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**CHEMICAL FATE OF BUNKER C FUEL OIL IN A SUBTROPICAL
MARINE ENVIRONMENT FOLLOWING A SPILL IN TAMPA BAY,
FLORIDA**

Dana Lynn Wetzel
University of South Florida

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Graduate School
University of South Florida
Tampa, Florida

CERTIFICATE OF APPROVAL

Master's Thesis

This is to certify that the Master's Thesis of

DANA LYNN WETZEL

with a major in Marine Science has been approved by
the Examining Committee on July 5, 1995
as satisfactory for the thesis requirement
for the Master of Science degree

Examining Committee:

Major Professor: Edward S. Van Vleet, Ph.D.

Member: ~~Richard~~ Richard H. Pierce, Ph.D.

Member: ~~Gregg R.~~ Gregg R. Brooks, Ph.D.

Member: Mark E. Luther, Ph.D.

CHEMICAL FATE OF BUNKER C FUEL OIL IN A SUBTROPICAL MARINE
ENVIRONMENT FOLLOWING A SPILL IN TAMPA BAY, FLORIDA

by

DANA LYNN WETZEL

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science
Department of Marine Science
University of South Florida

August 1995

Major Professor: Edward S. Van Vleet, Ph.D.

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An Abstract

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Major Professor: Edward S. Van Vleet, Ph.D.

A hydrocarbon chemistry study was performed on sediments, oil masses and mangrove prop roots of a mangrove island in Boca Ciega Bay, Florida following a spill of Bunker C fuel oil in Tampa Bay. Normal alkane (n-alkane) and polycyclic aromatic hydrocarbon (PAH) profiles were monitored for effects of degradation and weathering in these mediums for a period of one year. Initial findings indicated a loss of lower molecular weight n-alkanes and PAH's in sediments and prop roots. There was little or no loss of these low molecular weight components in the oil mass samples. Hydrocarbon profiles at the end of the year long study indicated a loss of many of the n-alkanes with a corresponding increase in the unresolved complex mixture, and a shift in the profile towards higher molecular weight compounds. One and two ring PAH's were also lost during the year, while three and four ring PAH's (phenanthrene, pyrene and chrysene) showed little evidence of degradation and/or weathering. Increased exposure to physical processes appeared to enhance the weathering of the petroleum hydrocarbons. Mangrove prop roots, exposed to such additional processes, clearly degraded more rapidly than

sediments or oil masses. Sediments exhibited more weathering than did oil mass samples which were protected from these natural weathering processes and showed little change from the original Bunker C composition throughout the year. The lack of significant weathering effects on the PAH's indicates probable long term residual toxicity for biological communities in and around Eleanor Island.

Abstract approved: Edward S. Van Vleet

Major Professor: Edward S. Van Vleet, Ph.D.
Professor, Department of Marine Science

Date Approved: July 5, 1995

1. INTRODUCTION

There are several means by which petroleum hydrocarbons can enter the marine environment including natural seepage, offshore oil production, atmospheric deposition, coastal, municipal, and industrial wastes and runoff, ocean dumping and marine transportation. Once in the environment, petroleum can impact many organisms, some quite adversely. An ever increasing dependence on oil is accompanied by an increased risk of exposure to oil contamination from spills, particularly those due to marine transportation of oil. While there are many contributors to marine oil pollution, marine transportation is responsible for the largest single share (NAS 1985). The National Research Council (NRC 1985), estimated losses of oil from marine transportation to be 1.45 million metric tons per year from major (>7 metric tons) and minor (<7 metric tons) spills.

In the early morning of August 10, 1993, a major oil spill occurred when approximately 1.2 million liters (1164 metric tons) of Bunker C (No. 6) fuel oil spilled from the fuel tanker *Bouchard 155* after it collided with the phosphate freighter *Balsa 37* in a shipping channel at the entrance to Tampa Bay, Florida. The position of the leaking tanker at 0600 that morning, was N 27°36.41', W 82°40.30'.

The *Balsa 37*, carrying 6000 tons of phosphate, was outbound in a shipping channel leading from Tampa Bay. It cut left across the bow of the jet fuel barge *Ocean 255*, which was carrying 30 million liters (7.9 million gallons) of jet fuel and 6.8 million liters (1.8 million gallons) of gasoline. The *Ocean 255* was passing to the left of the *Bouchard 155* as both vessels were headed inbound, when the *Balsa 37* collided first with the *Ocean 255* and then with the *Bouchard 155*. The *Ocean 255* exploded and burned sending flames over 35 meters in the air. Although approximately 0.12 million liters (32,000 gallons) of the *Ocean 255's* mixed product were discharged into Tampa Bay, most of the highly volatile jet fuel and gasoline quickly burned or volatilized. The *Balsa 37* sustained no serious damages and no phosphate cargo discharge. However, the *Bouchard 155* suffered severe injury, and spilled approximately 7800 barrels of highly viscous, high molecular weight Bunker C fuel oil, resulting in a 27 km long oil spill.

The barge began leaking the fuel oil at the point of impact, before eventually coming to rest near the Sunshine Skyway Bridge which spans the mouth of Tampa Bay. Although early hydrodynamic conditions with ebbing tides caused most of the oil to be carried several kilometers out of Tampa Bay and into the Gulf of Mexico, subsequent onshore winds and spring tides caused significant quantities of the oil to be deposited on nearby beaches and in mangrove, seagrass and estuarine habitats north of the mouth of Tampa Bay. The oil

that was washed ashore extended 23 km along the beaches of Sand Key, Treasure Island and Long Key in southern Pinellas County (Madeira Beach to Pass-a-Grille). A considerable mass of the oil was also transported through the John's Pass tidal inlet during a flooding spring tidal cycle and oiled the shallow to subtidal sand inlet containing several mangrove islands (Davis et al. 1994). The mangrove island most extensively oiled was Eleanor Island (Figure 1).

Eleanor Island is the largest mangrove island in this flood tidal delta system. It is the southernmost island in the pass and located just north and east of the John's Pass bridge and directly east of Treasure Island. Eleanor Island has a mean elevation of 30 cm and a maximum elevation of 1 m (Davis et al. 1994). It is covered with dense mangles of Rhizophora mangle (red mangrove) and Avicennia germinans (black mangrove), and is banded by several relatively thick oyster banks. It is bound on the northeast and southeast sides by shallow seagrass beds which drop into 3 m tidal channels. The west side is bordered by extensive intertidal to shallow subtidal sand shoals. Because of the eastward trajectory of the approaching oil mass, the north, west and the south sides of the island were most heavily impacted, with oil permeating the oysters in the intertidal zone and coating the pneumatophores of the black mangroves and the prop roots of the red mangroves. A visual assessment of the island showed a distinct line of oil on the mangroves to the height of the spring high tides (0.8 m) (Davis et al. 1994).

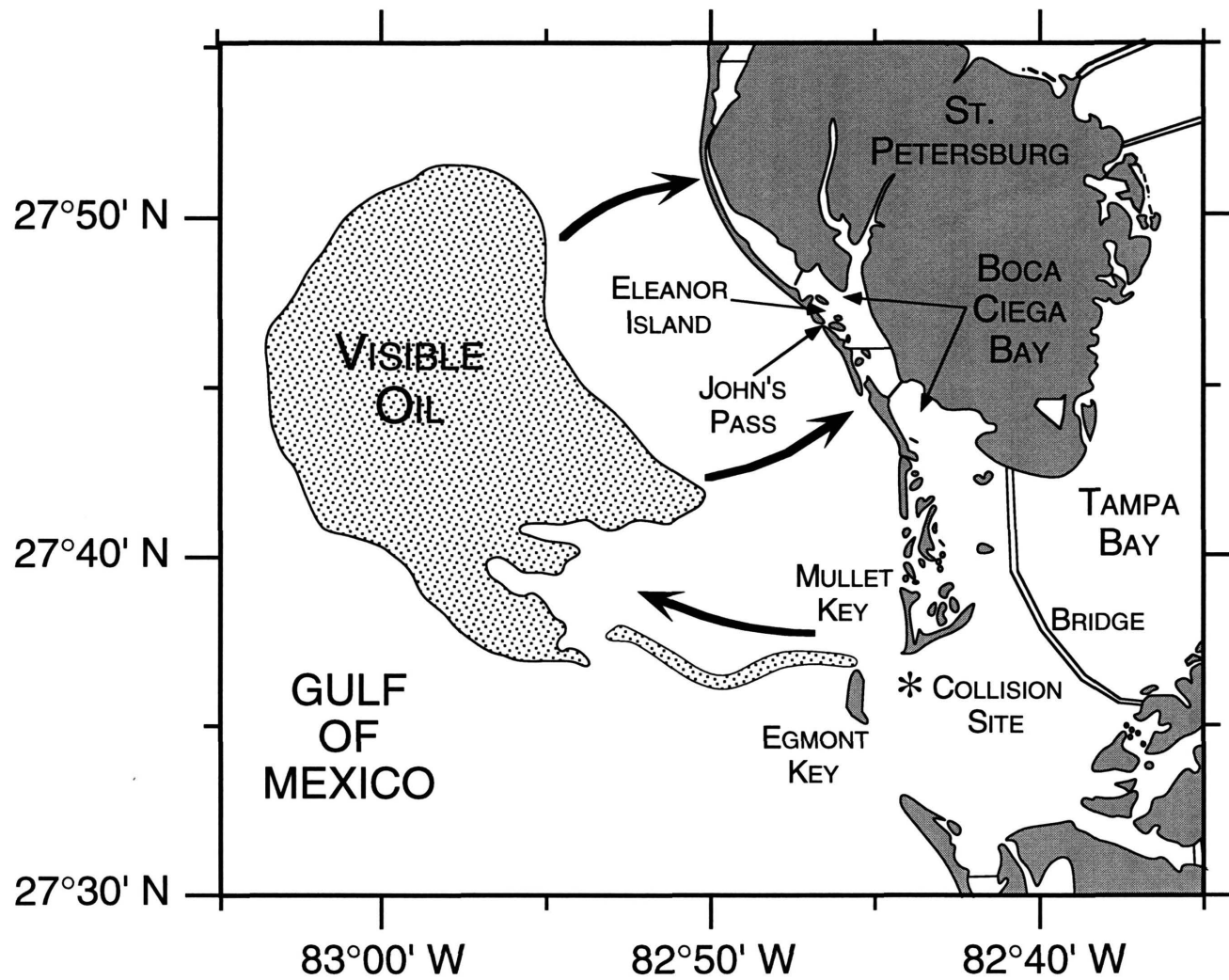


Figure 1. Bunker C Fuel Oil Spill Trajectory Map

Large patches of oil patties were randomly distributed within the mangrove fringe, shallow subtidal sand shoals and seagrass beds on the south, north and west sides of the island.

Sediments are widely recognized as likely sinks for contaminants, especially fine-grained sediments associated with mangrove islands. Because of the extreme amount oiling on Eleanor island, it was chosen as the site to conduct a time series study of the chemical fate of Bunker C fuel oil in a subtropical marine environment, not only in sediments, but also on oil-coated mangrove prop roots. This study was carried out to provide insight on the behavior of high molecular weight oils in this subtropical environment.

Characteristics of Weathered Oil

The persistence of oil in the marine environment has long been a concern, and there is relatively little known of the fate of Bunker C in subtropical environments. Physical and chemical properties of oil and environmental conditions affect the distribution and weathering of oil (changing its viscosity, solubility and toxicity). Processes that contribute to the alteration of the chemical composition and distribution of oil in the marine environment include: interactions with suspended sediments, evaporation, dissolution, emulsification, photooxidation, and microbial degradation (Figure 2).

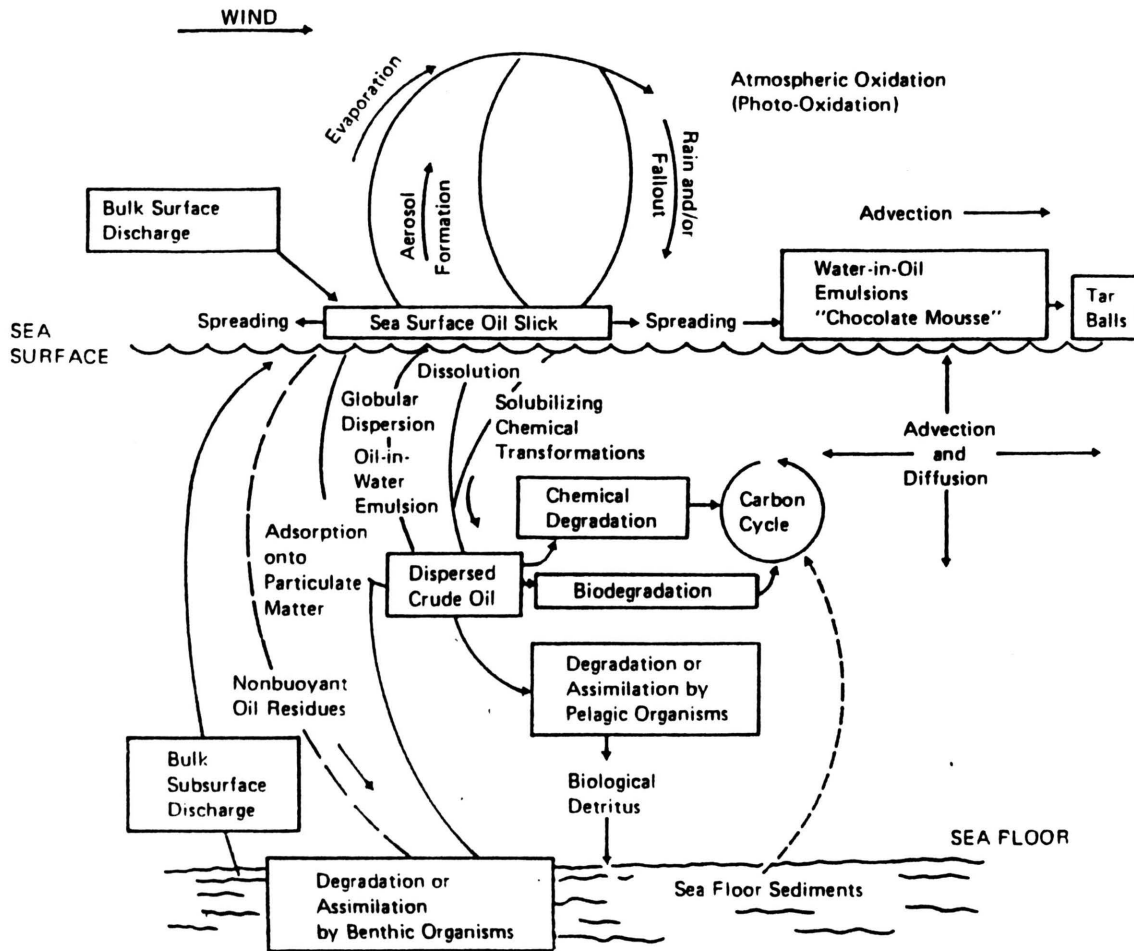


Figure 2. Schematic of Physical and Biological Processes Affecting Oil in the Marine Environment (Burwood and Speers 1974)

There have been numerous studies regarding the significance of each of these processes on the fate and effect of oil once it enters the marine environment. Meyers and Quinn (1973), suggested that as hydrocarbons become more soluble with increasing temperature and/or interaction with other dissolved organic matter, correspondingly smaller amounts of hydrocarbons are available to associate with suspended mineral particles in seawater. The extent of this association decreases with increasing solubility of the hydrocarbons. Meyers and Oas (1978), found that there was a linear association between suspended sediments and increasing n-alkane concentration and carbon chain length. However, this trend was not true for polycyclic aromatic hydrocarbons (PAH's), the degree of association of PAH's with mineral particles was lower in comparison than for n-alkanes.

The physical process of evaporation contributes significantly to changes in the chemical composition and physical properties of oil in the environment. Jordan and Payne (1980) found that evaporation alone can be responsible for the loss of from one- to two-thirds of an oil spill mass in a period of a few hours or a day. Low molecular weight components of oil are the most volatile and therefore will be subject to evaporation most easily. However, higher molecular weight components will not be readily evaporated. It is these compounds, some of which carry a high degree of

toxicity for marine biota, that will remain longest in the environment.

The solubility (dissolution) of hydrocarbons in seawater is of particular concern because of the potential toxicity to marine organisms. The more soluble components of crude oil are the low molecular weight aromatics such as benzene, toluene, and the xylenes. These low molecular weight aromatics, however, have been shown to be some of the most toxic as well (NRC 1985).

Emulsion formation is an important physical process, as its formation aids in photooxidation of oil, which in turn alters the chemical fate and biological effects of oil in water. It has been shown that heavier molecular weight oils will form emulsions more easily than light distillates and light diesel fuels (Bocard and Gatellier 1981). By increasing the exposure of oil to photooxidation through emulsification, it has been shown that there is an increased formation of soluble organics/carbon, leading to an increase in the toxicity of the petroleum to various organisms and a decrease in primary productivity (NRC 1985).

All of these physical processes inherently affect the toxicity of oil in the environment, but it is the biodegradation of oil that is believed to be the most effective mechanism for the removal of petroleum from the environment. This is particularly true for the nonvolatile components of oil. There are two distinct pathways for the biological degradation of petroleum. One pathway is through

bacterial degradation, while the other is by the uptake and subsequent metabolic processes in eukaryotic invertebrate and vertebrate systems (NRC 1985). Since dissolution, emulsification and sedimentation, have been shown to intensify potential toxicity, collateral biological processes could essentially increase the exposure of epibenthos and benthos to lethal and sublethal effects. In a subtropical marine environment, where temperatures are elevated and metabolic rates are increased, the damage to marine biota may be both acutely enhanced and exposed for long terms.

Petroleum hydrocarbons consist primarily of alkanes, cycloalkanes, and aromatic compounds. Weathering of these compounds occurs simultaneously, however differential degradation or dissolution causes a change in the hydrocarbon profile over time. Petroleum hydrocarbon alteration from weathering can be summarized as follows: loss of low boiling ($<nC_{20}$) hydrocarbons through evaporation, loss of low boiling ($<nC_{15}$) hydrocarbons through dissolution, microbial degradation leading to normal alkane to isoprenoid (pristane and phytane) ratio decreases from much greater than 1 in fresh oil to much less than 1 in degraded oil, biodegradation of the n-alkanes with a proportional increase in the percent of the unresolved complex mixture (UCM) and polycyclic aromatic hydrocarbons (PAH's), followed by a subsequent shift in the relative abundance within the UCM towards higher molecular weight

compounds (Farrington 1980, Van Vleet et al. 1984, NRC 1985, Pierce et al. 1986, Burns et al. 1993).

The oil spilled near Tampa Bay, Florida by the *Bouchard 155* consisted of Bunker C fuel oil, a viscous, heavy molecular weight, high boiling fraction of crude oil. Bunker C fuel oil is of moderate toxicity and is extremely persistent when spilled into the environment, particularly when spilled into protected, poorly flushed ecosystems such as mangrove forests. Due to its high viscosity and high molecular weight, it is among the most difficult oils to clean up or recover and is relatively resistant to microbial degradation.

Additional Oil Spill Studies

Several spills of Bunker C fuel oil have occurred in the marine environment, however most of these spills took place in temperate or cold water climates. These include the *Pennant* spill (0.3 million liters) in Narragansett Bay, Rhode Island (MPB 1973), the *Arrow* spill (1.3 million liters) in Chedabucto Bay, Nova Scotia (Michalik 1971, Scarratt 1972, Vandermuelen 1977, Vandermuelen et al. 1977, Keizer et al. 1978), the *Algol* spill (0.6 million liters) in Buzzards Bay, Massachusetts (NOAA 1977), the *Argo Merchant* (28.9 million liters) in Nantucket Shoals, Massachusetts (NOAA 1977), the *Metula* spill (2.1 million liters of Bunker C spilled with 53 million liters of crude oil) in the Strait

of Magellan (Hann 1977), the San Francisco Bay spill (3.2 million liters; Chan 1977), the *Sansinena* spill in outer Los Angeles Harbor (5.1 million liters; Soule et al. 1978), the *Kurdistan* spill (7.4 million liters) between Nova Scotia and Newfoundland (Vandermuelen 1985), the *Blue Magpie* spill (0.3 million liters) in Yaquina Bay, Oregon (Kemp et al. 1986), and the *Nestucca* spill (0.9 million liters) off the Washington coast (Strand et al. 1992). No reports have been found of major spills of Bunker C fuel oil in tropical (regions parallel to and within 23.5 degrees of each side of the equator) or subtropical (regions bordering the tropics) environments prior to the *Bouchard 155* spill.

In studies following several of the spills in cold water environments, acute toxicity and lethal effects of Bunker C fuel oil were observed. Effects on the soft-shell clam, *Mya arenaria*, following the *Arrow* spill included lowered total numbers, fewer mature adults, lower tissue and shell growth rates, lower carbon assimilation rates, and poor recovery (Gilfillan and Vandermuelen 1978). Following the *Sansinena* spill, Soule and Oguri (1978) observed reduced phytoplankton productivity and reduced benthic populations. Kemp et al. (1986) observed reduced populations and lowered recruitment of the amphipod, *Rhepoxnius abronius* following the *Blue Magpie* spill. In a laboratory study on the toxicity of Bunker C fuel oil to cod eggs and larvae, Kuhnhold (1978) observed reduced survival, retarded growth, loss of buoyancy, abnormal development and lower heartbeat

rates. In addition, Fry and Lowenstine (1985) found that seabirds, Ptychramphus aleuticus and Uria aalge, exhibited hepatocellular dissociation and hemosiderosis, renal tubular necrosis and hemolytic anemia, when exposed to Bunker C fuel oil.

One of the most studied oil spills in a tropical marine environment was the Bahia Las Minas refinery spill in Galeta, Panama. In 1986, a major spill occurred devastating many coastal environments of Panama (Garrity et al. 1993). The spill occurred at a petroleum refinery where approximately 38.3 million liters of medium weight crude oil drained from a ruptured storage tank near the Smithsonian Tropical Research Institute. Several kilometers of mangrove islands (similar to the mangroves of Eleanor Island), sea grass beds, and shallow coral reefs were severely oiled. While the oil of this spill was Venezuelan and Mexican Isthmian light crude and not Bunker C fuel oil, there can be information gained from that work and applied to the *Bouchard 155* spill, as both the Bunker C and the spilled refinery oil share some of the same chemical composition. Comparisons to the Bahia Las Minas spill will be made in the Discussion section of this thesis.

2. RESEARCH OBJECTIVES

The intent of this research was to examine temporal changes in the hydrocarbon profile of Bunker C fuel oil found in oil masses, sediments, and on mangrove prop roots following the *Bouchard 155* spill. The objectives of this research were as follows:

- To collect sediment and oil mass samples for a period of one year, biweekly for the first six months and monthly for the last six months, from four sites on Eleanor Island (Figure 3). This island was heavily impacted by the Bunker C fuel oil when it entered the bay through John's Pass.
- To analyze these samples for hydrocarbons by high resolution gas chromatography and combined gas chromatography-mass spectrometry in order to assess the changes in chemical properties of the Bunker C oil over the one year period. This allowed the investigation of the persistence and biodegradation of the oil in this environment. In addition, specific toxic components were targeted in order to examine changes in the potential toxicity of the residual oil with time.

Eleanor Island

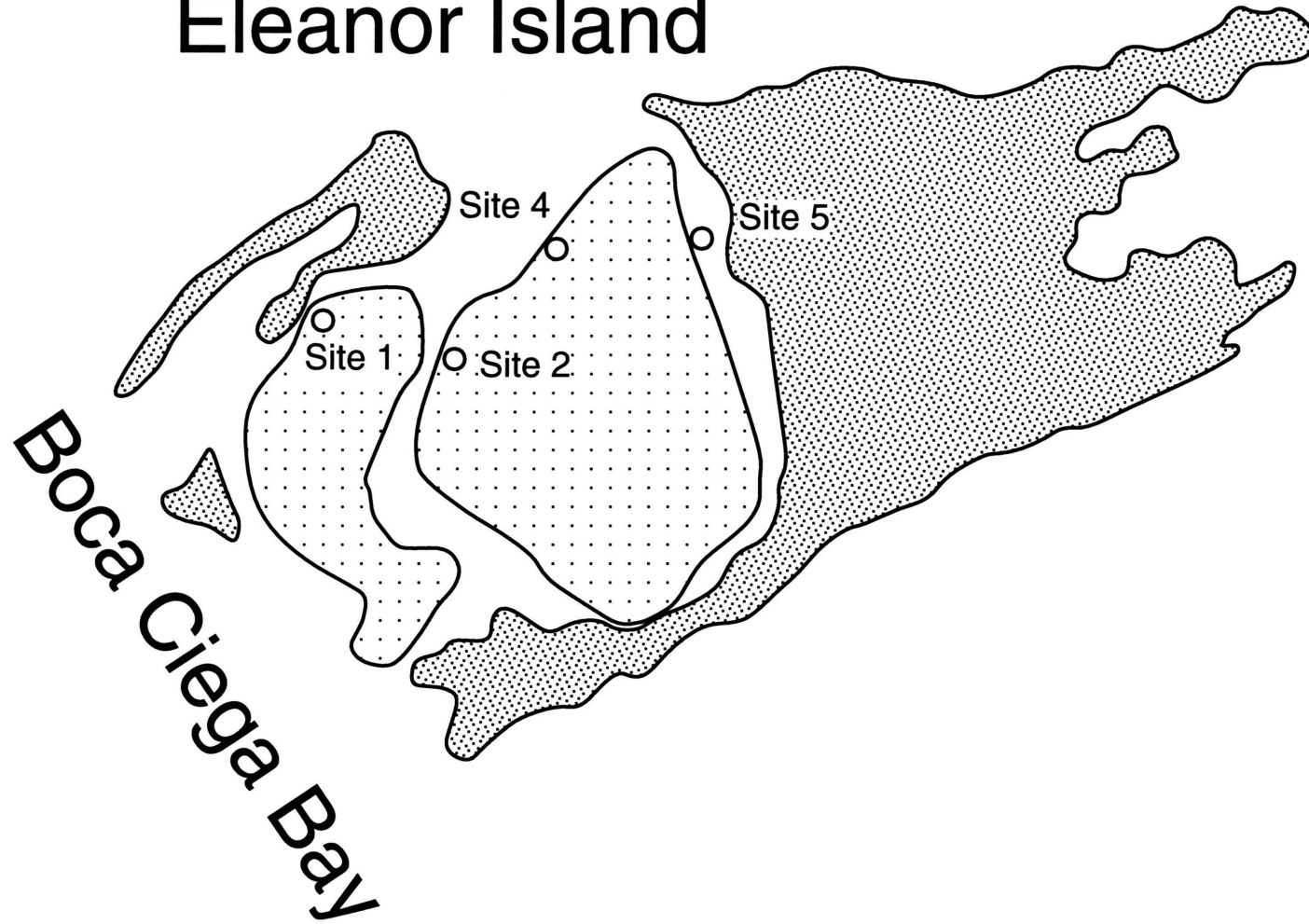


Figure 3. Eleanor Island Sampling Station Sites

- To collect visibly oiled mangrove prop roots and non-oiled mangrove prop roots (1 each per each site per sampling period) to investigate chemical changes in the oil associated with the exposed mangroves.

2. METHODS

Surface sediments (approximately top 5 cm) were collected with a metal trowel and cleaned between collections with hexane and stored in sterilized glass jars, from stations 1, 2 and 5 (Station 3 was deleted early in project as it was in close proximity to stations 2 and 4, and was assumed to be similar to these other stations). Bulk oil masses (approximately 5 g) were also collected and stored as above, from the sediment surface at Station 4. Prop root samples, both oiled and non-oiled, (approximately 4-5 cm in length) were collected from all stations. Samples were collected with non-petroleum based gloves and stored as above, beginning on September 24, 1993 (five weeks after the spill), and continued biweekly for the first six months and monthly for the last six months of the study. Station 5 was used as a reference station as it is located on the easternmost side of the island and was impacted the least.

Approximately 100 g (wet weight) of each sediment sample was extracted by refluxing for two hours with a five-fold volume excess of 2:1 (v/v) dichloromethane:methanol. Approximately 2-5 g were also removed for determination of sediment moisture content. Internal standards (5 α -androstane and o-terphenyl) were added to each sample prior

to extraction for quantitative hydrocarbon analysis. Following extraction, the organic phase was partitioned with water and separated. The aqueous phase was re-extracted twice more with hexane. The combined organic phase was then evaporated to near dryness, and redissolved in 1 ml hexane. The extracts were separated into F1 (aliphatics/saturated) and F2 (aromatics/unsaturated) fractions by silica gel-alumina column chromatography, and eluted with 25 ml hexane for the F1 fraction and 25 ml 1:1 (v/v) hexane:toluene for the F2 fraction (Caripol 1980). Each fraction was evaporated to near dryness and redissolved in 1 ml of hexane.

Each bulk oil mass sample (approximately 0.5 g) from Station 4, was dissolved in 1 ml of hexane in the presence of the internal standards and separated by column chromatography as above. Oiled prop root samples (approximately 2.5 cm) were saponified in a capped 15 cm culture tube by extracting with 10 ml of 70:30 (v/v) 0.5N KOH/methanol solution: toluene in the presence of the internal standards (fifteen percent water was added to prevent transesterification). The tubes were flushed with nitrogen, capped, and placed in a 100° water bath for 30 minutes. After cooling, the organic phase was isolated and separated into F1 and F2 fractions by column chromatography as above. Non-oiled prop roots were also analyzed in this manner to investigate natural background hydrocarbons.

A sample of the Bunker C fuel oil taken from the *Bouchard 155* by NOAA was similarly analyzed after separating into F1 and F2 fractions, for matching the alkane characteristics of the Bunker C fuel oil with those found in the samples.

All hydrocarbon fractions were analyzed by high resolution gas chromatography (GC) using a splitless injection capillary gas-liquid chromatograph. A Shimadzu GC-14A equipped with a 25 m x 0.2 mm (i.d.) DB-5 fused silica column (J.W. Scientific) and flame ionization detector was used with hydrogen as the carrier gas. Oven temperature was programmed from 80°C to 280°C at 4°C min⁻¹ and held at 280°C for ten minutes for sediment and oil mass samples. For prop root samples and the original Bunker C fuel oil, the oven temperature was programmed from 80°C to 280°C at 6°C min⁻¹ and held at 280°C for fifteen minutes. The peaks in the F1 fraction were identified by comparing peak retention times with known alkane standards or by co-injection with authentic standards. Hydrocarbon fractions were quantitated by comparison of the areas (corrected for individual response factors) with the area of the internal standard. Selected F2 fractions were analyzed by combined gas chromatography-mass spectrometry (GCMS) for qualitative and quantitative identification of individual PAH's. Samples were analyzed by electron impact ionization (70 eV) using a Finnigan INCOS-50 GCMS system interfaced with a Hewlett Packard 5890 gas chromatograph. Gas

chromatographic conditions were the same as those used above, however helium was used as the carrier gas. The mass spectrometer was scanned from mass 40-500 in 0.5 sec. All mass spectral data were compared to spectra produced by authentic standards and by comparison to previously published spectra.

4. RESULTS

Aliphatic Hydrocarbons

Bunker C Fuel Oil

A sample of Bunker C fuel oil was obtained from the holding tanks of the *Bouchard 155* and analyzed for baseline data to be used in identifying chemical changes over the year long monitoring project. Normal-alkanes (n-alkanes) in the F1 fraction were distributed from nC₁₃-nC₃₃ (Figure 4-A). Values of the percent composition of the individual alkanes relative to the total n-alkanes, ranged from $\cong 1\%$ to $\cong 15\%$ (Figure 4-B). The individual percent compositions of n-alkanes from nC₁₄-nC₁₉ (including the isoprenoids pristane and phytane) were approximately 1% of the total composition of these n-alkanes in the Bunker C fuel oil. From nC₂₀-nC₃₁, the percentages increased consistently with a maximum of 15% at nC₃₁. The percent composition of n-alkanes then steadily declined for nC₃₂-nC₃₃. The F1 (aliphatic) hydrocarbon concentration represented 86% of the total hydrocarbons (F1 + F2) of the Bunker C fuel oil. An unresolved complex mixture (UCM) hump was present in the nC₂₅-nC₃₁ range. A determination of nC₁₇/pristane and nC₁₈/phytane ratios were

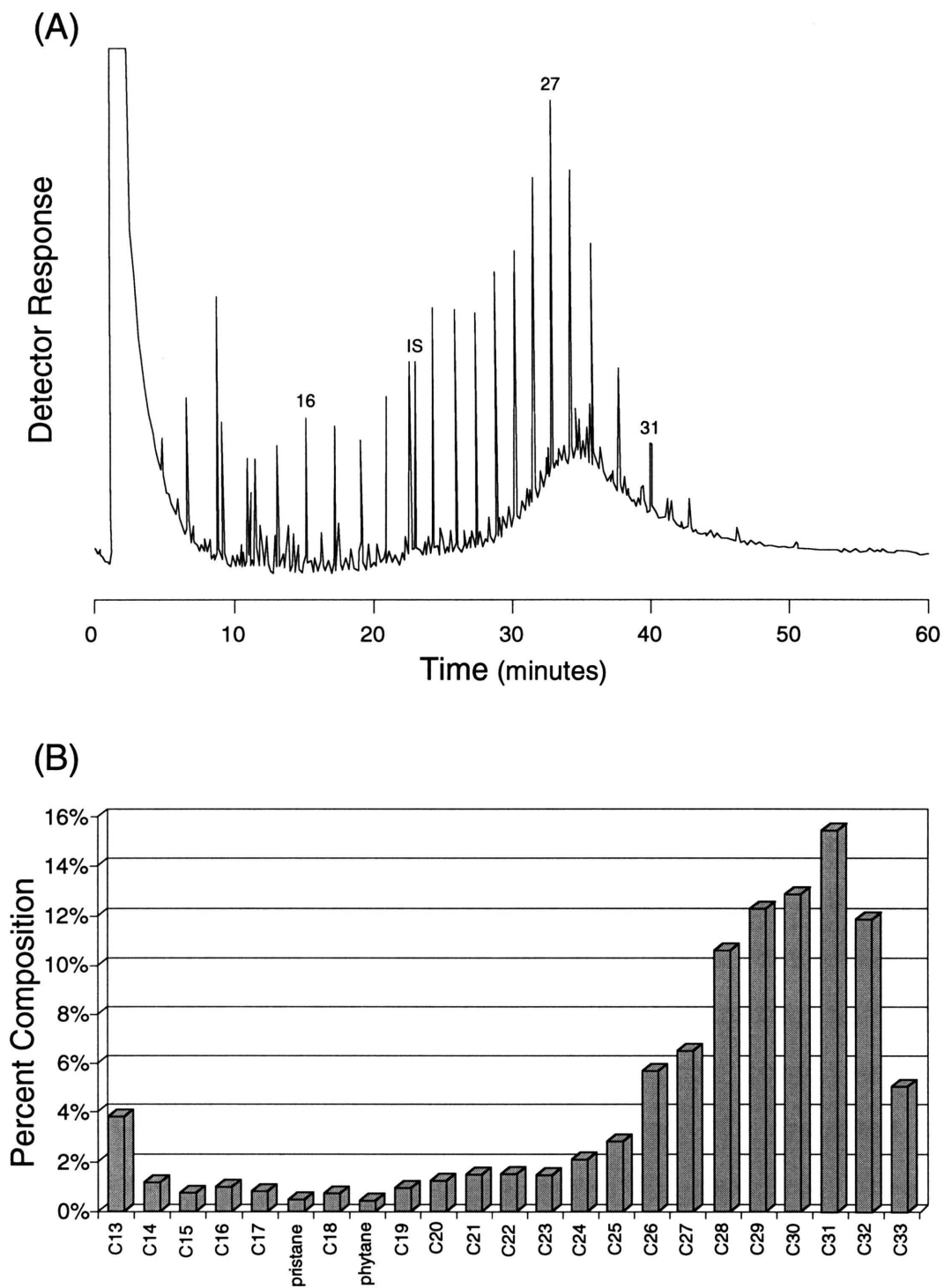


Figure 4. Bunker C Fuel Oil: A. Chromatogram, B. Percent Composition

ascertained to monitor the degradation of n-alkanes over time with respect to the less easily degraded isoprenoids. The nC_{17} /pristane ratio was 1.9 and the nC_{18} /phytane ratio was 1.7 in the intact Bunker C fuel oil. Concentrations of odd-carbon compounds equaled those of the even-carbons with an odd to even preference (OEP) of 1.0 (total abundance of odd-carbon n-alkanes from nC_{14} - nC_{33} /total abundance of even-carbon n-alkanes from nC_{14} - nC_{33}).

Station 4 oil mass samples

The oil sample collected on September 24, 1993, (six weeks after the spill), showed n-alkanes distributed from nC_{15} - nC_{32} (Figure 5-A). There was a slight shift towards higher molecular weight hydrocarbons in this sample from the Bunker C profile, with a maximum at nC_{32} (Figure 5-B). The nC_{17} /pristane ratio increased to 2.2 and the nC_{18} /phytane ratio increased to 2.6. The OEP remained at 1.0, although no concentrations of nC_{13-14} or nC_{33} were detected. The relative area of the UCM increased, beginning now at nC_{21} and ending at nC_{32} . Aliphatic hydrocarbons comprised 15% of the total (Table 1). A comparison of F1 resolved to F1 unresolved areas [$F1 \text{ resolved area} / (F1 \text{ resolved area} + F1 \text{ unresolved area})$] showed that the resolved portion of the oil was 26% of the total F1 area.

Samples from October 8, through December 17, 1994, showed similar n-alkane percent composition characteristics to the

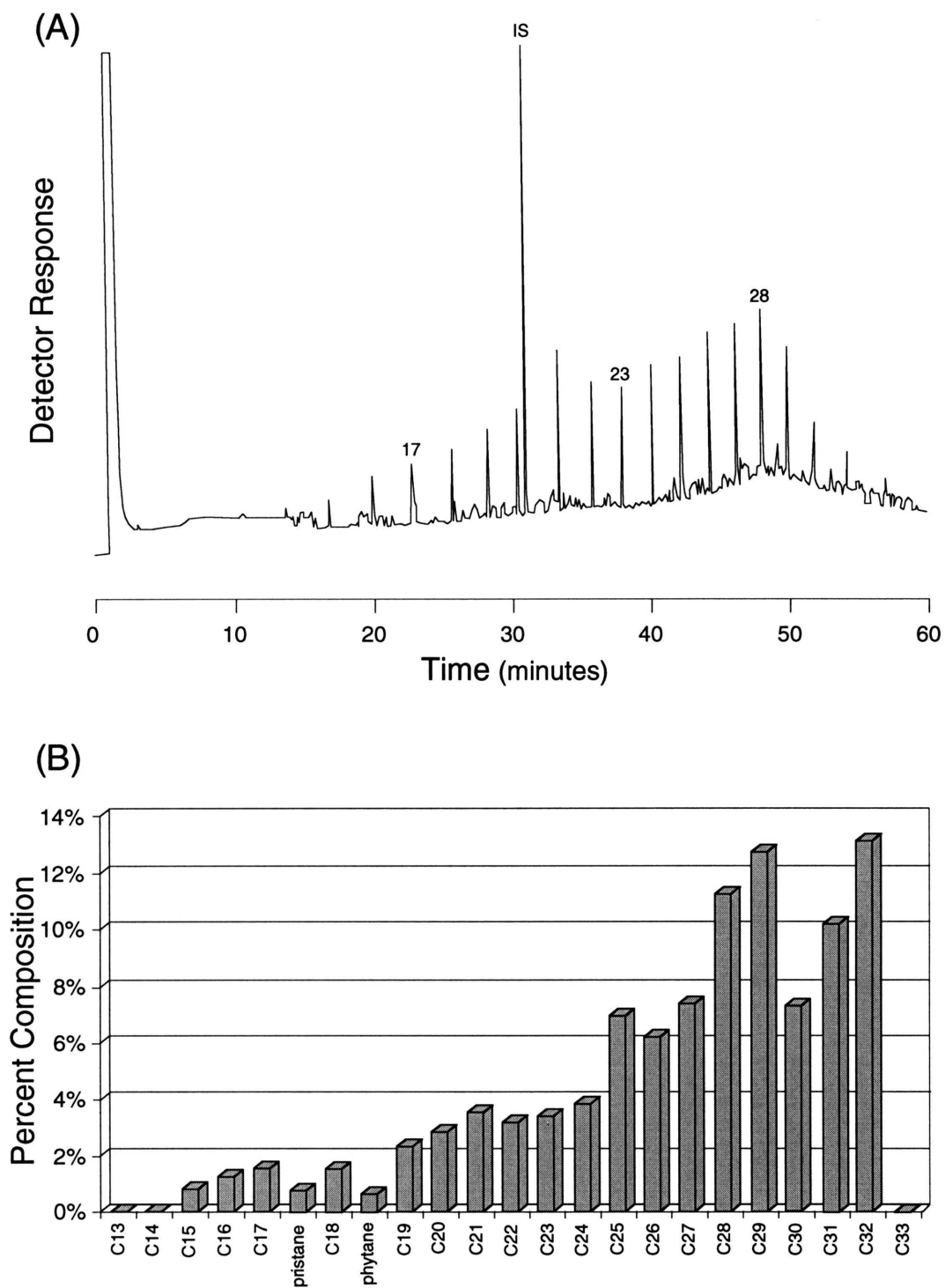


Figure 5. September 1993, Station 4 Oil Mass Sample:
A. Chromatogram, B. Percent Composition

Table 1. Station 4 Oil Mass Sample Characteristics.

Sample Date	N-alkane Range	Alkane Maxima	UCM Range Dominant Minor	nC ₁₇ /Pr ^a	nC ₁₈ /Phy ^b	%F1 ^c	%R _{F1} ^d	OEP ^e	Pr/Phy
09/24/93	nC ₁₅ -nC ₃₂	nC ₃₂	nC ₂₁ -nC ₃₂	2.2	2.6	15%	26%	1.0	1.2
10/08/93	nC ₁₅ -nC ₃₂	nC ₂₉	nC ₂₄ -nC ₃₂	1.5	1.6	38%	17%	1.2	1.2
10/24/93	nC ₁₅ -nC ₃₂	nC ₃₀	nC ₁₆ -nC ₂₄ nC ₂₅ -nC ₃₂	1.6	1.6	34%	18%	0.9	1.0
11/05/93	nC ₁₅ -nC ₃₂	nC ₃₁	nC ₂₅ -nC ₃₂	1.1	1.9	19%	25%	1.0	1.8
11/19/93	nC ₁₅ -nC ₃₂	nC ₂₉	nC ₁₆ -nC ₂₃ nC ₂₄ -nC ₃₂	1.8	1.7	56%	45%	1.1	1.0
12/03/93	nC ₁₅ -nC ₃₂	nC ₂₈	nC ₁₈ -nC ₃₂	1.9	1.9	54%	27%	1.0	1.0
12/17/93	nC ₁₅ -nC ₃₂	nC ₃₁	nC ₁₆ -nC ₂₅ nC ₂₃ -nC ₃₂	1.4	1.3	82%	18%	1.2	1.0
01/14/94	nC ₁₅ -nC ₃₂	nC ₃₂	nC ₂₀ -nC ₃₂	2.0	2.0	86%	17%	0.9	1.1
01/28/94	nC ₁₅ -nC ₃₂	nC ₁₉	nC ₁₅ -nC ₂₅ nC ₂₆ -nC ₃₂	0.7	0.8	56%	12%	1.1	1.1
02/25/94	nC ₁₅ -nC ₃₂	nC ₂₉	nC ₂₄ -nC ₃₂	1.5	1.4	79%	19%	1.1	1.1
03/11/94	nC ₁₅ -nC ₃₂	nC ₂₇	nC ₁₆ -nC ₂₃ nC ₂₄ -nC ₃₂	1.6	1.7	75%	20%	1.1	1.0
04/15/94	nC ₁₅ -nC ₃₂	nC ₂₈	nC ₁₆ -nC ₂₄ nC ₂₅ -nC ₃₂	1.4	1.4	90%	21%	1.1	1.0
05/13/94	nC ₁₅ -nC ₃₂	Pr; Phy	nC ₁₆ -nC ₂₄ nC ₂₅ -nC ₃₂	0.2	0.2	68%	4%	1.1	1.0
06/10/94	nC ₁₅ -nC ₃₂	nC ₂₁	nC ₁₉ -nC ₃₂	2.2	2.3	75%	27%	1.0	1.0
07/12/94	nC ₁₅ -nC ₃₂	nC ₂₀	nC ₁₅ -nC ₂₅ nC ₂₆ -nC ₃₂	0.5	0.6	28%	7%	1.0	0.6
09/06/94	nC ₁₅ -nC ₃₂	Pr; Phy	nC ₁₇ -nC ₂₄ nC ₂₅ -nC ₃₂	0.1	0.1	49%	2%	1.6	1.0

^a pristane; ^b phytane; ^c % (F1) hydrocarbon concentration (F1 + F2);
^d %F1 resolved area / (F1 resolved + unresolved); ^e odd-even predominance.

previous sample. The small shift in composition to higher molecular weight compounds continued with the n-alkane maximum varying from nC₂₈ to nC₃₂. The UCM remained at approximately the nC₂₁-nC₃₂ alkane range. However, the F1 resolved to unresolved areas fluctuated from 17% to 45%. The nC₁₇/pristane and nC₁₈/phytane ratios also varied from 1.5 to 1.9. The OEP remained fairly constant at 0.9 to 1.2 and the F1 hydrocarbon concentration ranged from 19% to 54% of the total. There was a minor secondary UCM hump developing in each of the October 24 and November 19, 1993 samples that were not present in the other samples.

Sample profiles throughout January to April were similar to previous months with the following minor exception. The January 28, March 11, and April 13, samples also exhibited minor secondary UCM humps. The OEP ratio remained at approximately 1.0, while total F1 hydrocarbon concentration fluctuated from 75% to 90%. The F1 resolved percentage varied from 12% on January 28, to 21% on April 15. The nC₁₇/pristane and nC₁₈/phytane ratios ranged from 0.7 to 2.0, and 0.8 to 2.0 respectively. The F1 hydrocarbons comprised from 56% to 90% of the total. The OEP was constant at approximately 1.0 for these samples.

The May 13, 1994 sample was also similar to the above profiles with some changes in the individual characteristics. The alkane maxima were pristane and phytane comprising approximately 15% each of the total n-alkane (plus pristane and phytane) composition for this

sample. Correspondingly the nC_{17} /pristane and nC_{18} /phytane ratios declined dramatically to 0.2 each. The F1% of the total was similar to the previous samples at 68%, but the F1 resolved area decreased to 4%.

By June 10, 1994, the n-alkane range had not changed, however the UCM at the nC_{17} - nC_{23} range became somewhat more dominant than the UCM at the nC_{24} - nC_{32} range (Figure 6-A). The F1 hydrocarbon concentration was 75% of the total and the F1 resolved area was 27% of the total F1 area. The OEP was 1.0, and the n-alkane maximum was nC_{21} (Figure 6-B). The nC_{17} /pristane and nC_{18} /phytane ratios increased to 2.2 and 2.3 respectively.

The July 12 sample was very similar in characteristics to the January 28, 1994, sample. There was a minor UCM around the nC_{26} - nC_{32} range, and a major UCM at nC_{15} - nC_{25} . The n-alkane maximum was nC_{20} . The nC_{17} /pristane and nC_{18} /phytane ratios decreased to 0.5 and 0.6 respectively.

The final sample from September 6, 1994, showed many similarities to the May 13 sample. The range of measurable n-alkanes was nC_{15} - nC_{28} (Figure 7-A). The concentrations of nC_{29} - nC_{32} were undetectable as these compounds were essentially degraded and the degradation products incorporated into the UCM. The secondary UCM, now from nC_{16} - nC_{23} , was significantly larger than the original from nC_{24} - nC_{28} . The OEP increased to 1.6 and the alkane maxima was at pristane and phytane (Figure 7-B). The total F1 hydrocarbon concentration was 49% of the total. The F1

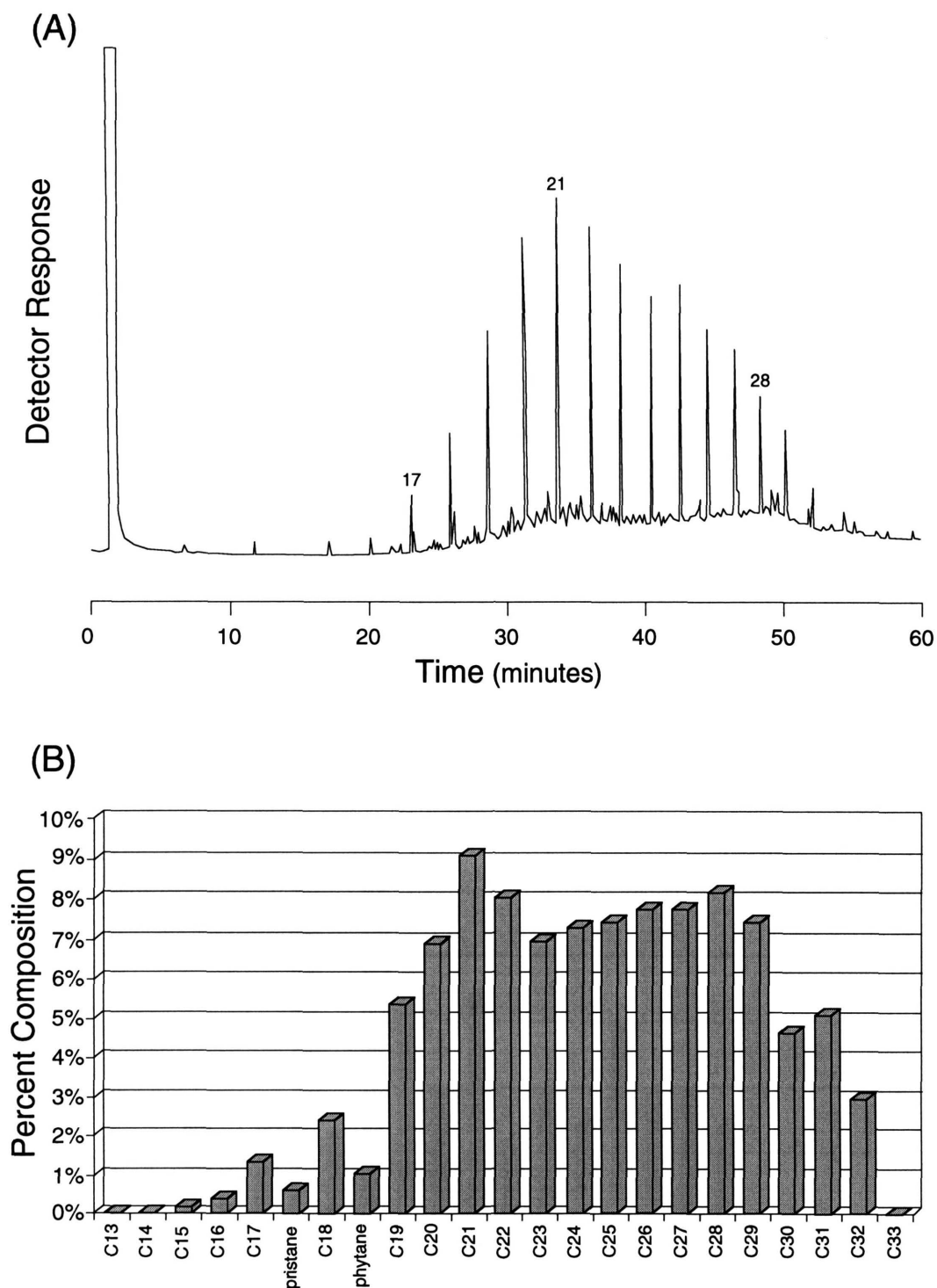


Figure 6. June 1994, Station 4 Oil Mass Sample:
A. Chromatogram, B. Percent Composition

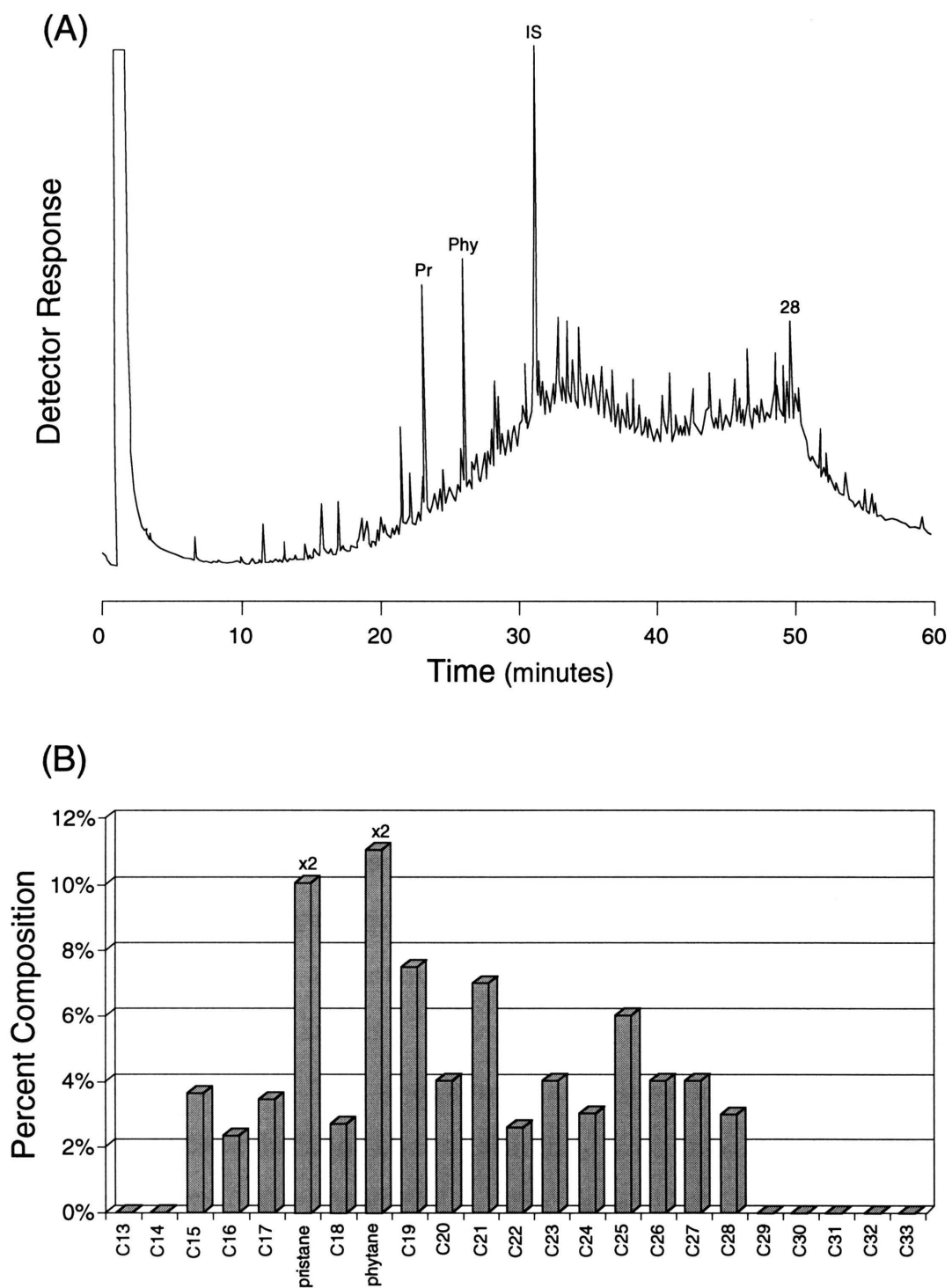


Figure 7. September 1994, Station 4 Oil Mass Sample:
A. Chromatogram, B. Percent Composition

resolved area decreased to 2%. The nC_{17} /pristane and nC_{18} /phytane ratios both declined from the previous date to 0.1 each.

Sediments

The n-alkane range in the first sediment sample from Station 1 collected on September 24, 1993 was from nC_{17} - nC_{32} (Figure 8-A). There were two UCM humps in this sample, the first and smaller UCM began at nC_{18} and then merged into an even larger UCM beginning at nC_{25} and extending through nC_{32} . The n-alkane maximum was nC_{29} which composed 16% of the total n-alkane composition (Figure 8-B). The OEP was 1.3. The total hydrocarbon concentration was 47.5 $\mu\text{g/g}$ dry sediment, and the F1 hydrocarbons comprised 80% of the total (Table 2). The nC_{17} /pristane ratio was 2.6 while the nC_{18} /phytane ratio was comparatively low at 0.2. The F1 resolved area comprised 8% of the total F1 area.

The Station 1 October through December 1993, samples consistently changed several of the compositional characteristics. The n-alkane range and the number of UCM's did not alter during these months, but the location of the dominant UCM did change. The area of dominance during October was in the nC_{15} - nC_{24} range, while for November it was nC_{24} - nC_{32} . By December both UCM's were equivalent in strength (Figure 9-A). The nC_{17} /pristane ratio was essentially the same for October and December at 1.0, but

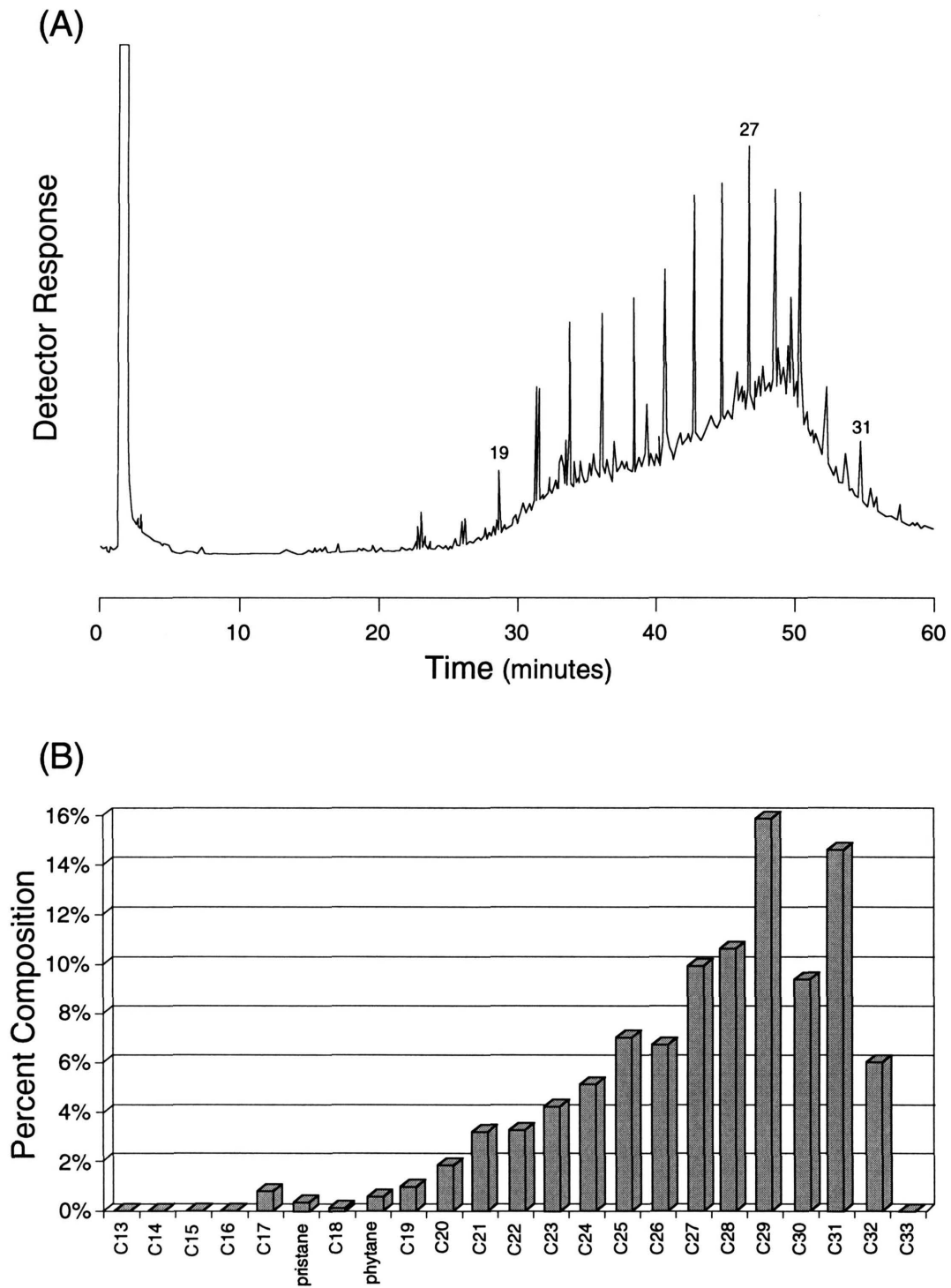


Figure 8. September 1993, Station 1 Sediment Sample:
 A. Chromatogram, B. Percent Composition

Table 2. Station 1 Sediment Sample Characteristics.

Sample Date	N-alkane Range	Alkane Maxima	UCM Range Dominant Minor	nC ₁₇ /Pr ^a	nC ₁₈ /Phy ^b	%F1 ^c	%R _{F1} ^d	OEP ^e	Pr/Phy	ΣHC ^f μg/g
09/24/93	nC ₁₇ -nC ₃₂	nC ₂₉	nC ₁₉ -nC ₂₃ nC ₂₄ -nC ₃₂	2.6	0.2	80%	8%	1.3	0.5	47.5
10/24/93	nC ₁₅ -nC ₃₁	nC ₁₇	nC ₁₅ -nC ₂₄ nC ₂₄ -nC ₃₂	12.2	0.2	80%	3%	2.0	1.2	48.6
11/19/93	nC ₁₄ -nC ₃₁	nC ₂₇	nC ₁₈ -nC ₂₃ nC ₂₄ -nC ₃₂	1.1	0.3	85%	3%	1.5	0.8	48.9
12/17/93	nC ₁₄ -nC ₃₁	nC ₃₀	nC ₁₅ -nC ₂₃ nC ₂₄ -nC ₃₂	1.0	0.5	90%	3%	1.0	1.0	33.6
01/28/94	nC ₁₅ -nC ₃₁	nC ₂₁	nC ₂₃ -nC ₃₂	3.5	-	60%	19%	4.6	-	3.6
02/25/94	nC ₁₅ -nC ₃₂	nC ₂₉	nC ₂₃ -nC ₃₂	2.0	-	72%	8%	4.2	-	7.4
03/11/94	nC ₁₆ -nC ₃₀	nC ₂₁ ;nC ₃₀	nC ₁₉ -nC ₂₂ nC ₂₃ -nC ₃₂	0.3	-	70%	6%	2.1	-	34.1
04/15/94	nC ₁₅ -nC ₃₀	nC ₃₀	nC ₁₇ -nC ₂₃ nC ₂₄ -nC ₃₂	4.1	-	59%	3%	0.8	-	31.5
05/13/94	nC ₁₅ -nC ₃₀	nC ₁₇	nC ₁₅ -nC ₂₃ nC ₂₄ -nC ₃₂	15.6	0.1	65%	4%	4.0	0.7	28.0
06/10/94	nC ₁₅ -nC ₂₉	nC ₂₉	nC ₂₃ -nC ₃₂	- ^g	-	81%	22%	23.6	-	29.2
07/12/94	nC ₁₅ -nC ₃₀	nC ₂₃	nC ₁₇ -nC ₂₃ nC ₂₄ -nC ₃₂	0.3	-	33%	8%	3.1	-	20.4
09/06/94	nC ₁₇ -nC ₃₀	Pr	nC ₁₅ -nC ₂₆ nC ₂₇ -nC ₃₂	<0.1	0.8	68%	4%	1.4	31.5	15.8

^apristane; ^bphytane; ^c%(F1) hydrocarbon concentration (F1 + F2);

^d%F1 resolved area/(F1 resolved + unresolved); ^eodd-even predominance;

^ftotal hydrocarbons/gram dry sediment; ^gnot calculated, insufficient data.

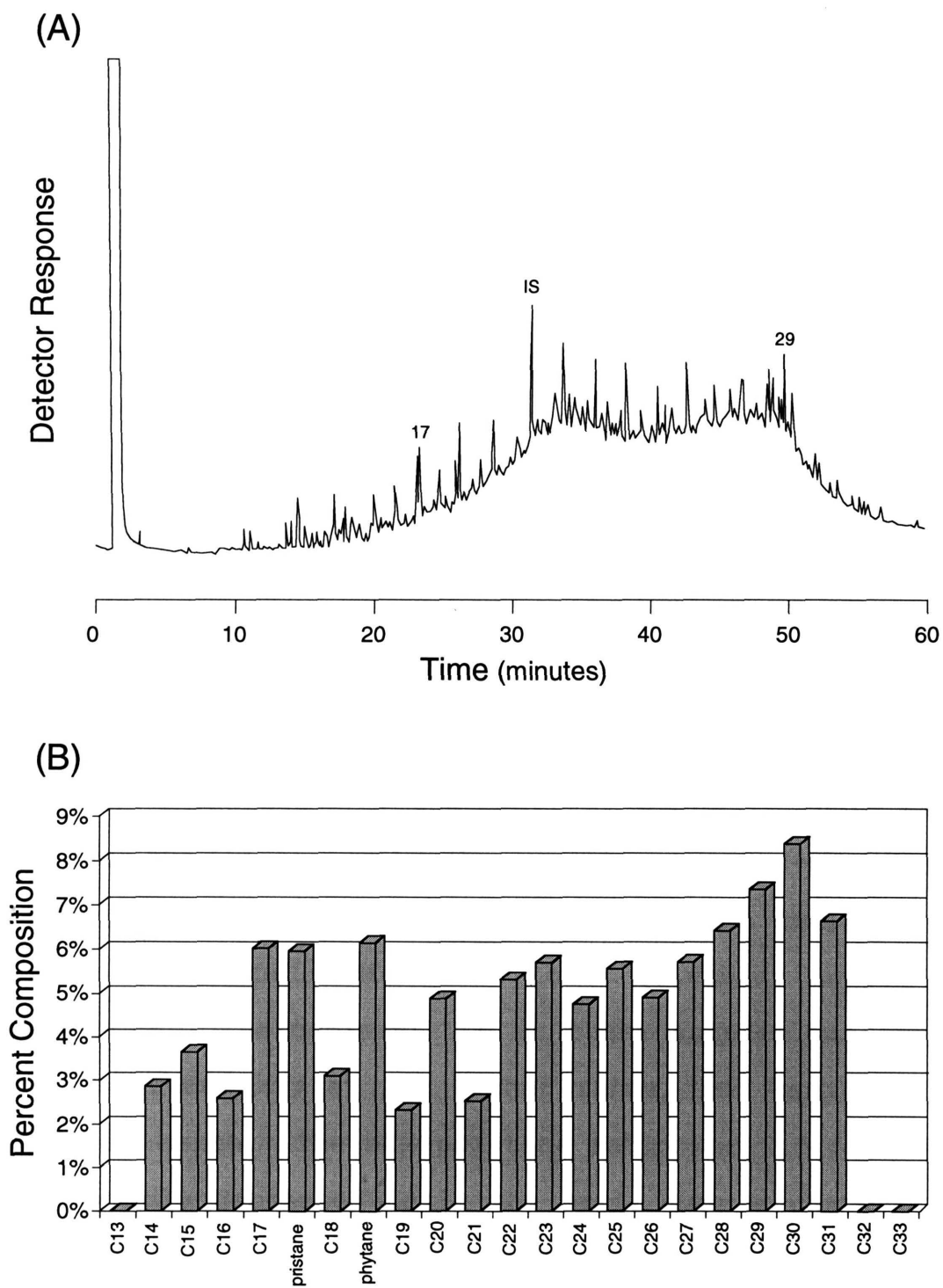


Figure 9. December 1993, Station 1 Sediment Sample:
 A. Chromatogram, B. Percent Composition

showed a marked increase during November to 12.2. The n-alkane maximum steadily increased from nC₁₇ in October to nC₃₀ in December (Figure 9-B). The nC₁₈/phytane ratios remained very low at 0.2 to 0.5 for these months. The F1 hydrocarbons comprised between 80-90% of the total. The F1 resolved area was consistent at 3% of the F1 area. The OEP for these samples decreased from 2.0 in October to 1.0 in December. The total hydrocarbon concentration ranged from 33.6 to 48.9 µg/g dry sediment.

The January to May 1994, samples were comparable to the previous dates (Table 2). However, there was also a loss of detectable amounts of selected alkanes throughout this period. There were similar losses of n-alkanes in the March through May samples, however there was a small amount of detectable phytane in the May sample. The n-alkane range remained unchanged from the previous samples. There was one UCM at the higher molecular weight range (nC₂₄-nC₃₂) for January and February, but for March, April, and May there was an additional UCM at the lower molecular weight range (nC₁₅-nC₂₃). The dominant UCM in these samples was the same for April and May at the higher range, and equal for both UCM's in March. The nC₁₇/pristane ratio was 3.5 for January and rapidly decreased until the April sample where it then increased to 4.1. By May, the ratio had increased to 15.6. There were no nC₁₈/phytane ratios made for January through April, because no phytane was detected during these sample times. The nC₁₈/phytane ratio for May was very low at only

0.1. The F1 hydrocarbons comprised between 59-72% of the total during these months. The OEP fluctuated from a low of 0.8 in April to a high of 4.6 in January. The n-alkane maximum also changed variably from nC_{17} - nC_{30} , with March having two maxima at nC_{21} and nC_{30} . The total hydrocarbon concentration ranged from 3.6 and 7.4 $\mu\text{g/g}$ dry sediment for January and February respectively, and increased to approximately 28.0-34.1 $\mu\text{g/g}$ dry sediment for March, April and May.

The June 10, 1994, Station 1 sample indicated a continued loss of many of the n-alkanes and the isoprenoid pristane (Figure 10-A). This sediment contained detectable amounts of nC_{15} , nC_{20-21} , nC_{23-25} , and nC_{29} only. The n-alkane maximum was nC_{29} and comprised 59% of the n-alkanes (Figure 10-B). The total hydrocarbon concentration in this sample was 29.2 $\mu\text{g/g}$ dry sediment, and the F1 hydrocarbon concentration was 89% of the total. The F1 resolved area was 11% of the total F1 area, and the OEP increased significantly from the previous date to 23.6. Since there were no detectable amounts of these compounds, ratios of nC_{17} /pristane and nC_{18} /phytane could not be calculated. There was a large UCM in the higher molecular weight compounds beginning at approximately nC_{23} and extending to the end of the Bunker C n-alkane range, nC_{33} .

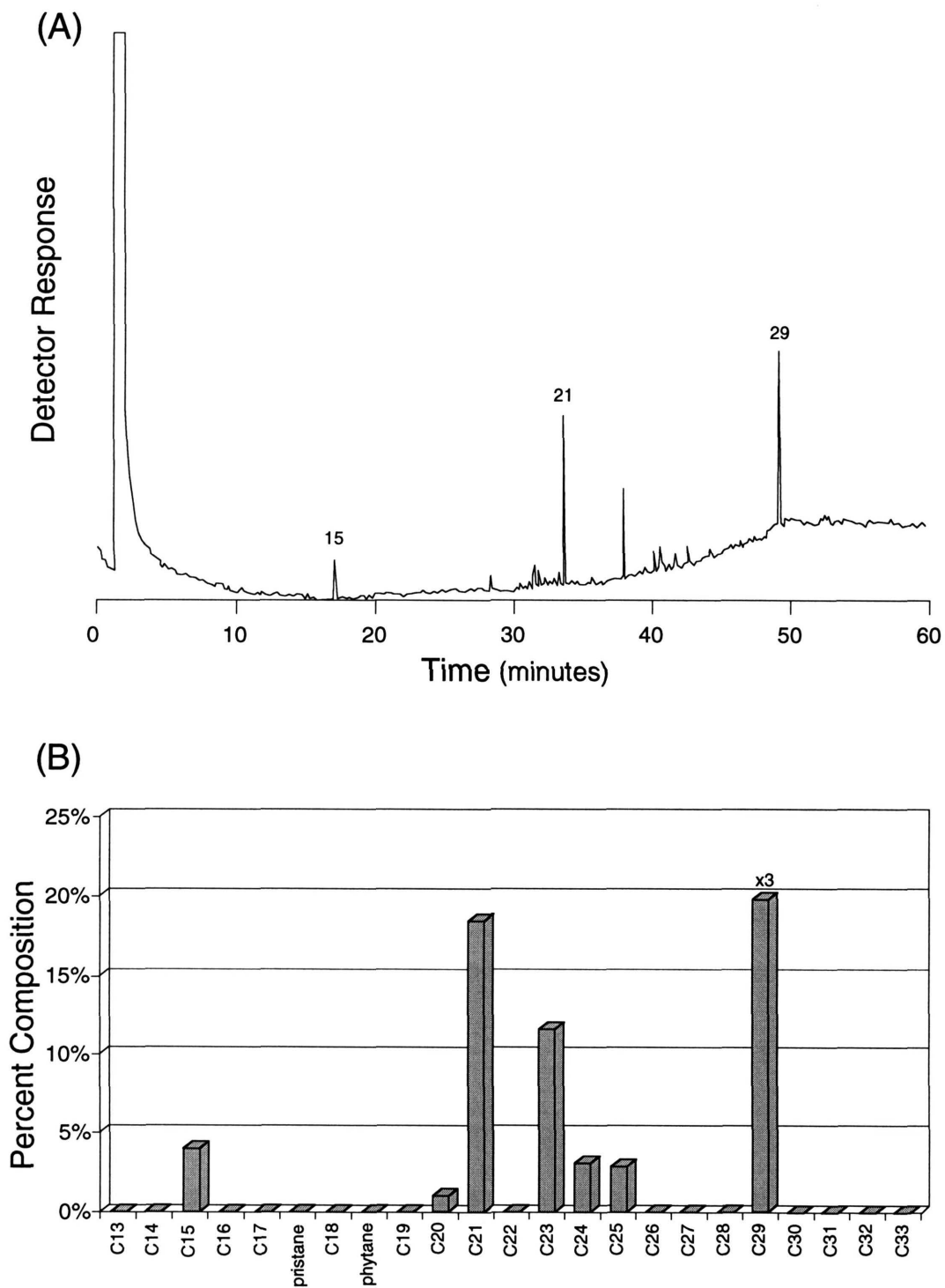


Figure 10. June 1994, Station 1 Sediment Sample:
A. Chromatogram, B. Percent Composition

The July 1994 sediment sample was comparable to the March and April sample dates. The nC_{17} /pristane ratio was 0.3, the same as the March sample. There was no detectable phytane. The n-alkane maximum was nC_{23} . The OEP was 3.1 and the F1 hydrocarbons represented 33% of the total. The F1 resolved area was 8% of the total area. The total hydrocarbon concentration was 20.4 $\mu\text{g/g}$ dry sediment. There were two UCM's in this sample, the dominant UCM at the nC_{24} - nC_{32} range, and the minor UCM at the nC_{17} - nC_{23} range.

In the last Station 1 sediment sample of the monitoring program (September 6, 1994), the n-alkanes ranged from nC_{17} - nC_{29} (Figure 11-A). There were two strong UCM's, with the major one occurring at the nC_{15} - nC_{25} range and the second at nC_{26} - nC_{33} . Pristane dominated in abundance composing 56% of the n-alkanes plus isoprenoids (Figure 11-B). The OEP declined from the previous sample to 1.4. There were 15.8 $\mu\text{g/g}$ dry sediment of total hydrocarbons. The F1 hydrocarbon concentration was 68% of the total, and the F1 resolved area represented only 4% of the total area. The nC_{17} /pristane and nC_{18} /phytane ratios were <0.1 and 0.8 respectively.

At Station 2, the September 24, 1993 sediment sample had similar characteristics to those found in Station 1 sediments of the same sampling time (Table 3). The hydrocarbon profiles were similar in range and composition of n-alkanes (Figures 12-A and 12-B). The OEP was the same at approximately 1.4, as was the location and dominance of

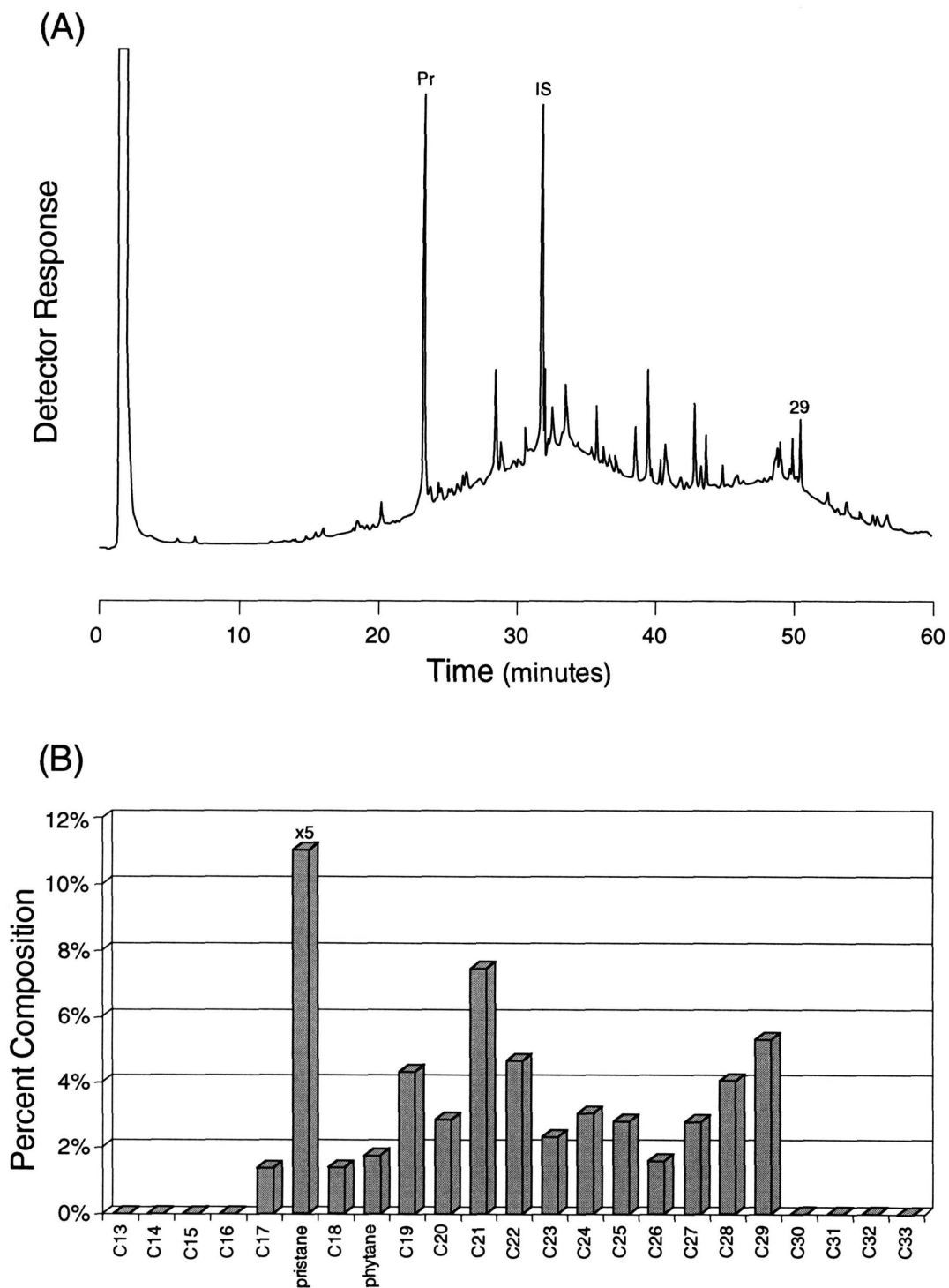


Figure 11. September 1994, Station 1 Sediment Sample:
A. Chromatogram, B. Percent Composition

Table 3. Station 2 Sediment Sample Characteristics.

Sample Date	N-alkane Range	Alkane Maxima	UCM Range Dominant Minor	nC ₁₇ /Pr ^a	nC ₁₈ /Phy ^b	%F1 ^c	%R _{F1} ^d	OEP ^e	Pr/Phy	ΣHC ^f μg/g
09/24/93	nC ₁₅ -nC ₃₁	nC ₃₁	nC ₁₈ -nC ₂₃ nC ₂₄ -nC ₃₂	1.3	1.0	84%	12%	1.4	1.0	29.4
10/24/93	nC ₁₇ -nC ₃₁	nC ₂₉	nC ₂₀ -nC ₃₁	4.0	-	49%	19%	2.6	-	9.4
11/19/93	nC ₁₇ -nC ₃₁	nC ₂₉	nC ₂₀ -nC ₃₁	4.9	-	34%	17%	3.0	-	14.6
12/17/93	nC ₁₅ -nC ₃₁	nC ₁₇	nC ₁₉ -nC ₃₁	86.0	0.4	53%	22%	5.8	0.6	16.6
01/28/94	nC ₂₁ -nC ₃₁	nC ₂₅	nC ₂₃ -nC ₃₀	- ^g	-	62%	29%	1.9	-	10.9
02/25/94	nC ₁₅ -nC ₃₂	nC ₂₉	nC ₁₈ -nC ₃₂	8.0	0.4	62%	24%	1.7	0.9	8.6
03/11/94	nC ₁₅ -nC ₃₂	nC ₂₉	nC ₁₇ -nC ₃₂	12.0	0.5	56%	22%	2.6	0.9	11.7
04/15/94	nC ₁₅ -nC ₃₂	nC ₂₉	nC ₁₉ -nC ₃₂	6.4	0.9	40%	29%	1.7	1.0	15.9
05/13/94	nC ₁₇ -nC ₃₂	nC ₂₉	nC ₂₂ -nC ₃₂	-	-	71%	36%	1.5	-	8.9
06/10/94	nC ₁₇ -nC ₃₂	nC ₂₉	nC ₂₀ -nC ₃₁	-	-	42%	47%	1.6	-	10.3
07/12/94	nC ₁₅ -nC ₃₂	nC ₂₉	nC ₂₄ -nC ₃₁	8.8	0.7	96%	22%	2.5	0.8	4.6
09/06/94	nC ₁₅ -nC ₃₁	nC ₁₇	nC ₁₈ -nC ₃₂	63.5	1.0	34%	26%	1.9	1.2	10.5

^apristane; ^bphytane; ^c% (F1) hydrocarbon concentration (F1 + F2);

^d%F1 resolved area/(F1 resolved + unresolved); ^eodd-even predominance;

^ftotal hydrocarbons/gram dry sediment; ^gnot calculated, insufficient data.

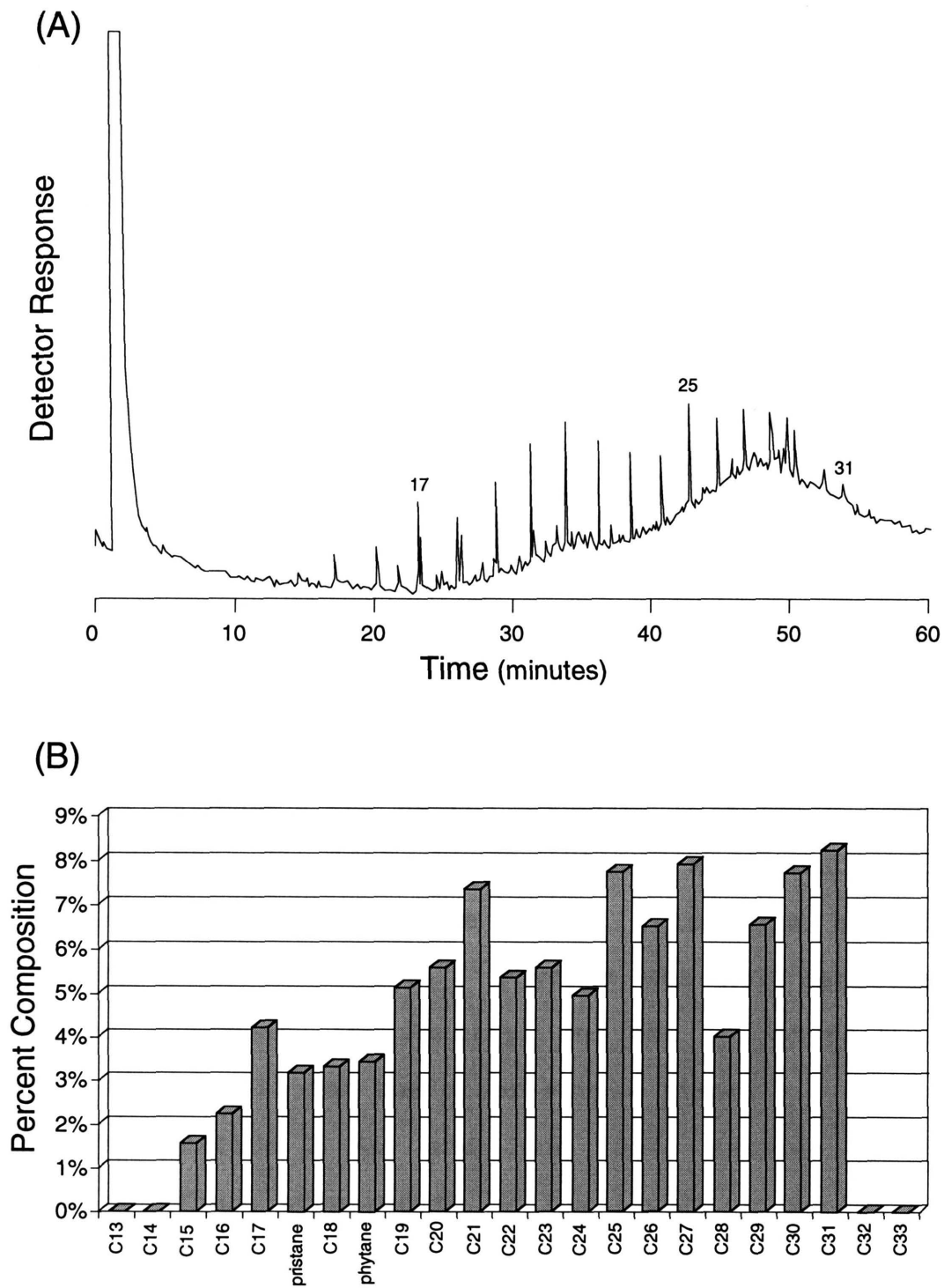


Figure 12. September 1993, Station 2 Sediment Sample:
 A. Chromatogram, B. Percent Composition

the two UCM's. The amount of oiling at this site was 29.4 $\mu\text{g/g}$ dry sediment of total hydrocarbons. F1 hydrocarbons accounted for 84% of the total. The F1 resolved area was 12%.

Station 2 samples from October through December 1993, and January through March 1994, did not seem to contain the typical Bunker C signature as the previous samples. They were dominated by an odd-carbon compound composition of probable biogenic origin (Figures 13-A and 13-B). The total hydrocarbon concentration ranged from 8.6-16.6 $\mu\text{g/g}$ dry sediment. The F1 hydrocarbon composition of the total ranged from 34-62%, and the F1 percent resolved area ranged from 17-29%. There was a small UCM approximately at the nC_{17} - nC_{31} range in each sample. The OEP ranged from 1.7-5.8. The nC_{17} /pristane ratio varied from 4.0-12.0 for October, November, February and March. However this ratio increased significantly to 86.0 in December, and then was not calculated for January due to no detectable amounts of pristane for that month. Phytane was not detected for October, November, and January, and the nC_{18} /phytane ratios were only 0.4-0.5 for the other sample times.

The Station 2 May and June 1994, samples were also similar. There appeared to be low levels of Bunker C fuel oil present in these samples (Figure 14-A). The n-alkane profile ranged from nC_{21} - nC_{32} , plus a 2% component of nC_{17} (Figure 14-B). All other n-alkanes including the isoprenoids, pristane and phytane, were at undetectable

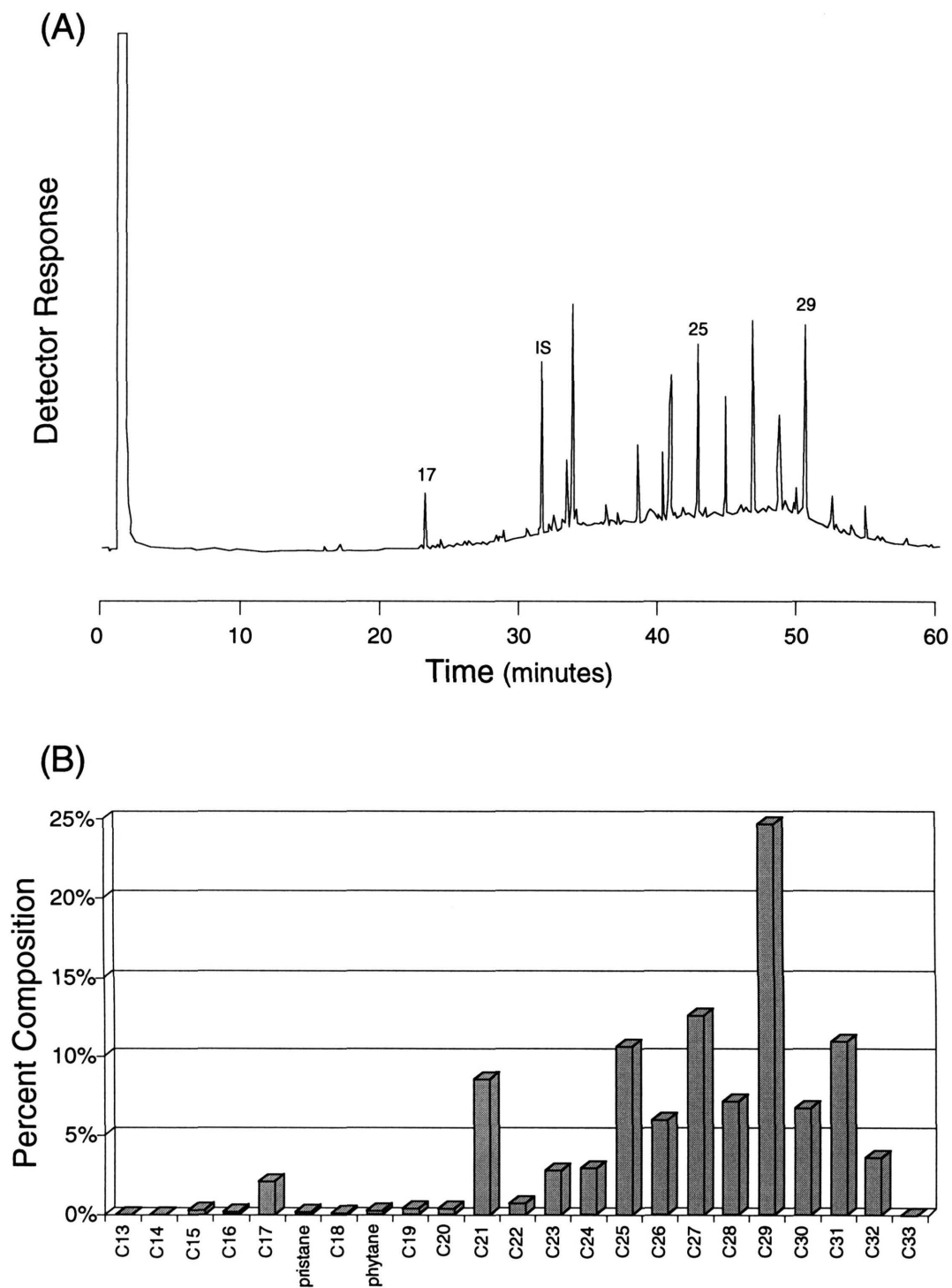


Figure 13. March 1994, Station 2 Sediment Sample:
A. Chromatogram, B. Percent Composition

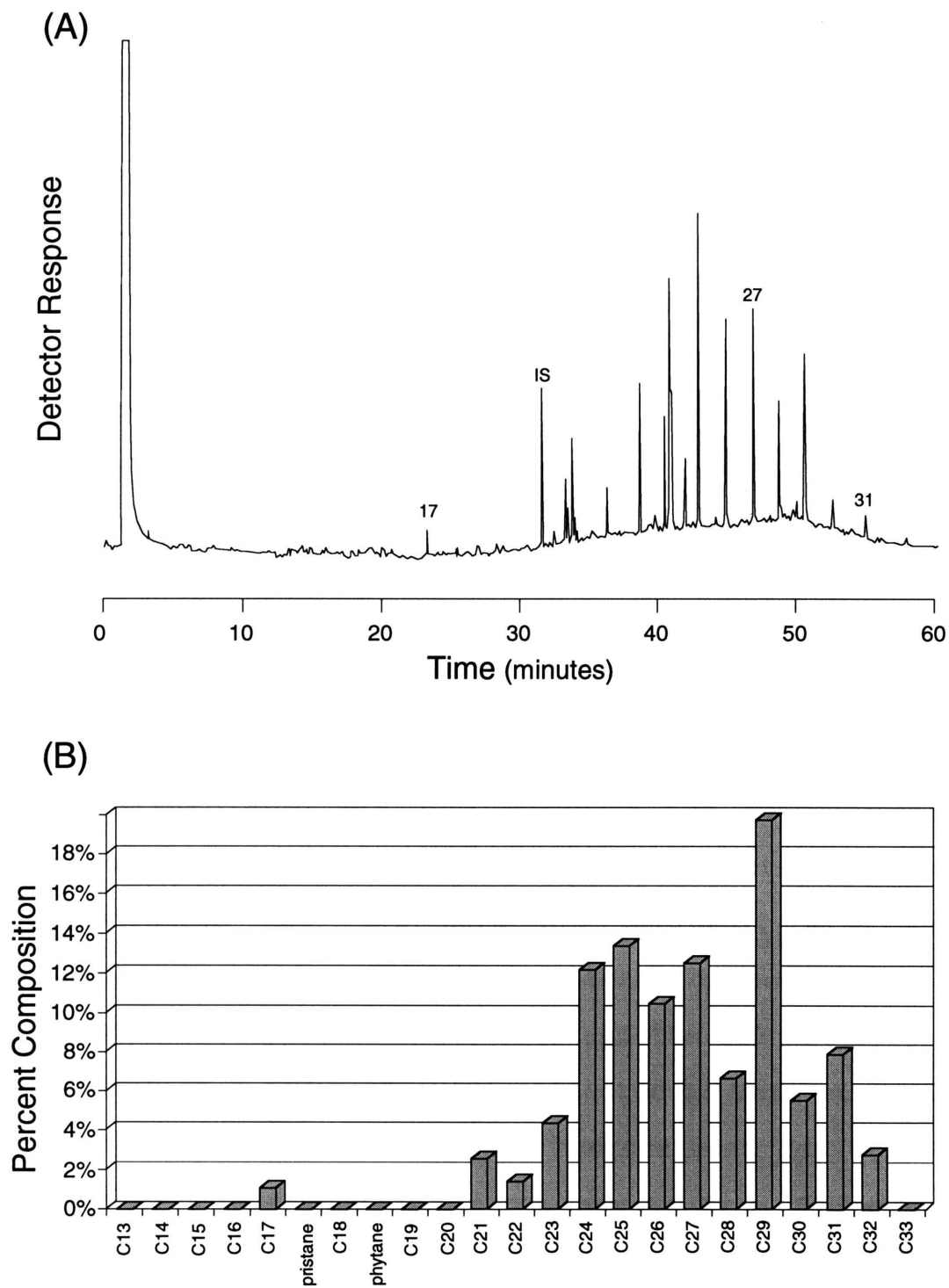


Figure 14. June 1994, Station 2 Sediment Sample:
A. Chromatogram, B. Percent Composition

levels. The UCM in each of these two samples were in the range of nC_{21} - nC_{32} , although they were very minor. The F1 resolved area was from 36-47%, and the total hydrocarbon concentration ranged from 8.9-10.3 $\mu\text{g/g}$ dry sediment in these samples. The F1 hydrocarbon concentration decreased from 71% of the total in May, to 42% in June. The OEP for these two sample months was relatively the same at approximately 1.5 each.

The September 6, 1994, Station 2 sample contained n-alkanes from nC_{15} - nC_{31} . Once again, as in the previous samples, there appeared to be lower levels of Bunker C oil than in the Station 1 sample of the same time. This sample had a minor UCM in the nC_{18} - nC_{32} range (Figure 15-A). The compound nC_{17} dominated the F1 composition with 25% (Figure 15-B). The nC_{17} /pristane ratio was high at 63.5 and the nC_{18} /phytane ratio was 1.0, although the concentration of each of the latter was very low. The total hydrocarbon concentration was 10.5 $\mu\text{g/g}$ dry sediment, with the F1 fraction comprising 34% of the total hydrocarbons. The percent F1 resolved area was 26%, and the OEP was 1.9.

Station 5 sediments were collected as reference samples to ascertain normal background hydrocarbons for comparison (Table 4). Although the first sample from September 24, 1993 exhibited a large amount of the initial Bunker C fuel oil, subsequent samples showed normal odd-carbon hydrocarbons typically derived from terrigenous sources and no detectable level of Bunker C fuel oil (Figures 16-A and B).

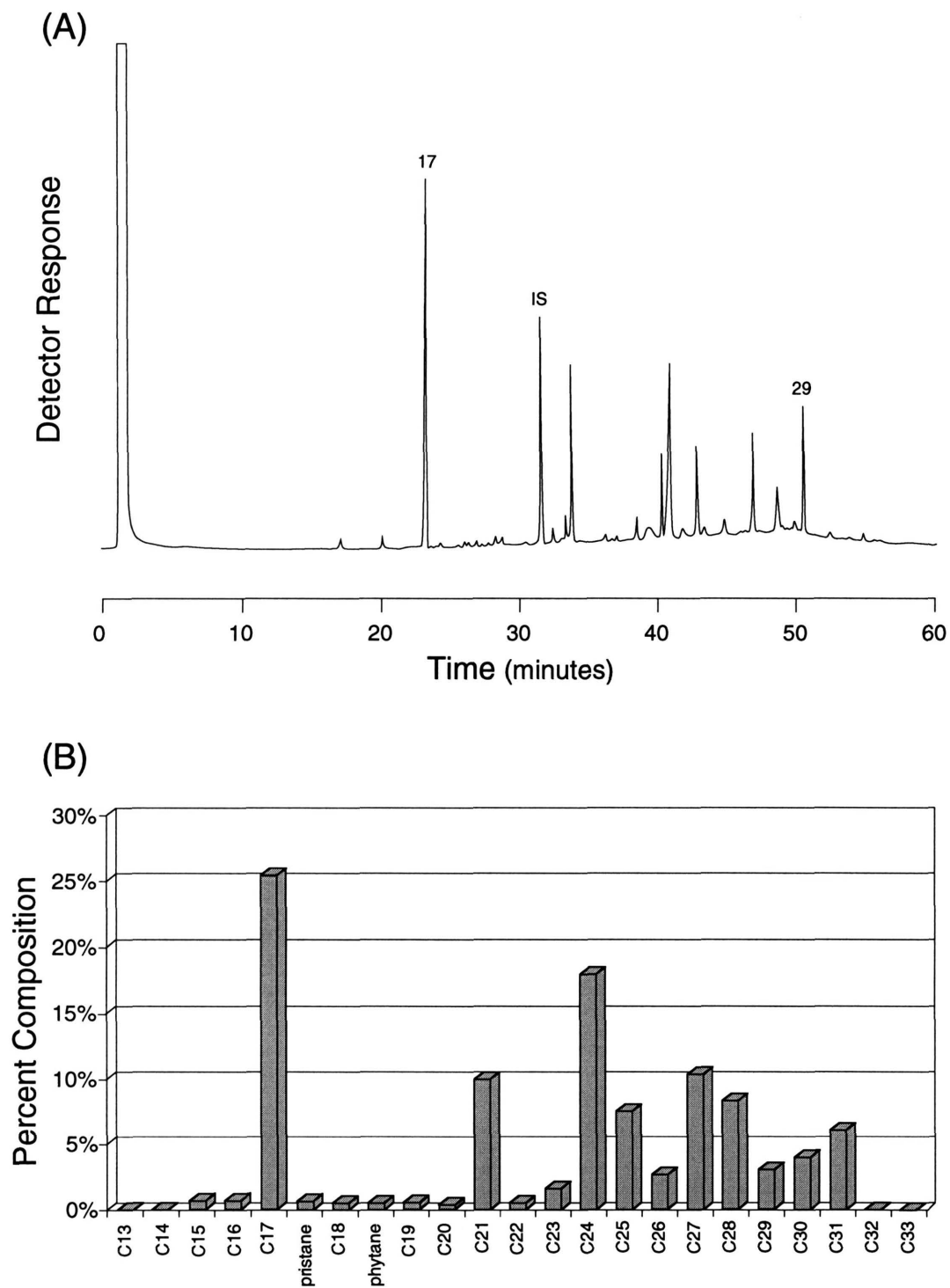


Figure 15. September 1994, Station 2 Sediment Sample:
A. Chromatogram, B. Percent Composition

Table 4. Station 5 Sediment Sample Characteristics.

Sample Date	N-alkane Range	Alkane Maxima	UCM Range Dominant Minor	nC ₁₇ /Pr ^a	nC ₁₈ /Phy ^b	%F1 ^c	%R _{F1} ^d	OEP ^e	Pr/Phy	ΣHC ^f μg/g
09/24/93	nC ₁₃ -nC ₃₂	nC ₂₁	nC ₁₄ -nC ₂₄ nC ₂₅ -nC ₃₂	1.7	1.5	98%	19%	1.0	1.1	204.1
10/24/93	nC ₁₇ -nC ₂₉	nC ₂₉	nC ₂₀ -nC ₃₂	- ^g	-	67%	8%	8.1	-	7.2
11/19/93	nC ₅₇ -nC ₃₁	nC ₂₉	none	2.9	-	47%	24%	1.5	-	8.2
02/25/94	nC ₁₇ -nC ₂₉	nC ₂₉	none	7.5	-	55%	14%	-	-	3.8
05/13/94	nC ₁₇ -nC ₃₁	nC ₂₉	none	4.9	-	24%	44%	3.0	-	4.1
09/06/94	nC ₁₅ -nC ₃₁	nC ₁₇	none	-	-	67%	27%	6.9	-	10.8

^apristane; ^bphytane; ^c% (F1) hydrocarbon concentration (F1 + F2);

^d%F1 resolved area/(F1 resolved + unresolved); ^eodd-even predominance;

^ftotal hydrocarbons/gram dry sediment; ^gnot calculated, insufficient data.

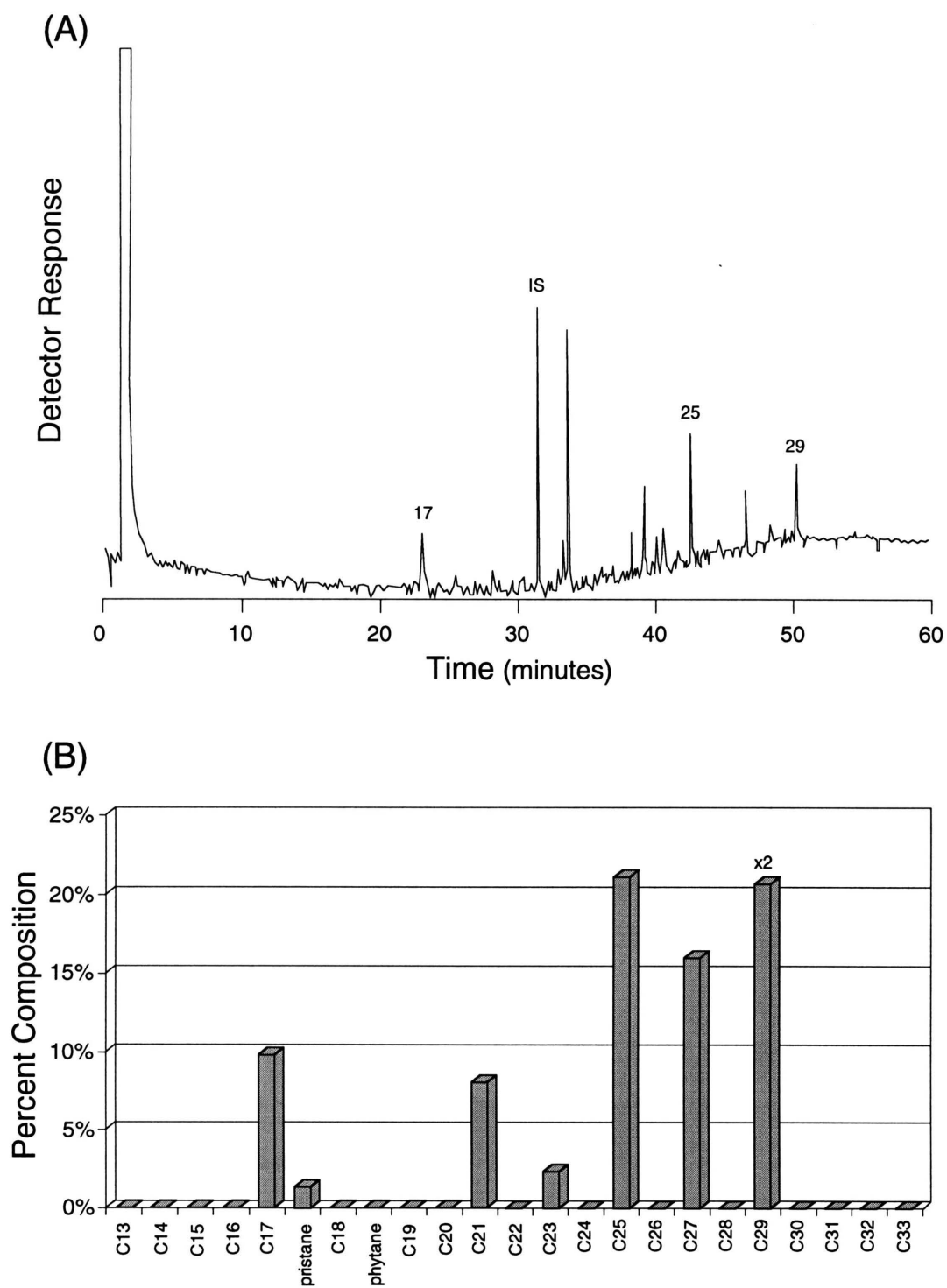


Figure 16. February 1994, Station 5 Sediment Sample:
A. Chromatogram, B. Percent Composition

Prop Roots

The first oiled prop root collected on October 24, 1993, showed a loss from the original Bunker C oil profile of nC_{13} - nC_{20} alkanes (Figure 17-A). There were no detectable levels of either pristane or phytane in this sample. The n-alkane range was from nC_{21} - nC_{31} . There was a UCM around the nC_{23} - nC_{31} area with an n-alkane maximum at nC_{29} (Figure 17-B). The F1 resolved area made up 15% of the area, and the F1 hydrocarbons comprised 30% of the total (Table 5).

There was virtually no monthly change in these characteristics until the January 28, 1993 sample where there was a loss of all n-alkanes from nC_{19} - nC_{31} to the UCM with the exception of a small amount of discernible nC_{29} (Figures 18-A and 18-B). The resolved area was only 6% of the total F1 area and the F1 hydrocarbons comprised 60% of the total.

This trend continued until April 15, 1994 when the two UCM's began to emerge. The smaller UCM at approximately nC_{18} - nC_{23} , merging into a larger UCM at around nC_{24} - nC_{31} (Figure 19-A). The F1 hydrocarbon concentration was 53% of the total and the F1 resolved area remained relatively unchanged at 5%. The nC_{17} /pristane and nC_{18} /phytane ratios could not be determined due to the lack of detectable levels

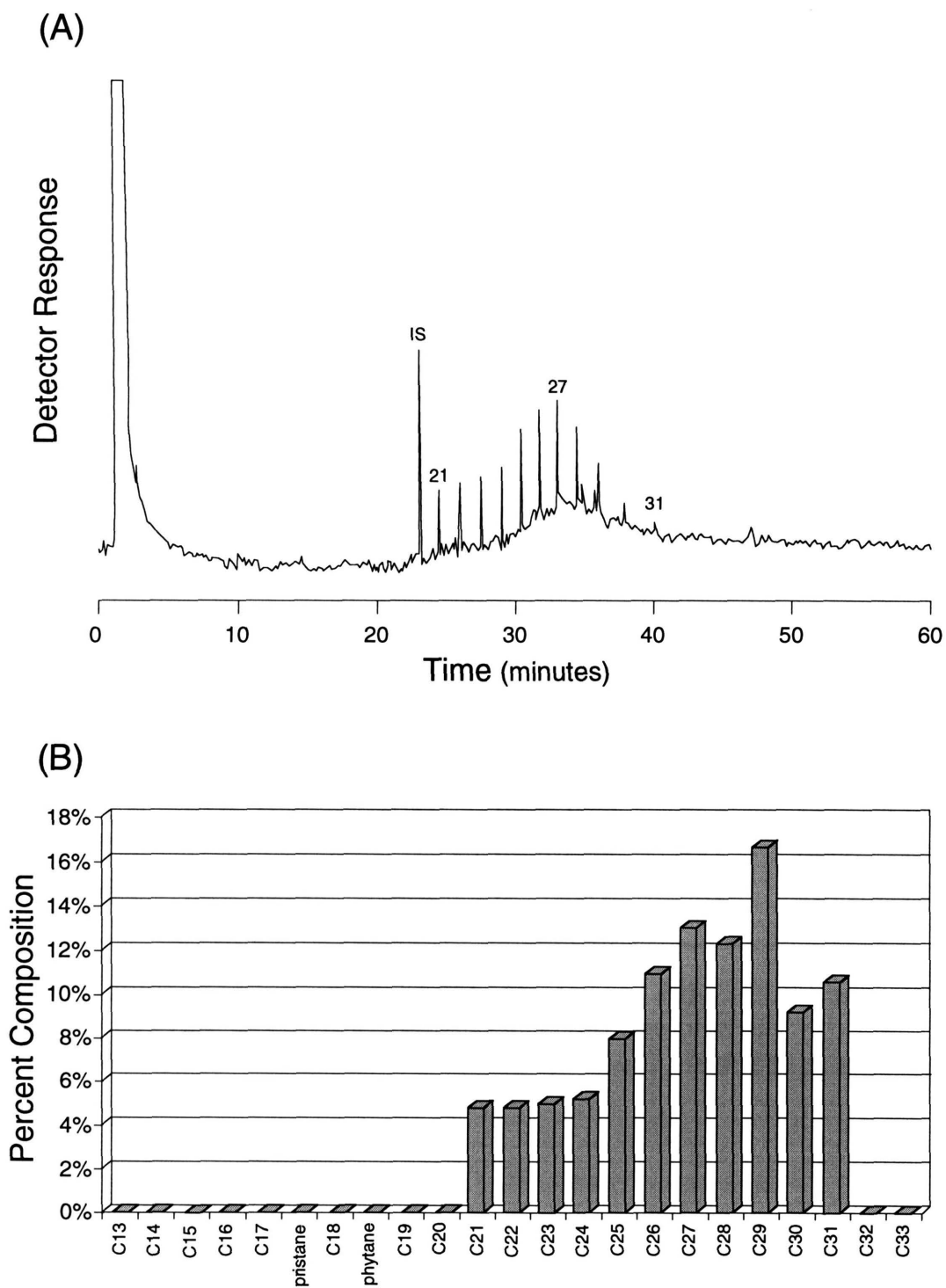


Figure 17. October 1993, Oiled Prop Root Sample:
A. Chromatogram, B. Percent Composition

Table 5. Oiled Prop Root Sample Characteristics.

Sample Date	N-alkane Range	Alkane Maxima	UCM Range	%F1 ^a	%R _{F1} ^b	OEP ^c
10/24/93	nC ₂₁ -nC ₃₁	nC ₂₉	nC ₂₃ -nC ₃₁	30%	15%	1.4
11/19/93	nC ₂₁ -nC ₃₁	nC ₃₁	nC ₂₃ -nC ₃₁	55%	10%	1.3
12/17/93	nC ₁₇ -nC ₃₁	nC ₂₇	nC ₂₃ -nC ₃₁	45%	18%	1.1
01/28/94	nC ₁₇ -nC ₃₁	nC ₂₉	nC ₂₀ -nC ₃₁	60%	6%	-
02/25/94	nC ₁₇ -nC ₃₀	nC ₁₇	nC ₂₀ -nC ₃₁	63%	2%	4.7
03/11/94	nC ₂₄ -nC ₃₀	nC ₂₅	nC ₂₀ -nC ₃₁	72%	1%	1.1
04/15/94	nC ₂₀ -nC ₃₀	nC ₂₉	nC ₁₉ -nC ₃₁	53%	5%	0.9
05/15/94	nC ₁₉ -nC ₃₁	nC ₂₉	nC ₂₀ -nC ₃₁	75%	8%	1.2
06/10/94	nC ₂₅ -nC ₃₁	nC ₂₉	nC ₂₀ -nC ₃₁	82%	1%	1.5
07/12/94	- ^d	-	nC ₂₀ -nC ₃₁	44%	0%	-
09/06/94	nC ₂₁ -nC ₃₂	nC ₂₈	nC ₂₀ -nC ₃₁	50%	9%	1.1

^a% (F1) hydrocarbon concentration (F1 + F2);

^b%F1 resolved area/(F1 resolved + unresolved);

^codd-even predominance; ^dnot calculated, insufficient data.

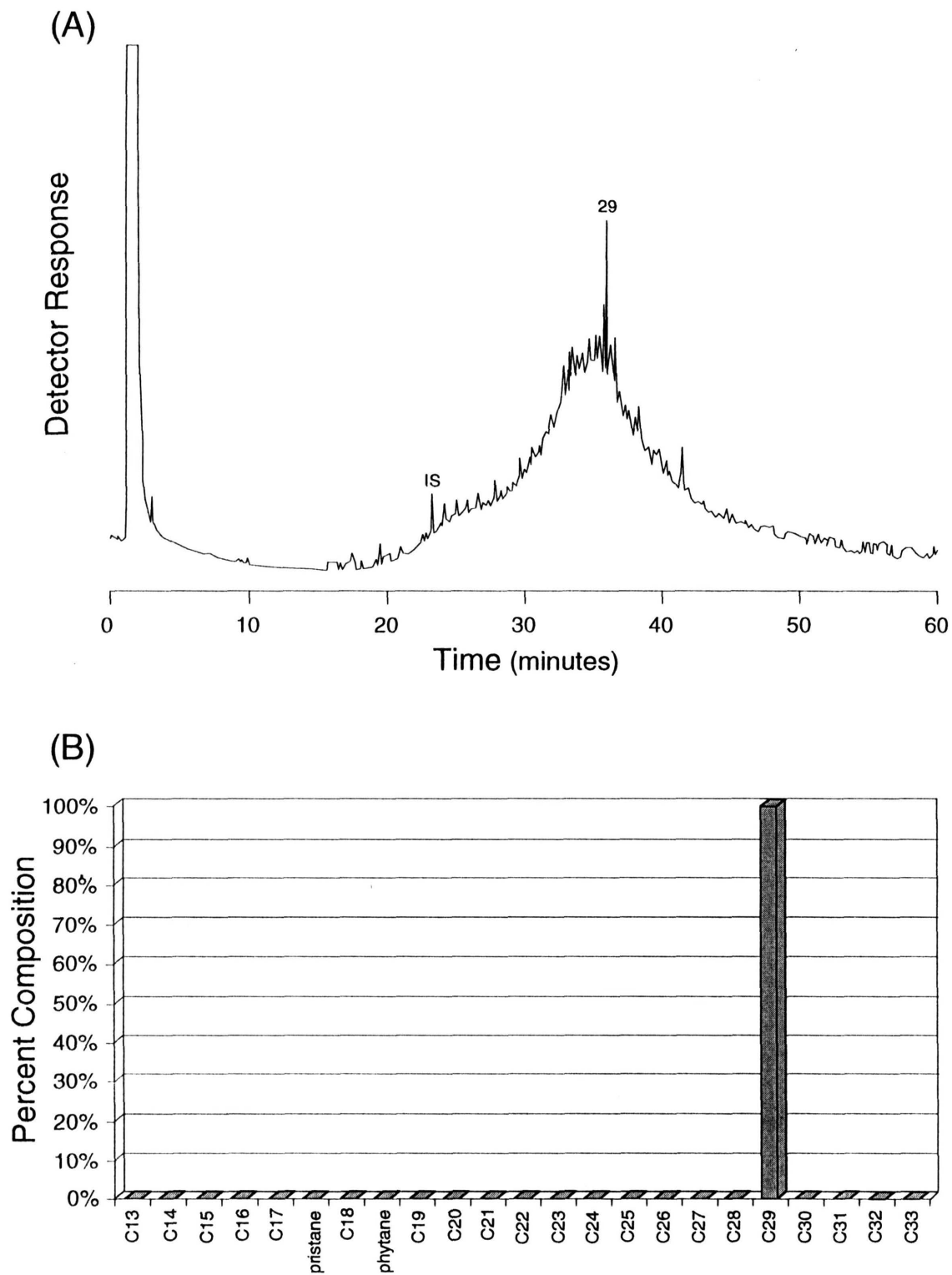


Figure 18. January 1994, Oiled prop Root Sample:
A. Chromatogram, B. Percent Composition

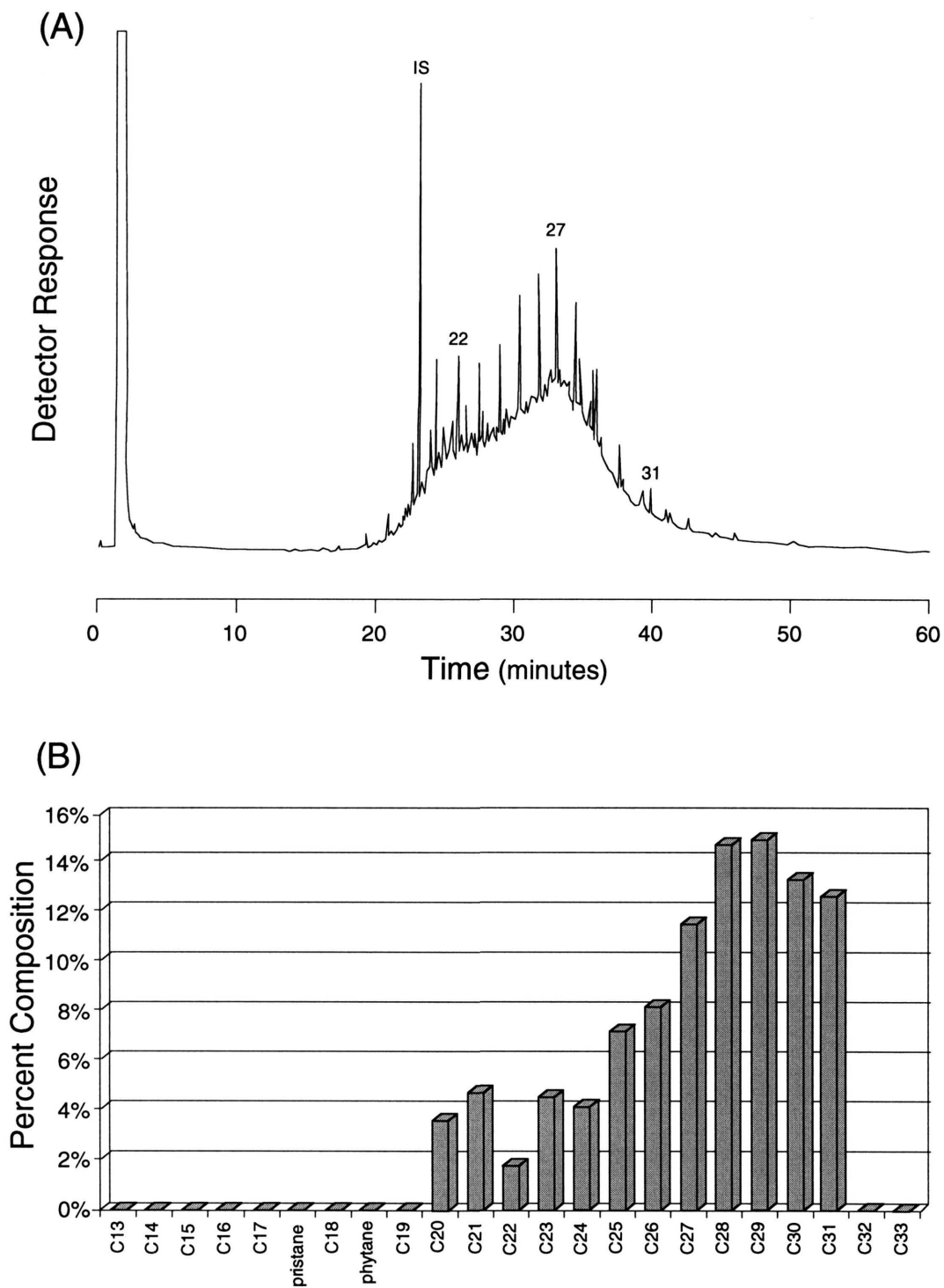


Figure 19. April 1994, Oiled prop Root Sample:
A. Chromatogram, B. Percent Composition

of these compounds (Figure 19-B). The remaining five months' samples were analogous to this April sample, with the percent resolved areas ranging from 0.8-1.0%. The F1 hydrocarbon concentration ranged from 50-75% of the total.

Non-oiled prop roots were collected and analyzed for determination of background hydrocarbons. There were no F1 hydrocarbons detected in the three prop roots sampled on three separate dates, January, May and September, 1994.

Analytical Precision

In order to determine analytical precision for laboratory techniques, replicate injections were made on the n-alkane standards. The standard was injected five times to verify response factors, and to ascertain reproducibility. Standard deviations for the 22 n-alkanes used as standards indicated a maximum laboratory error of $\pm 11\%$, and an average standard deviation of $\pm 3\%$.

Aromatic Hydrocarbons

Bunker C Fuel Oil

An analysis of selected PAH's was performed on the certified sample of Bunker C fuel oil obtained from NOAA. The sample was scanned for the following 35 PAH's and verified with authentic standards, to ascertain if they were present, and in what percent composition:

- acenaphthene
- acenaphthalene
- benzene (C₀-C₄)
- naphthalene (C₀-C₄)
- dibenzothiophene
- phenanthrene (C₀-C₄)
- anthracene (reported as phenanthrene)
- fluorene (C₀-C₄)
- pyrene (C₀-C₄)
- fluoranthrene (reported as pyrene)
- chrysene (C₀-C₄)
- benzo(a)anthracene (reported as chrysene)
- benzo(a)pyrene
- benzo(e)pyrene

The Bunker C fuel oil indicated a dominance of the naphthalene and phenanthrene homologous series, C₀-C₄ (C₀ is the parent compound and C₁-C₄ are substituents containing from one to four carbon atoms, in the attached side chain). These compounds comprised between \cong 1-11% each of the total

percent composition of these selected PAH's (Figure 20). The remaining PAH's represented between 1.0 and 6.0% each of the total scanned. Present in the Bunker C sample, were all homologs (C₀-C₄) of naphthalene, phenanthrene, fluorene, and pyrene, and the C₀-C₃ homologs of chrysene. There were no measurable levels of benzene, C₄ chrysene, benzo(a)pyrene or benzo(e)pyrene detected. Because anthracene coelutes with phenanthrene, and benzo(a)anthracene with chrysene, these compounds could not be separated and therefore their areas are reported as indicated above.

Station 4 Oil Mass Samples

The first oil mass sample collected on September 24, 1993, indicated a profile identical to the Bunker C fuel oil certified sample. In this sample, all of the PAH's found in the Bunker C fuel oil sample were present, and in the same percent composition (Figure 21). This profile exhibited the same high percent compositions of the two ring aromatic, naphthalene with approximately 1-12% of the total. This profile was no different than the Bunker C oil sample. The phenanthrene series was the most abundant of the remaining multiple ring aromatics with approximately 2-8% of the total. This trend continued, with slight variations throughout the February, June, and September 1994 oil mass samples (Figure 22). The distribution of homologs for these five compounds did not change significantly over the course

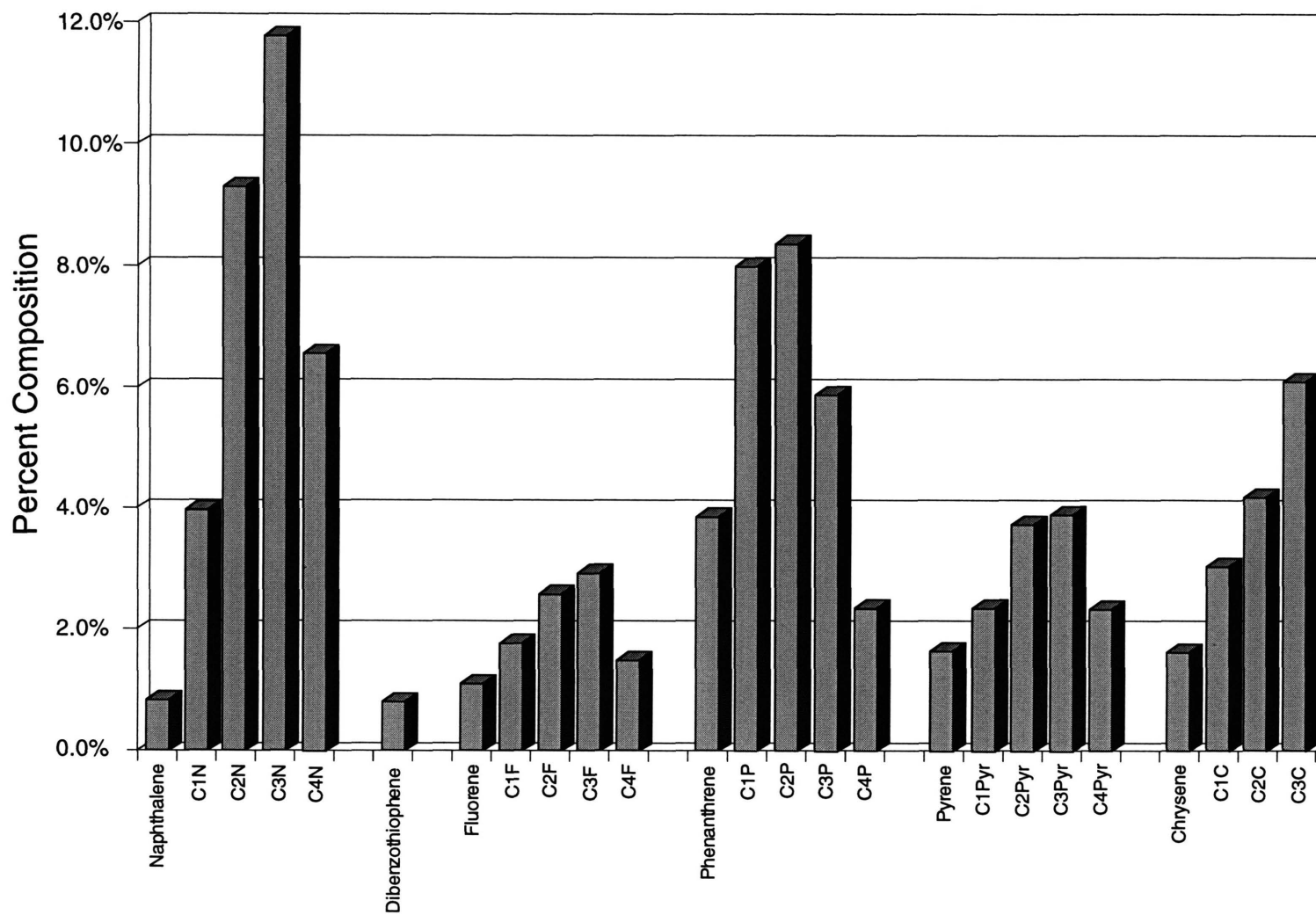


Figure 20. Bunker C Fuel Oil Selected PAH Homologs Percent Composition

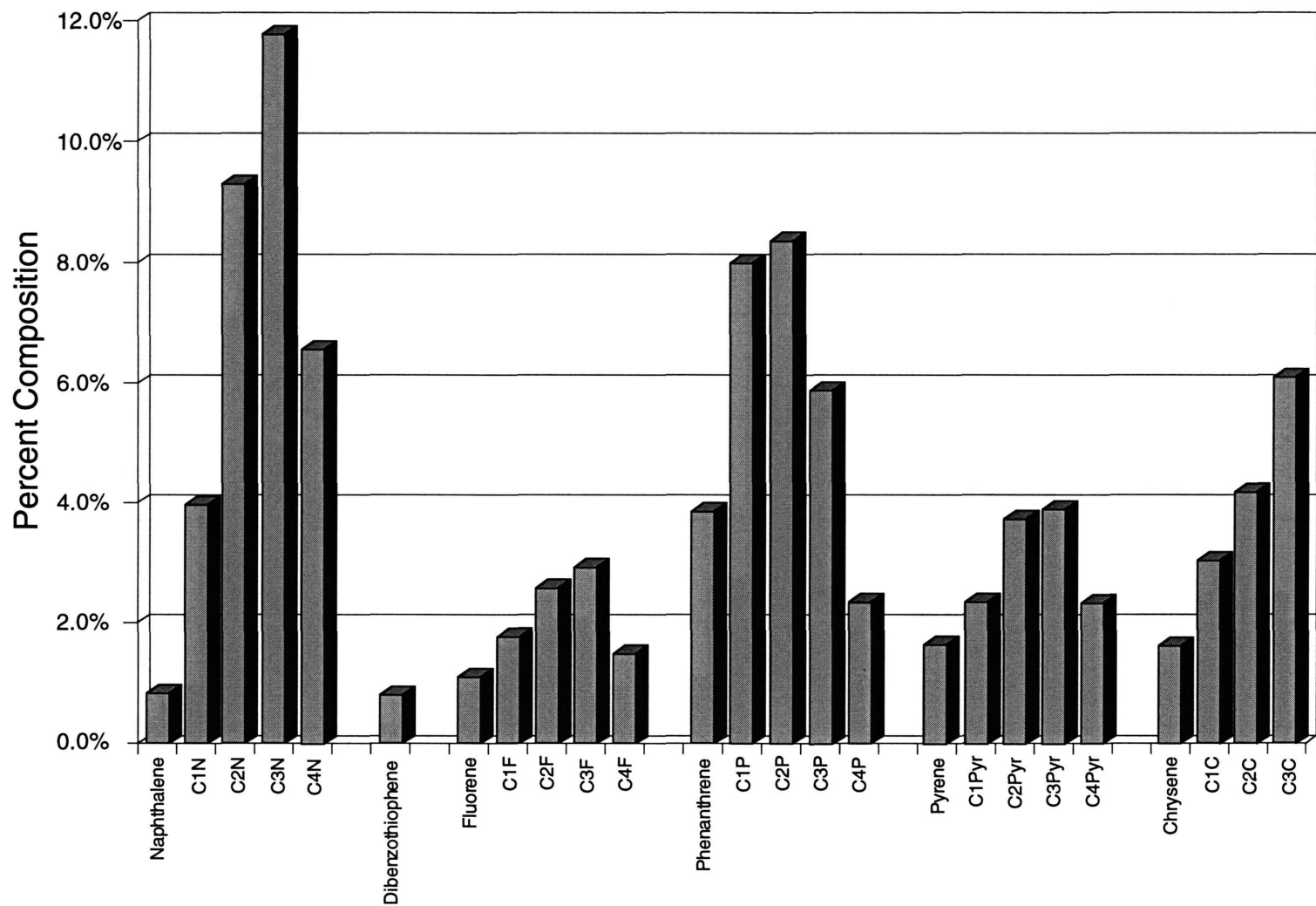


Figure 21. September 1993, Station 4 Oil Mass Sample Selected PAH Homologs Percent Composition

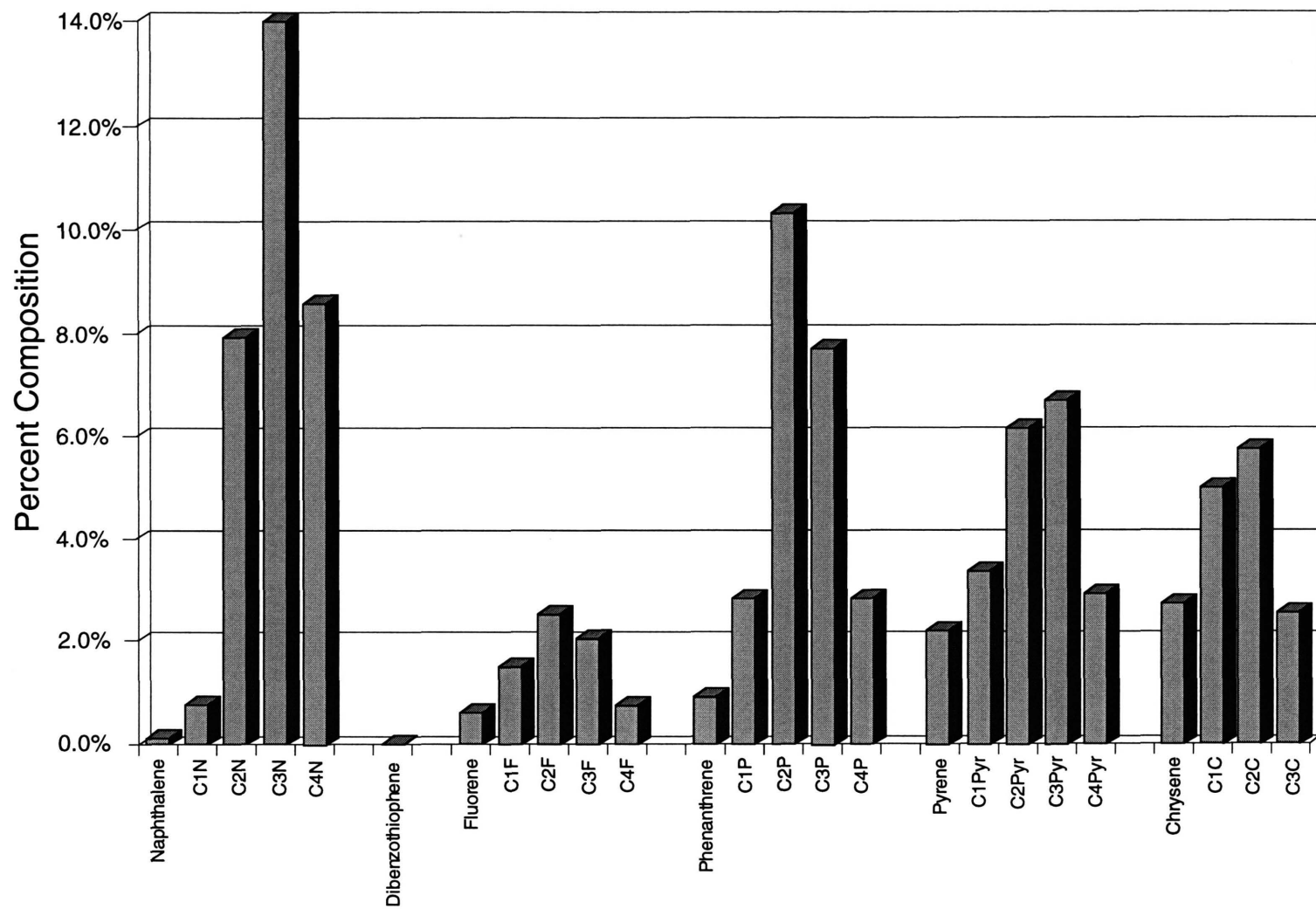


Figure 22. September 1994, Station 4 Oil Mass Sample Selected PAH Homologs Percent Composition

of this study, and were analogous to the Bunker C fuel oil profile (Figure 23). In the Bunker C oil sample, there appeared to be a somewhat stronger predominance in the naphthalene series than in the December 1993, to September 1994, Station 4 samples. This loss from the September 1994, sample is a characteristic of weathering as the naphthalenes are much more soluble than the other targeted PAH's.

Sediments

Although there did not seem to be many changes within the Station 4 oil mass samples throughout the year, there were significant deviations from the original Bunker C fuel oil in the Station 1 sediments. There was a small change in the percent composition of the PAH's found in the sediments between September 1993, to September 1994, (Figure 24). Both the first sediment sample collected on September 24, 1993 and the last sediment sample from September 6, 1994, showed a loss of all detectable levels of, naphthalene, and dibenzothiophene from the original oil. The fluorene series decreased in the September 1993, sample to only about 1% of the total composition, and was lost completely in the September 1994, sample. What did not appear to abate, were the phenanthrene, pyrene and chrysene series. Because of the absence of the above PAH's, there was a marked increase in the percentages of the pyrenes and

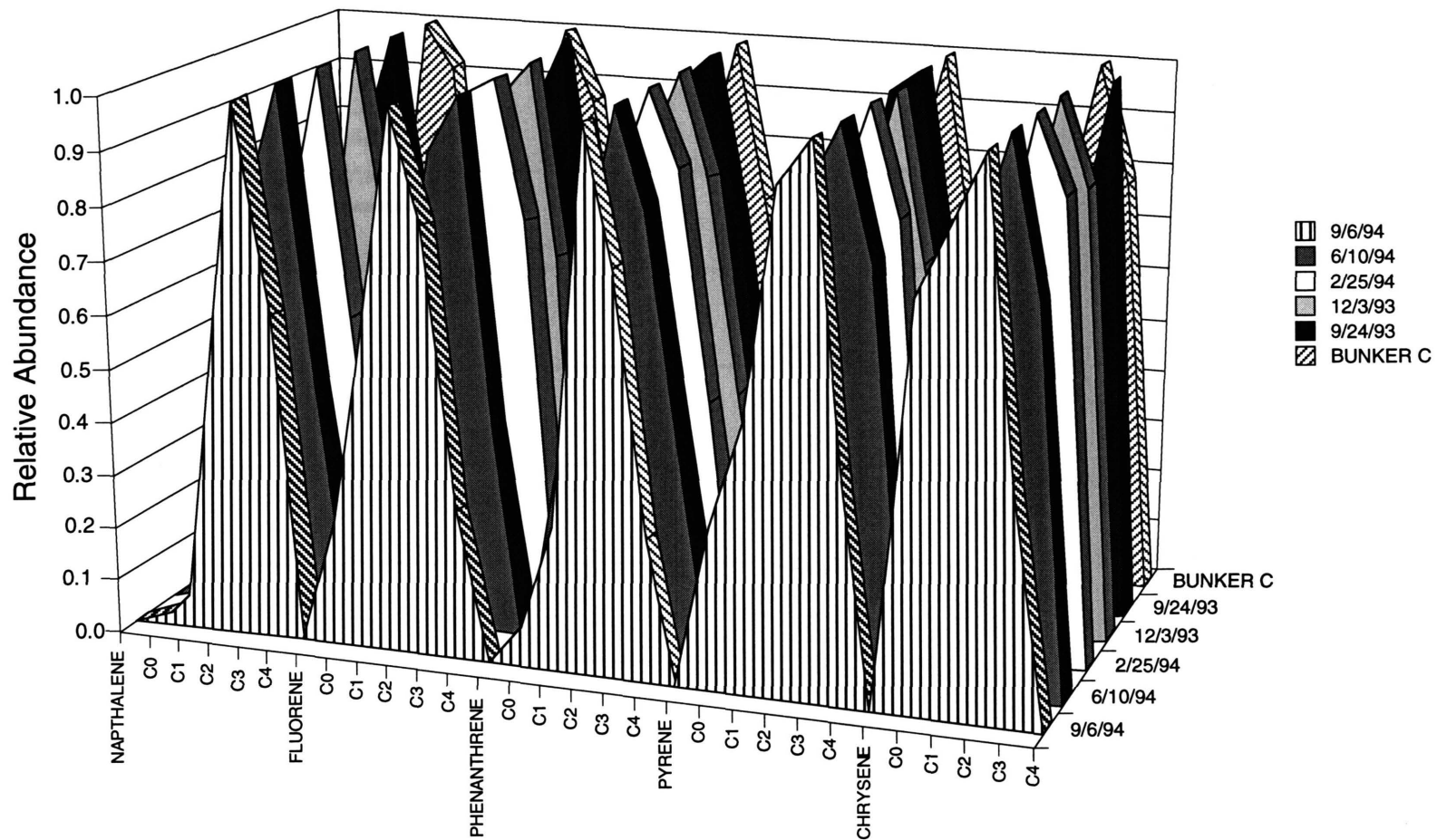


Figure 23. Selected PAH Relative Abundances of Bunker C Fuel Oil and Station 4 Oil Mass Samples

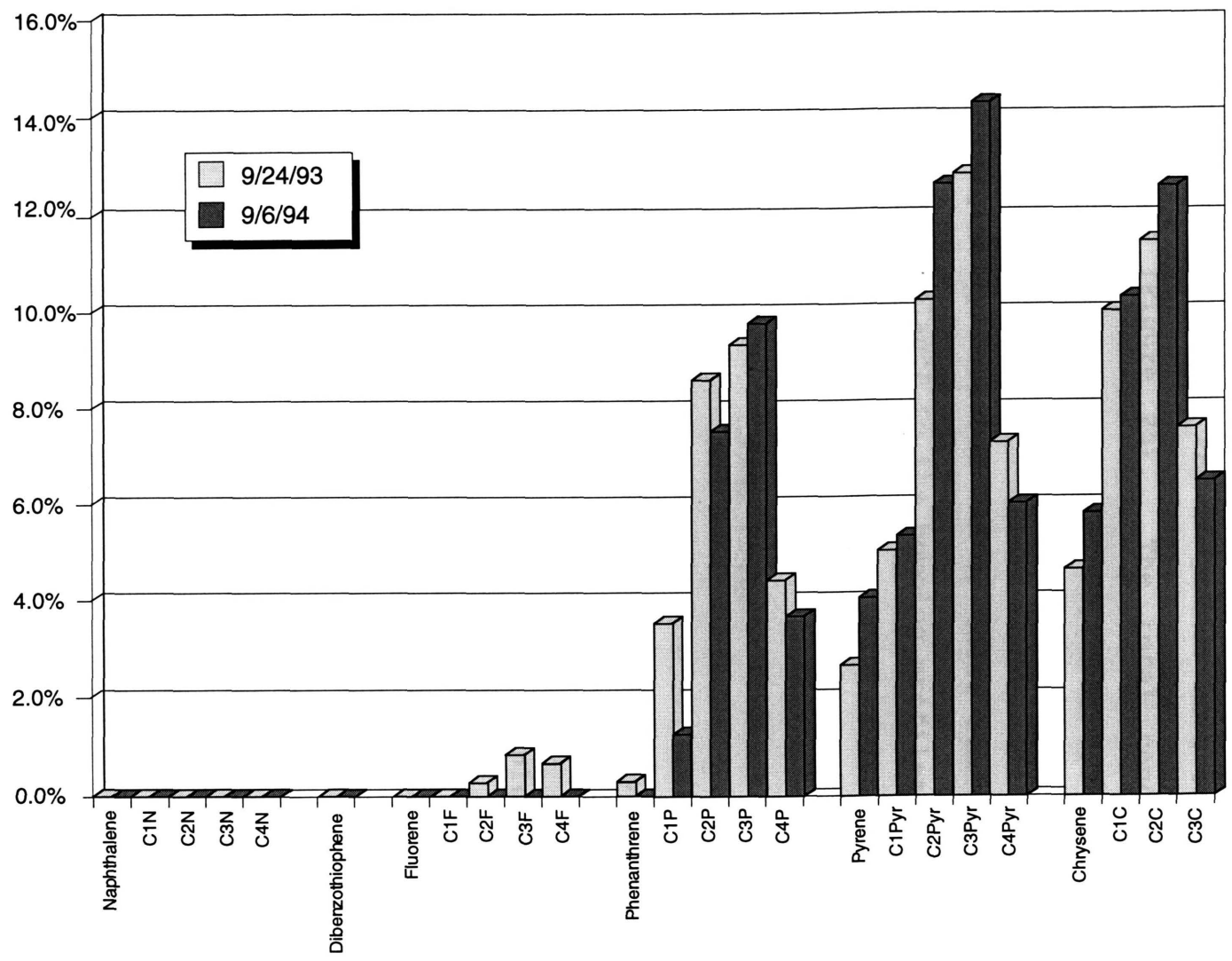


Figure 24. Station 1 Sediments Selected PAH Homologs Percent Composition

chrysenes to about 12% of the total. The percent composition of phenanthrene did not increase, and stayed at approximately 9% of the total PAH's. The total hydrocarbon concentration for these PAH compounds however did decrease substantially (Figure 25). The total concentration for September 1993, and September 1994, were 7.7 and 0.03 $\mu\text{g/g}$ dry sediment respectively. While there was a loss of many of the originally detected PAH's, those remaining showed a remarkable resemblance to the homolog profiles determined in the Bunker C fuel oil (Figure 26).

Prop Roots

The prop root samples appeared to display the same type of characteristic changes as were found in the sediments. There was an immediate loss of all detectable PAH's in the October 1993, prop roots, except phenanthrene, pyrene and chrysene (Figure 27). This loss of PAH's was also observed for the September 1994, sample. The percent composition for these dates was similar with phenanthrenes comprising approximately 10%, and pyrenes and chrysenes comprising 10-16% of the total. The September 1994, prop root sample was dominated by the chrysene series, specifically C_1 and C_2 chrysenes. Nonetheless, temporal differences in the profiles existed in the relative abundance's of the homologs of each compound (Figure 28). The September 1994, sample decreased in C_1 - C_3 phenanthrenes from the previous October.

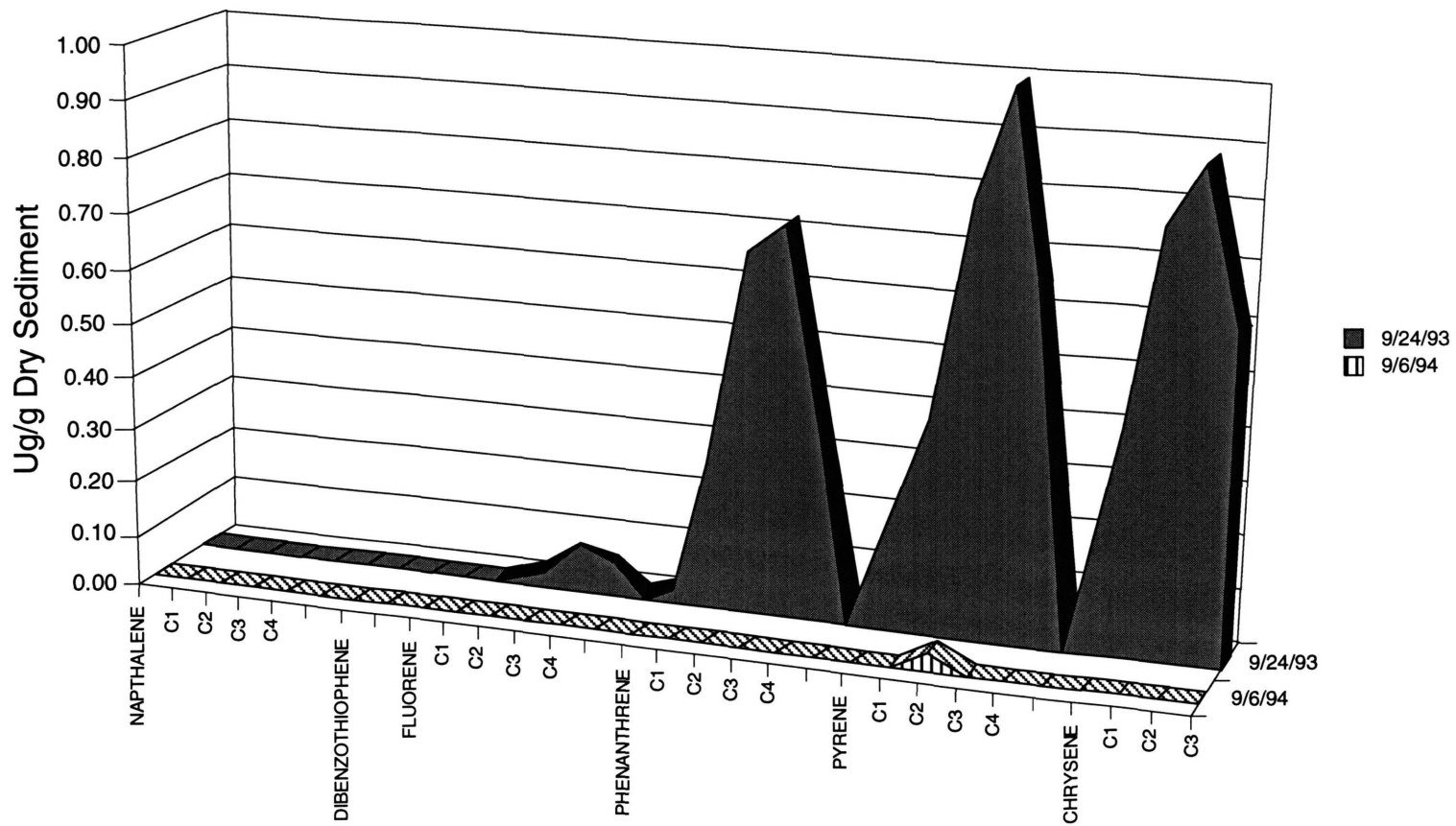


Figure 25. Station 1 Sediments Selected PAH Homologs Concentrations

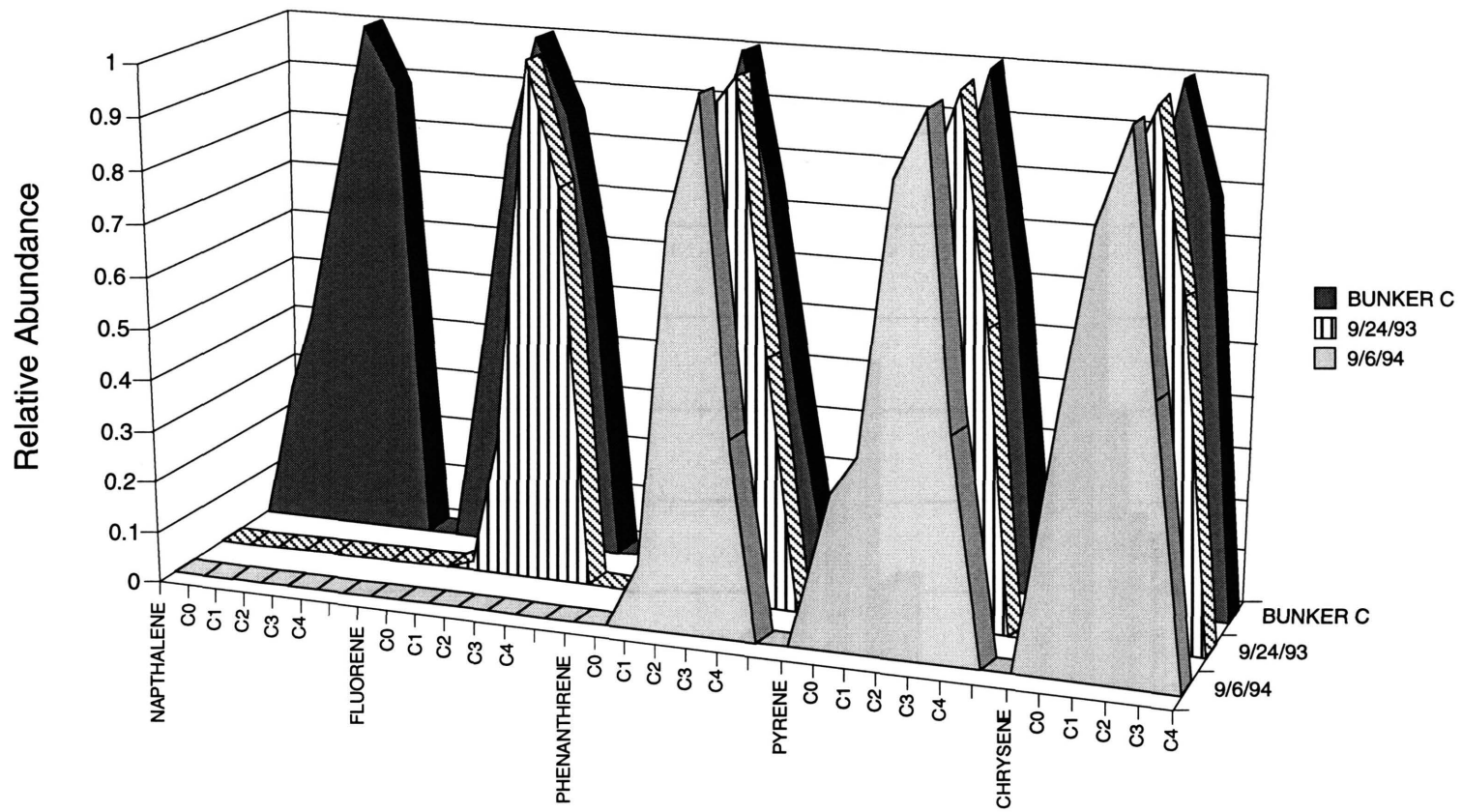


Figure 26. Selected PAH Relative Abundances of Bunker C Fuel Oil and Station 1 Sediments

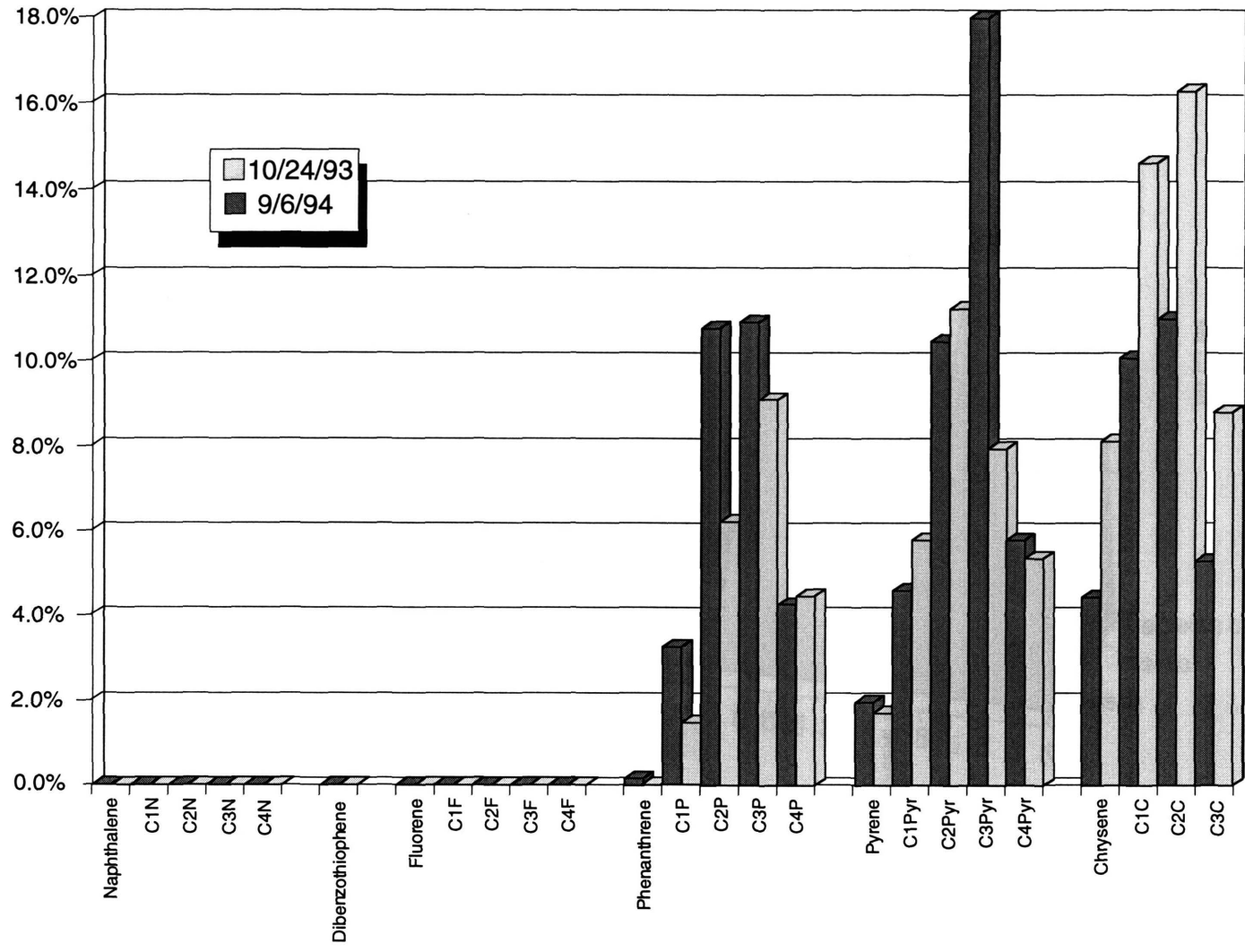


Figure 27. Oiled Prop Roots Selected PAH Homologs Percent Composition

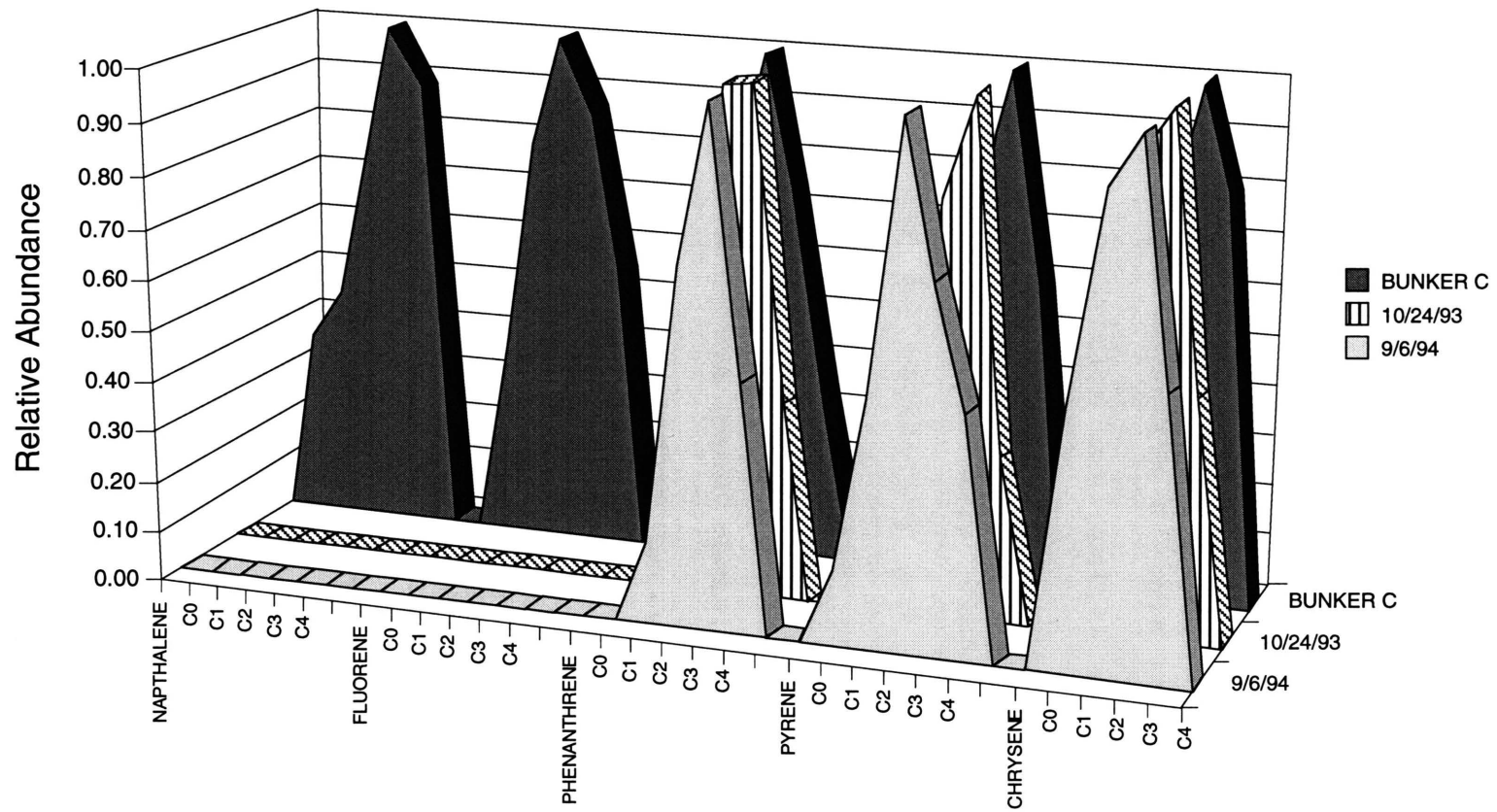


Figure 28. Selected PAH Relative Abundances of Bunker C Fuel Oil and Oiled Prop Root Samples

The relative abundance of phenanthrene, pyrene and chrysene, homologs, however, changed only very slightly from the original oil sample, with only a small shift towards the lower homologs in the pyrene series.

5. DISCUSSION

Diagnostic Tools for Fingerprinting Oil Spills

One important objective of this study was to identify the chemical composition and profile of the Bunker C fuel oil spilled from the *Bouchard 155* into Tampa Bay in 1993. By "fingerprinting" this oil, changes in its chemical composition due to weathering and microbial degradation could be monitored over a one year period. Changes in the oil were examined in three different mediums: oil masses, sediments and mangrove prop roots. Eleanor Island was chosen as the monitoring site because of the heavy oiling incurred after the spill trajectory altered course from the Gulf of Mexico onto the Gulf beaches, and also because of the dense mangrove forests which covered the island. Since most previous Bunker C fuel oil spills have occurred in temperate climates, Eleanor Island provided a unique geographical location to study the behavior of Bunker C fuel oil in a subtropical marine environment.

Bunker C fuel oil is a heavy, viscous, high molecular weight fraction of refined oil. The NRC (1985) has characterized Bunker C as having n-alkanes ranging from nC₁₃-nC₃₂₊, and PAH's which include benzene, naphthalene,

phenanthrene, fluorene, pyrene, and chrysene. Petroleum can be further characterized as having an OEP of near unity. Since biogenic hydrocarbons are typically dominated with odd-numbered n-alkanes, OEP was used in discriminating biogenic hydrocarbons from those derived from the Bunker C fuel oil. In addition, there are few PAH's found in non-petroleum sources, which further identify petroleum-derived inputs.

The use of pristane to phytane ratios is also a common tool for diagnosing sources of hydrocarbons. Pristane and phytane belong to a class of alkanes called isoprenoids. Isoprenoids are acyclic alkanes with regularly-repeating methyl branching points in their structures. Pristane is formed from phytol (a side chain of chlorophyll) by various oxidation and decarboxylation reactions, and phytane is formed by hydrogenation and dehydration of phytol. In oxidizing environments, pristane can be formed, and in reducing environments, such as are needed for the formation of petroleum, phytane is also formed (Philp 1985). Therefore, petroleum hydrocarbons have been found to have concentrations of phytane that are not found in biogenic sources. Isoprenoids are also widely used as a means of determining the extent of degradation of an oil. Because of the multiple branching sites found in isoprenoids, they are not degraded as rapidly as are the n-alkanes. Consequently, ratios of nC_{17} /pristane and nC_{18} /phytane can be monitored to

ascertain the magnitude of degradation of n-alkanes relative to the isoprenoids.

The NRC (1985) has shown that weathered petroleum will exhibit losses of low boiling ($<nC_{20}$) saturated and aromatic hydrocarbons. The hydrocarbon profile will shift from lower molecular weight compounds to higher molecular weight compounds. There will also be an increased importance of the unresolved complex mixture due to a decrease in resolution from the degraded alkanes, and an increased predominance of PAH's relative to all saturated compounds. Phenanthrene, pyrene and chrysene have been shown to become the dominant PAH's as the weathering process continues and there is a loss of lower PAH's relative to higher.

Although not all aromatics found in Bunker C fuel oils were monitored in this study, the dominant PAH's commonly reported were examined. While standards of non-alkylated PAH's are available, most of the alkylated PAH's are not easily obtained. Therefore, when calculating percent compositions of these compounds, response factors were not considered. Nonetheless, since the basic premise of the study was to observe changes in selected compounds relative to other targeted compounds, this did not alter the results.

All of these characteristics and diagnostic tools were applied to the Bunker C fuel oil, oil mass, sediment and prop root samples. By using these tools, and evaluating percent compositions, which has been suggested by the NRC (1985) as being as important as determining the absolute

values of hydrocarbon components, a thorough analysis of weathering patterns of Bunker C fuel oil in a subtropical marine environment was achieved.

Bunker C Fuel Oil

Aliphatics

The Bunker C fuel oil obtained for baseline data analysis showed the expected profile and composition of n-alkanes and PAH's found in all Bunker C oils (Figures 4 and 20). The range and percent composition of n-alkanes was consistent with published data (NRC 1985). The OEP and pristane/phytane ratio was 1.0 for each, indicative of petroleum hydrocarbons. The nC_{17} /pristane and nC_{18} /phytane ratios were 1.9 and 1.7 respectively, which provided a reference to compare all other samples as weathering occurred. According to previous studies, the aliphatic hydrocarbons are usually more abundant than aromatics, in fresh oil (NRC 1985). Such was the case with the Bunker C sample, in which the aliphatics comprised 86% of the total hydrocarbon concentration.

Aromatics

Typical Bunker C oils contain a large percentage of naphthalenes and phenanthrenes in addition to smaller

percentages of pyrenes, chrysenes, and fluorenes. The Bunker C oil sample from the Tampa Bay spill showed the same predominance of naphthalenes and phenanthrenes, and similar compositions of the remaining PAH's (Figure 20). These characteristics found in the Tampa Bay Bunker C fuel oil were corroborated by the study on Bunker C fuel oil from the Arrow spill in Chedabucto Bay, Nova Scotia (Wang et al. 1994). In that study, it was also found that the Bunker C source oil contained a high percentage of the naphthalene and phenanthrene homologous series of PAH's.

Station 4 Oil Mass Samples

Aliphatics

All of the oil mass samples from Station 4 appeared to have lost all detectable amounts of nC_{13-14} and nC_{33} from the original Bunker C profile. The range of n-alkanes was from nC_{15} - nC_{32} . This loss of nC_{13-14} can be attributed to evaporation and dissolution, as this is common for low molecular weight compounds. The oil mass samples in this study were transported from near Egmont Key, through John's pass, and then deposited on Eleanor Island. Through this transport, it is likely that these soluble components were lost to dissolution. Conversely, nC_{33} is not highly soluble, and its absence cannot be attributed to the same process. It has been shown that higher molecular weight

hydrocarbons can, however, adsorb onto small particles within the water column (Meyers and Oas 1978). These data are also in agreement with a study by Mote Marine Laboratory (Sherblom et al. 1993), on the analysis of water samples from the Tampa Bay oil spill. In this study, the authors found unexpected amounts of nC_{23} - nC_{35} in the water column. As some of the Bunker C fuel oil was transported to its final location on Eleanor Island, it is likely that some higher molecular weight components (i.e. nC_{33}), were preferentially adsorbed onto small particles and became the source of unexpected hydrocarbons found in the Mote Marine water column study. This would explain in part, the absence of this component from the Station 4 oil samples.

Another circumstance to consider is that when the Station 4 samples were analyzed, a small amount of oil was removed from the larger mass collected. Depending on whether that sample was taken from the outside of the mass, or the inside of the mass had some effect on several characteristics of that sample. The nC_{17} /pristane ratios for example, did not remain at or near the original Bunker C fuel oil ratio of 1.9. Instead, it fluctuated from as high as 2.2 on September 24, 1993, to as low as 0.1 on September 6, 1994 (Table 1). This would, without further analysis, appear to be consistent with expected weathering patterns. Since, as oil becomes more degraded this ratio becomes smaller. However, later in the study (June 10, 1994) the nC_{17} /pristane ratio was as high as the first sample

collected on September 24, which showed the least weathering. The same pattern was found with nC_{18} /phytane ratios for these months. The highest ratio was 2.6-2.3 on September 24, 1993 and on June 10, 1994, respectively, and the lowest was 0.1 for September 6, 1994 (Table 1). The percent resolved F1 area correspondingly declined or increased along with the n-alkane/isoprenoid ratios. This trend appears contrary to what would be expected for the uniform weathering of these oil mass samples except that some of these samples were collected inside of the oil mass and were therefore protected from weathering, hence the unweathered profiles. Others were collected from the outside of the oil mass and were exposed to weathering, indicating typical weathering patterns. Therefore, the characteristics of the oil mass samples often reflected whether the oil sample was taken primarily from the inside or outside of the sample.

In addition, those samples having nC_{17} /pristane ratios of less than 1.8 (i.e. degradation of the alkanes) often had two UCM's, which may be attributed to further weathering of the alkanes. While most oil mass samples had alkane maxima of nC_{28} - nC_{32} , those samples that had the lowest nC_{17} /pristane and nC_{18} /phytane ratios had alkane maxima of pristane and phytane, again indicative of a further stage of microbial degradation (Figure 7-A). The sample collected on January 28, 1994, however, had an alkane maxima of nC_{19} . Since this sample also had low nC_{17} /pristane and nC_{18} /phytane ratios,

the n-alkane probably was biogenically derived, as there were algal mats (common sources for nC₁₉) found on these oil mass samples at this time and until the end of the study.

The pristane/phytane ratios also fluctuated somewhat throughout the year, with a range of 0.6 to 1.8 (Table 1). Since the input of biogenic hydrocarbons with pristane would increase this ratio, it can be surmised that phytoplankton, algae, bacteria, and terrigenous organics could be a source of pristane, and consequently increase the pristane/phytane ratios.

Aromatics

The PAH data from the Station 4 September 24, 1993, oil mass sample indicated profiles indistinguishable from the Bunker C fuel oil. The naphthalenes, two ring compounds expected to weather first, were present in the same relative percent compositions as were found in the Bunker C oil sample (Figure 21). Phenanthrene, a three ring compound, was still the most abundant of the remaining PAH's. By the end of the year-long study (September 6, 1994 sample) only slight variations from the first collection were identified. The C₀ naphthalene component seemed to decrease slightly from the September 24, 1993, sample to 0.1% of the total (Figures 21 and 22). While there were small changes in the overall profile of the homologs of the PAH's, there were some slight losses of the higher homologs of pyrene and

chrysene (Figure 23). While these modest differences may be attributed to deviations in laboratory recovery rates, similar results were also reported by Overton et al. (1980). These authors noted that microbial degradative processes on C₃₊ PAH homologs exist and are more selective towards specific homologs due to enzymatic preferences. They suggest that photooxidative processes can also affect these homologs, however they tend to be less selective. Although this work is relatively new and still unconfirmed, according to these authors and others, these processes can aid in the degradation of some higher homolog PAH's (NRC 1985).

Summary of Oil Mass Samples

The oil mass samples collected from Station 4 exhibited very similar compositional characteristics throughout the year. There was a general loss of the lowest molecular weight alkanes (nC₁₃₋₁₄) from the original Bunker C fuel oil, due to evaporation and dissolution. There was also a loss in nC₃₃ from the Station 4 samples attributed to particle adsorption. The fluctuations in nC₁₇/pristane and nC₁₈/phytane ratios were used as markers for comparing weathering patterns from inside and outside the oil mass samples. The most identifiable changes in PAH's were in small losses of the highly soluble naphthalenes found in those samples which had been collected from outside of the oil masses. The slight deviations in the higher homologs of

pyrene and chrysene could be attributed to laboratory recovery rates or selective microbial and non-selective photooxidative processes.

Sediments

Aliphatics

Sediment samples from Station 1, generally had n-alkane ranges from approximately nC_{14} - nC_{32} . There was a loss of the lower molecular weight n-alkanes, again probably due to evaporation and/or dissolution. The alkane maxima from this station fluctuated from nC_{17} - nC_{30} , possibly correlating to the absence or presence of small tar balls within the analyzed sediments (Table 2).

All the sediment samples contained UCM's that correspond to expected weathered petroleum hydrocarbon profiles. These UCM's were normally located with the higher molecular compounds, however additional UCM's within the lower molecular weight ranges were identified in many of the samples. This may be due to secondary degradation by bacteria within this lower range.

The nC_{17} /pristane ratio varied significantly from one sample time to another. The ratio ranged from < 0.1 in the September 6, 1994, sample to 15.6 in the May 13, 1994 sample (Table 2). These variances can be attributed to: 1) the degradation of nC_{17} to give low nC_{17} /pristane ratios and

2) complete or almost complete depletions of pristane, and significant contributions of nC_{17} originating from biogenic sources, bacteria and algae, which would give rise to high nC_{17} /pristane ratios (Philp 1985). The loss nC_{18} in many of the sediment samples provided for low nC_{18} /phytane ratios. The complete absence of phytane from other sediment samples did not allow the computation of this ratio.

As the year progressed, there was a general increase, supported by station 5 sediment samples, in predominance of nC_{15} , nC_{17} , and nC_{29} which were evidently biogenically derived from bacteria, algae or higher terrigenous plants (Philp 1985). Because of these additional biogenic inputs, the OEP in some sediment samples increased substantially to as much as 23.6 (Table 2). Further, these inputs influenced the pristane/phytane ratios. With an input of biogenics comes the probable increase of pristane derived from oxidized chlorophyll.

The increase in pristane caused an increase in the pristane/phytane ratio in the September 6, 1994, sediment sample to 31.5. In many of the samples, this ratio could not be measured as phytane had completely degraded. Along with these weathering characteristics, there was a corresponding decrease in the percent resolved F1 area to as low as 3% in a large number of the samples (Table 2).

Station 2 sediments showed very similar characteristics to those found in Station 1 sediments, only to a lesser degree. The n-alkane ranges were fairly consistent at the

nC_{15} - nC_{32} range (Table 3). The alkane maxima varied little from nC_{29} . There was only one UCM in samples from this station, consistently at the higher range of n-alkanes except for the September 24, 1993 sample which had an additional UCM at the lower range. The resolved F1 area comprised a larger percent of the total F1 area than was found at Station 1. The nC_{17} /pristane and nC_{18} /phytane followed the same pattern as was found in the Station 1 sediments, but the fluctuations did not occur to those extremes.

Perhaps the reason for the milder degree of weathering at Station 2 can be explained by the location of this station relative to the location of Station 1. Station 1 was located on the western side of the island, and was exposed to higher energy physical processes. Conversely, Station 2 was located within a protected lagoon, not associated with higher energy processes. Since these sediments were protected from wave action and greater photooxidation, they did not weather as significantly as the Station 1 sediments. These data are similar to those found in a study on the Panama oil spill by Burns and Yelle-Simmons (1994), who found that mangrove sediments from sheltered channels exhibited the least amount of weathering.

The sediment samples from Station 5 were collected to ascertain natural background hydrocarbons for sediments from this island. Although the first sample from September 1993, exhibited the typical hydrocarbon Bunker C fuel oil profiles

found in the previous sediment samples of the same time, subsequent samplings indicated characteristics expected from purely biogenic sources. The OEP for these stations was generally $>>1.0$, and there were no concentrations of phytane, denoting a biogenic profile (Table 5).

A cooperative study by the University of South Florida and the office of the Tampa Bay Physical Oceanography Real-Time System (PORTS) found Bunker C fuel oil in sediments collected northeast and northwest of the spill site, twenty days after the spill. In this study it was determined that while the characteristic Bunker C oil was present, only n-alkanes nC_{19} - nC_{33} were found. Evidently, as some of the oil dispersed, the larger molecular weight n-alkanes adsorbed on to particulate material and were transported to the sediments, while the lower molecular weight n-alkanes were rapidly dissolved or evaporated. No PAH data from this study were available for comparison (Luther et al. 1993).

Sediments are widely recognized as likely sinks for contaminants. Areas of known accumulation of fine-grained sediments, such as found around mangrove islands, are known to accumulate contaminants to a greater degree than areas with larger grained sediments (Doyle et al. 1989). Mud, classified as sediments $<63\mu\text{m}$ in size, are known to be reactive and are often associated with contaminants. In a study of the characterization of Tampa Bay sediments, the sediments surrounding Eleanor Island contain from 23-56% mud-size surface sediments and the average, ambient

hydrocarbon concentration from the Boca Ciega area (where Eleanor Island is located) was found to be approximately 13 $\mu\text{g/g}$ dry sediment (Doyle et al. 1989).

Aromatics

There was a complete loss of naphthalene, dibenzothiophene, and the lower homologs of fluorene, along with a substantial decrease in the higher homologs in the fluorene series in the Station 1 September 1993, sediment sample (Figure 24). The same losses were observed in September 1994, along with the additional loss of the remaining fluorene series. Since these compounds are between naphthalene and phenanthrene in ring structure, they will be more soluble than the three and four ring compounds, therefore they will weather the most rapidly of the remaining PAH's. Their loss is an expected weathering characteristic, and is consistent with data found in previous work (Van Vleet et al. 1984, NRC 1985, Burns 1993, Wang 1994). The homologs of phenanthrene, pyrene and chrysene in the September 1994, sample indicate some losses in percent composition from the C_4 homolog of each of these PAH's (Figure 24). It was suggested by Overton et al. (1980), that when these PAH series are weathering, one possible pathway (microbial degradative processes) of degradation begins with the C_4 homolog first degrading to a C_3 by the cleaving of one methyl group.

Summary of sediment samples

The Station 1 sediment samples showed typical weathering characteristics. There was an increasing loss of lower molecular weight n-alkanes and an increase in the importance of the UCM found within the higher molecular weight n-alkanes. There were additional concentrations of odd-numbered hydrocarbons from biogenic sources that increased the OEP ratio over the year-long sampling period. While both Station 1 and Station 2 indicated expected weathering characteristics, Station 2 due to its protected location exhibited a more mild weathering profile. The PAH's for these sediments, showed an immediate loss of the naphthalenes, dibenzothiophene, and almost all of the fluorenes within six weeks of the spill. There were also changes within the homologs of many of the targeted PAH's indicating losses of the lower PAH's relative to the higher PAH's over time. At the end of one year, however, there still were significant quantities of the higher molecular weight PAH's present in the sediments.

Prop Roots

Aliphatics

The oiled prop root samples appeared to weather more rapidly than any of the oil mass or sediment samples. The prop roots immediately lost the n-alkanes from nC₁₃-nC₁₇ by the first sample from October 1993 (Figure 17). They exhibited a common UCM range of around nC₂₀-nC₃₁. With this evidence of immediate weathering, came further data substantiating this rapid process of degradation. The percent resolved area decreased from 15% in September 1993, to 0% in June 1994 (Table 5). No nC₁₇/pristane or nC₁₈/phytane ratios could be determined to monitor the degradation of alkanes compared to isoprenoids because both pristane and phytane were weathered or degraded completely in the first prop root sample. By September 1994, the UCM dominated the aliphatic hydrocarbons with nC₂₉ as the only detectable n-alkane present, a characteristic biogenic hydrocarbon.

The apparent rapid weathering of these prop roots can be attributed to their exposure to increased physical processes. Whereas the sediments were exposed to wave action, erosion, and photooxidation, the mangrove prop roots were also exposed to increased temperatures, wind action,

and higher exposure to photochemical decomposition. These factors would increase the rate of degradation. Prop roots analyzed in the Panama oil spill showed similar losses of the alkanes, resulting in a large UCM and an aliphatic profile comparable to the Eleanor Island mangrove prop roots (Burns 1993).

Aromatics

The prop roots exhibited many of the same weathering trends for aromatic hydrocarbons as the sediments. There was a complete loss of detectable amounts of naphthalene, dibenzothiophene, and fluorene in the first sample taken in October 1993 (Figure 27). These losses were also observed in the prop roots throughout the entire study. There were no amounts of the parent compound of phenanthrene in either sample.

Differences in the PAH profiles for the October 1993, and September 1994 samples existed in the homologs of phenanthrene, pyrene and chrysene (Figure 28). In the October 1993, prop root sample, there was a larger percent composition of the C₁-C₃ homologs of phenanthrene. These percentages decreased in the subsequent prop root sample. The C₃ homolog of pyrene also lost significant percent composition of the total, declining from 18% on October 1993, to 11% on September 1994. However, chrysene increased approximately 4-5% in composition for each homolog, from the

September 1993, sample (Figure 28). These data too, suggest that chrysene appears to weather least of these selected PAH's.

Summary of prop root samples

Prop root samples clearly indicated the greatest degree of weathering in all of the three types of mediums sampled (oil masses, sediments and prop roots). There was an immediate loss of many of the n-alkanes by the first sampling time of October 1993. The F1 resolved area was low (15%) in the first sample, compared to oil mass and sediment samples, and decreased to no F1 resolved area by the last sample of September 1994. There was a rapid and complete loss of the naphthalene, dibenzothiophene and fluorene parent compounds in the prop roots. The homologs of the remaining targeted PAH's indicated losses in all but the chrysene series.

6. Conclusions

The objectives of this project were to examine temporal changes in the hydrocarbon profile of Bunker C fuel oil found in oil masses, sediments, and on mangrove prop roots. The differences in these three mediums provided a comparison of weathering characteristics are a function of physical and biological processes.

The oil mass samples allowed for the investigation of compositional changes within an intact oil mass. Since not all oil spills result in the even dispersal of oil droplets, more vulnerable to weathering, this work offered some insight on the degradation of large oil deposits. The data suggest that in subtropical marine environments, virtually no weathering of the oil in a mass, occurs within at least one year after a spill of Bunker C fuel oil. The presence of almost all of the original n-alkanes and all of the targeted PAH's, points to the conclusion that without adequate exposure to physical and biological processes, Bunker C will not degrade for a long time. Studies on the Panama crude oil spill, while not Bunker C fuel oil, indicate that five years past the spill, pockets of oil were found that had the original crude oil profiles (Burns et al. 1994). A similar situation was also found in Chedabucto

Bay, seven years after the Arrow spill. In that study, Vandermeulen et al. (1977) observed that aromatics and cycloalkanes were still resistant to weathering.

Sediments afforded the most information on weathering of oil contaminants affected by subtropical climates. Since previous studies on weathering of Bunker C fuel oil were carried out in temperate regions, this geographic location provided an opportunity to compare and contrast degradation patterns in a subtropical setting. In general, by increasing the surface area of oil in the sediments through wave action, turbation, and availability to biological processes, a significant amount of weathering appears to occur. However, it was also concluded that deposition of the oil masses in protected lagoons delays the natural weathering process. Sediments collected in a lagoon area were much less degraded than those found on the exposed side of the island.

The study of weathering on mangrove prop roots was valuable in terms of remediation of oiled mangrove forests. This information could be of value when used in conjunction with studies regarding mangrove mortality and anticipated recovery of mangrove forests after an oil spill. The oil deposited on prop roots was the most completely weathered of all the oil samples. The immediate loss of almost of the n-alkanes and many of the PAH's was in contrast to the more slowly degrading sediment samples, and the essentially non-degrading oil mass samples. With increased exposure to

physical elements, came an increase in weathering of the exposed oil. This is useful information with regards to determining effects on mangroves as well as fauna which may depend on mangroves for food and/or protection.

Results of this study of the fate of Bunker C fuel oil shows that while most of the low molecular weight n-alkanes have degraded in the sediments and all have degraded on the mangrove prop roots, significant levels of PAH's still remain in all samples after one year. The loss of n-alkanes, while encouraging, is not of paramount importance since it is the PAH's that are toxic and threaten communities within the contaminated area. It is apparent that much of this oil will remain on and around Eleanor Island for a period of years to decades. Further studies of bioaccumulation and metabolism of these Bunker C components would complement the data from this project, offering a more complete analysis of the effect of Bunker C fuel oil in a subtropical marine environment.

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