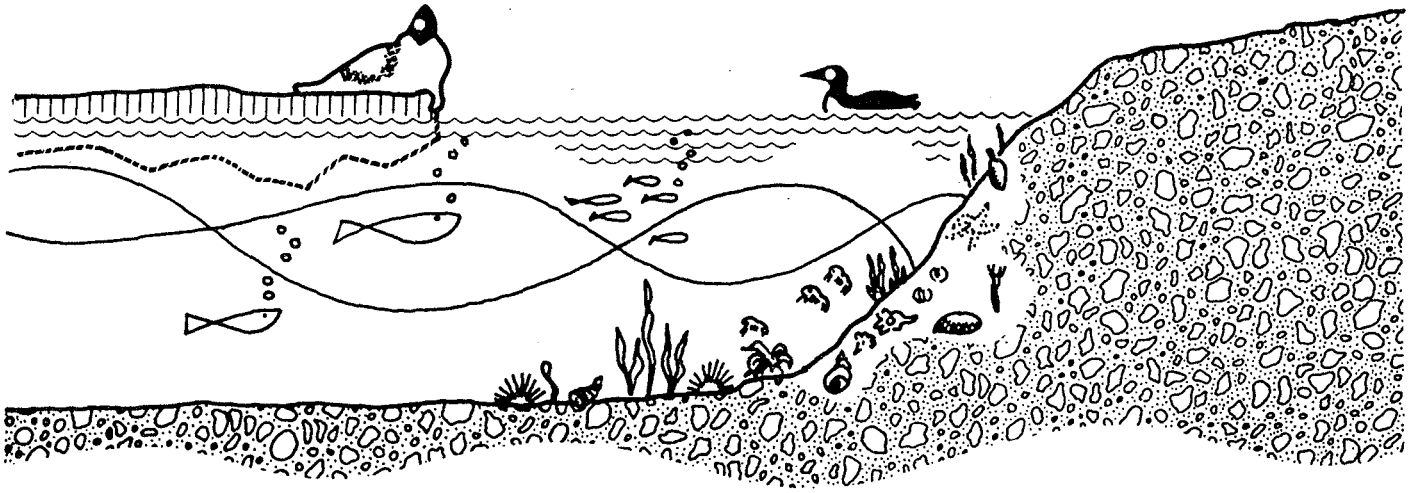
CHEMISTRY

2. Analytical Biogeochemistry



Baffin Island Oil Spill Project

WORKING REPORT SERIES

1982 STUDY RESULTS

The Baffin Island Oil Spill Project

OBJECTIVES

The Baffin Island Oil Spill (BIOS) Project is a program of research into arctic marine oil spill countermeasures. It consists of two main experiments or studies. The first of these, referred to as the Nearshore Study, was designed to determine if the use of dispersants in the nearshore environment would decrease or increase the impact of spilled oil. The second of the two experiments in the BIOS Project is referred to as the Shoreline Study. It was designed to determine the relative effectiveness of shoreline cleanup countermeasures on arctic beaches.

The project was designed to be four years in length and commenced in 1980.

FUNDING

The BIOS Project is funded and supported by the Canadian Government (Environment Canada: Canadian Coast Guard; Indian and Northern Affairs; Energy, Mines & Resources; and Fisheries & Oceans), by the U.S. Government (Outer Continental Shelf Environmental Assessment Program and U.S. Coast Guard), by the Norwegian Government and by the Petroleum Industry (Canadian Offshore Oil Spill Research Association; BP International [London] and Petro-Canada).

WORKING REPORT SERIES

This report is the result of work performed under the Baffin Island Oil Spill Project. It is undergoing a limited distribution prior to Project completion in order to transfer the information to people working in related research. The report has not undergone rigorous technical review by the BIOS management or technical committees and does not necessarily reflect the views or policies of these groups.

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Baffin Island Oil Spill Project
Chemistry Component 2
Analytical Biogeochemistry

Report on 1982 Field Experiments

Final Report
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ABSTRACT

The third year of the analytical biogeochemistry program as part of the BIOS experiments was conducted. The program focused on the persistence of oil in the benthic system, its weathering, and its transport. Water column samples were taken as well to examine possible movement of low levels of water-borne oil through the system.

The results indicate that oil is being transported from the Bay 11 beach and impacting this bay and perhaps the others as well at low levels. Significant biodegradation, as evidenced by an enhanced degradation of n-alkanes relative to the isoprenoid alkanes, was occurring on Bay 11 beach, but not in the offshore sediments. The presence of biodegraded residues in the heavily impacted (>10 ppm oil) offshore sediments and sediment floc of Bay 11 was due to offshore transport of beached residues. Levels in benthic animals decreased overall, the filter-feeders depurating oil to a greater extent than the deposit feeders due to the continued oil in Bay 11 and the increased presence of oil in these sediments.

Low levels (parts per trillion) of low molecular weight aromatics and saturates are apparently being introduced into the system as evidenced by the changing chemistry of the oil in benthic animals and by direct measurements of the water column and beach sediments.

Possible transport mechanisms that are responsible for persistant and some increasing oil levels in the various environmental compartments are discussed.

EXECUTIVE SUMMARY

The 1982 (one year post spill) field sampling and chemical analytical program was conducted to assess the fate of oil from the untreated surface oil spill and from the chemically dispersed spill which took place in areas designated as Bays 11 and 9 respectively along the east coast of the Ragged Channel area of Cape Hatt.

A combination of UV/fluorescence, gas chromatography (GC), and gas chromatography/mass spectrometry (GC/MS) measurements were conducted on water column, sediment, and animal tissue samples from the region.

Results indicated that although oil levels in the surface sediments of Bays 9 and 10 tend to decrease to levels in the 2-4 ppm range one year after the spill, the residual oil did not weather significantly during this time. Indications of significant microbial degradation were not observed in the GC patterns. While oil levels were higher at 7 meters depth than at 3 meters, there was no indication in these bays that higher concentrations of oil were not detected in sediments further offshore.

The animals in Bays 9, 10, and 7, while still containing low levels (1-20 ppm) of oil, had depurated substantial amounts of their original petroleum burden (100-500 ppm) during the year following the spills. Deposit feeders retained more oil than their filter-feeding counterparts. Of compositional significance was an observed "overprint" of low boiling saturates and aromatics seen in the filter feeders, Mya and Serripes. The source of these low boiling compounds, also found in water samples from the area, was probably the water soluble fraction of oil leaching off of the Bay 11 beach or trapped in the interstitial "groundwater" of the Bay 9 beach.

The composition of oil found in the Bay 9 beach sediments (1-20 ppm) closely resembled a water soluble fraction of the spilled oil. Oil found in

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SECTION ONE

INTRODUCTION

1.1 Project Goals

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

1. Establishing the concentrations of residual oil, its transport paths, fates, and weathering in the four bays in the various basic environmental compartments (i.e., water column, benthic sediments, organisms, shoreline) from samples of these compartments taken during the spring and summer of 1982.

2. Performing chemical measurements of the oiled shoreline plots (shoreline study) to determine concentration and composition of residual oil.

Once again, 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., glass capillary (fused silica) gas chromatography (GC^2), and computer-assisted gas chromatographic mass spectrometry (GC^2/MS), to give detailed compositional information, 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 identical to that used previously and involved the following sample types: surface sediments, sediment floc, sediment cores, sediment traps, beached sediments, benthic animal tissues (5 species), water column samples. The types of analyses

Table 1-1. Hydrocarbon biogeochemistry (Year 3) goals

1. To compare the composition and fates of oil as it impacted the four bays.

2. To examine the composition and concentration of high molecular weight petroleum components in a limited set of column samples taken from the four bays.

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

4. To explore the compositional fractionation of water-borne oil into dissolved and particulate classes.

5. To examine the composition and concentration of oil in bottom sediments and the related presence of oil in the suspended materials in the water column through sediment-trap samplings.

6. To analyze bottom sediments from all bays for oil content, composition, and weathering changes and 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.

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

used: UV/fluorescence, capillary gas chromatography and gas chromatographic mass spectrometry were 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. More emphasis was placed on GC^2 GC^2/MS analyses this year as it was assumed that the greater sensitivity and selectivity of these methods would yield more useful information during this phase of the study.

1.3 Summary of Previous Results

1.3.1 Summary of 1980 (Pre-Spill) Results (First-Year Study)

The goals of the first year study (see Boehm, 1981) were to fully characterize the Lagomedio oil used in the study and to determine the baseline levels of hydrocarbons in seawater, sediment and tissue from the Ragged Channel and Z-Lagoon areas. The results can be summarized as follows:

1. The oil was characterized as a high-Vanadium waxy crude having the chemical and physical properties shown in Table 1-2 and in Boehm et al.(1982a).

2. Seawater samples were "clean" with respect to petrogenic hydrocarbons, but 1-2 ng/liter of petroleum-like hydrocarbons were detected in large volume (200-liter) samples.

3. Sediment samples contained marine and terrigenous biogenic hydrocarbons, but low levels (1-4 ppb = ng/g) of pyrogenic polynuclear aromatic hydrocarbons (mainly phenanthrene, methyl phenanthrenes and perylene) were quantified as well. Their sources are global and/or local atmospheric transport of PAH from combustion of fossil fuels and *in situ* geochemical diagenesis.

4. Tissue hydrocarbon components were, for the most part, of biogenic origin although very low levels of some aromatic hydrocarbons could be detected (1-10 ppb).

Table 1-2. Saturated and aromatic hydorcarbon parameters of Lagomedio crude oil[a]

	Fresh Oil	Aged Oil
Saturates		
SHWR	2.87	2.28
ALK/ISO	2.36	2.50
PRIS/PHY	0.85	0.74
PRIS/n-C_{17}	0.51	0.38
PHY/n-C_{18}	0.61	0.62
Aromatics		
AWR	4.29	3.47

[a]Key:

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

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

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

PRIS = pristane

PHY = phytane

Details of baseline and oil characterization studies can be found in Boehm 1981.

1.3.2 Summary of Results of 1981 Oil Spill Experiment (Second-Year Study)

Discussed here are some of the most important observations and trends as they pertain to the behavior of oil in the experiments, and to specific important oil transport paths and biotal impacts. It is reproduced from Section Four of Boehm et el. (1982a).

The quantities of oil driven into the water column as a result of chemical dispersion were far greater than those that resulted from transport of untreated surface oil into the water column. Concentrations of chemically dispersed oil ranged from 1 to greater than 50 ppm ($\sim$100 ppm) during the dispersed oil discharge and for as long as twelve hours after discharge ceased at some points in Bay 9. Differential movement of oil released at different points along the diffuser resulted in direct northward movement of oil at greater depths of release (10 m,) and initial southerly movement of oil at shallower depths followed by subsequent reversal of direction and "reinvasion" of Bays 9 and 10 four hours after formal oil/dispersant discharge ceased. The dispersed oil plume formed a very stable layer of oil in the water column for perhaps 6-13 hours after dispersal. Dispersed oil droplets carried by strong shore currents were advected for considerable distances without a significant change in the composition of the oil. Whether this occurred due to the stability of the small ($\sim$10 μm) oil droplets, thus retarding fractionation (i.e., dissolution or evaporation), or whether particulate and dissolved parcels of oil traveled coherently due to strong advection (0.5 knot currents), is difficult to ascertain. Results of large volume water samplings that were taken outside of these concentrated plumes and after the passage of the highest concentrations indicated that a physical-chemical fractionation of hydrocarbon compounds did occur. It was, however, quite significant that fresh oil with its full suite

of low molecular weight saturated and aromatic components persisted as a coherent plume for considerable periods of time (6-13 hours), apparently cut off from evaporative loss from either the dissolved state or by advection to the surface. Indeed, confirmation of this coherent oil layer was made by fluorescence profiling and by discrete sampling, sometimes indicating a tenfold increase in water-borne oil concentrations within a water layer sandwiched by lower concentrations of more highly weathered oil. The persistence of low molecular weight saturates (C_6-C_{10} alkanes) and alkylated benzenes and naphthalenes in the plume in similar proportion to the total petroleum in the neat pre-aged oil was unexpected. Surely the subsurface release of dispersed oil accounted for this persistence. A surface release followed by application of chemical dispersants would have allowed some loss of light aromatics to occur by evaporation.

The very striking similarity between the BIOS dispersed oil plume behavior and that observed in the Ixtoc I spill is of no small importance. A subsurface release of oil that creates small oil droplets either through shear (Ixtoc) or through stabilization through chemical dispersion (BIOS) with resulting droplets advected by strong currents, results in subsurface coherent plumes of unweathered fresh oil with a full contingent of toxic aromatics. The similarities between the two events is also striking given the 25° C water column temperature differential between Gulf of Mexico and Arctic waters. Of course these initial high levels of oil (roughly 10 ppm in the Ixtoc I and 10 ppm and greater in the BIOS scenarios) will eventually be reduced through dilution and diffusion even if the coherent subsurface plume persists as it did for 20 km or so in the Ixtoc I spill.

During and after the dispersed oil experiment there was little evidence for either the large scale beaching of dispersed oil or the surfacing, in the water column, of dispersed oil. However, both phenomena did occur to minor extents and resulted in some important information. Oil that was found adhering to the Bay 9 beach was present at low levels (5-10 ppm). The oil had weathered significantly, due mainly to losses of low molecular weight components. Both the concentration of oil on the beach and its composition

were nearly identical to those found in the offshore benthic sediments implying a detectable but low sorptive affinity of dispersed oil. Oil which did appear to have coalesced at the sea surface was highly weathered through loss of low boiling saturates and aromatics. The state of weathering of this surface oil which was sampled several hours after initial dispersed oil discharge, was equivalent to that of nine day old beached surface oil (Bay 11). Thus it appears that the coalesced oil formed after solubles were stripped from the oil in the water column, with the coalesced oil forming from a weathered residue.

Oil did impact the sediments of Bays 9 and 10 immediately after the dispersed oil spill where initially a significant amount of the sedimented oil (~20%) resided in the surface floc. Sedimentation rates were estimated to be in the 2-10 $mg/m^2/day$ range. Subsequently, the floc was transported elsewhere, probably offshore, because floc from all bays sampled in the second post-spill period (September 11) was free of any detectable oil. Levels of oil in the sediments, however, remained elevated (1-5 ppm) in Bays 9 and 10. The overall sediment impact due to passage of dispersed oil through Bays 9 and 10 was minimal, with less than 1% of the discharged oil probably residing in the sediment at any time.

Results from the initial sampling of sediments indicated that 80% of the oil detected in the top 0-3 cm was not associated with the floc. This is in contrast to results from other spills (e.g., Boehm et al., 1982b) and to experimental tank studies in which most of the initially sediment-associated oil was in the floc layer. What appears to have occurred in the BIOS dispersed oil spill was a low level, direct and rapid penetration of dispersed oil into the bulk surface sediment, presumably a process mediated by the decrease of the oil's interfacial tension due to chemical dispersion allowing for penetration of the solid interface and perhaps into interstitial waters. Indeed chemical results from polychaete analyses in Bays 9 and 10 (Norstrom and Engelhardt, 1982) revealed an uptake of an alkylated benzene and naphthalene

(i.e., water soluble fraction) enriched petroleum hydrocarbon assemblage in Bays 9 and 10 only, perhaps associated with interstial water penetration of fractions of the oil.

The Bay 7 "control" did receive 50-100 ppb of dispersed oil in the first few days after the discharge. This quantity of oil was measured directly (Green et al., 1982) and was monitored indirectly through hydrocarbon body burdens in filter-feeding bivalves (i.e., Mya, Serripes). Direct sediment analyses and indirect evidence from deposit feeding animals (Macoma, Strongylocentrotus) indicate, however, that oil impact to Bay 7 sediments was quite minimal with only patchy low level inputs noted. The Bay 7 analytical results point to an important conclusion regarding application of UV/F and GC^2 techniques to the BIOS study. While background (by UV/F) levels of "oil equivalents" in the sediments was $\sim$0.5 ppm, many samples did exhibit post-spill oil levels of 1.0-1.5 ppm. In this concentration range, levels were too low to unambiguously yield an oil/no oil decision based on GC^2. Oil levels of $\sim$1.0 ppm would contain individual component concentrations (i.e., n-alkanes) of .01 ppm (or 10 ng/g). Due to significant biogenic background in the GC^2 traces, this level of individual components was often too low to see in the GC^2 traces. Thus UV/F becomes a key to assessing oil concentrations in sediments. However, in several cases in Bay 7 sediments, low UV/F levels ($\sim$0.3 ppm), generally associated with background levels, were shown by GC^2 to contain small amounts of oil. The weathering of oil while in transit to Bay 7 with resulting loss of water soluble aromatics and a concomitant decrease in UV/F response, caused whatever oil was seen in Bay 7 sediments to be relatively enriched in saturates (not detectable by UV/F). Thus the two techniques of UV/F and GC^2 proved to be an extremely powerful complementary set.

Water-borne oil in Bay 11 was initially confined to the surface (0-2 meters) layer during which time large scale transport of oil to the benthos via sorption and sinking did not occur. Through large volume water samples, low levels (ppb) of oil were detected in mid depth and bottom waters largely in a particulate form, prior to any possible cross contamination from the

dispersed oil spill occurring a week later. That oil did impact the sediment in Bay 11 prior to the dispersed oil spill is evident from uptake patterns of all of the benthic animals, especially those of the deposit feeders Macoma and Nuculana and of the filter-feeder Serripes, which revealed uptake of oil, albeit at lower levels relative to those which were acquired in the dispersed oil scenario, prior to any possible cross contamination from Bays 9 and 10. We do know that the dispersed oil's influence was far ranging including a transient water column impact at Bay 7 causing elevated levels of oil in all benthic biota, especially the filter feeders Mya and Serripes. Thus it may be logical to "subtract" the observed Bay 7 animal levels from the Bay 11 values to derive a "pure" Bay 11 result for the second post-spill sampling. Given the correctness of this logic, it can be concluded that, although low levels of oil are acquired in Bay 11 by the filter-feeders, the major Bay 11 impact is to the deposit feeders which are more closely linked to the sediments and which acquire weathered oil from off of the beach face.

The most significant findings of the study concern the relationship between water-borne and sediment concentrations of oil and levels in benthic biota. Initial uptake of oil by Mya and Serripes is from the water column wherein oil is acquired through pumping of contaminated seawater through the gills. Most of this oil initially resides in the animal's gut as confirmed through Serripes dissections. Chemically, even the initial oil residues in the gut and muscle tissue are different. The more water soluble aromatics (napththalene, alkylated benzenes) are transported to the muscle tissues (including gills) rapidly, while the less water-soluble aromatics (phenanthrenes and dibenzothiophenes) preferentially located in the gut. During the first two weeks after the spill however, it is these higher molecular weight aromatics which persist, the water soluble aromatics being depurated more readily. Initial levels of oil in filter feeders from Bay 7 are equal to or greater than those from Bays 9 and 10 where water column levels of oil were 20 to 200 times as great. Sediments can be ruled out as an oil-biotal intermediary due to the near absence of oil in Bay 7 sediments. Thus one must postulate that, while Mya and Serripes from Bays 9 and 10 either cease pumping due to water column levels or die after initial accumulation of oil,

animals in low-to-moderately contaminated waters continue to pump and acquire oil as long as it is present in the water. At water column concentrations of 50 µg/l (50 ppb) a clam (1 g dry weight) pumping at a rate of 1 liter per hour would pass ∿1.2 mg of oil through its body in 24 hours, more than enough to acquire a 100-500 ppm concentration. As levels of oil in Bays 9 and 10 were much higher, 1-50 ppm initially and 100-200 ppb for at least a day to a day and a half after cessation of the oil spillage, opportunities for greater bioaccumulation in Bays 9 and 10 were available but were probably not achieved due to either saturation in the gut, an inability to transport oil across the membranes fast enough to acquire more oil, or a wholesale cessation of pumping.

Whereas Mya and Serripes acquire oil through the water column and depurate 60-75% of it in two weeks time, Macoma and Nuculana acquire oil mostly through the sediments. Initially low-to-moderate oil levels in Macoma and Nuculana increase in Bays 9 and 10 where sediment impacts are greatest, and also in Bay 11 where offshore movement of beached oil results in higher initial (1 day) accumulation of oil in Macoma than with the filter-feeders and in higher concentrations in Macoma two weeks later as well. GC^2 profiles show evidence of uptake of oil from sediment rather than from the water column in deposit feeders after perhaps an initial (∿30-50 ppm) water column uptake. Bay 9 and 10 deposit feeders continue to take up oil as evidenced by increasing absolute levels and maintenance of a relatively unbiodegraded GC^2 profile and a low CPI (i.e., oil dominates terrigenous n-alkanes).

As previously discussed the two oil spill experiments conducted introduced oil into the nearshore system in two distinct manners. The Bay 11 surface oil (untreated) spill resulted in detectable water-borne oil concentrations only in the top meter or so of the water column (Green et al., 1982). That low levels of water soluble oil may have penetrated to the benthos during the first day or so following the spill can not be confirmed from direct chemical evidence of water samples, but may have occurred, causing the low initial increases in petroleum hydrocarbon levels and levels of water soluble aromatics in some of the filter feeders (Mya, Serripes, Astarte). That oil did impact the Bay 11 benthos as soon as one day after

the spill is indicated by the uptake of oil by Macoma, Pectinaria and Strongylocentrotus revealed in the immediate post-spill period. Subsequent benthic impact of oil in Bay 11 is clearly indicated in increased sediment concentrations (~5 ppm) as well as by the increased uptake of oil by the deposit (detrital) feeders. The oil reaching the benthos during the 1 day to 3 week post-spill period was weathered due to evaporation/dissolution as evidenced by the loss of alkylated benzene and napthalene compounds relative to the spilled oil.

The uptake and depuration curves during the first several days are difficult to reconstruct due to differences in sampling times. For example, it is not clear whether higher levels of oil in Serripes in Bay 10 versus Bay 9 were due to a combination of animal behavior and water column concentration or due to the additional day during which they acquired oil. Alternatively, filter feeders may very well have "shut down" their pumping systems in Bay 9 (or were narcotized or killed outright) due to high water column levels, while those animals in Bay 10 may have continued to pump and acquire more oil. Indeed this seems to have been the case in Bay 7. Low levels of oil (50-100 ppb) were detected in Bay 7 two days after the spill (Green et al. 1982), as were these same levels in Bays 9, 10 and at other Ragged Channel locations. Bay 7 Serripes were especially efficient at concentrating oil from these lower water column levels with oil residing primarily in the gut initially. The fact that Serripes and Mya from Bay 7 were probably not physiologically affected by those lower levels of oil probably resulted in their normal pumping of water throughout the first several days after the spill.

As alike as Mya and Serripes behave vis-a-vis routes of oil uptake, they differ in the compositional nature of the oil which they retain. During the two week post-spill period of depuration, an in vivo biodegradation presumably by a microbial population within the animals guts occurred to a significant extent. At this point the similarity between Mya and Serripes erodes because although on a gross level both species depurated oil, on a detailed chemical basis Serripes preferentially retained a high molecular weight saturated

hydrocarbon assemblage as well as the higher alkylated naphthalene, phenanthrene and dibenzothiophene compounds. Mya on the other hand depurated all hydrocarbon components, although the water soluble alkyl benzenes and naphthalenes were depurated somewhat faster.

Thus as the exposure levels in the water column decreased, levels in Mya decreased as well as did the gross oil levels in Serripes. This plus the fact that whole, undegraded (microbial) oil resided in Bay 11, 9 and 10 sediments without a concommitant increase in concentrations in oil levels in the filter feeders effectively decouples sedimentary sources of hydrocarbons from these animals. This decoupling is accented by the fact that while oil residues in sediments were not degraded, residues in the animals were microbially degraded.

Macoma, Nuculana, Strongylocentrotus and Pectinaria clearly are influenced by oil levels in the sediments more so than by those in the water column. Though there is some indication that low levels of soluble aromatics in the water were reflected in early oil compositions in the deposit feeders, steady uptake of sediment-bound oil by this group dominates. Thus the lack of detectable sediment-bound oil in Bay 7 is reflected in much lower petroleum body burdens in deposit feeders from this bay. Additionally over two weeks we see much less of an indication of microbial degradation in the Bay 9, 10 and 11 deposit-feeding animals due to the acquisition of undegraded oil from the sediments appearing as a constant compositional overprint. Furthermore, those aromatic hydrocarbon components longest lived in the sediments (i.e., alkylated dibenzothiophene and phenanthrene compounds) steadily increase in the deposit feeders.

Thus the various filter feeders and deposit/detrital feeders reflect the fate of oil in the system quite well. The fact that the polychaete acquires whole oil, dominated somewhat by a water-soluble grouping of alkylated benzenes and napthalenes, may reflect the association of oil with interstitial waters in the upper sediment column.

Parallel behavior to that related here of filter-feeding versus detrital feeding bivalves has recently been noted in an accidental spill (Boehm et al. 1982b). In this study the authors have found that the benthic-dwelling Macoma balthica was slower to initially acquire oil than was the filter-feeder Mytilus edulis which resided in the phytal zone. After beaching and erosional transport, and/or direct sedimentation of oil, the petroleum body burden increased in Macoma and only slowly decreased as the sediment levels dropped. Mytilus, on the other hand, exposed to a massive initial amount of water-borne oil, depurated rapidly and almost completely over one year's time.

During the first two to three weeks after the spills there was a notable lack of significant biodegradation of oil in the water column and in the sediments. No chemical evidence was found for the existence of biodegradation as a removal mechanism with the short-term post-spill period (3 weeks) either in the water column or in the sediment. One would have predicted higher rates of biodegradation in surface sediments, especially in the surface floc, but none was observed through degradation of the "easily" degraded n-alkanes. However, degradation of n-alkanes in the oil resulting in the classic loss of n-alkane relative to isoprenoid and other highly branched alkanes, was observed within Mya and Serripes and to lesser extents in other benthic species. Rapid degradation of alkanes only occurred in vivo. Whether or not this unique finding can be ascribed to microbiotal populations within the organism itself, a likely mechanism, must be independently confirmed. We suspect that, given an unspecified amount of time, microbial populations will begin to utilize the hydrocarbons as an energy source (i.e., biodegradation will become more significant).

The use of a variety of biological monitors or sentinel organisms in the BIOS study has served to both delineate oil transport paths and changing environmental compartment levels with time during the immediate post-spill (0-3 weeks) period. Furthermore, this study has shown that although similarly behaving animals (e.g., Mya/Serripes; Macoma/strongylocentrotus) may on a gross level appear to act in concert, the details of in vivo modifications and retentions of individual petroleum components are quite different and may

be initimately associated with long-term biological effects on the individual benthic species.

One question persists: What transport processes may act in the short term to move oil within the Ragged Channel system? Evidence from the initial post-spill period does indicate that (1) the oil-contaminated floc is a transient phenomenon, and (2) sediment concentrations tend to increase with depth (3 m to 7 m). This implies that initial deposition of oil increased with distance offshore and that subsequent movement and transpot of oil may cause more of a benthic impact farther offshore into Ragged Channel. Of course the movement of sediment-bound oil in Bay 11 is linked to erosion of beached oil as well.

Thus the major findings of the 1981 program were that: (1) very important trends in Arctic biotal uptake mechanisms and depuration trends were revealed, (2) the lack of significance of sedimentation of chemically dispersed oil was ascertained (<1%), (3) the rapid penetration of small, but significant quantities of dispersed oil residues into benthic sediments (below the floc layer) was established, (4) the coherent subsurface movement of "fresh" dispersed oil without evaporation of toxic components was observed, (5) the lack of significant biodegradation inthe 3-week post-spill period was determined, (6) the *in vivo* biotal microbial degradation of oil was observed, and (7) the relative retention of three-ringed alkylated aromatic hydrocarbon and organic sulfur compounds in tissues and in sediments was confirmed, thus implying their usefulness as long-term markers of the oil in all environmental compartments.

SECTION TWO

SAMPLING AND ANALYTICAL METHODOLOGY

2.1 Sampling

Samples of seawater, offshore sediments, beach sediments, benthic animals, and surface oil were collected from the experimental bays on Cape Hatt, Baffin Island, during May, August and September, 1982 (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 summary of the sampling design and methodology is presented here.

The sediment and tissue sampling design centered around the grid shown in Figure 2.3, which was identical to that used in 1981 collections. Sampling activities occurred during three times during which a large amount of over-sampling took place (vis-a-vis number of samples eventually analyzed). In May, sediment samples, Mya and Strongylocentrotus (urchins) were collected in each bay by divers at points along the 7m depth stratum. The sampling focused around the sample types shown in Figure 2.4.

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 droebochiensis). Surface floc was obtained from these tissue plots in Bay 11. Sediment cores (0-15 cm) were obtained at the north and south ends of the 7m stratum in each bay. Several sediment samples were also obtained in Bays 9 and 11 further offshore in 15m of water, one in line with transect 1 and one with transect 3. Samples were obtained at the microbiology stations in each bay during seven "cycles" from early August through mid-September.

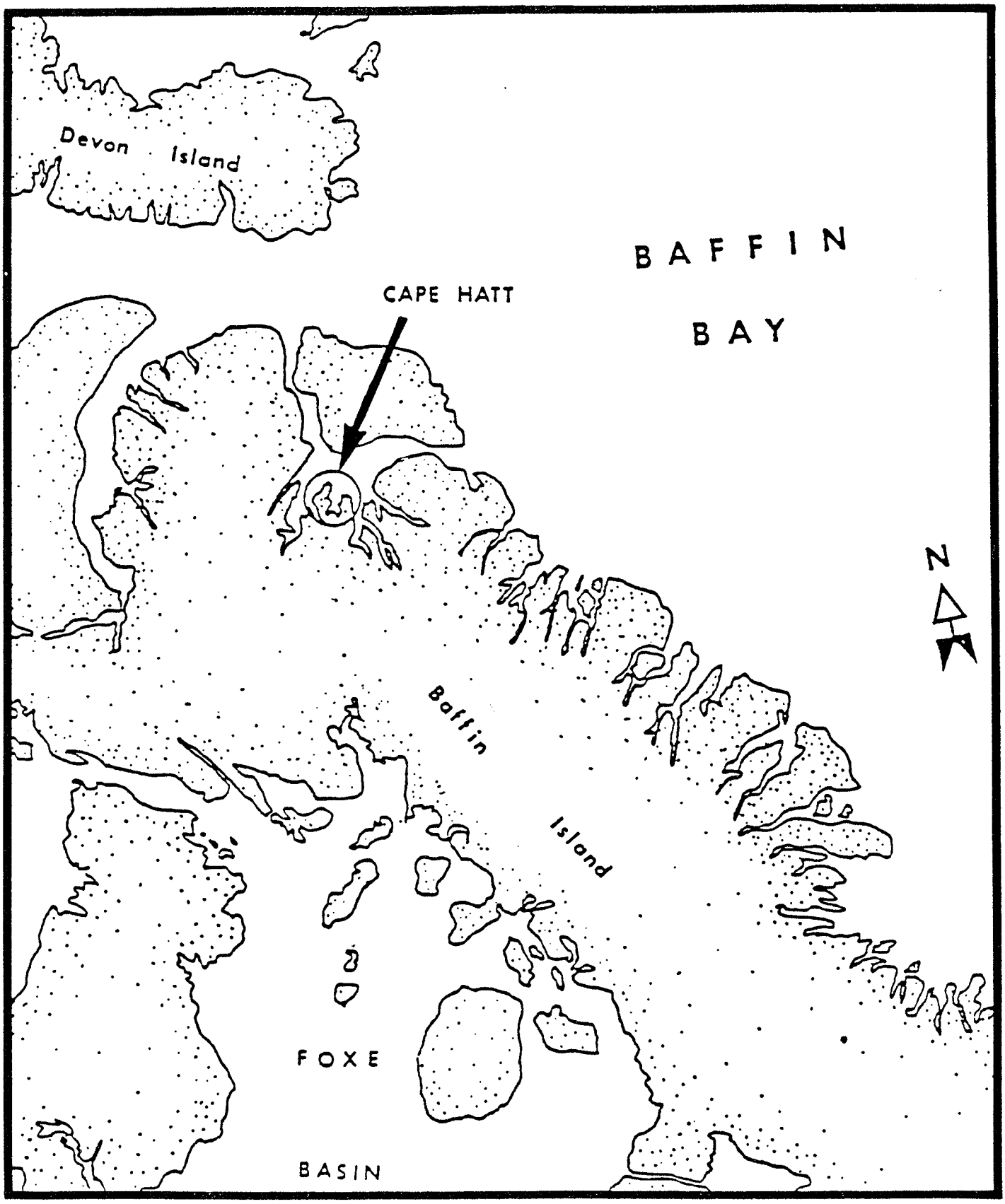


Figure 2.1. Location of Cape Hatt, Baffin Island.

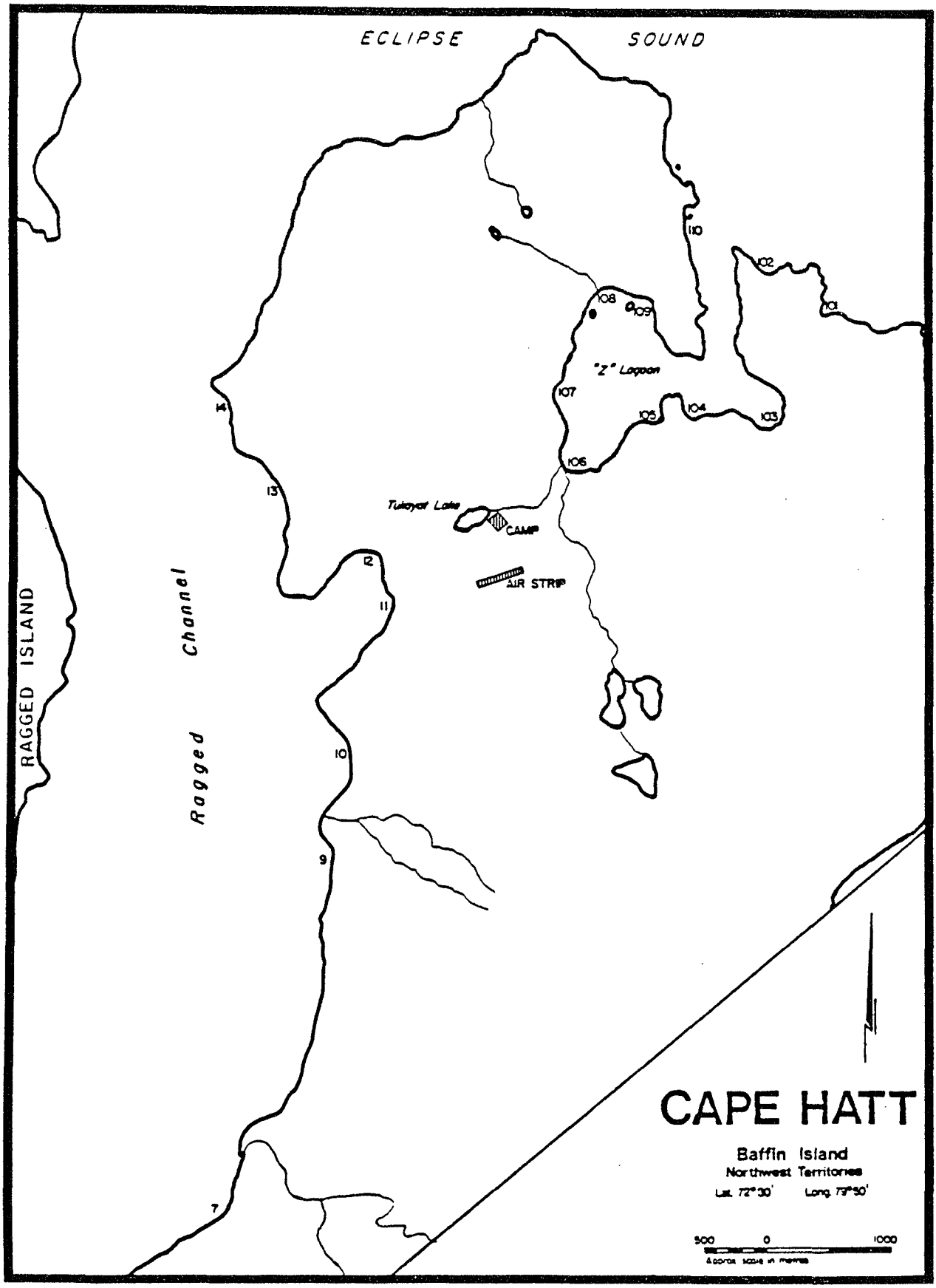


Figure 2.2. Detail of test bay locations.

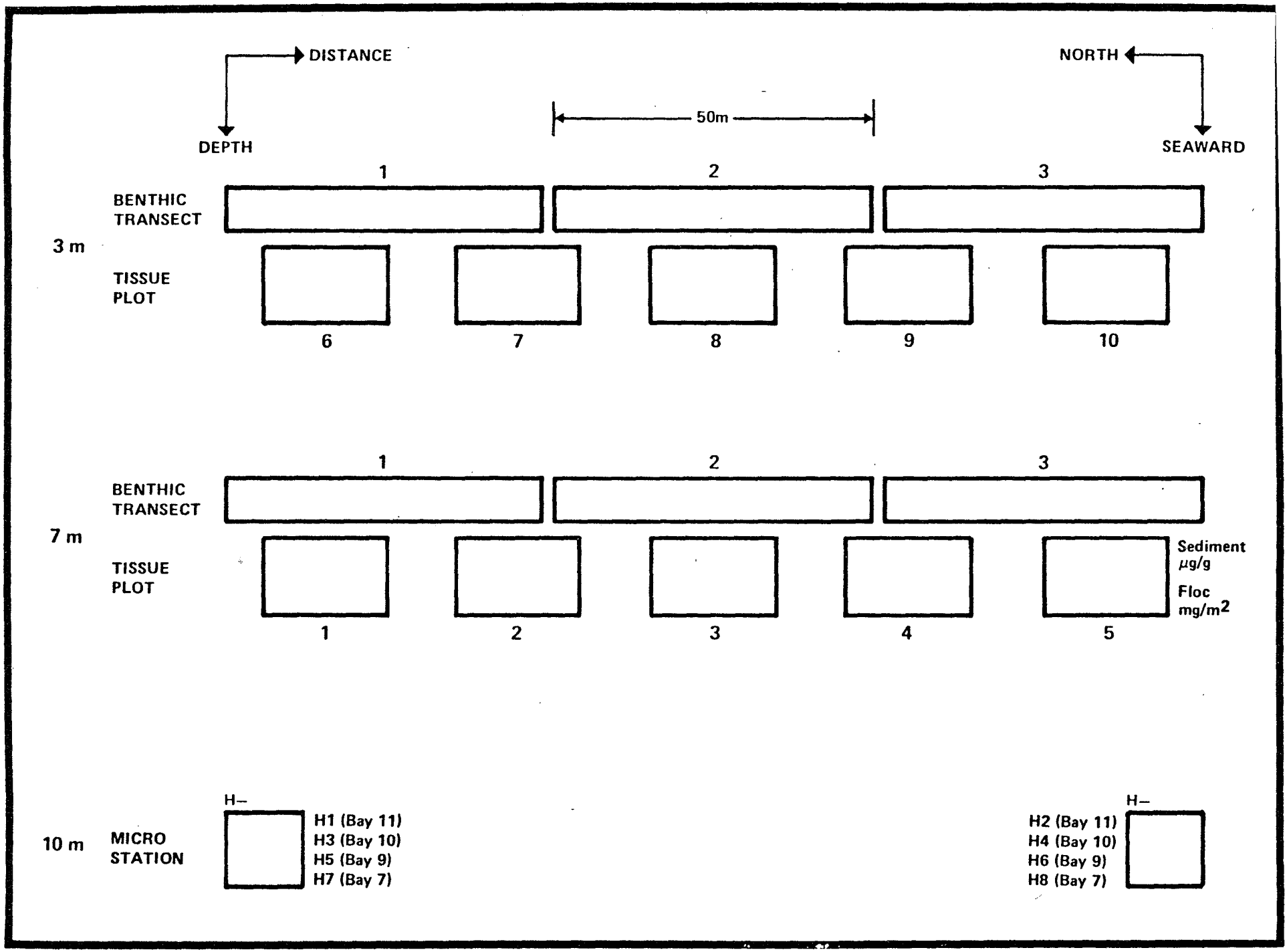


Figure 2.3. General description of benthic sampling grid used in each bay.

Figure 2.3. General description of benthic sampling grid used in each bay.

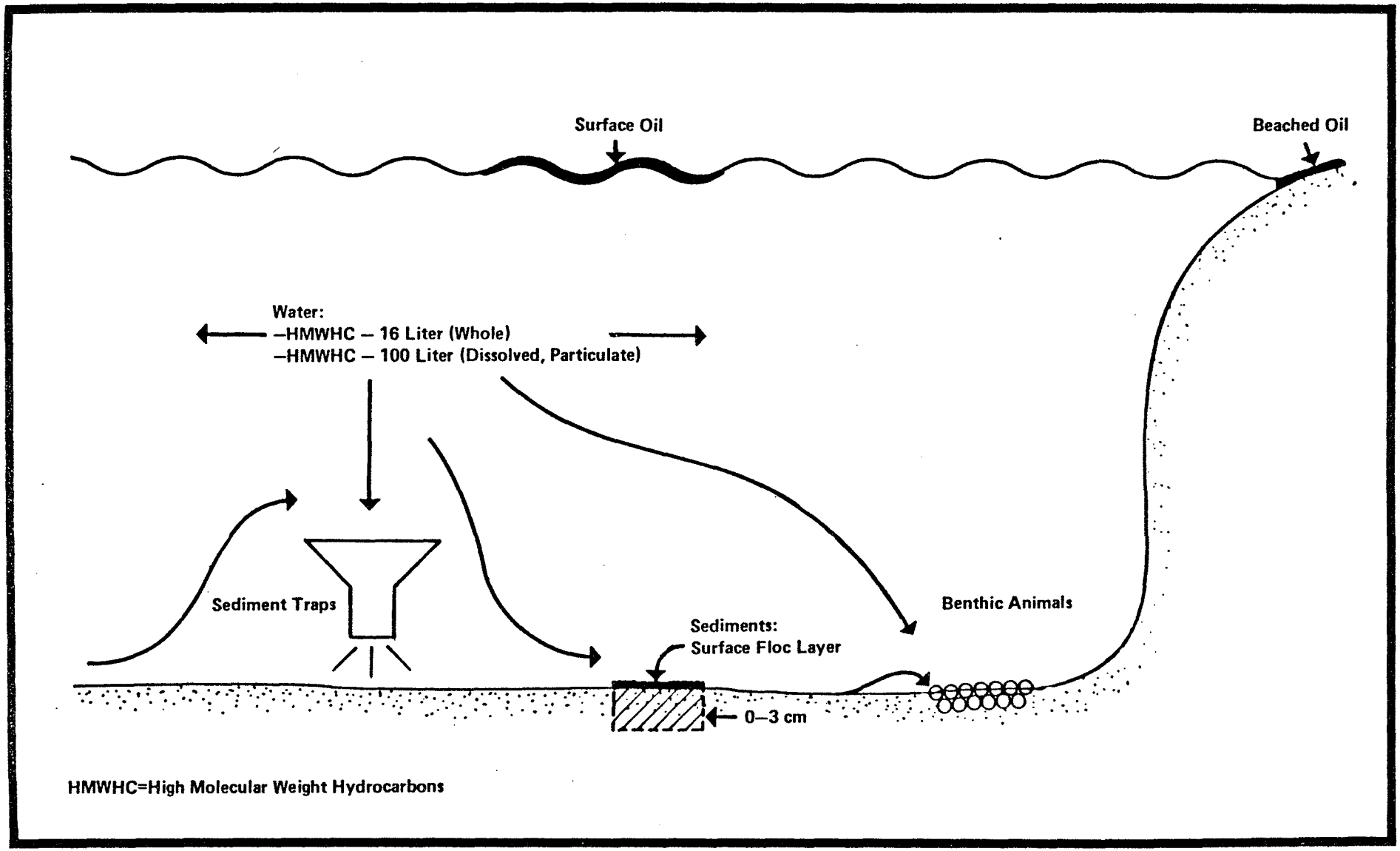


Figure 2.4. Sample Types Acquired for BIOS Chemistry Studies (Nearshore Study).

The water column sampling design is described in Humphrey et al. (1982) and the shoreline sampling design in Owens et al. (1982).

2.1.1 Seawater Sampling

Seawater was collected for two types of analyses: (1) high-molecular-weight hydrocarbon analysis from 16 liter samples, and (2) high-molecular-weight hydrocarbon analyses from large volume samples (100 liters). The latter sample type (large volume) were collected also in Bays 9, 7 and 10.

A National Bureau of Standards (NBS) water sampler was used to collect the 16-liter sample. 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/adsorption 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 10 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 for storage 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, 10, 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 and 1981 countermeasures plots (shoreline study in Z-lagoon) were taken from randomly predesignated subareas within a test plot. Beach sediments from Bay 11 were sampled from three stations (high-, mid- and low-tide marks) along each of two transects. Beach sediments from two transects in Bay 9 were collected once.

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 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 was as follows. A glass fiber filter (Gelman Type AE) was placed in the filter holder, the apparatus was lowered over the side of an inflatable boat and the pump was primed with clean water. With the diverter valve in the "Waste" position, the pump was turned on and lowered to the bottom. When positioned, the diver placed the funnel on the sediment surface and turned the diverter valve to the "Collect" position which directed the seawater/ floc slurry to the filter holder. The diver held the funnel in position for

30 seconds at each of four locations, thereby collecting floc from a surface area of approximately 0.1 m^2.

Suspended sediments were collected in sediment traps deployed by divers at easily found locations such as the end of a transect or the Baffin Queen anchor. The traps were left in place for several days to two weeks. Samples were collected in all four bays.

The trap, which consisted of a glass beaker inside a PVC cylinder (11 cm diameter x 50 cm length) mounted on a base, was capped and held vertically during deployment and recovery operations. When recovered, the water in the top of the trap was drained through a bung. The contents of the beaker were poured into a glass jar and frozen. Typically, biological detritus and fine sediment were collected by the sampler.

2.1.3 Benthic Animal Sampling

Benthic animals were collected from Bays 9, 10, 11, and 7.

Divers picked *Mya truncata* and *Strongylocentrotus* 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 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 2.5). 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 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.

Four types of samples (water, sediments, tissues, and oils), 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 2.6).

2.2.1 Water Sample Processing

2.2.1.a High Molecular Weight Hydrocarbon Analysis (6 liter)

Sixteen-liter seawater samples were analyzed for high molecular weight hydrocarbons by GC^2. The water was processed in the field laboratory by extracting with Freon three times, and 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 ERCO, the extracts were dried with sodium sulfate, evaporated to <1 ml by rotary evaporation, and displaced with hexane. Three

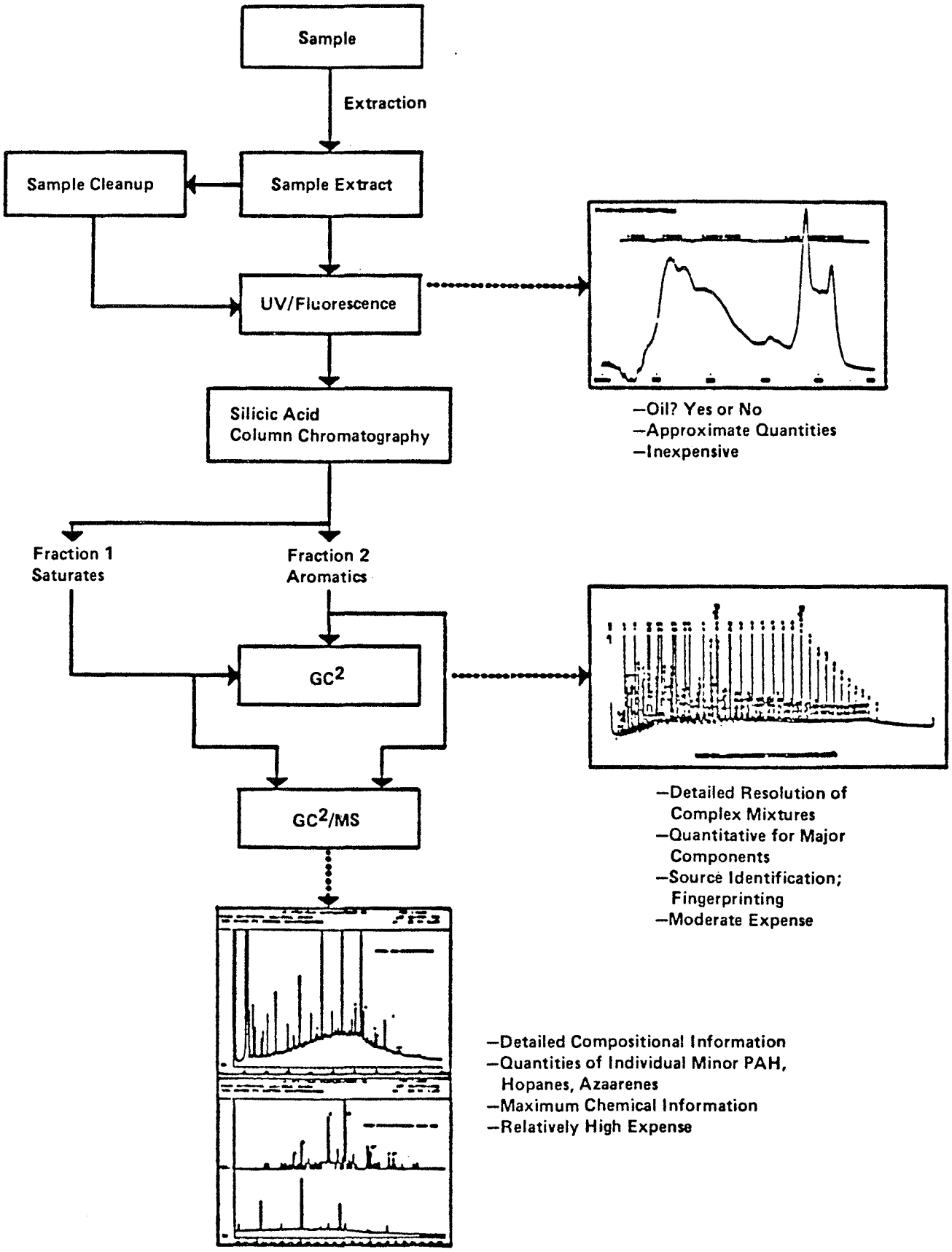


Figure 2.5. Schematic of Analytical Strategy.

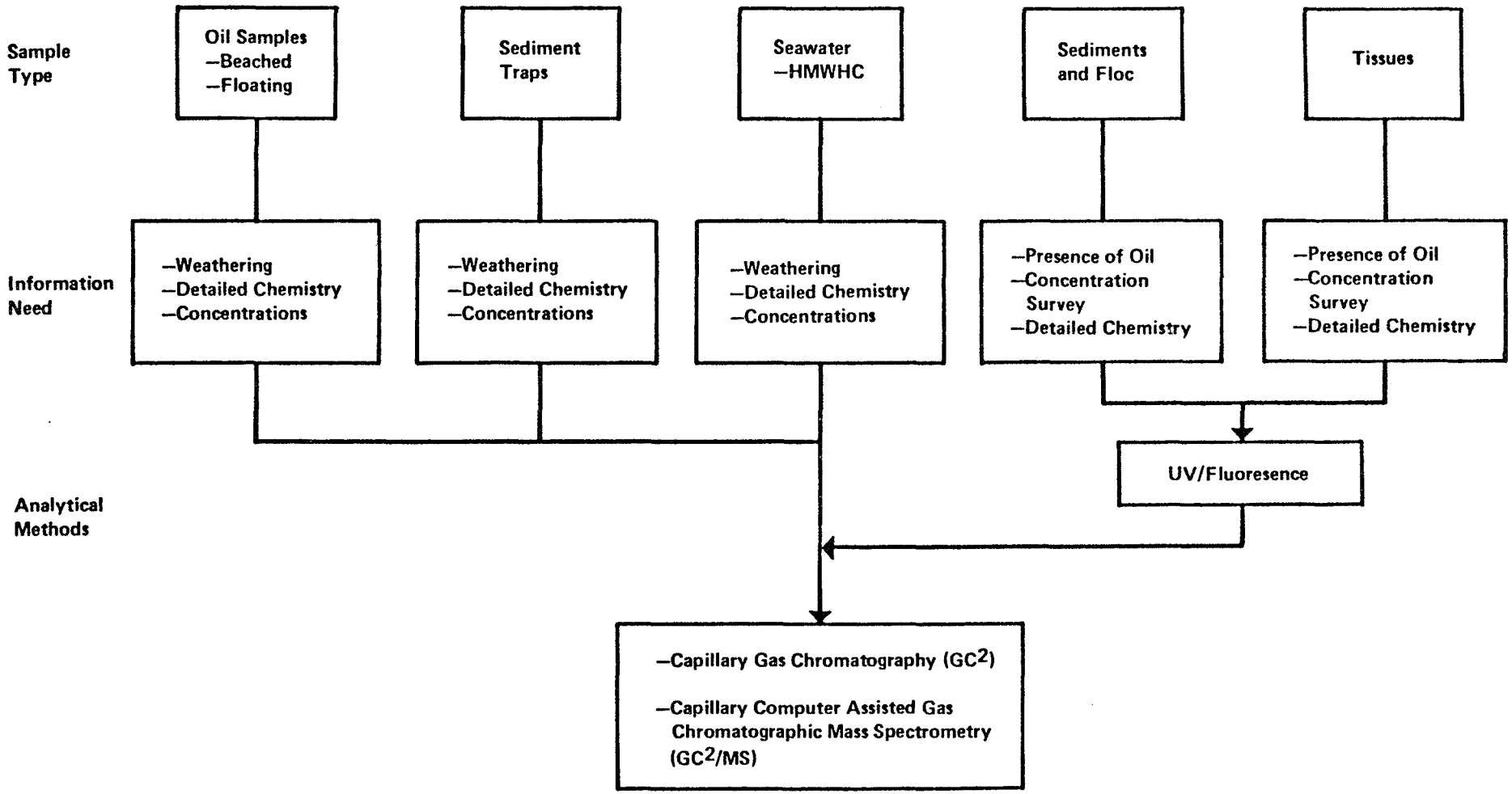


Figure 2.6. BIOS Analytical Protocols.

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. Those samples containing high levels of total extractables were 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). Those samples containing low levels of total extractables were analyzed directly by GC^2 without column chromatography. Aromatic fractions and total extracts of selected samples were analzyed by GC^2/MS (see Boehm et al. 1982a).

2.2.1.b High Molecular Weight Hydrocarbon Analysis (Large Volume)

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, dried with sodium sulfate, reduced in volume to <1 ml by rotary evaporation and displaced with hexane and 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 Boehm et al. 1982a) into saturated and unsaturated/aromatic fractions which were analyzed by GC^2 (see Boehm et al. 1982a). Aromatic fractions of selected samples were analyzed by capillary GC^2/MS (see Boehm et al. 1982a).

The plugs were processed 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, reduced in volume to <1 ml by rotary evaporation and the solvent 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 2.2.7) into saturated and unsaturated/aromatic fractions which were analyzed by capillary GC^2. Aromatic fractions of selected samples were analyzed by capillary GC^2/MS.

2.2.2 Sediment Sample Processing

Four types of sediment samples were collected and analyzed: surface sediment samples (0-2 cm), sediment floc samples, oiled beach sediments, and sediment trap samples. Each was analyzed by a unique set of analytical methodologies.

2.2.2.a Surface Sediment Sample Analysis (0-2 cm)

Surface sediment samples were analyzed for high-molecular-weight hydrocarbons using both UV/F and GC^2 techniques. Ten gram subsamples from the tissue plots and microbiology stations were analyzed by UV/F using the analytical method described below. Selected samples from individual tissue plots and microbiology stations were analyzed by GC^2 using an additional subsample ($\sim$100 g). Selected sediments collected from the benthic transects were analyzed by UV/F using a 10 g subsample. Extracts were fractionated by silica gel/ alumina column chromatography into saturated and unsaturated/ aromatic fractions which were analyzed by GC^2.

The extraction method for the UV/F analyses of sediment samples was a modified version of the GC[2] method described below. Approximately 10 g of wet sediment was weighed into a 50 ml glass centrifuge tube with a Teflon closure. The sediment was dried by extracting 3 times with 15 ml of methanol. The dry sediment was then extracted four times with 20 ml of dichloromethane: methanol (9:1) by shaking for 10 minutes on an orbital shaker for each extraction. All solvent extracts were transferred to a 250 ml separatory funnel containing 50 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 three times with 15 ml of dichloromethane. The dichloromethane extracts were combined, reduced in volume to < 1 ml by rotary evaporation and the solvent displaced with hexane.

Polar compounds which interfered with the UV/F analysis were removed from the extract by alumina column chromatography. The procedure was based on the methodology of Georlitz and Law (1974) and is summarized below. The total extract was charged to a chromatography column (9 mm ID) containing 6.5 g of a 7.5% water deactivated alumina that was wet-packed in hexane and prepared by eluting with 30 ml of hexane. The column was eluted with 25 ml of hexane to isolate the saturated, unsaturated, and aromatic compounds. The hexane fraction was concentrated by rotary evaporation, displaced with cyclohexane and analyzed by UV/F.

The extraction method for the capillary GC[2] analysis (see Boehm et al. 1982a) 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. An aliquot of the extract was 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.

2.2.2.b Surface Floc Analysis

Surface floc samples were analyzed for high-molecular-weight hydrocarbons using both UV/F and GC^2 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 interfere with the UV/F by alumina column chromatography as described for surface sediments. All samples 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.

2.2.2.c Oiled Beach Sediment Analysis

Oiled beach sediments were analyzed for high molecular weight hydrocarbons using only GC^2 techniques. The analytical methodology was, with one exception, the same as that described for GC^2 analysis of surface sediments. The sediments contained small amounts of water and were not dried with methanol prior to extracting them with dichloromethane:methanol (9:1). The

total extracts were fractionated by silica gel/alumina column chromatography into saturated an unsaturated aromatic fractions which were analyzed by capillary GC^2 Aromatic fractions of selected samples were analyzed by GC^2.

2.2.2.d Sediment Trap Analysis

Sediment trap samples were analyzed for high-molecular weight hydrocarbons using only GC^2 techniques. The sediment/water slurry (125 ml) was thawed, poured into a 250-ml separatory funnel and extracted three times with 50 ml of dichloromethane. Three micrograms of two internal standards, androstane and o-terphenyl, were added to the extract which was dried with sodium sulfate, reduced in volume to <1 ml and displaced with hexane. An aliquot of the extract was weighed on a Cahn Model 25 electrobalance to determine total extractable organics. Those samples collected during the first week after the experimental spills were fractionated by silica gel/alumina column chromatography into saturated and unsaturated aromatic fractions which were analyzed by GC^2 . Those samples collected during the second week after the spills were directly analyzed by GC^2.

2.2.3 Benthic Animal Tissue Processing

Five species of benthic bivalves were analyzed: Mya truncata, Serripes groenlandica, 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, bay and sampling time 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. (1982b).

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 Vitris tissue homogenizer, and a 10 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 methanol solution, and extracted 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, respectively, to isolate the saturated, unsaturated and aromatic compounds. The fraction was concentrated and transferred into cyclohexane for UV/F analysis.

After UV/F analysis, the extract from the tissue plot stations along each depth stratum were combined and concentrated by rotary evaporation and the solvent displaced with hexane. The pooled extracts were fractionated by silica gel/alumina column chromatography into saturated and unsaturated/aromatic fractions which were analyzed by GC^2 . Selected extracts from individual tissue plot stations were similarly fractionated and analyzed by GC^2. Aromatic fractions from selected samples were analyzed by GC^2/MS.

2.2.4 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 fluorecence response. The intensity of the fluorescence spectra was measured at 355 nm

Table 2-1. UV spectrofluorometry analytical conditions

Instrument:	Farrand Mark I spectrofluorometer
Features:	Corrected excitation Corrected emission
Slits:	
Excitation:	2.5 nm
Emission:	5.0 nm
Scan speed:	50 nm/min
Cell:	10 mm quartz
Monochrometers:	Synchronous
Excitation:	225-475 nm
Emission:	250-500 nm
Daily calibration:	Bay 11 Lagomedio oil
Quantification:	External standard

(or the nearest spectral maxima) 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 the Bay 11 oil standard curve.

2.2.5 Fractionation

Those sediment, tissue, and water samples chosen for GC^2 analyses and all of the oil samples were fractionated by silica gel/alumina column chromatography prior to fused silica capillary gas chromatography. 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 procedure was that of Boehm et al. (1982b) and is summarized below.

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 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.

2.2.6 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, and the weathering age of the 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 SE52 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 analytical outputs from the GC^2 analysis are listed in Tables 2-3 and 2-4. The concentrations of n-alkanes and isoprenoids were reported on a dry weight basis. From these concentrations a series of key diagnostic parameters were calculated. These ratios are useful in establishing the composition of the oil, the contribution of biogenic hydrocarbons, and the degree that the oil was weathered.

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

Selected samples found to contain petroleum by the GC^2 analyses were analyzed by GC^2/MS to measure the concentration of 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.

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 SE 52 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° Æ 3° C/min
Daily calibration:	Alkane/aromatic mixture
Quantification:	Internal standard (F_1 androstane, f_2 o-terphenyl)

TABLE 2-3

COMPOUNDS QUANTIFIED BY FUSED SILICA CAPILLARY GAS CHROMATOGRAPHY

COMPOUND	ANALYTICAL TECHNIQUE	USE
Saturated hydrocarbons		
n-alkanes ($n\text{-}C_{10}$ to $n\text{-}C_{34}$)	Capillary GC	Weathering and source indicators, especially when ratios are derived
Isoprenoids (farnesane, pristane, phytane, 1650, 1380)	Capillary GC	Weathering indicator (marker compounds as a group in lightly weathered samples)

TABLE 2-4

EXPLANATION OF PETROLEUM WEATHERING RATIOS

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.

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.

The Aromatic Weathering Ratio (AWR)

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

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

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 SE52 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. If necessary, the mass spectrum and retention time of an identified peak was retrieved and compared with an authentic standard or to a mass spectrum library to aid in identification of the compound. An in-house probability-based computer matching system, the HP 7920 multi-disc system containing EPA/NIH probability-based mass spectral libraries, was utilized for this purpose.

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 SE52 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
Alkyl benzenes (AB)
C_3 to C_6 Benzenes (C_3AB-C_6AB)
Naphthalenes (N) Naphthalene (C_0N) 2-Methyl naphthalene (C_1N) 1-Methyl naphthalene (C_1N) C_2 to C_4 Alkyl naphthalenes (C_2N-C_4N)
Biphenyl
Acenaphthene
Fluorene C_1 to C_3 Fluorenes
Phenanthrenes (P) Phenanthrene (C_0P) C_1 to C_4 Phenanthrenes (C_1P) - C_4P)
Dibenzothiophenes (DBT) Dibenzothiophene (C_0DBT) C_1 to C_3 Dibenzothiophene (C_1DBT-C_3DBT)
Fluoranthene
Pyrene C_1 Pyrene
Benzo(a)anthracene
Chrysene C_1 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 slick)

A group of three surface samples collected in areas of visible sheening in Bay 11 were analyzed to examine the extent of weathering of these hydrocarbons as they were emitted from the beached oil. Concentrations of oil in the surface sheen water ranged from 350-640 µg/l (ppb), far higher than bulk water values. The ALK/ISO and phytane/ $n\text{-}C_{18}$ values (Table 3.1) were nearly equal to that in the aged Lagomedio crude oil in which the ALK/ISO and phytane/ $n\text{-}C_{18}$ values were 2.6 and 0.63, respectively. The saturated hydrocarbons in the sheen appear to be relatively unweathered (Figure 3.1), with respect to the saturated hydrocarbons, the SHWR values being quite similar to that of the aged crude oil. No evidence of significant biodegradation is seen as well in the ALK/ISO or phytane/$n\text{-}C_{18}$ values.

GC^2/MS results, Figure 3.2, however, indicate that the aromatic component of the sheen is moderately to highly weathered due to physical-chemical weathering. The aromatic weathering ratio (AWR) values shown in Table 3.1 indicate that $\sim$80% of the naphthalenes, fluorene, and alkylated benzenes have been weathered from these samples compared to the aged Lagomedio. Thus we see differing extents of saturated and aromatic hydrocarbon weathering, the latter being much more extensive probably due to solubility losses rather than evaporative losses.

3.1.2 Oil in the water column

Two types of samples were taken. Three 16-liter bulk water samples were taken from Bay 11. Fourteen samples of particulates and filterable hydrocarbon

Table 3.1. Water sample oil concentrations and composition: Bay 11

Sample	Oil Concentration (μg/liter)	SHWR	Phy/n-C_{18}	ALK/ISO	AWR[b]
Surface sheen (3009)	350	2.0	.64	2.5	1.40
Surface sheen (3010)	610	2.4	.85	1.8	-
Surface sheen (3011)	640	2.1	.63	2.2	1.36
Surface water (3012)	(1.0)[c]	-	.57	3.1	-
Bottom water (3013)	(1.3)[c]	-	.33	11.1[a]	-
Intertidal water (3014)	(0.9)[c]	-	-	10.6[a]	-
Aged Lagomedio	-	2.3	.63	2.6	3.5

[a]Values suspect due to low levels and possible contaminants.

[b]By GC^2/MS.

[c]Numbers in parentheses represent quantity of n-alkanes in the n-C_{22} to n-C_{32} region (see text).

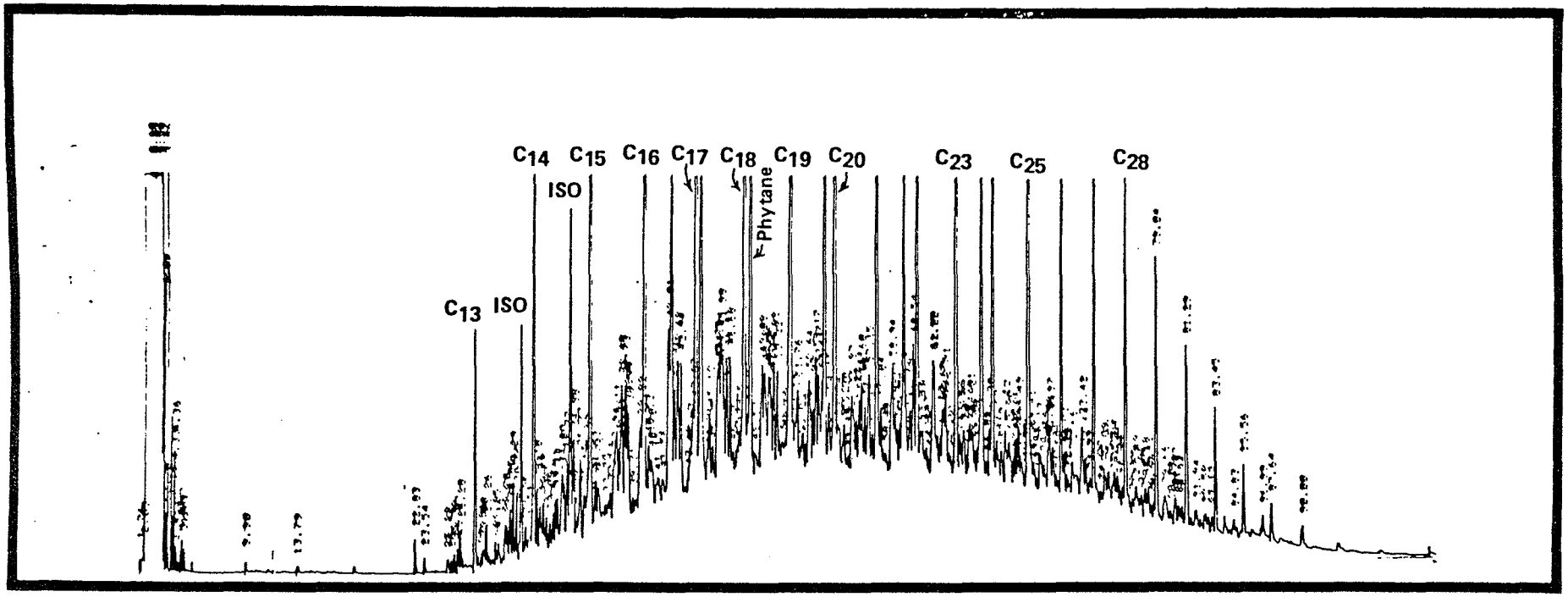


Figure 3.1. GC^2 trace of Bay 11 surface sheen water (16L Sample).

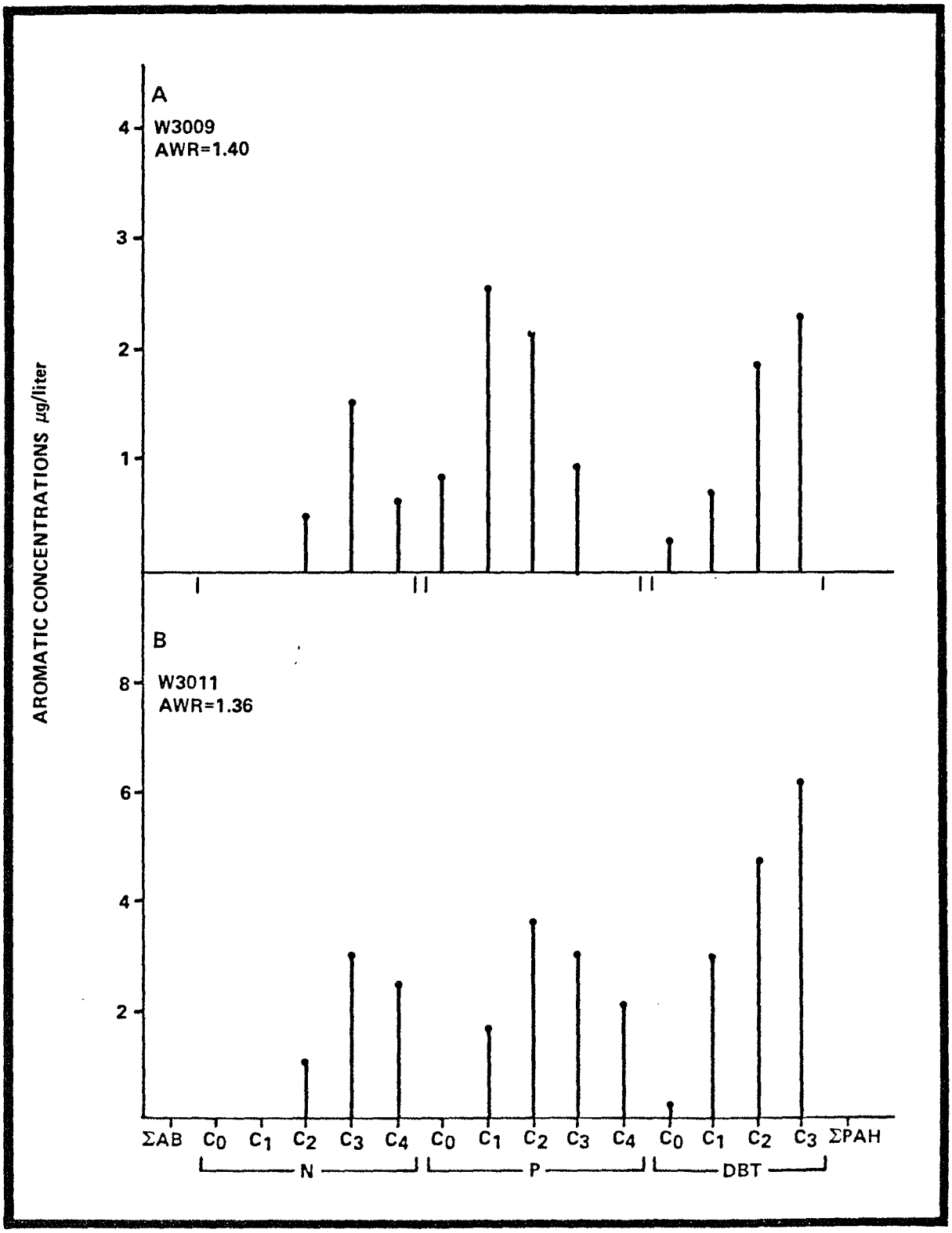


Figure 3.2. Surface sheen water from Bay 11: GC^2/MS results.

material were obtained from the four bays through the large volume (100 liter) water sampling (foam plug) method.

3.1.2.a High molecular weight hydrocarbons (16-liter samples - Bay 11)

Three four-liter samples (Table 3.1) were obtained from the water column in Bay 11. GC^2 analyses of these samples revealed a saturated hydrocarbon composition quite unlike that of the spilled oil in that a smooth distribution of n-alkanes in the boiling range n-C_{22} to n-C_{33} (maximum at n-C_{26}) range was seen in all of the samples. The source of this distribution is unknown and is probably not directly related to the oil. N-alkane levels were ∿0.1 µg/l each in this range and comprise 90-95 percent of the "total oil" value reported in Table 3.1. Actual total values of oil in the "normal" Lagomedia boiling range were 0.04 to 0.1 µg/liter.

3.1.2.b High molecular weight hydrocarbons (large volume samples)

3.1.2.bi Bay 9

Two large volume water samples were obtained from Bay 9. The filterable material obtained in the polyurethane plug contained only trace quantities of n-alkanes and no aromatic components (Table 3.2). Likewise the filters, which would contain any particulate oil, only contained traces of petrogenic residues.

3.1.2.bii Bay 10

The two samples from Bay 10 (Table 3.2) contained trace quantities of oil with total alkane levels in the .03 µg/liter range for the dissolved and particulate fractions each. By GC^2 the aromatic fractions contained no detectable components. Figure 3.3 illustrates the composition of a typical sample from Bay 10 containng trace levels of oil.

Table 3.2. Large volume water samples: Data summary - All Bays (GC^2 and GC^2/MS)

Bay	Sample No.	Date	Status	Total Petroleum (µg/liter)	Phy/ $n\text{-}C_{18}$	ΣAromatics (ng/liter)	AWR
Plugs ("Dissolved" or Filterable Oil)							
9	L3005 (N-micro)	8-18	ND	.01	-	-	-
9	L3011	8-25	Trace oil	.01	-	-	-
10	L3004 (N-micro)	8-18	ND	<.01	-	-	-
10	L3010	8-25	Trace oil	.03	-	-	-
7	L3006 (N-micro)	8-18	Trace oil	.03	-	-	-
7	L3012	8-25	Trace oil	<.01	-	-	-
11	L3001 (Baffin Queen 10m)	8-17	Trace oil	.04	-	-	-
11	L3002 (Baffin Queen 0.5m)	8-17	Trace oil	.04	-	-	-
11	L3007 (Near Bottom)	8-25	Trace oil	<.01	-	-	-
11	L3008	8-25	Trace oil	<.01	-	-	-
11	L3009 Intertidal	8-25	Low oil	.29	.57	140	1.5
11	L3013 Intertidal (.3m)	8-21	Low oil	.94	-	100	1.5

Table 3.2. Continued

Bay	Sample No.	Date	Status	Total Petroleum (µg/liter)	Phy/ n-C_{18}	ΣAromatics (ng/liter)	AWR
Filters (Particulate Oil)							
9	L3005	8-18	ND	.02	.30	-	-
9	L3011	8-25	Trace oil	.02	-	-	-
10	L3004	8-18	Trace oil	.04	.30	-	-
10	L3010	8-25	Trace oil	.03	.2	-	-
7	L3006	8-18	Oil	.08	.25	-	-
7	L3012	8-25	Trace oil	.01	-	-	-
11	L3001	8-17	Oil	.09	.25	-	-
11	L3002	8-17	Trace oil	.06	.50	-	-
11	L3007	8-25	ND	<.01	-	-	-
11	L3008	8-25	Trace oil	.03	.30	-	-
11	L3009	8-25	Oil (degraded)	.04	1.5	4	1.0
11	L3013	8-21	Oil (degraded)	1.1	2.8	130	1.1

ND = None detected.

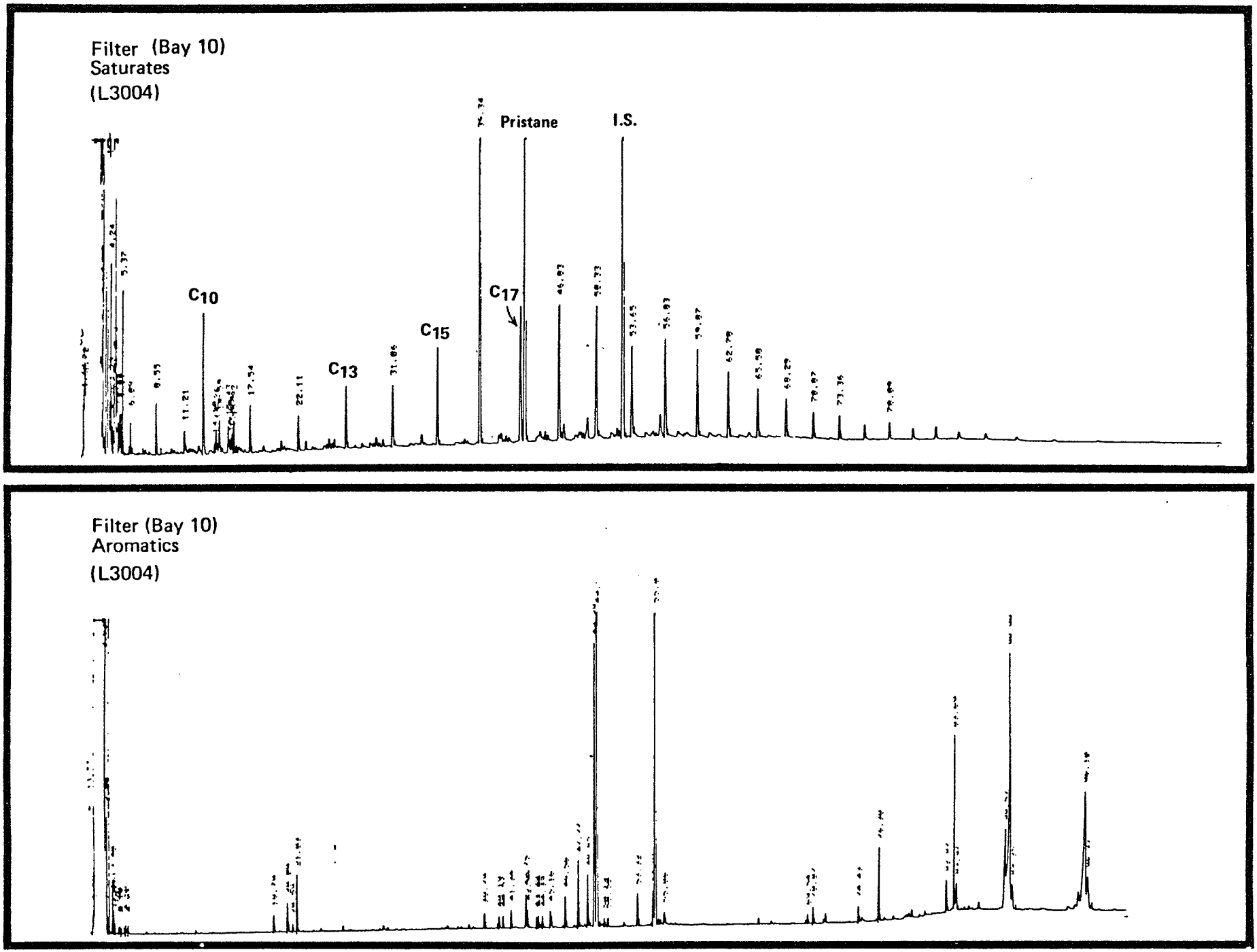


Figure 3.3. GC^2 traces, large volume water samples, Bay 10.

3.1.2.biii Bay 7

The results from Bay 7 (Table 3.2) are quite interesting because not only do both samples obtained contain measurable levels of oil but also one sample (L3006) contains moderate quantities of oil in both the particulate (Figure 3.4a) and dissolved fractions. The filter contained low molecular weight alkanes as low as n-C_{10} (Figure 3.4a). These low boiling n-alkanes may be related to the source of a different, lower boiling range oil seen in Bay 7 sediments as well (see Section 3.2.3). This oil is perhaps a lower boiling distillate of unknown origin. The total quantity of petroleum hydrocarbons in this sample is about 0.2 µg/liter.

3.1.2.biv Bay 11

Six large volume water samples were obtained from Bay 11. Trace levels of oil were found in four of the samples (L3001, 3002, 3007, 3008) with total levels of oil in the dissolved fraction equal to .01 - .02 µg/l and in the particulates, .01-.09 µg/l. Two of the samples contained larger quantities of petroleum hydrocarbons. Sample L3009 contained larger quantities of oil in the dissolved fraction (.29 µg/l total and .10 µg/l of aromatics) than on the particulate fraction .04 µg/l. The particulate oil (Figure 3.4b) appeared mildly biodegraded as seen by the phy/n-C_{18} ratio greater than 1. The dissolved fraction (Figure 3.5) contained a different alkane distribution with the n-C_{23} to n-C_{30} distribution of possible microbial origin seen in the saturate fraction, along with singificant aromatic compounds in the aromatic fraction. The particulate oil from sample L3013 (Figure 3.6) contains significant saturated and weathered aromatic material.

GC^2/MS results on the four analyses shown in Figure 3.7 indicate that in the L3009 sample aromatics were primarily found in the dissolved fraction (i.e., plug). In 3013, similar amounts of aromatics were found in both the particulate and dissolved fractions. However, the aromatic compositions were different with the more soluble two ringed naphthalenes in the dissolved fraction and the three ringed aromatics preferentially on the particulates.

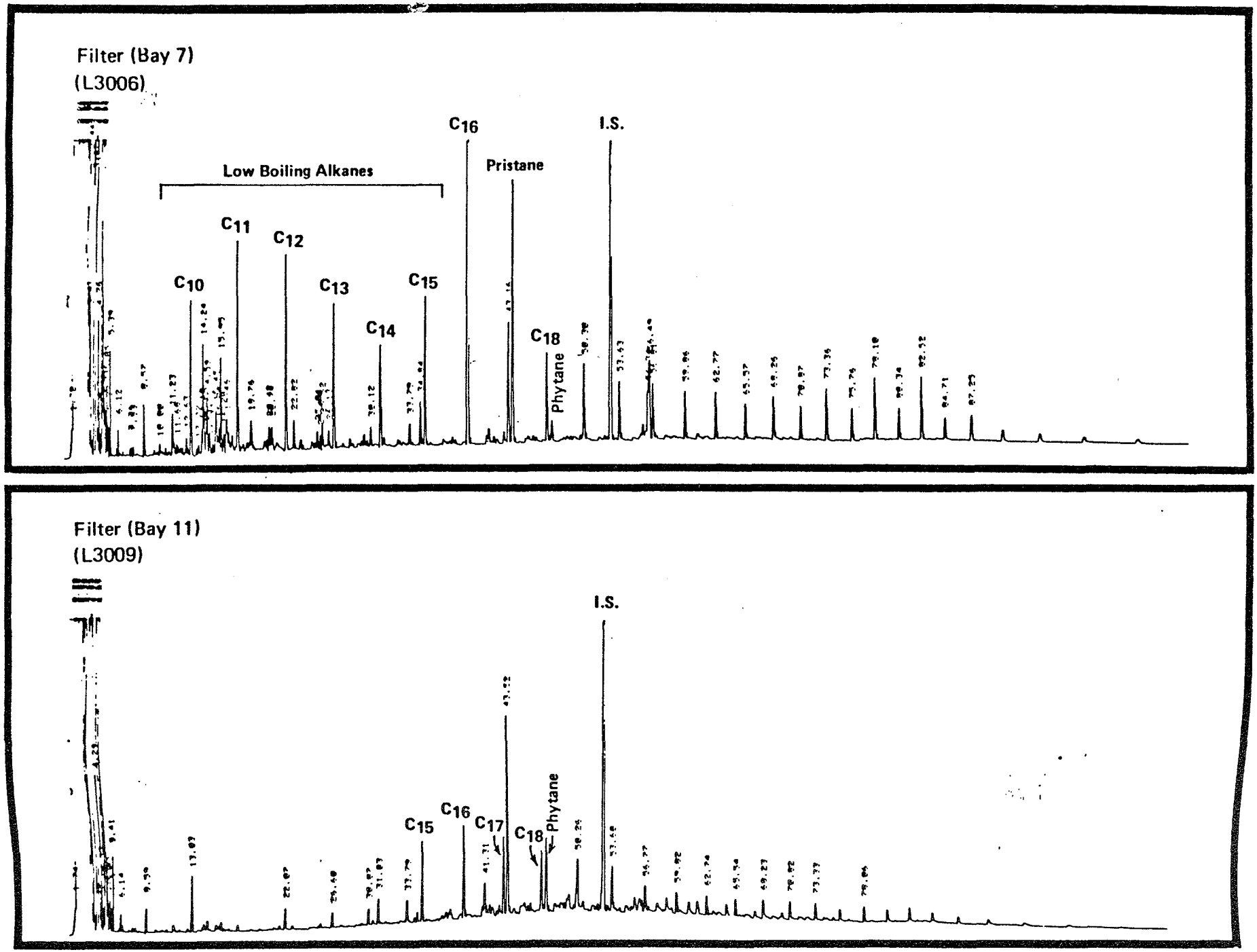


Figure 3.4. GC^2 *saturated* hydrocarbon traces, large volume water samples, Bays 7 and 11 (particulate oil).

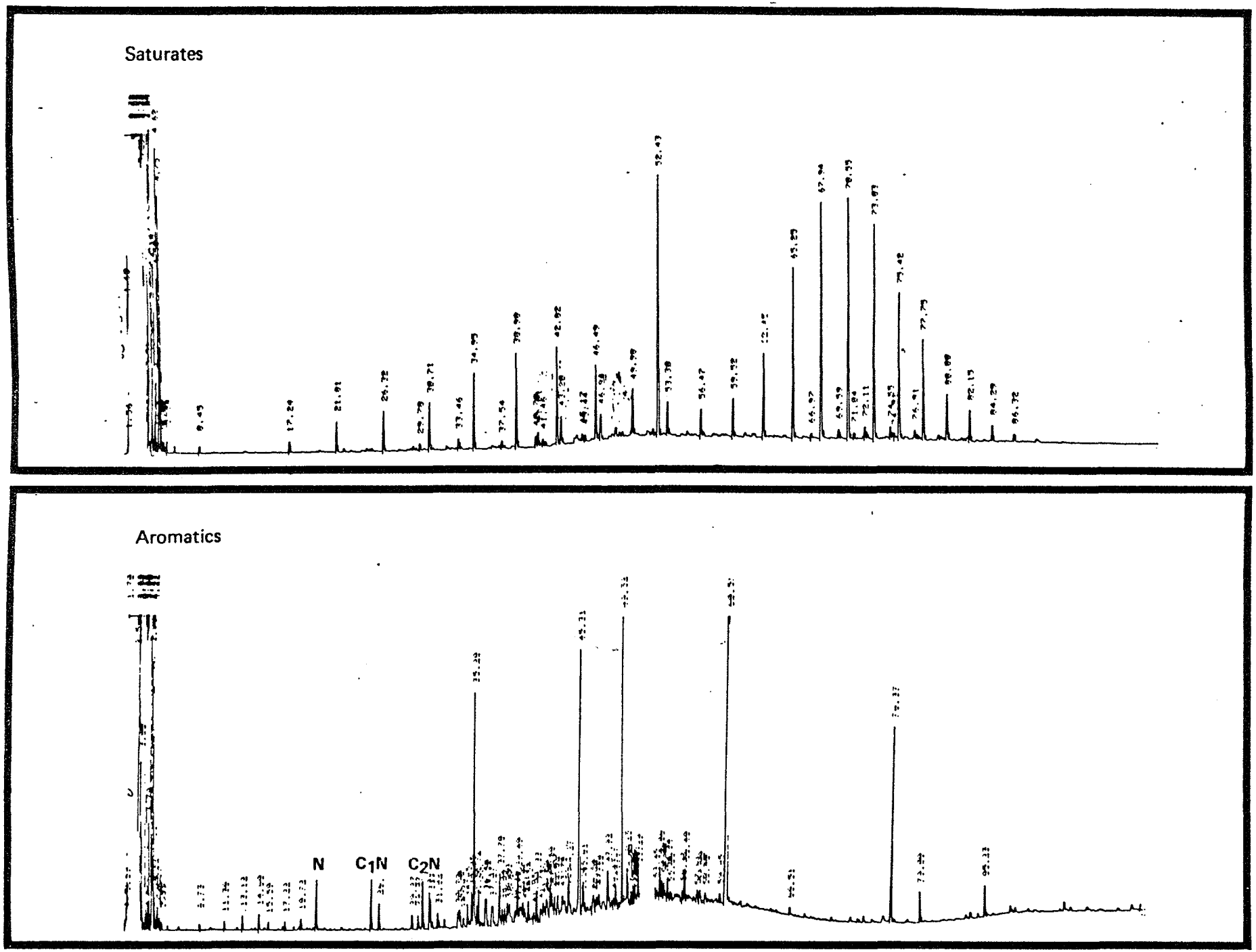


Figure 3.5. GC^2 trace of large volume water sample (L3009), Bay 11, dissolved fraction.

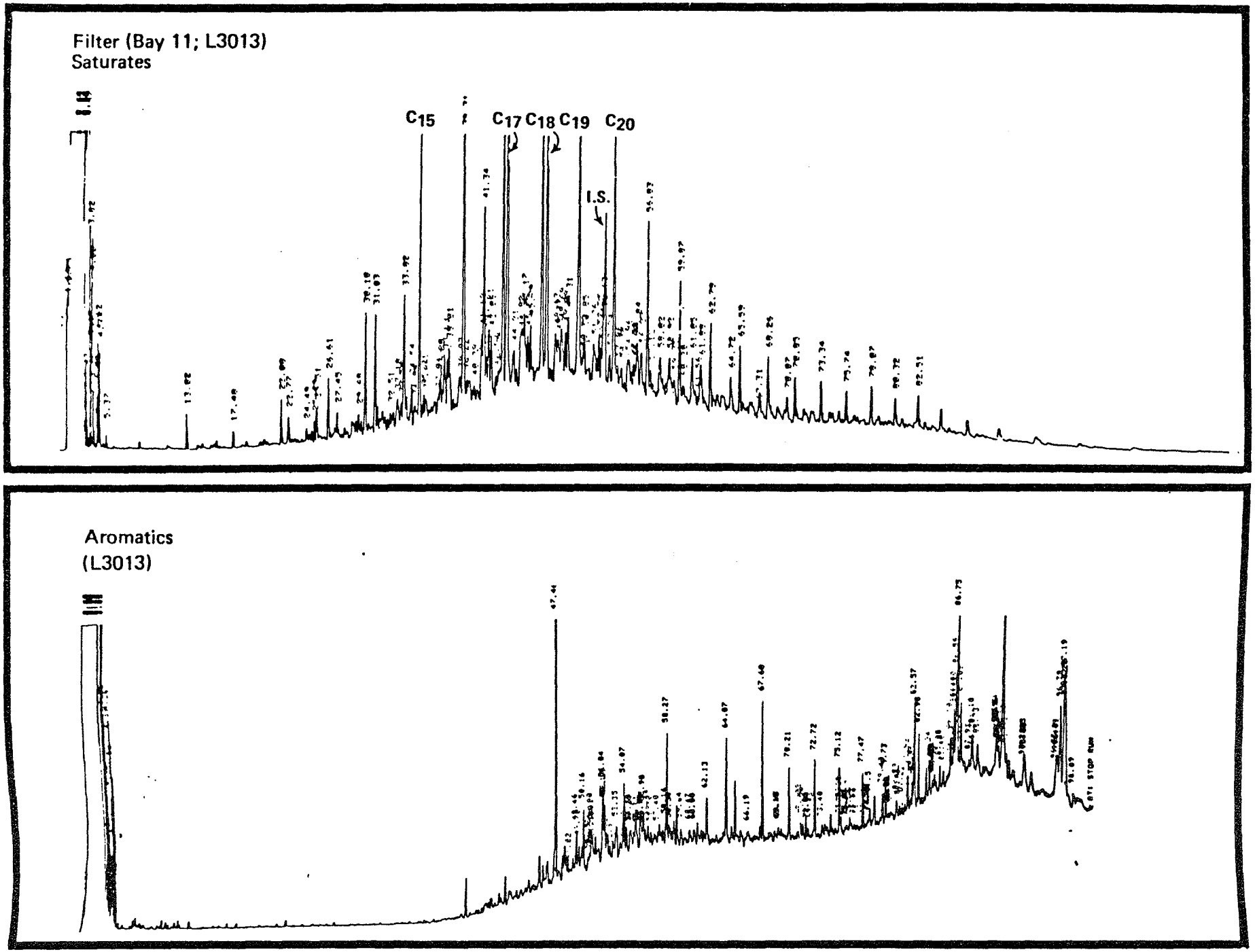


Figure 3.6. GC^2 trace of large volume water sample, Bay 11 (particulate oil).

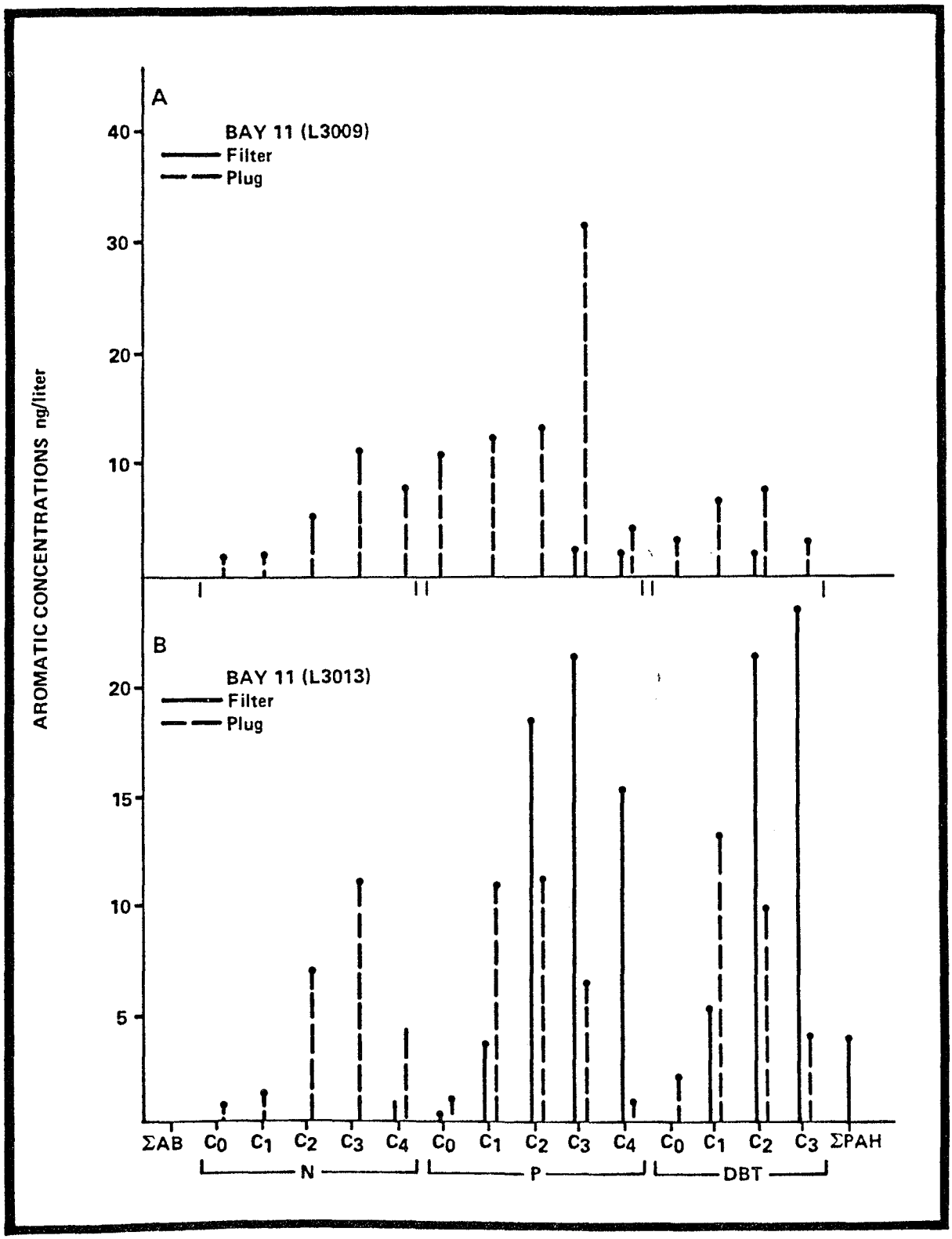


Figure 3.7. Large volume water samples, Bay 11: GC^2/MS results.

3.2 Oil in the Sediments

Several different sets of sediment samples were taken for analysis. A limited set of diver-obtained samples were acquired in May prior to ice breakup at the microbiology station. The main sampling occurred in August, at which time surface sediment samples were obtained by divers from within the tissue plots. The benthic biology transects were also sampled in August.

In addition to the surface sediment (0-2 cm) surface floc was obtained by divers from the 3 and 7m tissue plots in Bay 11. Sediments were also obtained at four sites seaward of the 7m tissue plots (two each in Bays 9 and 11) to determine if oil had been transported to deeper areas in the Ragged Channel area. To examine vertical penetration of oil into the sediments, sediment cores (15 cm) were obtained from Bays 9, 10, and 11. Finally, suspended or resuspended sediments were analyzed for possible petrogenic residues by virtue of a series of sediment trap samplings.

A summary of oil concentration data in sediments is presented in Table 3.3.

3.2.1 Bay 9

3.2.1.a Tissue plots (surface sediments)

3.2.1.ai Oil concentrations by UV/F

Samples of surface sediment were collected from Bay 9 tissue plots on August 17, 1982. Concentrations in sediments shown in Table 3.3 and Figure 3.8 are in µg/g dry weight. The levels of petroleum fluorescent equivalents observed averaged 2.2 µg/g. The pre-spill values observed in 1981 were 0.3-0.4 µg/g. The 1-day and 2-week post-spill results in 1981 were 2.1 and 9.0 µg/g respectively for the 7m tissue plots. It appears that significant levels of petroleum still reside in these sediments, levels

Table 3.3. Summary of surface sediment oil concentrations (August 1982)

Bay	Tissue plot	Benthic transect	Micro station (cycle 2)	No. of samples	Concentration: Arithmetic Mean (µg/g) (X±S)	Concentration: Geometric[a] Mean
9	7m	--	--	9	2.5±1.6	2.2 (1.5,3.1)
	--	1 (3m)	--	3	1.1±0.4	1.0 (.66,1.6)
	--	2 (3m)	--	3	.63±0.4	.52 (.23,1.2)
	--	3 (3m)	--	3	.91±.08	.91 (.83,1.5)
	--	--	H5	1	6.2	--
	--	--	H6	1	3.3	--
10	7m	--	--	9	1.7±.54	1.7 (1.4,2.0)
	--	1 (3m)	--	3	.85±.26	.83 (.58,1.2)
	--	2 (3m)	--	3	.68±.02	.68 (.66,.70)
	--	3 (3m)	--	3	.81±.53	.65 (.24,1.8)
	--	--	H3	1	3.3	--
	--	--	H4	1	3.7	--
7	7m	--	--	9	1.2±.39	1.2 (.96,1.4)
	--	1 (3m)	--	3	--	--
	--	2 (3m)	--	3	--	--
	--	3 (3m)	--	3	--	--
	--	--	H7	1	1.2	--
	--	--	H8	1	2.2	--
11	7m	--	--	9	9.5±15.2	5.3 (2.7,10.1)
	3m	--	--	9	10.3±21.2	3.0 (1.1,8.1)
	--	1 (3m)	--	3	4.5±2.7	4.0 (2.1,7.6)
	--	2 (3m)	--	3	1.7±0.9	1.4 (.66,3.1)
	--	3 (3m)	--	3	16±18	10.3 (3.0,35)
	--	1 (7m)	--	3	6.6±1.1	6.6 (5.4,8.0)
	--	2 (7m)	--	3	4.8±1.5	4.7 (3.3,6.6)
	--	3 (7m)	--	3	4.4±2.6	4.0 (2.1,7.5)
	--	--	H1	1	6.5	--
	--	--	H2	1	9.0	--

[a]Log transformed data: Geometric mean (lower 95 percent interval, upper 95 percent interval).

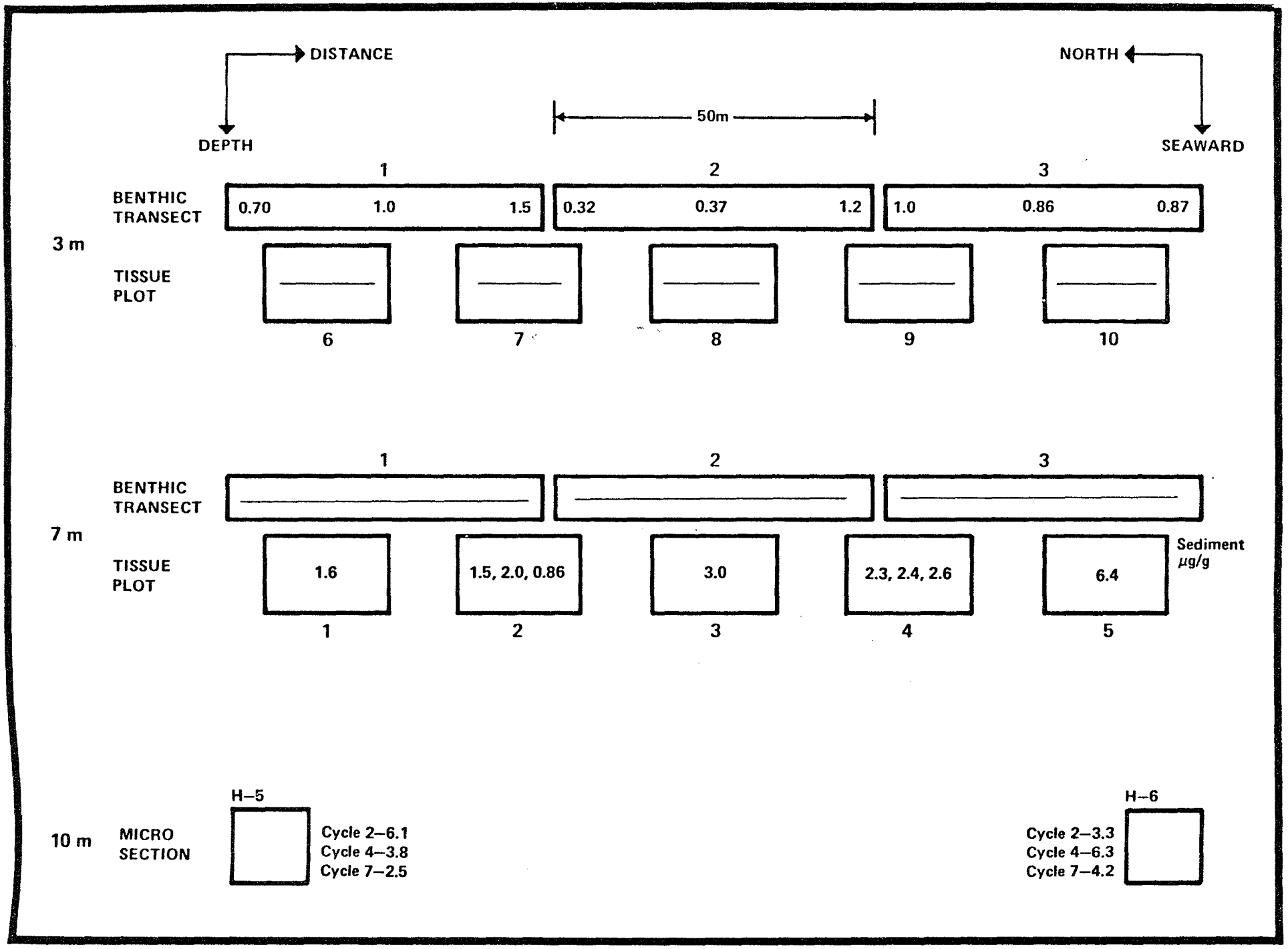


Figure 3.8. Sediment petroleum hydrocarbon content, by UV/F; Bay 9 (August 1982).

similar to those observed 1 day after the spill. Note (Figure 3.8) that at several stations (plot #5, H5, H6), the oil values at various times were determined to be $\sim$6 µg/g, indicating that significant sedimented oil still resided in the benthos.

The within-plot variation in oil content was determined on two sets of triplicate samples from each Bay. The results for Bay 9 and the other bays (Table 3.4) show that coefficients of variation ranged from 0.06 to 0.83 with the average variability being 0.38 (or 38%).

3.2.1.aii Oil Composition by GC^2

Two samples from the Bay 9 tissue plots were analyzed by GC^2 (plot 3 and 5) as these samples apparently contained the highest oil levels in this bay by UV/F analysis (3.0 and 6.4 µg/g respectively). Relevant data are tabulated in Table 3.5. As Figure 3.9 illustrates, a combination of weathered oil and terrigenous odd carbon n-alkanes (n-C_{23} to n-C_{31}) characterize the saturated hydrocarbon assemblage. A significant degree of physical-chemical weathering is indicated by the loss of alkanes smaller than n-C_{16}. However, biodegradation is not a very significant weathering process as the phytane/ n-C_{18} ratio is similar to that observed in the Lagomedio oil.

3.2.1.aiii Aromatic Hydrocarbon Composition By GC^2/MS

Two samples from the 7m tissue plots (numbers 3 and 5) were analyzed by GC^2/MS. Concentrations of aromatic hydrocarbons (Figure 3.10) were higher than those observed in 1981 when isomeric groupings (e.g., C_3P = trialkylated phenanthrenes) were less than 5 ng/g. In the 1982 sampling, concentrations were two to three times as high with the phenanthrenes and dibenzothiophenes the dominant remnants of the crude oil. There were compositional differences between plots 3 and 5.

Table 3.4. Variations in surface sediment oil levels (patchiness) (µg/g dry weight).

Bay	Tissue Plot Number	Mean[a] ± S.D.	Coefficient of Variation
9	2	1.5 ± .57	.38
	4	2.4 ± .15	.06
10	2	1.8 ± .69	.38
	4	1.7 ± .57	.34
7	2	1.1 ± .35	.32
	4	1.1 ± .25	.23
11	2	6.7 ± 1.4	.21
	4	3.1 ± 1.6	.52
	7	1.8 ± 1.5	.83
	9	.71 ± .34	.48

[a]Arithmetic mean of three replicates.

Table 3.5. Surface sediment hydrocarbon data summary: GC^2 results Bay 9

Sample Bay/Depth	Tissue Plot	Benthic Transect	Deep Sediment	Micro Station	Phytane (µg/g)	Pris/ Phy	Phy/ n-C_{18}	CPI	Status
Aged oil	-	-	-	-	-	1.5	.61	1.0	Oil
9/7	3	-	-	-	.007	4.4	.54	4.3	Oil
9/7	5	-	-	-	.013	2.0	.71	3.8	Oil
9/3	-	1	-	-	.007	3.0	.35	5.7	Oil
9/3	-	2	-	-	.003	1.0	.25	4.7	Oil
9/3	-	3	-	-	.006	2.7	.86	3.8	Oil
9/15	-	-	+	-	.003	6.3	.25	6.3	Low oil
9/15	-	-	+	-	.002	8.5	.18	8.5	Low oil
9/10 (May)	-	-	-	M5	.003	2.0	.75	4.0	Low oil
9/10 (May)	-	-	-	M6	.012	1.7	.58	6.0	Oil
9/10 (Cycle 2)	-	-	-	H5	.002	7.5	.20	4.3	Low oil
9/10 (Cycle 2)	-	-	-	H6	.004	6.5	.29	4.3	Low oil
9/10 (Cycle 7)	-	-	-	H5	.002	15	.18	3.8	Low oil
9/10 (Cycle 7)	-	-	-	H6	.005	4.0	.38	5.8	Low oil

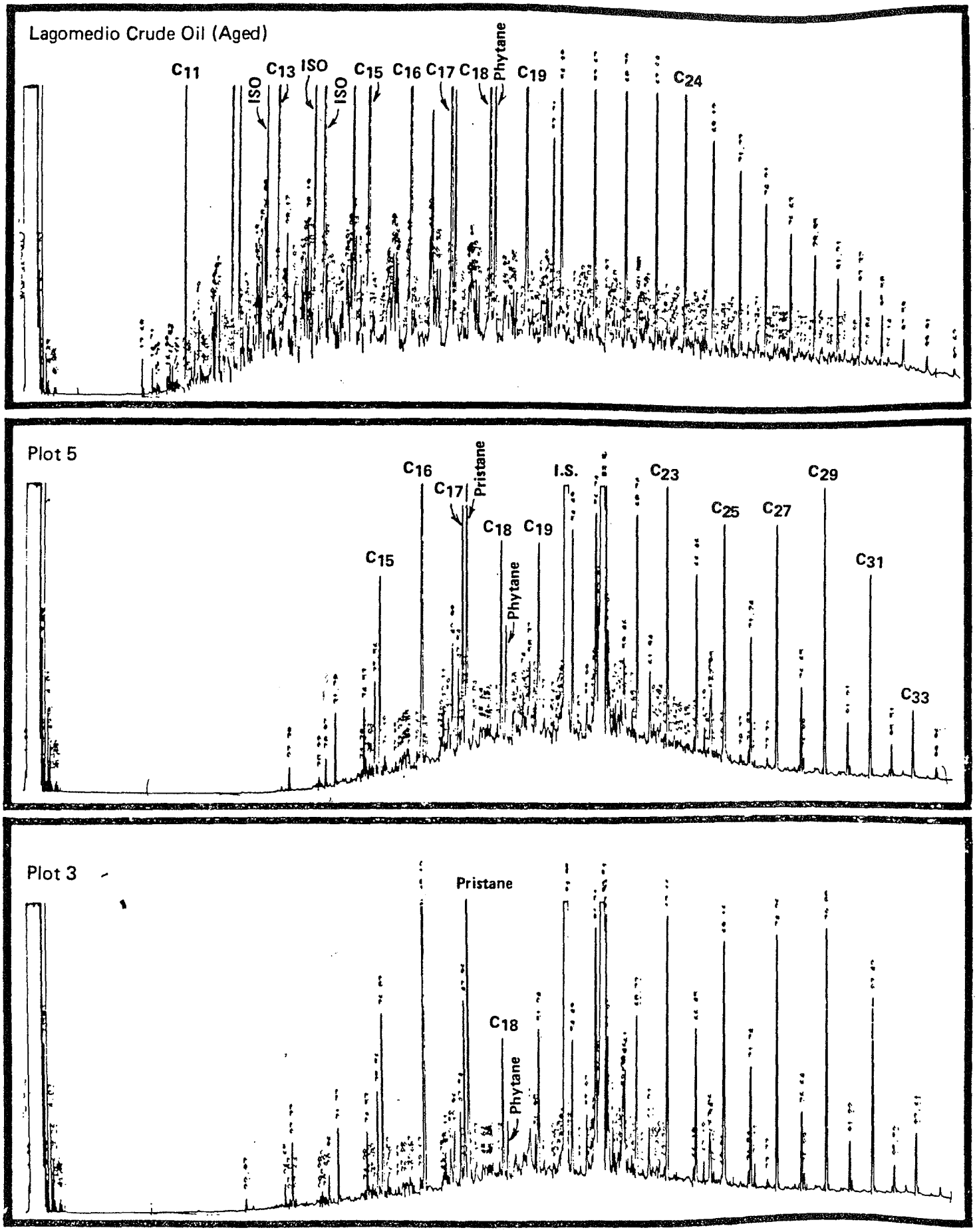


Figure 3.9. GC^2 traces of surface sediments from tissue plots, Bay 9, showing mixed petroleum and plant wax alkanes.

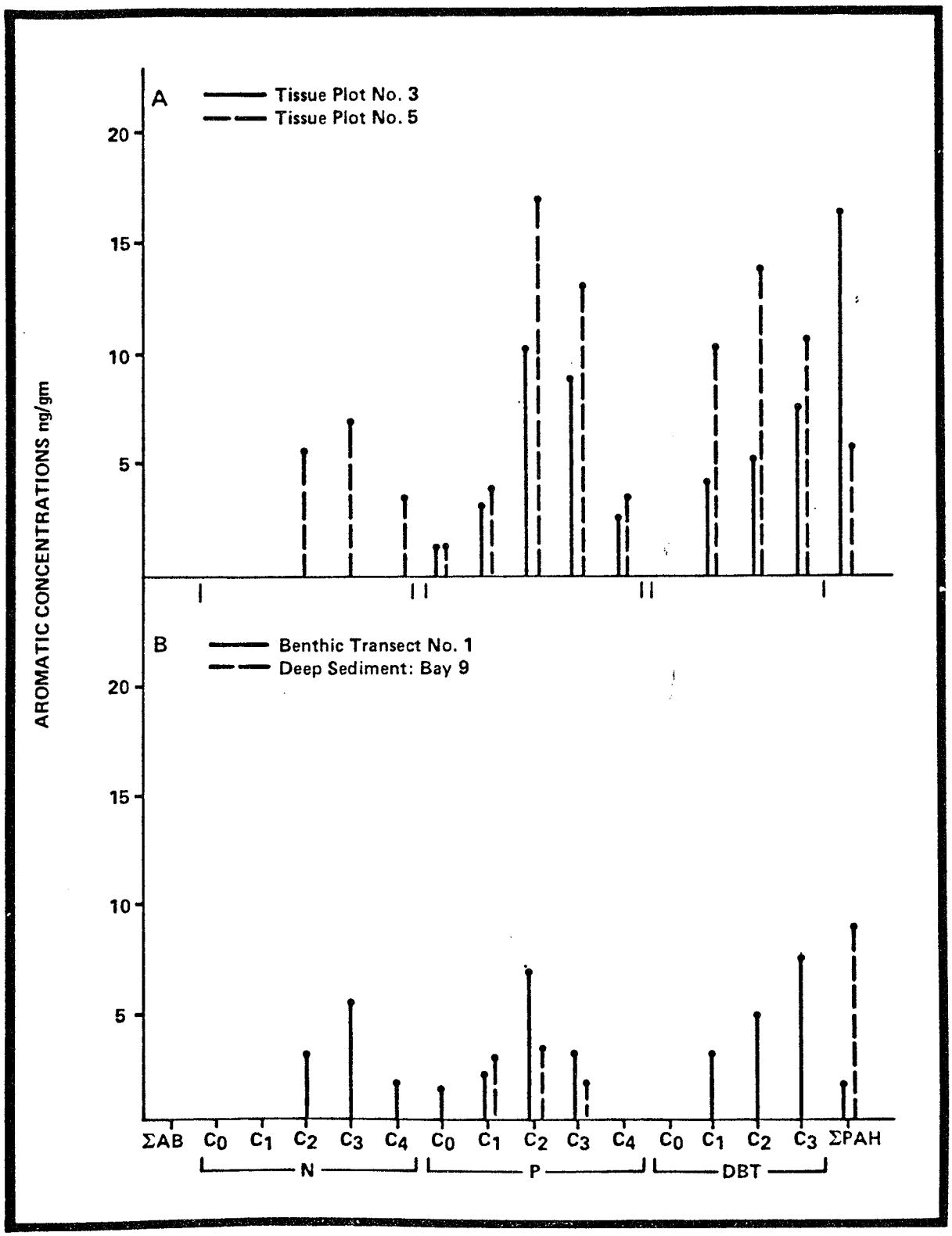


Figure 3.10. Sediments from Bay 9: GC^2/MS results.

Surprisingly, naphthalenes were detected at the 5 ng/g level in plot 5, but none were detected in plot 3. Non-petrogenic PAH in the sediments were in the 5-15 ng/g range with the five-ringed compound perylene being a major (25-30 percent of PAH) contributor.

3.2.1.b Benthic transects

3.2.1.bi Oil concentrations by UV/F

Oil concentrations in the benthic transects along the 3m depth stratum were obtained through the analyses of three samples within transect station. Concentrations in transect 1 at 3m were 1.0 (.66, 1.6) µg/g; in transect 2 they were .52 (.23,1.2) µg/g; and in transect 3 they were .91 (.83,1.5) µg/g (see Figure 3.8). Sediment oil concentrations at two of the three locations were a factor of ten higher when sampled in September 1981 at which time the mean values were 1.2, 4.1, 4.3 µg/g, respectively.

3.2.1.bii Oil composition by GC^2

Three samples, one from each transect at the 3m depth, were analyzed by GC^2. All samples exhibited saturated hydrocarbon features characteristic of low amounts of oil mixed with equal amounts of terrigenous plant wax alkanes. The GC^2 results are summarized in Table 3.5. A GC^2 trace is shown in Figure 3.11 illustrating some presence of lower boiling n-alkanes ($n\text{-}C_{10}$ to $n\text{-}C_{15}$) of a similar chemical nature to those seen in the Bay 7 water samples (Figure 3.4).

3.2.1.biii Aromatic hydrocarbon composition by GC^2/MS

One sample from transect #1 at 7m was analyzed. The aromatic composition of this sample (Figure 3.10) closely resembled that from tissue plot 5. The

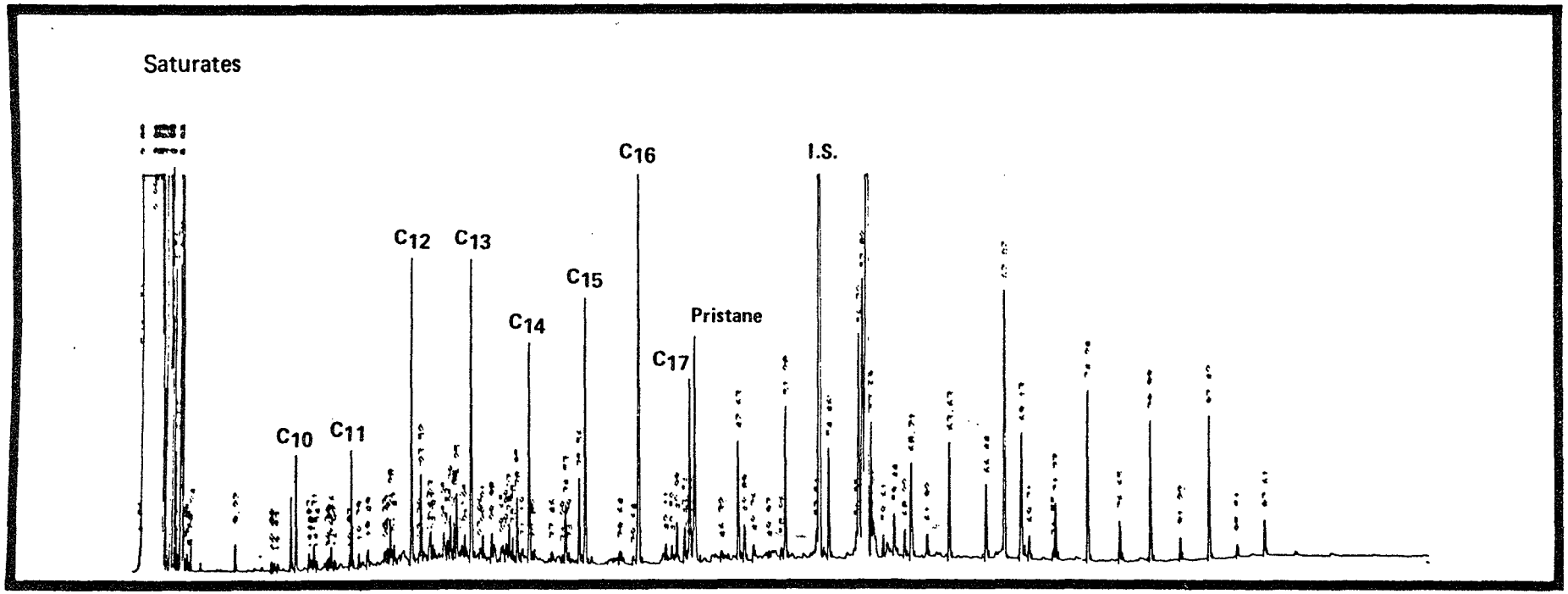


Figure 3.11. GC^2 trace, benthic sediments of Bay 9, Transect 1 (3 m).

alkylated naphthalenes, phenanthrenes and dibenzothiophenes are of similar concentration. Again the presence of small quantities of the naphthalenes is of interest in that the typical weathered crude oil should be depleted in these compounds. In the limited set of GC^2/MS analyses performed in 1981, these alkylated naphthalenes were absent from the Bay 9 sediments after two weeks although still present in Bay 10 sediments.

3.2.1.c Microbiology stations (surface sediments)

3.2.1.ci Oil concentrations by UV/F

Oil concentrations in the microbiology sediments were determined from May to September 1982. Concentration data for the "M" and "H" stations are presented in Table 3.6, and in Figure 3.7. In general, concentrations were no higher at these stations at 10m than they were at the 7m stations with values ranging from 2 to 6 µg/g at both sets of stations.

3.2.1.cii Oil Composition by GC^2

Relevent GC^2 information for the microbiology stations is presented in Table 3.5. Very low levels of oil are indicated by the GC^2 data which shows low phytane values, and low alkane values for these samples. No evidence of significant microbial degradation is seen as evidenced in the phytane/n-C_{18} ratio.

3.2.1.ciii Aromatic hydrocarbon composition by GC^2/MS

The importance of the GC^2/MS technique for determining if petrogenic residues are present in samples is demonstrated for the one sample analyzed for the Bay 9 microbiology station set. The May, M5 station results shown in Figure 3.12A indicate "normal" Bay 9 aromatic levels are present in this

Table 3.6. Surface sediment oil concentrations: Microbiology stations, Bay 9

Bay	Station	Cycle (date)	Oil Concentration (µg/g oil equivalents)
9	M5	(5/82)	3.0
		5 (9/3/82)	2.3
		5 (9/8/82)	2.7
	M6	(5/82)	1.9
		5 (9/8/82)	2.9
	H5	2 (8/11/82)	6.1
		4 (8/25/82)	3.8
		7 (9/82)	2.5
	H6	2 (8/11/82)	3.3
		4 (8/25/82)	6.3
		7 (9/82)	4.2

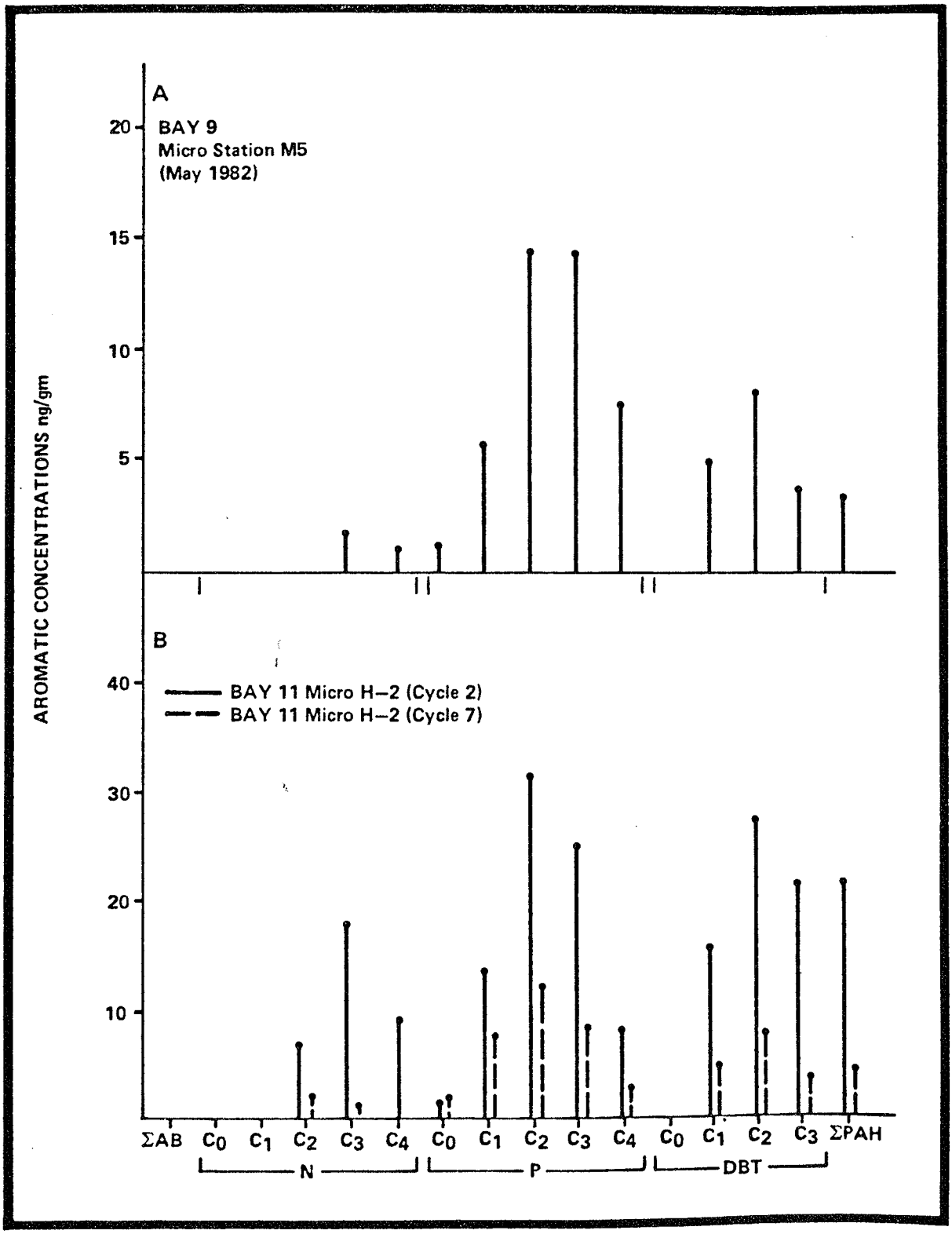


Figure 3.12. Surface sediment, microbiology stations, Bays 9 and 11: GC^2/MS results.

sample with the alkylated phenanthrene and dibenzothiophenes (5-15 ng/g) present. These data are definitive indicators of petroleum residues, while the saturated hydrocarbon values (Table 3.5) only weakly indicate the presence of oil.

3.2.1.d Sediment Cores

3.2.1.di Composition by GC^2

The five centimeter-thick sediment core fractions from Bay 9 showed that only low amounts of oil were present as evidenced by phytane values greater than approximately .002 µg/g and a pristane/phytane value of approximately 2 to 3 in the sample (Table 3.7). These criteria had previously been used (Boehm et al., 1982a) to readily detect the presence of oil in sediments. Apparently small amounts of oil have mixed into the 5-10 cm segment in the core at the south end of the 7m depth stratum, while the 5-10 cm segment at the northern end of the 7m stratum appears to be free of any oil contamination.

3.2.1.dii Aromatic Hydrocarbon Composition by GC^2/MS

Three core samples from Bay 9 were analyzed to examine the presence of trace levels of petrogenic aromatics and their vertical penetration. Results are presented in Figure 3.13. The phenanthrene and dibenzothiophene compounds are present in the 0-5 cm section of the north end (7m stratum) core, but only at low levels. The lower concentrations in this sample as compared to the tissue plot and benthic transect sediments is probably due to the fact that the core sample represents a 5 cm segment while the other samples are 2 cm segments. Thus, just based on the amount of sediment "dilution", we would expect the core segment to have two and a half times less oil than the surface scoop samples.

Table 3.7. Sediment core data: GC^2 results Bays 9, 10, 11

Bay	Location	Core Section	Phytane µg/g	Pristane/ Phytane	CPI	Status[a]
11	North (7m)	0-5	.005	5.4	6.3	Low oil
		5-10	.006	4.6	8.7	Low oil
		10-15	.001	9.1	9.3	No oil
	South (7m)	0-5	.002	12	7.8	No oil
		5-10	.001	7.3	20	No oil
9	North (7m)	0-5	.006	3.0	9.8	Low oil
		5-10	.001	6.6	9.0	No oil
	South (7m)	0-5	.009	2.9	4.0	Low oil
		5-10	.003	4.9	9.6	No oil
10	North (7m)	0-5	.003	3.0	19	Low oil
		5-10	.001	5.0	12	No oil
	South (7m)	0-5	.001	7.0	12	No oil
		5-10	.001	10.0	13	No oil

[a]Status determined by pristane/phytane ratio and absolute amount of phytane.

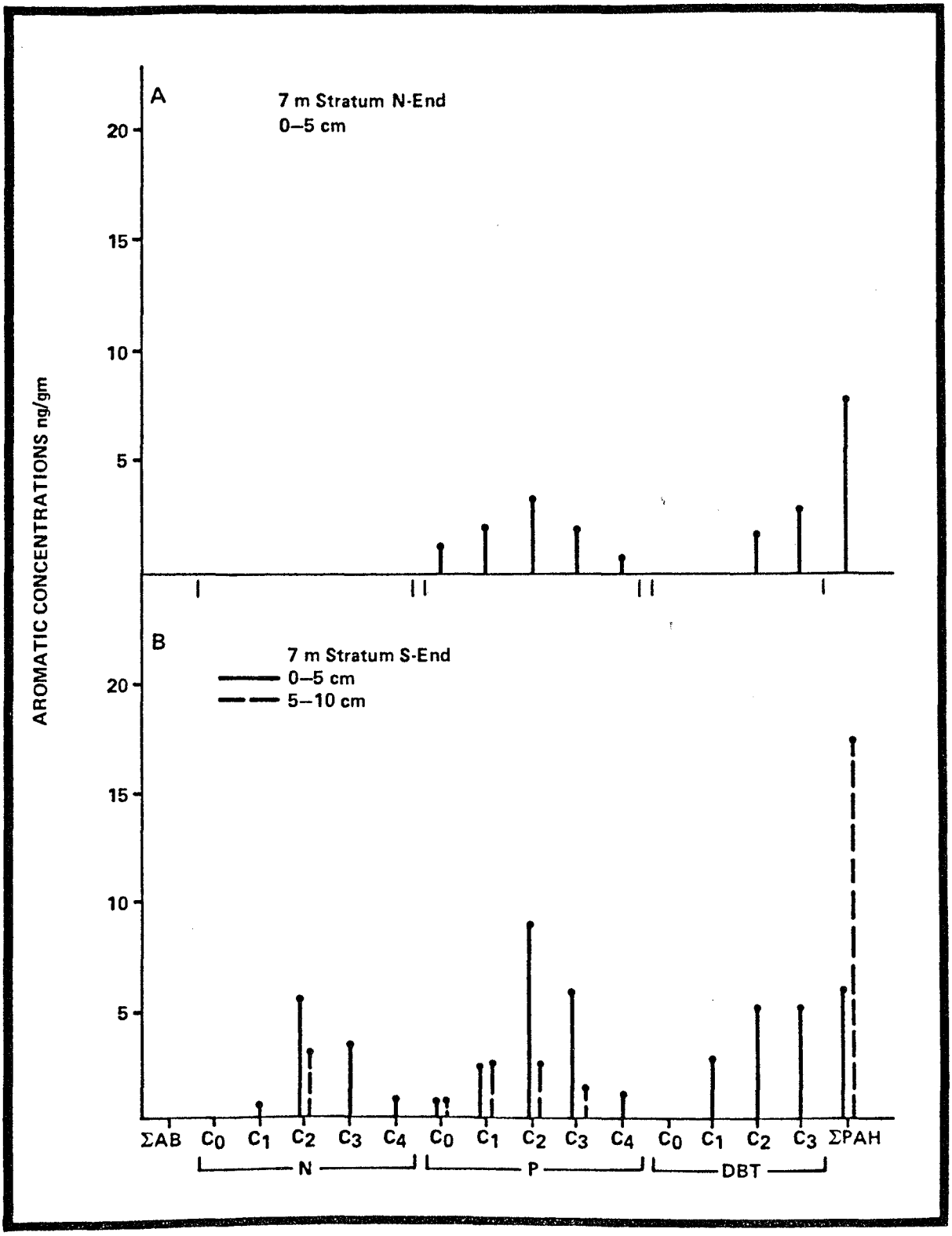


Figure 3.13. Sediment cores from Bay 9: GC^2/MS results.

The core from the south end of the stratum had three to five times more aromatic hydrocarbon in the 0-5 cm segment (Figure 3.13B). In this sample naphthalenes, phenanthrenes and dibenzothiophenes are of equal importance while naphthalenes were not detected in the north end core. Petroleum aromatics were not definitively identified in the 5-10 cm segment (Figure 3.13B), although their presence is suggested by the low amounts of the phenanthrenes. However, the absence of detectable dibenzothiophenes casts some doubt of the presence of crude oil residues. Note that the PAH levels are much higher in the deeper core segment (18 ng/g versus 6 ng/g), primarily due to the presence of perylene and other five-ringed aromatics of diagenetic origin.

3.2.1.e Deep sediments

3.2.1.ei Oil composition by GC^2

Table 3.5 in Section 3.2.1.aii presents the relevant GC^2-derived information. Low absolute quantities of phytane and moderate pristane/phytane ratios lend doubt to the presence of significant amounts of oil in these sediments. However, low levels (.01 µg/g) of n-alkanes do suggest low level oil contamination lower than that observed along the 3 and 7m depth strata.

3.2.1.eii Aromatic hydrocarbon composition by GC^2/MS

The one sample examined (Figure 3.14A) reveals very low levels of alkylated phenanthrenes. Thus we cannot definitely conclude that oil is present in this sample although its presence is suggested by the appearance of these compounds at the 1-5 ng/g level.

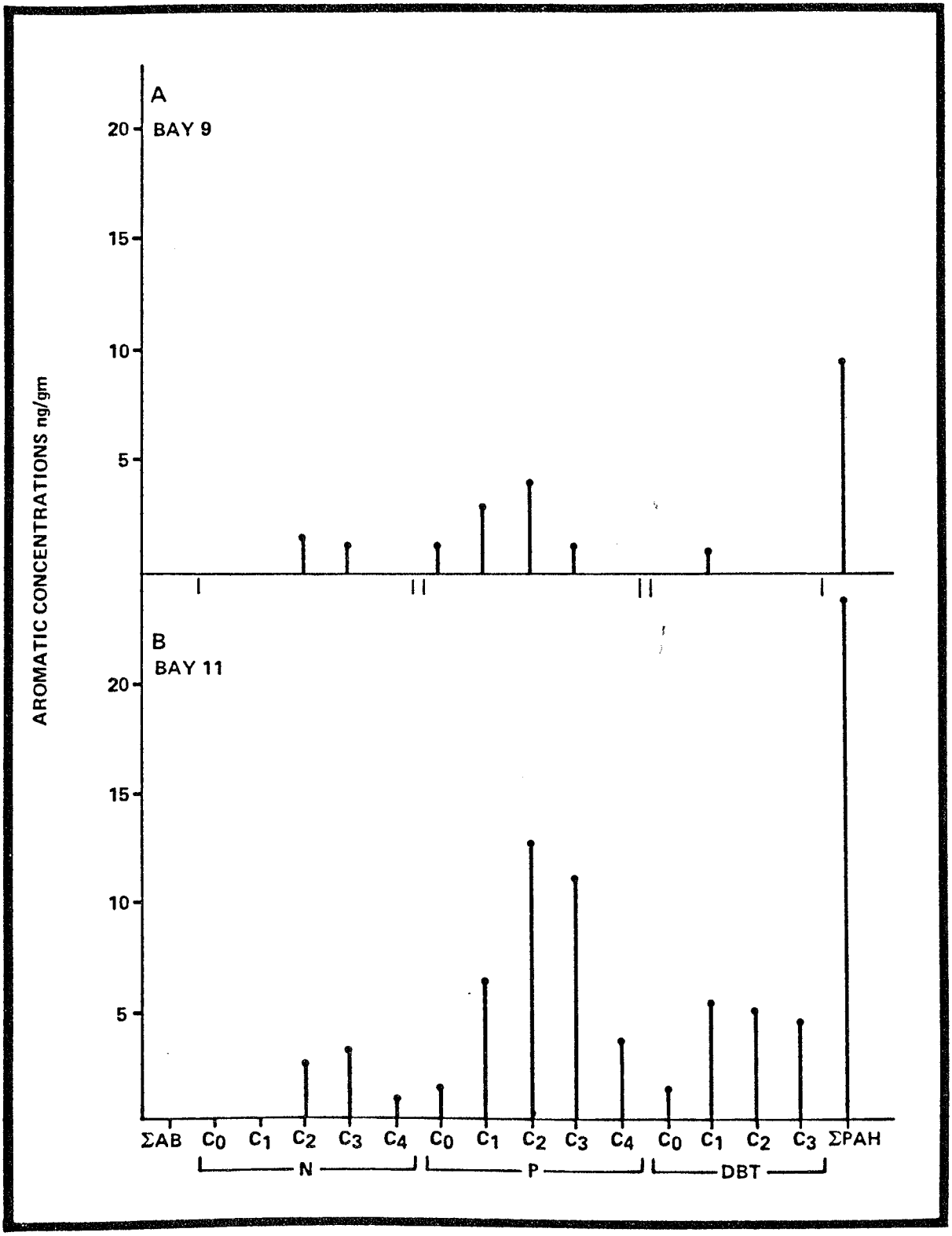


Figure 3.14. Surface sediments from deep station, Bays 9 and 11: GC^2/MS results.

3.2.2 Bay 10

3.2.2.a Tissue plots (surface sediments)

3.2.2.ai Oil concentrations by UV/F

Oil concentrations (Figure 3.15) in Bay 10 7m tissue plots were 1.7 (1.4,2.0) µg/g. The highest value observed was 2.6 µg/g. Concentrations observed in 1981 ranged from 0.5 to 3.0 µg/g in these Bay 10 sediments. When viewed in the context of a 0.5 µg/g background, we consider the 1982 Bay 10 levels to be similar to those observed in 1981.

3.2.2.aii Oil composition by GC^2

One sample from 7m tissue plot number 3 was analyzed. This sample, which contained 2.4 µg/g "oil equivalents" by UV/F, exhibited no GC^2 characteristics which would indicate the presence of oil through the contamination of the saturated fraction. No phytane was detected; therefore the pristane/ phytane ratio is infinite (pristane levels were 0.16 µg/g). The CPI was 4.8. No alkanes lower than n-C_{15} were detected.

3.2.2.1.aiii Aromatic Hydrocarbon Composition By GC^2/MS

One tissue plot sediment sample from Bay 10 (number 3 from 7M) was analyzed by GC^2/MS. Low levels of residual alkylated naphthalenes (Figure 3.16B) (1-2 ng/g), higher levels of alkylated phenanthrenes (3-8 ng/g) and low levels of dibenzothiophenes (1-5 ng/g) indicate that petroleum residues are detected here. Levels of background PAH values are higher.

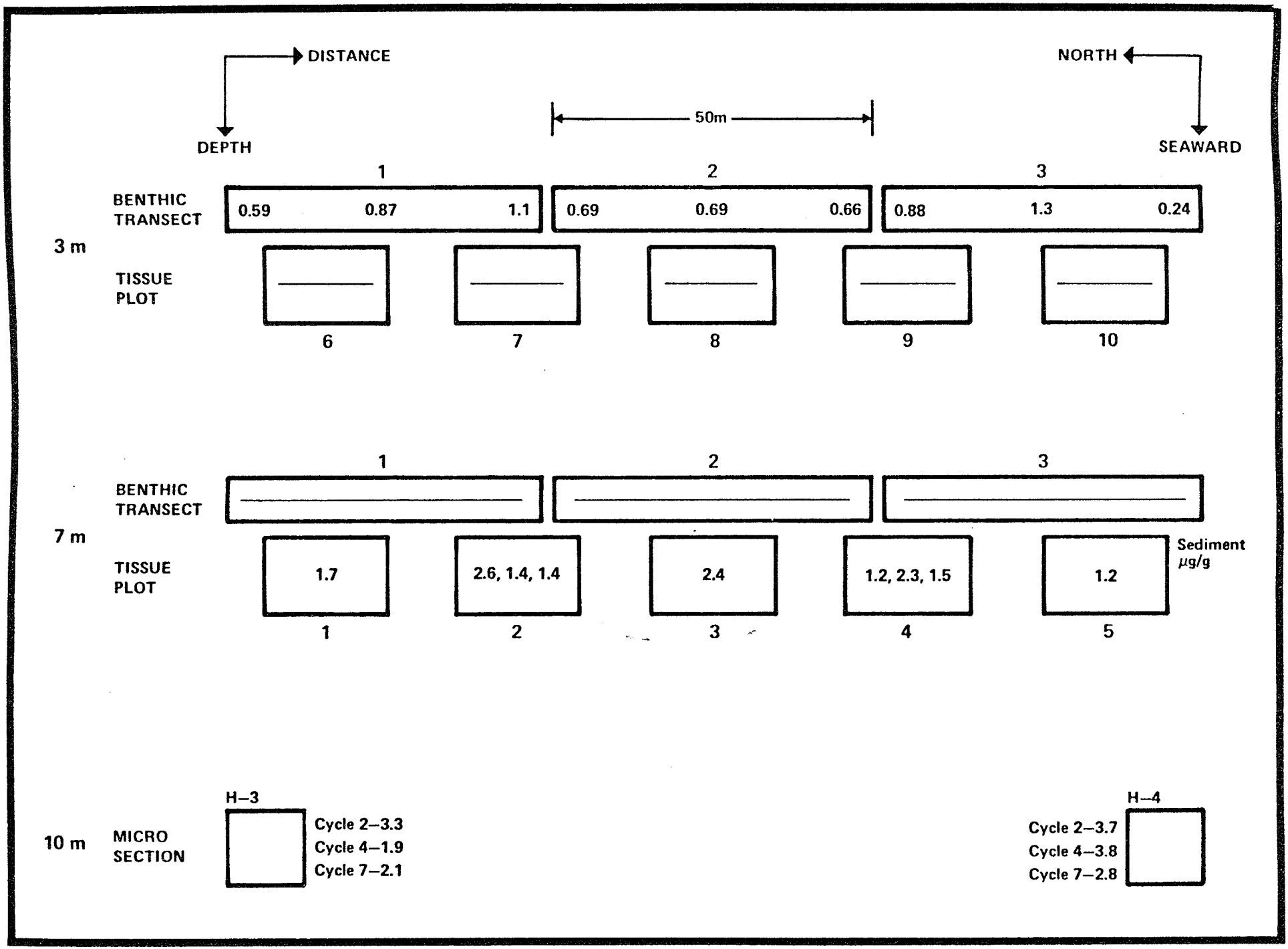


Figure 3.15. Sediment petroleum hydrocarbon content, by UV/F; Bay 10 (August 1982).

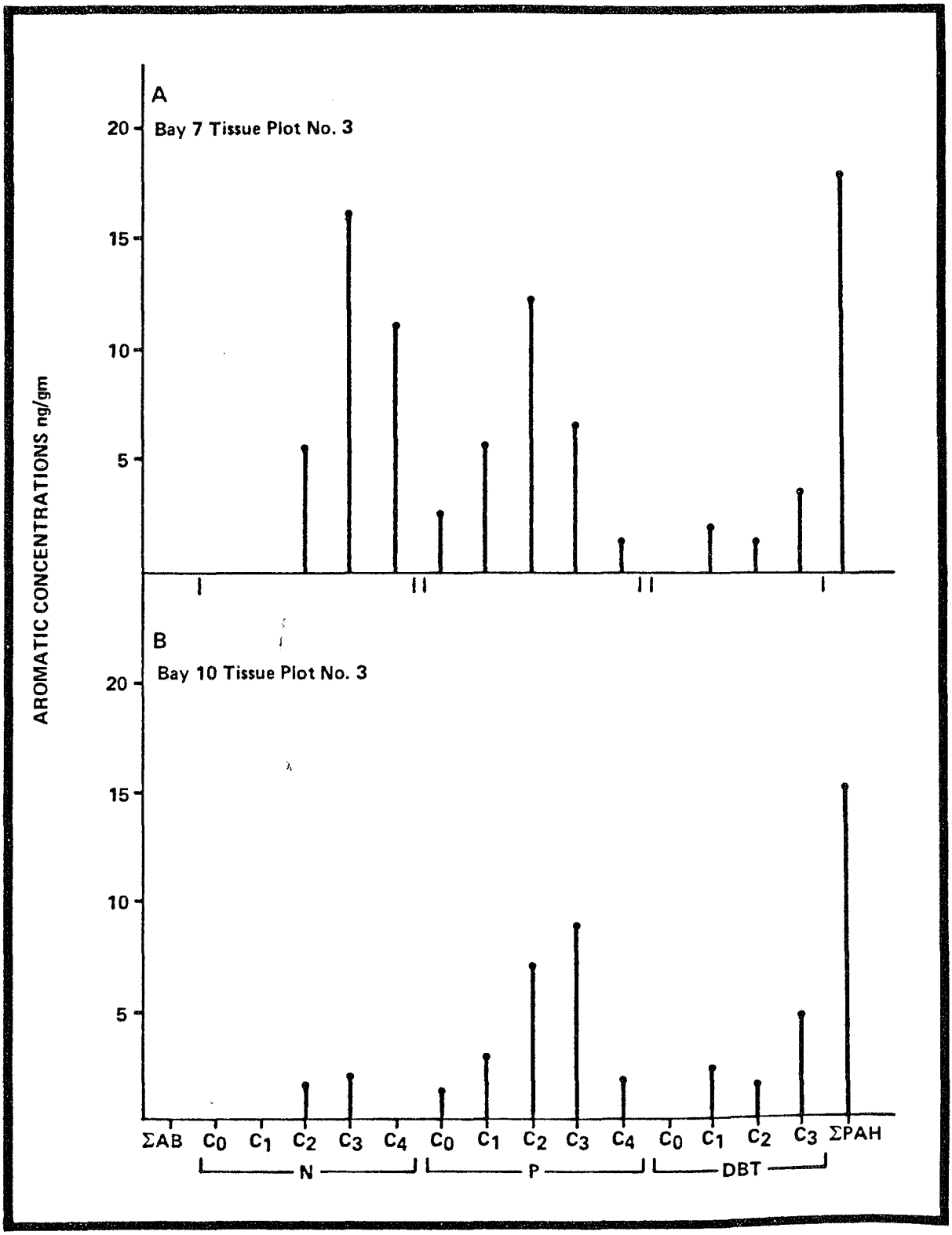


Figure 3.16. Sediments from Bays 7 and 10 tissue plots: GC^2/MS results.

3.2.2.b Benthic transects (surface sediments) Bay 10

3.2.2.bi Oil concentrations by UV/F

As Figure 3.15 shows, oil concentrations in the nine 3m samples were quite low, averaging .83 (.58,1.2), .68 (.66,.70), .65 (.24,1.8) µg/g for transects 1, 2 and 3, respectively. When sampled last in September 1981 the corresponding mean oil equivalents values were 1.8, .79, and 1.4 µg/g. The 1981 set exhibited sporadic high oil values with values of 5.4 and 3.7 µg/g being observed in samples from transects 1 and 3. The highest values encountered here in 1982 were 1.1 and 1.3 µg/g in these transects.

3.2.2.bii Oil Composition by GC^2

The two samples of highest concentration (1.1 and 1.3 µg/g) were analyzed by GC^2. Low levels of phytane (.001 and .003 µg/g) and high pristane/phytane ratios (30 and 19, respectively) indicate that an oil "signature" in the saturated hydrocarbons fractions of these samples is only weakly apparent in the GC^2 trace. However, the presence of low levels of n-alkanes in the $n\text{-}C_{13}$ to $n\text{-}C_{20}$ range ($\sim$.005 µg/g each) do indicate that very low levels of undegraded oil are present.

3.2.2.biii Aromatic Hydrocarbon Composition by GC^2/MS (Bay 10)

No samples were analyzed from the Bay 10 benthic transects.

3.2.2.c Microbiology Stations (Surface Sediments)

3.2.2.ci Oil Concentrations by UV/F

The May sampling in Bay 10 revealed low levels of oil "equivalents" (approximately .8 µg/g) (Table 3.8). However, oil levels rose between May

Table 3.8. Surface sediment oil concentrations: Microbiology stations, Bay 10

Bay	Station	Cycle (date)	Oil Concentration (µg/g oil; equivalents)
10	M3	(5/82)	0.90
	M4	(5/82)	0.76
	H3	2 (8/11/82)	3.3
		4 (8/25/82)	1.9
		7 (9/82)	2.1
	H4	2 (8/11/82)	3.7
		4 (8/25/82)	3.8
		7 (9/82)	2.8

and August when values at both H_3 and H_4 were 3-4 µg/g). Thereafter through cycle 7 levels remained about the same (2-3 µg/g).

3.2.2.cii Oil Composition by GC^2

GC^2 analyses were only conducted on the May samples from M3 and M4. At that time, no evidence of oil impact was seen. No detectable phytane was observed and no petrogenic alkanes were detected. Only the biogenic compounds, pristane and the terrigenous plant wax alkanes were found in the saturated hydrocarbon fraction.

3.2.2.ciii Aromatic Hydrocarbon Composition by GC^2/MS

No samples were analyzed from the Bay 10 microbiology stations.

3.2.2.d Sediment Cores (Bay 10)

3.2.2.di Oil Composition by GC^2

Two cores were examined from Bay 10 by analyzing two sections from each (0-5 cm; 5-10 cm). The GC^2 results are summarized in Table 3.4. Low levels of oil are detected in the top segment from the north end of the 7m stratum by virtue of the low pristane/phytane ratio. However, the GC^2 parameters indicate that no oil has been detected in either the 5-10 cm section of this core or in the other one from the south end of the 7m transect.

3.2.2.dii Aromatic Hydrocarbon Composition by GC^2/MS

No samples were analyzed from the Bay 10 cores.

3.2.3 Bay 7

3.2.3.a Tissue plots (surface sediments)

3.2.3.ai Oil concentrations by UV/F

UV/F-determined levels in Bay 7 stations (Figure 3.17) averaged 1.2 (.96,1.4) µg/g. These levels are lower than those for the other bays and are similar to those reported for Bay 7 in 1981. As in 1981, several isolated stations contained higher amounts of "oil equivalents" with station 3 containing 2.1 µg/g. Further analysis of this sample by GC^2 was warranted.

3.2.3.aii Oil Composition by GC^2

The one sample which was seen to contain 2.1 µg/g of "oil equivalents" was analyzed to see if oil could be definitively detected to Bay 7 surface sediments. That this sample does contain small amounts of oil is indicated by the presence of n-alkanes (.01-.02 µg/g) from n-C_{12} to n-C_{22} with small quantities of branched alkanes present (Figure 3.18). The low absolute quantity of phytane (.003 µg/g) indicates low overall abundance of oil. The petrogenic residues present are undegraded as the n-alkanes still dominate over the branched and isoprenoid alkanes. The phytane/n-C_{18} ratio in this sample was 0.19, much lower than in the original Lagomedio crude oil (0.61). Therefore, as this ratio can only increase with weathering, a source other than the Lagomedio crude oil for these petrogenic residues in Bay 7 is indicated by the data.

3.2.3.aiii Aromatic Hydrocarbon Composition By GC^2/MS

One sample from Bay 7 was analyzed. This sample was of some interest due to the slightly elevated "oil equivalents" levels as determined by UV/F

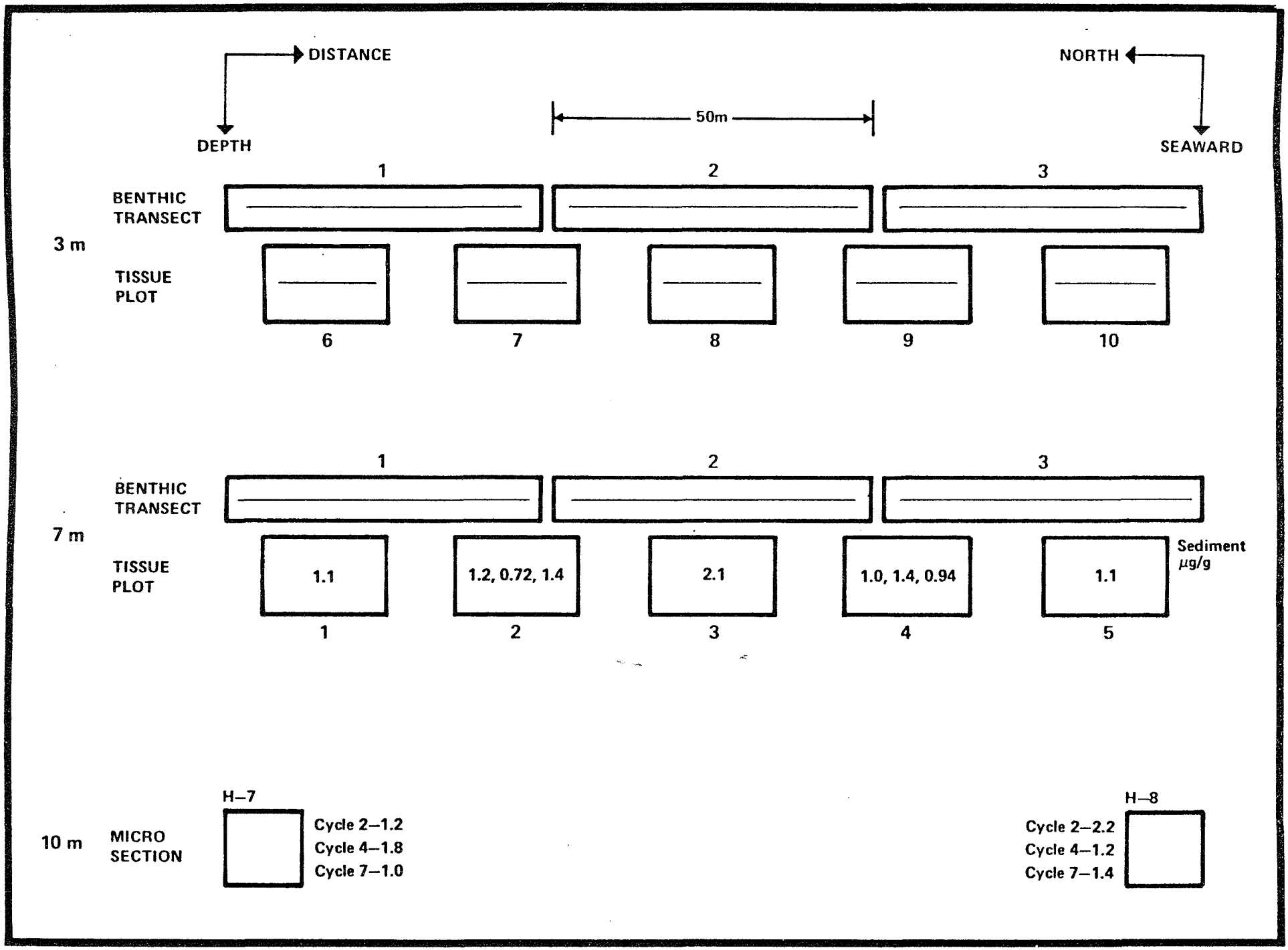


Figure 3.17. Sediment petroleum hydrocarbon content by UV/F; Bay 7 (August 1982).

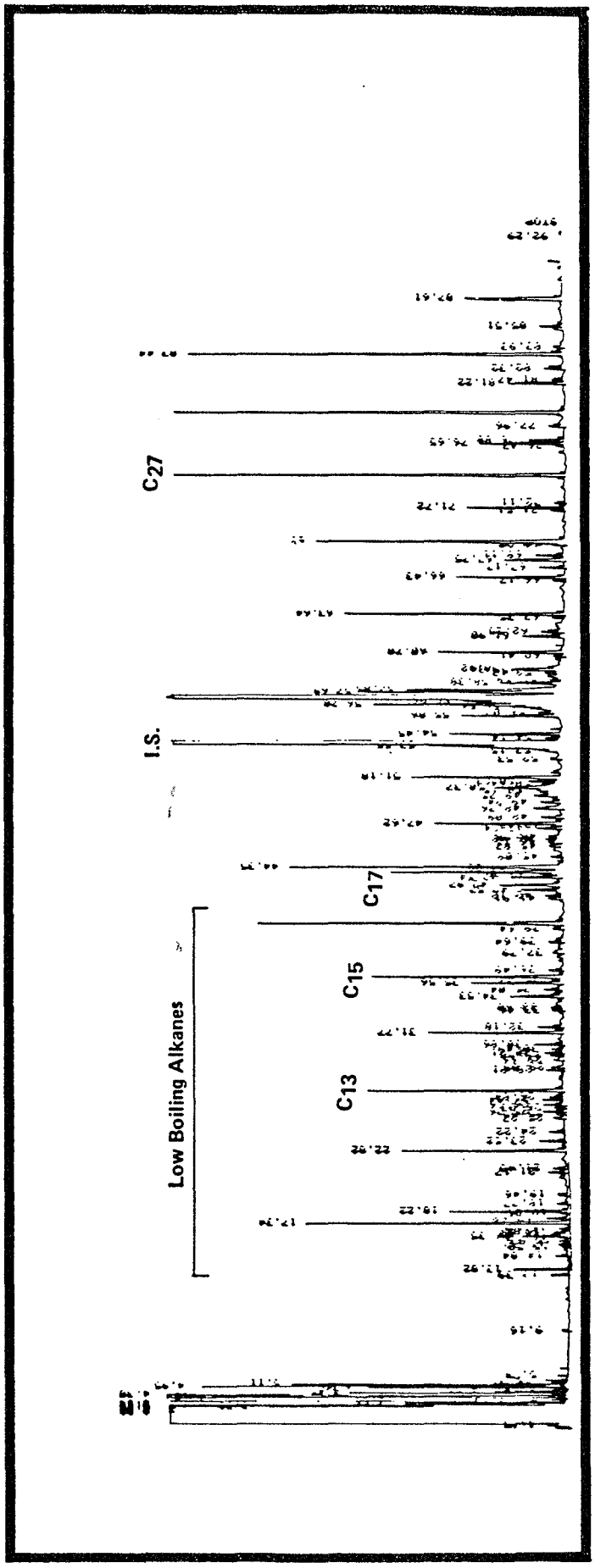


Figure 3.18. GC^2 trace of tissue plot sediments, Bay 7 Plot 3.

measurements (2.1 µg/g; see previous sections) The results (Figure 3.15A) are interesting in that the aromatic composition is quite different from the typical weathered crude oil assemblage seen in other samples. In the "typical" aromatic hydrocarbon profile, the phenanthrenes and dibenzothiophenes are dominant with naphthalenes, if present, equal to or less than the phenanthrenes. In this sample, the C_2-C_4 naphthalenes are dominant, with only small amounts of the dibenzothiophenes detected. A different oil input is suspected here; a light crude or perhaps a weathered fuel oil. Its source is unknown.

3.2.3.b Microbiology Stations (Surface Sediments)

3.2.3.bi Oil Concentrations by UV/F

Concentration data for the Bay 7 microbiology station is presented in Table 3.9. In May only background values were observed. Thereafter, it appears that oil is present in Bay 7 sediments as concentrations from 1-2 µg/g are observed through September at both H7 and H8.

3.2.3.bii Oil Composition by GC^2

The two samples from M7 and M8 analyzed by GC^2 yield saturated hydrocarbon profiles indicating no petrogenic residues are present at all and that only very low levels of the biogenic compounds are present.

3.2.3.biii Aromatic Hydrocarbon Composition by GC^2/MS

No samples were analyzed by GC^2/MS.

Table 3.9. Surface sediment oil concentrations: Microbiology stations, Bay 7 and BISIS

Bay	Station	Cycle (date)	Oil Concentration (µg/g; oil equivalents)
7	M7	(5/82)	.45
	M8	(5/82)	.40
	H7	2 (8/11/82)	1.2
		4 (8/25/82)	1.8
		7 (9/82)	1.0
	H8	2 (8/11/82)	2.2
		4 (8/25/82)	1.2
		7 (9/82)	1.4
BISIS	6A	2 (8/11/82)	6.0
		4 (8/25/82)	5.1
		6	2.3
	6B	2 (8/11/82)	5.8
		4 (8/25/82)	5.8
		6	5.7

3.2.4 Bay 11

3.2.4.a Tissue plots (surface sediments)

3.2.4.ai Oil concentrations by UV/F

Bay 11 sediments contain the highest oil concentrations of all the bays (Figure 3.19). Concentrations were 3.0 (1.1,8.1) µg/g in the 3-m tissue plots, with high values of 10.9 and 66.0 µg/g observed. Concentrations in the 7-m tissue plots were similar to transect 3m (5.3 (2.7,10.1) µg/g)). These values are considerably higher than those observed in September 1981 at which time concentrations were roughly 1.0 µg/g. Substantial oil transport to Bay 11 sediments appears to have taken place after the breakup of the ice. Bay 11 values from May 1982 are still quite low (0.5-1.1 µg/g). That active deposition due to erosional processes acting on the beached oil are occurring is apparent from the patchy distributions observed. Note that the southern ends of both depth strata contain an order of magnitude more oil than do the other stations along the strata.

3.2.4.aii Oil composition by GC^2

Samples were analyzed from the 3m and 7m depth strata to determine the chemical nature of petroleum residues in Bay 11. A summary of the pertinent GC^2 data is presented in Table 3.10. Included here are GC^2 analyses of three replicate samples from tissue plot 2. The levels of oil in these replicates determined by UV/F and the levels of phytane (Table 3.10) are in good agreement, as are the pristane/ phytane ratio and the microbial degradation-sensitive ratio, phytane/n-C_{18}. A small but significant degree of biodegradation appears to have caused this ratio to increase somewhat to 0.90-1.0 in the plot 2 samples and in the heavily impacted 3m tissue plot number 10. Thus there is some evidence that biodegraded oil is present at these stations.

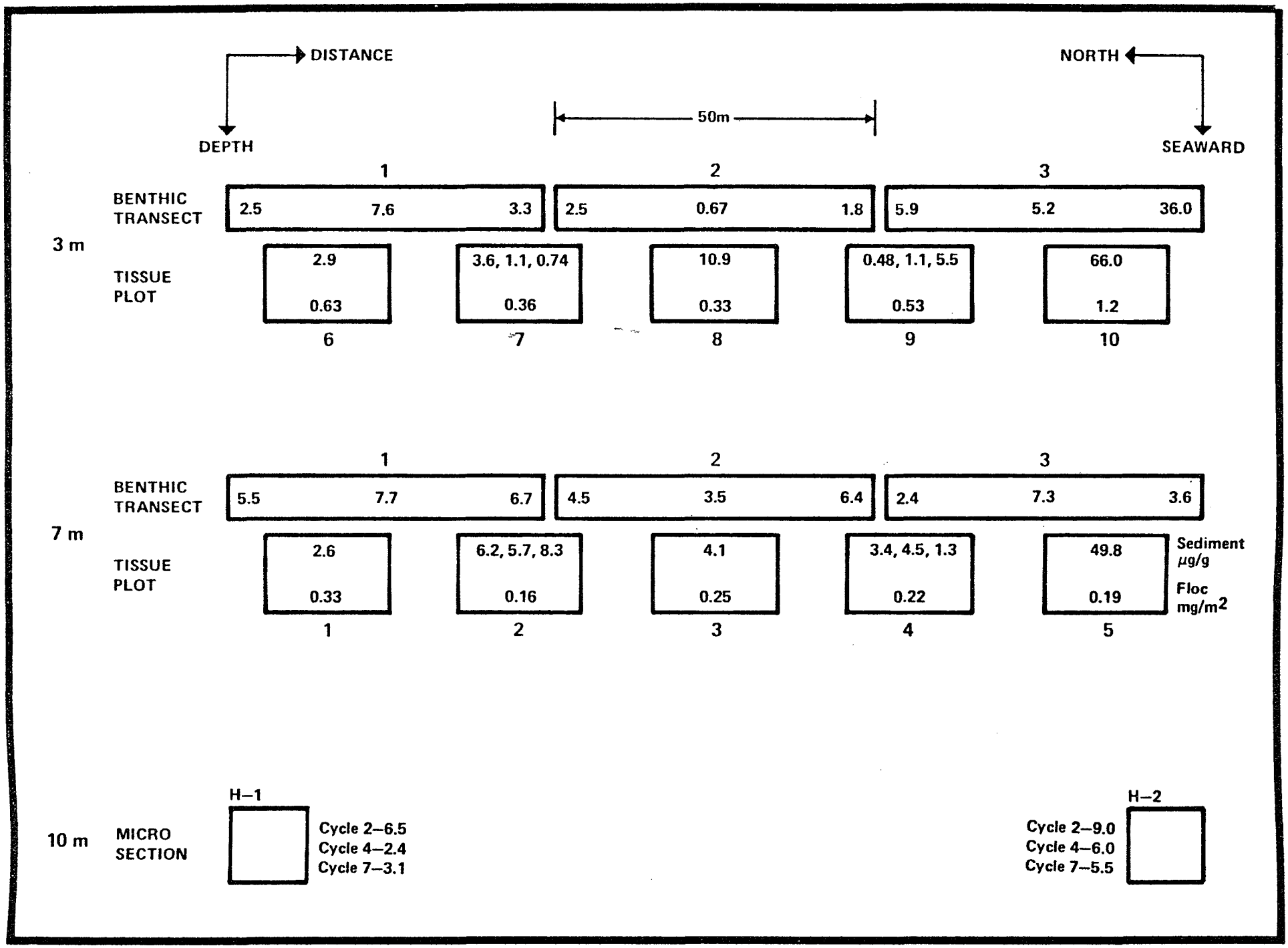


Figure 3.19. Sediment petroleum hydrocarbon content, by UV/F; Bay 11 (August 1982).

Table 3.10. Surface sediment hydrocarbon data summary: GC[2] results Bay 11

Sample Bay/Depth	Tissue Plot	Benthic Transect	Deep Sediment	Micro Station	Phytane µg/g	Pris/ Phy	Phy/ n-C_{18}	CPI	Status
Aged crude	-	-	-	-	-	1.5	.61	1.0	Oil
11/3	8	-	-	-	.057	1.6	.83	2.5	Oil
11/3	10	-	-	-	.410	.87	1.1	1.4	Oil
11/7 (1)	2	-	-	-	.012	3.5	.90	3.1	Oil
11/7 (2)	2	-	-	-	.011	2.5	.79	3.3	Oil
11/7 (3)	2	-	-	-	.018	2.0	1.0	3.0	Oil
11/7	5	-	-	-	.058	1.4	.84	2.6	Oil
11/3	-	1-1	-	-	.018	2.7	.69	3.4	Oil
11/3	-	1-2	-	-	.013	1.6	.87	3.3	Oil
11/3	-	1-3	-	-	.061	1.5	1.1	2.6	Oil
11/3	-	3-1	-	-	.068	1.3	1.1	2.2	Oil
11/3	-	3-2	-	-	.18	1.0	1.2	1.6	Oil
11/3	-	3-3	-	-	.42	.78	1.1	1.9	Oil
11/7	-	1-1	-	-	.010	3.2	.52	4.2	Oil
11/7	-	1-2	-	-	.019	2.7	.95	3.5	Oil
11/7	-	1-3	-	-	.022	1.9	.92	3.7	Oil
11/7	-	2-1	-	-	.010	2.2	.78	4.2	Oil
11/7	-	2-2	-	-	.039	1.3	.72	2.9	Oil
11/7	-	2-3	-	-	.014	1.6	.78	4.1	Oil
11/15	-	-	+	-	.003	5.0	.30	5.0	Low oil
11/15	-	-	+	-	.007	3.7	.44	5.2	Low oil
11/7 (May)	-	-	-	M1	.002	4.0	.40	20	No oil
11/7 (May)	-	-	-	M2	.002	3.5	.50	20	No oil
11/10 (Cycle 2)	-	-	-	H1	.009	3.2	.36	4.3	Low oil
11/10 (Cycle 2)	-	-	-	H2	.052	1.2	.71	23.5	Oil
11/10 (Cycle 7)	-	-	-	H1	.005	2.6	.23	5.3	Low oil
11/10 (Cycle 7)	-	-	-	H2	.007	2.4	.41	4.6	Low oil

GC^2 traces of two oil-impacted sediments are shown in Figure 3.20 ranging from 6.2 µg/g (Figure 3.20A) to 50 µg/g (Figure 3.20B). The most heavily oiled sample from plot number 10 is comprised of a slightly biodegraded residue with a phytane/n-C_{18} ratio of 1.1 and the prominence of the other important isoprenoids (Figure 3.21A) is obviously highly weathered, with components smaller than the C_3 naphthalenes not detected by GC^2.

3.2.4.aiii Aromatic Hydrocarbon Composition by GC^2/MS (Bay 11)

Five samples were analyzed from the Bay 11 tissue plots including two of the three sediment replicates taken from plot 2 (7 m). The results in Figure 3.22 for the replicates illustrate good agreement between the sampling replicates. The UV/F-determined "oil equivalents" results were similar as well (6.2 and 5.7 µg/g). One of the two replicates did contain small quantities of alkylated naphthalenes.

The results from plot 5 (Figure 3.22B) are striking. As had been determined by UV/F, this sample contains considerable quantities of oil (50 µg/g). The aromatic assemblage reveals a relatively unweathered crude oil, similar to the Lagomedio crude composition. Note the considerable quantities (10-20 ng/g) of the naphthalenes. The alkylated phenanthrenes were in the 20-50 ng/g range, five times higher than in plot 2 (see Figure 3.22A).

The results from the 3m tissue plots (Figure 3.23A) indicate again the presence of relatively unweathered oil by virtue of the important C_1-C_4 naphthalene concentrations. Note again how the naphthalenes, phenanthrenes and dibenzothiophene series are all at the same concentratation. This differs markedly from the Bay 7 result (Figure 3.15A) where naphthalenes were greater in concentration than the other compound series.

At tissue plot 10 (Figure 3.23) where UV/F results indicated a large oil input (66 µg/g), considerable quantities of phenanthrenes and dibenzothiophenes (50-150 ng/g) and lesser quantities of naphthalenes (approximately

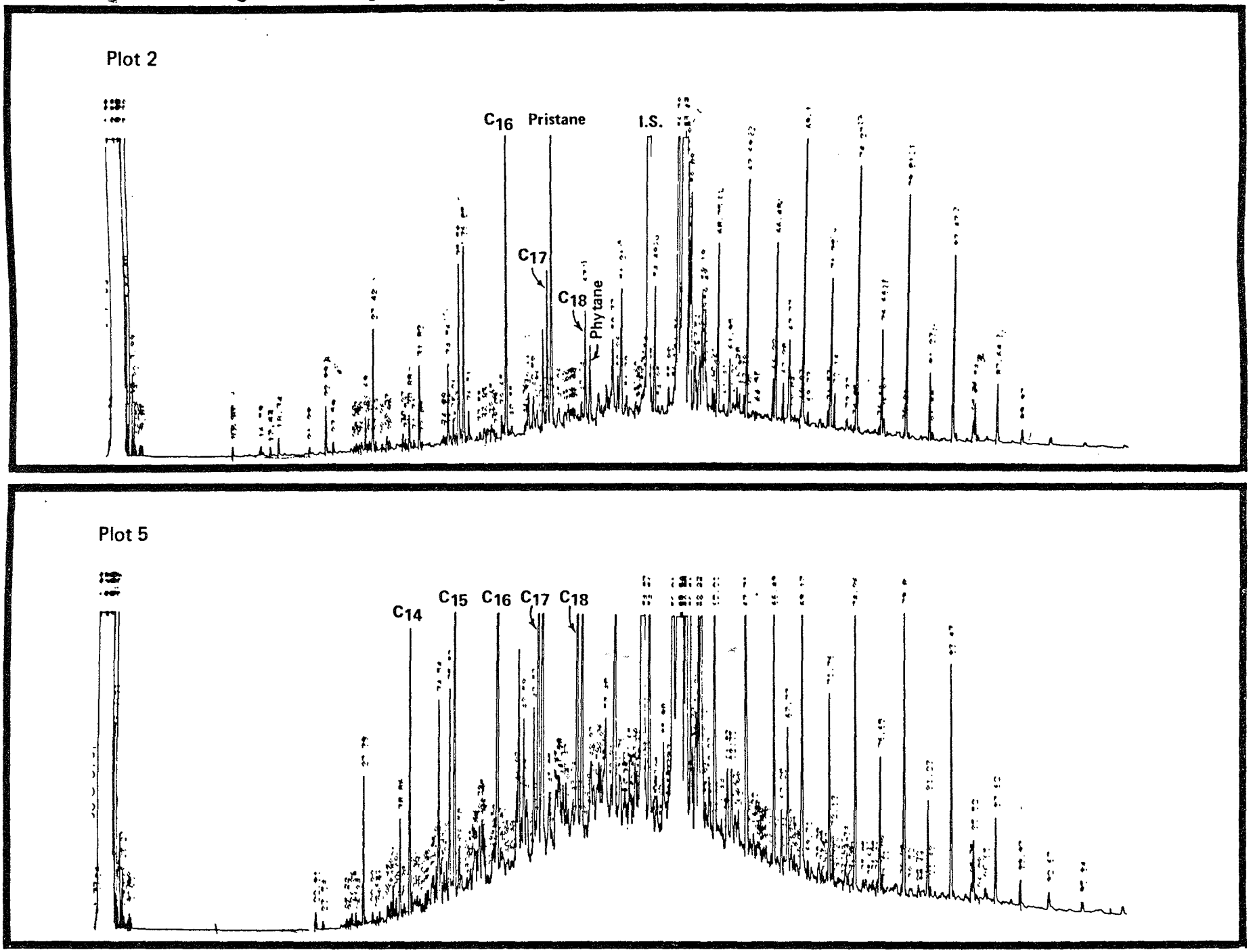


Figure 3.20. GC^2 traces, tissue plot sediments, Bay 11.

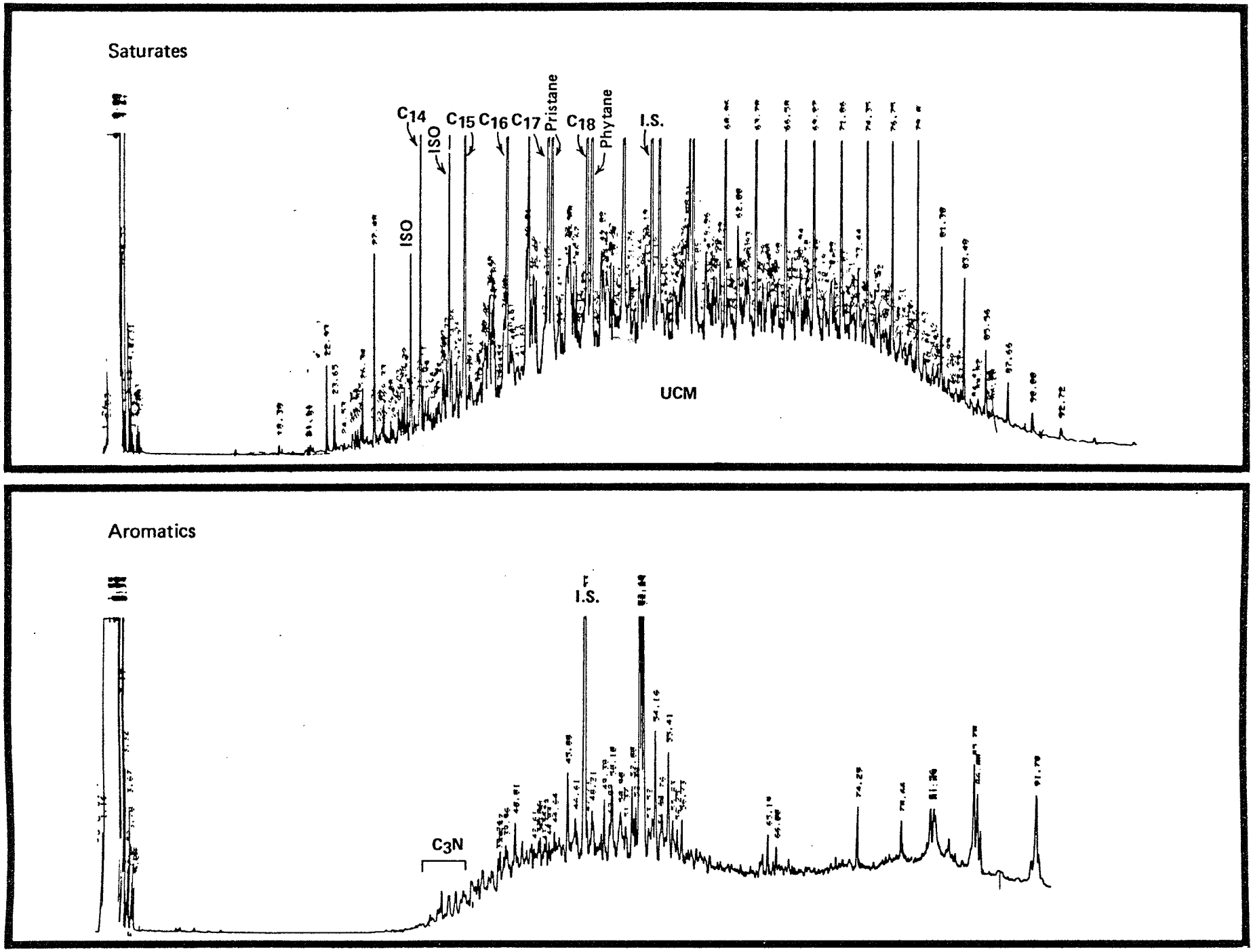


Figure 3.21. GC^2 traces of tissue plot (No. 10) sediment, Bay 11.

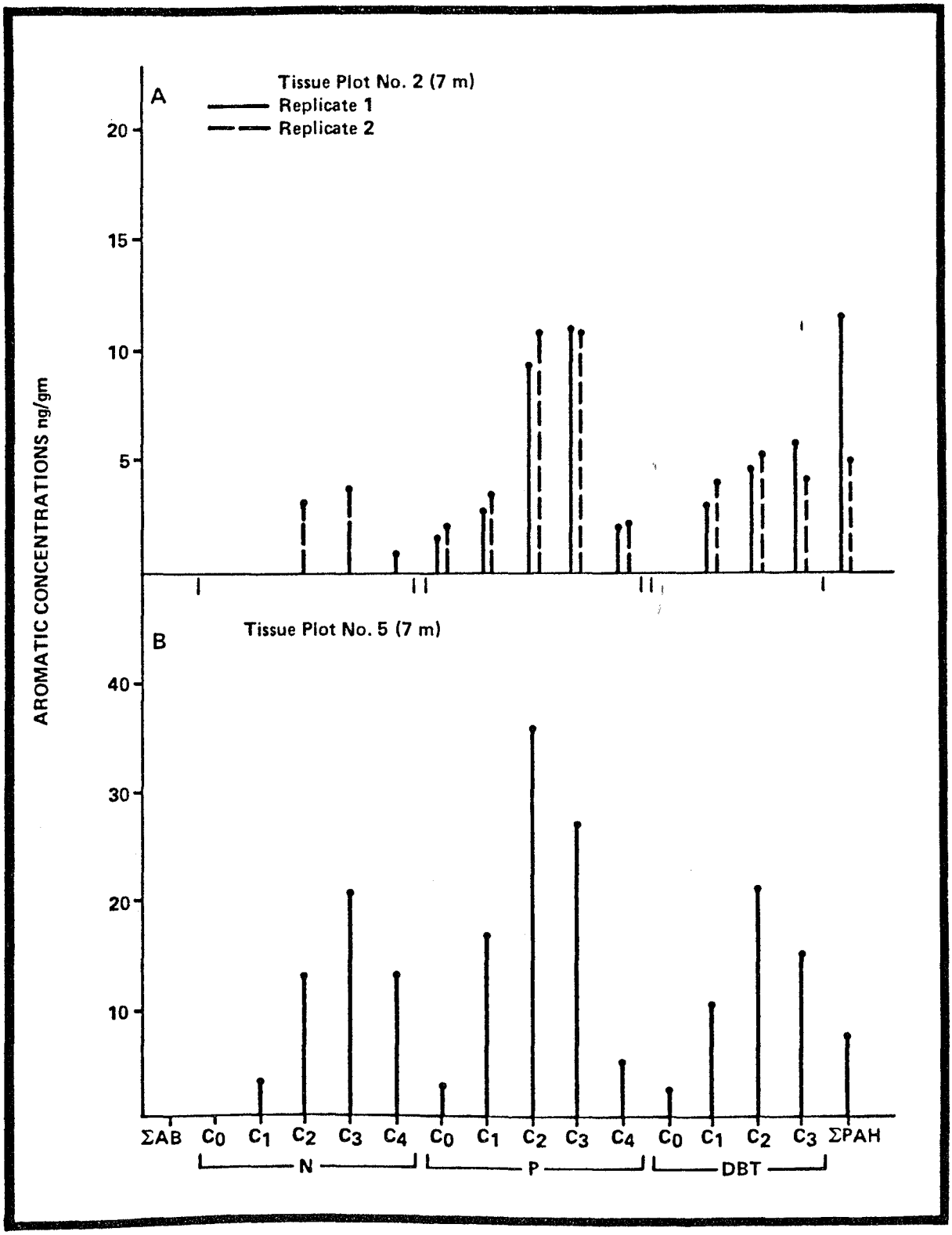


Figure 3.22. Sediments from Bay 11, tissue plots: GC^2/MS results.

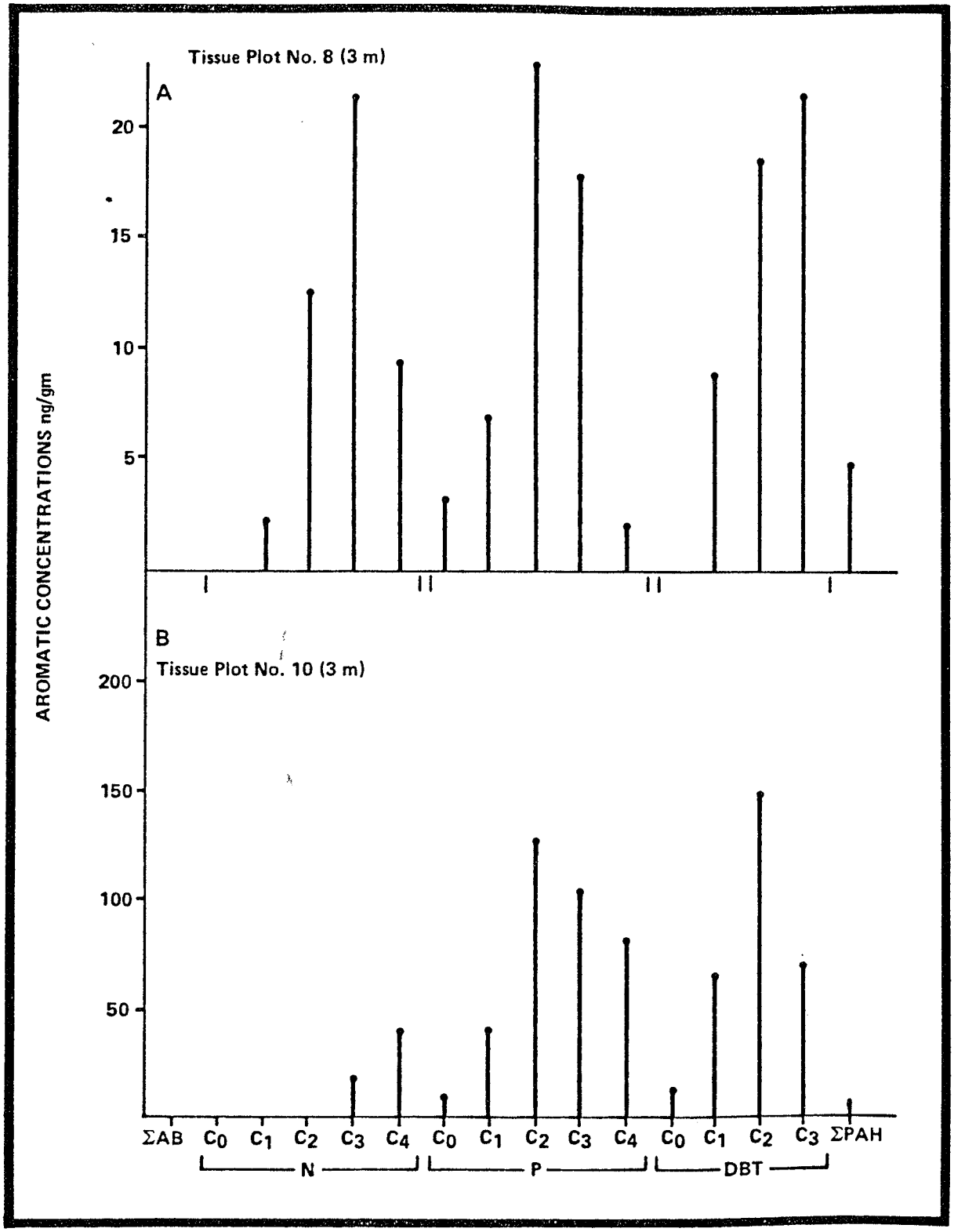


Figure 3.23. Sediments from Bay 11 tissue plots: GC^2/MS results.

30 ng/g) are present. The Figure 3.23A and B results indicate the two main compositions of the sediment bound oil that was observed; one in which the presence of the naphthalenes indicates a low degree of weathering (Figure 3.23A) and one in which the three-ringed aromatics remain dominant due to weathering in spite of higher oil levels (Figure 3.23B).

3.2.4.b Tissue plots (floc)

3.2.4.bi Oil concentrations by UV/F

Ten samples of surface floc were obtained from Bay 11. The 1981 results had illustrated that in Bays 9 and 10 a significant amount of oil was present in this surface floc in the first day after the dispersed oil spillage (up to 33 mg/m^2 in Bay 9). Two weeks later, however, no significant oil was found in the floc layer probably due to its transport elsewhere in the Ragged Channel area. Floc samples in 1982 were obtained only from Bay 11, the hypothesis being that erosional transport of beached oil might affect the levels of oil in the floc in Bay 11, and the likelihood for further input to the floc in Bays 9 and 10 being minimal.

The floc results are shown in Figure 3.19. Concentrations of oil equivalents by fluorescence were .23 $\pm$ .065 mg/m^2 in the 7-m samples and 0.61 $\pm$ mg/m^2 at the 3-m depth stratum. Thus significantly more oil is seen in the floc at 3 m. A value of 1.2 mg/m^2 is observed at plot 10, also the site of the highest oil levels in the surface sediment in both the tissue plots and in the benthic transects.

When last sampled in 1981 the floc in Bay 11 contained .07 $\pm$ .04 mg/m^2 at 3 m and .12 $\pm$ .08 mg/m^2 at 7 m indicating no significant oil in the floc at that time. Oil-in-floc levels had been on the order of 0.2 mg/m^2 one day after the surface oil spill in Bay 11. By contrast, it is well documented that in 1981 the floc in Bays 9 and 10 contained oil one day after the dispersed oil spill, 9.0 mg/m^2 and 4.3 $\pm$ 1.9 mg/m^2 respectively.

Therefore small relative amounts of oil have returned to the sediments of Bay 11.

3.2.4.bii Oil composition by GC^2

The presence of oil in the station 6 and 10 plots is clearly demonstrated from the GC^2 traces of the saturated hydrocarbon fractions shown in Figure 3.24. Both samples show a significantly weathered petroleum with low pristane/phytane ratios (1.9 and 1.1 respectively) indicative of oil rather than a biogenic input of pristane, and pristane/n-C_{17} ratios of 1.4 and 1.1, and phytane/n-C_{18} ratios of 0.7 and 0.95. That this oil has been biodegraded slightly is evident from the increasing relative importance of the isoprenoids pristane and phytane relative to the adjacent alkanes, n-C_{17} and n-C_{18}. The phytane/n-C_{18} and pristane/n-C_{17} ratios in the spilled oil were 0.62 and 0.38 respectively. The SHWR values were 1.2 and 1.3 respectively indicating a high degree of physico-chemical weathering.

3.2.4.biii Aromatic hydrocarbon composition by GC^2/MS

Two of the surface floc samples (plots 6 and 10) were analyzed by GC^2/MS. Both results (Figure 3.25) illustrate that the oiled floc is comprised of a weathered aromatic assemblage, consistent in its composition to that previously observed in September 1981 surface sediments. The 1981 floc samples from Bay 9 (1 day post-spill) did contain sizeable quantitites of naphthalenes, characteristic of relatively unweathered oil. Here in 1982 we see definite evidence for a recontamination of the floc in Bay 11 with a weathered oil similar in composition to most of the oil beached on the Bay 11 shoreline.

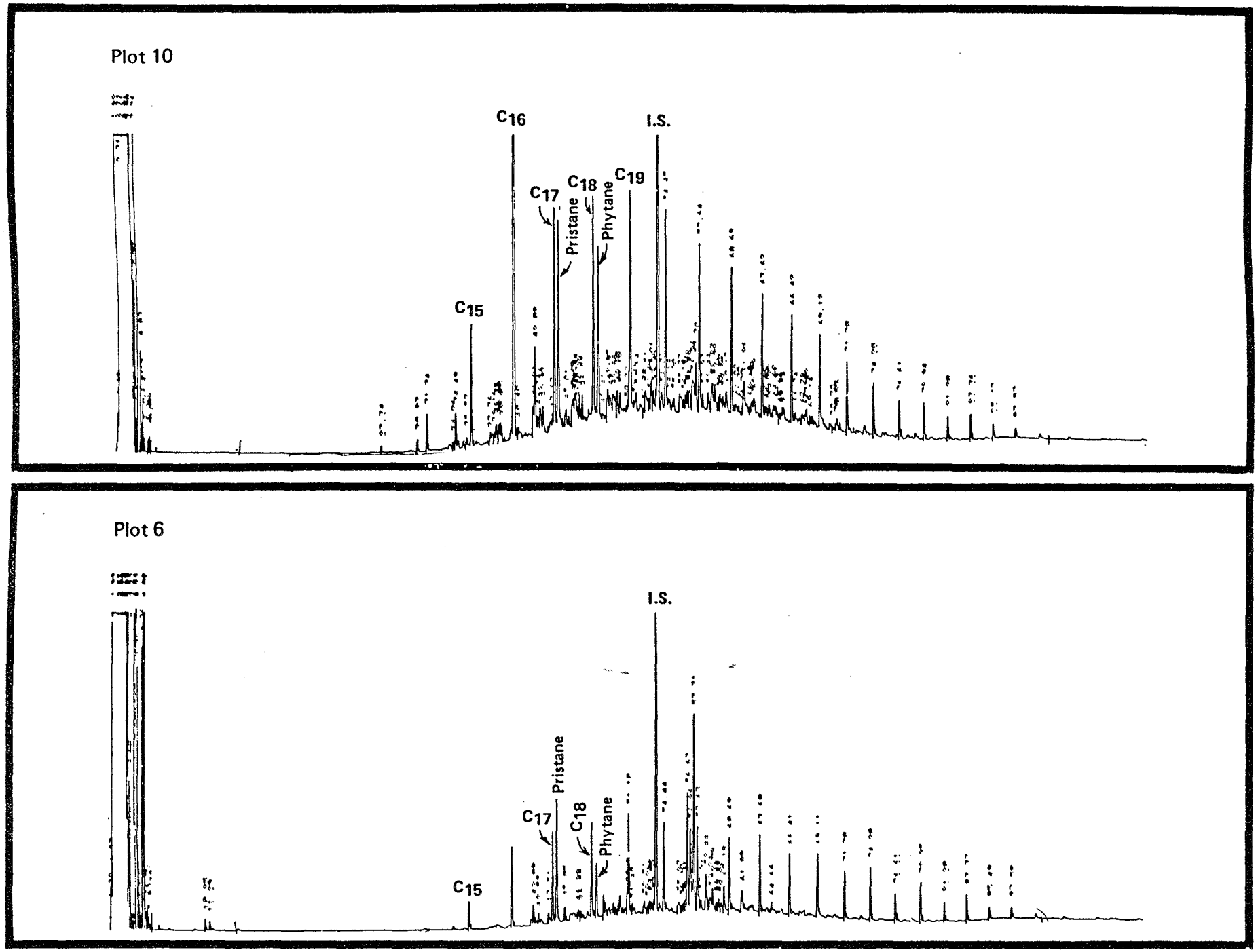


Figure 3.24. GC^2 traces of sediment floc from tissue plots, Bay 11, showing indications of biodegradation in Plot 10.

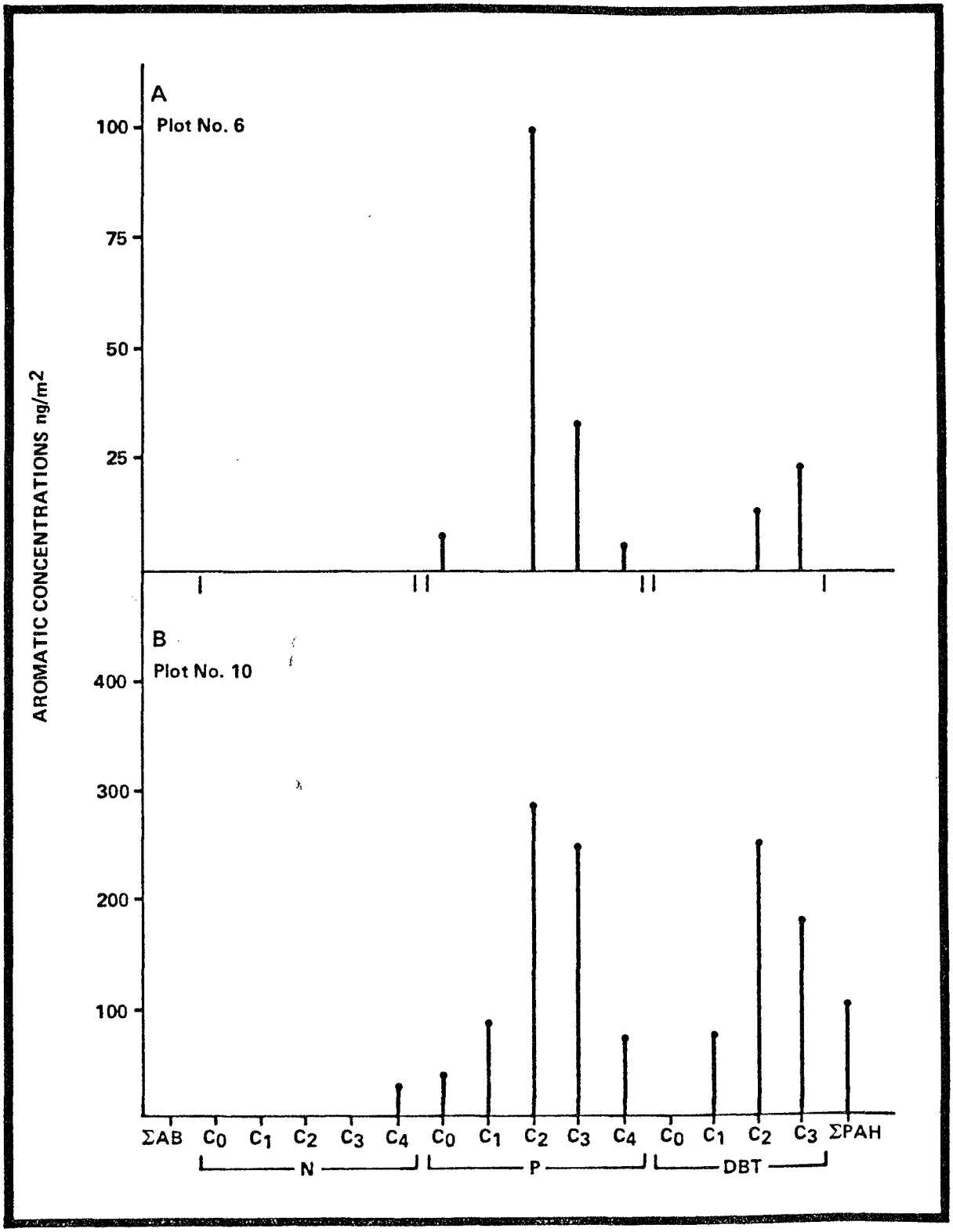


Figure 3.25. Surface sediment floc, Bay 11: GC^2/MS results.

3.2.4.c Benthic transects (surface sediments) Bay 11

3.2.4.ci Oil concentrations by UV/F

Concentrations of oil in sediments from the three transects at both the 3m and 7m depths are presented in Figure 3.19. Concentrations in transect 1 were 4.0 (2.1,7.6) µg/g at 3m and were higher, 6.6 (5.4,8.0) µg at 7m. Concentrations in transect 2 were 1.4 (.66,3.1) µg/g at 3m and 4.7 (3.3,6.6) µg/g at 7m. Concentrations in transect 3 were 10.3 (3.0,35) µg/g at 3m and 4.0 (2.1,7.5) µg/g at 7m. Along transects 1 and 2 concentrations increased with depth. Concentrations in transect 3 were much higher at 3m owing to an obvious patchy input of oil to the south end of the test area. Oil levels were much higher in the shallower (3m) end of all of the transects than were found in 1981. Levels at 7m were similar to the 1981 values. Thus, movement of oil off the beach and into the shallow sediments, probably by beach erosion, is indicated.

3.2.4.cii Oil composition by GC^2

The pertinent GC^2-derived data from 12 surface sediments of the Bay 11 benthic transects are presented in Table 3.10. It is clear from these data and from the overall appearance of the GC^2 traces that all Bay 11 samples contain moderate to high quantities of unbiodegrated-to-slightly degraded oil. The phytane/n-C_{18} ratio in several of the sample approaches 1.0 which indicates the decreased relative abundance of n-C_{18} compared to phytane. Moderate to high quantities of phytane (.01-.4 µg/g), which are directly correlated to the total oil, are present. The CPI values, which should be greater than 3 (up to 6) for only lightly impacted sediments, are in several cases less than 3 indicating a high degree of oiling.

GC^2 traces are very similar to those previously shown for the tissue plots. Note that the larger amounts of oil appear to be the most degraded vis-a-vis the phytane/n-C_{18} ratio, perhaps indicating that biodegradation is a beach-related phenomenon.

3.2.4.ciii Aromatic hydrocarbons composition by GC^2/MS

Four samples were examined by GC^2/MS. The results are presented graphically in Figure 3.26. The samples varied widely in their aromatic hydrocarbon concentrations, but compositionally the samples were quite similar. The common composition consisted of the main alkylated two and three-ringed compound series with the phenanthrenes dibenzethiophrenes naphthalenes. The presence of the naphthalenes confirms relatively recent inputs of oil. The samples from the 7m depth of the transects were very similar to concentrations (5-20 ng/g) and composition. The 3m transect 1 sample (Figure 3.26A) was lower in concentration than its 7m counterpart (Figure 3.26B), with naphthalenes below the detection limit. Large amounts of aromatics are present at 3m on transect 3 where isomer groupings ranged up to 150 ng/g in concentration.

3.2.4.d Microbiology Stations (Surface Sediments)

3.2.4.di Oil Concentrations by UV/F

The Bay 11 oil results in Table 3.11 and Figure 3.19 illustrate two apparent trends. First there is a strong apparent trend towards increasing oil concentrations at M2 ranging from 1 µg/g in May and to 7 and 13 µg/g in early September. Results at H1 and H2 illustrate the opposite trend with mid-August values 6.5 and 9 µg/g, respectively, and thereafter decreasing to 3 and 5.5 µg/g, respectively. The increasing trend at M2 is clearly a strong indication of increasing oil levels in the Bay 11 7m depth station.

3.2.4.dii Oil Composition by GC^2

GC^2-derived compositional data is placed in context with the other Bay 11 sediment data in Table 3.10. Representative GC^2 traces are shown in

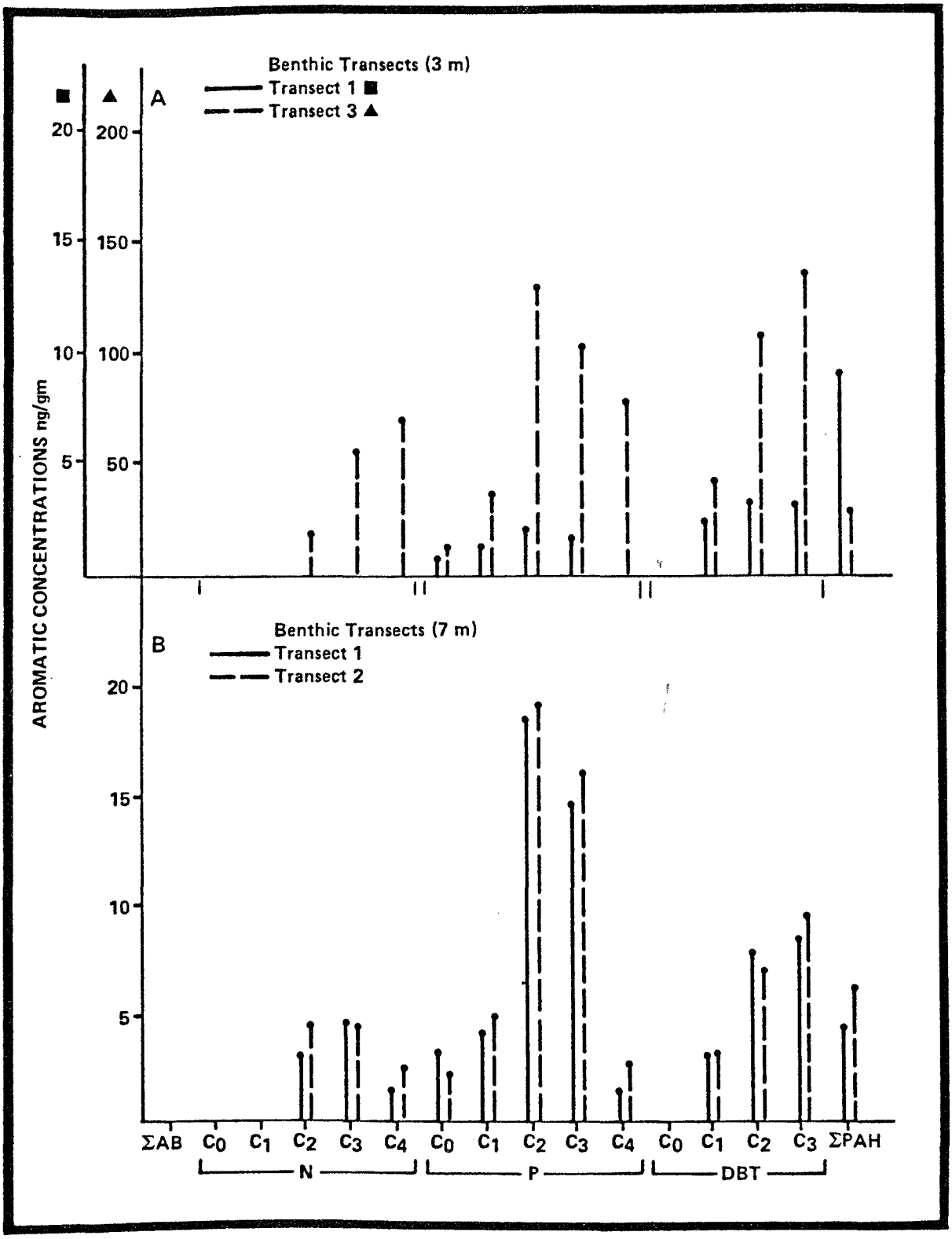


Figure 3.26. Surface sediments from benthic transects, Bay 11: GC^2/MS results.

Table 3.11. Surface sediment oil concentrations: Microbiology stations, Bay 11

Bay	Station	Cycle (date)	Oil Concentration (µg/g; oil equivalents)
11	M1	(5/82)	.54
	M2	(5/82)	1.1
		5 (9/3/82)	6.9
		7 (9/3/82)	12.8
	H1	2 (8/11/82)	6.5
		4 (8/25/82)	2.4
		7 (9/82)	3.1
	H2	2 (8/11/82)	9.0
		4 (8/25/82)	6.0
		7 (9/82)	5.5

Figure 3.27 for station H2. Low levels of oil are detected at these stations from August through September 1982. The H2, cycle 2 sample contains the most oil (Figure 3.27A), which exhibits no evidence of being biodegraded (phytane/n-C_{18} = 0.71). The cycle 7 sample of lower oil concentration also shows no evidence of biodegradaion. Note, however, that evidence for the biodegradation of oil is clearly seen (Table 3.10) for several of the other Bay 11 (3 and 7 m depths) samples by virtue of the near equivalence of phytane and n-C_{18} and by the relative importance of the other isoprenoid alkanes.

3.2.4.diii Aromatic Hydrocarbon Composition by GC^2/MS

GC^2/MS results from the two Bay 11 microbiology stations examined are shown in Figure 3.12. The "typical" aromatic assemblage is seen with compound levels being elevated in cycle 2 (8/11/82) (10-30 ng/g) over those observed during cycle 7 (9/8/82). Again, the presence of significant quantities of the naphthalenes indicates the presence of only moderately weathered oil in these samples.

3.2.4.e Sediment cores

3.2.4.ei Oil composition by GC^2

Pertinent GC^2 data on the two Bay 11 cores examined is presented in Table 3.10. Although the surface sediments of Bay 11 have been shown to contain moderate quantities of oil, the surface (0-5 cm) core sections from Bay 11 are very low in phytane, and show a high pristane/phytane ratio indicating only very low levels of oil, if any. An n-alkane distribution in the n-C_{13} to n-C_{20} range in the 0-5 and 5-10 cm sections does demonstrate the presence of oil at trace levels.

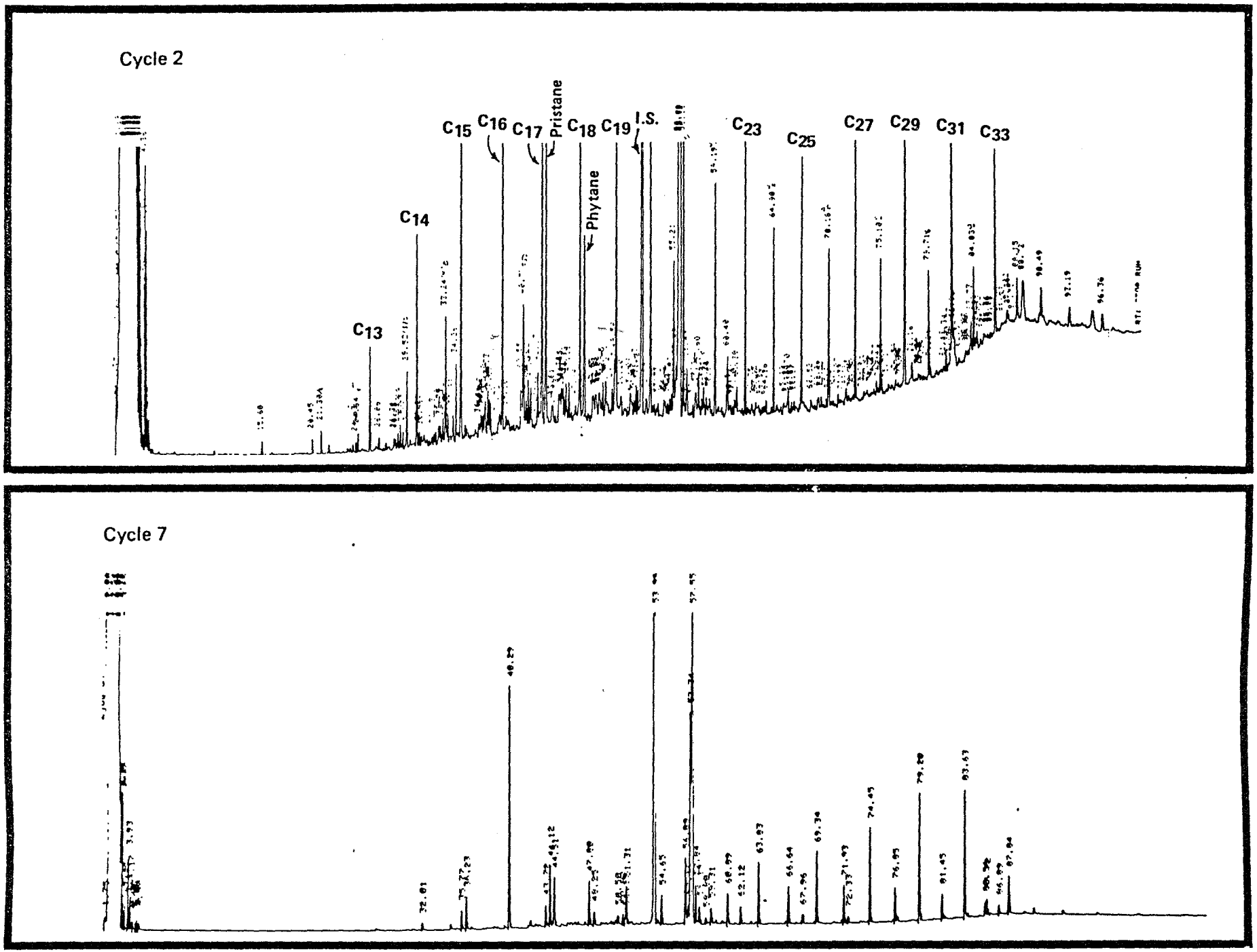


Figure 3.27. Surface sediments from microbiology stations Bay 11, Station H2, indicating the greater presence of oil in Cycle 2 (unbiodegraded).

3.2.4.eii Aromatic hydrocarbon composition by GC^2/MS

Three samples were analyzed from the Bay 11 core at the north end of the 7m deep stratum. The results are presented in Figure 3.28. PAH compounds are of similar levels in each section with a total of 10-15 ng/g in each (85% perylene). Dibenzothiophenes are only detected in the 0-5 cm section. Evidence is shown for the presence of the alkylated phenathrenes and some alkylated naphthalenes for the 5-10 and 10-15 cm sections and for the absence of dibenzothiophenes. Thus it is possible that low levels of petrogenic phenanthrenes have mixed down to the 10-15 cm level in the sediments, but due to the very low levels observed, this is a weakly supported contention.

3.2.4.f Deep sediments

3.2.4.fi Oil composition by GC2

GC^2 compositional data for those samples is summarized in Table 3.10. Owing to low phytane levels, very low alkane levels and moderate pristane/phytane ratio, it is concluded that very low levels of oil are observed in these sediments, thus voiding the hypothesis of offshore transport of oil to these slightly deeper stations. However, significant post-spill transport to even deeper stations in Ragged Channel cannot be ruled out.

3.2.4.fii Aromatic hydrocarbon composition by GC^2/MS

Although only weakly revealed in the GC^2 results, oil in the deeper Bay 11 sediments is confirmed by the GC^2/MS results (see Figure 3.14) where moderate levels of the phenanthrene and dibenzothiophene series with lesser amounts of the alkylated naphthalenes are detected.

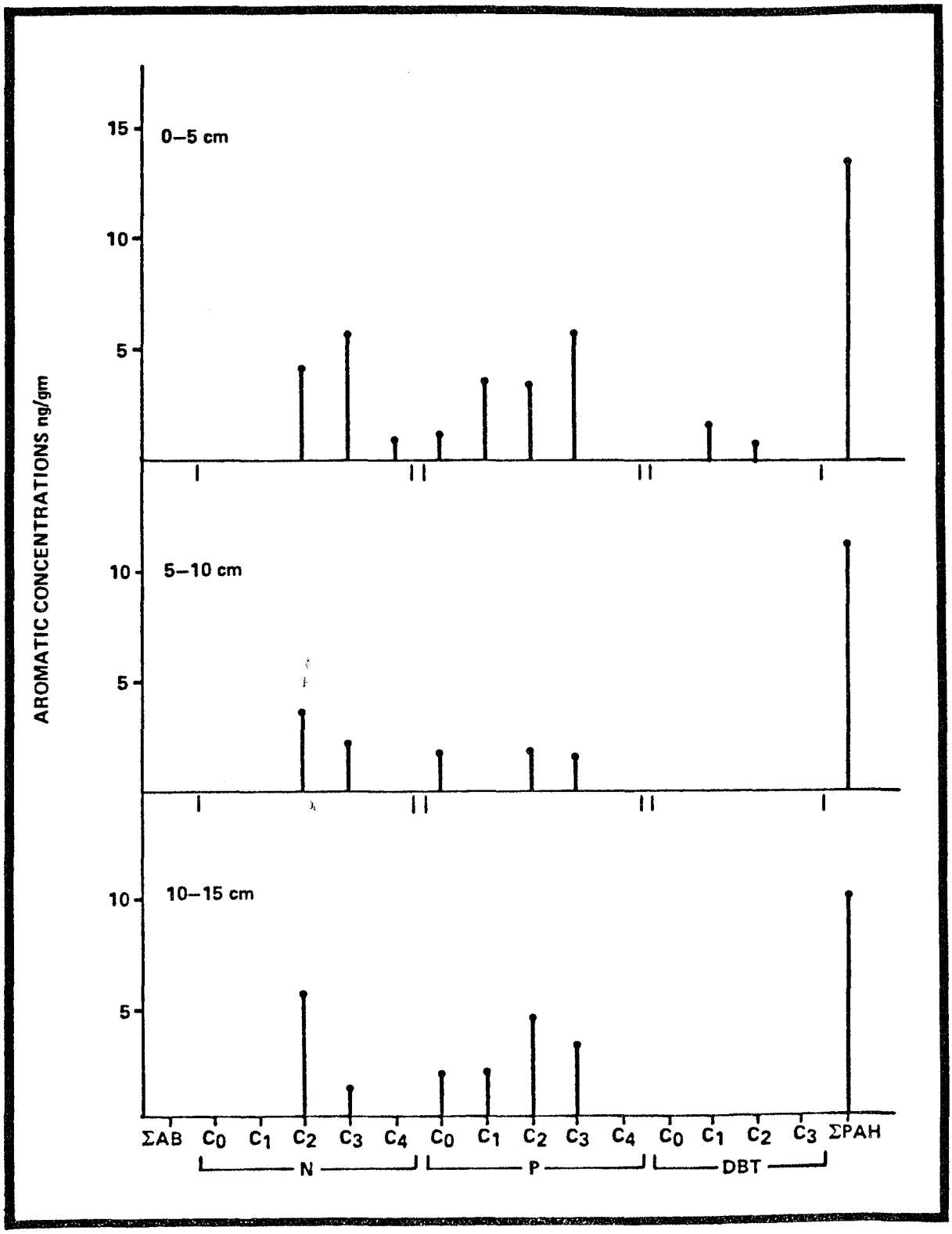


Figure 3.28. Sediment core; Bay 11; North end of 7 m tissue plots; GC^2/MS results.

3.2.5 Oil in Beach Sediments

Twelve sample of beach sediment were obtained to establish both residual oil concentrations and weathering profiles (GC^2 analyses) for these samples.

3.2.5.a Bay 11 Beach

Six samples were obtained on August 10, 1982 from two beach transects in Bay 11 (see Figure 3.29). These transects had been previously sampled in 1981. Results are summarized in Table 3.12. the results are very important in that they demonstrate that the residual oil is highly weathered (SHWR 1.0) and moderately biodgraded. That microbial activity is changing the chemistry is shown in the ALK/ISO and Phy/N-C_{18} ratios. The ALK/ISO ratios of 1.0 indicate near equivalence of the normal and isoprenoid alkanes indicating preferential degradation of the alkanes. The phy/n-C_{18} ratio demonstrates this as well. This value is equal to .62 in the spilled oil and as n-C_{18} is preferentially degraded the ratio increases. Figure 3.30A illustrates these GC^2 characteristics. Figure 3.30B illustrates a typical aromatic hydrocarbon profile in Bay 11 beached oil indicating the persistence of alkylated phenanthrenes and dibenzothiophenes in these samples. It is interesting to compare the GC^2 traces of surface floc in Bay 11 and the beached oil as quite similar GC^2 compositions are revealed.

3.2.5.b Bay 9 Beach

Results for a parallel set of six samples from Bay 9 are also presented in Table 3.12. Note that the Bay 9 oil residues, presumably from the dispersed oil experiment, are much lower in oil concentration (1-20 µg/g) than the Bay 11 beach sediments (700 - 7200 µg/g). Along with the lower concentrations of oil on Bay 9 we find a totally different composition than that observed on Bay 11 beach. The saturates (Figure 3.31) illustrate that n-alkane components as low as n-C_{11} are observed in these samples and that the

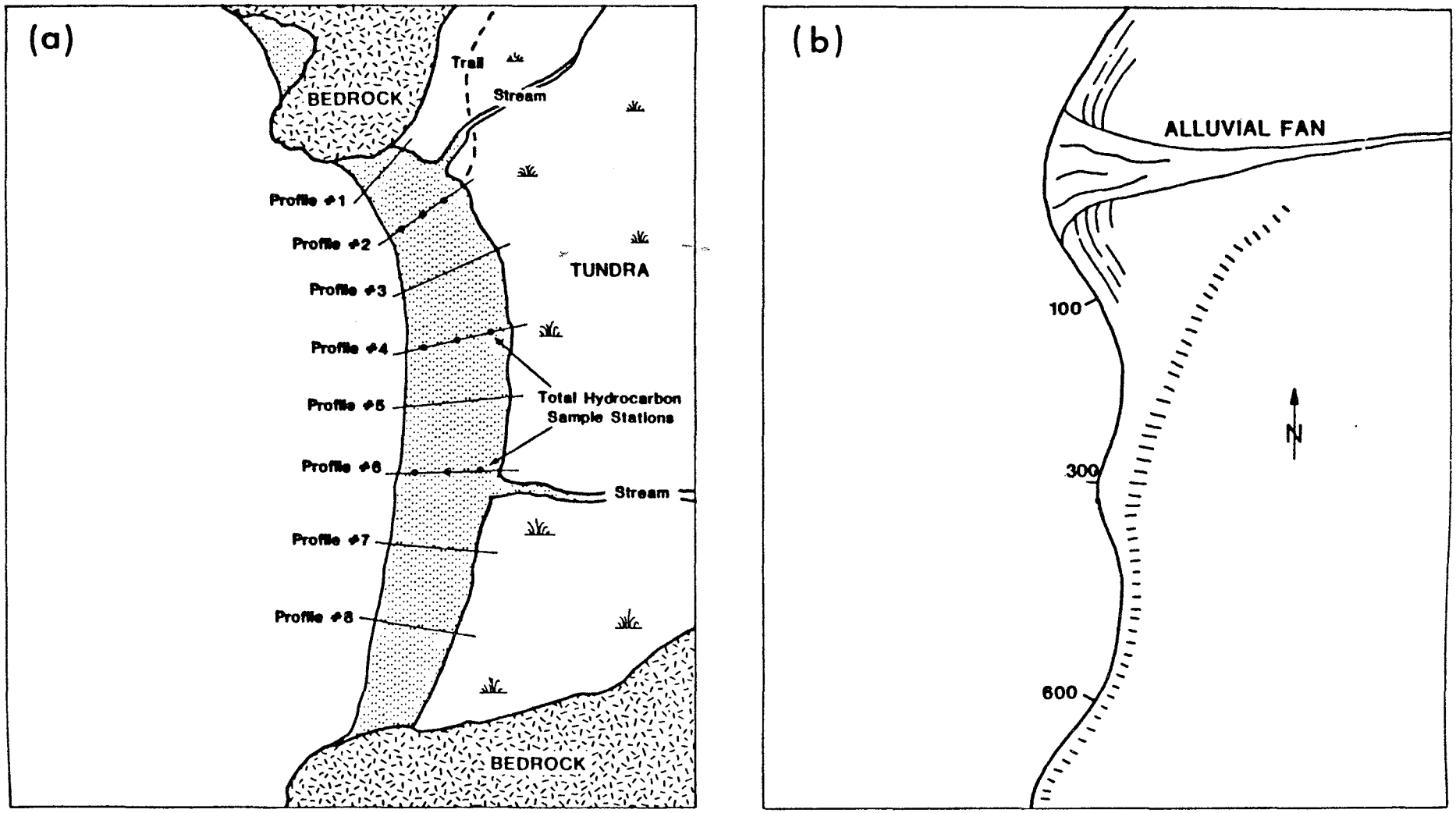


Figure 3.29. Location of surveyed beach profiles from (a) Bay 11, and (b) Bay 9.

TABLE 3.12

BAY 9 AND 11 BEACHED OIL (GC^2 DATA)

BAY	TRANSECT/ LOCATION	SATURATES (µg/g)	AROMATICS (µg/g)	TOTAL (µg/g)	ALK[a] ISO	PRIS[a] PHY	PHY[a] (n-C_{18}	SHWR[a]
11	P2 (upper)	1250	880	2130	1.0	.62	1.0	1.0
	P2 (mid)	2030	1640	3670	1.1	.78	1.3	1.2
	P2 (lower)	420	280	700	0.6	.70	2.3	1.1
	P6 (upper)	4230	2990	7220	1.8	.78	.74	1.2
	P6 (mid)	1030	610	1640	0.9	.63	2.0	1.1
	P6 (lower)	2420	1940	4360	1.3	.77	1.1	1.2
9	P100 (upper)	0.2	1.1	1.3	1.9	4.6	.31	1.1
	P100 (mid)	0.5	0.7	1.2	3.6	2.2	.53	1.3
	P100 (lower)	12	9.2.	21.2	2.2	.65	.69	1.1
	P300 (upper)	0.2	1.1	1.3	2.8	2.8	.35	1.6
	P300 (mid)	0.6	0.5	1.1	3.9	1.3	.41	1.7
	P300 (lower)	0.2	0.6	0.8	3.9	2.5	.30	1.5

[a] In aged Lagomedio these values are:
ALK/ISO = 2.50
PRIS/Phy =0.74
PHY/N-c_{18} = 0.62
SHWR = 2.30

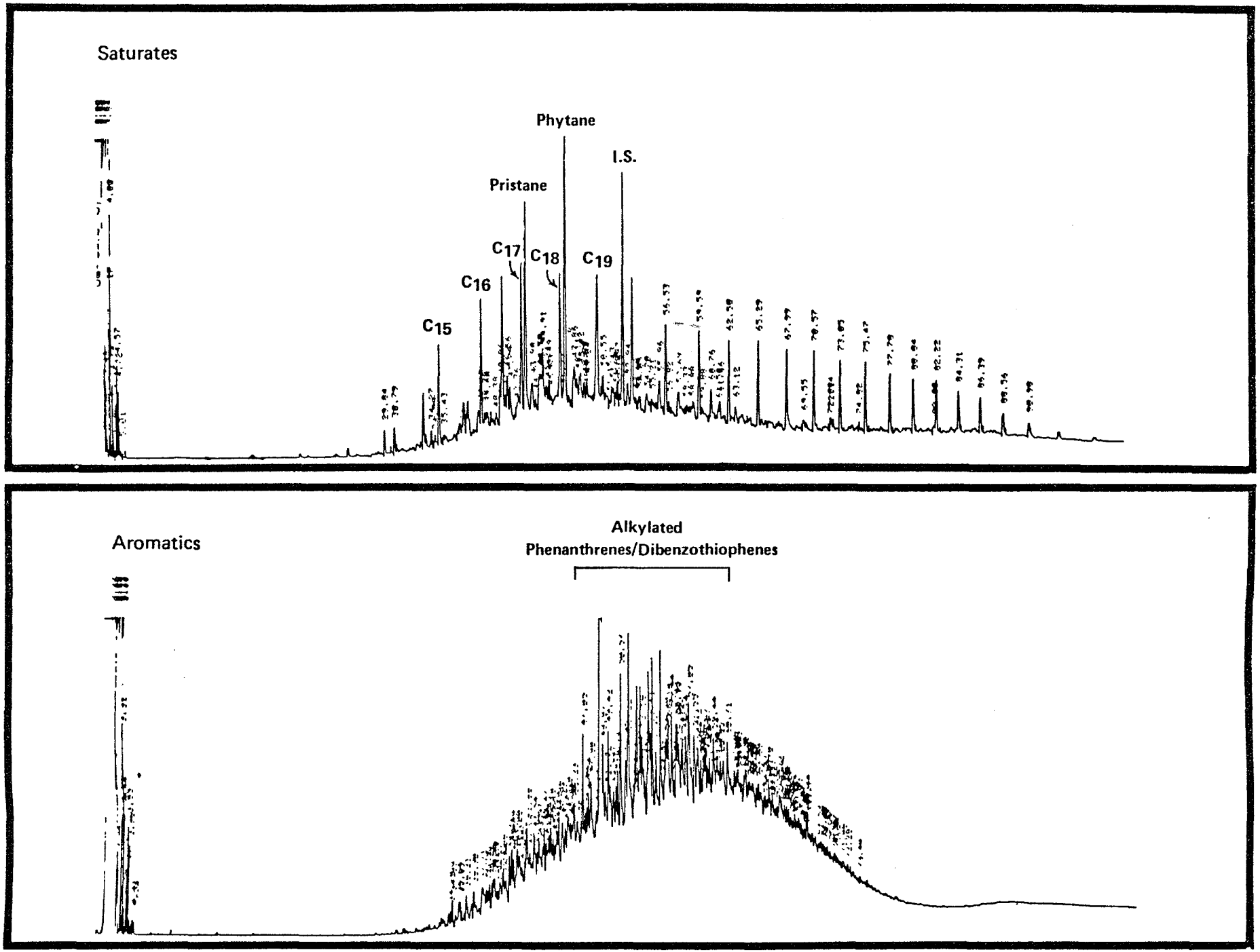


Figure 3.30. GC^2 traces of beach sediments, Bay 11, PR2.

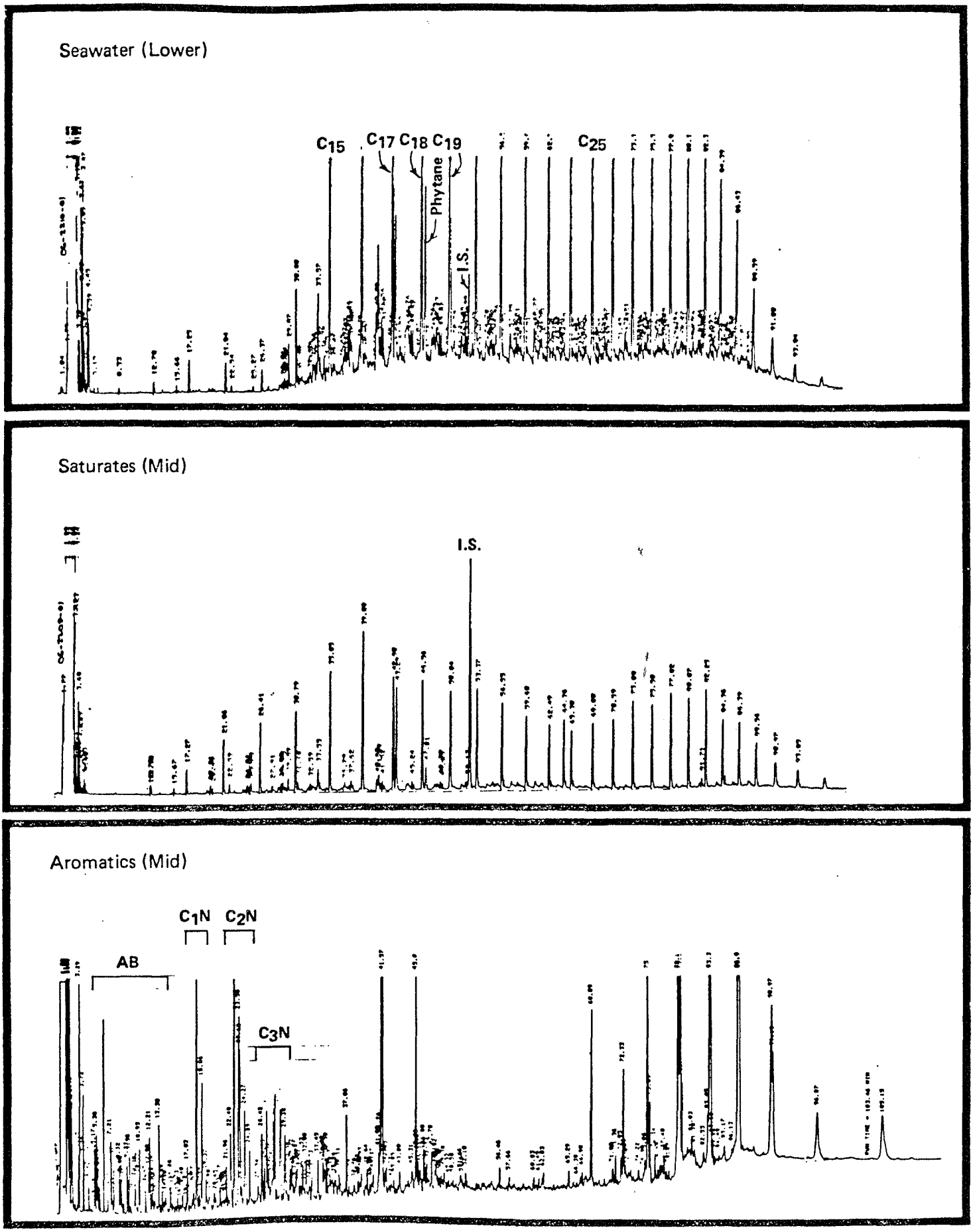


Figure 3.31. GC^2 traces of oiled beach sediments, Bay 9 (Transect 100).

residues are not biodegraded as evidenced by the high ALK/ISO ratios and the low phytane/n-C_{18} ratios. The oil on Bay 9 beach is less weathered physico-chemically as evidenced by the high SHWR values (1.5 - 1.7).

The presence of the light aromatics in all of the Bay 9 samples is striking. These compounds are easily weathered and should be quickly weathered once exposed to the environment. The aromatic composition closely resembles a water soluble fraction of the oil.

Note that these low molecular weight compounds were not observed in the beach sediments when sampled during pre-spill studies (Boehm, 1981b).

3.2.6 Comparison of UV/F "Oil Equivalents" Concentrations with GC-Derived Results

As in the report on the 1981 field results (Boehm et al. 1982a), we compared the UV/F-derived results on oil concentrations in sediments with those derived from the GC results. A plot of the concentration of oil in sediments measured by UV/F versus the concentration of phytane found in sediments appears in Figure 3.31A. The equivalence line is a plot of the concentration of phytane in oil as determined from knowledge of the amount of phytane in the original Lagomedio crude (6.4 mg phytane/gram oil).

In 1981 (see Boehm et al. 1982a; Figure 3.66) most samples clustered around this equivalence line. Here in 1982 we see that the lower concentrations of oil in sediments (6.0 ppm) as determined by UV/F fall somewhat below this equivalence line indicating a "loss" of phytane in the samples or in general a greater abundance of residual aromatics as compared to saturates in the samples. Note at the higher concentrations (6.0 to 70 ppm) the relationship is still strong. This probably indicates that for the recently deposited oil (especially in Bay 11), UV/F is a good estimate of the actual oil concentration while at lower concentrations the relationship is less strong due to weathering losses in the sediments. Overall the relationship seems as good as that observed in 1981.

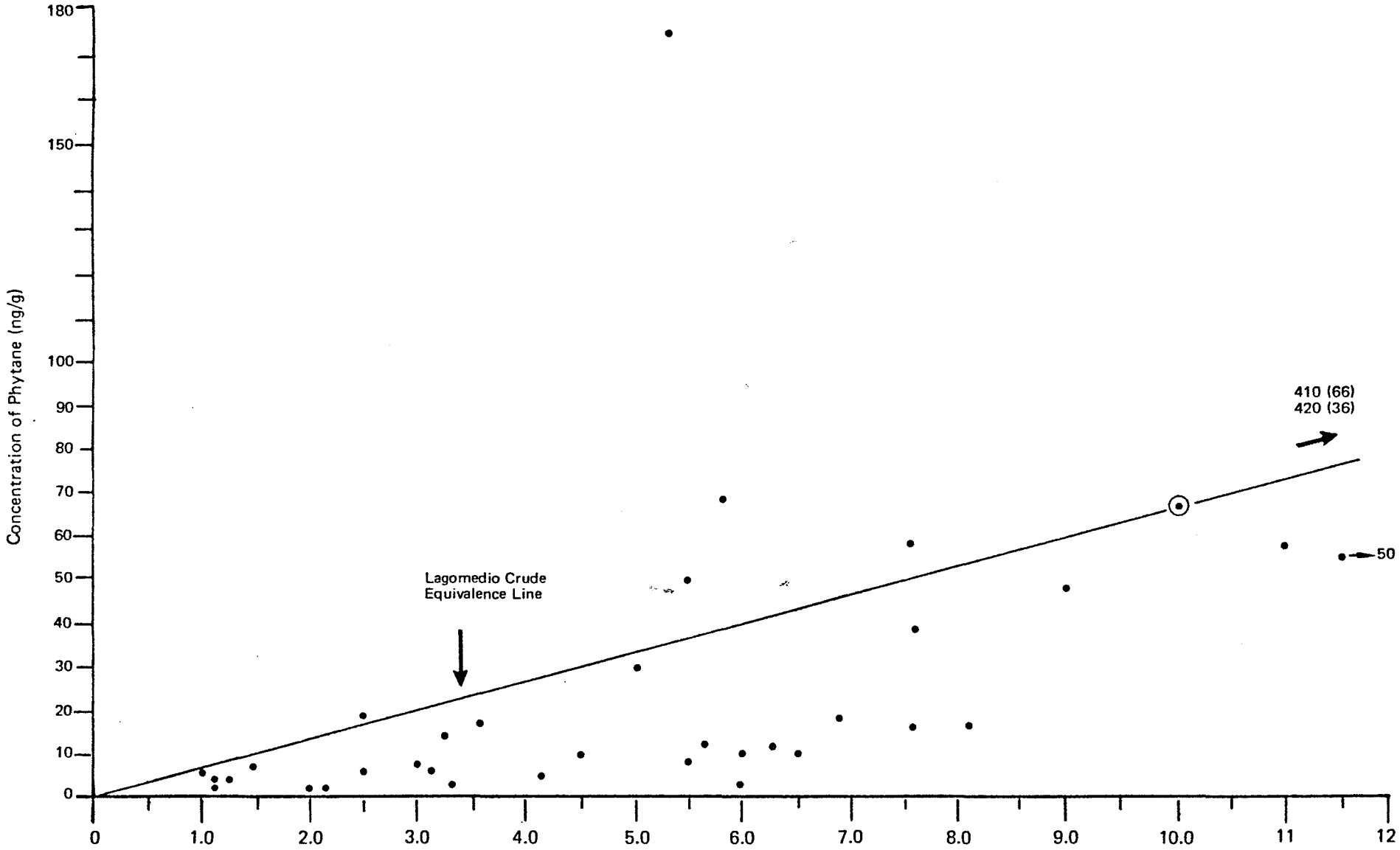


Figure 3.31A. Concentrations of oil by UV/F (ug/g).

3.3 Oil in the Sediment Traps

Eight samples of sediment trap material were obtained for GC^2 and selected GC^2/MS analyses. These consisted of traps which were allowed to collect material during the winter (i.e., the overwinter traps), one in each bay. Additionally four traps were deployed in Bay 11 near the bottom at the ends of the 7-m depth stratum and at the north and south micro plots.

Small amounts of weathered oil were observed only in the overwinter traps from Bays 9 and 10. The GC^2 traces of the saturated fractions of these samples are shown in Figure 3.32A,B. Traces of oil at extremely low levels were also observed in the Bay 7 overwinter trap. By comparison of the absolute phytane levels as an indication of the weathered oil there were .05 µg phytane/trap in Bay 7 while the Bay 9 and 10 traps contained 2.8 µg/trap and 0.16 µg/trap, respectively. The overwintering trap from Bay 11 contained no detectable hydrocarbons.

The traps deployed in Bay 11 after ice breakup, ostensibly to capture oil on beach-eroded particulates, contained no detectable petrogenic residues and only evidence of some terrigenous odd carbon chain alkanes from plant waxes. A sediment trap data summary is shown in Table 3.13.

GC^2/MS analyses were performed on three samples indicated in Table 3.13. The phenanthrene series is the most abundant series of aromatics. Significant quantities of phenanthrene (6.0 ng/trap), C_1phenanthrene (64 ng/trap), C_2phenanthrene (40 ng/trap), C_3phenanthrene (48 ng/trap), and C_4phenanthrene (6 ng/trap) were detected in the Bay 9 overwinter trap. Sizeable quantities of non-petroleum polynuclear aromatics (PAH) were detected here as well (60 ng/trap).

The other overwintering traps examined (Bays 7 and 10) contained less quantities of aromatics but nevertheless still detectable levels of the phenanthrenes (25-70 ng/trap). Thus it appears that very low levels of sediment-bound oil are circulating in the study area. Note that naphthalenes were detected in the traps as well, albeit at very low levels.

Table 3.13. Sediment trap data summary

Bay	Time	Location	Pristane mg/g	Phytane mg/trap	UCM	Status	GC²/MS Results (ng/trap) SN[a]	SP[b]	SPAH[c]
7[d]	Overwinter	-	5.1	.05	No	Trace Oil	5.0	72	2.8
9[d]	Overwinter	-	10.1	2.8	Yes	Weathered Oil	8.0	160	60
10[d]	Overwinter	-	38.3	.16	Low	Low Weathered Oil	3.0	25	ND
11	Overwinter	-	~.05	~.05	No	Clean			
11	August	7 meters north end	~.05	~.05	No	Clean			
11	August	7 meters south end	~.06	~.06	No	Clean			
11	August	N-micro	~.04	~.04	No	Clean			
11	August	S-micro	~.06	~.06	No	Clean			

[a] SN = sum of all members of naphthalene homologous series.
[b] SP = sum of all members of phenanthrene homologous series.
[c] Sum of four- and five-ringed aromatics (m/e 202 + 228 + 252).
[d] GC²/MS performed.

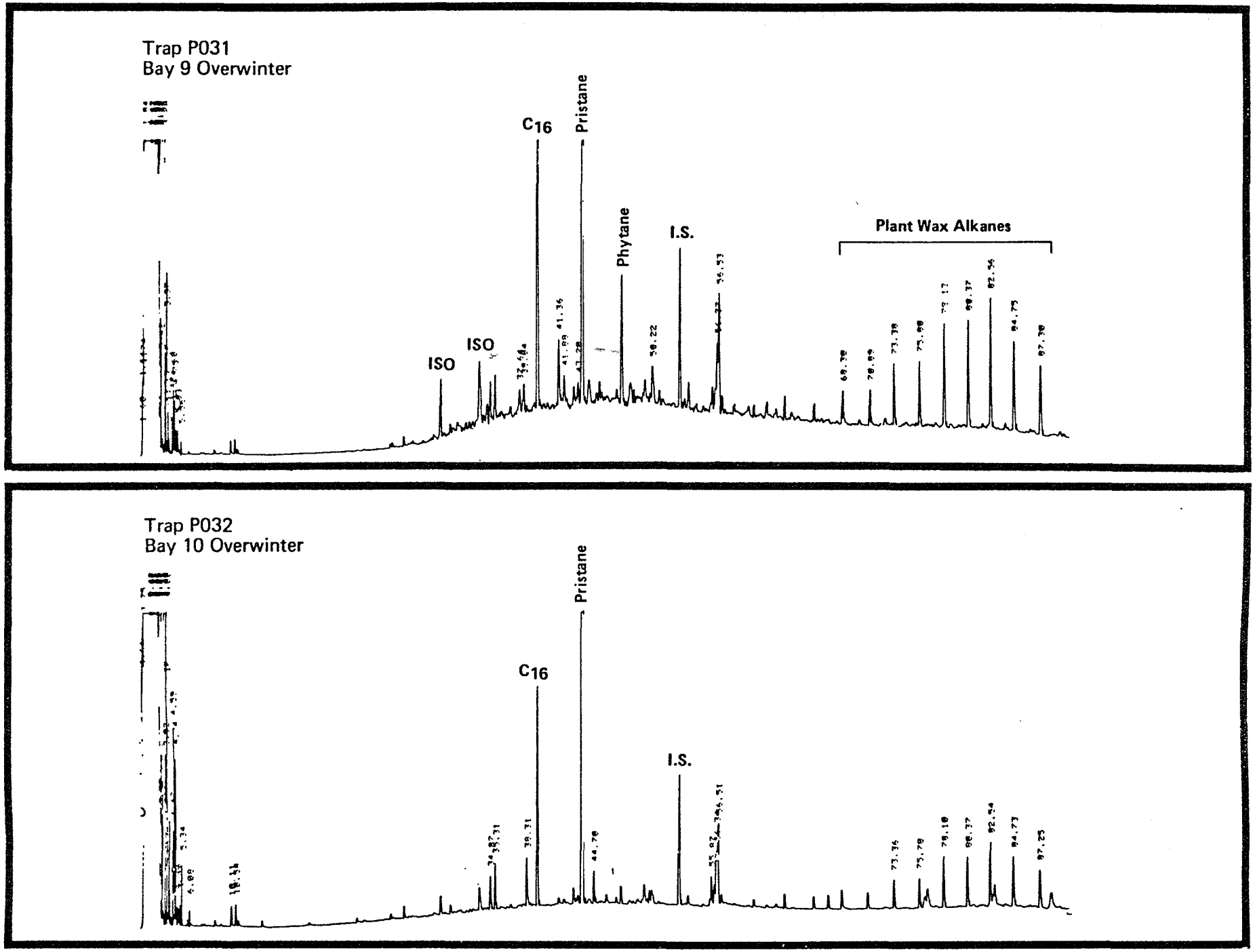


Figure 3.32. GC^2 traces of sediment trap material indicating some biodegraded petroleum residues in over-winter traps.

3.4 Oil in Marine Organisms

3.4.1 Mya truncata

UV/F analyses to determine oil concentrations were performed on a total of 29 Mya samples. These samples consisted of those taken in August from five individual tissue plot stations at the 7-meter depth in each of the four bays; those taken in May from one station along the 7-meter depth in Bays 7, 9, and 10, and at two stations in Bay 11; and those taken in September from the five tissue plots along the 7-meter depth in Bay 11 only.

GC^2 and GC^2/MS analyses were performed on pooled extracts from the five tissue plot stations sampled in August and on a pooled sample from the five tissue plots sampled in September. A total of five GC^2 and GC^2/MS analyses were performed on Mya samples.

Additional normal quality control activities included the analyses of three subsamples of a single homogenate at a single station.

All tissue data is reported as the geometric mean and the 95% confidence intervals for each data group.

3.4.1.a Bay 9

3.4.1.ai Oil Concentrations by UV/F

The UV/F results (Figure 3.33, 3.34) indicate that oil concentrations in the Mya sample from May contained 6.5 µg/g of oil and that oil concentrations declined to the 0.96 µg/g level in August. Only the 7m tissue plots was sampled so no comparisons of the 3m and 7m tissue plots are possible. When last sampled in September of 1981 oil concentrations in these animals had been 114 µg/g. UV/F replicate analyses were quite good. Triplicate samples taken from station 5 in August averaged 1.01 $\pm$ .04 µg/g (arithmetic means and standard deviation).

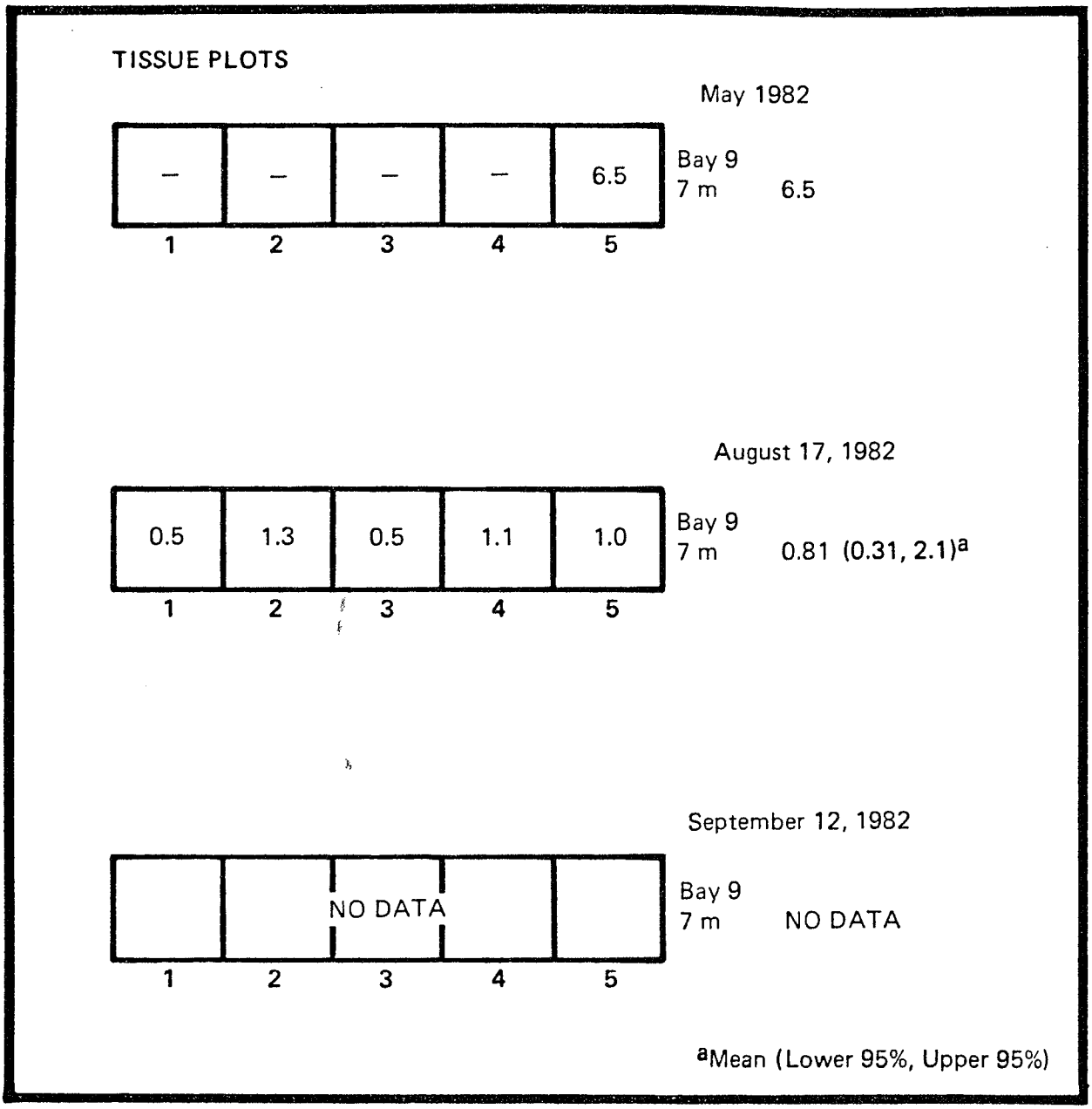


Figure 3.33. Concentrations of oil in *Mya*, Bay 9, by UV/F (μg/g dry wt.).

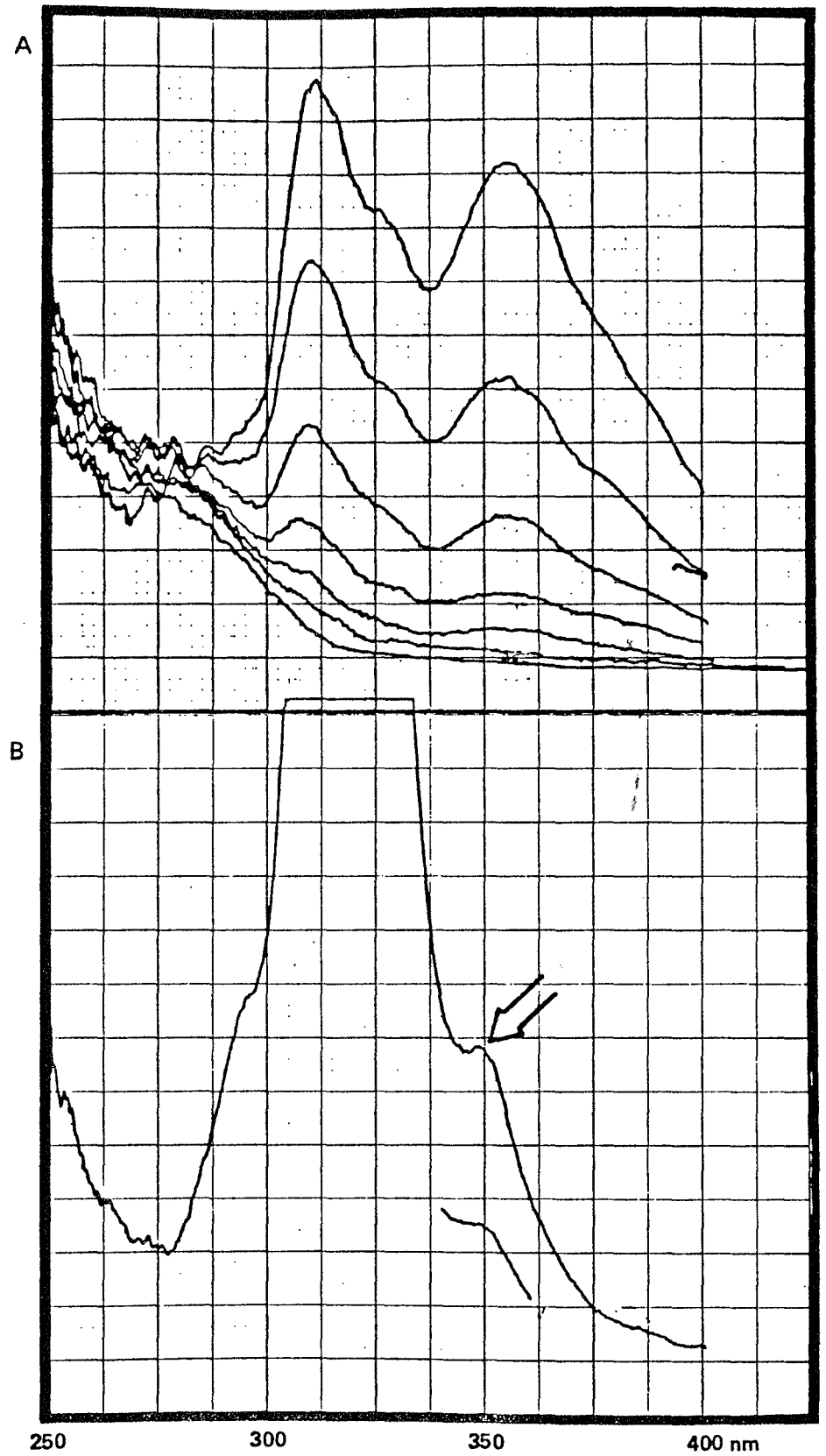


Figure 3.34. UV/F spectra of Lagomedio reference oil (A) and *Mya truncata* sample (B).

3.4.1.aii Oil Composition by GC2

Although the UV/F "oil equivalents" values for Bay 9 Mya indicate that levels were around 1 µg/g for the August pooled 7m sample, the GC^2 traces for this pooled sample reveal a considerable amount of saturated petroleum hydrocarbon (4.3 µg/g) material remaining in the sample. Note that the UV/F result is specific for fluorescing aromatic hydrocarbons (Figure 3.34). Thus, if an oil weathers so that aromatics are preferentially "lost" while saturates remain, the utility of the UV/F result decreases. In this case oil at the 6 µg/g level apparently remains in these samples, not the 0.8 µg/g indicated (Figure 3.33) by UV/F.

The residual saturated composition (Figure 3.35) is of considerable interest. The previously observed (Boehm et al. 1982a) uptake and depuration/weathering of the oil in vivo had indicated that the n-alkanes were degraded during the first two weeks after the spill, presumably owing to bacterial activity within the animal's gut. The GC^2 pattern seen in August of 1982 indicates that while the oil levels are far lower than observed in September 1981, we now see a petrogenic assemblage of hydrocarbons consisting of:

1. a weathered petroleum as indicated by the considerable residual UCM.
2. a "new n-alkane overprint of compounds from n-C_{10} to n-C_{22}.
3. beyond n-C_{22} an alkane assemblage resembling that in sediments (i.e., an odd alkane chain predominance).
4. an abundance of pristane due to dietary planktonic input.

Note that the phytane/n-C_{18} ratio which was very high in September 1981, indicating preferetial loss of C_{18} due to biodegradation is now 0.59, not much different from that in the spilled oil, 0.62. Thus, we are apparently seeing small amounts of relatively unweathered saturated hydrocarbons being

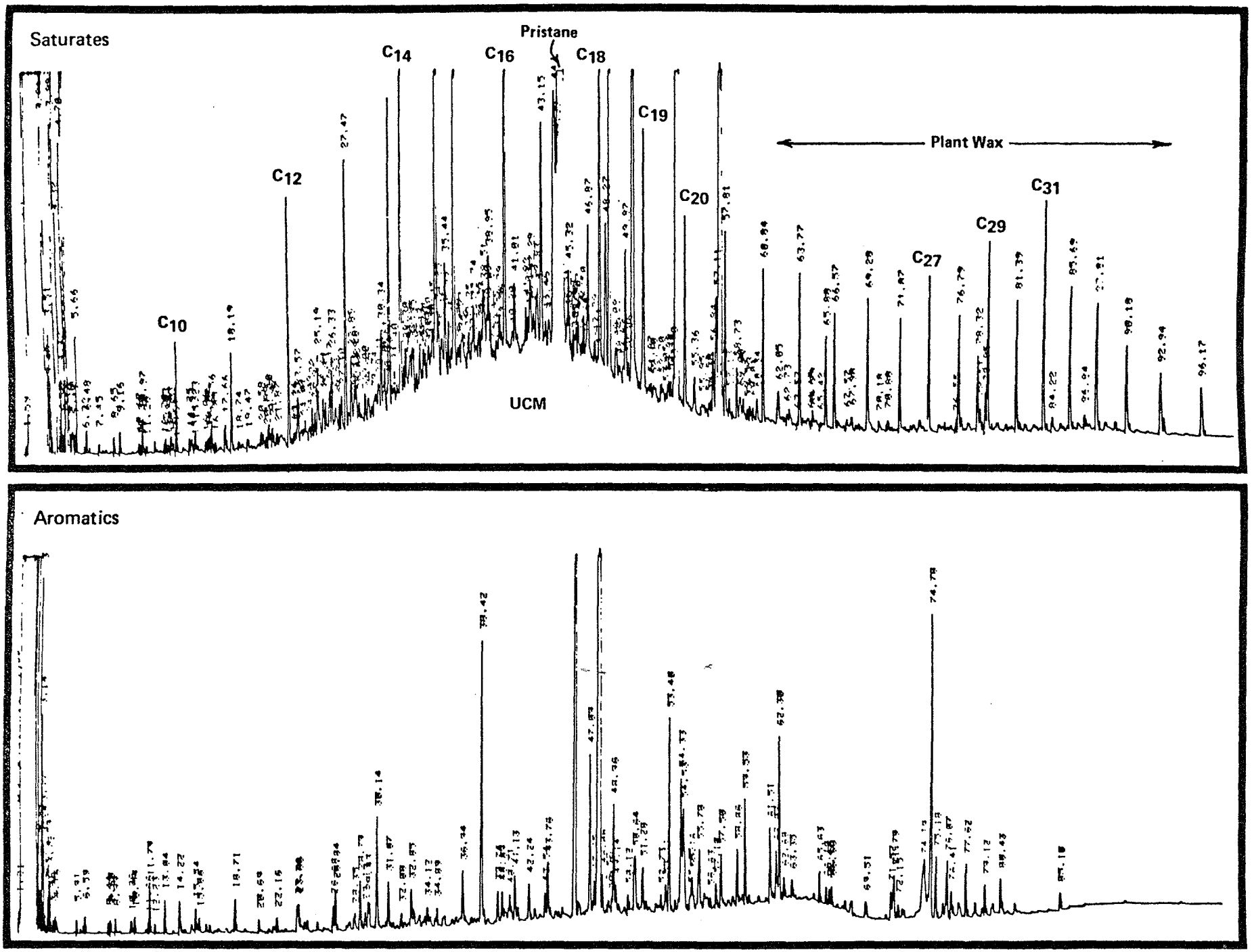


Figure 3.35. Hydrocarbon GC[2] traces, *Mya truncata*, Bay 9.

introduced to the animals. The SHWR in the animals is ∿2.7 while that in the original oil is 2.3. It is, however, not clear where the "new" n-alkane originated but the presence of this distribution has been previously noted in seawater and sediments. It should be kept in mind that the concentration differences between GC^2 traces in Figures 3.35 and those presented in Boehm et al. (1982a) are two orders of magnitude.

The aromatic hydrocarbon GC^2 trace indicates mainly biogenic material and low amounts of petroleum aromatics which are best investigated by GC^2/MS analyses.

3.4.1.aiii Aromatic Hydrocarbon Composition by GC^2/MS

The detailed aromatic hydrocarbon profiles of Mya from Bay 9 are shown in Figure 3.36. Absolute compound levels are one to two orders of magnitude lower than when last observed in 1981. Naphthalene and phenanthrene isomeric groupings (e.g., C_3N) are roughly 5-10 ng/g compared with 100 ng/g in September of 1981. As the absolute levels have decreased the composition has as well. During the two week post-spill period in 1981, the alkylated naphthalene-dominated initial composition gave way to a more weathered alkylated phenanthrene and alkylated dibenzothiophene-dominated assemblage (see Boehm et al. 1982a) One year later (Figure 3.36), however, the naphthalenes are again the most dominant group. This observation of an apparent shift in composition (albeit at low levels) along with the GC^2 data indicating a "new" input of n-C_{10} to n-C_{22} alkanes indicates that low levels of relatively unweathered oil still persist in the water column, and are acquired by Mya.

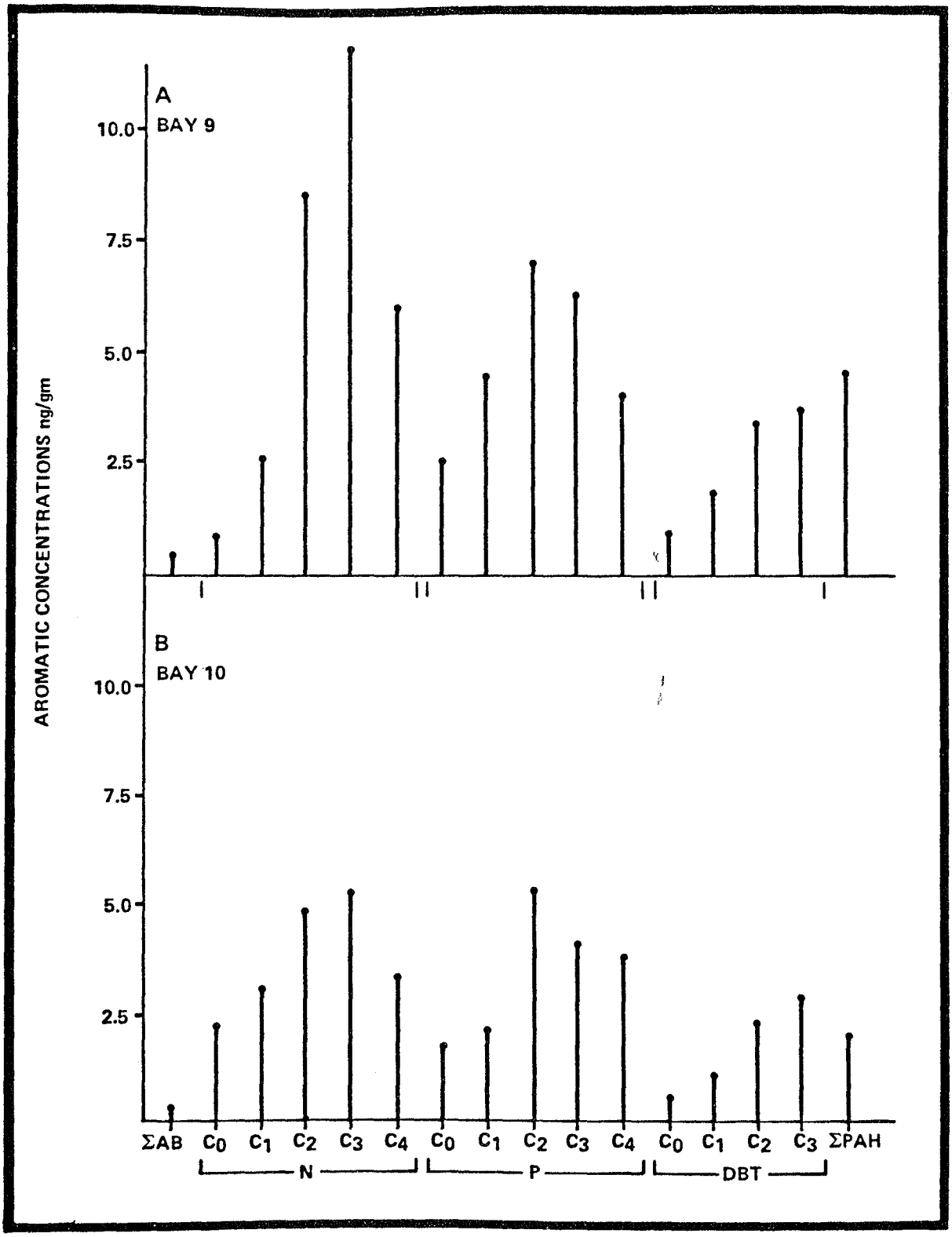


Figure 3.36. *Mya* GC^2/MS results, Bays 9 and 10.

3.4.1.b Bay 10

3.4.1.bi Oil Concentrations by UV/F

Oil concentration levels in Mya from Bay 10 were quite similar to those from Bay 9 (Figure 3.37). In May the single sample contained 6.8 µg/g and concentrations apparently decreased betwen May and August at which time concentrations were .96 (.68, 1.4) µg/g. When last sampled in September of 1981, oil concentrations were 157 (110,230) µg/g.

3.4.1.bii Oil Composition by GC2

As was the case for Bay 9 Mya, it is apparent that Bay 10 Mya also contain more saturated petroleum hydrocarbons than would be expected based on the UV/F result ($\sim$1 µg/g). Saturated hydrocarbons are 5.4 µg/g by GC^2 of the f_1 or saturated fraction alone.

The GC^2 assemblage (Figure 3.38) again contains elements 1-4 as indicated in Section 3.4.1.bii.

3.4.1.biii Aromatic Hydrocarbon Composition by GC^2/MS

The Bay 10 aromatic profile (Figure 3.36) is quite similar to that observed in Bay 9. The two-ringed aromatics, i.e., the naphthalenes, are dominant along with the phenanthrenes at the 2 to 5 µg/g level for isomeric groupings (e.g., C_3N). Total naphthalene (C_0N through C_4N) levels are 18 ng/g. Therefore, the overprint of a relatively unweathered assemblage is seen here as in Bay 9.

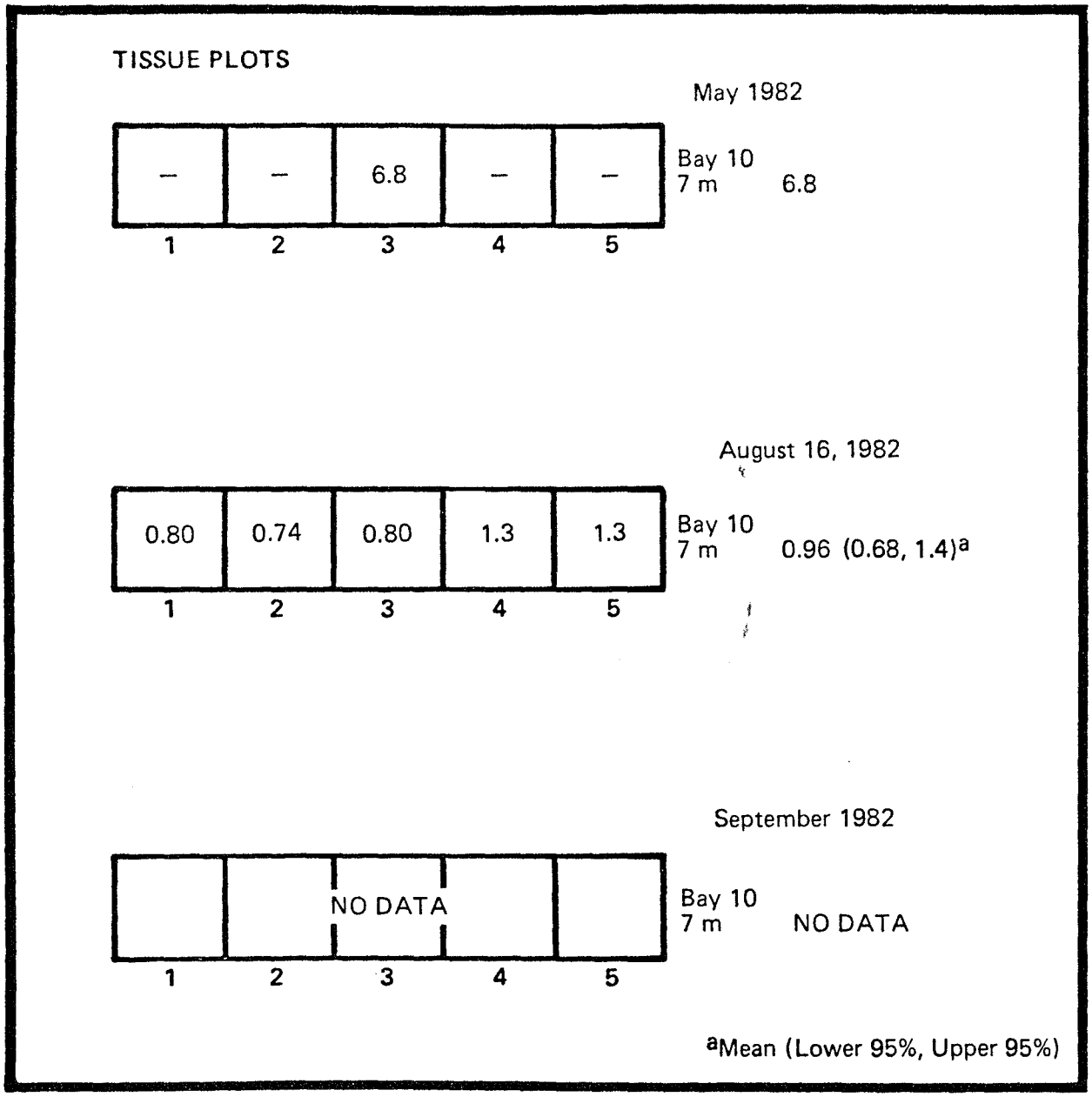


Figure 3.37. Concentrations of oil in *Mya*, Bay 10, by UV/F (μg/g dry wt.).

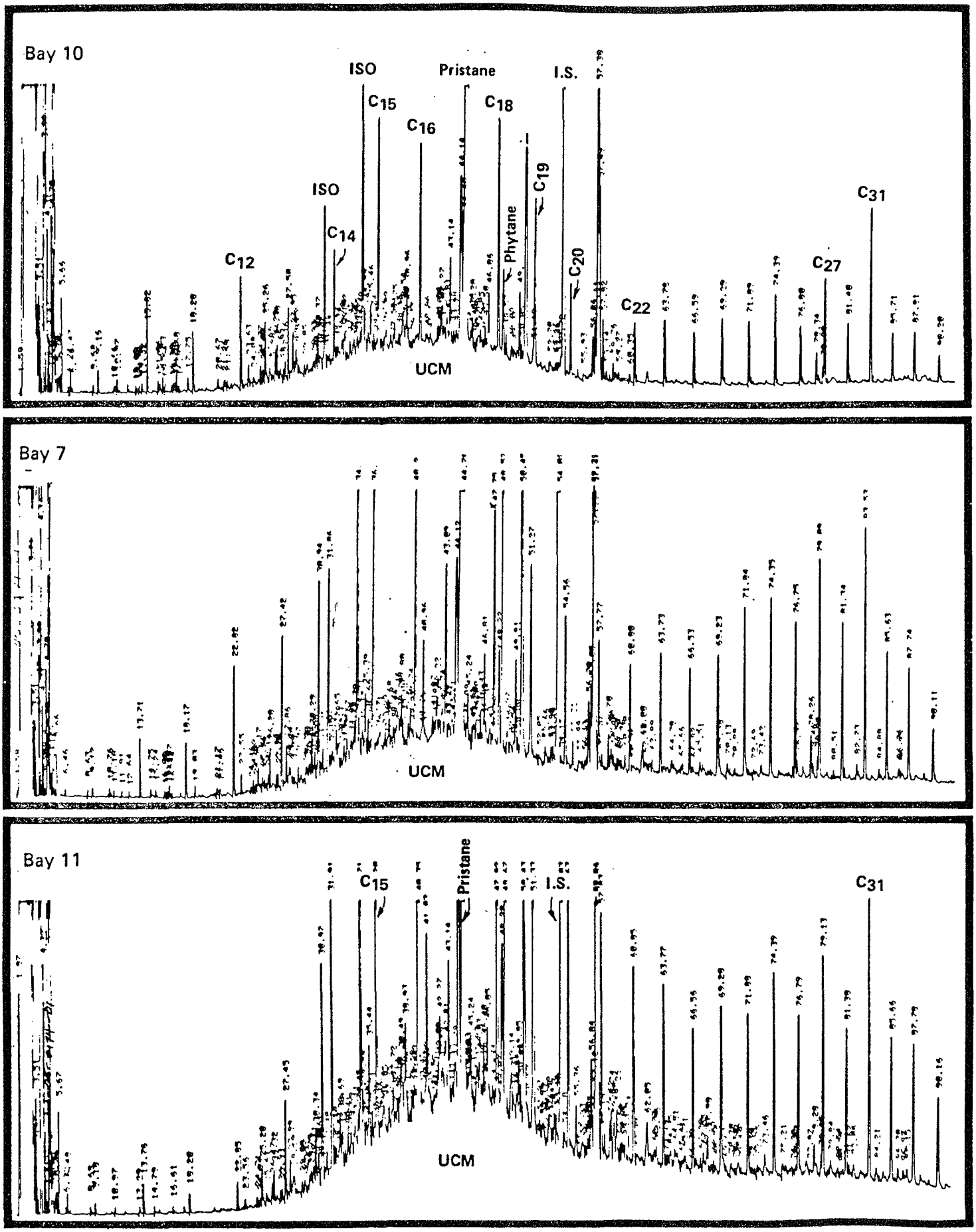


Figure 3.38. GC^2 traces of *Mya truncata*, saturated hydrocarbons (Bays 10, 7, 11).

3.4.1.c Bay 7

3.4.1.ci Oil Concentrations by UV/F

In May 1982, oil concentrations in Mya from Bay 7 (2.1 µg/g) were somewhat elevated over background or pre-spill levels (.34 µg/g) determined prior to the 1981 dispersed oil release. However, background levels were reached (Figure 3.39) by the August 1982 sampling when levels were .41 (.28, .59) µg/g. When last sampled in September of 1981, these animals contained 47 (31,70) µg/g of oil.

3.4.1.cii Oil Composition by GC2

The Bay 7 animals also contain detectable saturated hydrocarbons (3.4 µg/g). The UV/F results presented in the previous section illustrate near pre-spill levels of 0.4 µg/g. However, petrogenic material remains of the same composition as those in Bays 9 and 10 (Figure 3.38). The disproportionately large amounts of n-C_{15} and n-C_{16} may with pristane be of biogenic origin as are the plus alkanes larger than n-C_{22}.

3.4.1.ciii Aromatic Hydrocarbon Composition by GC^2/MS

GC^2/MS results for Bay 7 Mya (Figure 3.40) are similar to those observed in Bays 9 and 10. Compound levels of 2-10 ng/g as well as the naphthalene-dominated assemblage at those low levels are seen. Thus, this low level overprint affects the reference bay as well. This is consistent with 1981 results where a water-column mediated oil uptake was observed in Bay 7 along with Bays 9 and 10.

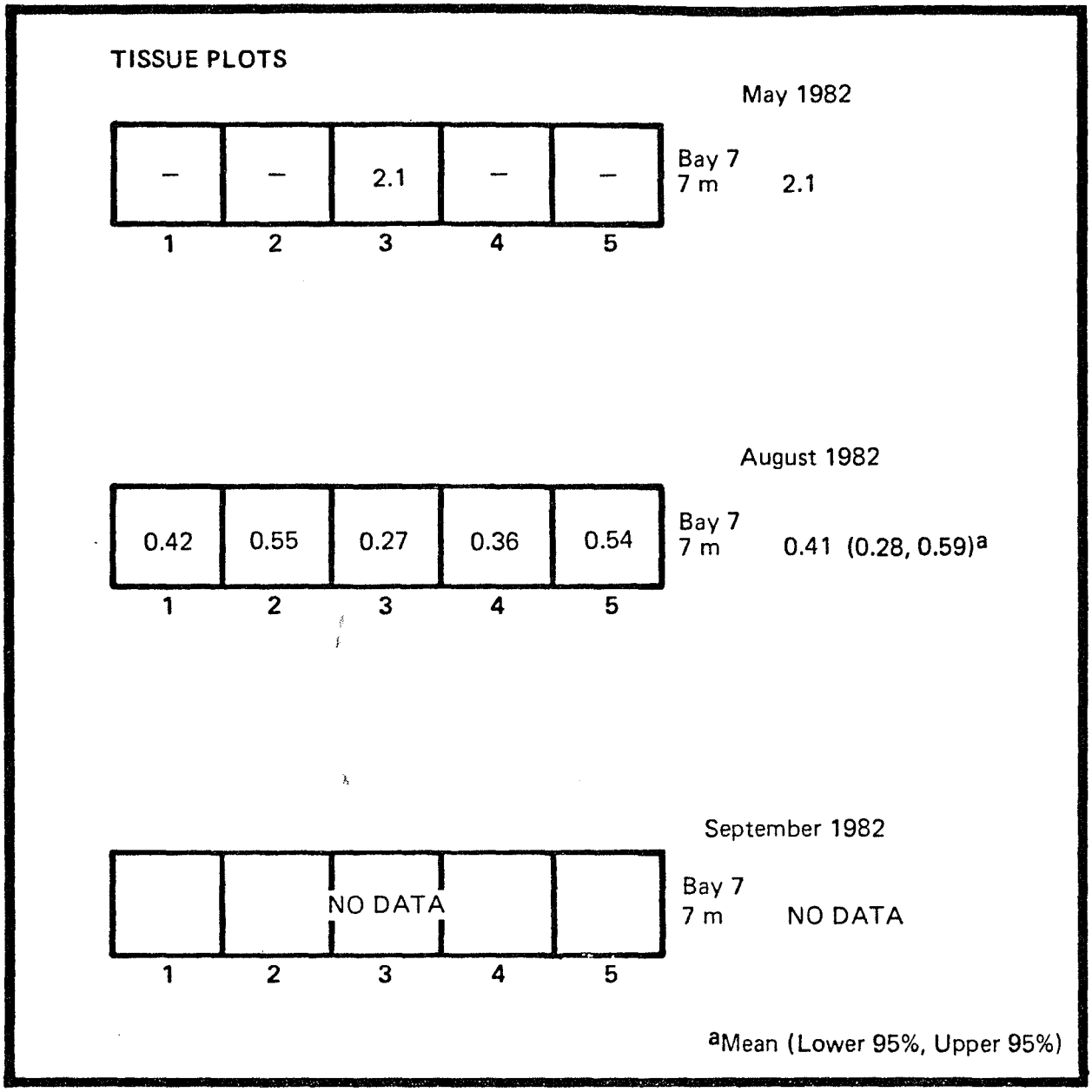


Figure 3.39. Concentrations of oil in *Mya*, Bay 7, by UV/F (μg/g dry wt.).

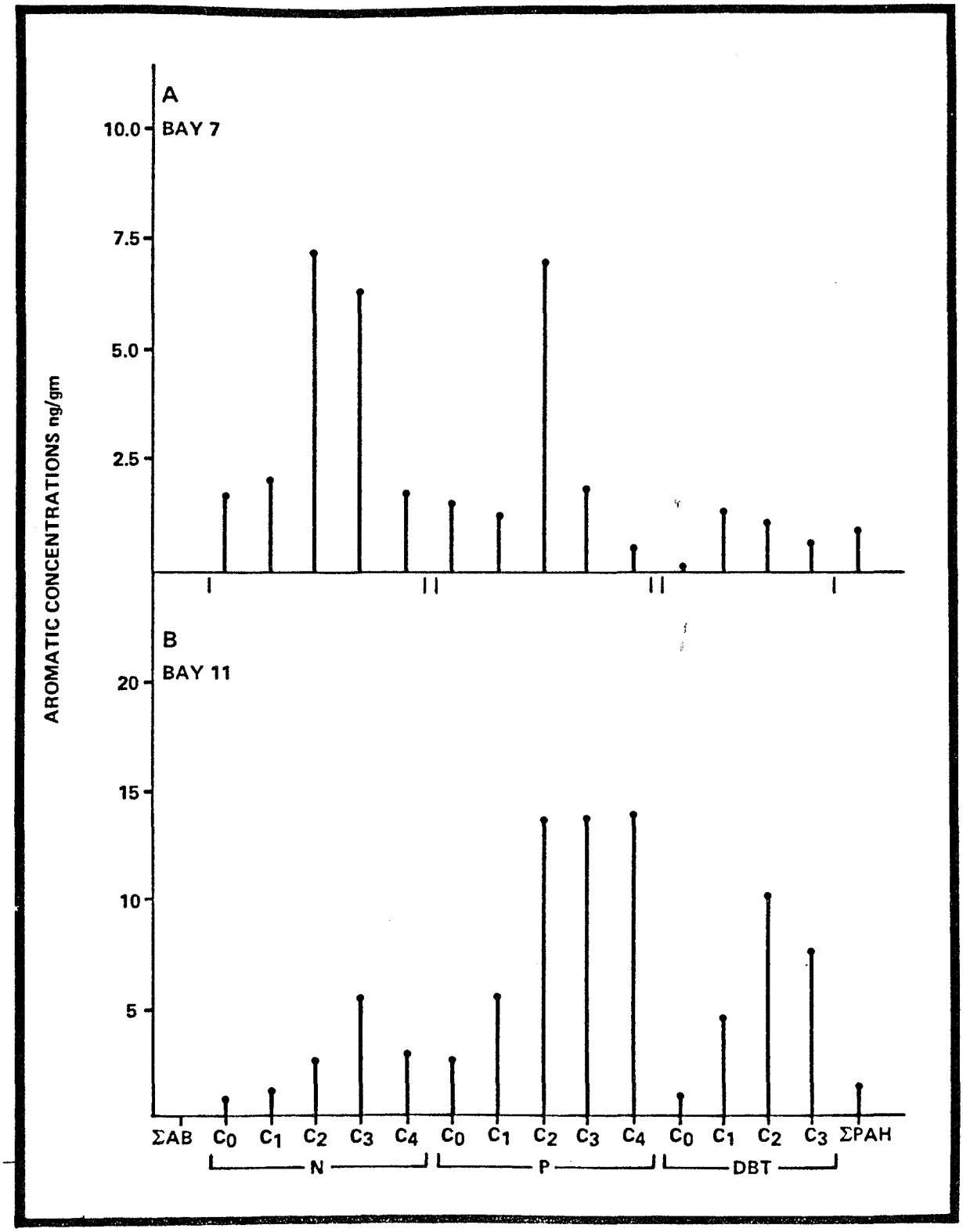


Figure 3.40. *Mya* GC^2/MS results, Bays 7 and 11.

3.4.1.d Bay 11

3.4.1.di Oil Concentrations by UV/F

Levels of oil in Mya samples (Figure 3.41) taken in May 1982 averaged 6.5 µg/g. Concentrations appeared to decrease between May and August when levels decreased to 1.3 (.91, 1.9) µg/g. However, Bay 11 was resampled in September at which time oil levels along the entire depth stratum increased three- to fourfold to 4.7 (4.69, 4.71) µg/g. When last sampled in September of 1981, levels in these animals were 93 (73,120) µg/g.

3.4.1.dii Oil Compositions by GC^2

Bay 11 Mya animals contain 8.0 µg/g of petrogenic saturated hydrocarbons. UV/F-determined values of oil for these samples were 1.3 ppm. Therefore, UV/F has underestimated the amount of petroleum hydrocarbons by roughly a factor of 5-6. The composition of the Bay 11 residual oil is quite similar to that observed in the other bays (Figure 3.38).

An additional sampling in September 1982 was analyzed (see Figure 3.42). The GC^2-determined oil content was 20 µg/g in the saturated fration alone. Again, the UV/F-determined value of $\sim$5 µg/g underestimates the oil content by at least a factor of four. Clear evidence of weathered oil is observed here. The n-alkane overprint observed earlier (Figure 3.42) is present, but at a reduced levels than those observed in August due to the higher overall oil levels present. The most dominat GC^2 characteristics in September 1982 are the large UCM, and the isoprenoid abundances, identical features to those observed in 1981, albeit now at much lower levels than in 1981 but higher than in August 1982.

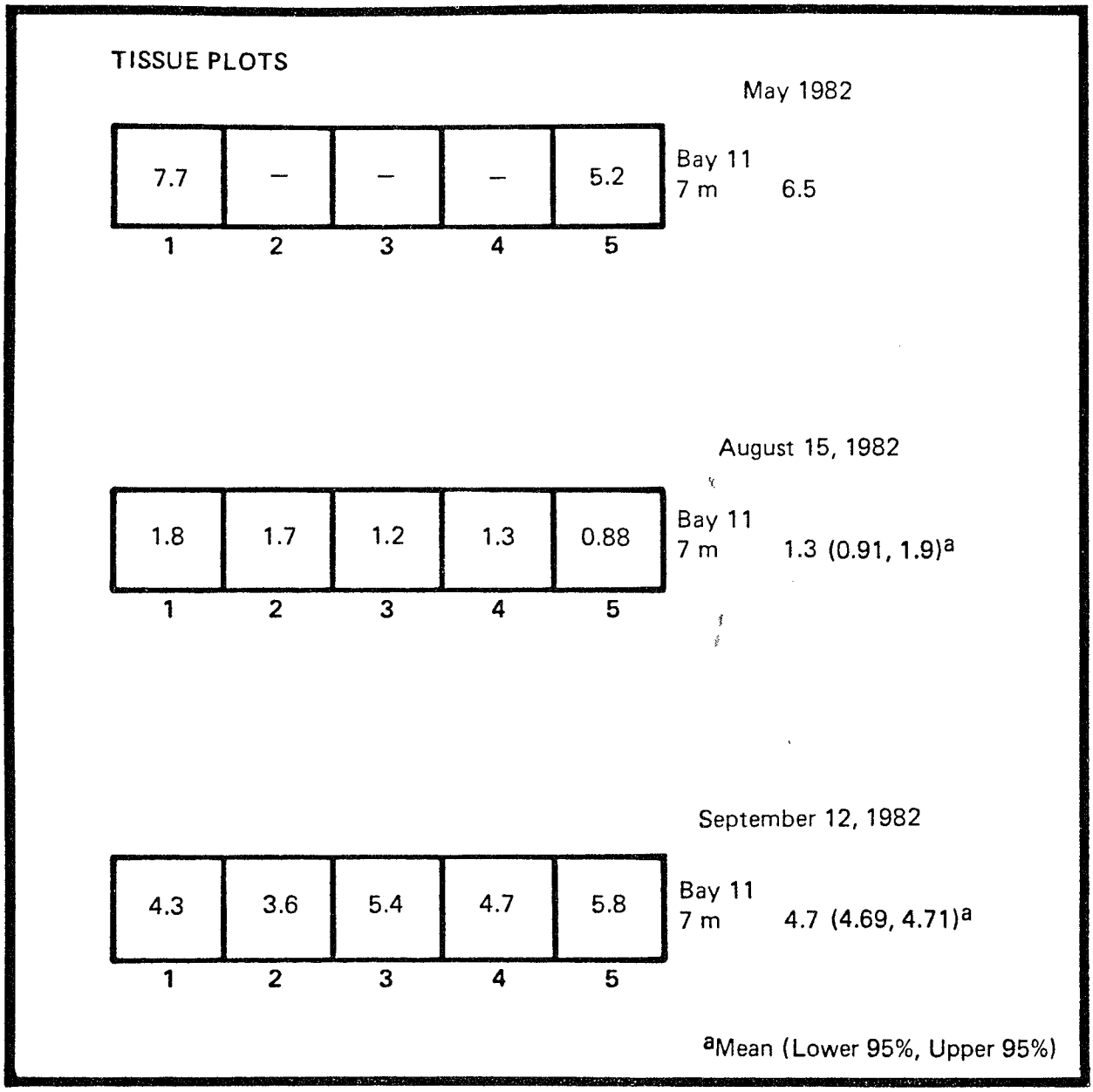


Figure 3.41. Concentrations of oil in *Mya*, Bay 11, by UV/F (μg/g dry wt.).

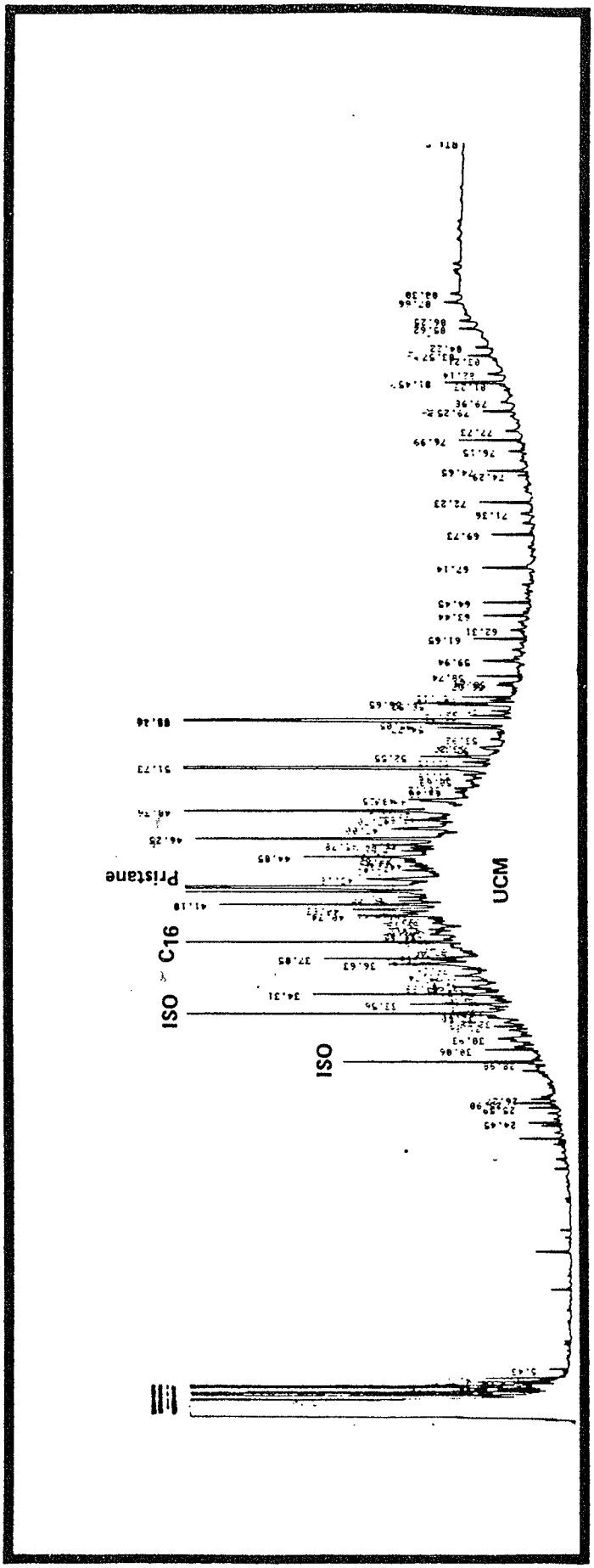


Figure 3.42. GC^2 trace of Bay 11 *Mya*, September sample.

3.4.1.diii Aromatic Hydrocarbon Composition by GC^2/MS

The Bay 11 aromatic composition is different than those observed in the other bays. In Figure 3.40, we can see that an aromatic assemblage dominated by the phenanthrene and dibenzothiophene series characterizes the Bay 11 *Mya* unlike the strong naphthalene overprint seen in the other bays. The composition observed in Bay 11 is quite consistent with that observed in September 1981 (see Figure 3.83 of Boehm et al., 1982a). The aromatic levels seen in 1981 (200-800 ng/g) are, however, much higher than the 10-15 ng/g levels observed in 1982. It does appear that in addition to the fact that Bay 11 *Mya* contain more aromatic hydrocarbons than those in the other bays, a different source of petrogenic material (more weathered) is reaching the Bay 11 animals than that reaching those in Bays 9, 10 and 7.

GC^2/MS results from the September 1982 sampling are shown in Figure 3.43. The phenanthrenes and dibenzothiophenes are greater in prominance than in August. Thus both the saturate and aromatic profiles of the September 1982 animals are consistant with a more weathered composition suggesting that the alkane overprint acquired in August has been modified just as the one day post-spill assemblage had been modified after the initial two week sampling in 1981.

3.4.2 *Serripes groenlandicus*

UV/F analyses were performed on 19 *Serripes* samples. The five tissue plots from the 7m depth in each of the four bays were sampled (one sample from Bay 11 was not taken). GC^2 and GC^2/MS analyses were performed on pooled extracts from each of the four bays (i.e., four samples).

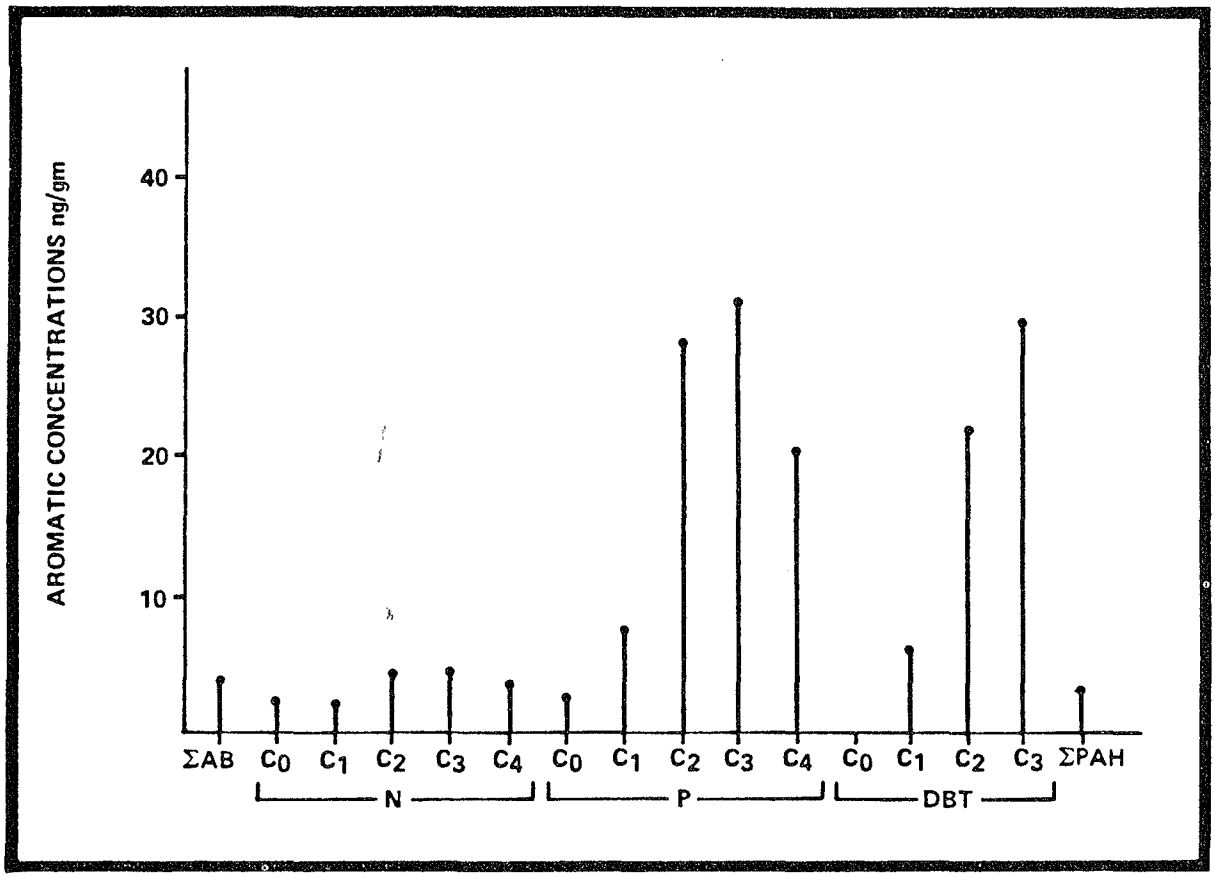


Figure 3.43. *Mya* GC^2/MS results, September 1982, Bay 11.

3.4.2.a Bay 9

3.4.2.ai Oil Concentrations by UV/F

Figure 3.44 illustrates the oil concentration results along the 7-meter depth stratum in Bay 9 along with the results from the other bays. Concentrations were 5.2 (3.9, 6.9) µg/g compared with 116 (69,190) µg/g when last sampled in September 1981. Note that the oil levels in Bay 9, although much reduced from 1981, are still significantly (95% level) higher than those in Bays 7 and 10.

3.4.2.aii Oil Composition by GC2

The saturated hydrocarbon GC^2 trace from the pooled Serripes sample from Bay 9 strongly suggests that relatively unweathered oil, or the lower boiling fractions of a crude oil, are being acquired by Serripes in Bay 9. The GC^2 trace in Figure 3.45 shows a clear indication of this low molecular weight overprint. Concentrations of the individual alkanes shown in Figure 3.45 are 0.1-0.5 µg/g. This low boiling n-alkane and branched alkane overprint is similar to that observed for Mya as well. Petrogenic inputs are also quite apparent in the aromatic GC^2 trace (not shown). When last sampled in 1981, the saturated hydrocarbon assemblage in Serripes resembled a biodegraded (n-alkane-free) composition, although overall concentrations were much higher.

3.4.2.aiii Aromatic Hydrocarbon Composition by GC^2/MS

Serripes from Bay 9 contain far greater residual aromatic hydrocarbons than do Mya from the same bay (Figure 3.46). The C_3N for example are present at the 370 ng/g level, as high as levels observed in 1981 for these compounds. The mass chromatograms for the naphthalene series (Figure 3.47) clearly show the abundant naphthalene series. The phenanthrenes are lower in

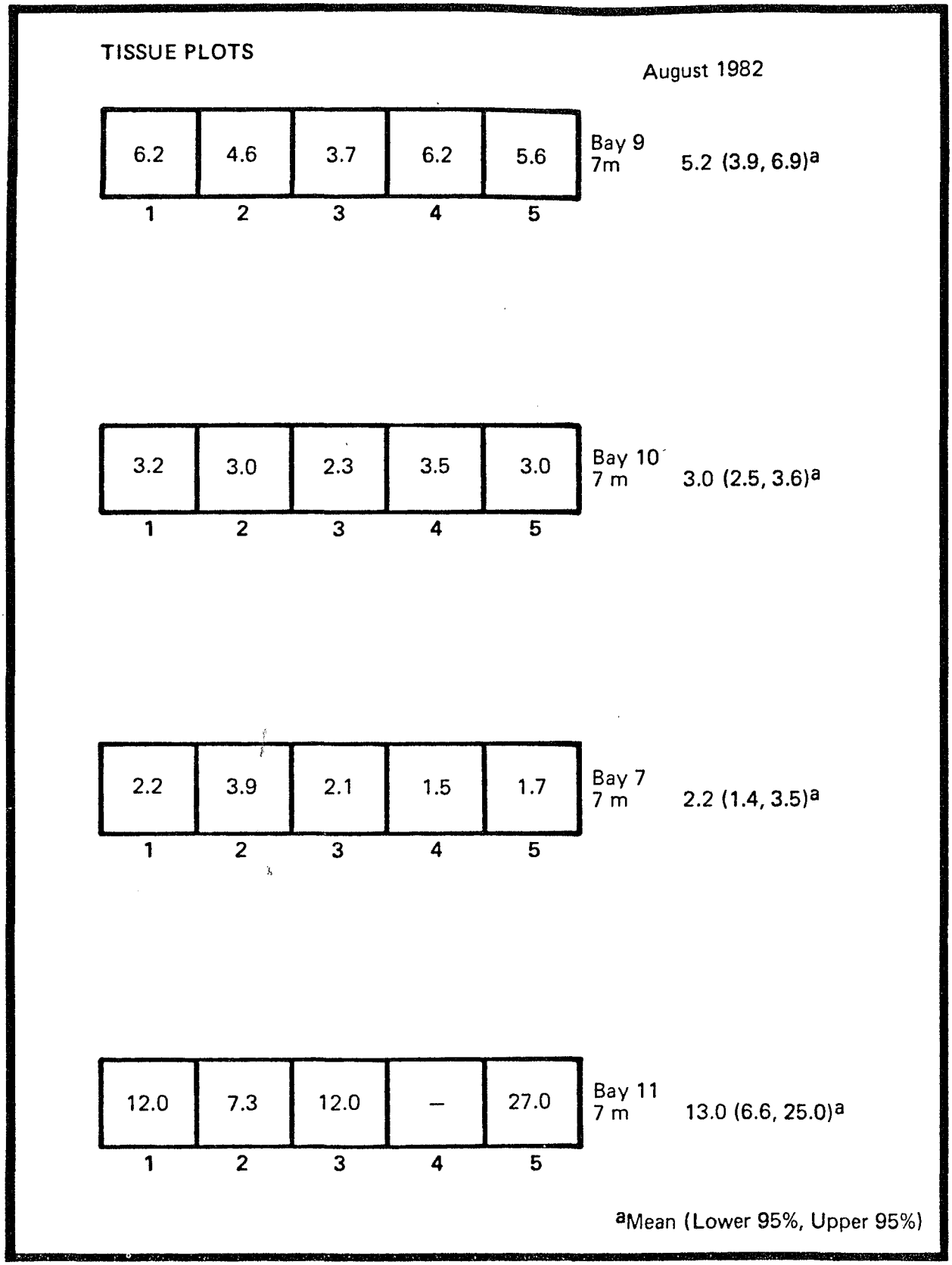


Figure 3.44. Summary of oil concentrations in *Serripes*, by UV/F (μg/g dry wt.).

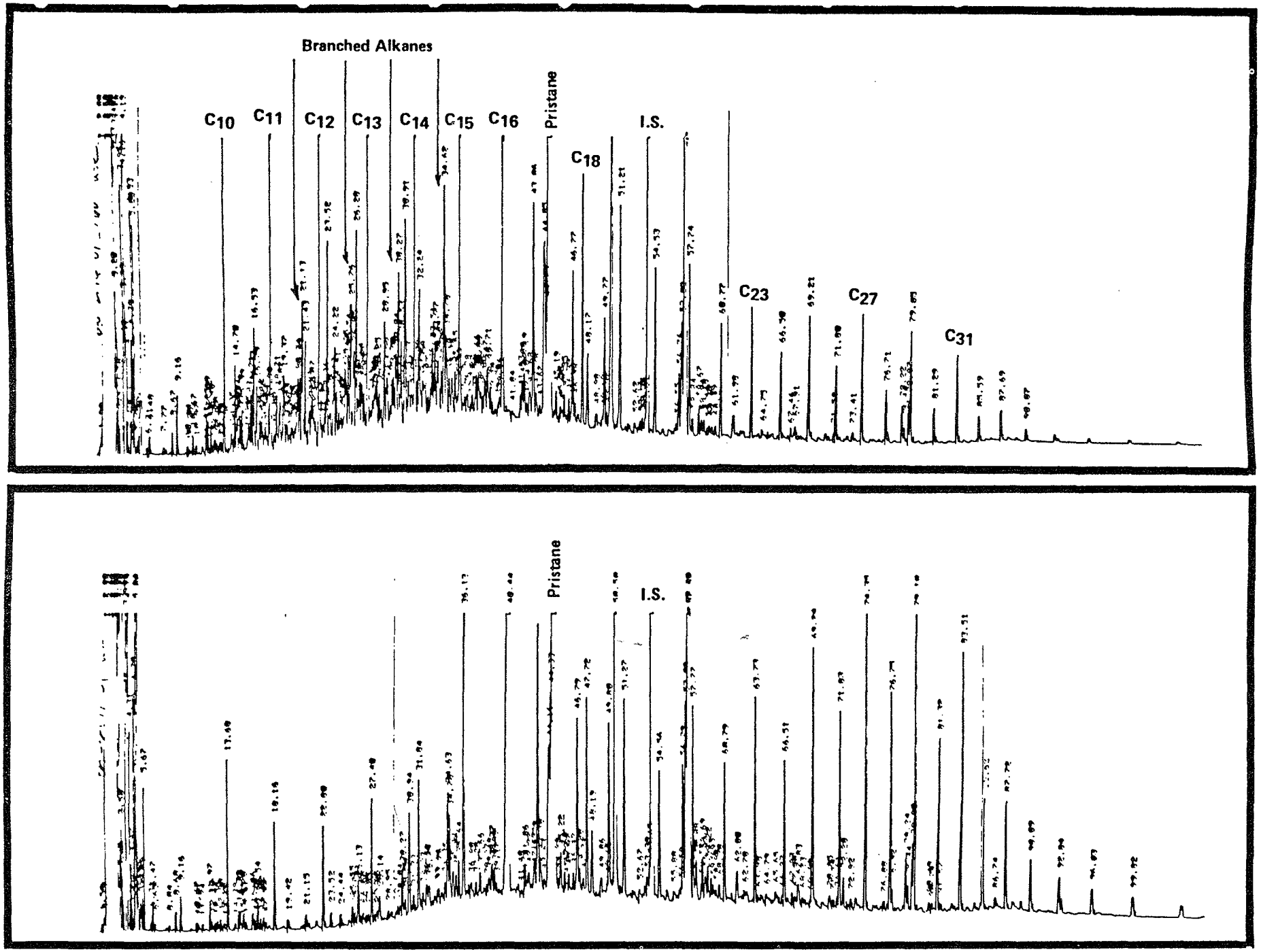


Figure 3.45. GC[2] traces of *Serripes groenlandicus*, saturated hydrocarbons (Bays 9 and 10).

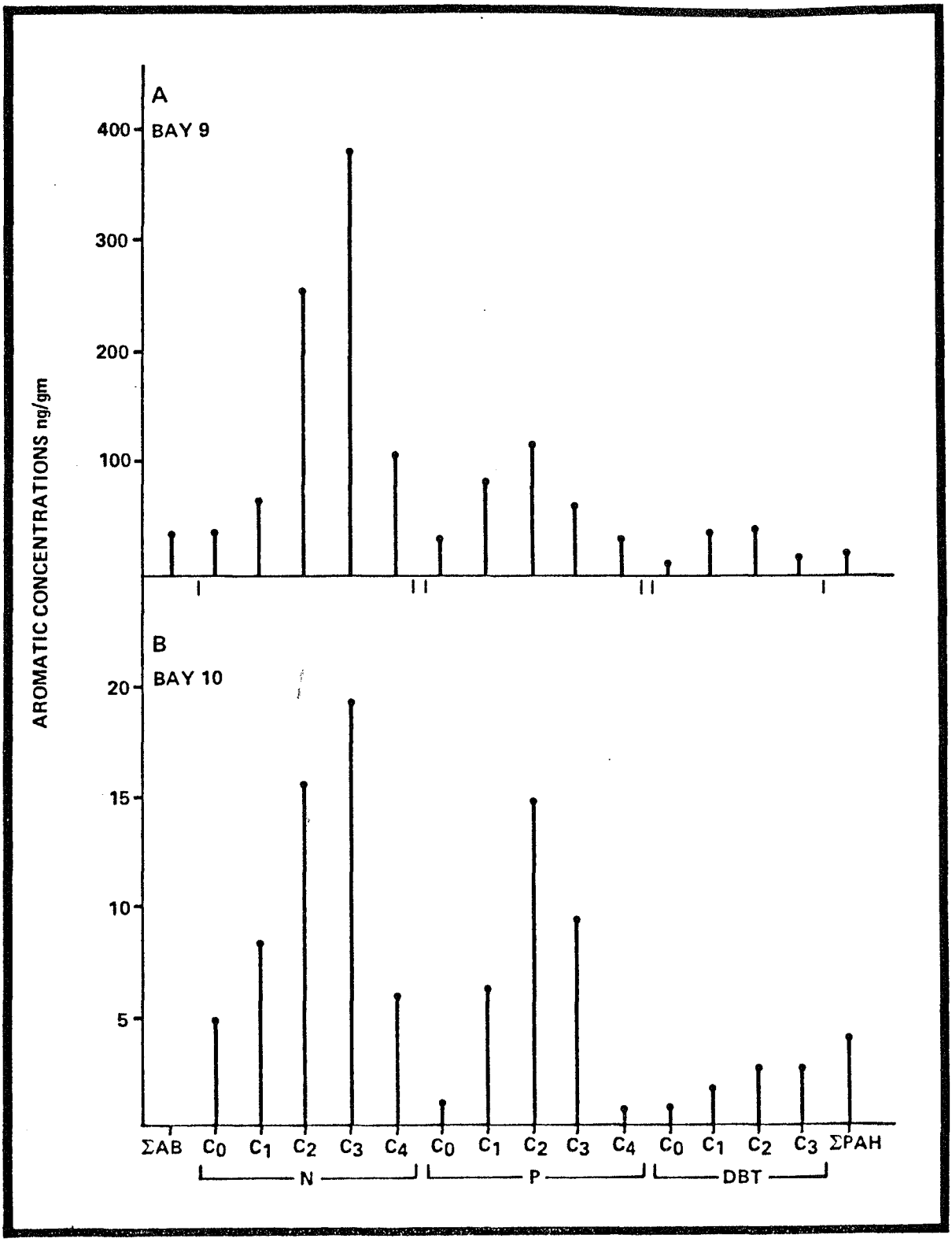


Figure 3.46. *Serripes* GC^2/MS results, Bays 9 and 10.

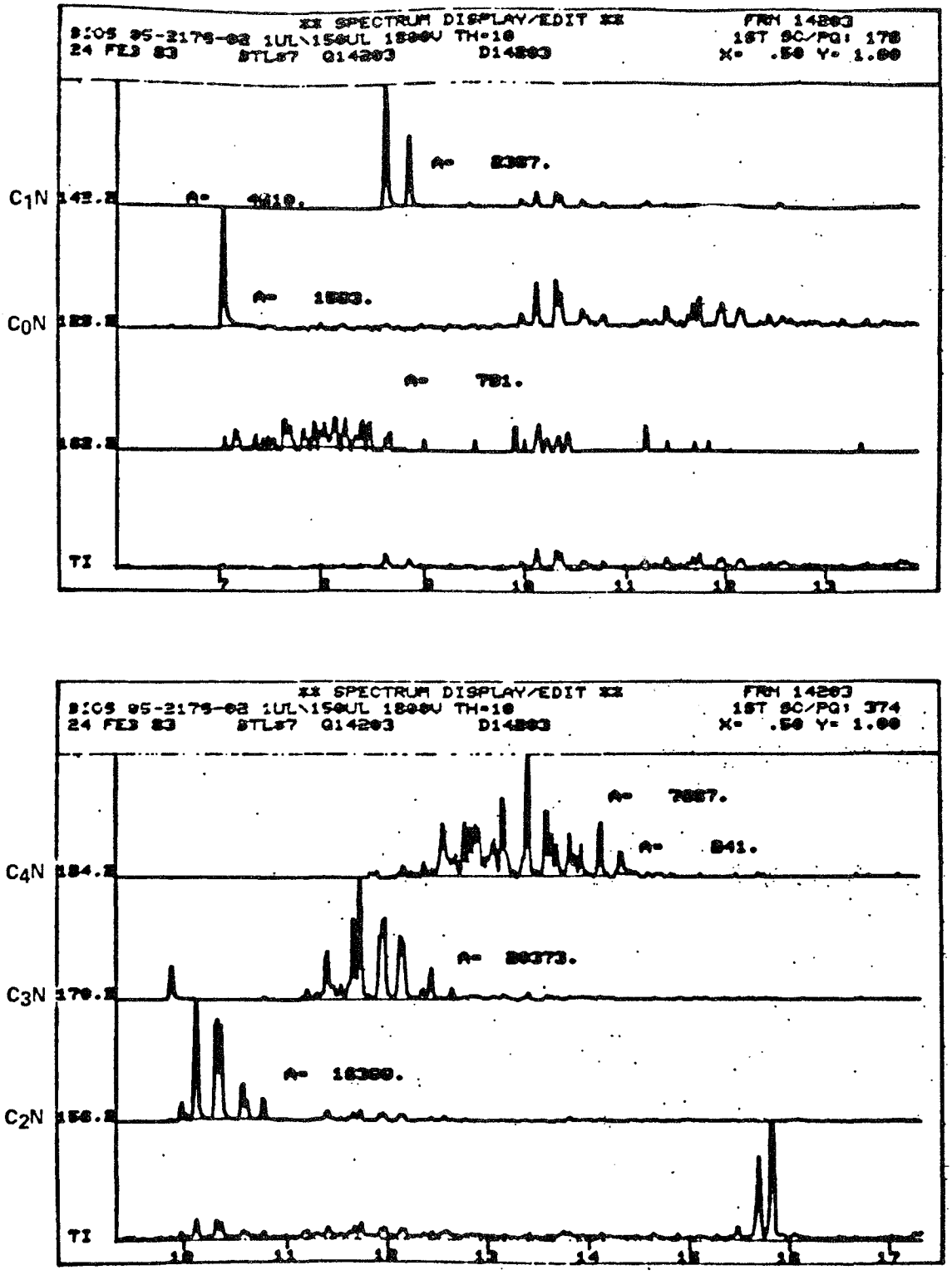


Figure 3.47. Mass chromatograms of alkylated naphthalenes in *Serripes* from Bay 9.

concentration than observed in 1981, yet still high at 20-100 ng/g. In 1981 the phenanthrenes and dibenzothiophenes dominated the aromatic assemblage after two weeks. However, here in the 1982 samples we see what appears to be considerable quantities of light to moderately weathered oil being retained by these animals.

It is very important to note that this aromatic hydrocarbon trend was not detected by UV/F results, which had indicated that Serripes' Bay 9 and Bay 10 oil content results were similar. The GC^2/MS results clearly show this is not the case. Thus as had been suspected in comparing UV/F trends with GC^2 results on the saturated hydrocarbons, inputs of the naphthalenes are not detected through limitations in the method by which the 355 nm band is measured, not the two ring (305 nm) band due to background interferences with the latter (Figure 3.48).

3.4.2.b Bay 10

3.4.2.bi Oil Concentrations by UV/F

Oil levels in Bay 10 at the time of the August 1982 sampling (Figure 3.44) were 3.0 (2.5 , 3.6) µg/g. These values were far lower than those taken 2 weeks after the spill, in September 1981 - 149 (130,170) µg/g. Levels in Bay 10 were lower than for Bay 9 but statistically similar to those in Bay 7.

3.4.2.bii Oil Composition by GC^2

The Bay 10 Serripes appear to be less affected by the input of new low boiling components than the animals in Bay 9. Figure 3.45B illustrates that the Bay 10 sample contained smaller quantities (.01-.05 µg/g) of the low-boiling n-alkanes. Elevated quantities of n-C_{15} (0.9 µg/g) and n-C16 (1.8 µg/g) are observed from unknown, but probably biogenic sources. The presence

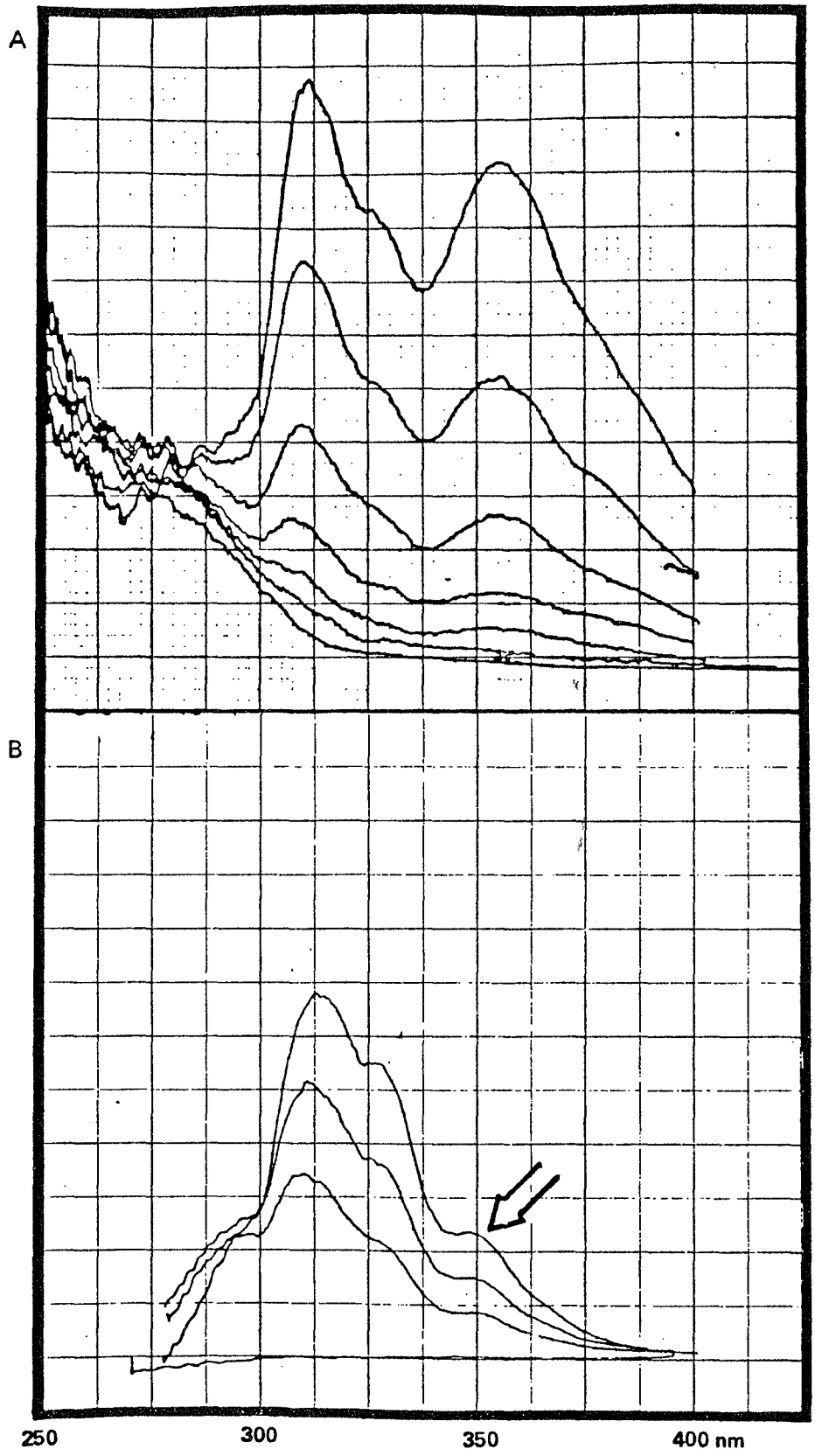


Figure 3.48. UV/F spectra of Lagomedio reference oil (A) and *Serripes groenlandicus* sample (B).

of two unidentified components (retention indices 1880, 1980) are noted as well. Significant quantities of terrigenous alkanes are observed in the sample.

3.4.2.biii Aromatic Hydrocarbon Composition by GC^2/MS

The Bay 10 aromatic levels are much lower than those in Bay 9. The aromatic assemblage (Figure 3.46) dominated again by alkylated naphthalene inputs and alkylated phenanthrenes contains compound levels in the 5-20 ng/g range, far below those observed in 1981 (200-300 ng/g). When last observed in 1981, these animals contained abundant dibenzothiophene series compounds (see Figure 3.94 in Boehm et al. 1982a). Note that in 1982, the dibenzothiophene compounds are of minimal importance. Thus, a profound compostional shift along with the obvious concentration differences has occurred.

3.4.2.c Bay 7

3.4.2.ci Oil Concentrations by UV/F

When last sampled in 1981 Serripes from Bay 7 contained 73 (31,170) µg/g. Oil concentrations determined in 1982 and shown in Figure 3.44 were 2.2 (1.4, 3.5) µg/g, levels still higher than pre-spill values of x_G = 1.2 µg/g and similar to those in Bay 10.

3.4.2.cii Oil Composition by GC^2

The low boiling petrogenic alkane components (.1-.3 µg/g) are again observed in Bay 7 indicating that low levels of this new oil input have reached the Bay 7 animals as well (Figure 3.49A).

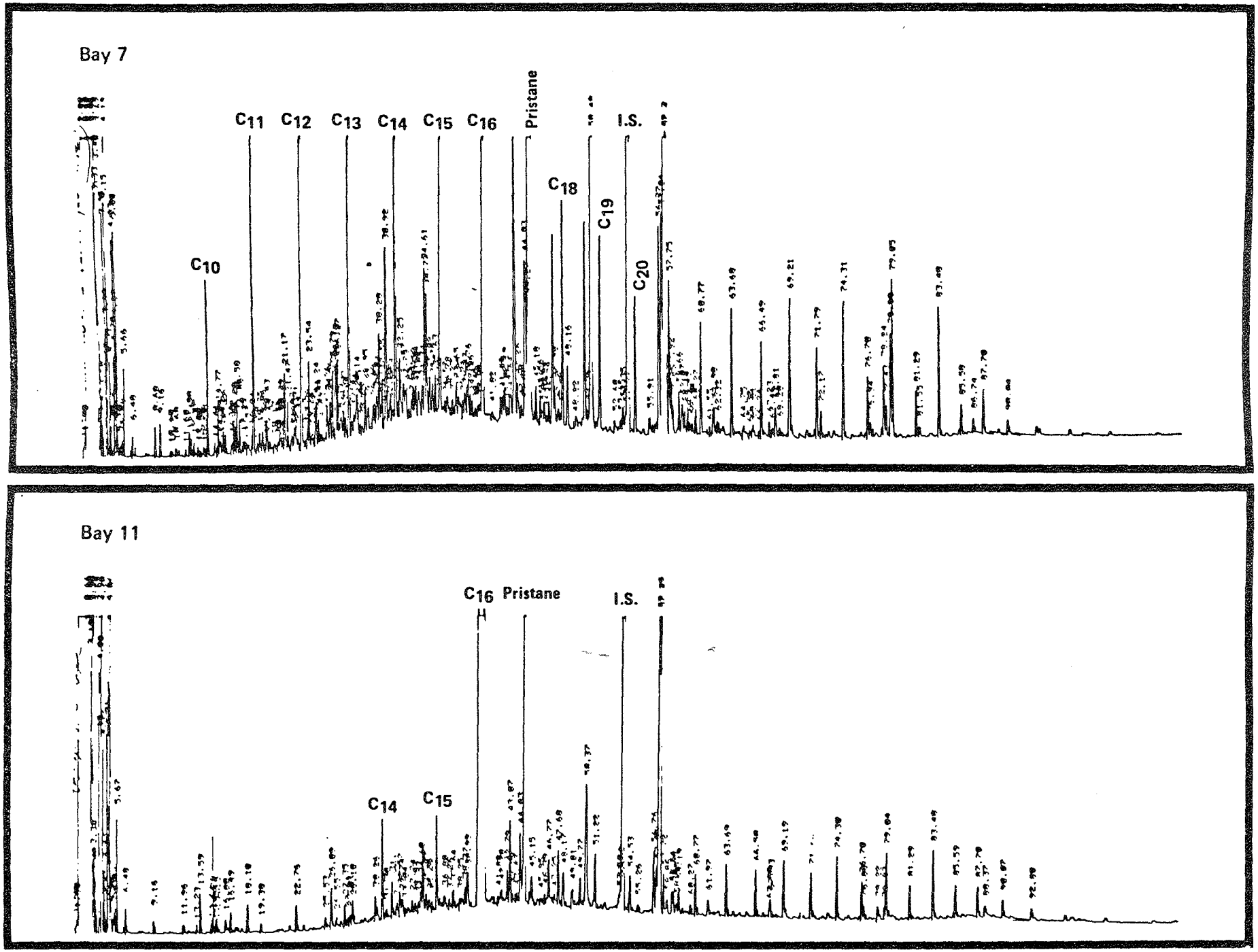


Figure 3.49. GC^2 traces of *Serripes groenlandicus*, Bays 7 and 11.

3.4.2.ciii Aromatic Hydrocarbon Composition by GC^2/MS

Unlike the Serripes from Bays 9 and 10 the aromatics in Serripes from Bay 7 are dominated by relatively low levels of the alkylated phenanthrenes (Figure 3.50) rather than by the naphthalenes. No dibenzothiophenes were observed in these samples unlike the situation in the 1981 sample from Bay 7 which contained 100-400 ng/g of these compounds.

3.4.2.d Bay 11

3.4.2.di Oil Concentrations by UV/F

Oil levels in Serripes from Bay 11 were higher than in any of the other bays, 13 (6.6, 25) µg/g with the highest value, 27 µg/g, found adjacent to tissue plot 5. These values were, however, all significantly lower than those obained when Serripes were previously sampled in September 1981 when values were 394 (200, 780) µg/g.

3.4.2.dii Oil Compbsition by GC^2

Serripes from Bay 11 contain lower levels of the low boiling alkanes (.02-.10 µg/g). The saturates in Bay 11 animals (Figure 3.49B) show an isoprenoid dominance as they last did in 1981. Note the large amounts of n-C16 here which may indicate the presence of a contaminant in the sample. Also note that since the analysis shown in Figure 3.49B was run at a different scale, the alkanes, which are as abundant as those from Bay 10 appear much less concentrated.

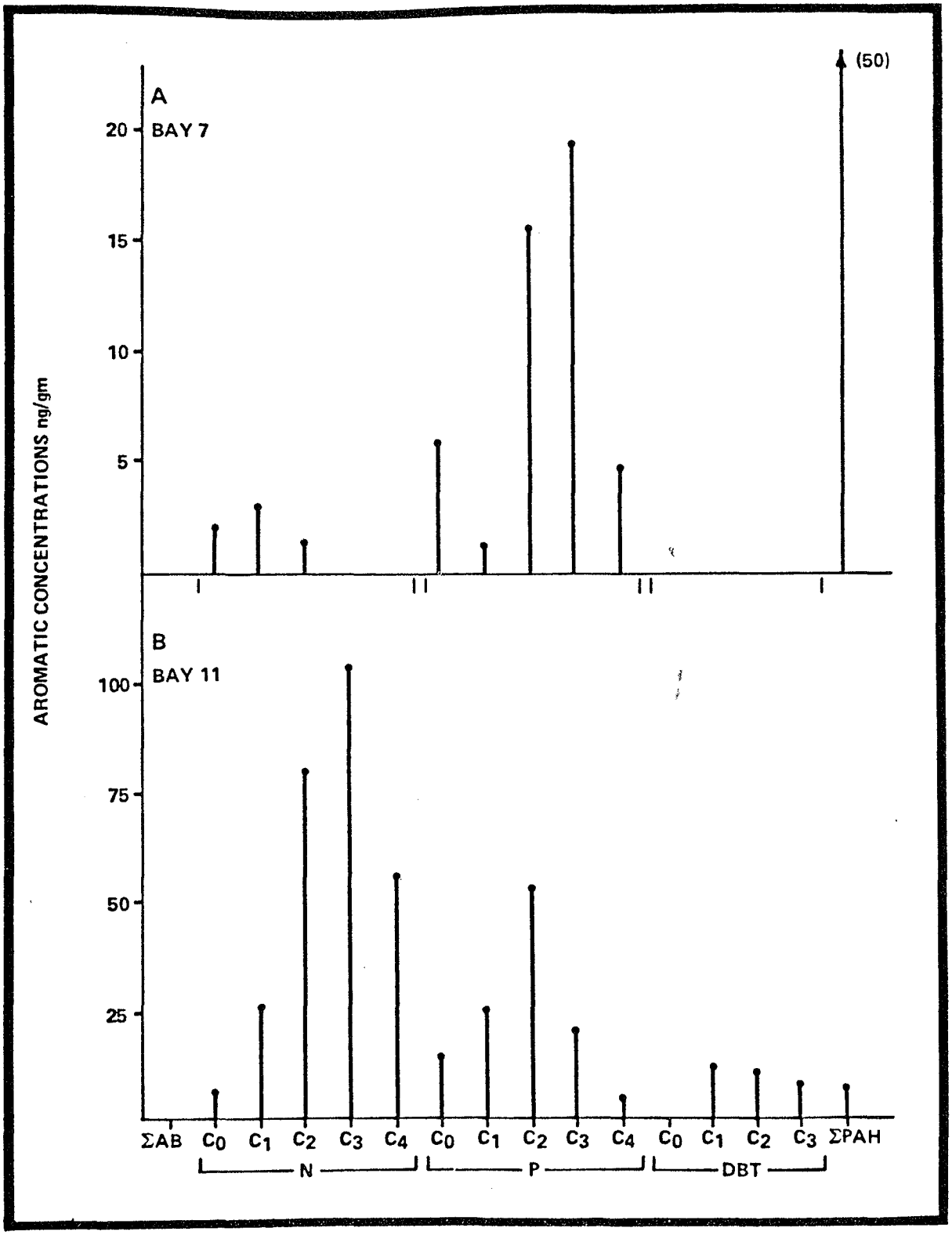


Figure 3.50. *Serripes* GC^2/MS results, Bays 7 and 11.

3.4.2.diii Aromatic Hydrocarbon Composition by GC^2/MS

The Bay 11 aromatics in Serripes (Figure 3.50) were not unlike those from Bay 9 sampled at the same time. The introduction of naphthalenes at the 50-100 ng/g (lower than the larger Bay 9 levels) is nevertheless striking. Bay 11 animals in 1981 were dominated by 500-1000 ng/g of phenanthrenes and dibenzothiophenes which are of much less importance one year later. An input of low levels of a new oil again is suspected, thus creating the assemblage shown in Figure 3.50B. Again, the UV/F result has probably underestimated not only the quantity of total oil in the sample as reflected in the saturated hydrocarbon trace, presented in Section 3.4.2.dii, but the levels of naphthalene-dominated aromatics.

3.4.3 Macoma calcarea

Twenty samples of Macoma, five stations from each of the four bays were analyzed by UV/F. The transects were pooled for GC^2 and GC^2/MS analyses yielding four samples.

3.4.3.a Bay 9

3.4.3.ai Oil Concentrations by UV/F

During the 1981 sampling and analysis Macoma behaved quite differently from either Mya or Serripes. Higher oil levels were found with time in samples from Bay 9. In September of 1981, the mean oil levels were high, 840 (610, 1140) µg/g. Pre-spill levels were 0.7 µg/g. Values reported here (Figure 3.51) for the August 1982 samples were significantly lower 25 (17, 36) than previous samples.

A typical UV/F spectra for Macoma is presented in Figure 3.52.

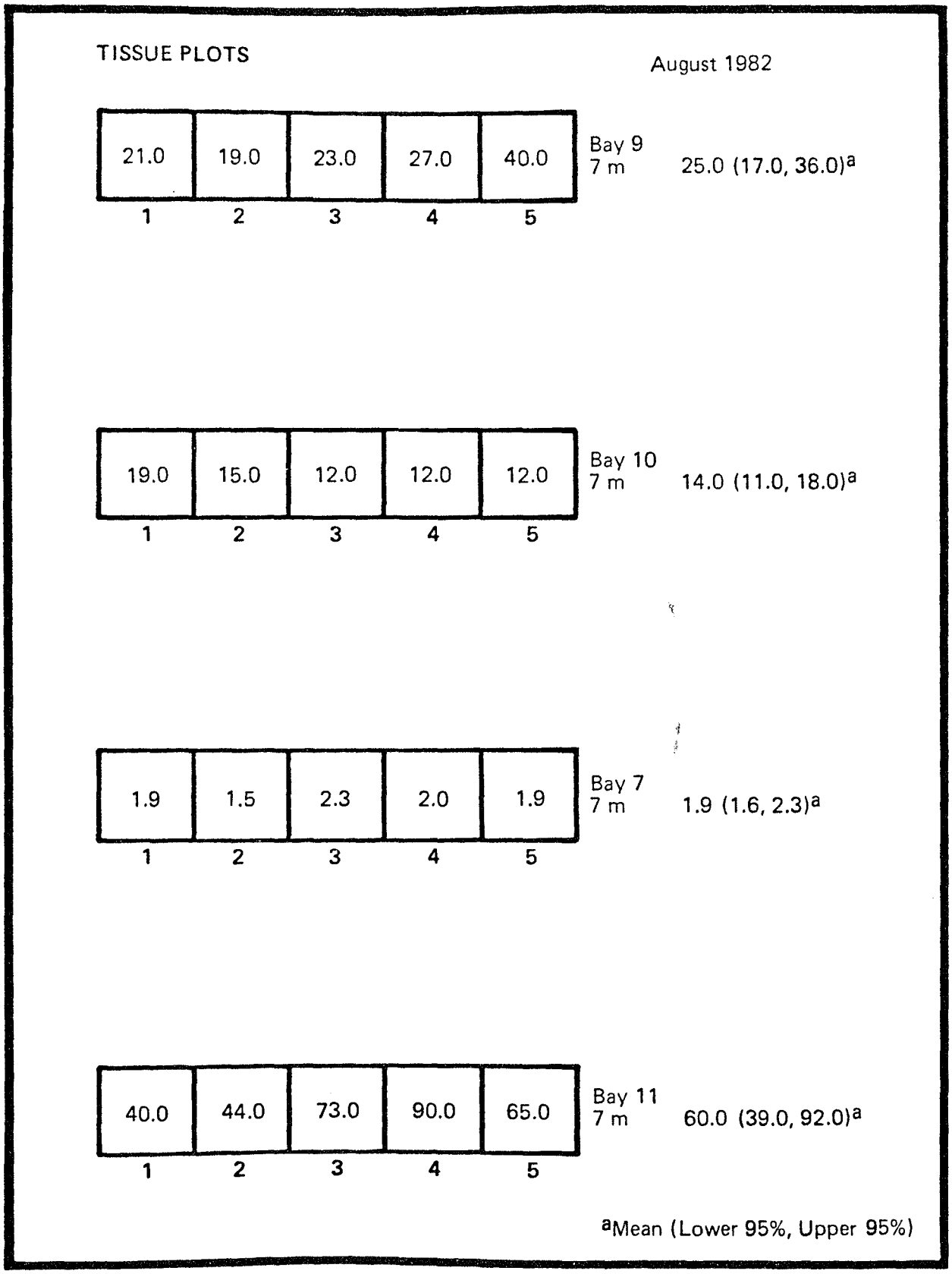


Figure 3.51. Summary of oil concentrations in *Macoma*, by UV/F (μg/g dry wt.).

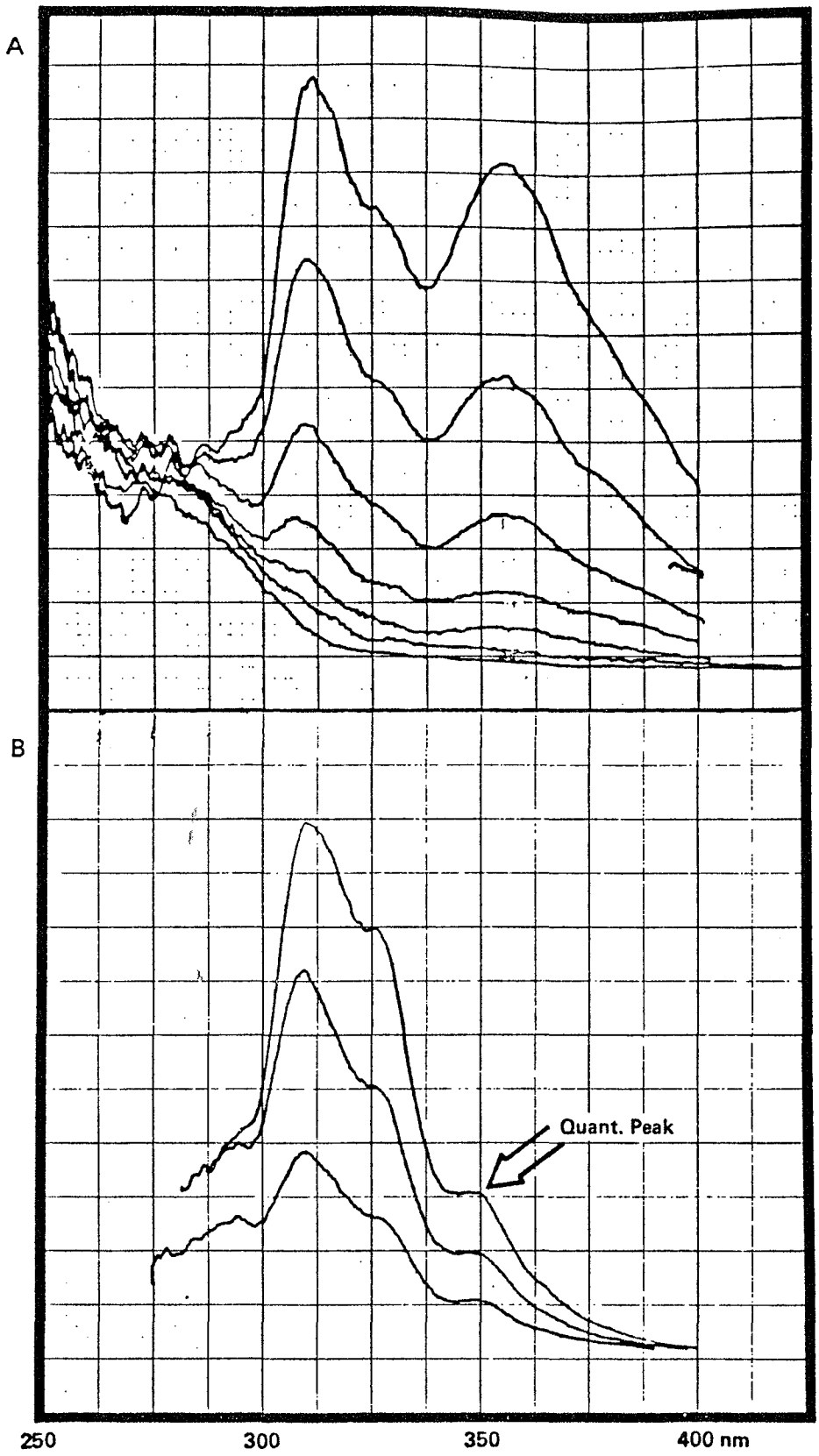


Figure 3.52. UV/F spectra of Logamedio reference oil (A) and *Macoma calcarea* sample (B).

Nevertheless, levels in Macoma were still much higher than pre-spill values and higher than for Mya or Serripes taken at the same stations.

3.4.3.aii Oil Composition by GC^2

Macoma samples in Bay 9 contained a combination of the biodegraded residual petrogenic material seen in September 1981 as indicated by the dominance of the isoprenoid alkanes over the normal alkanes (Figure 3.53). In addition, sizeable quantities of two biogenic compounds, pristane and an olefin, at retention index of 2089 are observed. An odd chain alkane sequence beginning with n-C_{21} and continuing to n-C_{31} indicates that terrigenous biogenic material linked to the sediments is present in these deposit feeders. Thus, the hydrocarbon assemblage unlike those for Mya and Serripes are consistent with the 1981 results.

The aromatic assemblage revealed by GC^2 does not give any indication that petroleum aromatics are in the sample. The assemblage in Figure 3.53 is purely biogenic.

3.4.3.aiii Aromatic Hydrocarbon Composition by GC^2/MS

The GC^2/MS-generated data for Macoma from Bay 9 (Figure 3.54) shows quite significant differences than those for the Mya and Serripes previously discussed. The aromatic assemblage in Macoma is dominated by the alkylated phenanthrenes and dibenzothiophenes. This pattern is unlike that from the Mya and Serripes filter-feeders in that the naphthalenes are essentially absent in Macoma while they are more important qualitatively in other species. The Macoma composition observed in Figure 3.53 is also different from that previously observed in 1981, when the naphthalenes were still present in significant (200-300 ng/g) levels, although lower than the phenanthrenes (200-700 ng/g) and dibenzothiophenes (250-1300 ng/g). Here in 1982 the naphthalenes are absent, the phenanthrenes are present (50-150 ng/g), as are

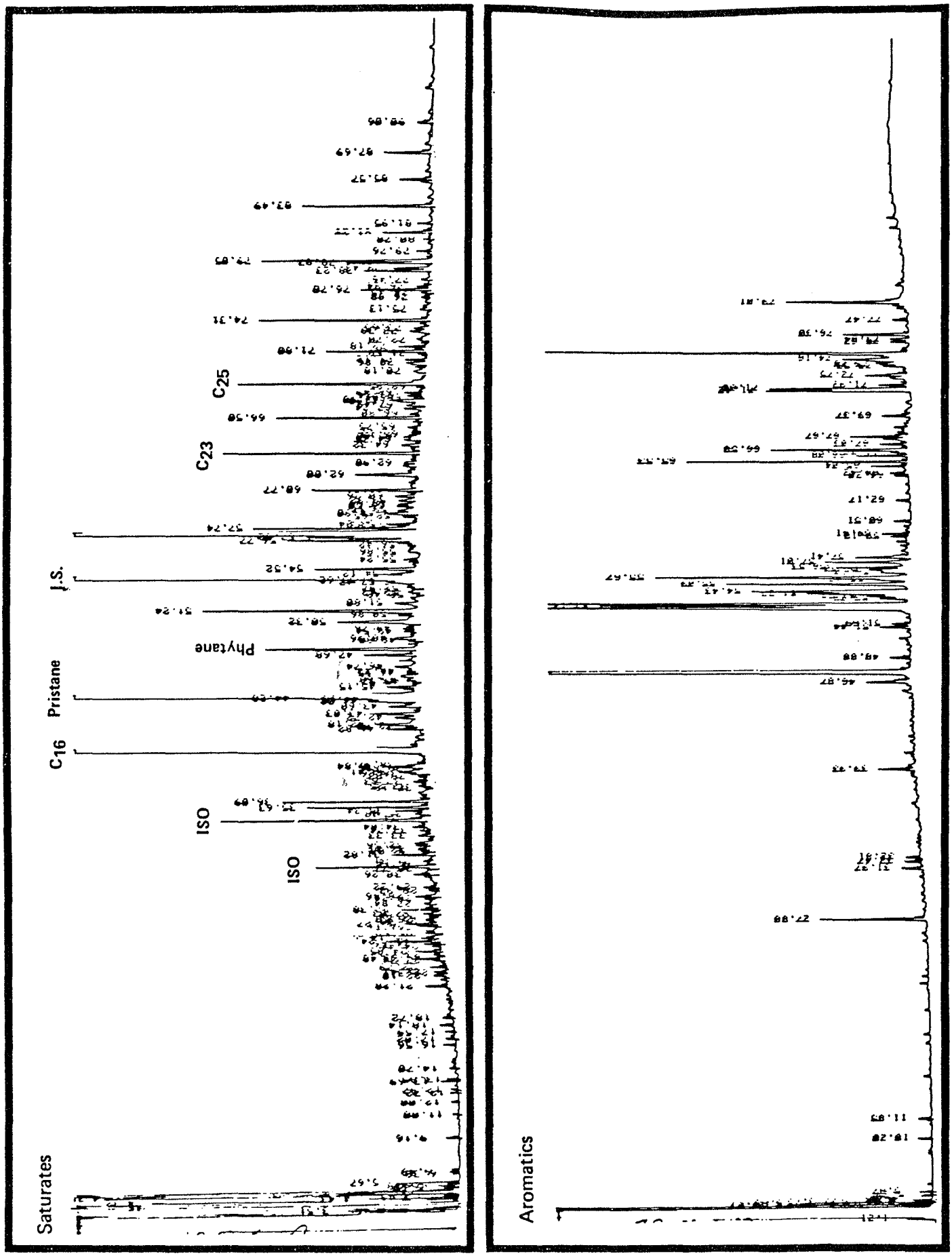


Figure 3.53. GC^2 traces of *Macoma*, Bay 9.

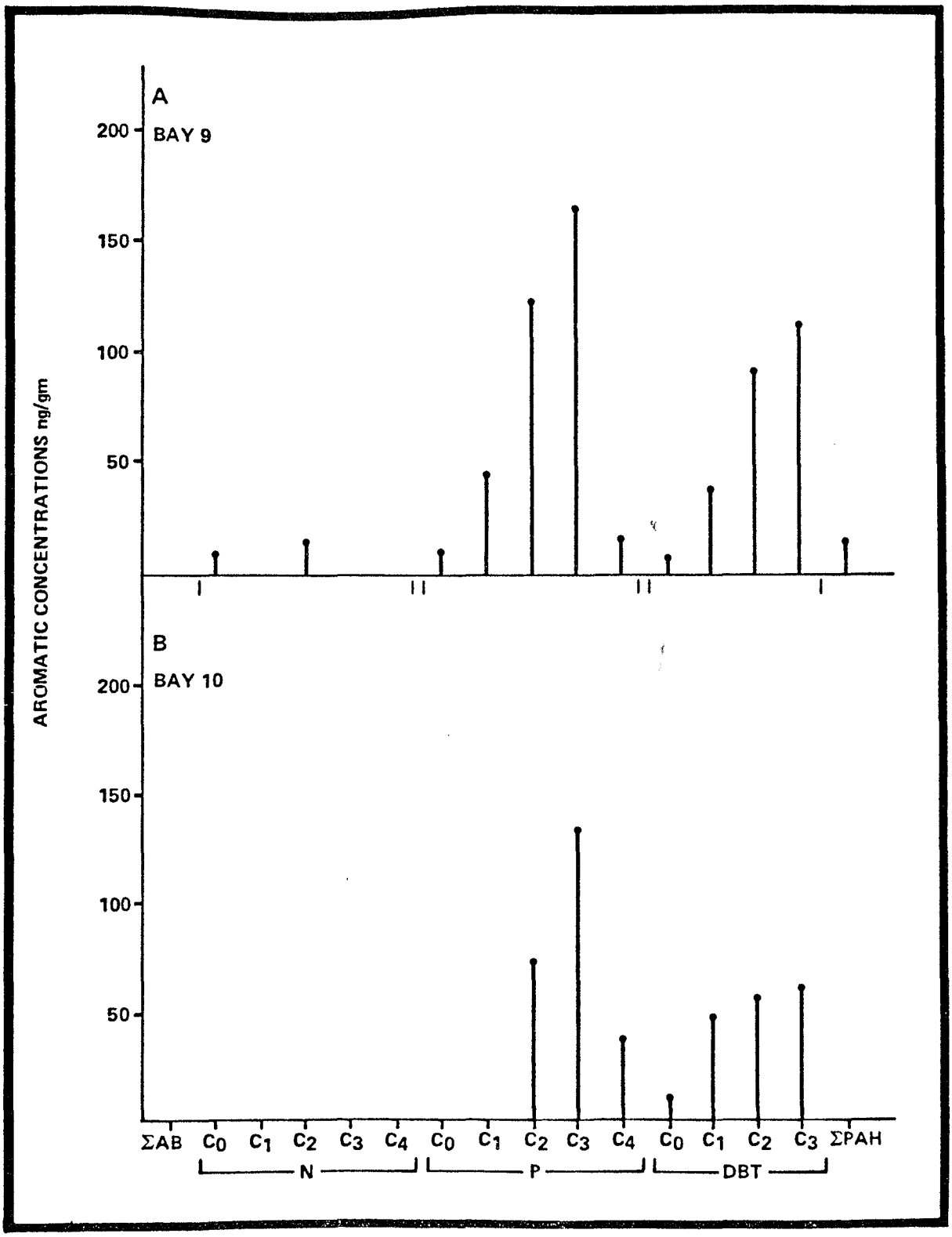


Figure 3.54. *Macoma* GC^2/MS results, Bays 9 and 10.

the dibenzothiophenes (30-100 ng/g). It appears that Macoma is still primarily influenced by sediment-bound aromatics which do contain these three-ringed compound series.

3.4.3.b Bay 10

3.4.3.bi Oil Concentrations by UV/F

Macoma pre-spill values were 2.1 µg/g and after the dispersed oil release increased to 406 µg/g and held at 440 (250,760) µg/g at the time of the second post-spill sampling in September 1981. Levels encountered 1 year later, in August 1982, were much lower, 14 (11, 18) µg/g indicating continued oil impact. Levels were lower, however, than those in either Bays 9 or 11 (see Figure 3.51).

3.4.3.bii Oil Composition by GC2

Macoma samples from Bay 10 (Figure 3.55A) were comprised of the same saturated hydrocarbon assemblage as that revealed in Bay 9: residual petrogenic isoprenoid alkanes; biogenic pristane; other petrogenic branched alkanes; terrigenous plant wax alkanes. Thus we are observing decreased amounts of degraded petroleum in these animals in the 1982 sample set.

3.4.3.biii Aromatic Hydrocarbon Composition by GC^2/MS

The aromatic hydrocarbons in Bay 10 Macoma are quite similar in composition and concentration to those in the Bay 9 animals (Figure 3.54A and B). Again, unlike Mya and Serripes, no naphthalenes are present.

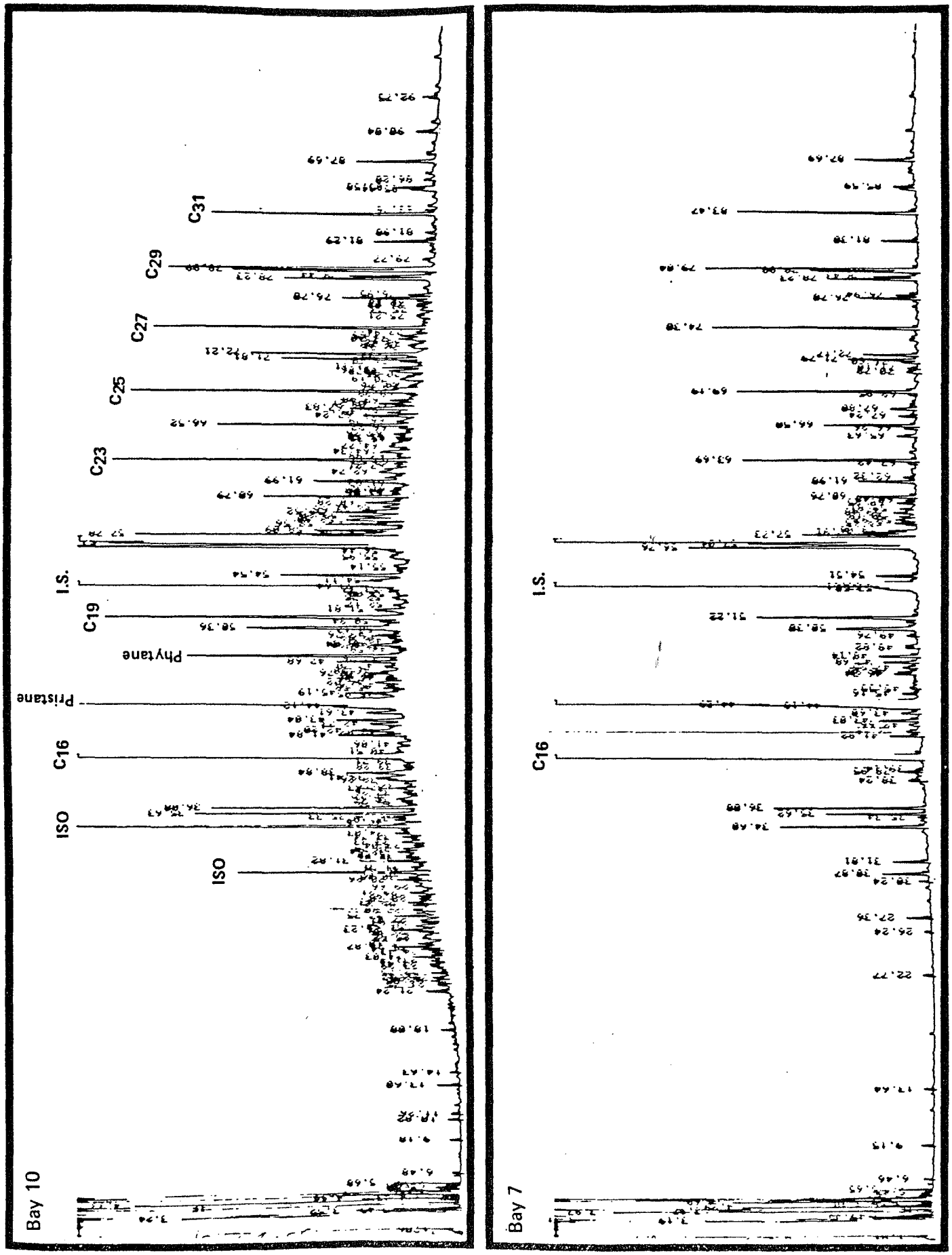


Figure 3.55. Saturated hydrocarbon GC^2 traces, *Macoma*, Bays 10 and 7.

3.4.3.c Bay 7

3.4.3.ci Oil Concentrations by UV/F

In 1981 while Macoma in Bays 9, 10, and 11 were high and reflected a sediment impact, levels in Bay 7 were lower 85 (39,190) µg/g, but still much higher than pre-spill values (∿1 µg/g). The lack of any detectable sediment-bound oil in Bay 7 led to the conclusion that the 80-90 µg/g values reflected an initial water-mediated uptake rather than from the surface sediment as was the case in the other bays. The values found here for the August 1982 set were back to nearly background levels 1.9 (1.6, 2.3) µg/g. The persistence of oil in animals from Bays 9, 10, 11 at levels at least ten times the Bay 7 levels underscores the lack of sediment-mediated impact in Bay 7 and its lingering quantitative importance in the other bays.

3.4.3.cii Oil Composition by GC^2

Unlike the Bay 9 and 10 results the Bay 7 Macoma sample (Figure 3.55B) extracts were "clean" with major amounts of pristane and other biogenic compounds present and with an absence of UCM material and petrogenic branched alkanes. Thus the samples can be considered to be petroleum-free.

3.4.3.ciii Aromatic Hydrocarbon Composition by GC^2/MS

Very low levels of phenanthrenes (0-20 ng/g) are observed in Bay 7 Macoma (Figure 3.56), much lower levels than observed in the other bays, and at very similar levels and composition to those observed in 1981 (see Figure 3.108 in Boehm et al., 1982a).

3.4.3.d Bay 11

3.4.3.di Oil Concentrations by UV/F

Although oil levels found in August 1982 ~60 (39, 92) µg/g were lower than those previously found 1 year earlier ~246 (76,790) µg/g , it is evident that the chemical impacts of oil in Bay 11 are of greater duration than those in either Bays 9 and 10. Although the September 1981 oil levels in Bay 9 and 10 Macoma (840 and 440 µg/g respectively) were higher than those found at the same time in Bay 11 (246 µg/g) residual Bay 11 values in 1982 are two to three times higher in Bay 11, indicating longer term impacts and certainly reflecting the additional oil inputs to the sediments previously presented.

3.4.3.dii Oil Composition by GC^2

Figure 3.57 illustrates the GC^2 composition of the saturated and aromatic hydrocarbon fractions of the Bay 11 Macoma. Considerable quantities of degraded petroleum remain in the saturated fraction. Note the relative lack of importance of the n-C_{22} plus odd chain alkanes which were prominent features of the other Macoma chromatograms. The total area indicated by the f_1 GC^2 trace yields a petrogenic saturated hydrocarbon value of 99 µg/g compared to the UV/F total oil value of 60 µg/g. Thus, again UV/F has underestimated the oil content, probably by a factor of two.

The composition of the f_2 trace (Figure 3.57B) is largely biogenic.

3.4.3.diii Aromatic Hydrocarbon Composition by GC^2/MS

The aromatic hydrocarbons levels and composition are very similar to those observed in Bay 11 Macoma in September 1981 when the aromatic assemblage was dominated by alkalyted phenanthrenes and dibenzothiophenes. In the 1982 sample, we see identical results. The compound levels in Figure 3.56B

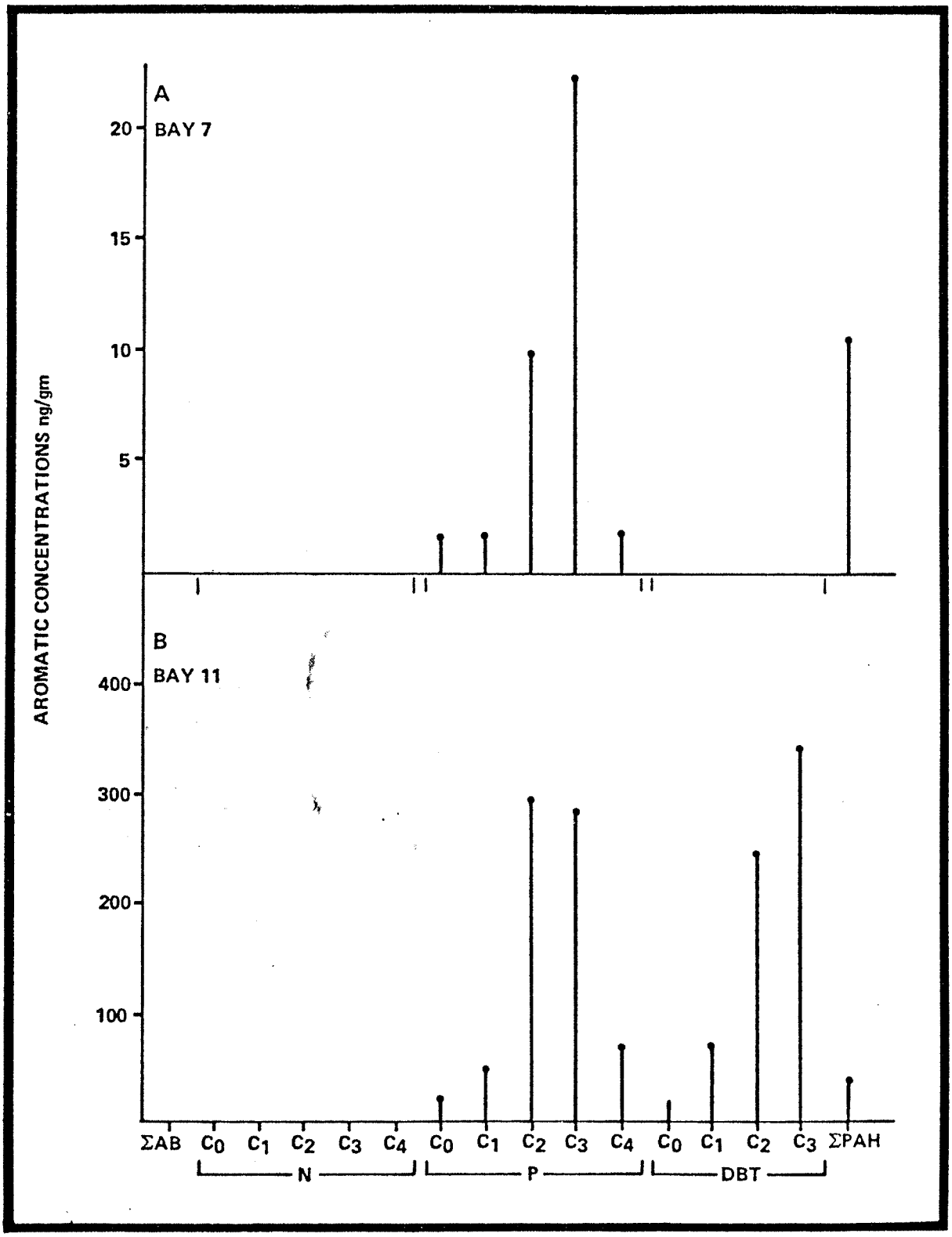


Figure 3.56. *Macoma* GC^2/MS results, Bays 7 and 11.

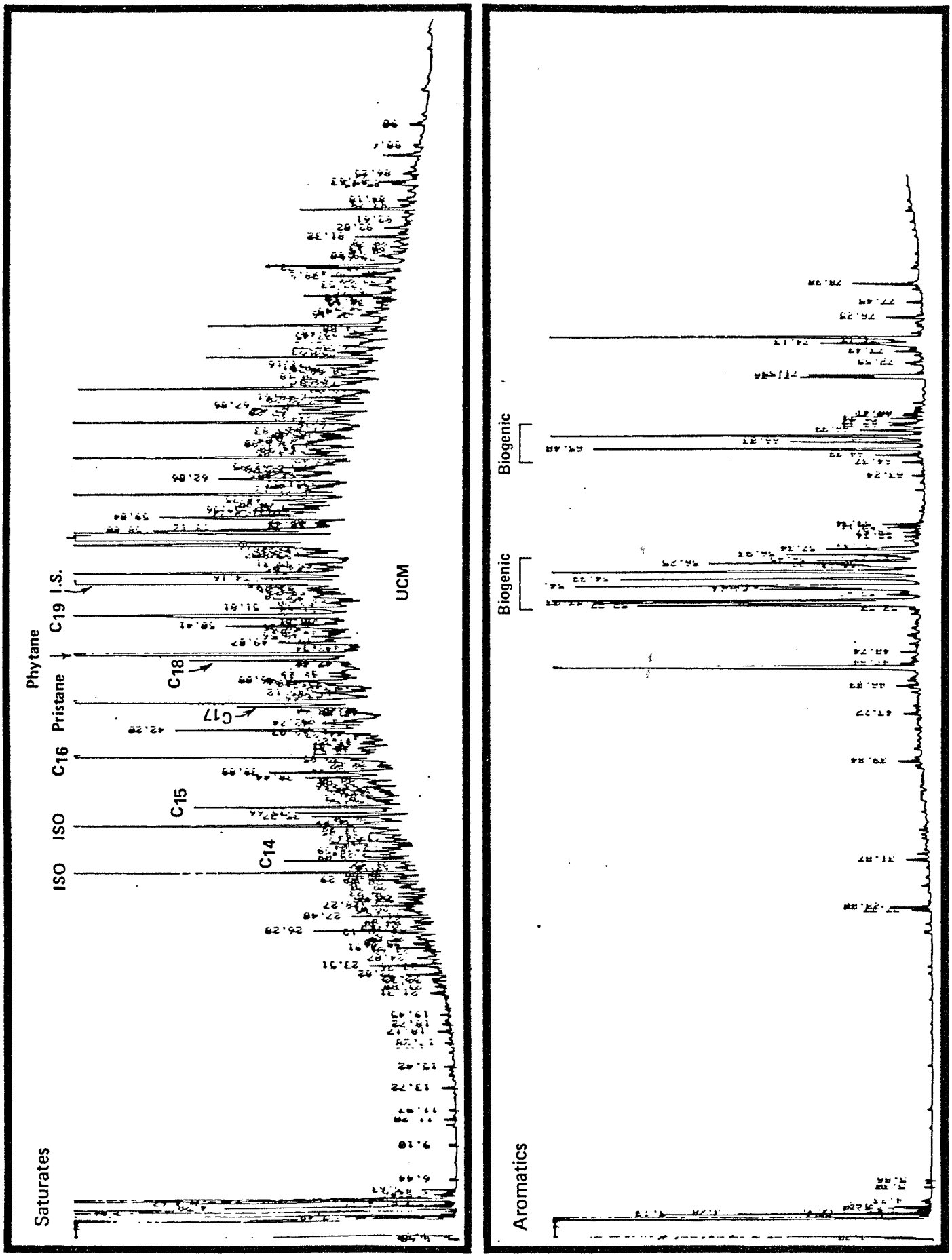


Figure 3.57. GC^2 traces of *Macoma*, Bay 11.

are in the 100-300 ng/g range as they were in 1981, and of equal importance is the dibenzothiophene series. Macoma is apparently quite influenced by the sediment-bound hydrocarbons which display this weathered assemblage.

Although the UV/F-determined "total oil" levels were three to four times lower in 1982 than they were in 1981, the concentrations of the important aromatic compound series shown in Figure 3.56B are identical, thus illustrating steady-state behavior with respect to uptake/depuration due to increased oil levels in the Bay 11 sediments.

3.4.4 Astarte borealis

Twenty samples of Astarte were analyzed by UV/F corresponding to five tissue plots in each of the four bays. GC^2 and GC^2/MS analyses were performed on four samples corresponding to one pooled extract in each of the four bays.

3.4.4.a Bay 9

3.4.4.ai Oil Concentrations by UV/F

Concentrations of oil in Astarte (Figure 3.58) from the August 1982 collection in Bay 9 were 19 (10,40) µg/g. When last sampled in 1981, these samples averaged 171 (88,330) µg/g. The parallel decreases in Mya and Serripes oil levels in Bay 9 were 114 down to 0.8 µg/g (99% decrease) and 116 down to 5.2 µg/g (96% decrease), respectively. Astarte apparently had retained more oil (88% decrease) at the time of the August sampling (see Section 3.4.6). A typical UV/F spectra is shown in Figure 3.59.

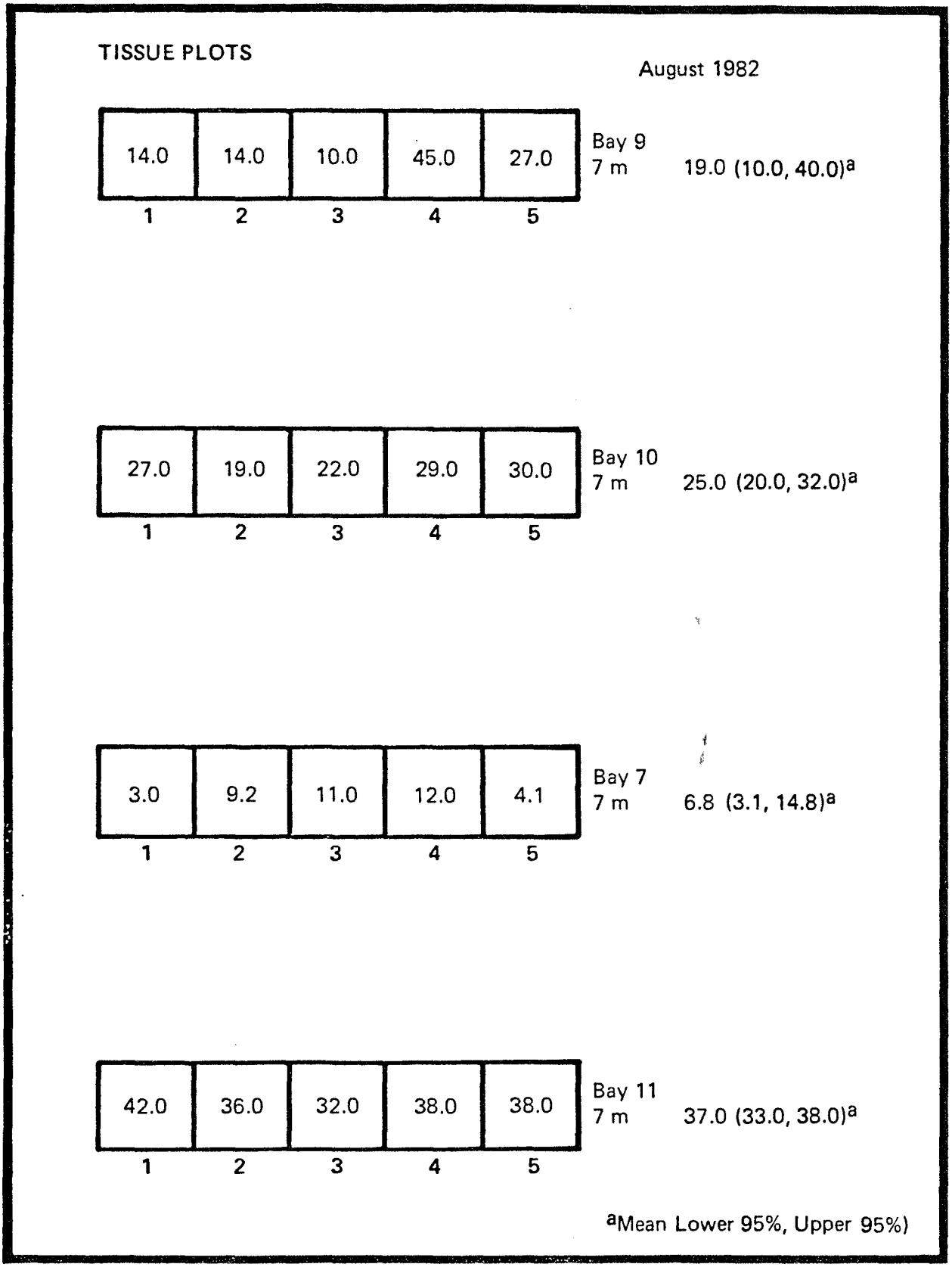


Figure 3.58. Summary of oil Concentrations in *Astarte*, by UV/F (μg/g dry wt.).

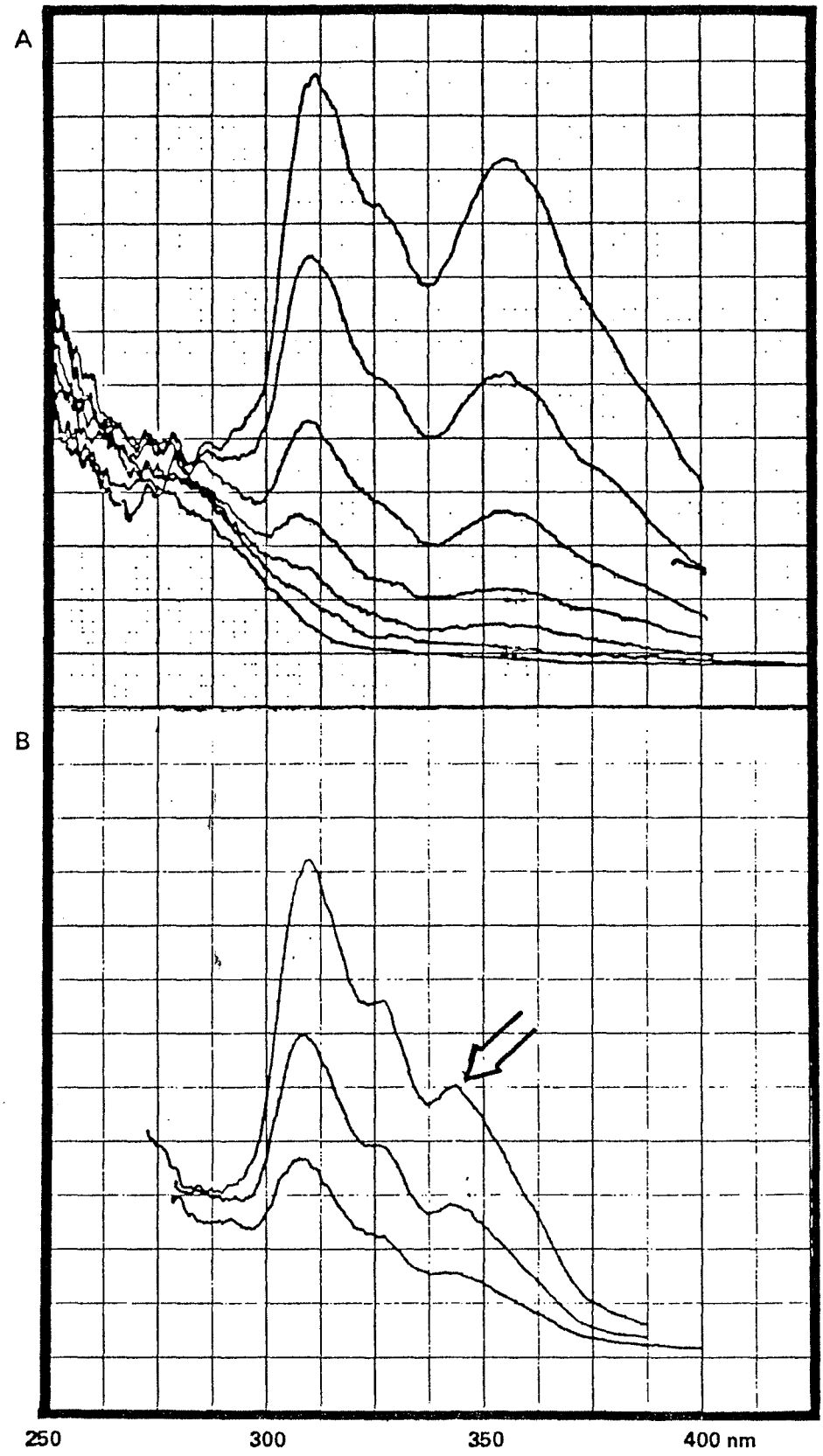


Figure 3.59. UV/F spectra of Lagomedio reference oil (A) and *Astarte borealis* sample (B).

3.4.4.aii Oil Composition by GC^2

The GC^2 profiles of Astarte from Bay 9 (Figure 3.60A,B) show little evidence of residual petroleum material. When last sampled in 1981, a degraded petrogenic assemblage was quite evident through an abundance of isoprenoid alkanes in the saturated fraction and through obvious alkylated phenanthenes in the aromatic fration. In Figure 3.60A, the only suggestion of prior oil impact is the presence of phytane. The pristane observed is of a biogenic origin. The aromatic fraction shown in Figure 3.60B is free of obvious petrogenic influence. Any aromatic hydrocarbons are of very low levels relative to the biogenic clusters, and require GC^2/MS analysis for their detection and quantification.

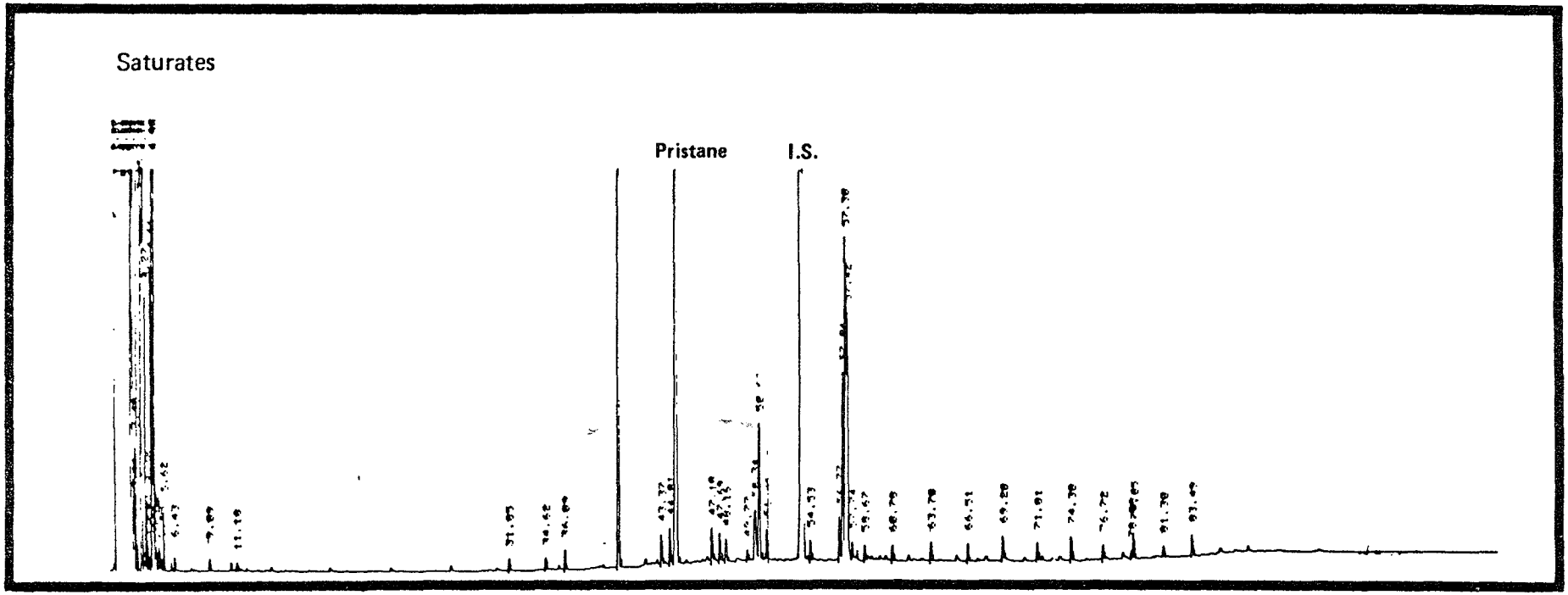
3.4.4.aiii Aromatic Hydrocarbon Composition by GC^2/MS

The one sample analyzed by GC^2/MS (Figure 3.61) contains 10-40 ng/g of alkylated phenanthrenes and 10-20 ng/g of the alkylated dibenzothiophenes. No evidence of naphthalene introduction is seen here.

3.4.4.b Bay 10

3.4.4.bi Oil Concentrations by UV/F

Average concentrations of oil in Astarte (Figure 3.58) from Bay 10 were slightly higher than those from Bay 9. Levels in Bay 10 of 25 (20,32) µg/g, down from 149 µg/g in 1981. Again, the residual oil levels in Astarte were higher than those from the Mya (1 µg/g) and Serripes (3 µg/g) taken at the same time in 1982.



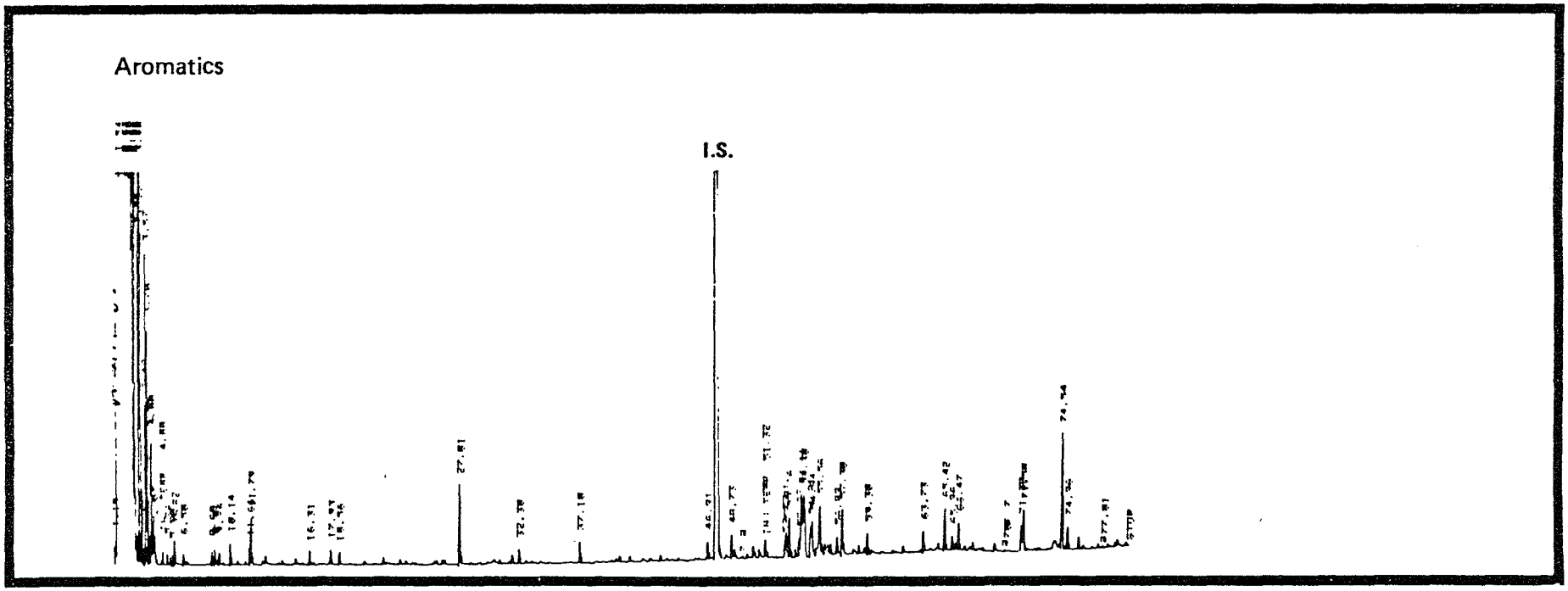


Figure 3.60. GC^2 traces of *Astarte*, Bay 9.

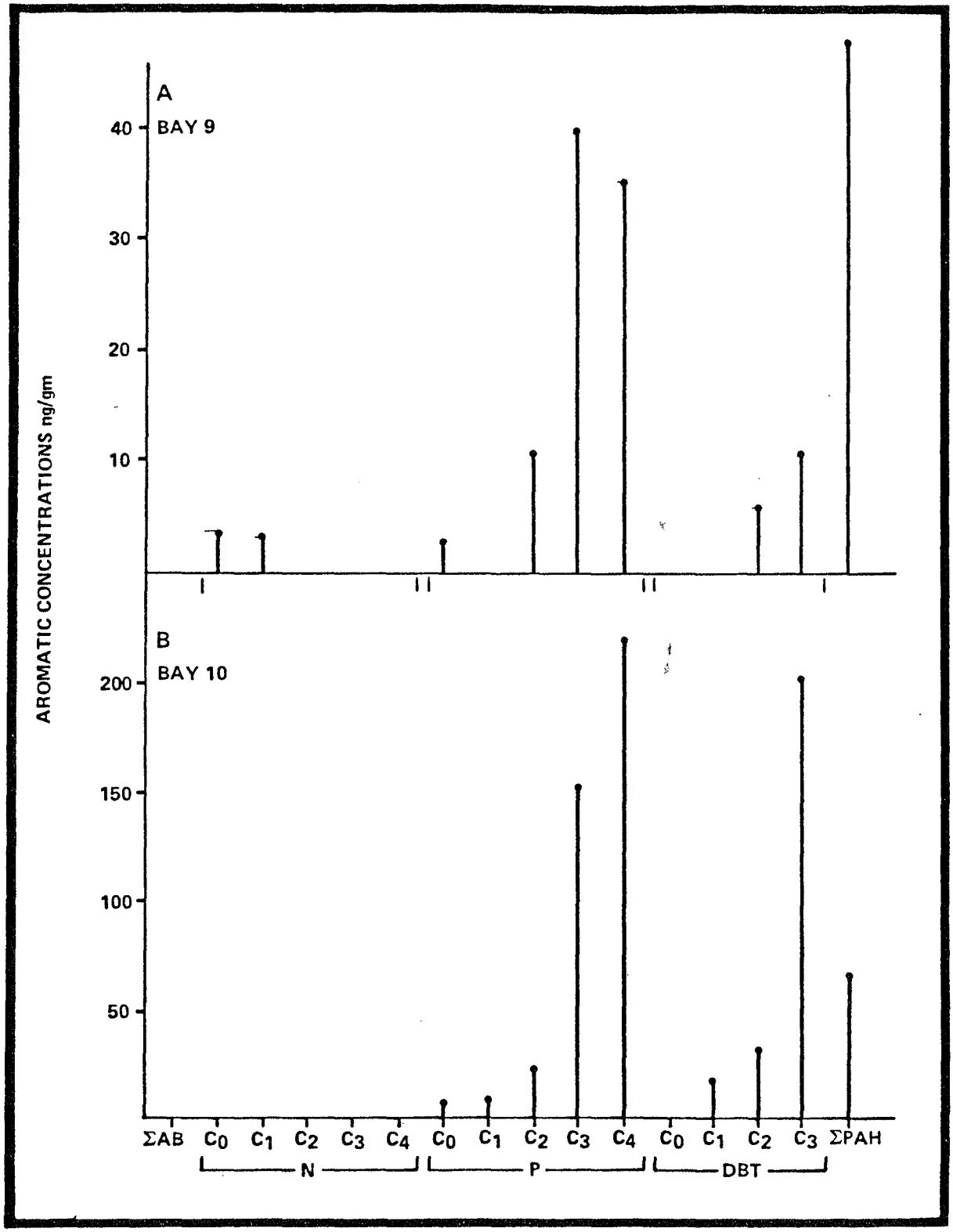


Figure 3.61. *Astarte* GC^2/MS results, Bays 9 and 10.

3.4.4.bii Oil Composition by GC^2

Astarte GC^2 profiles in Bay 10 again do not demonstrate a marked petroleum influence. They are very similar to those observed in Bay 9 with the biogenic compounds by far the most dominant input.

3.4.4.biii Aromatic Hydrocarbon Composition by GC^2/MS

Astarte apparently behaves similarly to Macoma with respect to aromatic hydrocarbon content. The petrogenic compounds in the phenanthrene and dibenzothiophene series are present (Figure 3.61B) in Astarte at the 100-200 ng/g level higher than the Bay 9 residual levels. Note that Astarte contained the highest aromatic levels of any of the bivalves in 1981 with compound levels in the 1000-4000 ng/g range. Thus, this considerable residual aromatic material in 1982 Bay 10 Astarte may be due to this initial heavy loading. Note again that unlike Mya and Serripes, Astarte contains no naphthalene compounds.

3.4.4.c Bay 7

3.4.4.ci Oil Concentrations by UV/F

Residual oil levels in Bay 7, 6.8 (3.1,15) µg/g were lower than those in Bays 9, 10, and 11. When last sampled in September, 1981, these filter-feeders contained an average of 56 µg/g. Background levels had previously been determined to be 2 µg/g. However, it is interesting to note that the decrease of 56 to 6.8 µg/g, a decrease of 88%, is nearly identical to the percentage decreases in Astarte in Bays 9 and 10.

3.4.4.cii Oil Composition by GC^2

GC^2 results for Bay 7 Astarte reveal purely a biogenic assemblage in the saturated and aromatic hydrocarbon fractions.

3.4.4.ciii Aromatic Hydrocarbon Composition by GC^2/MS

While Astarte did contain detectable aromatics (phenanthrenes and dibenzothiophenes) in 1981, no aromatics were detected in the 1982 sample, indicating that these animals, after receiving an initial water column-mediated dosing in 1981, have been subjected to no new inputs. We suspect that Astarte interacts more with sediment than with the water column vis-a-vis food uptake, and as the Bay 7 sediments have been and still are largely oil-free, Astarte in Bay 7 have merely depurated the oil initially acquired.

3.4.4.d Bay 11

3.4.4.di Oil Concentrations by UV/F

Oil concentrations were observed to be 37 (33,38) µg/g in August 1982 (Figure 3.58). When last sampled in September 1981, Astarte from Bay 11 contained 140 (50,390) µg/g. The 73% decrease in oil levels in Bay 11 Astarte observed between September 1981 and August 1982 is somewhat less than the 83-88% decreases observed in the other bays. The absolute oil levels remaining in Bay 11 are higher than those in the other bays. Both of these factors indicate that additional low level oil exposure may be a cause for this lesser decrease observed in Bay 11.

3.4.4.dii Oil Composition by GC^2

Astarte from Bay 11 yield GC^2 profiles of the hydrocarbon distribution, closely resembling the weathered oil profiles seen in September 1981. As Figure 3.62 indicates, the phytane abundance and the moderate abundance of other isoprenoid and branched alkanes along with a substantial UCM all suggest residual oil contamination. The pristane seen in this sample however, is largely biogenic accounting for its much higher levels than phytane. Total oil levels averaged 37 µg/g by UV/F. The GC^2 oil value

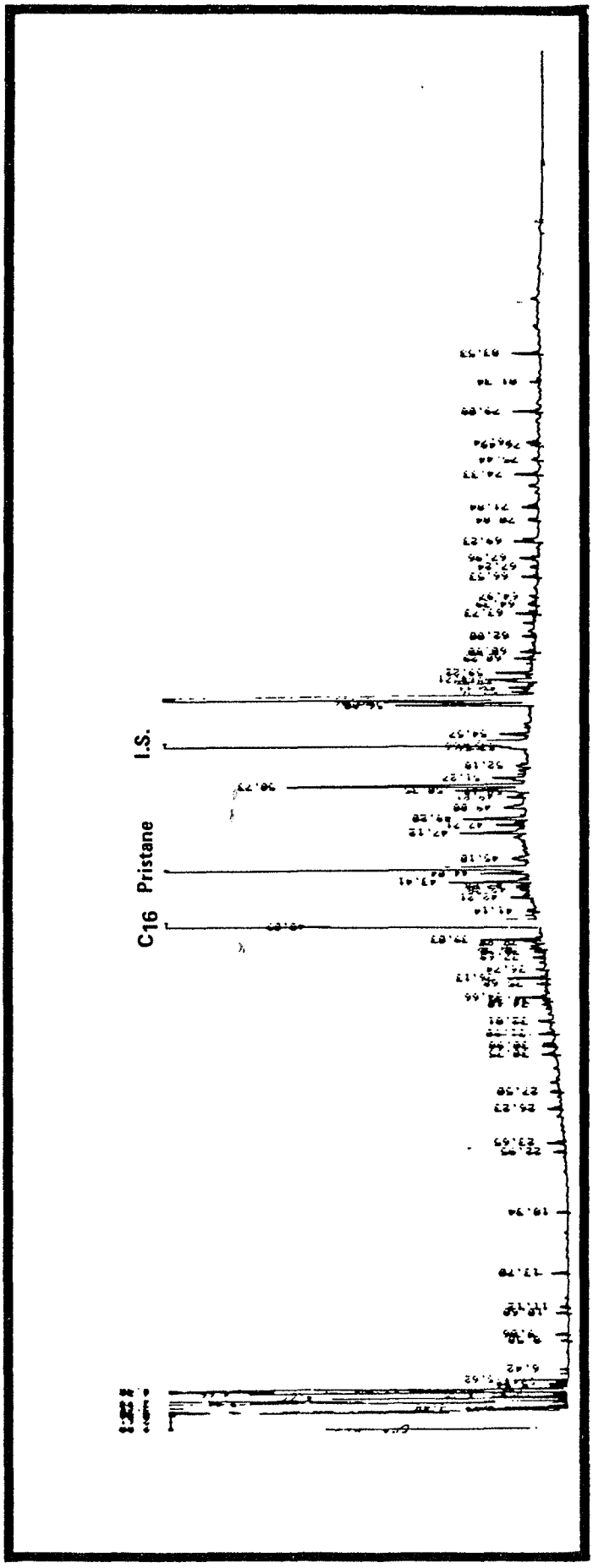


Figure 3.62. GC^2 trace of Bay 11 *Astarte*.

computed just from the saturated fraction is approximately 17 µg/g. This is reasonable agreement unlike the situation for Mya and Serripes where the UV/F underestimated oil content by a factor of five or so.

3.4.4.diii Aromatic Hydrocarbon Composition by GC^2/MS

Astarte in Bay 11 contain about four to five times less aromatic hydrocarbons in 1982 (Figure 3.63B) (50-150 ng/g) than they did in September of 1981 (300-700 ng/g). However, the aromatic composition is the same as in 1981, indicating no naphthalene overprint as was observed in Mya and Serripes.

3.4.5 Strongylocentrotus droebachiensis (Urchins)

Forty urchin samples were analyzed by UV/F for total oil concentrations. These included (1) a May 1982 collection consisting of one sample from Bays 7, 9, and 10 and two samples from Bay 11; (2) an August 1982 set of five samples from the seven meter depth stratum in each of the four bays; (3) five samples from Bay 11 in September 1982; (4) ten individual animal specimens, five from each of Bays 9 and 11 taken in August.

GC^2 and GC^2/MS analyses to determine oil composition were performed on one sample pooling from each bay in August plus the Bay 11 September sample pooling, or a total of five samples.

3.4.5.a Bay 9

3.4.5.ai Oil Concentrations by UV/F

When last sampled in September of 1981, urchins from Bay 9 contained 237 $\pm$ 57 µg/g of oil (Engelhardt and Norstrom, 1982). Animals obtained in May of 1982 (Figure 3.64) from one station contain three times as much oil,

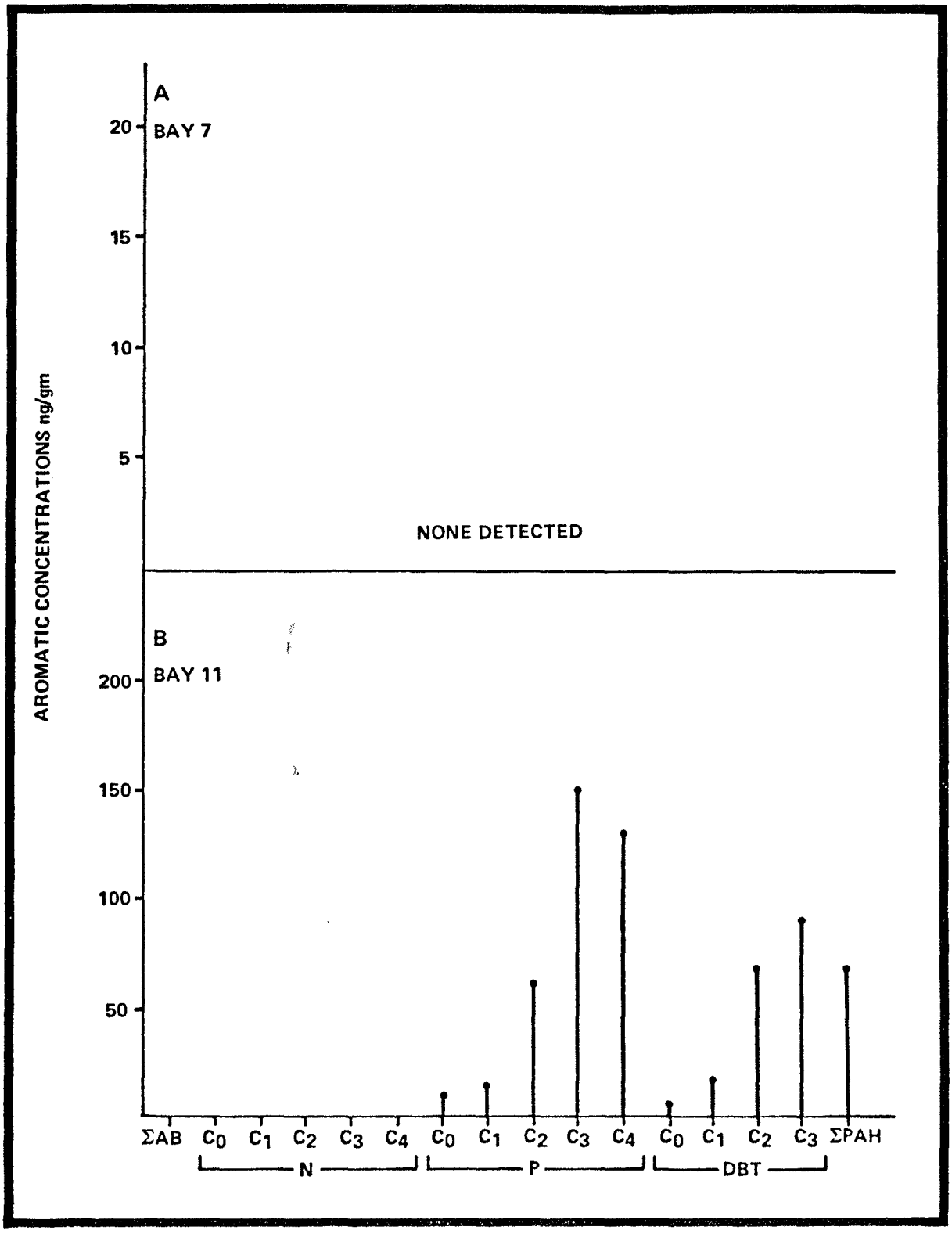


Figure 3.63. *Astarte* GC^2/MS results, Bays 7 and 11.

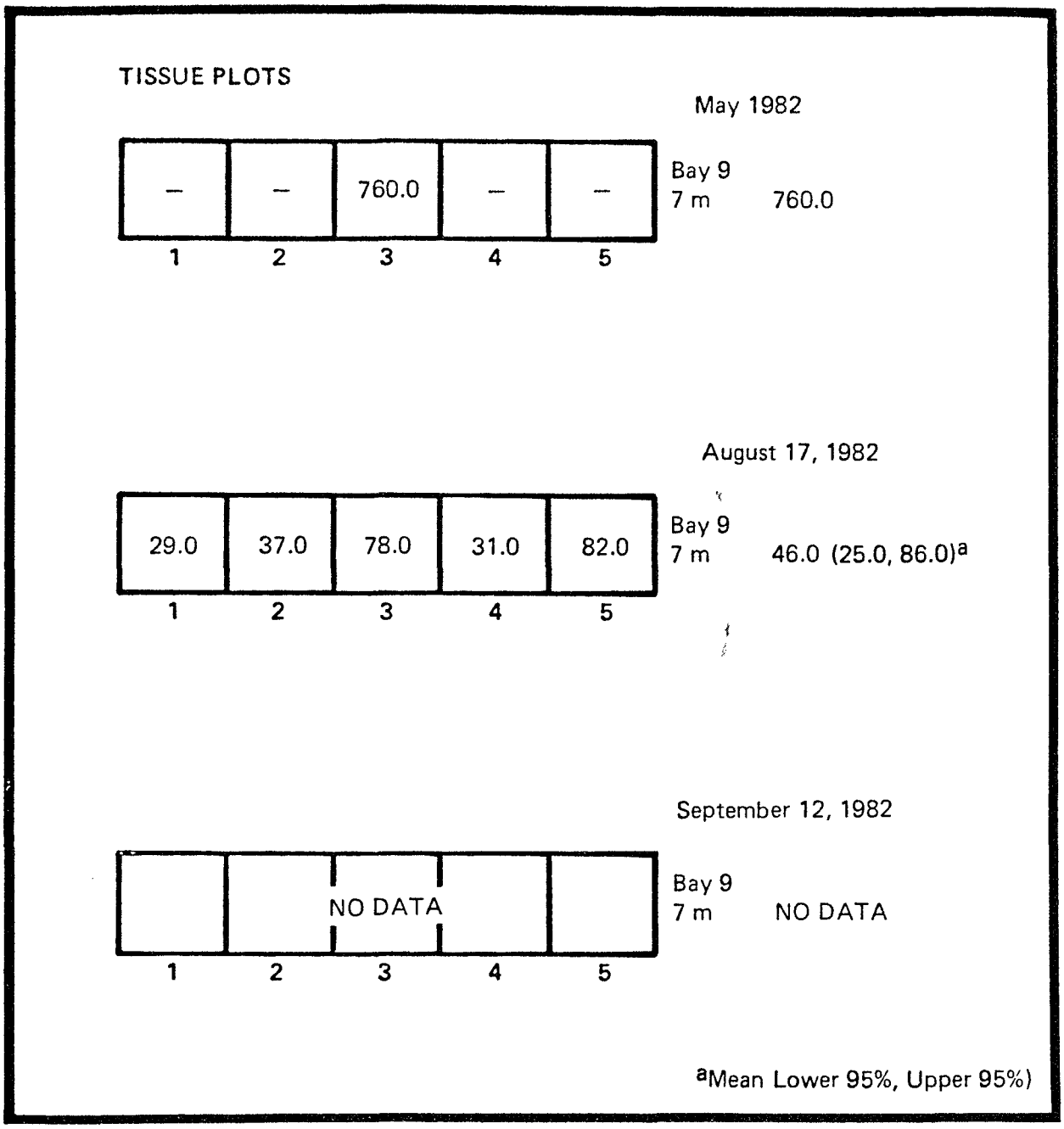


Figure 3.64. Summary of oil concentrations in *Strongylocentrotus* , by UV/F, Bay 9, (μg/g dry wt.).

760 µg/g. However, by the time of the August 1982 sampling, these values had decreased to 46 (25,86) µg/g, thus indicating either an abnormally high May value or rapid May to August depuration of oil. Results from Bays 10 and 11, however, confirm that the urchins contained much more oil in May than they did three months later in August.

A set of five individual animals from Station 1 in Bay 9 were analyzed for oil content to determine the variability of the individual level. Table 3.14 shows that values were 45 ± 29 µg/g (coefficient of variation of 64%). This mean value compares reasonably well with the combined animal sample from this station (29 µg/g). A typical spectrum is shown in Figure 3.65.

3.4.5.aii Oil Composition by GC^2

The GC^2 trace for the saturated hydrocarbons in urchins from Bay 9 (Figure 3.66A) clearly illustrate a strong petrogenic influence on the hydrocarbon composition. The normal and branched alkanes along with phytane and the UCM are linked with petroleum residues in the animals. The aromatic hydrocarbon profile for this sample (not illustrated) is largely comprised of biogenic olifins. Thus, GC^2/MS analysis is needed to detail aromatic hydrocarbon levels in this sample.

3.4.5.aiii Aromatic Hydrocarbon Composition by GC^2/MS

Urchins in Bay 9 (Figure 3.67A) contain low to moderate levels of residual aromatic hydrocarbons. When last observed in September 1981, levels of phenanthrenes and dibenzothiophenes were very high, 1000-2500 ng/g. These animals have apparently lost most of these compounds through depuration or perhaps through metabolic transformations to the point where phenanthrenes are 25-75 ppm, dibenzothiophenes are nearly absent and small amounts of naphthalenes, 5-25 ng/g reappear.

Table 3.14. Analyses of individual urchins from Bays 11 and 9.

Bay	Station	Individual animal Oil concentrations/µg/g dry wet	Pooled sample concentration
11	5	137	
		187	
		90	
		308	
		110	
		$\overline{X}$ = 167 ± 87	43
9	1	30	
		21	
		20	
		79	
		74	
		$\overline{X}$ = 45 ± 29	29

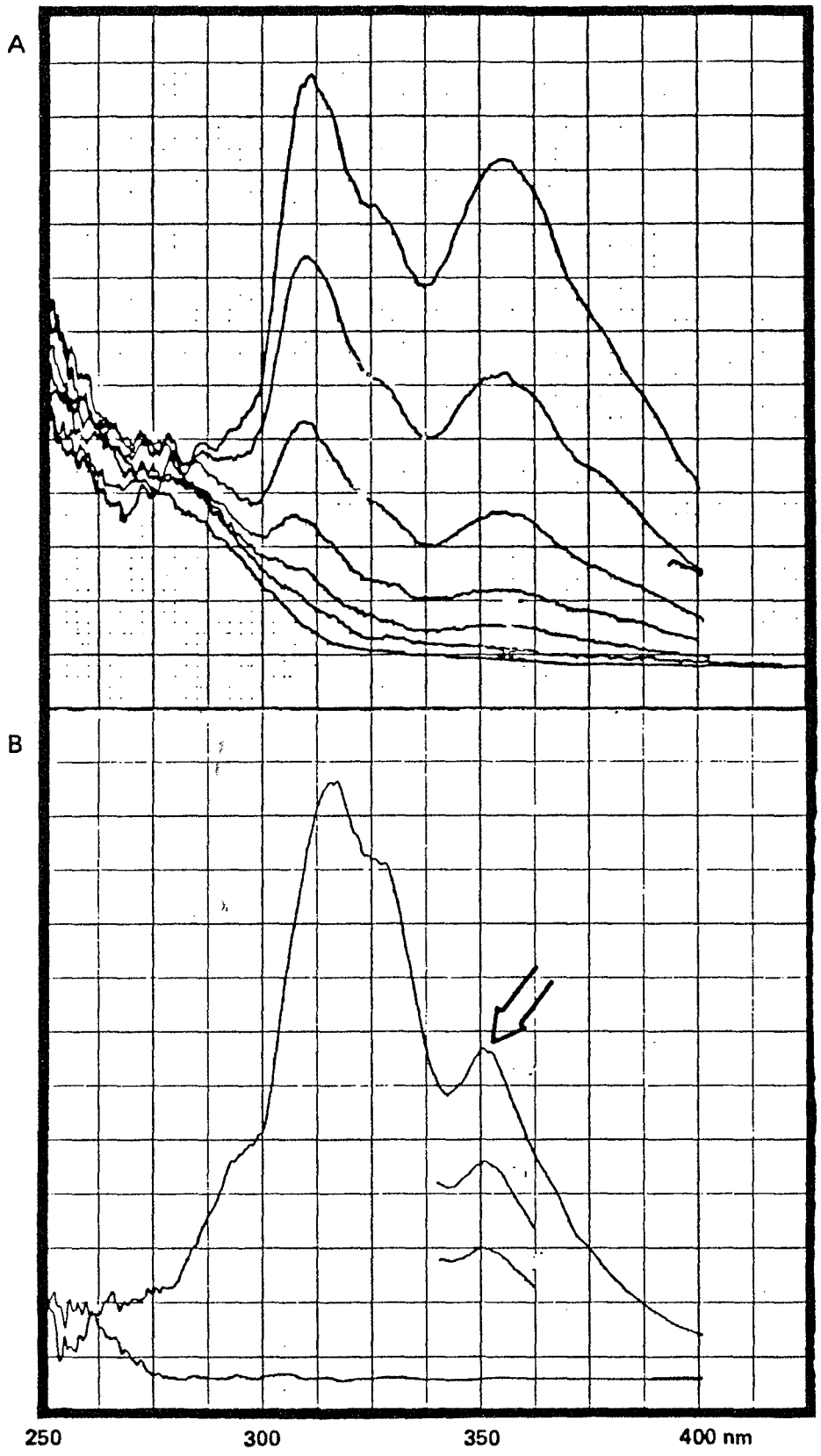


Figure 3.65. UV/F spectra of Lagomedio reference oil (A) and *S. droebachiensis* sample (B).

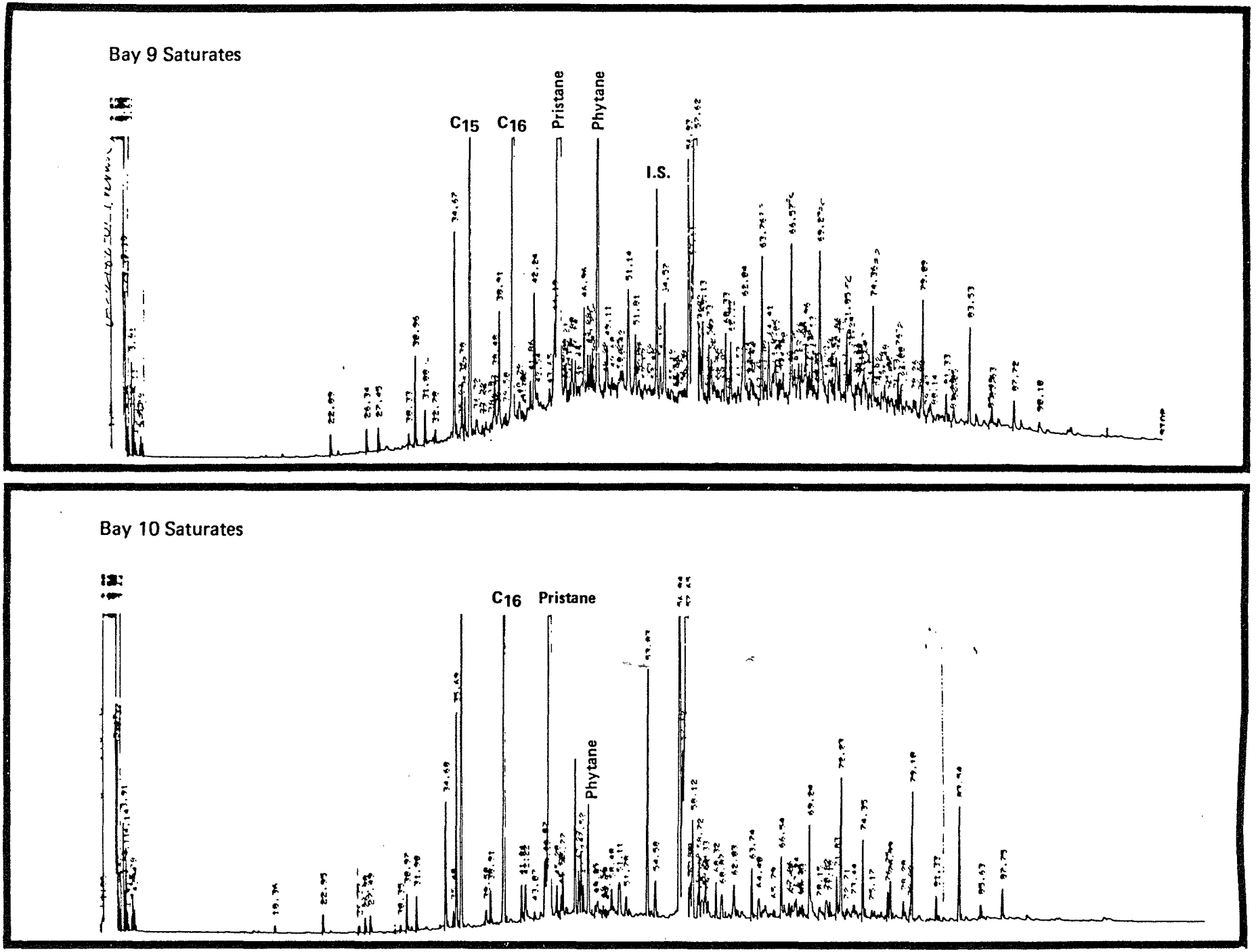


Figure 3.66. GC^2 traces of *Strongylocentrotus,* Bay 9 and 10.

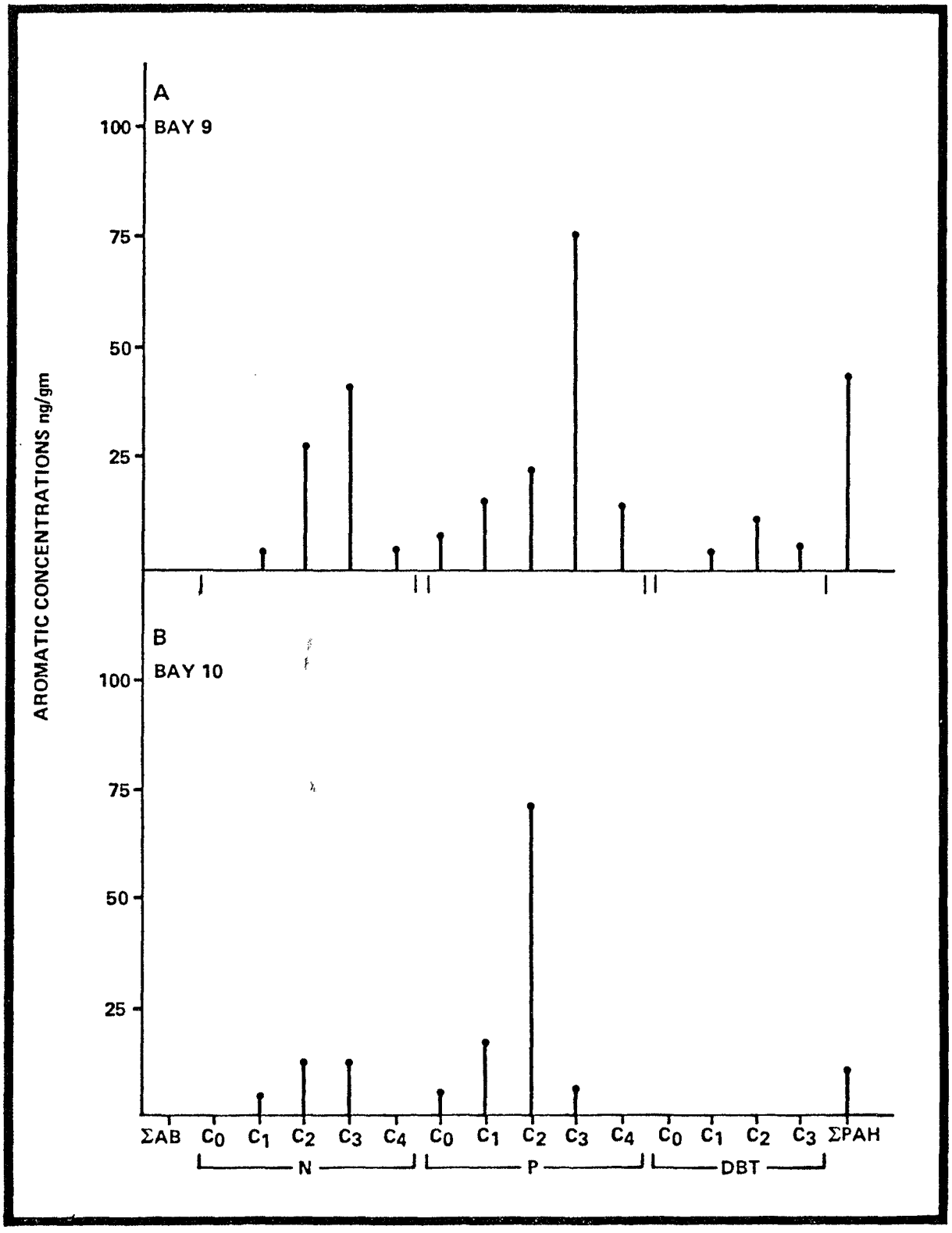


Figure 3.67. *Strongylocentrotus* GC^2/MS results, Bays 9 and 10.

3.4.5.b Bay 10

3.4.5.bi Oil Concentrations by UV/F

Bay 10 urchins contained less oil (217 µg/g) than in the corresponding Bay 9 animals in May (see Figure 3.68). This value was higher than that reported at the end of the 1981 field sampling program by Engelhardt and Norstrom (1982). At that time, oil values averaged 111 ± 12 µg/g. The apparent increase in May was followed by a sharp decrease in oil levels observed in August, down to 20 (15,26) µg/g. Thus, here as in Bay 9 we see that the urchins did apparently acquire new oil over the winter, most likely from the sediments. Thereafter, values decreased probably due to accelerated metabolic and feeding activity.

3.4.5.bii Oil Composition by GC^2

The petrogenic influence is much less apparent in Bay 10's urchin GC^2 profile (Figure 3.66B). Here, biogenic compounds dominate (as they do in the aromatic GC^2 trace - not shown) with pristane, nC_{16}, $n\text{-}C_{15}$ dominant as is the mono-olefin at index 2089. Any UCM is much less apparent. Therefore, petroleum residues are becoming more difficult to see by GC^2 analysis.

3.4.5.biii Aromatic Hydrocarbon Composition by GC^2/MS

Bay 10 urchins have similarly low to moderate levels (20-70 ng/g) of aromatics as had Bay 9 animals (Figure 3.67B). Bay 10 animals contained roughly 500-900 ng/g of individual aromatic compounds series in 1981.

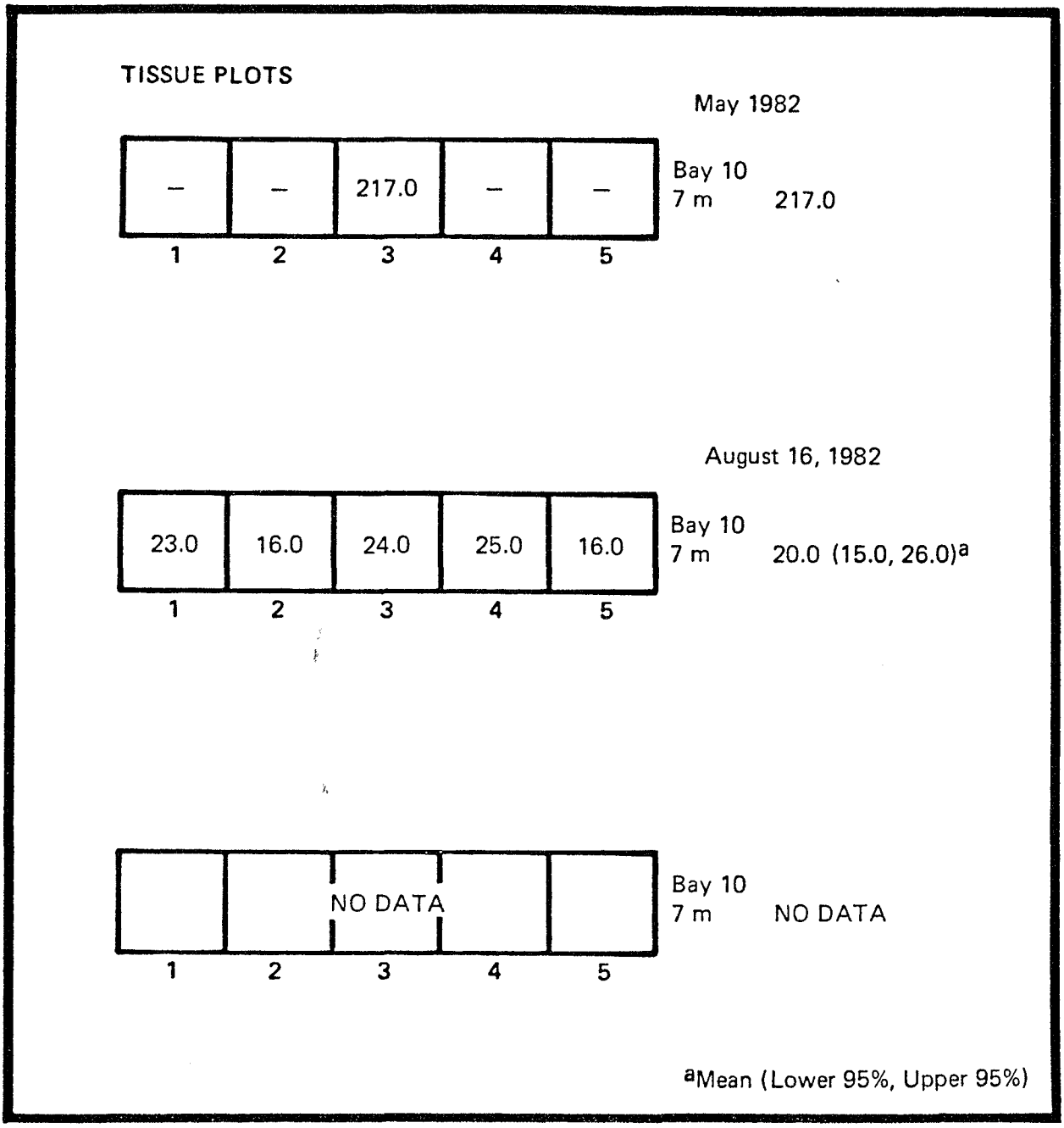


Figure 3.68. Summary of oil concentrations in *Strongylocentrotus*, Bay 10, by UV/F, (μg/g dry wt.).

3.4.5.c Bay 7

3.4.5.co Oil Concentrations by UV/F

Urchin samples from Bay 7 contained 23 µg/g in May 1982 (Figure 3.69) and thereafter decreasing to pre-spill levels of 4.6 (2.3,9.2) µg/g. When last sampled in 1981, these animals contained 44 ± 5.6 µg/g a factor of three to five lower than in Bays 10 and 9. Thus, it appears from the UV/F data that Bay 7 urchins have been able to depurate all or nearly all of the assimilated oil, which presumably was initially acquired from the water column rather than the sediments. Thus, Bay 7 urchins differ from the other bays due to their lack of exposure to sedimented oil.

3.4.5.cii Oil Composition by GC^2

The f_1 and f_2 urchin profiles illustrating only biogenic hydrocarbons for the Bay 7 urchins is shown in Figures 3.70. No petroleum influence is evident in these traces.

3.4.5.ciii Aromatic Hydrocarbon Composition by GC^2/MS

Bay 7 urchins (Figure 3.71A) contained low levels (10-40 ng/g) of the naphthalene compound series in 1982, lower values than in 1981 when these "reference" animals did contain higher (100 ng/g) levels of these compounds. Small amounts of C_3 phenanthrene were also observed in August 1982.

3.4.5.d Bay 11

3.4.5.di Oil Concentrations by UV/F

The data from Bay 11 illustrates some very interesting trends in urchin oil content (Figure 3.72). Urchins were obviously impacted by oil starting

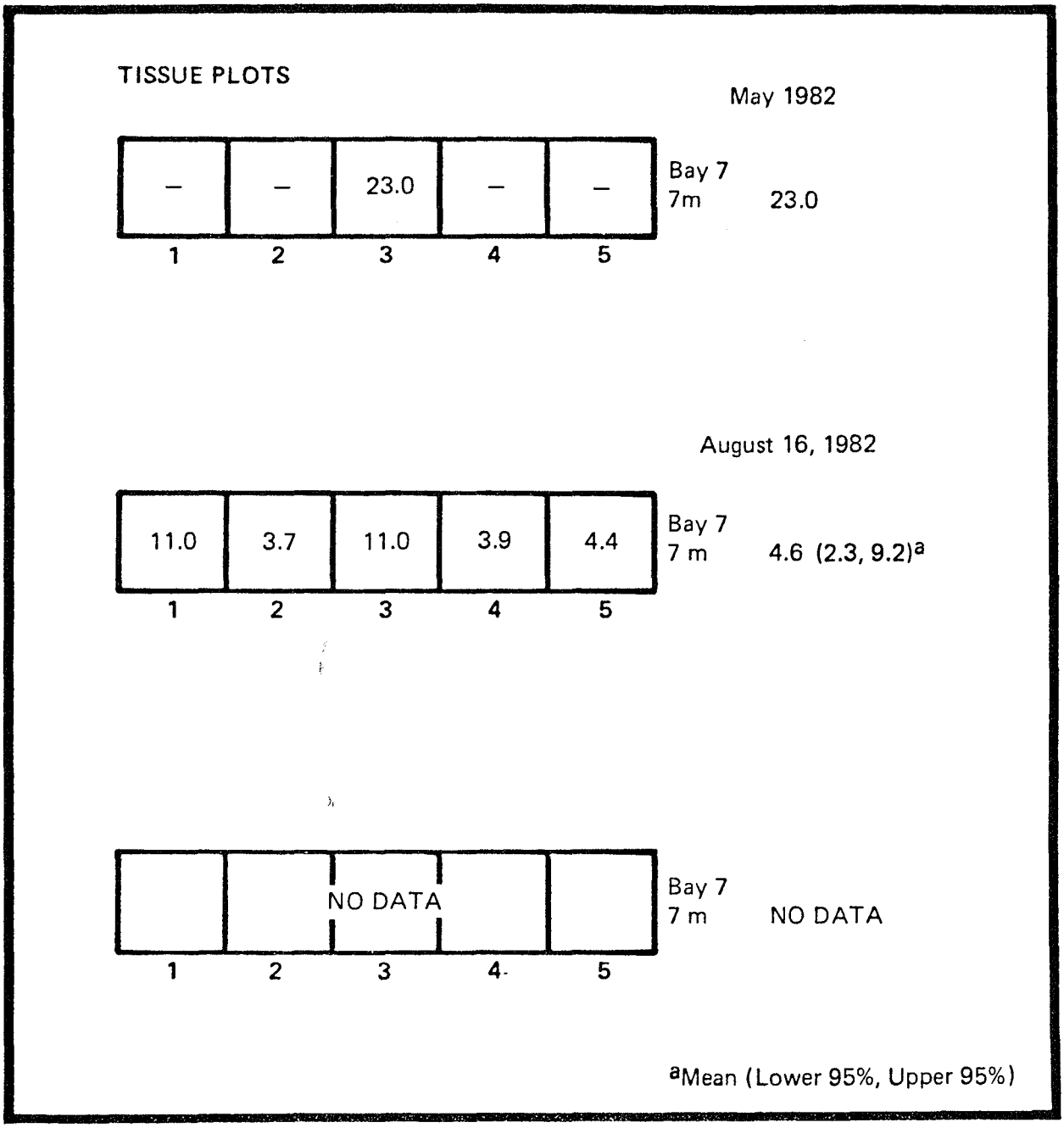


Figure 3.69. Summary of oil concentrations in *Strongylocentrotus*, by UV/F, Bay 7, (µg/g dry wt.).

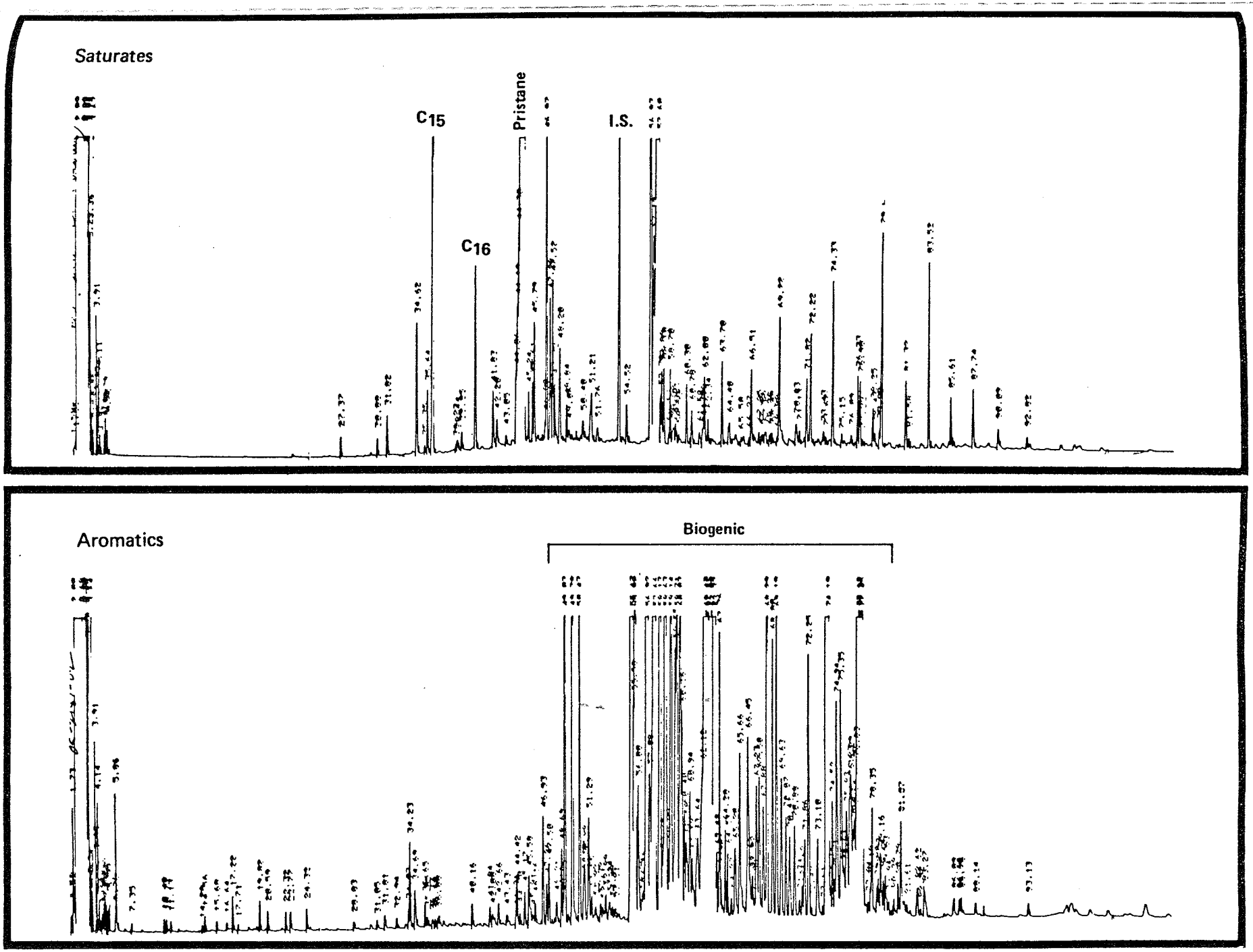


Figure 3.70. GC^2 traces of *Strongylocentrotus* from Bay 7 indicating negligible petroleum contamination.

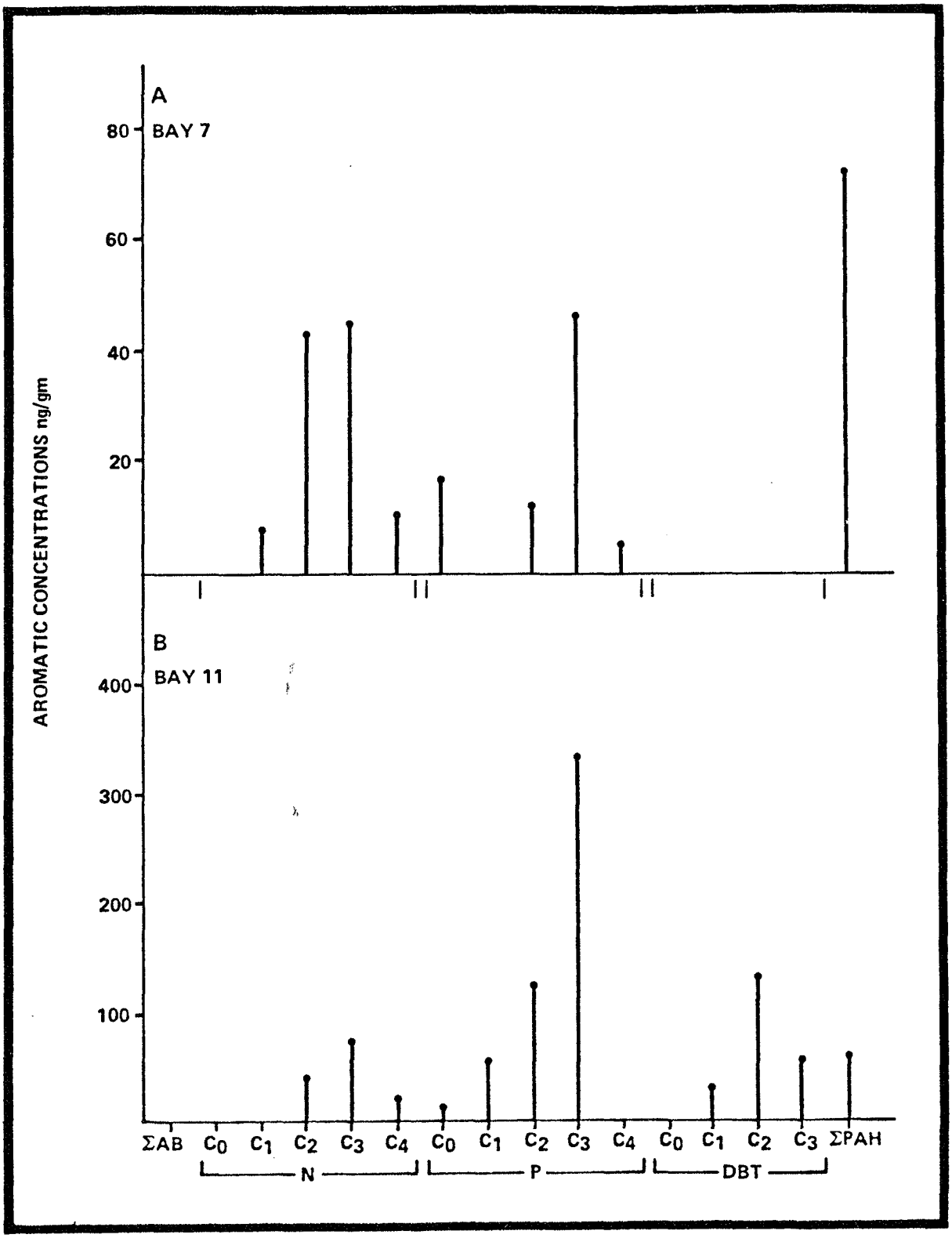


Figure 3.71. *Strongylocentrotus* GC^2/MS results, Bays 7 and 11.

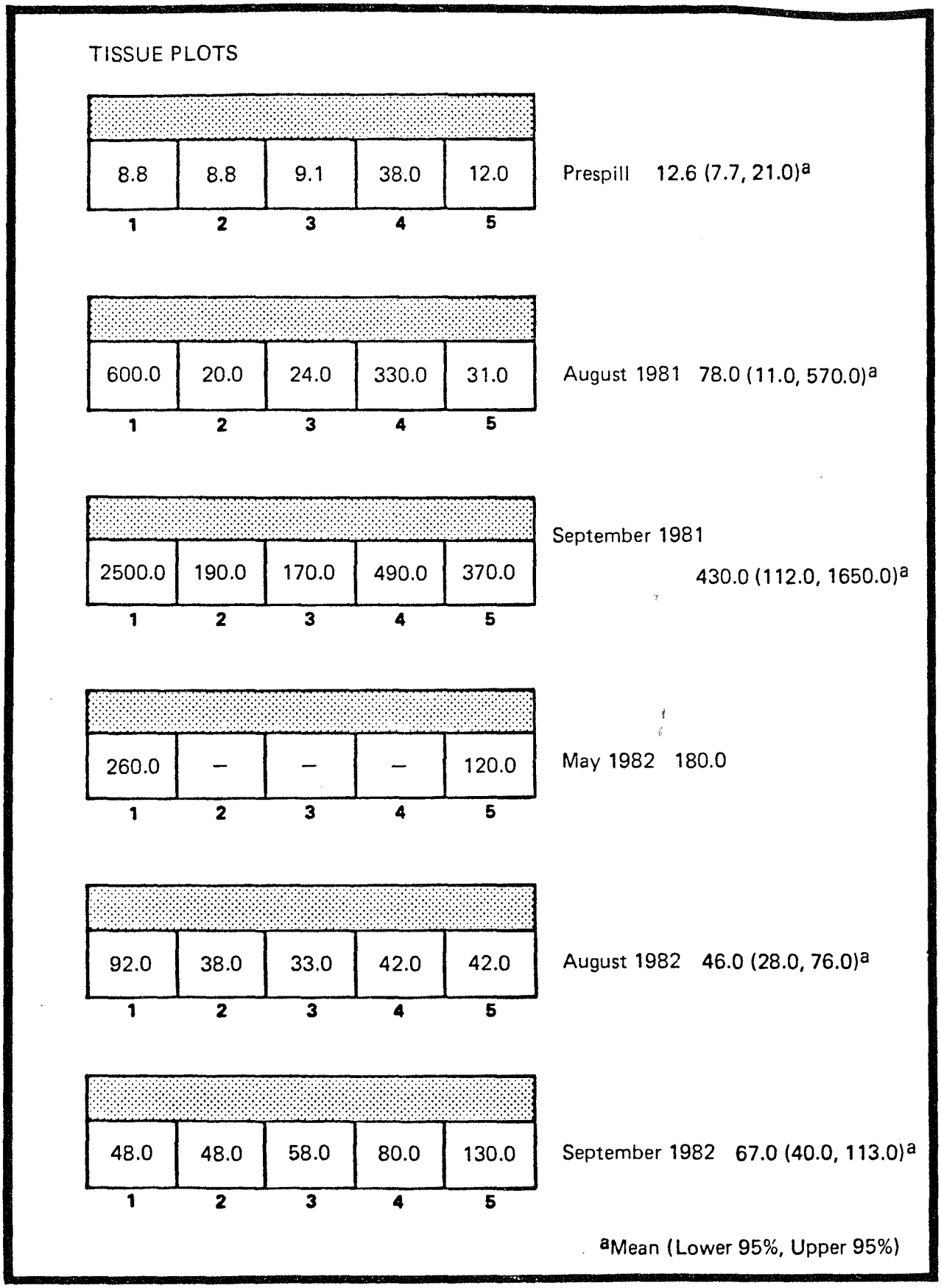


Figure 3.72. Summary of *Strongylocentrotus* oil concentration data, 1981–1982, Bay 11.

in August 1981 and peaking at 430 (112,1650) µg/g in September 1981. The May 1982 sampling, 180 µg/g was lower as was the August 1982, 46 (28,76) µg/g sampling. The 7-m depth value increased to 67 (40,113) largely on the basis of one high value at Station 5 without which the mean value would be 57 µg/g. The September 1982 sampling in Bay 11 for urchins indicates that oil levels after decreasing substantially from May 1982 have apparently leveled off. Whether this is true for the other bays is not known as only Bay 11 was sampled in September. The sample of "caged urchins," first caged in 1981 but taken in September 1982 for analysis, contained 140 µg/g of oil.

As in Bay 9, individual urchins were analyzed in Bay 11, this time at the southern end of the depth stratum, Station 5. The mean value of the five individuals, 167 µg/g (Table 3.14) is four times the station value. We suspect that a combination of water loss by the individuals due to thawing and refreezing, and the low sample weights (dry weights) could have introduced absolute errors to the individual urchin analyses for Bay 11. Thus, while the conclusions analytical precision or variability between individuals is probably valid (±52%) the absolute values are suspect. The station result wherein several animals were combined (the lower value) is probably the accurate oil content result.

3.4.5.dii Oil Composition by GC^2

The important influence of residual petroleum on the Bay 11 urchins is revealed in Figure 3.73. The saturated hydrocarbon profile definitely illustrates petrogenic character. However, the petroleum aromatics are obscured in the f_2 by the much more abundant biogenic material.

GC^2 profiles of the saturates from the three individual urchins (Figure 3.74) reveal close compositional similarities although the concentration of the No. 3 sample is about five times as great. This compositional simularity suggests a uniform source of degraded oil to these animals rather than any direct input of weathered, but undegraded eroding shoreline oil.

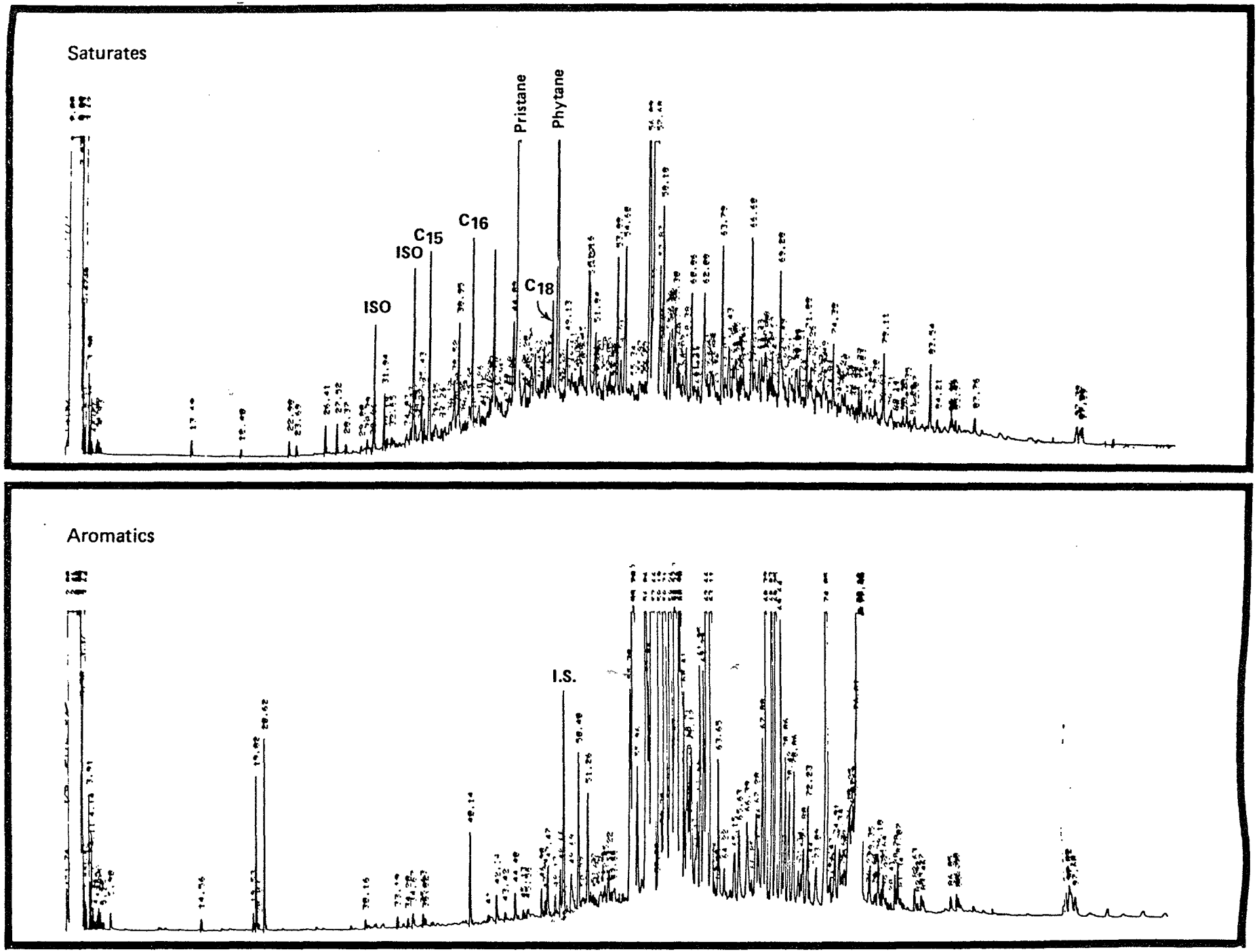


Figure 3.73. GC^2 traces of *Strongylocentrotus*, Bay 11.

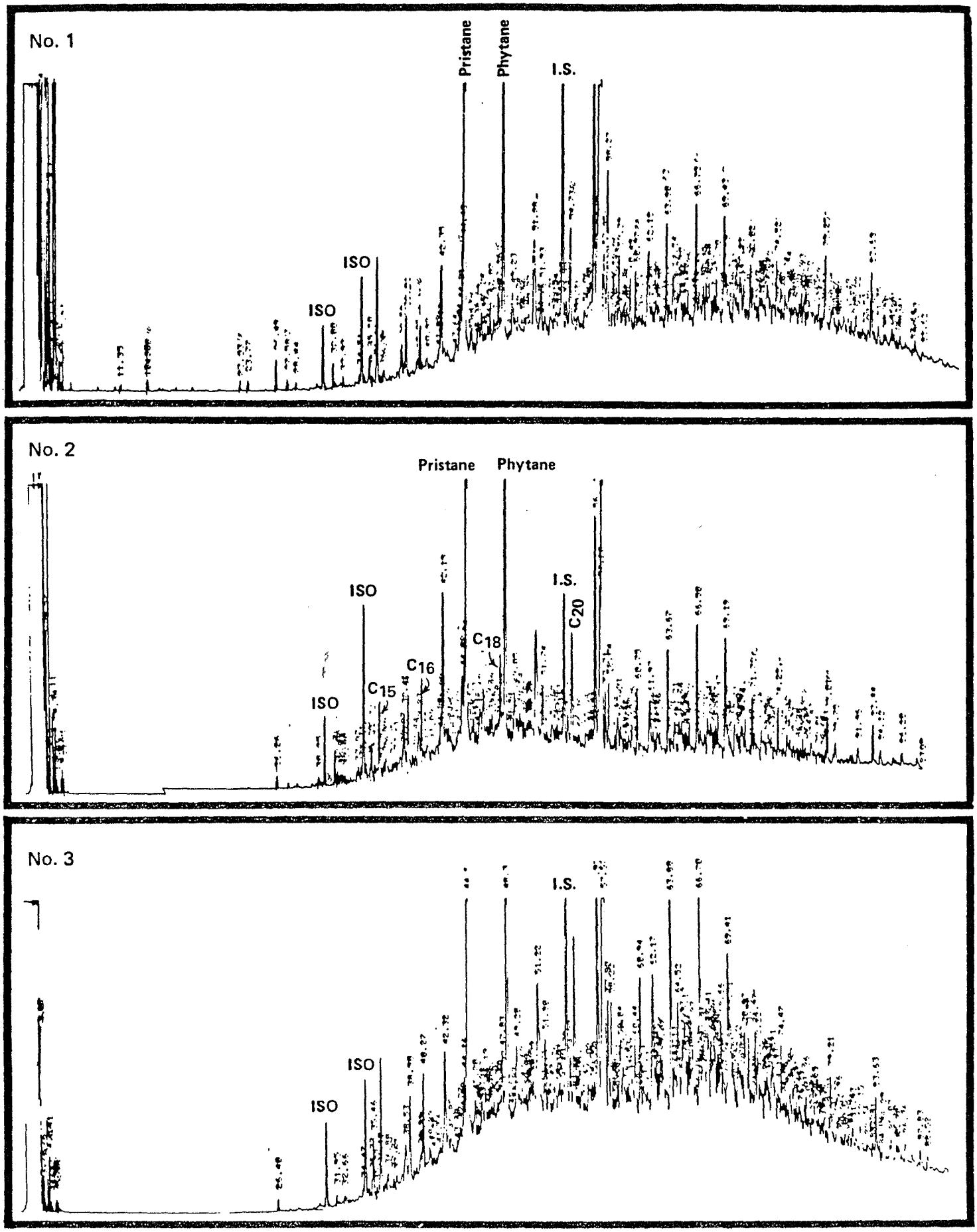


Figure 3.74. GC^2 traces of *Strongylocentrotus* (urchin) individuals, Bay 11, Plot 5.

An additional sampling in September of 1982 yielded a very similar GC profile indicating that no additional unbiodegraded oil was making its way directly into the animals. The alkane/isoprenoid ratio remained quite low (.08), thus verifying that new alkane inputs from shore were not significant here.

3.4.5.diii Aromatic Hydrocarbon Composition by GC^2/MS

A more detailed study of aromatic content and composition of urchins in Bay 11 was conducted than in the other bays. Figure 3.71B shows the results from August 1982. Here 100-300 ng/g of the phenanthrene compounds were present, higher than for urchins in any of the other bays. Dibenzothiophenes (50-120 ng/g) were also present. When last observed in September 1981, correspoding levels of the phenanthrenes were ∿200 ng/g and of the dibenzothiophenes were 300-600 ng/g. Thus while absolute values of dibenzothiophenes have decreased by a factor of perhaps four, the phenanthene values are similar. Only in Bay 11 did the urchins maintain their aromatic hydrocarbon content, indicating that significant new inputs of oil into the Bay 11 system occurred.

An additional analysis was conducted on a set of urchins taken in September 1982, one month later. Levels of both the phenanthrene and dibenzothiophenes apparently decreased by an additional factor of three. However, naphthalenes achieved a relative importance in the September 1982 animals (Figure 3.75) being present at the 50-100 ng/g level. While naphthalenes were present in the samples taken one month earlier (Figure 3.71B), they were not nearly as abundant as the three-ringed aromatics. Thus, a shift in apparent aromatic composition has occurred.

Three individual urchins were analyzed from station 5 in Bay 11 in August 1982. The three results shown in Figure 3.76 are quite different indicating much compositional heterogenity. The No. 1 animal contained significant naphthalenes and phenanthrenes (60-100 ng/g); the No. 2 animal

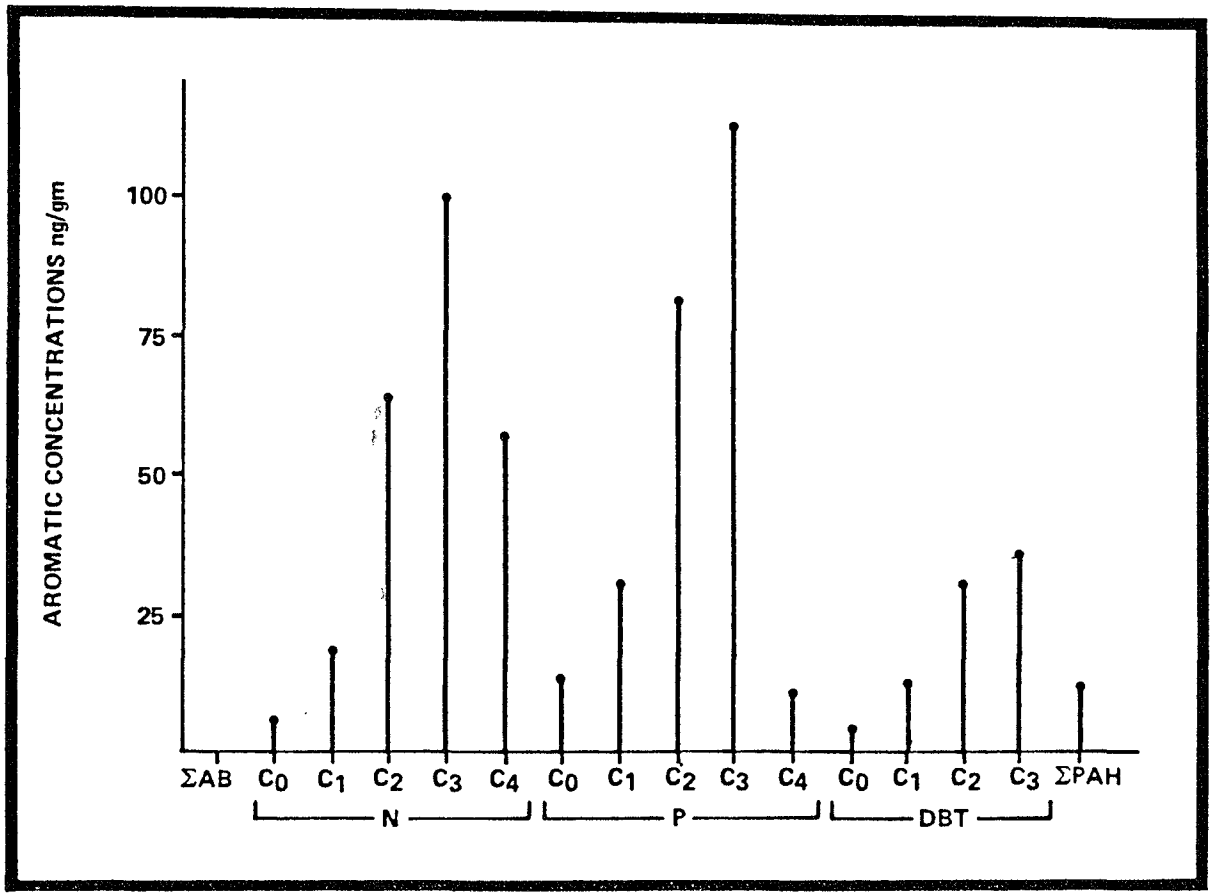


Figure 3.75. *Strongylocentrotus* GC^2/MS results, September 1982, Bay 11.

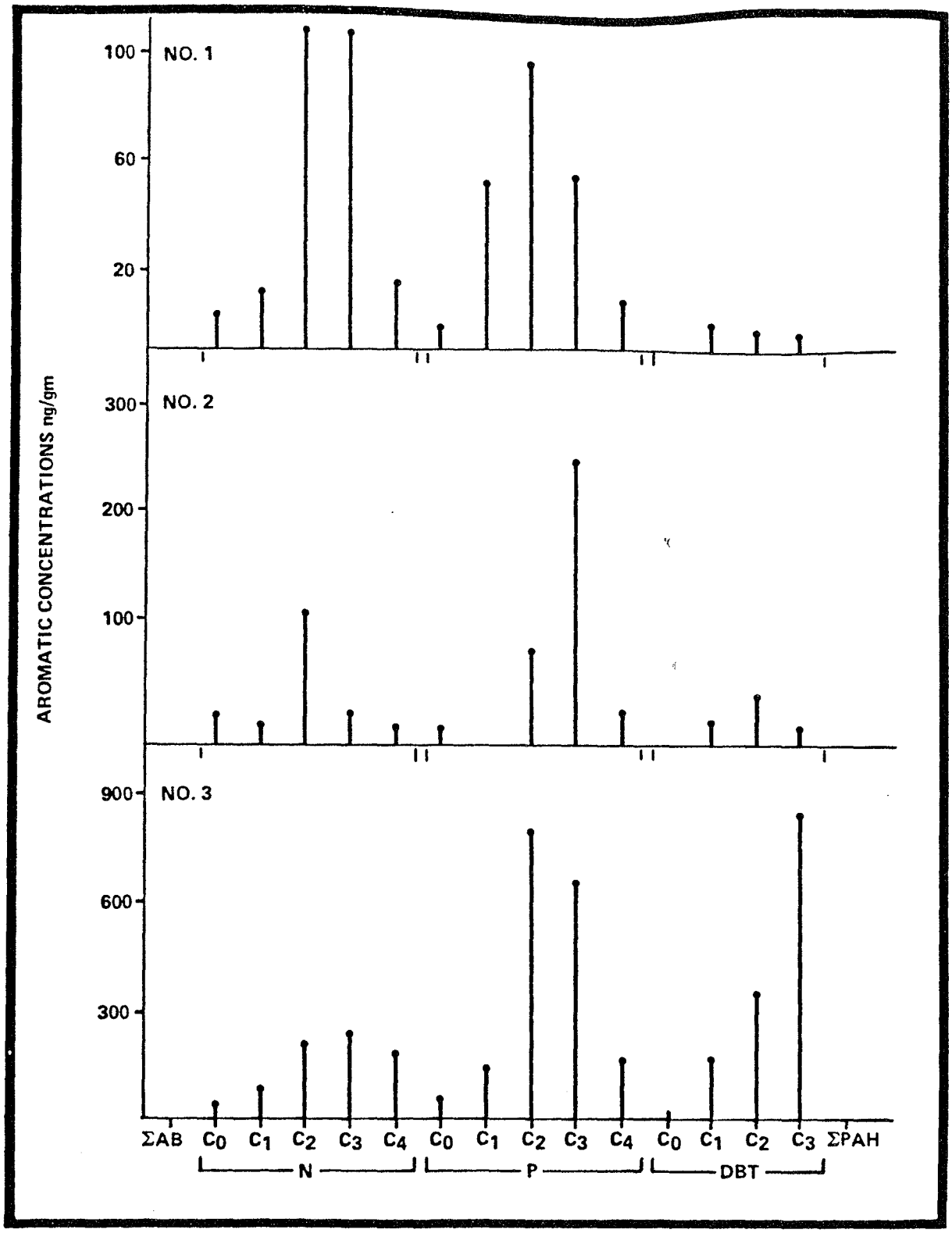


Figure 3.76. *Strongylocentrotus* GC^2/MS results, Individuals Bay 11.

contained similar levels of naphthalenes, but nearly twice as much C_3 phenanthrene; the No. 3 animal contained more oil with abundant naphthalene (100-300 ng/g) phenanthrene (100-800 ng/g) and dibenzothiophene (200-900 ng/g) series compounds. Note that dibenzothiophenes were only significant in the No. 3 animal as this animal apparently had recently acquired weathered oil. Only this animal's composition was similar to that observed in the Bay 11 pooled extract (Figure 3.71B) and to that observed in 1981.

Thus we see that most of the GC^2/MS results for this and for the other species must be considered an "average" of differing compositions in many animals pooled along a certain depth stratum.

3.4.6 Results by Bay

3.4.6.a Bay 9

The oil concentration results for all species from Bay 9 are presented in Figure 3.77. All species are seen to have lost considerable amounts of the oil that they acquired in 1981. Several interesting points are: (1) the urchins apparently continued to increase their body burdens over the winter after which time levels decreased to ∿50 ppm, (2) levels in Macoma are still elevated (∿25 ppm) but down from 1981, (3) levels in Astarte (∿20 ppm) are still higher than baseline (∿.5 pm), (4) only Mya levels are apparently back down to single ppm values although oil is still present in their tissues, (5) there apparently had been lags in the uptake of oil by the detrital feeders, Macoma, which peaked several weeks after the spill and the urchins which apparently peaked in May 1982.

3.4.6.b Bay 10

Results from all of the species are summarized in Figure 3.78. Very similar trends as those observed in Bay 9 are seen here. The Macoma and

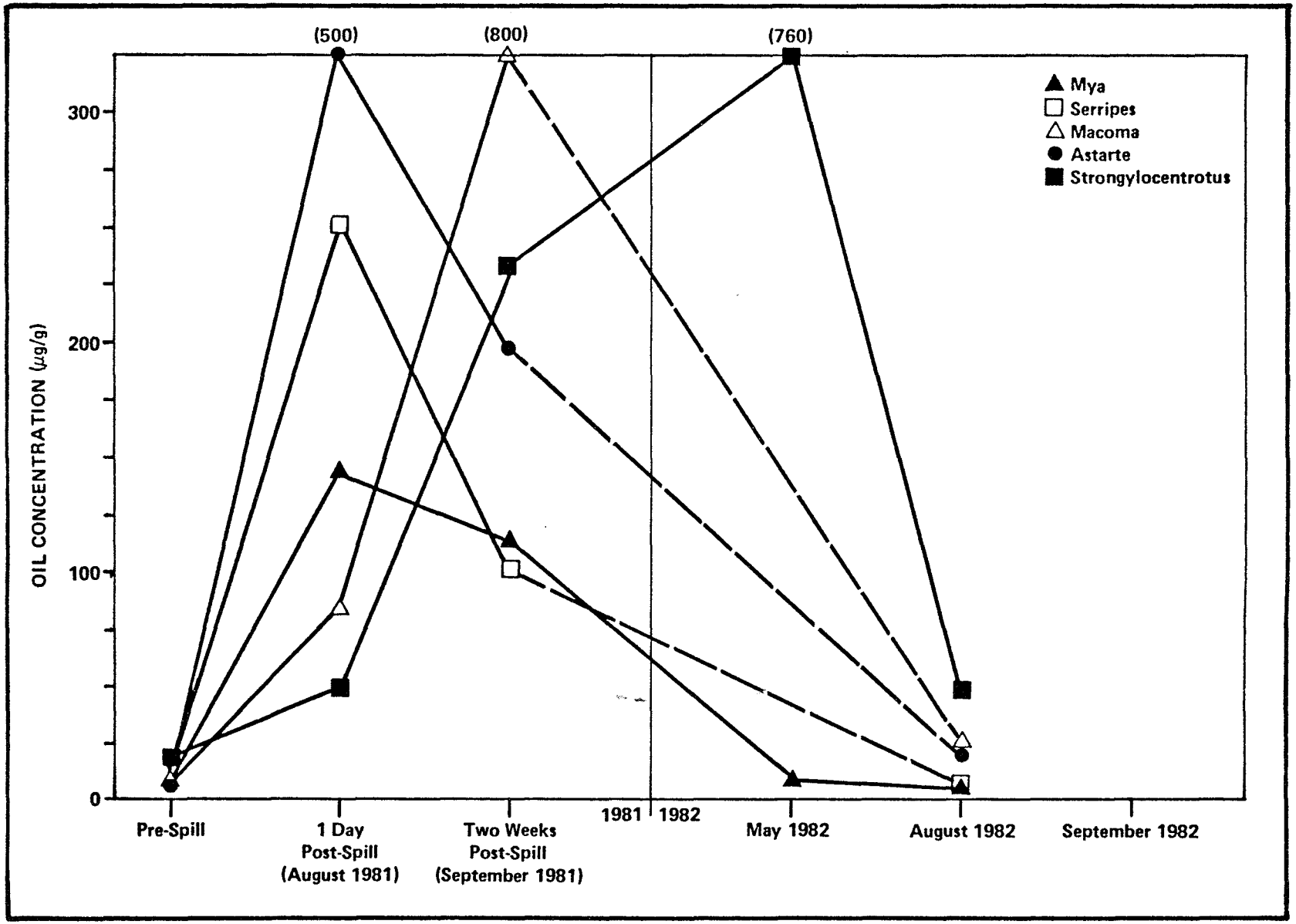


Figure 3.77. Oil concentrations in animals: Bay 9 (µg/g; by UV/F).

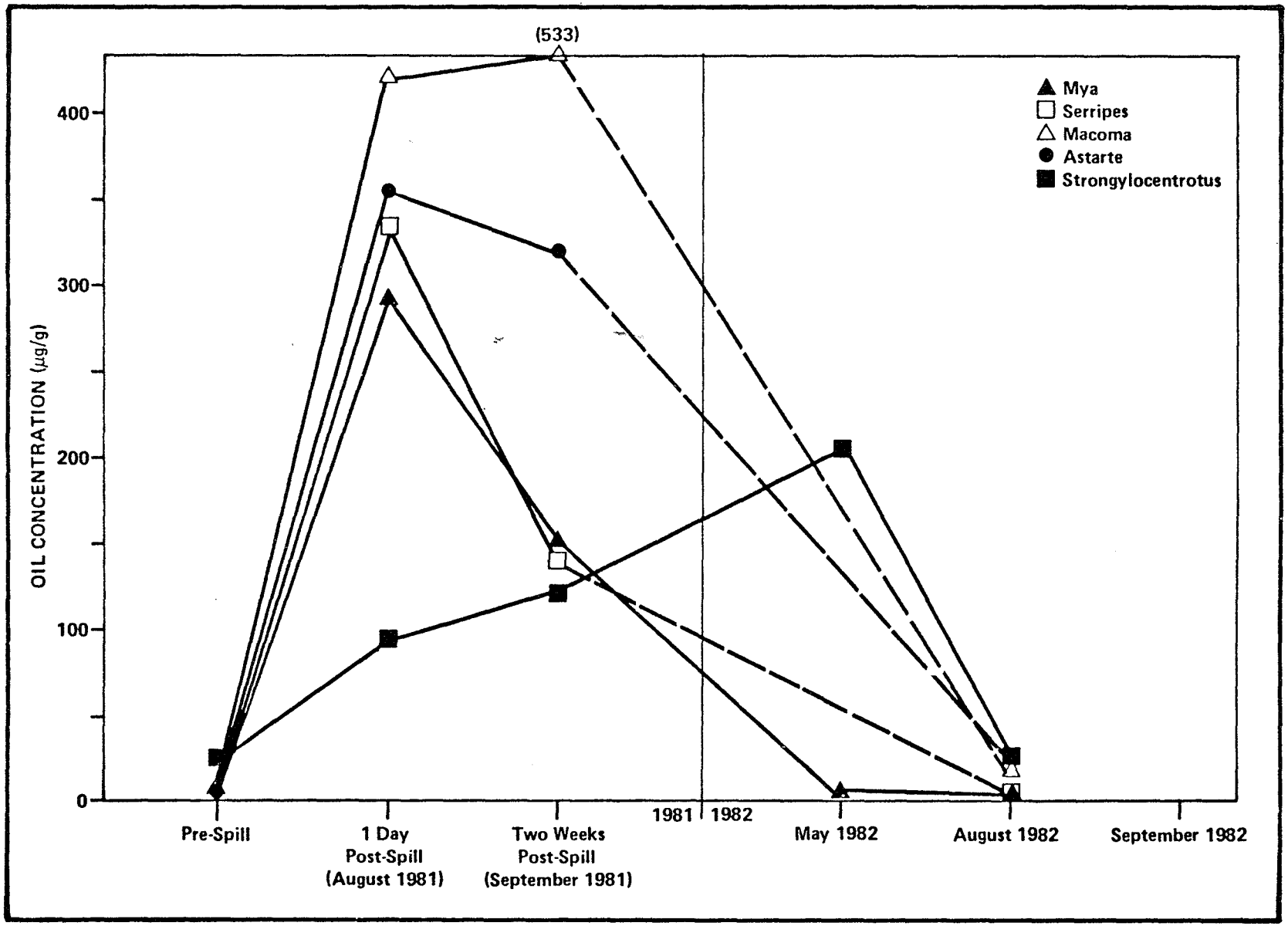


Figure 3.78. Oil concentrations in animals: Bay 10 (µg/g; by UV/F).

urchin concentrations peaked at times out of phase with the other species and again levels of oil in urchins apparently increased over the winter. By August the residual petroleum levels in urchins, Macoma, and Astarte are similar but higher than those for the filter-feeding Serripes and Mya.

3.4.6.c Bay 7

Bay 7 uptake and depuration patterns are simpler than for Bays 9 and 10 owing to the lack of sediment-mediated uptake in Bay 7. Levels of oil in all animals decreased markedly during the year after the spills. Residual values present in August 1982 oil are in the single ppm range for all animals. Note that in May 1982, levels in Mya and urchins were still somewhat higher than finally observed later in August.

3.4.6.4 Bay 11

After the initial lag (1981) in oil uptake due to the lag in transport of beached oil offshore, levels in the animals decreased over the winter (Figure 3.80). Mya was nearly depleted in oil content by May but experienced a minor increase from August to September 1982. The same increase was seen for the urchins. (The other species were not sampled in September 1982.) Levels of oil in Macoma and Astarte were higher in August than those observed in the other bays, probably owing to offshore transport of beached oil.

3.4.7 Comparison of UV/F and GC Results for Organisms

Only a limited set of data exists for purposes of making a comparison of UV/F "oil equivalents" values to total petroleum hydrocarbons by GC. The UV/F results (Table 3-15) were obtained directly from instrument readings. The oil (GC) results were calculated by quantifying the amount of phytane in each sample and applying a known phytane-to-total oil conversion factor (6.4 mg phytane/gram oil; Boehm et al. 1982a, p. 188-189).

As the results in Table 3.15 indicate, the relationship between the two sets of results varies according to the species. While UV/F seemed to underestimate the oil content in Mya by a factor averaging 8.7, the equivalent "factors" for the other species were Serripes 1.1; Macama 2.7; Astarte .25; Strongylocentrotus 6.0. Thus the application of any correction factor would vary from species to species. However, such an application assumes that the GC numbers are "right" while UV/F numbers are incorrect. Although it is known that UV/F measurements are based on a certain fraction of the oil and that as the oil weathers the relative abundance of this fraction may change, the same may be said for the GC results. Thus we note this discrepancy, but recommend the continued use of UV/F measurements in the program with GC and GC/MS backup. The UV/F data still serves as a good comparative set of data on gross oil levels which are probably internally consistent.

TABLE 3-15

COMPARISON OF UV/F AND GC RESULTS FOR ORGANISMS

Species	Bay	Phytane (µg/g)	Oil (GC) (µg/g)	Oil (UV/F) (µg/g)	Total Phenanthrenes (ng/g)
Mya	7	.052	8.1	0.41	10
	9	.045	7.0	0.81	20
	10	.017	2.7	0.96	14
	11	.030	4.7	1.3	47
Serripes	7	.021	3.3	2.2	50
	9	.040	6.3	5.2	290
	10	.023	3.6	3.0	34
	11	.053	8.3	13.0	130
Macoma	7	.040	6.3	1.9	35
	9	.028	4.4	25	350
	10	.19	29	14	270
	11	1.1	170	60	720
Astarte	7	.048	7.5	19	ND
	9	.028	4.4	19	90
	10	.029	4.5	29	400
	11	.052	8.1	37	400
Strongyloncentrotus					
	7	.28	44	4.6	70
	9	1.5	230	46	140
	10	.31	480	20	100
	11	3.5	550	78	450

ND = None detected.

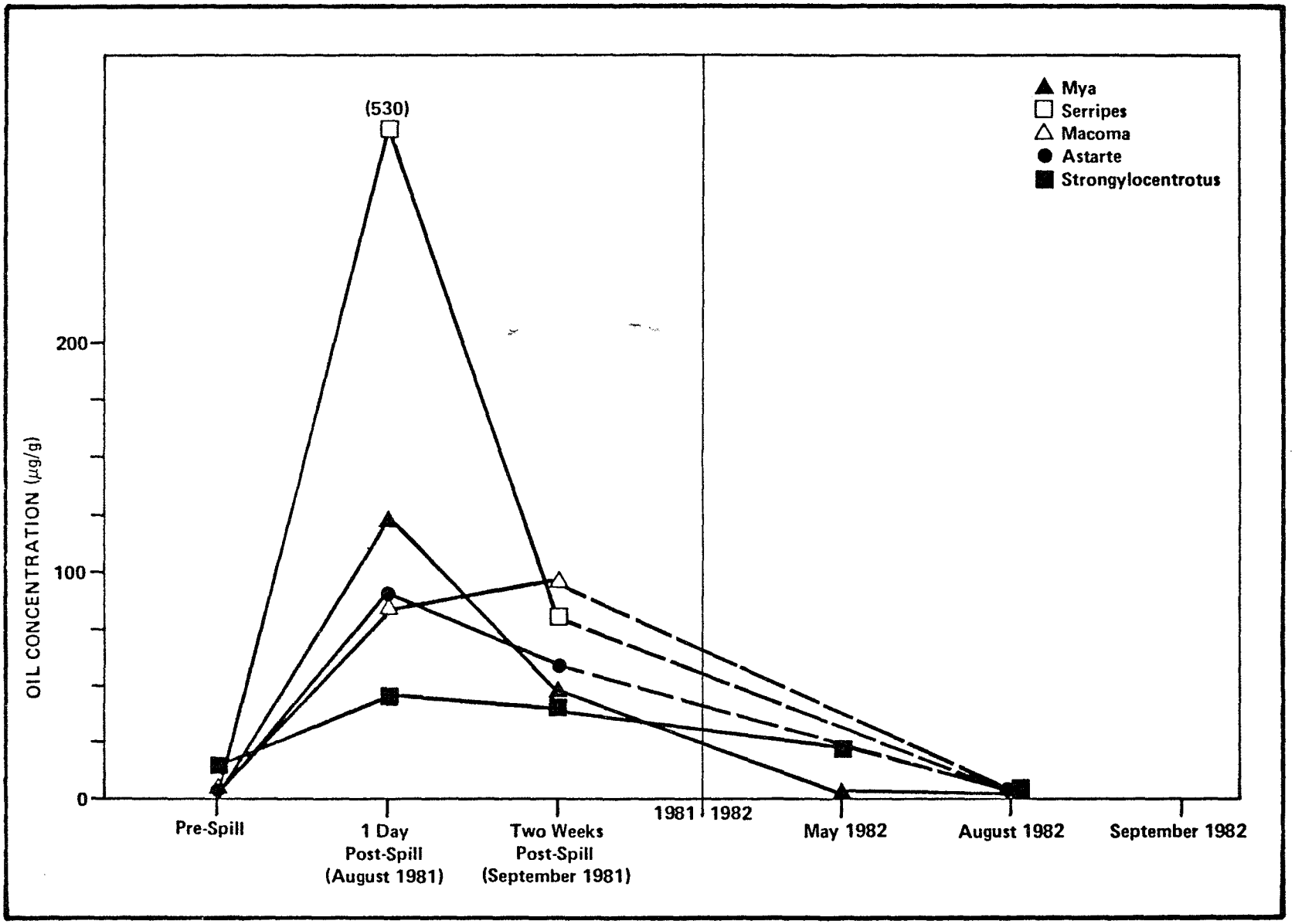


Figure 3.79. Oil concentrations in animals: Bay 7 (μg/g; by UV/F).

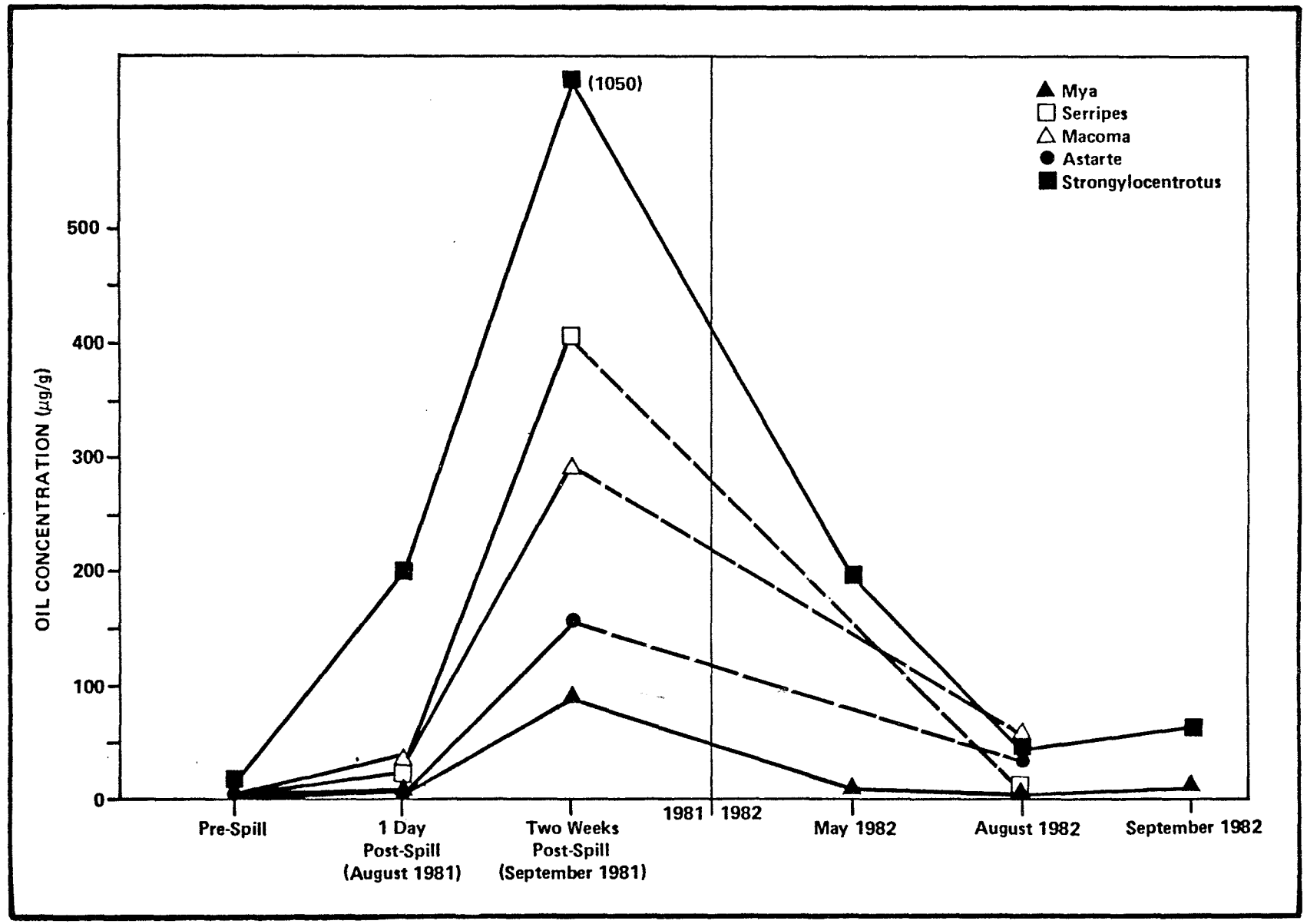


Figure 3.80. Oil concentrations in animals: Bay 11 (µg/g; by UV/F).

SECTION FOUR

DISCUSSION

The 1982 field sampling and analytical program focused mainly on the persistence of petroleum residues in the benthic system. Although water column sampling and related sample analyses were conducted, these samples only served to monitor the water column in a qualitative way for the transport of water-bourne oil.

It appears that oil levels in Bay 9 and Bay 10 sediments decreased between the 1981 and 1982 samplings by roughly a factor of two in Bay 9, down to 3.0 ppm, and by a similar factor in Bay 10 (down to 2.0 ppm). Petroleum in the sediments of these bays are more concentrated at the 7m depth in shallower water, but there is no evidence that oil concentrations increase out to a depth of 15 m where the so-called "deep" samples were taken. Therefore, if oil from the spills has been transported further offshore, it resides in sediments in deeper waters of Ragged Channel. However, this is speculative at this point.

The composition of the low level oil residues is quite similar to that observed in 1981. No significant further weathering of the oil is noted in the sediments. This includes weathering through biodegradation. There is no chemical evidence that the microbial population is preferentially using the small amounts of petrogenic n-alkanes in the sediments. Therefore, the biodegradation parameters of ALK/ISO and phytane/n-C18 remain constant. Additional physical-chemical weathering is also not significant as the aromatic hydrocarbon composition still is characterized by the occassional presence of highly alkylated naphthalenes, and the definitive alkylated phenanthrene and dibenzothiophrene homologous series. Absolute levels of these important components apparently increased significantly (factor of 2 to 4) from those observed in 1981, but this apparent increase may be due to the larger amount of GC^2/MS analytical information generated in 1982.

In any event, levels of the aromatic hydrocarbons quantified (namely the phenanthrenes and dibenzothiphenes) are certainly not decreasing in the sediments. This apparent contradiction with the UV/F-generated oil concentration data is probably more a function of the fact that GC^2/MS analyses focused on specific individual components while the UV/F measurements focused on a much less defined "fluorescene property" of the extract. One can have confidence in both sets of results as being internally consistent during 1982 and with previous sediment data.

The oil that resides in the sediment for the most part is confined to the top layer (0-5 cm) of sediment. However, there was GC^2/MS evidence of some vertical penetration of the alkylated phenanthrenes thus suggesting some vertical movement of certain oil components in the sediment. Low to moderate levels of oil (1-20 ppm) are present on the Bay 9 beach, far lower than observed on Bay 11 beach (20,000 ppm). The beached Bay 9 oil is chemically much less weathered than that found on the Bay 11 beach and there is no evidence of its having been biodegraded as was the case for the larger quantities of oil on Bay 11 beach. The presence of alkylated benzenes and naphthalenes in the Bay 9 oil residues is quite surprising and significant. Oil in such low quantities would be quickly stripped of these compounds by evaporation and dissolution. This oil must be "new" or newly exposed to the environment.

By far the most dynamic situation vis-a-vis oil transport is seen in Bay 11. After ice breakup (i.e., after May) oil is introduced to the bay 11 water and sediments. Apparently erosion or tidal flushing of the Bay 11 beach introduces important quantities of oil to the 3m and 7m depths. The significant quantities of oil in the surface sediments, 10-70 ppm, has been weathered substantially although occasionally "pockets" of only lightly to moderately weathered oil are observed (i.e., naphthelenes are present). There is ample evidence to postulate that oil has been significantly biodegraded and physico-chemically weathered while on the Bay 11 beach and has been transported while bound to sediment particles on the beach to the offshore sediment. The highest concentrations of oil in the surface sediment offshore are more highly weathered than where lesser quantities are found.

There are also significant amounts of oil in the floc layer. The major oil concentrations appear along benthic transect number 3, the southernmost transect, thus suggesting offshore transport concentrates oiled particles here. Interestingly it appears that this ofshore transport of oil has not affected the microbiology sediments because although concentrations of oil are higher at these sites (~6 ppm) than they were in September 1981 (~2 ppm) the oil present is chemically different (i.e., no biodegradation evident) than that observed in the 3m and 7m samples of high (10-60 ppm) concentration. The oil at these microbiology stations is apparently the result of a different path of transport than that found in the shallower sediments (i.e., not directly from summer 1982 beach erosion). (The deep sediments (15m) in Bay 11 do not reveal significant offshore transport in this bay as well.) The further offshore movement of oil in Bay 11 merits detailed study.

The Bay 7 sediments did contain small quantities (1-2 ppm) of petroleum-type material. When analyzed by GC^2 and GC/MS it was quite interesting to find a relative abundance of naphthalenes (but toxicologically insignificant) in these sediments and only trace levels of dibenzothiophene suggesting one of two things: (1) that a leachable or water soluble fraction of some Lagomedio source (e.g., Bay 11 beach or Bay 9 beach) has made its way to Bay 7 in small quantities and has been incorporated at low levels into the sediments, or (2) that a new source of oil, a distillate oil, has been introduced into the system. The large-volume-water sample taken in Bay 7 confirms the presence of light petroleum fractions in the water column at low (10-30 ng/l; parts per trillion) levels.

If one takes the entire water volume (0-10m depth) to be $4.25 \times 10^8 m^3$ (Humphrey, personal communication) it would only take 13 kg of these oil components from any source to achieve these water column concentrations. If these components are assumed to be 5% of a suspected source, such as the Bay 11 beached oil, then erosion of 260 kg of oil would yield these levels. This is equivalent to an introduction of merely $0.3 m^3$ of oil (or 300 liters). Therefore, these water column levels could have been achieved by the introduction and mixing of oil from the Bay 11 beach into the Ragged Channel area.

The most powerful set of monitoring measurements relate to the benthic marine organisms. The urchins and Macoma (deposit feeders) have been seen to be good sentinels of oil input to sediments. Mya and Serripes bivalves reflect the water-borne contaminants and Astarte appears to reflect both equally well. Absolute concentrations in all animals observed at the end of the 1982 sampling season were much lower than in 1981. Oil levels in the deposit-feeders are higher than those in the filter-feeders. Mya and Serripes apparently depurated acquired oil so that as early as May (for Mya) levels were down to the low single ppm levels. The deposit-feeders continued to reflect inputs to the sediments. Urchins in Bay 11 actually increased in their oil concentration before decreasing to their final levels in 1982; 20 ppm in Bay 9 and 60 ppm in Bay 11. Oil contamination was not fully expunged from any of the species with detectable oil levels seen in all samples other than the filter-feeders in Bay 7 which were nearly "clean" at the time of the September sampling. Thus on gross concentration levels, oil in the animals was observed to be on the rapid decline to near zero in some species.

Of great interest is the chemical composition of the petrogenic residues in the animals, because they tie the water column, sediment and oil transport data together quite well. Both Mya and Serripes animals from all of the bays contain a low molecular weight n-alkane compositional "overprint" on top of the degraded oil composition seen in these animals in 1981. Note that these low level "overprints" are only easily seen due to the very low levels of residual oil (low ppm) in these animals. Where concentrations of oil in the animals was greater than 10 ppm or so, these overprints are not detectable. In addition, the homologous series of naphthalenes, apparently eliminated by depuration of oil in the 1981 samples, has been reintroduced at low levels to many of the benthic animals.

Where are these low molecular weight fractions coming from that are observed in the Ragged Channel system? It is possible that oil leaching off of the Bay 11 beach could introduce these low molecular weight aromatics and alkanes into the system. As little as 300 liters of oil introduced into Bay 11 waters could produce water soluble material (estimated to be 5% of the oil

content of Bay 11 oil) mixed in the water column to yield concentrations of 30 ng/l in all of Ragged Channel. Indeed 10-50 ng/l were observed in the Bay 7 water sample. Alternatively, and also requiring further study, is the possibility that contamination of groundwater on the Bay 9 beach during and after the dispersed oil release could have occurred. The composition of the Bay 9 beach petroleum residues strongly suggests a water soluble material in the wet sediment which has the capacity to leach into the system and impact the animals at very low levels. The source of the Bay 9 beach residues is not known. It too could have come from Bay 11, but the highly unweathered nature of the Bay 9 residues makes this connection quite tenuous. The great efficiency of the animals in concentrating water-borne petroleum had been previously established in the 1981 Bay 7 results (Boehm et al. 1982a).

In conclusion, a number of facts were revealed in the 1982 studies and a number of hypotheses are suggested by the data.

Conclusions

1. Biodegraded, physico-chemically weathered oil was eroded from Bay 11 beach and impacted the 3m and 7m sediments and floc.

2. This oil apparently has not impacted deeper (10m, 15m) stations.

4. There is no evidence for the occurrence of biodegradation of oil in offshore sediments.

5. There is evidence for only minimal vertical mixing of oil into the sediment column.

6. There is evidence for the occurrence of low levels of low molecular weight aromatics and saturates in the water column of Ragged Channel.

7. Filter-feeding bivalves have depurated most of their petroleum body burdens, but are left with a low-molecular- weight saturate and aromatic hydrocarbon overprint.

8. Deposit feeding animals are much lower in oil concentration than in 1981, but still have 20-60 ppm of petrogenic residues.

Hypothesis

1. Oil in Bay 9 or Bay 11 beach/groundwater was/is a source of low level petroleum contamination to the water column and hence to the animals.

2. Oil leaching off of Bay 11 beach is affecting the chemistry of the entire Ragged Channel area.

3. Oil will continue to increase in concentration in Bay 11 sediments with the possibility of offshore (deeper) transport and vertical penetration into the sediment increasing with time.

4. The opportunity for biodegradation to occur in Bay 11 sediments will increase as oil concentrations increase.

SECTION FIVE

RESULTS: SHORELINE STUDY

Three sets of shoreline countermeasure experimental plots were sampled during the 1982 field season for subsequent analyses by GC^2 and a subset for GC^2/MS. These included the 1980 control test plots: eight samples from H1 (crude), H2 (emulsion), L1 (crude), L2 (emulsion), T1 (crude), T2 (emulsion) TE1 (crude), TE2 (emulsion), each sampled once (August 10, 1982); the eight 1981 test plots: plots D(E)C, D(E)E, ME, CE, CC, MC, D(B)E, D(B)C each at two times (August 8 and 29, 1982); the four Norwegian test plots: E,F,G,H, each sampled once (August 27, 1982); the fourteen 1982 test plots: ID(E)C, ID(E)E, ID(B)C, ID(B)E, ICC, ICE, IMC-e, IMC-C, IME-e, IME-c, BD(B)c, BD(B)G, BD(E)C, BD(E)F (August 12, 20 and September 15). Details of the experiments and sampling methods are found in Owens (1983).

The analytical tasks were to subject all samples to extraction, fractionation and analysis of saturated and aromatic hydrocarbons by gravimetry and by GC^2 to determine (1) oil concentrations, and (2) oil composition and weathering. A sample subset are then analyzed by GC^2/MS to determine the details of aromatic hydrocarbon weathering.

5.1 Hydrocarbon Concentrations

A summary of the data on the gross compositional features (i.e., GC^2 peaks or resolved components) and total (i.e., by microgravimetry) hydrocarbons are presented in Tables 5.1 - 5.3. The results from the shoreline sampling of beached oil from Bays 9 and 11 in Ragged Channel have been previously presented in the context of the nearshore study (see Section 3.2.6).

Concentrations of hydrocarbons in the 1980 test plots range from 1.7 µg/g at H2, remaining low at H1 (2.4 µg/g) and L2 (4.3 µg/g). Increased

Table 5.1. Shoreline Study: GC[2] data on 1980 countermeasure test plots

Plot	Date	Field ID	Saturated Hydrocarbons (µg/g) Resolved	Saturated Hydrocarbons (µg/g) Total[a]	Aromatic Hydrocarbons (µg/g) Resolved	Aromatic Hydrocarbons (µg/g) Total[b]	Total PHC (a+b)	Total Extractable Material (µg/g)
H1	Aug 10	53041	0.1	0.8	~0.1	1.6	2.4	4.7
H2	Aug 10	53042	0.2	0.7	~0.1	1.0	1.7	5.5
L1	Aug 10	53043	180	1060	14	750	1810	2710
L2	Aug 10	53044	0.5	2.2	~0.1	2.1	4.3	12.7
T1	Aug 10	53045	2640	11,700	270	7050	18,800	26,400
T2	Aug 10	53046	1210	6670	100	4190	10,900	15,800
TE1	Aug 10	53047	6670	10,400	1040	9900	20,300	30,900
TE2	Aug 10	53048	3030	8020	320	6450	14,500	22,300

Table 5.2. Shoreline Study: GC[2] data on 1981 countermeasure test plots

Plot	Date	Field ID	Saturated Hydrocarbons (µg/g) Resolved	Saturated Hydrocarbons (µg/g) Total[a]	Aromatic Hydrocarbons (µg/g) Resolved	Aromatic Hydrocarbons (µg/g) Total[b]	Total PHC (a+b)	Total Extractable Material (µg/g)
ME	Aug 8	53123	18.	32.	.33	9.0	41.	60
	Aug 29	53173	6.7	26.	.20	16.	42.	82
CE	Aug 8	53124	7.0	33.	.32	20.	53.	84
	Aug 29	53174	17.	51.	.36	28.	79.	111
MC	Aug 8	53126	12.	52.	.59	42.	94.	140
	Aug 29	53176	2.4	19.	.15	13.	32.	53
CC	Aug 8	53125	13	51	.50	32.	83.	140
	Aug 29	53175	4.2	14	.11	8.6	23.	41
D(E)C	Aug 8	53121	7.4	32	.55	21.	53.	88
	Aug 29	53171	2.2	14	.12	10	24.	41
D(E)E	Aug 8	53122	20.	53.	.99	46	99	140
	Aug 29	53172	0.7	5.0	.07	3.1	8.1	15
D(B)C	Aug 8	53128	.17	1.3	.04	2.6	3.9	9.9
	Aug 29	53178	.05	0.5	.02	1.0	1.5	3.5
D(B)E	Aug 8	53127	.64	2.1	.03	2.8	4.9	10
	Aug 29	53177	.11	0.6	.02	1.6	2.2	4.4
			(mg/g)		(mg/g)		(mg/g)	(mg/g)
E	Aug 27	53181	2.5	11.	.26	7.9	19.	25.
F	Aug 27	53182	2.5	9.8	.25	7.4	14.	25.
G	Aug 27	53183	3.6	15.	.46	10.3	25.	35.
H	Aug 27	53184	2.0	9.0	.19	8.0	17.	25.

Table 5.3. Shoreline Study: GC[2] data on 1982 test plots

Plot	Date	Field ID	Saturated Hydrocarbons (mg/g) Resolved	Saturated Hydrocarbons (mg/g) Total[a]	Aromatic Hydrocarbons (mg/g) Resolved	Aromatic Hydrocarbons (mg/g) Total[b]	Total PHC (a+b)	Total Extractable Material (mg/g)
ID(B)C	Aug 12	53433	--	380	--	315	700	770
	Aug 14 (top)	53635	9.5	14	.18	2.2	16	19
	Aug 14 (plot)	53643	1.6	3.0	.08	.53	3.5	3.6
	Aug 20	53733	2.6	12	.30	3.6	16	19
	Sep 15	53833	2.3	6.5	.09	1.5	8.0	10
ID(B)E	Aug 12	53434	--	180	--	120	300	360
	Aug 14 (top)	53636	2.9	16	.47	2.6	19	20
	Aug 14 (plot)	53644	4.6	8.5	.24	2.0	11	14
	Aug 20	53734	6.5	10	.24	1.8	12	14
	Sep 15	53834	1.2	3.6	.06	.71	4.3	5.2
ID(E)C	Aug 12	53431	--	310	--	310	620	800
	Aug 14 (top)	53637	1.5	6.6	.23	4.9	12	14
	Aug 14 (plot)	53645	.04	.12	.01	.09	.21	.27
	Aug 20	53735	1.4	5.1	.13	3.4	8.5	12
	Sep 15	53835	1.2	4.4	.12	3.3	7.7	11
ID(E)E	Aug 12	53432	--	130	--	110	240	330
	Aug 14 (top)	53638	.20	.98	.03	.72	1.7	2.7
	Aug 14 (plot)	53646	.14	.53	.02	.38	.90	1.5
	Aug 20	53736	1.6	6.9	.18	4.2	11	15
	Sep 15	53836	.65	2.5	.05	2.0	4.5	6.8
ICC	Aug 12	53435	--	350	--	310	660	770
	Aug 20	53731	.22	.87	.02	.53	1.4	2.0
	Sep 15	53831	.03	.13	.002	.08	.21	0.3
ICE	Aug 12	53436	--	120	--	110	230	290
	Aug 20	53732	.02	.09	.002	.06	.15	.22
	Sep 15	53832	.22	.84	.025	.61	1.4	2.3
IMC	Aug 13	53437	--	380	--	280	660	740
IMC-e	Aug 15	53639	5.4	22	.96	16	38	46
(BMC)	Aug 22	53737	5.1	17	.68	12	29	46
IMC-c	Aug 15	53640	2.5	7.5	.37	5.7	13	19
(BMC)	Aug 22	53738	2.2	8.3	.27	5.5	14	19
IME-e	Aug 15	53642	2.0	7.2	.30	4.8	12	17
(BCE)	Aug 22	53740	3.1	11	.40	8.0	19	31
IME-c	Aug 15	53641	1.8	6.1	.33	4.1	10	14
(BME)	Aug 22	53739	1.4	5.9	.16	3.6	9	14
BD(B)C		53837	.40	1.2	.03	.38	1.6	3.8
BD(B)E		53838	.96	3.3	.11	1.1	4.4	8.9
BD(E)C		53839	.13	.42	.01	.15	.57	1.4
BD(E)E		53840	2.0	6.0	.23	1.8	7.8	16

oil levels are seen at T1, T2, TE1, TE2 where concentrations are 10-20 mg/g. These are similar trends and similar absolute levels as observed one year earlier (see Boehm et al. 1982a). Concentrations in the crude oil plots, H1, L1, T1, TE1 are consistently higher than the corresponding emulsified oil plots.

Highest concentrations in the 1981 test plots were observed at D(E)E (99 µg/g) on August 8. Concentrations decreased twenty days later to 8.1 µg/g. Other modest decreases in concentrations were seen at plots MC and CC. Lower residual concentrations were observed at plots D(B)C and D(B)E where single ppm values were found. Concentrations in all plots were lower than when last sampled in 1981.

The 1981 Norwegian plots contained much higher concentrations of oil with values from 15-25 parts per thousand (mg/g).

Concentrations of oil in the various 1982 test plots are presented in Table 5.3.

5.2 Saturated Hydrocarbon Composition

Through the saturated hydrocarbon weathering ratio (SHWR) which reflects physico-chemical weathering and the ALK/ISO ratio which reflects biodegradation, the compositional status of the residual oil in the samples can be determined. These parameters define the chemical nature of the oil vis-a-vis weathering properties and the related phsycial and toxicological properties of the oil. These results are presented in Table 5.4. The ALK/ISO and SHWR for the "Aged" Lagomedio oil are presented at the end of the table for reference.

Weathering is observed to occur to varying extents. The SHWR for the 1980 plots is about what was observed in 1981 indicating little further weathering. Significant beach biodegradation has occurred at the H1, H2, L1 and L2 plots, but not at the other plots.

Table 5.4. Shoreline Study: GC^2 and GC^2/MS weathering parameters

	Plot	Date	SHWR	ALK/ISO	AWR
1980 Plots	H1	Aug 10	1.8	1.4	--
	H2	Aug 10	1.7	1.4	--
	L1	Aug 10	1.3	1.7	None detected
	L2	Aug 10	1.1	1.1	--
	T1	Aug 10	1.6	2.4	--
	T2	Aug 10	1.3	2.4	--
	TE1	Aug 10	3.4	2.6	--
	TE2	Aug 10	2.0	2.5	--
1981 Plots	ME	Aug 18	12.1	4.7	None detected
		Aug 29	1.0	1.1	--
	CE	Aug 18	1.1	1.6	--
		Aug 29	1.0	1.5	--
	MC	Aug 18	1.9	1.9	--
		Aug 29	1.1	1.7	--
	CC	Aug 18	1.3	2.2	--
		Aug 29	1.1	1.6	--
	D(E)C	Aug 18	2.4	3.2	None detected
		Aug 29	1.1	1.2	--
	D(E)E	Aug 18	2.6	3.0	1.5
		Aug 29	1.4	2.2	--
	D(B)C	Aug 18	1.5	1.2	--
		Aug 29	1.8	0.7	--
	D(B)E	Aug 18	2.7	2.2	--
		Aug 29	1.8	2.2	--
	E	Aug 27	1.8	1.9	--
	F	Aug 27	1.8	2.6	--
	G	Aug 27	1.8	2.5	--
	H	Aug 27	1.7	2.4	--
1982 Plots	ID(B)C	Aug 12	2.7	2.6	--
		Aug 14(T)	34	5.6	--
		Aug 14(P)	17	5.2	--
		Aug 20	9.3	4.6	--
		Sep 15	16.	4.6	--
	ID(B)E	Aug 12	3.6	2.6	--
		Aug 14(T)	26	4.6	--
		Aug 14(P)	14	5.2	--
		Aug 20	21	5.2	--
		Sep 15	16	4.6	--

Table 5.4. (Continued)

	Plot	Date	SHWR	ALK/ISO	AWR
1982 Plots (contd.)	ID(E)C	Aug 12	3.6	2.6	--
		Aug 14(T)	2.6	2.6	--
		Aug 14(P)	1.8	2.6	--
		Aug 20	2.1	2.6	--
		Sep 15	1.7	2.6	--
	ID(E)E	Aug 12	3.4	2.6	--
		Aug 14(T)	2.0	2.8	--
		Aug 14(P)	2.2	2.6	--
		Aug 20	1.9	2.7	--
		Sep 15	1.4	2.6	--
	ICC	Aug 12	3.2	2.7	2.4
		Aug 20	1.9	2.6	1.7
		Sep 15	1.6	2.8	1.5
	ICE	Aug 12	2.9	2.6	2.3
		Aug 20	1.6	2.6	1.4
		Sep 15	1.8	2.7	1.8
	IMC	Aug 13	3.6	2.7	2.3
	IMC-e	Aug 15	2.0	2.6	--
		Aug 22	2.2	2.7	--
	IMC-c	Aug 15	2.6	2.5	2.8
		Aug 22	2.0	2.7	2.0
	IME-e	Aug 15	2.3	2.6	--
		Aug 22	1.8	2.9	--
	IME-c	Aug 15	2.3	2.6	2.4
		Aug 22	2.0	2.6	2.1
	BD(B)C	--	1.7	2.6	--
	BD(B)E	--	2.0	2.6	2.0
	BD(E)C	--	1.6	2.4	1.8
	BD(E)E	--	2.0	2.6	--

SHWR = saturated hydrocarbon weathering ratio; varies from ~2.8 to 1.0 as oil weathers; higher values due to kerosene-type inputs from dispersant formulations.

AWR = aromatic weathering ratio; by GC^2/MS; varies from ~3.5 to 1.0 as oil weathers.

ALK/ISO = biodegradation ratio; varies from 2.5 to 1.0 as alkanes are preferentially degraded; may be higher if kerosene inputs are noted.

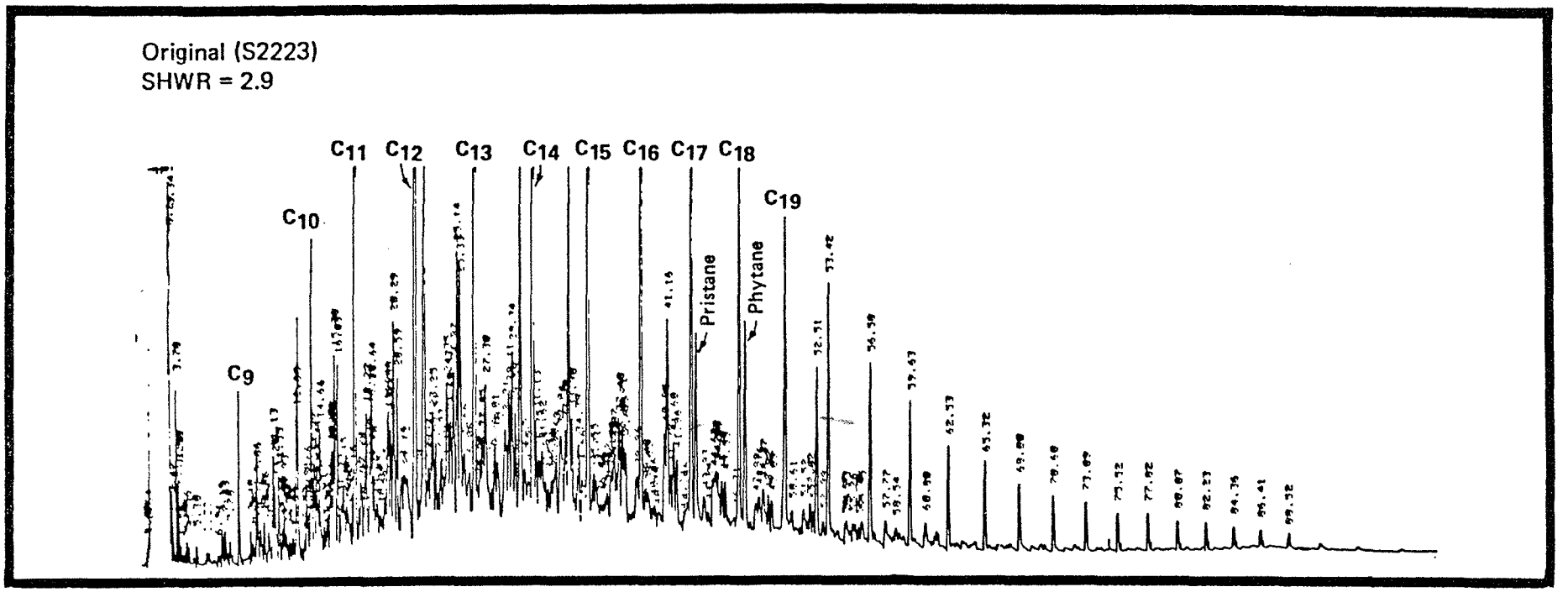
In the 1981 test plots, various degrees of weathering are observed with substantial physico-chemical (i.e., SHWR) and some biodegradation weathering having occurred at ME, CE, MC, CC. Plot D(E)C weathered substantially between August 8 and 29, while D(B)C appears moderately weathered and biodegraded (ALK/ISO = 0.7) by the end of August 1982. One sample (ME, August 18) appears contaminated thus giving spurious ratios.

Results for the 1982 test plots are also presented. The additions of kerosene-type material (B-dispersant) in some of the dispersant formulations is easily noted by the high SHWR and ALK/ISO ratios. Compare the compositions of petroleum material before and after dispersant application in Figures 5.1A versus B and 5.2A versus B. No detectable biodegradation is observed in any of these samples. However, the physico-chemical weathering of the oils are noted in the SHWR time sequence for plots (ID(E)C (3.6 to 1.7), ID(E)E (3.4 to 1.9), ICC (3.2 to 1.6) and others.

5.3 Aromatic Composition (GC^2/MS)

Twenty samples were analyzed by GC^2/MS to obtain the aromatic weathering ratio. This ratio is more subject to loss by dissolution of hydrocarbons than is the SHWR which is primarily an evaporation indicator. Note that the AWR was not quantifiable in the 1980 or 1981 test plots due to low aromatic concentrations. Only in the D(E)E is AWR computed which shows that although substantial amounts of aromatic weathering has occurred, "weatherable" aromatics remain (i.e., AWR ¨1.0).

The AWR results from the 1982 plots are also presented in Table 5.4. Weathering sequences were determined for plots ICC, ICE, IMC-e, IMC-c, IME-c as well as for other selected samples. Note that the AWR which was 3.5 in the original "aged" Lagomedio oil was seen to be somewhat lower in the various "barrel" oils examined (e.g., ICC = 2.4; ICE 2.3, IMC = 2.3). Therefore, from the chemical evidence it appears that some weathering of



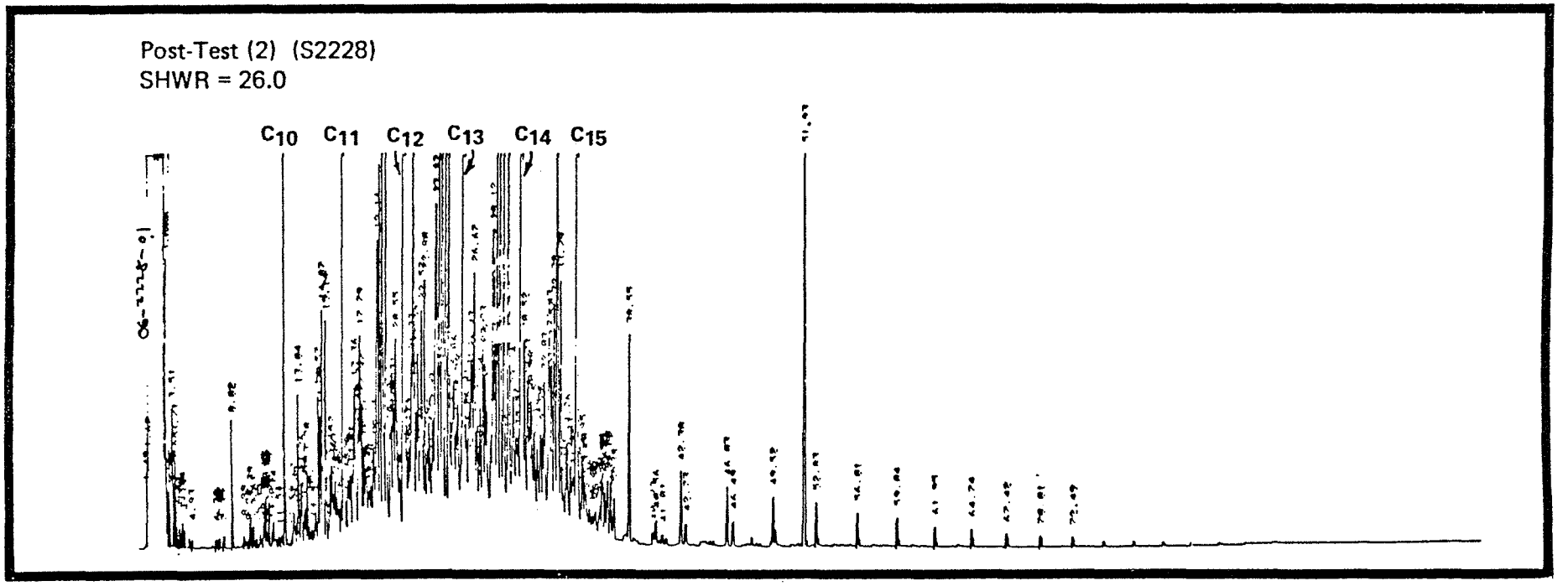


Figure 5.1. Saturated hydrocarbon GC^2 traces of Plot ID(B)E.

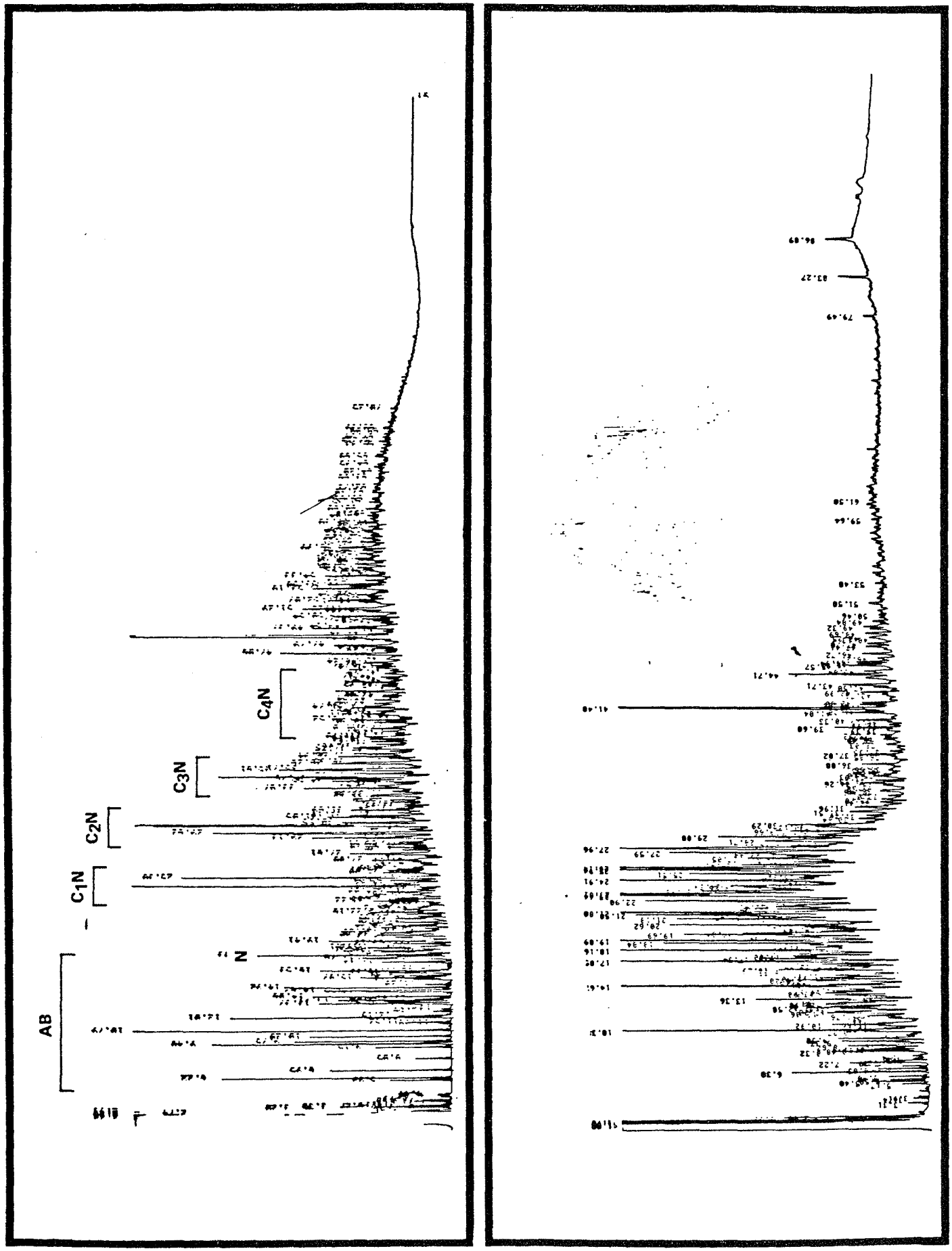


Figure 5.2. Aromatic hydrocarbon GC^2 traces of Plot ID(B)E.

light aromatics had taken place prior to oil application. Subsequent to application, further weathering of the aromatics occurred as the AWR decreased to values of 1.5 in plot ICC and 1.8 in plot ICE. If the range of weathering is assumed to be AWR 3.5 to 1.0 then the oil as applied was already 40% weathered (i.e., loss of alkyl benzenes, naphthalenes, fluorenes) and weathered further to about 80% as defined by this ratio.

SECTION SIX

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