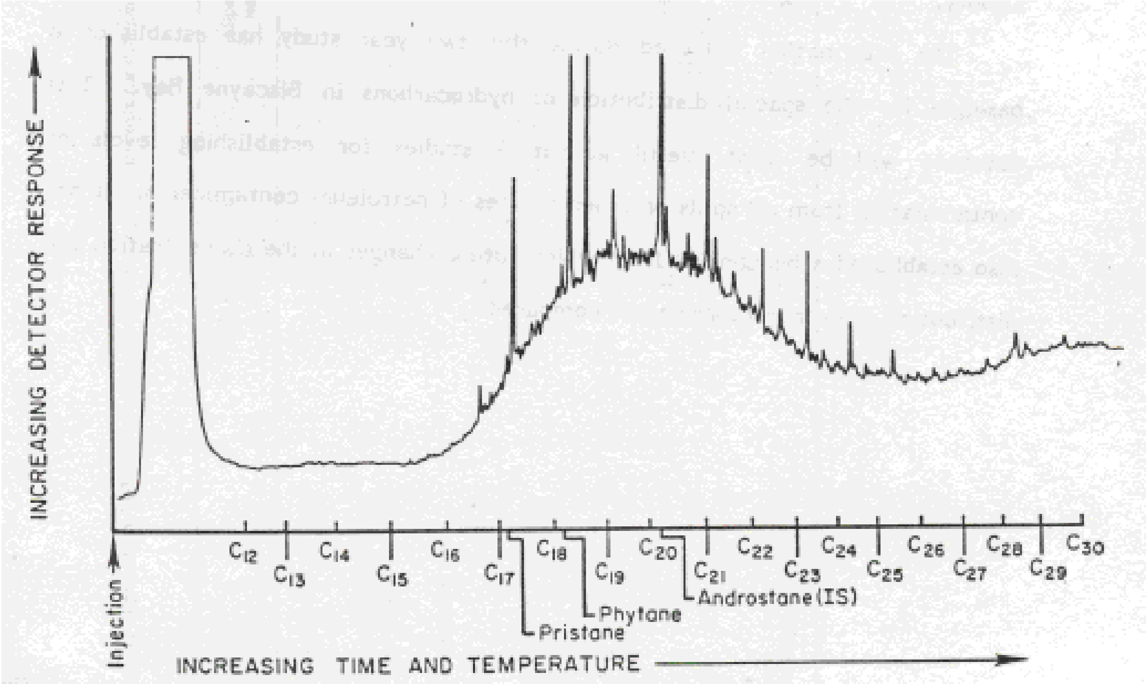

Figure 25. Chromatograms of aliphatic (f_1) fraction. Flat tree oyster collected from marina.

4.5. Summary

During the two year duration of this study 205 surface sediments, 21 biota and 27 surface water samples were collected and analyzed for hydrocarbon content. The total hydrocarbon content in the surface sediments ranged from below our detection limits to 2663.4 μg/g. The surface waters ranged from 0.8 to 64.5 μg/L and the biota samples ranged from 0.3 to 600.8 μg/g. The samples containing the highest concentrations for both water and sediment were collected from the Miami River. The concentration of hydrocarbons found in the sediment of the Miami River are as high as those found in Chesapeake Bay, New York Bight (Table 24) and at least ten times greater than those in Charlotte Harbor and the St. Johns River.

The sediments were the best indicator of petroleum contamination since they are the ultimate sink for this pollutant. The surface sediment samples which contained petroleum contaminants were usually associated with two main usage patterns: 1) areas associated with boats and ships (e.g., major transportation routes, moorings, cargo handling, and construction and maintenance); and 2) areas which receive runoff and other inputs from highly urbanized regions of Dade County.

The information gathered during this two-year study has established a baseline for the spatial distribution of hydrocarbons in Biscayne Bay. This database will be most useful in future studies for establishing levels of contamination from oil spills or other sources of petroleum contaminants. It has also established a benchmark from which future changes in the concentration and distribution of hydrocarbons can be compared.

Table 24. Summary of petroleum hydrocarbon concentrations in surface sediments for different geographical areas.

Location	Total Hydrocarbons µg/g	Aliphatics µg/g	Aromatics µg/g	Citation
COASTAL AREAS				
Australia				
Western Port Bay (polluted area)	42	-	-	Burns and Smith, 1977
Western Port Bay (unpolluted area)	7	-	-	Burns and Smith, 1977
Bermuda				
South Shore inside boiler reefs	262	42	221	Sleeter, 1980
Chesapeake Bay	3200	1950	1210	Walker *et al.*, 1975
Dungeness Bay (Juan de Fuca)	-	3	30	Macleod *et al.*, 1977
English Channel	31	-	-	Tissier and Oudin, 1973
Narragansett Bay				
Providence River	2060			Farrington and Quinn, 1977
West Passage	263	-	-	Farrington and Quinn, 1977
Upper Bay	1990	1900	29	Zatrion, 1973
New York Bight	1346-2900	866-1800	479-1100	Farrington and Tripp, 1977
Orinoco Delta	59	30	28	Smith, 1954
Port Angeles H. (Juan de Fuca)	-	530	260	Macleod *et al.*, 1977
CONTINENTAL SHELFS				
Bermuda	19	7	12	Sleeter, 1980
Black Sea	170	-	34	Shishenina *et al.*, 1974
California Shelf	-	36	64	Smith, 1954
Gulf of Mexico				
South Eastern area	5	3	2	Lytle and Lytle, 1977
Eastern area	2	2	2	Lytle and Lytle, 1977
North Central area	4	2	2	Gearing *et al.*, 1976

Table 24. Summary of petroleum hydrocarbon concentrations in surface sidements for different geographical areas (cont.).

Location	Total Hydrocarbons μg/g	Aliphatics μg/g	Aromatics μg/g	Citation
North Atlantic				
Hudson Canyon	16	5	11	Farrington and Tripp, 1977
Hudson Channel	81	35	60	Farrington and Tripp, 1977
Continental shelf	11	5	5	Farrington and Tripp, 1977
Continental slope	14	5	9	Farrington and Tripp, 1977
Norwegian Sea	11	-	3	Shishenina *et al.*, 1974
Scotian Shelf				
Halifax transect	2	-	-	Keizer *et al.*, 1977
Well sites	1	-	-	Keizer *et al.*, 1977
Sable Island	3	-	-	Keizer *et al.*, 1977
West Africa				
West of Cape Verde	33	20	12	Smith, 1954
Southwest of Cape Verde	29	17	13	Smith, 1954
ABYSSAL PLAIN and OPEN OCEAN				
Pacific	14-16	-	3	Shishenina *et al.*, 1974
Norwegian Sea	10	-	3	Shishenina *et al.*, 1974
North Atlantic	5	3	2	Farrington and Tripp, 1977
Canary Islands	12	2	10	Sleeter, 1980

5. Acknowledgments

The authors would like to acknowledge the following people at the Rosenstiel School of Marine and Atmospheric Science for their scientific, technical and monetary support: Associate Dean Warren Wisby and Dr. Richard Robins for supplying the funds to refurbish the analytical laboratory, Dr. Harold Wanless for his valuable input concerning the geology of Biscayne Bay, Mr. Steve Berkeley and Mr. Steve Carney for their assistance in acquisition of the biota samples, Todd S. Payne, Ludy Diaz de Carrasco, Emilio Perez and Richard Fitzpatrick who were of great assistance in maintaining the everyday operation of the laboratory; Mark Pikur, Enrique Lahmann and Christy Thomas for their assistance with the field collections, Mrs. Kay Hale and her excellent library staff for their valuable assistance, Shelley McCarthy for her kindness, patience and excellent job typing the manuscript and Catherine Sikkema who prepared the graphics. We would like to thank the Dade County Department of Environmental Resources Management for letting us participate in the Biscayne Bay Restoration and Enhancement Program and all the members of this group for their valuable input and cooperation. We certainly appreciate the constructive input and assistance supplied by the project reviewer Dr. Pat Parker. The assistance and cooperation supplied by the Mote Marine Laboratory and Jacksonville University is also appreciated. Our thanks are expressed to Dr. Edward S. Van Vleet for his excellent GC-MS work and to Alan Huff, the Project Officer, for his kindness, patience, and administrative assistance.

[Rescue of this work in 2005 was funded through a grant of the South Florida Ecosystem Restoration Prediction and Modeling Program (SFERPM) - a competitive program conducted by the Center for Sponsored Coastal Ocean Research (CSCOR), in association with the South Florida Living Marine Resources Program (SFLMR) - for Coastal and Estuarine Data/Document Archeology and Rescue (CEDAR) for South Florida. We wish to thank J. Browder, S. Markley, R. Skinner, A. Gangitano, G. G. Lauenstein and M. J. Bello for their assistance.]

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