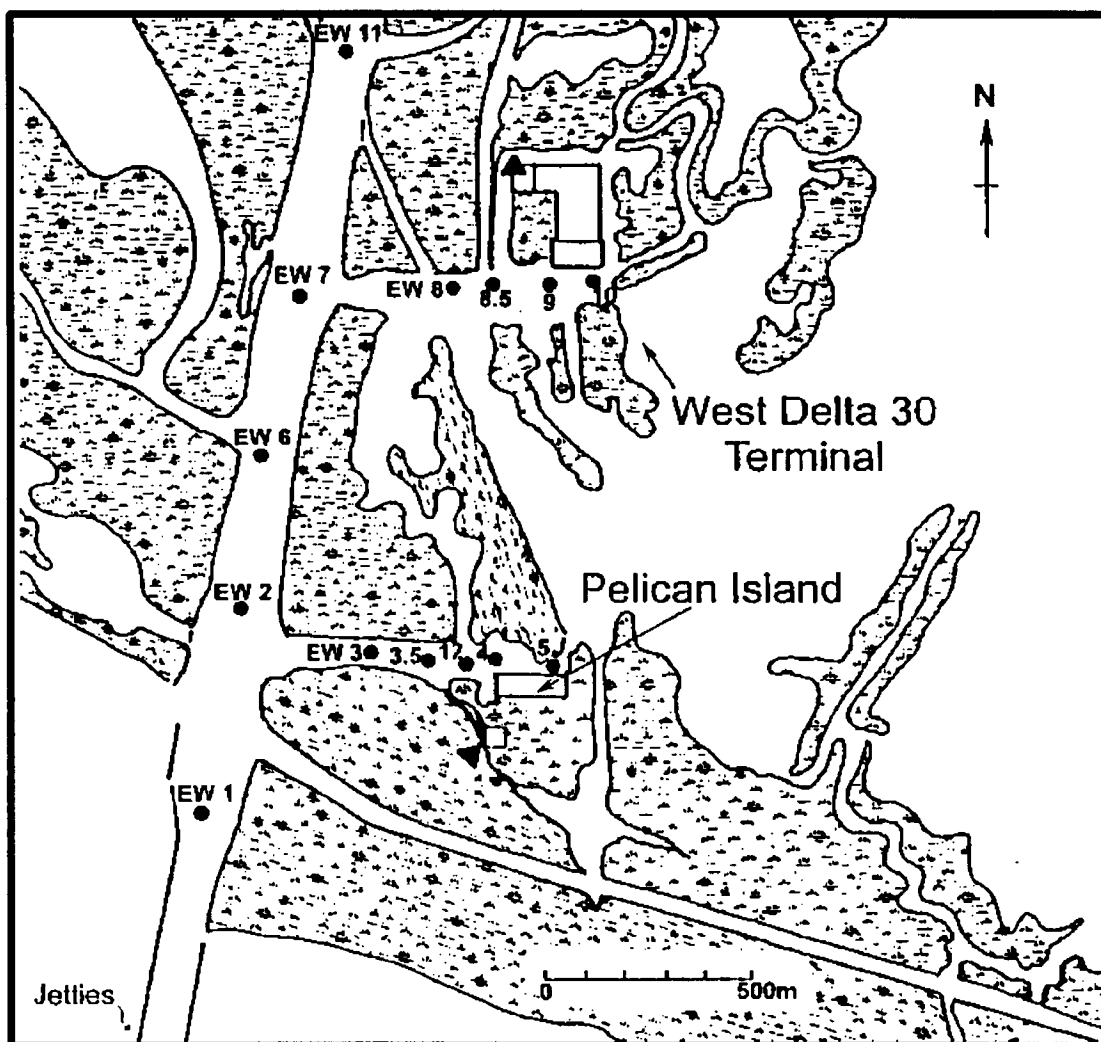


Coastal Marine Institute

# Long-term Effects of Contaminants from OCS Produced-water Discharges at Pelican Island Facility, Louisiana



U.S. Department of the Interior  
Minerals Management Service  
Gulf of Mexico OCS Region



Cooperative Agreement  
Coastal Marine Institute  
Louisiana State University

**Coastal Marine Institute**

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## ABSTRACT

The receiving environment for an OCS produced water discharge abandoned for two years at Pelican Island was examined in 1989 and again in 1996 (nine-years post-discharge) for the presence of produced water contaminants in sediments and possible effects on benthos. The effluent stream averaged 12,000 to 15,000 bbl·d<sup>-1</sup> when discontinued in July 1987, and the area was characterized in a previous study as having a medium potential for the dilution of produced water discharge contaminants. Two years following the cessation of the effluent, surficial sediments were moderately contaminated with produced water derived hydrocarbons, and these hydrocarbons were more concentrated with depth at two stations closest to the original discharge point. At the station closest to the abandoned discharge, the benthic infauna was significantly reduced in species and abundance at the two-year mark compared to adjacent stations in the same access canal.

Side-by-side comparisons of hydrocarbon analytical data from 1989 and 1996 were not possible, because improved analytical techniques allowed for a wider range of target analytes and reduced the detection limits. Following nine years of no discharge, the TTAH concentrations and composition for the station closest to the discontinued discharge indicated a reduced concentration of mostly weather petroleum source hydrocarbons. Additional hydrocarbon compounds present in a vertical core from this same station were most similar to creosote and indicated an additional contaminant not present in cores collected from that station seven years before. Cores collected in 1989 and again in 1996 from another station in the access canal next to the abandoned facility were compositionally dissimilar. There were high levels of a petroleum source hydrocarbon deeper in the sediments that were not observed in 1989, and the source was characteristically similar to produced water discharges. The sediments collected at nine years post-discharge, therefore, revealed some weathering of the produced water petroleum source contaminants, a persistence of other produced water sources contaminants or new sources, and some additional sources of contaminants not previously documented. The infauna from the station that was characterized as affected by produced water contaminants in 1989 did not differ from adjacent stations in the access canal in 1996, with the exception of a single station that was characterized by a different sediment type.

The surficial sediment contamination and effects seen at two-years post-discharge were not apparent at nine-years post-discharge. There were still contaminants present, including weathered petroleum source hydrocarbons and creosote, accumulated in higher concentrations vertically in the sediments (up to 10 cm). Results from this abandoned produced water discharge facility are transferable to similar sites (similar volumes and physiography and hydrography of receiving environment), but not to sites with high contaminant levels to greater depths in the sediments and to greater distances from the point of discharge.

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The field work for this project was conducted at the site of the former Exxon Pipeline Company Pelican Island facility near Empire Waterway. Mr. Brian Magruder and Mr. Dale Cooper of Exxon Pipeline Company provided information concerning the condition of the facility in 1996.

We thank the captain and crew of the R/V *Acadiana* for assistance in sampling in November 1996. Dr. Nancy N. Rabalais and Ms. Paulene O. Roberts conducted the field sampling. Benthic sample analysis was conducted by Ms. Lorene E. Smith. Ms. Paulene O. Roberts was the primary laboratory chemist for the hydrocarbon analyses. Mr. Charles B. Henry, Jr. was the primary data synthesis chemist. Dr. Edward B. Overton was the project manager. Mr. Ron LeBlanc assisted with hydrocarbon sample analysis. Trace metal analyses were conducted by Dr. Robert P. Gambrell of LSU Wetland Biogeochemistry Institute.

## EXECUTIVE SUMMARY

There were over 1,200 produced water discharges in the coastal habitats of Louisiana and Texas by the late 1980s (Boesch and Rabalais 1989a, Rabalais et al. 1991). Fifteen of these discharges contained produced waters generated from the Outer Continental Shelf (OCS). In order to meet requirements of Federal and State regulations to end produced water discharges by January 1999, many of the produced water treatment facilities have been dismantled, or the waste product is being reinjected or transported offshore for disposal. Some effluents are continuing under an emergency order of the Louisiana Department of Environmental Quality.

Several studies have documented the fate and effects of produced water discharges on sediment contamination, benthic communities and bioaccumulation potential (Boesch and Rabalais 1989a,b, St. Pe' 1990, American Petroleum Institute 1991, Rabalais et al. 1991). The effects depend on the volume of the discharge, the chemical characterization of the discharge, and the physiography and hydrography of the receiving environment. Produced water derived contaminant signals and/or effects on benthic organisms may be minimal near the discharge, but they may also be substantial and extend great distances from the discharge. Produced water derived contaminants may accumulate in the sediments adjacent to and downstream from a discharge point resulting in high concentrations of hydrocarbons to depths of 25 to 30 cm in vertical sediment cores (Rabalais et al. 1991). Hydrocarbon contamination resulting from these discharges may also persist through time both in surficial sediments and vertically into subsurface sediments (Rabalais et al. 1991).

The receiving environment for a produced water discharge abandoned for two years at Pelican Island was examined in 1989 (Rabalais et al. 1991) and again in 1996 (this study) for the presence of produced water contaminants in sediments and possible effects on benthos. The effluent stream averaged 12,000 to 15,000 bbl d<sup>-1</sup> when discontinued in July 1987, and the area was characterized in the previous study as having a medium potential for the dilution of produced water discharge contaminants. Our objective was to determine the temporal differences in the fate of the produce water contaminant accumulation, persistence and effects on the macroinfauna.

Sampling was conducted in November of both years along an expected gradient of contamination away from the point of the discontinued effluent. Sediments from the surface and vertical cores were analyzed by gas chromatography/mass spectrometry (GS/MS) for hydrocarbon contamination and by inductively coupled argon plasma emission spectroscopy (ICP) for metals. The macroinfauna retrieved on a 0.5-mm sieve was used to characterize the benthic community.

Sediment contaminants of a produced water origin were present in moderate concentrations in the surface sediments two years post-discharge, and higher concentrations were present with depth in vertical cores. There were no obvious impacts to the benthic infauna after two years of no discharge, with the exception of the station closest to the discharge (EW4),

where the numbers of species and individuals were significantly reduced. These reductions were associated with higher levels of alkylated polynuclear aromatic hydrocarbons (PAH) and total hydrocarbons in the surface and subsurface sediments. These results indicated that a legacy of impacts may remain within the coastal environment after the cessation of oil and gas production activities.

Improvements in hydrocarbon analytical methods between 1989 and 1996 reduced detection limits and expanded the ability to characterize the source compounds. Some of the higher concentrations of selected AH were due, in part, to a wider range of target analytes. Overlapping concentrations of TTAH occurred at two stations (EW3 and EW4) sampled at both two years and nine years post-discharge. The signature of relatively fresh low-sulfur petroleum at depth in the EW3 core from 1996 was compositionally dissimilar to the 1989 data. The source of petroleum detected at EW3 was characteristically similar to produced water discharges characterized in the 1989 study. In addition, a slight increase in Zn in the EW3 vertical profile for 1996 was observed to correlate with AH concentration. This finding suggested a possible connection to past produced water contamination.

The overall petroleum-source pollution was reduced at the station closest to the abandoned discharge (EW4) and represented a weathering of the contaminants. A high level of creosote with depth in the core for EW4 in 1996, however, represented an additional AH content that was not present in 1989. Heavily degraded petroleum characterized sections of vertical cores from station EW4 in 1989. This same signature was present in 1996 but with lower concentrations. These similarities/changes are consistent with weathering of the contaminant and no new inputs. The higher AH concentrations in the vertical cores for station EW3, however, indicated a buried fresh oil signature that was not as degraded as the petroleum contamination at EW4.

Metals concentrations were not of any environmental significance. The higher concentration of Zn in the vertical core for EW3 corroborated a petroleum source for the hydrocarbons.

The benthic communities were significantly different among stations within the canal adjacent to the Pelican Island facility after nine years of no effluent. The differences, however, were not related to any contaminant signal in the sediments. The station with the most different fauna was station EW5 which was also subjected to stronger currents, and which had sediments that were sandier, better sorted, and more consolidated. The abundance and species richness of the most affected station sampled at two-years post-discharge were significantly greater in the nine-year post-discharge samples. The position of the benthic community along a recovery response trajectory could not be determined from the two sample dates, but the infaunal species composition had shifted from those organisms considered opportunistic or indicative of stressed environments to a more diverse fauna with more individuals.

The surficial sediment contamination and effects seen at two-years post discharge were not apparent at nine-years post-discharge. There were still contaminants, including weathered petroleum source hydrocarbons and creosote, accumulated in higher concentrations vertically in

the sediments (up to 10 cm). Results from this abandoned produced water discharge facility are transferable to similar sites (similar volumes and physiography and hydrography of receiving environment), but not to sites with high contaminant levels to greater depths in the sediments and to greater distances from the point of discharge.

## INTRODUCTION

During the production of crude oil, condensates or natural gas, water that is trapped within permeable sedimentary rock may also be brought to the surface. This water is called formation water, produced water or oil field brine. The water is generally removed from the oil, condensate or gas as completely as possible in order to transport the product. The separated waste may be reinjected down a well, either for disposal or to enhance recovery of hydrocarbons, or, as has been the case of a vast majority of production from the northern Gulf of Mexico region, they may be discharged into the surface waters of the ocean or coastal areas.

By the late 1980s, there were over 1,200 produced water discharge sites in the coastal habitats of Louisiana and Texas (Boesch and Rabalais 1989a, Rabalais et al. 1991). Of these, 15 sites (all within Louisiana) discharged produced waters generated from the Outer Continental Shelf into State waters (Rabalais et al. 1991). Current Louisiana Department of Environmental Quality regulations and General Permits of the U.S. Environmental Protection Agency call for the cessation of discharge of all produced water effluents into surface waters of coastal habitats. Presently, the Louisiana Department of Environmental Quality is acting under an emergency order to allow the continued discharge of oil and gas produced water in open water coastal systems until January 1999. In preparation for cessation of produced water discharges and/or poor economics of production water treatment facilities, operations have been discontinued at several produced water facilities, including some carrying OCS produced waters.

During a previous MMS-funded study of the effects of OCS produced water discharges in coastal environments, Rabalais et al. (1991, 1992) documented (1) the presence of high concentrations of produced water derived hydrocarbons to depths of 25 to 30 cm in vertical sediment cores in some study areas, (2) indications of long-term accumulation of contaminants and their resistance to degradation, (3) presence of produced water origin hydrocarbons with depth in vertical sediment cores adjacent to an abandoned produced water facility, and (4) persistent effects of accumulated or residual produced water contaminants on the benthic infauna adjacent to an abandoned produced water facility. These results indicate that a legacy of impacts may remain within the coastal environment after the cessation of OCS oil and gas production activities.

Two facilities near Empire Waterway handled OCS produced water (Figure 1). Chevron's West Delta 30 Terminal (11,000 bbl·d<sup>-1</sup>) was in operation in 1989 (Rabalais et al. 1991) and was scheduled to be shut down by August 1992. Exxon Co., USA's Pelican Island Terminal ceased discharging produced water (12,000 to 15,000 bbl·d<sup>-1</sup>) in July 1987. Collection of samples during the previous study in 1989 was approximately two years since the cessation of a produced water effluent at Pelican Island. The present study was designed to examine the sediments and fauna adjacent to the abandoned discharge at an interval of nine years since the cessation of the discharge. During the present study, we noticed that the West Delta 30 Terminal had been abandoned and the facility cleared from the marsh since our field trip there in 1989. Even though there were minimal contaminants observed at this site in the 1989 study, we

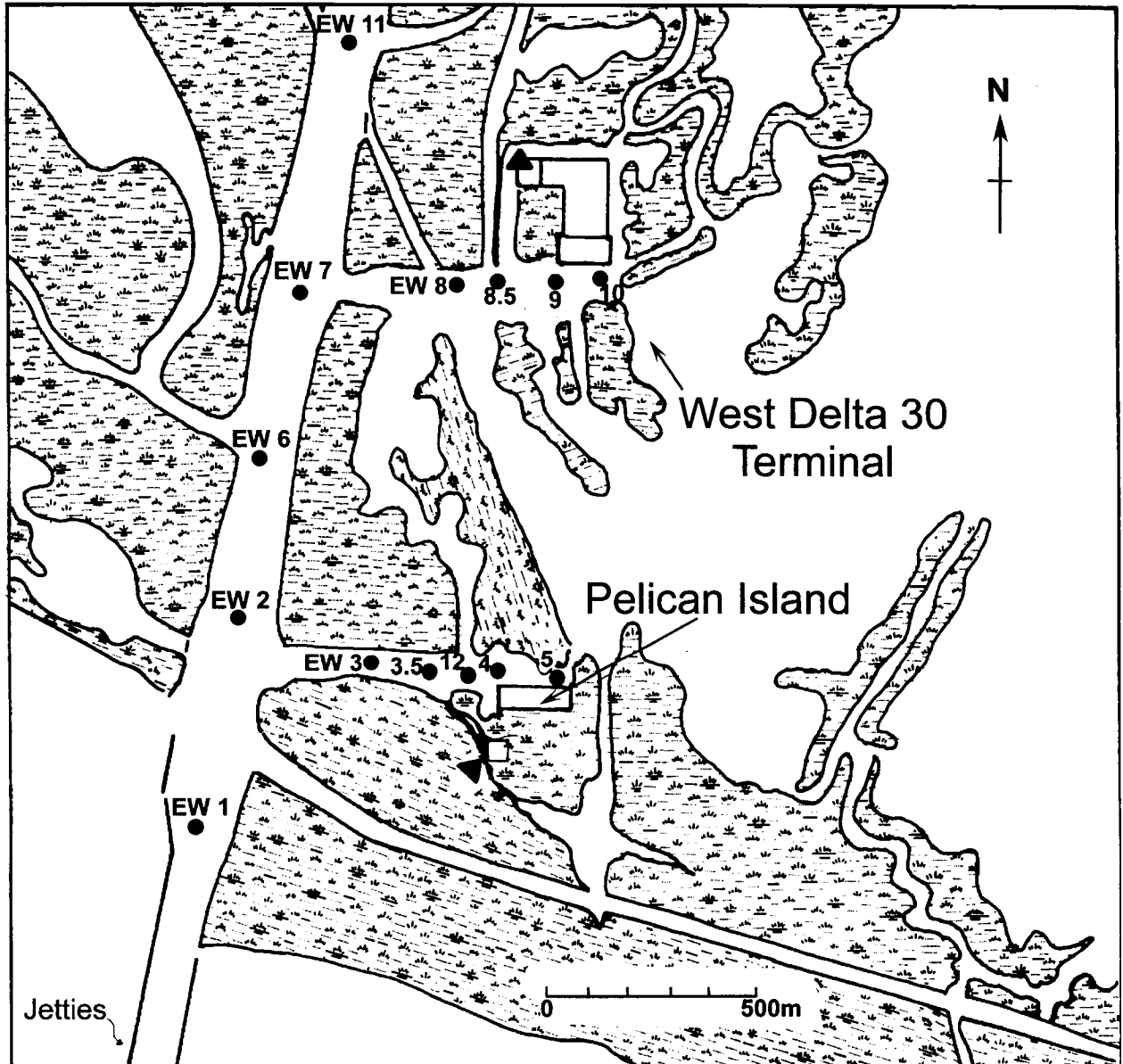


Figure 1. Empire Waterway study area (modified from Rabalais et al. 1991). Black triangles denote the locations of the discontinued produced water discharge points.



collected a few sediment cores in 1996 for chemical analyses. The time since abandonment was estimated to be four years.

Surficial sediments, vertical sediments, and benthic infauna were sampled in a gradient away from the discharge at the Pelican Island facility (Figure 1) two years after cessation of the effluent in 1989. Alkylated polynuclear aromatic hydrocarbons (PAH) were detected at low concentrations at several stations along the transect near the abandoned discharge. The maximum value was located close to the discharge point and decreased away from there (Figure 2). The FFPI (fossil fuel pollution index) indicated a petrogenic source contaminating the sediments with elevated PAH. Metal concentrations for surface sediments were generally low with higher values being found near the facility.

The 1989 analysis of vertical sediment cores from the transect adjacent to the abandoned discharge revealed the highest concentrations of alkylated PAH and total hydrocarbons for the study area; these were in the subsurface (2-5 cm) and deeper (20-25 cm) sections of the core at EW4 (Figure 3). Other peaks in hydrocarbons were also found in subsurface and deeper vertical cores at EW3 and EW2, but not to the same degree as found at EW4. Data from the vertical cores point to the accumulation and subsequent persistence of produced water-associated hydrocarbons for at least two years after the effluent was stopped. There were no obvious impacts to the benthic infauna in 1989 with the exception of station EW4 near the old discharge, where the numbers of species and individuals were reduced. These reductions were associated with higher levels of alkylated PAH and total HC in the surface, and subsurface sediments.

In light of the persistence of produced water-derived hydrocarbons and their effects on benthic fauna, we examined the same study area in 1996 for a nine-year post-discharge assessment. Our objective was to:

- determine the temporal differences in the fate of OCS produced water contaminant accumulation, persistence, and effects at a single location within Louisiana state waters where produced waters were no longer discharged, specifically at two- and nine-years post-discharge.

Our null hypotheses were:

H<sub>0</sub>: Produced water origin contaminants are not present in surface or in vertically accreted sediments after nine years.

H<sub>0</sub>: There are no differences in the benthic infauna with distance from the historical point of produced water origin contaminant signal.

We predicted lower concentrations of hydrocarbons in the surficial sediments, with possibly no benthic impacts. We predicted, however, that there would still be contaminants at depth. We based these predictions on our previous results from a discontinued discharge and other than current discharges (Rabalais et al. 1991).

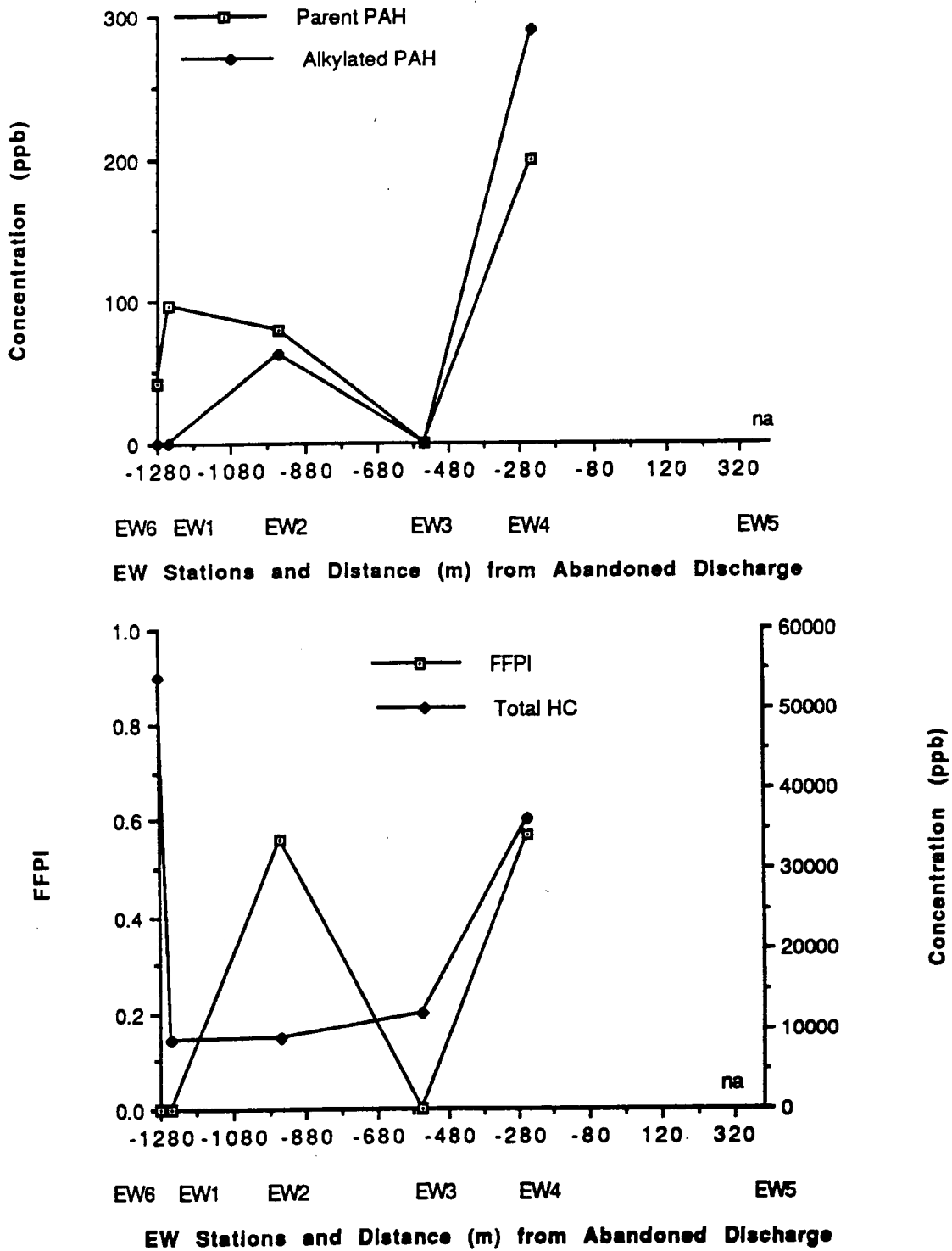


Figure 2. Spatial distribution of PAH and total HC concentrations and FFPI in surface sediments from stations near the abandoned discharge in Empire Waterway, November 1989 (from Rabalais et al., 1991).

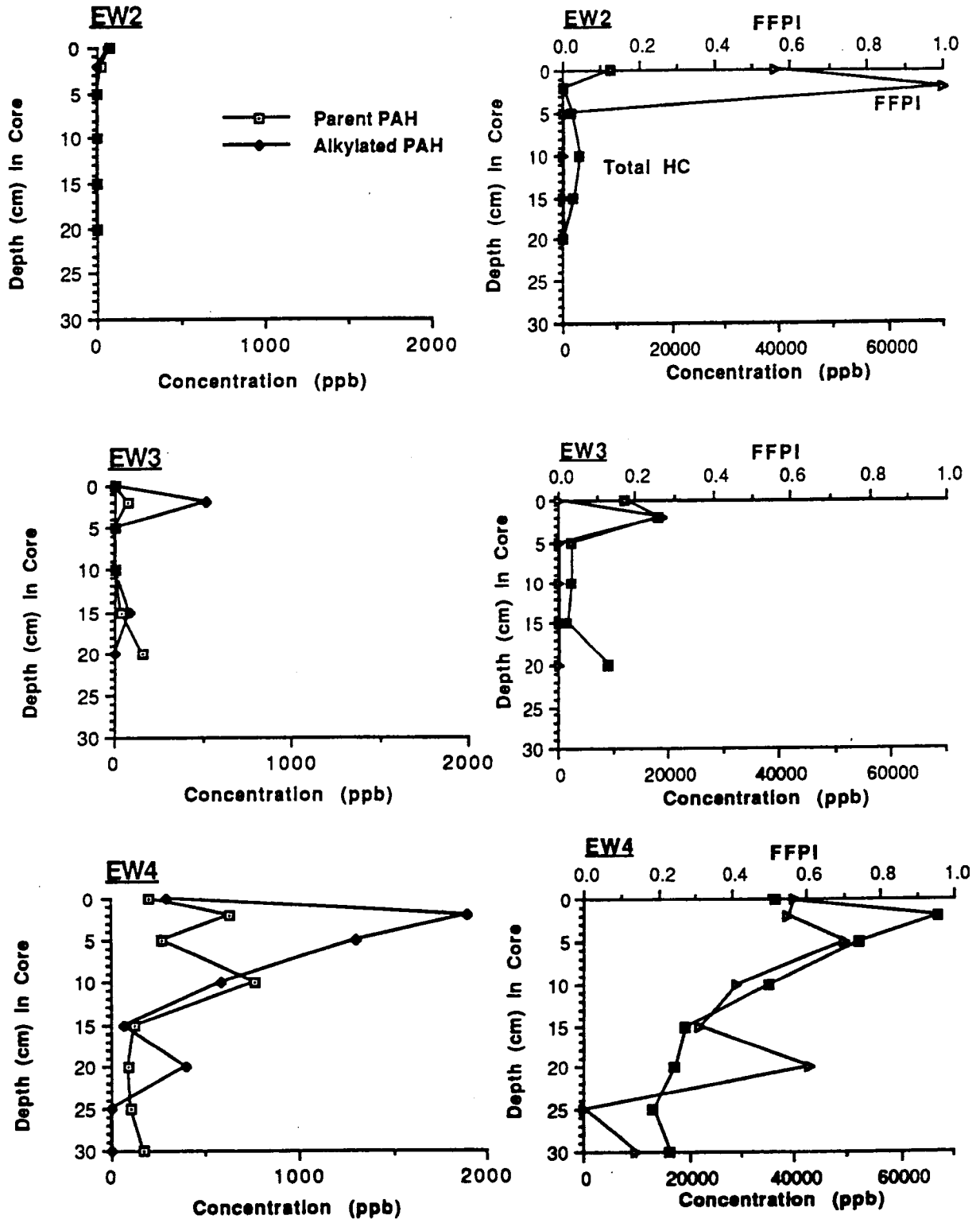


Figure 3. Total parent and alkylated PAH concentrations, FFPI and total HC concentrations in vertical sediment core sections from stations near the abandoned discharge in Empire Waterway, November 1989. (Value for each core section is plotted at the top of that section; for example, the value for 15-20 cm is plotted at 15 cm.) (from Rabalais et al. 1991).

## METHODS

### Study Area

The site of the discontinued produced water discharge is the Exxon Co. USA's Pelican Island Terminal near the Empire Waterway. The site is located at the terminus of a dredged canal that joins the Empire Waterway near the jetties (Figure 1). When discharging, the volume reported for the Pelican Island facility was 12,000 to 15,000 bbl d<sup>-1</sup>. The facility began operations in 1956 and continued to July 1987. The site was initially sampled by Rabalais et al. (1991) in November 1989 for produced water contaminants and effects on benthic infauna, at a time approximately two years after the end of the discharge. From aerial photographs taken in November 1988, Rabalais et al. (1991) determined that the discharge was from a pipe near a slough in the marsh with likely movement of the discharge into the access canal. The presence of produced water origin contaminants in the access canal (Rabalais et al. 1991) confirmed this prediction.

### Sampling Design

We sampled in November 1996 to replicate as closely as possible the seasonal aspect of the benthic infauna. This sample date provided a nine-year post-discharge assessment of the presence of produced water contaminants and their potential effects on the benthic infauna.

During the 1989 collections, we sampled stations EW4 and EW3, but were not able to access EW5 because of a barricade (Figure 1). We intended to reoccupy stations EW4 (contaminant signal) and EW3 (limited contaminant signal) as well as two other stations to provide a more detailed gradient away from the original source of the produced water effluent. Because of difficulty in positioning the research vessel and obtaining intact box cores, the sample design was modified.

### Field Sampling

The R/V *Acadiana* was used as the sampling platform, because of the need to deploy a box corer. An Ekman-type closure 0.1-m<sup>2</sup> box corer was used to collect sediment samples. The box corer has an average penetration of 50 cm in soft sediments and a minimum of 30 cm in sandy sediments. The general characteristics of the water column at three stations were determined with a Hydrolab Surveyor 3 CTD unit.

Surface grain size samples (upper 3 cm) and TOC samples were taken using a 50-cc syringe corer. Sediment interstitial salinity measurements were not above average in the previous study (Rabalais et al., 1991) and were not repeated. Vertical sediment cores ( $n = 9$  from six stations) were taken with 7.5-cm acrylic tubes placed within the larger box corer. All sediment samples were stored on ice until return to the laboratory where they were stored frozen until analysis.

Sediment samples for benthic macroinfauna analysis were subsampled from replicate box cores ( $n = 5$ ) with a smaller ( $0.025 \text{ m}^2$ ) Ekman grab to a depth of 10 cm. The entire contents were sieved in the field through a 0.5-mm screen. The organisms retained on the sieve and the debris were preserved in 10% buffered formalin in ambient water stained with Rose Bengal. Within 48-hr of return to the laboratory, the samples were transferred to 70% ethanol.

The field survey was conducted on 13 November 1996. While at the study site, we noticed that the West Delta 30 Terminal had been abandoned and the facility cleared from the marsh since our field trip there in 1989. Even though there were no contaminants observed at this site in the 1989 study, we collected a few sediment cores for chemical analyses anyway. These were taken from the canal adjacent to the marsh creek most likely to carry contaminants away from the old facility (station E8.5). No benthos were collected.

Sampling efforts at the Pelican Island facility were designed to replicate as closely as possible our collections in November 1989 (Figure 1). We collected sediment cores and benthos from four of the five stations attempted. Adequate samples could not be taken at one of the stations between EW4 and EW5 (hydrographic station DW13) because of the extensive shell pad in the channel adjacent to former shore facilities. The station to the east of the historic discharge point (EW5) that was inaccessible in 1989 was sampled in 1996. Currents at this location, however, were strong and it was difficult to maneuver the research vessel in the same spot for each box core. We reoccupied the station with the most contaminants in the 1989 study (station EW4) and two others in a presumed down plume gradient (stations EW12 and EW3.5).

### **Sedimentary Characteristics**

Grain size distributions were determined using a Coulter Multisizer with 256 channelizer capability. Three aperture tube sizes were used in the analysis: 280  $\mu\text{m}$ , 140  $\mu\text{m}$  and 50  $\mu\text{m}$ . Samples were sieved through 60- $\mu\text{m}$  Nitex before analysis with the 140- $\mu\text{m}$  aperture tube and were sieved through 20- $\mu\text{m}$  Nitex before analysis with the 50- $\mu\text{m}$  aperture tube. Coulter Accucomp software was used to overlay distributions from each tube, and sand, silt and clay fractions were identified using the final combined distribution. TOC samples were ground, and difference in weight after ignition in a muffle furnace at 360 °C for 16 h was used to estimate carbon.

### **Hydrocarbon Analytical Methods**

#### *Analytical Approach*

The analytical approach was designed to provide quantitative and qualitative information relative to trace level aromatic hydrocarbon (AH) contamination in marine sediments. The analytical approach is based on a solvent extraction and concentration technique followed by instrumental analysis using Gas Chromatography/Mass Spectrometry (GC/MS). The GC/MS analysis provides highly selective source-fingerprinting information as well as compound specific quantitative results for specific AH that are strongly correlated with observed toxicity in crude oil, creosote, and incomplete combustion derived pollutants. GC/MS is an extremely

powerful technique and the method of choice for most oil pollution studies (Overton et al. 1981, Boehm and Farrington 1984, Michel et al. 1991, Sauer and Boehm 1991, Henry and Overton 1993, Henry et al. 1993, Sauer et al. 1993, Roques et al. 1994). Since the previous study at the Empire Waterway site, advances in analytical instrumentation and detailed oil analysis methods have significantly reduced method detection limits and expanded the scope of the target analytes.

Fingerprinting is a term used to describe the analytical process of characterizing petroleum in a manner such that results from a known crude oil or petroleum product can be compared to an unknown sample to determine if the unknown sample is characteristically the same and, therefore, possibly from the same source. The GC/MS target compounds utilized are useful in monitoring oil weathering and biodegradation as well as source-fingerprinting. Petrogenic (oil or petroleum derived) and pyrogenic (combustion-derived AH) are monitored as well as alkanes, sulfur heterocycles, sterane, triterpanes, and hopanes. The AH target compounds include constituents within crude oil and petroleum refined products that are very resistive to natural biodegradation and are often linked with chronic toxicity; many of these compounds are known mammalian carcinogens (e.g., benzo(a)pyrene).

### *Sample Receipt and Storage*

Nine sediment cores were received at the Louisiana State University, Institute for Environmental Studies (IES) on 14 November 1996. Each core was logged into the laboratory and assigned a unique identification code. Each core was then frozen upright in a standard upright freezer. The cores remained frozen until March 1997; at which time, each was transferred to a refrigerator to await sample preparation, extraction, and analysis.

### *Sample Preparation*

Each core (still partially frozen) was carefully extruded onto a clean stainless steel pan. The sides of the sediment core which had been in direct contact with the polycarbonate core tube were cut-away and discarded. The total length of the core was recorded. From the top, the core was sliced into 5 cm sections, and the top section subdivided into 0-2 cm and 2-5 cm sections. Each section was transferred into certified clean, 4-oz jars with a Teflon lined cap. Each sample was homogenized by mechanical stirring and returned to the refrigerator to await extraction.

### *Sample Extraction*

Samples were extracted by a solvent extraction method designed to partition nonpolar and slightly polar organic pollutants from the sediment matrix into an organic solvent. Trace level pollutants were then concentrated in the solvent by an enrichment process. For each core section or slice, 20 g was accurately weighed into a precleaned 150 ml beaker. A series of surrogate standards (acenaphthylene-d10, phenanthrene-d10, and terphenyl-d14) was added. Anhydrous sodium sulfate was added and mixed into the sediment until a "dry" sand-like matrix was created. Immediately, 50 ml of high purity dichloromethane (DCM) was added followed by approximately one minute of stirring. The beaker was covered with two layers of aluminum foil (dull side down) and placed in a warm (roughly 25 °C) sonication bath for 25 min. The warm

solvent and the vigorous sonication aid in enhancing extraction efficiency. The extract was then poured through a funnel packed with precleaned glass wool and anhydrous sodium sulfate into a 250 ml round bottom rotary evaporation flask. Again, 50 ml of DCM was added and the extraction repeated a second and a third time. During the last two extraction series, the sonication time was reduced to 15 min. Subsequent extracts were combined in the round bottom flask and reduced to a final volume of 1.0 ml by a combination of rotary evaporation and “blow-down” under a gentle stream of purified nitrogen. Activated copper granules were used to remove inorganic sulfur.

#### *Detailed Chemical Analysis (GC/MS)*

All samples were analyzed by GC/MS to quantify specific target AH pollutants associated with produced water pollutants as well as other sources of AH contamination. The following provides a descriptive outline of the instrumental analyses.

GC Operation. The GC/MS analysis used was a Hewlett Packard 5890 GC configured with a DB-5 high resolution capillary column (0.25 mm ID, 30 meter, 0.25 micron film, J&W Scientific) directly interfaced to a Hewlett Packard 5971 MS detector system. The GC flow rates, etc. were optimized to provide the required degree of separation (i.e., phytane and *n*-C18 should be baseline resolved and pristane and *n*-C17 should be near baseline resolved). The GC was operated in the temperature program mode with an initial column temperature of 55 °C for 3 min then increased to 290 °C at a rate of 5 °C/min and held at the upper temperature for 15 min. The injection temperature was set to 250 °C and only high-temp, low thermal bleed septa were used. The interface to the MS was maintained at 290 °C. All gasses used were of the highest purity available.

MS Operation. The MS was operated in the Multiple Ion Detection mode (MID or SIM, Selected Ion Mode) to maximize the detection of several trace target constituents in crude oil. The instrument was operated such that the selected ions for each acquisition window were scanned at a rate greater than 1.4 scans/sec. The targeted constituents and the quantitative ions monitored for each is provided in Table 1. At the start of any analysis period, the MS was tuned to PFTBA, and a NSC Reference and daily quantification standard analyzed prior to the analysis of unknowns. An internal standard mix composed of naphthalene-d8, anthracene-d10, chrysene-d12, and perylene-d12 was coinjected with each analysis to monitor the instruments performance during each run. All injections were made using a manual technique.

Data Processing. All collected spectral data was processed by HP Chemstation™ software using a specially written macro developed by IES. Each macro printout contains the extracted ion chromatography data in addition to raw integration data which is exported to an Excel™ spreadsheet for quantitative analysis. Each macro printout was carefully reviewed and reintegrated as required

Quantitative Analysis. The concentration of specific target AH was determined by an internal standard method compared to a 5-point calibration curve using authentic standards where available. A single point standard and reference oil were analyzed daily to insure and verify

Table 1. Target compounds by GC/MS.

Compound	Quant. Ion	Abbrev.
alkanes (nC-10 through nC-36)	85	
naphthalene	128	NAPH
C-1 naphthalenes	142	C-1 NAPH
C-2 naphthalenes	156	C-2 NAPH
C-3 naphthalenes	170	C-3 NAPH
C-4 naphthalenes	184	C-4 NAPH
fluorene	166	FLU
C-1 fluorenes	180	C-1 FLU
C-2 fluorenes	194	C-2 FLU
C-3 fluorenes	208	C-3 FLU
dibenzothiophene	184	DBT
C-1 dibenzothiophenes	198	C-1 DBT
C-2 dibenzothiophenes	212	C-2 DBT
C-3 dibenzothiophenes	226	C-3 DBT
phenanthrene	178	PHEN
C-1 phenanthrenes	192	C-1 PHEN
C-2 phenanthrenes	206	C-2 PHEN
C-3 phenanthrenes	220	C-3 PHEN
C-4 phenanthrenes	234	C-4 PHEN
naphthobenzothiophene	234	NBT
C-1 naphthobenzothiophenes	248	C-1 NBT
C-2 naphthobenzothiophenes	262	C-2 NBT
C-3 naphthobenzothiophenes	276	C-3 NBT
fluoranthrene	202	FLANT
pyrene	202	PYR
C-1 pyrenes	216	C-1 PYR
C-2 pyrenes	230	C-2 PYR
C-3 pyrenes	244	C-3 PYR
C-4 pyrenes	258	C-4 PYR
chrysene	228	CHRY
C-1 chrysenes	242	C-1 CHRY
C-2 chrysenes	256	C-2 CHRY
C-3 chrysenes	270	C-3 CHRY
C-4 chrysenes	284	C-4 CHRY
hopanes (191 family)*	191	
sterenes (217 family)*	217	
benzo(b)fluoranthene/benzo(k)fluoranthene	252	B(b+k)F**
benzo(e)pyrene	252	B(e)P
benzo(a)pyrene	252	B(a)P
perylene	252	PERYL
indeno(g,h,i)pyrene	276	INDPYR
dibenzo(a,h)anthracene	278	BENZP
benzo(1,2,3-cd)perylene	276	DIBENZ

\* Used primarily for source-fingerprinting and generally not quantified.

\*\* Benzo(b)fluoranthene and benzo(k)fluoranthene are combined as a single value.



instrument performance. A key value used for data synthesis is the sum of the target aromatic hydrocarbons, total target aromatic hydrocarbons (TTAH).

Pyrogenic vs. Petrogenic Determination. The Fossil Fuel Pollution Index technique developed by Boehm and Farrington (1984) can aid the characterization of the relative contribution between combustion related AH and oil pollution. A modified FFPI technique (\*FFPI) was used in the current study to include the expanded list of target analytes and was quantified as follows:

$$\text{Modified FFPI} = (\text{naphthalene} + \text{C-1 naphthalenes} + \text{C-2 naphthalenes} + \text{C-3 naphthalenes} + \text{C-4 naphthalenes} + \text{fluorene} + \text{C-1 fluorenes} + \text{C-2 fluorenes} + \text{C-3 fluorenes} + \text{dibenzothiophene} + \text{C-1 dibenzothiophenes} + \text{C-2 dibenzothiophenes} + \text{C-3 dibenzothiophenes} + \text{C-2 phenanthrenes} + \text{C-3 phenanthrenes} + \text{naphthobenzothiophene} + \text{C-1 naphthobenzothiophenes} + \text{C-2 naphthobenzothiophenes} + \text{C-3 naphthobenzothiophenes} + \text{C-2 pyrenes} + \text{C-3 pyrenes} + \text{C-4 pyrenes} + \text{C-2 chrysenes} + \text{C-3 chrysenes} + \text{C-4 chrysenes} + (0.5 * (\text{phenanthrene} + \text{C-1 phenanthrenes} + \text{C-1 pyrenes} + \text{C-1 chrysenes}))) / \text{TTAH} - \text{perylene}$$

### **Metals Analytical Methods**

A 1-g subsample of sediment was acid digested/extracted and analyzed directly by a inductively coupled argon plasma emission spectroscopy (ICP) for the following target metals: Cu, Zn, Cd, Pb, Ni, As, Fe, Mn, Ca, Mg, Al, K, Cr, Na, P. Quantitative determinations were made using response factors calculated from authentic standards and a serial dilution calibration curve. Standard reference materials were analyzed to insure QA/QC. Metals analyses were conducted by the Wetland Biogeochemistry Institute, Louisiana State University.

### **Benthic Community Structure**

Macroinfaunal samples were transferred to the sorting laboratory at LUMCON where they were logged and inventoried. The organisms were sorted from the debris in gridded dishes under a dissecting microscope. The debris from the sample was rechecked by another technician or the laboratory supervisor for any missed organisms. If organisms were found, the sample was resorted. Organisms were counted and identified to the lowest possible taxon. Organisms normally considered part of the meiofauna (nematodes and harpacticoid copepods) were not included in the macroinfaunal analysis. A collection of voucher specimens was retained in a Reference Collection that already houses specimens from the previous study (Rabalais et al. 1991).

The number of species and individuals per replicate was determined for each station. Standard benthic community parameters (Rabalais et al. 1991, 1993, 1995) were determined for each station and included number of species, number of individuals, diversity (H') and evenness (J').

Diversity was calculated by the formula:

$$H' = - \sum_{i=1}^s ((n_i / N) \log_{10}(n_i / N))$$

where  $s$  = total number of species collected,  $n$  = number of individuals of each species, and  $N$  = total number of individuals.

Evenness was calculated by the formula:

$$J' = H' / \log_{10}s$$

Infaunal data were analyzed using the General Linear Model procedure for analysis of variance (SAS Institute Inc. 1990). Normal distribution of the species and abundance data was achieved with a  $\ln(x+1)$  transformation; diversity and evenness data were not transformed. Where significant differences existed, Duncan's multiple range test was performed to identify groups of significantly different stations. The level of significance was established at  $\alpha = 0.05$ .

## RESULTS

### Hydrography

The salinity and temperature data (Appendix 1) indicated that the water column was generally well-mixed at stations EW8.5 (2 m depth) and EW11 (2.9 m depth between EW4 and EW5 with a moderately strong current). Station EW3.5 in 3.9 m was stratified in both temperature and salinity. Bottom dissolved oxygen concentration was also depleted compared to the surface concentration (4.12 mg l<sup>-1</sup> compared to 7.21 mg l<sup>-1</sup>). A fairly strong ebb current was moving through the canal during sample collection.

### Sedimentary Characteristics

The sediments were primarily silts with minor clay and sand fractions. Large shell hash from oyster shell pads near the location of the previous shoreline facilities (docks, pilings) was abundant between stations EW4 and EW5 to the point that efforts to core there were abandoned. Sediments at station EW5 and EW4 were muddier, but still contained many large oyster shells. Shell hash was abundant in sediment samples from EW5. EW5 sediments also had the greatest sand fraction. Sediments at EW12 and EW3.5 were silty, without the shell hash. Sediments in one replicate for station EW3.5 were black, and smelled of hydrogen sulfide; in another, there was an abundance of marsh plant detritus.

### Sediment Hydrocarbons

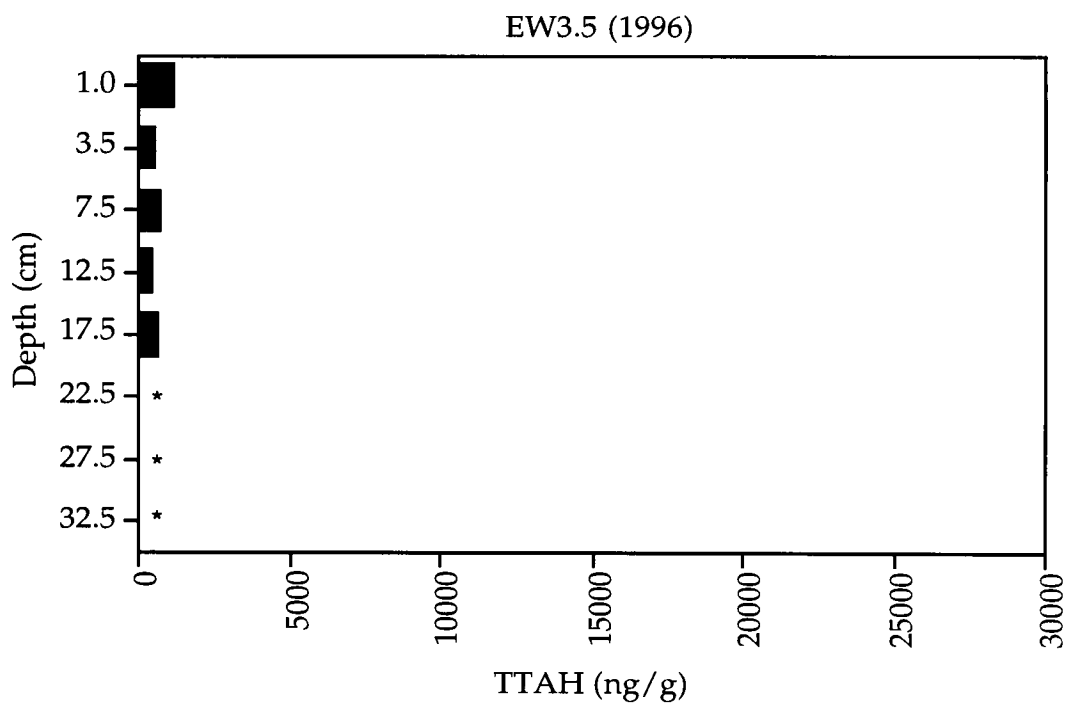
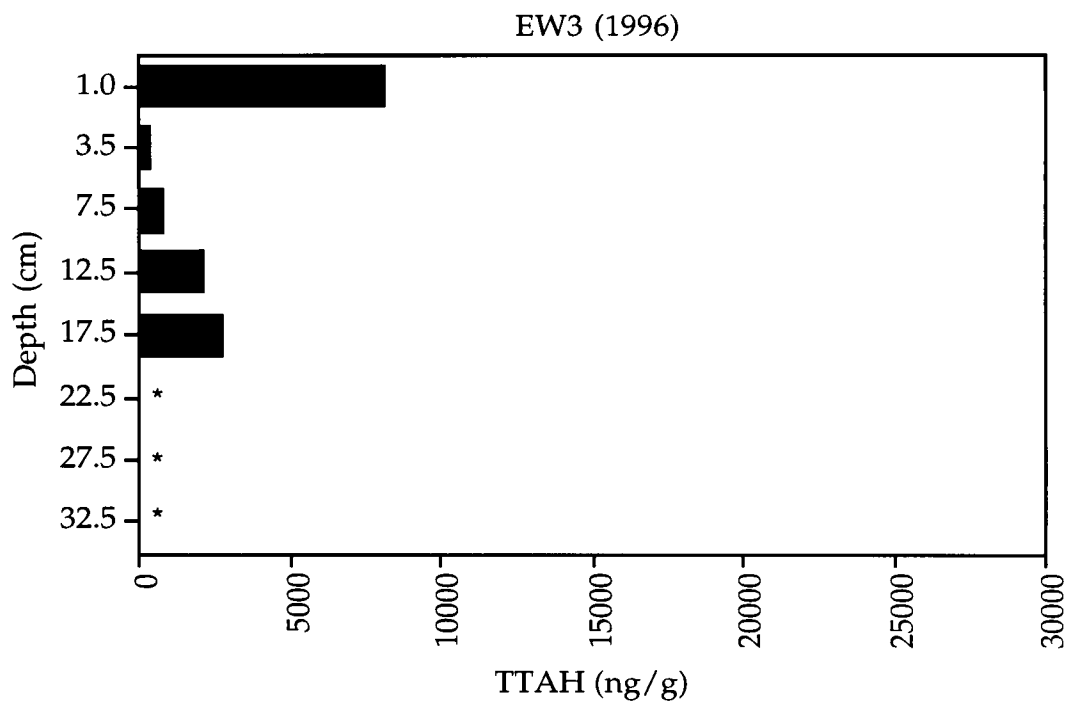
A summary of the GC/MS values are provided in Appendix 3.

#### *TTAH Concentration Relative to Depth*

Figures 4 through 6 provide a characterization of the total targeted aromatic hydrocarbons (TTAH) concentration with respect to sediment depth for the cores collected at Empire Waterway in November 1996. Stations EW3, EW3.5, EW4, EW11 and EW12 are in the canal adjacent to the Pelican Island facility. Station EW8.5 is in the canal adjacent to the abandoned West Delta 30 Terminal. A wide range of quantitative values were observed from a low value of 0.27 ng/mg to a high value of 230 ng/mg TTAH (dry weight basis). The distribution of TTAH relative to depth did not adhere to any readily apparent trend. TTAH concentrations were minimal in surface samples and to depth at station EW8.5, which is consistent with previous lack of a contaminant signal for the West Delta 30 Terminal facility in 1989.

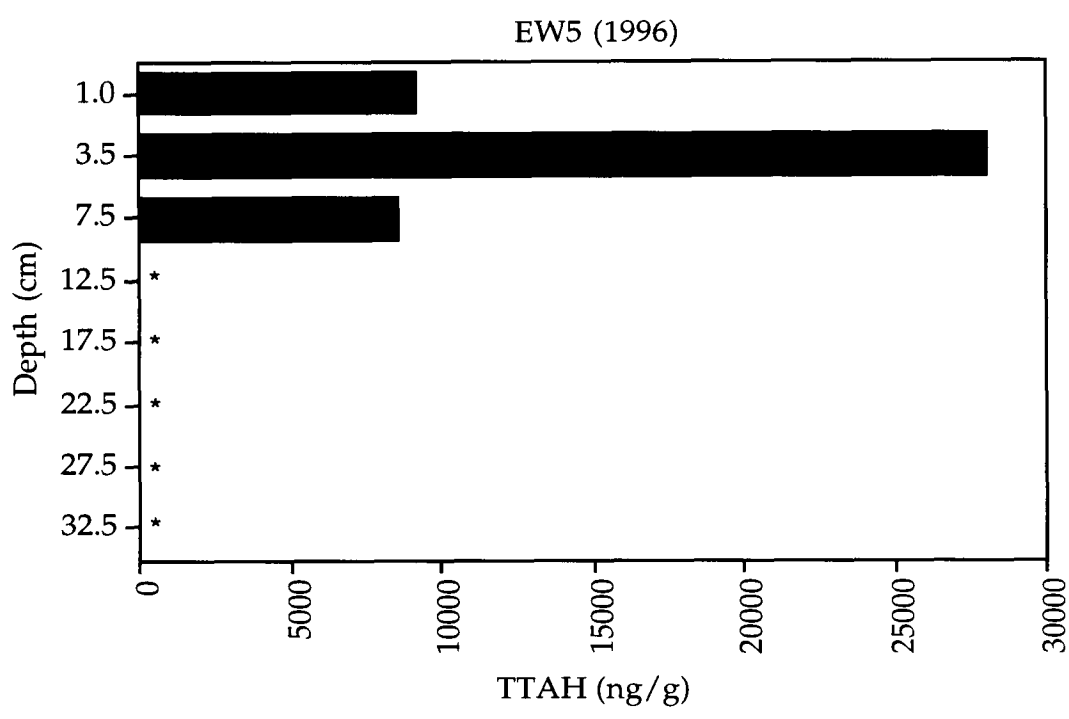
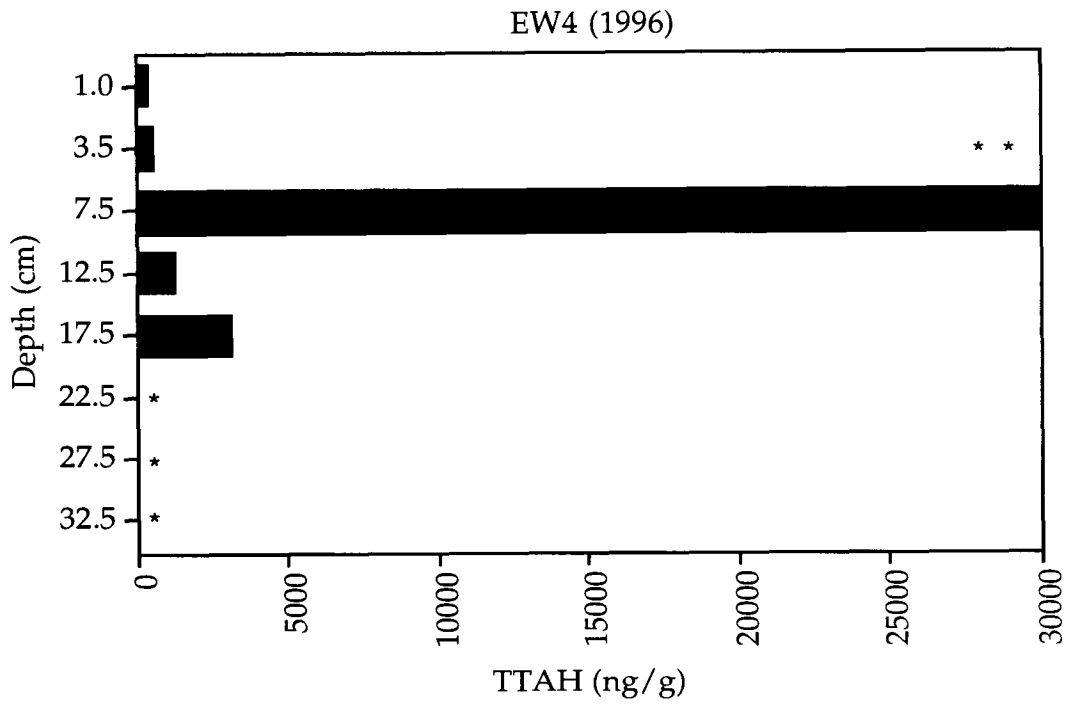
#### *TTAH Concentration Relative to Fossil Fuel Pollution Index (\*FFPI)*

The TTAH value lacks source specificity, but when combined with a qualitative value such as the FFPI, pollution sources can be differentiated. Figure 7 is a comparison of TTAH concentration vs. \*FFPI for three different AH pollution sources--unweathered crude oils ( $n = 4$ ), fresh and weathered creosote from a variety of locations ( $n = 10$ ), and a sample of wood smoke



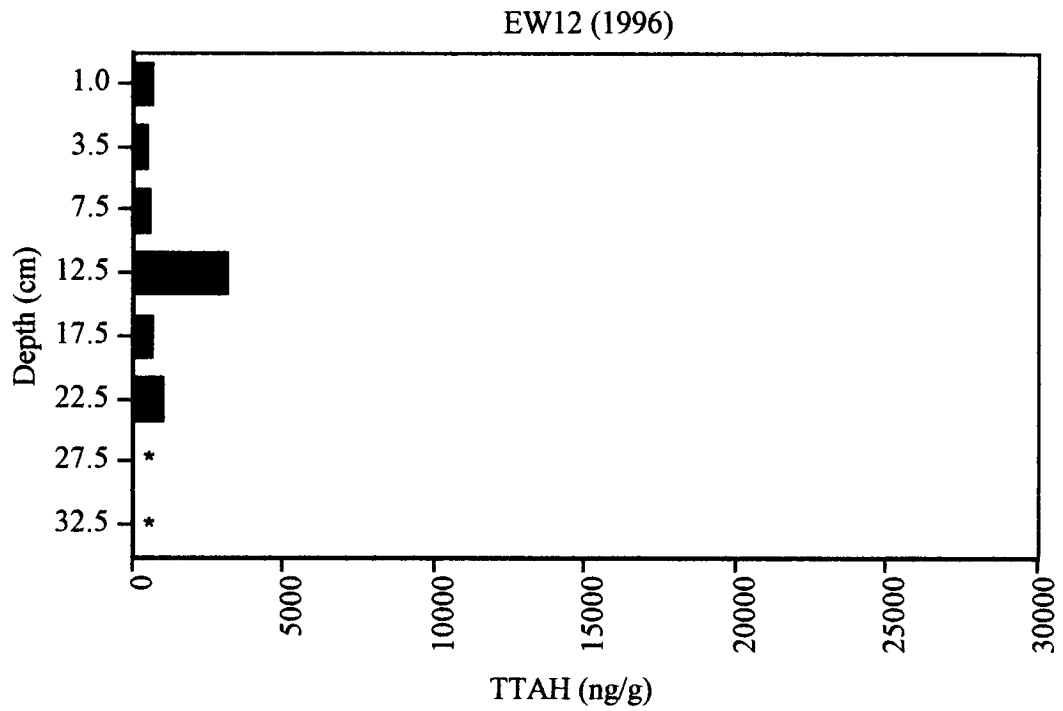
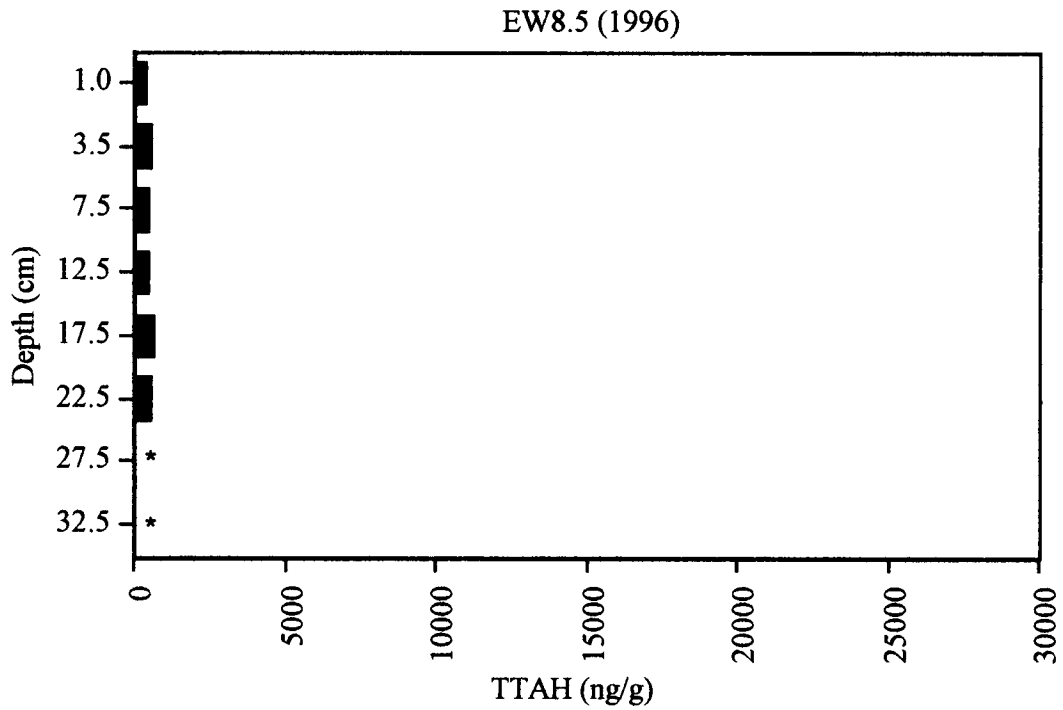
\* No sample was collected at this depth.

Figure 4. TTAH concentration relative to depth at Station EW3 (top) and Station EW3.5 (bottom). Both cores were collected in 1996.



\* No sample was collected at this depth.

Figure 5. TTAH concentration relative to depth at Station EW4 (top) and Station EW5 (bottom). Both cores were collected in 1996.



\* No sample was collected at this depth.

Figure 6. TTAH concentration relative to depth at Station EW8.5 (top) and Station EW12 (bottom). Both cores were collected in 1996.

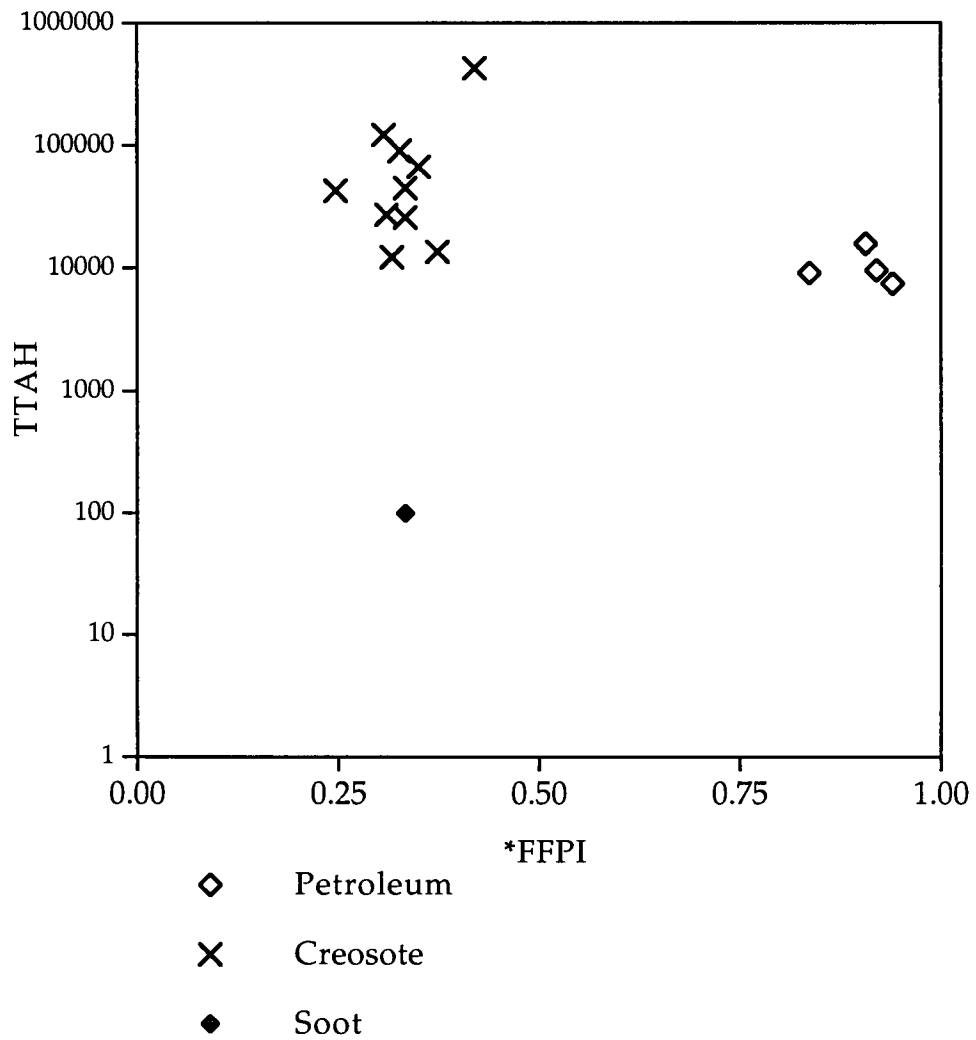


Figure 7. Comparison of TTAH concentration versus \*FFPI for three different hydrocarbon sources.

or soot. The petroleum oils are clearly differentiated from the creosote and soot relative to the \*FFPI value. Creosote and wood smoke both exhibit low \*FFPI values, but are differentiated in Figure 7 by concentration. AH, as characterized by TTAH, are minor constituents in soot generally representing less than 1% the total mass. The same suite of aromatic hydrocarbons represent less than 5% of most oils, but generally constitute more than 50% of most creosote oils.

Figure 8 is the same comparison of TTAH concentration vs. \*FFPI for the Empire Waterway sample population in 1996. Where high concentrations of TTAH were detected, the \*FFPI exhibited a low value suggesting that the AH was not petroleum derived. Core sections with \*FFPI values greater than 0.75 are dominated by residual oil contamination and are identified as set B (EW3 2-5 cm, EW3 5-10 cm, EW3.5 2-5 cm, EW3.5 10-15 cm, EW3.5 15-20 cm). Core sections with high TTAH concentrations and a \*FFPI less than 0.5 appear to be contaminated by creosote and are identified as set A (EW3 0-2 cm, EW4 5-10 cm, EW5 0-2 cm, EW5 2-5 cm, EW5 5-10 cm, EW12 10-15 cm). Within set A, samples EW3 0-2 cm and EW12 15-20 cm also contain a weathered petroleum signature. Samples which fall outside these two clearly defined regions are probably contaminated by a combination of pollution sources including weathered petroleum, weathered creosote, and incomplete combustion by-products. The latter represent a pollution source which is essentially ubiquitous in the marine environment.

#### *AH Profile Relative to Depth*

Figures 9 and 10 provide the AH profile (or signature) for selected reference materials. Each plot is a histogram with the specific AH identified on the x-axis and the quantitative value presented as a scaled bar. The relative distribution of the individual AH constituents is useful in characterizing the type and source of AH pollution detected in individual samples. Clearly, the AH profiles for crude oil and creosote are highly different, in spite of the high degree of variability that exists for both. Petroleum is dominated by 2- and 3-ring AH compounds which are highly alkylated. Pyrogenic-sourced pollution is characterized by 3-, 4-, and 5-ring AH, and the non-alkylated (parent) structures dominate. Creosote is similar to the latter and difficult to differentiate based on AH data alone. For oil pollution, changes in the AH profile are indicators of oil weathering or degradation.

Figures 11 through 23 provide a systematic presentation of the AH profile (or signature) for each core section analyzed. Source characterization based on the AH profile is primarily qualitative; although the differences in sources characterized above are the principle for the FFPI concept. FFPI or \*FFPI alone discount the full information content of the AH profile. Samples EW4 5-10 cm, EW5 0-2 cm, EW5 2-5 cm, and EW5 5-10 cm exhibit a strong creosote signature while samples EW3 2-5 cm and EW3 5-10 cm exhibit a strong petroleum signature. Perylene is present as the most abundant AH in many of the samples analyzed, but is not derived principally from anthropogenic pollution.

#### *Comparison of 1989 and 1996 Samples*

Two stations were sampled both in 1989 and 1996, EW3 and EW4. Lacking specific information as to the site history such as sediment depositional rates or dredging, it was very



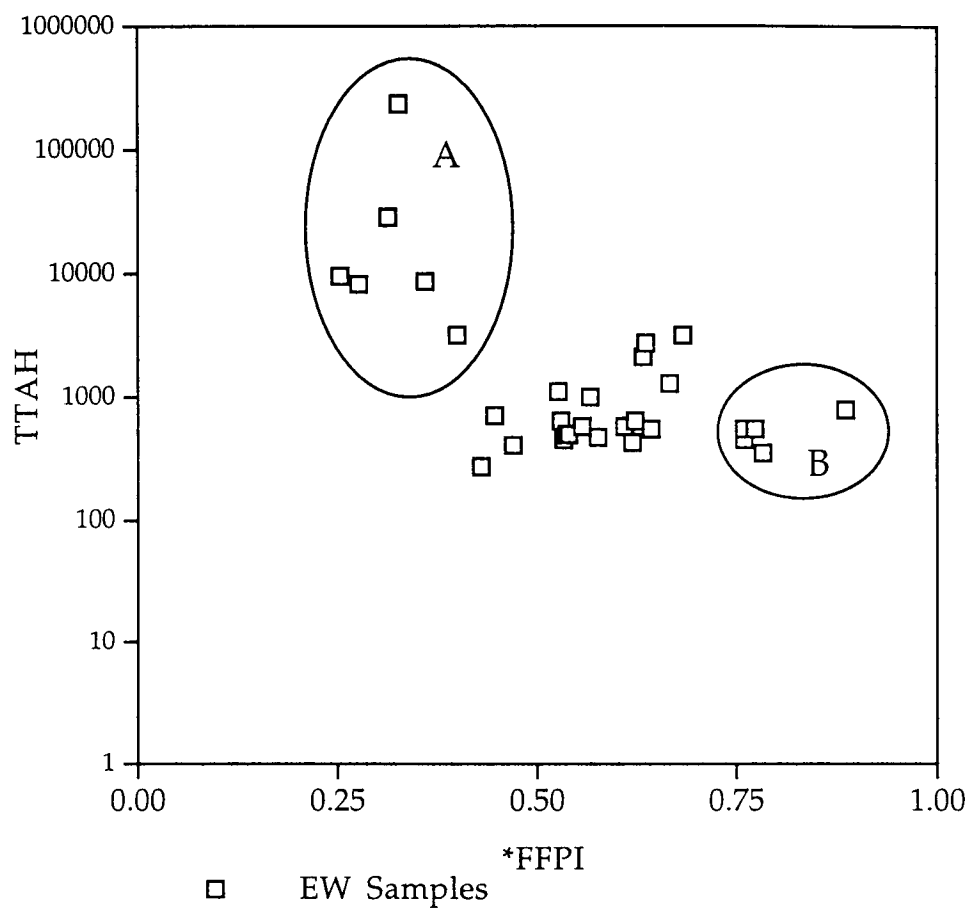


Figure 8. Comparison of TTAH concentration versus \*FFPI for samples collected from Empire Waterway collected in 1996. Sample population A is dominated by creosote derived AH while population B is petroleum derived and probably associated with persistent produced water contamination. All other samples demonstrate Ahs derived from a combination of sources including oil, creosote, and incomplete combustion products.

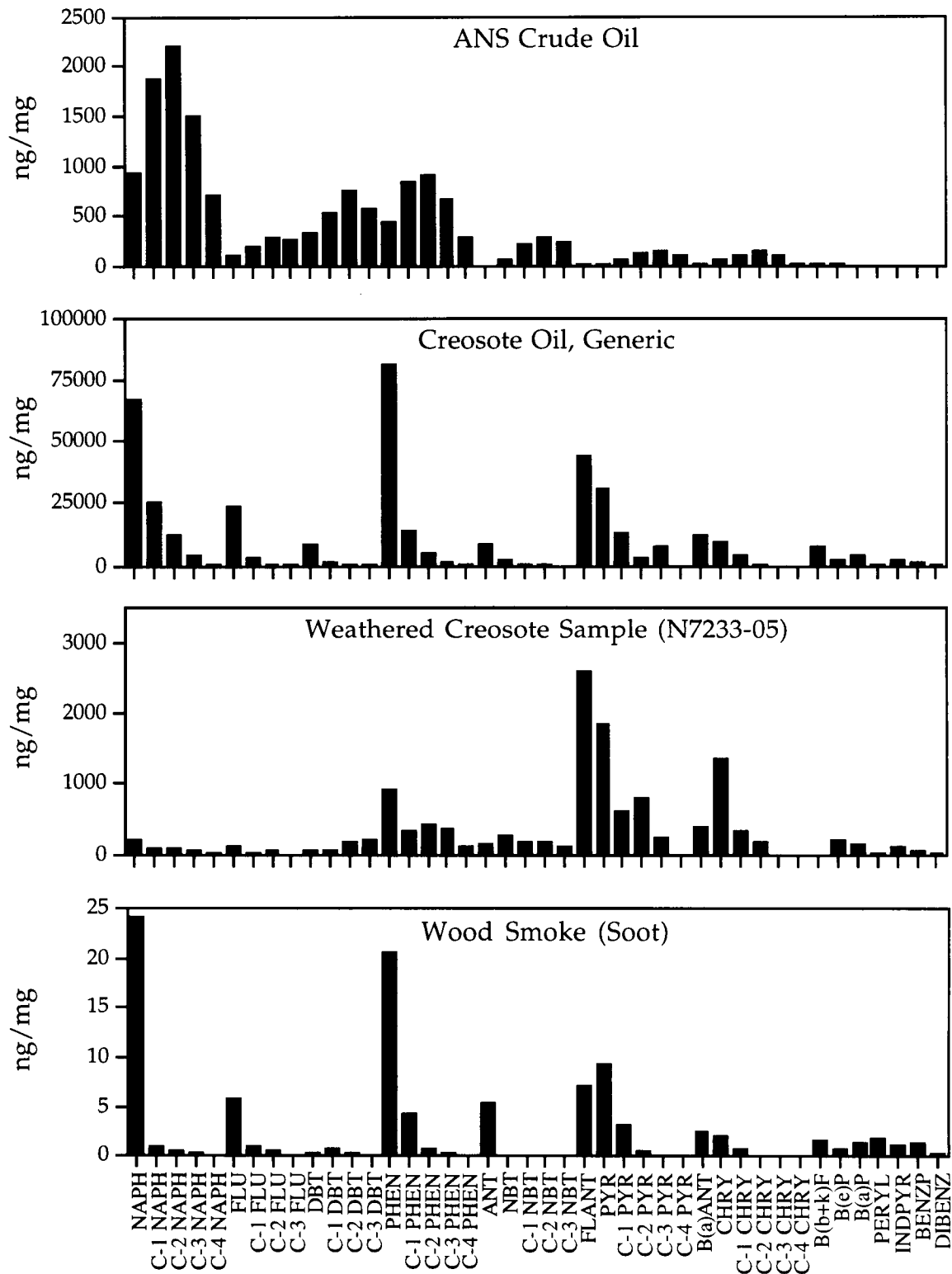


Figure 9. AH profile comparison of ANS crude oil, two weathered creosote samples, and pyrogenic AH extracted from smoke.

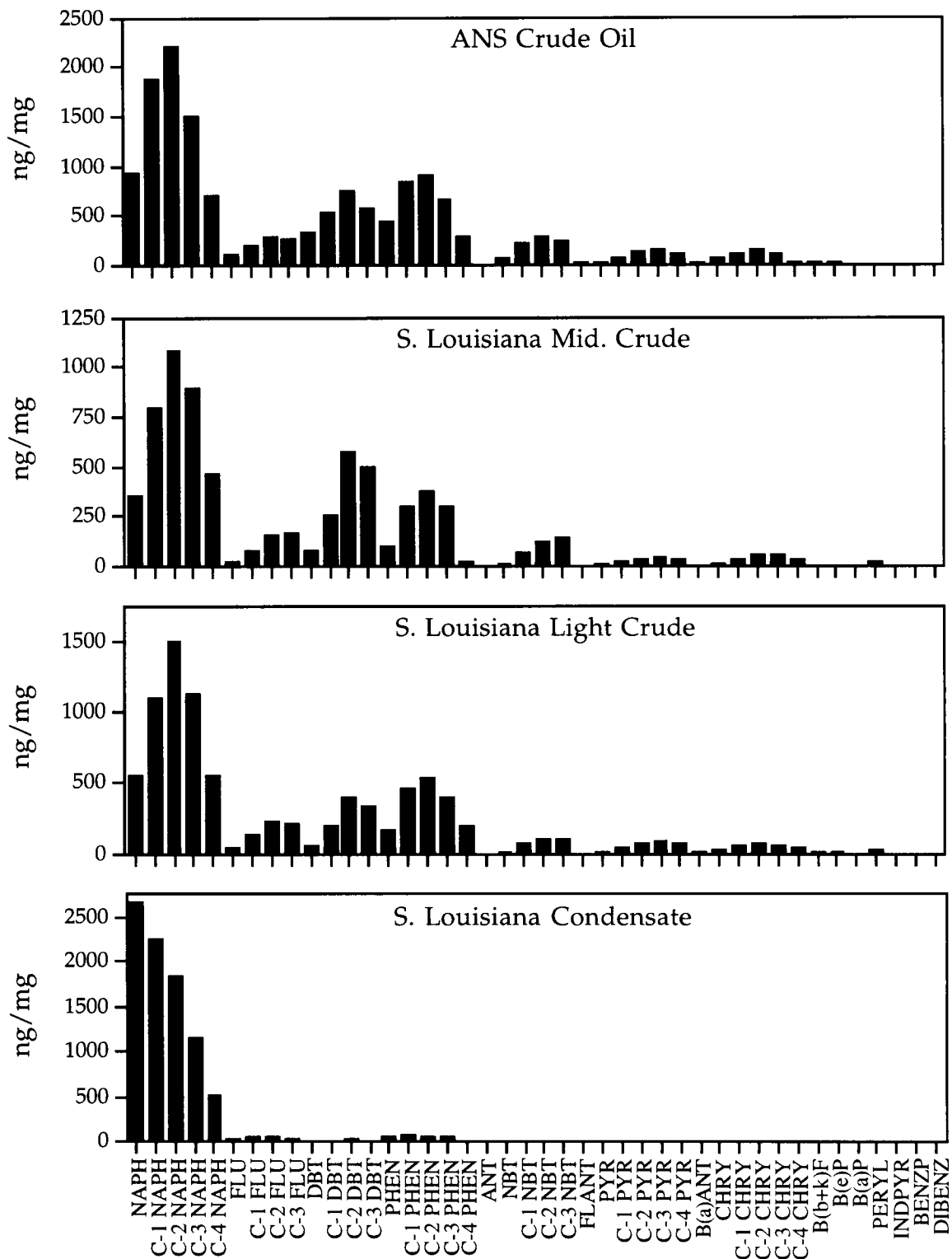


Figure 10. AH profile comparison of ANS crude oil and three different South Louisiana crude oils.

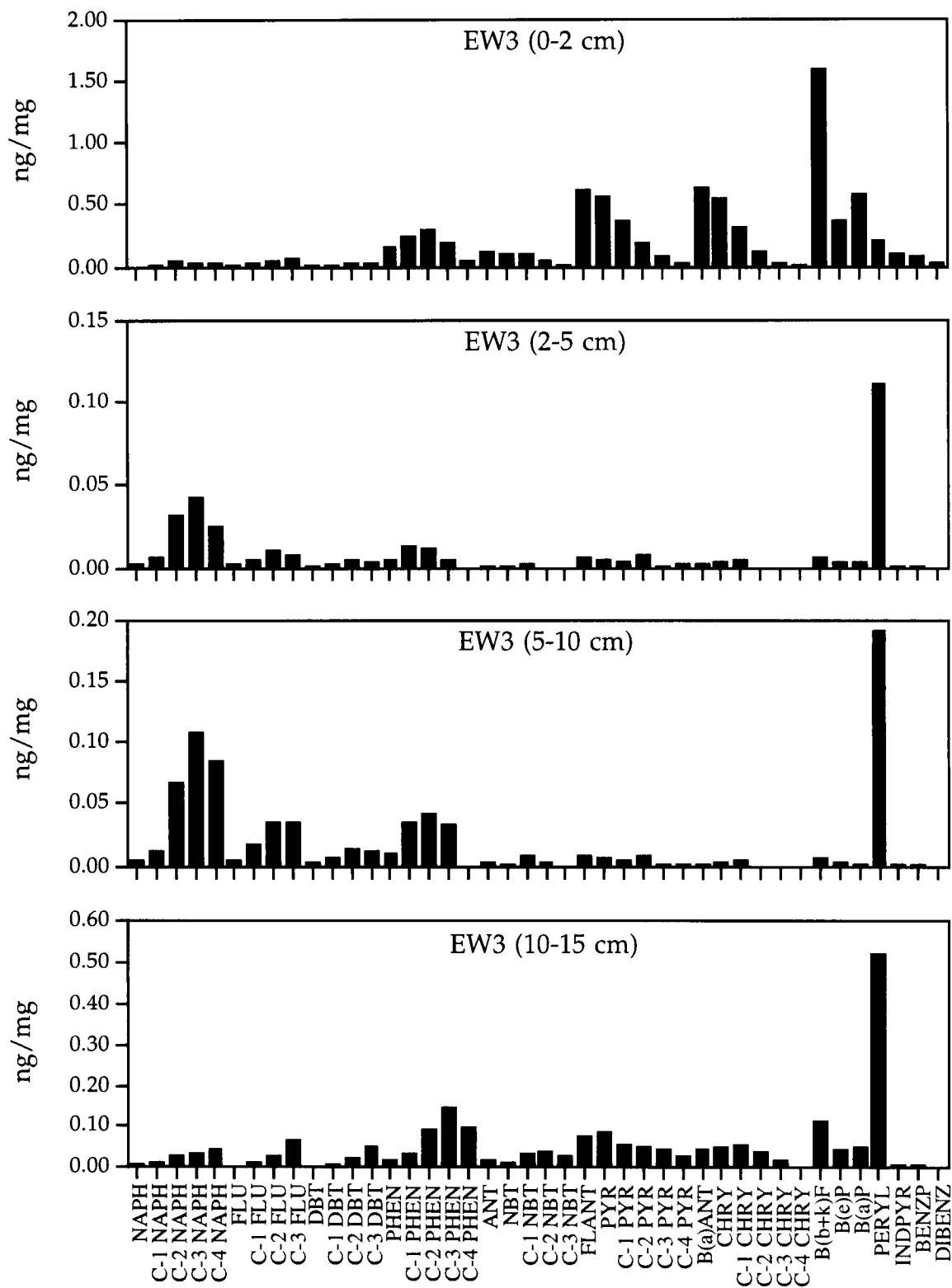


Figure 11. AH profile comparison of the top four core slices collected at Station EW3 (1996).

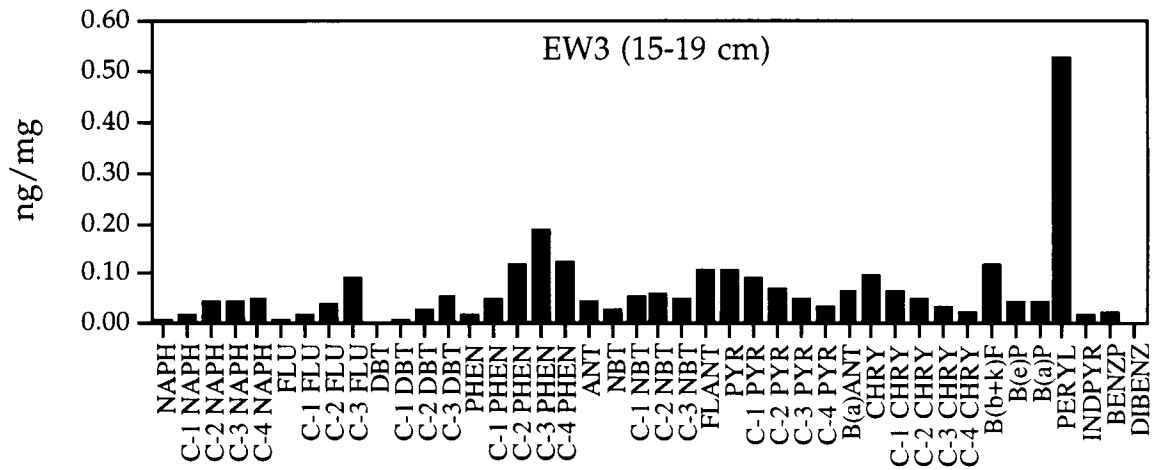


Figure 12. AH profile comparison of core slice #5 (15-19 cm) collected at Station EW3 (1996).

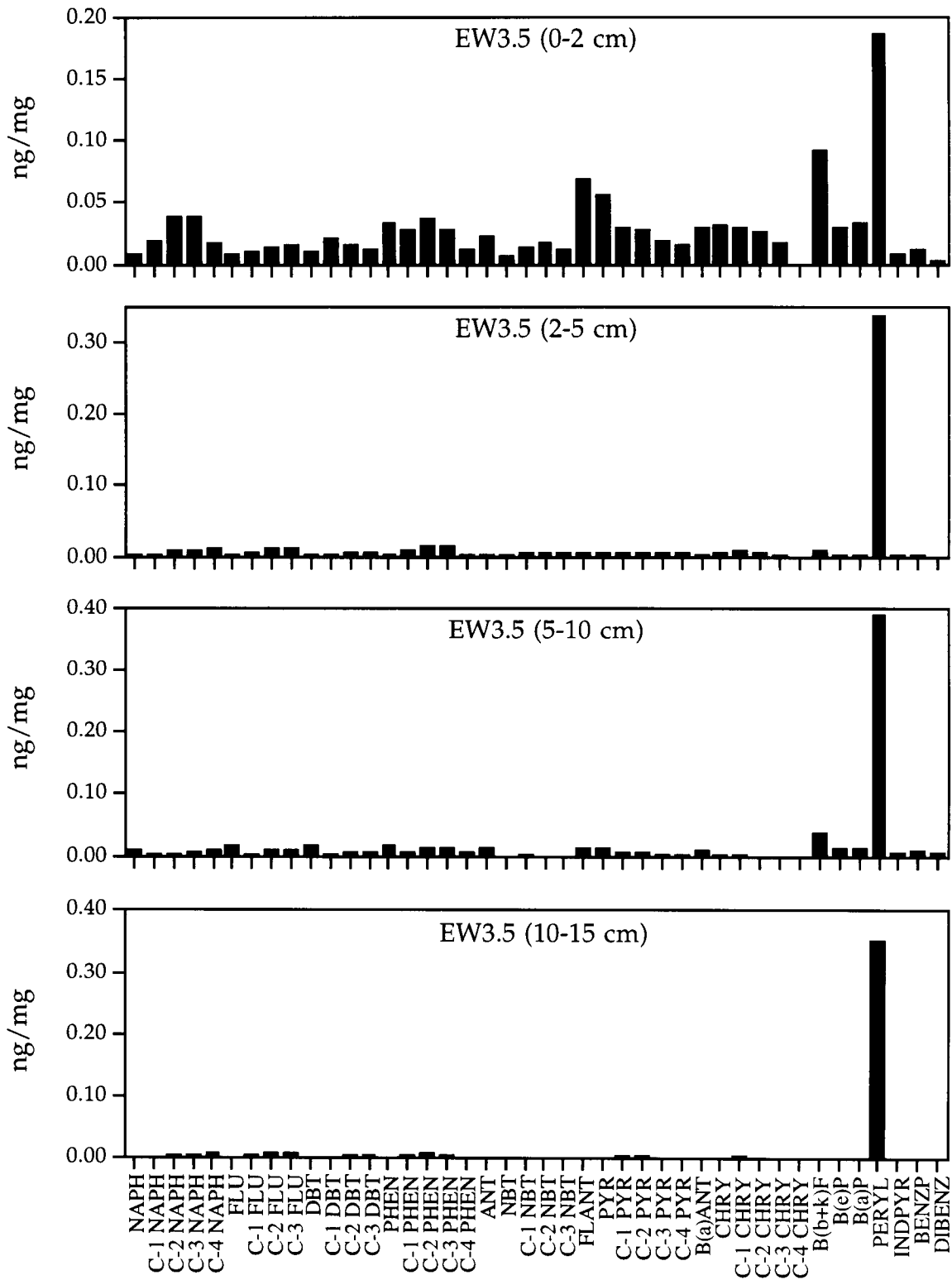


Figure 13. AH profile comparison of the top four core slices collected at Station EW3.5 (1996).

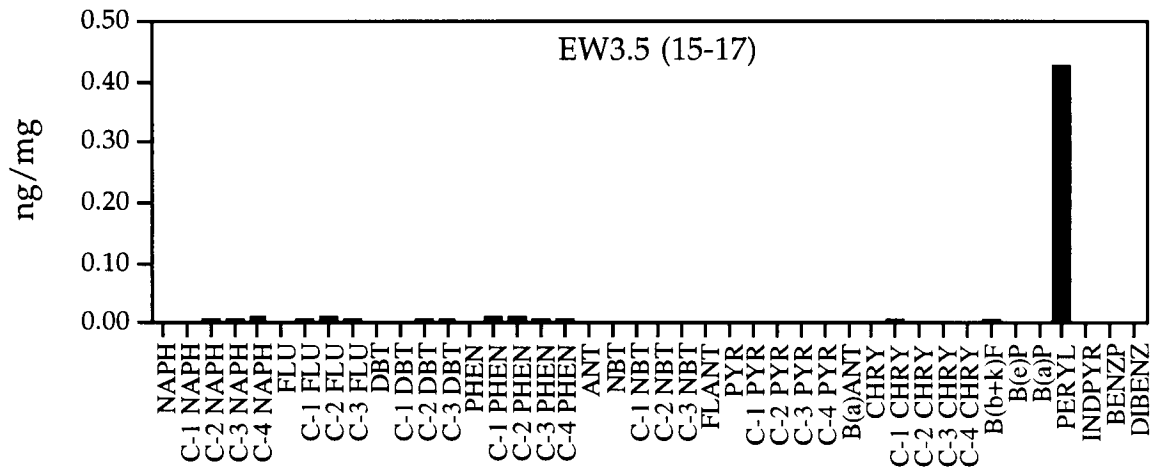


Figure 14. AH profile comparison of core slice #5 (15-17 cm) collected at Station EW3.5 (1996).

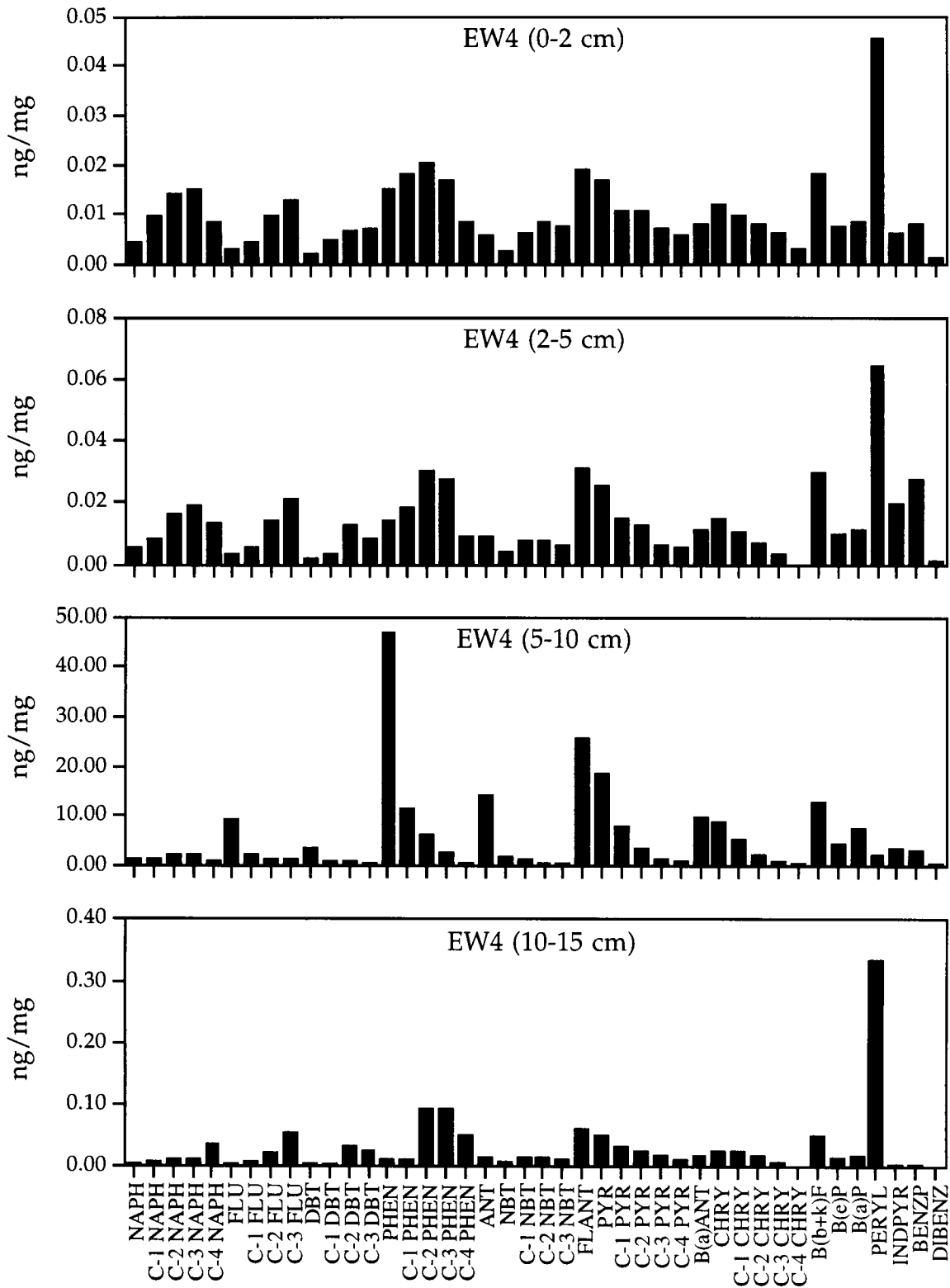


Figure 15. AH profile comparison of the mean values (n=3) of the top four core slices collected at Station EW4 (1996).



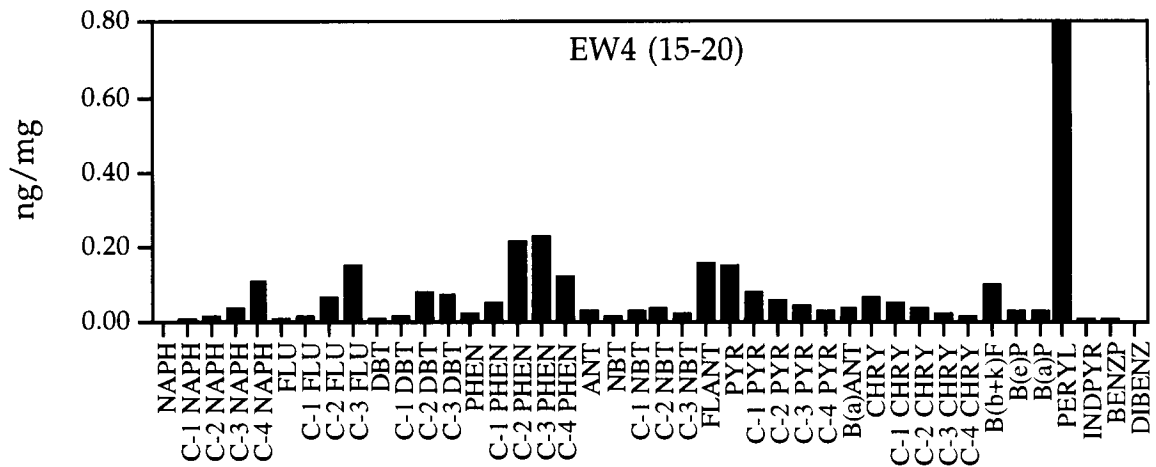


Figure 16. AH profile comparison of core slice #5 (15-20 cm) collected at Station EW4 (1996).

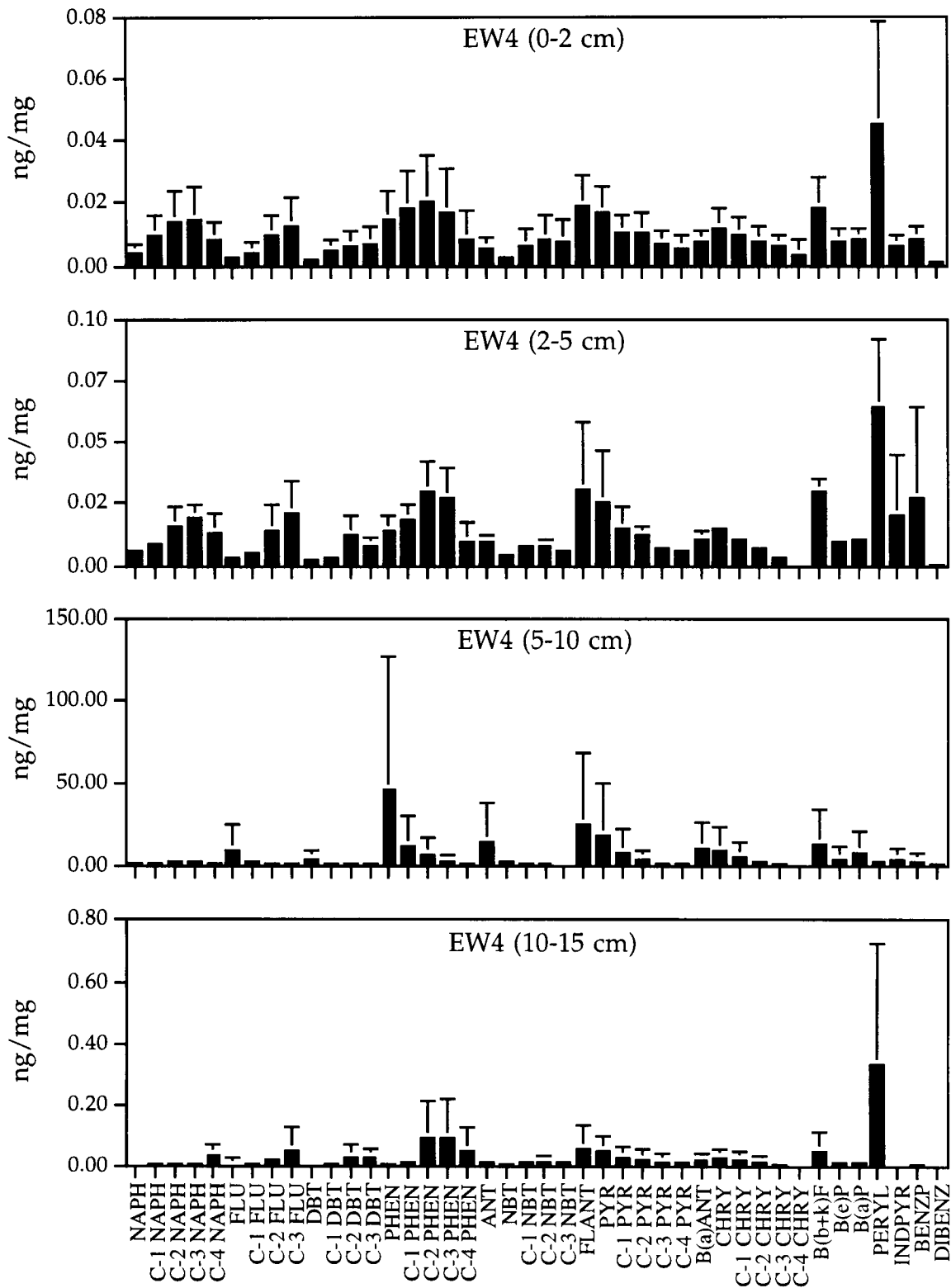


Figure 17. AH profile comparison of the top four core slices collected at Station EW3. Variance shown is standard deviation (n=3).

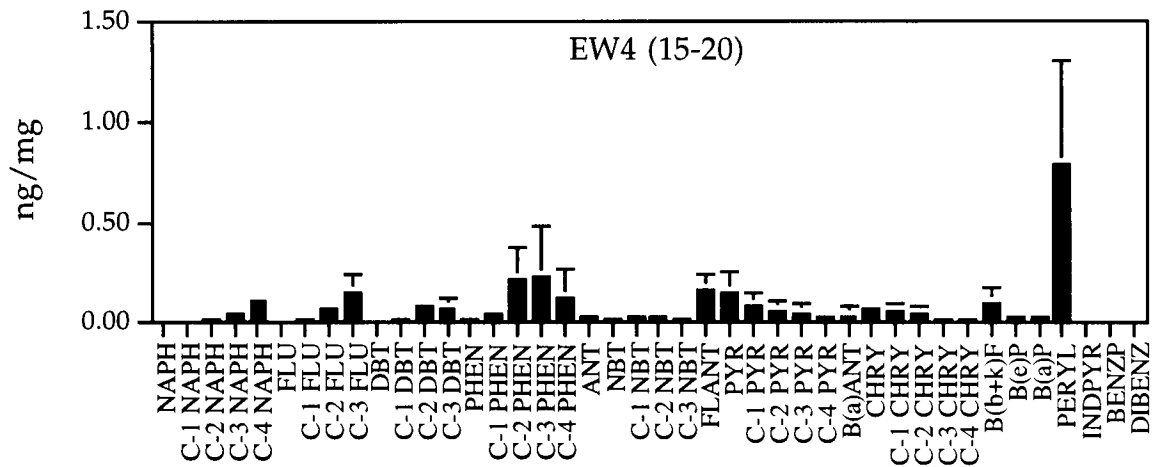


Figure 18. AH profile comparison of the mean values (n=3) from core slice #5 (15-20 cm) collected at Station EW4. Variance shown is standard deviation (n=3).

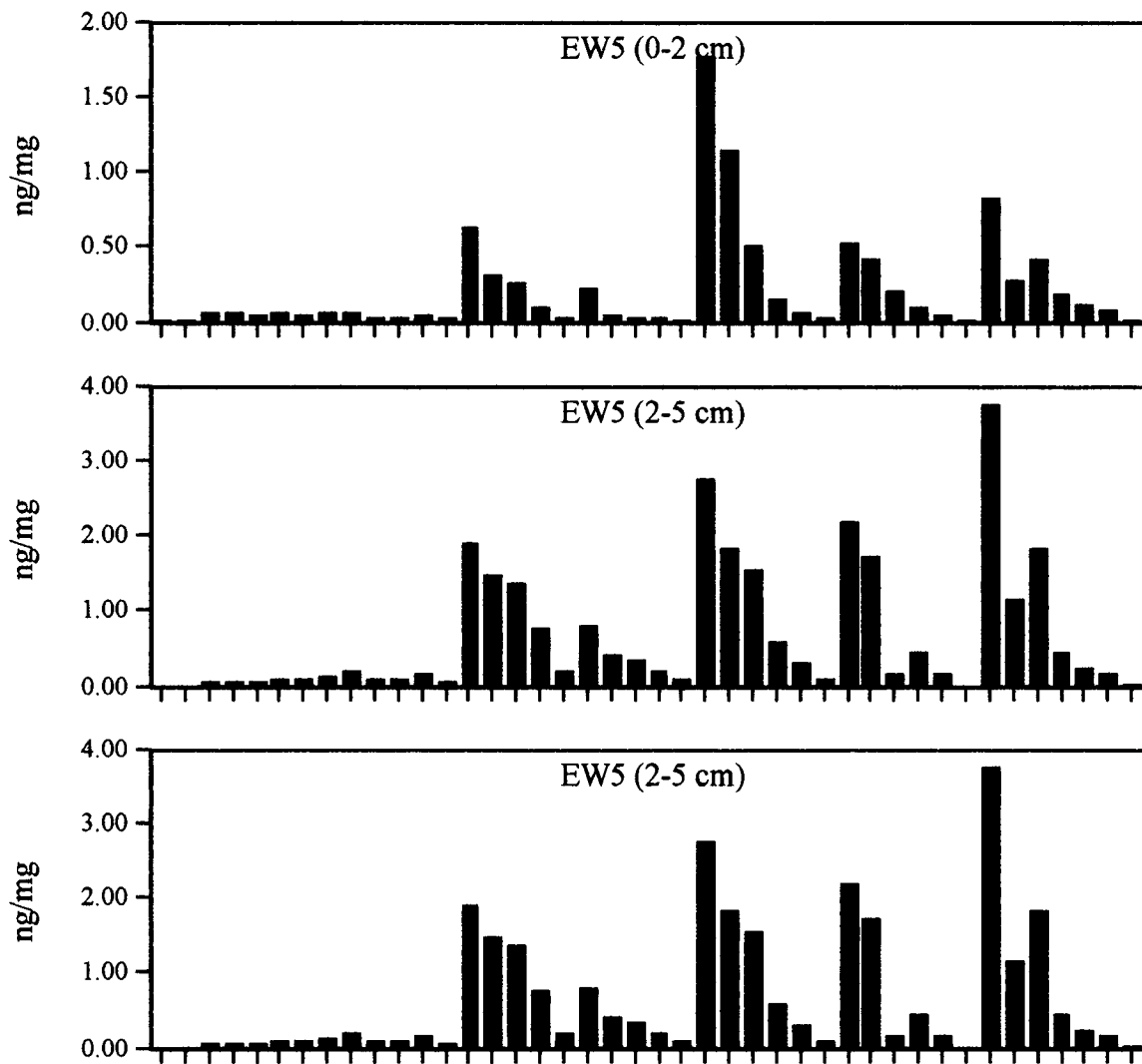


Figure 19. AH profile comparison of the top four core slices collected at Station EW5 (1996).

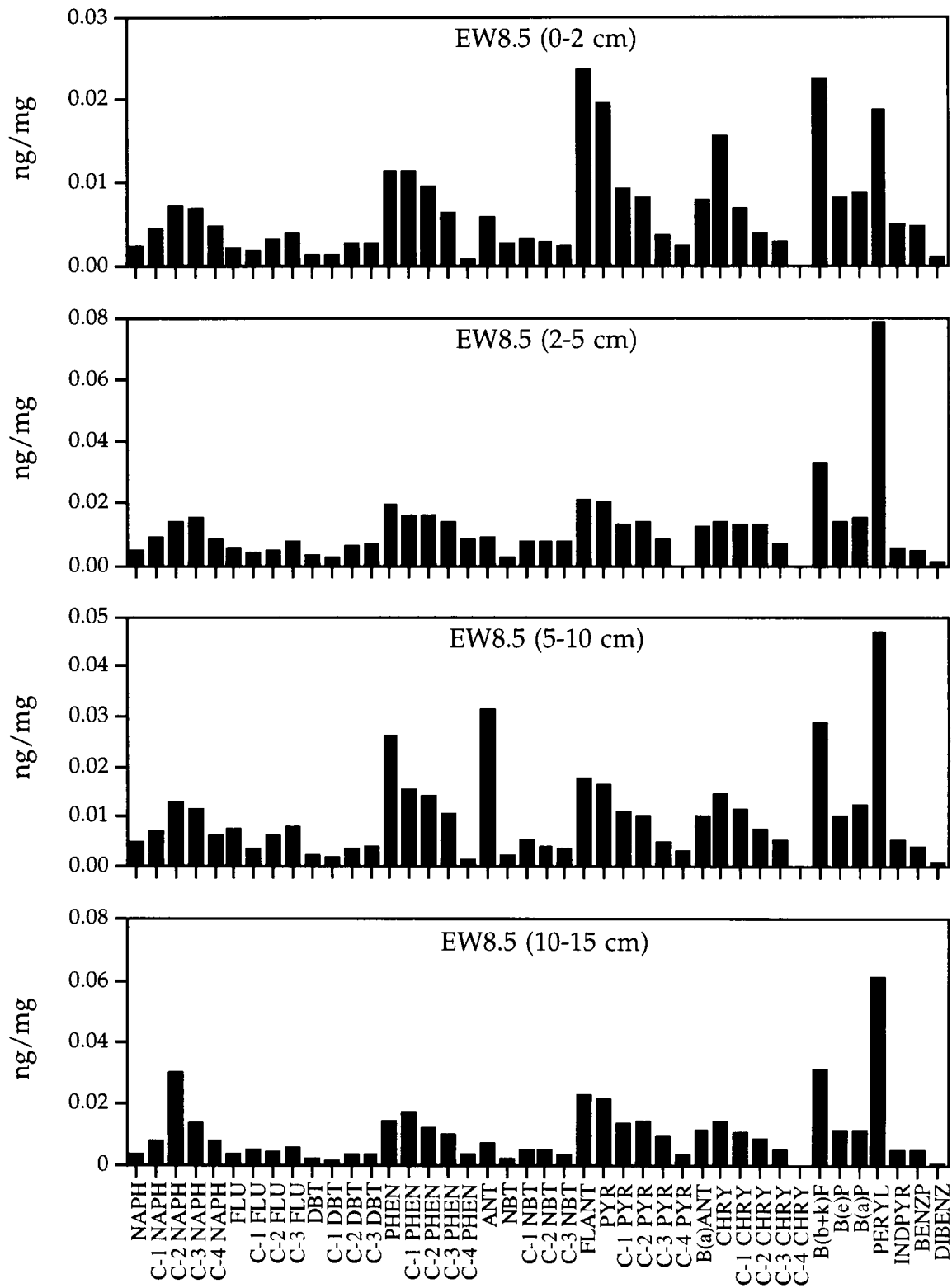


Figure 20. AH profile comparison of the top four core slices collected at Station EW8.5 (1996).

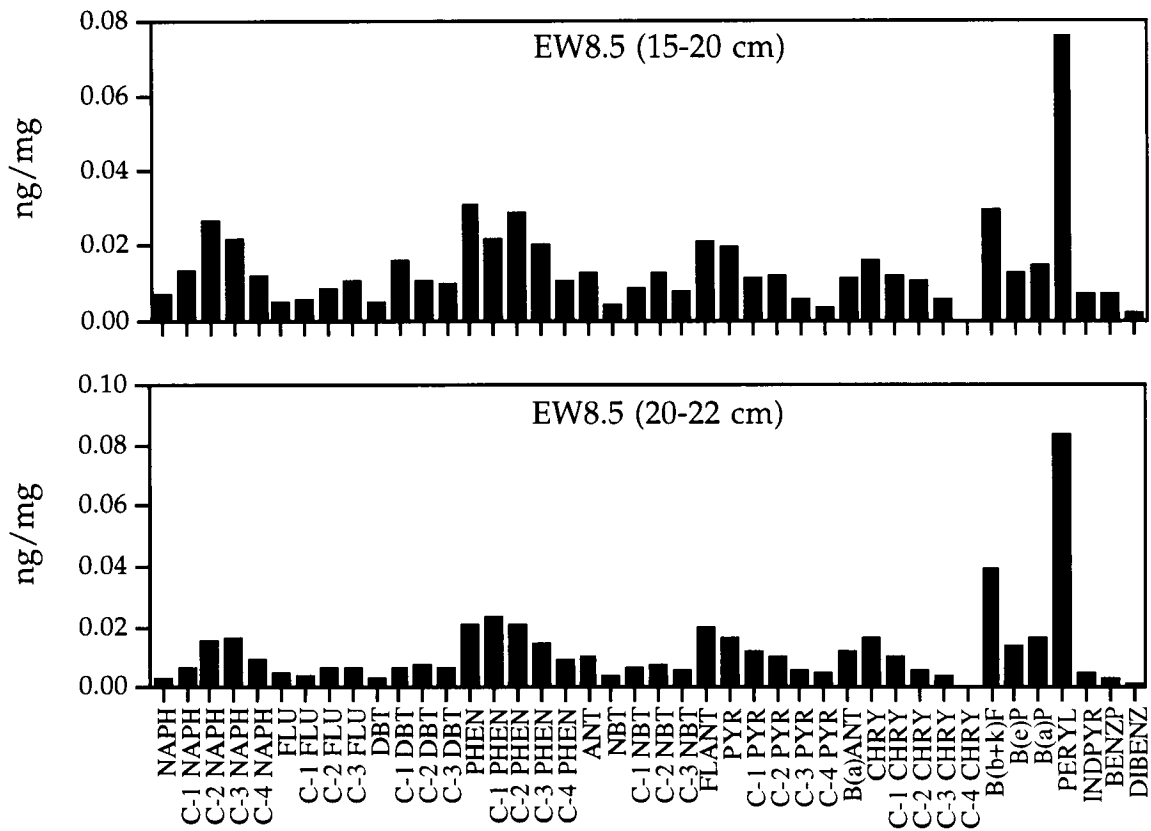


Figure 21. AH profile comparison of core slice #5 and #6 collected at Station EW8.5 (1996).

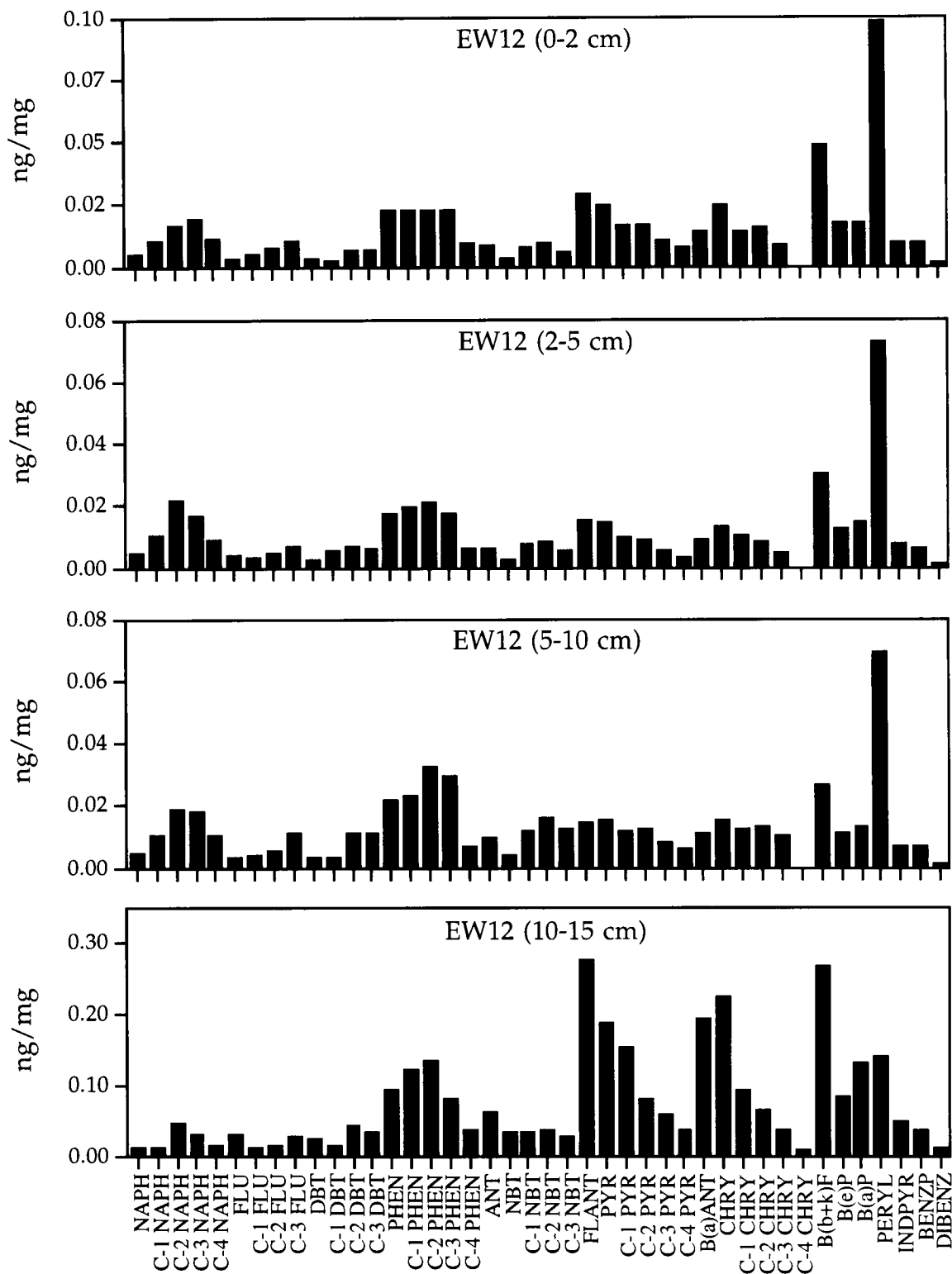


Figure 22. AH profile comparison of the top four core slices collected at Station EW12 (1996).

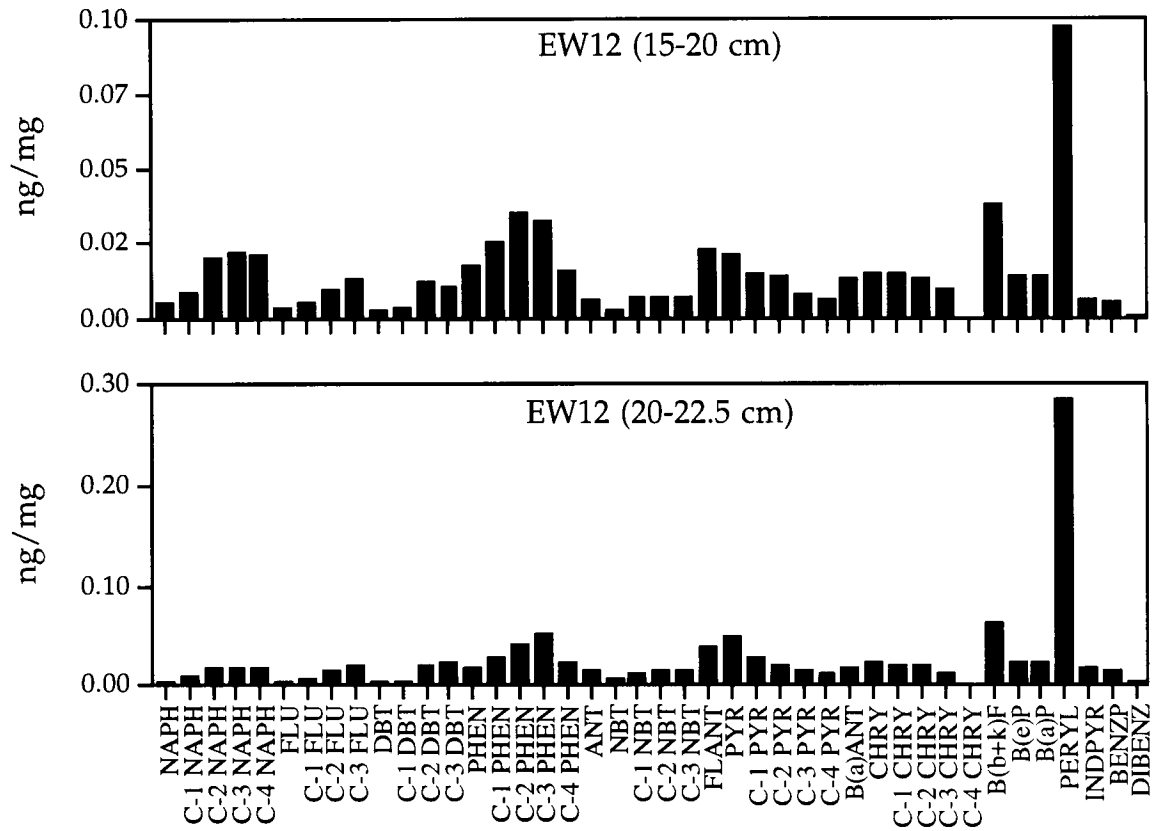


Figure 23. AH profile comparison of core slice #5 and #6 collected at Station EW12 (1996).



difficult to make direct comparisons. In addition, analytical method differences existed between the 1989 and the 1996 data sets due in part to advancements in analytical techniques and equipment. Without a depositional history, we were forced to simply plot TTAH relative to depth for both sites using both 1989 and 1996 data sets (Figures 24 and 25). Trends in the TTAH values relative to depth between the two sample periods were not readily apparent. The observed differences are only in part associated with the small difference in the target compounds summed to generate the TTAH values in 1989 and 1996.

Figures 26 through 35 are AH profile comparisons between the 1989 and 1996 sampling periods for individual core sections. These figures clearly demonstrate the improvements in analytical analyses reflected in the 1996 data set relative to the 1989 analytical period. Minimum detection limits are improved by at least an order of magnitude, and the expanded target list aids in the identification of pollution source. Overall, it is difficult to compare the 1989 data set relative to the 1996 data set since the latter provided a greater scope and lower detection limits.

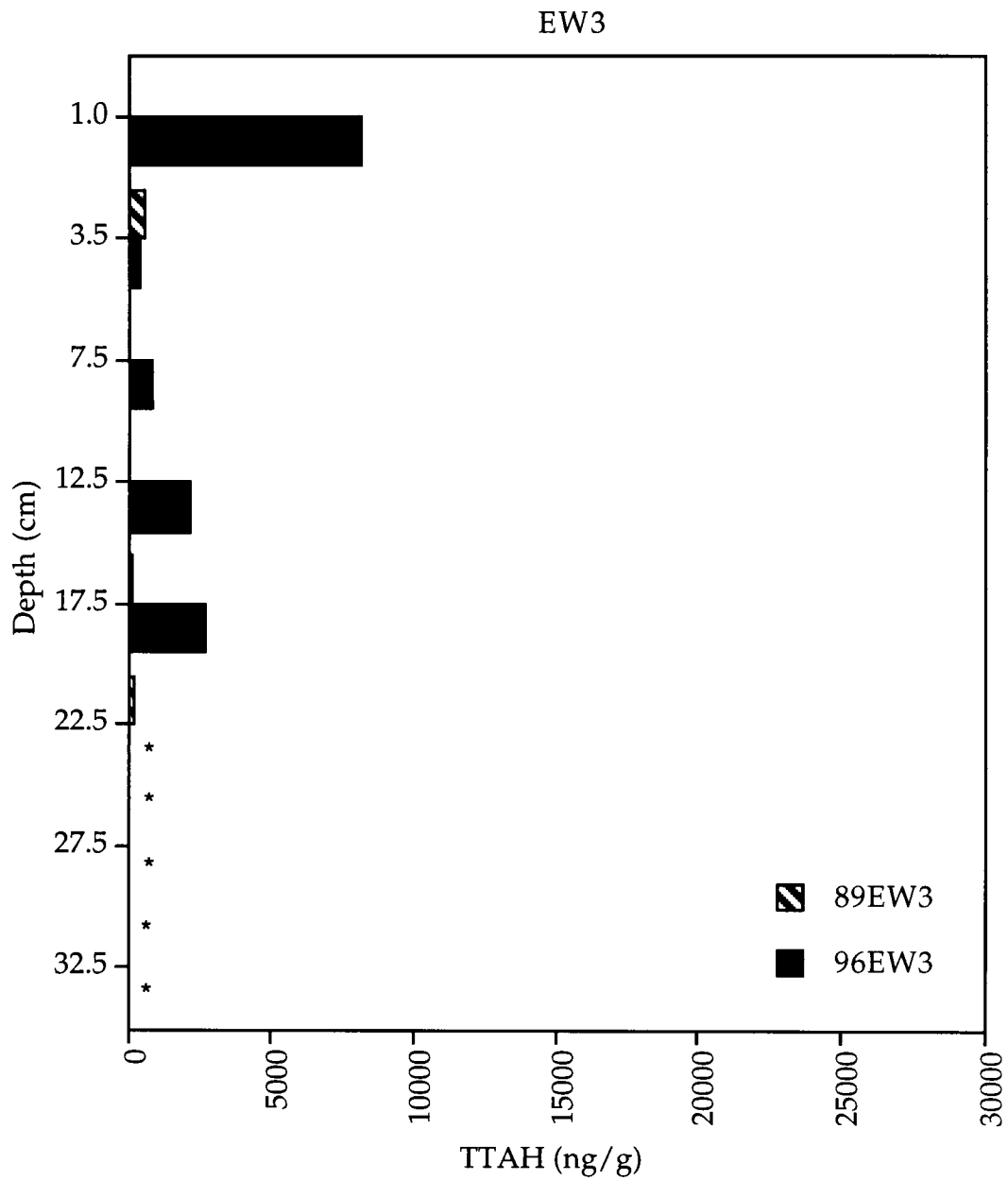
### **Sediment Metals**

As in 1989, the 1996 metal concentrations were generally low (see Appendix 4). Most of the trace metal results were similar to each other and probably represent background metal distributions. While none of the metals appear to be of any environmental significance, selected metals, such as Zn, may be useful in tracking produced water impacts. Zn concentrations ranged from a low of 56 ppm (dry weight basis) to a high of 420 ppm. The mean Zn concentration for all stations except EW3, EW3.5 and EW4 (stations nearest the discharge) was 114 ppm. The highest Zn concentration was detected in one of the cores for station EW4 (10-15 cm), a sample that also exhibited elevated petroleum hydrocarbons characteristically similar to persistent produced water pollutants. A similar elevated Zn concentration, but less pronounced, was observed in the same vertical section of the EW3 core.

### **Benthos**

Stations for collection of benthos in 1996 were restricted to the canal adjacent to the Pelican Island facility. The benthic infauna was a combination of marine and intermediate salinity organisms, primarily polychaetes (see Appendix 5 for benthic community parameters and Appendix 6 for species list). The dominant polychaetes were *Paraprionospio pinnata* and *Mediomastus* sp. A. There were several other species of polychaetes, oligochaetes, nemertean worms, bivalves, gastropods, ophiuroids and decapod crustaceans.

Among the stations sampled in 1996, station EW5 was much more diverse than the other stations (EW3.5, EW4 and EW12) (Table 2). Additional dominant organisms at EW5 were tubificid oligochaetes, the polychaete *Streblospio benedicti*, nemerteans, several gastropods, and ophiuroids. This station was characterized by more shell hash and a higher sand fraction than the other stations. Located in the waterway between the canal and the adjacent bay, EW5 was subject to swift currents. Benthic infauna was more abundant at both stations EW5 and EW12 than either of stations EW4 and EW3.5 which were similar to each other (Table 2).



\*No sample collected at this depth.

Figure 24. Comparison of TTAH concentration with depth for sediment cores from station EW3 in 1989 (hatched) and in 1996 (solid).

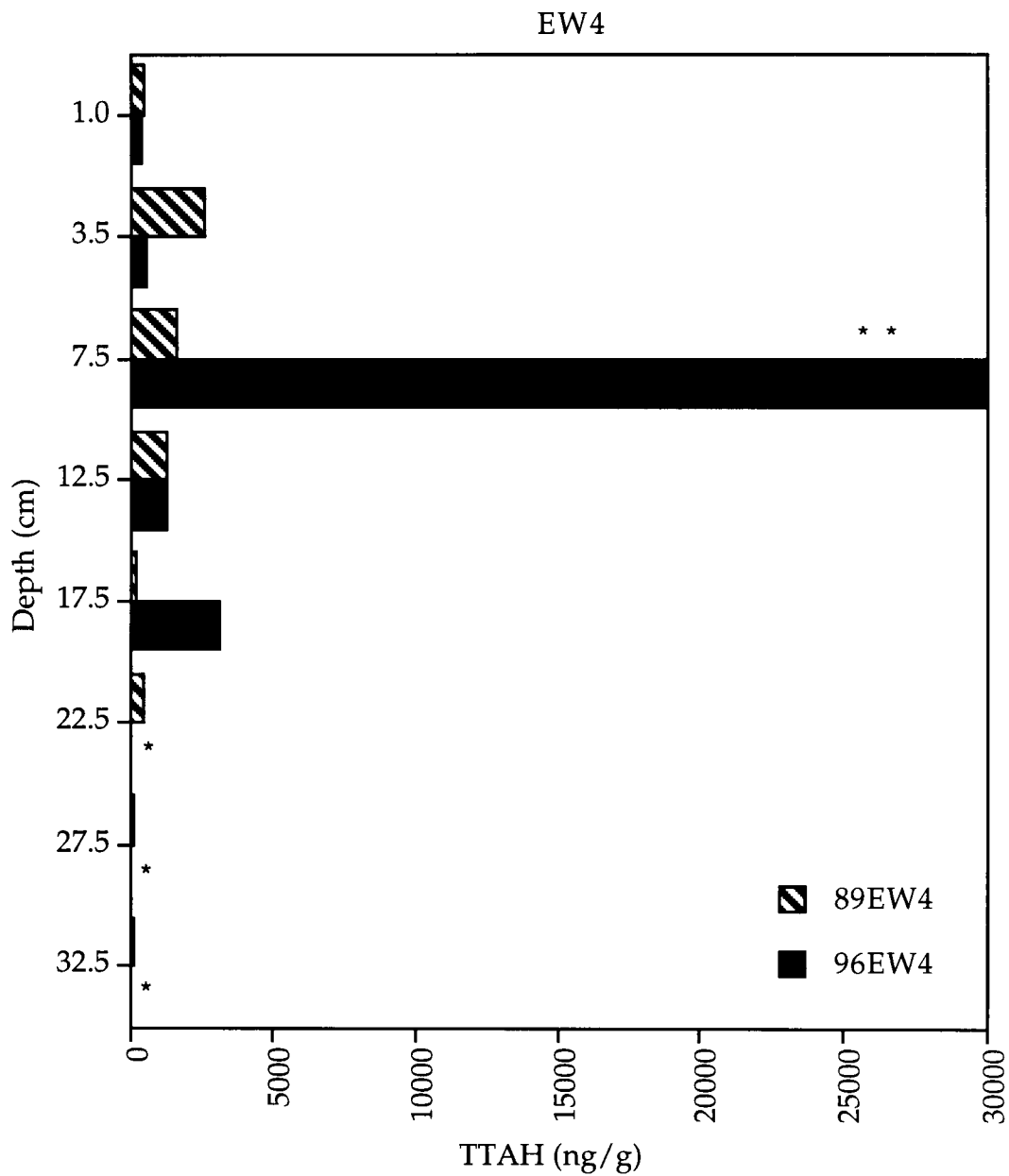


Figure 25. Comparison of TTAH concentration with depth for sediment cores from station EW4 in 1989 (hatched) and in 1996 (solid).

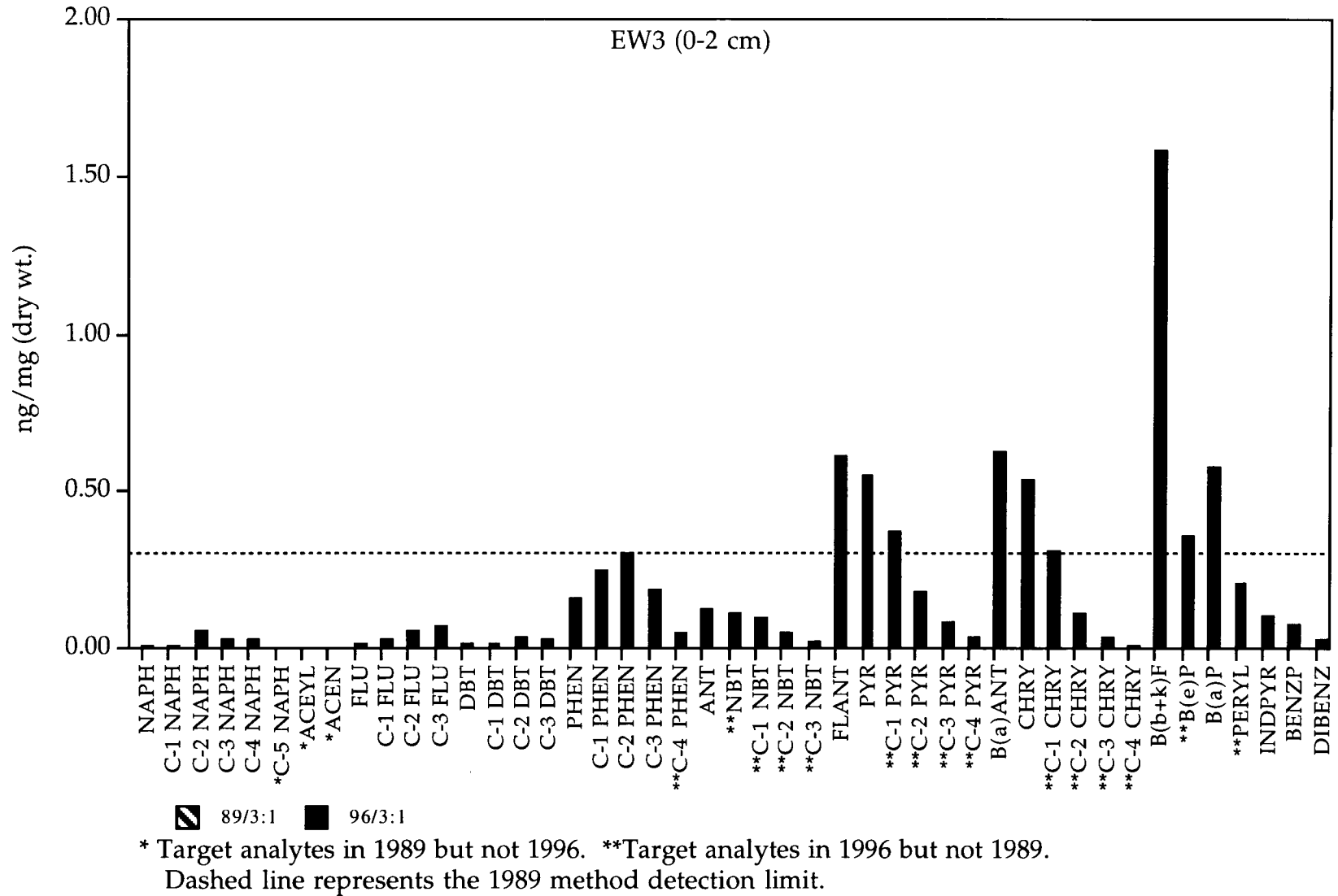


Figure 26. Comparison of AH concentration profile between the 1989 and 1996 cores at station EW3 (0-2 cm).

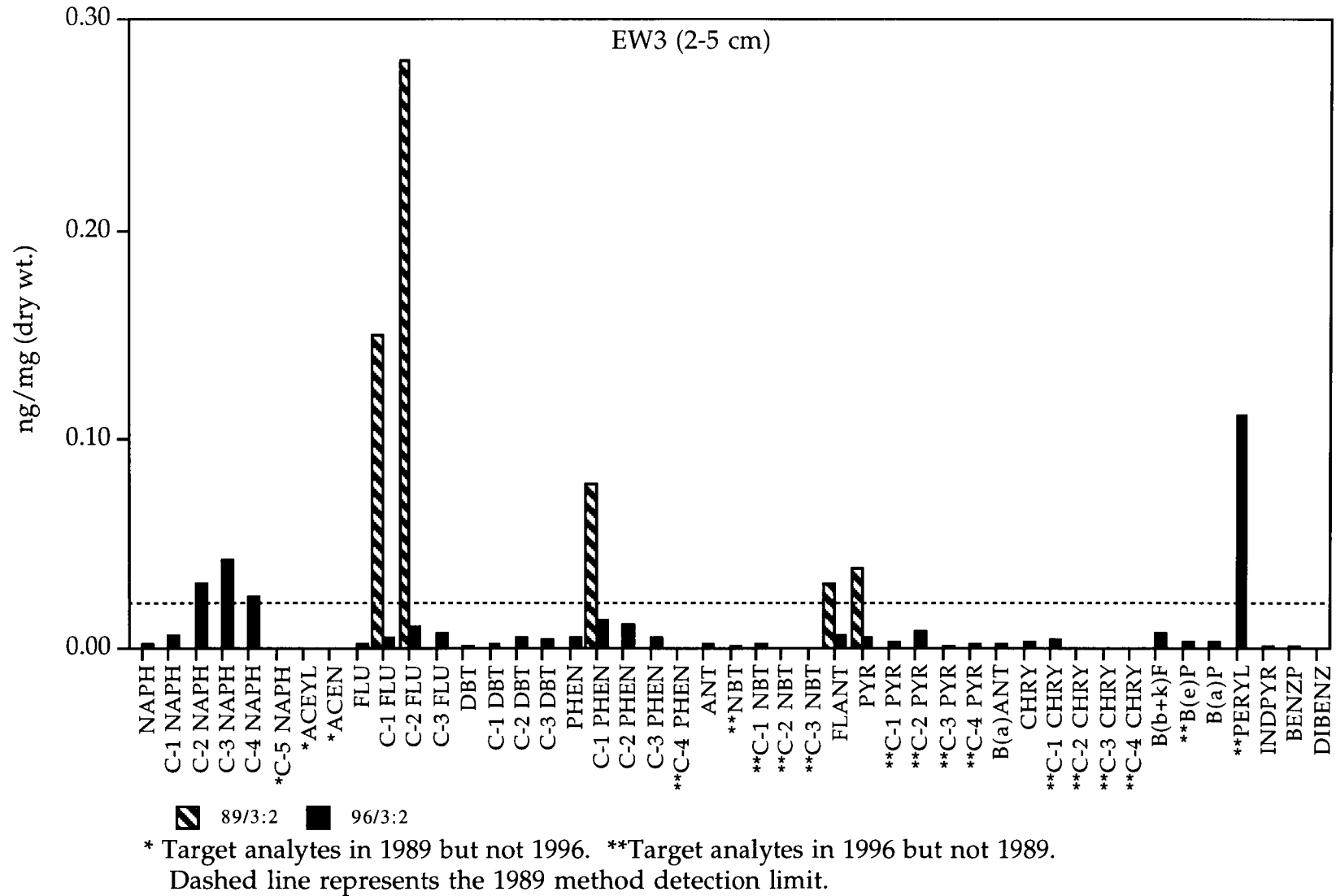


Figure 27. Comparison of AH concentration profile between the 1989 and 1996 cores at station EW3 (2-5 cm).

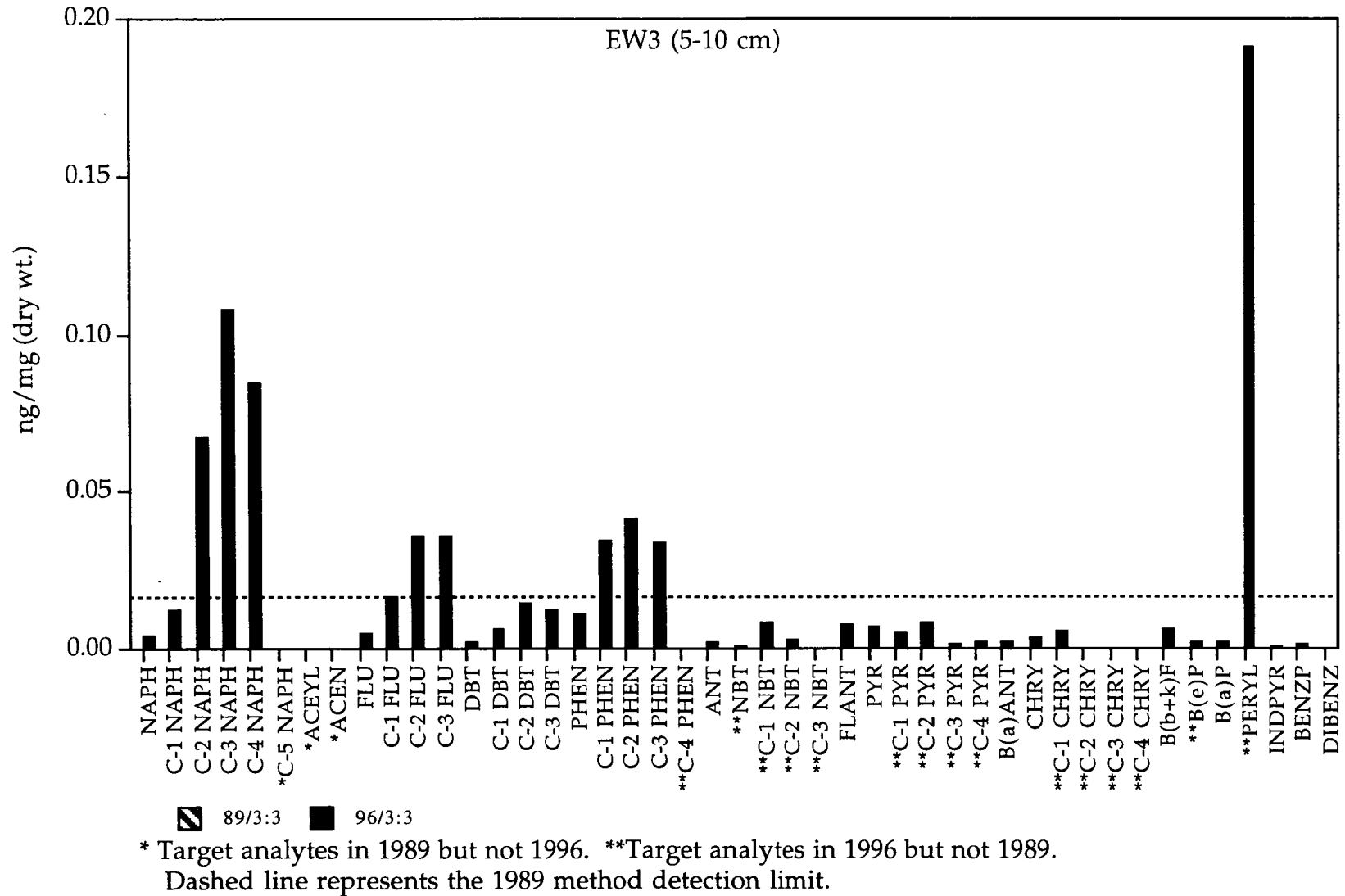


Figure 28. Comparison of AH concentration profile between the 1989 and 1996 cores at station EW3 (5-10 cm).

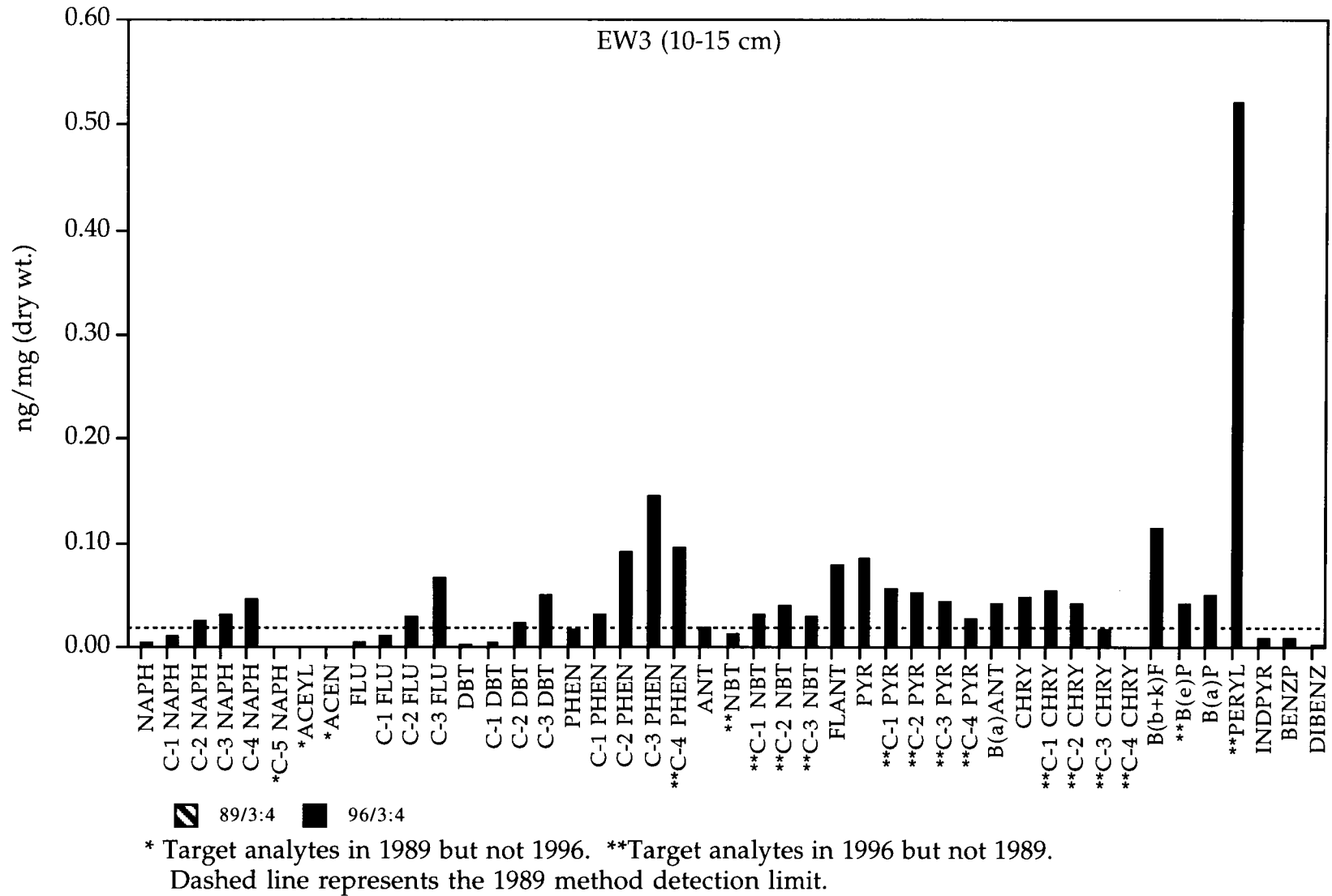


Figure 29. Comparison of AH concentration profile between the 1989 and 1996 cores at station EW3 (10-15 cm).

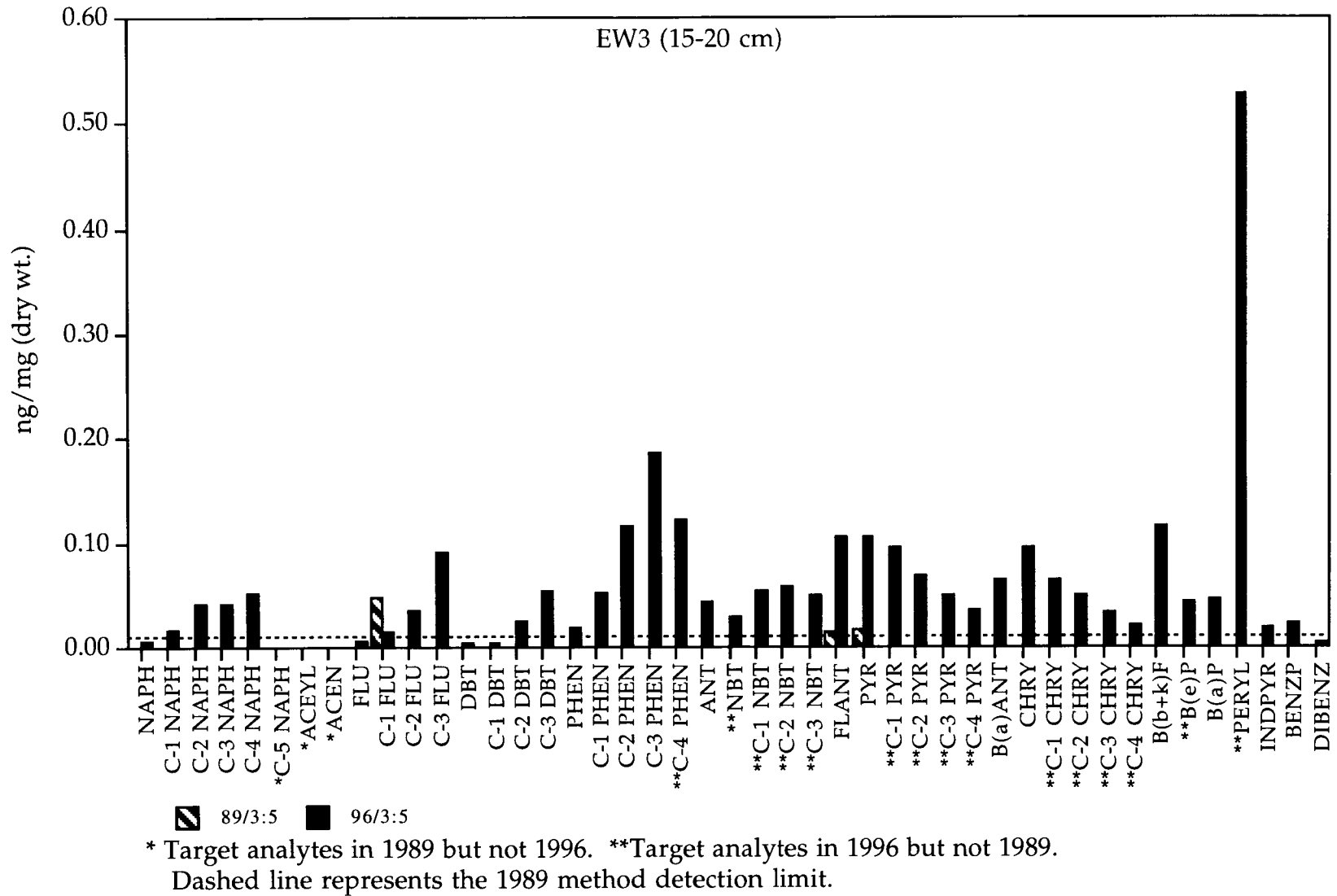


Figure 30. Comparison of AH concentration profile between the 1989 and 1996 cores at station EW3 (15-20 cm).



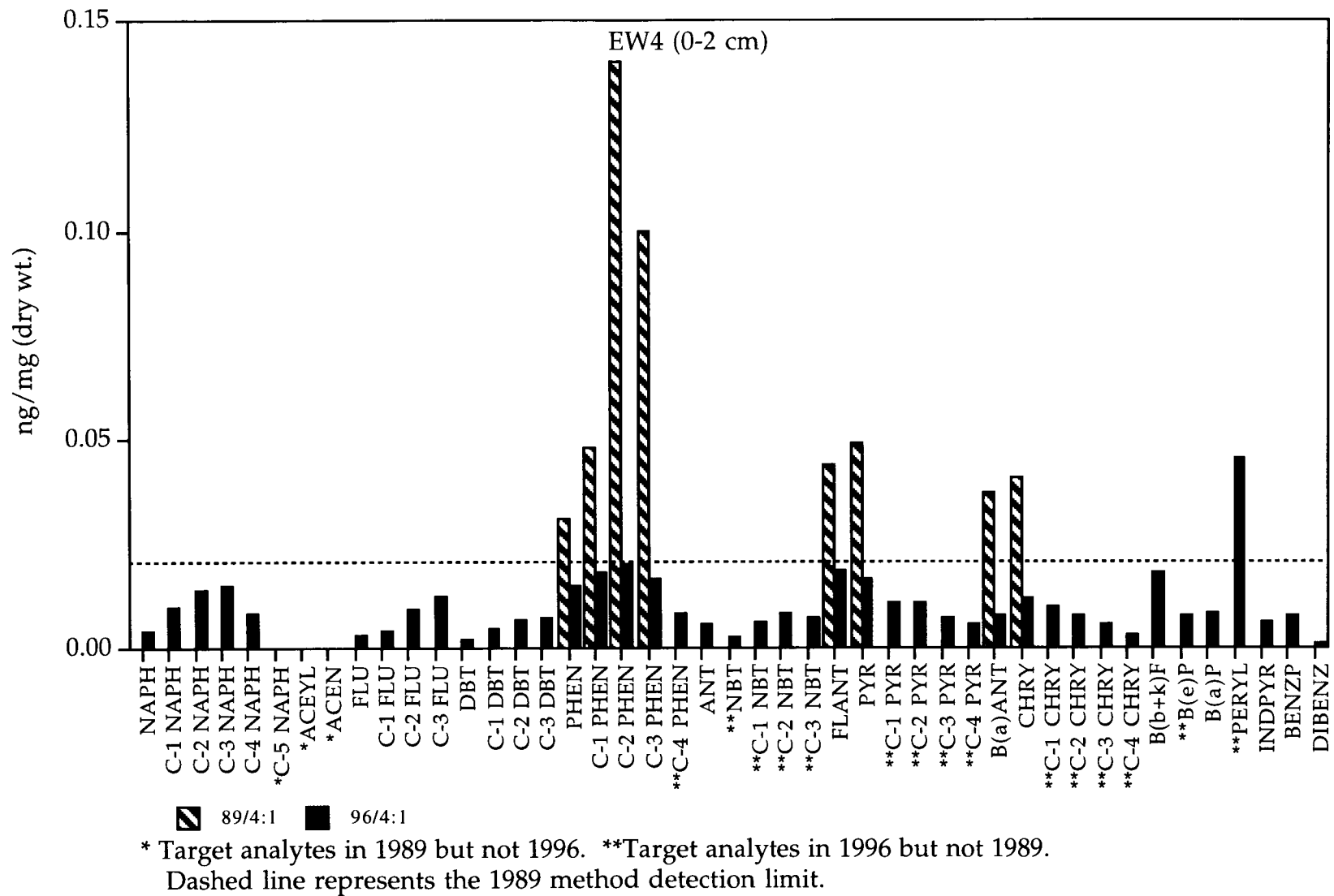


Figure 31. Comparison of AH concentration profile between the 1989 and 1996 cores at station EW4 (0-2 cm).

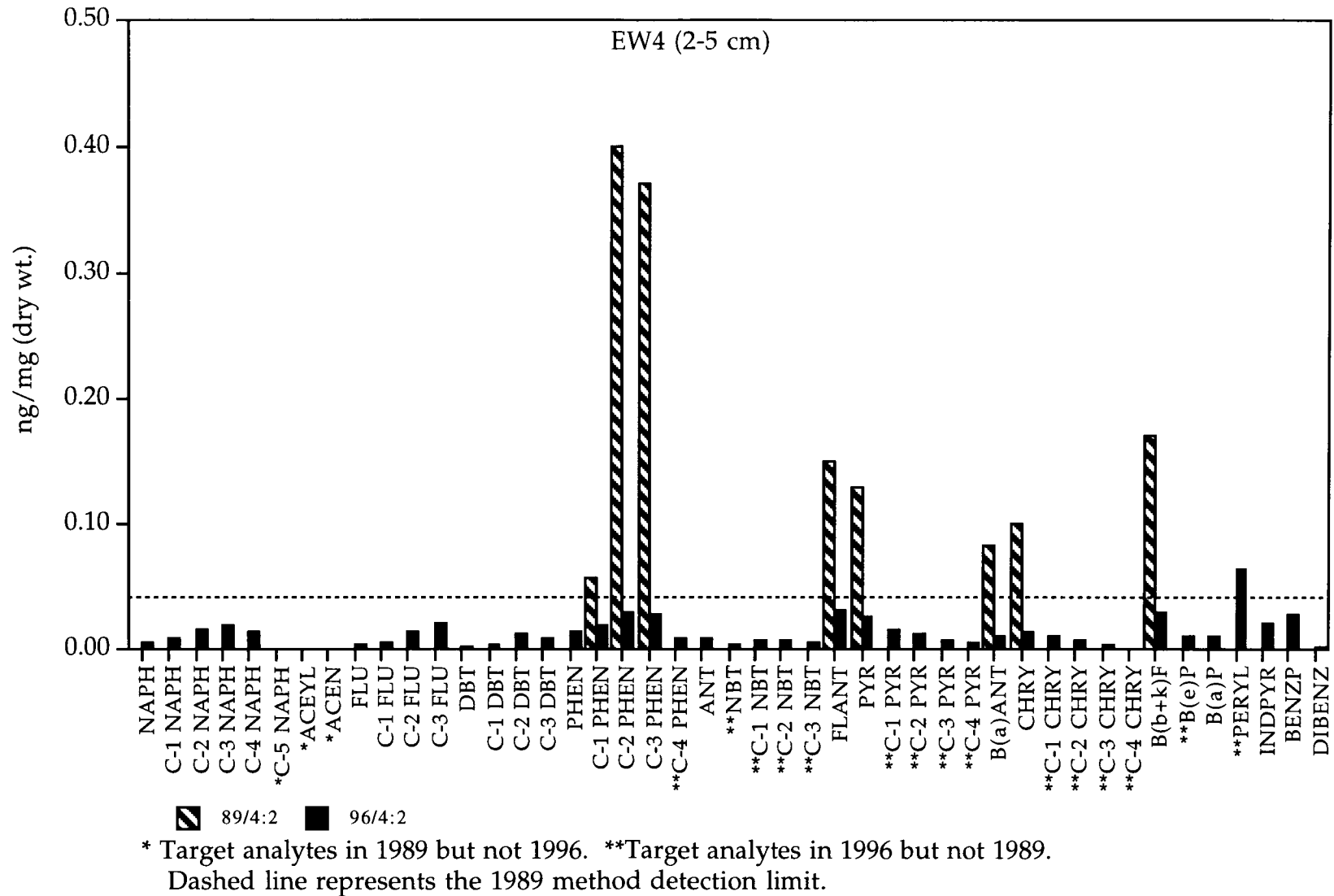


Figure 32. Comparison of AH concentration profile between the 1989 and 1996 cores at station EW4 (2-5 cm).

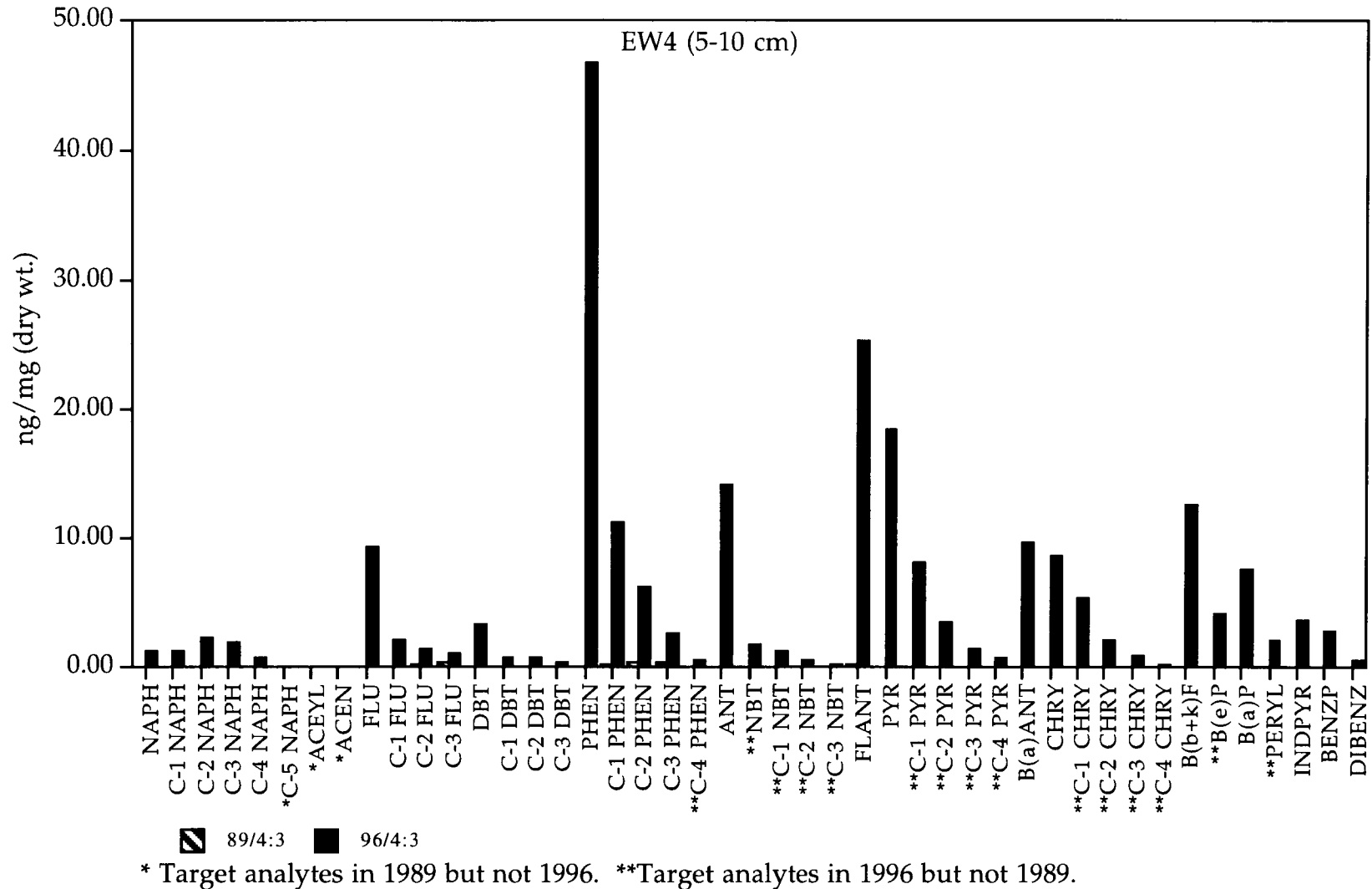


Figure 33. Comparison of AH concentration profile between the 1989 and 1996 cores at station EW4 (5-10 cm).

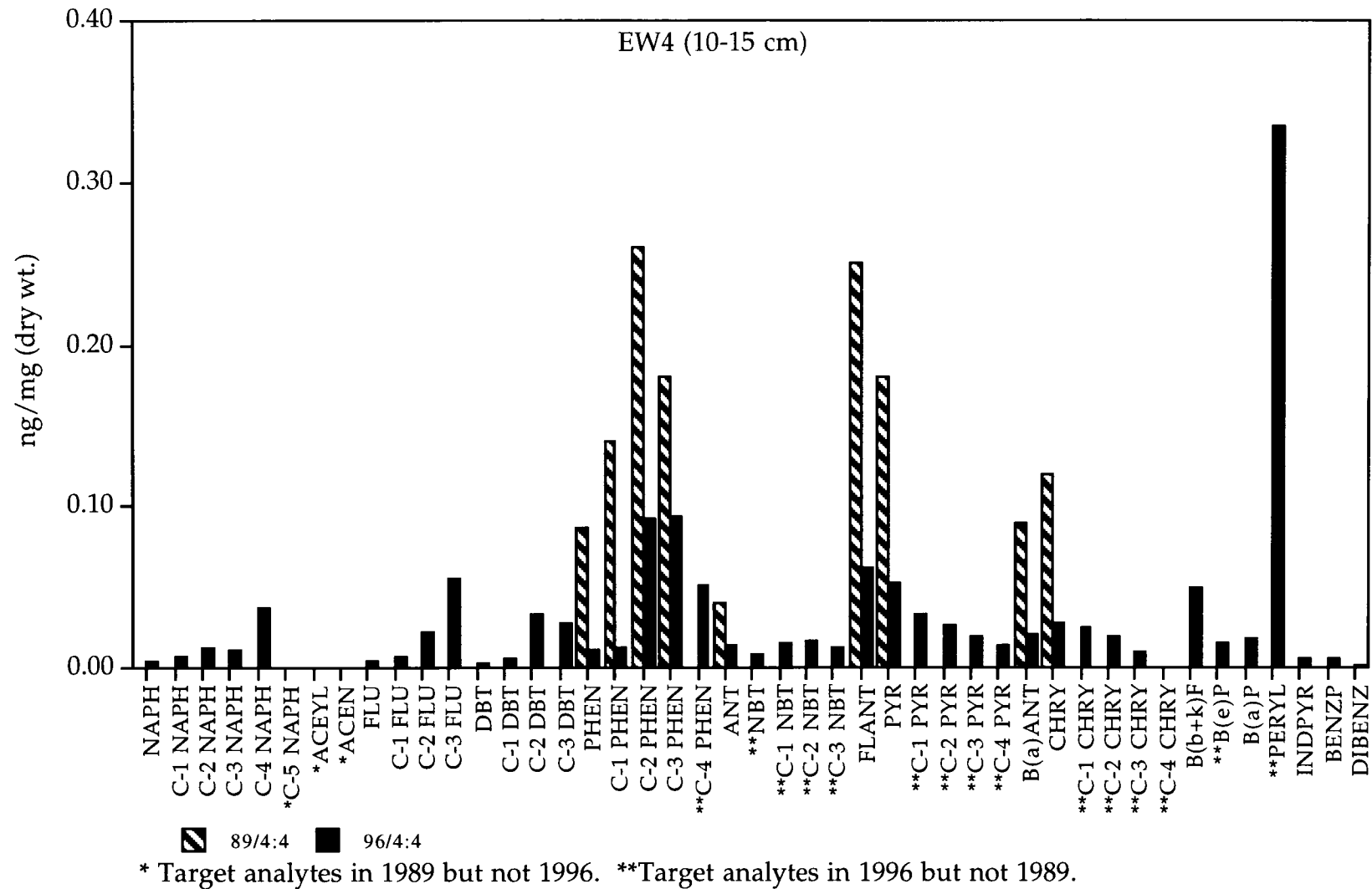


Figure 34. Comparison of AH concentration profile between the 1989 and 1996 cores at station EW4 (10-15 cm).

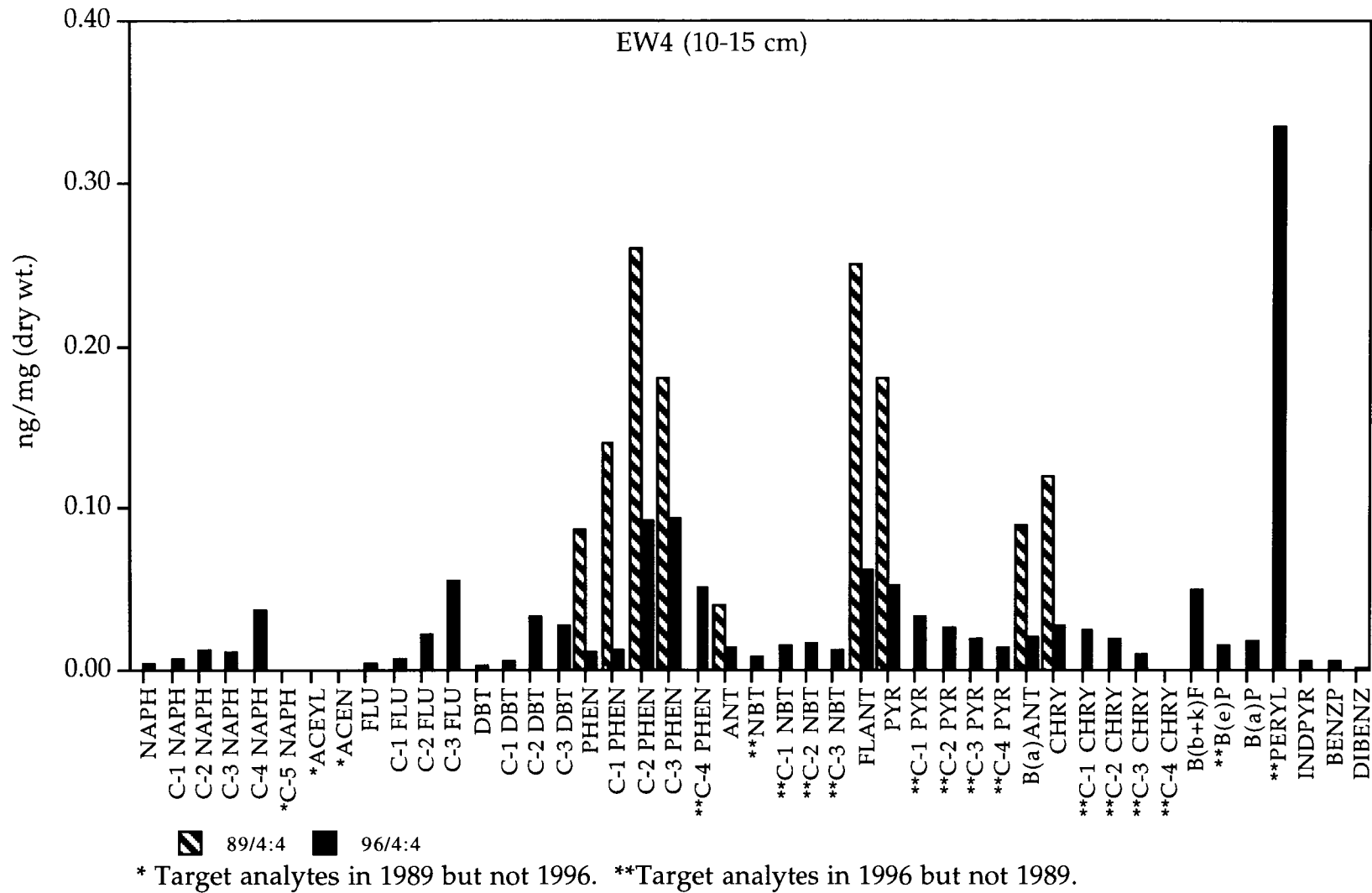


Figure 35. Comparison of AH concentration profile between the 1989 and 1996 cores at station EW4 (15-20 cm).

Table 2. Results of general linear model analysis variance of 1996 benthic community data ( $n = 5$ ) and comparison of means by Duncan's multiple range test ( $\alpha = 0.05$ ). Number of species and abundance data are  $\ln(x+1)$  transformed; diversity and evenness data are not transformed.

<b>Species</b>	$p < 0.0002^*$	<u>3.5</u>	<u>12</u>	<u>4</u>	<u>5</u>
<b>Individuals</b>	$p < 0.0002^*$	<u>4</u>	<u>3.5</u>	<u>12</u>	<u>5</u>
<b>H'</b>	$p < 0.0006^*$	<u>12</u>	<u>3.5</u>	<u>4</u>	<u>5</u>
<b>J'</b>	$p < 0.0079^*$	<u>12</u>	<u>3.5</u>	<u>5</u>	<u>4</u>

----- increasing means ----->

With the data combined for stations along the canal sampled in 1996 and 1989, station EW5 was again much more diverse than the other stations (Table 3, Figure 36). Station EW4 (1989) was less diverse than the other stations which were intermediate. There were significant differences among stations with regard to number of individuals for all station/dates combined (Table 3). Station EW5 (1996) had the most individuals, and Station EW4 (1989) had the least individuals (Figure 37). Otherwise, there was considerable overlap in abundance of organisms for the remaining stations sampled in either 1996 or 1989. The only station that was sampled in both 1989 and 1996 was station EW4 which had significantly fewer number of species and individuals in 1989 than in 1996 (Table 3).

A comparison of the infauna collected at station EW4 1989 versus 1996 is provided in Table 4. Differences are not due to technique (same laboratory methods and quality control) nor taxonomy (same taxonomist). Since only three replicate samples were taken at EW4 in 1989, the methods of Gaufin et al. (1956) were used to determine the average number of species yielded by three samples out of a total of five replicates taken in 1996. The calculated average of 27.6 species may be compared to the 10 species collected in 1989. The community in 1989 was represented by several species characterized as opportunists. These species were also present in 1996, even in moderate to high abundance, but many other species (including many higher order taxa) characteristic of a less stressed community (Pearson and Rosenberg 1978) were also present.

Table 3. Results of general linear model analysis variance of 1989 and 1996 benthic community data ( $n = 3$  for 1989 and 5 for 1996) and comparison of means by Duncan's multiple range test ( $\alpha = 0.05$ ). Number of species and abundance data are  $\ln(x+1)$  transformed; diversity and evenness data are not transformed.

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<b>Species</b>	$p < 0.0001^*$	<u>'89-4</u>	<u>'89-3</u>	<u>'96-3.5</u>	<u>'96-12</u>	<u>'96-4</u>	<u>'89-2</u>	<u>'96-5</u>
<b>Individuals</b>	$p < 0.0001^*$	<u>'89-4</u>	'89-2	'96-4	'96-3.5	'89-3	<u>'96-12</u>	<u>'96-5</u>
<b>H'</b>	$p < 0.0004^*$	'96-12	'89-4	'89-3	'96-3.5	<u>'96-4</u>	<u>'89-2</u>	<u>'96-5</u>
<b>J'</b>	$p < 0.0072^*$	<u>'96-12</u>	<u>'89-3</u>	<u>'96-3.5</u>	'96-5	'96-4	'89-2	'89-4

----- increasing means ----->

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Although there was a relationship between the concentrations of alkylated PAH and total hydrocarbons and low diversity and abundance of infauna for those stations sampled in the Pelican Island facility canal in 1989, this relationship was not apparent in 1996. For the 1996 samples, there did not appear to be any relationship between the TTAH concentration and the number of species or the number of individuals. A comparison of the benthic community data for station EW4 for both years (Figure 36) and the TTAH for the same station/date (Figures 31-35) revealed that:

- the same pattern of relative concentration of TTAH (where there was overlap between years) was similar for 1989 and 1996.
- the concentrations of TTAH in 1989 (where there was overlap between years) were higher than in 1996, particularly for the petroleum-derived TTAH and particularly in the upper portions of the core.
- the benthic fauna were more diverse and more abundant in 1996 compared to 1989 corresponding to the pattern of reduction in TTAH concentrations noted above.

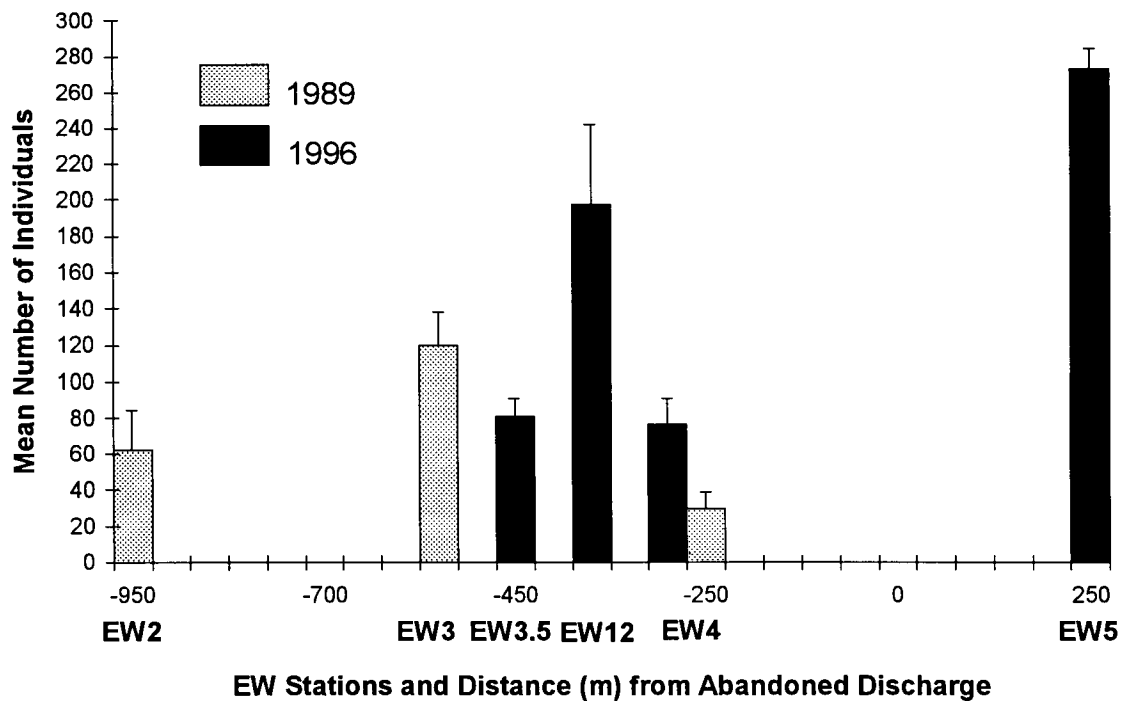
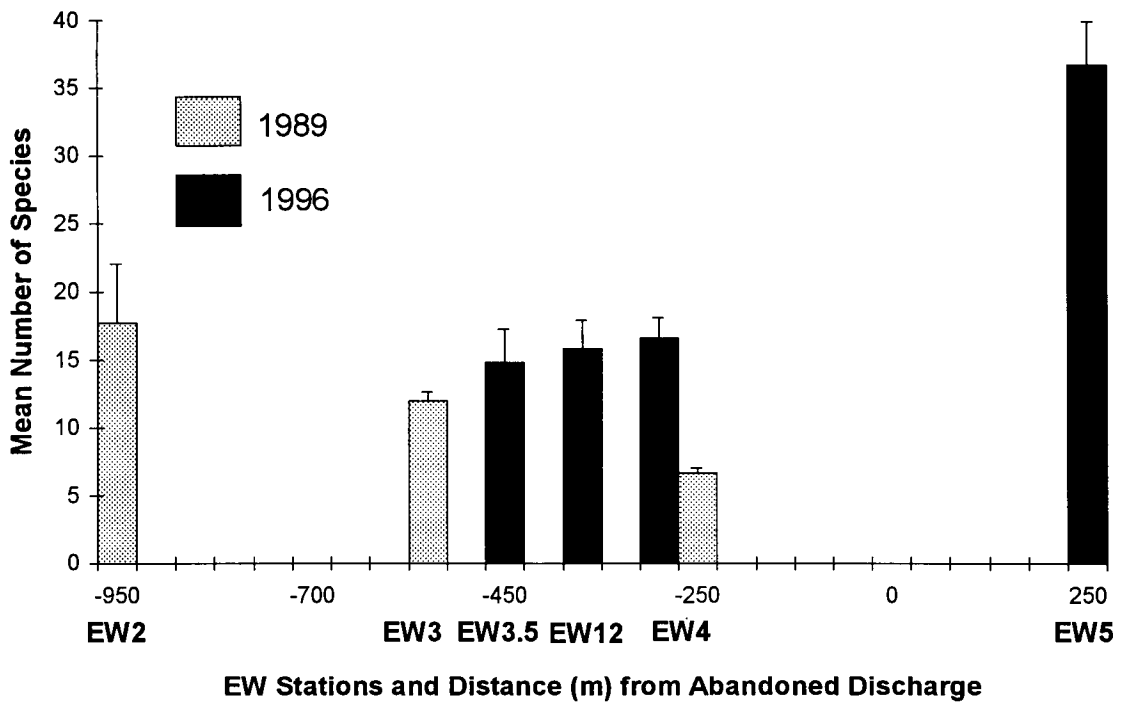


Figure 36. Comparison of mean number of species and mean number of individuals of macroinfauna from Empire Waterway Pelican Island facility in 1989 and 1996.



Table 4. Comparison of taxa for station EW4 in 1989 versus 1996.

Empire Waterway 1989 Station EW4	Empire Waterway 1996 Station EW4
Nemertea	Platyhelminthes
cf. <i>Carinomella</i> sp.	<i>Stylochus</i> sp.
Nemertea H	Nemertea
Polychaeta	cf. <i>Carinomella</i> sp.
<i>Mediomastus ambiseta</i>	cf. Cephalothricidae
<i>Parandalia</i> sp. A	Lineidae longgroove
<i>Paraprionospio pinnata</i>	Nemertea H
<i>Sigambra tentaculata</i>	Polychaeta
<i>Streblospio benedicti</i>	<i>Armandia maculata</i>
Oligochaeta	<i>Glycinde solitaria</i>
Tubificidae nc	<i>Malmgreniella taylori</i>
Bivalvia	<i>Mediomastus</i> sp. A
<i>Mulinia lateralis</i>	<i>Neanthes micromma</i>
Amphipoda	<i>Ophiodromus</i> sp. B
Amphilochidae A	<i>Parandalia</i> sp. A
	<i>Paraprionospio pinnata</i>
	<i>Phyllodoce arenae</i>
	<i>Prionospio perkinsi</i>
	<i>Sigambra bassi</i>
	<i>Sigambra tentaculata</i>
	<i>Streblospio benedicti</i>
	Oligochaeta
	Tubificidae nc
	<i>Tubificoides</i> wc
	Bivalvia
	<i>Mulinia lateralis</i>
	<i>Petricola pholadiformis</i>
	Semelidae
	Gastropoda
	<i>Acteocina canaliculata</i>
	Hydrobiidae C
	Hydrobiidae D
	<i>Texadina barretti</i>
	<i>Texadina sphinctostoma</i>
	Cumacea
	<i>Cyclaspis varians</i>
	Isopoda
	<i>Edotea montosa</i>
	Decapoda
	<i>Ogyrides alphaerostris</i>
	Ophiuroidea
	<i>Hemipholis elongata</i>
	<i>Microphiopholis atra</i>
	Ophiuroidea C

## DISCUSSION

### Temporal and Physical Setting

Sediment and benthos samples were collected from the canal adjacent to the Pelican Island produced water discharge that had been discontinued for two years (Rabalais et al. 1991) and again after a total of nine years (this study). Limited samples were collected from the West Delta 30 Terminal discharge site at an estimated four years after the discharge ended. Hydrocarbon contamination at the West Delta 30 Terminal was minimal in the adjacent canal in 1989, as was the case in 1996. Contaminant signals of a produced water effluent remained at the Pelican Island facility two years after continuation of the discharge, along with isolated effects on the benthic community. Between 1989 and 1996, all structures associated with the Pelican Island facility had been removed, including those along the waterway, and the wetlands were restored. A pipeline relay station was situated at the end of the access canal near station EW5, and another at the West Delta 30 Terminal.

Shear velocity values calculated from previous current meter profiles taken near EW9 in 1989 established a clear potential for sediment entrainment in that canal during both flood and ebb tides. The ebb current moving past station EW5 in November 1996 was also probably sufficient to entrain sediments. The Empire Waterway study site was designated by Rabalais et al. (1991) as an environment in which the potential for dilution of produced water discharges would be medium, based on the bed shear stress calculations and the high percentage silt sediment and accumulated hydrocarbons.

### Contaminants

Petrogenic source hydrocarbons were present in the canal adjacent to the discontinued produced water discharge from the Pelican Island Terminal two years after cessation of the effluent. Concentrations were highest at the station closest to the discharge point. Total hydrocarbons and alkylated PAH were more concentrated in deeper sections of vertical sediment cores. These data support a conclusion of accumulation and subsequent persistence of produced water-associated hydrocarbons for at least two years after the effluent was stopped.

Re-examination of sediments nine years post-discharge (1996) indicated that hydrocarbons in sediment cores exhibited a wide range of AH pollution with respect to both concentration and source. Concentration of AH was minimal at EW8.5 consistent with previous observations (Rabalais et al. 1991). Improvements in analytical methods between 1989 and 1996 reduced detection limits and expanded the source characterization and fingerprinting capability. An increase in the concentration of AH for the 1996 study is due, in part, to a wider range of target analytes.

Concentrations of overlapping TTAH at two stations (EW3 and EW4) sampled in both years provided a mixed signal. EW3 showed a strong signature of relatively fresh low-sulfur

petroleum compositionally dissimilar to the 1989 data for the same location. The source of petroleum detected at EW3 for 1996 was characteristically similar to produced water discharges characterized in the 1989 study. In addition, a slight increase in Zn in the EW3 1996 vertical profile was observed to correlate with AH concentration. This finding suggests a possible connection to past produced water contamination. Petroleum-source pollution was reduced at the station closest to the abandoned discharge (EW4) compared to 1989 values. Creosote contamination was high and accounted for additional AH content. The high concentrations of creosote in the 1996 sediment cores compared to the 1989 sediment cores is likely due to possible contamination from placement of creosote pilings during the initial building of the facility or in subsequent deterioration. Patchiness in the either the distribution of creosote-contaminated wood chips or the deployment of the box corer would be a reasonable explanation for differences between sample dates.

Heavily degraded petroleum characterized sections of the vertical profiles from station EW4 in 1989. This same signature was present in 1996 but with lower concentrations. These similarities/changes are consistent with weathering of the contaminants and no new inputs. The higher AH concentrations in vertical cores for station EW3, however, indicated a buried fresh oil signature that was not as degraded as the petroleum contamination at EW4.

Reduced concentrations of AH in the upper layers of the sediments may be explained by resuspension and advection of sediments from the area, movement of cleaner sediments into the area, or a combination of both. The potential for entrainment was established with current meter measurements in 1989, and observations of strong ebb current during sampling in November 1996. The lower concentrations of AH with depth for the EW4 cores indicates weathering, so this may be case for surface sediments as well. The nine-year post-discharge samples for EW4 matched what would be expected from weathering and/or entrainment or accumulation of surface sediments. The high concentration of petroleum-source AH at depth in the EW3 core was not expected and cannot be explained by any of the mechanisms discussed above.

None of the metals appeared to be of any environmental significance. Selected metals, however, were used as source indicators. Zn has been shown to correlate to some degree with produced water contamination of sediments (Neff et al. 1987, Rabalais et al. 1991). A similar correlation was observed in the 1996 survey, especially for vertical profiles of station EW3.

## **Benthos**

Two years following cessation of the produced water discharge, there were effects of petroleum-derived hydrocarbons on benthic abundance and species numbers at one station adjacent to the Pelican Island facility. Nine years following the cessation of the discharge, there were significantly different numbers of species and individuals at the four stations sampled. These differences, however, did not appear to be related to any differences in the contaminant concentrations in the surface sediments (0-2 cm and 2-5 cm) or with greater depth where there was still a pattern of contaminants similar to the two-year post-discharge samples.

The numbers of individuals and species at station EW4 which were affected by the petroleum-derived hydrocarbon contamination in the two-year post-discharge samples were significantly greater in the nine-year post-discharge samples. These results are consistent with the reduction in concentration of TTAH that overlapped between the two sampling events—the two-year post-discharge and the nine-year post-discharge. The differences in benthic abundance and diversity between nine-year post-discharge and two-year are real. The same laboratory techniques were used, and the same taxonomist identified the organisms.

Unfortunately, there are only two points (collection dates) on this temporal recovery response trajectory curve. Thus, we do not know the manner in which the benthic community has changed over the years, or whether it will continue to progress from a community that was stressed (contaminant effects) to one that is not (lesser contaminant signal). Either of stations EW2 or EW5 might serve as a “reference” station; however, both vary from the series in the canal adjacent to the Pelican Island facility (EW3, EW3.5, EW4, EW12) in depth, possibly currents, activity in the overlying water column (e.g., vessel traffic), and sediment grain size composition.

### **Re-examination of Hypotheses and Predictions**

In the development of the proposal for this research project we hypothesized that:

H<sub>0</sub>: Produced water origin contaminants would not be present in surface or in vertically accreted sediments after nine years.

H<sub>0</sub>: There would be no differences in the benthic infauna with distance from the historical point of produced water origin contaminant signal.

We predicted lower concentrations of hydrocarbons in the surficial sediments, with possibly no benthic impacts. We predicted, however, that there would still be contaminants at depth. We based these predictions on our previous results from a discontinued discharge and other current discharges (Rabalais et al. 1991).

The first null hypothesis was rejected, because hydrocarbon contaminants were still present at depth in cores taken from areas closest to the abandoned discharge point. The surface sediment contaminant levels, however, were reduced compared to the two-year post-discharge samples. The second null hypothesis was also rejected, because there were significant differences in the benthic community parameters with distance from the historical discharge point. These differences, however, were not related to hydrocarbon contamination in the surface sediments. In fact, the number of species and total abundance of individuals in the sediments collected from the station most affected previously, were significantly higher than the two-year post-discharge samples and similar to adjacent stations in the canal.

## Applicability to Other Sites and Management Concerns

The level of contaminants at the Pelican Island discontinued discharge two-years post-discharge were several orders of magnitude lower than the concentrations of contaminants at an active produced water discharge site at Pass Fourchon (Rabalais et al. 1991). The Pass Fourchon site, however, had a total combined effluent of > 50,000 bbl d<sup>-1</sup> in 1989 compared to the historic discharge rate of the Pelican Island facility of 12,000 to 15,000 bbl d<sup>-1</sup>. Contaminated surficial and vertical sediments at Pass Fourchon had alkylated PAH at levels of 20,000 to 30,000 ppb compared to similar samples at the discontinued discharge (300 ppb surficial, but up to 1,500 to 2,000 ppb at depth).

Because of these differences, we would predict that the persistence of contaminated sediments and benthic impacts will be less severe at the Pelican Island facility, two-years post-discharge and nine-years post-discharge than other more severely impacted environments. Other produced water discharge sites in coastal Louisiana received higher volume effluents and potentially more toxic effluents than the Pelican Island facility. These other sites were also areas where highly contaminated sediments and benthic impacts were documented during the period of discharge (Boesch and Rabalais 1989b, St. Pe' 1990, American Petroleum Institute 1991, Rabalais et al. 1991). Such an environment is exemplified by the OCS/state produced water discharge site at Pass Fourchon (Rabalais et al. 1991).

Our results document the decrease in surface sediment contamination but the persistence of accumulated contaminants in a dredged canal with a medium potential for dilution (Rabalais et al. 1991) nine years after the cessation of a medium-sized effluent (of unknown characterization). These results are transferable to similar sites, but not to sites with high contaminant levels, for example the Pass Fourchon site. Other studies will be necessary for sites with low to medium dilution potential and/or evidence of high sediment contamination and benthic impacts. These will need to be conducted over a series of years post-discharge. Our completed research is a preliminary examination of a good candidate abandoned discharge site because of the previous two-year post-discharge study. Similar studies are justified for other sites because of the differences in effluents, receiving environments, documented contaminant levels, and variable time since discontinuation of the discharge.

Additional OCS and non-OCS produced water discharge facilities are located within Louisiana state waters that will eventually dispose of produced waters by alternative technologies, or dismantle the facility. In either case, contaminated sediments will remain in the receiving environment and become a reservoir for continued dispersal under natural events (resuspension and transport) or human activities (dredging). Knowing the extent, concentration, and persistence of produced water origin contaminants will aid resource managers in decisions concerning restoration/recovery of contaminated sites, impacts of dredging activities, or potential beneficial uses of dredged materials in wetland restoration programs (e.g., Coastal Wetland Protection, Preservation and Recovery Act, CWPPRA).

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## **APPENDICES**



Appendix 1. Hydrographic data for Empire Waterway samples, 13 November 1996.

Date	Time	Temp	pH	SpCond	Salin	DO	DO	Depth
MMDDYY	HHMMSS	degC	units	mS/cm	ppt	%Sat	mg/l	meters
Annotation at 111396 092645 : EW8.5								
11/13/96	8:28:05	17.73	7.82	36.1	22.8	90.8	7.63	1.9
11/13/96	8:28:33	17.71	7.83	35.9	22.7	91	7.65	1.4
11/13/96	8:29:16	17.71	7.83	35.9	22.7	90.6	7.63	1.1
11/13/96	8:29:41	17.69	7.84	35.8	22.6	90.7	7.64	0.8
11/13/96	8:30:02	17.69	7.84	35	22	90.2	7.63	0.3
Annotation at 111396 112527 : EW11								
11/13/96	10:29:06	18.41	7.95	35.3	22.2	100	8.32	2.9
11/13/96	10:29:14	18.4	7.96	35.3	22.2	100	8.32	2.5
11/13/96	10:29:22	18.4	7.96	35.1	22.1	99.8	8.32	1.9
11/13/96	10:29:29	18.36	7.96	35	22	99.6	8.31	1.6
11/13/96	10:29:36	18.35	7.97	34.8	21.9	99.3	8.29	1.2
11/13/96	10:29:43	18.33	7.98	34.4	21.6	99.3	8.31	1.0
11/13/96	10:29:53	18.33	7.98	34.4	21.6	99.5	8.32	0.4
Annotation at 111396 141737 : EW3.5								
11/13/96	13:21:49	21.21	7.82	46.1	29.9	54.7	4.12	3.9
11/13/96	13:22:00	21.12	7.82	45.8	29.7	55	4.15	3.5
11/13/96	13:22:21	20.32	7.86	42.6	27.5	66.8	5.19	2.9
11/13/96	13:22:49	20.46	7.86	43.9	28.4	72.1	5.55	2.6
11/13/96	13:22:58	20.4	7.87	43.1	27.8	66.3	5.13	2.0
11/13/96	13:23:34	19.19	7.89	39	24.9	84.1	6.78	1.5
11/13/96	13:23:41	19.05	7.90	38.4	24.4	87	7.06	1.1
11/13/96	13:23:55	19.07	7.90	38.4	24.4	89	7.21	0.4

Appendix 2. Sediment grain size analysis.

Sample ID	% Sand	% Silt	% Clay	Sand:Mud	% Organic
EW3.5A	12.55	78.01	9.44	0.14	9.70
EW3.5C	5.18	86.54	8.28	0.05	6.45
EW4A	8.05	82.85	9.10	0.09	8.78
EW4C	9.74	83.46	6.80	0.11	10.57
EW5A	25.15	70.10	2.75	0.37	5.35
EW5C	34.61	61.75	3.64	0.53	6.50
EW12A	2.24	89.64	8.12	0.02	10.19
EW12C	13.22	81.09	5.69	0.15	8.92

Appendix 3. Hydrocarbon data for Empire Waterway, 13 November 1996.

MS FILE:	HP7092F	HP7097C	HP7097E	HP7092E	MEAN
LAB ID:	N6319-04:01	N6319-04:02	N6319-04:03	N6319-04:04	N6319-04:05M
SAMPLE NAME:	EW3	EW3	EW3	EW3	EW3
% Water	58.3	61.0	56.9	46.6	43.7
COMP./Conc.:	ng/mg (dry)	ng/mg (dry)	ng/mg (dry)	ng/mg (dry)	ng/mg (dry)
NAPH	0.0035	0.0024	0.0042	0.0047	0.0068
C-1 NAPH	0.0100	0.0061	0.0126	0.0099	0.0175
C-2 NAPH	0.0538	0.0311	0.0676	0.0256	0.0417
C-3 NAPH	0.0307	0.0427	0.1081	0.0317	0.0420
C-4 NAPH	0.0254	0.0244	0.0847	0.0450	0.0511
FLU	0.0151	0.0022	0.0050	0.0034	0.0061
C-1 FLU	0.0277	0.0049	0.0166	0.0094	0.0153
C-2 FLU	0.0570	0.0102	0.0358	0.0282	0.0362
C-3 FLU	0.0721	0.0075	0.0358	0.0672	0.0906
DBT	0.0132	0.0012	0.0023	0.0022	0.0037
C-1 DBT	0.0141	0.0021	0.0059	0.0041	0.0051
C-2 DBT	0.0341	0.0047	0.0142	0.0233	0.0258
C-3 DBT	0.0300	0.0037	0.0121	0.0490	0.0534
PHEN	0.1600	0.0055	0.0109	0.0166	0.0187
C-1 PHEN	0.2450	0.0131	0.0344	0.0319	0.0507
C-2 PHEN	0.3000	0.0118	0.0414	0.0900	0.1168
C-3 PHEN	0.1850	0.0050	0.0336	0.1439	0.1861
C-4 PHEN	0.0495	nd	nd	0.0945	0.1211
ANT	0.1275	0.0016	0.0023	0.0185	0.0425
NBT	0.1090	0.0006	0.0009	0.0123	0.0283
C-1 NBT	0.0954	0.0024	0.0085	0.0319	0.0536
C-2 NBT	0.0454	nd	0.0026	0.0384	0.0584
C-3 NBT	0.0200	nd	nd	0.0298	0.0498
FLANT	0.6105	0.0064	0.0076	0.0778	0.1056
PYR	0.5536	0.0054	0.0068	0.0842	0.1058
C-1 PYR	0.3756	0.0036	0.0046	0.0555	0.0942
C-2 PYR	0.1819	0.0079	0.0081	0.0514	0.0688
C-3 PYR	0.0811	0.0013	0.0017	0.0431	0.0503
C-4 PYR	0.0336	0.0020	0.0019	0.0267	0.0354
B(a)ANT	0.6252	0.0025	0.0019	0.0424	0.0637
CHRY	0.5372	0.0035	0.0032	0.0470	0.0956
C-1 CHRY	0.3110	0.0044	0.0054	0.0529	0.0646
C-2 CHRY	0.1131	nd	nd	0.0411	0.0505
C-3 CHRY	0.0339	nd	nd	0.0167	0.0332
C-4 CHRY	0.0082	nd	nd	nd	0.0202
B(b+k)F	1.5873	0.0069	0.0061	0.1139	0.1167
B(e)P	0.3611	0.0036	0.0023	0.0424	0.0437
B(a)P	0.5782	0.0034	0.0020	0.0498	0.0451
PERYL	0.2103	0.1113	0.1909	0.5205	0.5269
INDPYR	0.1047	0.0006	0.0005	0.0076	0.0187
BENZP	0.0774	0.0008	0.0011	0.0078	0.0220
DIBENZ	0.0283	0.0002	nd	0.0015	0.0034
TTAH	8.1355	0.3468	0.7838	2.0940	2.6857

Note, all values valid to two significant figures only.

## Appendix 3. Continued.

MS FILE:	HP7141E	MEAN	MEAN	MEAN	HP7093F
LAB ID:	N6319-05:01	N6319-05:02M	N6319-05:03M	N6319-05:04M	N6319-05:05
SAMPLE NAME:	EW3.5	EW3.5	EW3.5	EW3.5	EW3.5
% Water	64.2	48.7	43.2	42.4	42.1
COMP./Conc.:	ng/mg (dry)	ng/mg (dry)	ng/mg (dry)	ng/mg (dry)	ng/mg (dry)
NAPH	0.0076	0.0016	0.0110	0.0009	0.0014
C-1 NAPH	0.0185	0.0026	0.0020	0.0017	0.0021
C-2 NAPH	0.0388	0.0081	0.0036	0.0034	0.0052
C-3 NAPH	0.0388	0.0071	0.0056	0.0040	0.0062
C-4 NAPH	0.0169	0.0101	0.0105	0.0078	0.0080
FLU	0.0083	0.0016	0.0164	0.0009	0.0012
C-1 FLU	0.0106	0.0039	0.0037	0.0028	0.0039
C-2 FLU	0.0134	0.0102	0.0092	0.0075	0.0096
C-3 FLU	0.0157	0.0115	0.0098	0.0062	0.0077
DBT	0.0105	0.0009	0.0153	0.0006	0.0008
C-1 DBT	0.0214	0.0021	0.0017	0.0013	0.0017
C-2 DBT	0.0162	0.0056	0.0062	0.0034	0.0043
C-3 DBT	0.0123	0.0059	0.0058	0.0030	0.0039
PHEN	0.0334	0.0034	0.0163	0.0017	0.0023
C-1 PHEN	0.0282	0.0083	0.0054	0.0039	0.0092
C-2 PHEN	0.0359	0.0139	0.0138	0.0075	0.0092
C-3 PHEN	0.0282	0.0139	0.0131	0.0059	0.0069
C-4 PHEN	0.0113	0.0032	0.0051	nd	0.0042
ANT	0.0217	0.0020	0.0144	0.0004	0.0006
NBT	0.0063	0.0012	0.0007	nd	0.0004
C-1 NBT	0.0140	0.0058	0.0020	nd	0.0019
C-2 NBT	0.0174	0.0067	0.0008	nd	nd
C-3 NBT	0.0117	0.0061	nd	nd	nd
FLANT	0.0683	0.0040	0.0120	0.0023	0.0016
PYR	0.0555	0.0044	0.0124	0.0023	0.0018
C-1 PYR	0.0299	0.0048	0.0053	0.0034	0.0030
C-2 PYR	0.0277	0.0067	0.0057	0.0056	0.0019
C-3 PYR	0.0198	0.0049	0.0033	0.0020	0.0019
C-4 PYR	0.0147	0.0046	0.0022	0.0024	0.0029
B(a)ANT	0.0297	0.0022	0.0115	0.0007	0.0008
CHRY	0.0321	0.0046	0.0043	0.0016	0.0020
C-1 CHRY	0.0294	0.0074	0.0029	0.0058	0.0061
C-2 CHRY	0.0262	0.0061	0.0006	0.0007	0.0026
C-3 CHRY	0.0166	0.0032	nd	nd	nd
C-4 CHRY	nd	nd	nd	nd	nd
B(b+k)F	0.0916	0.0083	0.0369	0.0012	0.0040
B(e)P	0.0300	0.0029	0.0139	0.0020	0.0020
B(a)P	0.0329	0.0025	0.0123	0.0015	0.0015
PERYL	0.1850	0.3376	0.3894	0.3525	0.4272
INDPYR	0.0085	0.0014	0.0071	0.0009	0.0008
BENZP	0.0118	0.0025	0.0090	0.0016	0.0012
DIBENZ	0.0023	0.0002	0.0059	0.0001	0.0002
TTAH	1.1493	0.5440	0.7072	0.4497	0.5521

Appendix 3. Continued.

MS FILE:	MEAN	STDEV	MEAN	STDEV	MEAN
LAB ID:	xx:01	xx:01	xx:02	xx:02	xx:03
SAMPLE NAME:	EW4	EW4	EW4	EW4	EW4
% Water	59.7533	1.9782	58.7600	4.4877	48.4433
COMP./Conc.:	ng/mg (dry)	ng/mg (dry)	ng/mg (dry)	ng/mg (dry)	ng/mg (dry)
NAPH	0.0043	0.0026	0.0056	0.0017	1.1695
C-1 NAPH	0.0096	0.0065	0.0082	0.0005	1.1363
C-2 NAPH	0.0139	0.0097	0.0158	0.0079	2.2017
C-3 NAPH	0.0148	0.0105	0.0190	0.0059	1.8862
C-4 NAPH	0.0082	0.0056	0.0133	0.0074	0.7616
FLU	0.0029	0.0017	0.0035	0.0006	9.2917
C-1 FLU	0.0042	0.0035	0.0054	0.0018	2.1065
C-2 FLU	0.0095	0.0068	0.0137	0.0106	1.3324
C-3 FLU	0.0125	0.0096	0.0211	0.0136	1.0037
DBT	0.0020	0.0013	0.0021	0.0004	3.2368
C-1 DBT	0.0047	0.0039	0.0031	0.0005	0.7599
C-2 DBT	0.0065	0.0047	0.0125	0.0074	0.7353
C-3 DBT	0.0070	0.0055	0.0081	0.0034	0.3571
PHEN	0.0149	0.0091	0.0138	0.0065	46.7496
C-1 PHEN	0.0181	0.0119	0.0183	0.0061	11.2528
C-2 PHEN	0.0204	0.0150	0.0300	0.0126	6.2712
C-3 PHEN	0.0167	0.0140	0.0274	0.0121	2.5272
C-4 PHEN	0.0083	0.0089	0.0091	0.0088	0.4436
ANT	0.0056	0.0036	0.0093	0.0030	14.1670
NBT	0.0024	0.0018	0.0038	0.0010	1.7863
C-1 NBT	0.0062	0.0054	0.0076	0.0024	1.2758
C-2 NBT	0.0083	0.0076	0.0077	0.0030	0.5139
C-3 NBT	0.0074	0.0073	0.0060	0.0013	0.2511
FLANT	0.0187	0.0099	0.0309	0.0277	25.3400
PYR	0.0166	0.0090	0.0254	0.0210	18.5303
C-1 PYR	0.0107	0.0056	0.0150	0.0085	8.0441
C-2 PYR	0.0107	0.0061	0.0126	0.0034	3.3856
C-3 PYR	0.0070	0.0043	0.0065	0.0011	1.3070
C-4 PYR	0.0058	0.0042	0.0058	0.0011	0.7191
B(a)ANT	0.0078	0.0034	0.0108	0.0033	9.7102
CHRY	0.0119	0.0061	0.0146	0.0025	8.5494
C-1 CHRY	0.0097	0.0055	0.0101	0.0016	5.2605
C-2 CHRY	0.0078	0.0050	0.0067	0.0017	2.1349
C-3 CHRY	0.0059	0.0036	0.0036	0.0019	0.9046
C-4 CHRY	0.0031	0.0054	nd	nd	0.2487
B(b+k)F	0.0180	0.0100	0.0299	0.0054	12.6593
B(e)P	0.0076	0.0040	0.0097	0.0010	4.0941
B(a)P	0.0085	0.0036	0.0108	0.0009	7.5234
PERYL	0.0454	0.0332	0.0641	0.0275	2.0151
INDPYR	0.0063	0.0034	0.0199	0.0254	3.5711
BENZP	0.0080	0.0044	0.0273	0.0368	2.8145
DIBENZ	0.0012	0.0005	0.0010	0.0001	0.4660
TTAH	0.4190	0.2838	0.5689	0.2895	228.4953

Appendix 3. Continued.

MS FILE:	STDEV	MEAN	STDEV	MEAN	STDEV
LAB ID:	xx:03	xx:04	xx:04	xx:05	xx:05
SAMPLE NAME:	EW4	EW4	EW4	EW4	EW4
% Water	9.4985	48.3267	3.2366	46.8950	1.4354
COMP./Conc.:	ng/mg (dry)	ng/mg (dry)	ng/mg (dry)	ng/mg (dry)	ng/mg (dry)
NAPH	2.0172	0.0033	0.0027	0.0049	0.0036
C-1 NAPH	1.9541	0.0064	0.0043	0.0074	0.0052
C-2 NAPH	3.7860	0.0113	0.0060	0.0164	0.0056
C-3 NAPH	3.2329	0.0102	0.0072	0.0395	0.0162
C-4 NAPH	1.2686	0.0373	0.0319	0.1105	0.0055
FLU	16.0573	0.0042	0.0250	0.0079	0.0006
C-1 FLU	3.6309	0.0067	0.0045	0.0162	0.0052
C-2 FLU	2.2715	0.0216	0.0197	0.0652	0.0130
C-3 FLU	1.6681	0.0548	0.0712	0.1487	0.0965
DBT	5.5656	0.0029	0.0147	0.0060	0.0004
C-1 DBT	1.2946	0.0055	0.0045	0.0125	0.0003
C-2 DBT	1.2229	0.0326	0.0408	0.0809	0.0363
C-3 DBT	0.5834	0.0267	0.0325	0.0705	0.0509
PHEN	80.2679	0.0104	0.0063	0.0222	0.0067
C-1 PHEN	19.4368	0.0124	0.0062	0.0479	0.0096
C-2 PHEN	10.6695	0.0913	0.1235	0.2163	0.1581
C-3 PHEN	4.2515	0.0927	0.1312	0.2308	0.2472
C-4 PHEN	0.7229	0.0508	0.0767	0.1201	0.1523
ANT	24.5183	0.0138	0.0134	0.0322	0.0100
NBT	3.0096	0.0072	0.0082	0.0178	0.0073
C-1 NBT	2.1497	0.0150	0.0199	0.0286	0.0292
C-2 NBT	0.8567	0.0156	0.0219	0.0338	0.0392
C-3 NBT	0.4149	0.0124	0.0173	0.0219	0.0269
FLANT	43.4551	0.0617	0.0734	0.1564	0.0873
PYR	31.7324	0.0515	0.0513	0.1480	0.1084
C-1 PYR	13.7574	0.0323	0.0330	0.0829	0.0626
C-2 PYR	5.7033	0.0260	0.0298	0.0581	0.0556
C-3 PYR	2.2070	0.0187	0.0243	0.0411	0.0529
C-4 PYR	1.2193	0.0131	0.0163	0.0310	0.0366
B(a)ANT	16.6660	0.0196	0.0218	0.0341	0.0429
CHRY	14.5609	0.0271	0.0296	0.0661	0.0345
C-1 CHRY	9.0106	0.0241	0.0269	0.0518	0.0441
C-2 CHRY	3.6423	0.0182	0.0218	0.0393	0.0458
C-3 CHRY	1.5422	0.0090	0.0115	0.0225	0.0269
C-4 CHRY	0.4307	nd	0.0026	0.0143	0.0203
B(b+k)F	21.5175	0.0492	0.0649	0.0977	0.0755
B(e)P	6.9455	0.0150	0.0156	0.0289	0.0224
B(a)P	12.8443	0.0173	0.0185	0.0326	0.0209
PERYL	3.1668	0.3343	0.3888	0.7928	0.5156
INDPYR	6.1167	0.0050	0.0065	0.0087	0.0044
BENZP	4.8086	0.0055	0.0004	0.0081	0.0033
DIBENZ	0.7902	0.0012	0.0024	0.0020	0.0014
TTAH	390.9675	1.2738	1.5290	3.0746	2.1872

Appendix 3. Continued.

MS FILE:	MEAN	HP7122D	HP7128D	MEAN (n=3)	MEAN
LAB ID:	N6319-09:01M	N6319-09:02	N6319-09:03	N6319-10:01M	N6319-10:02M
SAMPLE NAME:	EW5	EW5	EW5	EW8.5	EW8.5
% Water	42.9	40.4	36.8	64.5	63.1
COMP./Conc.:	ng/mg (dry)	ng/mg (dry)	ng/mg (dry)	ng/mg (dry)	ng/mg (dry)
NAPH	0.0061	0.0064	0.0086	0.0024	0.0048
C-1 NAPH	0.0080	0.0068	0.0153	0.0045	0.0088
C-2 NAPH	0.0660	0.0469	0.0632	0.0072	0.0138
C-3 NAPH	0.0663	0.0682	0.0767	0.0069	0.0152
C-4 NAPH	0.0456	0.0682	0.0307	0.0046	0.0083
FLU	0.0704	0.1083	0.1448	0.0020	0.0054
C-1 FLU	0.0483	0.1083	0.0525	0.0019	0.0041
C-2 FLU	0.0588	0.1483	0.0332	0.0032	0.0051
C-3 FLU	0.0690	0.2167	0.0344	0.0039	0.0078
DBT	0.0370	0.1078	0.0753	0.0012	0.0032
C-1 DBT	0.0288	0.0912	0.0233	0.0013	0.0024
C-2 DBT	0.0514	0.1700	0.0260	0.0025	0.0060
C-3 DBT	0.0248	0.0788	0.0219	0.0025	0.0069
PHEN	0.6339	1.8905	1.2947	0.0113	0.0199
C-1 PHEN	0.3166	1.4755	0.4417	0.0114	0.0163
C-2 PHEN	0.2672	1.3833	0.2133	0.0094	0.0161
C-3 PHEN	0.1058	0.7839	0.1447	0.0062	0.0143
C-4 PHEN	0.0246	0.2075	0.0099	0.0008	0.0084
ANT	0.2312	0.7950	0.0657	0.0058	0.0092
NBT	0.0558	0.4105	0.4041	0.0025	0.0029
C-1 NBT	0.0378	0.3400	0.0664	0.0030	0.0075
C-2 NBT	0.0227	0.2073	0.0432	0.0029	0.0076
C-3 NBT	0.0141	0.1078	0.0466	0.0023	0.0075
FLANT	1.7604	2.7678	0.7119	0.0235	0.0213
PYR	1.1465	1.8318	0.5721	0.0196	0.0202
C-1 PYR	0.5094	1.5570	0.3366	0.0093	0.0134
C-2 PYR	0.1633	0.5862	0.1414	0.0081	0.0138
C-3 PYR	0.0730	0.2931	0.0606	0.0037	0.0083
C-4 PYR	0.0374	0.1117	0.0337	0.0023	nd
B(a)ANT	0.5314	2.1812	0.5343	0.0080	0.0126
CHRY	0.4266	1.7110	0.4035	0.0155	0.0140
C-1 CHRY	0.2028	0.1813	0.2440	0.0068	0.0130
C-2 CHRY	0.0979	0.4341	0.1361	0.0040	0.0135
C-3 CHRY	0.0422	0.1634	0.0657	0.0028	0.0068
C-4 CHRY	0.0080	nd	0.0244	nd	nd
B(b+k)F	0.8226	3.7420	0.8278	0.0226	0.0334
B(e)P	0.2875	1.1480	0.2676	0.0081	0.0138
B(a)P	0.4142	1.8220	0.4349	0.0086	0.0155
PERYL	0.1842	0.4365	0.1658	0.0188	0.0787
INDPYR	0.1218	0.2452	0.1356	0.0049	0.0052
BENZP	0.0829	0.1758	0.0851	0.0047	0.0048
DIBENZ	0.0168	0.0407	0.0173	0.0010	0.0010
TTAH	9.2191	28.2565	8.5345	0.2716	0.4909

Appendix 3. Continued.

MS FILE:	MEAN	MEAN	HP7134C	HP7136F	MEAN
LAB ID:	N6319-10:03M	N6319-10:04M	N6319-10:05	N6319-10:06	xx:01
SAMPLE NAME:	EW8.5	EW8.5	EW8.5	EW8.5	EW12
% Water	62.5	65.0	66.4	54.0	59.9
COMP./Conc.:	ng/mg (dry)	ng/mg (dry)	ng/mg (dry)	ng/mg (dry)	ng/mg (dry)
NAPH	0.0046	0.0036	0.0068	0.0029	0.0055
C-1 NAPH	0.0070	0.0080	0.0133	0.0068	0.0106
C-2 NAPH	0.0128	0.0297	0.0266	0.0152	0.0170
C-3 NAPH	0.0112	0.0137	0.0217	0.0158	0.0191
C-4 NAPH	0.0061	0.0080	0.0121	0.0090	0.0110
FLU	0.0075	0.0035	0.0045	0.0046	0.0036
C-1 FLU	0.0034	0.0048	0.0058	0.0038	0.0047
C-2 FLU	0.0061	0.0046	0.0081	0.0063	0.0074
C-3 FLU	0.0079	0.0058	0.0103	0.0067	0.0103
DBT	0.0022	0.0023	0.0050	0.0030	0.0032
C-1 DBT	0.0017	0.0014	0.0161	0.0064	0.0027
C-2 DBT	0.0034	0.0035	0.0101	0.0069	0.0067
C-3 DBT	0.0040	0.0038	0.0095	0.0063	0.0073
PHEN	0.0258	0.0141	0.0308	0.0205	0.0225
C-1 PHEN	0.0153	0.0170	0.0220	0.0230	0.0224
C-2 PHEN	0.0140	0.0120	0.0286	0.0205	0.0231
C-3 PHEN	0.0104	0.0103	0.0204	0.0148	0.0229
C-4 PHEN	0.0014	0.0039	0.0106	0.0090	0.0091
ANT	0.0315	0.0071	0.0128	0.0099	0.0083
NBT	0.0021	0.0022	0.0038	0.0041	0.0037
C-1 NBT	0.0050	0.0052	0.0085	0.0068	0.0080
C-2 NBT	0.0039	0.0051	0.0123	0.0073	0.0093
C-3 NBT	0.0033	0.0040	0.0075	0.0053	0.0062
FLANT	0.0178	0.0228	0.0212	0.0197	0.0290
PYR	0.0163	0.0215	0.0193	0.0162	0.0247
C-1 PYR	0.0108	0.0133	0.0110	0.0118	0.0163
C-2 PYR	0.0099	0.0145	0.0119	0.0101	0.0168
C-3 PYR	0.0048	0.0092	0.0055	0.0051	0.0103
C-4 PYR	0.0031	0.0037	0.0035	0.0047	0.0077
B(a)ANT	0.0102	0.0116	0.0109	0.0118	0.0141
CHRY	0.0144	0.0143	0.0159	0.0165	0.0243
C-1 CHRY	0.0115	0.0105	0.0122	0.0097	0.0142
C-2 CHRY	0.0075	0.0086	0.0102	0.0058	0.0155
C-3 CHRY	0.0050	0.0051	0.0054	0.0042	0.0083
C-4 CHRY	nd	nd	nd	nd	nd
B(b+k)F	0.0287	0.0311	0.0295	0.0388	0.0483
B(e)P	0.0102	0.0116	0.0127	0.0136	0.0172
B(a)P	0.0121	0.0115	0.0147	0.0158	0.0178
PERYL	0.0467	0.0611	0.0757	0.0838	0.0977
INDPYR	0.0054	0.0048	0.0072	0.0050	0.0098
BENZP	0.0037	0.0053	0.0068	0.0029	0.0099
DIBENZ	0.0009	0.0011	0.0017	0.0010	0.0019
TTAH	0.4095	0.4355	0.5824	0.4916	0.6283



Appendix 3. Continued.

MS FILE:	MEAN	MEAN	MEAN	MEAN	MEAN
LAB ID:	xx:02	xx:03	xx:04	xx:05	xx:06
SAMPLE NAME:	EW12	EW12	EW12	EW12	EW12
% Water	62.0	62.7	60.5	57.1	51.8
COMP./Conc.:	ng/mg (dry)	ng/mg (dry)	ng/mg (dry)	ng/mg (dry)	ng/mg (dry)
NAPH	0.0046	0.0047	0.0130	0.0051	0.0036
C-1 NAPH	0.0105	0.0105	0.0132	0.0083	0.0084
C-2 NAPH	0.0215	0.0186	0.0464	0.0204	0.0162
C-3 NAPH	0.0166	0.0181	0.0315	0.0218	0.0176
C-4 NAPH	0.0088	0.0105	0.0175	0.0210	0.0176
FLU	0.0043	0.0033	0.0313	0.0031	0.0030
C-1 FLU	0.0036	0.0043	0.0131	0.0055	0.0053
C-2 FLU	0.0049	0.0056	0.0165	0.0093	0.0132
C-3 FLU	0.0070	0.0113	0.0278	0.0132	0.0180
DBT	0.0028	0.0035	0.0256	0.0025	0.0029
C-1 DBT	0.0057	0.0031	0.0159	0.0034	0.0045
C-2 DBT	0.0071	0.0113	0.0431	0.0121	0.0188
C-3 DBT	0.0064	0.0109	0.0336	0.0107	0.0232
PHEN	0.0175	0.0217	0.0947	0.0177	0.0157
C-1 PHEN	0.0195	0.0233	0.1213	0.0250	0.0266
C-2 PHEN	0.0214	0.0322	0.1330	0.0354	0.0399
C-3 PHEN	0.0175	0.0297	0.0803	0.0323	0.0508
C-4 PHEN	0.0059	0.0070	0.0380	0.0156	0.0218
ANT	0.0064	0.0099	0.0624	0.0058	0.0133
NBT	0.0030	0.0042	0.0337	0.0023	0.0059
C-1 NBT	0.0079	0.0118	0.0342	0.0071	0.0122
C-2 NBT	0.0080	0.0163	0.0394	0.0069	0.0133
C-3 NBT	0.0053	0.0129	0.0283	0.0065	0.0144
FLANT	0.0154	0.0149	0.2760	0.0226	0.0380
PYR	0.0148	0.0157	0.1854	0.0209	0.0479
C-1 PYR	0.0097	0.0117	0.1525	0.0149	0.0271
C-2 PYR	0.0092	0.0123	0.0802	0.0141	0.0198
C-3 PYR	0.0052	0.0086	0.0588	0.0078	0.0130
C-4 PYR	0.0037	0.0061	0.0380	0.0064	0.0115
B(a)ANT	0.0093	0.0109	0.1933	0.0128	0.0178
CHRY	0.0135	0.0151	0.2242	0.0152	0.0207
C-1 CHRY	0.0102	0.0126	0.0923	0.0144	0.0195
C-2 CHRY	0.0083	0.0130	0.0668	0.0127	0.0183
C-3 CHRY	0.0050	0.0102	0.0385	0.0095	0.0107
C-4 CHRY	nd	nd	0.0086	nd	nd
B(b+k)F	0.0304	0.0265	0.2679	0.0377	0.0624
B(e)P	0.0125	0.0114	0.0856	0.0141	0.0211
B(a)P	0.0144	0.0130	0.1324	0.0143	0.0214
PERYL	0.0725	0.0692	0.1412	0.0973	0.2851
INDPYR	0.0074	0.0068	0.0493	0.0059	0.0155
BENZP	0.0062	0.0068	0.0375	0.0051	0.0135
DIBENZ	0.0014	0.0011	0.0145	0.0010	0.0034
TTAH	0.4653	0.5506	3.1366	0.6177	1.0332

Appendix 3. Continued.

MS FILE:	MEAN	STDEV	STERR	MEAN	HP7225G
LAB ID:	NSC Ref	NSC Ref	NSC Ref	N7212-01	N6239-01
SAMPLE NAME:	REF	REF	REF	Verm16 Ref	G.House
% Water	na	na	na	(SLA #1)	(SLA #2)
COMP./Conc.:	ng/mg	ng/mg	ng/mg	ng/mg	ng/mg
NAPH	933.5857	239.1623	173.3625	2669.9643	560.9608
C-1 NAPH	1870.4743	493.9190	347.3384	2248.3910	1094.5576
C-2 NAPH	2203.8271	689.7329	409.2404	1826.8177	1505.0167
C-3 NAPH	1498.7598	514.6175	278.3127	1152.3004	1121.9216
C-4 NAPH	706.8185	277.1141	131.2529	519.9404	560.9608
FLU	102.4350	61.2908	19.0217	27.4023	44.4664
C-1 FLU	191.0298	95.5970	35.4733	45.6704	129.8419
C-2 FLU	279.2634	125.3669	51.8579	51.1509	231.2253
C-3 FLU	251.2671	110.8475	46.6591	36.5364	213.4387
DBT	317.9358	69.7975	59.0392	10.6657	62.9291
C-1 DBT	535.4259	119.9916	99.4261	12.7047	190.6941
C-2 DBT	748.3452	158.4791	138.9642	20.3902	400.4577
C-3 DBT	570.9809	122.5046	106.0285	13.3321	343.2494
PHEN	433.1263	93.8434	80.4295	64.3077	173.5317
C-1 PHEN	840.4729	182.3144	156.0719	86.2664	457.6659
C-2 PHEN	902.7898	182.1905	167.6439	65.8762	533.9436
C-3 PHEN	660.5814	157.5913	122.6669	45.4859	400.4577
C-4 PHEN	274.8525	90.0887	51.0388	nd	190.6941
ANT	nd	nd	nd	9.0972	nd
NBT	53.8549	18.6543	10.0006	nd	12.7765
C-1 NBT	217.5830	71.0475	40.4042	nd	68.6499
C-2 NBT	292.8847	96.8546	54.3873	nd	110.6026
C-3 NBT	237.4463	83.4309	44.0927	nd	97.2540
FLANT	5.8186	2.4352	1.0805	1.7223	2.7679
PYR	11.3477	3.7425	2.1072	2.9524	7.1966
C-1 PYR	71.0441	21.3342	13.1926	8.7343	40.1346
C-2 PYR	128.5061	38.8795	23.8630	7.5041	73.3495
C-3 PYR	140.4789	41.3796	26.0863	4.7977	87.1890
C-4 PYR	105.9487	32.9397	19.6742	2.0913	67.8137
B(a)ANT	10.0302	17.3559	1.8626	0.8216	4.2013
CHRY	53.0198	18.7926	9.8455	0.8496	20.5863
C-1 CHRY	101.4567	25.7878	18.8400	1.9606	57.3475
C-2 CHRY	142.9178	35.9541	26.5392	4.0519	80.8747
C-3 CHRY	113.8696	31.1429	21.1451	3.5291	61.7589
C-4 CHRY	11.9692	28.1744	2.2226	nd	35.2908
B(b+k)F	9.0542	3.5368	1.6813	nd	4.6134
B(e)P	12.5319	4.5529	2.3271	nd	5.8671
B(a)P	4.7839	5.0886	0.8884	nd	2.0387
PERYL	1.7002	2.8546	0.3157	nd	32.5950
INDPYR	1.8647	2.6359	0.3463	nd	nd
BENZP	4.6846	4.4671	0.8699	nd	nd
DIBENZ	1.3809	2.1111	0.2564	nd	nd
TTAH	15056.1483	4377.6018	2795.8566	8945.3146	9088.9210

## Appendix 3. Continued.

MS FILE:	HP7226A	MEAN	SD	HP7255E	HP7234C
LAB ID:	N7142-01	na	na	N7247-04	SWP Creosote
SAMPLE NAME:	L. Barre Ref	SLA M(n=3)	SLA M(n=3)	Creosote	Creosote
% Water	(SLA #3)	na	na	na	na
COMP./Conc.:	ng/mg	ng/mg	ng/mg	ng/mg	ng/mg
NAPH	356.3066	1195.7439	1280.8065	6.5740	67338.5558
C-1 NAPH	793.0695	1378.6727	768.1349	101.5986	25858.0054
C-2 NAPH	1080.4135	1470.7493	374.3802	370.5361	11851.5858
C-3 NAPH	896.5133	1056.9118	139.7371	197.2208	4040.3133
C-4 NAPH	459.7504	513.5505	50.9068	33.4678	888.8689
FLU	21.2400	31.0362	12.0320	988.8207	23237.9234
C-1 FLU	76.1102	83.8742	42.6195	144.5199	2896.7822
C-2 FLU	152.2203	144.8655	90.2622	nd	986.8159
C-3 FLU	159.3004	136.4252	90.6425	nd	604.8227
DBT	75.0726	49.5558	34.2228	382.3558	8562.4060
C-1 DBT	256.8273	153.4087	126.2601	54.6223	1556.8011
C-2 DBT	572.9225	331.2568	282.6916	28.9498	817.3206
C-3 DBT	493.8987	283.4934	245.7929	11.4707	284.1162
PHEN	97.5707	111.8033	55.9857	9285.7836	80867.1675
C-1 PHEN	298.6858	280.8727	186.3394	1365.5564	14335.5433
C-2 PHEN	378.3354	326.0517	238.3736	322.2713	4778.5144
C-3 PHEN	298.6858	248.2098	182.7898	81.9334	1433.5543
C-4 PHEN	14.1378	68.2773	106.2515	13.1093	312.4413
ANT	nd	3.0324	5.2523	229.4135	8951.6062
NBT	11.2609	8.0125	6.9803	65.5467	2724.4019
C-1 NBT	63.2190	43.9563	38.1640	15.8405	895.1606
C-2 NBT	122.4869	77.6965	67.5490	5.4622	307.4682
C-3 NBT	136.3160	77.8567	70.1976	nd	116.7601
FLANT	2.2027	2.2309	0.5234	6226.9373	43826.2488
PYR	3.0127	4.3872	2.4331	3453.1198	30678.3741
C-1 PYR	18.3384	22.4024	16.0898	503.8158	13147.8746
C-2 PYR	27.5076	36.1204	33.7571	566.0852	3371.2499
C-3 PYR	36.6767	42.8878	41.5453	84.9128	7416.7498
C-4 PYR	28.8174	32.9075	33.0515	nd	155.0775
B(a)ANT	1.8608	2.2945	1.7311	211.6288	11956.6997
CHRY	9.8037	10.4132	9.8825	768.1341	9608.0622
C-1 CHRY	30.3024	29.8702	27.6960	94.0572	4117.7410
C-2 CHRY	51.6923	45.5397	38.7792	21.9467	1052.3116
C-3 CHRY	53.4748	39.5876	31.5011	nd	160.1344
C-4 CHRY	26.7374	20.6761	18.4096	nd	nd
B(b+k)F	1.1950	1.9361	2.3944	459.3985	7659.7607
B(e)P	1.8565	2.5745	2.9987	114.8496	2352.6408
B(a)P	0.4986	0.8458	1.0627	62.0188	4445.3968
PERYL	23.6652	18.7534	16.8435	13.1930	1084.4814
INDPYR	nd	nd	nd	31.4000	2544.1348
BENZP	nd	nd	nd	24.6544	1827.8974
DIBENZ	nd	nd	nd	nd	683.9072
TTAH	7131.9860	8388.7405	4775.0714	26341.2053	409735.6782

Appendix 3. Continued.

MS FILE:	HP7234D	HP7238D	HP7234E	HP7233D	HP7237C
LAB ID:	N7233-02	N7233-03	N7233-05	N7233-01	N7233-04
SAMPLE NAME:	Creosote	Creosote	Creosote	Creosote	Creosote
% Water	na	na	na	na	na
COMP./Conc.:	ng/mg	ng/mg	ng/mg	ng/mg	ng/mg
NAPH	846.7560	3357.7534	198.4766	2664.2124	557.0209
C-1 NAPH	629.6391	1984.1270	88.5098	732.6584	458.7231
C-2 NAPH	143.2972	946.2759	72.4171	216.4673	524.2550
C-3 NAPH	30.3964	335.7753	59.0065	63.2750	311.2764
C-4 NAPH	3.6910	68.6813	34.8675	12.9880	88.4680
FLU	410.5484	3607.5036	120.4514	938.8941	275.6193
C-1 FLU	33.3571	561.1672	31.6977	91.2814	699.6491
C-2 FLU	nd	360.7504	41.2070	nd	424.0298
C-3 FLU	nd	nd	nd	nd	nd
DBT	184.6629	2028.7795	55.5487	565.3329	1570.1906
C-1 DBT	28.5388	368.8690	53.3268	74.0781	224.3129
C-2 DBT	21.8238	158.6137	175.5340	27.2919	138.3263
C-3 DBT	14.1015	40.5756	213.3071	5.2634	31.7777
PHEN	3012.4302	24099.4419	923.3431	7212.8676	20705.8096
C-1 PHEN	317.0979	4303.4718	335.7611	740.7810	4486.2588
C-2 PHEN	91.9584	206.5666	419.7014	161.8022	1207.8389
C-3 PHEN	36.4663	344.2777	356.7462	37.0390	310.5871
C-4 PHEN	9.8300	46.4775	115.4179	nd	465.8807
ANT	94.0102	1428.7526	157.7584	232.3063	931.7614
NBT	82.2589	959.0594	266.6339	169.5999	429.9331
C-1 NBT	25.1813	221.3214	186.6437	17.7398	121.5028
C-2 NBT	20.1450	55.3304	191.0876	4.2887	28.0391
C-3 NBT	10.5761	nd	131.0950	nd	nd
FLANT	2773.0021	15272.5564	2602.5505	5233.2794	12086.5632
PYR	1611.8074	10220.8647	1861.8246	2887.3266	8527.9758
C-1 PYR	207.9752	2349.6241	600.5886	342.8700	2842.6586
C-2 PYR	242.6377	2114.6617	800.7848	415.0532	1484.4995
C-3 PYR	38.1288	352.4436	240.2354	41.5053	268.4733
C-4 PYR	nd	nd	nd	nd	nd
B(a)ANT	81.2259	1469.5830	405.7309	181.3602	1815.3118
CHRY	682.1090	3289.4737	1358.4742	787.4527	2560.0551
C-1 CHRY	61.1546	610.9023	326.0338	61.5197	628.3772
C-2 CHRY	18.3464	156.6416	165.7338	9.8432	121.0208
C-3 CHRY	nd	nd	nd	nd	nd
C-4 CHRY	nd	nd	nd	nd	nd
B(b+k)F	378.4562	3424.6575	nd	447.8030	1716.0501
B(e)P	102.4058	1137.1049	218.3009	121.7926	415.1093
B(a)P	47.3070	750.1631	161.4517	52.4769	468.8294
PERYL	5.9631	143.1018	27.2876	9.1596	84.6626
INDPYR	32.3914	580.4833	103.6929	38.8507	202.6296
BENZP	22.7681	345.6564	66.9787	23.3368	122.6169
DIBENZ	3.8263	107.3431	24.1609	5.4329	53.6707
TTAH	12356.2713	87808.8324	13192.3679	24627.2303	67389.7647

Appendix 3. Continued.

MS FILE:	HP7255D	HP7258C	HP7258D
LAB ID:	Creosote #A	N7247-02	N7247-03
SAMPLE NAME:	Creosote	Creosote	Creosote
% Water	na	na	na
COMP./Conc.:	ng/mg	ng/mg	ng/mg
NAPH	8818.3422	133.9286	355.1136
C-1 NAPH	3086.4198	36.4583	866.4773
C-2 NAPH	815.6966	27.5298	681.8182
C-3 NAPH	220.4586	17.1131	255.6818
C-4 NAPH	28.6596	nd	28.4091
FLU	3928.1706	635.3775	1459.7039
C-1 FLU	392.8171	139.9984	226.1513
C-2 FLU	476.9921	107.6911	nd
C-3 FLU	5.4489	nd	nd
DBT	1902.6187	492.1737	754.2999
C-1 DBT	24.5499	110.0915	132.3583
C-2 DBT	94.1080	64.7597	62.6211
C-3 DBT	20.4583	233.1349	25.6177
PHEN	3273.3224	9066.3580	14232.0736
C-1 PHEN	34779.0507	1554.2328	2419.4525
C-2 PHEN	777.4141	466.2698	626.2112
C-3 PHEN	184.1244	123.0434	142.3207
C-4 PHEN	nd	24.6087	24.1945
ANT	1718.4943	841.8761	327.3377
NBT	756.9558	582.8373	156.5528
C-1 NBT	130.9329	90.6636	39.8498
C-2 NBT	26.5957	27.8467	15.6553
C-3 NBT	nd	nd	nd
FLANT	25510.2041	9729.8535	9609.6612
PYR	15109.8901	6295.7875	5397.2070
C-1 PYR	2158.5557	1774.2674	789.8352
C-2 PYR	2747.2527	1144.6886	1303.2280
C-3 PYR	333.5950	177.4267	210.6227
C-4 PYR	nd	nd	nd
B(a)ANT	1412.8728	744.0476	239.5833
CHRY	5162.4200	4525.6505	1534.8859
C-1 CHRY	516.2420	299.1532	176.4237
C-2 CHRY	111.3996	69.0353	45.8702
C-3 CHRY	nd	nd	nd
C-4 CHRY	nd	nd	nd
B(b+k)F	3597.5929	1477.9491	1064.4055
B(e)P	1019.3180	430.5993	268.7327
B(a)P	569.6189	227.5827	99.5617
PERYL	116.2299	40.2499	19.0968
INDPYR	279.8128	158.0131	64.0994
BENZP	222.4512	115.8763	42.7329
DIBENZ	39.8084	23.5615	nd
TTAH	120368.8947	42009.7354	43697.8466

Appendix 4. Trace metal data for Empire Waterway, 13 November 1996.

Sample ID	Station	mid- depth cm	Sample Weight g	Sample inal Vol ml	Cu ppm, dry weight	Zn ppm, dry weight	Cd ppm, dry weight	Pb ppm, dry weight	Cr ppm, dry weight	Ni ppm, dry weight
4:01	EW3	1.0	1.006	35	22.9	94.7	1.97	0	32.8	18.4
4:02	EW3	3.5	1.003	35	21.6	79.2	2.19	0	35.8	20.8
4:03	EW3	7.5	1.004	35	19.3	82.4	2.21	0	37.6	20.5
4:04	EW3	12.5	1.001	35	24	131.2	2.6	0	46.7	23.6
4:05	EW3	17.5	1.003	35	23	117.4	2.54	0	46.5	24
5:01	EW3.5	1.0	1.006	35	26.3	102.4	2.35	0	34.2	23.4
5:02	EW3.5	3.5	1.009	35	18.3	82.2	2.17	0	33.3	21.7
5:03	EW3.5	7.5	1.005	35	19.3	78.4	2.08	0	29	21.1
5:04	EW3.5	12.5	1.002	35	21.9	76.3	2.68	0	30.2	21.9
5:05	EW3.5	17.5	1.001	35	19.2	77.1	2.1	0	27.8	21.4
6:01	EW4a	1.0	1	35	23.7	104.1	2.47	0	37.7	24.4
6:02	EW4a	3.5	1.002	35	20.2	86.8	2.22	0	28.7	20.2
6:03	EW4a	7.5	1.004	35	23.1	81.4	2.32	0	30.7	20.7
6:04	EW4a	12.5	1.004	35	21.2	106.4	2.3	0	36.2	24.7
6:05	EW4a	17.5	1.001	35	21.6	93.4	2.4	0	40.9	25.2
7:01	EW4b	1.0	1.003	35	22.1	106	2.54	0	40.8	23.9
7:02	EW4b	3.5	1.004	35	20.7	109.3	2.13	0	26.4	19.5
7:03	EW4b	7.5	1	35	22.6	89.7	2.09	0	31.4	23.1
7:04	EW4b	12.5	1.002	35	22.9	100	2.36	0	37.1	25.7
8:01	EW4c	1.0	1.003	35	19.4	91.4	2.22	0	34.9	21.1
8:02	EW4c	3.5	1.005	35	27.1	107.3	2.59	0	40.5	24.7
8:03	EW4c	7.5	1	35	23.8	150.5	2.47	0	39.7	24
8:04	EW4c	12.5	1	35	24.4	419.8	2.57	0	33.8	23.8
8:05	EW4c	17.5	1.001	35	24.6	208.7	2.45	0	33.7	23.5
9:01	EW5	1.0	1	35	9.7	83.5	1.55	0	19.5	14.2
9:02	EW5	3.5	1.004	35	11.3	93.4	1.33	2.65	15.3	12.1
9:03	EW5	7.5	1.003	35	8.8	56	1.05	14.7	13.3	10.2
10:01	EW8.5	1.0	1.007	39	27.6	118.9	2.7	0	37.8	25.2
10:02	EW8.5	3.5	1.005	39	25.1	104.4	2.58	0	35.1	24.9
10:03	EW8.5	7.5	1.003	39	26.6	118.8	2.91	0	46.5	27
10:04	EW8.5	12.5	1.004	39	30.3	141.5	2.85	0	41.1	26.9
10:05	EW8.5	17.5	1	39	26.5	147	2.7	0	39.1	25.4
10:06	EW8.5	22.5	1.002	32.9	32	126.4	2.97	0	42	28.5
11:01	EW12a	1.0	1.001	32.9	22.5	115.1	2.47	0	35.6	24
11:02	EW12a	3.5	1	32.9	25.4	116.5	2.69	0	33.8	24.7
11:03	EW!2a	7.5	1.001	32.9	23.3	105.6	2.34	0	33.3	22.9
11:04	EW12a	12.5	1.003	32.9	18.9	85.2	2	0	30.1	19
11:05	EW12a	17.5	1.002	32.9	23.7	114.6	2.6	0	38.8	25.8
12:01	EW12b	1.0	1	35	27.2	168.1	2.65	0	39.1	26
12:02	EW12b	3.5	1.001	35	23.8	109.8	2.45	0	36	24
12:03	EW12b	7.5	1.002	35	24.3	128.5	2.39	0	33.9	23.6
12:04	EW12b	12.5	1.005	35	26.9	131	2.91	0	44.1	27.4
12:05	EW12b	17.5	1.002	35	20.8	102.5	2.21	0	30.8	21.9
12:06	EW12b	22.5	1.004	35	23	121.3	2.42	0	35.8	24.9

just below detection limits (=0); just above detection limits (+.001); below linear range (-0.1); above linear range (+1)

## Appendix 4. Continued.

Station	mid- depth cm	As ppm, dry weight	Fe ppm, dry weight	Mn ppm, dry weight	Ca ppm, dry weight	Mg ppm, dry weight	P ppm, dry weight	Al ppm, dry weight	K ppm, dry weight	Na ppm, dry weight
EW3	1.0	82.2	23256	367	16497	8241	432	33119	9213	10632
EW3	3.5	59.3	26322	427	8552	11292	378	37996	8309	17832
EW3	7.5	125	23704	434	7892	10242	1107	33712	5334	16029
EW3	12.5	139.7	27506	431	6076	10008	358	40194	5497	7420
EW3	17.5	98.7	28924	446	6391	10215	363	43059	5866	7398
EW3.5	1.0	71.8	28757	484	9352	9878	510	35647	1564	13840
EW3.5	3.5	106.1	23077	464	8246	9127	392	28781	3663	6788
EW3.5	7.5	70.9	23586	412	7635	9098	369	26701	5025	7529
EW3.5	12.5	28.3	24823	385	8186	9617	346	32811	6417	7206
EW3.5	17.5	75.4	21352	382	7930	8554	367	23878	3262	8930
EW4a	1.0	115.2	27188	448	5611	9107	477	32428	4326	8036
EW4a	3.5	68.9	25813	412	16365	8986	431	26466	5407	15076
EW4a	7.5	60.3	26047	364	6598	9319	312	31845	8677	10542
EW4a	12.5	99.4	24839	603	6696	9634	360	30820	3772	7432
EW4a	17.5	113	26962	423	6630	10294	360	34261	4465	6066
EW4b	1.0	120	27810	510	6290	9600	487	35687	4659	8242
EW4b	3.5	60.1	25901	418	18726	8821	488	24107	5428	16883
EW4b	7.5	85.3	22579	464	17192	9482	376	29782	5625	7896
EW4b	12.5	115.9	24243	583	8472	9917	440	33530	3954	7024
EW4c	1.0	112.1	24270	433	6385	8178	481	30125	3999	6204
EW4c	3.5	90.3	30343	573	5952	9910	518	41299	8296	10692
EW4c	7.5	87.3	28665	522	11819	10062	439	40344	7102	9667
EW4c	12.5	69.5	27820	475	5840	9680	388	30223	6111	9163
EW4c	17.5	76.1	27851	461	6139	9891	417	30435	5906	11003
EW5	1.0	38.9	12954	257	38455	6178	378	16508	2436	4956
EW5	3.5	36.1	11584	249	27233	5834	1373	13230	4291	8150
EW5	7.5	38.4	9453	199	21325	4518	296	9164	1493	3849
EW8.5	1.0	85.5	29734	504	6467	10378	523	34891	6309	13338
EW8.5	3.5	97.4	27618	539	6797	9926	543	30690	3819	14242
EW8.5	7.5	118.6	30702	620	6904	10754	556	41072	6155	12209
EW8.5	12.5	85.2	30199	603	5794	10278	525	37491	5675	11933
EW8.5	17.5	107.3	29492	652	5937	11048	557	35405	6517	18139
EW8.5	22.5	92.7	34117	646	6895	11805	607	40847	7358	14437
EW12a	1.0	89.2	26539	542	6100	8434	529	30072	4562	7651
EW12a	3.5	67.9	27401	640	5745	8802	542	30261	5017	9824
EW12a	7.5	82.7	26062	581	5322	8990	499	29914	5863	10899
EW12a	12.5	77.1	21602	348	10112	7873	352	27340	5071	9063
EW12a	17.5	82.7	28153	597	6501	9571	410	33828	5076	9223
EW12b	1.0	86.9	29304	553	5240	9320	541	35780	5600	9643
EW12b	3.5	90.8	28203	587	6202	9435	520	32594	6014	10329
EW12b	7.5	87.1	26774	583	5987	8993	534	30559	5666	9812
EW12b	12.5	116	30577	579	5384	10414	498	38637	6074	10242
EW12b	17.5	73	23598	381	9793	8487	364	26547	4436	9414
EW12b	22.5	83.4	28551	517	7540	9780	384	32445	6149	8095

just below detection limits (=0); just above detection limits (+.001); below linear range (-0.1); above linear range (+1)

Appendix 5. Benthic community parameters for Empire Waterway study site. Number of replicates = 3 for 1989, 5 for 1996. Values are mean  $\pm$  standard error.

Date	Station	Number of Species	Number of Individuals	Diversity (H')	Evenness (J')
11/89	EW2	17.6 $\pm$ 4.3	62.3 $\pm$ 21.7	0.94 $\pm$ 0.12	0.78 $\pm$ 0.07
11/89	EW3	12.0 $\pm$ 0.6	119.3 $\pm$ 18.8	0.75 $\pm$ 0.07	0.69 $\pm$ 0.06
11/89	EW4	6.7 $\pm$ 0.3	29.3 $\pm$ 10.0	0.67 $\pm$ 0.00	0.81 $\pm$ 0.02
11/96	EW3.5	14.8 $\pm$ 2.4	80.6 $\pm$ 10.2	0.82 $\pm$ 0.08	0.71 $\pm$ 0.04
11/96	EW4	16.6 $\pm$ 1.5	76.6 $\pm$ 13.9	0.92 $\pm$ 0.03	0.75 $\pm$ 0.03
11/96	EW5	36.8 $\pm$ 3.2	273.4 $\pm$ 11.3	1.13 $\pm$ 0.08	0.72 $\pm$ 0.04
11/96	EW12	15.8 $\pm$ 2.1	197.8 $\pm$ 44.4	0.63 $\pm$ 0.05	0.54 $\pm$ 0.05



Appendix 6. Species list for stations in Pelican Island canal and adjacent Empire Waterway.

Empire Waterway November 1989 Stations 2, 3, 4	Empire Waterway November 1996 Stations 3.5, 4, 5, 12
Anthozoa	Anthozoa
Thenaria	Thenaria
Nemertea	Platyhelminthes
<i>Cerebratulus lacteus</i>	<i>Stylochus</i> sp.
cf. <i>Carinomella</i> sp.	Nemertea
cf. <i>Zygeupolia</i> sp.	cf. <i>Carinomella</i> sp.
Lineidae unidentified	cf. Cephalothricidae
Nemertea A	Lineidae longgroove
Nemertea H	<i>Lineus socialis</i>
Nemertea unidentified	Nemertea F
Polychaeta	Nemertea G
<i>Ancistrosyllis jonesi</i>	Nemertea H
<i>Ancistrosyllis papillosa</i>	Nemertea I
<i>Cossura delta</i>	Nemertea striped
<i>Magelona</i> sp. H	Nemertea unidentified
<i>Malacoceros vanderhorsti</i>	Polychaeta
<i>Malmgreniella taylori</i>	<i>Apoprionospio pygmaea</i>
<i>Mediomastus ambiseta</i>	<i>Armandia maculata</i>
<i>Mediomastus californiensis</i>	<i>Capitella capitata</i>
<i>Neanthes micromma</i>	<i>Diopatra cuprea</i>
<i>Neanthes succinea</i>	<i>Glycinde solitaria</i>
<i>Parandalia</i> sp. A	<i>Gyptis vittata</i>
<i>Paraprionospio pinnata</i>	<i>Magelona</i> sp. H
<i>Polydora cornuta</i>	<i>Malmgreniella maccrarya</i>
<i>Polydora socialis</i>	<i>Malmgreniella</i> sp. D
<i>Sigambra bassi</i>	<i>Malmgreniella taylori</i>
<i>Sigambra tentaculata</i>	<i>Mediomastus</i> sp. A
<i>Streblospio benedicti</i>	<i>Neanthes micromma</i>
Oligochaeta	<i>Nereis lamellosa</i>
Tubificidae nc	<i>Ophiodromus</i> sp. B
<i>Tubificoides</i> sp. A	<i>Ophiodromus</i> sp. C
Gastropoda	<i>Paramphinome</i> sp. B
<i>Anachis obesa</i>	<i>Parandalia</i> sp. A
<i>Nassarius acutus</i>	<i>Paraprionospio pinnata</i>
Bivalvia	<i>Pectinaria gouldii</i>
Bivalvia G	<i>Phyllodoce arenae</i>
<i>Mulinia lateralis</i>	<i>Podarkeopsis levifuscina</i>
<i>Petricola pholadiformis</i>	<i>Polydora socialis</i>
Bivalvia unidentified	<i>Polygordius</i> sp.
Amphipoda	<i>Prionospio perkinsi</i>
Amphilochidae A	<i>Sigambra bassi</i>
<i>Cerapus</i> sp.	<i>Sigambra tentaculata</i>
Decapoda	<i>Stenoninereis martini</i>
<i>Alpheus</i> sp.	<i>Streblospio benedicti</i>
<i>Callinectes sapidus</i>	Oligochaeta
	Tubificidae cap 2

Appendix 6. Continued.

Empire Waterway November 1989 Stations 2, 3, 4	Empire Waterway November 1996 Stations 3.5, 4, 5, 12
<i>Hexapanopeus angustifrons</i> <i>Trachypenaeus</i> sp. <i>Pagurus</i> sp. <i>Pinnixa</i> sp. <i>Upogebia affinis</i> Xanthidae	Tubificidae nc <i>Tubificoides</i> wc
Phoronida	Gastropoda
<i>Phoronis</i> sp.	<i>Acteocina canaliculata</i>
Ophiuroidea	<i>Anachis obesa</i>
<i>Microphiopholis atra</i>	Caecidae
Ophiuroidea unidentified	<i>Cantharus cancellarius</i>
Vertebrata	<i>Corambe obscura</i>
<i>Myrophis punctatus</i>	Hydrobiidae C
	Hydrobiidae D
	Hydrobiidae unidentified
	<i>Nassarius acutus</i>
	<i>Odostomia</i> sp. A
	<i>Texadina barretti</i>
	<i>Texadina sphinctostoma</i>
	Bivalvia
	<i>Abra aequalis</i>
	Arcidae sp. A
	Bivalvia G
	<i>Mulinia lateralis</i>
	<i>Petricola pholadiformis</i>
	Cumacea
	<i>Cyclaspis varians</i>
	Isopoda
	<i>Edotea montosa</i>
	Amphipoda
	Amphilochidae B
	<i>Cerapus</i> sp. A
	<i>Corophium</i> sp. B
	<i>Corophium louisianum</i>
	<i>Melita</i> sp.
	<i>Monoculodes</i> sp. A
	Decapoda
	<i>Hexapanopeus angustifrons</i>
	<i>Ogyrides alphaeostris</i>
	Paguridae w/o rostrum
	Paguridae w/ rostrum
	<i>Upogebia</i> sp. A
	Phoronida
	<i>Phoronis</i> sp.
	Ophiuroidea
	<i>Hemipholis elongata</i>
	<i>Microphiopholis atra</i>
	Ophiuroidea C
	Hemichordata
	Enteropneusta



### **The Department of the Interior Mission**

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering sound use of our land and water resources; protecting our fish, wildlife, and biological diversity; preserving the environmental and cultural values of our national parks and historical places; and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to ensure that their development is in the best interests of all our people by encouraging stewardship and citizen participation in their care. The Department also has a major responsibility for American Indian reservation communities and for people who live in island territories under U.S. administration.



### **The Minerals Management Service Mission**

As a bureau of the Department of the Interior, the Minerals Management Service's (MMS) primary responsibilities are to manage the mineral resources located on the Nation's Outer Continental Shelf (OCS), collect revenue from the Federal OCS and onshore Federal and Indian lands, and distribute those revenues.

Moreover, in working to meet its responsibilities, the **Offshore Minerals Management Program** administers the OCS competitive leasing program and oversees the safe and environmentally sound exploration and production of our Nation's offshore natural gas, oil and other mineral resources. The **MMS Royalty Management Program** meets its responsibilities by ensuring the efficient, timely and accurate collection and disbursement of revenue from mineral leasing and production due to Indian tribes and allottees, States and the U.S. Treasury.

The MMS strives to fulfill its responsibilities through the general guiding principles of: (1) being responsive to the public's concerns and interests by maintaining a dialogue with all potentially affected parties and (2) carrying out its programs with an emphasis on working to enhance the quality of life for all Americans by lending MMS assistance and expertise to economic development and environmental protection.