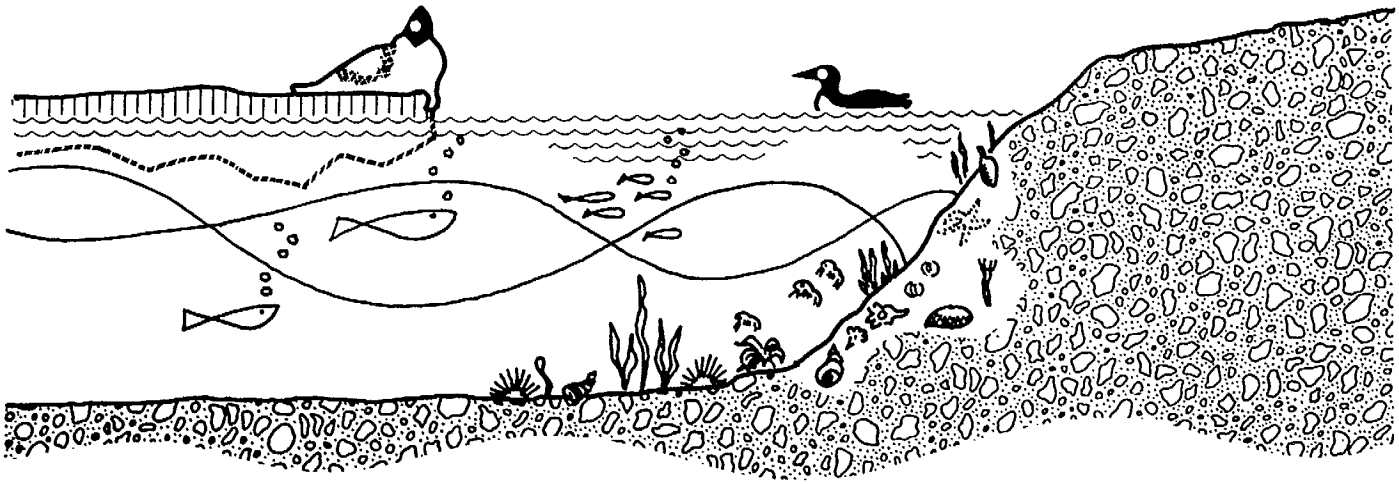
CHEMISTRY

2. Analytical Biogeochemistry



Baffin Island Oil Spill Project

WORKING REPORT SERIES
83-2

1983 STUDY RESULTS

BAFFIN ISLAND OIL SPILL PROJECT
WORKING REPORT SERIES

The Baffin Island Oil Spill (BIOS) Project is a multidisciplinary program of research on arctic marine oilspill fate, effects and countermeasures. The Project commenced in the spring of 1980 and has now completed the fourth and final year of planned field work at an experimental site located on the northern end of Baffin Island, Canada. The results of work performed in each of the various study components under the Project have been made available on a yearly basis through this working report series. This has been done prior to a complete integration of findings and interpretation with respect to the Project objectives. The working report series should therefore be considered as interim or data reports. The contents do no necessarily reflect the views or policies of the BIOS Project management or funders.

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BAFFIN ISLAND OIL SPILL PROJECT
CHEMISTRY COMPONENT-2:
ANALYTICAL BIOGEOCHEMISTRY

REPORT ON 1983 FIELD EXPERIMENTS

FINAL REPORT
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EXECUTIVE SUMMARY

The fourth year of a continuing series of analytical chemical studies of oil fate and transport from the Baffin Island Oil Spill (BIOS) program has been undertaken. Weathered oil continues to erode off the Bay 11 (untreated oil spill test site) beach resulting in increasing oil levels in the Bay 11 sediment. An overall sixfold concentration increase (up to 410 ppm) has been detected in the 3 meter and 7 meter sediments with concentrations decreasing offshore. Transport of oil residues to the deeper areas (35 m) of the Bay 11/12 Area (1-8 ppm) has been detected. Oil in the sediments is more highly weathered than was observed in 1982, although pockets of relatively fresh oil remain on the Bay 11 beach.

Oil concentrations in the sediments of Bay 9 after reaching a high of ~10 ppm in 1981 decreased to 1-3 ppm in 1982, but were seen to increase to levels of 5-10 ppm in 1983.

Detrital feeding benthic animals in Bay 11 appear to have achieved a balance of uptake and depuration of oil while decreasing (through metabolism?) their toxic aromatic hydrocarbon burden. Highest levels of oil are found in Macoma (~60 ppm) and urchins (~100 ppm) from Bay 11. Oil was detected in urchins at similar concentrations in Bay 9 although values for the other animals were much lower. Bay 7 remains relatively unimpacted.

Levels of oil in the water column are very low, generally less than 0.5 ppb. Correspondence of the 16 Liter and large volume water samples is fair with levels being somewhat lower (factor of 2) in the large volume samples. Oil at concentrations of ~1 ppb in was detected in Ragged Channel both types of samples with the compositions being similar.

Levels of aromatic hydrocarbons were lower in both the sediments and animals and were not directly related to absolute UV/F-determined oil levels.

Correspondence of UV/F with GC/GCMS data is very weak as was observed in the 1982 study. However, the UV/F signal should be considered to be most useful on a comparative basis as the detection of individual saturated and aromatic components becomes more difficult.

Continuing and increasing oil introduction to Bay 11 sediments caused by erosion of oil off the Bay 11 beach, and transport of sediment offshore are likely future scenarios in light of the above findings.

SECTION ONE

INTRODUCTION

1.1 Project Goals

The analytical chemistry component of the Baffin Island oil spill (BIOS) project involved two major tasks during the fourth year of the project:

1. Nearshore Study - Establishing the concentrations of residual oil, its transport paths, fates, and weathering in the three bays (Bay 11, 9, 7) in the various basic environmental compartments (i.e., water column, benthic sediments, organisms, shoreline) from samples of these compartments taken during the summer of 1983.

2. Shoreline Study - Performing chemical measurements of the oiled shoreline plots to determine concentration and composition of residual oil.

As in previous years (see Boehm et al., 1982a,b; Boehm, 1981; 1983a,b), a tailored analytical program combining analytical property measurements [i.e., ultraviolet fluorescence (UV/F) to determine oil concentrations in the various environmental components] with detailed compositional measurements [i.e., fused silica capillary gas chromatography (GC^2) combined with and computer-assisted gas chromatographic mass spectrometry (GC^2/MS)] was utilized.

The specific goals of the analytical chemistry program are given in Table 1.1.

1.2 Technical Plan

The analytical plan used in this study was nearly identical to that used previously and involved the following sample types: surface sediments, sediment floc, sediment cores, beached sediments, benthic animal tissues (5 species), water column samples. The types of analyses used: UV/fluorescence, capillary gas chromatography and gas chromatographic mass spectrometry were also used previously. The rationale for each type of analytical procedure is presented in detail in Section Two of this report. The overall plan was to carefully blend analytical techniques of varying sophistication and resolution to best enable the program goals to be achieved within budgetary constraints. Such blends have been successfully employed previously in this and other programs.

TABLE 1.1. HYDROCARBON BIOGEOCHEMISTRY (YEAR 4) GOALS

Nearshore (Ragged Channel)

1. To compare the composition and fates of oil as it impacted the three bays (11, 9, 7).

2. To examine the composition and concentration of high molecular weight petroleum components (n-C_{10} to n-C_{32}; alkylated benzenes to perylene) in a limited set of water column samples taken from the four bays.

3. To examine the chemical nature and weathering of residual surface slick oil and beached oil.

4. To examine the composition and concentration of oil in bottom sediments.

5. To analyze bottom sediments from Bays 11, 9 and 7 for oil content, composition, and weathering changes; to examine the relation of bulk sediment hydrocarbon chemistry; to that of the deposited surface flocculent layer in Bay 11; to examine possible trends in biodegradation; to examine possible offshore transport of the oil.

6. To examine the depuration of petroleum residues by several species of benthic marine organisms, and to examine how these processes varied by species and by bay.

7. To analyze a set of sediment samples from the Milne Inlet subtidal sediments (unimpacted area).

Shoreline Study (Z:Lagoon Area)

1. To determine the concentration and composition of residual oil remaining from several sets of shoreline oil spill countermeasure experiments.

SECTION TWO

SAMPLING AND ANALYTICAL METHODS

2.1 Sampling

Samples of seawater, offshore subtidal sediments, sediment cores, beach sediments, and benthic animals were collected from the experimental bays on Cape Hatt, Baffin Island, during August, 1983 (Figures 2.1, 2.2). Bay 11 had been the site of the untreated surface oil spill; Bay 9 had been the site of the chemically dispersed oil spill (Figure 2.2). A detailed description of the sampling techniques used appears in Boehm (1981a) and Boehm et al. (1982a). A brief summary of the sampling design and methodology is repeated here.

The sediment and tissue sampling design centered around the grid shown in Figure 2.3 which was identical to that used in 1981 and 1982 collections. Sampling activities occurred during one time during which a large amount of oversampling took place (vis-a-vis number of samples eventually analyzed).

In August a complete surface sediment collection (tissue plots and benthic transects) was obtained from each bay as was a complete collection of the five benthic species (Mya truncata, Serripes groenlandicus, Macoma calcarea, Astarte borealis, Strongylocentrotus droebachiensis). Surface floc was obtained from the tissue plots in Bay 11. Sediment cores (0-15 cm) were obtained at the north and south ends of the 3 and 7 m stratum in Bay 11 only. Several deep sediment samples were also obtained in the Bay 11/12 area further offshore in 35 m of water. Sediment samples were obtained at two microbiology transects in Bays 11 and 7 during August.

The water column sampling design is described in Humphrey et al. (1983) and the shoreline sampling design in Owens et al. (1983).

2.1.1 SEAWATER SAMPLING

Two parallel sets of seawater samples were collected. These consisted of 16 liter whole water samples, and large volume samples ($\sim$ 100 liters). The water samples

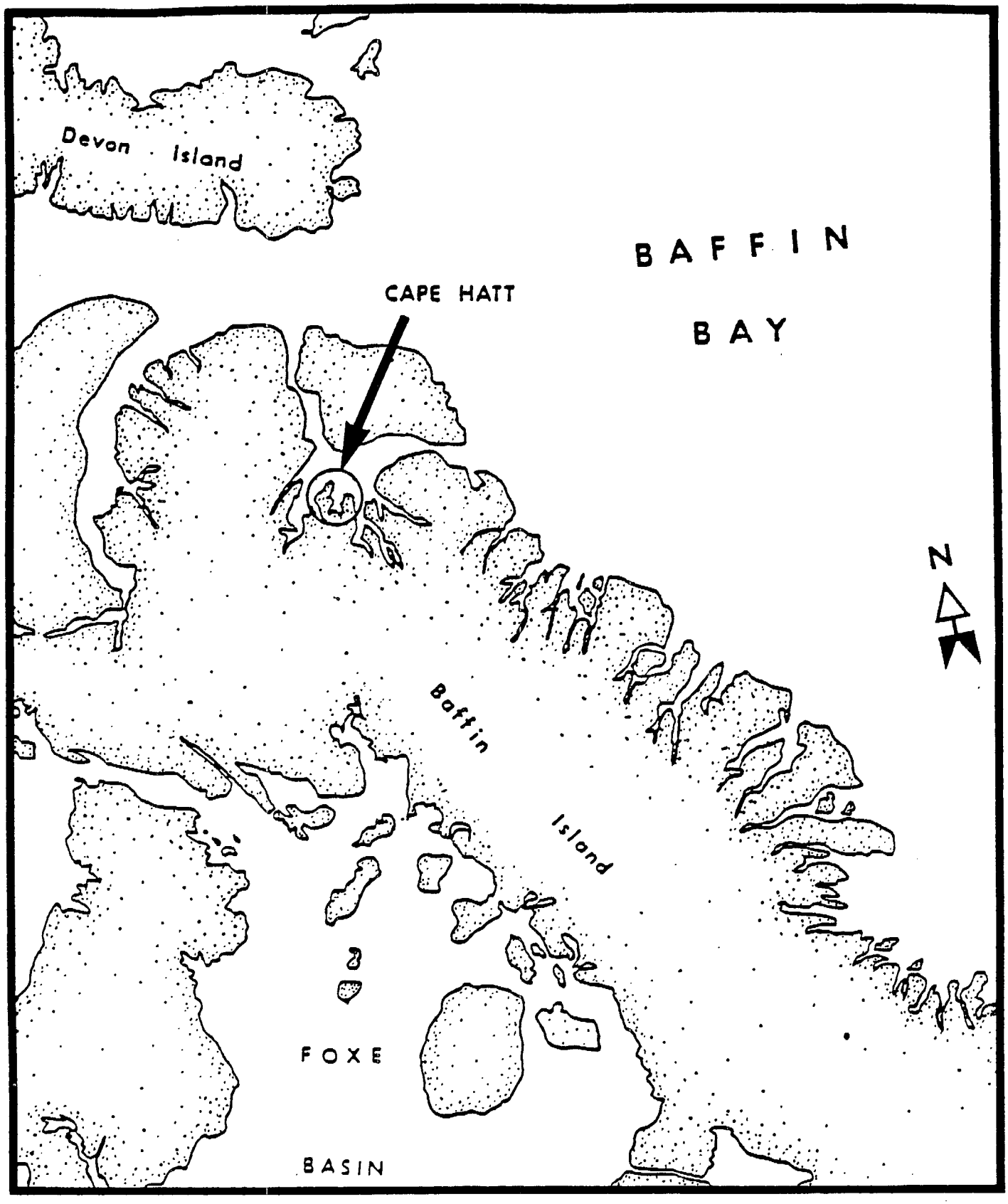


FIGURE 2.1. LOCATION OF CAPE HATT, BAFFIN ISLAND.

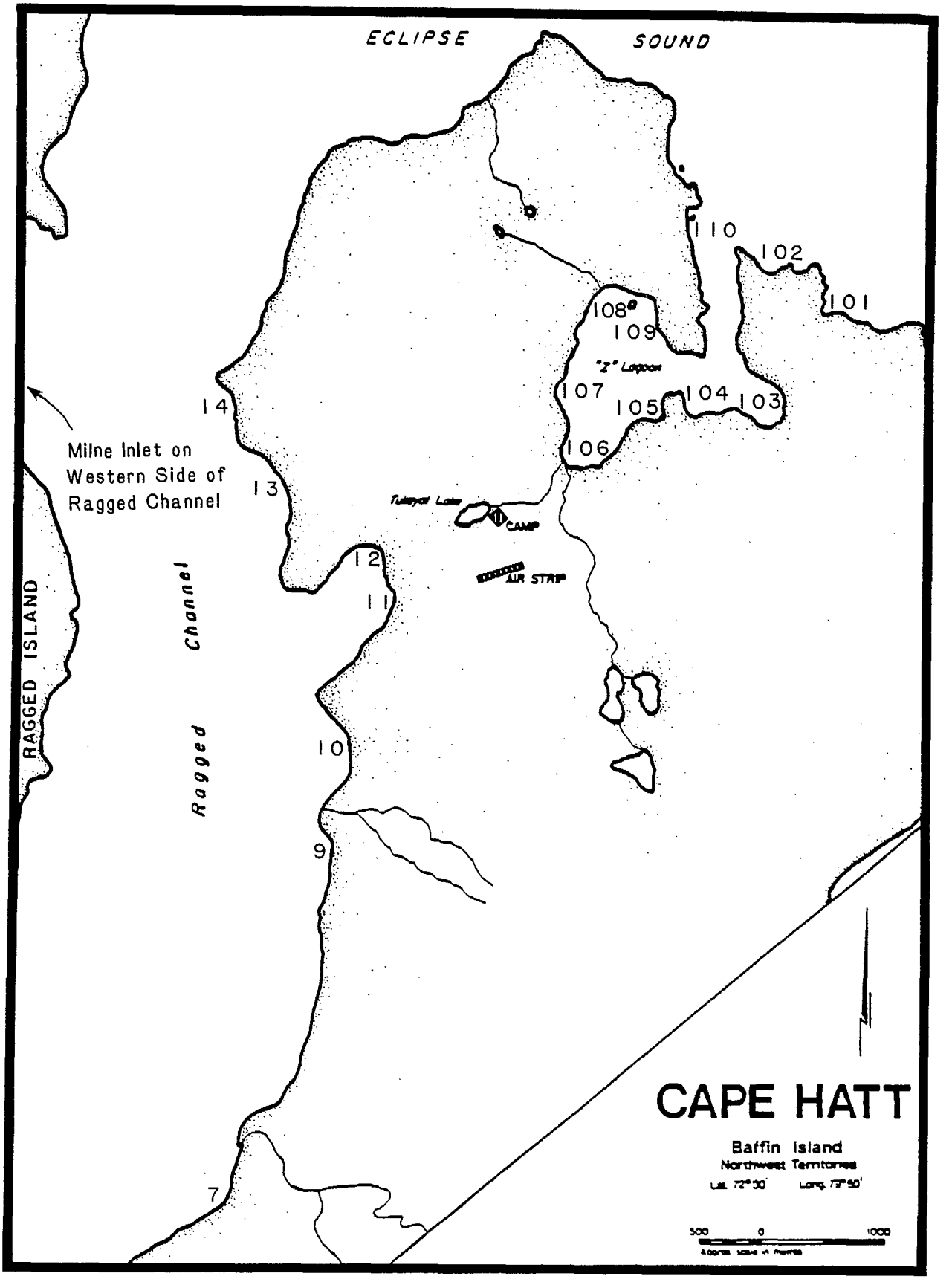


FIGURE 2.2. DETAIL OF TEST BAY LOCATIONS.

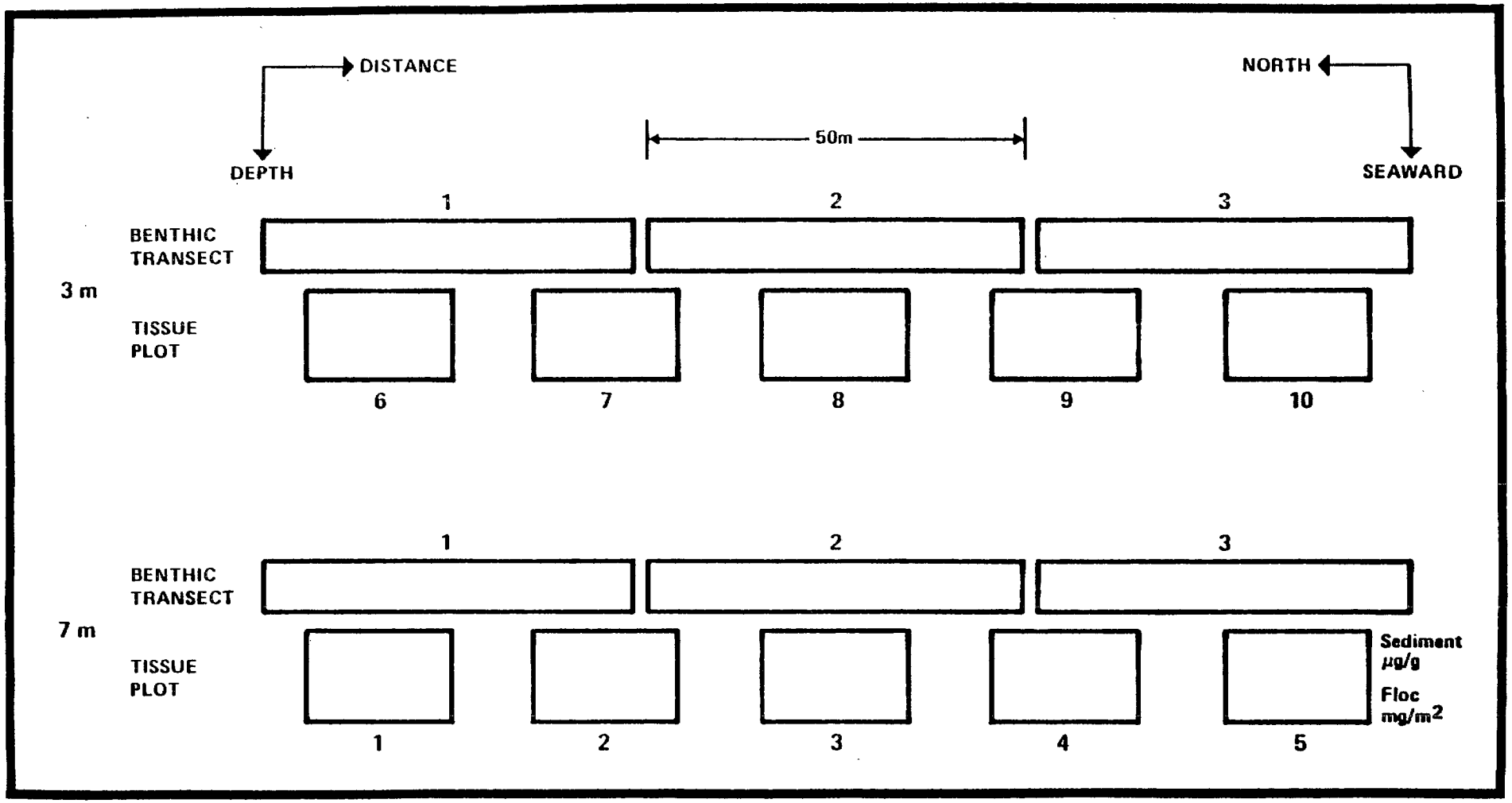


FIGURE 2.3. GENERAL DESCRIPTION OF BENTHIC SAMPLING GRID USED IN EACH BAY.

were collected mainly in Bay 11 although samples were obtained from Ragged Channel Milne Inlet and two from Bay 7 (The reader is referred to Humphrey, 1984 for station locations).

A pumping system was used to collect the seawater samples. A 4-liter solvent-rinsed glass bottle was filled with seawater (four times at each station), sealed with a sheet of Teflon and a screw cap, and stored at ambient temperatures until transported to the field laboratory (within 8 hours). At the field laboratory, the samples were preserved by adding 75 ml of Freon 113 to the bottle and then stored at room temperature until extraction.

Samples for large-volume high-molecular-weight hydrocarbon analysis were collected with an in situ filtration/absorption sampler. The sampler consisted of a submersible pump, a 293-mm glass fiber filter held in a stainless steel holder, a series of polyurethane plugs in a glass cylinder held in a Teflon sleeve and a flow measurement device. The apparatus was deployed for a period of 4 to 12 hours during which ~100 liters of seawater were pumped through the sampler. Particulates in the seawater were trapped on the filter which was simply folded, placed in an aluminum foil pouch and frozen. Dissolved organics were adsorbed to the polyurethane plugs in the glass cylinder which was sealed on each end with a sheet of Teflon and frozen.

2.1.2 SEDIMENT SAMPLING

Sediments were collected from the beaches in Bay 9, Bay 11 and the countermeasures test area (shoreline study) and from the subtidal bottom in Bays 9, 11 and 7 for high-molecular-weight hydrocarbon analysis. Beach sediment stations were located using transect markers established in Bay 9 and Bay 11 and from beach plot markers in the counter-measures test area. The samples from the 1980, 1981, 1982 countermeasures plots (shoreline study in Z-lagoon) were taken from randomly predesignated subareas within a test plot. Beach sediments from Bays 9 and 11 were sampled from a variety of surface and subsurface locations on each beach.

At each station, beach material was scooped into a solvent-rinsed glass jar with a stainless steel trowel. Surface sediment was taken from the top 5 centimeters, subsurface sediment from a depth of 10-15 cm. Care was taken to ensure that the subsurface sample was not contaminated with surface sediment. The samples were transported to the field laboratory and frozen.

Divers collected offshore surface sediment (0-2 cm) by scooping a glass jar along the sediment surface. Unfilled jars were taken through the water surface in a PVC tube whose ends were capped with PVC screw caps and sealed with polyethylene bags. Once below the surface the bags were cut, allowing the tube to flood with seawater and become negatively buoyant. Jars were dispensed from the bottom of the tube and replaced at the top of the tube when filled with sediment.

Divers collected sediment floc with a sampler that consisted of an inverted polyethylene funnel (diameter = 20 cm), a length of Tygon tubing (1 cm diameter x 1 m length), a submersible pump, a metal diverter valve and a stainless steel filter holder (142 mm diameter). The collection procedure is described in Boehm, 1983a.

2.1.3 BENTHIC ANIMAL SAMPLING

Benthic animals were collected from Bays 11, 9 and 7.

Divers picked Mya truncata and Strongylocentrotus droebachiensis using clean gloves. Animals collected from individual stations were placed in nylon mesh bags which were sealed in plastic bags underwater before being carried through the water surface. The contents of the mesh bag were transferred to a plastic bag, labeled, and transported to the field laboratory. The animals were then sorted by species, wrapped in aluminum foil, and frozen.

Other species Macoma calcarea, Astarte borealis and Serripes groenlandicus were airlifted from the sediment by divers. The airlift transferred animals, rocks and mud from the sediment surface into a mesh bag at the opposite end of the airlift. The mesh bag was carried through the water surface in a plastic bag and transported to the field laboratory. The animals were picked from the agglomeration of debris, sorted by species, wrapped in aluminum foil, and frozen.

2.2 Analytical Methods

The general analytical strategy for the chemical assessment consisted of three levels (Figure 2.4). In the first level, samples were extracted and analyzed by ultraviolet spectrofluorometry (UV/F) to measure the concentration of petroleum. Those samples either containing high levels of petroleum or of interest due to sampling time and position

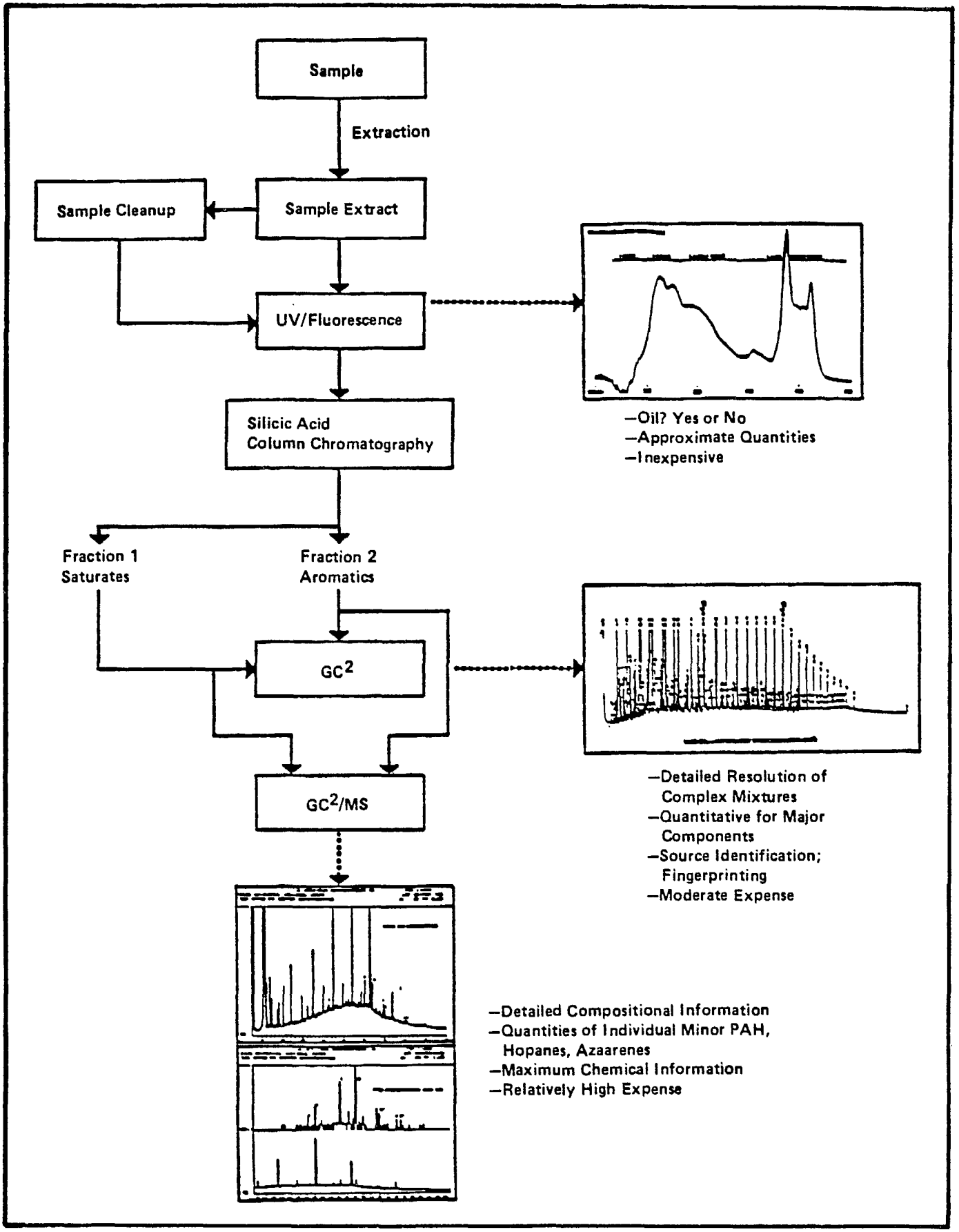


FIGURE 2.4. SCHEMATIC OF ANALYTICAL STRATEGY.

were carried through to the second level, fused silica glass capillary gas chromatography with flame ionization detection (GC^2). This technique was used to quantify hydrocarbons, to distinguish petroleum hydrocarbons from biogenic hydrocarbons, and to evaluate the composition of petroleum. Measurement of levels of individual aromatic hydrocarbons was accomplished during the third phase when computer-assisted gas-chromatographic/mass spectrometry (GC^2/MS) was used.

The basic types of samples (water, sediments, and tissues) were analyzed within this study, each according to a slightly different analysis scheme. Each sample type required a unique initial processing/sample extraction protocol and followed its own analytical scheme (see Figure 2.5). All samples were spiked with internal standards, androstane (saturated hydrocarbons) and o-terphenyl (aromatic hydrocarbons) prior to solvent extraction.

2.2.1 SAMPLE PROCESSING

2.2.1.1 Water Samples (16 Liters)

Sixteen-liter seawater samples were analyzed for high molecular weight hyrocarbons by GC^2. The water was processed in the field laboratory by extracting three times with Freon. The three extracts were combined, reduced in volume to 10 ml by rotary evaporation and transferred to a glass tube for shipment. Procedural blanks were processed periodically to check for contamination during the field processing.

When received at Battelle, the extracts were dried with sodium sulfate, evaporated to <1 ml by rotary evaporation, and displaced with hexane. Three micrograms of two internal standards, androstane and o-terphenyl, were added to the extract. An aliquot of the extract was weighed on a Cahn Model 25 electrobalance to determine total extractable organics. All samples contained large amounts of total extractable organics (natural lipids) and were therefore fractionated by silica gel/alumina column chromatography (see Boehm et al., 1982a) into saturated and unsaturated/aromatic fractions which were analyzed by GC^2 (see Boehm et al., 1982a). Aromatic fractions and total extracts of selected samples were analyzed by GC^2/MS (see Boehm et al., 1982a).

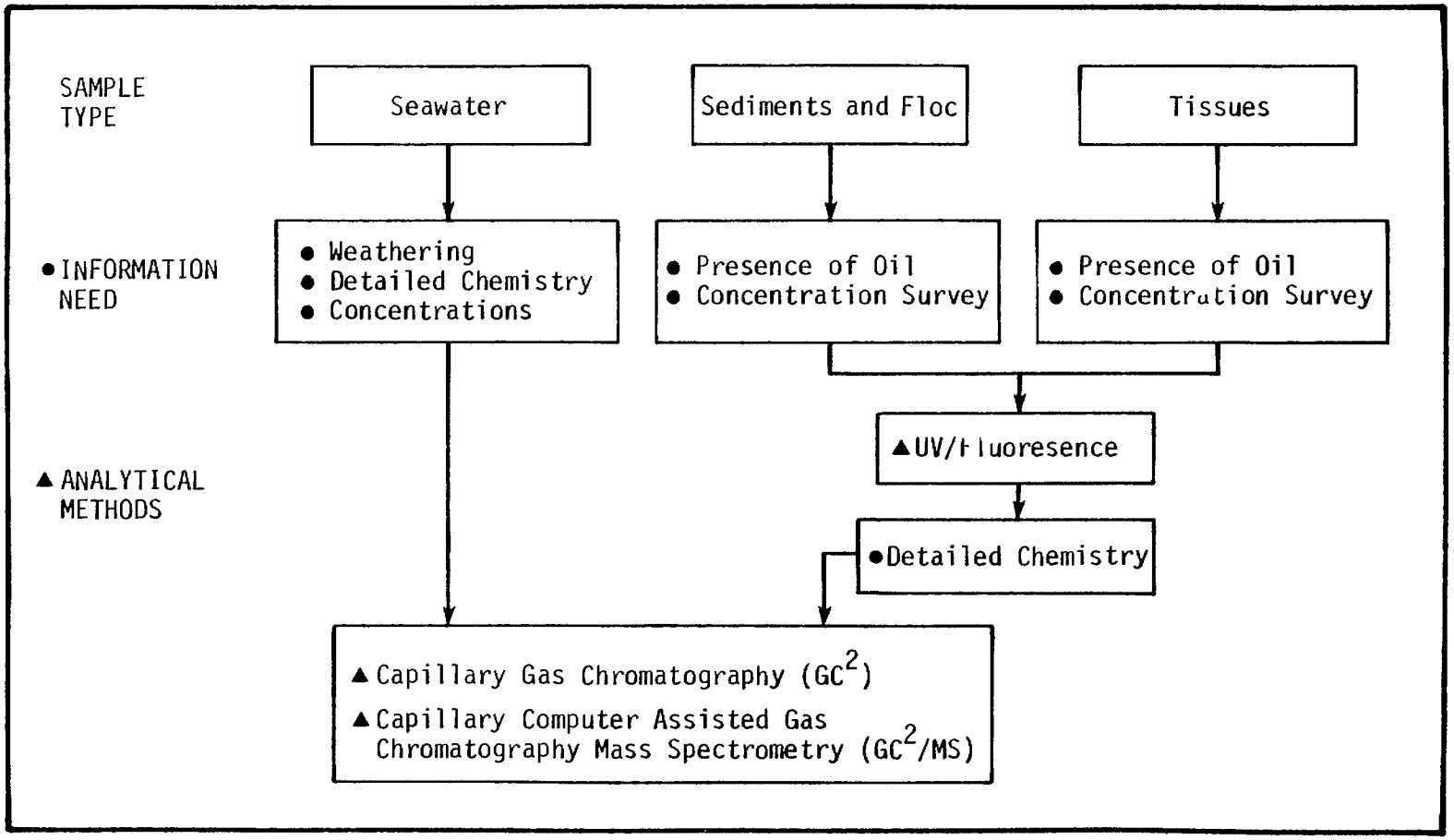


FIGURE 2.5. BIOS ANALYTICAL PROTOCOLS.

2.2.1.2 Large Volume Water Samples (90-100 Liters)

Each large volume water sample consisted of a glass fiber filter containing particulate organics and a polyurethane plug containing dissolved organics, both of which were analyzed for high-molecular weight hydrocarbons by GC^2. The filters were processed by cutting them into small pieces which were placed into 250-ml Teflon jars. Three micrograms of two internal standards (androstane and o-terphenyl) and 100 ml of a mixture of dichloromethane and methanol (9:1) were added. The jars were shaken for four hours, and the solvent was decanted. The extraction was repeated with two additional portions of solvent, and the three extracts were combined.

The plugs were processed by squeezing them in the presence of methanol followed by extracting them in a Soxhlet extractor for 24 hours with methanol to remove water and then with dichloromethane:methanol (9:1) to extract organic compounds. All solvent extracts from a sample were combined in a one-liter separatory funnel, the dicholoromethane layer was drawn off, and the remaining water/methanol was extracted three times with 75 ml of dichloromethane. The dichloromethane extracts from a sample were combined with the combined filter extracts to yield one combined "dissolved" plus particulate hydrocarbon sample. The combined extracts reduced in volume to <1 ml by rotary evaporation and displaced with hexane. An aliquot of each of the extracts was weighed on a Cahn Model 25 electrobalance to determine total extractable organics. The extracts were fractionated by silica gel/alumina column chromatography (see Section 2.2.2.2) into saturated and unsaturated/aromatic fractions which were analyzed by capillary GC^2. Aromatic fractions of selected samples were analyzed by GC^2/MS.

2.2.1.3 Sediment Sample Processing

Three types of sediment samples were collected and analyzed: surface sediment samples (0-2 cm), oiled beach sediments and, surface floc samples. The sediment and floc were analyzed by different protocols.

2.2.1.3a Surface Sediments (Benthic Transects, Tissue Plots, Microbiology Sediments, Sediment Cores). Surface sediment samples from the benthic transects and tissue plots were analyzed for high-molecular-weight hydrocarbons using UV/F. One hundred gram subsamples were analyzed by UV/F using the analytical method described

below. Selected samples from individual tissue plots and benthic transects and all microbiology sediment samples were analyzed by GC^2.

The extraction method for the sediment UV/F and GC^2 analysis of sediment samples was based on methods of Brown et al. (1979) and Boehm et al. (1981). Approximately 100 g of wet sediment was weighed into a 250-ml Teflon jar and dried by extracting three times with 75 ml of methanol. Five micrograms of two internal standards, androstane and o-terphenyl were added to the sediment. The dry sediment was then extracted three times with 100 ml of dichloromethane: methanol (9:1) by shaking on a platform shaker for a minimum of 4 hours for each extraction. All solvent extracts were transferred into a 1-liter separatory funnel containing 100 ml of water (Millipore RO) and acidified to a pH of 2 with hydrochloric acid. The dichloromethane layer was drawn off and the aqueous methanol phase was extracted 3 times with 50 ml of dichloromethane. The dichloromethane extracts from a sample were combined, reduced in volume to 1 ml by rotary evaporation and displaced with methanol. The extract was transferred to a 50 ml glass tube containing 10 ml of methanol and 4 ml of 10N aqueous KOH, sealed with a Teflon cap and heated at 80°C for 4 hours to saponify interfering polar compounds. The mixture was cooled then extracted 3 times with 15 ml of hexane. The combined hexane extracts were dried over sodium sulfate and concentrated by rotary evaporation to approximately 1 ml. The extract was then analyzed by UV/F (see Section 2.2.2.1).

Single aliquots of extracts to be further analyzed by GC^2 and/or GC^2/MS were weighed on a Cahn Model 25 electrobalance to determine total extractable organics. The extracts were fractionated by silica gel/alumina column chromatography into saturated and unsaturated/aromatic fractions which were analyzed by GC^2. Aromatic fractions of selected samples were analyzed by capillary GC^2/MS.

2.2.1.3b Surface Floc Analysis. Surface floc samples were analyzed for high-molecular-weight hydrocarbons using UV/F. A selected subset were analyzed by GC^2 and GC^2/MS techniques. The glass fiber filters containing the floc were extracted with dichloromethane:methanol (9:1) using the techniques described for the large volume water sample filters. The total extracts were freed of polar compounds which interface with the UV/F by saponification as described for surface sediments. All sample extracts were analyzed by UV/F and selected samples were fractionated by silica gel/alumina column chromatography into saturated and unsaturated aromatic fractions which were analyzed by GC^2. Selected aromatic fractions were analyzed by GC^2/MS.

2.2.1.3c Oiled Beach Sediment Analysis. Oiled beach sediments were analyzed for high molecular weight hydrocarbons using only GC^2 techniques. The analytical methodology was the same as that described for GC^2 analysis of surface sediments.

2.2.1.4 Benthic Animal Tissue Processing

Five species of benthic bivalves were analyzed: Mya truncata, Serripes groenlandicus, Macoma calcarea, Astarte borealis, and Strongylocentrotus droebachiensis (sea urchin). Samples from individual tissue plot stations were analyzed by UV/F. Subsequently, extracts from all five tissue plot stations at a given depth and bay were combined and analyzed by GC^2.

The extraction and analytical procedure (see Boehm et al., 1982a) was based closely on that of Warner (1976) as revised by Boehm et al. (1982c). Clam tissues (guts, muscle, gills) were removed from the shells with solvent-rinsed utensils. Samples with more than 10 grams wet weight tissue were homogenized with a Polytron tissue homogenizer, and a 10-30 g aliquot was taken for analysis. Otherwise, the entire sample was homogenized. A small aliquot of the tissue homogenate was taken for wet weight/dry weight determination. Tissue was digested overnight with a 5 N aqueous potassium hydroxide and were then extracted in a separatory funnel with hexane. Hexane extracts were combined, dried with sodium sulfate and concentrated to 0.5 ml by rotary evaporation. Polar and biogenic compounds which interfered with the UV/F analysis were removed from the extract by aluminia column chromatography. One of two sizes of columns, one containing 6.5 g and the other containing 25 g of 7.5% water deactivated alumina, were used depending on the amount of tissue. The column was eluted with 25 ml or 75 ml of hexane/dichloromethane (9:1) to isolate the saturated, unsaturated and aromatic compounds. The fraction was concentrated and transferred into hexane for UV/F analysis.

After UV/F analysis, the extracts from the tissue plot stations along each depth stratum were combined, concentrated by rotary evaporation and displaced with hexane. The pooled extracts 5 species x 3 bays were fractionated by silica gel/alumina column chromatography into saturated and unsaturated/aromatic fractions which were analyzed by GC^2. Aromatic fractions from these fifteen combined samples were analyzed by GC^2/MS.

2.2.2 SAMPLE ANALYSIS

2.2.2.1 UV/F Analysis

The synchronous excitation/emission technique used has been extensively described previously (Boehm et al., 1982a). The analytical conditions are shown in Table 2.1. This technique measures aromatic hydrocarbons with a two- to five-ring aromatic structure (Lloyd, 1971). The extract was repeatedly diluted by 50% and reanalyzed until a comparison of two consecutive dilutions indicated that the analysis was done within the linear range of fluorescence response. The intensity of the fluorescence spectra was measured at 350-360 nm which corresponded to a peak maximum present in a Lagomedio Bay 11 reference oil sample. The fluorescence spectra were converted to relative concentration units by comparing the peak height at each wavelength to that of a Bay 11 oil standard curve.

2.2.2.2 Fractionation

Those sediment, tissue, and water samples chosen for GC^2 analyses were fractionated by silica gel/alumina column chromatography prior to GC^2 analysis. Column chromatography isolated the saturated and aromatic hydrocarbons from the total extract, thereby facilitating the identification and quantification of individual hydrocarbon compounds which were present in the sample extract.

The total extract was charged to a 100% activated silica gel/5 percent deactivated alumina/activated copper (11 g, 1 g, 2 g) chromatography column that was wet-packed in dichloromethane and prepared by eluting with 30 ml each of dichloromethane and hexane. The column was eluted with 18 ml of hexane followed by 21 ml of hexane:dichloromethane (1:1) to isolate the saturated (f_1) and aromatic/unsaturated (f_2) hydrocarbons, respectively. After concentrating each fraction by rotary evaporation, the total gravimetric concentration was determined by weighing a measured aliquot on a Cahn Model 25 electrobalance.

TABLE 2.1. UV SPECTROFLUOROMETRY ANALYTICAL CONDITIONS

Instrument:	Farrand System 3 spectrofluorometer
Features:	Corrected excitation
Slits:	
Excitation:	2.5 nm
Emission:	5.0 nm
Scan Speed:	50 nm/min
Cell:	10 nm quartz
Monochrometers:	Synchronous
Excitation:	225-475 nm
Emission:	250-500 nm
Daily Calibration:	Bay 11 Lagomedio oil
Quantification:	External calibration curves

2.2.2.3 GC^2 Analysis

GC^2 analysis served to identify and quantify the petroleum hydrocarbon compounds present in the sample. The relative concentrations of individual compounds identified the composition of oil present, and the absolute concentrations served as a measure of the amount of oil present. The concentrations of certain compounds were also used to calculate indicator ratios that reveal the type of hydrocarbons present, i.e., biogenic or petroleum.

Each fraction was analyzed by fused silica capillary gas chromatography on a Hewlett Packard 5840 or 5880 gas chromatograph equipped with a splitless injection port and a flame ionization detector. Wall coated open tubular (WCOT) fused silica columns (0.25 mm x 30 m, J&W Scientific) coated with SE30 and SE54 stationary phases were used to analyze, respectively, the f_1 and f_2 fractions from the column chromatography. The instrumental conditions are listed in Table 2.2. Compounds were identified by comparing retention indices of peaks in the samples to retention indices of known compounds in a standard mixture that was analyzed daily. Concentrations were calculated by comparing the integrated areas of peaks with the area of the appropriate internal standard (androstane for the f_1, o-terphenyl for the f_2). The total concentrations of saturated and aromatic hydrocarbons were determined by planimetering the unresolved area, converting it to integrator area units, adding it to the total resolved integrated area, and calculating a concentration using the internal standard method.

The concentrations of n-alkanes and isoprenoids were determined from GC^2 on a dry weight basis. From these concentrations, a series of key diagnostic parameters were calculated (Tables 2.3 and 2.4). These ratios are useful in establishing the composition of the oil, the contribution of biogenic hydrocarbons, and the degree that the oil was weathered when compared to values for the spilled oil itself (Table 2.4).

Concentrations of the chromatographically unresolved complex mixture (UCM) appearing as a "hump" on the GC^2 traces were quantified relative to the internal standard by plainimetry. This UCM is characteristic of residual petroleum hydrocarbons in the samples.

TABLE 2.2. FUSED SILICA CAPILLARY GAS CHROMATOGRAPHY/FLAME IONIZATION DETECTION ANALYTICAL CONDITIONS

Instrument:	Hewlett Packard 5840 or 5880 gas chromatograph
Features:	Split/splitless capillary inlet system Microprocessor-controlled functions
Inlet:	Splitless
Detector:	Flame ionization
Column:	
f_1:	0.25 mm I.D. x 30 m SE30 fused silica (J&W Scientific)
f_2:	0.25 mm I.D. x 30 m SE54 fused silica (J&W Scientific)
Gases:	
Carrier:	Helium 2 ml/min
Make-up:	Helium 30 ml/min
Detector:	Air 300 ml/min (500 ml/min for 5880)
Temperatures:	
Injection port:	250°C
Detector:	300°C
Column oven:	40°-290° 3°C/min
Daily calibration:	Alkane/aromatic mixture
Quantification:	Internal standards (F_1 androstane; f_2 o-terphenyl)

TABLE 2.3. EXPLANATION OF PETROLEUM WEATHERING AND SOURCE RATIOS

1. The Biodegradation Ratio (Alkane/Isoprenoid)

$$ALK/ISO_{14-18} = \frac{1400 + 1500 + 1600 + 1700 + 1800}{1380 + 1470 + 1650 + 1708 + 1810}$$

The ALK/ISO ratio approaches 0 as the n-alkanes are depleted.

2. The n-C_{18}/Phytane Ratio

The C_{18}/Phy ratio also approaches 0 as n-C_{18} is preferentially depleted

3. The Pristane/Phytane Ratio

The Pris/Phy ratio is equal to ~0.7 in aged Lagomedio oil. As the amounts of the biogenic isoprenoid, pristane increase relative to the petrogenic isoprenoid, phytane, this ratio becomes large.

4. The Saturated Hydrocarbon Weathering Ratio (SHWR)

$$SWHR = \frac{\text{sum of n-alkanes from n-}C_{10}\text{ to n-}C_{25}}{\text{sum of n-alkanes from n-}C_{17}\text{ to n-}C_{25}}$$

The SWHR approaches 1.0 as low-boiling saturated hydrocarbons (n-C_{10} to n-C_{17}) are lost by evaporation.

5. The Aromatic Weathering Ratio (AWR)

$$AWR = \frac{\text{Akyl benzenes + naphthalenes + fluorenes + phenanthrenes + dibenzothiophenes}}{\text{Total phenanthrenes + dibenzothiophenes}}$$

The AWR approaches 1.0 as low-boiling aromatics are lost by evaporation and/or dissolution.

6. Carbon Preference Index (CPI)

$$CPI = \frac{2(\text{n-}C_{27} + \text{n-}C_{29})}{\text{N-}C_{26} + 2nC_{28} + \text{n-}C_{30})}$$

CPI $\cong$ 1.0 for petroleum
CPI ranges from 3-6 for terrigenous plant waxes.
The relative amounts of petroleum alkanes to terrigenous biogenics can be assessed through this ratio.

TABLE 2.4. SATURATED AND AROMATIC HYDROCARBON PARAMETERS OF LAGOMEDIO CRUDE OIL[a]

	Fresh Oil	Aged Oil
Saturates		
SHWR	2.9	2.3
ALK/ISO	2.4	2.5
Pris/Phy	0.85	0.74
n-C_{18}/Phy[b]	1.6	1.6
Aromatics		
AWR	4.3	3.5

[a]Key

$$\text{SHWR} = \frac{(\sum \text{n-alkanes; } C_{10}\text{-}C_{25})}{(\sum \text{n-alkanes: } C_{17}\text{-}C_{25})}$$

$$\text{AWR} = \frac{\text{(Alkyl Benzenes + Naphthalenes + Fluorenes + Phenanthrenes + Dibenzothiophenes)}}{\text{Phenanthrenes + Dibenzothiphenes}}$$

$$\text{ALK/ISO} = \frac{(\sum \text{alkanes; } C_{14}\text{-}C_{18})}{(\sum 5 \text{ isoprenoids; in n-}C_{13} \text{ boiling range})}$$

PRIS = pristane

PHY = phytane

[b] Note: This ratio was expressed as the inverse in previous BIOS reports. It is reformulated here to be consistent in concept to the ALK/ISO ratio.

2.2.2.4 Gas Chromatography/Mass Spectrometry (GC^2/MS)

Selected samples suspected to contain petroleum by the GC^2 analyses were analyzed by GC^2/MS to measure the concentration and composition of individual aromatic hydrocarbons in the samples. The concentrations of a series of polynuclear aromatic hydrocarbons, in particular the alkylated phenanthrenes and dibenzothiophenes, serve as a fingerprint of weathered petroleum.

The f_2 (aromatic fraction) from the silica gel/alumina column chromatography was analyzed for polynuclear aromatic hydrocarbons by GC^2/MS. An aliquot of the fraction was analyzed using a Finnegan 4530 instrument equipped with a 0.25 mm x 30 m SE54 fused silica capillary column (J&W Scientific), which was threaded directly into the ion source. Instrumental conditions are listed in Table 2.5.

Selected ion searches were used to obtain ion chromatograms for aromatic compounds with known retention indices and suspected to be present in the samples. Concentrations of the identified compounds were determined by measuring peak areas of the appropriate peaks in the selected ion chromatograms and relating them to that of the internal standard. Relative response factors for each component were calculated from analyses of analytical standards, if available, or were extrapolated. The compounds reported from the GC^2/MS analyses are listed in Table 2.6 and are presented in a series of Figures in the results section with compound designations as in Table 2.6.

TABLE 2.5 GAS CHROMATOGRAPHY/MASS SPECTROMETRY INSTRUMENTAL CONDITIONS

INSTRUMENT:	Finnegan 4530 gas chromatograph/mass spectrometer
FEATURES:	Data General Nova 3 data system with Incos data system Finnegan MAT 9610
INLET:	Splitless
DETECTOR:	Quadrupole mass spectrometer
SCAN RATE:	450 amu/sec (45-450 amu)
IONIZATION VOLTAGE:	70 eV
COLUMN:	0.25 mm i.d. x 30 m SE54 fused silica (J&W Scientific)
INTERFACE:	Direct insertion of column into source
CARRIER GAS:	Helium 2 ml/min
TEMPERATURES:	
INJECTION PORT:	270°C
SEPARATOR OVEN:	280°C
SOURCE:	250°C
GC OVEN:	40-290°C, 10°C/min (temperature program)
DAILY CALIBRATION:	FC43, DFTPP and aromatic mixture
QUANTIFICATION:	Internal standard (o-terphenyl) (response factors)

TABLE 2.6 GAS CHROMATOGRAPHY/MASS SPECTROMETRY ANALYTICAL OUTPUTS

POLYNUCLEAR AROMATIC HYDROCARBONS	
Abbreviation	Compound or Compound Grouping
AB	Alkyl benzenes (C_3 to C_6)
N	Naphthalene homologous series
C_0N	Naphthalene
C_1N	Methyl naphthalenes
C_2N-C_4N	Alkyl naphthalenes
F	Fluorene homologous series
C_0F	Fluorene
C_1-C_3F	Alkylated fluorenes
P	Phenanthrene homologous series
C_0P	Phenanthrene
C_1PC_4P	Alkylated phenanthrenes
DBT	Dibenzothiophene homologous series
C_0DBT	Dibenzothiophene
C_1DBT-C_3DBT	Alkylated dibenzothiophenes
PAH	Fluoranthene Pyrene Benzo(a)anthracene Chrysene Benzofluoranthene Benzo(a)pyrene Benzo(e)pyrene Perylene

SECTION THREE

RESULTS (NEARSHORE STUDY)

3.1 Water Column

3.1.1 OIL ON THE WATER'S SURFACE (SURFACE SHEEN SLICK)

Two 16 Liter samples of seawater were collected in an area of visable sheening in Bay 11. These sheens, which originated from the stranded oil residues on the Bay 11 beach, were analyzed mainly to determine the composition of the surface sheens, their weathering characteristics as well as the total oil concentrations in the 16 Liter surface water sample.

Concentrations of petroleum in these samples (Table 3.1) were 1870 and 1030 µg/sample. These samples represent the source petroleum leached from the Bay 11 beach. The compositional characteristics of the two samples are similar (Figures 3.1 and 3.2). The petroleum is highly weathered having lost much of its n-alkane material in the n-C_{10} to n-C_{17} range. Normal alkanes remain prominent in the n-C_{20} to n-C_{34} range. SHWR ratios for both samples are ~1.0. That the residual oil has been extensively biodegraded is evident from the low C_{18}/Phy ratios (~0.26). The higher molecular weight normal alkanes appear to be exempted from this microbial attack. Similar weathered residues from temperate spills (e.g., Amoco Cadiz, Boehm et al., 1981) exhibit near-total depletion of all n-alkanes throughout the boiling range (see Figure 1.4 in Boehm et al., 1982a).

Surface sheen samples taken in 1982 (see Boehm, 1983a) were weathered to a lesser extent (SHWR - 2.0; C_{18}/Phy = 1.6) than the samples taken in 1983.

Both of these samples were analyzed by GC^2/MS. The results are presented in Figure 3.3. The aromatic compositions are comprised entirely of alkylated phenanthrene and dibenzothiophene (DBT) compounds. Sample W4022 also contained tri and tetramethyl naphthalenes. These compositions convert to the AWR ratios presented in Table 3.1

TABLE 3.1. SEAWATER ANALYTICAL RESULTS (16 LITER)

Sample ID	Volume (L)	Description	Hydrocarbon Concentrations (µg/L) Saturates	Aromatics	Total	SHWR	C_{18}/Phy	AWR	Oil?
W4021	NA	Bay 11; Surface Slick 8-12-83; 1300	330[a]	1540[a]	1870[a]	1.1	.27	1.0	Yes
W4022	NA	Bay 11; Surface Slick	460[a]	570[a]	1030[a]	1.0	.26	1.1	Yes
W4003	15.9	Bay 11; S. Micro; 10m 8-12-83; 1017	.26	.11	.37	--	--	ND	No
W4004	15.4	Bay 11; S. Micro; 1m 8-12-83; 1243	.20	.33	.53	--	--	ND	Trace
W4008	16.1	Bay 11; S. Micro; 10m 8-13-83; 1540	<.1	<.1	<.1	--	--	--	No
W4009	12.2	Bay 11; S. Micro; 1m 8-13-83; 1949	<.1	<.1	<.1	--	--	--	No
W4010	15.8	Bay 11; S. Micro; 10m 8-15-83; 1131	.14	.17	.31	--	--	--	No
W4011	16.0	Bay 11; S. Micro; 1m 8-15-83; 0750	.18	.18	.36	--	--	--	No
W4013	15.8	Bay 11; S. Micro; 10m 8-16-83; 0810	1.1	<.1	1.1	--	--	--	Trace
W4014	15.7	Bay 11; S. Micro; 1m 8-16-83; 1131	.18	.10	.28	--	--	--	No
W4015	15.6	Bay 11; S. Micro; 10m 8-19-83; 0810	.26	.1	.36	--	--	--	Trace
W4016	15.2	Bay 11; S.Micro; 1m 8-19-83; 1207	.27	<.1	.27	--	--	--	No
W4006	15.5	Bay 7; N. Micro; 5m 8-12-83; 1555	.26	.20	.46	--	--	ND	No
W4017	15.5	Bay 7; N. Micro; 5m 8-18-83; 0820	.17	<.1	.17	--	--	--	No
W4005	15.8	Ragged Channel; 5m 8-16-83; 1735	1.7	1.0	2.7	--	--	--	Yes
W4012	16.1	Milne Inlet; 5m 8-15-83; 1521	<.1	<.1	<.1	--	--	--	No

a = Values in µg/sample; no volume reported.
ND = No aromatics detected.

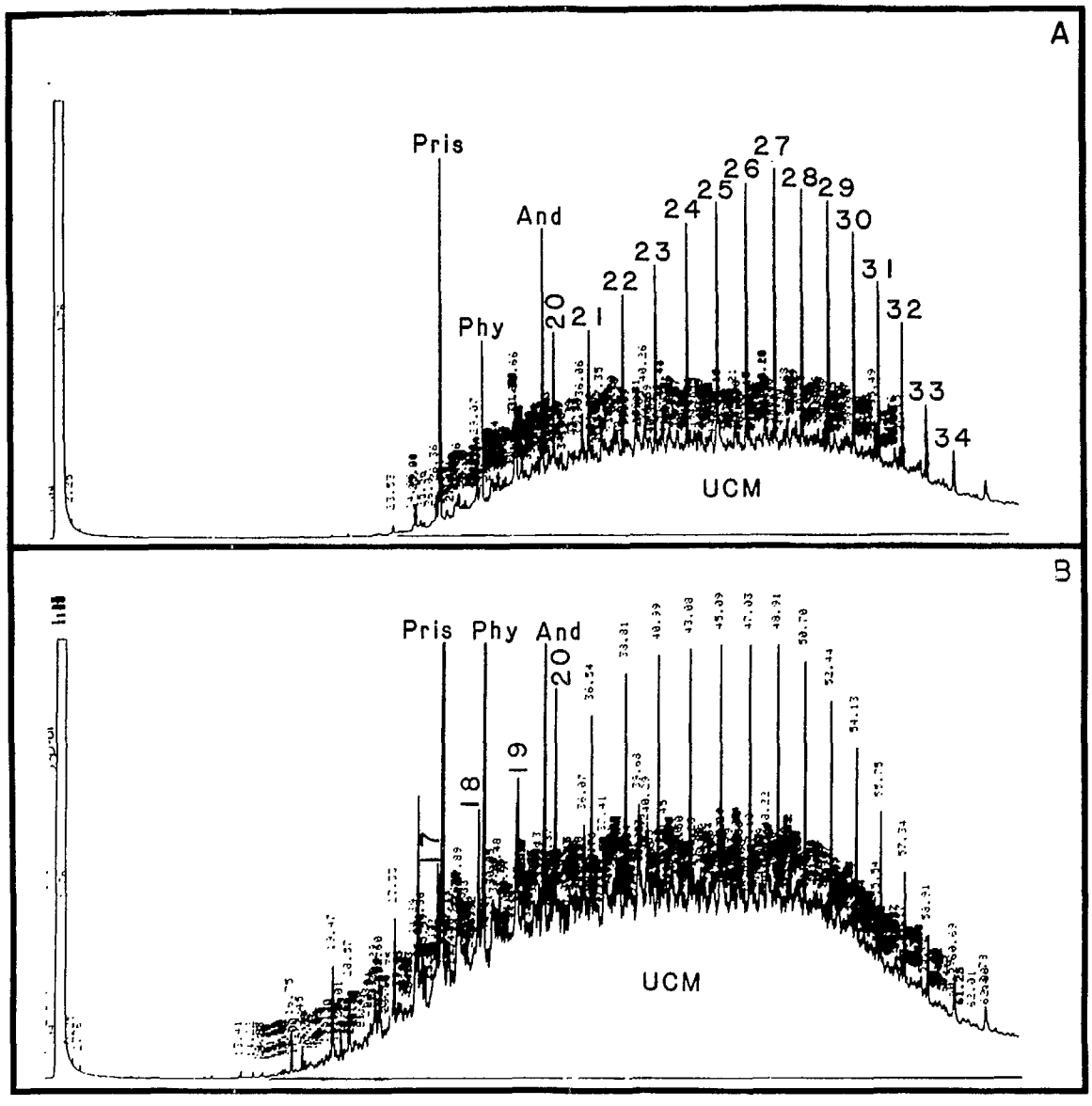


FIGURE 3.1. GC^2 TRACES OF SATURATED HYDROCARBONS FROM BAY 11 SLICK/SHEEN SAMPLES.

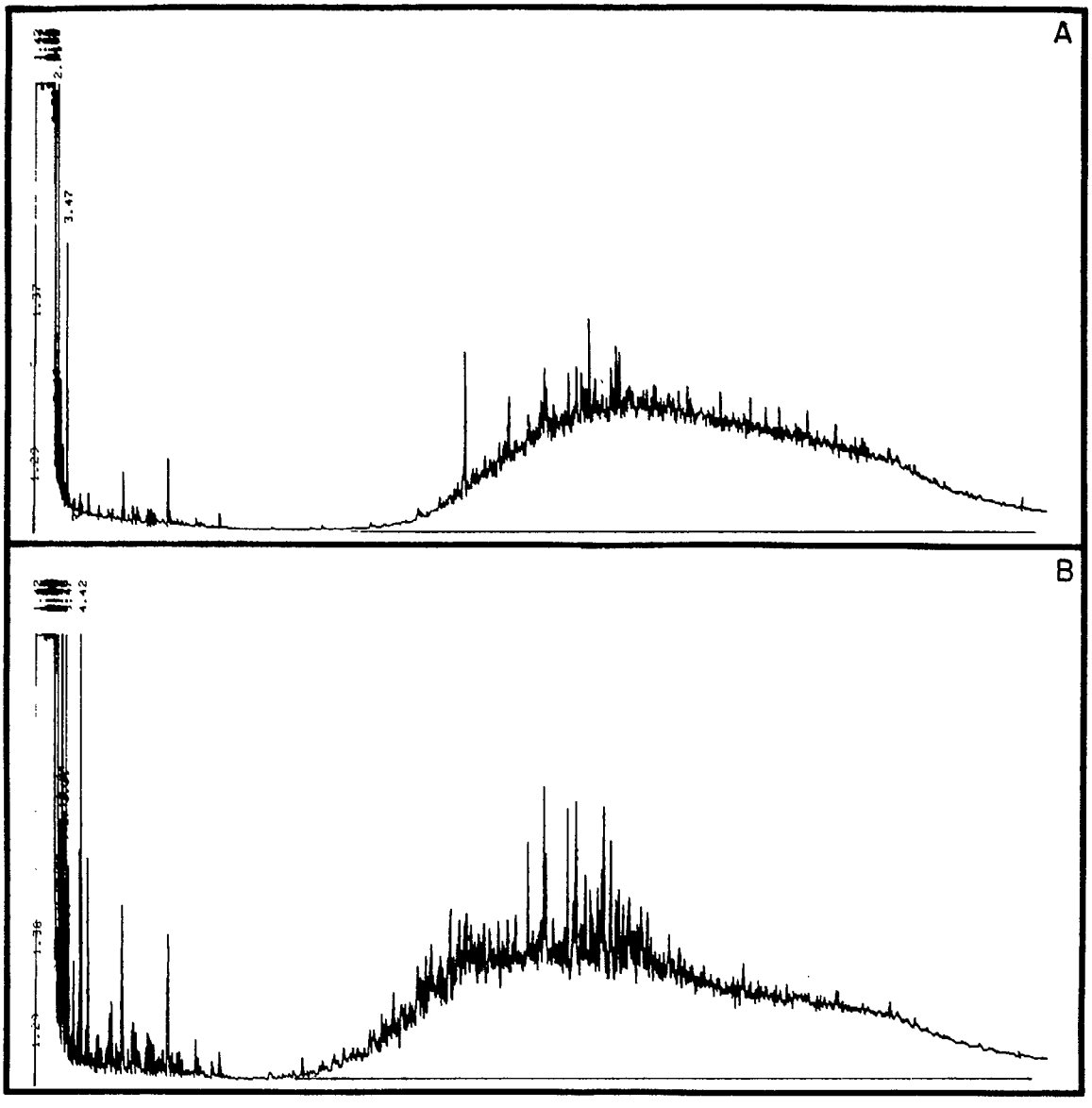


FIGURE 3.2. GC^2 TRACES OF AROMATIC HYDROCARBONS FROM BAY 11 SLICK/SHEEN SAMPLES.

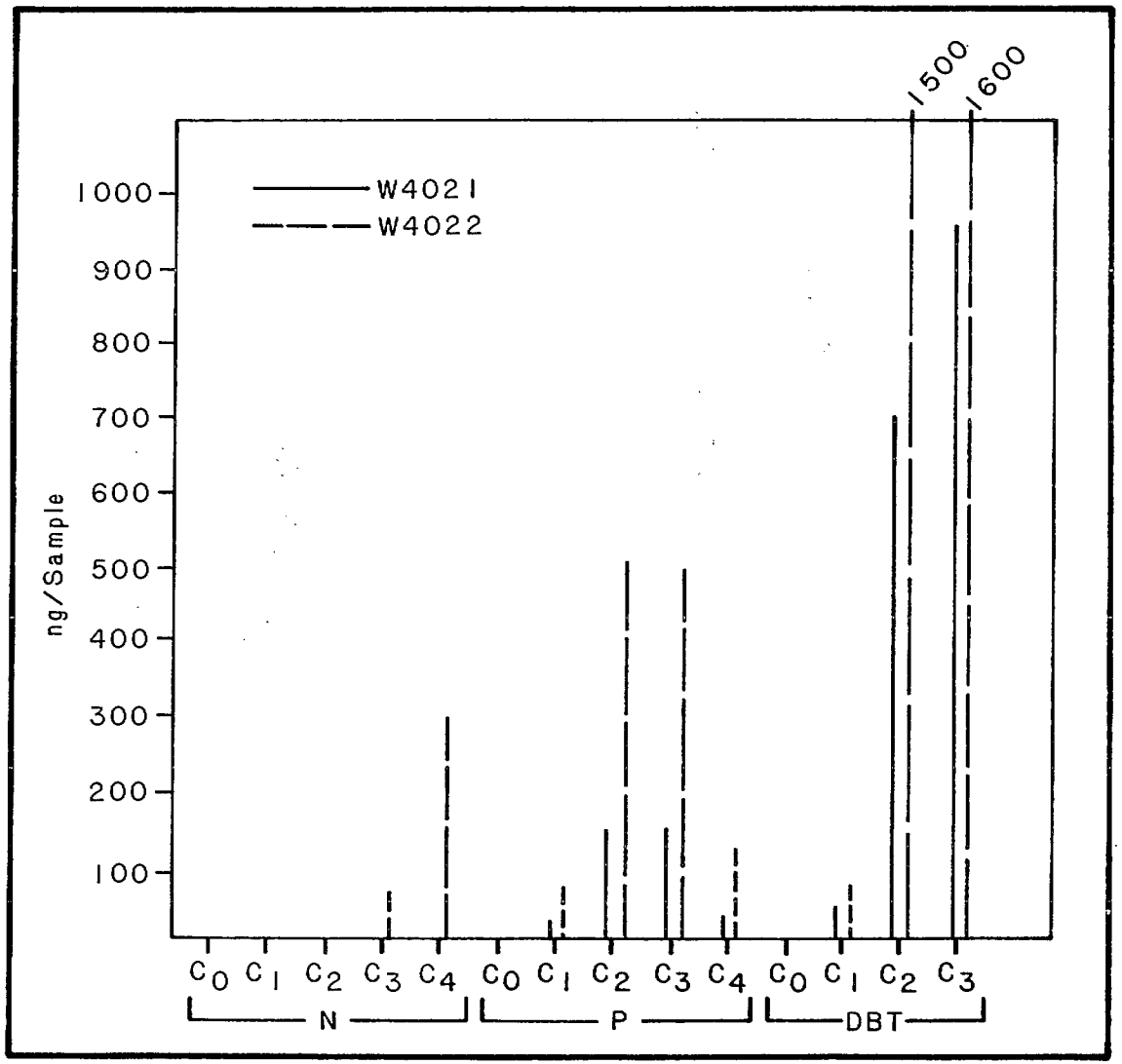


FIGURE 3.3. BAY 11 SLICK/SHEEN AROMATIC PROFILES BY GC^2/MS.

3.1.2 OIL IN THE WATER COLUMN

3.1.2.1 16 Liter Samples

Analytical results obtained from the 16 Liter water samples are also presented in Table 3.1. Traces of petroleum material diagnosed from the presence of a petrogenic series of n-alkanes (n-C_{20} to n-C_{30}) were detected in the saturated hydrocarbon fractions of several of the samples (Figure 3.4). The biogenic isoprenoid, pristane, was prominent in nearly all of the water samples, much more so than indicated in Figure 3.4A. GC^2 analysis of most of the 16 Liter samples failed to indicate the presence of any petrogenic aromatic compounds. Levels of "aromatics" shown in Table 3.1 for the most part are actually indicative of biogenic unsaturated hydrocarbon components eluting in the "aromatic" fraction.

The four samples in which trace quantities (<1.0 µg/L) or greater were detected, include three from Bay 11 (two at 10 meters depth, one at 1 meter depth) and one from Ragged Channel. Levels less than 0.5 µg/L represent biogenic material only. The maximum quantity of oil detected, 2.7 µg/L, was seen in one of the Ragged Channel samples. The composition of this sample is illustrated in Figure 3.4. A small amount of unresolved naphthenic material is observed in the saturated hydrocarbon fraction as well as a prominent series of n-alkanes from C_{20} to C_{33}. The aromatic fraction (Figure 3.4B) contains a series of low boiling components as well as a significant amount of unresolved material as well.

Absolute maximum concentrations in these water samples are similar to those found in a small set of 16 L samples taken in 1982, with n-alkane values ~1.0 µg/L in both years.

GC^2/MS analyses were performed on four additional 16L samples. No detectable aromatics (i.e. >1.0 ng/L) were observed in three of the samples. Sample W4005 contained very low levels (<1-5mg/L) of alkylated phenanthrene and DBT compounds.

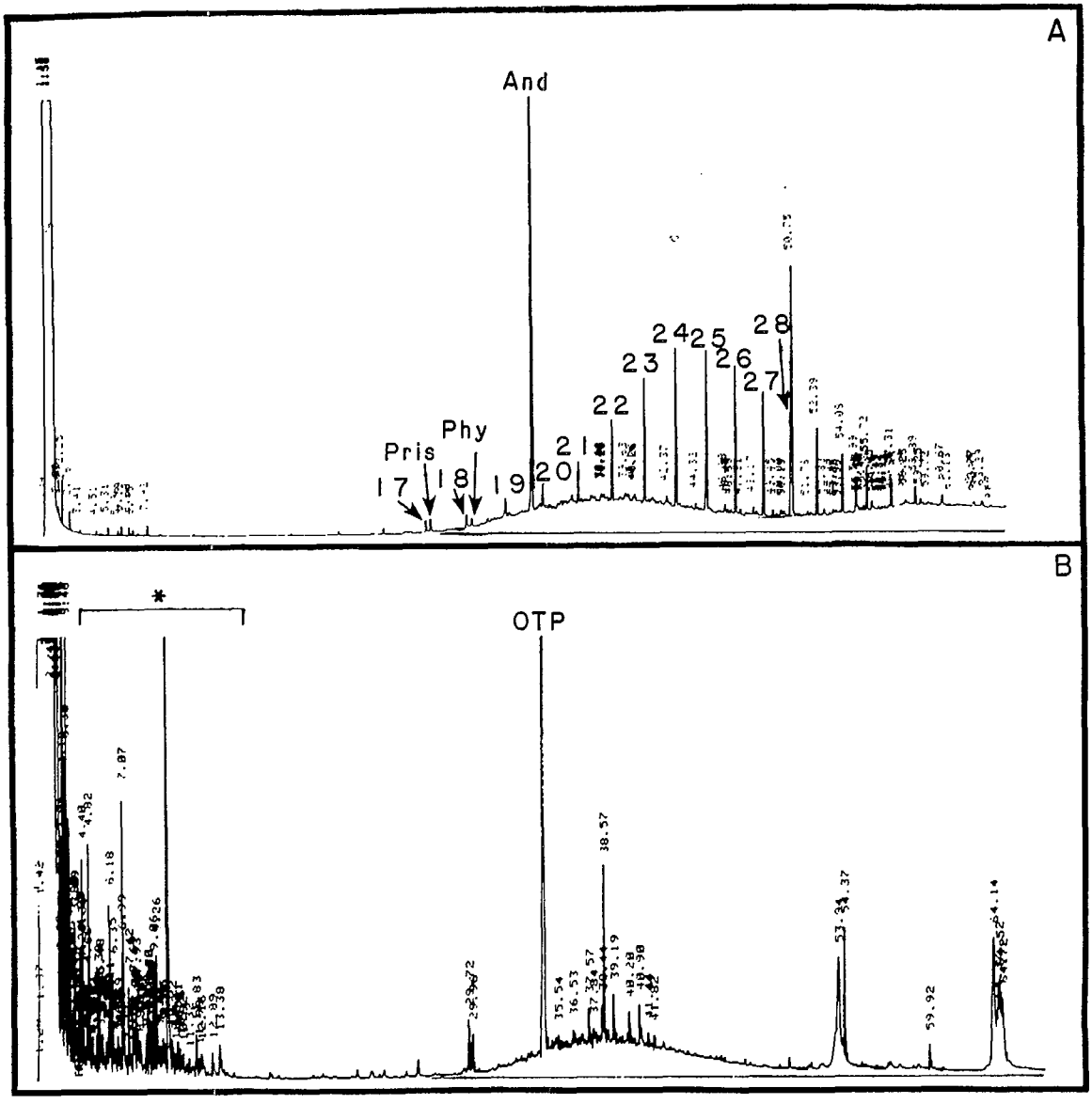


FIGURE 3.4. GC^2 TRACES 16 LITER WATER SAMPLE, RAGGED CHANNEL (W4005): A- SATURATES; B- AROMATICS; *-LOW MOLECULAR WEIGHT AROMATICS.

3.1.2.2 Large Volume Water Samples

The combined dissolved and particulate fractions were analyzed as one water column sample. The results of these analyses are presented in Table 3.2. Although large quantitites of biogenic lipids were captured in the samples, cleanup and analyses of the hydrocarbon fractions revealed little evidence of oil in the water column. These samples were obtained in a pair with a 16 L sample in order to compare the quantitative and qualitative results from both sample types. There is generally reasonable agreement between the two sets. The large volume samples contained trace quantities of oil in four samples at levels of 0.1-0.3 μg/Liter. Two of the four "trace level" large volume samples from Bay 11 corresponded to paired 16 L samples in which traces of oil were also found (L4004; W4004:L4015; W4015) although the large volume sample levels were about a factor of two to three lower in concentration. The results on the 16 Liter Ragged Channel sample (W4005, Table 3.1), exhibiting higher levels of detected petroleum, were confirmed by the parallel large volume sample (L4005, Table 3.2) although again the large volume sample was lower in concentration by a factor of two. Compositionally, this Ragged Channel large volume sample (Figure 3.5) agreed closely with the 16 L sample results (Figure 3.4). The lower molecular weight components were present in the aromatic fractions from both the large volume sample and the 16L sample.

The 1983 results differed from the previous years results in that the 1983 petroleum residues appeared to be more substantially weathered than those detected in the water column during the 1982 field sampling season. Normal alkanes in the n-C_{12} to n-C_{17} boiling range which were frequently detected in the 1982 large volume samples were absent in the 1983 samples. Low levels of naphthalenes detected in the 1982 samples were not seen in the GC^2 traces from 1983.

Two samples were analyzed by GC^2/MS. No detectable (>1.0ng/L) aromatics were seen in the L4004 or the L4005 sample. The Ragged Channel L4005 sample contained the same low boiling compounds as did the W4005 samples. However, data on these components were not acquired in the GC^2/MS analysis, and therefore the nature of these compounds remains unknown.

TABLE 3.2. SEAWATER ANALYTICAL RESULTS (LARGE VOLUME SAMPLES)

Sample ID	Volume (L)	Description	Hydrocarbon Concentrations (µg/L) Saturates	Aromatics	Total	SHWR	C_{18}/Phy	AWR	Oil?
L4003	99	Bay 11; S. Micro; 10m 8-12-83; 1017	.09	.11	.20	NA	NA	--	Trace
L4004	86	Bay 11; S. Micro; 1m 8-12-83; 1243	.23	.02	.25	NA	NA	ND	Trace
L4008	100	Bay 11; S. Micro; 10m 8-13-83; 1540	<.01	<.01	<.01	NA	NA	--	No
W4009	109	Bay 11; S. Micro; 1m 8-13-83; 1949	<.01	<.01	<.01	NA	NA	--	No
W4010	91	Bay 11; S. Micro; 10m 8-15-83; 1131	.05	.07	.12	NA	NA	--	No
L4011	117	Bay 11; S. Micro; 1m 8-15-83; 0750	.02	.07	.09	NA	NA	--	No
L4013	90	Bay 11; S. Micro; 10m 8-16-83; 0810	.04	.04	.08	NA	NA	--	NO
L4014	91	Bay 11; S. Micro; 1m 8-16-83; 1131	.07	.03	.10	NA	NA	--	Trace
L4015	99	Bay 11; S. Micro; 10m 8-19-83; 0810	.10	.03	.13	NA	NA	--	Trace
L4016	92	Bay 11; S. Micro; 1m 8-19-83; 1207	.08	.04	.12	NA	NA	--	No
L4006	90	Bay 7; N. Micro; 5m 8-12-83; 1555	.08	.03	.11	NA	NA	--	No
L4017	92	Bay 7; N. Micro; 5m 8-18-83; 0820	.06	.03	.09	NA	NA	--	Trace
L4005	85	Ragged Channel; 5m 8-16-83; 0735	.67	.47	1.1	NA	0.9	ND	Yes
L4012	100	Milne Inlet; 5m 8-15-83; 1521	<.01	<.01	<.01	NA	NA	--	No

NA = Compounds not detected.
ND = No aromatics detected.

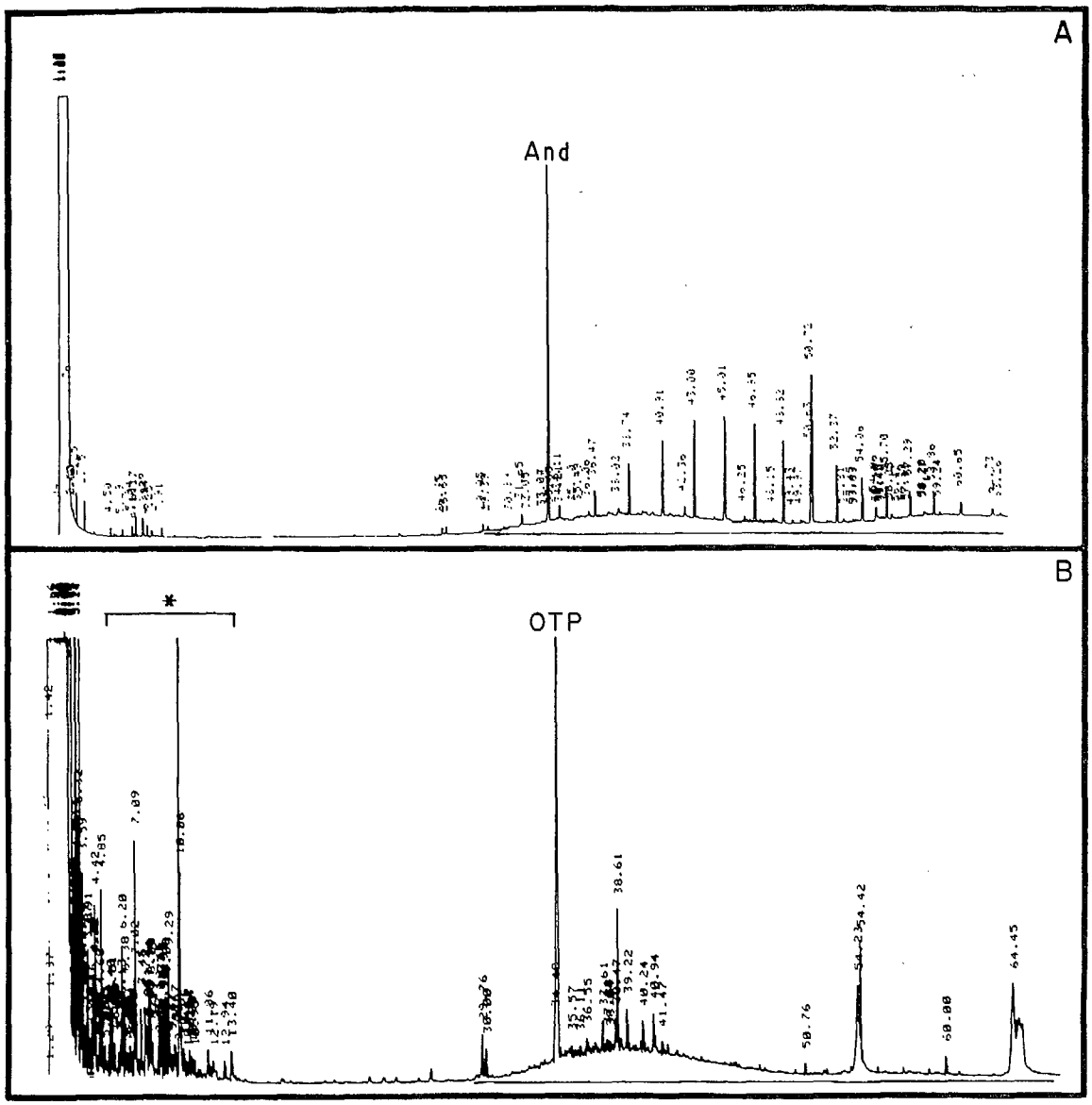


FIGURE 3.5. GC^2 TRACES OF LARGE VOLUME WATER SAMPLE, RAGGED CHANNEL (L4005): A- SATURATES; B- AROMATICS; *-LOW MOLECULAR WEIGHT AROMATICS.

3.2 Oil in the Sediments

3.2.1 BAY 11

Six types of sediment samples were analyzed from the Bay 11 beach and subtidal region during 1983. Sediment samples (0-2 cm) were analyzed from the tissue plots at 3 m and 7 m depth adjacent to the area from which animal samples were acquired for tissue analysis; from the three benthic transects at the same depths in which benthic communities were quantified; from the tissue plot surface floc to determine levels and composition of oil in newly deposited sediment; from a microbiology transect to examine offshore distributions of oil along a intertidal to 10 meter water depth transect; from a series of deep water sediments to determine transport of oil to deeper areas (~35m) in the Bay 11/12 area; from the Bay 11 beach to determine quantities and composition of stranded oil.

3.2.1.1 Tissue Plots

3.2.1.1a Oil Concentrations by UV/F. Figure 3.6 and Table 3.3 presents a summary of the petroleum concentrations in UV/F-determined Lagomedio oil equivalents in Bay 11 subtidal sediments. The Bay 11 sediments contained high levels of oil. Concentrations on a log transformed basis [i.e. $\bar{X}_G$ (Lower 95% confidence limit, upper 95% confidence limit)] in the 3 m tissue plots were 22.5 (8.9, 57.8) µg/g compared with 3.0 (1.1, 8.1) µg/g last observed in 1982. The highest value found in 1983, 123 µg/g, is only twice the highest 1982 value, 66 µg/g. However, on the average roughly two times more oil has impacted the three meter stratum in Bay 11. Concentrations at the 7 m stratum [12.6 (9.1, 17.5)] µg/g were lower than at 3 m and were more tightly grouped in concentration. This illustrates the patchy nature of the 3 m distributions caused by active oil deposition at this depth. Further offshore (7 m) distributions are more homogeneous although a factor of three separates the lowest (8.1 µg/g) and highest (21.2 µg/g) concentration at the 7 m depth. The 1982 sampling revealed levels of oil at 7 m to be 5.3 (2.7, 10.1) µg/g, or on the average, a factor of two lower than in 1983.

Active erosion of beached oil is occurring in Bay 11 as it was in 1982. Concentrations of oil are higher at the southern end of the 3 m sampling line, as was also the case in 1982.

TABLE 3.3 SUMMARY OF BAY 11 SEDIMENT HYDROCARBON CONCENTRATION DATA

Sample Type	Depth	Concentration: X (-95%, +95%) (µg/g)	
		1982	1983
Tissue Plot	3m	3.0(1.1, 8.1)	22.5(8.9, 57.8)
Tissue Plot	7m	5.3(2.7, 10.1)	12.6(9.1, 17.5)
Benthic Transect 1	3m	4.0(2.1, 7.6)	21.2(8.6, 51.9)
	7m	6.6(5.4, 8.0)	22.5(18.7, 27.1)
Benthic Transect 2	3m	1.4(.66, 3.1)	14.0(4.7, 41.3)
	7m	4.7(3.3, 6.6)	12.0(10.9, 13.2)
Benthic Transect 3	3m	10.3(3.0, 35.0)	119 (86.7, 162)
	7m	4.0(2.1, 7.5)	18.8(9.9, 35.8)
Deep Sediment	35m	-----	4.6(2.5, 8.3)

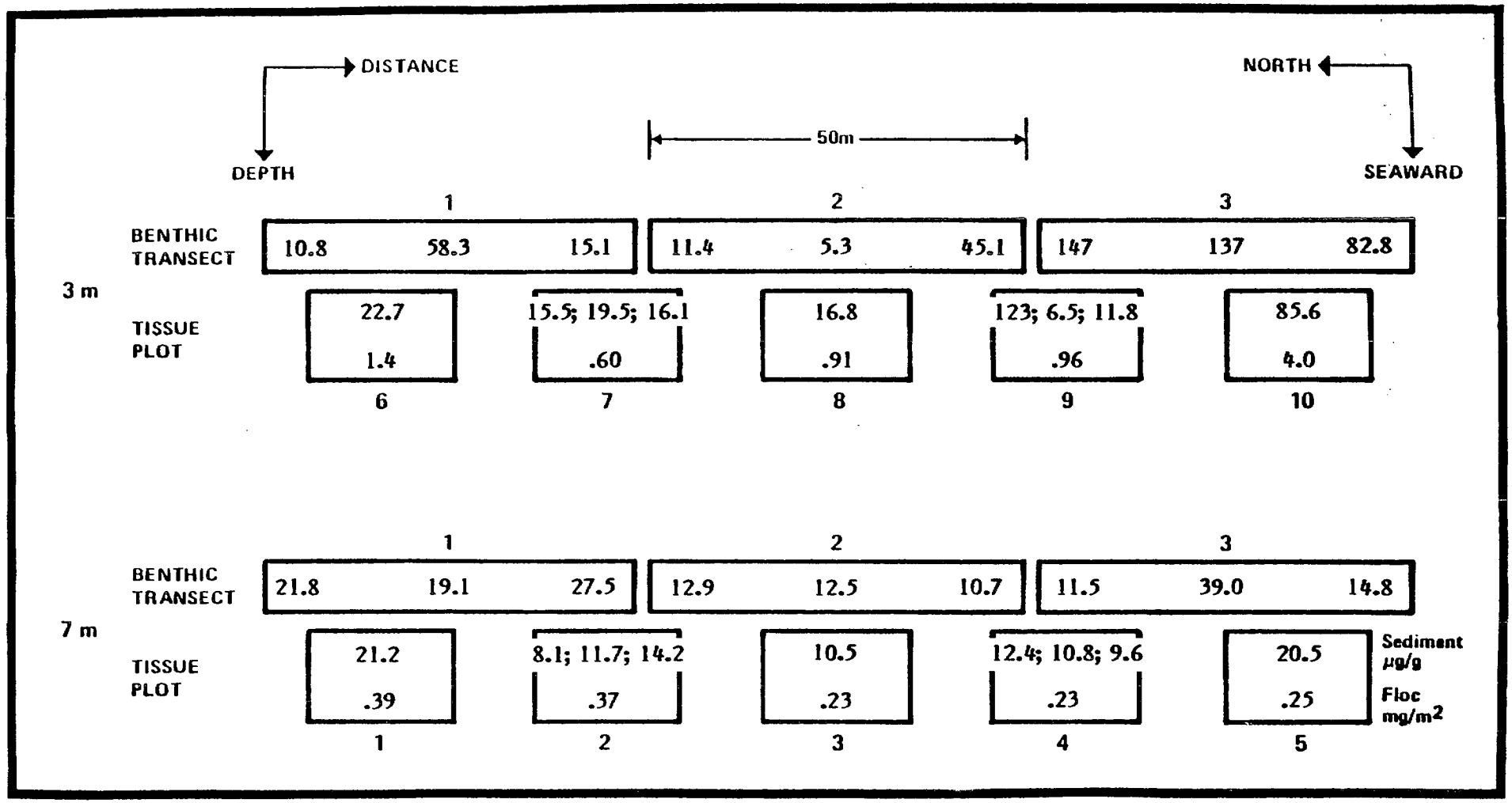


FIGURE 3.6. BAY 11 SEDIMENT PETROLEUM HYDROCARBON CONTENT; UV/F (AUGUST 13, 1983).

3.2.1.1b Oil Composition by GC^2. Four samples of Bay 11 tissue plot sediments were analyzed by GC^2 to determine the oil's composition. These results are summarized in Table 3.4. Two representative saturated hydrocarbon GC^2 traces are presented in Figure 3.7. A combination of weathered oil (SHWR = 1.1) illustrating a moderate degree of biodegradation (C_{18}/Phy = .43) and terrigenous alkanes is illustrated by the GC^2 trace in Figure 3.4a (tissue plot 8 at 3 meters depth). The UCM material also characterizes this weathered oil residue. Higher concentrations of oil are found (Table 3.4) at tissue plot #10 at 3 meters and the GC^2 trace of this sample illustrates the same features of weathered oil. The SHWR for this sample is slightly higher (SHWR = 1.3) which indicates that n-alkanes in the C_{10} to C_{17} range are still present in this sample. Notice how the increase amount of oil depresses the CPI further (CPI = 1.4) as the relative influence of the terrigenous n-alkanes is less due to the increased amount of oil.

The biodegradation indicator used here, C_{18}/Phy, varies from values of 0.4 to 1.0, indicative of moderately degraded oil, to 1.5 to 2.0 indicative of an undegraded oil.

3.2.1.1c Aromatic Hydrocarbon Composition by GC^2/MS. Three tissue plot samples were analyzed by GC^2/MS, the results summarized in Figure 3.8. The aromatic hydrocarbon concentration ranges agree well with those determined from the 1982 sample set. Tissue plot 10, however, contained lower concentrations of those quantified homologous series, by a factor of 3, than detected in 1982. The alkylated phenanthrene and DBT series are the most prominent quantifyable aromatic compounds.

3.2.1.2 Surface Floc Samples

3.2.1.2a Oil Concentrations by UV/F. UV/F determinations on floc samples from each of the Bay 11 tissue plots are presented in Figure 3.6. Concentrations are reported as mg oil/m^2 assuming a 0.1 m^2 sampling area as has been used previously. Petroleum levels of .23 to 4.0 mg/m^2 were observed in the samples. Background levels are ~0.05 mg/m^2. The 3 m samples had substantially more oil associated with the floc, .93 (.65, 1.3) mg/m^2, than did the 7 m samples, .29 (.22, .37) mg/m^2, again indicating the more substantial ongoing impact along the 3m stratum.

The 1981 results had previously indicated that maximum floc impact in the dispersed oil spill (Bay 9) had achieved at 33 mg/m^2 impact. Bay 11 floc samples taken in 1982 had indicated a lesser but very significant oil impact to the surface floc at 3 m, .54

TABLE 3.4 BAY 11 SEDIMENT HYDROCARBON COMPOSITIONAL DATA BY GC[2]

Sample Depth (m)	Tissue Plot	Benthic Transect	Floc	Deep Sediment	Phytane (µg/g)	Pris/ Phy	C_{18}/Phy	CPI	Status
3	6	—	--	—	.05	1.0	2.0	2.5	Oil
3	8	—	--	—	.04	1.7	.43	2.6	Oil
3	10	—	--	—	.27	.68	.70	1.4	Oil
7	1	—	--	—	.01	5.9	1.2	2.8	Low Oil
7	5	—	--	—	.06	1.2	.67	2.1	Oil
3	—	1b	--	—	.18	.67	.39	1.8	Oil
3	—	3b	--	—	.50	.68	.47	1.2	Oil
7	—	1a	--	—	.04	2.7	.92	2.3	Oil
7	—	2c	--	—	.02	2.8	4.2	3.0	Oil
7	—	3b	--	—	.07	1.7	.65	2.0	Oil
35	—	—	—	(4222)	.008	3.7	2.3	2.8	Trace Oil
35	—	—	—	(4221)	.010	3.0	3.7	3.0	Low Oil
3	—	—	6	—	.011[a]	1.4	.81	2.4	Low Oil
3	—	—	8	—	.010[a]	2.4	.90	1.7	Low Oil
3	—	—	10	—	.051[a]	0.9	.22	1.7	Oil
7	—	—	1	—	.009[a]	11.0	3.0	1.6	Trace Oil
7	—	—	5	—	.008[a]	1.9	2.6	1.6	Trace Oil

[a]Concentrations in µg/m^2.

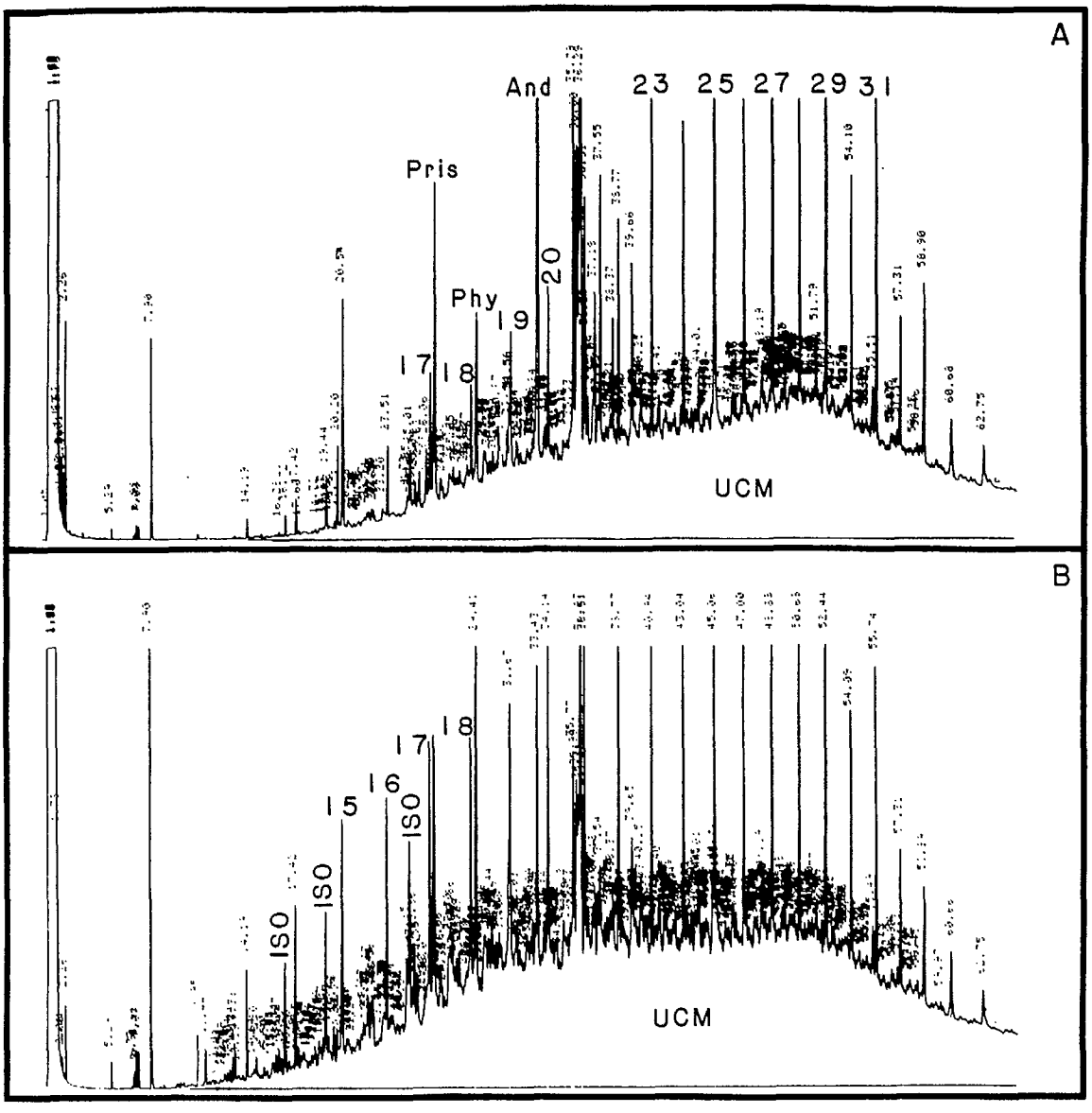


FIGURE 3.7. GC^2 TRACES OF BAY 11 TISSUE PLOT SEDIMENT SATURATED HYDROCARBONS: A- NO. 8; B- NO. 5.

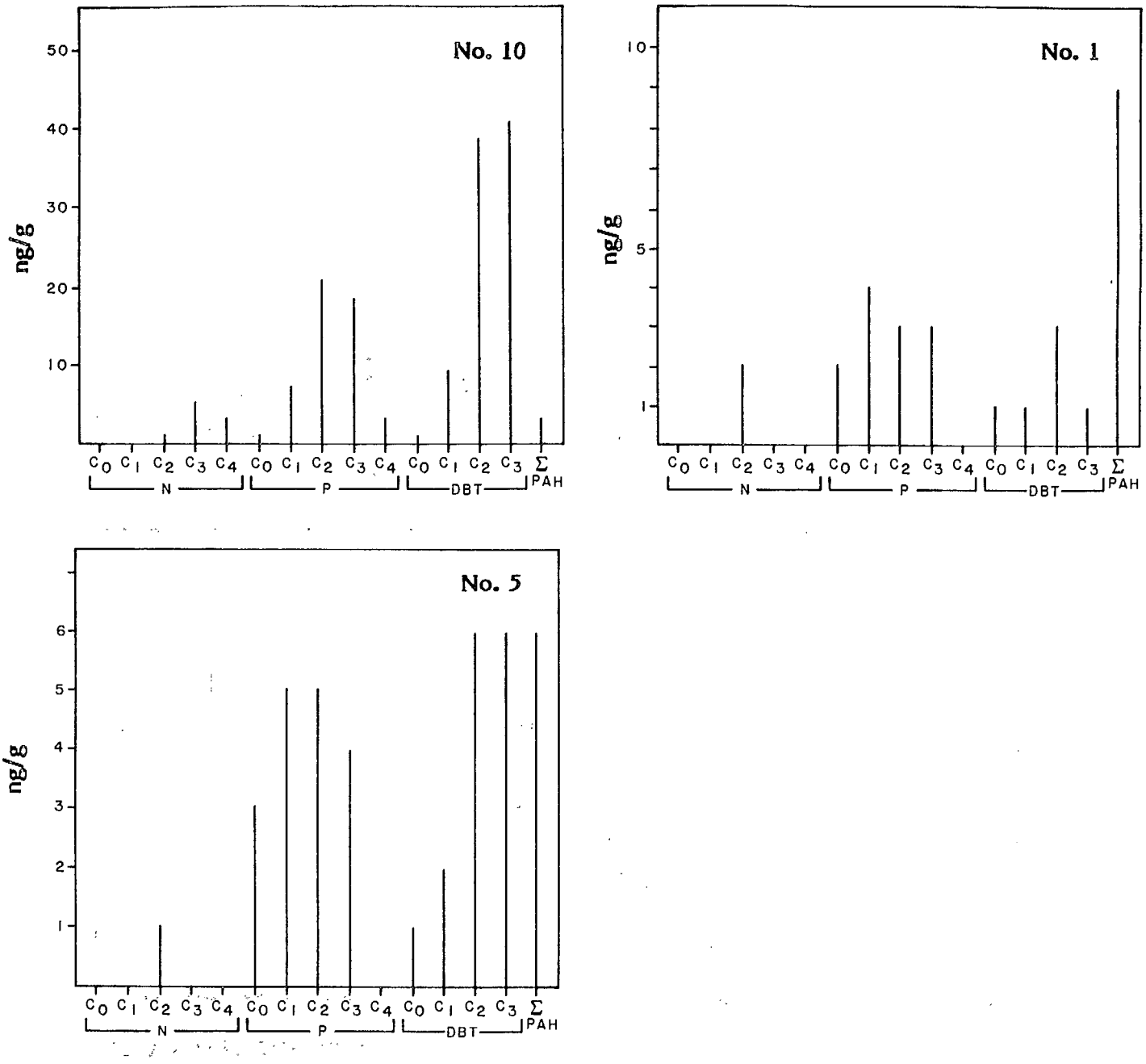


FIGURE 3.8. AROMATIC PROFILES BY GC^2/MS OF BAY 11 SEDIMENT

(.33, .90) mg/m^2, at at 7 m, .23 (.17, .29) mg/m^2). Thus the 1983 values are very similar to those previously reported in 1982, in spite of the much larger bulk sediment (0-2 cm) reported in 1983. Thus, it appears that oil is being mixed into the upper sediment column in Bay 11 leaving a "steady state" concentration of oil in the floc layer.

3.2.1.2b Oil Composition by GC^2. A series of five Bay 11 floc samples were analyzed by GC^2 (Table 3.4). Small to moderate quantities of oil were noted (Figure 3.9) in these samples when the petrogenic components (i.e. UCM material, phytane, etc.) were viewed against the background biogenic material. The saturated hydrocarbon weathering ratios (SHWR) of all of these samples approximated 1.0 indicating that the oil residues had been depleted of the lower molecular weight n-alkanes (C_{10} to C_{17}). Petrogenic material in the floc at 3 meters depth was more highly biodegraded than that at 7m as judged by the C_{18}/Phy ratio which ranged from 0.2 to 0.9 at 3 m, with the lowest value corresponding to the highest oil concentration found in tissue plot #10. The C_{18}/Phy ratio was 2.5 to 3.0 at 7m depth.

3.2.1.2c Aromatic Hydrocarbon Composition by GC^2/MS. The aromatic hydrocarbon composition of the sediment floc from Bay 11 was determined on three samples. The results are summarized in Figure 3.10. Aromatic compositions and concentrations were quite similar to those reported in the 1982 samples. For example, C_2phenanthrene and C_2 DBT were each present at ~300ng/m^2 in 1982. Comparable levels in 1983 were ~200 ng/m^2.

3.2.1.3 Benthic Transects

3.2.1.3a Oil Concentrations by UV/F. Concentrations of oil in the sediments taken from the three transects are presented in Figure 3.6 and are summarized in Table 3.3. Concentrations in Transect 1 were similar at 3 and 7 m, 21.2 (8.6, 51.9) µg/g and 22.5 (18.7, 27.1) µg/g respectively, although the range (10.8-58.3 µg/g) was greater at the 3 m stations. Concentrations in Transect 2 were also similar at 3 m, 14.0 (4.7, 41.3) µg/g, and 7 m, 12.0 (10.9, 13.2) µg/g. Again the range at 3 m (5.3 to 45.1 µg/g) was greater owing to the patchiness observed repeatedly at the 3 m stations. Levels of oil in Transect 3 were much greater at 3 m, 119 (86.7, 162) µg/g than at 7 m, 18.8 (9.9, 35.8) µg/g. This observation is both consistent with the observations for the adjacent tissue plots as well as with the 1982 observations.

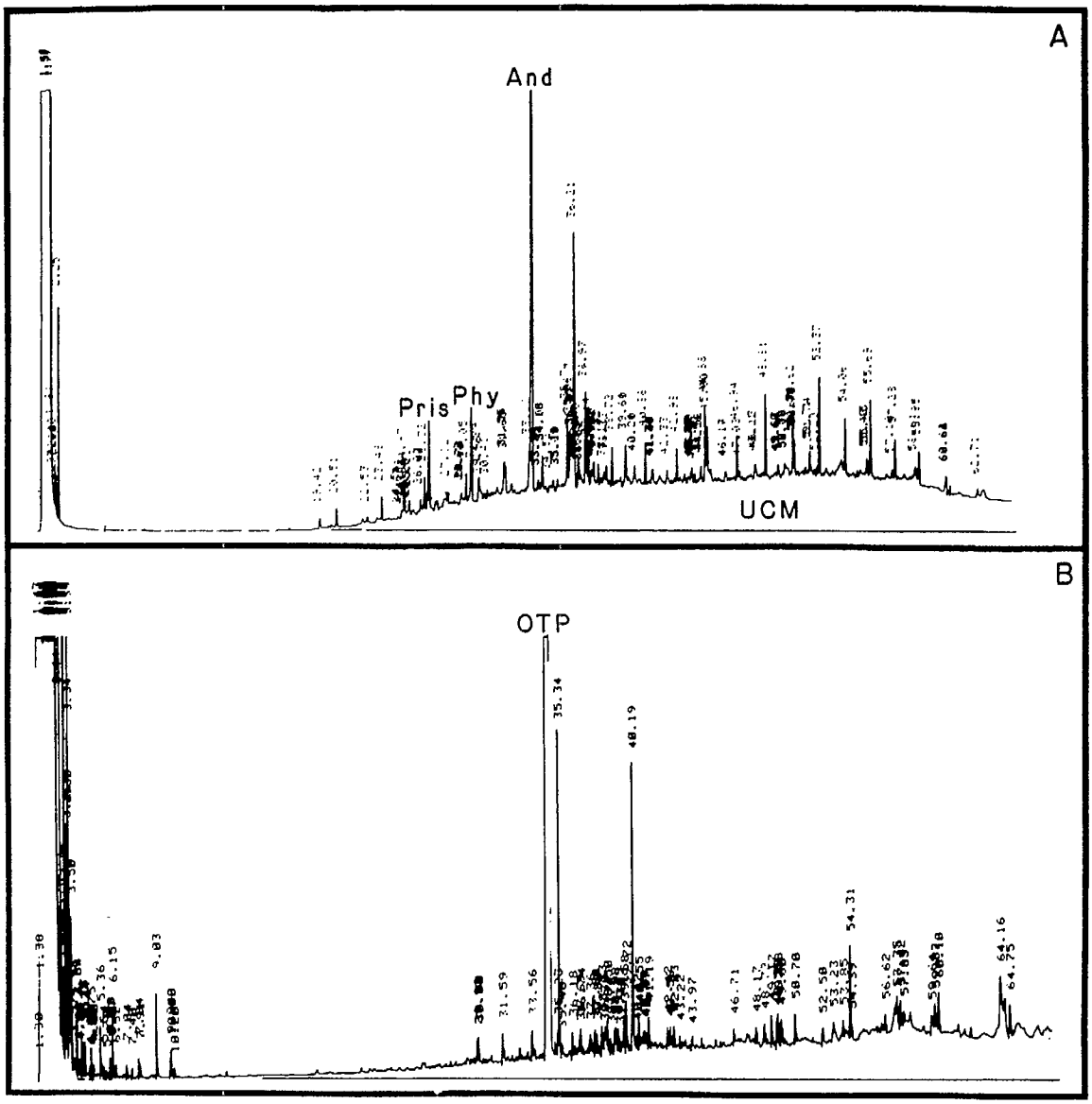


FIGURE 3.9. GC^2 TRACES OF BAY 11 FLOC SAMPLES: A- SATURATED HYDROCARBONS; B- AROMATICS.

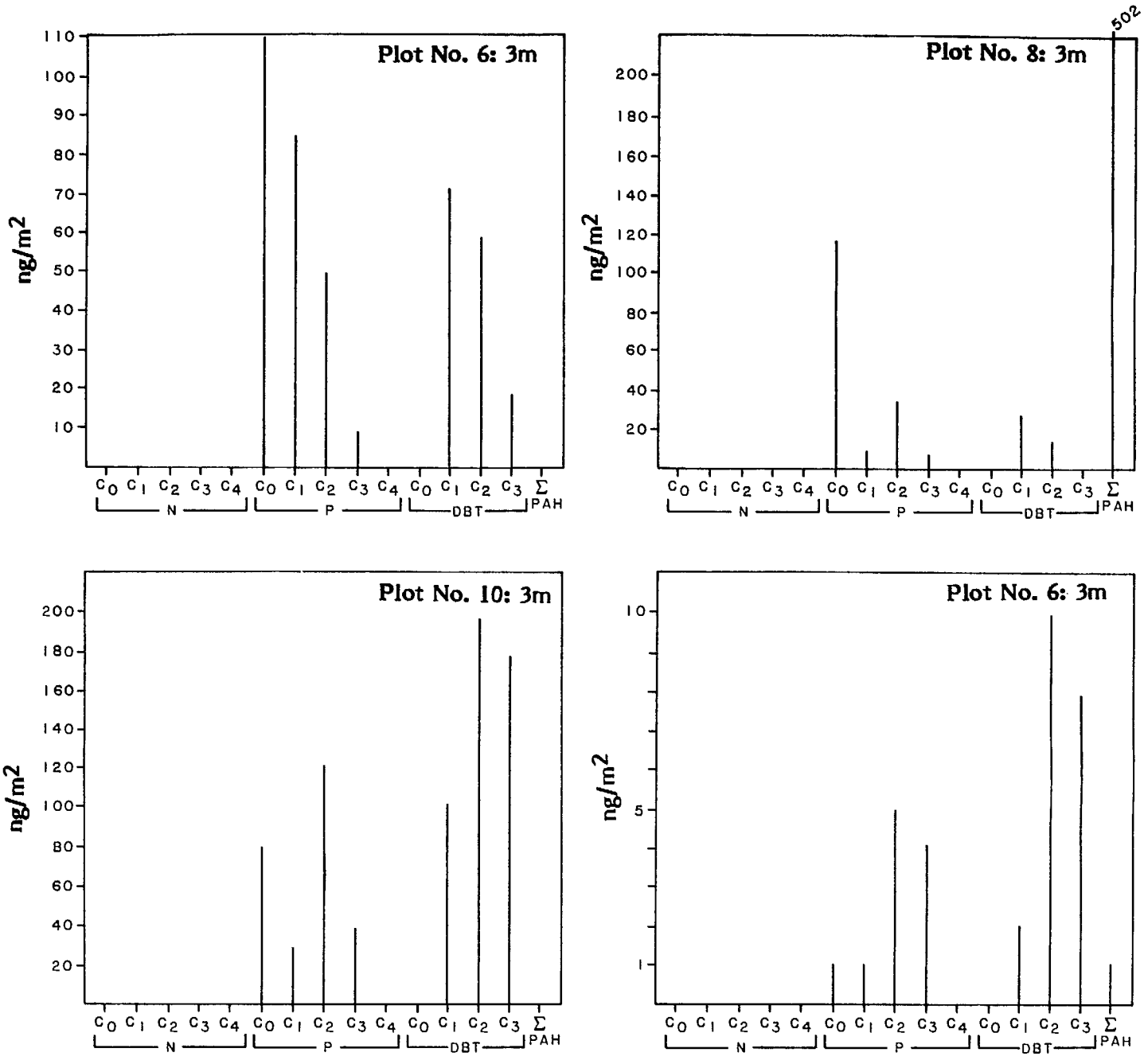


FIGURE 3.10. AROMATIC PROFILES BY GC^2/MS OF SEDIMENT FLOC FROM BAY 11

The 1983 oil levels in the benthic transects were much higher (4-10 times) than previously observed in 1982.

3.2.1.3b Oil Composition by GC^2. Five benthic transect sediment samples were analyzed by GC^2 (Table 3.4). The compositional profiles of all of these samples closely resemble those from the tissue plots (see Figure 3.7). GC^2 analyses confirmed the presence of oil in all of these benthic transect samples. At lower concentrations the PRIS/Phy ratio became larger than ~2.5 indicating an increased relative dominance of the biogenic isoprenoid, pristane. That the oil was moderately biodegraded is illustrated by the lower C_{18}/Phy ratio (0.4 to 1.0) compared to that in the undegraded oil. This extent of biodegradation is greater than was observed in samples taken from these locations in 1982. At that time, the lower extent of C_{18}/Phy ratio was ~1.0. Here in 1983, it has decreased further to 0.4 in some samples. The CPI values are all less than 3.0, indicating a higher degree of oiling than was the case in 1982, a finding that confirms the quantitative results presented previously.

3.2.1.3c Aromatic hydrocarbon compostion by GC^2/MS. The results on the single benthic transect sediment sample analyzed by GC^2/MS is presented in Figure 3.10D. Low levels (5-10 ng) of individual aromatics were detected.

3.2.1.4 Microbiology Transects

3.2.1.4a Oil Concentration and Composition by GC^2. A summary of the petroleum concentration data in the one microbiology transect is summarized along with relevant compositional parameters in Table 3.5. The locations of the transect is illustrated in Figures 3.11 and 3.12. Estimated petroleum concentrations ranged from 0.8 to 410 µg/g. Note that the total hydrocarbon levels are often higher at the lower levels than the estimated petroleum concentrations due to the presence of significant amounts, 2-3 µg/g, of biogenic hydrocarbons in petroleum-free sediment. Maximum concentrations were found at Station 14 and 13 at 2.4 and 4.0 meters depth, respectively. Concentrations decrease further offshore although petroleum residues were detected in all samples.

Representative compositional profiles are shown in Figures 3.13 and 3.14 and compositional parameters tabulated in Table 3.5. Note that a large amount of phytane present in these samples (> .001, background) directly indicates that large amounts of petroleum are present. The petroleum residues are moderately biodegraded with levels of

TABLE 3.5 SUMMARY OF MICROBIOLOGY SEDIMENT SAMPLE HYDROCARBON DATA.

Bay	Water Depth (m)	Station	Total Hydrocarbon Concentration[a]	Phytane (µg/g)	Pristane / Phytane	n-C_{18} / Phytane	CPI	Estimated Petroleum Concentration[b] (µg/g)
11	11.3	1	3.5	.011	4.3	.63	3.2	1.7
11	10.6	2	7.3	.005	6.1	1.1	3.3	.8
11	9.1	3	7.8	.005	6.2	1.4	3.1	.8
11	9.1	4	6.8	.008	7.6	1.1	1.4	1.2
11	7.6	5	5.2	.011	2.9	.83	1.4	1.7
11	6.9	6	5.2	.006	5.3	1.3	5.0	.9
11	6.4	7	7.8	.029	2.5	.59	2.0	4.4
11	6.1	8	13	.030	1.6	.59	2.6	4.50
11	5.5	9	34	.19	.81	.37	1.9	29.0
11	4.6	10a	37	.28	.83	.40	1.5	42.0
		10b	39	.30	.90	.37	1.5	45.0
		10c	30	.23	.82	.36	1.9	35.0
11	4.6	11	30	.28	2.1	.55	1.0	42.0
11	4.5	12	30	.24	0.7	.45	1.7	36.0
11	4.0	13	65	.78	.72	.38	0.6	120.0
11	2.4	14	300	2.7	.90	.91	1.2	410.0
11	1.5	15	24	.29	.67	.28	1.2	44
11	1.3	16	63	1.7	.77	.50	1.3	87.0
7	2	5	3.2	.001	45	1.7	3.3	<.5
7	4	4	3.7	<.001	-	4.0	7.4	<.5
7	6	3	1.8	<.001	33	-	6.3	<.5
7	8	2	1.9	<.001	-	-	7.0	<.5
7	10	1	5.1	.012	3.1	.45	1.7	1.8

[a]Includes any petroleum material plus biogenic compounds quantified by gas chromatography.

[b]Estimated from known Phytane Content of Aged Lagomedio crude oil (6.4 mg Phytane/g oil) (from Boehm et al., 1982a).

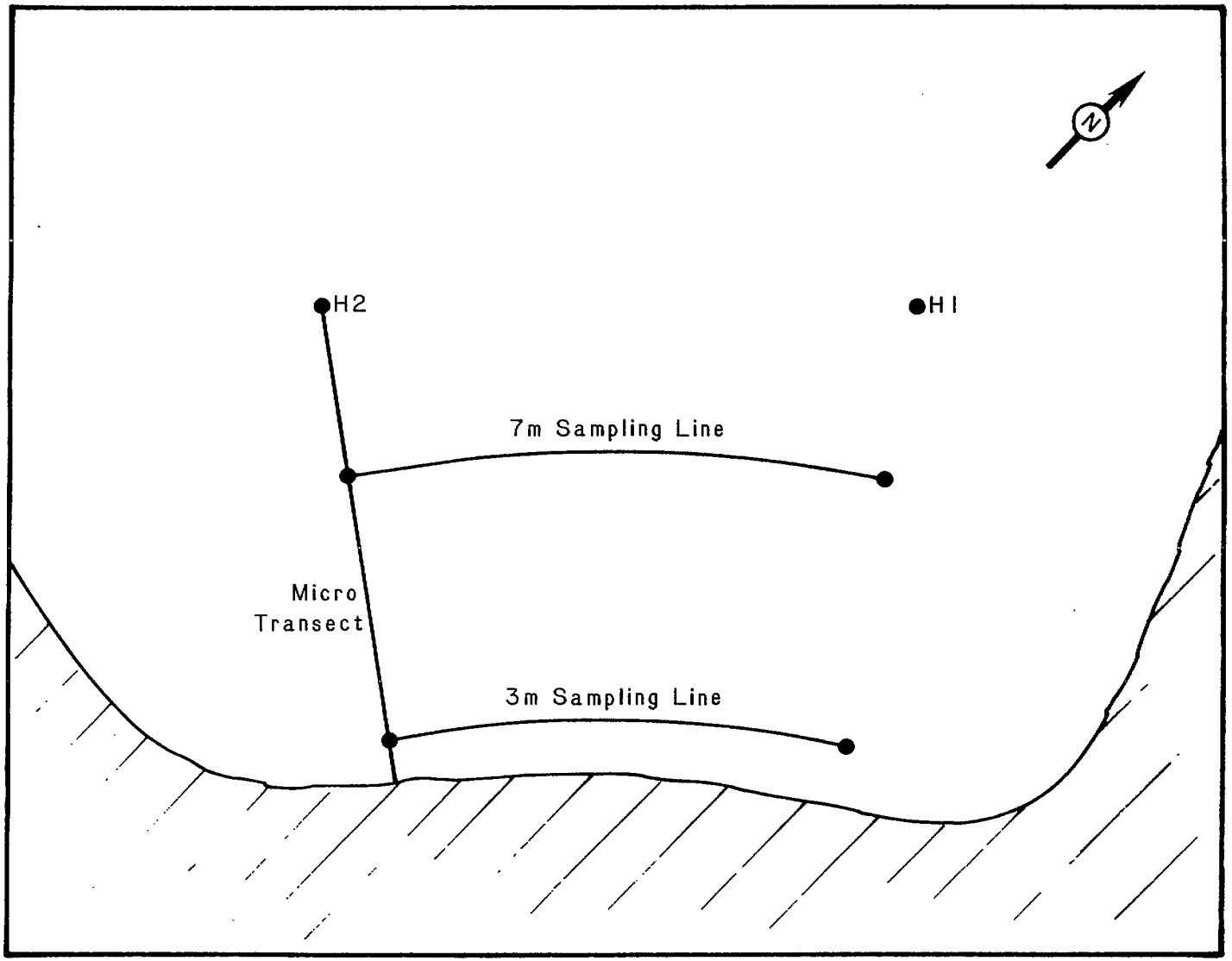
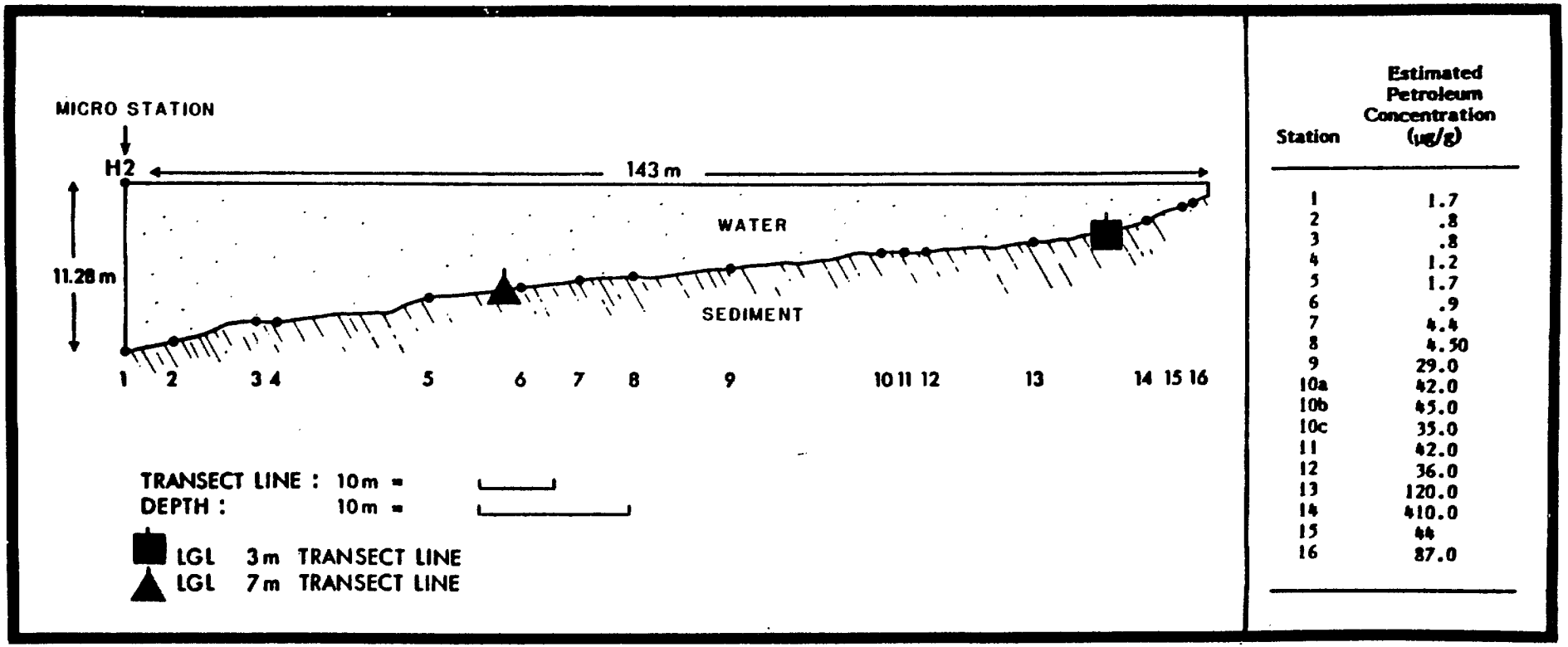


FIGURE 3.11. LOCATION OF BAY 11 MICROBIOLOGY SUBTIDAL SEDIMENT TRANSECT.



Station	Estimated Petroleum Concentration (µg/g)
1	1.7
2	.8
3	.8
4	1.2
5	1.7
6	.9
7	4.4
8	4.50
9	29.0
10a	42.0
10b	45.0
10c	35.0
11	42.0
12	36.0
13	120.0
14	410.0
15	44
16	87.0

FIGURE 3.12. CROSS-SECTIONAL DEPTH PROFILE ALONG BAY 11 MICROBIOLOGY SEDIMENT TRANSECT

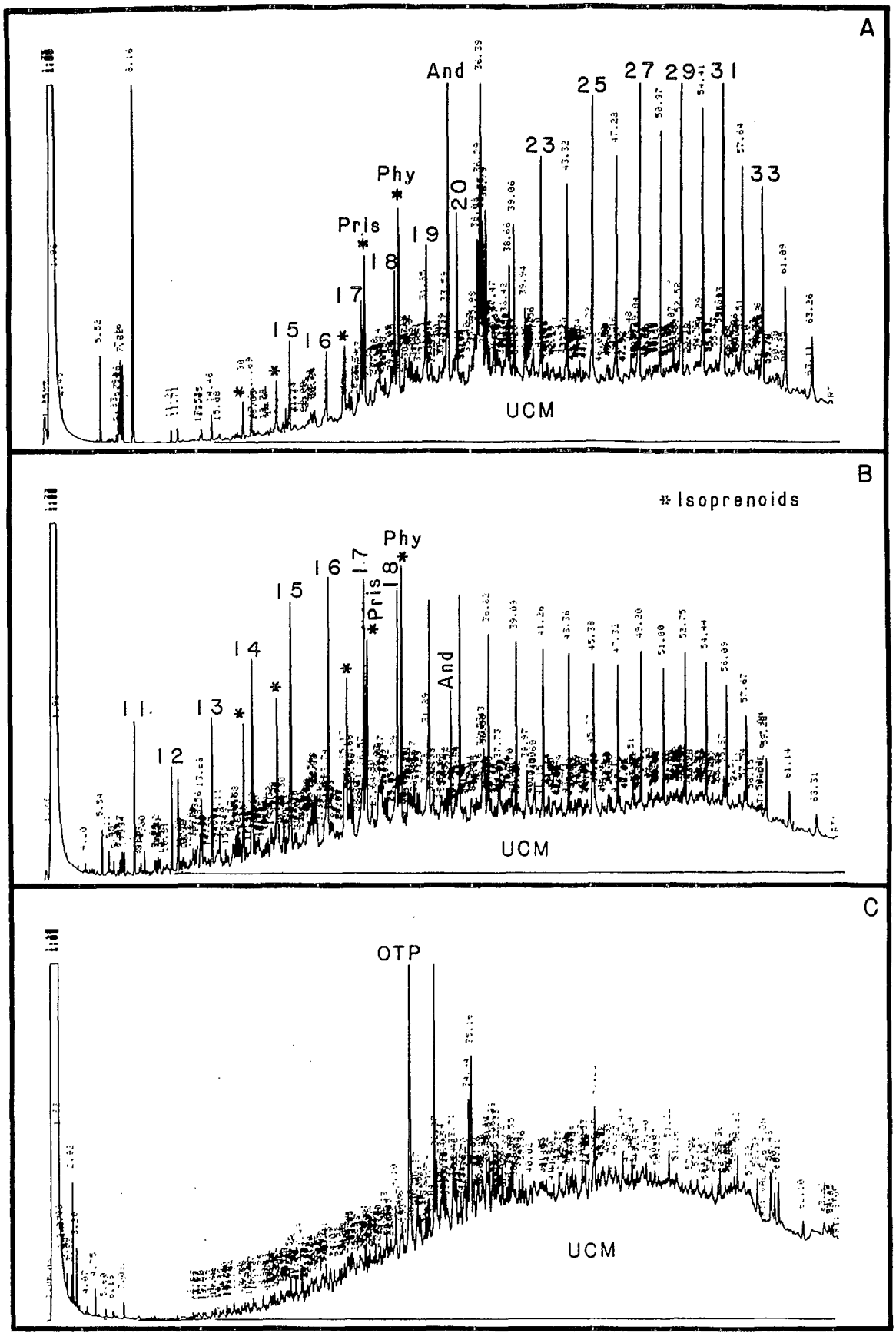


FIGURE 3.13. GC^2 TRACES IN MICROBIOLOGY SEDIMENT SAMPLES (BAY 11): A- STATION 12, 36 ppm (SATURATES); B- STATION 14, 410 ppm (SATURATES); C-STATION 14, 410 ppm (AROMATICS).

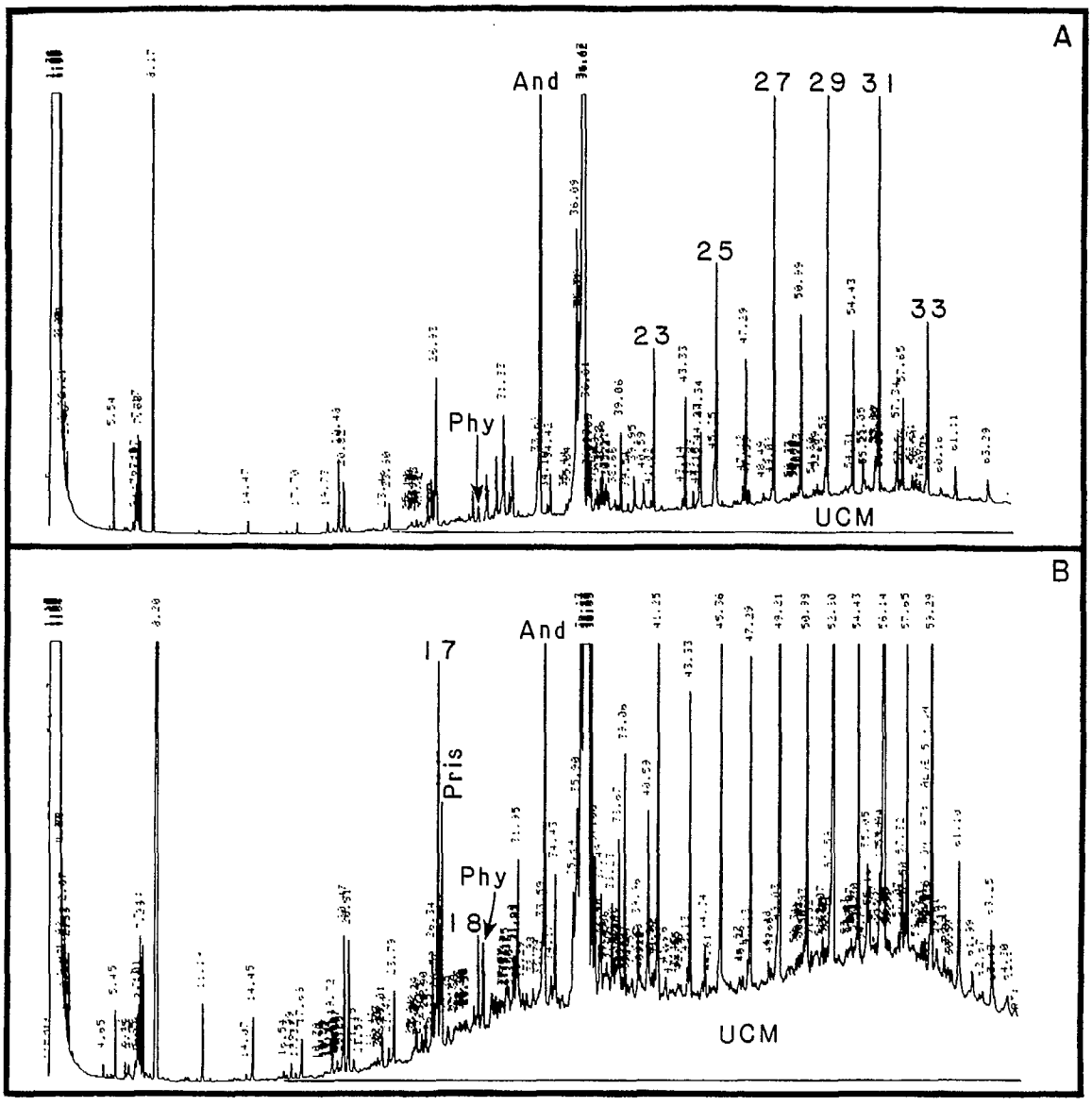


FIGURE 3.14. GC^2 TRACES IN MICROBIOLOGY SEDIMENT SAMPLES (LOW LEVEL OIL): A- STATION 2, 0.8 ppm (SATURATES); B- STATION 5, 1.7 ppm (SATURATES).

n-C_{18} substantially less than phytane in moderately to heavily oiled samples. A lesser degree of biodegradation is seen in the lightly oiled samples ($\sim$1.0 ppm). Normal alkanes in the C_{10} to C_{17} range are quite prominent in the most heavily oiled sample (Station 14; Figure 3.13), thus resulting in a SHWR value of $\sim$ 2.0. At lower absolute quantities of oil, the SHWR is lower 1.0-1.5 indicating a higher degree of physical/chemical weathering. Stations 2 and 5 (Figure 3.14) contain small quantities of oil, computed from the Phytane/total oil ratio of 6.4 mg/g, which are obscured by the much larger amounts of terrigenous odd chain n-alkanes. Nevertheless, weathered oil is definitely present as noted by the presence of UCM feature on the GC^2 traces.

3.2.1.5 Sediment Cores

A series of four sediment cores, segmented in 5 cm segments to 15 cm depth in the sediment column were analyzed to examine vertical oil penetration in the sediment column.

3.2.1.5a Oil Composition by GC^2. Relevant compositional data from the saturated hydrocarbon GC^2 traces are summarized in Table 3.6. Concentrations of phytane are converted to "total estimated petroleum" by multiplying by 156 (the ratio of total oil to phytane in the Lagomedio oil). Very little oil penetration into the sediment is observed in these results. Note that the surface sediment sample is a 5 cm segment as compared with the normal 2 cm surface sediment sample obtained in this study. It can be therefore concluded that oil present in the Bay 11 sediments resides primarily in the top 0-2 cm. We saw previously (Section 3.2.3.2a and 3.2.1.2a) that oil levels had increased in surface sediment samples between 1982 and 1983, yet the surface floc levels remained similar. Oil, therefore, must have been mixed into the sediment to achieve a higher bulk sediment (0-2 cm) level without increasing floc values. Apparently, from the core data this penetration is superficial, not extending below the 0-5 cm segment and undoubtedly residing mostly in the 0-2 cm segment. This accounts for the low oil values shown by the core samples. Another explanation is that the differing sampling techniques biased the results, a likely contributing factor.

In any event, representative GC^2 traces an oiled core segment (3.1 µg/g) is shown in Figure 3.15 along with the companion 5-10 segment and the aromatic fraction from this latter segment. This aromatic/olefenic profile is typical of all of the sediment

TABLE 3.6 BAY 11 SEDIMENT CORE GC2 DATA

Core	Section (cm)	Phy (µg/g)	Pris/Phy	C_{18}/Phy	Estimated Oil Concentrations[a] (µg/g)	Status
11 N	0-5	.005	>10	2.0	0.8	Trace Oil
(3 meters)	5-10	.002	3.4	2.3	<0.5	---
	10-15	.002	5.2	2.9	<0.5	---
11 S	0-5	.02	.88	.77	3.1	Oil
(3 meters)	5-10	.002	3.4	2.7	<0.5	---
11 N	0-5	.007	7.1	3.3	1.1	Oil
(7 meters)	5-10	.005	7.7	3.1	.8	Trace Oil
	10-15	<.001	55	17	<0.5	---
11 S	0-5	<.001	33	--	<0.5	---
(7 meters)	5-10	<.001	10	--	<0.5	---

a - Estimated from phytane/oil ratio.

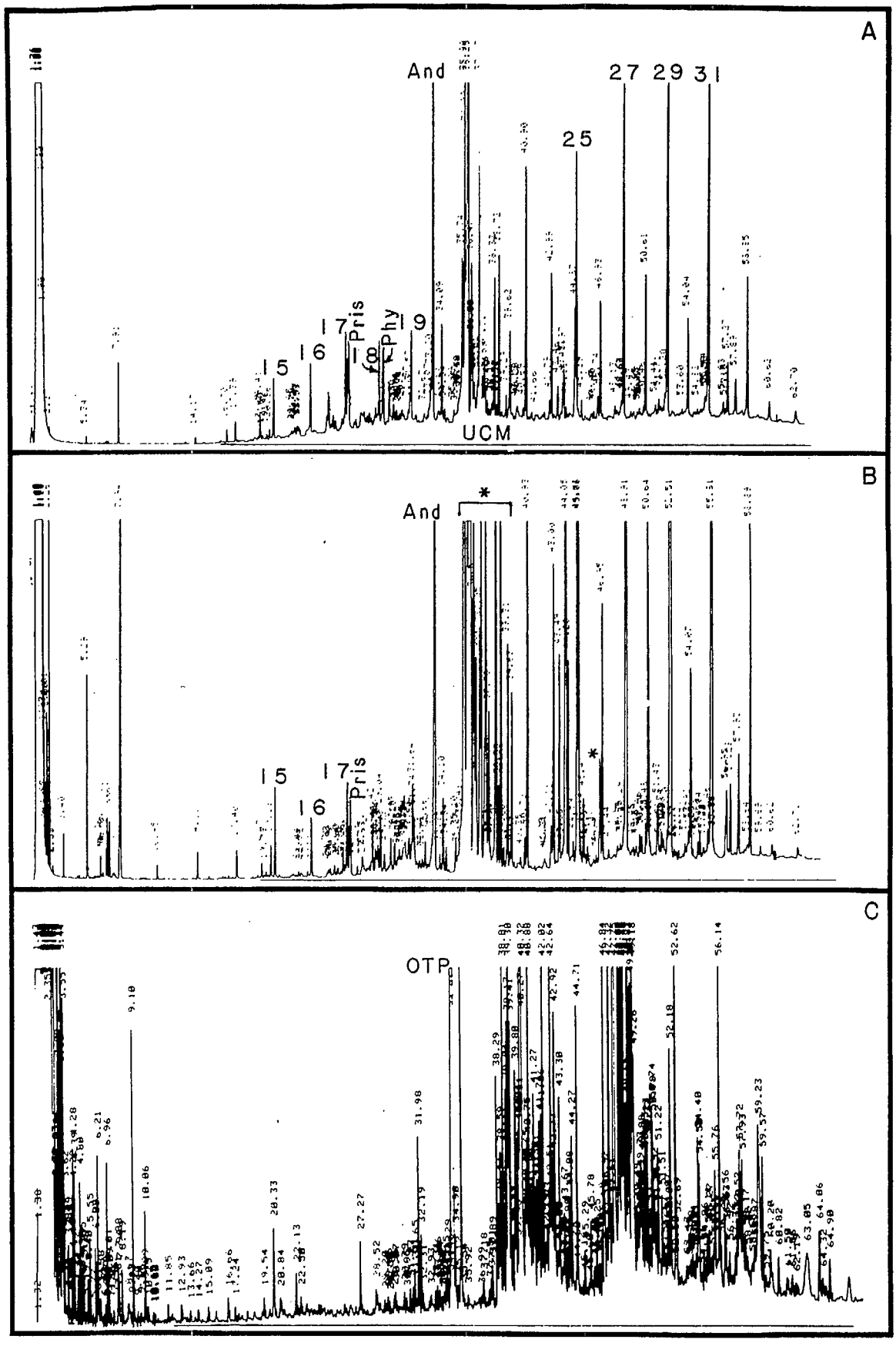


FIGURE 3.15. GC^2 TRACES OF BAY 11, S, 3m, SEDIMENT CORE: A- SATURATES 0-5 cm; B- SATURATES 5-10 cm; C-AROMATICS/UNSATURATES 5-10 cm; *- CYCLOALKENES.

samples. The aromatic fraction (Figure 3.15c) consists primarily of uncharacterized unsaturated hydrocarbon compounds of a biogenic or diagenetic origin. The saturate fraction of the 5-10 cm segment contains an abundance of cycloalkenes previously studied in other regions by Requejo and Quinn (1983). The Bay 11 north core at 3m illustrates no visable oil and only biogenic components (Figure 3.16).

3.2.1.5b Aromatic Hydrocarbon Composition by GC^2/MS. GC^2/MS analytical results for two cores are presented in Figures 3.17 and 3.18. The 0-5 cm segment of the 11 south (3m) core contains individual petrogenic aromatics in the 2-10 ng/g range. Small quantities of the alkylated aromatics are also present at 5-10 cm. The entire 11 north (3m) core, Figure 3.18, contains only traces of the C_0 and C_1 phenanthrene compounds, 1-5 ng/g, which are typical pre-spill values. Very low levels of the C_0 and C_1 DBT compounds (probably not associated with oil) are seen in the 10-15 cm segment of the 11 north core. It is not clear why the 0-5 cm segment is essentially "free" of petrogenic aromatics, in spite of the clear evidence for the presence of these compounds in the 0-2 cm segment (i.e. the tissue plots).

3.2.1.6 Deep Sediments (35 m)

A series of four deep sediments taken in the offshore basin in the central Bay 11/12 area at 35m water depth were analyzed to determine longer range offshore transport of sedimented oil.

3.2.1.6a Oil Concentrations by UV/F. As the results in Tables 3.3 and 3.7 and Figure 3.19 indicate, petroleum residues were clearly detected by UV/F in these deep water sediments with concentrations ranging from 1.7 to 8.2 µg/g. It appears that oil has been transported to deeper areas offshore although the distributions are quite patchy.

3.2.1.6b Oil Composition by GC^2. Two samples were analyzed by GC^2. Low levels of phytane (.008 and .01 µg/g) convert to 1.2 and 1.6 µg/g of oil respectively by GC^2. The GC^2 trace shown in Figure 3.20 shows the presence of C_{15}-C_{20} petroleum alkanes along with phytane and a small UCM, all characteristic of petroleum inputs to the deep sediments.

3.2.1.6c Aromatic Hydrocarbon Composition by GC^2/MS. The one deepwater sediment sample examined (B4221) contained 1-3 ng/g of the C_0 and C_1 phenanthrene compounds but not detectable petroleum aromatics in spite of the clear UV/F signal of the total extract which yielded a result of 8.2 µg/g of oil.

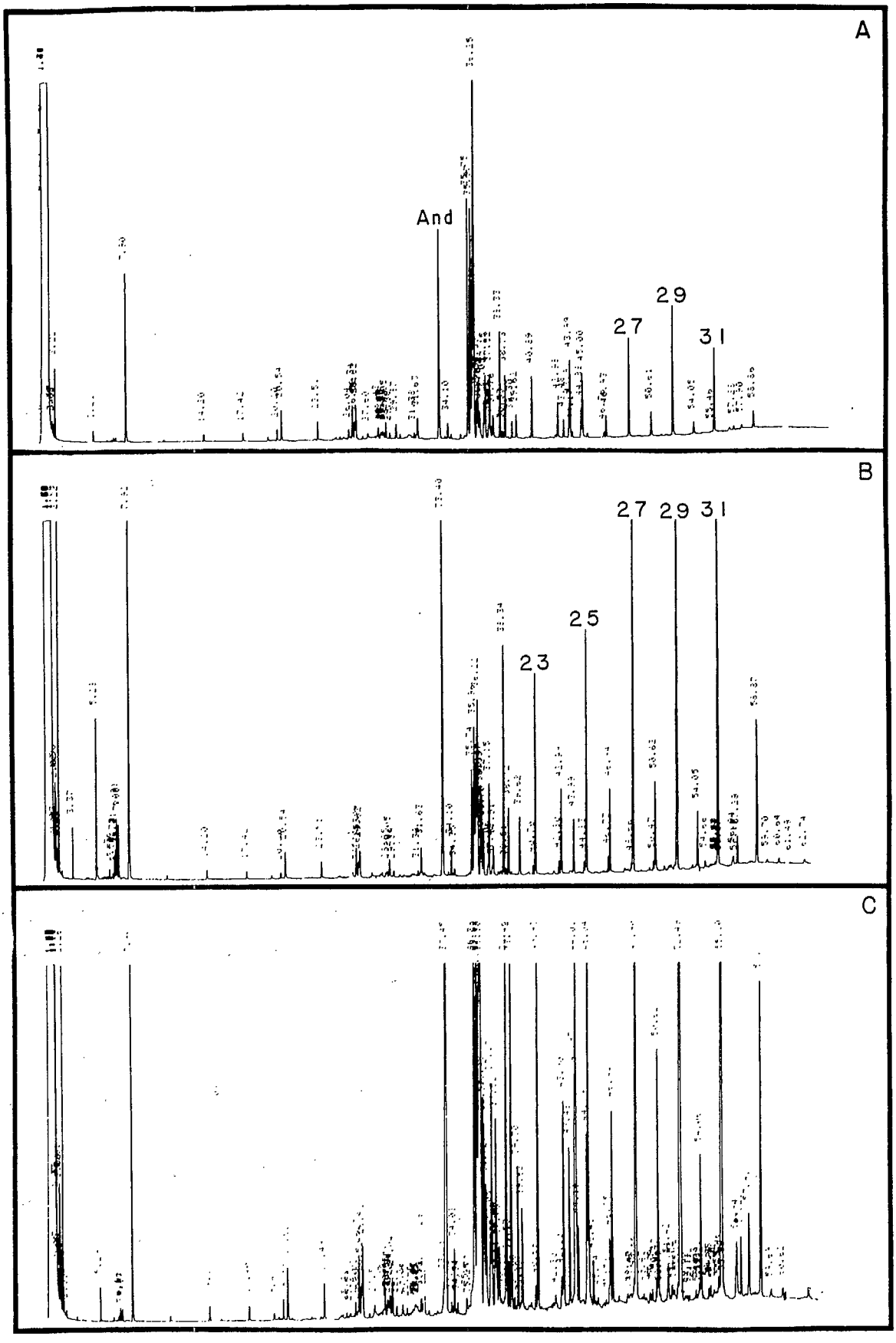


FIGURE 3.16. GC^2 TRACES OF SATURATED HYDROCARBONS IN BAY 11 N, 3m, SEDIMENT CORE: A- 0-5 cm; B- 5-10 cm; C- 10-15 cm.

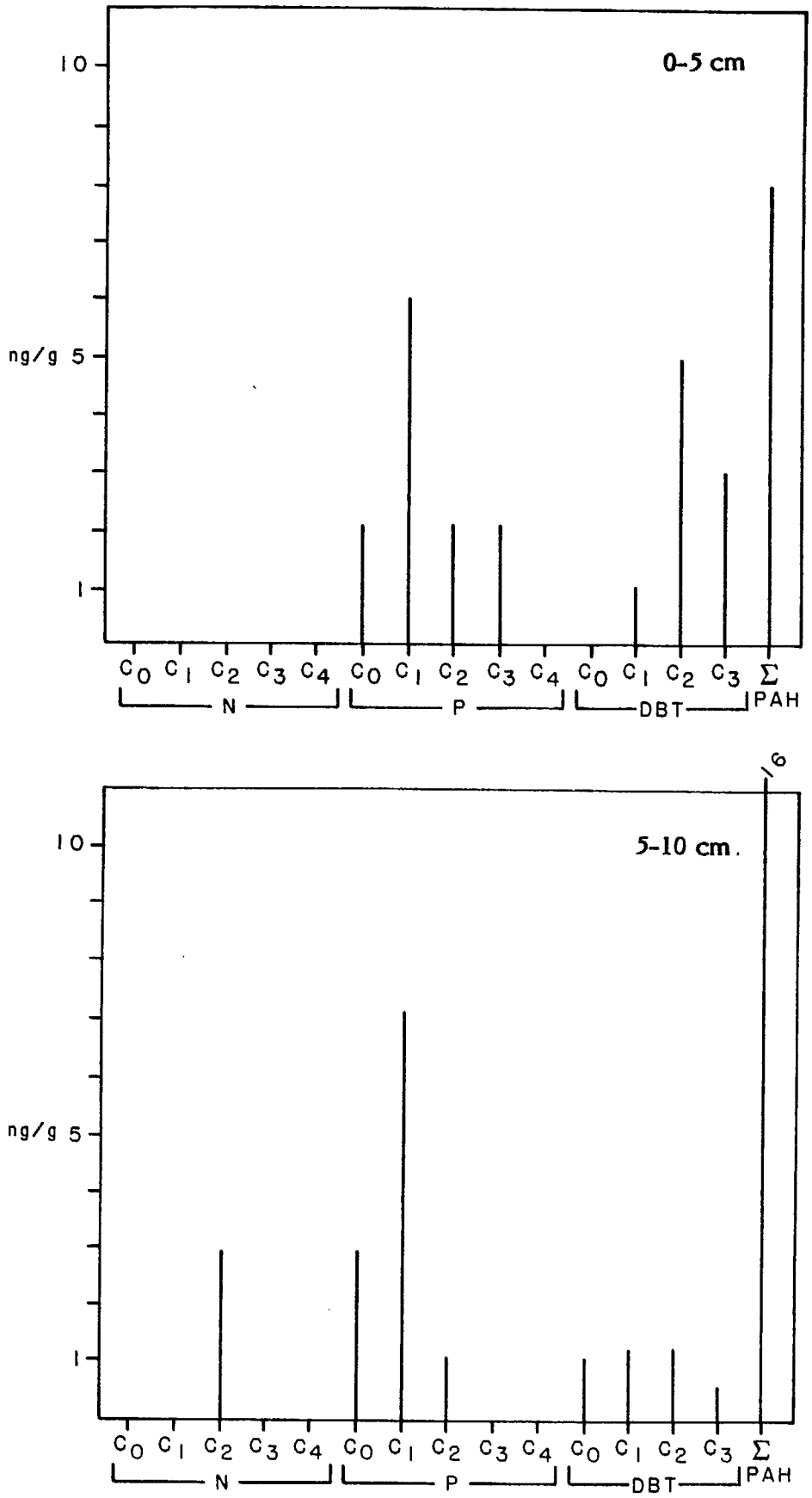


FIGURE 3.17. AROMATIC PROFILES BY GC2/MS OF BAY 11 SEDIMENT CORE 11 S, 3m

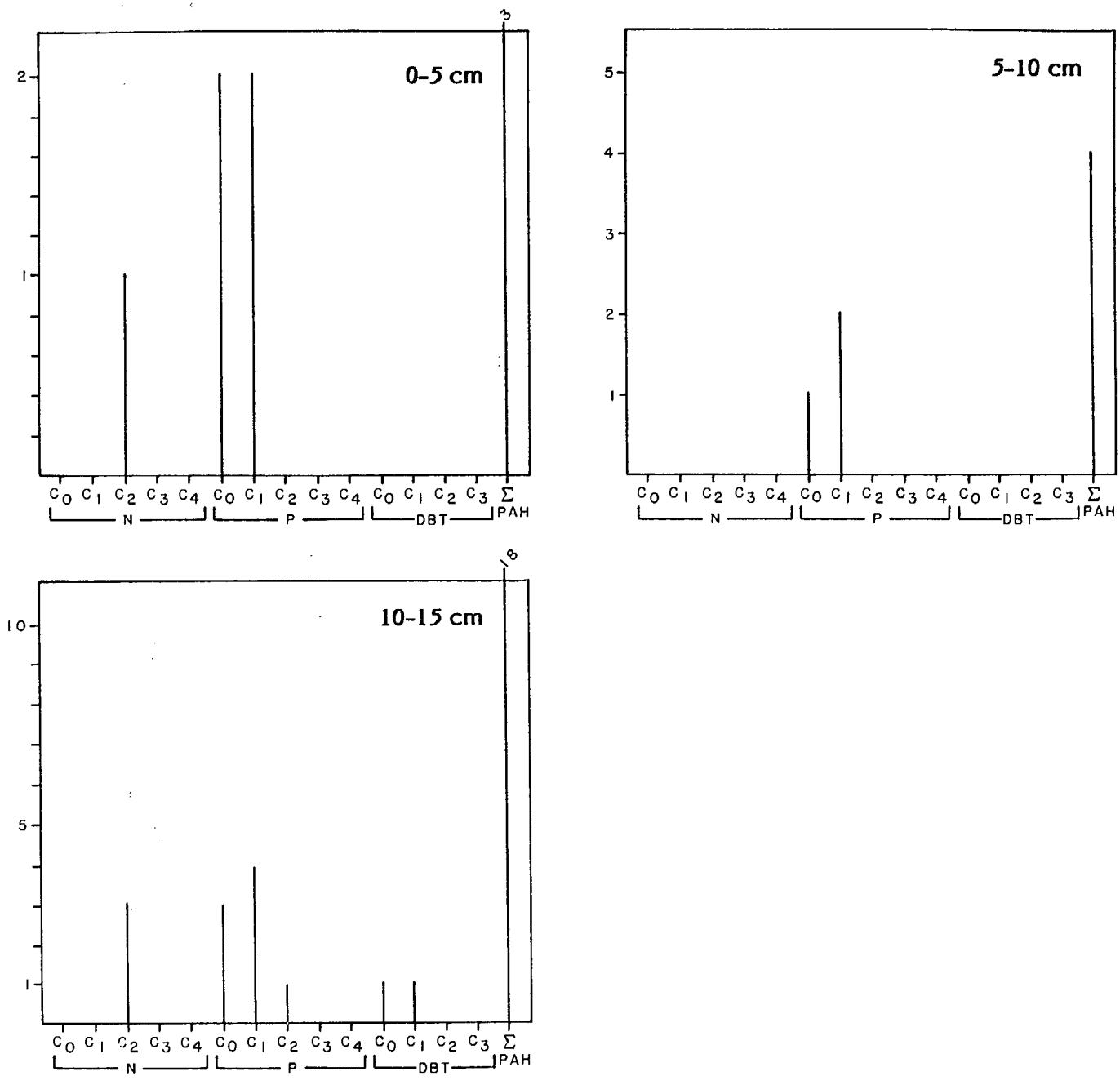


FIGURE 3.18. AROMATIC PROFILES BY GC^2/MS OF BAY 11 SEDIMENT CORE 11 N, 3m

TABLE 3.7 BAY 11/12 DEEP WATER DREDGES SEDIMENT PETROLEUM HYDROCARBONS BY UV/F

Sample I.D.	Petroleum Hydrocarbons (µg/g)
B4221	8.2
B4222	5.5
B4223	4.4
B4224	5.9
B4225	1.7

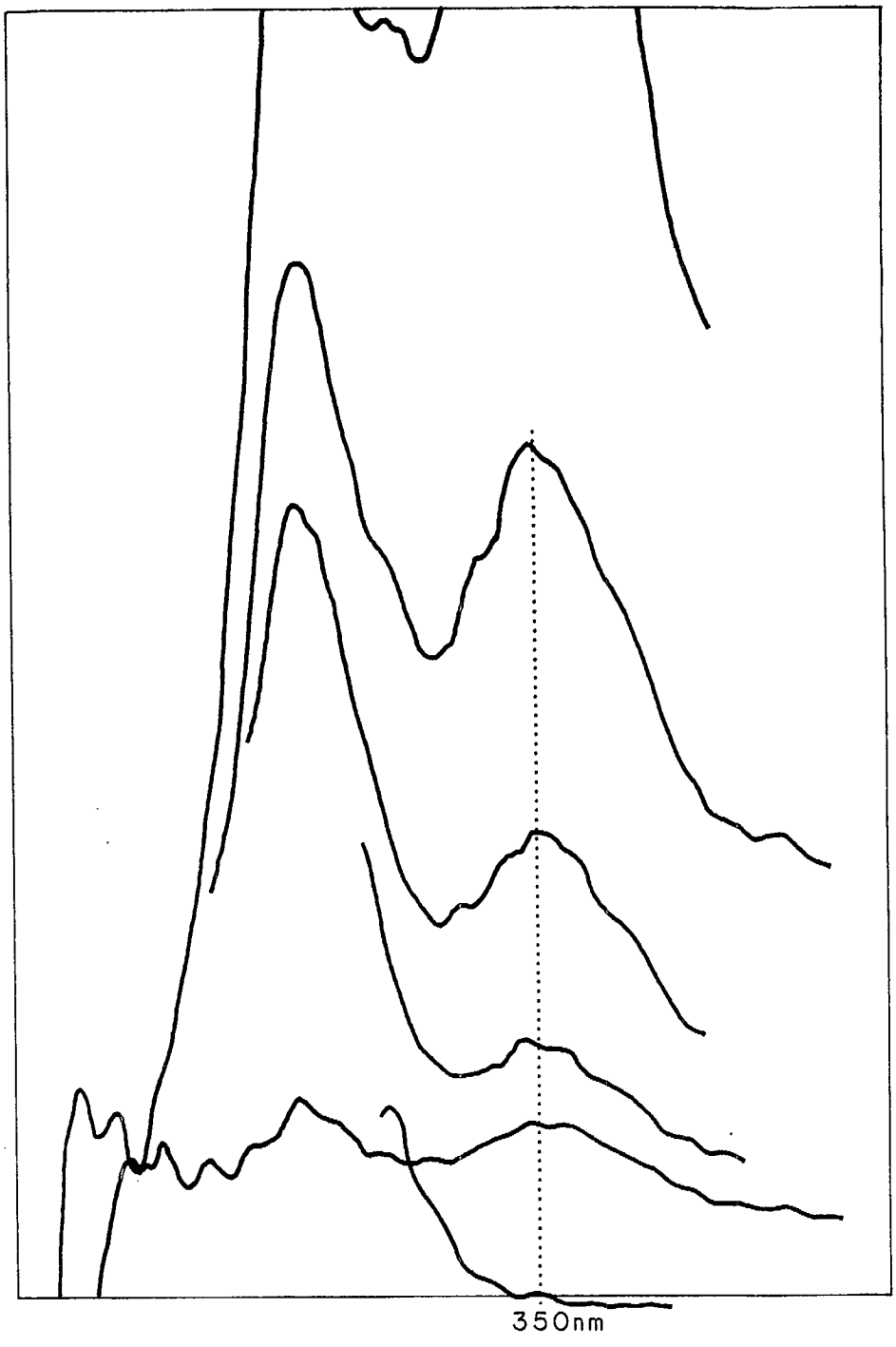


FIGURE 3.19. UV/F SPECTRA OF BAY 11/12 DEEPWATER SEDIMENT SAMPLE.

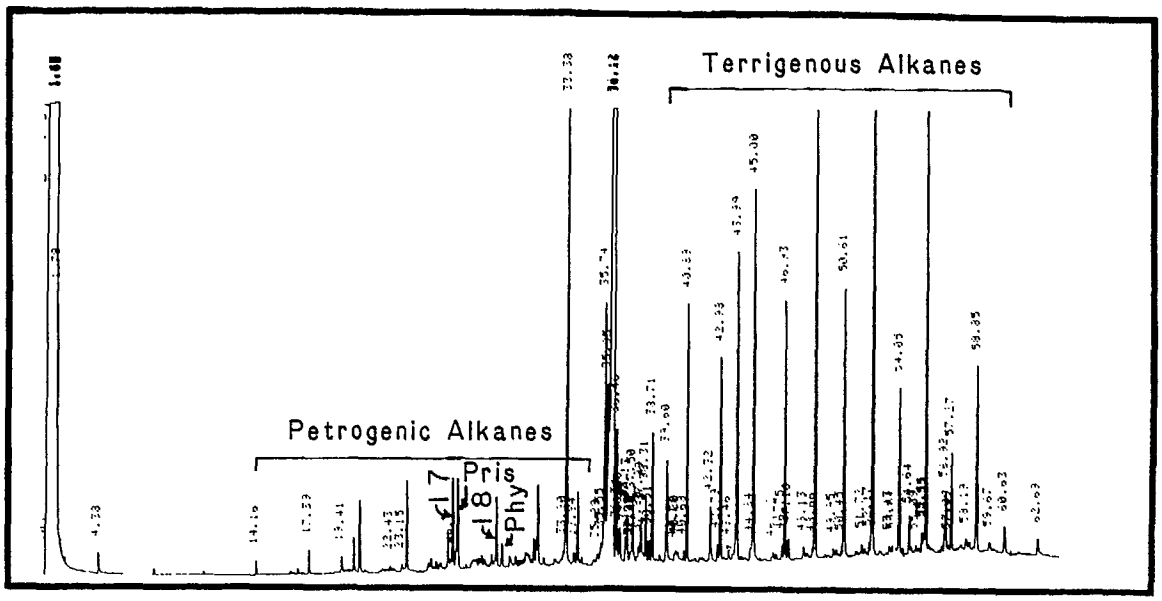


FIGURE 3.20. GC^2 TRACE OF DEEPWATER SEDIMENT SAMPLE; SATURATED HYDROCARBONS

3.2.1.7 Bay 11 Beach Sediments

The concentrations of oil found in beach samples from Bay 11 along with details of the composition of this oil are presented in Table 3.8. These oil residues represent the source of material for the Bay 11 subtidal sediments and perhaps to other sediments in the area. Note that the total extractable petroleum values include polar (i.e. non-hydrocarbon) material as well as petroleum hydrocarbons.

Concentrations of oil on the Bay 11 beach surface were quite patchy ranging from 72 to 19,400 μg/g. The mean concentration, with lower and upper 95% confidence limit values (log transformed data) was 1250 (192, 8090) μg/g. Sub-surface oil values were lower on the average 158 (5.9, 4220) μg/g although the range is very large.

Compositional details are also presented in Table 3.8 and two representative GC^2 traces are shown in Figure 3.21.

A range of weathering states are observed. The X1 surface sample exhibits an SHWR = 2.0 and, ALK/ISO value of 2.2 and an AWR of 2.5 all indicative of lightly weathered oil. The GC^2 trace of this sample is shown in Figure 3.21a. At the other compositional extreme (Figure 3.20b) observed for these samples in the Profile 6, lower surface sample (SHWR = 1.0; ALK/ISO = 0.3). The oil in this sample is highly weathered from both physical/chemical and microbial degradation viewpoints. In general, the lower surface samples are much more highly weathered than their counterparts on the upper end of the beach profile. Many intermediate values are observed.

3.2.2 BAY 9

Three types of sediment samples were analyzed from the Bay 9 beach and subtidal region during 1983. Sediment samples (0-2 cm) were analyzed from the 7m tissue plots and from the 3m benthic transect stations. In addition, a series of seven Bay 9 beach samples were analyzed.

3.2.2.1 Tissue Plots

3.2.2.1a Oil Concentrations by UV/F. The concentrations of oil in the Bay 9 subtidal sediments are presented in Figure 3.22. Concentrations of oil in the 7m tissue

TABLE 3.8 SHORELINE STUDY 1983 HYDROCARBON CHEMISTRY RESULTS - ANALYTICAL RESULTS; RAGGED CHANNEL BEACHES.

Sample ID	Plot	Depth	Saturated Hydrocarbon µg/g[a]	Aromatic Hydrocarbon µg/g[a]	Total Petroleum Hydrocarbons µg/g[a]	Total Extractable Organics[b] µg/g	SHWR	ALK/ISO	AWR
4124	Bay 9	100, Upper Surface	0.0	1.0	1.0	8.1	2.0	0.8	1.2
4126	Bay 9	100, Mid-Surface	0.9	0.4	1.3	6.9	1.2	1.4	NA
4127	Bay 9	100, Mid Sub-Surface	0.0	0.0	0.0	11.3	1.7	0.9	1.6
4128	Bay 9	100, Lower Surface	0.2	0.0	0.2	2.92	ND	ND	NA
4129	Bay 9	100, Lower Sub-Surface	0.8	0.8	1.6	11.6	1.0	0.9	NA
4952	Bay 9	300, Upper Surface	0.7	0.2	0.9	10.8	1.1	1.5	NA
4130	Bay 9	300, Mid-Surface	0.5	1.1	1.6	6.5	1.2	0.8	NA
4132	Bay 9	300, Lower Surface	0.0	0.7	0.7	9.7	1.2	1.6	NA
4134	Bay 11	2, Upper Surface	221.	180.	401.	1,260.	1.0	1.0	1.0
4135	Bay 11	6, Upper Surface	8,490.	5,380.	13,900.	17,300.	1.6	1.9	2.2
4136	Bay 11	2, Mid-Surface	601.	307.	908.	1,880.	1.1	0.4	1.1
4137	Bay 11	6, Mid-Surface	9,210.	4,280.	13,500.	16,700.	1.7	2.1	NA
4138	Bay 11	2, Lower Surface	55.1	16.9	72.0	197.	1.1	0.2	NA
4139	Bay 11	6, Lower Surface	2,580.	1,310.	3,890.	6,160.	1.0	0.3	NA
4140	Bay 11	4, Upper Surface	12,200.	7,230.	19,400.	25,400.	1.6	2.5	NA
4141	Bay 11	8, Upper Surface	2,380.	1,100.	3,480.	4,810.	1.1	1.4	NA
4142	Bay 11	4, Mid-Surface	4,220.	1,930.	6,150.	10,800.	1.0	0.7	NA
4143	Bay 11	8, Mid-Surface	1,010.	503.	1,510.	2,450.	1.0	1.4	NA
4144	Bay 11	4, Lower Surface	29.6	13.1	42.7	94.0	1.2	0.4	NA
4145	Bay 11	8, Lower Surface	835.	422.	1,260.	2,000.	1.1	0.3	NA
4146	Bay 11	X1 Surface	16,200.	1,050.	17,200.	26,900.	2.0	2.2	2.5
4147	Bay 11	X2 Surface	216.	107.	322.	600.	1.3	1.2	NA
4148	Bay 11	X3 Surface	332.	186.	518.	809.	1.8	2.1	NA
4149	Bay 11	X4 Surface	122.	69.8	192.	730.	1.6	1.8	2.1
4150	Bay 11	X5 Surface	7,670.	5,130.	12,800.	15,900.	1.4	1.0	NA
4946	Bay 11	X1 Sub-Surface	4,640.	2,380.	7,020.	8,980.	1.6	2.0	2.3
4947	Bay 11	X2 Sub-Surface	41.4	18.6	78.6	151.0	1.2	0.7	NA
4948	Bay 11	X3 Sub-Surface	2.4	2.3	4.7	72.2	1.3	1.4	NA
4949	Bay 11	X4 Sub-Surface	0.9	3.0	3.9	227.	1.3	1.4	3.5
4950	Bay 11	X5 Sub-Surface	3,430.	2,180.	5,600.	7,180.	1.8	1.8	NA
4951	Bay 11	X6 Sub-Surface	164.	105.	269.	688.	1.7	2.1	NA
4955	Crude Oil Point	X7 Surface	1,060.	467.	1,530.	2,600.	1.0	1.2	NA
4956	Crude Oil Point	X8 Sub-Surface	1,220.	724.	1,940.	3,000.	1.0	1.6	NA

a = determined gravimetrically.
b = contain petrogenic hydrocarbons, petrogenic polar compounds and biogenic compounds.
ND = none detected.

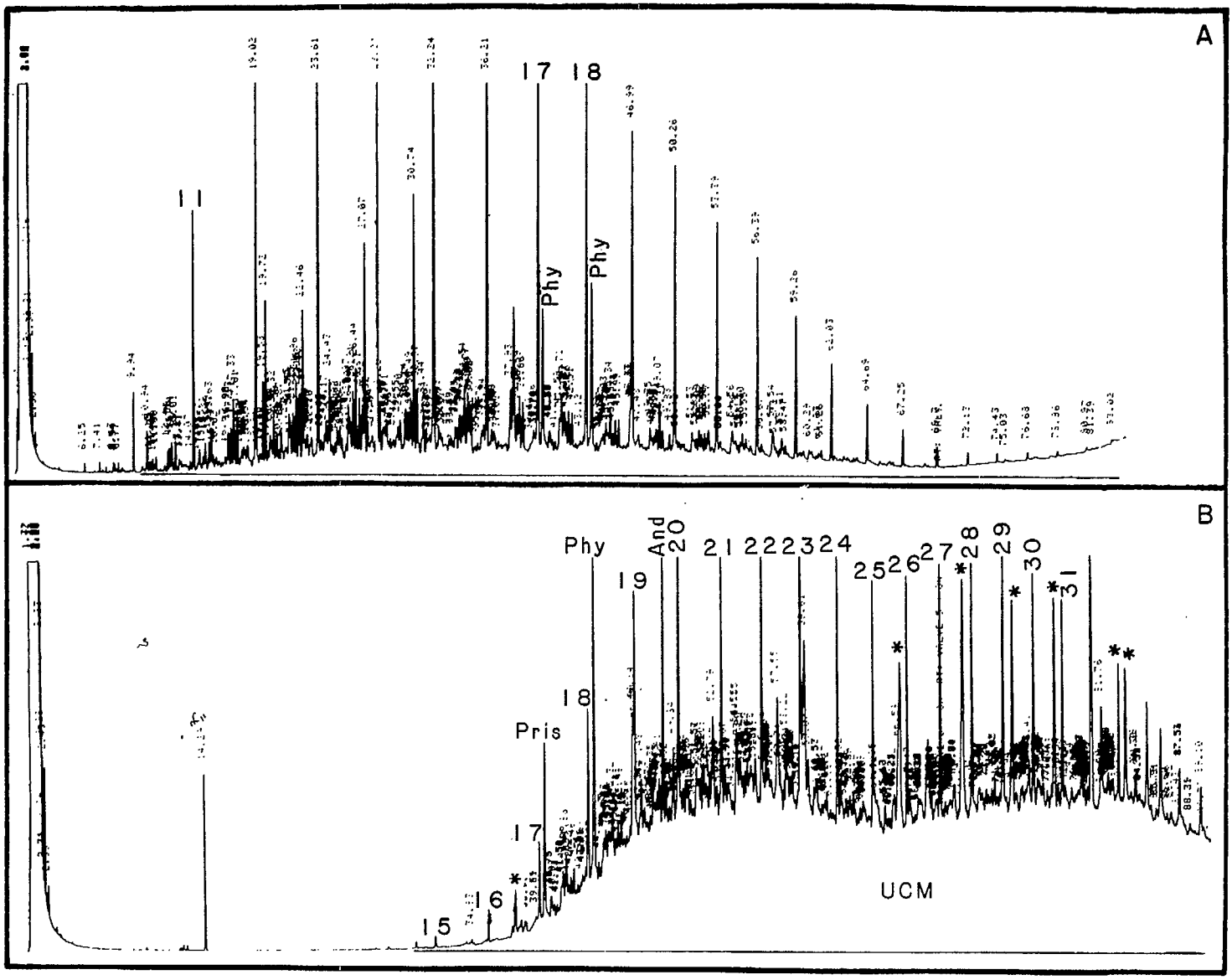


FIGURE 3.21. GC^2 TRACE OF BAY 11 BEACH SEDIMENTS: A- SATURATES S4146 (UNWEATHERED, UNDEGRADED); B- SATURATES S4139 (WEATHERED AND DEGRADED); *-UNIDENTIFIED CYCLIC ALKANES (TERPENOIDS).

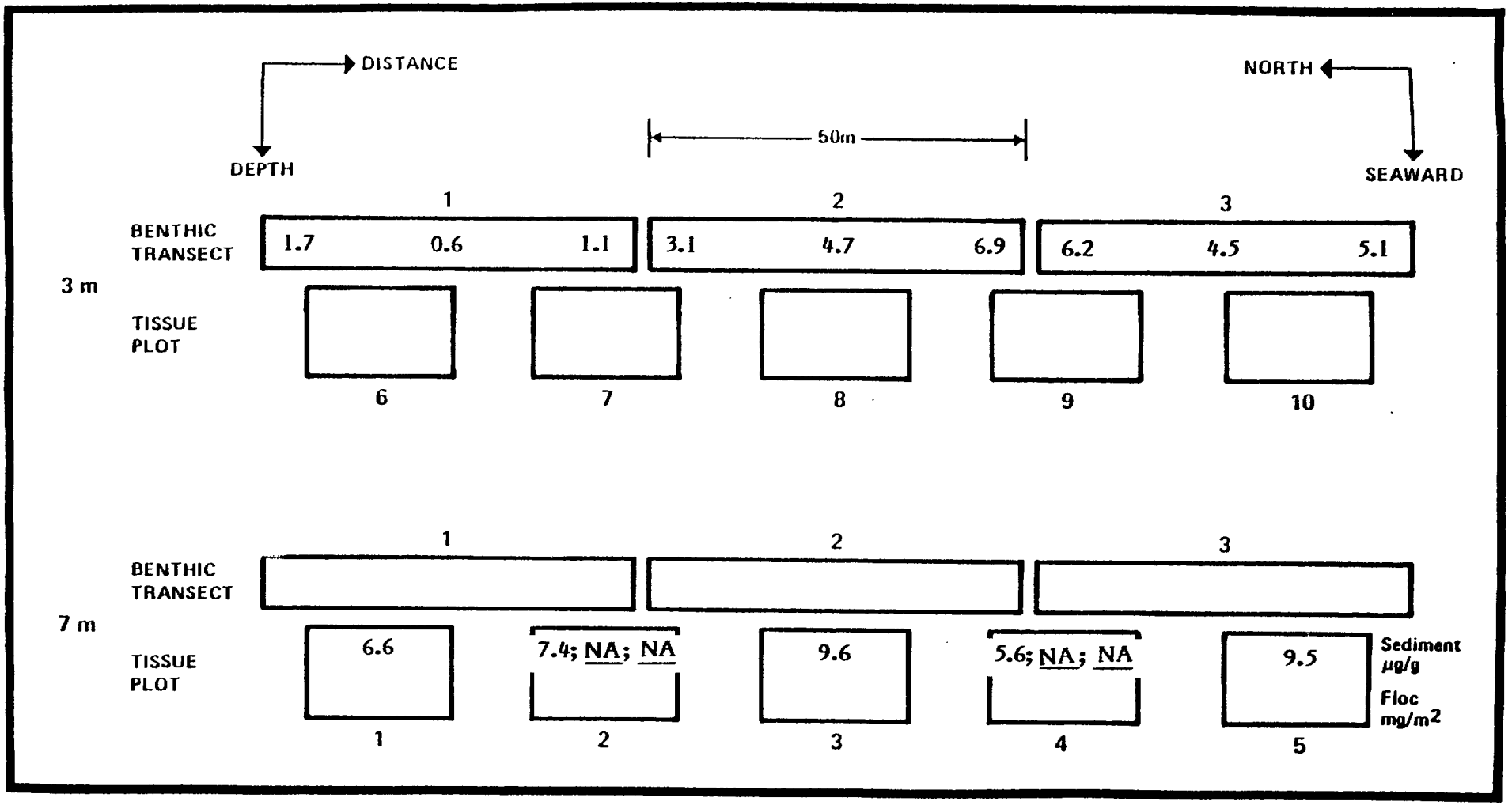


FIGURE 3.22. BAY 9 SEDIMENT PETROLEUM HYDROCARBON CONTENT; BY UV/F (AUGUST 15, 1983). (NA = NOT ANALYZED)

plots ranged from 5.6 to 9.5 μg/g with a mean of 7.6 (6.0, 9.5) μg/g as determined by UV/F. These values are higher than those reported for the 1982 samples which were 2.2 (1.5, 3.1) μg/g.

3.2.2.1b Oil Composition by GC^2. Three tissue plot sediments from Bay 9 were analyzed by GC^2 to confirm the presence of oil and to examine the sample's hydrocarbon composition. As can be seen from one of the GC^2 traces (Figure 3.23) low levels of identifyable petrogenic compounds (n-alkanes C_{13}-C_{19}, and phytane) are seen in the samples. Phytane is detected at levels of .002 to .005 μg/g which convert to concentrations of 0.3 to 0.8 μg/g compared with the much higher levels detected by UV/F. These discrepancies are examined in Section 3.2.5. The aromatic/olefinic fraction exhibits large amounts of biogenic/diagenetic unsaturates with possibly minor quantities of petroleum aromatics. These aromatics are discussed in the next section.

3.2.2.1c Aromatic Hydrocarbons Compositions by GC^2/MS. Two Bay 9 a tissue plot samples (B4054, 7m, No. 5 and B4077, 7m, No. 3) analyzed by GC^2/MS contained low levels 1-3 ng/g of petroleum aromatics (i.e. the alkylated phenanthrene and DBT compounds. These values were a factor of 5 lower than the levels observed in 1982. Note however, that the levels determined on the 1983 samples are quite similar to those reported after the spills in 1981 when bulk oil levels in the Bay 9 sediments were roughly the same concentration (1981: mean=9.0 μg/g).

3.2.2.2 Benthic Transects

3.2.2.2a Oil Concentrations by UV/F. Oil concentrations in the 3m benthic transects as determined by UV/F were as follows: Transect 1 = 1.0 (.62, 1.8) μg/g; Transect 2 = 4.6 (3.3, 6.4) μg/g; Transect 3 = 5.2 (4.4, 6.1) μg/g. The values in Transects 2 and 3 are higher than those reported on 1982 field samples at which time Transect 2 levels were .52 (.23, 1.2) μg/g and Transect 3 levels were .91 (.83, 1.5) μg/g. Levels in Transect 1 were similar in 1982 and 1983 (1982 Transect 1 = 1.0 (.66, 1.6) μg/g). Thus it appears that levels of 3-7 μg/g of oil were added to the benthic transect samples. These levels approximate those observed in the 1982 Bay 9 microbiology samples 3-6 μg/g in 1982.

3.2.2.2b Oil Composition by GC^2. GC^2 analyses of the two Bay 9 benthic transect samples analyzed reveal the presence of only low levels of any petrogenic compounds in the saturated hydrocarbon fraction (similar to Figure 3.23). Levels of

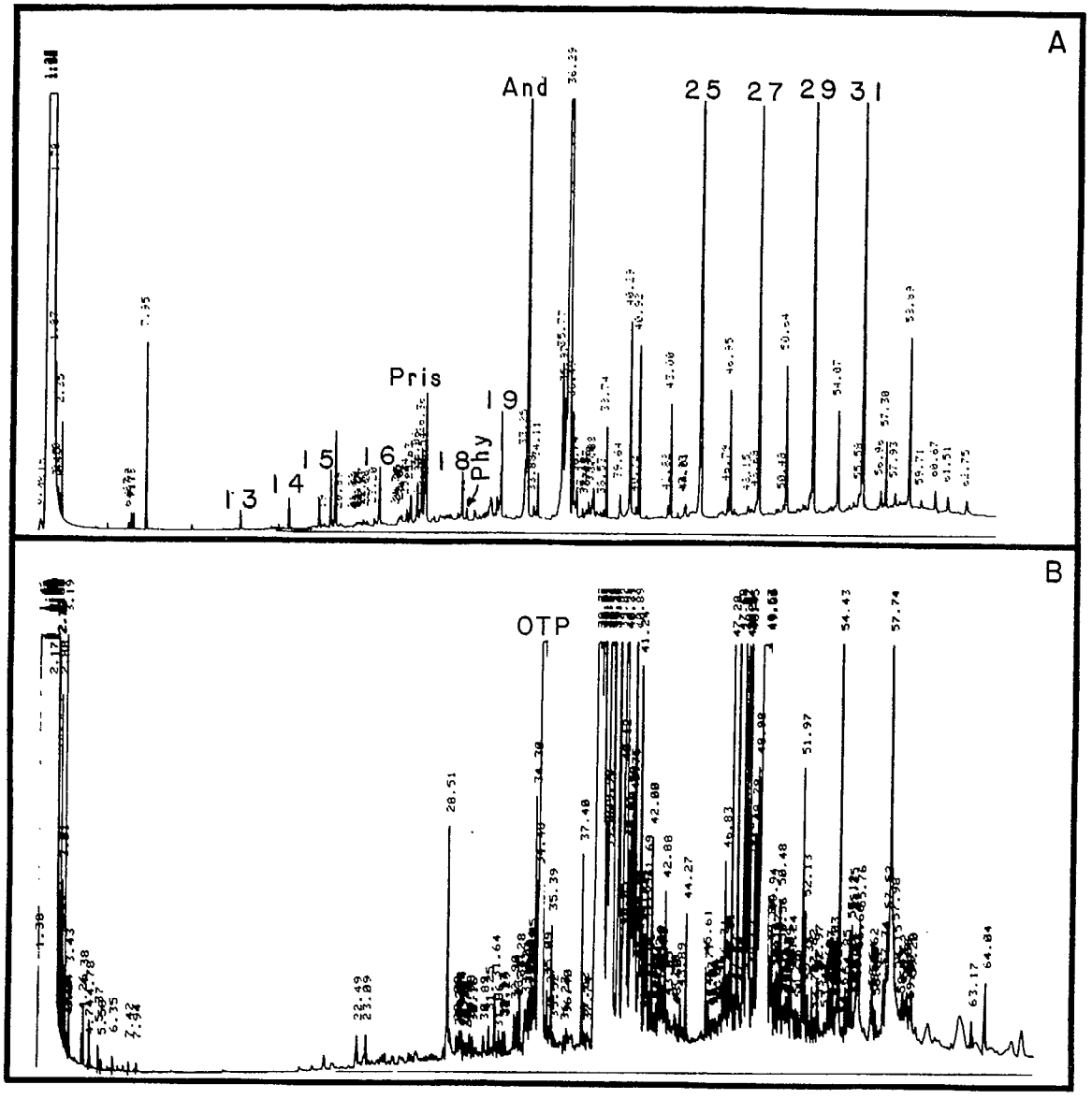


FIGURE 3.23. GC^2 TRACE OF BAY 9 TISSUE PLOT SEDIMENT: A- SATURATED HYDROCARBONS; B- AROMATIC/UNSATURATED HYDROCARBONS.

phytane in the two samples analyzed were detectable, but very low (.005 and .004 µg/g) albeit higher than the .001 (µg/g) background. However, these phytane levels convert to oil levels of .8 and .6 µg/g respectively, much lower than the UV/F determined values.

3.2.2.2c Aromatic Hydrocarbon Composition by GC^2/MS. The single benthic transect sample analyzed by GC^2/MS (B4088; 3m; Benthic Station 3a) contained individual aromatic hydrocarbon levels of 1-3 ng/g (alkylated phenanthrene and DBT compounds) amidst a 3 ng/g background of polycyclic aromatic hydrocarbons (4 and 5 rings).

3.2.2.3 Bay 9 Beach

The analytical results for a set of eight Bay 9 beach sediment samples are presented in Table 3.8. These oil concentrations range from 0.5 to 1.6 µg/g, in the range of those levels reported in 1982. The highest level samples were comprised of a weathered (SHWR = 1.2) undegraded (C_{18}/Phy = 3.4) saturated hydrocarbon composition (Figure 3.24). This oil is significantly different from that observed on the Bay 11 beach, as it is undegraded.

3.2.3 BAY 7

Two types of sediment samples were analyzed from the Bay 7 subtidal area: five tissue plot sediments and nine benthic transect samples.

3.2.3.1 Tissue Plots

3.2.3.1a Oil Concentrations by UV/F. UV/F-determined values of oil concentrations in Bay 7 stations (Figure 3.25) averaged 3.2 (1.4, 7.4) µg/g. Aside from the one high value, 12.8 µg/g/ tissue plot # 4, the mean value is 2.3 1.6, 3.3) µg/g, approximately twice the mean value determined in 1982, 1.2 (.96, 1.4) µg/g..

3.2.3.1b Oil Composition by GC^2. The existence of petroleum at tissue plot #4 was confirmed by the GC^2 data on this sample. This sample, shown in Figure 3.26A, contains .05 µg/g phytane (~7.8 µg/g of oil) and a small, but significant quantity of UCM material. The C_{18}/Phy ratio of 0.5 indicates that this petroleum material is significantly biodegraded. This ratio is equal to 1.6 in undegraded oil. The PRIS/Phy ratio of 2.8

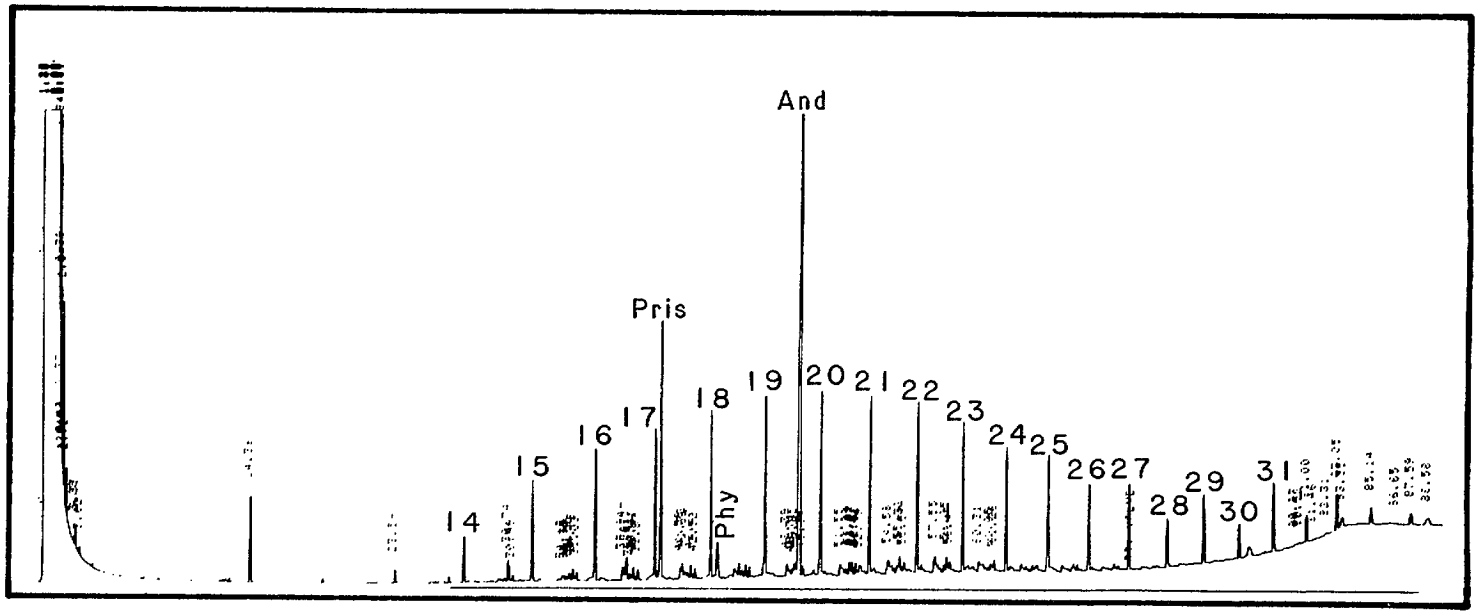


FIGURE 3.24. GC^2 TRACE OF REPRESENTATIVE BAY 9 BEACH SEDIMENT; SATURATED HYDROCARBONS.

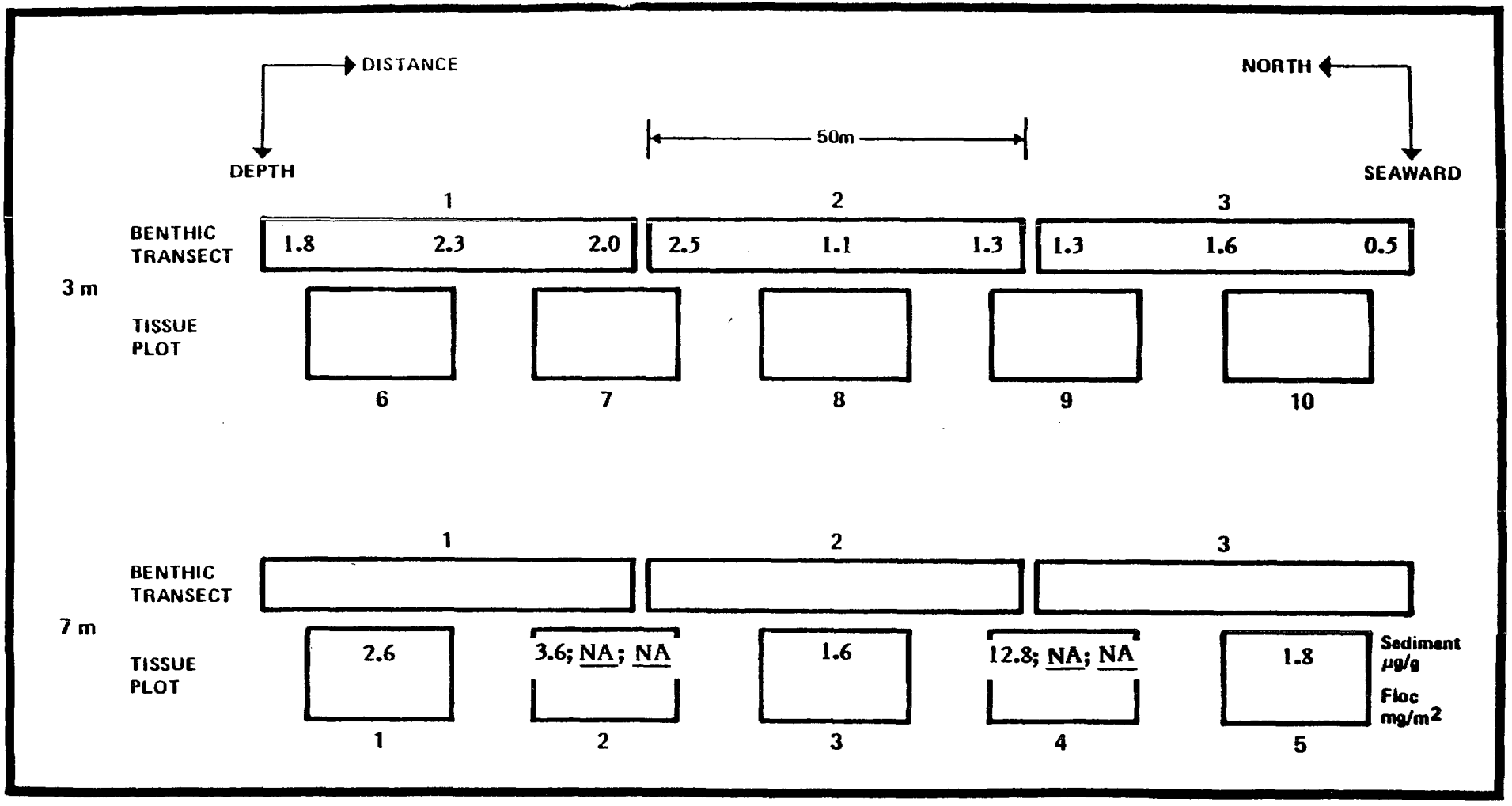


FIGURE 3.25. BAY 7 SEDIMENT PETROLEUM HYDROCARBON CONTENT; BY UV/F (AUGUST 14, 1983). (NA = NOT ANALYZED)

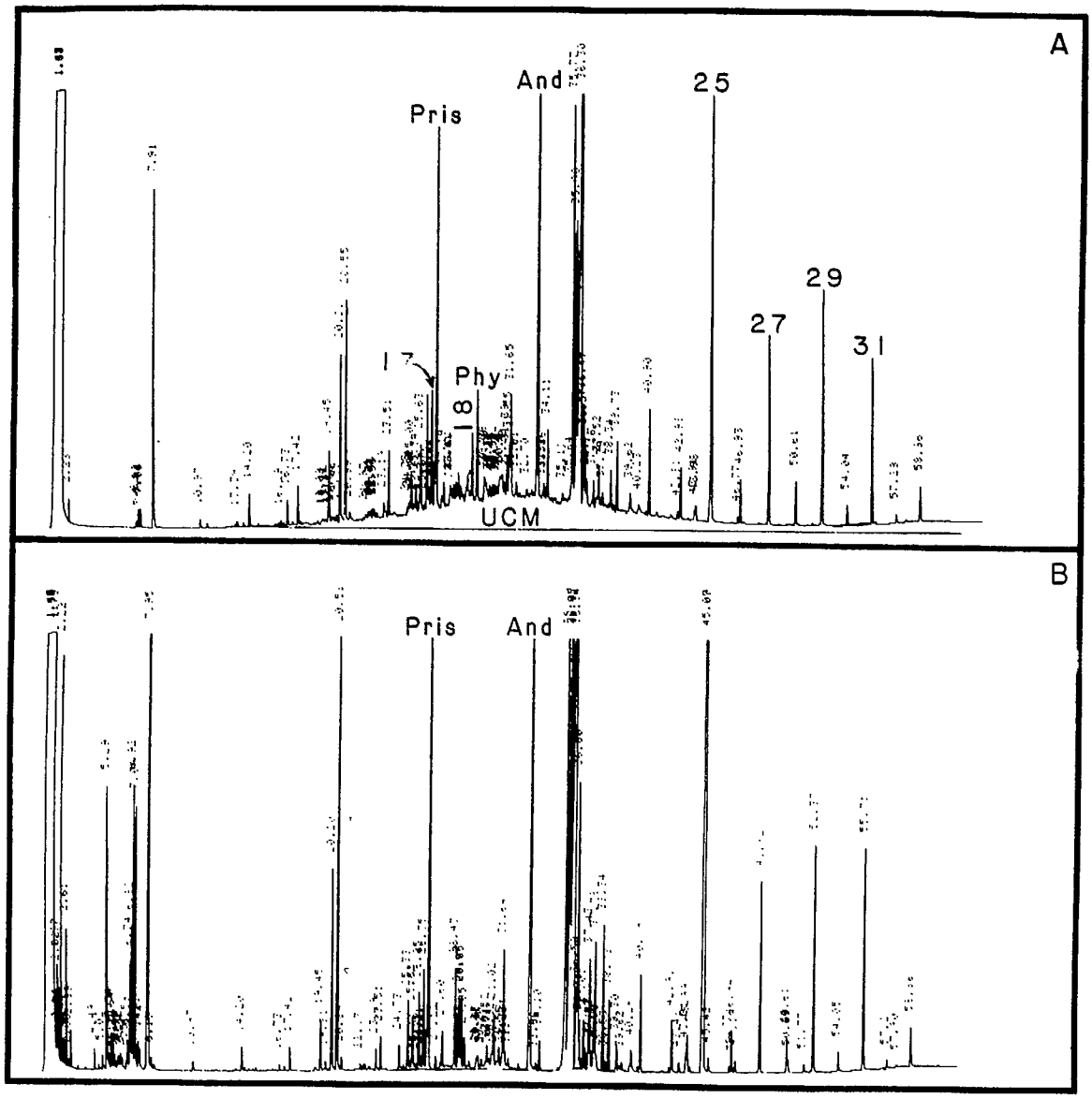


FIGURE 3.26. GC^2 TRACE BAY 7 SEDIMENTS: A- SATURATES TISSUE PLOT NO. 4; B- SATURATES BENTHIC TRANSECT.

indicates that biogenic pristane "overprints" any petrogenic pristane (PRIS/PHY in oil = 0.74). Petrogenic phytane was detected in tissue plot # 5 (.008 µg/g), tissue plot #3 (.009) and the agreement between UV/F and GC^2 results in Bay 7 is good (see Section 3.2.5).

3.2.3.1c Aromatic Hydrocarbon Composition by GC^2/MS. Two samples (Plot No. 4a and 5) were analyzed by GC^2/MS. The presence of petroleum in plot 4, corresponding to the Figure 3.26A sample, was confirmed (Figure 3.27A). Individual aromatics were present at the 1-4 ng/g level and a petroleum composition was noted, as opposed to the background distribution (Figure 3.27B) observed for the other sample from Bay 7.

3.2.3.2 Benthic Transects

3.2.3.2a Oil Concentrations by UV/F. Concentration data for the Bay 7 benthic transect sediments is shown in Figure 3.25. Values are low as follows: Transect 1 = 2.1 (1.9, 2.4) µg/g; Transect 2 = 1.5 (.99, 2.4) µg/g; Transect 3 = 1.0 (.55, 1.8) µg/g. These values are similar to those observed in the tissue plots in Bay 7 in 1982. No 3m samples were analyzed in 1982.

3.2.3.2b Oil Composition by GC^2. Two samples were analyzed to examine hydrocarbon compositions of the Bay 7 benthic transects. One of the two saturated hydrocarbon GC^2 traces is presented in Figure 3.26B. No phytane and hence no petroleum residues were detected in these 3m samples.

3.2.4 MILNE INLET SAMPLES

Five sediment samples taken from the subtidal area of Milne Inlet on the western side of Ragged Island were analyzed to determine if any oil residues were detectable in these reference areas.

3.2.4.1 Oil Concentrations by UV/F

No oil was detected in any of the five samples UV/F spectra (e.g., Figure 3.28) contained only small 350 nm responses. Resultant oil concentrations are shown in Table 3.9. The mean value is 0.78 µg/g, essentially a background level.

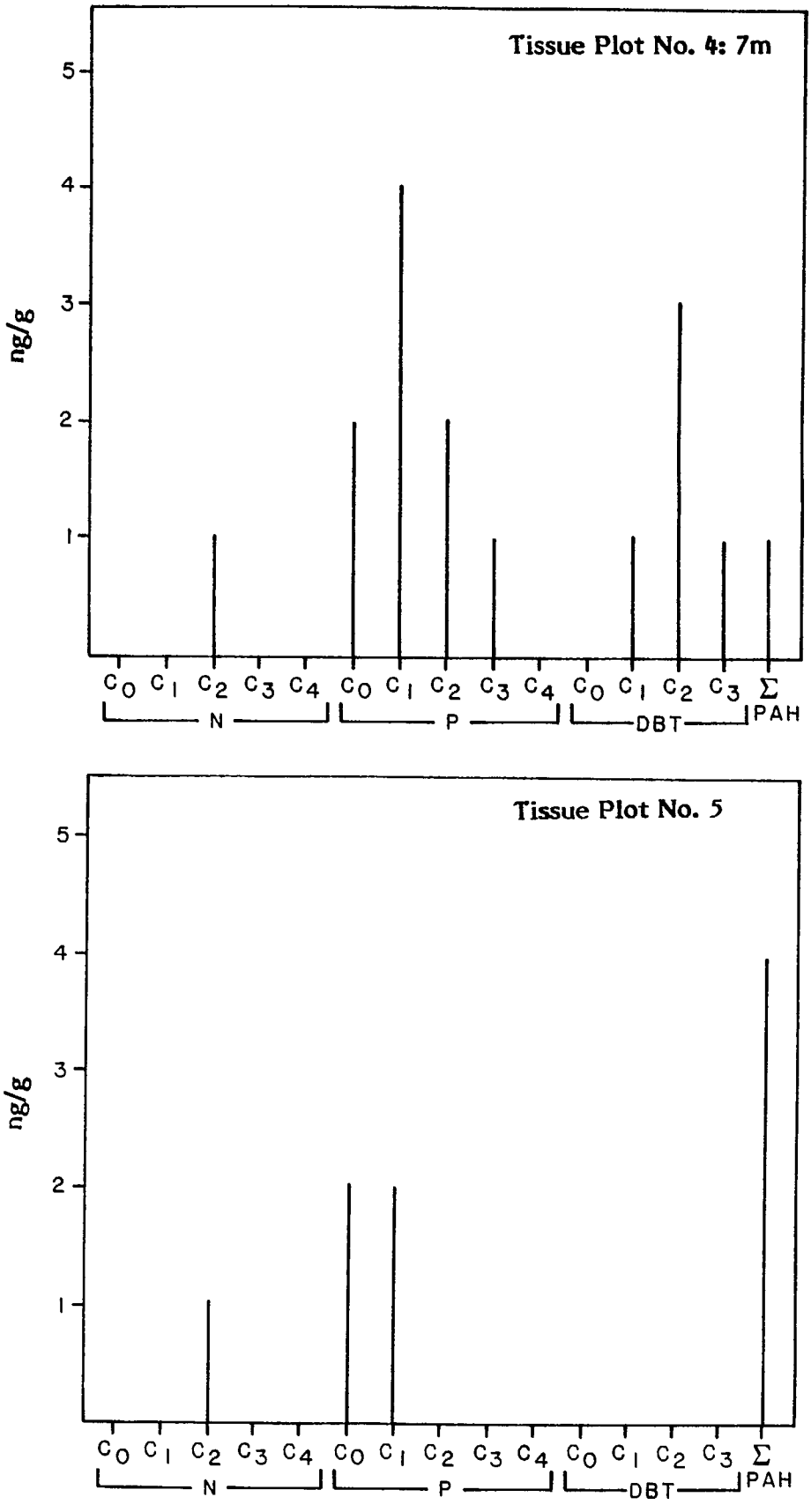


FIGURE 3.27. AROMATIC PROFILES BY GC^2/MS OF BAY 7 SEDIMENTS

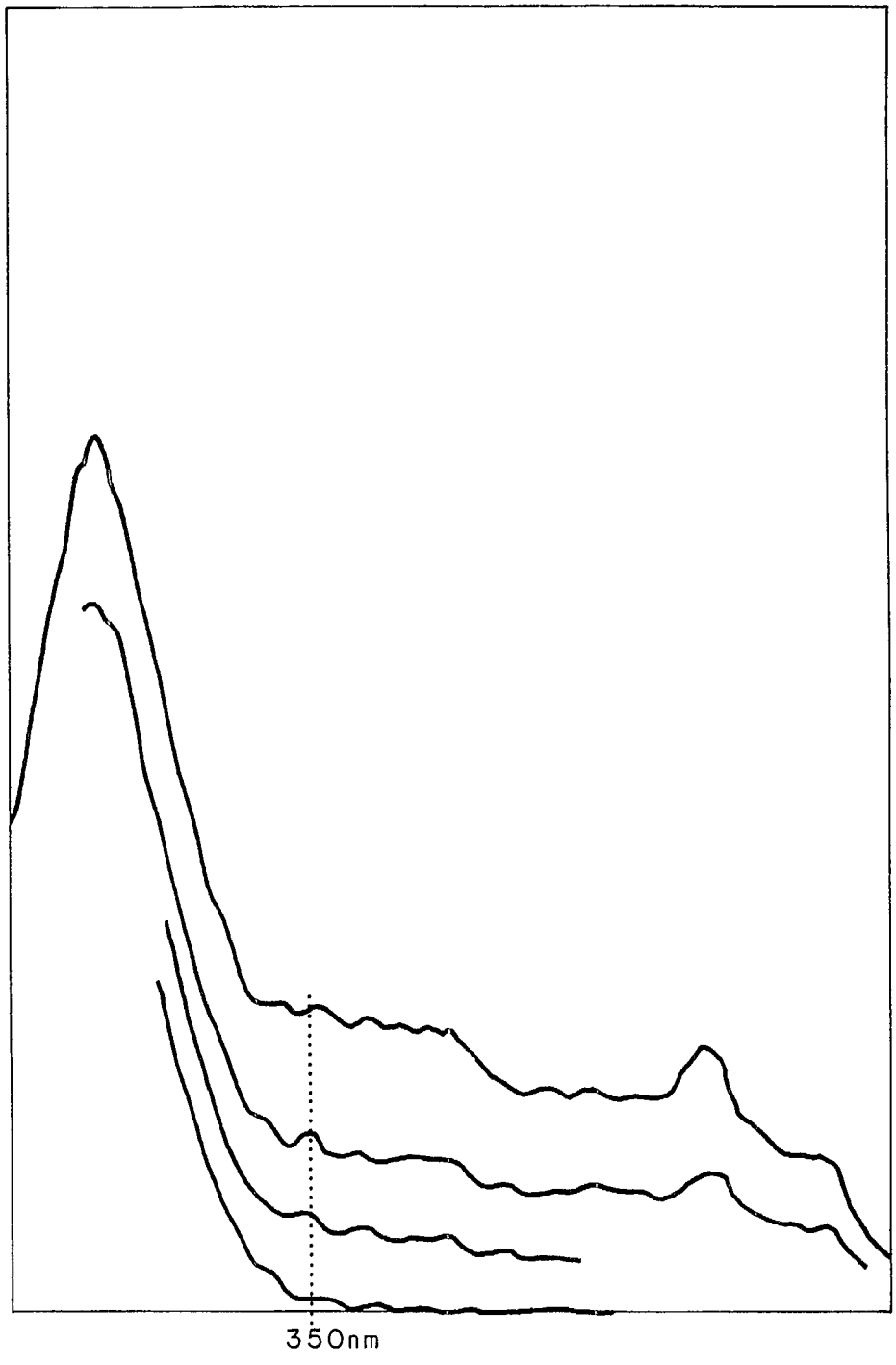


FIGURE 3.28. UV/F SPECTRA OF MILNE INLET SEDIMENT SAMPLE DILUTION SERIES, SHOWING NO OIL PRESENT.

TABLE 3.9 MILNE INLET SUBTIDAL SEDIMENT CONTROL SAMPLES - PETROLEUM HYDROCARBON CONTENT BY UV/F

Sample I.D.	Plot	Petroleum Hydrocarbons (µg/g)
B4091	1	0.8
B4092	2	0.7
B4093	3	1.1
B4094	4	0.5
B4095	5	0.8

3.2.4.2 Oil Compositions by GC^2

The two GC ^{2} analyses performed on the Milne Inlet samples confirm the purely biogenic composition of these samples. No phytane or UCM was detected in either sample. The composition consisted of terrigenous n-alkanes and olefinic material (Figure 3.29).

3.2.4.3 Aromatic Hydrocarbon Composition by GC^2/MS

The aromatic hydrocarbon composition of the one Milne Inlet sample examined is illustrated in Figure 3.30.

3.2.5 COMPARISON OF UV/F-DERIVED PETROLEUM CONCENTRATIONS AND GC^2-DERIVED RESULTS

A large discrepancy exists between UV/F and GC^2-derived hydrocarbon values as shown in Table 3.10. This discrepancy was noted in the 1982 study results (Boehm, 1983a) and has become wider with time. The original close agreement between these two sets of results Boehm et al. (1982a) apparently does not hold as oil residues get progressively more weathered. As we compute a GC^2-derived value from the phytane concentrations (i.e. Phytane/total oil = 6.4 mg/g phytane oil) this computation becomes less reliable as phytane itself is degraded. We know that the UV/F 350-360 nm band was nearly absent in prespill samples and is also absent in Milne Inlet sediment samples. Therefore, we must conclude that the UV/F data is reliable at least in a comparative sense when viewed against 1981-1982 data.

Note also that as the oil weathers, the correlation of the 350-360 nm intensity on the UV/F spectra with total oil concentrations breaks down. However, we conclude that the UV/F values should be used as the petroleum concentrations in this study.

3.2.6 REANALYSIS OF 1982 FIELD SAMPLES

As part of the QC/QA program performed as part of this study, three sediment samples from the 1982 field program representing a range of concentrations were

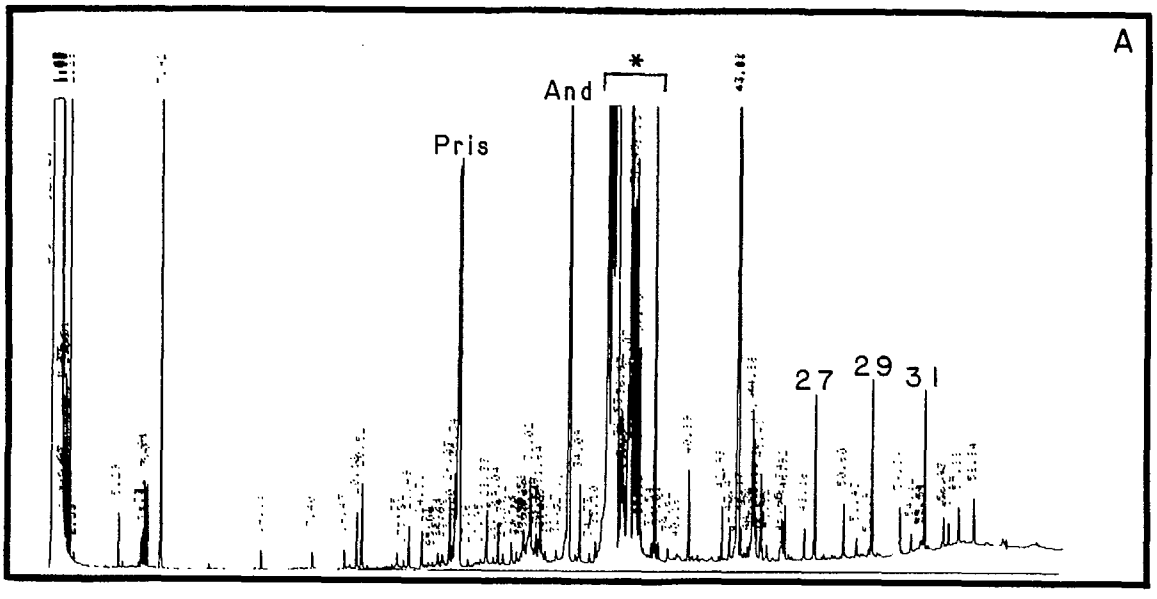


FIGURE 3.29. GC^2 TRACE MILNE INLET SEDIMENT SATURATED HYDROCARBONS; *-CYCLOALKENES.

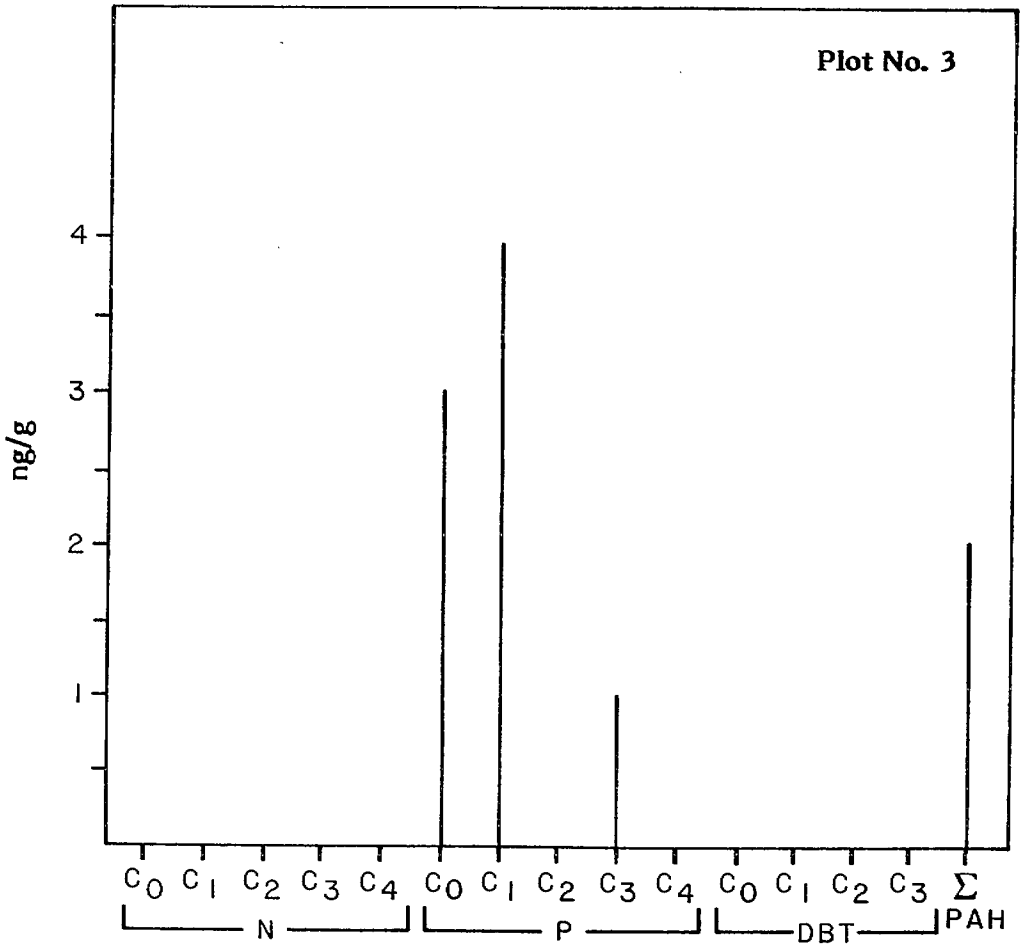


FIGURE 3.30. AROMATIC PROFILES BY GC^2/MS MILNE INLET SEDIMENT SAMPLE

TABLE 3.10 UV/F VERSUS GC^2 - DERIVED RESULTS ON SEDIMENTS

Bay	Tissue Plot	Benthic Transect	Oil Concentration UV/F (µg/g)	Phytane (µg/g)	Oil Concentration[a] GC^2 (µg/g)
11	1		21.2	.01	1.5
	5		20.5	.06	9.2
	6		22.7	.05	7.7
	8		16.8	.04	5.6
	10		85.6	.27	42
		1b(3m)	58.3	.18	28.5
		3b(3m)	137	.50	79.3
		1a(7m)	21.8	.04	5.5
		2c(7m)	10.7	.02	3.0
		3b(7m)	39.0	.07	10.8
9	2		7.4	.002	0.3
	3		9.6	.003	0.5
	5		9.5	.003	0.5
		2c(3m)	6.9	.005	0.8
		3a(3m)	6.2	.004	0.6
7	3		1.6	.008	1.3
	4		12.8	.05	7.8
	5		1.8	.009	1.4
		2a(3m)	2.5	.002	0.3
		3b(3m)	1.6	.003	0.5

[a] Phytane x 156 = Oil Concentration.

reanalyzed here. Other samples (e.g., tissues and shoreline sediments) were not available for this phase of the program. The UV/F and GC^2 results are summarized in Table 3.11. The agreement between the two data sets is generally quite good.

3.3 Oil In Marine Organisms

3.3.1 Mya truncata

Mya samples were analyzed from each of the 7 meter tissue plots in Bays 11, 9 and 7. Following UV/F analyses the extracts from each bay were pooled and one combined sample was analyzed by GC^2 and GC^2/MS; to determine compositional data.

3.3.1.1 Bay 11

3.3.1.1a Oil Concentrations by UV/F. Levels of UV/F-determined petroleum in the Bay 11 Mya samples ranged from <1.0 µg/g to 10.6 µg/g (dry weight basis). The concentrations, summarized in Figure 3.31, 4.0 (1.7, 9.7) µg/g are similar to those reported on the September 1982 samples, 4.7 (4.0, 5.7) µg/g although the distributions are more patchy in 1983.

3.3.1.1b Oil Composition by GC^2. The composition of saturated hydrocarbon fraction in Bay 11 Mya is shown by the GC^2 trace in Figure 3.32a. The three major features of the GC^2 trace are:

1. The significant quantity of UCM material indicative of weathered petroleum,
2. The terrigenous n-alkane content indicating that the animals contained sediment material,
3. The prominence of the isoprenoid hydrocarbons which indicate the oil in the animals was biodegraded.

Note that the GC^2 trace was expanded vertically to give the Figure 3.32A illustration.

The C_{18}/Phy ratio is 1.0 in this composite sample. This suggests that the animals are still acquiring oil from the Bay 11 system because in previous years this ratio

TABLE 3.11. QC/QA ANALYSES: COMPARISON OF RESULTS IN 1982 FIELD SAMPLES

	Oil Concentrations by UV/F (µg/g)		Phytane (µg/g)		Oil Concentration by Phytane Conversion (µg/g)		Pris/Phy		C_{18}/Phy	
	a	b	a	b	a	b	a	b	a	b
Bay 11 Tissue Plot No. 10 (B3187)	66	84	.41	.60	64	94	.87	1.3	.91	1.3
Bay 11 Tissue Plot No. 5 (B3037)	49	32	.06	.04	9.4	6.2	1.4	1.3	1.2	1.3
Bay 7 Tissue Plot	2.2	2.1	.003	.005	0.5	0.8	—	10	5.2	30

a = 1983 analyses (ERCO)
b = 1984 analyses (BATTELLE)

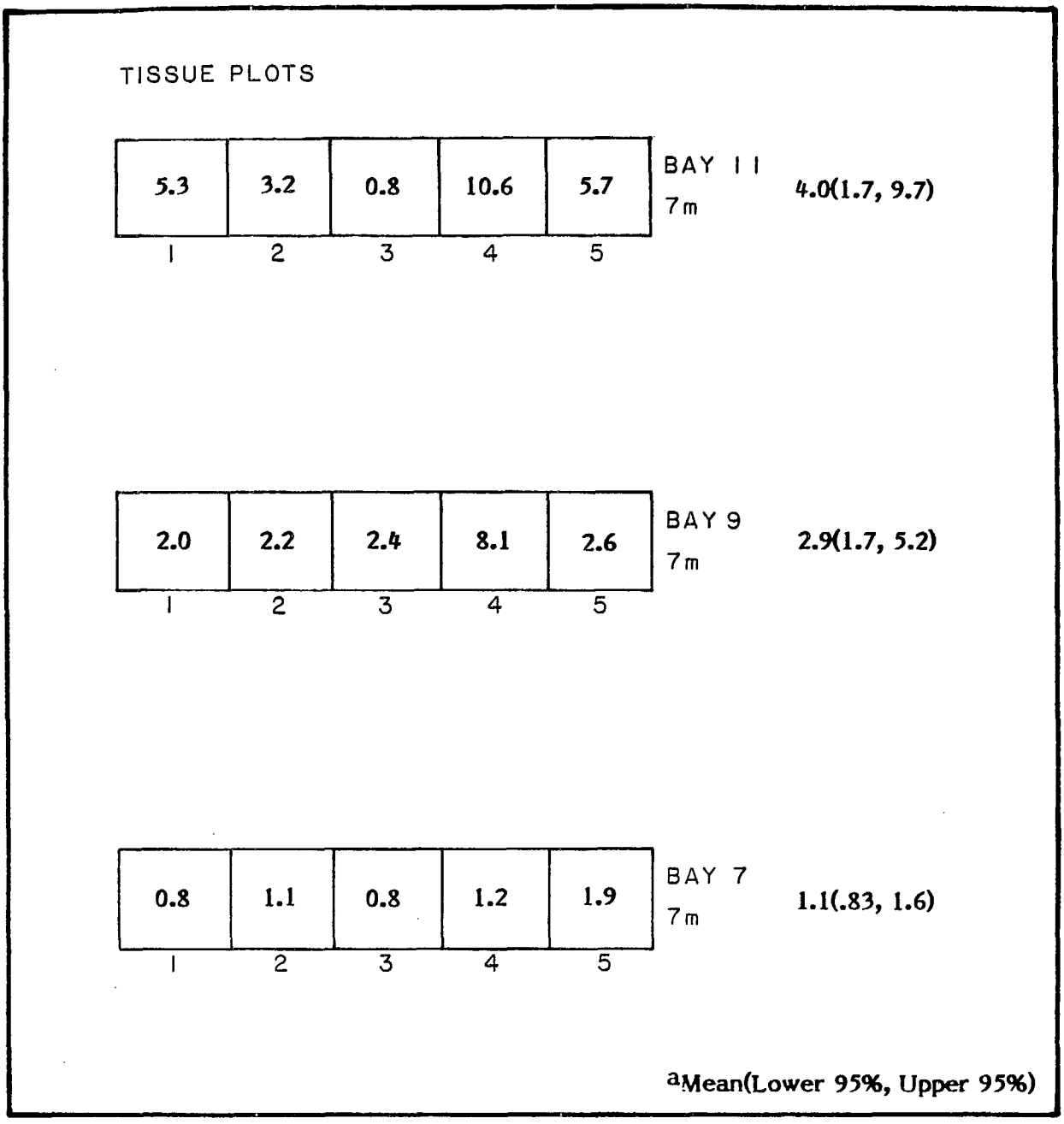


FIGURE 3.31. SUMMARY OF OIL CONCENTRATIONS IN Mya truncata, by UV/F, (µg/g dry wt.).

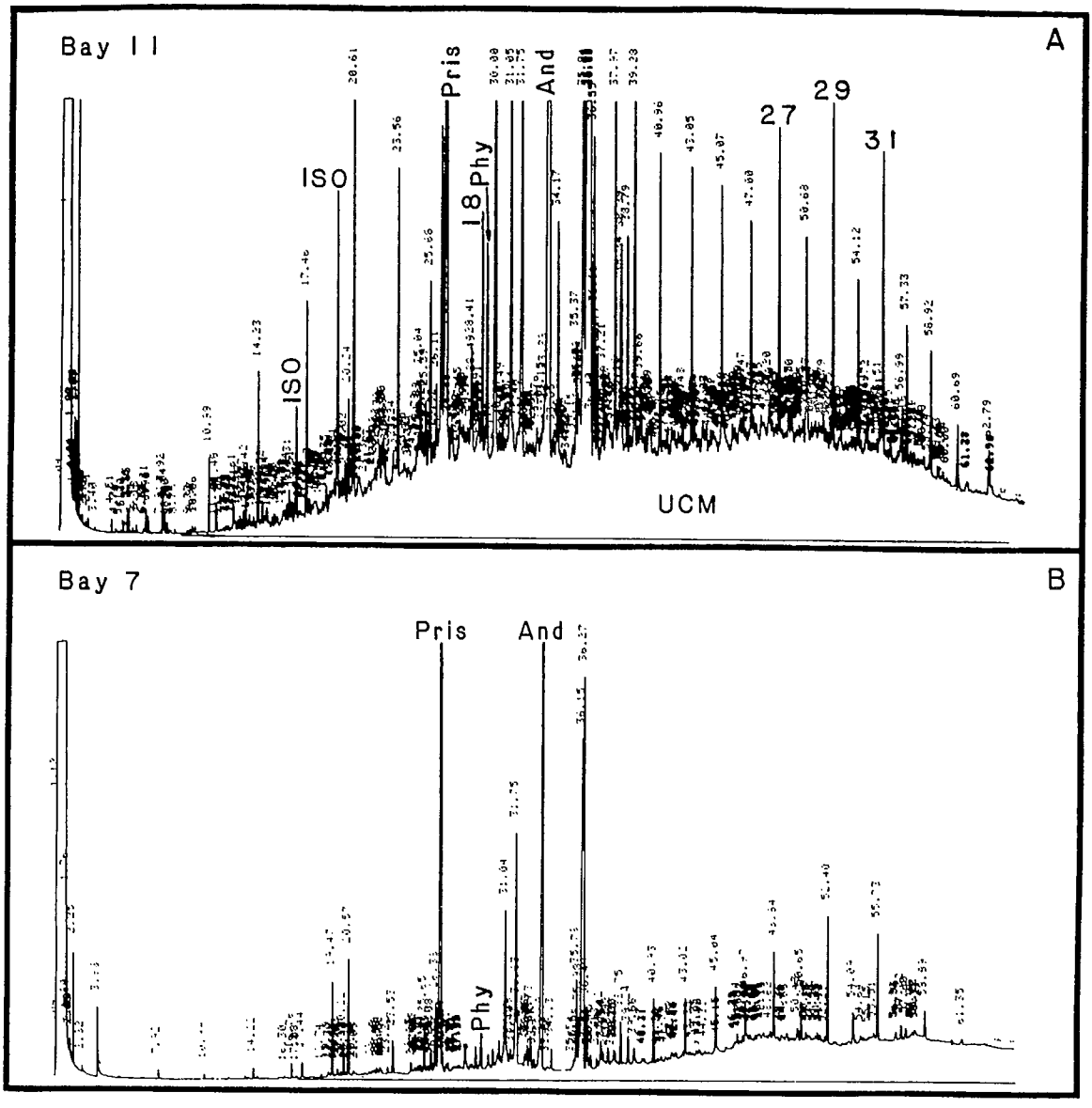


FIGURE 3.32. Mya truncata SATURATED HYDROCARBON GC^2 DETERMINATIONS.

had decreased to values much less than 1.0. The PRIS/Phy ratio in the animals equals ~14 suggesting that the marine biogenic material is quantitatively more important than the petrogenic input, a fact borne out by the biogenic character of the GC^2 trace in Figure 3.32a. Significant quantities of UCM material confirm the petroleum residues.

As a confirmatory step in the UV/F determinations, the combined f_2 fractions from all five samples was analyzed by UV/F. The resultant value of 7.5 μg/g is close to the arithmetic mean of the five separate plots (5.2 μg/g).

3.3.1.1c Aromatic Hydrocarbon Composition by GC^2/MS. The composite aromatic hydrocarbon fraction of this sample contained only very low quantitites of petroleum aromatics (Figure 3.33). Alkylated naphthalenes were present at the 1-5 ng/g level, down from the 10-15 ng/g levels observed in 1982. The alkylated phenanthrenes and dibenzothiophenes which were the dominant components in the 1982 animals are present only in trace levels 0.5 to 1.0 ng/g in the 1983 field samples. The alkylated naphthalenes are now dominating the aromatic composition albeit at very low levels (2-5 ng/g). Comparable levels in the summer of 1982 were 1-15 ng/g of individual aromatic compounds.

3.3.1.2 Bay 9

3.3.1.2a Oil Concentrations by UV/F. Mya samples from Bay 9 contain 2.9 (1.7, 5.2) μg/g of petroleum by UV/F (Figure 3.31). These concentrations are higher than those reported for the 1982 field samples at which time levels were near or at background levels 0.81 (.52, 1.3) μg/g. Confirmatory UV/F analysis of a combined f_2 fraction yielded a value of 3.3. μg/g very close to the mean of the values determined on unfractionated extracts.

3.3.1.2b Oil Composition by GC^2. GC^2 analysis of the combined sample yielded no definitive petrogenic component. A biogenic assemblage dominated with a PRIS/Phy value >50 and absolute phytane levels <0.001 μg/g.

3.3.1.2c Aromatic Hydrocarbon Composition by GC^2/MS. GC^2/MS analysis of the Bay 9 Mya sample yielded no detectable aromatic hydrocarbons (i.e. < 1 ng/g). This represents a tenfold decrease in indentifyable aromatics as the 1982 values were in the 2-10 ng/g range.

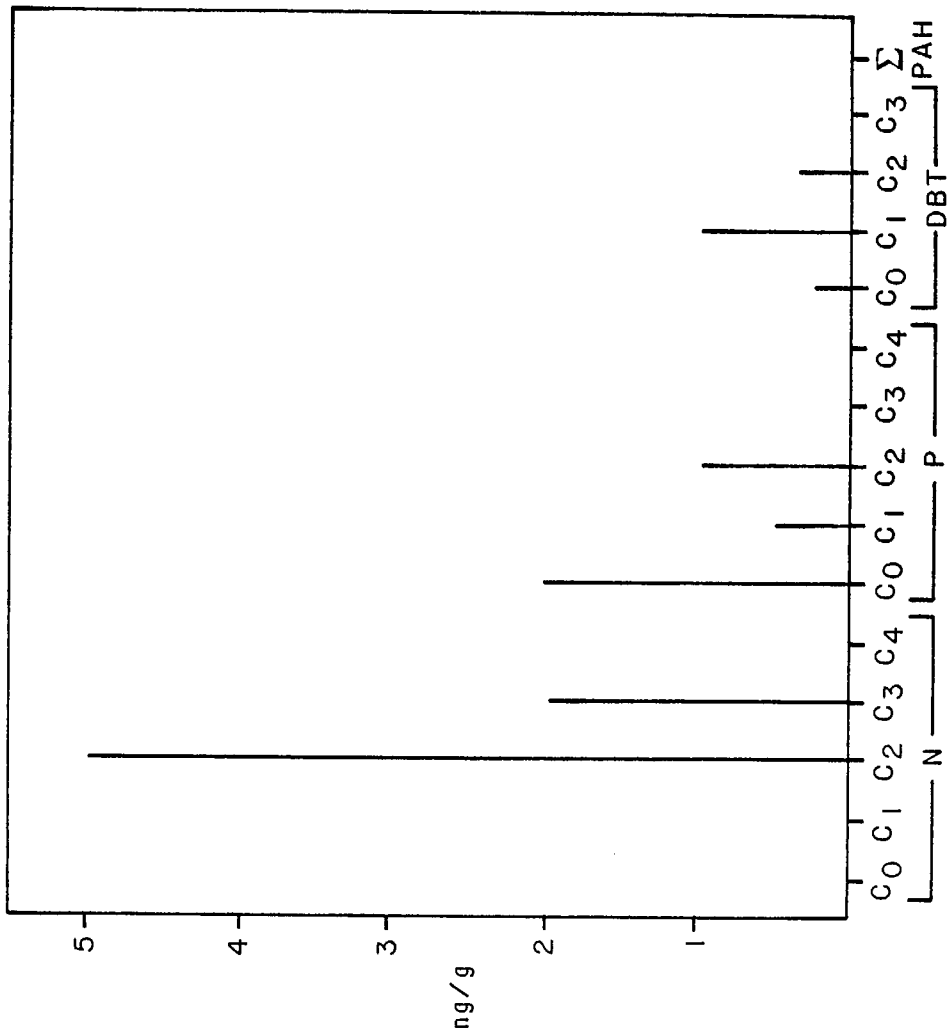


FIGURE 3.33. Mya AROMATIC PROFILES BY GC^2/MS (BAY 11).

3.3.1.3 Bay 7

3.3.1.3a Oil Concentration by UV/F. UV/F determined levels in Mya from Bay 7 (Figure 3.31) were 1.1 (.83, 1.6) µg/g which represents values near the detection limit (0.8 µg/g) and essentially containing only the smallest traces of a 355 nm shoulder on the UV/F trace. The combined f_2 UV/F value 1.1 µg/g was identical to the mean of the individual samples.

3.3.1.3b Oil Composition by GC^2. The saturated hydrocarbon GC^2 trace exhibits a nearly petroleum-free composition (Figure 3.32B) except for a low quantity of UCM material and detectable phytane levels (~.002 µg/g).

3.3.1.3c Aromatic Hydrocarbon Composition by GC^2/MS. Bay 7 Mya samples contained only trace levels 1-2 ng/g of alkylated naphthalenes and no phenanthrene or DBT compounds. When sampled in 1982, the comparable values were 2-8 ng/g.

3.3.2 Serripes groenlandicus

Samples of Serripes were collected and processed in a manner indentical to that used for Mya (see Section 3.3.1)

3.3.2.1 Bay 11

3.3.2.1a Oil Concentrations by UV/F. The concentration summary of the Bay 11 animals is presented in Figure 3.34 and the UV/F trace of the combined f_2 fractions shown in Figure 3.35. The concentrations in the tissue plots 10.9 (7.0, 17.0) µg/g is verified by the combined f_2 result, 9.1 µg/g. Oil levels in Bay 11 Serripes when previously sampled in 1982 were 5.2 (4.1, 6.4) µg/g. Thus the values in Serripes have increased by a factor of two on the average.

3.3.2.1b Oil Composition by GC^2. The GC^2 trace shown in Figure 3.36 exhibits low levels of petrogenic alkanes in the n-C_{20} to n-C_{30} range, a significant quantity of UCM material and the presence of .07 µg phytane, the latter of which converts to 11.2 µg/g of petroleum. Thus the GC^2 results confirm the levels of oil determined by UV/F and indicate that the oil present is biodegraded in the n-C_{10} to n-C_{20} range with petrogenic alkanes still present in the samples.

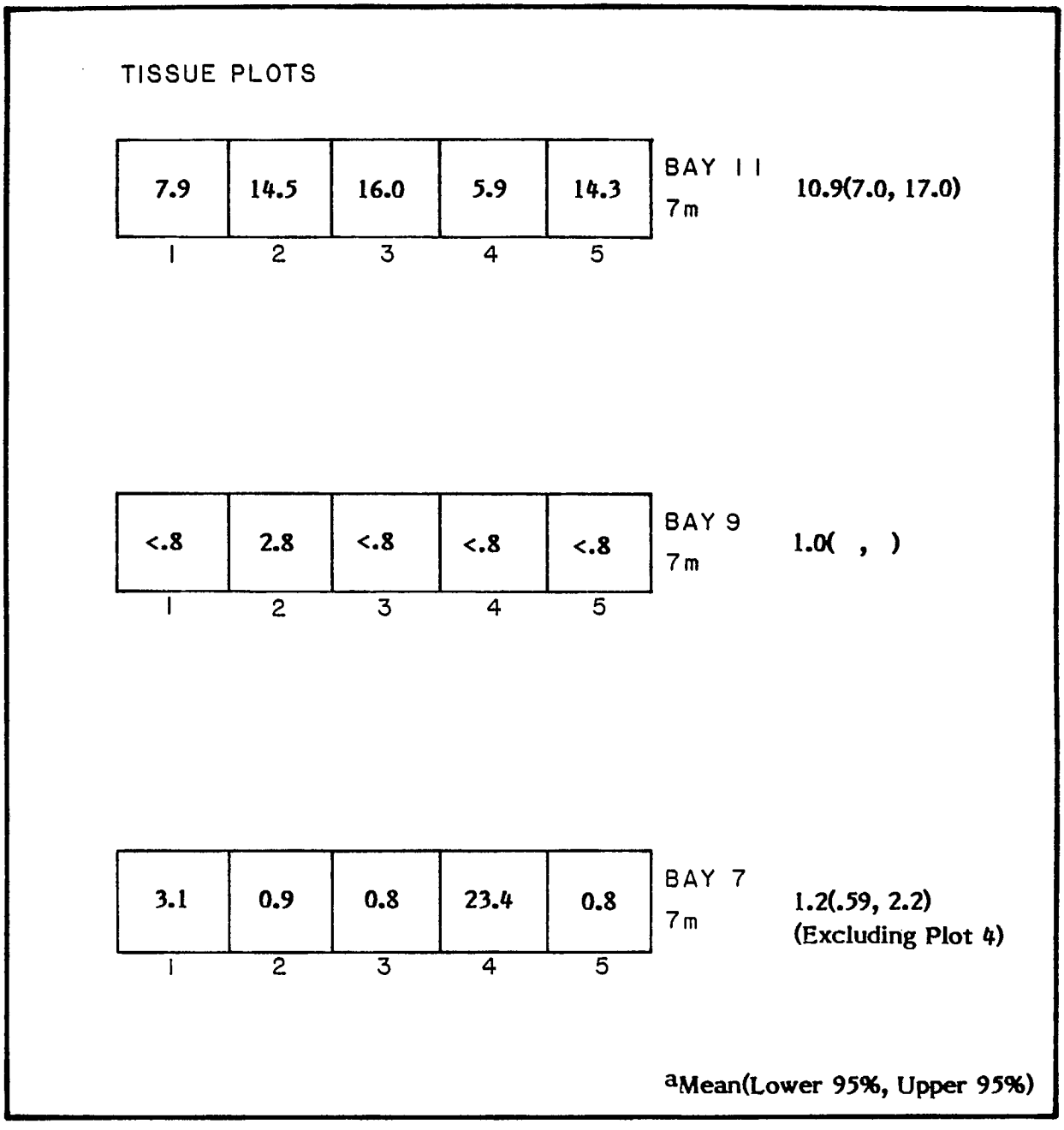


FIGURE 3.34. SUMMARY OF OIL CONCENTRATIONS IN Serripes groenlandicus, UV/F, (µg/g dry wt.).

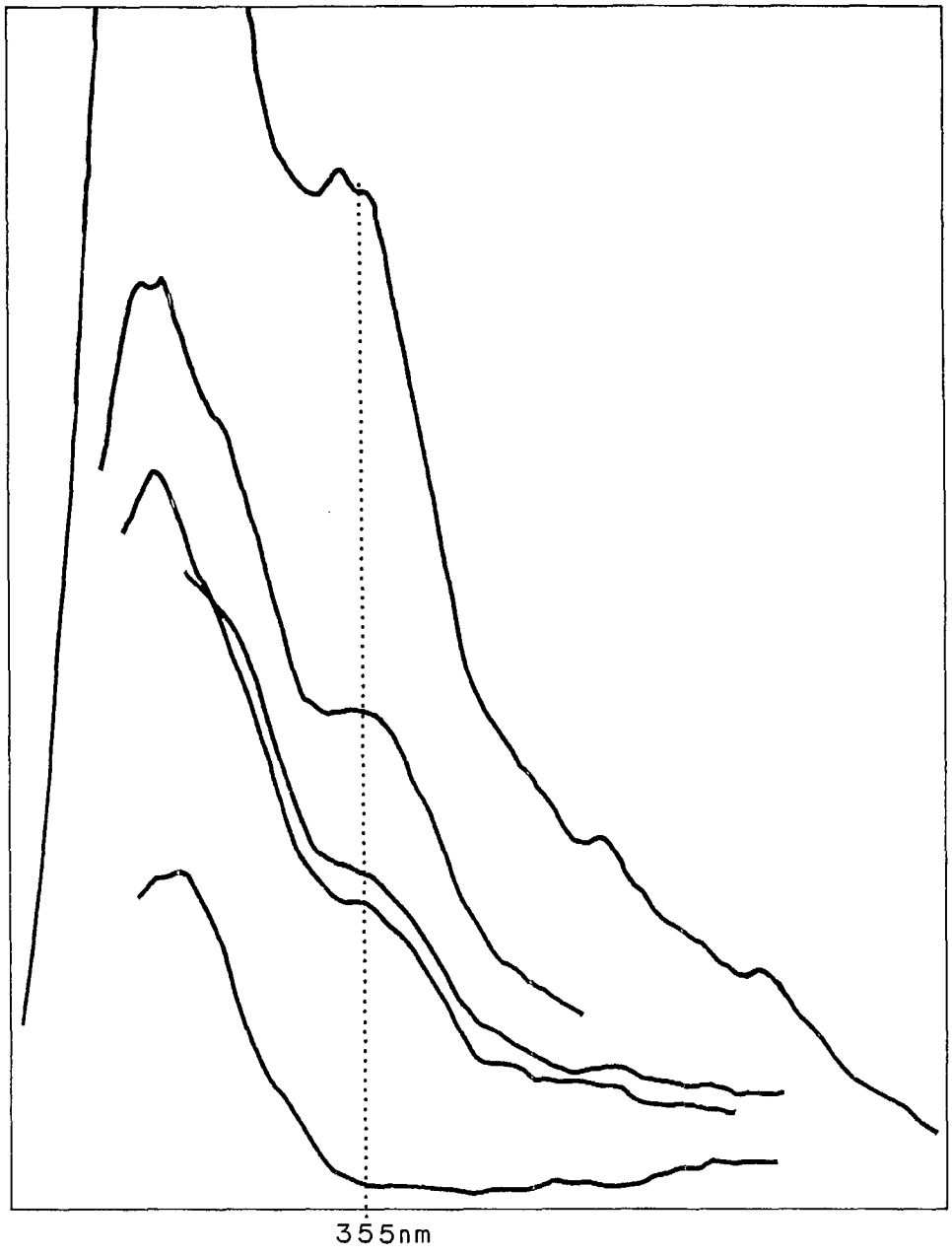


FIGURE 3.35. UV/F SPECTRA OF Serripes SAMPLE EXTRACT FROM BAY 11 COMBINED F_2 FRACTION.

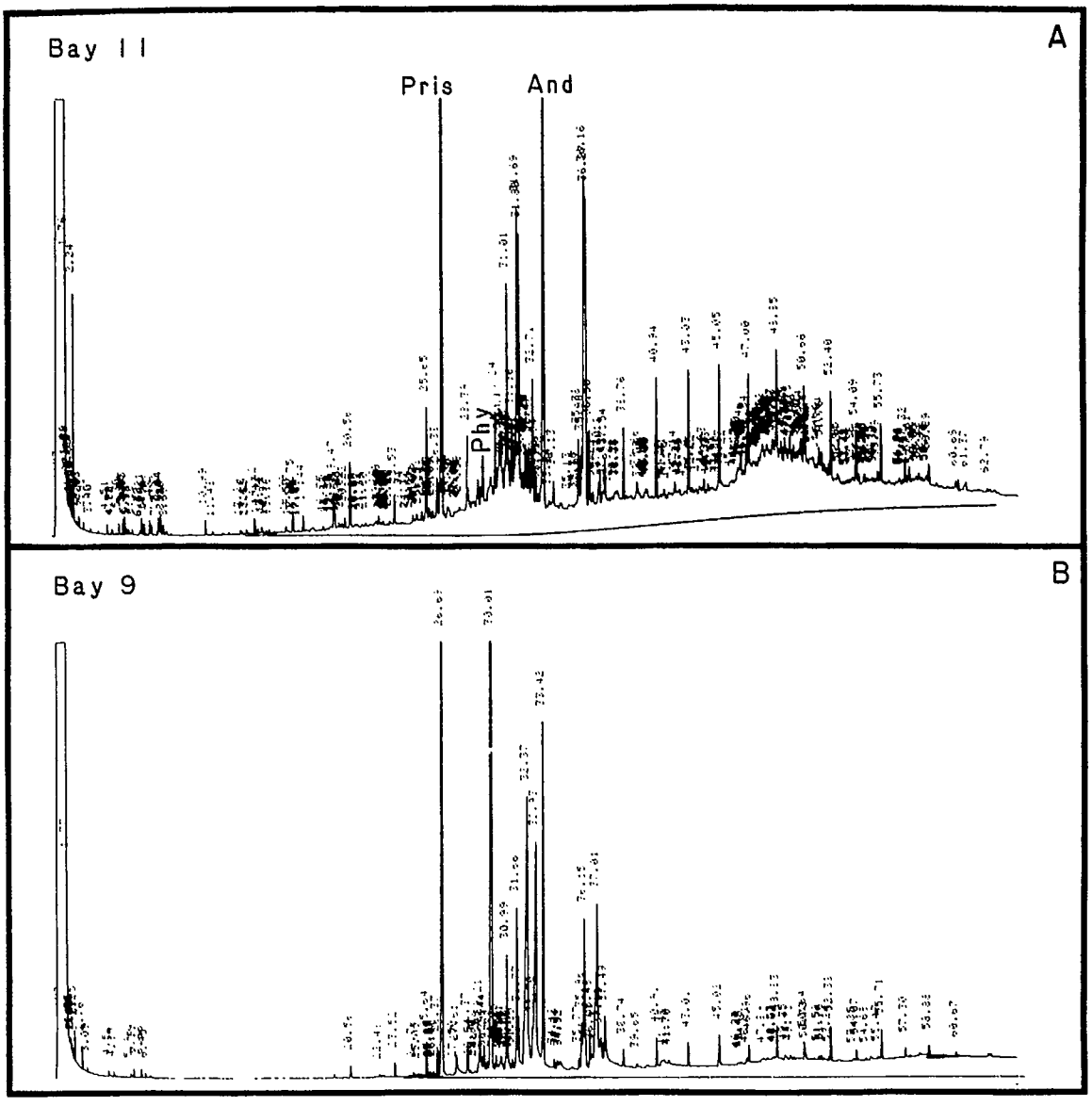


FIGURE 3.36. Serripes SATURATED HYDROCARBON GC^2 DETERMINATIONS.

3.3.2.1c Aromatic Hydrocarbon Composition by GC^2/MS. Analysis of the composite Serripes sample by GC^2/MS, detected trace quantities of alkylated naphthalenes (3 ng/g) and phenanthrenes (2 ng/g) with no DBT compounds detected. This represents a drastic decrease from the 10-100 ng/g values determined in 1982 (Boehm 1983a).

3.3.2.2 Bay 9

3.3.2.2a Oil Concentrations by UV/F. One of the Bay 9 Serripes UV/F spectra is shown in Figure 3.37. These values if quantified blindly would indicate the presence of large quantitites of oil in these animals and indeed the presence of oil is suggested by the UV/F traces (e.g., Figure 3.37). However, when the extract was fractionated and the f_2 was rerun by UV/F, the 355 nm peak was removed from the sample. We suspect that a polar, non-petroleum interference having a spectral maximum at ~380 nm contributed to the spurious 355 nm "oil peak" in the unfractionated extracts. Essentially, oil was detected in only one sample (Plot 2). The actual mean value which should be at 2.8 µg/g.

3.3.2.2b Oil Composition by GC^2. The Bay 9 Serripes composite gave a GC^2 saturated hydrocarbon trace as shown in Figure 3.36B. No detectable petroleum is seen in the sample. Only biogenic components were detected, confirming the absence of oil in Bay 9 Serripes.

3.3.2.2c Aromatic Hydrocarbons by GC^2/MS. No petroleum aromatics were detected in the Bay 9 Serripes composite.

3.3.2.3 Bay 7

3.3.2.3a Oil Concentrations by UV/F. The summary of the Bay 7 Serripes oil concentrations (Figure 3.34) shows values ranging from <0.8 µg/g to 23.4. We suspect that as in the Bay 9 samples the 23.4 value may be a spurious result, due to the spectral interference identical for that in Bay 9 (Figure 3.37B). However, it is interesting to note that this Serripes oil value coincided with the highest sediment oil value of 12 ppm at tissue plot 4 in Bay 7. The mean of the other four samples is 1.2 µg/g which is lower than the 2.2 µg/g value reported on the 1982 samples.

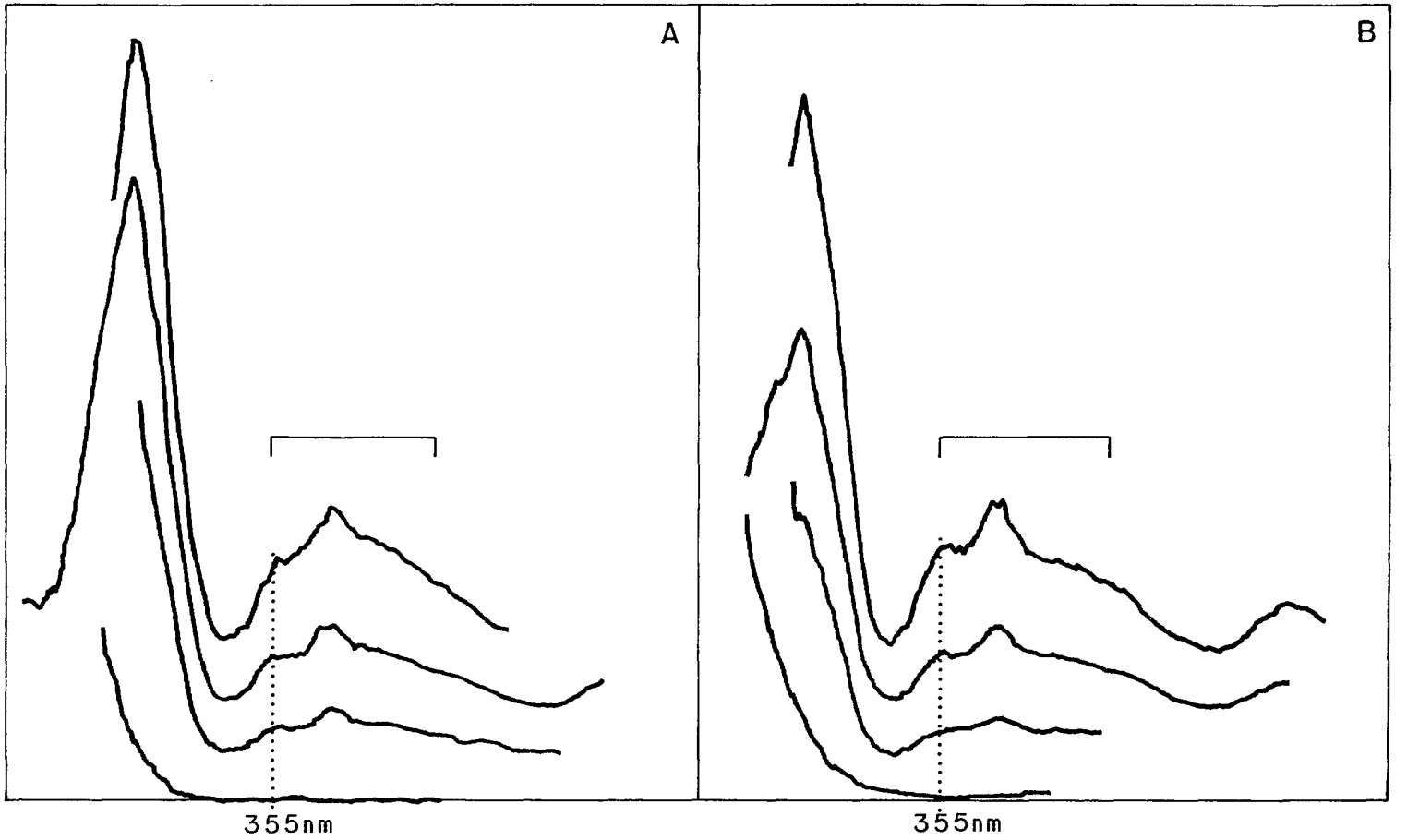


FIGURE 3.37. Serripes UV/F SPECTRA FROM BAYS 9(A) and 7(B) SHOWING NON-PETROLEUM SPECTRAL INTERFERENCE WHICH WAS ELIMINATED BY COLUMN CHROMATOGRAPHY.

3.3.2.3b Oil Composition by GC^2. The Bay 7 GC^2 trace confirmed the absence of oil in these samples. Only biogenic material was detected, the hydrocarbon assemblage being dominated largely by pristane.

3.3.2.3c Aromatic Hydrocarbon Composition by GC^2/MS. The Bay 7 Serripes sample contained no detectable petroleum aromatics.

3.3.3 Macoma calcarea

Samples were collected and processed as were Mya (Section 3.3.1).

3.3.3.1 Bay 11

3.3.3.1a Oil Concentrations by UV/F. The Bay 11 Macoma samples exhibited high concentrations of oil (Figure 3.38). The presence of oil was clearly discernable from the UV/F spectra (Figure 3.39). The concentrations in Bay 11, 63.8 (44.0, 92.7) µg/g are nearly identical to those determined from the 1982 samples 60.0 (39.0, 92.0) µg/g.

3.3.3.1b Oil Composition by GC^2. Moderate quantities of heavily weathered oil were detected in the combined Macoma samples including ~0.6 µg/g phytane (=94 µg/g oil by GC^2) and a significant amount of UCM material (Figure 3.40). The isoprenoids pristane and phytane are prominent confirming the highly biodegraded nature of the oil residues. This composition is similar to that observed in 1982. The smooth n-alkane (C_{20}-C_{30}) distribution further confirms the presence of considerable quantities of petroleum.

3.3.3.1c Aromatic Hydrocarbons Composition by GC^2/MS. Only the alkylated phenanthrene compounds were detected in the composite Macoma sample (Figure 3.41). The highest value of 12 ng/g is over an order of magnitude lower than the comparable values determined in 1982.

3.3.3.2 Bay 9

3.3.3.2a Oil Concentrations by UV/F. Macoma samples from Bay 9 contained 12.6 (6.7, 23.6) µg/g of petroleum by UV/F, values confirmed by the combined f_2, UV/F run. These values were lower than those previously observed in Bay 9 on the 1982 field samples: 25.0 (17.0, 36.0) µg/g, in spite of the higher apparent levels of oil seen in the 1983 surface sediments.

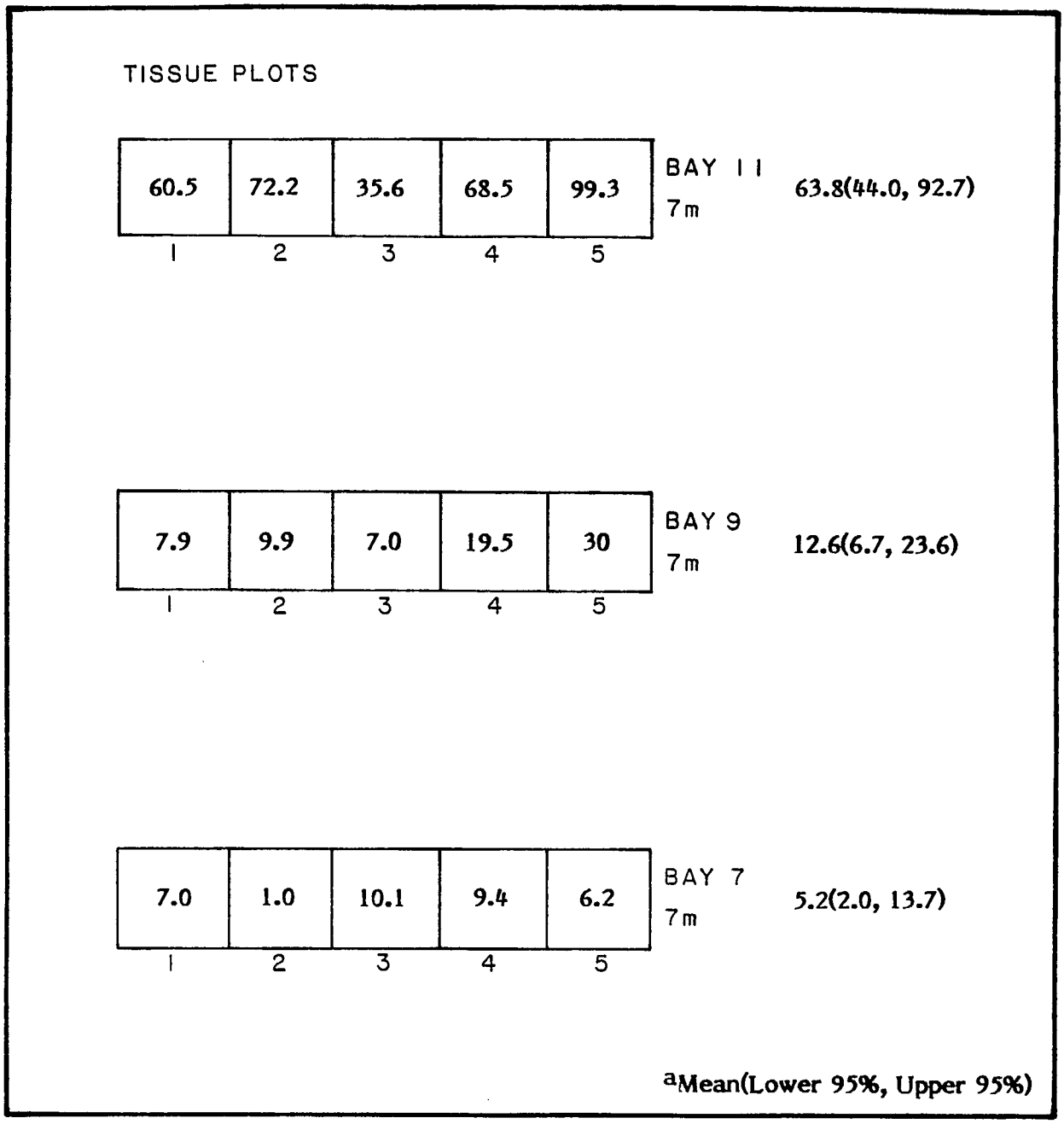


FIGURE 3.38. SUMMARY OF OIL CONCENTRATIONS IN Macoma calcarea, by UV/F, (µg/g dry wt.).

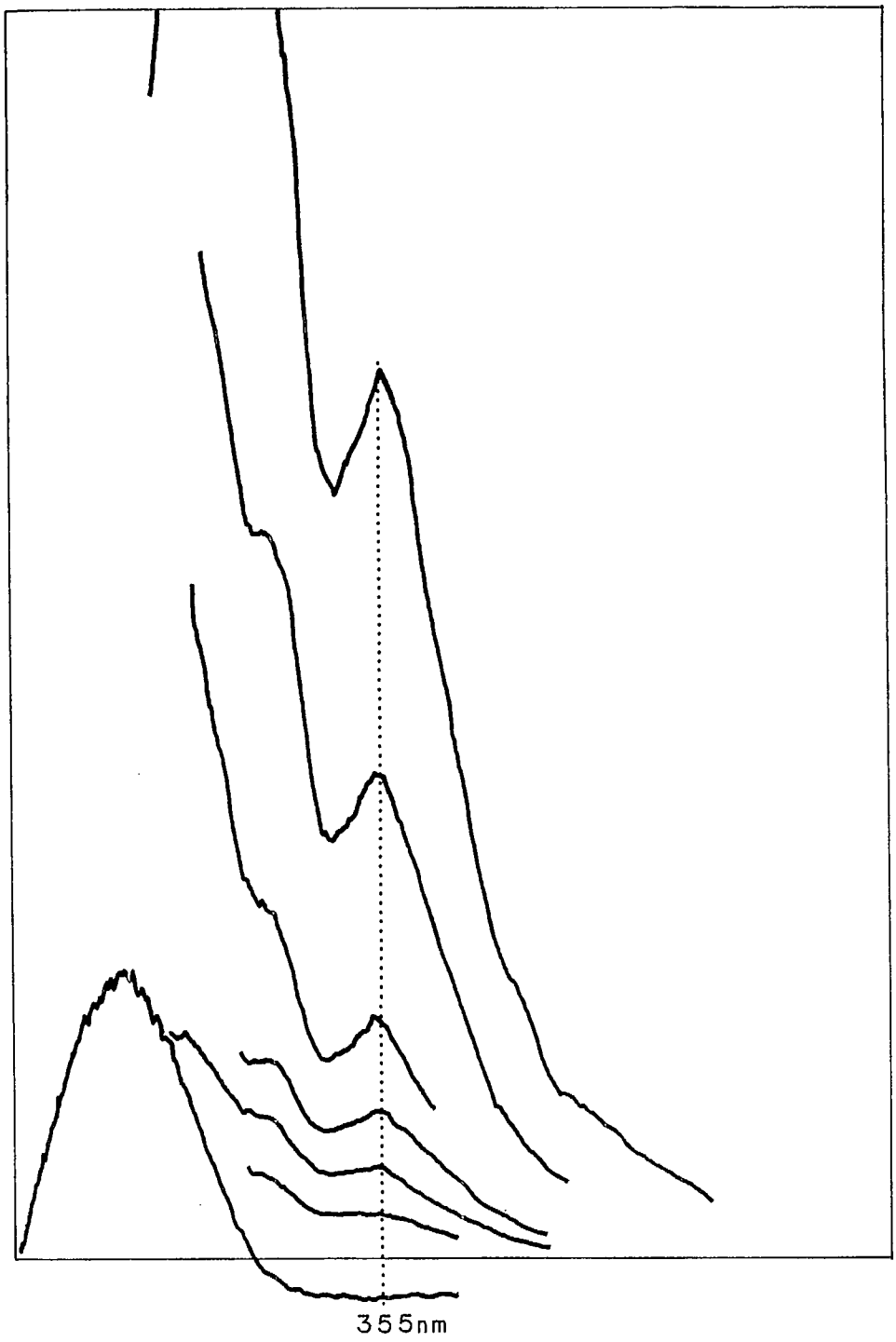


FIGURE 3.39. Macoma UV/F SPECTRA.

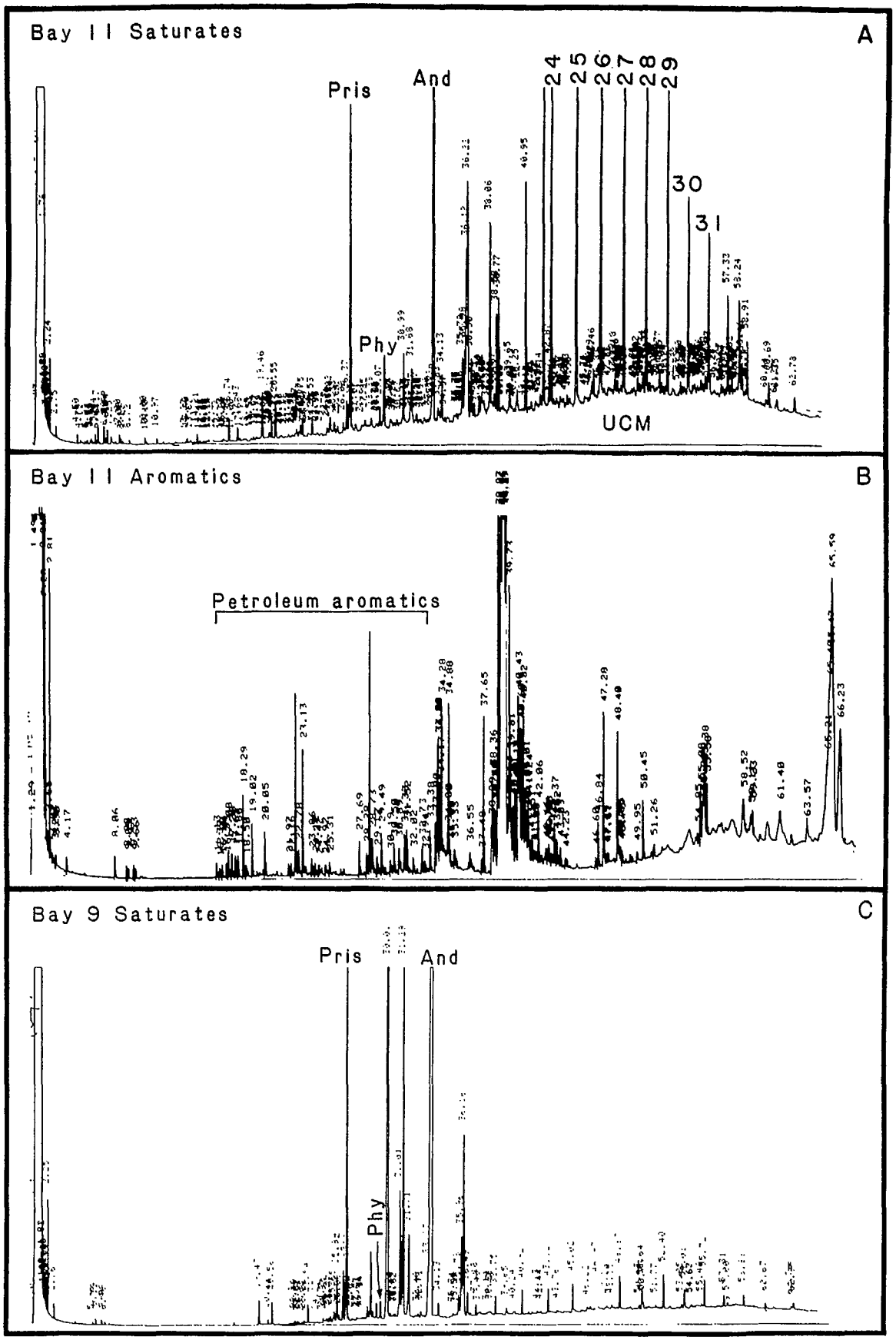


FIGURE 3.40. REPRESENTATIVE Macoma GC^2 DETERMINATIONS.

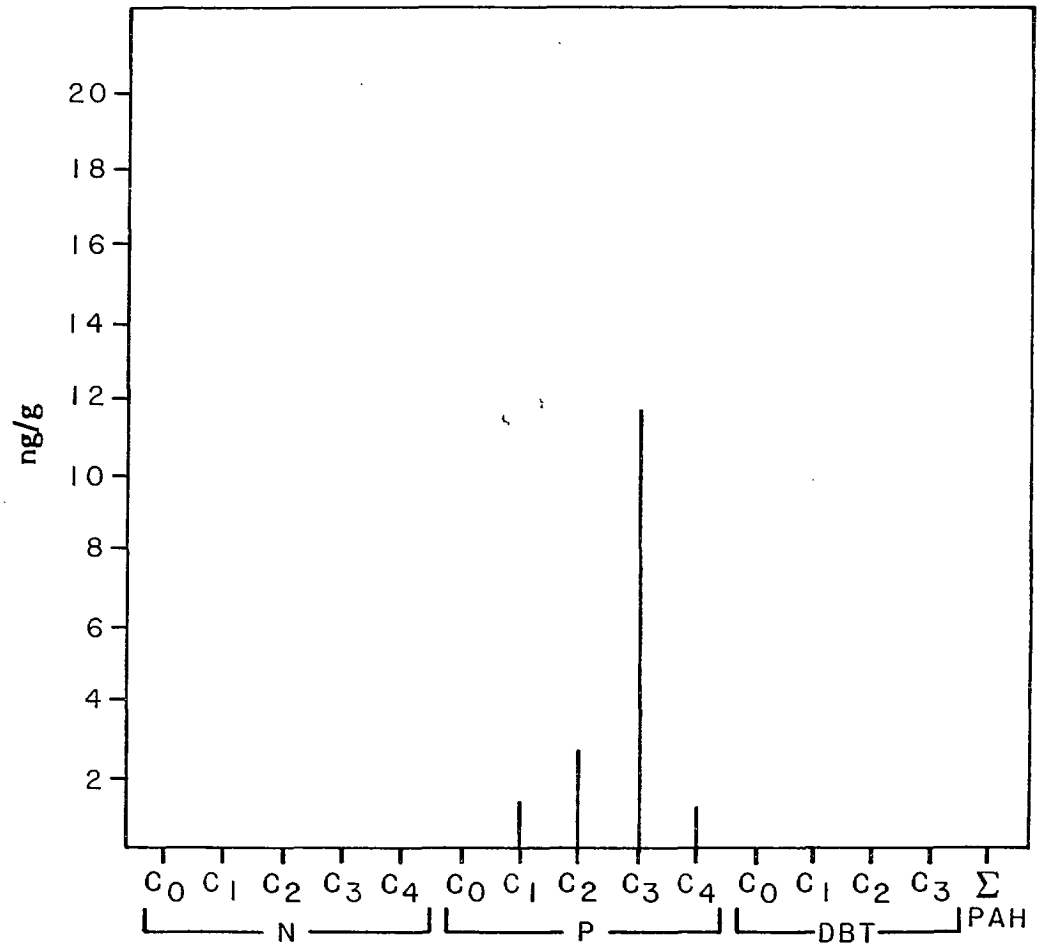


FIGURE 3.41. Macoma AROMATIC PROFILES BY GC^2/MS (BAY 11).

3.3.3.2b Oil Composition by GC^2. Levels of oil, lower than those observed in Bay 11, were seen in the combined Bay 9 sample. That oil is present is noted by the small quantity of UCM material and the presence of phytane (.02 µg/g) in the sample.

3.3.3.2c Aromatic Hydrocarbon Composition by GC^2/MS. Petroleum aromatics were detected in Macoma from Bay 9 in the 1-5 ng/g range with the phenanthrene most abundant. Alkylated phenanthrenes and DBT were detected at levels of up to 150 ng/g in 1982. The absence of these homologous series in the Macoma is unexpected and can not be adequately explained at present.

3.3.3.3 Bay 7

3.3.3.3a Oil Concentrations by UV/F. The Macoma samples from Bay 7 contained detectable quantities of oil in the 1.0 to 5 µg/g range. The combined f_2 UV/F analysis yielded an oil concentration value of 4.7 µg/g. The mean of the five tissue samples was 4.4 (3.7, 6.5) µg/g was higher than the 1.9 (1.6, 2.3) µg/g observed in 1982.

3.3.3.3b Oil Composition by GC^2. The GC^2 trace of the combined Bay 7 Macoma (Figure 3.42) sample did reveal the low level presence of UCM and phytane amidst a composition similar to sedimentary hydrocarbons. Biogenic material dominated although the phytane levels of .02 µg/g convert to an equivalent concentration of 2.9 µg/g.

3.3.3.3c Aromatic Hydrocarbon Composition by GC^2/MS. Petroleum aromatics in the 2-6 ng/g range were detected in the Bay 7 composite sample. Alkylated naphthalenes and phenanthrenes were the only compounds detected. Bay 7 animals contained 1-20 ng/g in 1982.

3.3.4 Astarte borealis

3.3.4.1 Bay 11

3.3.4.1a Oil Concentrations by UV/F. Concentrations of oil in Astarte (Figures 3.43 and 3.44) from 1983 were 15.2 (6.1, 38.4) µg/g. When last sampled in 1982, these samples averaged 37.0 (33.0, 38.0) µg/g which spanned the 1982 range as well. However, the lower 1983 mean values indicate that oil levels in Astarte are still decreasing.

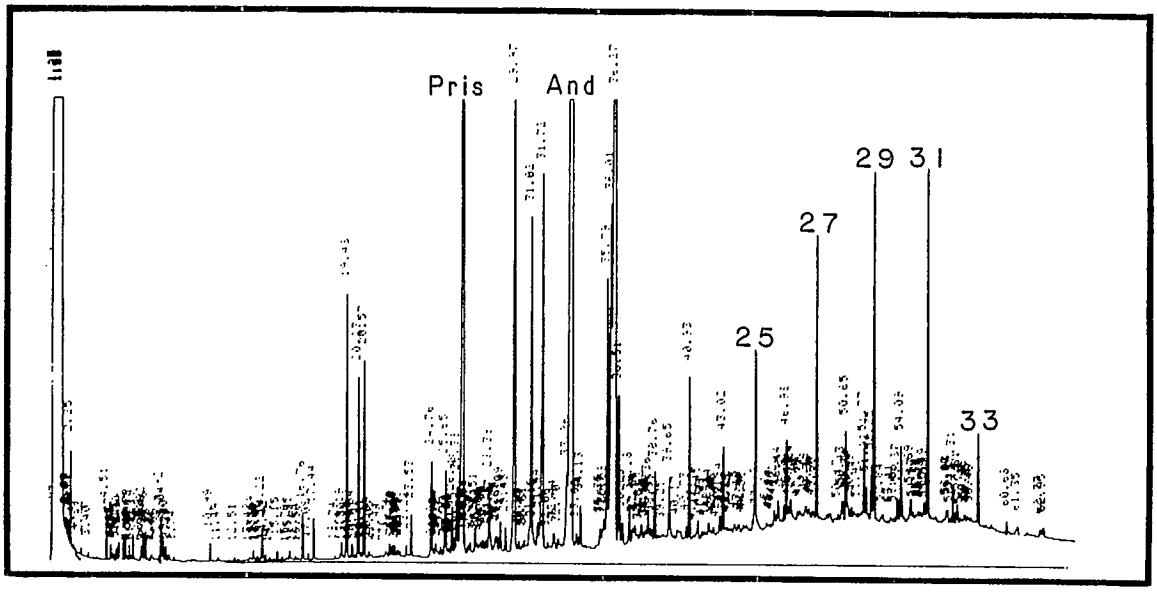


FIGURE 3.42. Macoma SATURATED HYDROCARBONS FROM BAY 7.

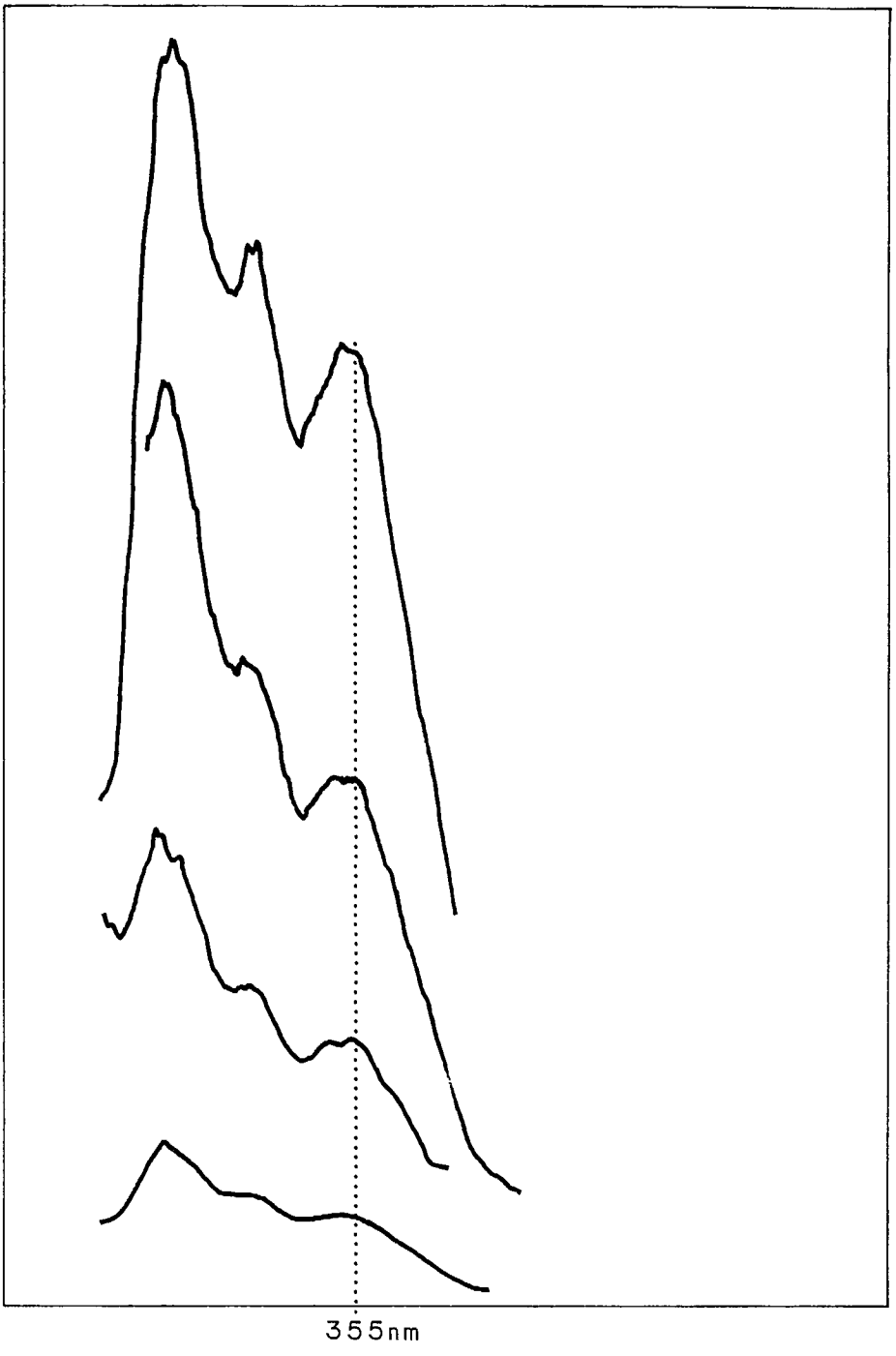


FIGURE 3.43. UV/F SPECTRA OF Astarte FROM BAY 11.

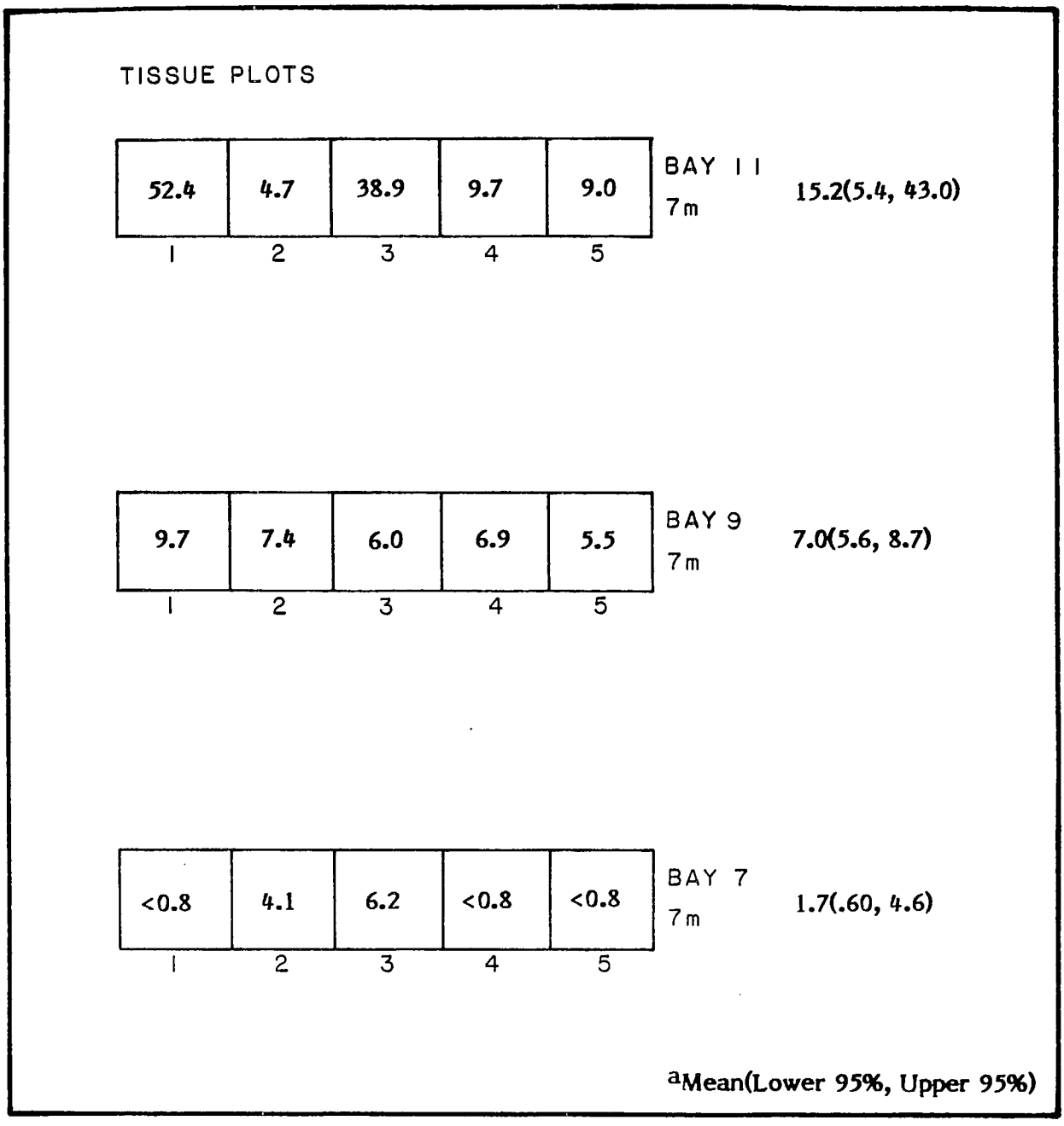


FIGURE 3.44. SUMMARY OF OIL CONCENTRATIONS IN Astarte borealis, by UV/F, (µg/g dry wt.).

3.3.4.1b Oil Composition by GC^2. GC^2 analysis of the Astarte composite revealed the same features characteristic of other low level samples: 1) a predominantly biogenic assemblage; 2) UCM material; 3) small quanties of phytane; 4) n-alkanes in the C_{20} to C_{30} range. Additionally, those Bay 11 (and other Astarte) contained a double UCM (see Figure 3.45) of unknown origin, but possibly resulting from biodegradation processes.

3.3.4.1c Aromatic Hydrocarbon Composition by GC^2/MS. Low levels of alkylated phenanthrene (1-3 ng/g) and dibenzpthiophenes (~1 ng/g) were detected in the 1983 field samples much lower than the 10-150 ng/g values observed in the 1982 field samples.

3.3.4.2 Bay 9

3.3.4.2a Oil Concentrations by UV/F. Concentrations of oil in Bay 9 Astarte (Figure 3.44) were 7.0 (5.6, 8.7) µg/g. When last sampled in 1982, the corresponding values were 19.0 (10.0, 40.0) µg/g. As in Bay 11, the Astarte values are continuing to decrease despite an input of oil to the sediments of both bays.

3.3.4.2b Oil Composition by GC^2. The Bay 9 Astarte chromatogram is shown in Figure 3.46. This GC^2 trace is enhanced in the vertical direction several times to illustrate several interesting features:

1. The double small unresolved areas of the chromatogram overlaying the larger more frequently encountered UCM.
2. The biogenic olefinic cluster at C_{18}-C_{19},
3. The n-alkane distribution from C_{20} to C_{30} characteristic of petrogenic paraffins,
4. The significant quantity of phytane (0.11 µg/g) equivalent to an 18.3 µg/g concentration of oil residues higher than that detected by UV/F.

3.3.4.2c Aromatic Hydrocarbon Composition by GC^2/MS. Alkylated phenanthrenes (C_1-C_3) were detected in the Astarte samples in the 5-10 ng/g range, lower by a factor of four than the levels seen in the previous, 1982, sampling.

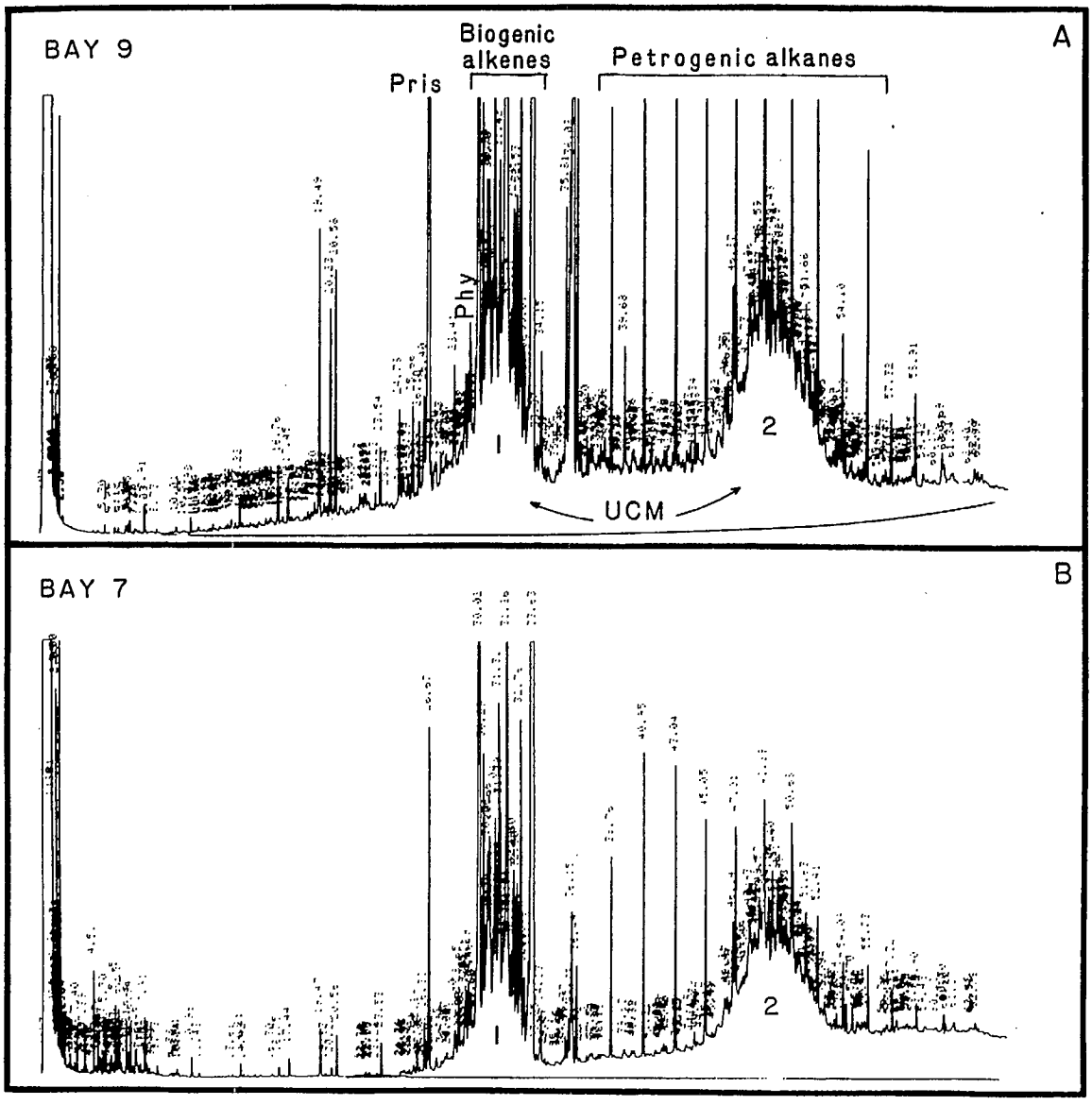


FIGURE 3.45. Astarte SATURATED HYDROCARBON GC^2 DETERMINATIONS.

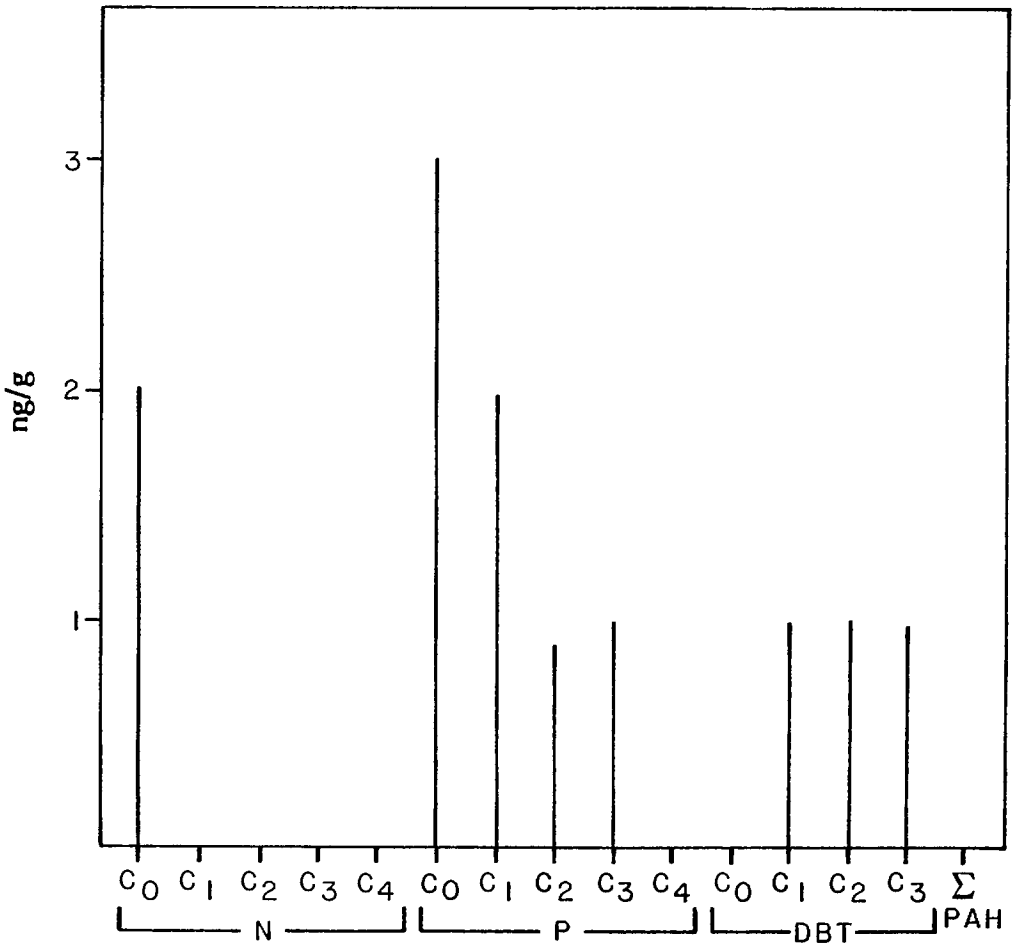


FIGURE 3.46. Astarte AROMATIC PROFILES BY GC^2/MS (BAY 11).

3.3.4.3 Bay 7

3.3.4.3a Oil Concentrations by UV/F. The Bay 7 Astarte oil concentrations determined by UV/F (Figure 3.44) were 1.7 (.60, 4.8) µg/g, less than the values detected in 1982, 6.8 (3.1, 14.8) µg/g. This decrease in oil levels parallels the decreases in Bays 11 and 9 for this species.

3.3.4.3b Oil Composition by GC^2. Traces of oil are seen in the Bay 7 Astarte GC^2 trace (Figure 3.45B). Note the double UCM, as was observed in Bay 9 and the residual n-alkane material in the mid-boiling range (C_{20}-C_{30}) in the chromatogram. These double UCM features may be sourced during the biodegradation of acquired oil residues in vivo although this is an untested hypothesis. This double UCM may also be an artifact resulting from an unusually complex array of biogenic hydrocarbons in these samples.

3.3.4.3c Aromatic Hydrocarbon Composition by GC^2/MS. Individual alkylated naphthalene (5-10 ng/g), phenanthrene (25 ng/g) and dibenzothiophene (10-15 ng/g) compounds were detected by GC^2/MS. No aromatics were previously detected in the 1982 sample set.

3.3.5 Strongylocentrotus droebachiensis (URCHINS)

3.3.5.1 Bay 11

3.3.5.1a Oil Concentrations by UV/F. When last sampled in September, 1982, level of oil in urchins were 67.0 (40.0, 113) µg/g. The current 1983 results show that higher levels are clearly present (Figure 3.47) and results are summarized in Figure 3.48. Concentrations are 103 (57.1, 187) µg/g, which are similar to levels observed in the spring of 1982.

A very important discrepency between the UV/F results obtained on the unfractionated extracts and that obtained on the combined f_2 fraction was noted. While the mean oil concentration demonstrated on the unfractionated extracts was 103 µg/g, the combined f_2 value was 6.1. The UV/F spectra for the unfractionated animals shows a clearly visable "oil peak" at 355 nm. This peak is much decreased in the f_2 fraction after column chromatography. (The internal standard is recovered.).

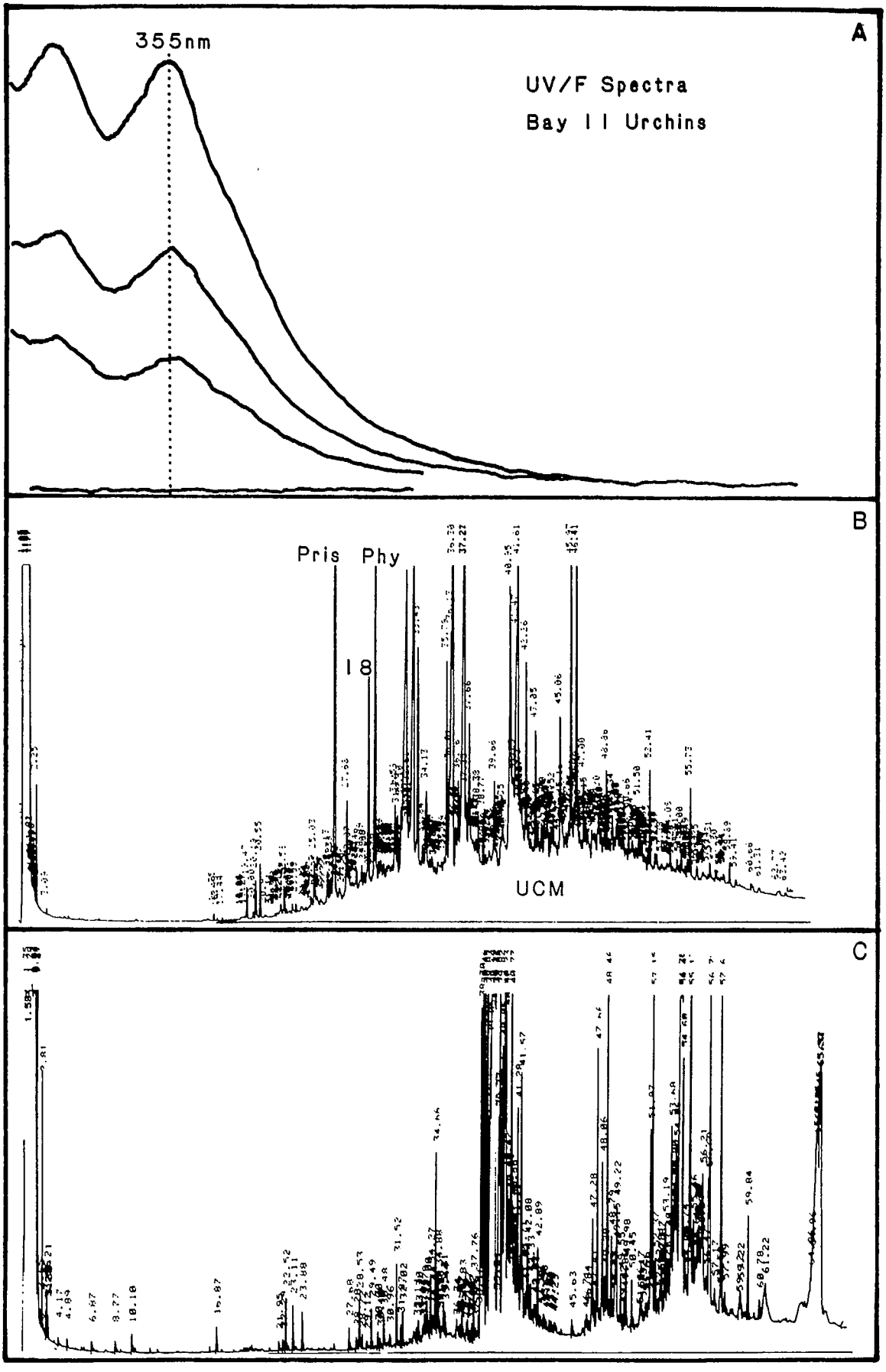


FIGURE 3.47. BAY 11 URCHIN RESULTS: A- UV/F; B- SATURATED HYDROCARBON GC^2; B- AROMATIC/UNSATURATED HYDROCARBON GC^2.

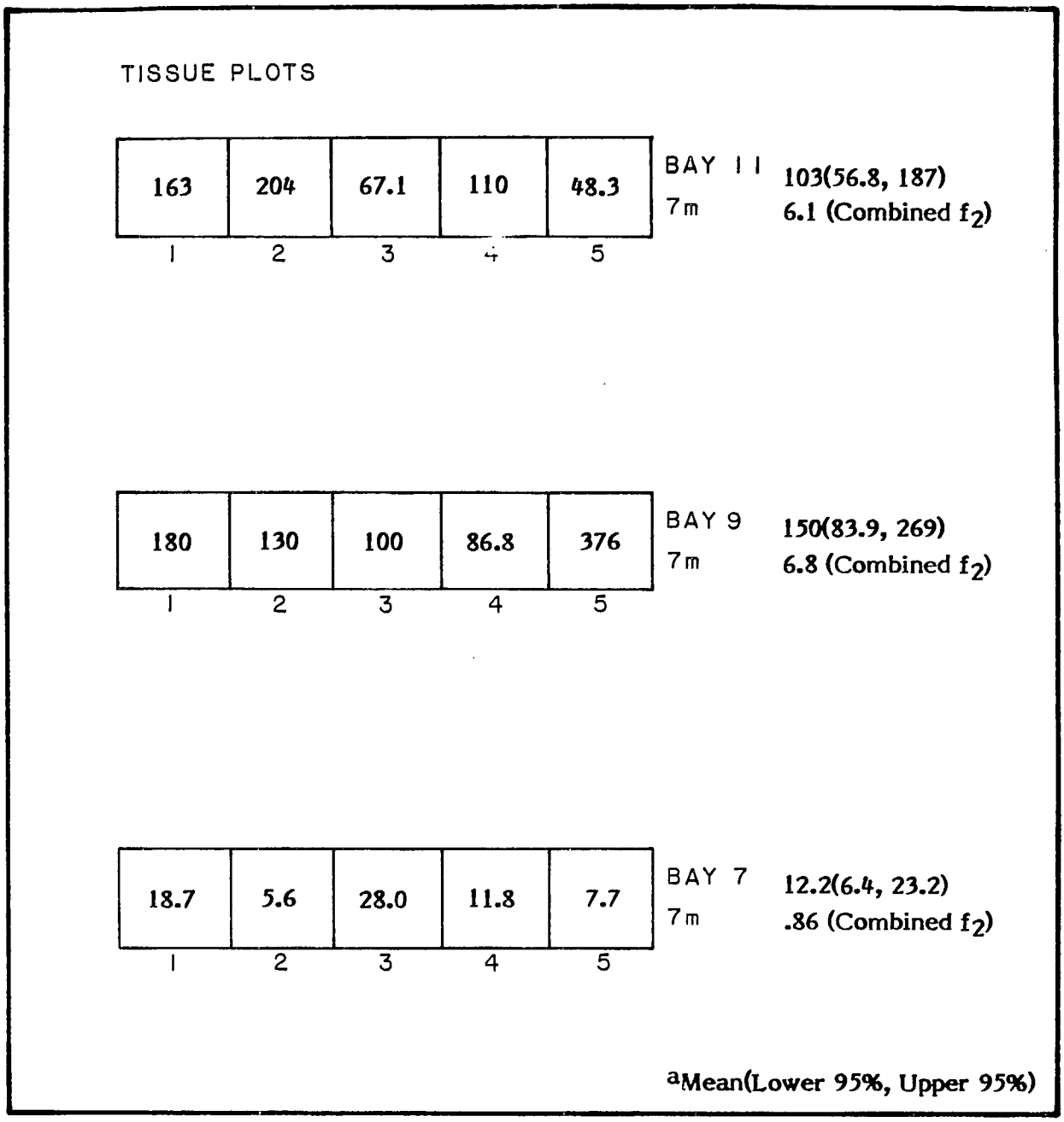


FIGURE 3.48. SUMMARY OF OIL CONCENTRATIONS IN Strongylocentrotus droebachiensis, by UV/F, (µg/g dry wt.).

3.3.5.1b Oil Composition by GC^2. Weathered oil residues are apparent in the GC^2 trace shown in Figure 3.47B, where petrogenic phytane, pristane and UCM are readily apparent. No prominent n-alkane distributions are observed in the C_{20} to C_{30} range for this species.

Aromatic hydrocarbon GC^2 traces (e.g. Figure 3.47C) indicate the low relative quantity of petroleum aromatics compared to biogenic olefins.

3.3.5.1c Aromatic Hydrocarbons by GC^2/MS. Large quantities of alkylated phenanthrenes were detected in the Bay 11 urchins. The values 10-190 ng/g are roughly equal to those detected on the 1982 samples. The composition, however, (Figure 3.49) is notably lacking in dibenzothiophene compounds.

3.3.5.2 Bay 9

3.3.5.1a Oil Concentrations by UV/F. UV/F determined oil concentrations on total extracts from Bay 9 were 150 (83.9, 269) µg/g. Inspite of the apparent unambiguous quantification of these extracts (Fig 3.50) the UV/F value of the combined f_2 fraction yielded a value of 6.8 µg/g. This is similar to the Bay 11 discrepancy. Note, however, that such comparisons were not made in previous years.

The comparable 1982 field sample result 46.0 (25.0, 86.0) µg/g is less than the 1983 values determined on the total contracts. Note that values as high as 760 µg/g were found in may, 1982 in Bay 9 urchins.

3.3.5.2b Oil Composition by GC^2. The GC^2 trace of the Bay 9 sample contained mainly biogenic compounds although a significant amount of UCM material was detected. The profile was similar in composition to that from Bay 11 (Figure 3.46) although of lesser concentration.

3.3.5.2c Aromatic Hydrocarbon Composition by GC^2/MS. The GC^2/MS analysis of the Bay 9 urchin's aromatic fraction failed to detect (>1 ng/g) any petroleum aromatics although significant quantities (15-150 ng/g) of four and five ringed aromatics were detected.

3.3.5.3 Bay 7

3.3.5.3a Oil Concentrations by UV/F. Although a significant discrepancy still exists between the UV/F total extract values, 12.2 (6:4, 23.2) µg/g and the UV/F of the

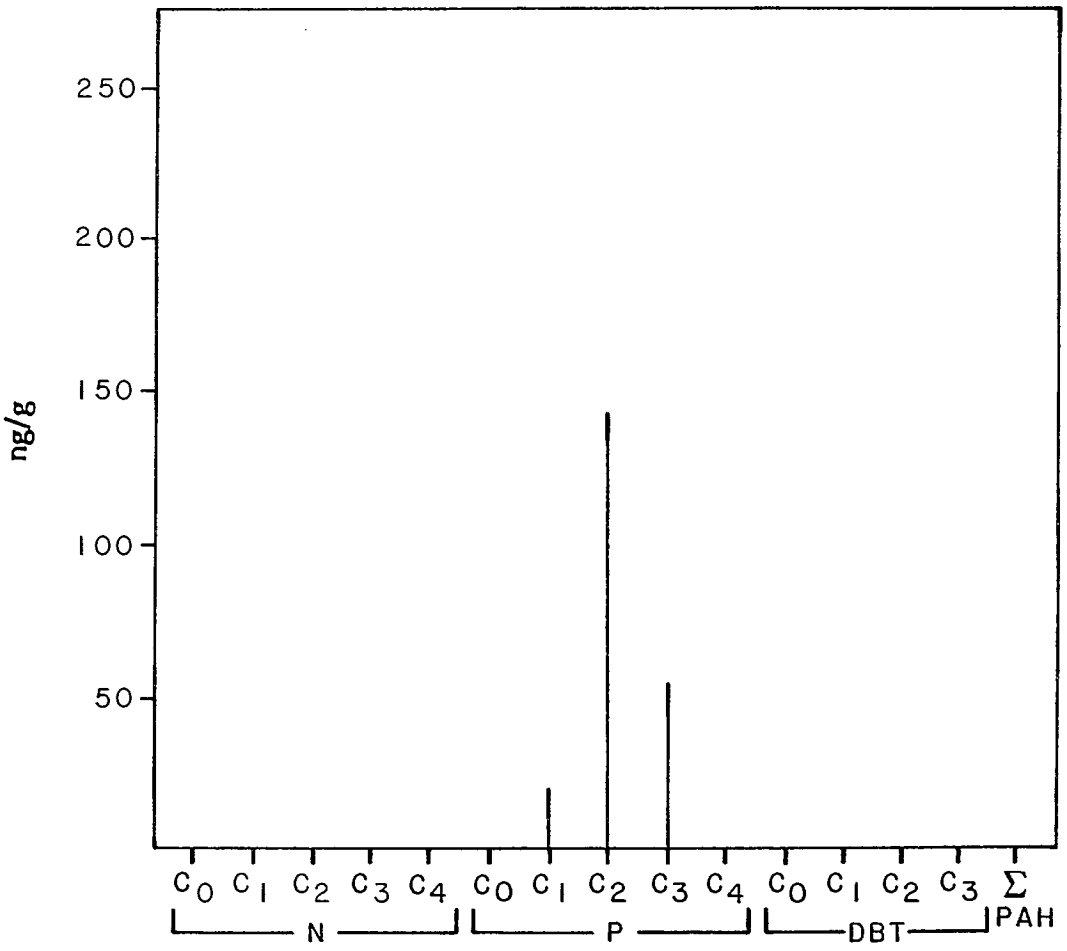


FIGURE 3.49. Strongylocentrotus AROMATIC PROFILES BY GC^2/MS (BAY 11).

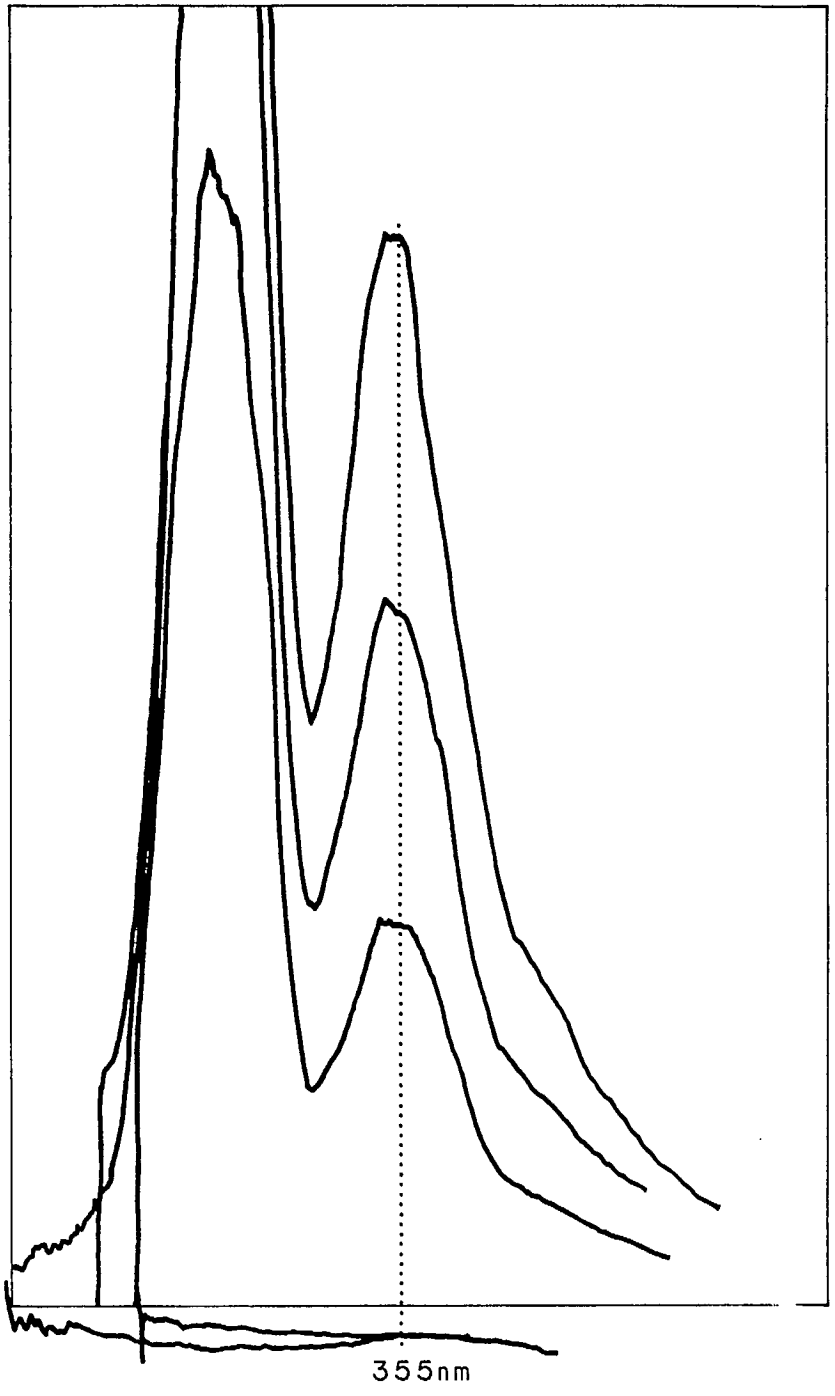


FIGURE 3.50. Strongylocentrotus UV/F SPECTRA, BAY 9.

fractionated extract (0.9 µg/g), the Bay 7 values are much lower than those from Bays 9 and 11. Last year's values were 4.6 (2.3, 9.2) µg/g.

3.3.5.3b Oil Composition by GC^2. Biogenic compounds dominated the saturated hydrocarbon GC^2 determination (Fig. 3.51) although petrogenic inputs are indicated by the presence of a UCM distribution and by small quantities of phytane.

3.3.5.3c Aromatic Hydrocarbon Composition by GC^2/MS. Small quantities 1-5 ng/g of C_0 and C_1 phenanthrene were detected in the composite sample. This finding is consistent with the GC^2 saturated composition which indicates that sediment material was present in the urchin tissues. C_0P and C_1P are common low level background components of sediments.

3.3.6 MILNE INLET ANIMALS

One composite sample of each species was obtained from the benthos of Milne Inlet and the western side (non-spill side) of Ragged Island. These animals were analyzed by UV/F, GC^2 and GC^2/MS.

UV/F results on the total extracts are as follows:

Mya	=	<0.8 µg/g
Sernpes	=	<0.8
Macoma	=	<0.8
Astarte	=	1.3
Str.	=	<0.8

GC^2 results detected only biogenic components, mainly pristane and no UCM material. Therefore, no petrogenic components were detected.

GC^2/MS results were as follows:

Mya	:	Phenanthrene detected at 1 ng/g
Serripes	:	none detected
Macoma	:	naphthalene = 2 ng/g
		phenanthrene = 4 ng/g
Astarte	:	naphthalene = 1 ng/g
		phenanthrene = 1 ng/g
Str.	:	phenanthrene = 1 ng/g

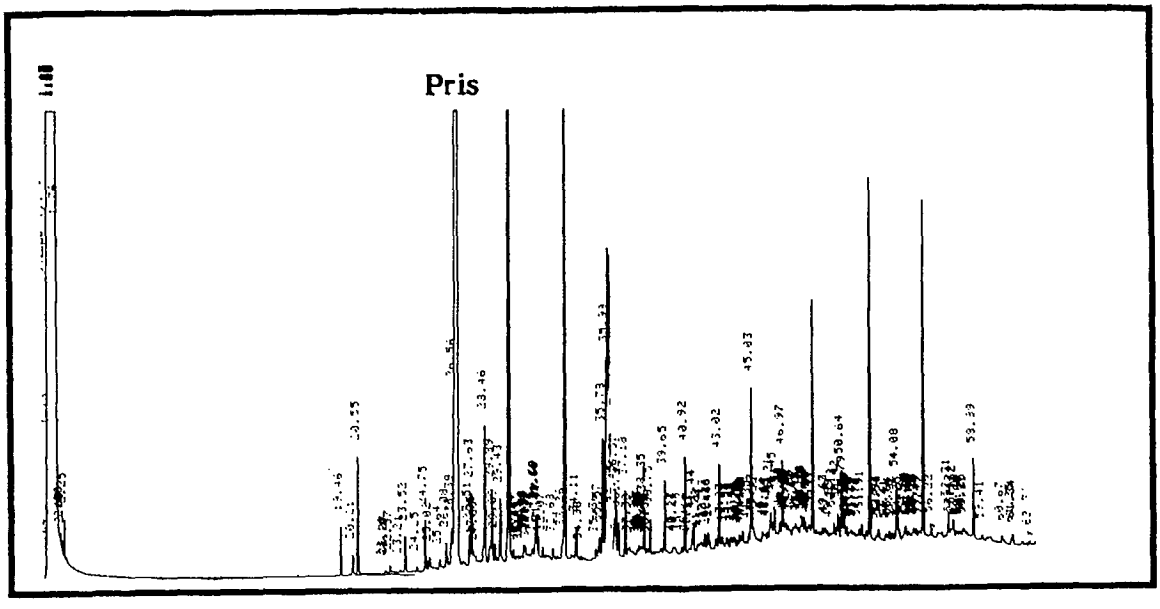


FIGURE 3.51. GC^2 TRACE OF Strongylocentrotus BAY 7 SATURATED HYDROCARBONS

3.4 Summary of Temporal Trends in Mean Oil Concentrations in Sediment and Animals

Details of the distributions of petroleum hydrocarbons in sediments and benthic animals determined from the 1983 sampling have been presented in Sections 3.2 and 3.3. To put these findings in temporal perspective, the 1980-1983 trends in petroleum residues for sediments and animals of Bay 11 are presented in Figures 3.52 and 3.53. These are geometric mean concentrations obtained from log-transformed concentration data. Confidence limits are defined in Sections 3.2 and 3.3. The important features of these plots are:

1. The general increase in sediment levels at all stations. Note that the 3m benthic transect (No. 3) value is off scale in Figure 3.52.

2. The August 1982 to August 1983 increase (or leveling off) of oil concentrations in Strongylocentrotus and Macoma. Note that the initial increase in oil levels (September 1981) for all animals is believed to have been caused by intrusion of dispersed oil from the Bay 9 release, not from the Bay 11 surface release.

The Bay 9 results are summarized in Figures 3.54 and 3.55. The important features to note are:

1. After an initial increase in Bay 9 sediment oil levels, values decreased in 1982 followed by a general increase, except at Benthic Transect No. 1 at 3m, in 1983. Note that oil levels remained elevated (approximately 4-6 ppm) in the 10m deep microbiology plots in 1982.

2. A long-term depuration is seen to occur in most of the Bay 9 benthic animals. However, after two years, oil levels in Macoma and Astarte are still 15-20 times background levels, while Strongylocentrotus has apparently acquired significantly more oil between 1982 and 1983 paralleling the increase in sediment levels.

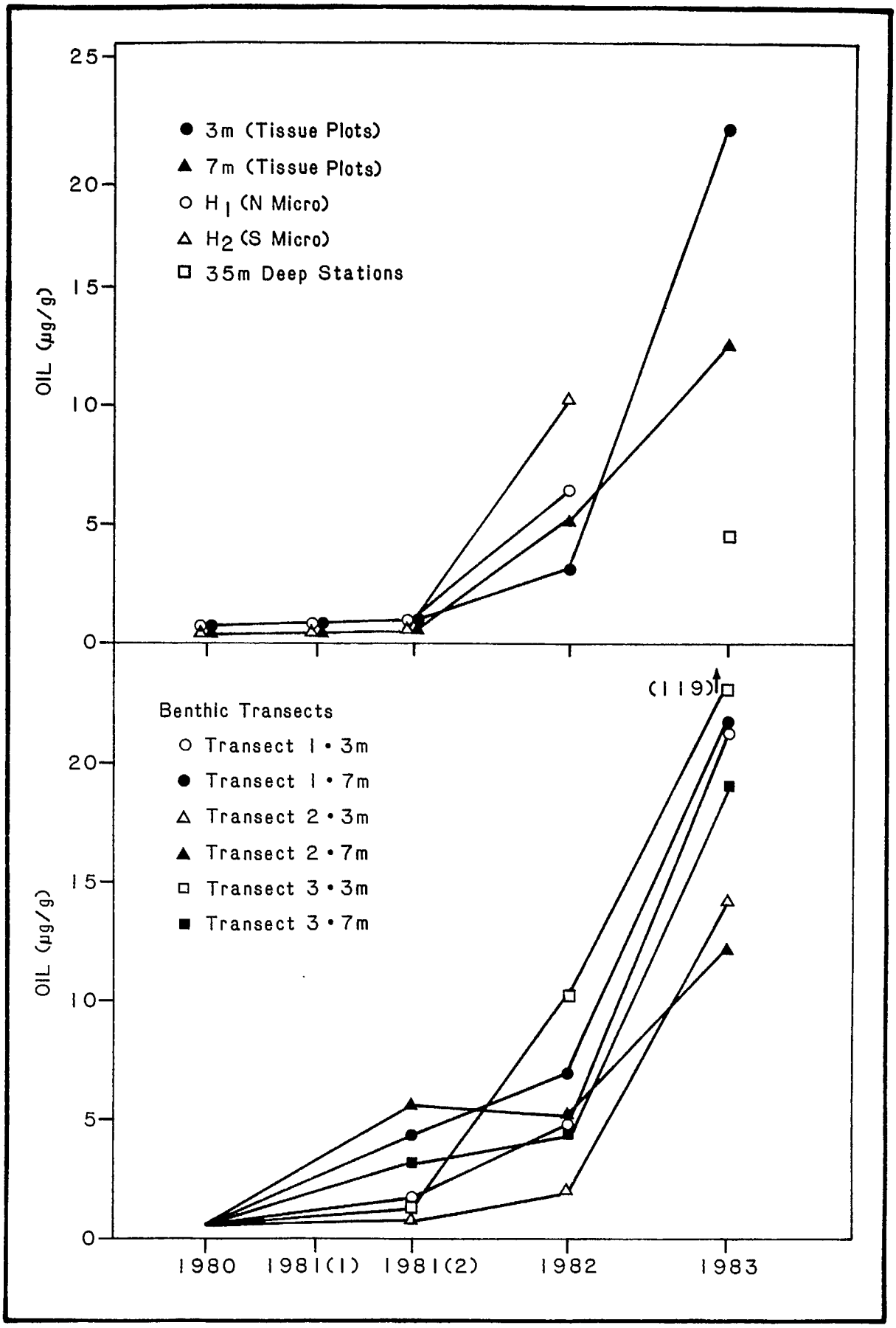


FIGURE 3.52. BAY 11 SEDIMENT OIL CONCENTRATIONS (1980-1983) (µg/g; BY UV/F)

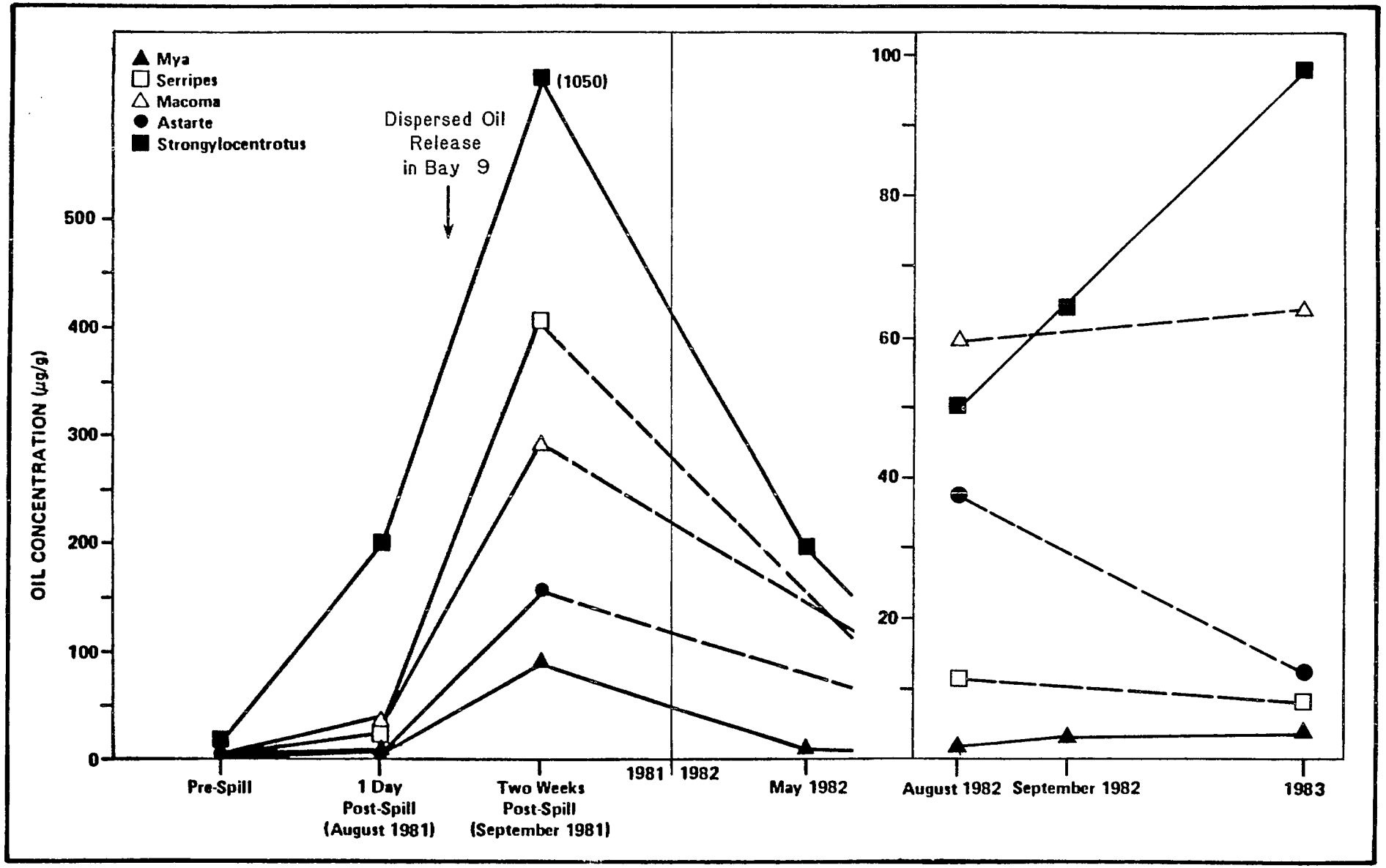


FIGURE 3.53. OIL CONCENTRATIONS IN ANIMALS: BAY 11 (µg/g; BY UV/F) (1980–1983).

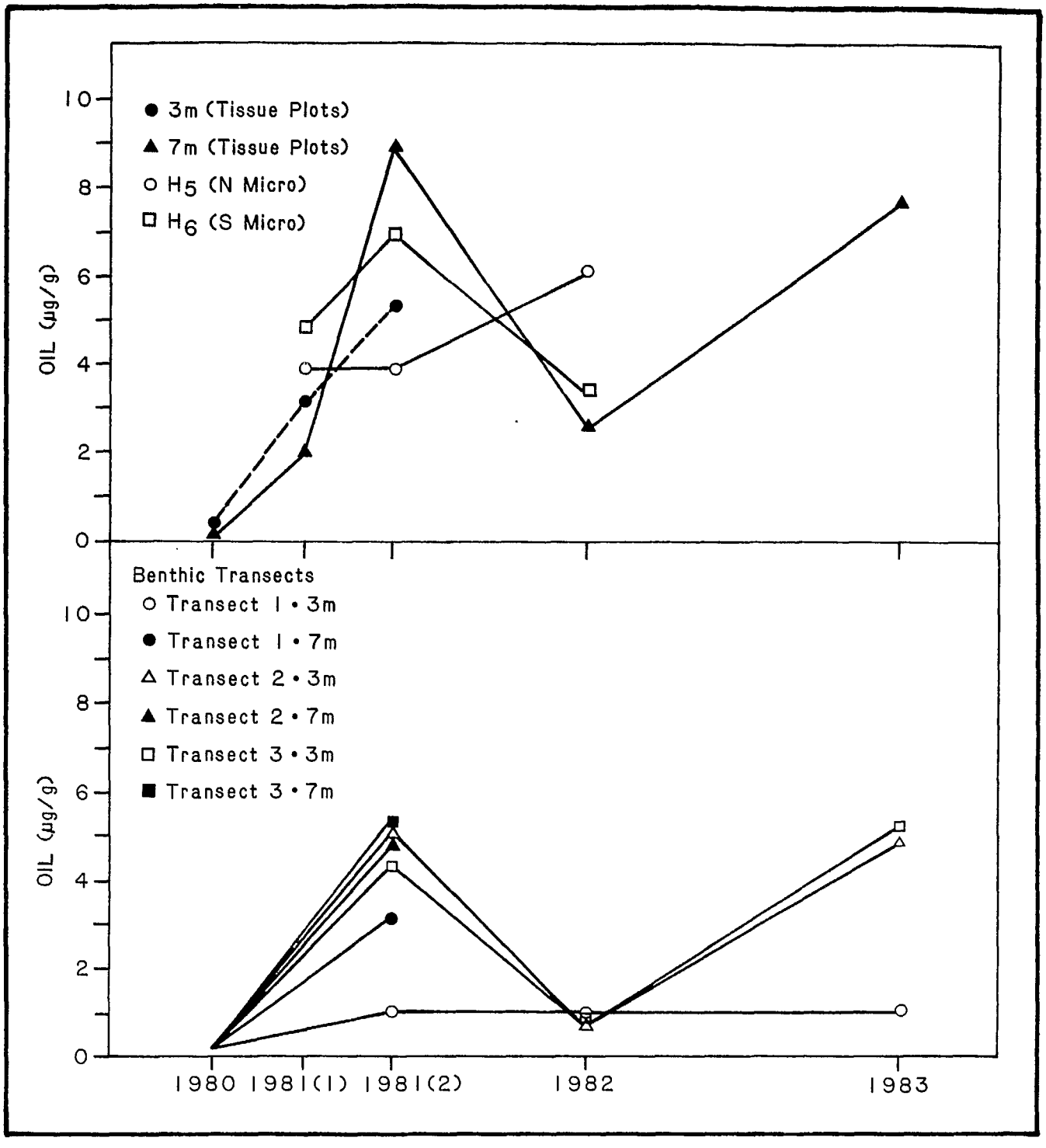


FIGURE 3.54. BAY 9 SEDIMENT OIL CONCENTRATIONS (1980-1983) (µg/g; BY UV/F)

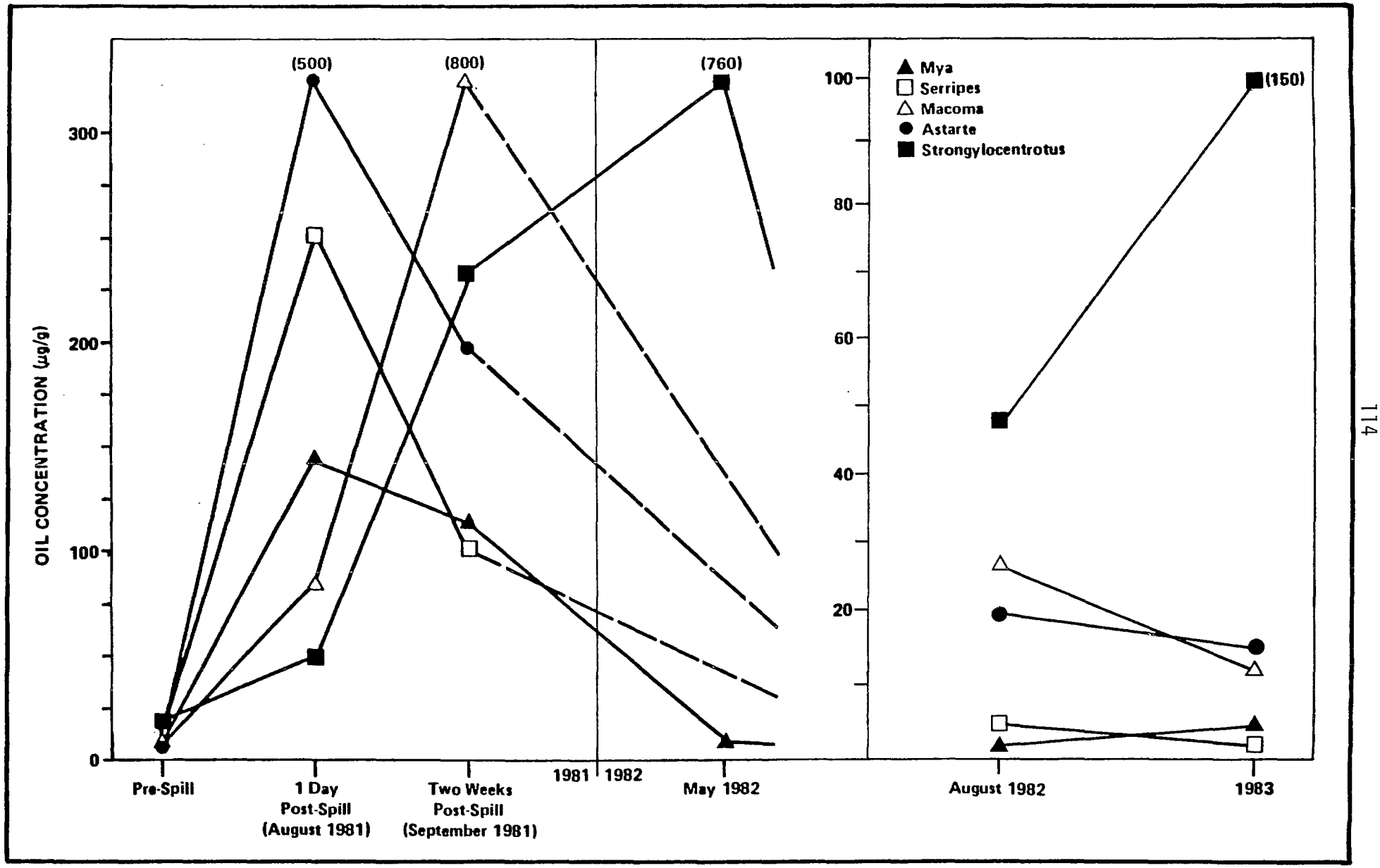


FIGURE 3.55. OIL CONCENTRATIONS IN ANIMALS: BAY 9 (µg/g; BY UV/F) (1980-1983).

Additional temporal information is presented for Bay 7 benthic animals (Figure 3.56). Note that the sediment levels in Bay 7 while still uniformly low in 1983 did apparently increase to about 2 ppm on the average in 1983. These are very low, but detectable levels which may be affecting Strongylocentrotus (Figure 3.56) in Bay 7 in 1983.

Bay 10 benthic animal temporal trends (Figure 3.57) were only followed through the 1982 field season.

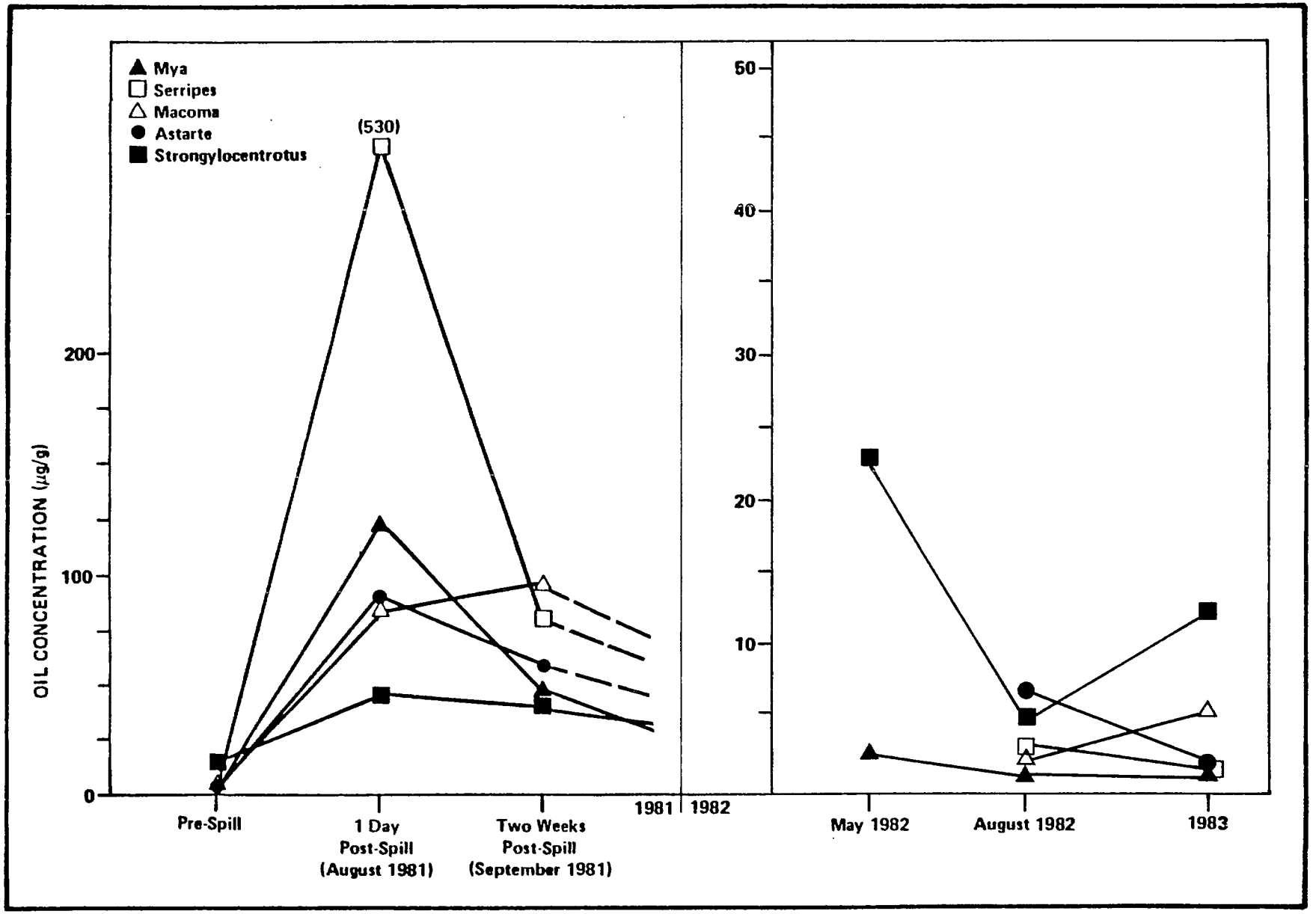


FIGURE 3.56. OIL CONCENTRATIONS IN BENTHIC ANIMALS: BAY 7 (µg/g; BY UV/F) (1980–1983).

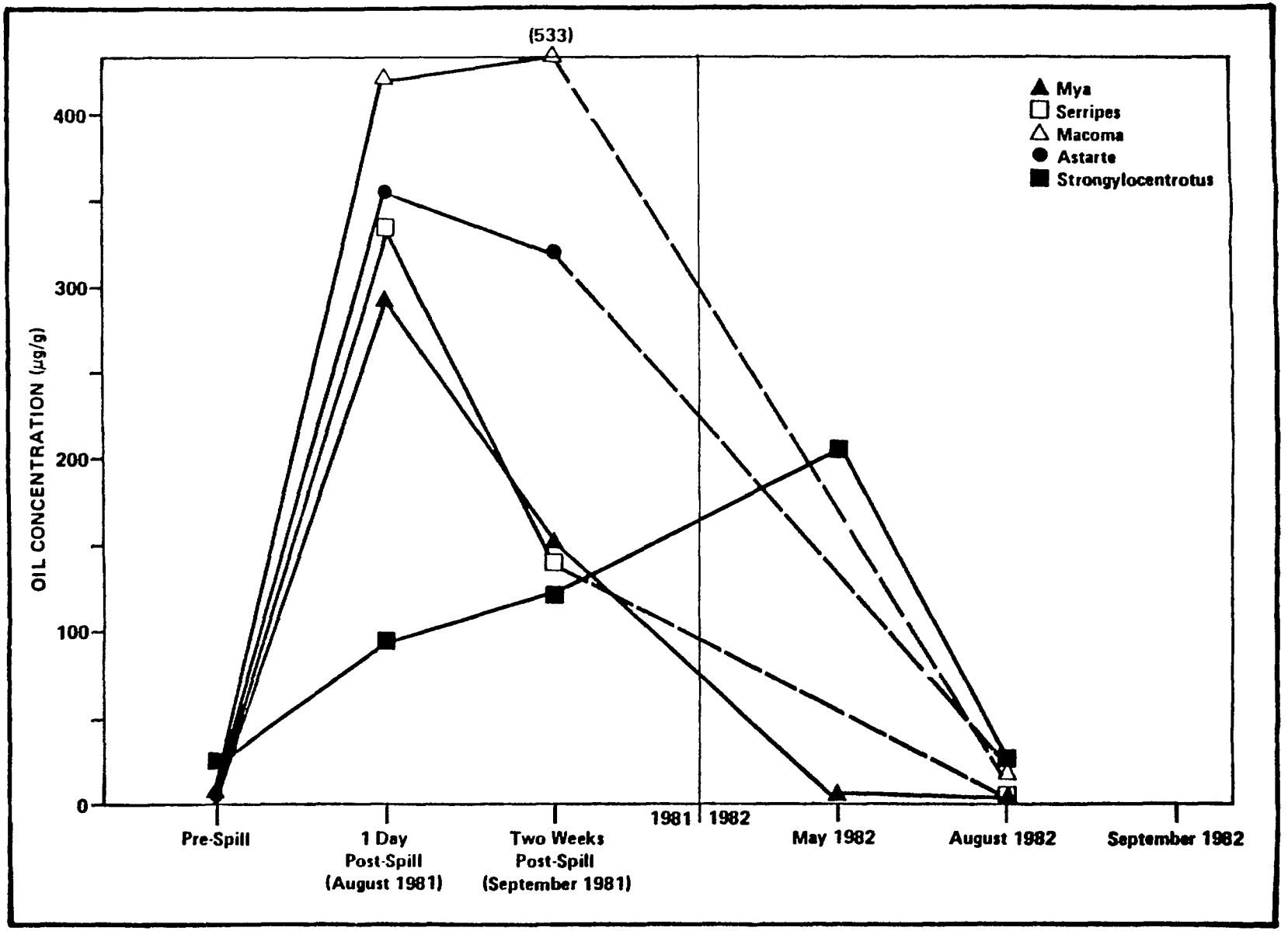


FIGURE 3.57. OIL CONCENTRATIONS IN ANIMALS: BAY 10 (µg/g; BY UV/F) (1980–1982)

SECTION FOUR

SHORELINE STUDY

A detailed study of the oil concentrations and compositions in a set of 96 beach sediment samples was conducted. A summary of the samples analyzed is shown in Table 4.1.

All samples were extracted and the extracts fractionated by column chromatography to yield a saturated and aromatic hydrocarbon fraction for each sample. Concentrations of petroleum hydrocarbons were detemined by microgravimetry of these fractions. The total extractable material was also weighed. This latter value represents the total petroleum value which includes the hydrocarbons plus polar material (non-hydrocarbon) in the stranded petroleum.

The saturated hydrocarbon composition was determined on all samples by GC^2 analysis. Two ratios best describe the GC^2-determined composition:

1. The SHWR reflects the weathering status due mainly to physical-chemical processes (i.e. evaporation, dissolution). As the n-C_{10} to n-C_{17} hydrocarbons are lost due to those processes, the SHWR approaches zero from an unweathered value of ~2.5. Note that where petroleum (kerosene) based dispersants have been used as part of the cleanup experiment, alkane components added in the C_{10} to C_{17} (from kerosene) range create SHWR > 2.5. Where SHWR exceeds that in the crude oil itself, kerosene additions are the likely explanation.

2. ALK/ISO ratio - In the Lagomedio oil, the ratio of n-alkanes to isoprenoid alkanes in the C_{13} - C_{19} boiling region is ~2.5. Normal alkanes are the most readily biodegraded components. Thus, as biodegradation proceeds, this ratio approaches zero, and the GC^2 trace becomes progressively depleted in n-alkanes. This is not to say that the isoprenoids themselves are not degraded; however, they are degraded more slowly than are the n-alkanes. Additions of kerosene or biogenic materials can confound the interpretation of this ratio. Kerosene (and diesel) additions add components in the boiling range of the components which make up this ratio. Also, at low levels of oil the inputs of biogenic pristane (one of the isoprenoids) and n-C_{15} and n-C_{17} (from plankton; two of the n-alkanes) can affect this ratio.

TABLE 4.1. SHORELINE STUDY HYDROCARBON CHEMISTRY RESULTS SAMPLE DESCRIPTIONS

Test Year	Sample ID	Plot		Depth	Date
1980	4050	Bay 102	Oil Patch		83-08-17
1980	4051		L1	Upper Surface	83-08-17
1980	4052		L1	Upper Sub-Surface	83-08-17
1980	4053		L1	Lower Surface	83-08-17
1980	4054		L1	Lower Sub-Surface	83-08-17
1980	4055		L2	Surface	83-08-17
1980	4056		L2	Sub-Surface	83-08-17
1980	4057		T1	Surface	83-08-17
1980	4058		T1	Sub-Surface	83-08-17
1980	4059		T2	Surface	83-08-17
1980	4060		T2	Sub-Surface	83-08-17
1980	4957		T2	Upper Sub-Surface	83-08-17
1981	4120		CC	Surface	83-08-17
1981	4121		CC	Sub-Surface	83-08-17
1981	4122		CE	Surface	83-08-17
1981	4123		CE	Sub-Surface	83-08-17
Ragged Channel	4124	Bay 9		100, Upper Surface	83-08-10
Beaches	4126	Bay 9		100, Mid Surface	83-08-10
Beaches	4127	Bay 9		100, Mid-Sub-Surface	83-08-10
Beaches	4128	Bay 9		100, Lower Surface	83-08-10
Beaches	4129	Bay 9		100, Lower Sub-Surface	83-08-10
Beaches	4130	Bay 9		300, Mid-Surface	83-08-10
Beaches	4132	Bay 9		300, Lower Surface	83-08-10
Beaches	4134	Bay 11		2, Upper Surface	83-08-16
Beaches	4135	Bay 11		6, Upper Surface	83-08-16
Beaches	4136	Bay 11		2, Mid-Surface	83-08-16
Beaches	4137	Bay 11		6, Mid-Surface	83-08-16
Beaches	4138	Bay 11		2, Lower Surface	83-08-16
Beaches	4139	Bay 11		6, Lower Surface	83-08-16
Beaches	4140	Bay 11		4, Upper Surface	83-08-16
Beaches	4141	Bay 11		8, Upper Surface	83-08-16
Beaches	4142	Bay 11		4, Mid-Surface	83-08-16
Beaches	4143	Bay 11		8, Mid-Surface	83-08-16
Beaches	4144	Bay 11		4, Lower Surface	83-08-16
Beaches	4145	Bay 11		8, Lower Surface	83-08-16
Beaches	4146	Bay 11		X1 Surface	83-08-16
Beaches	4147	Bay 11		X2 Surface	83-08-16
Beaches	4148	Bay 11		X3 Surface	83-08-16
Beaches	4149	Bay 11		X4 Surface	83-08-16
Beaches	4150	Bay 11		X5 Surface	83-08-16

TABLE 4.1.
(Continued)

Test Year	Sample ID	Plot	Depth	Date
Ragged Channel	4946	Bay 11	X1 Sub-Surface	83-08-16
Beaches	4947	Bay 11	X2 Sub-Surface	83-08-16
Beaches	4948	Bay 11	X3 Sub-Surface	83-08-16
Beaches	4949	Bay 11	X4 Sub-Surface	83-08-16
Beaches	4950	Bay 11	X5 Sub-Surface	83-08-16
Beaches	4951	Bay 11	X6 Sub-Surface	83-08-16
Beaches	4952	Bay 9	300, Upper Surface	83-08-16
Beaches	4955	Crude Oil Point	X7 Surface	83-08-17
Beaches	4956	Crude Oil Point	X8 Sub-Surface	83-08-17
1982	4301	ICC	Surface	83-08-17
1982	4302	ICC	Sub-Surface	83-08-17
1982	4303	ICE	Surface	83-08-17
1982	4304	ICE	Sub-Surface	83-08-17
1982	4305	IDEC	Surface	83-08-17
1982	4306	IDEC	Sub-Surface	83-08-17
1982	4307	IDEE	Surface	83-08-17
1982	4308	IDEE	Sub-Surface	83-08-17
1982	4309	IDBC	Surface	83-08-17
1982	4310	IDBC	Sub-Surface	83-08-17
1982	4311	IDBE	Surface	83-08-17
1982	4312	IDBE	Sub-Surface	83-08-17
1982	4313	IMC-C	Berm Surface	83-08-17
1982	4314	IMC-C	Berm Sub-Surface	83-08-17
1982	4315	IMC-M	Berm Surface	83-08-17
1982	4316	IMC-M	Berm Sub-Surface	83-08-17
1982	4317	IMC-C	Back Surface	83-08-17
1982	4318	IMC-C	Back Sub-Surface	83-08-17
1982	4319	IMC-M	Back Surface	83-08-17
1982	4320	IMC-M	Back Sub-Surface	83-08-17
1982	4321	IME-C	Berm Surface	83-08-17
1982	4322	IME-C	Berm Sub-Surface	83-08-17
1982	4323	IME-M	Berm Surface	83-08-17
1982	4324	IME-M	Berm Sub-Surface	83-08-17
1982	4325	IME-C	Back Surface	83-08-17
1982	4326	IME-C	Back Sub-Surface	83-08-17
1982	4327	IME-M	Back Surface	83-08-17
1982	4328	IME-M	Back Sub-Surface	83-08-17
Norwegian	4329	N1, T2 West	Surface	83-08-17
Norwegian	4330	N2, T2 West	Composite	83-08-17
Norwegian	4331	N3, T2 East	Surface	83-08-17
Norwegian	4332	N4, T2 East	Composite	83-08-17
Norwegian	4333	N5, 102E		83-08-17
Norwegian	4334	N6, 102F		83-08-17
Norwegian	4335	N7, 102G		83-08-17
Norwegian	4336	N8, 102H		83-08-17

TABLE 4.1.
(Continued)

Test Year	Sample ID	Plot	Depth	Date
Norwegian	4337	N9, 102A		83-08-17
Norwegian	4338	N10, 102B		83-08-17
Norwegian	4339	N11, 106A	Surface	83-08-17
Norwegian	4340	N12, 106A	Composite	83-08-17
Norwegian	4341	N13, 106C	Surface	83-08-17
Norwegian	4342	N14, 106C	Composite	83-08-17
Norwegian	4343	N15, 106D	Surface	83-08-17
Norwegian	4344	N16, 106D	Composite	83-08-17
Norwegian	4345	N17, 106E	Surface	83-08-17
Norwegian	4346	N18, 106E	Composite	83-08-17

Several examples illustrate these points. The GC^2 traces in Figure 4.1 illustrate:

1. Figure 4.1a, a relatively unweathered oil sample; SHWR = 2.0; ALK/ISO = 2.1; AWR (see below) = 3.0 (S4052; L1, upper subsurface; 8960 ppm).

2. Figure 4.1b - A moderately weathered oil sample; physical-chemical weathering due to evaporation, - SHWR = 1.1; little biodegradation, - ALK/ISO = 1.9 (S4057; T1; surface; 33800 ppm). Abundant UCM present.

3. Figure 4.1c - A sample to which a low boiling distillate has been added; SHWR = 12.0; ALK/ISO = 3.7 (S4309); IDBC; surface; 1620 ppm).

The GC^2 traces in Figure 4.2 indicate:

1. Figure 4.2a - A moderately weathered (SHWR = 2.0) biodegraded (ALK/ISO - 0.7) oil sample (S4121; CC; subsurface; 300 ppm). UCM present, bimodal.

2. Figure 4.2b - A sample which has received significant quantities of light distillate (e.g., kerosene or diesel); SHWR = 3.3, ALK/ISO = 3.2; (S4120 ; CC; surface; 130 ppm).

The results shown in Figure 4.3 illustrate:

1. Figure 4.3a - A relatively unweathered, unbiodegraded sample; SHWR = 1.8; ALK/ISO = 2.2 (S4330; N_2, T_2 west, composite, 28,600 ppm).

2. Figure 4.3b - A weathered (SHWR = 1.1) but unbiodegraded sample (ALK/ISO = 2.1) (S4332; N4, T2, east, composite; 36,300 ppm).

3. Figure 4.3c - A moderately weathered (SHWR = 1.5) biodegraded (ALK/ISO = 0.9) sample (S4340; N12, 106C, surface, 39,700 ppm). Bimodal UCM present.

Illustrations of biodegraded, weathered oil , the Bay 11 beach, have previously been shown in Section 3.2.1.7. (Figure 3.21).

The quantitative and compositional results on the shoreline sediments are summarized in Tables 4.2 through 4.6 for the various sample sets. These data include the gravimetric (oil concentrations) and GC^2 (saturated hydrocarbon compositions) as well as GC^2/MS determinations of the aromatic weathering ratio (AWR) in a selected set of

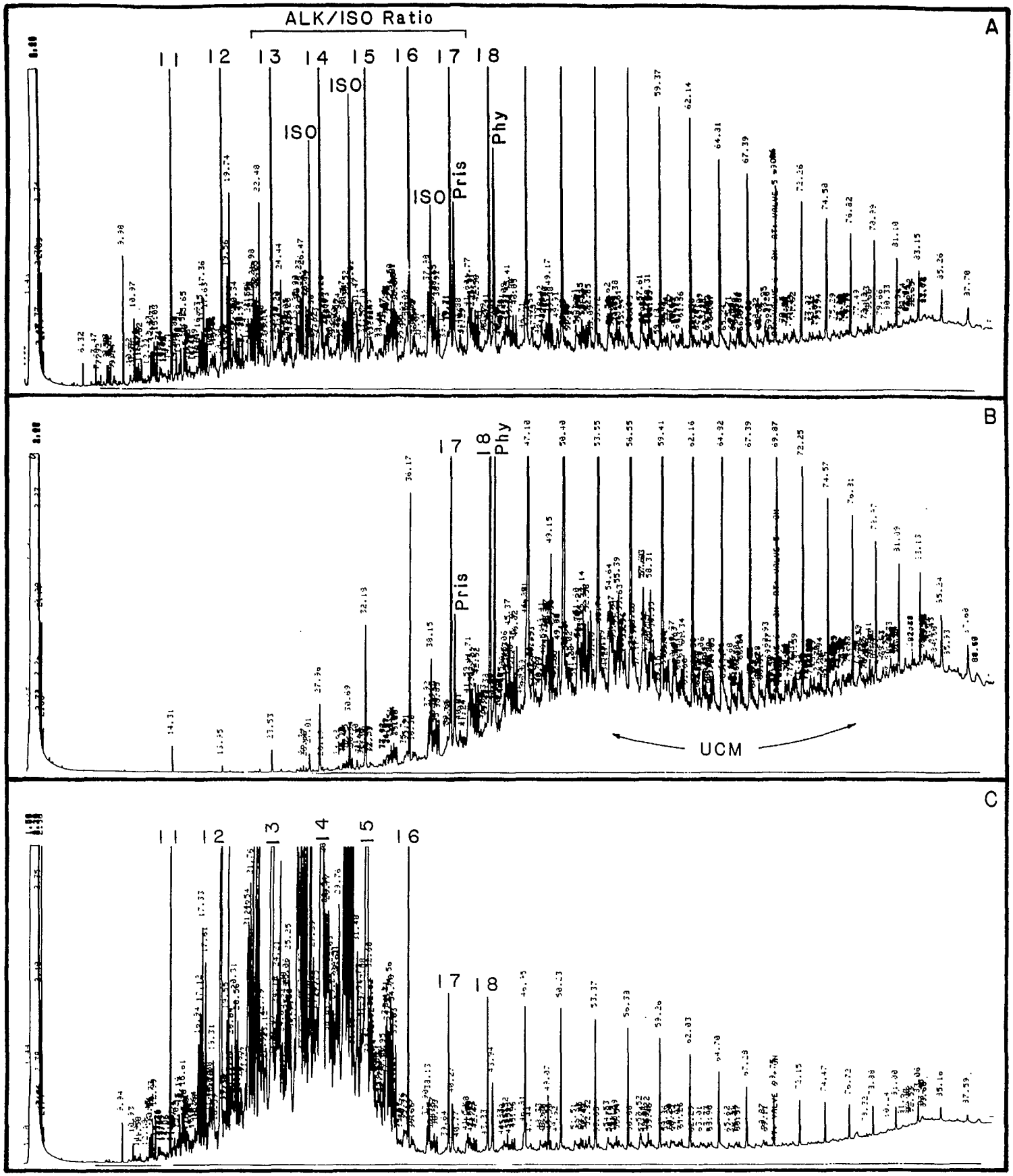


FIGURE 4.1. REPRESENTATIVE SHORELINE SEDIMENT SATURATED HYDROCARBON GC^2 DETERMINATIONS: A- S4052, LI; B- 4057, TI; C- 4309, IDBC.

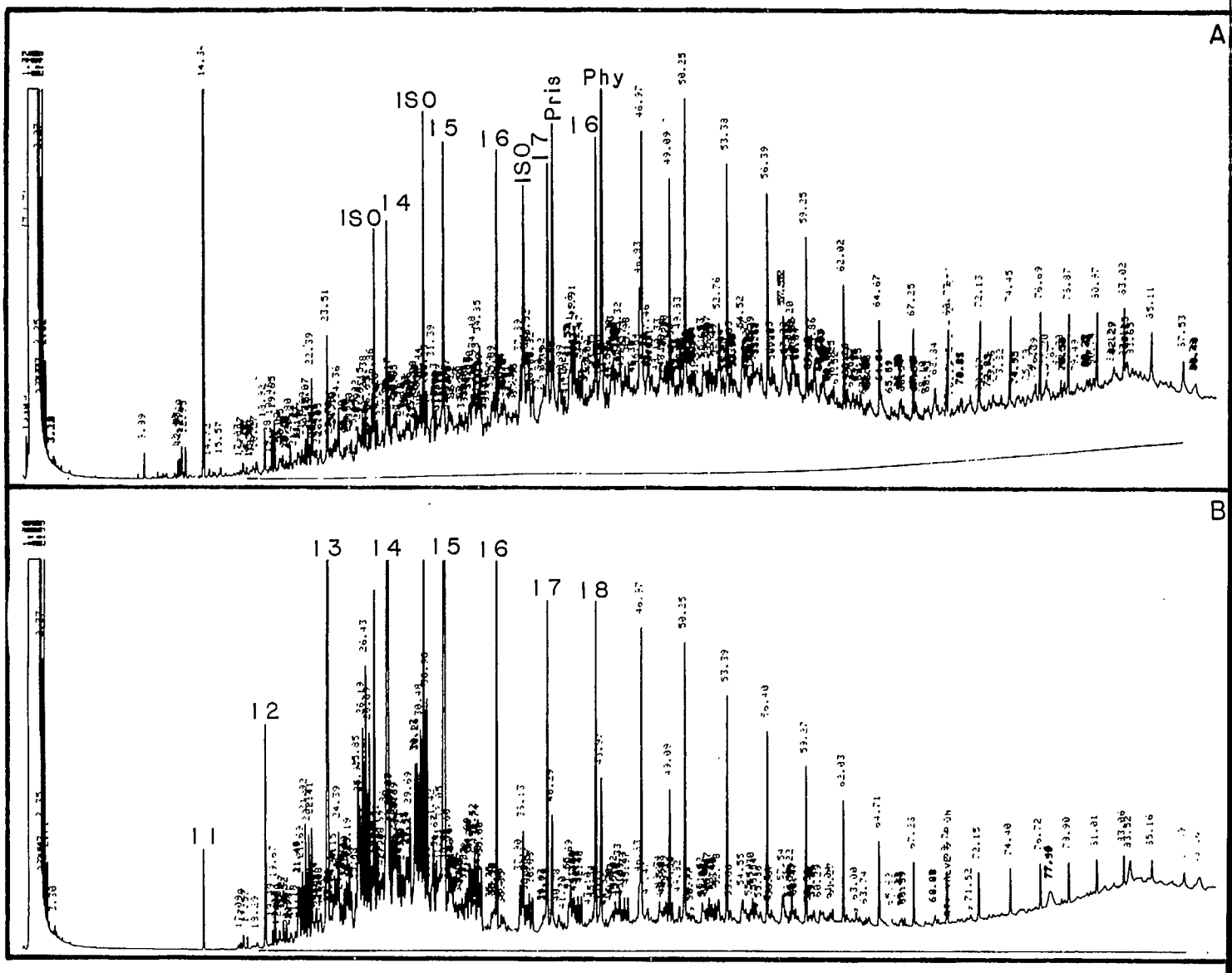


FIGURE 4.2. REPRESENTATIVE SHORELINE SEDIMENT SATURATED HYDROCARBON GC^2 DETERMINATIONS: A- 4124, CC; B- 4120, CC.

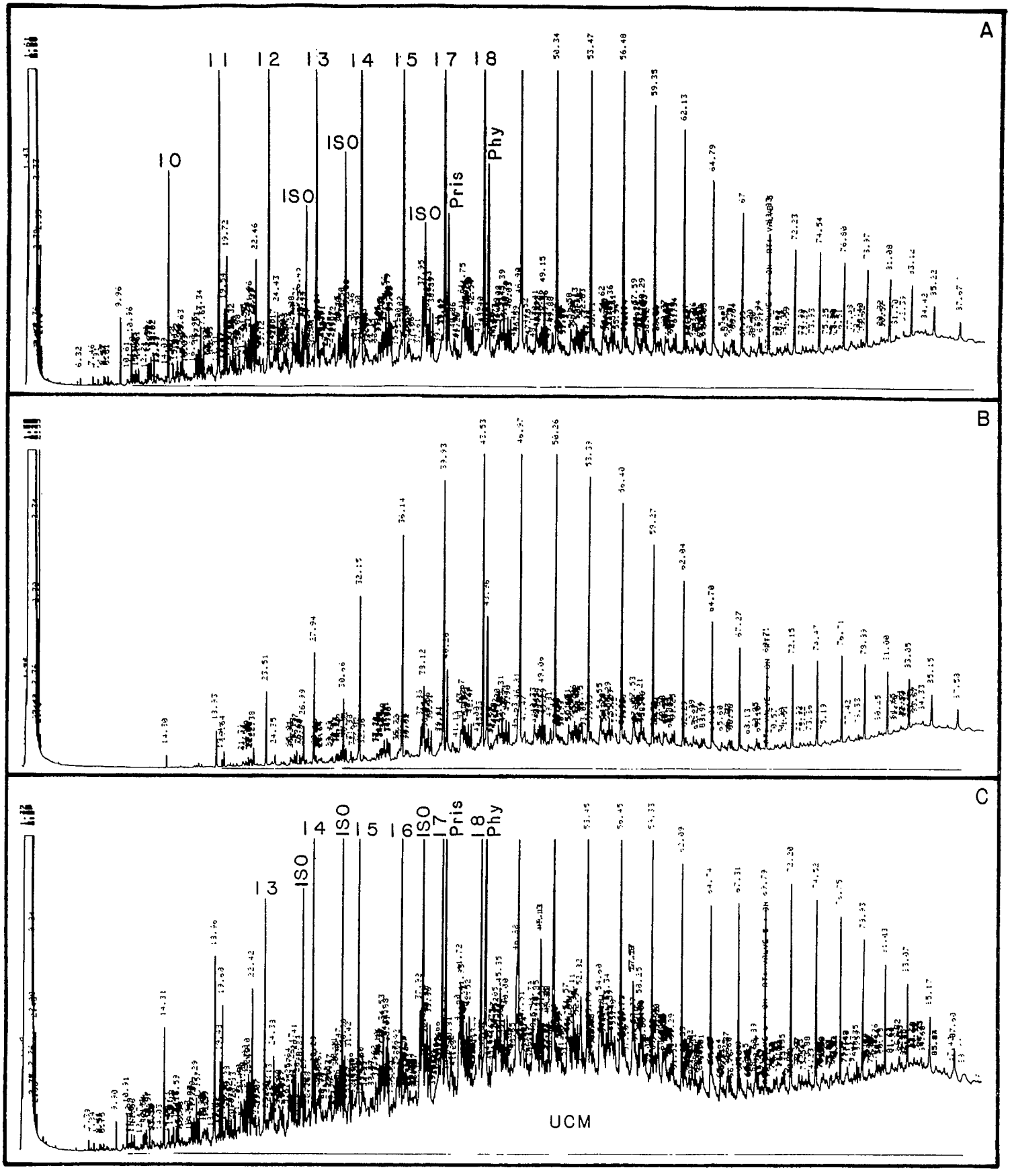


FIGURE 4.3. REPRESENTATIVE SHORELINE SEDIMENT SATURATED HYDROCARBON GC^2 DETERMINATIONS: A- S4330; B- S4332; C- S4340.

TABLE 4.2. SHORELINE STUDY 1983 HYDROCARBON CHEMISTRY RESULTS - ANALYTICAL RESULTS; 1980 TEST PLOTS.

Plot	Depth	Saturated Hydrocarbon µg/g	Aromatic Hydrocarbon µg/g	Total Hydrocarbon µg/g	Total Extractable µg/g	SHWR	ALK/ISO	AWR
Bay 102, Oil Patch		889.	526.	1,940.	1,930.	1.2	0.8	
L1	Upper Surface	686.	345.	1,030.	1,470.	1.2	0.9	1.3
L1	Upper Sub-Surface	4,890.	2,460.	7,350.	8,960.	2.0	2.1	3.0
L1	Lower Surface	18.3	9.4	27.7	55.0	1.0	1.7	1.5
L1	Lower Sub-Surface	0.0	1.9	1.9	16.0	1.2	1.0	
L2	Surface	4.2	5.1	9.3	34.2	1.3	1.7	
L2	Sub-Surface	2.0	0.9	2.9	23.7	1.4	1.1	
T1	Surface	2,780.	1,430.	4,210.	6,450.	1.1	1.9	
T1	Sub-Surface	6,170.	4,250.	10,400.	13,900.	1.8	2.2	
T2	Surface	17,100.	10,500.	27,600.	33,800.	1.4	2.2	
T2	Sub-Surface	9,590.	5,470.	15,100.	19,900.	2.2	2.2	
T2	Upper Sub-Surface	242.	159.	401.	635.	1.2	0.2	

TABLE 4.3. SHORELINE STUDY 1983 HYDROCARBON CHEMISTRY RESULTS - ANALYTICAL RESULTS; 1981 TEST PLOTS.

Plot	Depth	Saturated Hydrocarbon µg/g	Aromatic Hydrocarbon µg/g	Total Hydrocarbon µg/g	Total Extractable µg/g	SHWR	ALK/ISO	AWR
CC	Surface	33.7	19.8	53.5	131.	3.3	3.2	
CC	Sub-Surface	117.	78.6	196.	299.	2.0	0.7	
CE	Surface	6.9	5.6	12.5	62.0	2.0	2.1	
CE	Sub-Surface	18.1	14.7	32.8	78.5	1.9	1.4	

TABLE 4.4. SHORELINE STUDY 1983 HYDROCARBON CHEMISTRY RESULTS - ANALYTICAL RESULTS; 1982 TEST PLOTS.

Plot	Depth	Saturated Hydrocarbon µg/g	Aromatic Hydrocarbon µg/g	Total Hydrocarbon µg/g	Total Extractable µg/g	SHWR	ALK/ISO	AWR
ICC	Surface	112.	73.6	185.	437.	1.6	1.4	1.6
ICC	Sub-Surface	2.5	1.8	4.3	55.3	1.5	1.9	
ICE	Surface	356.	214.	570.	924.	1.5	1.7	1.5
ICE	Sub-Surface	1.8	4.7	6.5	230.	1.8	0.6	
IDEC	Surface	276.	163.	439.	709.	1.4	2.0	
IDEC	Sub-Surface	1.4	2.6	4.0	75.5	1.1	2.5	
IDEE	Surface	297.	188.	484.	887.	1.4	1.5	
IDEE	Sub-Surface	3.5	9.5	13.0	332.	2.5	0.4	
IDBC	Surface	523.	102.	624.	1,620.	12.	3.7	
IDBC	Sub-Surface	380.	54.7	435.	668.	17.	3.6	
IDBE	Surface	354.	75.6	429.	868.	14.	3.9	
IDBE	Sub-Surface	2.7	6.2	8.9	121.	2.8	1.9	
IMC-C	Berm. Surface	19,600.	11,600.	31,200.	45,200.	1.5	2.2	2.3
IMC-C	Berm Sub-Surface	3,860.	2,800.	6,660.	9,480.	2.4	2.3	
IMC-M	Berm Surface	19,300.	12,000.	31,300.	41,200.	1.6	2.3	
IMC-M	Berm Sub-Surface	5,960.	3,490.	9,460.	11,800.	2.1	2.3	
IMC-C	Back Surface	17,100.	10,500.	27,600.	41,000.	1.4	1.9	1.7
IMC-C	Back Sub-Surface	118.	87.8	206.	376.	1.9	2.1	3.1
IMC-M	Back Surface	8,230.	5,680.	13,900.	15,700.	1.7	2.2	
IMC-M	Back Sub-Surface	929.	679.	1,610.	2,410.	2.0	2.1	
IME-C	Berm Surface	6210.	3,790.	10,000.	11,900.	1.7	2.1	2.8
IME-C	Berm Sub-Surface	5,170.	2,860.	8,020.	9,670.	2.0	2.3	
IME-M	Berm Surface	6,070.	3,520.	9,600.	11,900.	1.7	2.3	
IME-M	Berm Sub-Surface	6,440.	3,650.	10,100.	11,700.	2.0	2.2	
IME-C	Back Surface	20,900.	13,300.	34,200.	44,100.	1.5	1.4	1.8
IME-C	Back Sub-Surface	389.	259.	648.	947.	1.6	2.0	2.0
IME-M	Back Surface	13,400.	6,000.	19,400.	20,400.	1.6	2.4	
IME-M	Back Sub-Surface	4,890.	3,300.	8,190.	12,900.	2.1	2.3	

TABLE 4.5. SHORELINE STUDY 1983 HYDROCARBON CHEMISTRY RESULTS - ANALYTICAL RESULTS; RAGGED CHANNEL BEACHES.

Plot	Depth	Saturated Hydrocarbon µg/g	Aromatic Hydrocarbon µg/g	Total Hydrocarbon µg/g	Total Extractable µg/g	SHWR	ALK/ISO	AWR
Bay 9	100, Upper Surface	0.0	1.0	1.0	8.1	2.0	0.8	1.2
Bay 9	100, Mid-Surface	0.9	0.4	1.3	6.0	1.2	1.4	
Bay 9	100, Mid Sub-Surface	0.0	0.0	0.0	11.3	1.7	0.9	1.6
Bay 9	100, Lower Surface	0.2	0.0	0.2	2.92	0	0	
Bay 9	100, Lower Sub-Surface	0.8	0.8	1.6	11.6	1.0	0.9	
Bay 9	300, Mid-Surface	0.5	1.1	1.6		1.2	0.8	
Bay 9	300, Lower Surface	0.0	0.7	0.7	9.7	1.2	1.6	
Bay 11	2, Upper Surface	221.	180.	401.	1,260.	1.0	1.0	1.0
Bay 11	6, Upper Surface	8,490.	5,380.	13,900.	17,300.	1.6	1.9	2.2
Bay 11	2, Mid-Surface	601.	307.	908.	1,880.	1.1	0.4	1.1
Bay 11	6, Mid-Surface	9,210.	4,280.	13,500.	16,700.	1.7	2.1	
Bay 11	2, Lower Surface	55.1	16.9	72.0	197.	1.1	0.2	
Bay 11	6, Lower Surface	2,580.	1,310.	3,890.	6,160.	1.0	0.3	
Bay 11	4, Upper Surface	12,200.	7,230.	19,400.	25,400.	1.6	2.5	
Bay 11	8, Upper Surface	2,380.	1,100.	3,480.	4,810.	1.1	1.4	
Bay 11	4, Mid-Surface	4,220.	1,930.	6,150.	10,800.	1.0	0.7	
Bay 11	8, Mid-Surface	1,010.	503.	1,510.	2,450.	1.0	1.4	
Bay 11	4, Lower Surface	29.6	1.1	42.7	94.0	1.2	0.4	
Bay 11	8, Lower Surface	835.	422.	1,260.	2,100.	1.1	0.3	
Bay 11	X1 Surface	16,200.	1,050.	17,200.	26,900.	2.0	2.2	2.5
Bay 11	X2 Surface	216.	107.	322.	600.	1.3	1.2	
Bay 11	X3 Surface	332.	186.	518.	809.	1.8	2.1	
Bay 11	X4 Surface	122.	69.8	192.	730.	1.6	1.8	2.1
Bay 11	X5 Surface	7,670.	5,130.	12,800.	15,900.	1.4	1.0	
Bay 11	X1 Sub-Surface	4,640.	2,380.	7,020.	8,980.	1.6	2.0	2.3
Bay 11	X2 Sub-Surface	41.4	18.6	78.6	151.0	1.2	0.7	
Bay 11	X3 Sub-Surface	2.4	2.3	4.7	72.2	1.3	1.4	
Bay 11	X4 Sub-Surface	0.9	3.0	3.9	227.	1.3	1.4	3.5
Bay 11	X5 Sub-Surface	3,430.	2,180.	5,600.	7,180.	1.8	1.8	
Bay 11	X6 Sub-Surface	164.	105.	269.	688.	1.7	2.1	
Bay 11	300, Upper Surface	0.7	0.2	0.9	10.8	1.1	1.5	
Crude Oil Point	X7 Surface	1,060.	467.	1,530.	2,600.	1.0	1.2	
Crude Oil Point	X8 Sub-Surface	1,220.	724.	1,940.	3,000.	1.0	1.6	

TABLE 4.6. SHORELINE STUDY 1983 HYDROCARBON CHEMISTRY RESULTS - ANALYTICAL RESULTS; NORWEGIAN TEST PLOTS.

Plot	Depth	Saturated Hydrocarbon µg/g	Aromatic Hydrocarbon µg/g	Total Hydrocarbon µg/g	Total Extractable µg/g	SHWR	ALK/ISO	AWR
N1, T2 West	Surface	34,200.	14,200.	48,400.	72,600.	1.4	2.0	
N2, T2 West	Composite	16,300.	9,140.	25,400.	28,600.	1.8	2.2	
N3, T2 East	Surface	18,200.	9,830.	28,100.	35,400.	1.3	2.1	
N4, T2 East	Composite	18,300.	9,950.	28,300.	36,300.	1.1	2.1	
N5, 102 E		5,490.	3,250.	8,740.	11,300.	1.4	1.2	
N6, 102 F		5,470.	3,690.	9,160.	11,700.	1.8	2.1	
N7, 102 G		10,700.	7,210.	17,900.	21,100.	1.8	2.2	
N8, 102 H		18,700.	11,800.	30,500.	35,800.	1.7	1.8	
N9, 102 A		12,700.	6,870.	19,500.	19,000.	1.6	2.1	
N10, 102 B		11,900.	5,920.	17,900.	20,900.	1.5	2.1	
N11, 106 A	Surface	29,200.	18,100.	47,300.	66,100.	1.3	1.1	
N12, 106 A	Composite	5,180.	3,700.	8,880.	11,600.	1.5	0.9	
N13, 106 C	Surface	24,400.	12,500.	36,800.	39,700.	1.4	2.0	
N14, 106 C	Composite	4,370.	2,380.	6,750.	8,970.	1.5	2.0	
N15, 106 D	Surface	25,000.	13,900.	38,800.	45,400.	1.4	1.5	
N16, 106 D	Composite	13,400.	7,770.	21,100.	24,900.	1.7	1.6	
N17, 106 E	Surface	9,660.	5,870.	15,500.	20,000.	1.4	2.0	
N18, 106 E	Composite	12,500.	7,360.	19,800.	20,600.	1.8	2.2	

samples. The AWR in the spilled oil was 3.5. As light aromatics are removed due to physical chemical weathering, this ratio decreases. Twenty such aromatic fractions were analyzed by GC^2/MS.

All of these results must be viewed as the latest in a time series of quantitative and qualitative results on the various test plots.

SECTION 5

DISCUSSION OF RESULTS

Two years after the Ragged Channel (nearshore) spills, the focus of the analytical biogeochemical studies is primarily on the movement of oil sourced from the stranded oil on the Bay 11 beach and its impact on the benthic biota.

In the summer of 1982, the oil levels in the subtidal sediments of Bay 11 had increased to 3.0 µg/g (range 0.7-66) at 3 meters and 5.3 µg/g (range 1.3-50) at 7 meters. One of the major findings of the 1983 study was the marked increase in subtidal sediment oil levels in Bay 11. Oil levels in sediments increased by a factor of 5-10 due to erosion of beached oil and deposition offshore to at least the 7m water depth contour. The microbiology transect in Bay 11 confirms that the bulk of the deposited offshore oil lies in the 3m to 7m depth range and the highest concentrations are found at the south end of the 3m line. However, we have confirmed that 1-8 ppm of oil have been transported further offshore in the deeper (35m) areas in the Bay 11/12 region.

Bay 9 sediment petroleum hydrocarbon values increased between 1982 and 1983. The source of elevated quantities of sedimented oil in the sediments of Bay 9 probably lies in the sediments just south of the Bay 9 study area. Large quantities of oil were observed to be transported from the oil/dispersant diffuser system south along the shoreline during the discharge in Bay 9 in 1981. It is possible that elevated oil levels in sediments resulting from this southerly transport may have eventually resulted in infiltration of these sediments into the study area of Bay 9, just north of the diffuser site. Values of 0.6-7 ppm of oil have been detected at 3m in Bay 9 and 6-10 ppm detected at 7 meters. On the average, this represents a threefold increase at 7m and at 3m in Bay 9.

Levels of oil in the Bay 7 sediments have increased slightly over the low levels (1-2 ppm) observed previously. One "hot spot" at 13 ppm was found which also corresponded to higher oil levels in one benthic animal species.

Judging from the compositional profiles of the subtidal sedimented oil in Bay 11, the residues are more highly weathered than they had been in 1982. The oil eroded off of the Bay 11 beach is compositionally very variable. It appears that weathering (i.e. the combined processes of evaporation, dissolution and biodegadation) is proceeding more rapidly in the lower end of the beach transects. Relatively unweathered oil is still present

in concentrated patches on the Bay 11 beach. However, for the most part it appears that both the oil leached into the water column (i.e. the slick samples) and the sedimented oil (floc samples) are largely depleted in low boiling alkanes (n-C_{10} to n-C_{15}) and aromatics (alkylated benzenes and naphthalenes).

The surface floc hydrocarbon levels in the Bay 3 meter samples were almost twice as high, on the average, than the comparable 1982 values (.93 mg/m^2 vs. .54 mg/m^2) although the 7m samples values were quite similar in both years (~.25 mg/m^2). The elevated bulk (0-2 cm) sediment levels probably result from a mixing of surface floc oil into the upper sediment column. However, the core samples revealed only trace levels of oil lower than 5 cm in the sediment column and less oil in general in the 0-5 cm section than in the 0-2 cm grab sample (i.e. the benthic transect and tissue plot samples). Oil is thus probably confined to the top few (0-2) centimeters. However, general lack of strong agreement between GC^2-determined (cores) and UV/F-determined (sediment samples) oil values may very well explain this difference.

The continuing use of UV/F as the main analytical tool to determine oil concentrations has created several interpretational dilemmas. Where high oil concentrations are present (e.g., Bay 11 sediments and floc) the UV/F and GC^2 methods agree generally within a factor of two. At lower concentrations, direct calculation of oil levels by GC^2 is impossible due to the biogenic interferences. The continuing use of the phytane:oil ratio to convert observed phytane levels in sediments to "oil concentrations" is risky at low levels due to the fact that phytane is not inert and the inevitability of its degradation causes the phytane to oil conversion to be grossly inaccurate, especially at low levels. Additionally, the UV/F 350-360 nm intensity measurement on total extracts could include polar aromatic compounds (metabolites of, or polar components of petroleum) and naphtheno-aromatics which would appear as unresolved material in the f_2 (aromatic-olefinic) fraction. Both these compound groupings which would be part of a "total oil" measurement are not detected in our conventional saturated and aromatic hydrocarbon determinations.

This situation is readily apparent in the tissue analyses where UV/F "oil values" on total extracts don't always agree with GC^2 value (phytane conversions), and don't agree with the UV/F analysis of the f_2 fraction. We had previously noted (Boehm, 1983a) the widening discrepancy between UV/F and GC^2 values. The discrepancy between UV/F (total extract) and UV/F (f_2 fraction) determinations is new data. It may have very well existed in previous years.

All signs point to the continued use of UV/F data to compare sediment and tissue data between sampling periods as being the wisest, most consistent path to take.

Evidence for petrogenic inputs to tissue samples by GC^2 and GC^2/MS has become difficult to establish. High, unambiguous, UV/F-determined oil values did not result, in 1983, in high aromatic hydrocarbon values by GC^2/MS. The UV/F-determined values for the five species indicated the following:

1. Bay 11: Mya oil concentrations were only slightly higher than they were in 1982; Macoma values were the same as in 1982 indicating a steady state uptake/depuration situation for these deposit-feeders; Serripes levels were the same in 1983 as in 1982 indicating also a steady state situation. Astarte values decreased by a factor of approximately two. Urchin levels increased somewhat (100 versus 67) over 1982. However, between August and September of 1982 the urchin values were seen to be on the increase.

2. Bay 9: Macoma, Astarte and Serripes all show concentration decreases between 1982 and 1983 in spite of apparent increases in the sedimentary oil concentrations in this Bay. Only Mya (slight increase) and urchins (50 versus 150 ppm) showed increases in the average oil levels in this Bay.

3. Bay 7: Serripes, Mya and Astarte all illustrated no increase of oil while urchins (slight increase) and Macoma samples (1.9 versus 5.2) were seen to increase in concentration.

The overall conclusion reached when reviewing these data is that the benthic detrital feeders in Bay 11 appear to reman significantly impacted by oil while for the most part the filter-feeders continue to decrease their oil burdens in this bay. The deposited oil seems generally unavailable to the filter-feeding animals. However, background values have not been reached in all of the Bay 11 species and several of the Bay 9 and 7 species, namely the urchins. It should be noted that we now consider that the initial (2-week postspill) increases in the Bay 11 benthic animal oil content were almost certainly due to intrusion of Bay 9 dispersed oil, not due to the Bay 11 untreated oil itself, waterborne oil levels due to the dispersed oil release in Ragged Channel in general were shown to be ~ 50 ppb and were higher, up to 140 ppb in Bay 11. Therefore, the impact of the Bay 11 release is probably just now (1983) being revealed in the increasing or steady-state oil levels seen in the Bay 11 benthic animals (See Figure 3.53).

While aromatic hydrocarbons were detected at low to moderate levels in many of the tissue samples, levels of the petroleum aromatics (i.e. alkylated dibenzothiophenes and phenanthrenes) are much lower than was observed in 1982. The aromatic hydrocarbon levels have apparently decreased markedly in spite of the "oil signal" being detected in the UV/F analysis (see discussion above). The vigorous in vivo biodegradation of oil components in all of the animals discussed at length in Boehm et al.(1982a,b) and Boehm, (1983) and recently demonstrated in our analyses of the animals from the DIAND tank experiments (Boehm, 1984) may very well be responsible for aromatic hydrocarbon degradation as well, after the saturated hydrocarbon substrate has been depleted. The lack of large amounts of GC^2/MS-determined aromatic hydrocarbons also does not mean that other aromatic compounds, (not original analytical targets of the GC^2/MS) are not present.

Both the Milne Inlet sediment and animal samples were free of any UV/F-determined oil, thus lending credence to the UV/F-measured oil levels in the test bays.

Large quantities of oil still remains on the Bay 11 beach. Based on this year's findings and/or by extrapolation of the relative impact curves shown in Figure 5.1, it can be predicted that:

1. Oil will continue to "weather" on the Bay 11 beach.

2. Oil will continue to be transported offshore to the Bay 11 sediments and that levels will further increase with time.

3. Oil may will be transported from Bay 11 subtidal sediments further offshore into the deeper parts of the Bay 11/12 system.

4. Deposit feeders in Bay 11 will continue to be impacted by the oil. Oil will become less available to filter-feeders as the primary transport mechanisms of weathered oil will be through the surface sediment.

5. In vivo degradation of saturated and aromatic hydrocarbons will be the main detoxification mechanism available to animals.

6. Low levels of water-borne oil will continue to leach off the Bay 11 beach and will result in low level petroleum contamination of the water column.

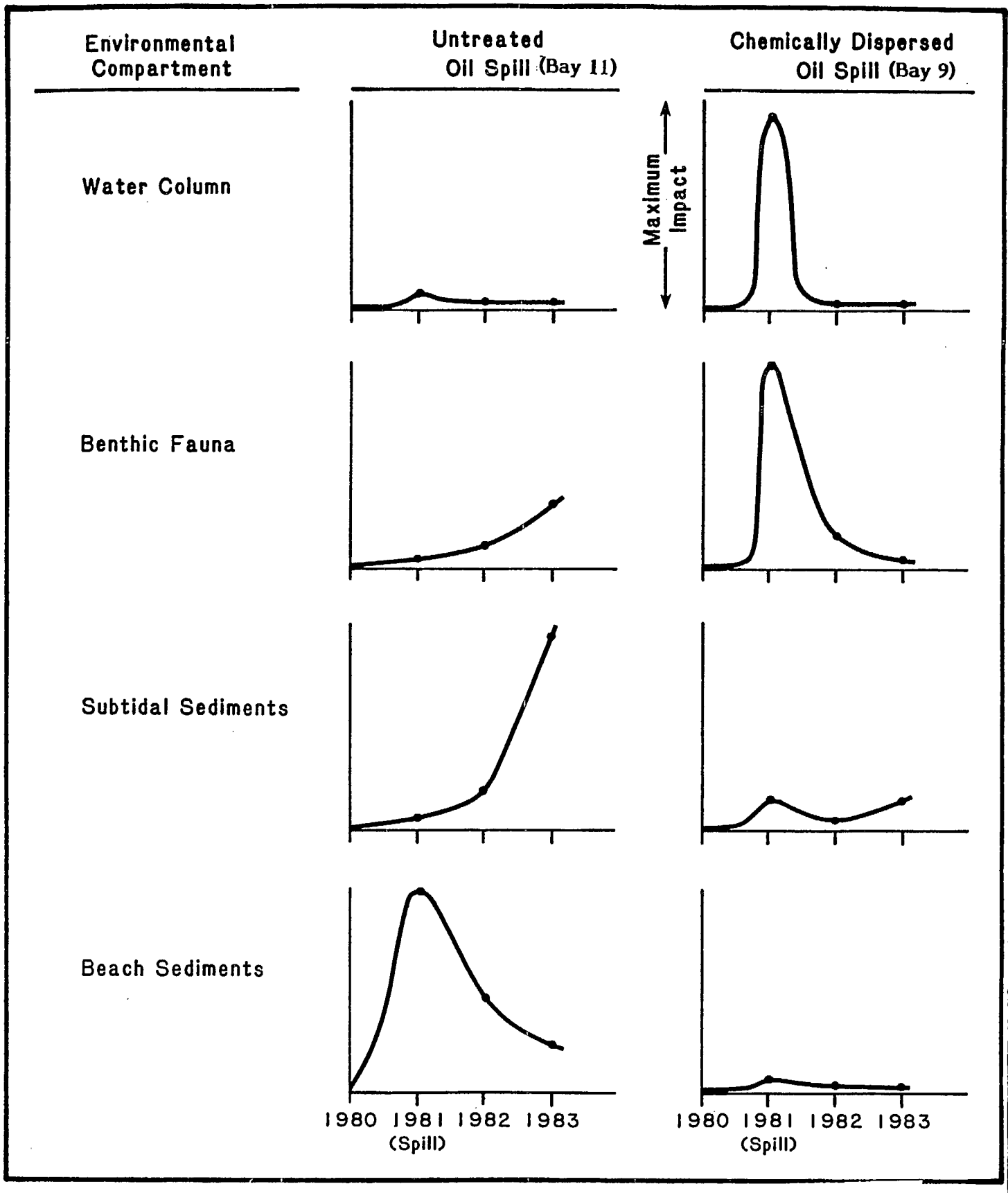


FIGURE 5.1. SUMMARY OF COMARATIVE FATES OF OIL FROM THE BIOS SPILLS.

The spill study should enter a new phase. The comparative aspects of the fate of dispersed versus untreated oils is at an end. The long term impacts of chronic oil pollutant inputs to an arctic nearshore environment has just begun. It is extremely important that this unique research opportunity not be lost as have others (e.g., Amoco Cadiz) in the past.

SECTION SIX

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