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MMS 93-0018

University Research Initiative

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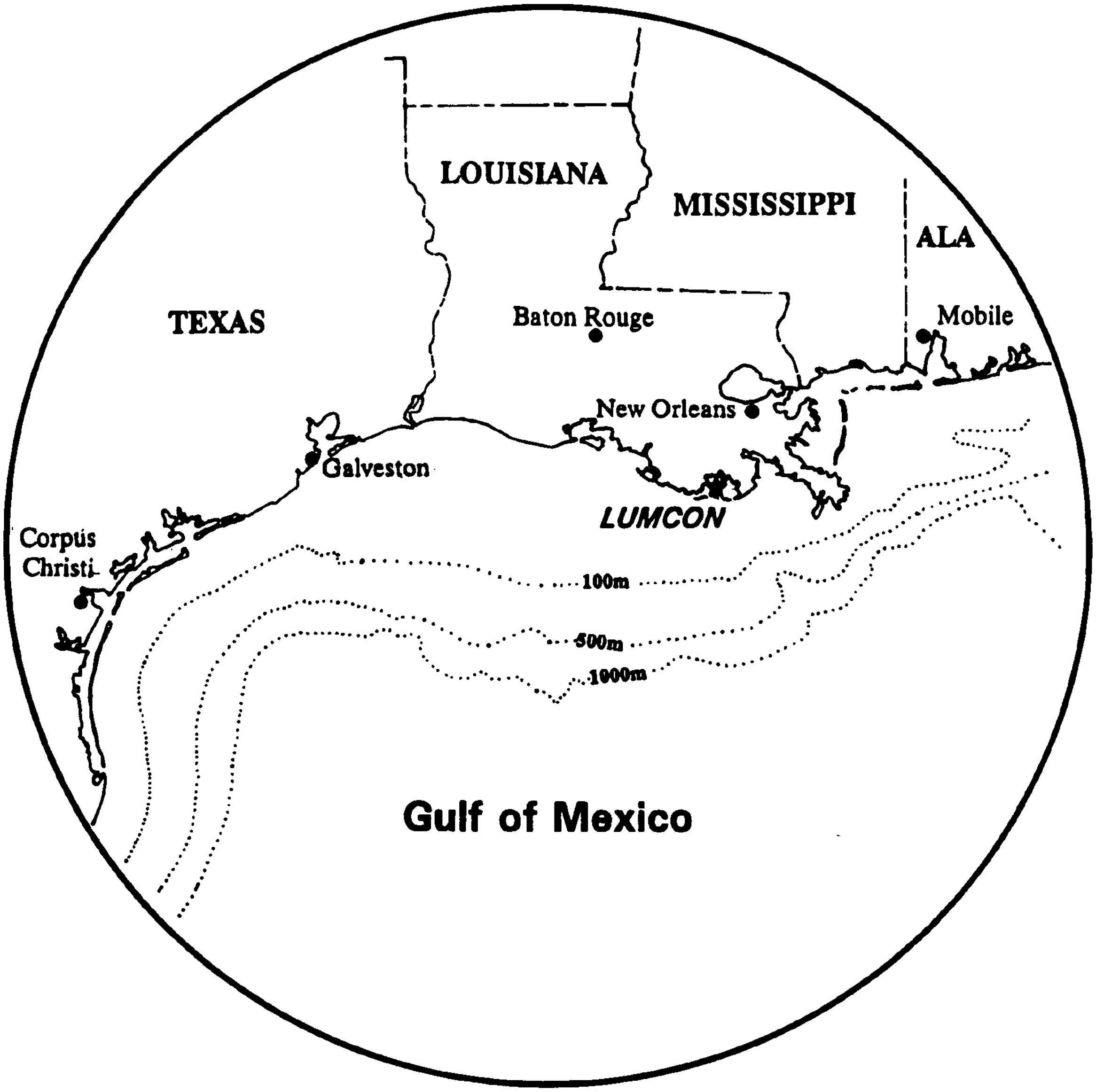

U.S. Department of the Interior
Minerals Management Service
Gulf of Mexico OCS Region

Cooperative Agreement
University Research Initiative
Louisiana Universities Marine Consortium

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Fate and Transport of Particle-Reactive Normal, Alkylated and Heterocyclic Aromatic Hydrocarbons in a Sediment-Water-Colloid System

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ABSTRACT

The overall study framework is designed to investigate the fate, transport and chemical transformations of normal, alkylated and heterocyclic aromatic hydrocarbons associated with spilled oil, operational discharges and produced water discharges in coastal marine and estuarine environmental systems. In the present research, the nature of the particle reactivity or sorption/desorption equilibria which control the fate, transport and chemical transformations of hydrocarbons has been investigated through: 1) studies of the sorption/desorption equilibria and kinetics of selected normal, alkylated and heterocyclic PAH on various sediment types (a range of organic carbon and particle sizes) over a range of salinities; 2) studies of the relationship between the carbon fraction of sediments and the equilibrium K_{OC} (partition coefficient) for selected normal, alkylated and heterocyclic PAH; and 3) study the role of colloidal organic material in the facilitated transport of hydrocarbons through aquatic systems and in mediating the particle reactive nature of selected normal, alkylated and heterocyclic PAH. This information may be used by environmental managers to determine or predict the extent and spatial distribution of hydrocarbon impacts of operational and accidental discharges of hydrocarbons as the result of oil production in marine and estuarine environments.

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Chapter 1

EXECUTIVE SUMMARY

The production of oil and gas reserves is historically and contemporarily one of the major economic resources within the Gulf of Mexico region and specifically within the state of Louisiana. Expansion of the industry throughout the region from the mid-1940s until the mid-1980s in a relatively unregulated environmental milieu has resulted in increasing concern over the potential impacts of long-term discharges of waste materials associated with oil exploration, drilling, and production and refining operations. While the effects of catastrophic spills and releases of oil into coastal and estuarine environments have been recognized for several decades, the potential environmental impacts of chronic discharges of waste streams associated with normal oil and gas operations upon sensitive coastal and estuarine ecosystems have not been extensively investigated or reported.

Produced waters are geologic formation waters present in the permeable subsurface sand and rock formations that are also the source of trapped oil and gas reservoirs. When the oil and/or gas reservoirs are discovered and production begins, large volumes of this formation water are brought to the surface along with crude oil, volatile hydrocarbon condensates or natural gas. This water variously called formation water, produced water or oil field brine is separated from the petroleum or gas phase by a variety of chemical and physical processes. The water may be re-injected into the subsurface or it may be discharged into surface waters. The latter is the practice employed in the majority of cases in the northern Gulf of Mexico. Approximately 95% of the oil and 98% of the gas produced from the OCS in the central and western regions of the Gulf of Mexico yield produced waters discharged to surface waters. The vast majority of the produced water generated by these production activities is separated and discharged at offshore platforms. However, approximately 254,000 barrels per day (1 barrel= 159 liters) of the estimated 1.2 million barrels per day of produced waters generated in the Gulf OCS are piped to shore and separated at facilities located in coastal or estuarine portions of Louisiana and discharged into surface waters there. This volume generated in the OCS represents only 25% of the total produced waters discharged into Louisiana waters and only 13% of the total discharged into surface water environments in the Gulf of Mexico (Rabalais et al., 1991).

Increasing concern over the cumulative potential environmental effects of such discharges into coastal and estuarine environments which serve as a spawning ground for many important economic species of fish and shellfish has developed in the last several years. Since produced waters represent essentially saturated solutions of many dissolved major, minor and trace elements as well as a broad spectrum of hydrocarbons including normal aliphatic, branched-chain and aromatic fractions, there is concern over the localized impacts of these effluents.

The aromatic fraction of the total hydrocarbon load of produced waters are generally the fraction of most environmental concern due to their persistence, relatively high bioaccumulation potential and wide spectrum of toxicological impacts including mutagenesis and carcinogenesis.

In previous studies funded by the Minerals Management Service (MMS), we have been able to characterize the chemical nature of produced water associated contaminants and to document the extent of contamination in sediments surrounding produced water discharge sites located in a variety of hydrologic regimes (Boesch and Rabalais, 1989a and b; Rabalais et al., 1991). However, in all of these studies, the issue of contamination was considered in a synoptic study design which did not address the dynamic chemical, physical or hydrologic processes which control the distribution of contaminants. Further, they did not address the fate of in-place contamination should regulations now in place or contemplated by state and the U.S Environmental Protection Agency be put into effect, stopping or phasing out the discharges, thus making the sediments a source of contamination rather than a sink for it.

In the present study, we have investigated some of the chemical and physical processes which control the distribution in aquatic environments, the binding and release of contaminants from sediments and the potential for recovery of impacted sediment environments should discharges be discontinued. The goals of the studies were focused on four specific tasks:

a. To investigate the sorption/desorption kinetics and equilibriums of selected polynuclear aromatic hydrocarbons (PAHs), heterocyclic and alkyl-PAHs on various sediments (a range of organic carbon contents and particle sizes) in various brackish and marine aqueous systems.

b. To investigate the relationship between carbon fraction and the equilibrium Kp_{OC} (partition coefficient) for selected alkyl-PAH, PAHs.

c. To investigate the role of colloidal material in facilitating transport of hydrophobic organics through aquatic systems and in mediating the particle reactive nature of selected contaminants.

d. To investigate the distribution of normal, alkylated and heterocyclic PAH in the field as compared to laboratory microcosms.

The sorption/desorption processes which control the distribution of organic contaminants between the particulate and dissolved phases were investigated in several types of laboratory studies. Results of these experiments established the rates of these processes as well as the equilibria for different chemicals. A thermodynamically-based model for predicting the effects on sorption processes of changes in salinity was developed and validated. Microcosm studies showed that the sorption of aromatic hydrocarbons of all types was controlled by the organic carbon content of the sediments in the receiving waters.

New analytical methodologies were developed as part of the study to allow the fingerprinting of specific patterns of contamination from a discharge and to follow that signal in the sediment record as a function of distance from the discharge or depth in the sedimentary record. These methods were applied to both field and laboratory experiments to investigate fate and transport processes in natural sediments.

Microcosms were designed and employed to investigate the desorption of in-place contamination from sediments. The results suggest that recovery of sediments in contaminated regions may be slow requiring several decades for the biologically important top 50 cm to be purged of aromatic hydrocarbon contamination. Preliminary modeling of the desorption data suggests that with more modelling effort, a predictive model of sediment recovery could be developed.

Chapter 2

INTRODUCTION

2.1 Background

Oil and gas reserves are historically and contemporarily one of the major economic resources within the Gulf of Mexico region and specifically within the state of Louisiana. As the industry has expanded in the region, increasing concern over the potential impacts of long-term discharges of waste materials associated with oil exploration, drilling, and production refining operations have developed. While the effects of catastrophic spills and releases of oil into coastal and estuarine environments have been recognized for several decades, the potential effects of chronic discharges of waste streams associated with normal oil and gas operations upon sensitive coastal and estuarine ecosystems have not been extensively investigated or reported.

Produced waters are geologic formation waters which are present in the permeable subsurface sand and rock formations that are the source of trapped oil and gas reservoirs. When the oil and/or gas reservoirs are discovered and production begins, large volumes of this formation water are brought to the surface along with crude oil, volatile hydrocarbon condensates or natural gas. This water variously called formation water, produced water or oil field brine is removed from the petroleum phase by a variety of chemical and physical processes such as gravity separation, centrifugation, pressure condensation, heat shocking or de-emulsification. Produced water is now the name of the total water discharged during extraction. While it is mostly formation water, it may contain injection water, used to improve extraction. Chemicals added during extraction and water separation processes to improve the efficiency of these processes may also be present. After separation the water may be re-injected into the subsurface or it may be discharged into surface waters. The latter is the practice employed in the majority of cases in the northern Gulf of Mexico. Approximately 95% of the oil and 98% of the gas produced from the OCS in the central and western regions of the Gulf of Mexico resul in produced water discharges to surface waters. The vast majority of the produced water generated by these production activities is separated and discharged at offshore platforms. However, approximately 254,000 barrels per day of the estimated 1.2 million barrels per day of produced waters generated are piped to shore and separated at facilities located in coastal or estuarine portions of Louisiana and discharged into surface waters there. This volume generated in the OCS represents only 25% of the total produced waters discharged into Louisiana waters and only 13% of the total discharged into surface water environments in the Gulf of Mexico (Rabalais et al., 1991).

Increasing concern over the cumulative potential environmental effects of such discharges into coastal and estuarine environments which serve as a spawning ground for many economically important species of fish and shellfish has developed in the last several years. Since produced waters represent essentially saturated solutions of many dissolved major, minor and trace elements as well as a broad spectrum of hydrocarbons including normal aliphatic, branched-chain and aromatic fractions, there is concern over the potential impacts on these important aquatic ecosystems. The aromatic fraction of the total hydrocarbon load of produced waters are generally the fraction of most environmental concern due to their persistence, high bioaccumulation potential and wide spectrum of toxicological impacts including mutagenesis and carcinogenesis.

Because of the limited water solubility of many of the compounds of concern, they are expected to rapidly associate with suspended sediment and bedded sediment particles in the vicinity of the discharge and be preserved there. Because of the high binding capacities of organic rich, fine-grained sediments found at many discharge sites, hydrocarbons may concentrate to levels far exceeding those observed in the water column of the receiving water body. Thus it is important to understand physical-chemical factors which govern such concentration processes and which will ultimately control the fate of the contaminants should such discharges of produced water increase, decease or cease due to changes in environmental regulations.

Among the various interactions which influence the transport and fate of organic contaminants in environmental systems, sorptive interactions with various particulate materials are considered to be of prime importance in determining the ultimate fate and, to some degree, the toxicity of organic contaminants to target species. Sorption results when a component in solution is concentrated at an interface (Bailey and White, 1964). For sediment/water systems, the interface of primary concern is the liquid/solid interface. The sorbing species is referred to as the solute when it is in solution and the sorbate when it is in contact with the solid (sorbent) surface. Sorption will occur when the forces of attraction between the sorbate and the solid (sorbent) surface are greater than the sum of the repulsive forces between the solid and the sorbate and the forces of attraction between the solute and the solvent (Adamson, 1976).

For neutral hydrophobic organic solutes (NHCs) or solutes having low solubilities in water, sorption occurs due to a weak solute-solvent interaction rather than a large specific sorbate-sorbent interaction. Here, even very weak sorbate-sorbent attraction (e.g., Van der Walls forces) will overcome the weak solute-solvent interaction and result in the sorption of the compound from solution. A weak interaction between solute and the sorbent (low water solubility) is the result of a large decrease in the entropy of the system upon solvation (Karickhoff et al., 1979; Means et al., 1980) and the absence of significant hydrophilic character in the molecule. This process is termed hydrophobic sorption because of the existence of the weak solute-solvent interaction.

Transport of NHCs in the solution phase as a result of aqueous leaching from contaminated sediments is expected to be quite low. This is based on their low aqueous solubility (<100 ppb) and high octanol-water partition coefficient (log Kow >5). These properties can be used in one of many available regression equations (Kenega and Goring, 1980; Chiou et al., 1979; Means et al., 1980) to predict sediment partition coefficients normalized on organic carbon (Koc) values of >4.5. Experiments to evaluate NHC movement in water through sediments have confirmed the lack of mobility (Helling, 1971). Many theories have been proposed to explain the "facilitated" transport of hydrophobic organics in aquatic systems including association with colloids and/or microparticulates (Means and Wijayaratne, 1982) and combination with surfactants to form micelles. Organic colloids are likely the primary facilitators at discharge sites at which high dissolved organic matter concentrations are observed. Two important questions to be addressed in extending the knowledge of solute transport in water/sediment systems to reflect the potential presence of colloids are: (1) what are the governing theories for the sorption processes and (2) what are the kinetic and equilibrium characteristics of sorption and desorption. Some progress has been made to address both of these questions.

Recent studies of the kinetic and equilibrium characteristics of sorption of NHCs to colloids from aqueous media have been guided by what is known regarding the sorption from water to sediment of other classes of hydrophobic organic contaminants such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) (Means et al., 1980; Karickhoff et al., 1979; Weber et al., 1983). The equilibrium aspect of the transport of these latter solutes in sediment systems can be expressed in terms of water-sediment partition coefficients (Kd) which have been found to be related to the octanol-water partition coefficient (Kow) of the solute and the fraction organic carbon content (f_{oc}) of the sediment or sediment (Means et. al., 1980). Kinetically, the sorption and desorption processes appear to involve two steps; the initial step is typically rapid (i.e., on the order of minutes) over which most of the sorption/desorption occurs, followed by a slower second step, which may occur over periods of several hours or longer. The literature regarding the reversibility of sorption of various classes of low solubility organic contaminants from sediments is limited and to some degree contradictory. Leenheer and Ahlrichs (1971) have reported complete reversibility of sorption of carbaryl and parathion by humified sediment organic matter. In contrast, DiToro and Horzempa (1982) and Horzempa and DiToro (1983) report that for studies of desorption of PCBs from lake sediments, a significant portion of sorbed solute appeared to be persistently sorbed. Isaacson and Frink (1984) studied the reversibility of sorption of phenol, 2-chlorophenol and 2,4-dichlorophenol on lake sediments, and have reported that up to 90% of the solute was irreversibly sorbed.

The role of colloidal organic matter in mediating the transport and fate of hydrophobic contaminants in water/sediment systems has been a developing field over the last five years. The role of colloidal organic matter in the sorption of pesticides and PAHs was pioneered in the Aquatic Chemistry and Toxicology Laboratory directed by Dr. Means (Means and Wijayaratne, 1982; Wijayaratne and Means, 1984) and has subsequently been confirmed by other laboratories for PCBs (Brownawell and Farrington,1986) and DDT (Carter and Suffett, 1982). Although Means and Wijayaratne(1982) postulated that colloid-enhanced transport might be important for NHCs in estuarine and marine environments, little quantitative research along these lines has been performed. A review of the role of colloids in contaminant transport was recently published by Sigleo and Means (1990).

2.2 Goals of Study

The specific aims of this project task are to investigate the potential for dispersion of potentially toxic chemicals associated with formation water discharges such as PAHs, their heterocyclic analogs, alkylated analogs and phenols from contaminated particulates at produced water sites into brackish or marine waters. Experimental studies employing both static and dynamic experimental systems were performed. Work was focused upon three specific tasks:

a. To investigate the sorption/desorption kinetics and equilibriums of selected PAHs, heterocyclic and alkyl-PAHs on various sediments (a range of organic carbon contents and particle sizes) in various brackish and marine aqueous systems.

b. To investigate the relationship between carbon fraction and the equilibrium Kp_{-OC} (partition coefficient) for selected alkyl-PAHs and normal PAHs.

c. To investigate the role of colloidal material in facilitating transport of hydrophobic organics through aquatic systems and in mediating the particle reactive nature of selected contaminants.

d. To investigate the distribution of normal, alkylated and heterocyclic PAHs in the field as compared to laboratory microcosms.

Chapter 3

STUDY DESIGN

3.1 Study Sites

In order to achieve the goals of the study, both laboratory and field studies were conducted. For the laboratory studies of the sorption/desorption properties of PAHs or batch sorption experiments, the investigation required that a range of both uncontaminated reference sediments and contaminated, fine-grained sediments be collected for various types of experiments. Another criterion used in site selection was the relative potential impact of sources of petroleum hydrocarbon pollution upon the specific aquatic system being studied. Based upon these criteria and taking advantage of previous studies (Boesch and Rabalais , 1989 a and b, Rabalais et al., 1991) that we had performed, we selected three stations in the Pass Fourchon/Lake Champagne region, identified as Lab Point, Westlake and Southlake, and three stations in Lafitte Bayou, identified as LR0, LR250N and LR500N, for collection of bulk quantities of reference sediments for study (See Figure 3.1.1-3).

Other project research objectives were addressed using two basic experimental approaches. First, sediment cores collected in the Pass Fourchon, Bayou Rigaud and Eugene Island (See Figure 3.1.1-2 and 3.1.4-5) were analyzed in detail for their normal, aromatic, alkyl- and heterocyclic PAHs in order to define the magnitude and extent of contamination as a function of distance from the discharge and depth in the sediment. The sediments collected exhibited organic carbon (OC) contents in the typical range of 1.5 to 4.0% (uncontaminated) to 5-7% carbon (heavily contaminated). Second, heavily contaminated bulk sediments located near the Pass Fourchon produced water discharges within Louisiana were identified and collected. Sediments were collected using a Ponar grab sampler in large quantities (~50 kg) and returned to the laboratory for subsequent homogenization, detailed chemical analysis and use in microcosm experiments.

3.2 Batch Sorption Experiments

The field sediments collected a the Lake Champagne and Lafitte Bayou sites were used as substrates in standard batch sorption experiments (Means et al., 1979) using liquid phases containing fresh, estuarine or marine water, or mixtures of these waters with produced water. Preliminary studies were performed with each substrate to confirm the adequacy of the centrifuging procedure required for phase separations, to verify solute mass balances, and to establish the linearity of sorption isotherms (to avoid saturation of either phase).

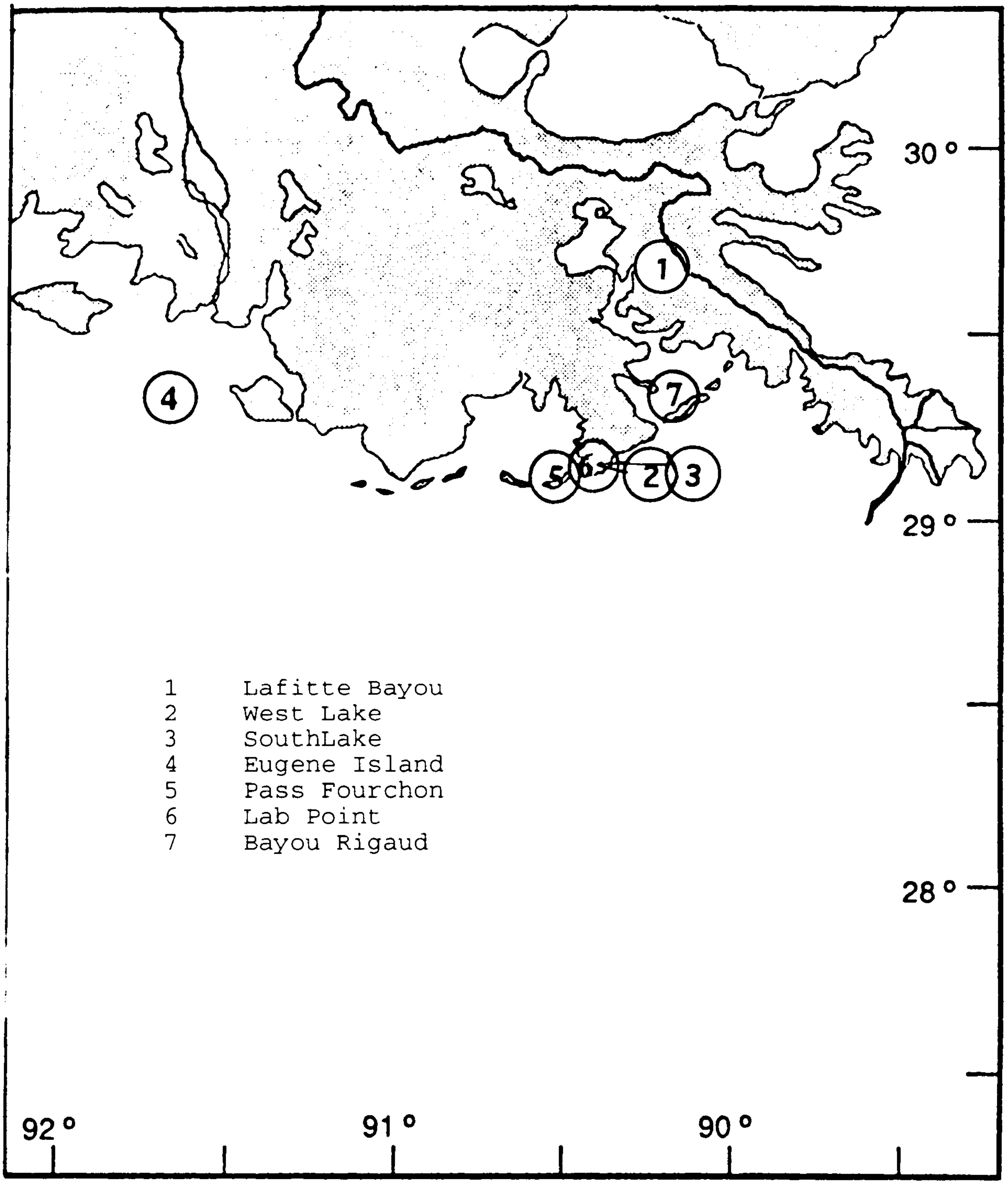


Figure 3.1.1. General Locations of Study Sites

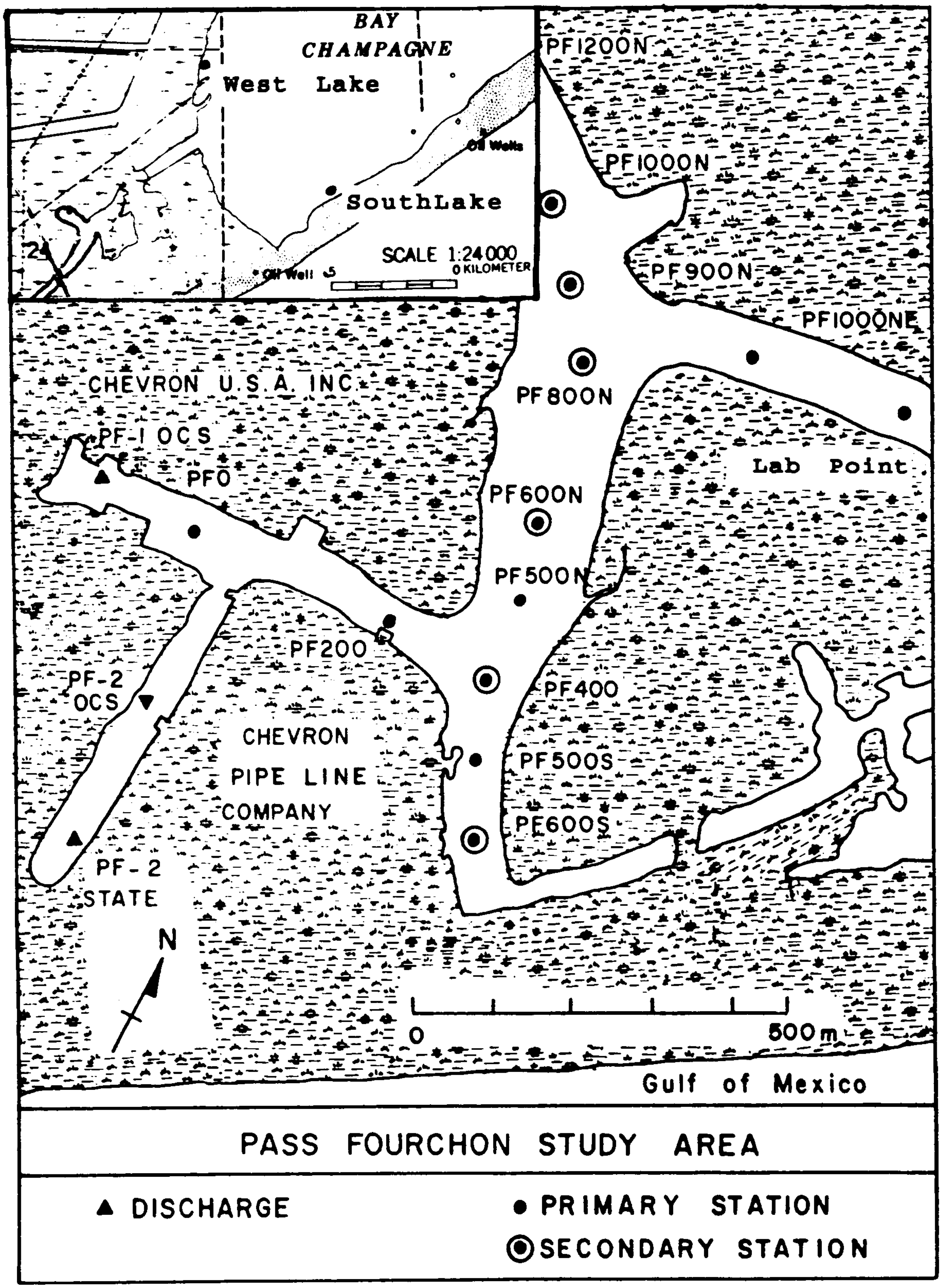


Figure 3.1.2. Locations of Pass Fourchon Study Sites and Lake Champagne Study sites (inset)

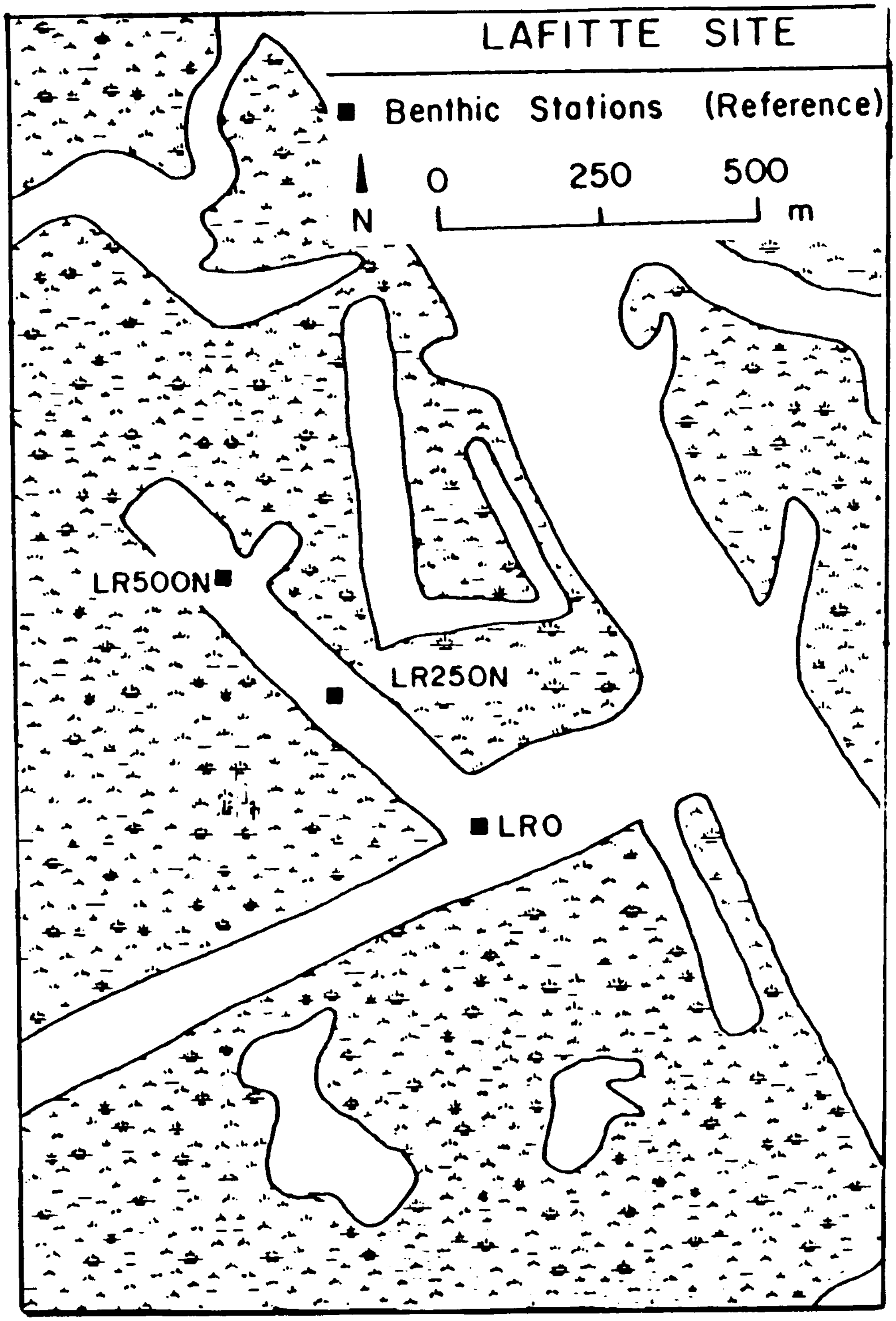


Figure 3.1.3. Locations of Lafitte Bayou Study Sites

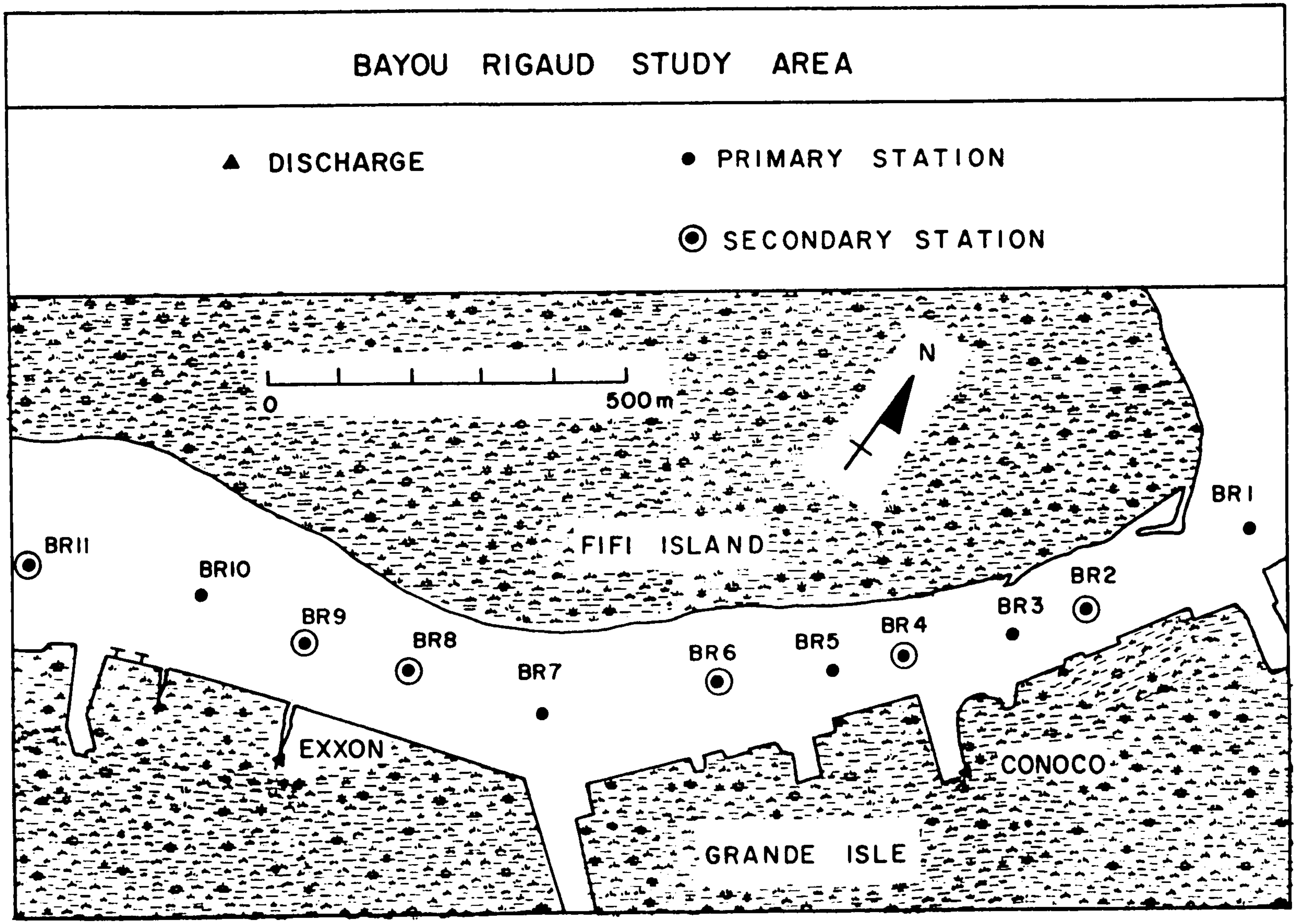


Figure 3.1.4. Locations of Bayou Rigaud Study Sites

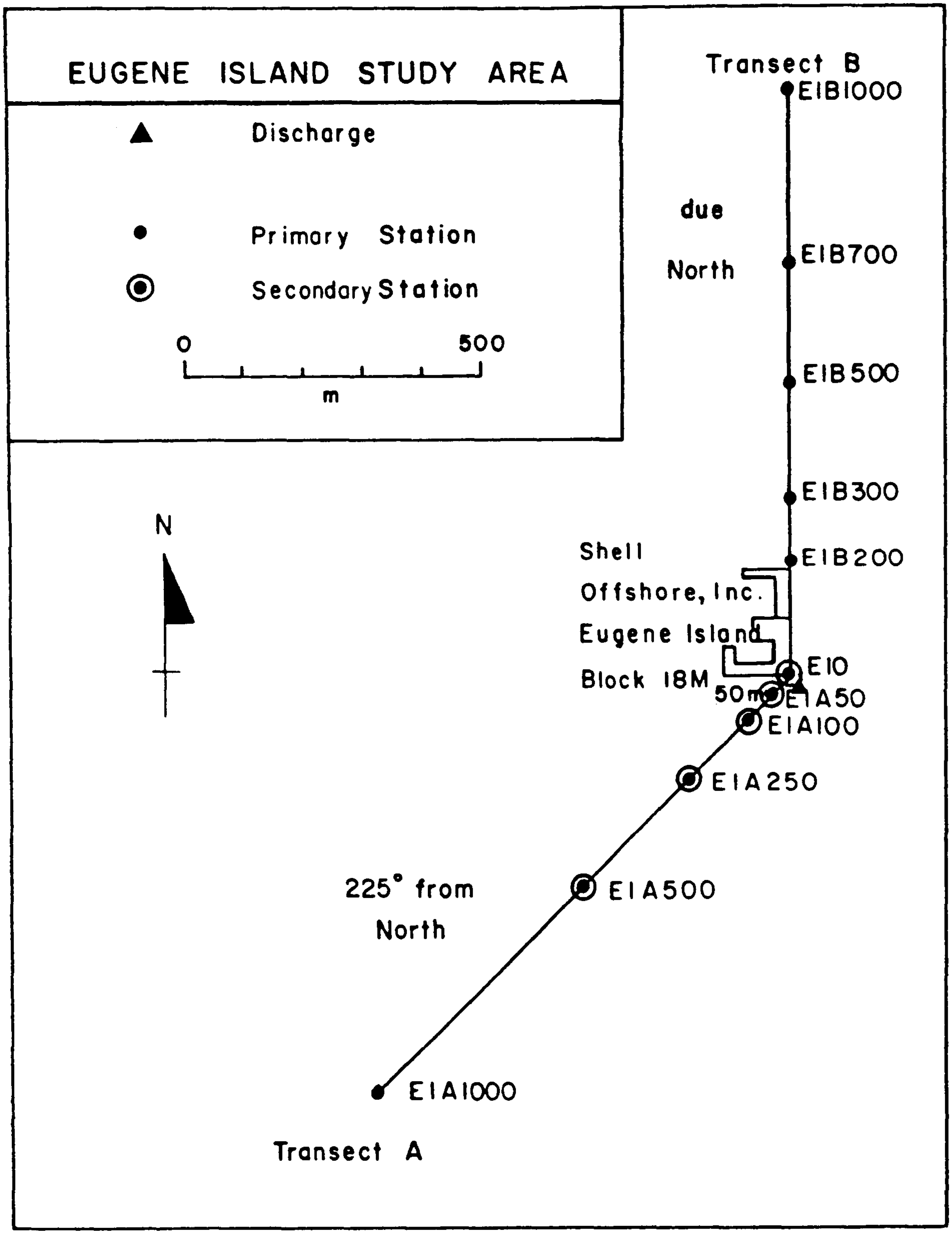


Figure 3.1.5. Locations of Eugene Island Study Sites

3.3 Microcosm Desorption Experiments

In addition to the batch sorption experiments, sediments collected from the field were homogenized and used in long-term (120 day) dynamic desorption experiments to determine desorption kinetics for the compounds of interest. This series of experiments was developed to take advantage of the modified approaches used to measure chemicals which were utilized in these studies and are reported in later sections of this document. These microcosm experiments ultimately yielded data which allowed a more rigorous evaluation of the fate of aromatic hydrocarbons in sediment systems using kinetic models.

3.3.1 Sediments

Approximately eight sorbents were used in this work. Most estuarine and marine sediments were collected with the aid of the LUMCON research vessels and were selected based on their proximity to OCS produced discharges and regional geology. Sediment samples from four produced water contaminated sites were used in this study. Uncontaminated sediments collected at two locations in Lake Champagne were used to establish baseline conditions and were also used to assess the effects of salinity upon sorption in synthetic contamination experiments to simulate sediment conditions at the time of initial contamination. Synthetically-contaminated sediments were utilized primarily as fresh materials. Each sediment was characterized for a number of physical and chemical properties known to be related to sorption properties including organic carbon content and texture (i.e., sand, silt, and clay fraction). The methods employed for these determinations are presented by Means et al. (1979).

3.3.2 Solute

The solutes to be used in these experiments included a variety of neutral hydrophobic compounds (NHCs): polycyclic aromatic hydrocarbons (PAHs) (i.e., naphthalene, phenanthrene, pyrene, benzanthracene, etc.), alkylated aromatic hydrocarbons (i.e., alkyl naphthalenes and alkyl phenanthrenes), as well as heterocyclic aromatic hydrocarbons (i.e., dibenzothiophene and alkylated dibenzothiophenes). These compounds are all found in produced water discharges and were used to investigate trends in behavior for solutes of differing solubilities.

3.3.3 Liquid

A variety of solution phases were used in both batch sorption and dynamic desorption microcosm experiments to investigate sorption and desorption of PAHs. Marine and estuarine waters were used in most experiments. In some experiments produced water (hypersaline) collected from actual discharge sites **may be** utilized in select experiments for comparison.

Chapter 4

EXPERIMENTAL METHODS

4.1 Field Logistics

4.1.1 Vessel and Boat Support

Samples of sediments used in these studies were collected from either the LUMCON vessels *Acadiana* or *Pelican* or from small boats operating in shallow waters. Bulk sediments and sediment cores at open water sites such as Eugene Island or deep bays such as Bayou Rigaud were obtained from the larger vessels, while smaller sediment samples and the reference sediment from Lake Champagne were obtained from a 22 ft Aquasport.

4.1.2 Field Sampling Equipment

Bulk sediment and sediment cores were obtained from the *Acadiana* or the *Pelican* using an Ekman-type box corer (0.1 m^2). At stations where large amounts of surficial sediments were desired a Ponar grab was used. Average penetration of the Ekman-type box corer was 50 cm in soft sediments and 30 cm in sandy sediments. Sub-cores which maintained the depositional strata of the sediments at the site were obtained by inserting a 10 cm X 50 cm polybutylene tube into the box corer. At shallow stations a small hand operated Ekman corer (0.025 m^2) was used from a small boat to obtain sediments to a depth of 10 cm.

4.2 Sediment Properties

Sediment properties were determined using the methods described in Means et al. (1979) on homogenized sub-samples of bulk sediments after sieving through a 2 mm^2 stainless steel sieve to remove debris, shell and live organisms.

4.3 Analytical Methodology for Hydrocarbons

4.3.1 Background and Rationale

In order to achieve the objectives of the study, analytical methods which were capable of meeting certain criteria in both field and laboratory-collected samples needed to be developed. These were:

- the method must have sensitivities in the sub-ppb range
- the methods must yield compound specific quantification in the presence of a complex hydrocarbon background
- the method must be able to discriminate between positional isomers of certain compounds or compound groups

- the methods must be applicable to field samples and spiked laboratory samples.

- the methods must be able to yield quantitative information on relatively small samples obtained from laboratory microcosm studies (2-4 g total)

In previous studies of the sorptive interactions of compounds with sediments and colloids, we have employed the use of 3H- or 14C-labelled compounds with a high level of success (Means et al., 1979, 1980, 1982, Means and Wijayaratne, 1982, Wijayaratne and Means, 1984). While this method of compound detection meets most of the criteria above and was used in some aspects of these studies, the compounds are very expensive to obtain commercially for custom syntheses ($2500-5000 per synthesis). Because of this expense and the limited amounts of funds available for this study, we chose to investigate a second alternative. This approach entailed the synthesis of stable isotopic labelling of aromatic hydrocarbons with deuterium to yield compounds which could be detected sensitively and discriminated from each other by gas chromatography/mass spectrometry techniques. This approach, while less expensive and theoretically feasible did not prove to be successful due to low chemical yields of the fully deuterated reaction products. The syntheses resulted in mixtures of partially deuterated products which were difficult to detect sensitively or discriminate one from another in complex mixtures of naturally occurring compounds. A detailed description of the results will be presented in a later portion of this report.

The third approach which was evaluated and which ultimately yielded most of the results presented in this report was the development of ultra-trace methods employing multiple selected ion monitoring techniques for the detection of a suite of 58 aromatic hydrocarbons. The methods meet the criteria stated above and are described in the following sections. It should be pointed out that without the development of these methods this study would have been severely limited in scope.

4.3.2. Sediment Extraction Methods

The sediment extraction method is a modification of that described by MacLeod et al. (1985), where samples, sodium sulfate and DCM are rolled for 8-16 hours, followed by decanting, and this procedure repeated 3 times. Twelve samples and a reagent blank are typically prepared at one time. A suite of deuterated PAH (Ultra Scientific, US-108) is added to each sample jar as surrogate standards to monitor extraction efficiency. The decanted DCM is filtered through sodium sulphate, concentrated by rotoevaporation, and then further concentrated under a nitrogen stream with solvent exchange to hexane. Final volumes range from 200-500 µl. Fine granular copper was added to reduce sulphur interferences. Extracts from the tumbling procedure were not subjected to further cleanup or fractionation. Part of the method development included the evaluation of the need for pre-analysis cleanup of extracts. Silica gel columns were used to separate aliphatic (F1), aromatic (F2), and polar (F3) classes using elution with hexane for F1, 50:50 hexane/dichloromethane for F2, and 100% DCM for F3 components. Comparison of the F2-fraction of silica gel eluants with unfractionated extracts showed that resolution of individual components was best with the unfractionated extracts, possibly due to contribution of aliphatic hydrocarbons present to "Grob effects" or solvent focusing effects (Onuska and Karasek, 1984) on the gas chromatographic column. In addition, use of unfractionated extracts allowed for the concurrent estimation of the aliphatic hydrocarbons in the same analysis.

4.3.3. GC/MS Analysis

A Hewlett-Packard 5890 Gas Chromatograph directly interfaced to a Hewlett-Packard 5970B Mass Selective Detector was operated using the parameters presented in Table 4.3.3.1. A series of linear temperature ramps was necessary for the maximal separation of isomers of alkylated PAH's and for separation of parent PAH compounds from alkylated PAH's with interfering ions, while keeping analysis time (60 min.) and band-broadening to a minimum.

Table 4.3.3.2 lists the target analytes and deuterated reference standards, their abbreviations, and the mass fragments used for quantitative evaluation ("primary ion") and for confirmation of identity ("confirming ion"). Alkylated PAH standards were purchased from Chiron Laboratories A.S. (Norway). The standards represent the two isomers of methylnaphthalene, all 10 of the dimethylnaphthalene isomers, isopropylnaphthalene and 1,6,7-trimethylnaphthalene for the class "C3" (three substituted carbon groups) naphthalenes, all four possible isomers of methyldibenzothiophene, 1,2-dimethyldibenzothiophene for the class "C2" dibenzothiophenes, five of five possible methylphenanthrenes, 16 of 25 isomers of dimethyl phenanthrene, and 1,2,8-trimethylphenanthrene for the class of "C3" phenanthrenes.

The chromatographic analysis method was developed by first determining the retention order and mass spectra of all of the individual alkylated PAH isomers, as listed in Table 4.3.3.2, then analyzing a mixture of all the analytes together, with adjustment to the temperature ramps to achieve maximum resolution. "Optimal resolution" is a trade off between increased separation and band-broadening that occurs with increased time spent in the column. After what was considered the best possible resolution was achieved, some of the individual mixtures had to be reanalyzed to confirm that retention orders had not changed. This is also necessary when the GC column is replaced, but is not required for all individual components because of the identification power (specificity) of the mass spectrometer. Spectra of the individual

Table 4.3.3.1. Gas Chromatography/Mass Spectrometry Instrument Parameters.

Heated Zones

Splitless Injection Port Temperature: 235°C.
Purge Time: 0.5 min.
GC/MS Transfer line temperature: 280°C

Gas Chromatography Column

Column: DB-5, 30 meter, 0.25 µ film thickness, 0.25 mm I.D.J&W Scientific,Inc.
Carrier Gas: Helium
Linear velocity: 40 cm/sec (butane injection at 100°C)

Gas Chromatograph Temperature Program

Initial Column Temperature: 50°C
Time at Initial Temperature: 3 min.
Temperature Ramp: #1: 6°C/min to 120°C
#2: 3°C/min to 190°C
#3: 12°C/min to 280°C
Time at Final Temperature: 14.5 min.

Mass Spectrometer Data Acquisition

Scan Range: 45-450 amu.
Scan Rate: 1.06 scans/sec

Table 4.3.3.2. Target Analytes

Analyte	Abbreviation	Primary Ion	Confirming ion
Naphthalene	Naphthalene	128	129
2-Methylnaphthalene	2-MN	142	141
1-Methylnaphthalene	1-MN	142	141
2-Ethylnaphthalene	2-EN	156	141
1-Ethylnaphthalene	1-EN	156	141
2,6/2,7-Dimethylnaphthalene	2,6/2,7-DMN	156	141
1,3/1,7-Dimethylnaphthalene	1,3/1,7-DMN	156	141
1,6-Dimethylnaphthalene	1,6-DMN	156	141
1,4/2,3-Dimethylnaphthalene	1,4/2,3-DMN	156	141
1,5-Dimethylnaphthalene	1,5-DMN	156	141
Acenaphthylene	Acenaphthylene	152	153
1,2-Dimethylnaphthalene	1,2-DMN	156	141
2-Isopropylnaphthalene	2-IPN	170	155
1,8-Dimethylnaphthalene	1,8-DMN	156	141
Acenaphthene	Acenaphthene	153	154
Fluorene	Fluorene	166	165
Dibenzothiophene	Dibenzothiophene	184	185
Phenanthrene	Phenanthrene	178	179
Anthracene	Anthracene	178	179
4-Methyldibenzothiophene	4-MDBT	198	197
2/3-Methyldibenzothiophene	2/3-MDBT	198	197
1-Methyldibenzothiophene	1-MDBT	198	197
3-Methylphenanthrene	3-MP	192	191
2-Methylphenanthrene	2-MP	192	191
4/9-Methylphenanthrene	4/9-MP	192	191
1-Methylphenanthrene	1-MP	192	191
4,5-Dimethylphenanthrene	4,5-DMP	206	191
3,6-Dimethylphenanthrene	3,6-DMP	206	191
3,5-Dimethylphenanthrene	3,5-DMP	206	191
2,6-Dimethylphenanthrene	2,6-DMP	206	191
2,7-Dimethylphenanthrene	2,7-DMP	206	191
3,9-Dimethylphenanthrene	3,9-DMP	206	191
1,6/2,5/2,9-Dimethylphenanthrene	1,6/2,5/2,9-DMP	206	191
1,7-Dimethylphenanthrene	1,7-DMP	206	191
1,9/4,9-Dimethylphenanthrene	1,9/4,9-DMP	206	191
Fluoranthene	Fluoranthene	202	101
1,5-Dimethylphenanthrene	1,5-DMP	206	191
1,8-Dimethylphenanthrene	1,8-DMP	206	191
1,2-Dimethylphenanthrene	1,2-DMP	206	191
9,10-Dimethylphenanthrene	9,10-DMP	206	191
Pyrene	Pyrene	202	101
Benzo(a)anthracene	Benzanthracene	228	226
Chrysene	Chrysene	228	226
Benzo(b)fluoranthene	Benzo(b)fluor	252	253
Benzo(k)fluoranthene	Benzo(k)fluor	252	253
Benzo(a)pyrene	Benzo(a)pyrene	252	253
Indeno(1,2,3-cd)pyrene	Indenopyrene	276	278
Dibenz(a,h)anthracene	Dibenzanthracene	278	276
Benzo(g,h,i)perylene	Benzoperylene	276	278

Deuterated Internal/Surrogate Standards		
d8-Naphthalene	d8-Naph	136
d10-Acenaphthene	d10-Ace	164
d10-Phenanthrene	d10-Phen	188
d12-Chrysene	d12-Chrys	240
d12-Perylene	d12-Peryl	264

isomers that were obtained initially can be used to distinguish some of the isomers from each other in the mixed standard.

Retention order of the alkylated PAH isomers was determined by preparing 10 ppm dilutions in hexane containing one of each type of isomer, i.e., a methylnaphthalene, a dimethylnaphthalene, a methylphenanthrene, a dimethyl-phenanthrene, etc. A final standard, containing all parent PAH compounds (Ultra Sci., US-106), alkylated PAH, and deuterated surrogate standards, was prepared at 5 ppm by dilution with dichloromethane and was analyzed with hexamethylbenzene (HMB) as an internal standard. HMB was also coinjected into the GC/MS with each sample aliquot to monitor performance of the instrument and injection technique, but was not used in the calculations of analyte final concentrations. Quantifications were made using the internal standard (I.S.) method based on the corresponding deuterated surrogate standard for each analyte.

Chromatographic data for parent and alkylated PAH were obtained from 20 daily calibration analyses of the standard mixture. In addition to the analytes listed, C4- and C5-naphthalenes, C3-dibenzothiophenes, and C3-phenanthrenes are estimated using relative response factors generated from similar class analytes represented by the standard mixture. For example, the C3-dibenzothiophenes were estimated using the relative response factor for C2-dibenzothiophenes, 1,2-dimethyldibenzothiophene. In this way, we were able to quantitate additional compound classes without the considerable expense of these additional standards. C1-C3-fluorenes were estimated using the response factor from the parent compound.

4.3.4. Quality Assurance/Quality Control

Standard QA/QC procedures were followed, including analysis of duplicate and spiked samples, and daily tuning and calibration of the GC/MS system.

4.4. Modifications of Analytical Method for Sediment Desorption Experiments

4.4.1. Extraction of Microcosm Soil Cores

Two methods of extraction were evaluated for preparation of sediment core samples. The method chosen for use is as follows: Three core jars were removed from each microcosm tank at sampling times of 0, 1, 3, 7, 14, 28, 60 and 120 days, for a total of 24 samples. The jars were capped and refrigerated until the day before extraction, when the overlying water was removed and the capped jar frozen overnight at -20°C. For extraction, the jar was broken and the frozen core placed in a coring device designed for these experiments. The device consisted of a longform beaker, with the same diameter as the core jars, to which a caliper was attached. The frozen core was placed into the device top side down and a glass plunger pushed through from the opposite end to force the core against a scraper while aligned with the caliper. The core was scraped against Stanley Sureform scrapers, a separate scraper for each 2-mm section, and which were sonicated in DCM and baked at 200°C overnight prior to each use. The scrapers were supported over 500 ml tared jars and the soil allowed to fall into the jar for each section. Residual soil on the scrapers was removed by tapping the scrapers against the lip of the jars. A subsample of ~0.5 gm was removed for dry-weight determination and the jar reweighed to obtain the wet weight of the sample. Wet weights were typically 2-3 g and moisture content averaged 60%, and was generally 1-2% higher in the top sections. Dichloromethane was added to each jar, then an aliquot of the deuterated surrogate standards, and finally 30 gm of sodium sulfate was mixed in thoroughly using a stainless steel spatula. The jars were sonicated for 10 mins in an ice-cooled bath, and the solvent decanted through sodium sulfate. The bath water was closely monitored to prevent losses of analytes due to increased temperature. The sonicating extraction procedure was repeated three times. The resulting extract was concentrated as described previously and sulfur removed by activated copper.

4.4.2. GC/MS Analysis of Microcosm Extracts and Determination of Desorption Rates for Alkylated PAH

Extracts were analyzed by GC/MS operated in the selected ion monitoring mode for enhanced sensitivity of the target analytes, utilizing the same temperature program as previously described for the GC. The standard mixture was diluted to 1 ppm for calibration of the instrument. Injections into the GC were made by autosampler, and hexamethylbenzene was added to each extract to monitor instrument performance. Because of the new analytical methodology which we have developed and employed, we are able to make several independent estimates of concentrations for several positional isomers of the same compound (i.e. 10 dimethylnaphthalenes) having similar sorption constants and aqueous solubility.

4.5 Batch Sorption/Desorption Testing

Batch shake testing was employed to evaluate both sorption/desorption kinetics and equilibrium of pyrene as a model PAH on several sediments. The experimental parameters investigated in these studies are summarized in Table 4.5.1.

For pyrene, batch sorption and desorption testing was performed in 15 mL glass centrifuge tubes. Sorption and desorption equilibrium isotherms were measured in triplicate. The mass of sediment which was used in each batch test was in the range of 0.9 to 1.0 g, with a solution volume of 10 mL.

Table 4.5.1. Experimental Parameters for Sorption/Desorption Systems.

Sorbents	Control sediments (3) Discharge site sediments (4)
Liquid Phases	Fresh water (0 ppt) Estuarine water (9,18 ppt) Marine water (32 ppt)
Solutes	Pyrene

In sorption these experiments, five different initial solute doses were used to result in five different equilibrium concentrations. Initial solute concentrations were determined in preliminary range-finding studies and were selected such that equilibrium solution concentrations (Cw) will span at least 1.2 orders of magnitude in Cw in the range of 1 to 50% of the solubility of the compound in the liquid phase. Time series experiments were performed using various time intervals and durations (three-day intervals for thirty days) to evaluate sorption and desorption kinetics. Desorption experiments consisted of an equilibration phase (determined by time course studies) followed by exchange of the solution phase and studies of both the kinetics and equilibrium desorption partition coefficients at five concentrations spanning at least 1-2 orders of magnitude.

Sediment/liquid separation prior to liquid scintillation analysis was accomplished by centrifugation. Centrifugation at 1000 x g for 20 minutes was sufficient for phase separation. Centrifuge speeds and times were determined in pilot experiments for each solute/sediment combination to insure sufficient phase separation of liquid and sediment to prevent the introduction of a negative experimental bias.

Previous experiments with marine systems have shown complete mass balances of several NHCs using experimental protocols utilized here (Means et al., 1979) Specifically, these studies showed negligible losses of compounds to centrifuge tube walls or through the teflon and/or foil cap liners. However, significant biases were introduced into the experimental data for less refractory compounds such as the PAHs which may be sensitive to light, volatilization, or microbial metabolism (Means et al., 1980, 1982). Therefore, solute material balances for each experimental system were confirmed in the current work using the procedures described in Means et al.(1980). No significant losses of compound were observed.

For relatively insoluble solute/liquid systems, some modifications to these procedures were made. For cases where the solute is sufficiently insoluble in the liquid phase, direct addition of solute to the liquid phase will not be possible.

Therefore, solute additions in these cases were accomplished by adding known volumes of the solute in methylene chloride or methanol to empty tubes followed by evaporation of the solvent under nitrogen (Means et al.,1979). Pilot experiments were performed to determine a mass balance for each solute when added in this manner, and to determine whether release of solute from the tube walls during subsequent sorption equilibration represents any significant kinetic factor.

Using this procedure, sediment, liquid, and solute were added and the tubes sealed with teflon-lined caps. Tubes were equilibrated in a shaking table contained with a glove box or hood. Tubes were shielded from light and held at 20 C ± 2 C. Following appropriate equilibration times, tubes were centrifuged and the supernatant liquid phase sampled in triplicate by withdrawing 1-mL aliquots for liquid scintillation counting (LSC) analysis. The concentration of solute sorbed to the solid phase were determined by difference between total solute added to the tube and mass of solute remaining in solution phase at equilibrium after correction for any impurities or degradation products. Mass balance studies were performed to determine the total mass of solute associated with the liquid, solid, and tube walls to confirm material balances, to check for degradation, and to confirm that wall effects were negligible.

Desorption isotherm data were determined using sediment samples containing sorbed solute prepared by the sorption techniques outlined above or environmentally contaminated. Following sorption equilibration, the sediment-water suspension were centrifuged, and the liquid phase supernatant were analyzed, discarded, and replaced with an equivalent volume of the same liquid phase. Equilibration and analysis were performed using the procedures of the sorption studies.

4.6 Radiochemical Analysis

The primary analytical technique used in batch sorption experiments was liquid scintillation counting (LSC) of H-3 or C-14 labeled PAHs, and PAH-analogs on an Packard 5400 counter. Fairly high specific activity, uniformly labeled compounds were available commercially (e.g., 30-115 mCi/mmol, Cambridge Isotope Laboratories, Cambridge, MA, and Pathfinders, St. Louis, MO) or have been synthesized by exchange tritiation (Means et al., 1980). Liquid samples were counted by transferring a 5 mL of sample (in triplicate) to LSC vials containing 5-15 mL of Aquagel counting cocktail and counted twice for 10 minutes. Longer counting times (greater than 10 minutes) were used for low-level samples to obtain good counting statistics. All data was corrected for quench using external standard correction on each sample. Corrections for chemiluminescence were also applied as needed but were minimized by the use of the luminescence suppressing cocktail Aquagel and dark equilibration of samples prior to counting.

4.7 Data Manipulation and Modeling

Results of sorption isotherm experiments were fitted to a linear form of the Freundlich partitioning equation:

$$C_S = K_{p\text{-}oc}\ C_W$$

where C_S = equilibrium solute concentration of the sorbent (ug/g), Cw = equilibrium solute concentration in the solvent phase (ug/ml) and $K_{p\text{-}oc}$ = partition coefficient (dimensionless assuming solution density of 1 g/ml). Partition coefficients were normalized to the fraction organic carbon content of the sediment (f_{OC}) to give:

$$K_{OC} = K_{p\text{-}oc}/f_{OC}$$

where K_{OC} = partition coefficient corrected on organic carbon content of the sediment.

Desorption isotherm data were fitted to a similar linear partition equation to determine whether desorption of PAHs was a reversible process. No significant deviations from reversibility were observed in the substrates tested.

4.8 Laboratory Microcosm Development

The goal of this aspect of the research was to develop a microcosm system which could be used to study the desorption of alkylated and heterocyclic PAH from contaminated sediments under a variety of conditions. We wanted to be able to use the microcosms for studies involving benthic organisms as well as abiotic conditions. Figure 4.8.1 shows the microcosm design which was developed and which has been used to study desorption of alkylated PAH from contaminated sediments over time courses up to 120 days.

The microcosm test apparatus was designed with the intent to limit possible complicating variability while retaining a necessary amount of flexibility. The test apparatus (Figure 4.8.1) consists of two 5 gallon aquaria in which are situated 28 clear, graduated glass sample jars of 110 ml volume, 24 of which have been filled with 100 ml of the test sediment. The jars have been arranged in four rows of seven with the four corner sample jars not filled with sediment but filled with cleaned glass spheres. Other sub-microcosms may also be used or a single bed of sediment can be used in the system. The pumping system can accommodate up to 6 additional microcosms.

The remaining volume of the tanks is filled,except for a 2 cm depth air space below the lids, with water having a salinity of 14 parts-per-thousand prepared from deionized water and Instant Ocean in this particular experiment. This water is circulated in such a manner to effect five water exchanges (volume of aquarium) in a 24 hour period. This exchange rate is satisfactory for biological experiments as well. The water enters and exits from opposite

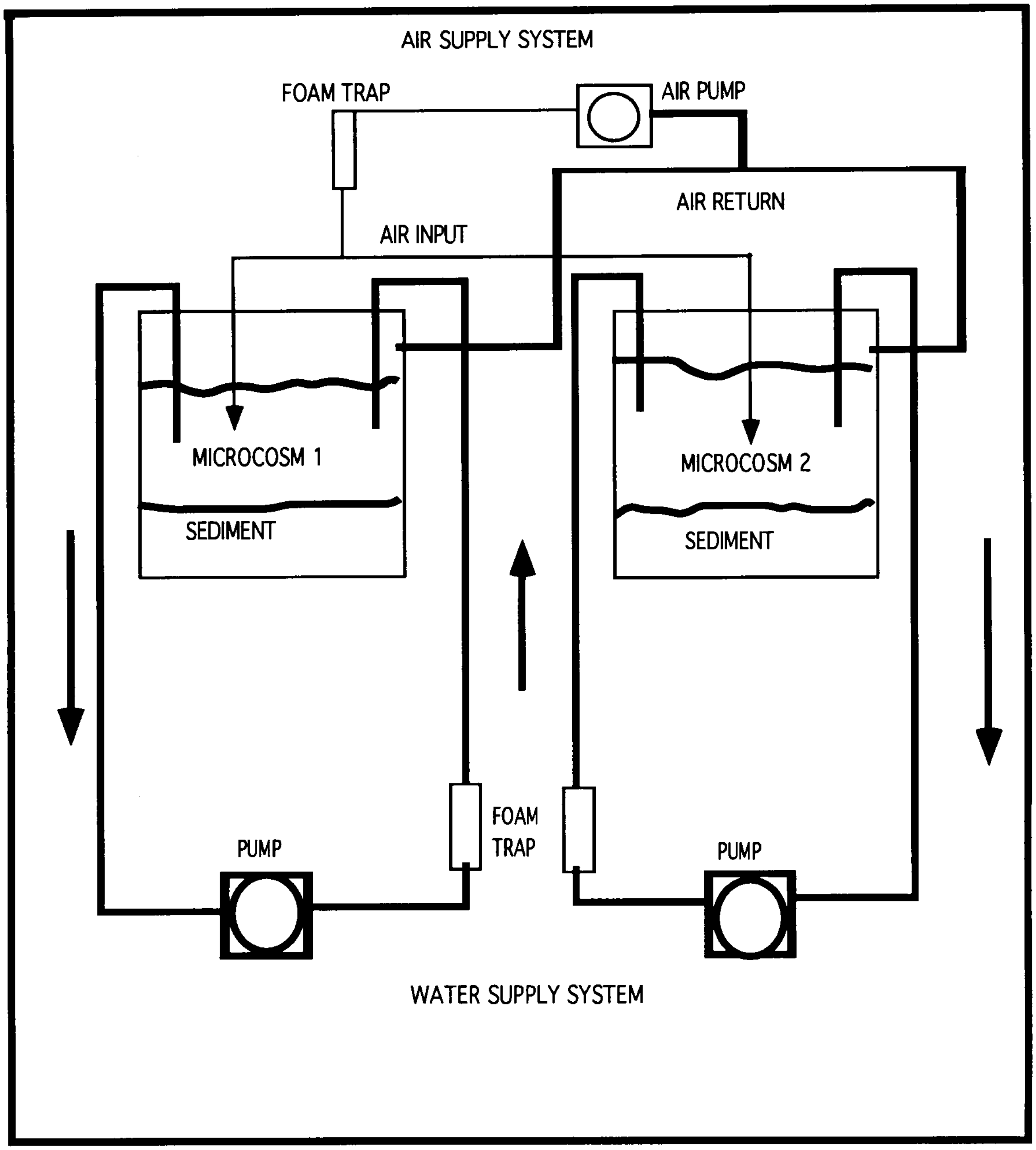


Figure 4.8.1. Design of Sediment Microcosm for Dynamic Desorption Studies

ends of the tanks via four nozzles which are situated 1 cm above the sample jar tops and are aligned with the 4 columns of sample jars that run the length of the aquaria. The nozzles are connected through a manifold to a common carrier line that feeds or collects flow from the nozzles evenly.

Upon exiting the tanks the water passes through a foam plug trap which removes the hydrocarbons that may have desorbed into solution. The water is then introduced to the other tank than that from which it was removed by the action of a peristaltic pump and the manifold/nozzle system previously discussed. The process of mixing the waters between tanks should prevent any variability in the waters flowing over the samples. The water volume of the system as well as the arrangement of the sample jars is preserved in the tanks after sampling events by replacing the samples taken with jars filled with clear glass spheres.

The potential for flow variation over the samples necessitated two design features. The first, already mentioned, is that the corner sample jars in the aquaria were not used due to poor water flow characteristics in these areas. Secondly, the flow and mixing within the tanks is enhanced by the use of an air-bubbling system. The 2200 ml of air per minute that are pumped into each tank via a submerged airstone create mixing and flows throughout the tank. The air from both tanks is recirculated constantly as the air that is pumped into the water is drawn from the air space above the water and passed through a urethane foam plug trap to remove any volatilized hydrocarbons.

The entire microcosm test apparatus is operated in a compartmentalized enclosure to exclude light and to provide thermal stability. The enclosure is only opened for brief periods for sampling and maintenance procedures which are performed under low light conditions.

Chapter 5

RESULTS AND DISCUSSION

5.1 Sorption/Desorption Studies of Neutral Hydrophobic Organic Contaminants from Estuarine Sediments

The normal parent PAH compound pyrene was selected for intensive study of the sorption/desorption kinetics of PAH in fresh, brackish and marine systems. Pyrene was selected for several reasons. Pyrene has a molecular weight (202 Daltons) which is near the median of those compounds of interest in these studies. Its aqueous solubility (135 µg/l ± 13 [0.668 µmol/l] and octanol-water partition coefficient Kow or P (124000±11000) are known and are also typical of the class of compounds of concern in these studies. Further, the sorption properties of pyrene have also been investigated in freshwater sediments (Means et al., 1979, 1980). Figures 5.1.1 though 5.1.5 show the sorption isotherms as a function of salinities from 0 to 32 ppt obtained on two contaminated sediments (Lab Point and Lafitte Bayou) and three control (uncontaminated) sediments (Westlake and Southlake-top and bottom). The latter sediment was collected at the same site but at a depth of approximately 20 cm below the sediment water interface.

Table 5.1.1 Characteristics of Study Sediments

Sediment Station	%organic carbon	texture %sand	%silt	%clay
Lab Point	3.5	19.1	51.4	29.5
Lafitte Bayou	4.3	35.4	57.4	7.2
Westlake	3.3	78.6	18.1	3.3
Southlake-top	4.0	38.5	56.6	4.9
Southlake-bottom	3.7	40.1	53.7	6.2

The data sets from each of the experiments were subjected to linear regression (Statview 512+ software, BrainPower Inc., Calabasas, CA) and the slopes of the lines and regression R^2 values determined. The Freundlich Kd constants derived from this analysis are summarized in Table 5.1.2.

Table 5.1.2 Freundlich Equilibrium Sorption Constants for Study Sediments

Station	Salinity 0 ppt	9 ppt	18 ppt	32 ppt
Lab Point	2273.4	2913.5	3337.9	4532.7
Westlake	2091.3	4533.6	5675.7	6233.8
Lafitte Bayou	3144.5	5146.5	ND	9578.8
Southlake-top	2615.2	2706.5	3450.2	4108.9
Southlake-bottom	2208	4671.9	5233.8	5736.1

ND= not determined

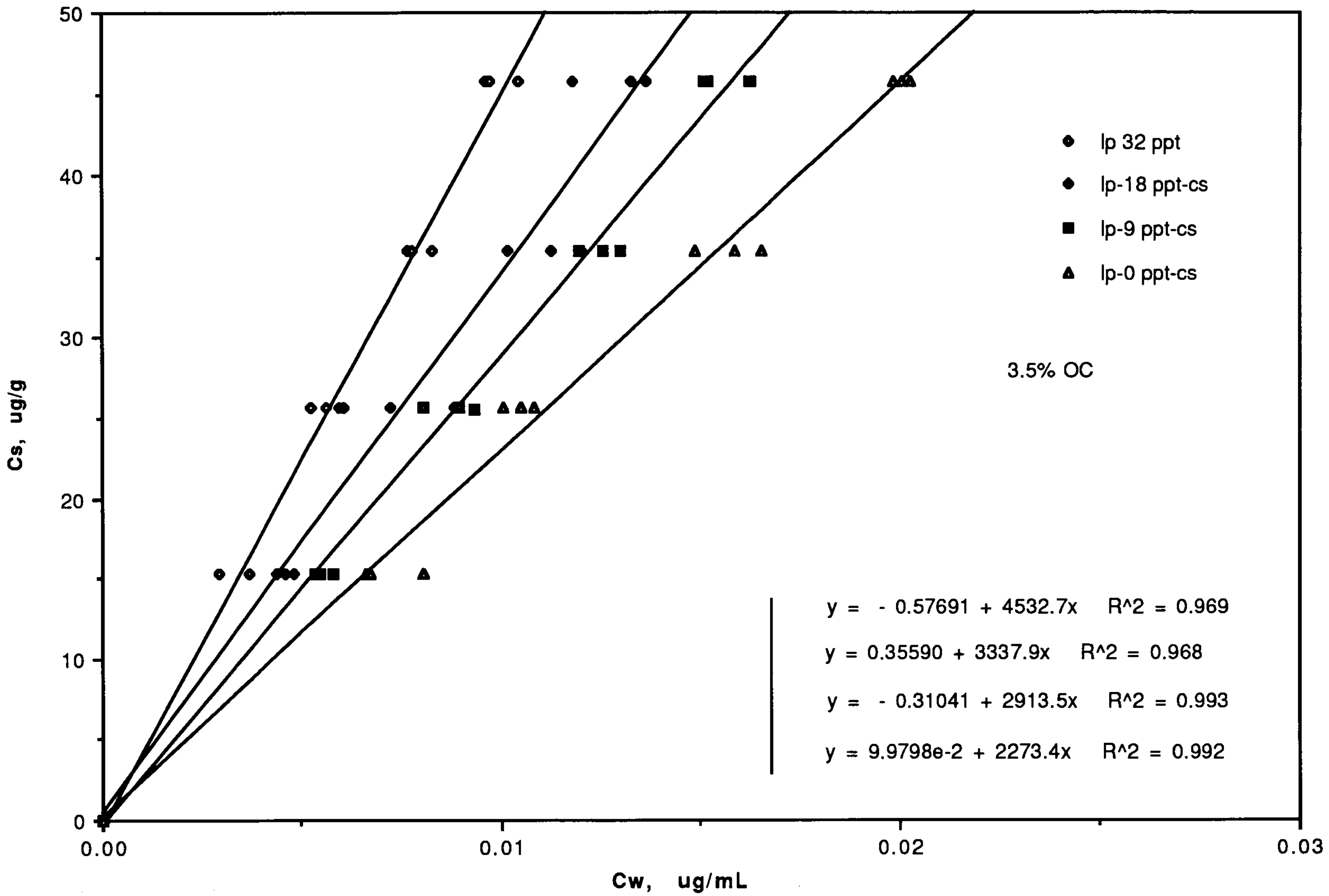


Figure 5.1.1. Sorption isotherms as a function of salinity obtained on contaminated sediment from Lab Point.

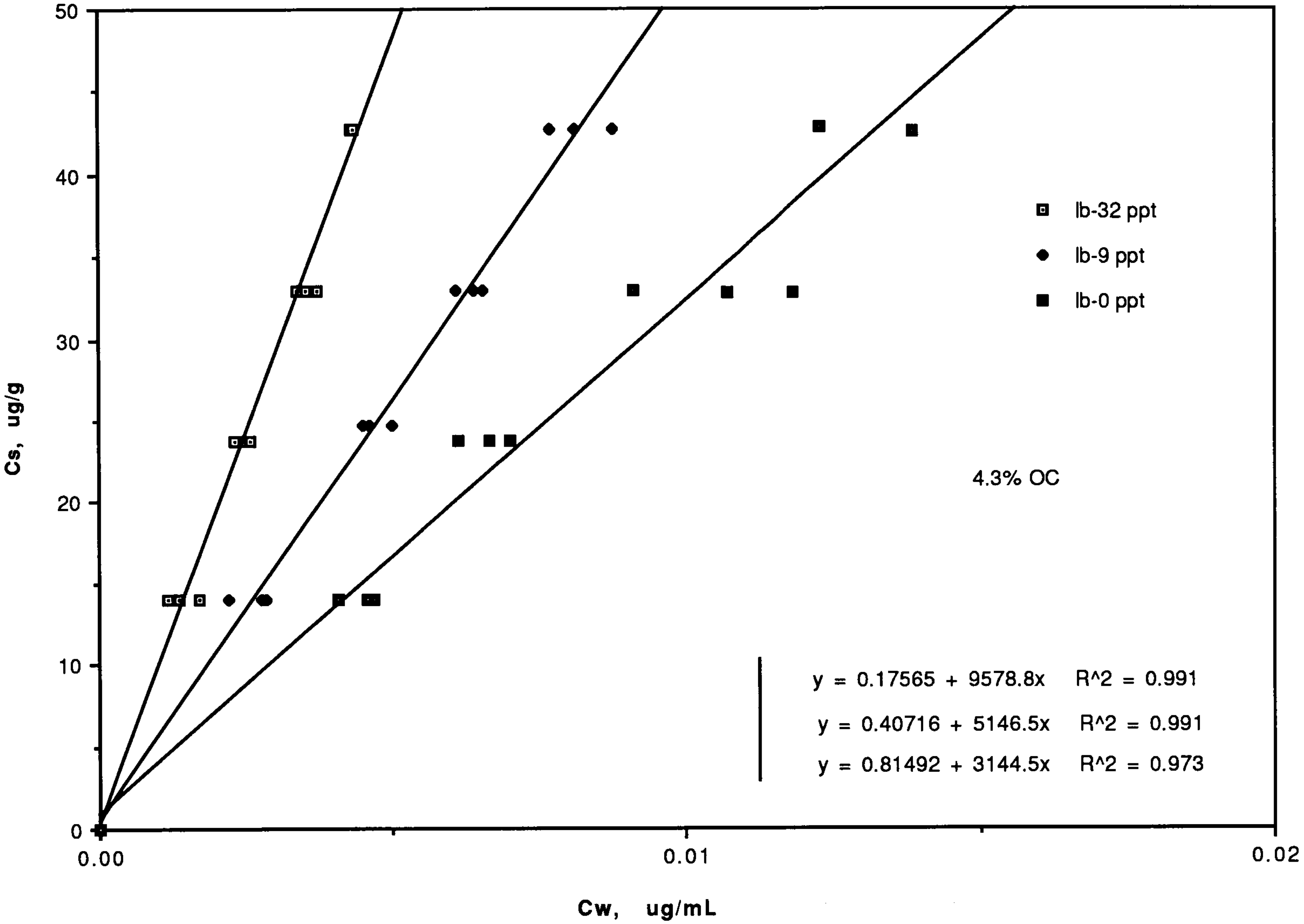


Figure 5.1.2. Sorption isotherms as a function of salinity obtained on contaminated sediment from Lafitte Bayou

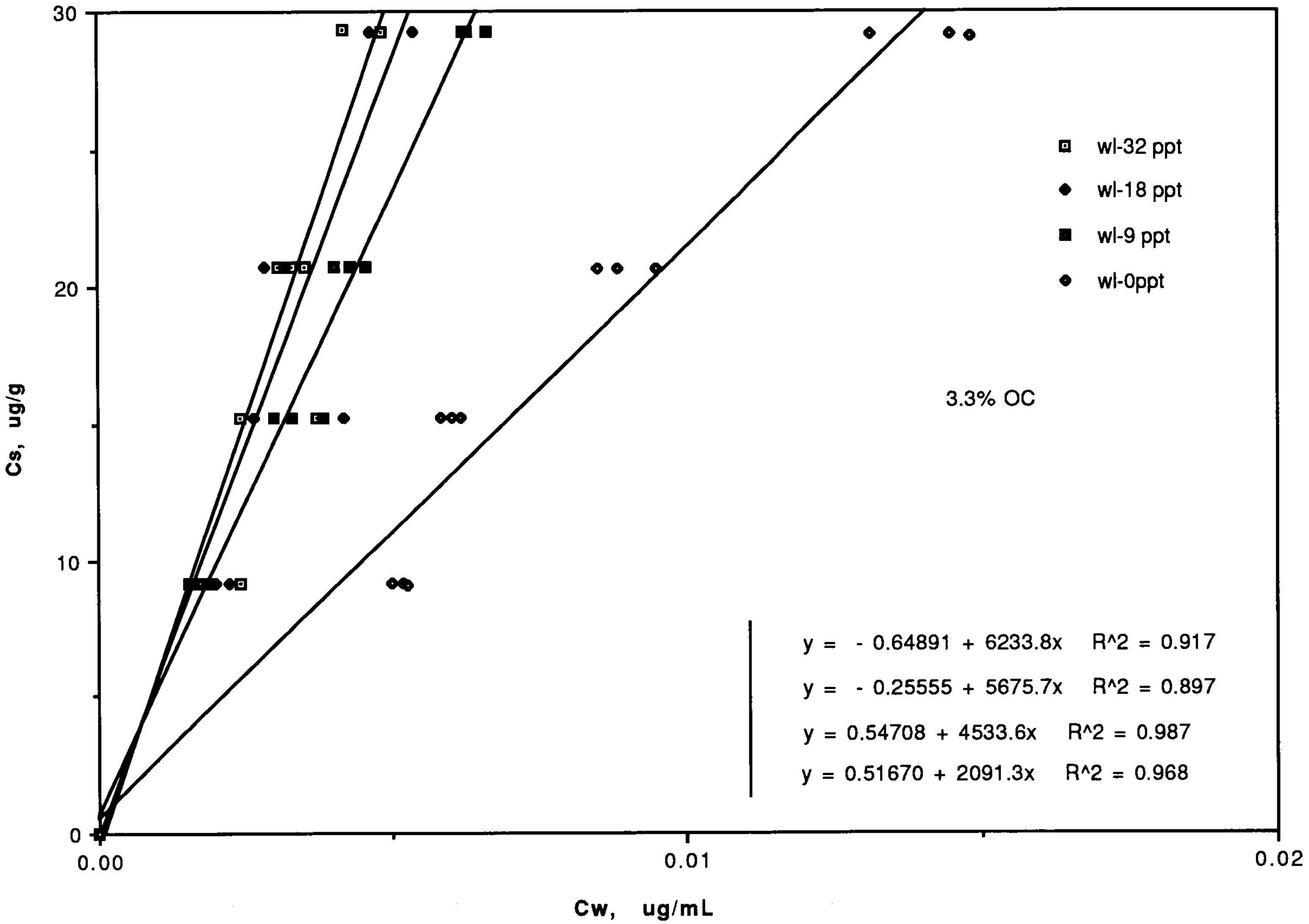


Figure 5.1.3. Sorption isotherms as a function of salinity obtained on control (uncontaminated) sediment from Westlake.

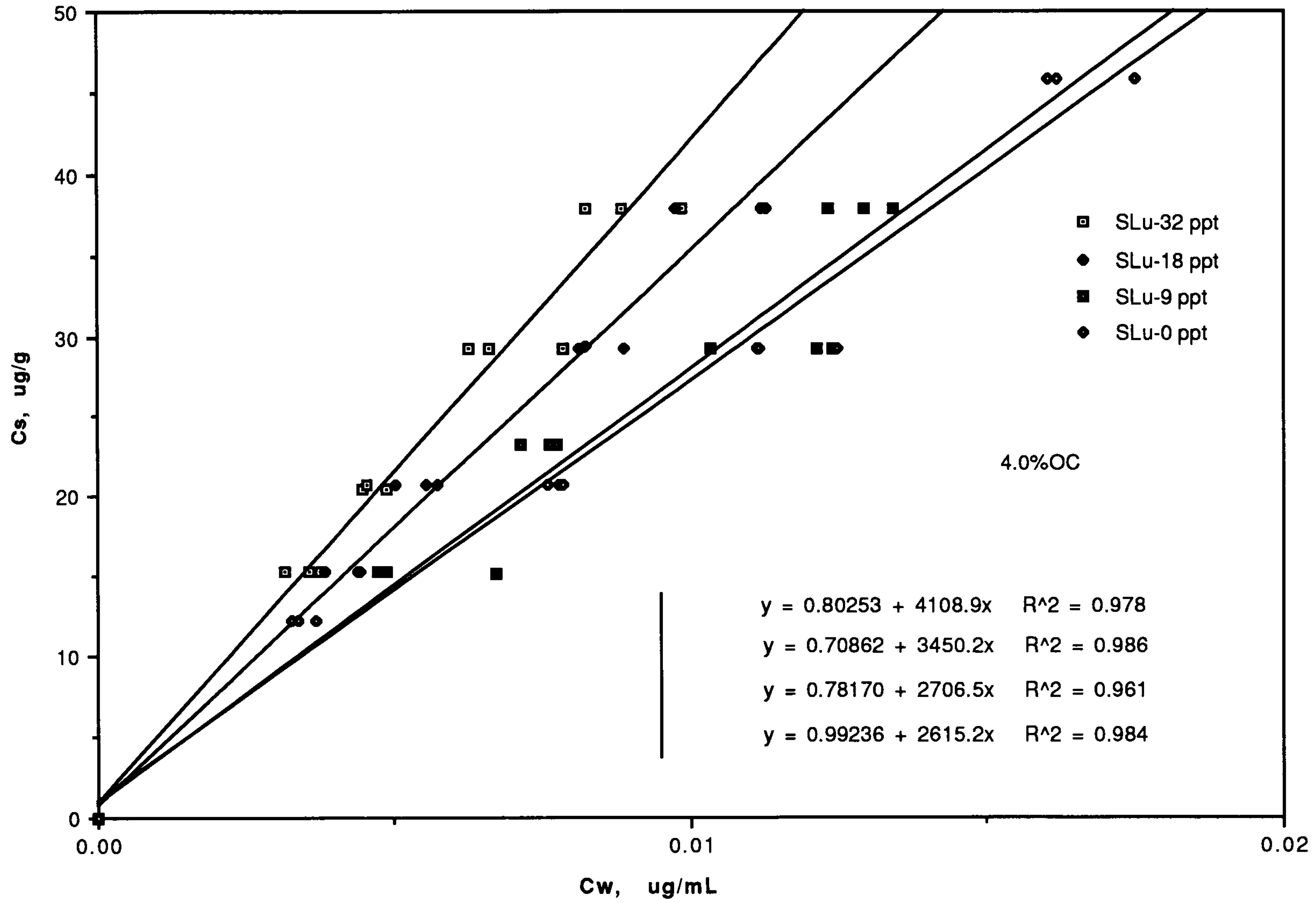


Figure 5.1.4. Sorption isotherms as a function of salinity obtained on control (uncontaminated) sediment from Southlake, top (sediment water interface).

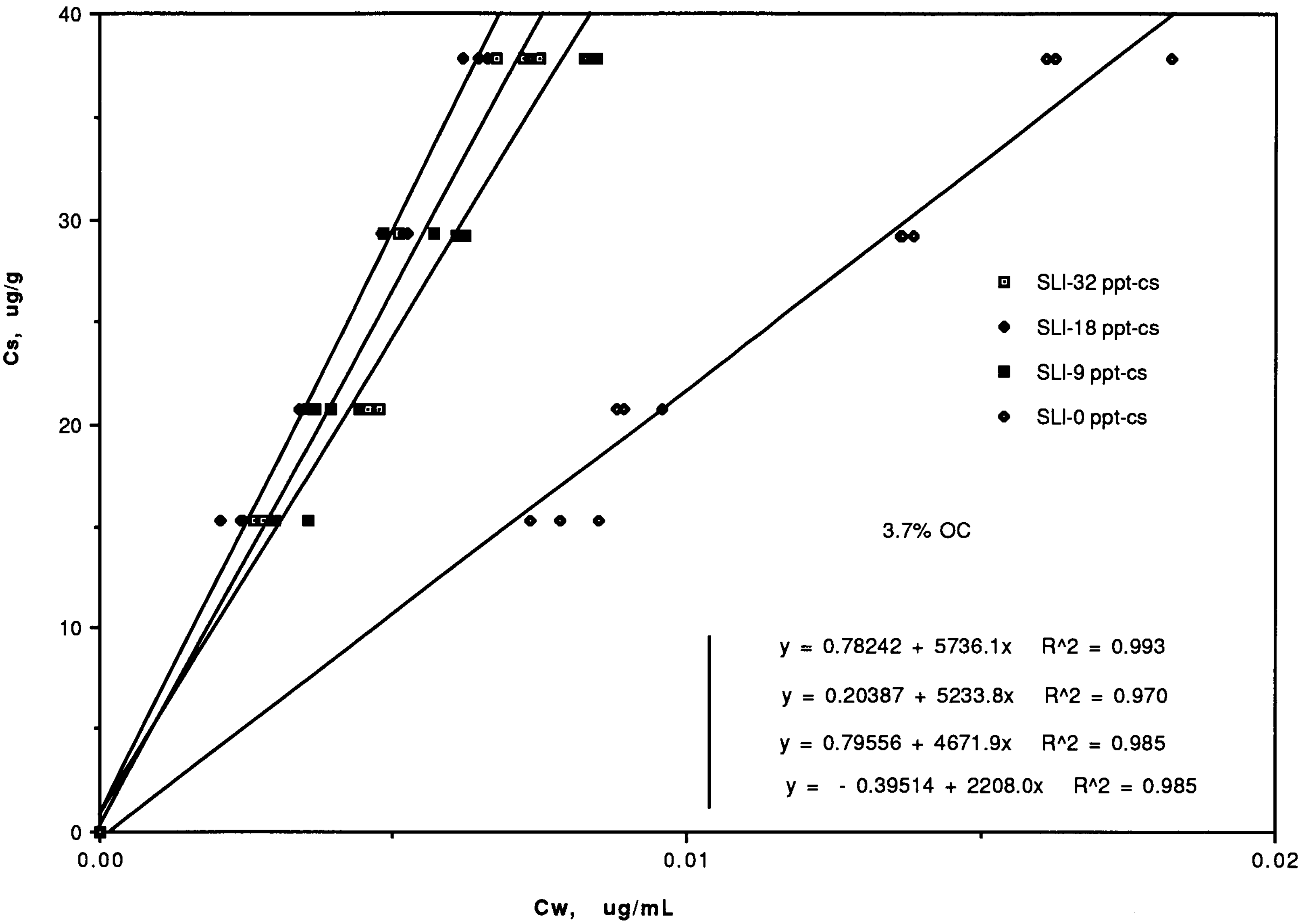


Figure 5.1.5. Sorption isotherms as a function of salinity obtained on control (uncontaminated) sediment from Southlake, bottom (approximately 20 cm below the sediment water interface).

The results obtained all suggest that the partitioning of pyrene on sediments and thus other PAHs is affected by changes in the salinity of the ambient waters. In all cases, as salinity was increased, there was an increase in the slope of the sorption isotherm, indicating that the binding of the pyrene molecule to the sediment organic carbon was increasing. Data for the sorption of pyrene at 0 salinity or in fresh water was compared to that determined in previous studies. Means et al. (1980) reported that the Kd values for pyrene as measured on fourteen different sediments and soils ranged from 71 to 1155 on substrates that contained between 0.11% and 2.38% organic carbon. They reported that the sorption capacity of the sediments was highly correlated with the organic carbon content, leading to the normalization of Kd values to Kocs for the sediments studied. Koc values exhibited a mean of 62700 ± 12000 and a range of 43800 to 85250 (Means et al., 1980). The sediment Kd values (range=2091 to 3144) in the present study all exceeded the range reported above but this was attributed to the higher organic carbon contents of the sediments studied here. Table 5.1.3 presents the Koc values for the sediments in the present study.

Table 5.1.3 Sorption Koc Values for Study Sediments as a Function of Salinity

Station	Salinity 0 ppt	9 ppt	18 ppt	32 ppt
Lab Point	64954.30	83242.90	95368.60	129505.70
Westlake	63372.70	137381.80	171990.90	188903.00
Lafitte Bayou	73127.90	119686.00	ND	222762.80
Southlake-top	65380.00	67662.50	86255.00	102722.50
Southlake-bottom	59675.70	126267.60	141454.10	155029.70
Mean	65302.12	106848.16	123767.15	159784.74
S.D	4918.06	29861.98	40216.07	47459.56

ND= not determined

In fresh water the Louisiana sediments exhibited pyrene Koc values in the range of 65302±4918. These results are very comparable with those reported earlier.

The desorption isotherm data gathered on three of the five sediments investigated in this study yielded both Kd and Koc values that were comparable to the sorption Kd and Koc values (Figures 5.1.6 to 5.1.8). Tables 5.1.4 and 5.1.5 present the values for Kd and Koc obtained.

The desorption Kd values for the three sediments ranged from 2055 to 2914, while the mean desorption Koc value was determined to be 70694±18520. Statistical comparisons of both the Kd and Koc values determined at all salinities indicated that all experimental sorption values were highly correlated with desorption values. A paired t-test of the sorption vs. desorption

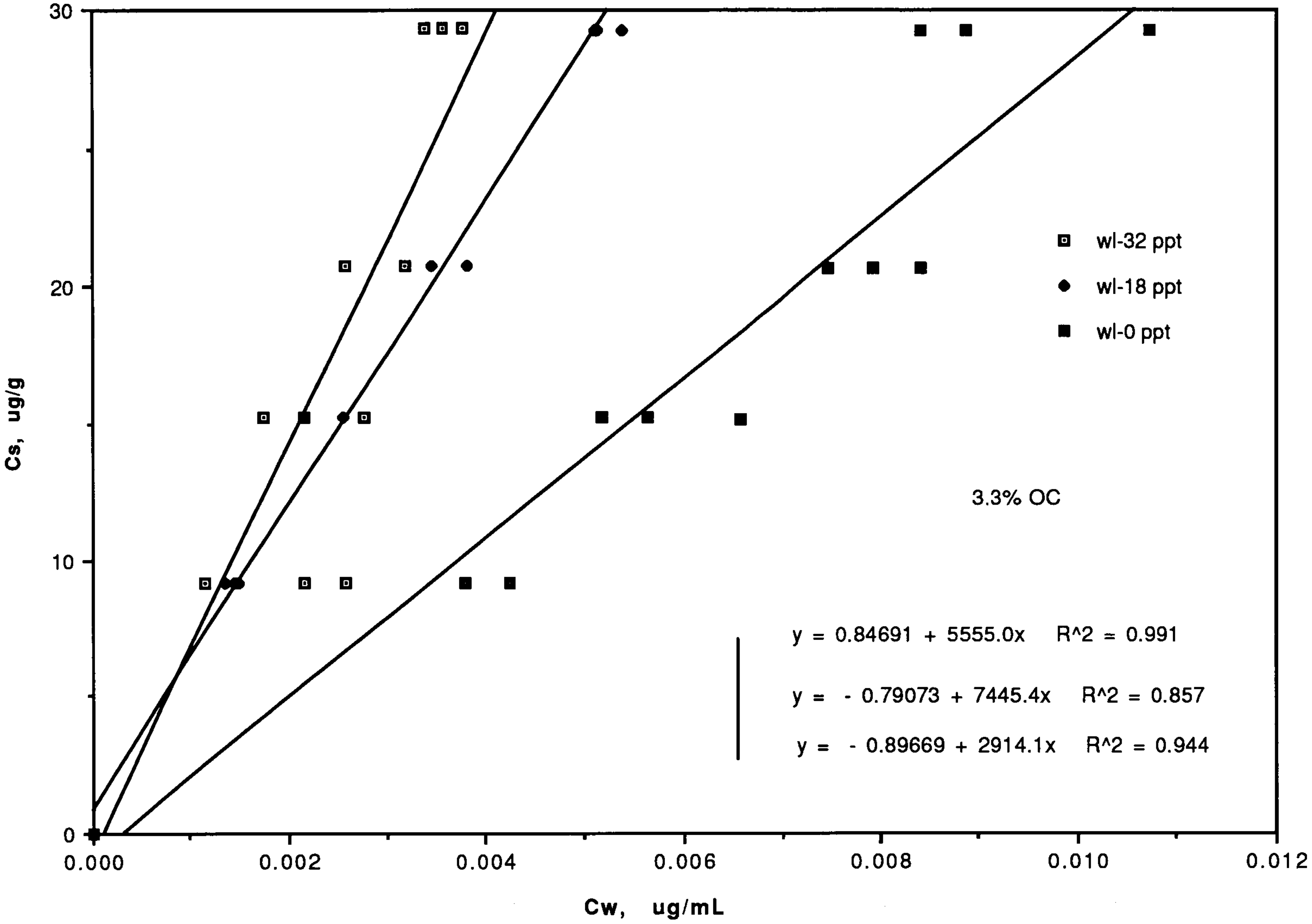


Figure 5.1.6. Desorption isotherms as a function of salinity obtained on control (uncontaminated) sediment from Westlake.

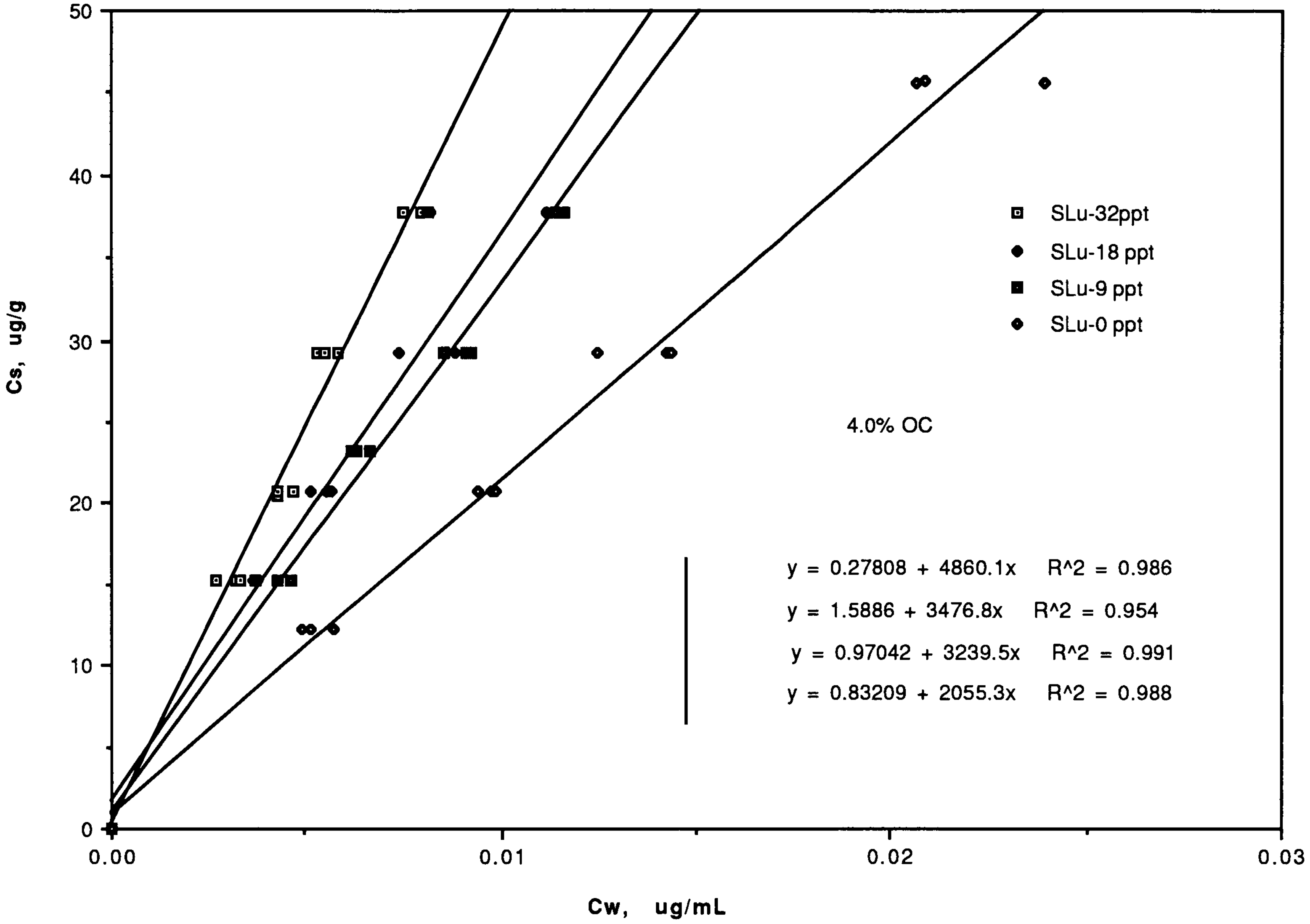


Figure 5.1.7. Desorption isotherms as a function of salinity obtained on control (uncontaminated) sediment from Southlake-top.

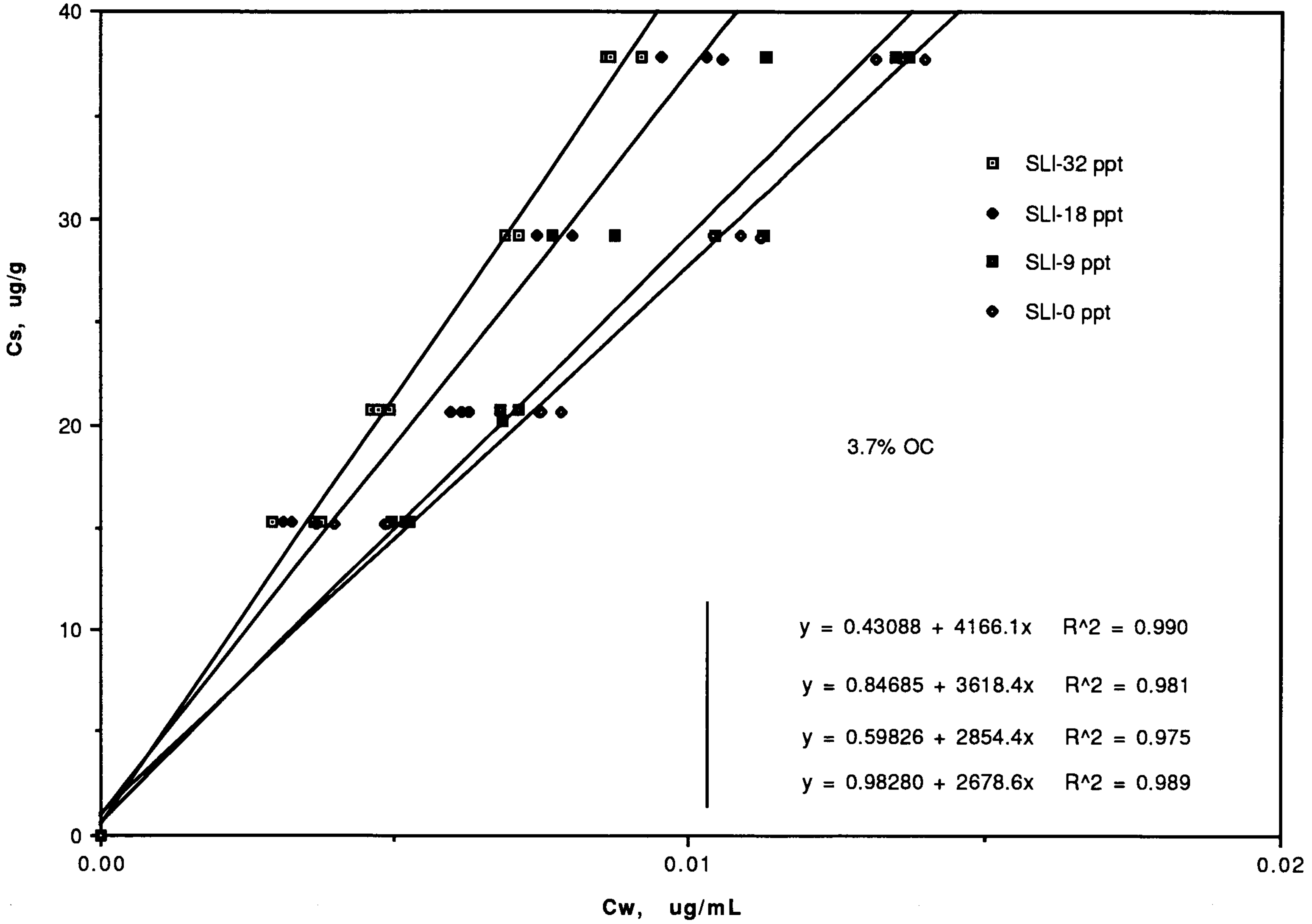


Figure 5.1.8. Desorption isotherms as a function of salinity obtained on control (uncontaminated) sediment from Southlake-bottom.

Table 5.1.4 Freundlich Equilibrium Desorption Constants for Study Sediments

Station	Salinity 0 ppt	9 ppt	18 ppt	32 ppt
Southlake-top	2055.3	3239.5	3476.8	4860.1
Southlake-bottom	2678.6	2854.4	3618.4	4166.1
Westlake	2914.1	ND	5555	7445.4

ND= not determined

Table 5.1.5 Desorption Koc Values for Study Sediments as a Function of Salinity

Station	Salinity 0 ppt	9 ppt	18 ppt	32 ppt
Southlake-top	51382.50	80987.50	86920.00	121502.50
Southlake-bottom	72394.60	77145.90	97794.60	112597.30
Westlake	88306.10	ND	168333.30	225618.20
Mean	70694.40	79066.70	117682.63	153239.33
S.D.	18520.42	2716.42	44200.47	62839.88

ND= not determined

Kd and Koc values indicated that they were not significantly different. Table 5.1.6 contains the results of these analyses.

Table 5.1.6 Statistical Analysis Results of Comparison of Sorption vs Desorption Constants

Station/ Parameter	n	Corr. coeff.	R-squared	d.f.	Probability
Southlake-top/Kd	4	0.914	0.836	3	0.566
Southlake-bot/Kd	4	0.819	0.671	3	0.126
Westlake/Kd	3	0.954	0.911	2	0.248
Southlake-top/Koc	4	0.914	0.836	3	0.566
Southlake-bot/Koc	4	0.819	0.0671	3	0.126
Westlake/Koc	3	0.954	0.911	2	0.248

The results of these analyses suggest that the sorption process on natural sediments investigated in this study were completely reversible and that the partition coefficients obtained from both types of equilibration processes are equivalent within experimental error. Results obtained on sediments heavily contaminated with petroleum-related hydrocarbons were not statistically different from natural uncontaminated sediments.

The results of the study on the effects of increasing salinity upon sorption and desorption equilibria represent some of the most detailed data published to date. In all cases, sorption/desorption Kd values were dependent upon salinity. Table 5.1.7 presents the results of an analysis of variance test of the influence of salinity upon the sorption/desorption Kd values for pyrene on estuarine sediments investigated as part of this study. The results of this analysis demonstrate that salinity has a very significant effect upon equilibrium partition constants on sediments (P<0.000145). In an examination of the variance in a Two-Factor test (Table 5.1.8), where the the differences associated with sorption vs. desorption results were partitioned from salinity effects, the results show that sorption/desorption Kds are not significantly different (P<0.729) regardless of salinity while salinity had a very significant effect (P<0.00144) on Kd values.

Table 5.1.7 One-way ANOVA for the Influence of Salinity upon Pyrene Sorption/Desorption Kd Values

Anova: Single-Factor

Summary

Groups	Count	Sum	Average	Variance
0 ppt	8	19980.40	2497.55	161912.20
9 ppt	7	26065.90	3723.70	1043438.85
18 ppt	7	30347.80	4335.40	1186803.18
32 ppt	8	46661.90	5832.74	3598467.43

ANOVA

Source of Variation	SS	df	MS	F	P-value
Between Groups	45940801	3	15313600.5	10.0280202	0.00014421
Within Groups	39704110	26	1527081.14		
Total	85644911	29		F crit 7.35690264	P<0.001

Table 5.1.8 Two-Factor ANOVA for Sorption/Desorption Experiments with Estuarine Sediments

	sorption	desorption	Total
0 ppt			
Count	3	3	6
Sum	6914.5	7648	14562.5
Average	2304.83333	2549.33333	4854.16667
Variance	75650.3233	196916.763	272567.087
9 ppt			
Count	3	3	6
Sum	11912	10637.9	22549.9
Average	3970.66667	3545.96667	7516.63333
Variance	1203369.74	784128.403	1987498.15
18 ppt			
Count	3	3	6
Sum	14359.7	12650.2	27009.9
Average	4786.56667	4216.73333	9003.3
Variance	1388225.8	1348230.89	2736456.7
32 ppt			
Count	3	3	6
Sum	16078.8	16471.6	32550.4
Average	5359.6	5490.53333	10850.1333
Variance	1235114.19	2986536.76	4221650.95
Total			
Count	12	12	
Sum	49265	47407.7	
Average	16421.6667	15802.5667	
Variance	3902360.06	5315812.82	

ANOVA

Source of Variation	SS	df	MS	F	P-value
Sample	28870817.2	3	9623605.73	8.35185528	0.00143549
Column	143731.804	1	143731.804	0.12473778	0.72856197
Interaction	729274.055	3	243091.352	0.21096706	0.88732181
Within	18436345.8	16	1152271.61		
Total	48180168.8	23			

F crit
5.29223598
8.53094662
5.29223598

Figures 5.1.9 through 5.1.10 show the regression of Koc values for pyrene vs salinity on the estuarine sediments studied. In most cases, the linear regression coefficients were 0.95 or greater. For two sediments (sorption-Westlake and sorption-

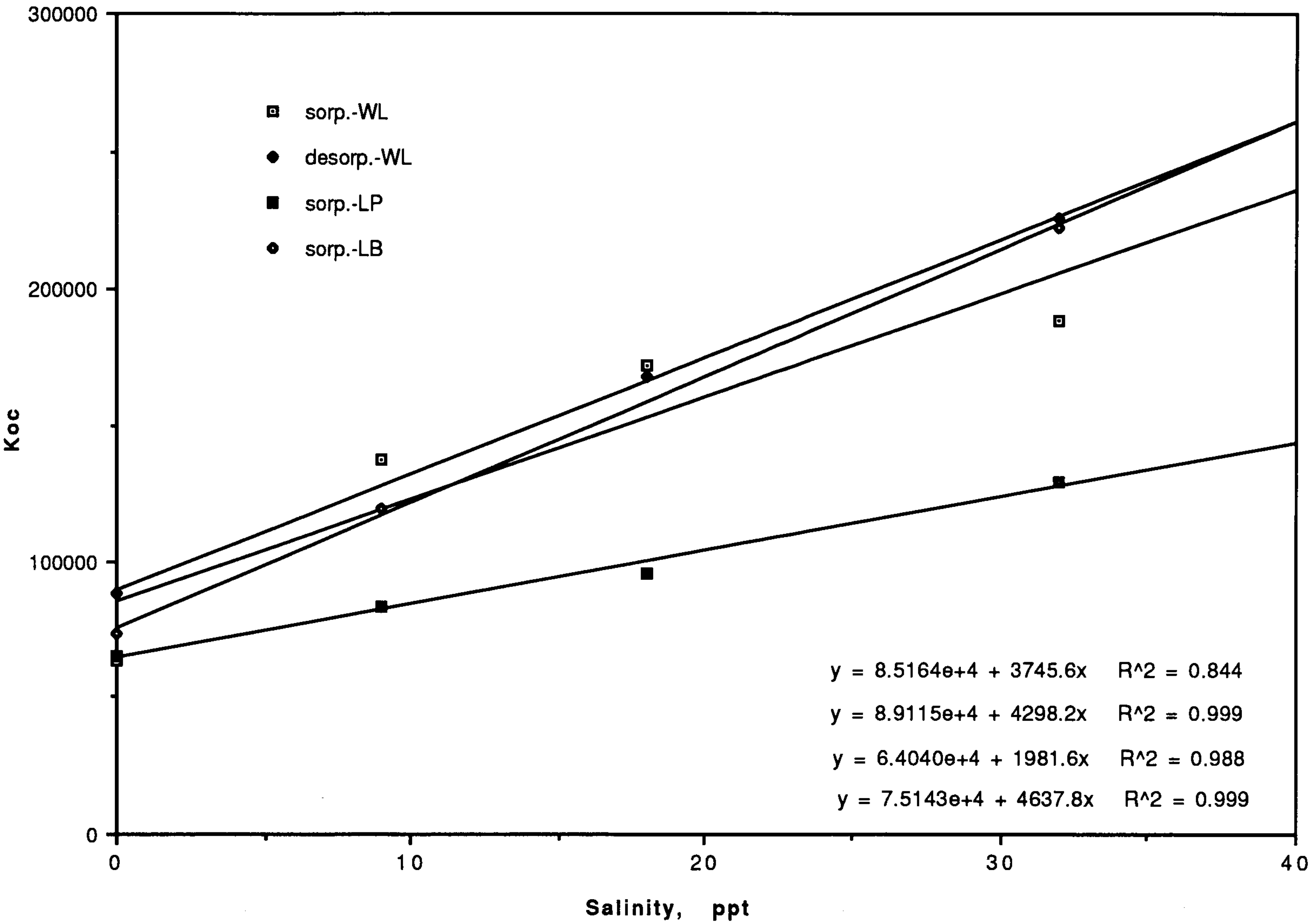


Figure 5.1.9. Regression of sorption/desorption Koc vs salinity on selected sediments.

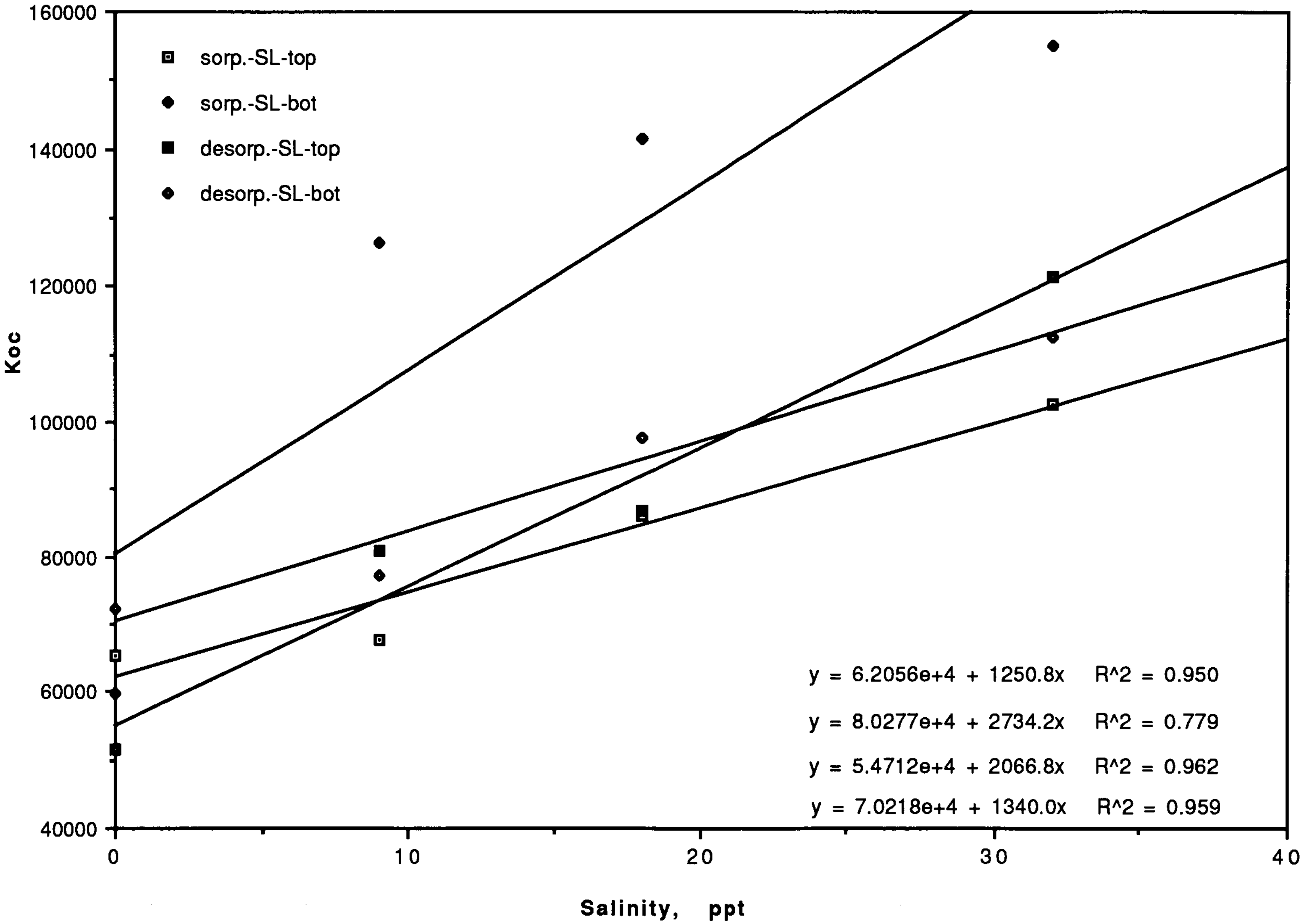


Figure 5.1.10. Regression of sorption/desorption Koc vs salinity on Southlake sediments.

Southlake-bottom), the results suggested that a non-linear regression should be applied. When this was done, regression coefficients increased to a level comparable to the other values observed. For six of the eight Koc values tested, Koc values increased linearly with increasing salinity. The slopes of these regressions ranged from 1250x to 4638x with intercepts between 54700 and 89100. For the two sediments that exhibited a nonlinear relationship of Koc with salinity the intercepts were approximately 64000. For these latter two sediments the rapid increase in Koc between 0 ppt and 9 ppt salinity seemed to be the primary difference between these sediments and the other sediments tested. Interestingly, the desorption Koc values for these two sediments changed linearly with changes in salinity.

Investigations of the effects of salinity upon the partitioning of neutral hydrophobic organic compounds upon sediments are fairly limited in the literature. Abernathy and Davidson (1971) investigated the influence of increasing the ionic strength of the solution phase in equilibrium and field soil mobility tests for the herbicides Prometryne and Flumeturon. They reported that increases of ionic strength using 0.01 and 0.5 N $CaCl_2$ increased sorption of Prometryne, a neutral triazine compound, while it decreased the sorption of the polar herbicide Flumeturon. Karickhoff (1984) investigated the influence of ionic strength using sodium chloride upon the sorption of pyrene and methoxychlor. They reported a small increase in sorption of both compounds on a soil. A maximum of a 15% increase in partition coefficients was observed with salt added to a mass equivalent to that of the soil in a 40:1 soil to water ratio system (Estimated salinity was ~25 ppt).

The relationship between aqueous solubility of organic compounds and their tendency to sorb to sediments has been investigated extensively (Means et al., 1979, 1980, 1982; Wijayaratne and Means, 1984). The relationships quantitatively relate decreases in aqueous solubility to corresponding increases in Kd and Koc values. By inference, factors which limit the solubility of a compound in solution would be expected to increase partitioning onto sediment particles. One such factor is the "salting out" effect of increasing dissolved solids in solution on the solubilities of neutral hydrophobic chemicals such as PAH.

The salting out effect has been known and investigated for a fairly long time. The first quantitative investigations of the phenomenon were performed by Setchenow in 1889. The effects of salts on solution properties of non-electolytes have been recognized and attributed to changes in chemical activity and reactivity (Long et al., 1951; Long and McDevit, 1951). The basic relationship is stated:

$$\log\ (\gamma_i/\gamma_i^o) = \log\ (S_i^o/S_i) = \sigma M$$

where σ is the Setchenow constant or salting out parameter, M is the molar concentration of the dissolved electrolyte and S and γ are the solubility and activity coefficient of the non-electrolyte in solution, respectively. The superscript (o) refers to the reference case of distilled water containing no dissolved electrolytes. The effects of the electrolytes upon the non-electrolytes are hypothesized to be the result of alterations of the structure of water and its interactions with neutral hydrophobic molecules in solution. The theory put forth by Long and McDevit states that ionic contributions to the Setchenow constant will be additive for different electrolytes (such as the mixture found in seawater) but there is little quantitative information on the behavior of mixed electrolytes (Gordon and Thorne, 1967a and b).

The effects of salts upon the solubility of PAH such as pyrene have been investigated by several laboratories. May and Wasik (1978) showed a decrease in solubility of several PAH as a function of increased salt content in the effluent of generator columns designed to generate saturated solutions of PAH and measure the Setchenow constant for pyrene at 0.25. Rossi and Thomas (1981) reported both calculated and experimentally determined Setchenow constants for three PAHs, including pyrene. The value was 0.319 l/m.

Long and McDevit (1951) showed that the differences in the concentrations of non-electrolytes in aqueous solution at different ionic strengths and in non-aqueous reference phases gave the following relationship in activity coefficients:

$$\gamma_i^O Ci^O = b\gamma_i^R Ci^R = \gamma_i^S Ci^S$$

where b is a constant and γ_i^O is the activity coefficient of the compound in pure water, γ_i^S is the activity coefficient of the compound in salt solution and γ_i^R is the activity coefficient of the compound in the reference (non-aqueous) phase. Values of Ci represent the concentrations of the compounds in the pure aqueous, saline and reference phases, respectively. From this relationship, we can infer that:

$$\gamma_i^S/\gamma_i^O = C_i^o/C_i^S$$

which is in the form of the Setchenow equation:

$$\gamma_i^S/\gamma_i^O = C_i^O/C_i^S = 10^{\sigma Ms}$$

where σ is the Setchenow constant and Ms is the molar concentration of the seawater.

Taking into consideration what we already know about partitioning on sediments with respect to Kd:

$$Kd=Cs/Cw$$

This may be restated as:

$$1/Kd\gamma_o{}^O C_o{}^O=\gamma_i{}^O C_i{}^O$$

where $\gamma_o{}^O$ is the activity coefficient of the compound in the organic phase of the sediment, $C_o{}^O$ is the concentration of the compound in the sediment organic matter, $\gamma_i{}^O$ is the activity coefficient of the compound in the aqueous phase and $C_i{}^O$ is the concentration of the compound in the pure aqueous phase. In our experiments where we are considering the effects of salinity upon the partitioning process, the changes in Kd may be the result of changes in the activity coefficient of pyrene in the aqueous phase alone or as the result of changes in the activity coefficients in both the aqueous phase and the sediment organic carbon phase.

$$1/Kd = \gamma_i{}^S/\gamma_o{}^O 1/Kd^S$$

Rearranging this equation we see that:

$$Kd^S/Kd= \gamma_i{}^S/\gamma_o{}^O$$

and substituting the log form of the Setchenow equation for $\gamma_i{}^S$

$$Kd^S/Kd= 10^{\sigma Ms}/\gamma_o{}^O$$

and taking the logarithm that:

$$\log Kd^S/Kd=\sigma Ms-\log\gamma_o{}^O$$

Thus a plot of log $\log Kd^S/Kd$ against the molar concentration of seawater should yield a slope of σ and an intercept of $-\log\gamma_o{}^O$. If sediment organic matter can be considered an "ideal" reference phase then the value of $\gamma_o{}^O$ should be close to unity or 1.0. Similarly, if salting out effects are solely responsible for the increases in sorption observed then the slope of the log Kd^S/Kod plots should approximate the Setchenow constants measured in solution or ~0.3. Figures 5.1.11 to 5.1.18 show the relationship of log Kd^S/Kd with Ms and Table 5.1.9 summarizes the results of all experiments performed.

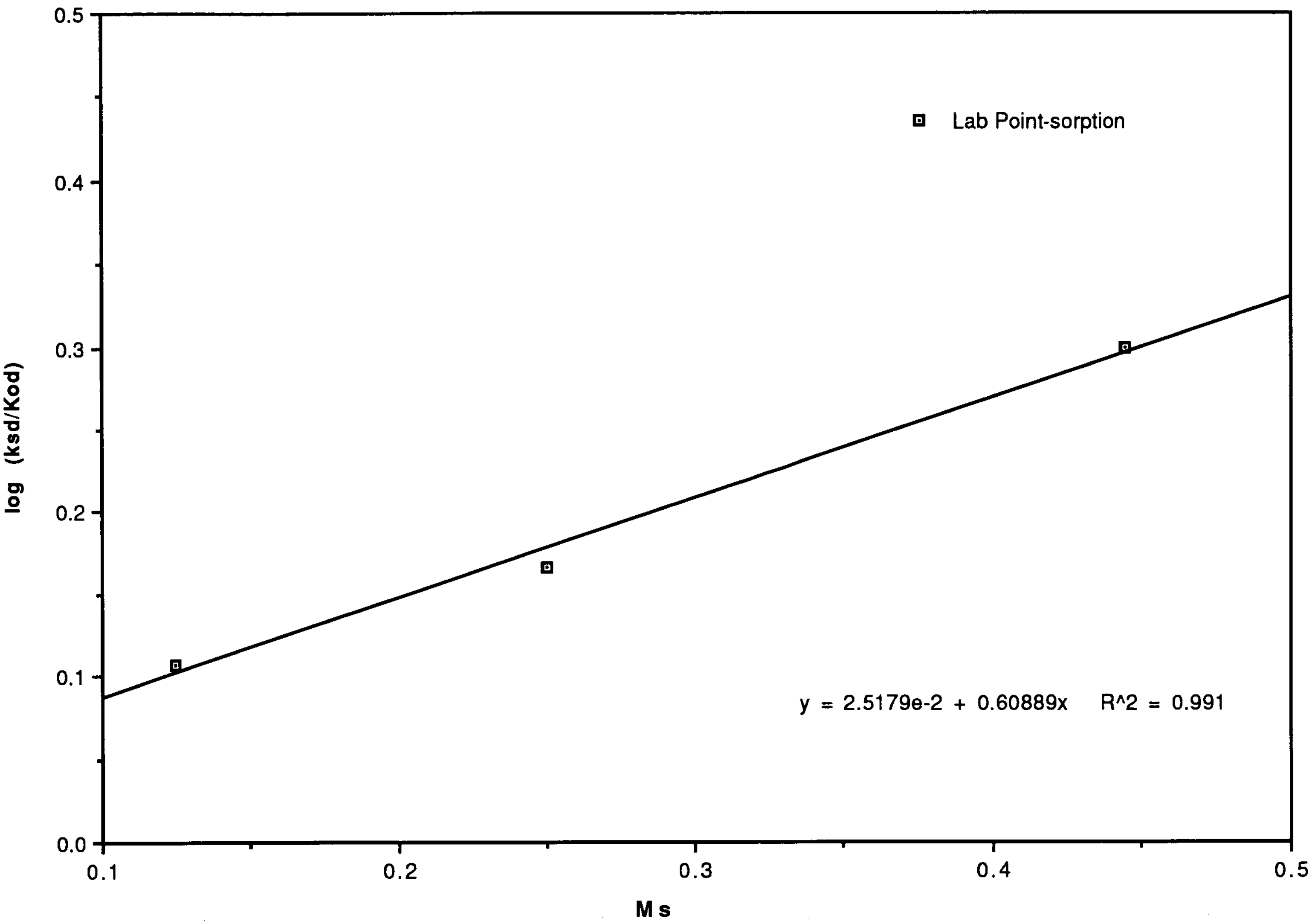


Figure 5.1.11. Estimate of Setchenow constant from sediment partitioning data, Lab Point-sorption.

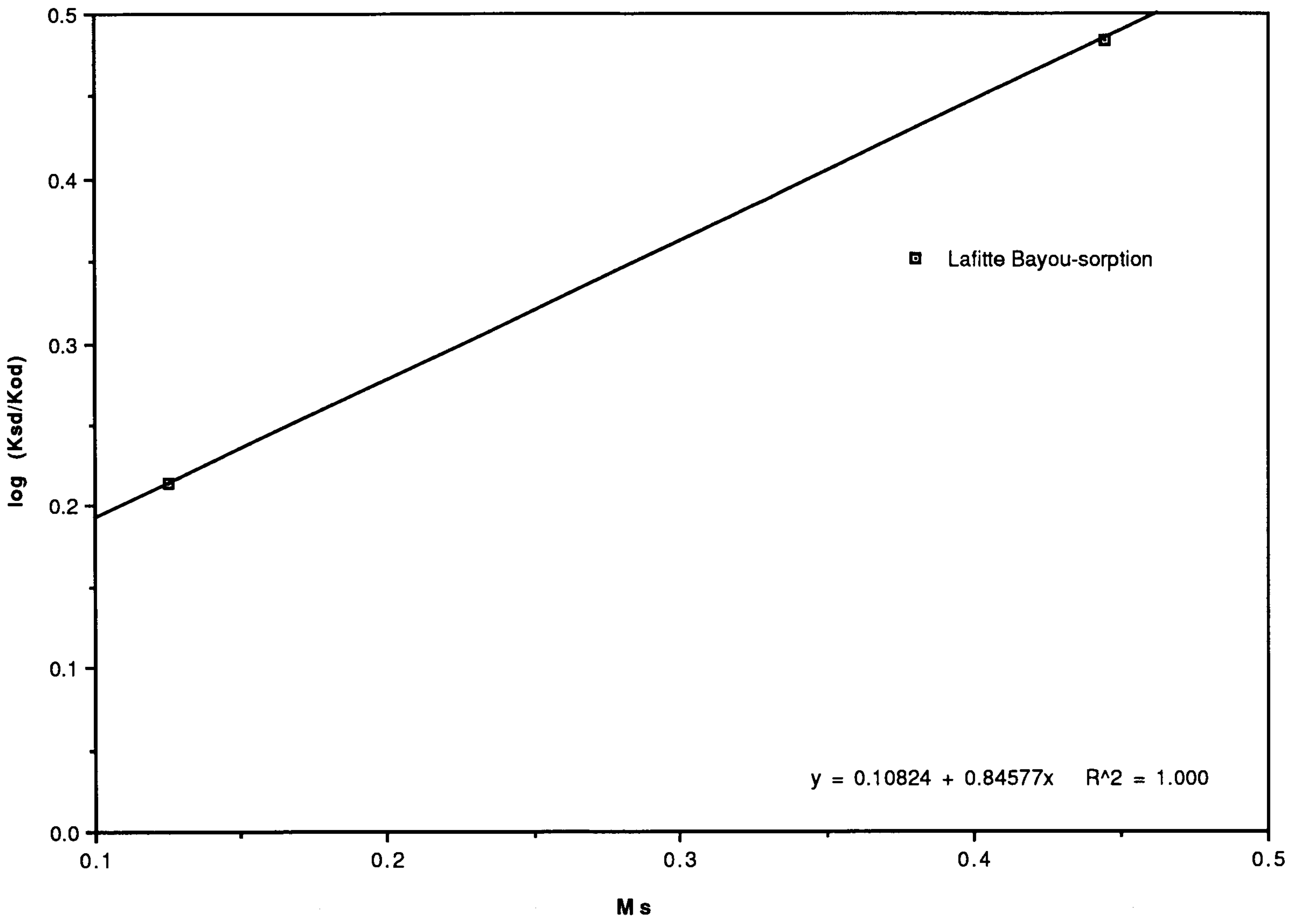


Figure 5.1.12. Estimate of Setchenow constant from sediment partitioning data, Lafitte Bayou-sorption.

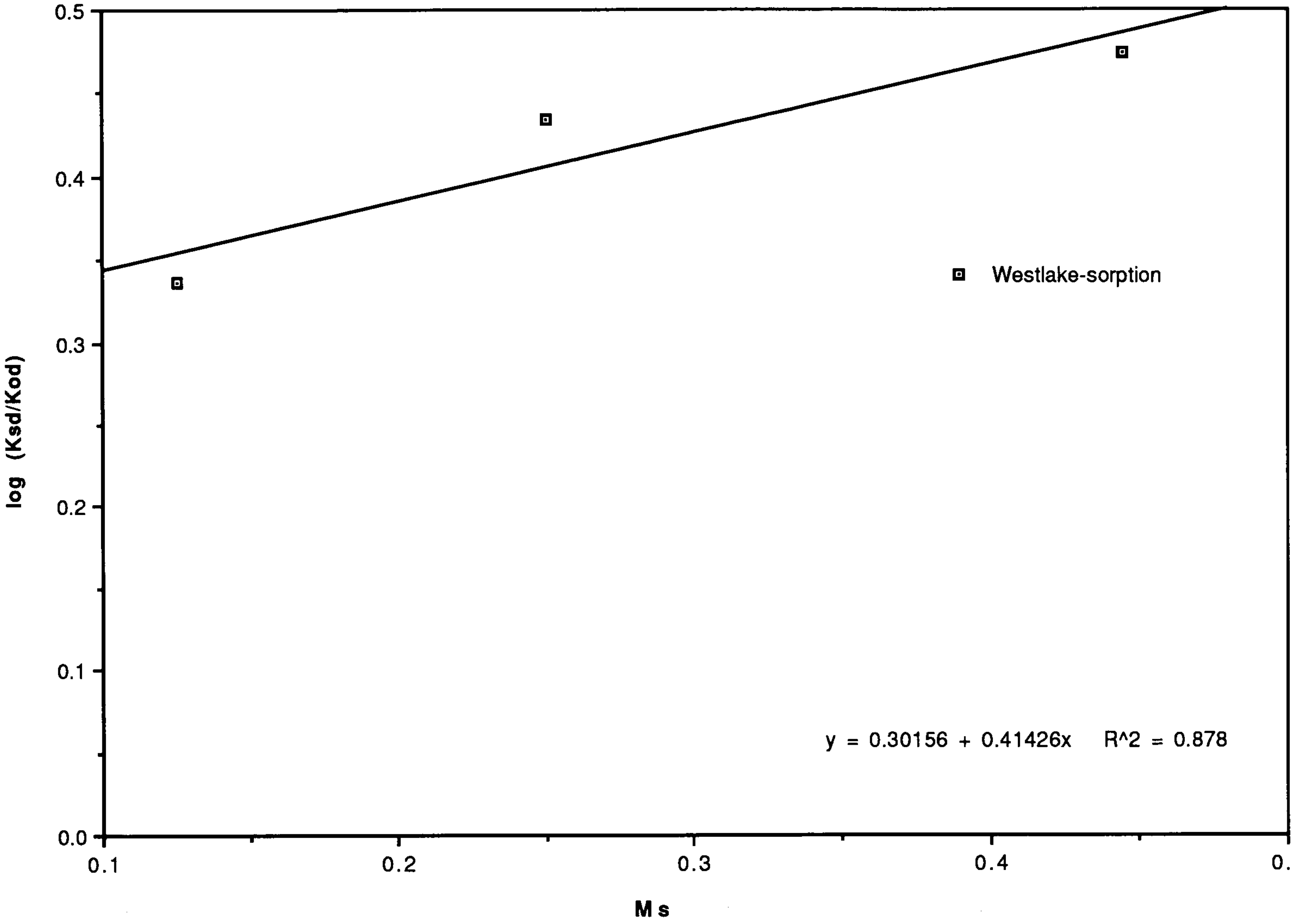


Figure 5.1.13. Estimate of Setchenow constant from sediment partitioning data, Westlake-sorption.

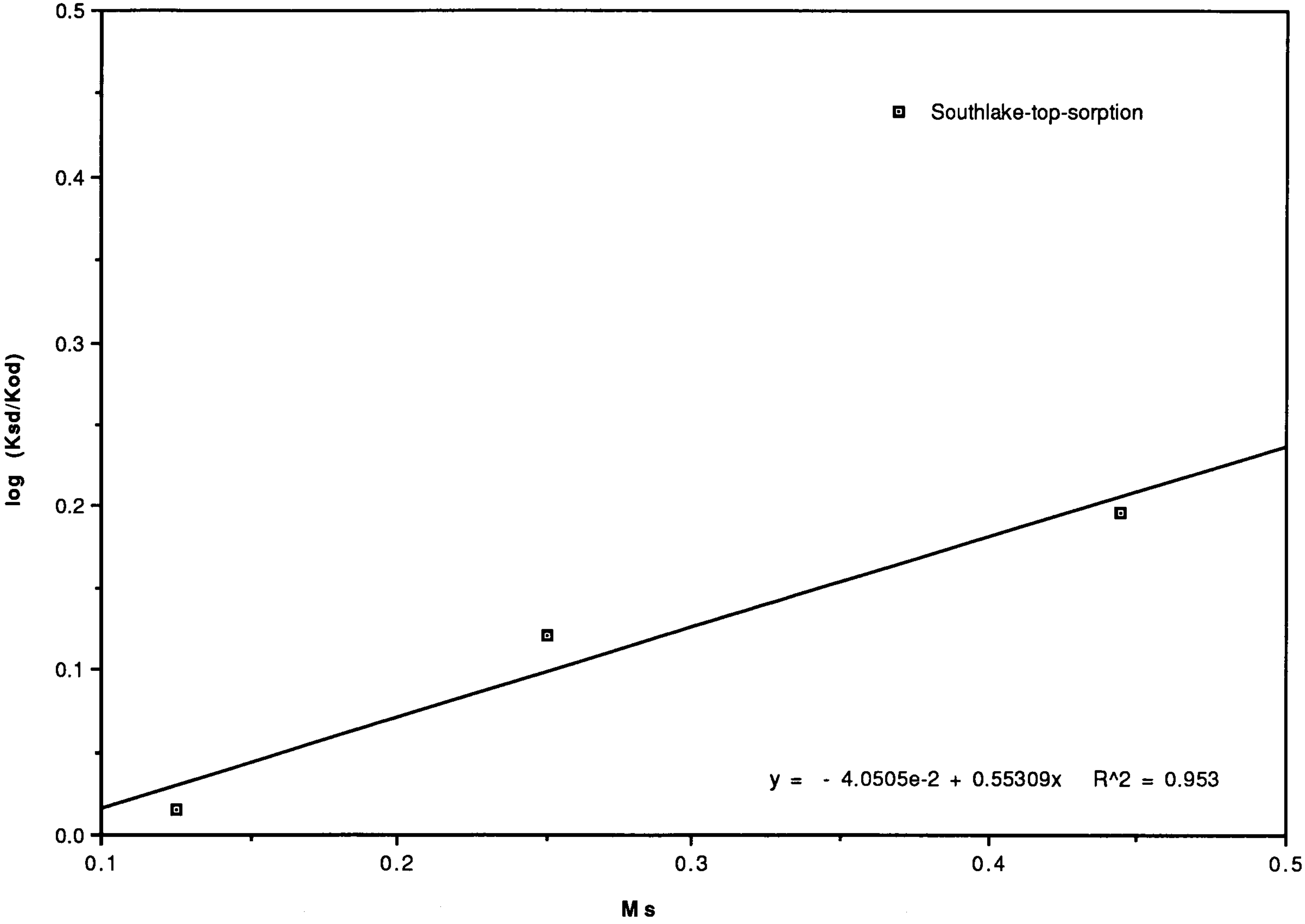


Figure 5.1.14. Estimate of Setchenow constant from sediment partitioning data, Southlake-top-sorption.

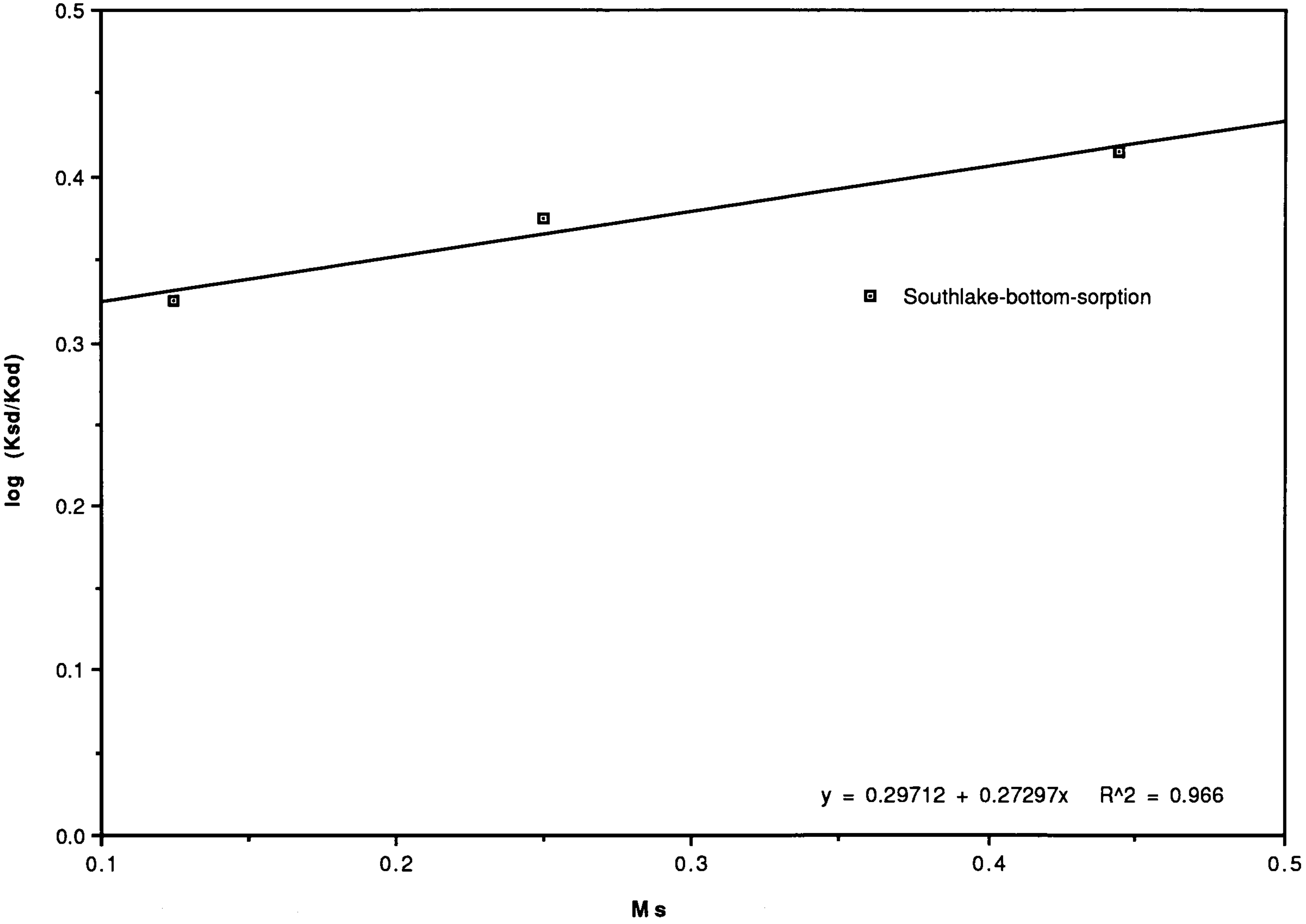


Figure 5.1.15. Estimate of Setchenow constant from sediment partitioning data, Southlake-bottom-sorption.

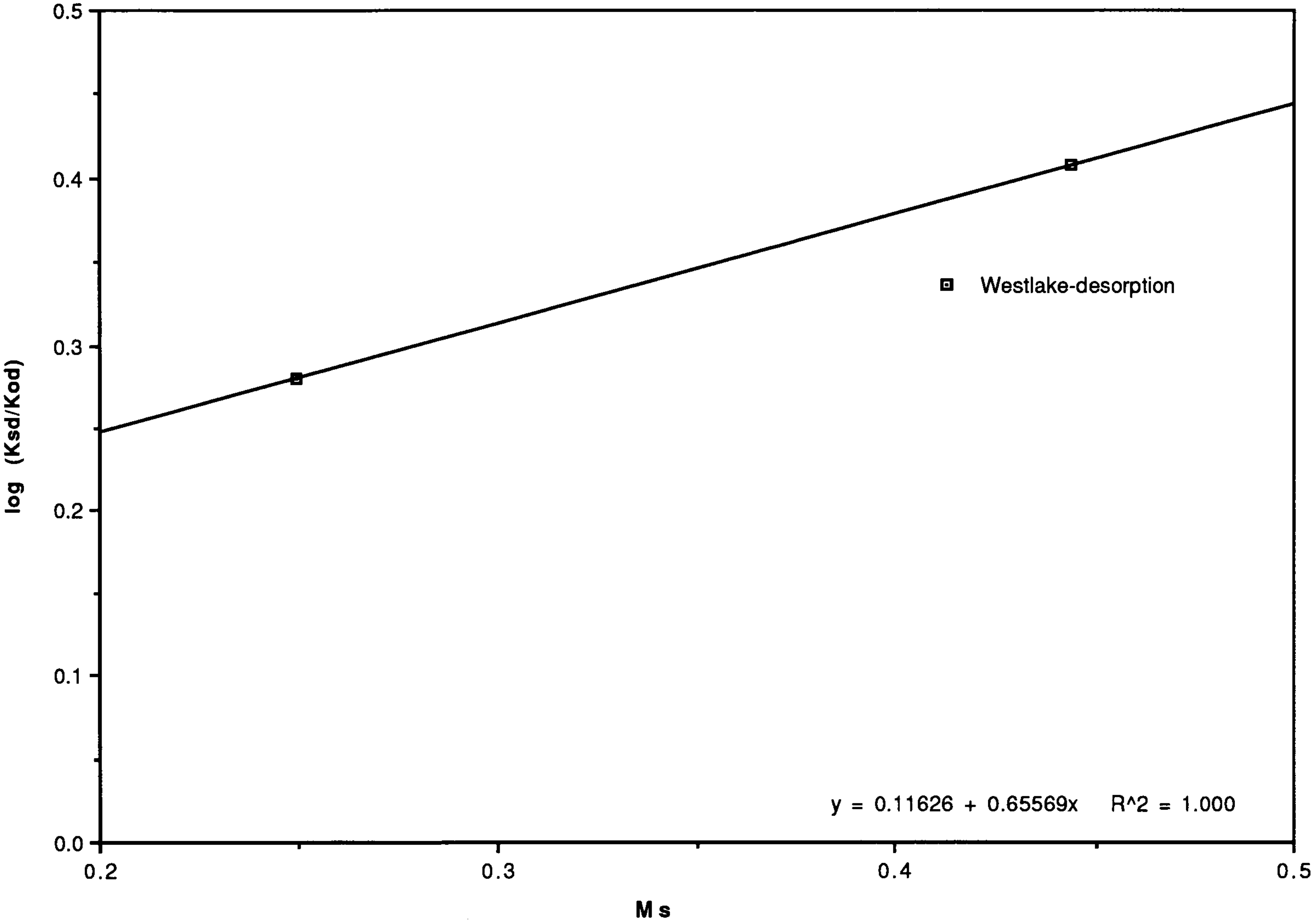


Figure 5.1.16. Estimate of Setchenow constant from sediment partitioning data, Westlake-desorption.

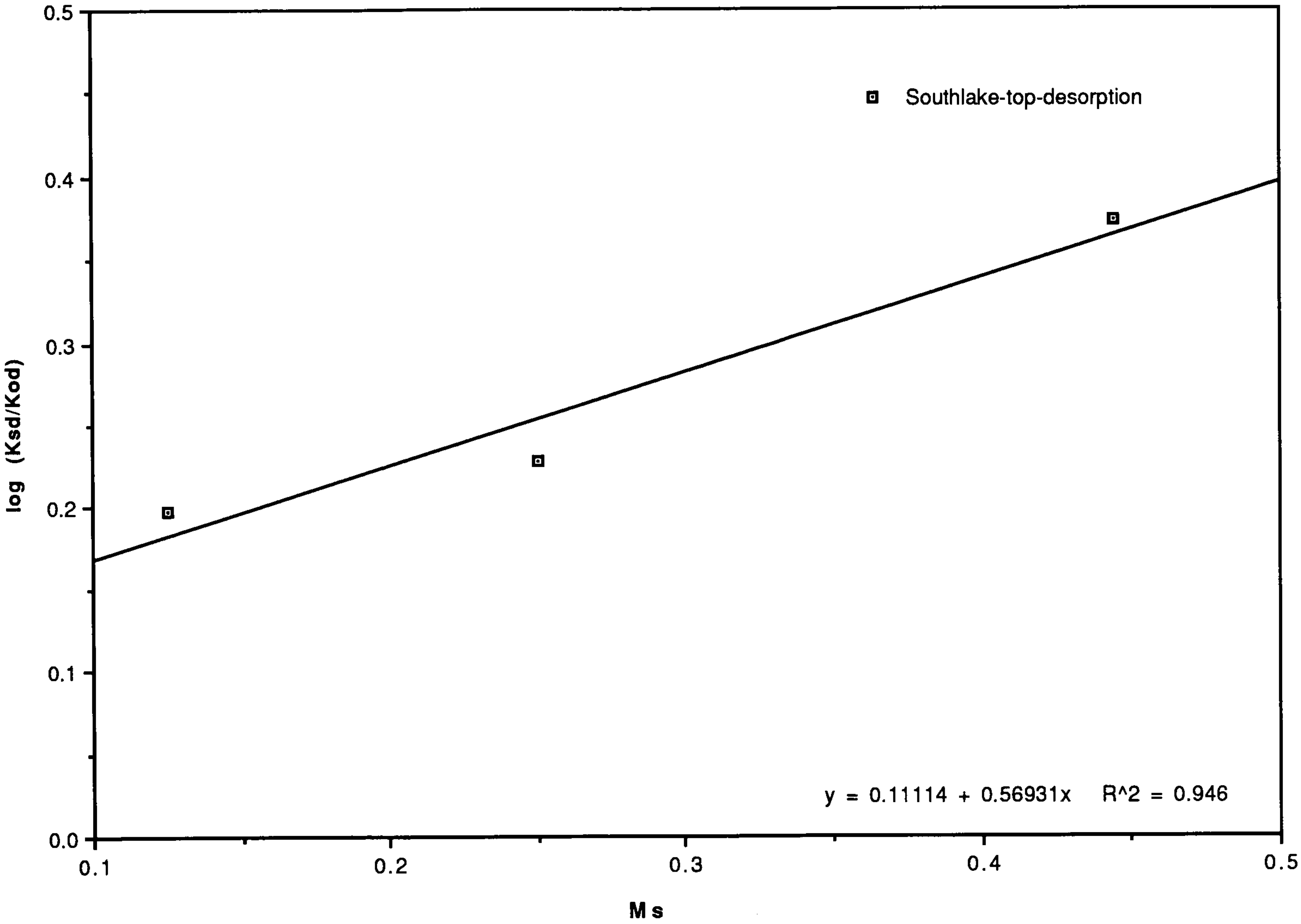


Figure 5.1.17. Estimate of Setchenow constant from sediment partitioning data, Southlake-top-desorption.

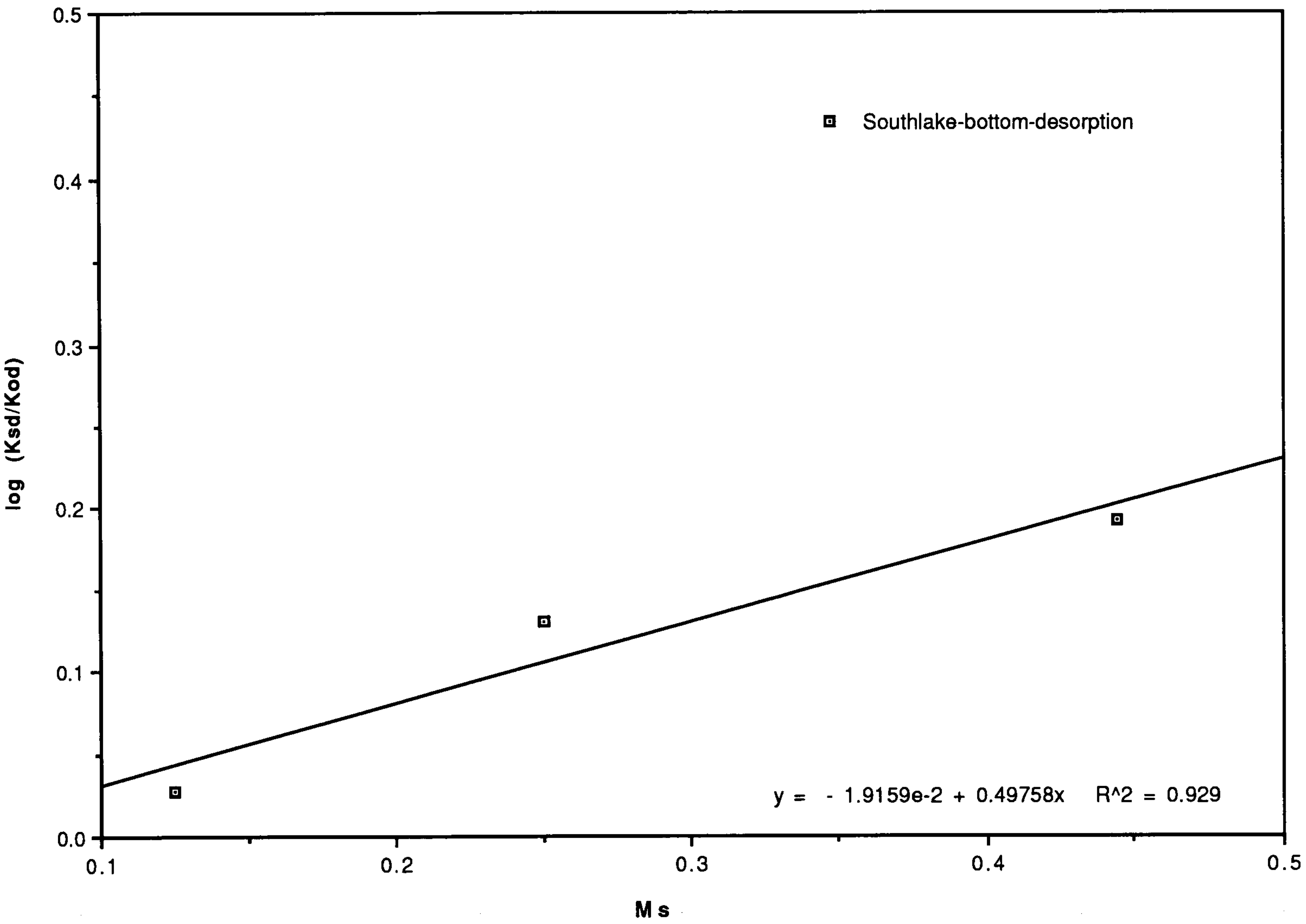


Figure 5.1.18. Estimate of Setchenow constant from sediment partitioning data, Southlake-bottom-desorption.

Table 5.1.9 Estimates of the Setchenow Constant for Pyrene from Sediment Partitioning on Estuarine Sediments

Sediment	R-squared	(-log γ_o)	γ_o	σ
Lab Point	0.991	0.02517	0.9436	0.6089
Westlake-s	0.878	0.3015	0.4995	0.4143
Lafitte Bayou		0.999	0.1082	0.7794
	0.8458			
Southlake-top-s		0.953	-0.04051	1.0977
	0.5531			
Southlake-bot-s		0.966	0.2971	0.5045
	0.2729			
Southlake-top-d		0.946	0.1111	0.7743
	0.5693			
Southlake-bot-d		0.929	-0.01915	1.0451
	0.4976			
Westlake-d	0.999	0.1162	0.7652	0.6557
Mean		0.11245125	0.8011625	0.5522
S.D.		0.12994647	0.22335936	0.16921136

The mean value of the Setchenow constant determined from the sediment partitioning experiments was 0.552, with a range of 0.273 to 0.846 and the mean estimate of γ_o^O was 0.801, with a range of 0.500 to 1.098. The fact that estimates of σ yield a value greater than that determined in solution phase experiments suggests that the increase in sorption as a function of salinity is only partially accounted for by the decrease in solubility as the result of the salting out effect. Deviations from the Setchenow constant observed from solution experiments may also suggest that the aqueous phase and the reference phase, in this case sediment organic matter, may not be completely immiscible (Long and McDevit, 1951; Long et al., 1951). Therefore, some changes associated with the organic phase of the sorbant may be responsible for the other increases observed. The fact that γ_o^O is less than unity suggests that changes in salinity also have some impact upon the activity coefficients of pyrene in the organic matter phase and further that these changes are resulting in sediment organic matter being a "better solvent" for pyrene at elevated salinities.

Means and Wijayaratne (1982) observed large alterations in the sorptive capacity of natural colloidal organic matter isolated from aquatic systems as a function of salinity. They interpreted this observation to changes in the conformation of the organic matter in 3-dimensional space. Freeman and Cheung (1981) proposed a gel permeation model for sediment organic matter in which the solution characteristics of solvent phase altered the swelling and contraction of the organic matrix associated with sediment particles. The results reported here suggest that sediment organic matter, although probably rich in polar functional characteristics (Chiou et al., 1983), may itself be "salted out" at elevated salinities, thus making the organic matter a better solvent for hydrophobic organic compounds such as pyrene.

5.2 Analytical Methods Development

5.2.1 Attempted Development of Stable Isotopic Labelling of Target Compounds

In order to be able to determine effects of previous sediment contamination on fate and transport of new contaminant inputs, stable isotopic labelling of compounds associated with petrogenic contamination was performed. The alkylated and heterocyclic polynuclear aromatic hydrocarbons (PAHs) were chosen to encompass a range of solubilities of PAH compounds and ensure adequate analytical resolution at low detection limits. Further, deuteration was initially chosen over tritiation or ^{14}C labelling because of cost considerations as well as handling and disposal methods. The six preliminary compounds were chosen for deuteration were 2-methylnaphthalene, 1-methylnaphthalene, dibenzothiophene, benz(a)anthracene, 2-methylphenanthrene, and 3,6-dimethylphenanthrene.

The compounds were deuterated using a tritiation procedure from Means et al. (1980), which was a modification of the method used by Hilton and O'Brien (1964). In this method, deuterated water was reacted with P_2O_5 to form deuterated phosphoric acid, which was then reacted with BF_3. The PAH compound was added to the reaction mixture in cyclohexane solution and stirred overnight to accomplish the exchange deuteration of the aromatic hydrogens on the molecules. The compound was then isolated by solvent extraction for further purification. We analyzed the deuterated products using GC-MS techniques to verify that deuteration had occurred and to determine the extent of exchange that had occurred.

Several technical problems were encountered in this procedure. Several of the compounds were not sufficiently soluble in cyclohexane as described in the original method. Therefore, xylenes were used throughout the deuteration procedure for those compounds. GC-MS analysis revealed that the compounds were not deuterated to a sufficient extent that their mass spectral patterns would be clearly discernible in chromatograms from co-eluting substances present in contaminated samples. After several attempts at these syntheses, it was decided that this approach was beyond our level of synthesis expertise and was becoming too expensive and time consuming. Therefore, tritiated pyrene was used for some studies and the new isomer-specific analytical techniques were developed as described and applied in this report to study fate and transport processes of normal, alkylated and heterocyclic aromatics. The following is a description of the analytical characteristic of these new methods as they were applied in field and laboratory applications.

5.2.2 Results of Analytical Method Development

Chromatographic data (Table 5.2.1) for parent and alkylated PAH were obtained from 20 daily calibration analyses of the standard mixture. Results showed that both relative retention times and relative response factors varied little over a two month period. These are based on analyses performed in full-scan mode of the mass spectrometer. The average detection limit (ng detected on-column) is based on extrapolation of response factors to a minimum integratable area, and agrees well with standard curves obtained in the scanning mode. The last column presents detection limits obtained from a standard curve from selected ion mode (SIM) acquisition. The average detection limit was 0.40 ng for scanning mode and 0.040 for SIM data, a tenfold increase in sensitivity. Several new analytes were added to the method during the development of the SIM method.

Table 5.2.2 shows the reproducibility of the extraction and analysis method. Three extractions of a laboratory reference sediment spiked with the EPA South Louisiana Crude Reference Oil had an average relative standard deviation (%RSD) of 11%, with a range from 1% to 48%. This indicates that the entire extraction and analysis procedure was very reproducible (Table 5.2.3). presents full-scan results from the analysis of three samples collected near produced water discharges and spiked with the standard mixture just prior to extraction. Average recovery was 101%, 83%, and 73% for naphthalenes, dibenzothiophenes, and phenanthrenes, respectively. Table 5.2.4 shows an example from the database that has been accumulated for surface sediments collected near produced water discharge sites in south Louisiana. The Minimum Detection Limit (MDL), in ppb, was calculated for each sample based on the detection limit established for phenanthrene from standard curve data, adjusted sample size (dry weight), and for the recovery of the corresponding surrogate standard, d10-phenanthrene, in the sample. The most significant contributor to MDL was the percentage of water in the sediment, and values for MDL in field samples averaged approximately 20 ppb, while the MDLs for microcosm cores averaged 2.0 ppb. (See Appendix tables.)

5.3 Field Applications of Methodology to Investigate the Fate of Produced Water Associated Contaminants

5.3.1 Surficial Sediments

An extensive body of information has been acquired for surface and depth sections of cores collected seasonally at various distances from produced water discharges located at Pass Fourchon, Bayou Rigaud and Eugene Island (OCS) in South Louisiana. Figures 5.3.1-4 show examples of data for alkylated PAH homologs in samples collected at Pass Fourchon, 600 meters north of the

Table 5.2.1. Chromatographic Data for Target Analytes

ANALYTE	I.S.	MEAN R.R.T*	RSD R.R.T.	MEAN RRF	RSD RRF	DETECTION LIMITS, ng	
			%		%	full-scan mode	SIM mode
Naphthalene	d8-Naph	1.005	0.012%	0.80	2.2%	0.14	0.010
2-MN	"	1.223	0.019%	1.02	2.9%	0.28	0.020
1-MN	"	1.259	0.018%	1.12	3.2%	0.34	0.020
2-EN	d10-Ace	0.878	0.025%	1.29	3.6%	0.74	0.041
1-EN	"	0.883	0.012%	1.45	4.1%	0.84	0.027
2,6/2,7-DMN	"	0.894	0.018%	0.80	3.4%	0.37	0.030
1,3/1,7-DMN	"	0.915	0.010%	0.67	2.3%	0.33	0.024
1,6-DMN	"	0.920	0.012%	0.74	3.9%	0.43	0.011
1,4/2,3-DMN	"	0.943	0.010%	0.87	2.9%	0.50	0.027
1,5-DMN	"	0.948	0.013%	0.87	3.9%	0.29	0.015
Acenaphthylene	"	0.956	0.009%	0.49	2.4%	0.14	NA
1,2-DMN/2-IPN	"	0.966	0.039%	1.29	4.2%	0.23	0.033
2-IPN	"	0.969	0.012%	1.80	3.6%	1.0	0.017†
1,8-DMN	"	0.996	0.012%	0.88	3.2%	0.39	0.024
Acenaphthene	"	1.008	0.013%	0.71	2.3%	0.20	NA
Fluorene	"	1.155	0.023%	0.64	4.6%	0.20	0.045
Dibenzothiophene	d10-Phen	0.976	0.016%	0.80	1.6%	0.22	NA
Phenanthrene	"	1.005	0.009%	0.92	2.1%	0.11	0.049
Anthracene	"	1.015	0.009%	0.93	2.2%	0.12	0.061
4-MDBT	"	1.081	0.014%	1.26	3.4%	0.31	0.027
2/3-MDBT	"	1.101	0.012%	1.23	3.3%	0.31	0.040
3-MP	"	1.124	0.010%	1.24	4.5%	0.30	0.054
1-MDBT	"	1.125	0.010%	1.49	3.8%	0.40	0.030
1,2-DMDBT	"	NA	NA	NA	NA	NA	0.021
2-MP	"	1.129	0.013%	1.06	3.5%	0.25	0.055
4/9-MP	"	1.149	0.010%	1.31	4.5%	0.31	0.073
1-MP	"	1.153	0.012%	1.07	7.1%	0.25	0.050
4,5-DMP	"	1.178	0.032%	2.46	27.9%	0.20	NA
3,6-DMP	"	1.220	0.040%	1.56	7.3%	0.39	0.025
3,5-DMP	"	1.223	0.040%	1.98	8.3%	0.29	NA
2,6-DMP	"	1.225	0.039%	0.92	7.1%	0.30	0.029
2,7-DMP	"	1.228	0.042%	1.08	6.5%	0.24	0.021
3,9-DMP	"	1.236	0.042%	1.16	7.6%	0.27	0.027
1,6/2,5/2,9-DMP	"	1.240	0.041%	1.44	5.7%	0.33	0.084
1,7-DMP	"	1.243	0.044%	1.06	7.2%	0.23	0.028
1,9/4,9-DMP	"	1.249	0.042%	1.47	6.5%	0.33	0.045
Fluoranthene	"	1.250	0.042%	0.77	7.1%	0.086	0.051
1,5-DMP	"	1.252	0.043%	1.69	7.6%	0.35	0.021
1,8-DMP	"	1.256	0.046%	1.11	8.0%	0.26	0.025
1,2-DMP	"	1.264	0.048%	1.49	8.1%	0.24	0.027
9,10-DMP	"	1.275	0.050%	1.56	9.0%	0.34	0.023
1,2,8-TMP	"	NA	NA	NA	NA	NA	0.021
Pyrene	"	1.276	0.047%	0.79	10.7%	0.082	0.034
Benzanthracene	d12-Chrys	0.999	0.005%	0.82	2.9%	0.092	0.057
Chrysene	"	1.001	0.032%	0.89	2.6%	0.090	0.041
Benzo(b)fluor	d12-Peryl	0.972	0.017%	0.62	9.7%	0.21	0.044
Benzo(k)fluor	"	0.974	0.020%	0.58	9.2%	0.21	0.044
Benzo(a)pyrene	"	0.995	0.009%	0.79	3.7%	0.33	0.042
Indenopyrene	"	1.107	0.051%	1.14	25.7%	1.3	0.030
Dibenzanthracene	"	1.112	0.043%	1.16	24.8%	3.5	0.22
Benzoperylene	"	1.138	0.073%	1.17	33.3%	1.0	0.024

IS = Internal Standard Reference Compound

R.R.T. = Relative retention time = R.T. x/R.T. IS

R.R.F. = Relative response factor = (Conc. x/Area x)/(Conc. IS/Area IS)

* n=20, data from daily calibrations over a 2-month period.

†detection limit is for 1,6,7-trimethylnaphthalene

Table 5.2.2. Replicate analyses of a laboratory reference sediment.

Analyte	A-01 ng/g	A-02 ng/g	A-03 ng/g	MEAN ng/g	STD.DEV.	R.S.D. %
DET. LIMIT	7.1	5.9	6.0	6.3	0.67	11%
Naphthalene	8.6	10	11	9.9	1.2	12%
2-MN	19	19	23	20	2.3	11%
1-MN	21	20	34	25	7.8	31%
2-EN	trc	trc	nd	trc	NA	NA
1-EN	trc	nd	nd	nd	NA	NA
2,6/2,7-DMN	25	22	19	22	3.0	14%
1,7/1,3-DMN	18	20	20	19	1.2	6%
1,6-DMN	17	18	15	17	1.5	9%
2,3/1,4-DMN	trc	6.9	10	8.5	2.2	26%
1,5-DMN	8.1	9.1	9.3	8.8	0.64	7%
Acenaphthylene	nd	trc	trc	trc	NA	NA
1,2-DMN/2-IPN	tr	tr	tr	tr	NA	NA
2-IPN	nd	nd	nd	nd	NA	NA
1,8-DMN	nd	nd	nd	nd	NA	NA
Acenaphthene	16	14	15	15	1.0	7%
Fluorene	22	22	21	22	0.58	3%
Dibenzothiophene	18	16	14	16	2.0	13%
Phenanthrene	58	58	59	58	0.58	1%
Anthracene	26	30	27	28	2.1	8%
4-MDBT	40	39	35	38	2.6	7%
2/3-MDBT	26	25	23	25	1.5	6%
1-MDBT	15	18	17	17	1.5	9%
3-MP	22	21	18	20	2.1	10%
2-MP	19	17	20	19	1.5	8%
4/9-MP	25	19	29	24	5.0	21%
1-MP	14	trc	14	14	0.21	2%
3,6-DMP	32	29	26	29	3.0	10%
3,5-DMP	27	30	26	28	2.1	8%
2,6-DMP	nd	nd	nd	nd	NA	NA
2,7-DMP	13	12	11	12	1	8%
3,9-DMP	53	57	48	53	4.5	9%
1,6/2,9/2,5-DMP	40	37	37	38	1.7	5%
1,7-DMP.	trc	trc	trc	trc	NA	NA
1,9/4,9-DMP	8.5	8.0	7.4	8.0	0.55	7%
Fluoranthene	420	430	390	413	21	5%
1,5-DMP	nd	nd	nd	nd	NA	NA
1,8-DMP	nd	nd	nd	nd	NA	NA
1,2-DMP	nd	6.3	7.2	6.8	0.64	9%
9,10-DMP	nd	nd	nd	nd	NA	NA
Pyrene	440	450	390	427	32	8%
Benzo(a)anthracene	91	87	82	87	4.5	5%
Chrysene	131	133	126	130	3.6	3%
Benzo(b)fluoranthene	68	61	57	62	5.6	9%
Benzo(k)fluoranthene	150	160	140	150	10	7%
Benzo(a)pyrene	41	24	31	32	8.5	27%
Indeno(1,2,3-cd)pyren	nd	nd	nd	nd	NA	NA
Dibenz(a,h)anthracene	43	65	23	44	21	48%
Benzo(g,h,i)perylene	nd	nd	nd	nd	NA	NA

Average R.S.D. 11%

Table 5.2.3. Recovery of target analytes spiked into sediment from near produced water discharges.

ANALYTE	Spike Amt. ng/µl	EW9 % Recov	EW3 % Recov	PF400NF % Recov	**MEAN RECOV**
d8-Naph	20	63%	64%	39%	**55%**
d10-Ace	20	74%	82%	52%	**69%**
d10-Phen	20	94%	149%	35%	**93%**
d12-Chrys	20	67%	99%	20%	**62%**
d12-Peryl	20	76%	68%	22%	**55%**
Naphthalene	20	75%	77%	85%	**79%**
2-MN	20	73%	88%	95%	**86%**
1-MN	20	80%	91%	104%	**92%**
2-EN	20	90%	97%	112%	**100%**
1-EN	20	87%	86%	129%	**101%**
2,6/2,7-DMN	40	92%	101%	99%	**98%**
1,3/1,7-DMN	39	94%	104%	86%	**95%**
1,6-DMN	20	97%	102%	112%	**104%**
1,4/2,3-DMN	40	100%	108%	103%	**104%**
1,5-DMN	20	97%	102%	100%	**100%**
Acenaphthylene	20	90%	105%	84%	**93%**
1,2-DMN/2-IPN	38	93%	106%	132%	**110%**
2-IPN	18	89%	98%	139%	**109%**
1,8-DMN	19	105%	114%	144%	**121%**
Acenaphthene	20	104%	108%	124%	**112%**
Fluorene	20	116%	130%	116%	**121%**
Dibenzothiophene	10	87%	83%	104%	**91%**
Phenanthrene	20	81%	91%	106%	**93%**
Anthracene	20	78%	100%	98%	**92%**
4-MDBT	10	85%	100%	81%	**88%**
2/3-MDBT	16	88%	111%	65%	**88%**
3-MP	20	84%	116%	58%	**86%**
1-MDBT	14	81%	103%	33%	**72%**
2-MP	30	79%	97%	72%	**83%**
4/9-MP	30	77%	110%	50%	**79%**
1-MP	20	81%	111%	48%	**80%**
3,6-DMP	10	94%	144%	8%	**82%**
3,5-DMP	10	80%	NA	NA	**80%**
2,6-DMP	10	69%	91%	8%	**56%**
2,7-DMP	5	75%	108%	31%	**71%**
3,9-DMP	10	54%	122%	23%	**51%**
1,6/2,9/2,5-DMP	32	72%	124%	17%	**71%**
1,7-DMP	11	76%	121%	18%	**71%**
1,9/4,9-DMP	18	82%	123%	24%	**76%**
Fluoranthene	20	72%	124%	21%	**72%**
1,5-DMP	8	70%	131%	0%	**67%**
1,8-DMP	9	82%	123%	17%	**74%**
1,2-DMP	10	73%	133%	0%	**69%**
9,10-DMP	10	67%	133%	30%	**76%**
Pyrene	20	60%	117%	21%	**66%**
Benzanthracene	20	73%	108%	120%	**100%**
Chrysene	20	75%	108%	127%	**103%**
Benzo(b)fluor	20	63%	77%	212%	**118%**
Benzo(k)fluor	20	58%	86%	112%	**85%**
Benzo(a)pyrene	20	62%	80%	0%	**47%**
Indenopyrene	20	60%	133%	0%	**64%**
Dibenzanthracene	20	60%	133%	0%	**64%**
Benzoperylene	20	70%	149%	0%	**73%**

AVE NAPHS=	**101%**
AVE DBTS=	**83%**
AVE PHENS=	**73%**

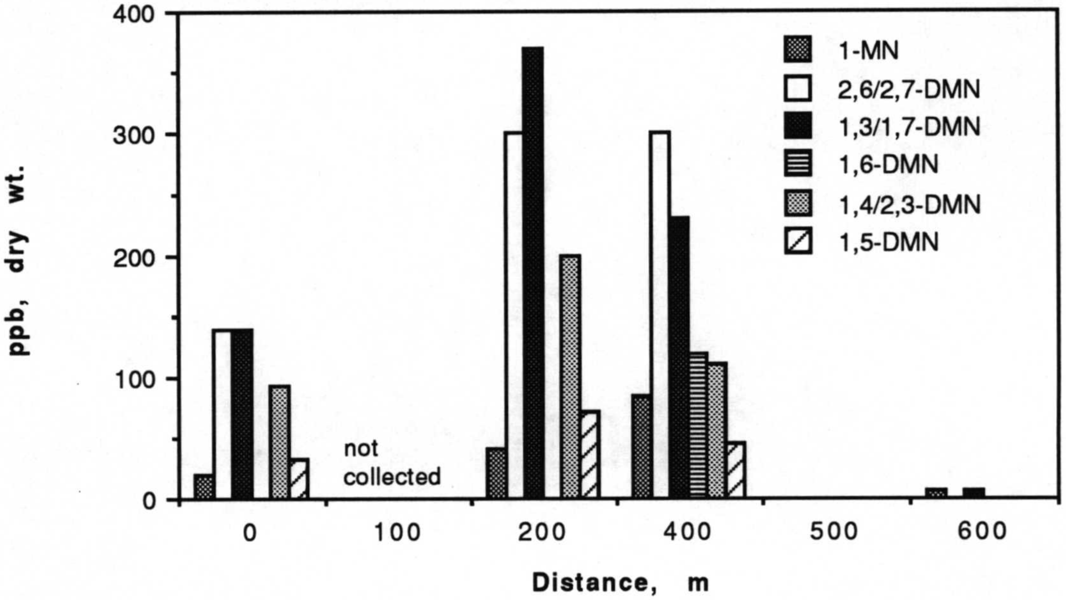
Table 5.2.4. Example of a dataset for samples collected in the vicinity of produced water discharges in Louisiana.

Analyte	PF--400	NORTH				SOUTH
	ppb	600 ppb	800 ppb	900 ppb	1000 ppb	600 ppb
Naphthalene	31	nd	37	tr	5.1	tr
2-Methylnaph.	trc	nd	68	nd	8.4	trc
1-Methylnaph.	20	41	84	tr	6.6	trc
2-Ethylnaph.	nd	nd	43	nd	nd	nd
1-Ethylnaph.	nd	nd	nd	nd	nd	nd
2,6/2,7-Dimethylnaph.	140	300	300	tr	trc	trc
1,3/1,7-DMN	140	370	230	nd	6.2	trc
1,6-DMN	nd	tr	120	nd	trc	nd
1,4/2,3-DMN	93	200	110	nd	trc	tr
1,5-DMN	32	72	46	nd	nd	nd
1,2-DMN/2-IPN	nd	trc	trc	nd	nd	nd
2-IPN	nd	trc	nd	nd	nd	nd
1,8-DMN.	nd	nd	nd	nd	nd	nd
C1-Naphthalenes, total	20	41	150	tr	15	tr
C2-Naphthalenes, total	410	940	850	tr	6.2	tr
C3-Naphthalenes	3,100	6,400	3,200	nd	33	trc
C4-Naphthalenes	5,300	5,000	920	nd	tr	nd
C5-Naphthalenes	1,800	tr	1,100	nd	tr	nd
Acenaphthylene	nd	nd	nd	nd	nd	nd
Acenaphthene	nd	nd	nd	nd	trc	nd
Fluorene	47	77	77	tr	nd	nd
C1-Fluorenes	250	500	410	nd	tr	tr
C2-Fluorenes	500	1600	630	nd	tr	tr
C3-Fluorenes	890	1400	720	nd	36	160
Dibenzothiophene	tr	27	31	tr	nd	nd
4-MDBT	120	270	150	trc	trc	15
2/3-MDBT	32	120	65	trc	nd	nd
1-MDBT	30	72	25	nd	nd	nd
C1-Dibenzothiophenes, total	180	460	240	tr	tr	15
C2-Dibenzothiophenes, est.	1,000	1,400	670	trc	7.0	150
C3-Dibenzothiophenes, est.	1,200	1,500	860	nd	11	330
Phenanthrene	nd	nd	180	10	18	14
3-MP	230	540	320	tr	7.8	tr
2-MP	35	120	270	tr	6.0	tr
4/9-MP	240	570	360	nd	7.7	tr
1-MP	150	310	260	nd	tr	tr
3,6-DMP	330	490	270	trc	11	49
3,5-DMP	nd	nd	nd	nd	nd	nd
2,6-DMP	150	310	180	tr	4.9	tr
2,7-DMP	170	250	110	tr	5.4	37
3,9-DMP	610	1,078	530	trc	15	74
1,6/2,5/2,9-DMP	480	800	400	tr	12	65
1,7-DMP	160	320	160	tr	4.7	tr
1,9/4,9-DMP	190	270	150	nd	tr	31
1,5-DMP	nd	nd	nd	nd	nd	nd
1,8-DMP	78	120	75	nd	tr	18
1,2-DMP	51	98	47	nd	tr	nd
9,10-DMP	nd	nd	36	nd	nd	tr
C1-Phenanthrenes, total	660	1,500	1,200	tr	22	tr
C2-Phenanthrenes, total	2,200	3,700	2,000	tr	53	270
C2-Phenanthrenes, est.	2,300	3,900	2,000	trc	60	300
C3-Phenanthrenes, est.	2,400	3,400	1,800	tr	44	610

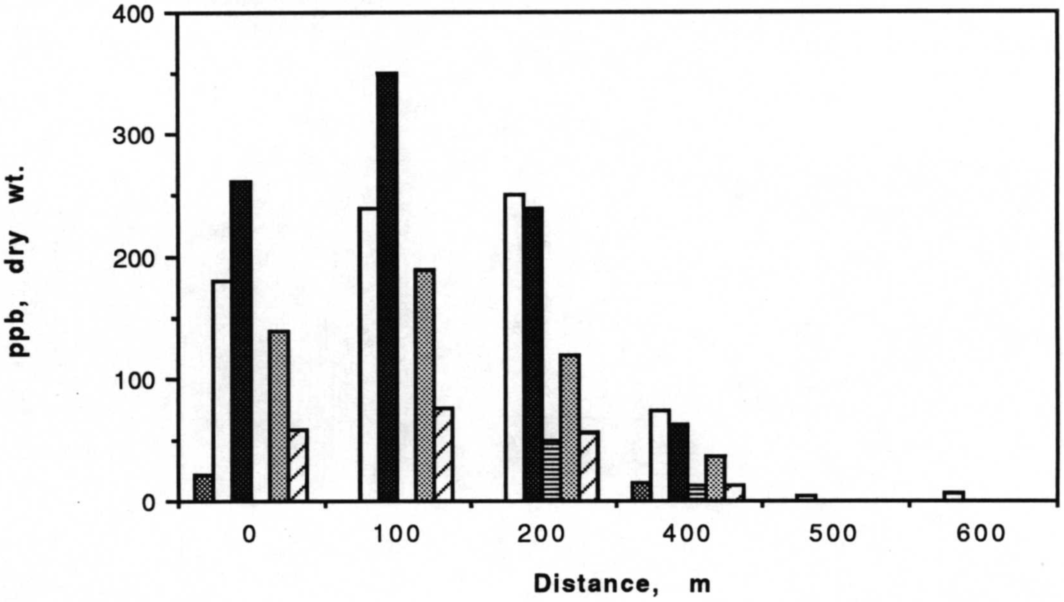
Table 5.2.4. Example of a dataset for samples collected in the vicinity of produced water discharges in Louisiana. (continued)

Analyte	PF--400	NORTH				SOUTH
		600	800	900	1000	600
	ppb	ppb	ppb	ppb	ppb	ppb
Anthracene	nd	nd	27	3.5	3.7	12
Fluoranthene	180	190	110	23	54	110
Pyrene	150	190	110	20	56	110
Benzanthracene	74	94	46	10	13	38
Chrysene	230	340	140	11	19	70
Benzo(b)fluoranthene	nd	nd	nd	8.0	15	nd
Benzo(k)fluoranthene	nd	nd	nd	6.0	8.2	nd
Benzo(a)pyrene	nd	nd	nd	7.4	tr	nd
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd	nd	nd
Dibenzo(a,h)anthracene	nd	nd	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd	nd	nd	nd
Total Pyrogenic PAH	710	920	760	99	190	350
Total Petrogenic PAH	20,010	28,041	14,750	tr	234	1,565
Total PAH	21,000	29,000	16,000	99	430	1,900
FFPI	0.92	0.92	0.90	0.05	0.52	0.80
Saturated Hydrocarbons						
Resolved	32,000	57,000	68,000	480	2,100	3,600
Unresolved	458,000	523,000	302,000	1,720	2,200	106,400
Total	490,000	580,000	370,000	2,200	4,300	110,000
MDL (ng/g)	19	24	21	2.5	3.6	9.9

MDL: Minimum Detection Limit
nd: Not detected
tr: Trace; one ion present, but below detection limits
trc: Trace confirmed; two ions present, but below detection limits
n/a: not analyzed



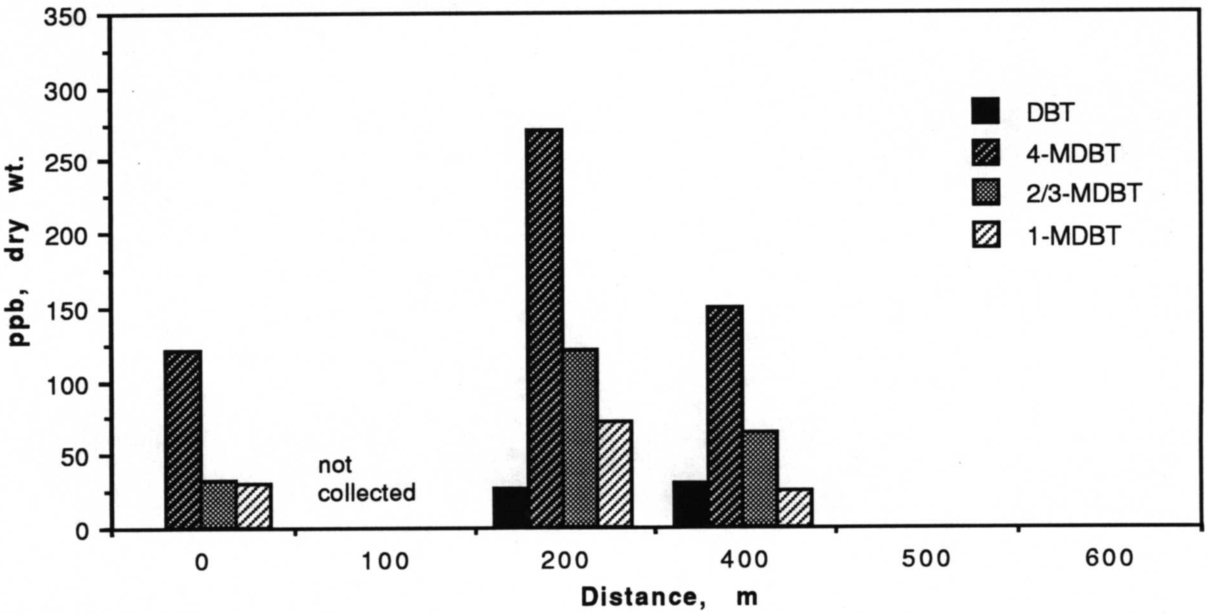
Feb. '89 collection



May '89 collection

Figure 5.3.1. Selected alkylated naphthalenes concentrations in surface sediments collected at Pass Fourchon, Louisiana, at two time periods.

Feb. '89 collection



May '89 collection

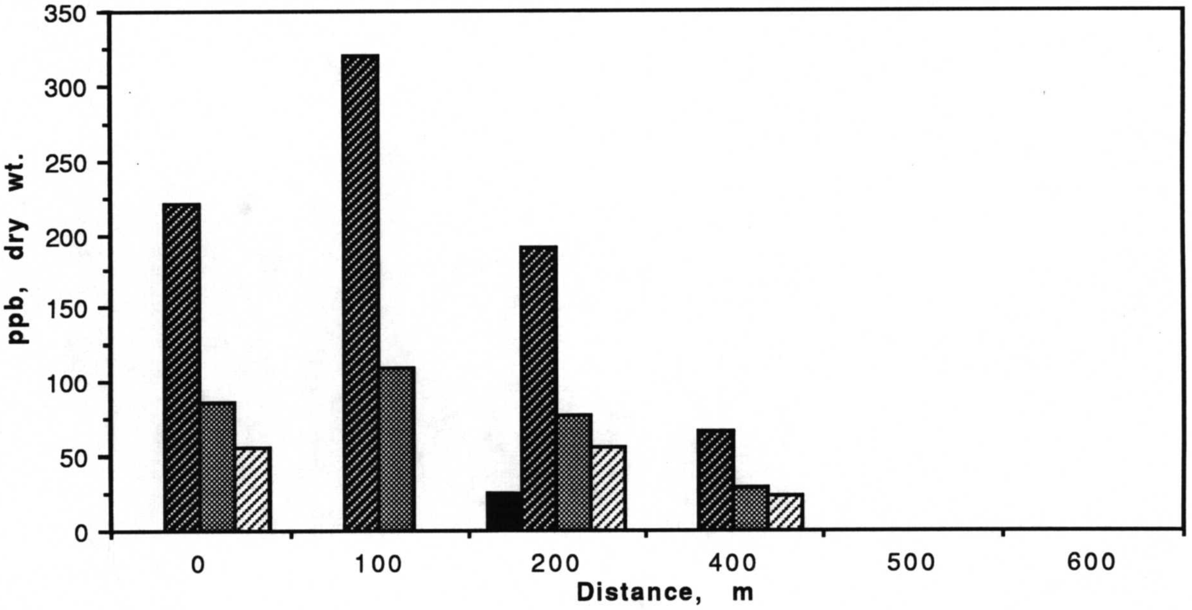
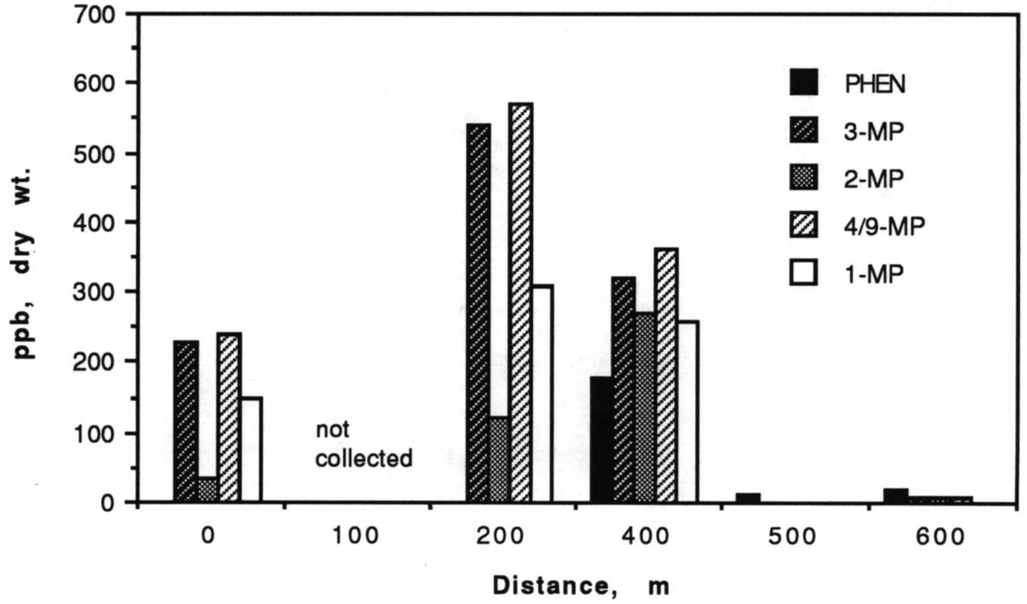


Figure 5.3.2. Methyl dibenzothiophenes concentrations in surface sediments collected at Pass Fourchon, Louisiana, at two time periods.

Feb. '89 collection



May '89 collection

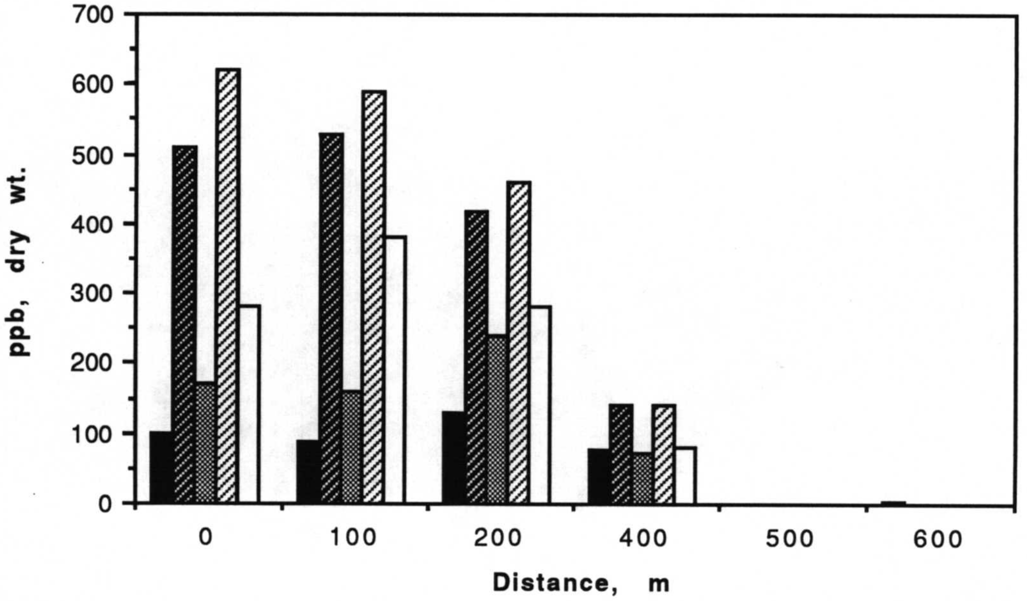
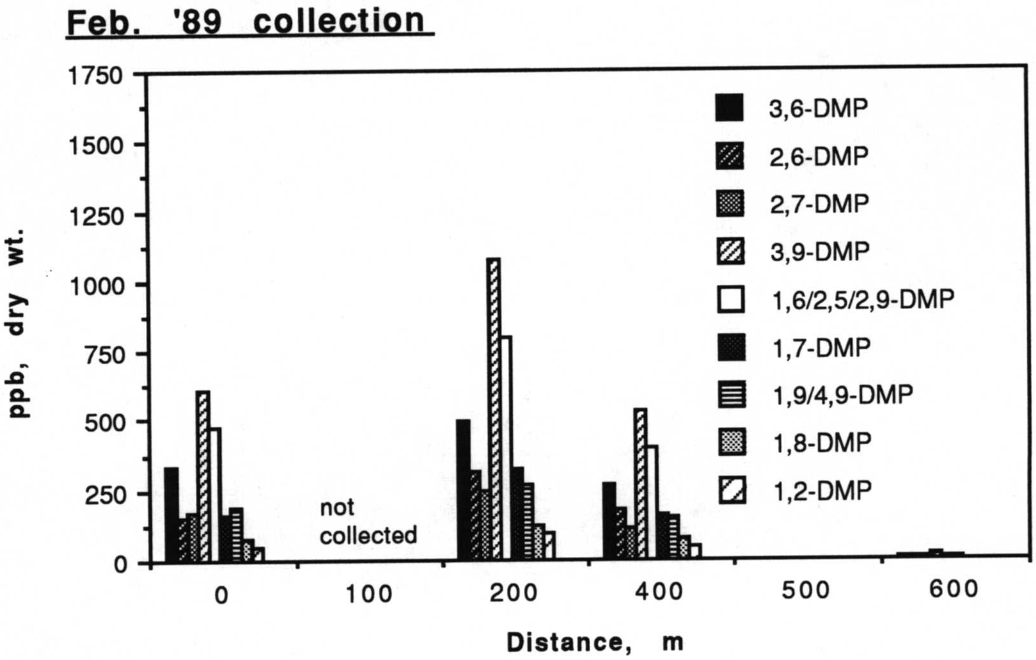
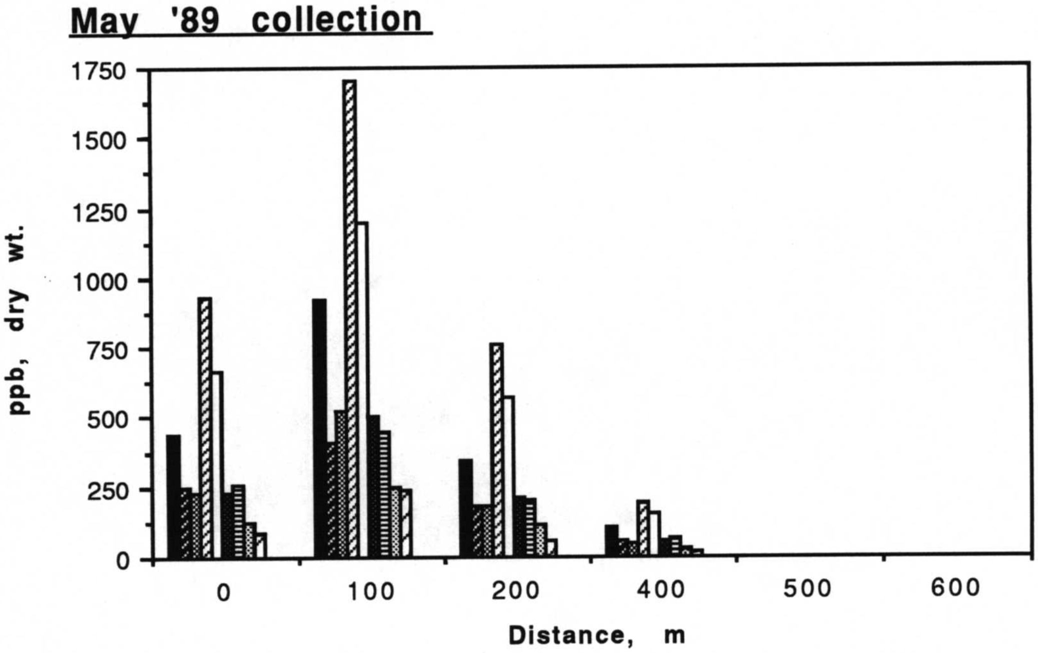


Figure 5.3.3. Methyl phenanthrenes concentrations in surface sediments collected at Pass Fourchon, Louisiana, at two time periods.



Feb. '89 collection



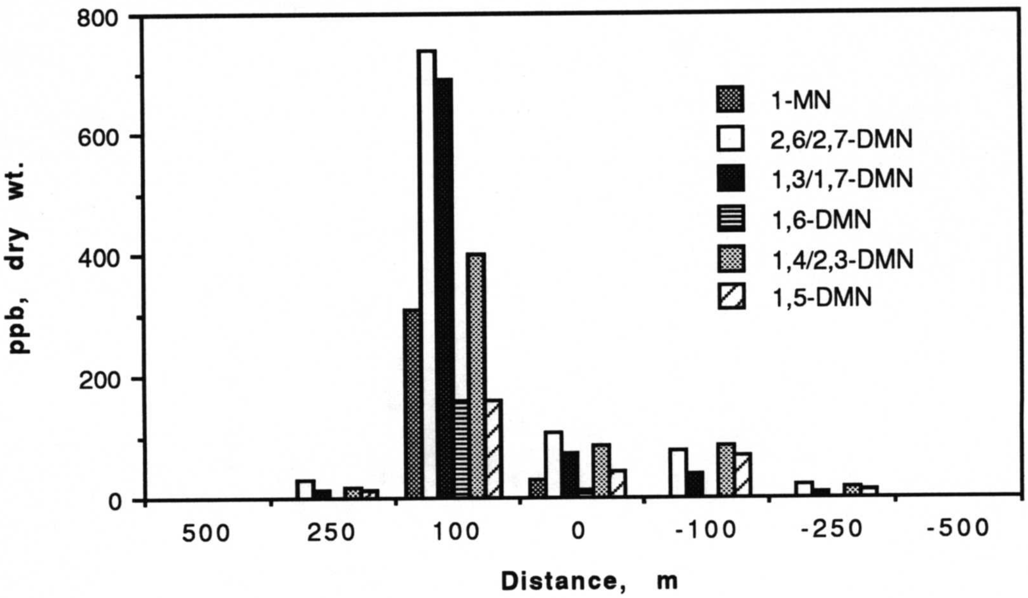
May '89 collection

Figure 5.3.4. Dimethyl phenanthrenes concentrations in surface sediments collected at Pass Fourchon, Louisiana, at two time periods.

discharge site during two seasonal collections. Variations in the relative concentrations of alkylated and heterocyclic PAH can be seen at various distances from the discharge site, however, similarities in pattern are apparent between seasons. For example, the concentration of 1,3- and 1,7-dimethylnaphthalenes (DMN) (coeluting) tends to be higher than the concentrations of 2,6- and 2,7-DMN (coeluting) nearest the discharge site, but this ratio was reversed as distance from the discharge increased (Figure 5.3.1). This was true for both seasons shown, but the distance from the discharge where the ratios reversed was not constant. Changes in alkylated aromatic hydrocarbon ratios were more easily observed for the naphthalenes, as these are the most susceptible to weathering effects. Another isomeric group of alkylated aromatics that was observed to show ratio changes were the methyl phenanthrenes (MP) (Figure 5.3.3), where the ratio of 1-MP to 2-MP was high (>1) at the collection nearest the discharge, but neared unity at 1000 m distant for both collections. Other ratios that were observed to change over distance from the discharge site were the dimethylphenanthrenes (DMP): 2,6-DMP:2,7-DMP, and 1,7-DMP:1,9- and 4,9-DMP (Figure 5.3.4).

Figures 5.3.5-9 show examples of data for alkylated PAH homologs in samples collected at Bayou Rigaud during two seasons. Again, variations in the relative concentrations of alkylated and heterocyclic PAH can be seen at various distances from the two discharge sites, the largest of which is the Conoco facility near the 0 m station, however, similarities seen at Pass Fourchon in pattern were absent in the two seasons shown. There is a dramatic decrease (to non-detectable in some cases) for alkylated naphthalenes (Figure 5.3.5), alkylated dibenzothiophenes (Figure 5.3.6), methyl phenanthrenes (Figure 5.3.7) and dimethylphenanthrenes (Figure 5.3.8) at the 0m, +100m and -100m stations at Bayou Rigaud between February and May of 1989. Smaller decreases as well as changes in the relative abundances of different isomers within the compound groups were also observed at the +250m, -250m, -500m and +500m stations. These figures illustrate the complexity of processes impacting the sediments, such as discharge parameters and weather patterns and dredging of the site between the two time points. In stark contrast, the similarity between samples from two seasons for the pyrogenic PAH (Figure 5.3.9) when contrasted to the large changes in the distribution of alkylated and heterocyclic PAH between February and May of 1989 suggest that intentional removal of surface sediments occurred in this time period.

A comparison of concentration patterns between the two sites, Pass Fourchon and Bayou Rigaud, using selected alkylated aromatic hydrocarbons shows that while the patterns within classes of alkylated aromatics are relatively constant, concentration ratios between classes vary considerably (Figures 5.3.10). This is an example of the usefulness of the analytical method for specific fingerprinting of petroleum discharge sources.


Feb. '89 collection

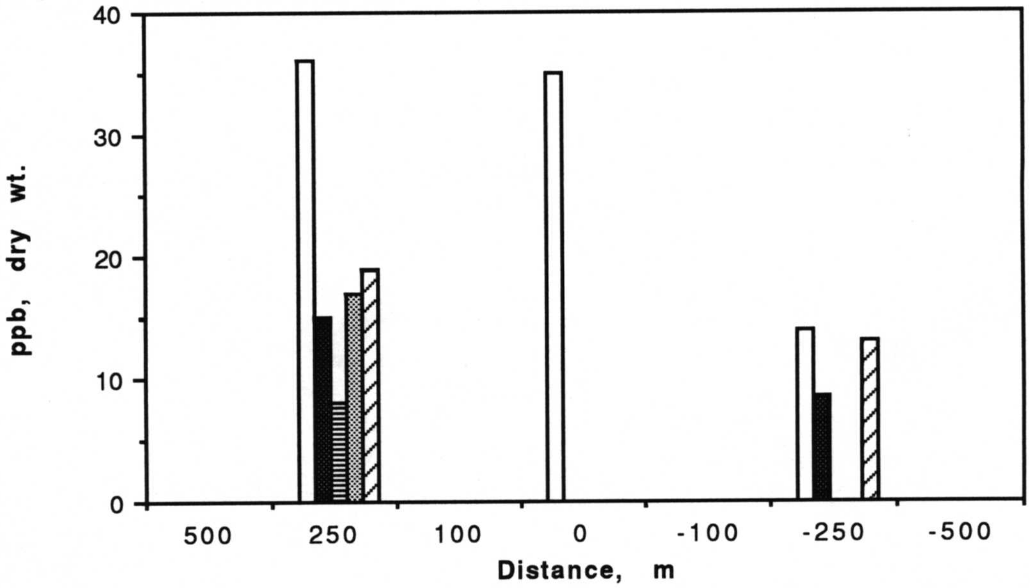
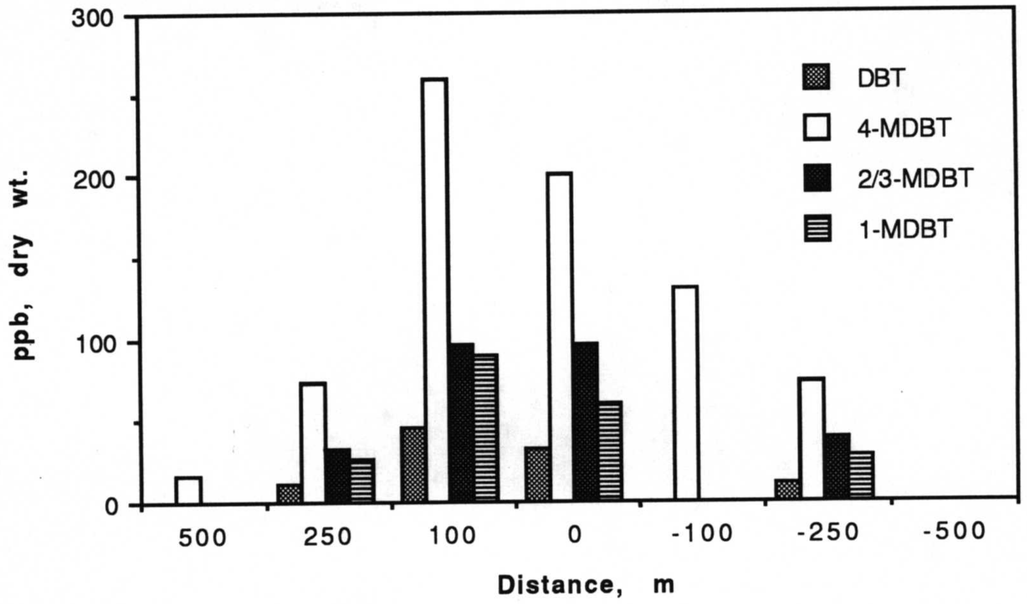

May '89 collection

Figure 5.3.5. Selected alkylated naphthalenes concentrations in surface sediments collected at Bayou Rigaud, Louisiana, at two time periods.

Feb. '89 collection



May '89 collection

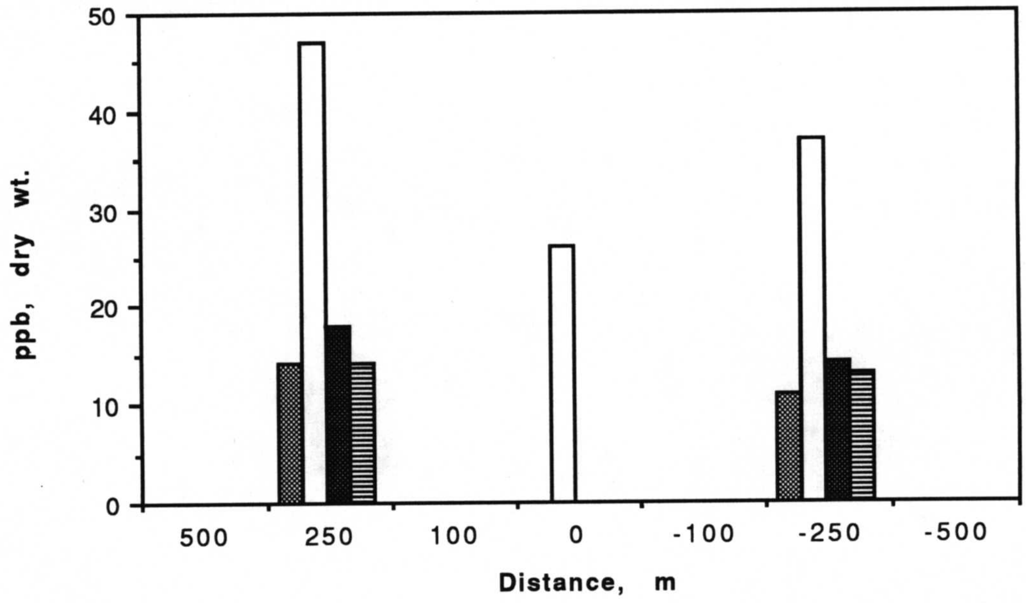
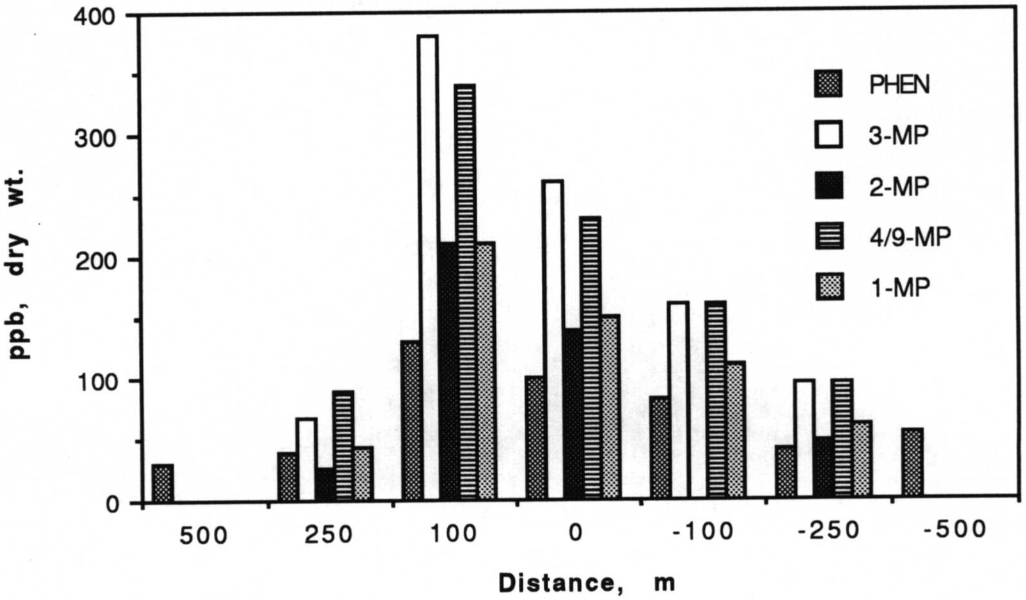
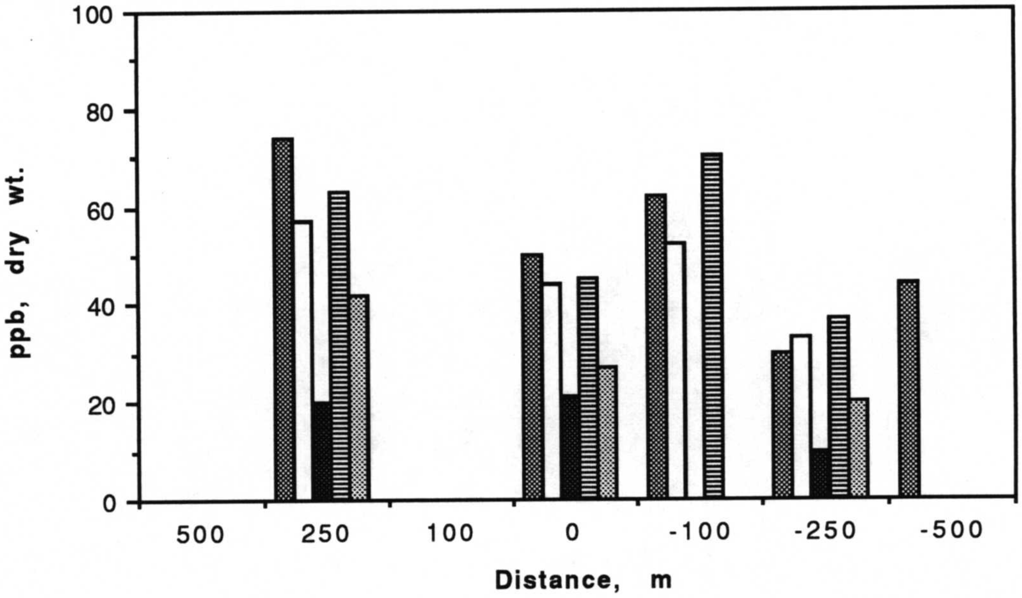


Figure 5.3.6. Methyl dibenzothiophenes concentrations in surface sediments collected at Bayou Rigaud, Louisiana, at two time periods.



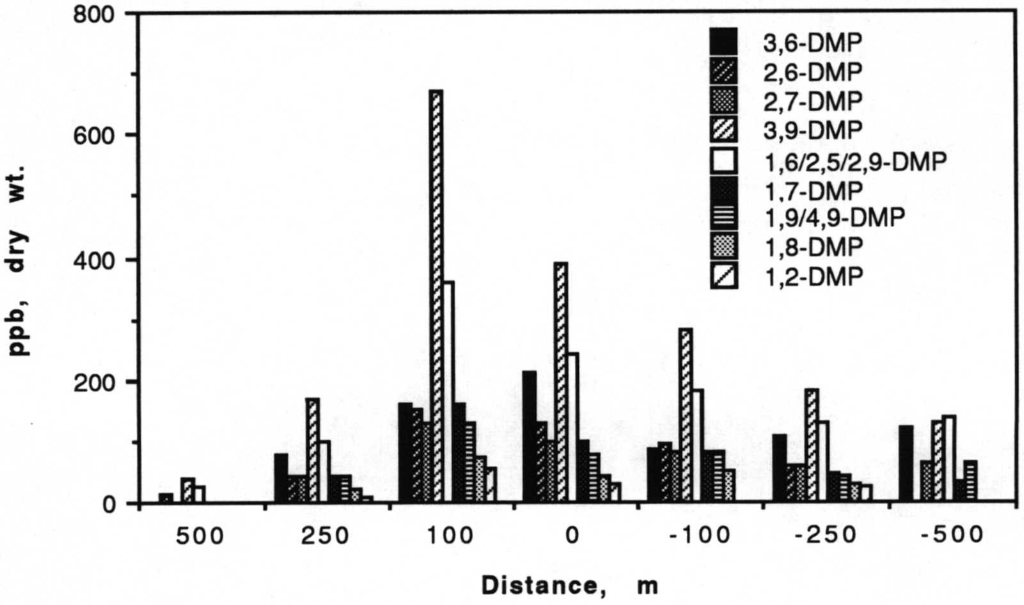
Feb. '89 collection



May '89 collection

Figure 5.3.7. Methyl phenanthrenes concentrations in surface sediments collected at Bayou Rigaud, Louisiana, at two time periods.

Feb. '89 collection



May '89 collection

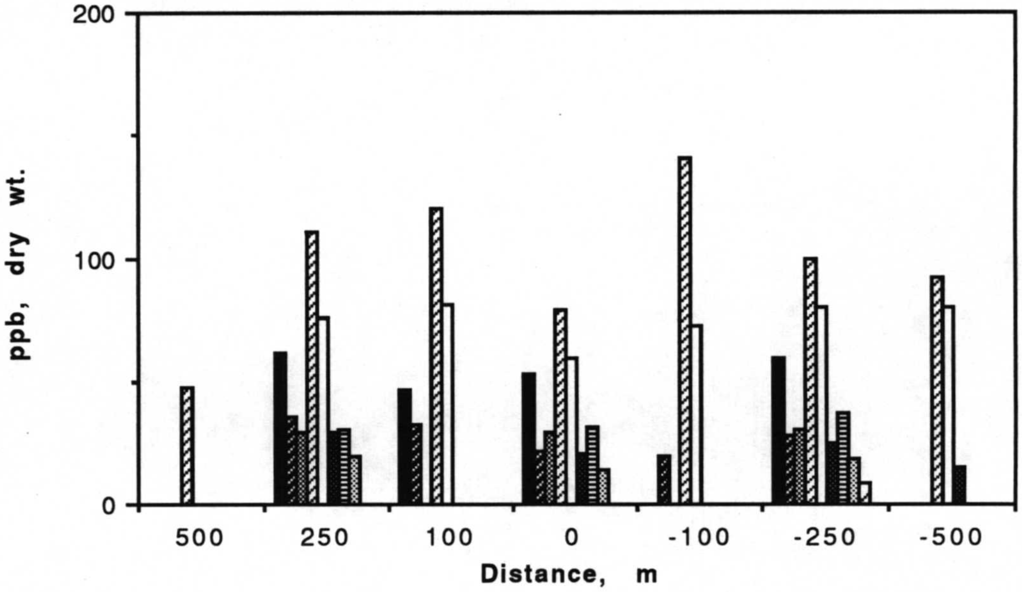
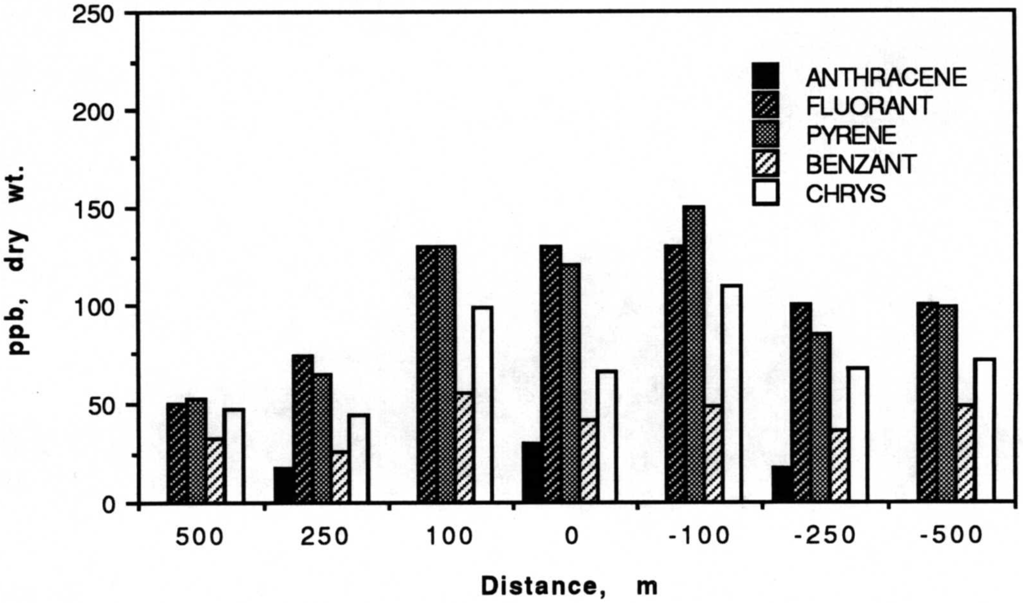


Figure 5.3.8. Dimethyl phenanthrenes concentrations in surface sediments collected at Bayou Rigaud, Louisiana, at two time periods.

Feb. '89 collection



May '89 collection

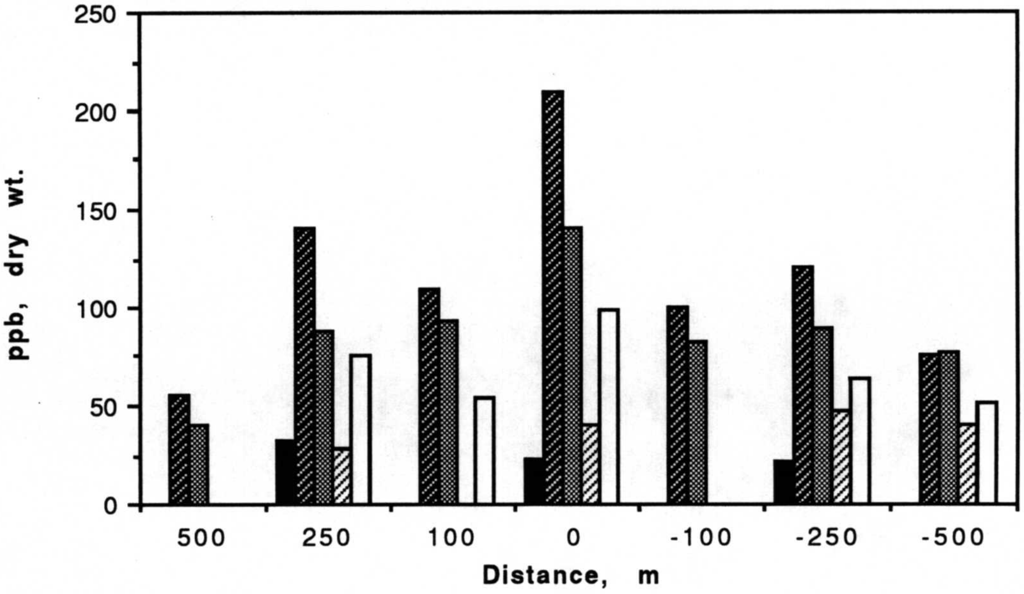
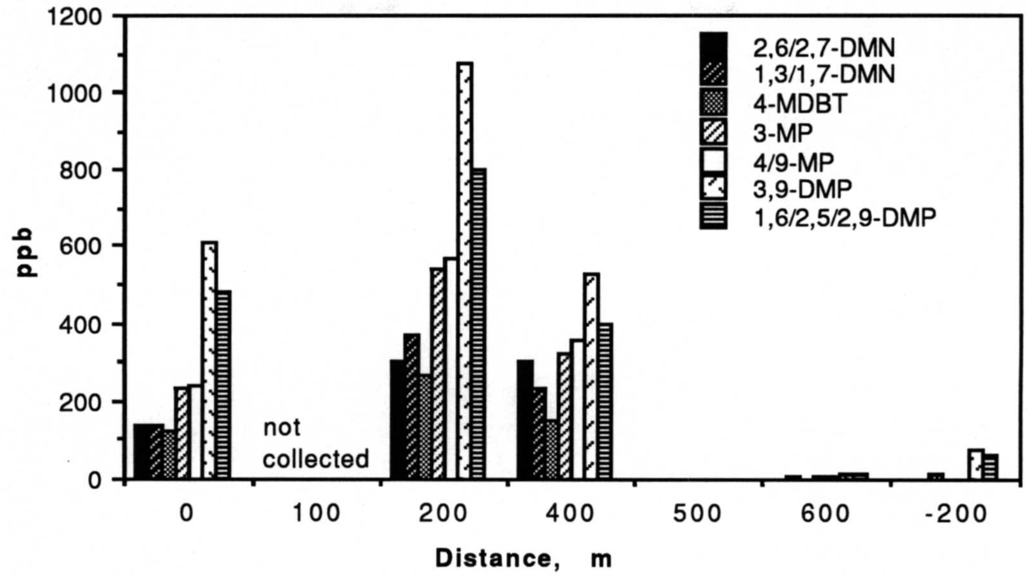
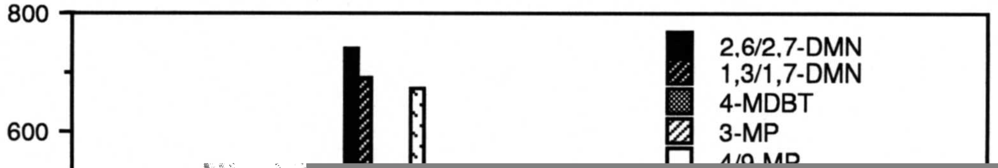


Figure 5.3.9. Selected parent PAH concentrations in surface sediments collected at Bayou Rigaud, Louisiana, at two time periods.

PASS FOURCHON SURFACE SEDIMENTS, FEBRUARY 1989.



BAYOU RIGAUD SURFACE SEDIMENTS, FEBRUARY 1989.



5.3.2 Subsurface Distribution of Hydrocarbons

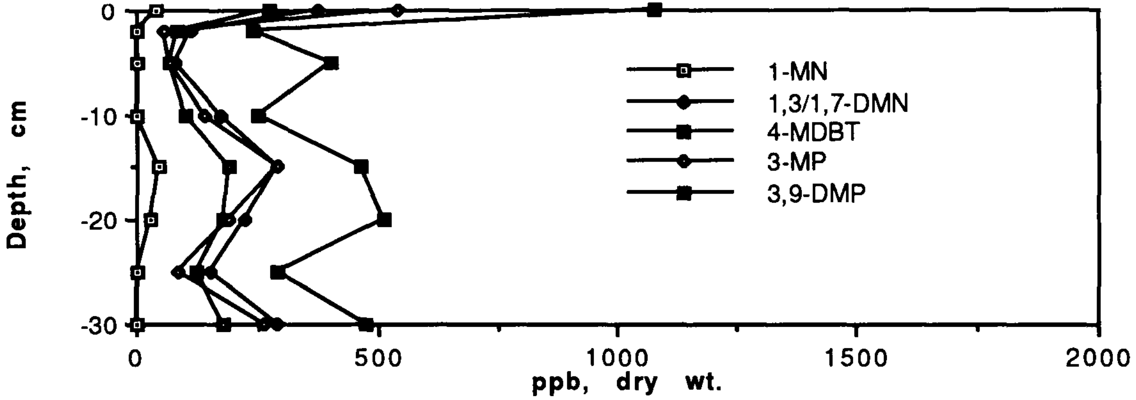
Figure 5.3.11 shows depth profile data for cores taken at a single site over four seasons, and illustrate again the dynamic nature of processes affecting these sediments. Note the similarity between cores from three seasons (one season had no detectable concentrations of any PAH except phenanthrene). The pattern of a subsurface decrease followed by an increase in concentrations lower in the core is often seen, and may indicate that chemical processes have more effect on PAH distributions than discharge parameters or sedimentation rates.

Figures 5.3.12-14 show the distribution of naphthalenes with depth in core for three sites, Pass Fourchon, Bayou Rigaud, and Eugene Island. Each figure shows two stations within each site; one contaminated and the other a reference station away from the discharging area. All data were graphed for each station and site, however, some analytes were not detected in any sections of a core, and therefore are not represented in the graph legends. The reference stations for all three sites show minimal numbers of naphthalenes detected and at minimal concentrations. The Bayou Rigaud station closest to the discharge (BR 9, Figure 5.3.13) shows unusually high concentrations of naphthalene and methyl naphthalenes at the lowest section examined, -30 cm (the data for the -2 cm section were eliminated from the figure due to low recovery of naphthalenes which raised the detection limit for this section to a value higher than the average concentrations for other sections). With the exception of the bottom section of the Bayou Rigaud core, the Eugene Island core sections showed a "signature" for napthalenes that was more predominant in naphthalene and methyl napthalenes than seen at the other sites. The Pass Fourchon core sections tended to be devoid of these three analytes. The unique signatures for Eugene Island samples are probably due to the fact that this is a gas field as opposed to an oil field and to the different treatment of the water prior to discharge at this site compared to that used for Pass Fourchon and Bayou Rigaud.

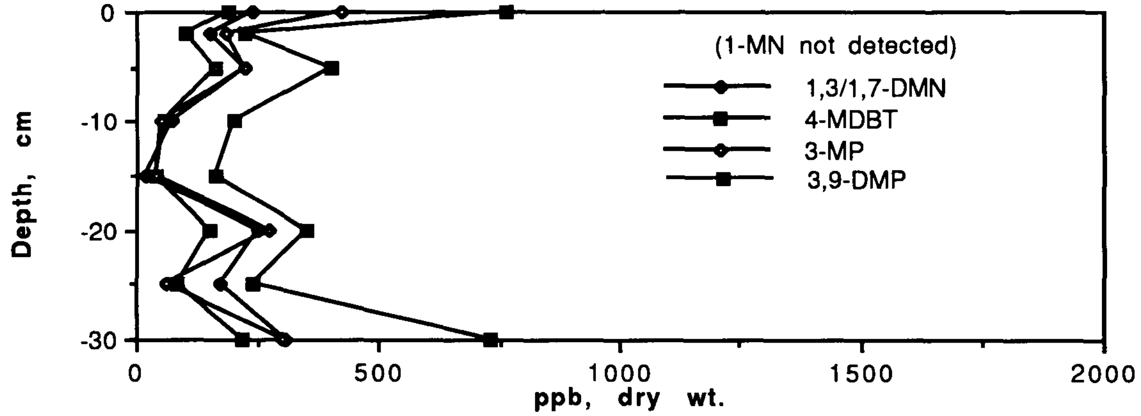
The C2-naphthalenes patterns in the Bayou Rigaud contaminated core were similar to those seen in the Pass Fourchon contaminated core (PF600N, Figure 5.3.12). The contaminated core from the Eugene Island site (Figure 5.3.14) had the highest concentrations of C2-naphthalenes, with a maximum in the middle depth of the core (-10 cm) and decreasing in either direction away from this.

Figure 5.3.15-17 show data for methyldibenzothiophene (MDBT) and methylphenanthrene (MP) isomers in the same format used for naphthalenes data. Concentrations of MPs and MDBTs in the Pass Fourchon core tended to be slightly lower than for naphthalenes, while concentrations at Bayou Rigaud were higher than naphthalenes, and not generally detected in the Eugene Island cores. Data for C2-phenanthrenes (see DMP, Figures 5.3.18-20) show lower, but detectable, concentrations in reference core sections. The distribution over depth sections in contaminated cores was

Feb. '89 collection



May '89 collection



Feb. '90 collection

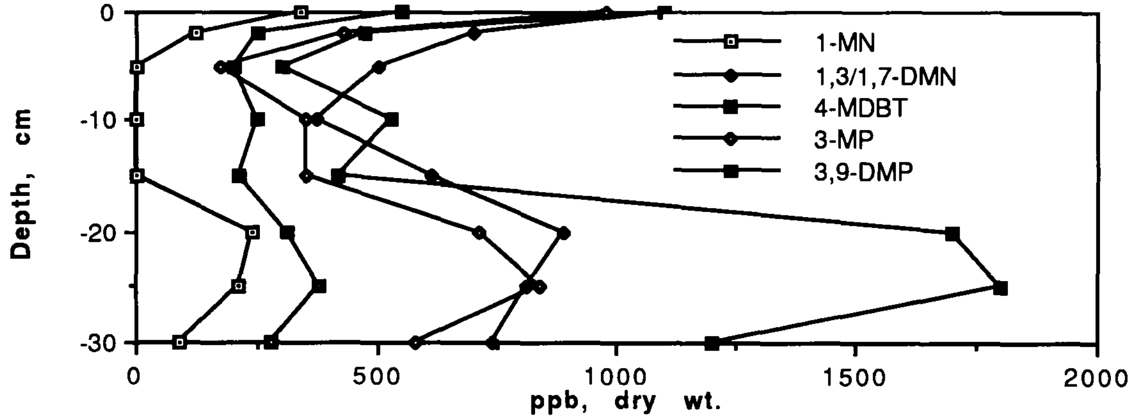


Figure 5.3.11. Depth profiles for selected alkylated aromatic hydrocarbons concentrations in cores taken at a single Pass Fourchon site (PF600N) over three seasons (October 1989 core showed no detectable concentrations).

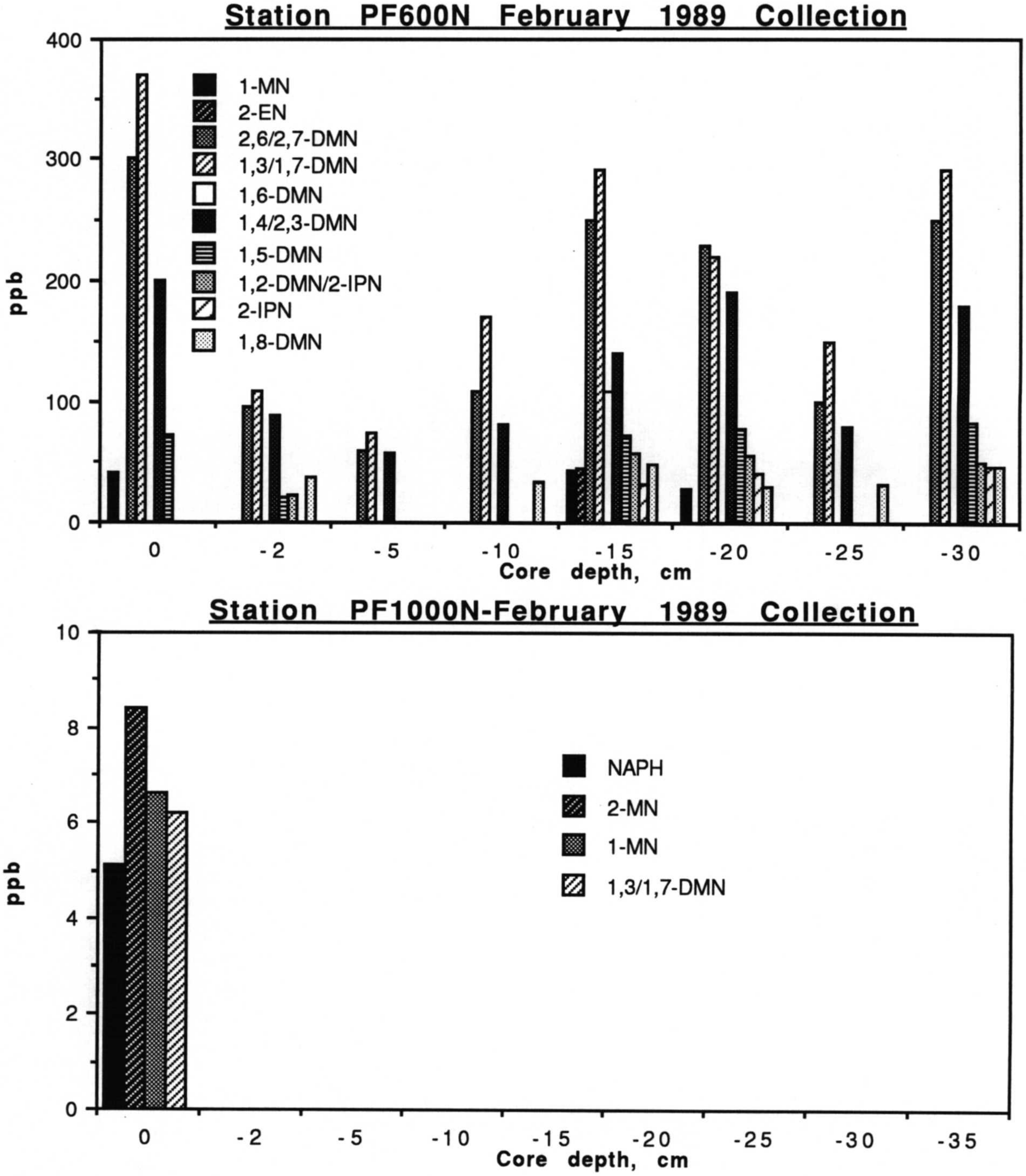
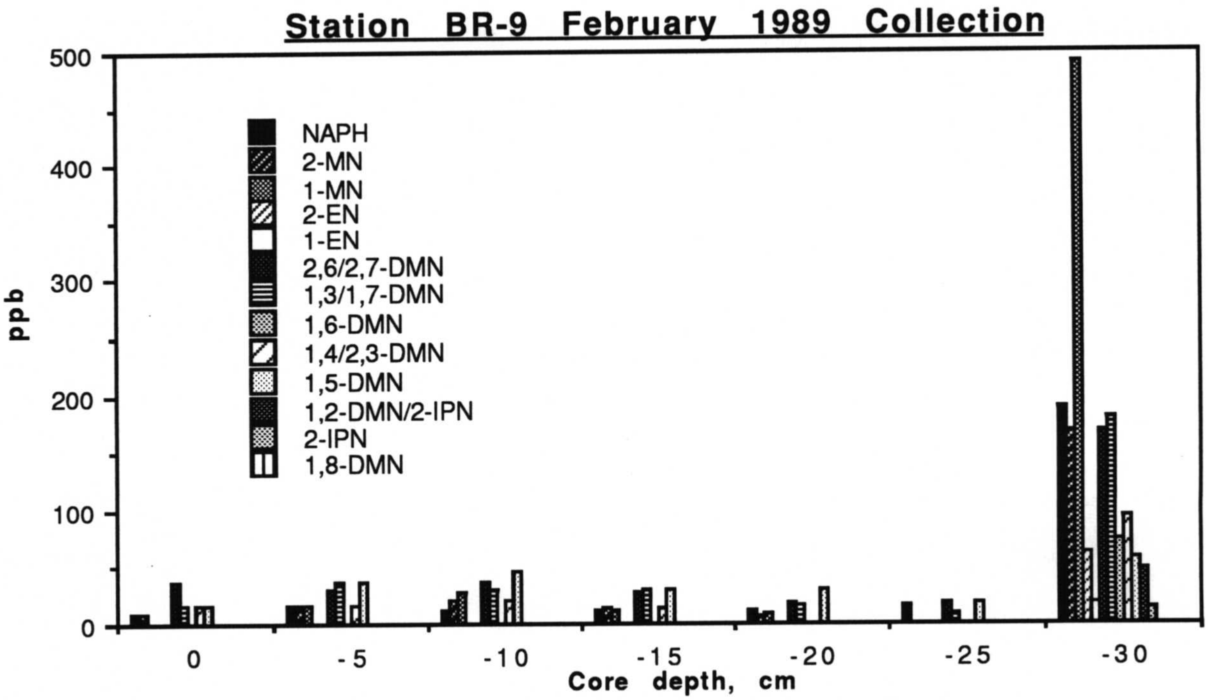


Figure 5.3.12 Alkylated naphthalenes concentrations in sections of two cores taken at Pass Fourchon, February 1989, at distances of 600 and 1000 meters from the discharge site.



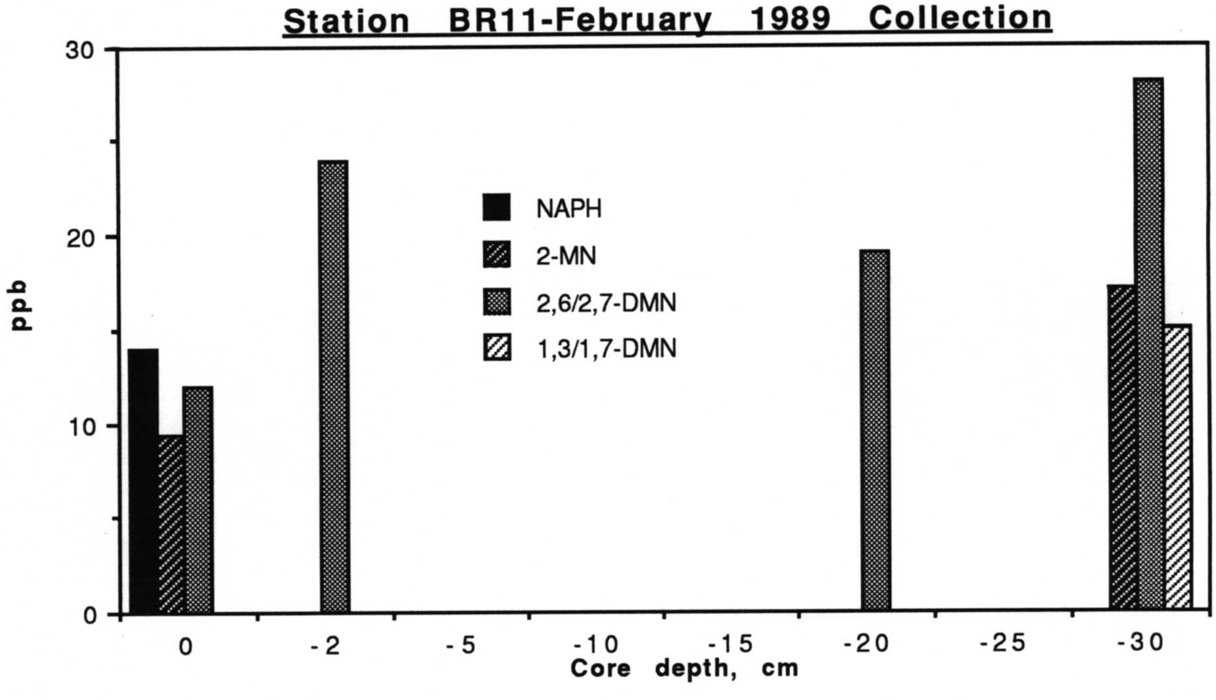
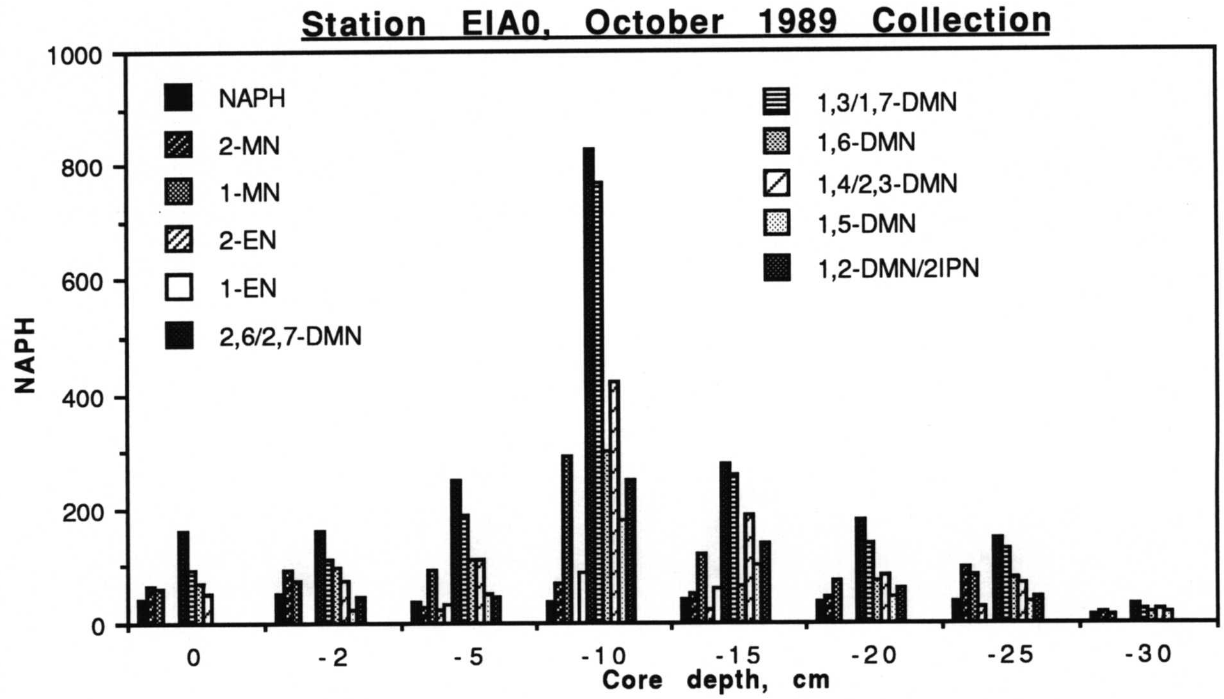


Figure 5.3.13 Alkylated naphthalenes concentrations in sections of two cores taken at Bayou Rigaud, February 1989, at distances of 0 and 300 meters from the discharge site.



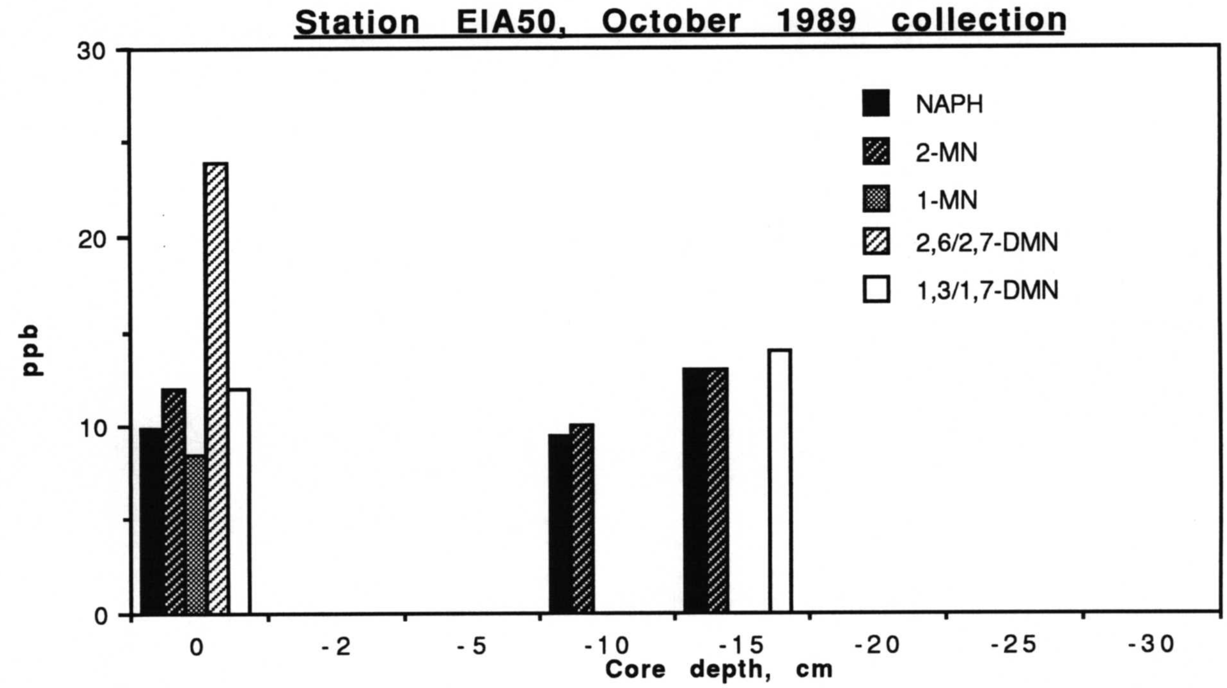


Figure 5.3.14 Alkylated naphthalenes concentrations in sections of two cores taken at Eugene Island, October 1989, at distances of 0 and 50 meters from the discharge site.

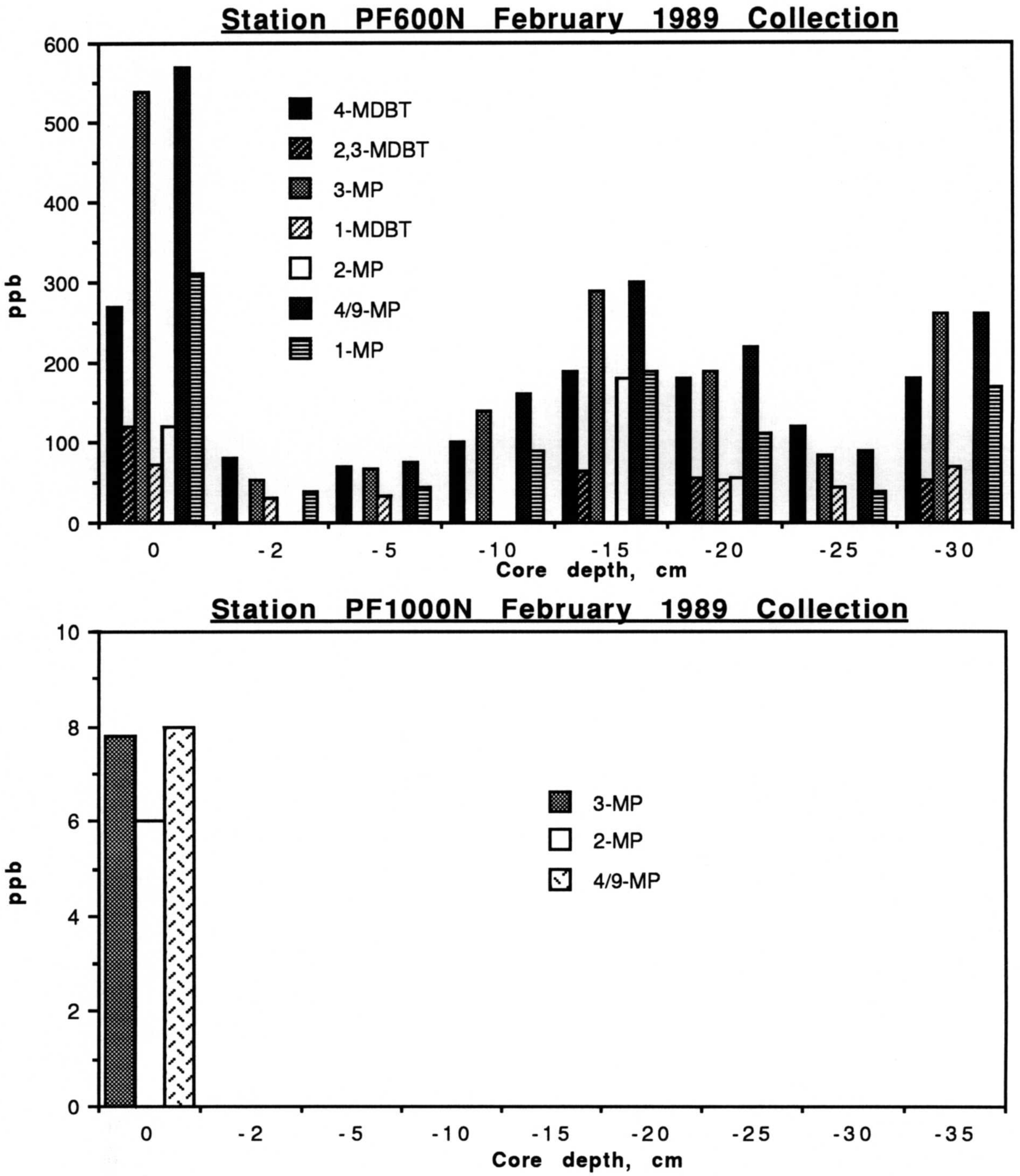
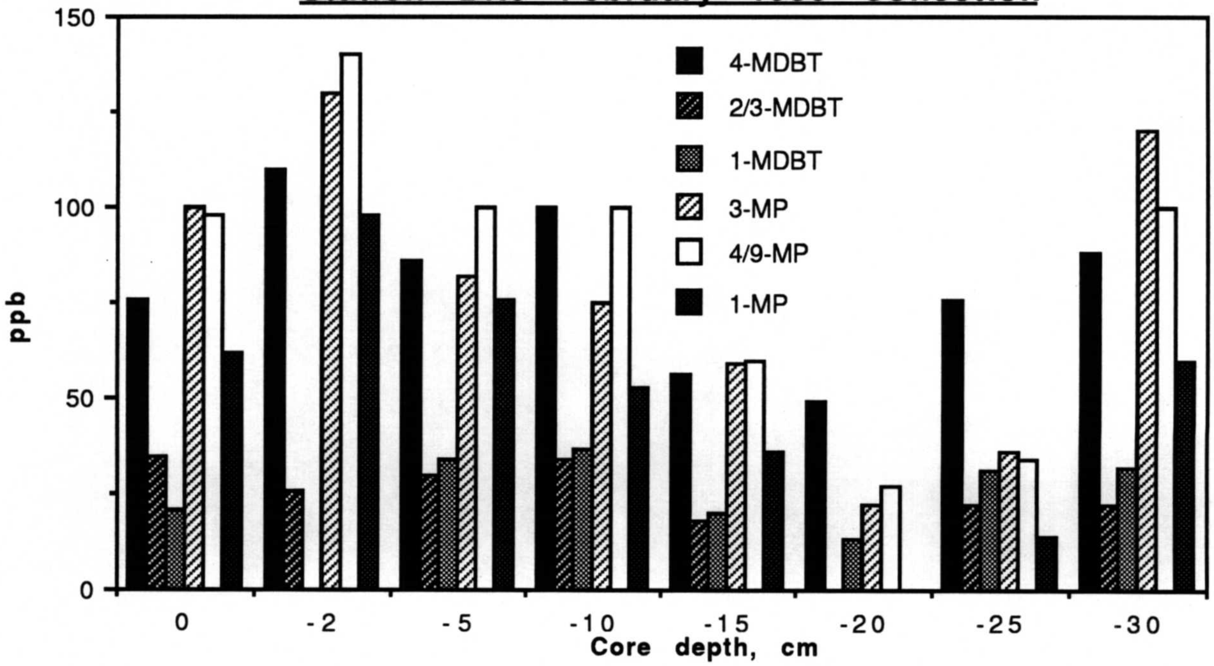
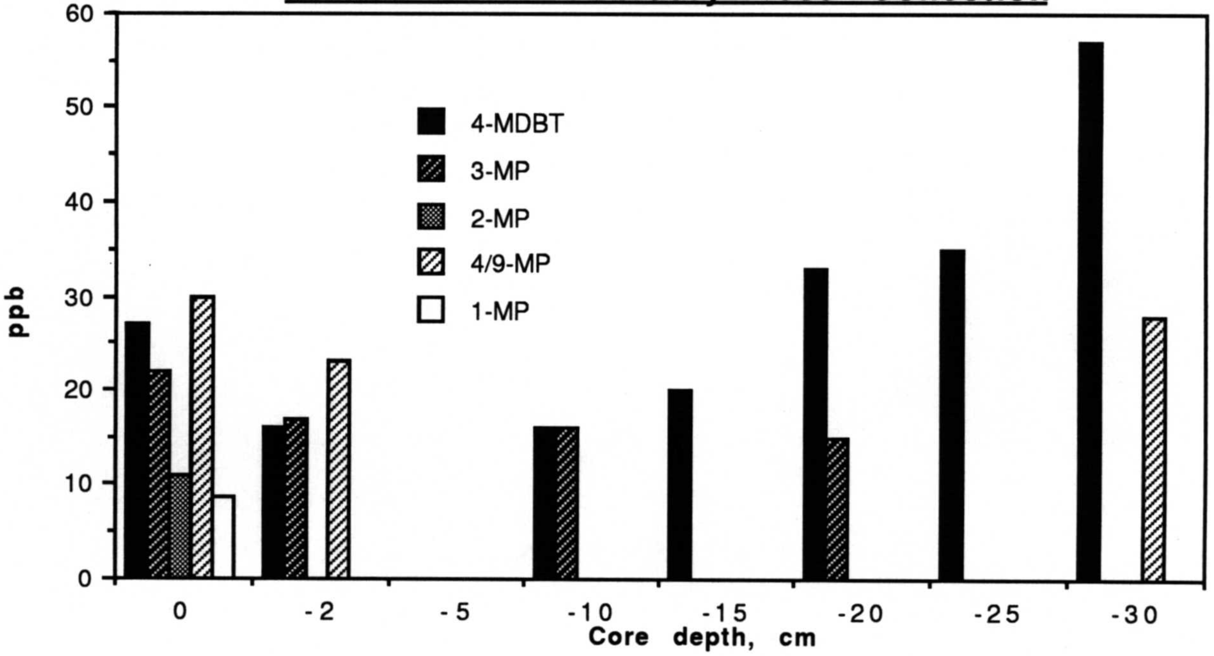


Figure 5.3.15 Alkylated methyldibenzothiophenes concentrations in sections of two cores taken at Pass Fourchon, February 1989, at distances of 600 and 1000 meters from the discharge site.

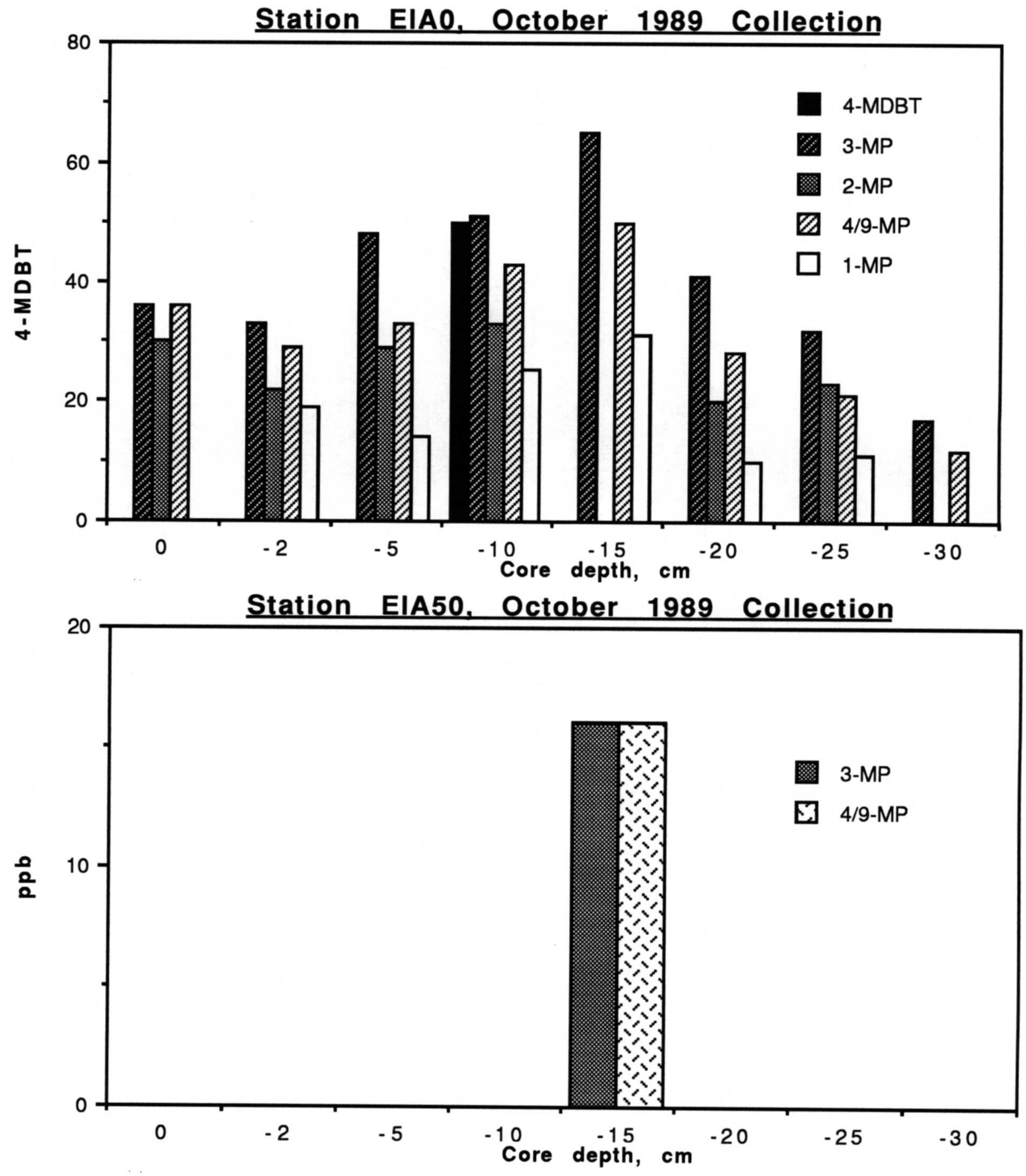


Station BR9 February 1989 Collection



Station BR11 February 1989 Collection

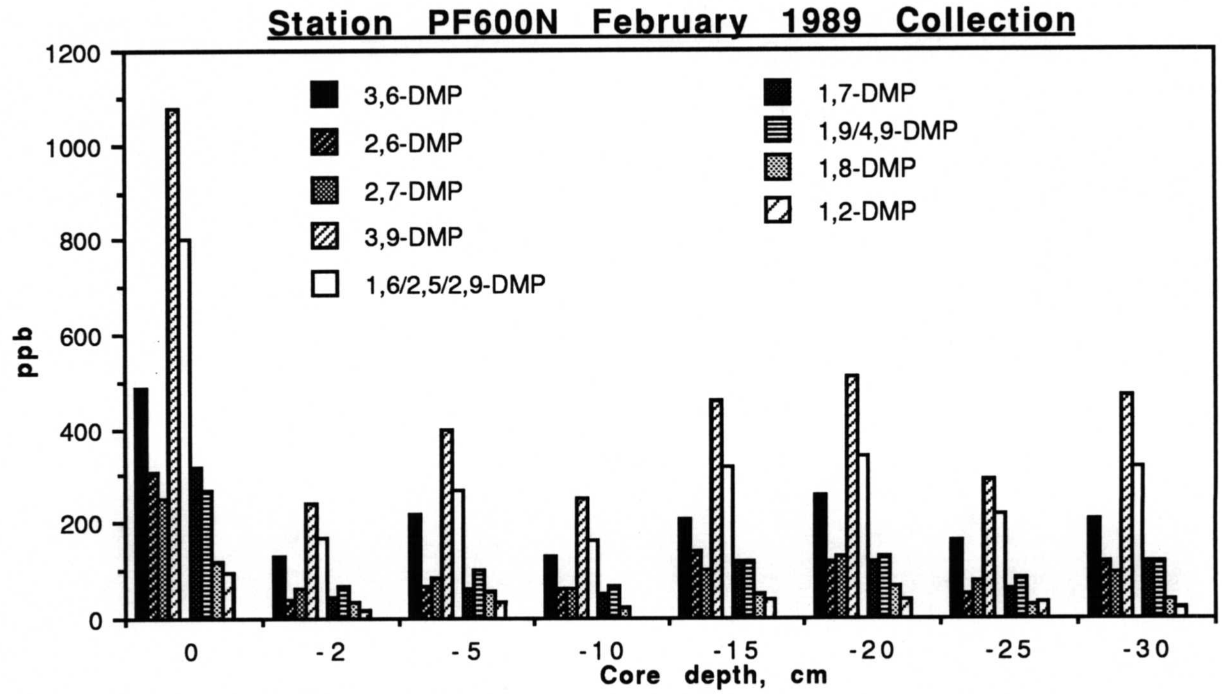
Figure 5.3.16 Methyldibenzothiophenes and methylphenanthrenes concentrations in sections of two cores taken at Bayou Rigaud, February 1989, at distances of 0 and 300 meters from the discharge site.



Station EIA0, October 1989 Collection

Station EIA50, October 1989 Collection

Figure 5.3.17 Methyldibenzothiophenes and methylphenanthrenes concentrations in sections of two cores taken at Eugene Island, October 1989, at distances of 0 and 50 meters from the discharge site.



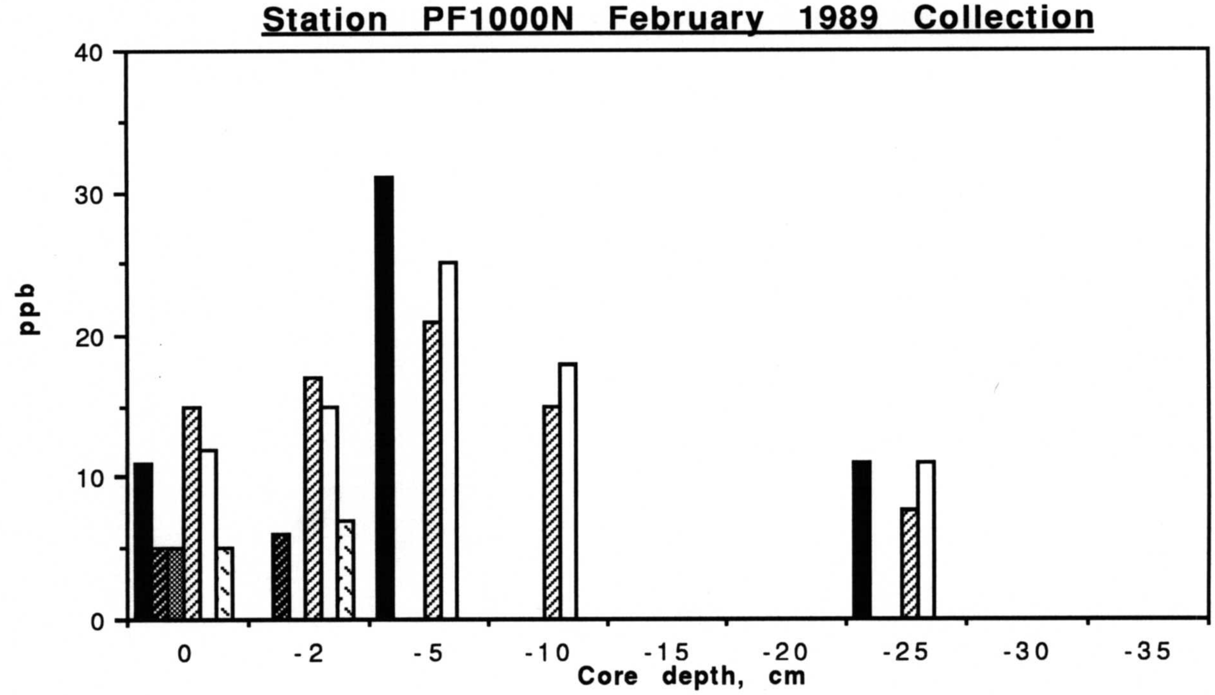
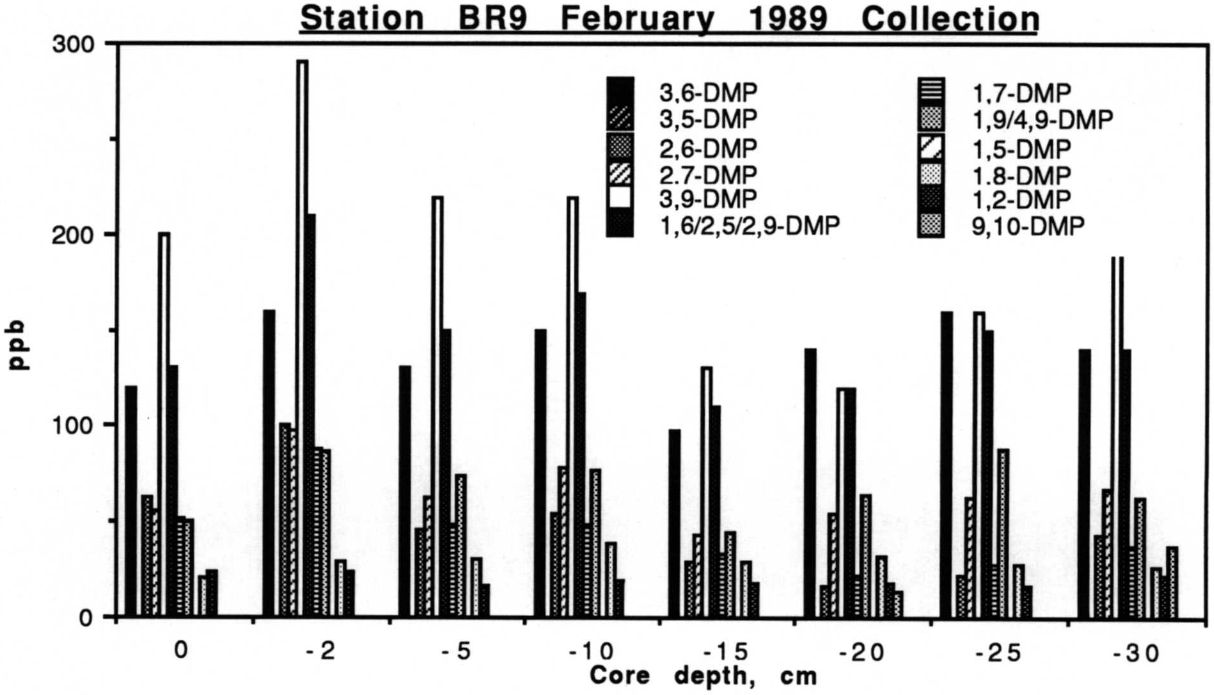


Figure 5.3.18 Dimethylphenanthrenes concentrations in sections of two cores taken at Pass Fourchon, February 1989, at distances of 600 and 1000 meters from the discharge site.



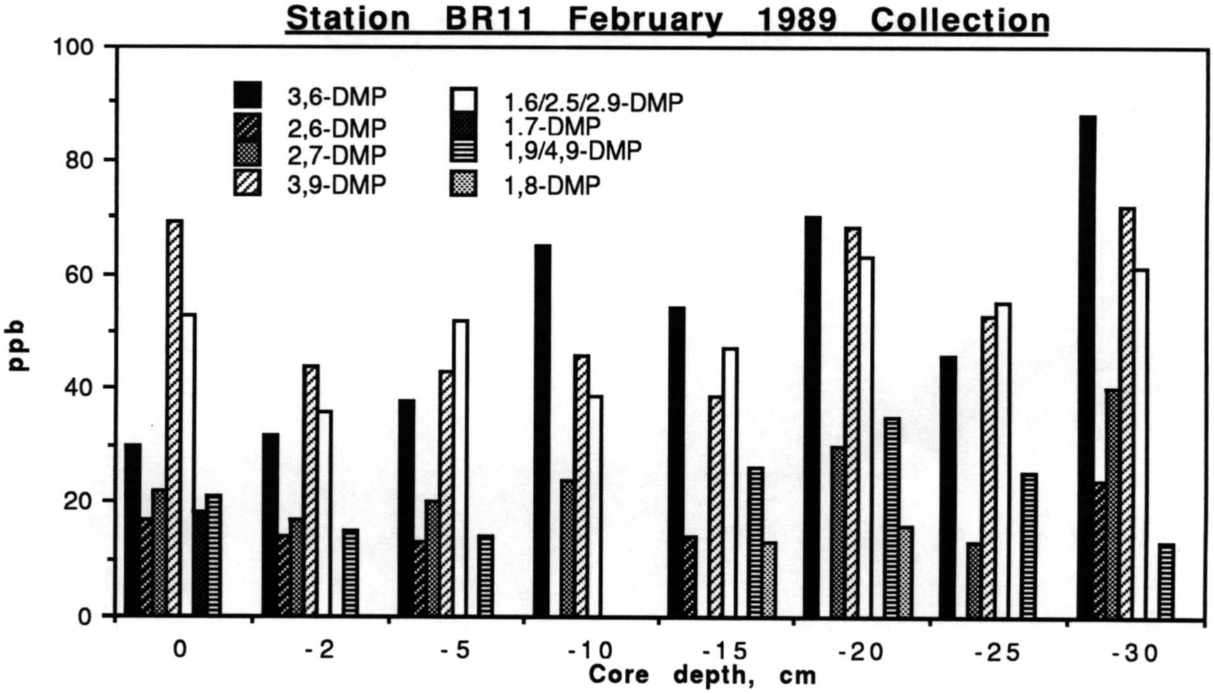
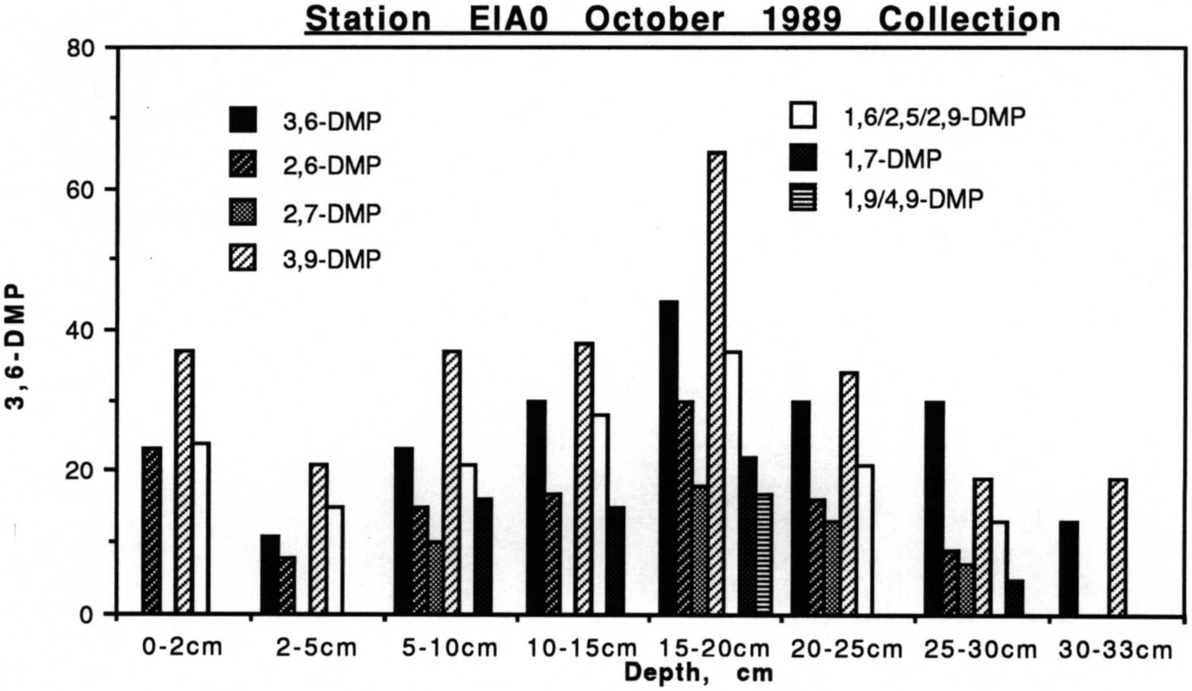


Figure 5.3.19 Dimethylphenanthrenes concentrations in sections of two cores taken at Bayou Rigaud, February 1989, at distances of 0 and 300 meters from the discharge site.



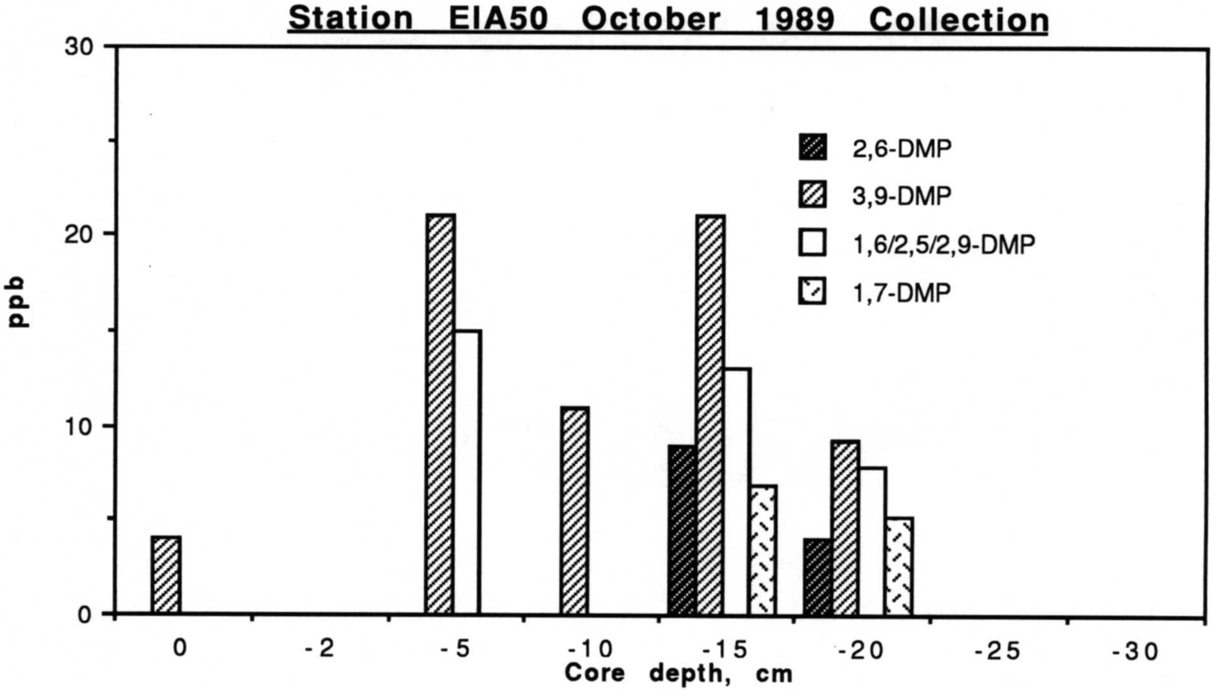


Figure 5.3.20 Dimethylphenanthrenes concentrations in sections of two cores taken at Eugene Island, October 1989, at distances of 0 and 50 meters from the discharge site.

similar to patterns observed for naphthalenes, MDBT, and MP in the Pass Fourchon and Bayou Rigaud cores, and most similar to MDBT, MP distributions in the Eugene Island core. The relative distribution of isomers was remarkably consistent throughout the depth of the PF600N core. The signature pattern was similar between all three sites, especially between the Pass Fourchon and Bayou Rigaud sites. Signatures are identifiable in the reference cores, especially for the Bayou Rigaud core. This is easily seen in the summary graphs, Figures 5.3.21-23. The relative distribution over depth of MDBT and MP in contaminated core sections was similar to naphthalenes distributions in the Pass Fourchon and Eugene Island cores, but the Bayou Rigaud core had a more even distribution over depth sections. Again, the Eugene Island core displayed a signature that differed from the other two sites, with methydibenzothiophenes not detected and an even distribution of all isomers of methylphenanthrenes. Overall, concentrations of MDBT and MP were lower in the Eugene Island core sections, but note that 2-MP was detected in all sections of this core, while it was absent in most sections of cores at the other two sites. These figures also show that the distribution of MDBT and MP was more similar between core sections than for the napthalenes data.

Comparisons between aromatic classes are shown in Figures 5.3.21-23 for the three sites. These plots show the most abundant isomers from each class for depth sections of the contaminated and reference cores. These figures show that: 1) The C2-naphthalenes concentrations are of major importance at the Eugene Island site, while other alkylated aromatics are much lower than seen at the other sites, and 2) The signatures are similar between the Pass Fourchon and Bayou Rigaud sites.

We have applied the examination of different ratios of analytes and multi-variant statistical analysis techniques in order to further examine this and other data to determine selective mobilization/removal processes active in the field for various members of the class of alkylated and heterocyclic PAH. Field data have been compared to microcosm data to compare and further elucidate transport processes and infer rates of processes.

5.4 Microcosm Desorption Results

Figure 5.4.1 shows an example of data obtained for selected alkylated naphthalenes for cores representing a "0-day" sample, (i.e., cores were capped and stored immediately after the sediments were bedded), a day-60 core and a day-120 core taken from the microcosm tanks. In spite of the lack of treatment of the "0-day" samples, concentrations of analytes were significantly lower in the top segment of the core than in lower sections of the core even after extensive homogenization of the sediments prior to introduction to the core jars. This may be the result of freezing the core or due to rapid desorption into overlying water that

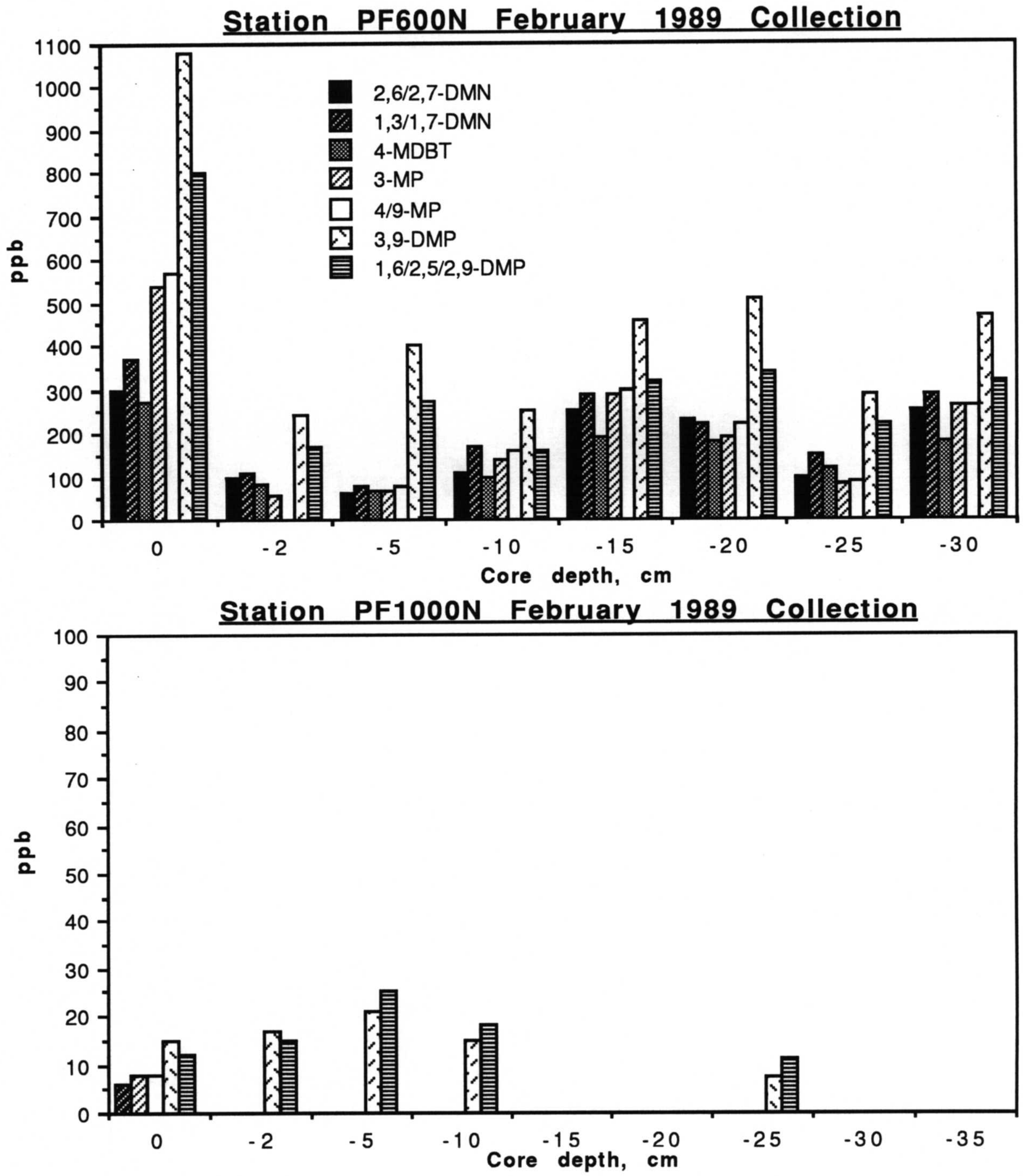


Figure 5.3.21 Selected alkylated aromatic hydrocarbons concentrations in sections of two cores taken at Pass Fourchon, February 1989, at distances of 600 and 1000 meters from the discharge site.

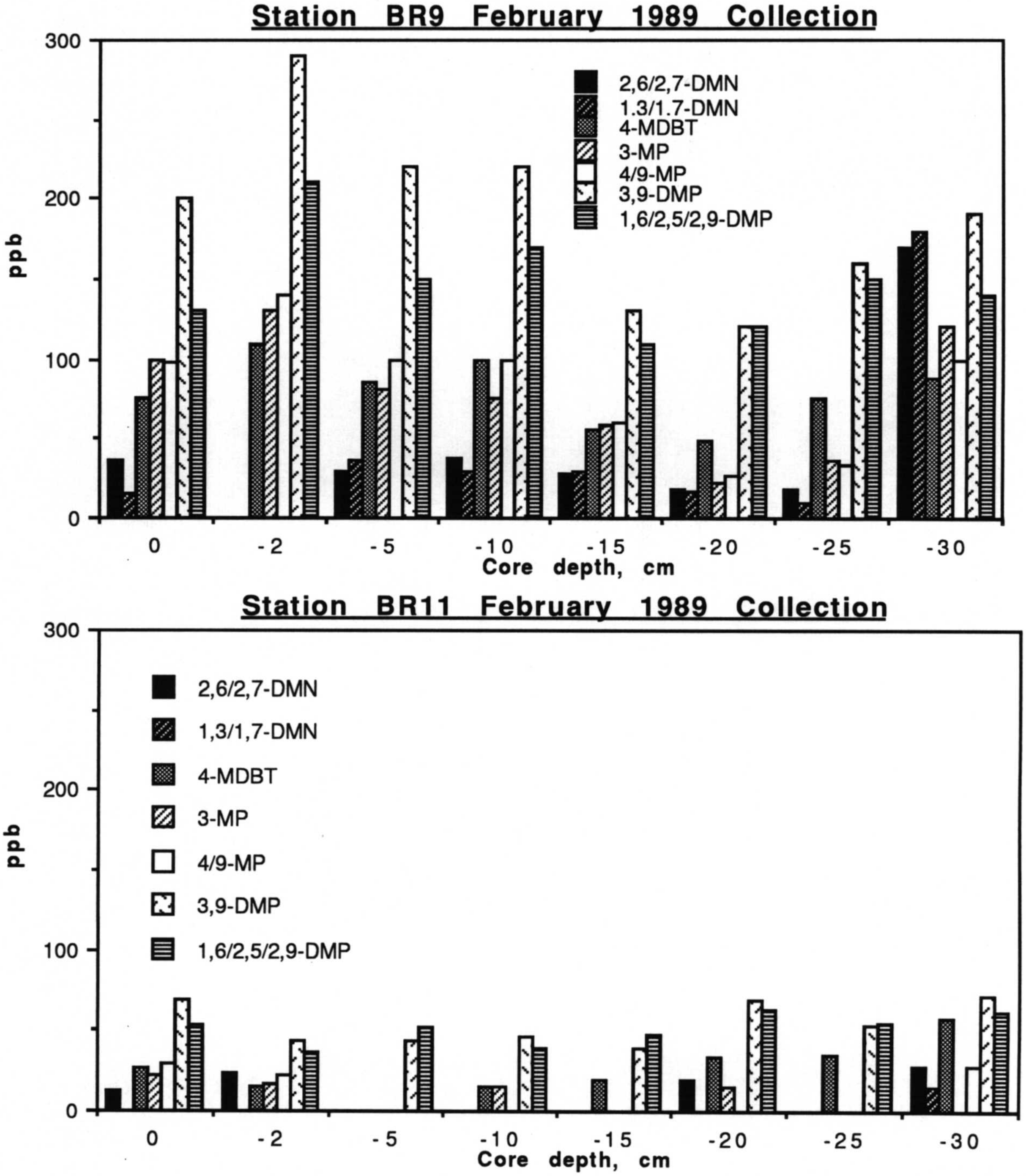


Figure 5.3.22 Selected alkylated aromatic hydrocarbons concentrations in sections of two cores taken at Bayou Rigaud, February 1989, at distances of 0 and 300 meters from the discharge site.

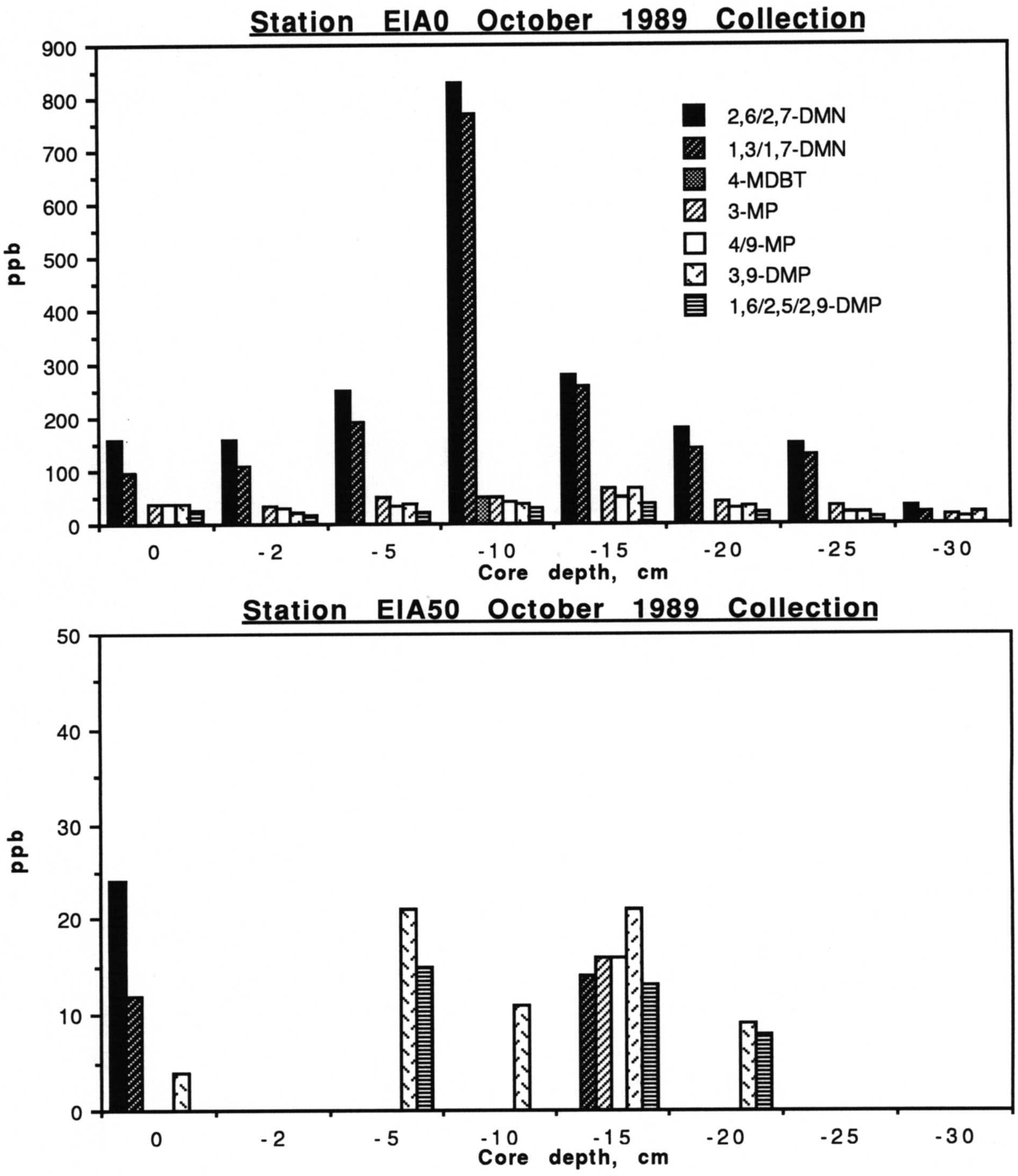


Figure 5.3.23 Selected alkylated aromatic hydrocarbons concentrations in sections of two cores taken at Eugene Island, October 1989, at distances of 0 and 50 meters from the discharge site.

separated from the sediment during the bedding process. The subsurface minimum which was observed in the day-0 core for all three compounds seems to suggest that a redox-related, selective destruction of the three compounds may be occurring in the cores. destruction of the three compounds may be occurring in the cores. The data for the day 60 core show that desorption of both dimethyl-naphthalenes is occurring from the top sections of the core while other compounds such as 1-ethylnaphthalene (1-EN) appear to be relatively unchanged with depth. By day 120, several of the dimethylnaphthalenes are greatly depleted in the core while 1-EN is still found at very similar concentrations below 8mm depth. Figure 5.4.2 shows the concentration profiles of three methyl-phenanthrenes as a function of depth and core age in the desorption microcosm. These data show that all three methyl-phenanthrene isomers desorb from sediments at similar rates but all are depleted in the cores after 120 days of incubation. Figures 5.4.3 through 5.4.6 show the average 120-day depth profiles for all alkylated species examined. These figures clearly show the depletion of all analytes in upper sections of the cores, with the notable exception of naphthalene, and also indicate that rates are similar for isomers within a class, but differ between classes. Figures 5.4.7 and 5.4.8 show the changes in relative concentration for a selected analytes from each class as a function of both depth and time. From these data and other data obtained on these and other cores, we are developing estimates of the desorption rate constants of alkylated and heterocyclic PAHs from sediments under different conditions of salinity, OC and colloid enrichments. We are able to make several independent estimates of these rates for several positional isomers of the same compound (i.e. 10 dimethylnaphthalenes) having similar sorption constants and aqueous solubility. We are also able to examine the potential for selective removal (degradation) of specific isomers.

5.5 Modeling of Microcosm Results

The results of the microcosm desorption experiments have been used to develop a model of contaminant transport from bedded sediment. In natural aquatic systems, because of the relatively rapid advective movements of the water masses overlying contaminated sediment beds, the type of equilibria studied and reported in an earlier part of this report are rarely if ever achieved. If new contaminants are consistently being added to the overlying waters then there will be a net flux of the chemical into the surficial sections of the sediment bed or alternatively suspended particulates within the overlying water will settle out on the surface of the sediment bed. However, in well flushed systems or in systems where the source of contamination is removed, the tendency will be for contaminants associated with the sediment bed to disassociate from the sediment particle surfaces and gradually be removed by diffusion to the sediment-water interface and then be mixed (diluted) and transported away with the movements of the water.

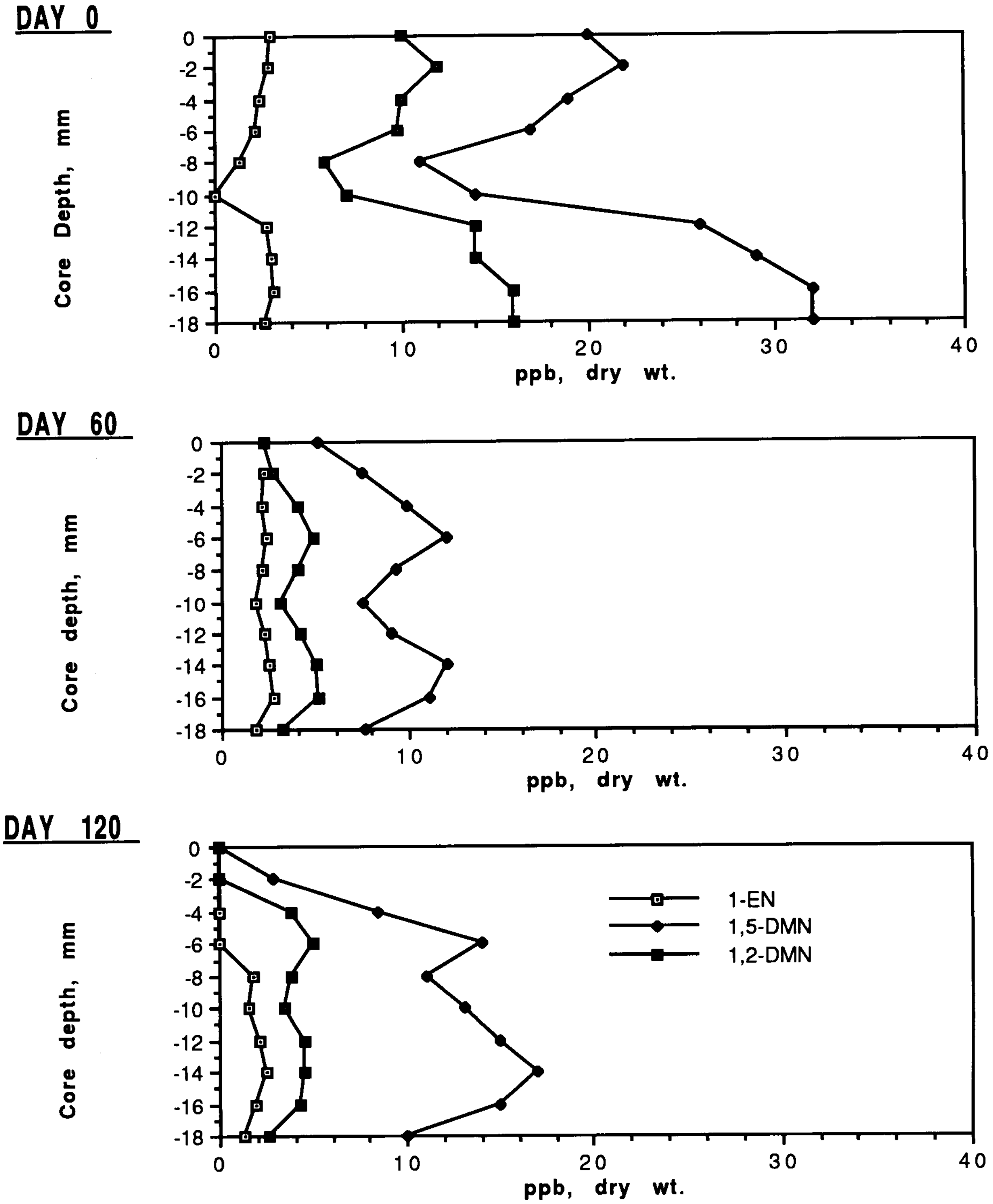


Figure 5.4.1. Depth profiles for selected alkylated naphthalenes concentrations in microcosm cores representing three sampling periods.

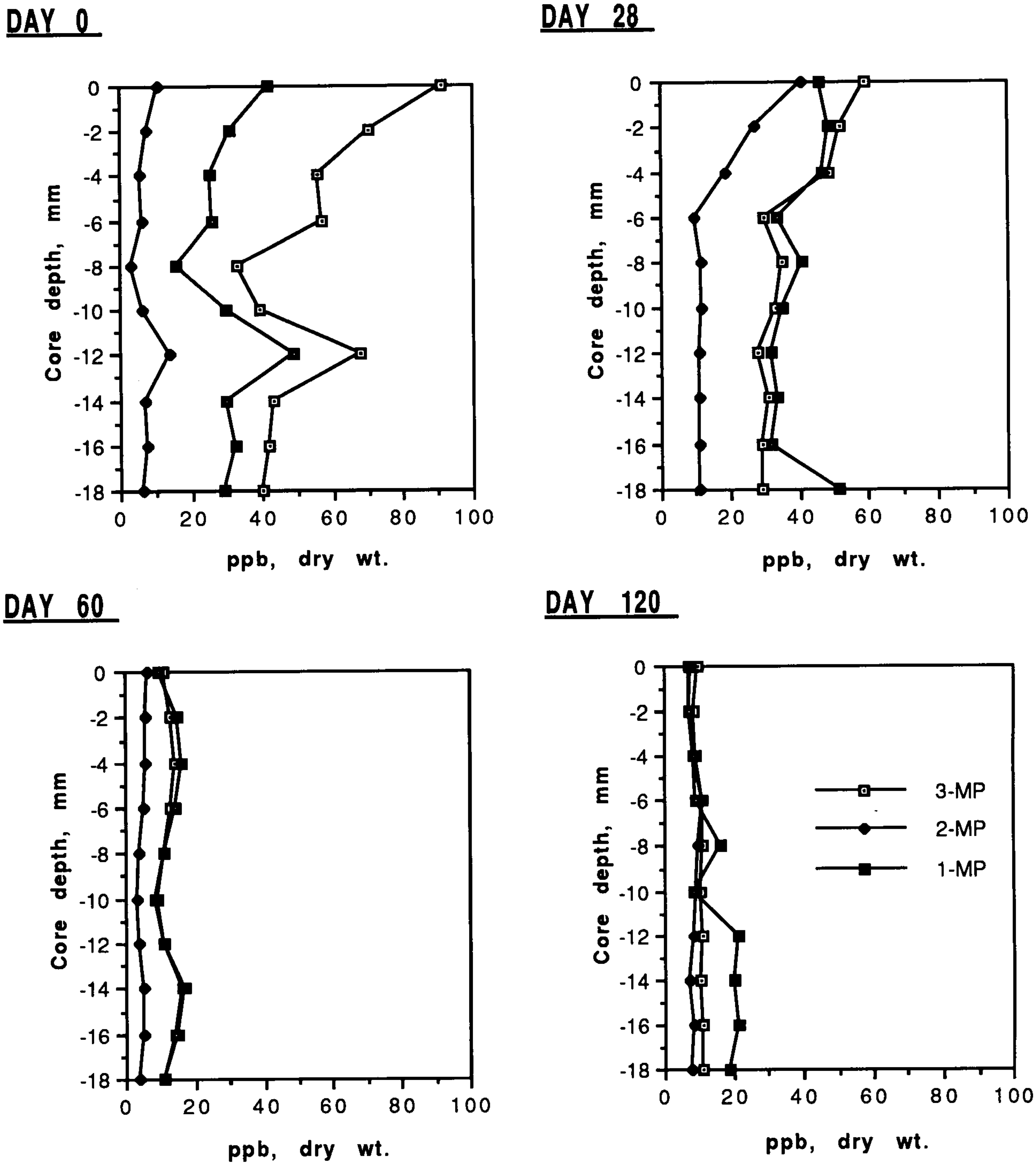


Figure 5.4.2. Depth profiles for selected methylphenanthrenes concentrations in microcosm cores representing four sampling periods.

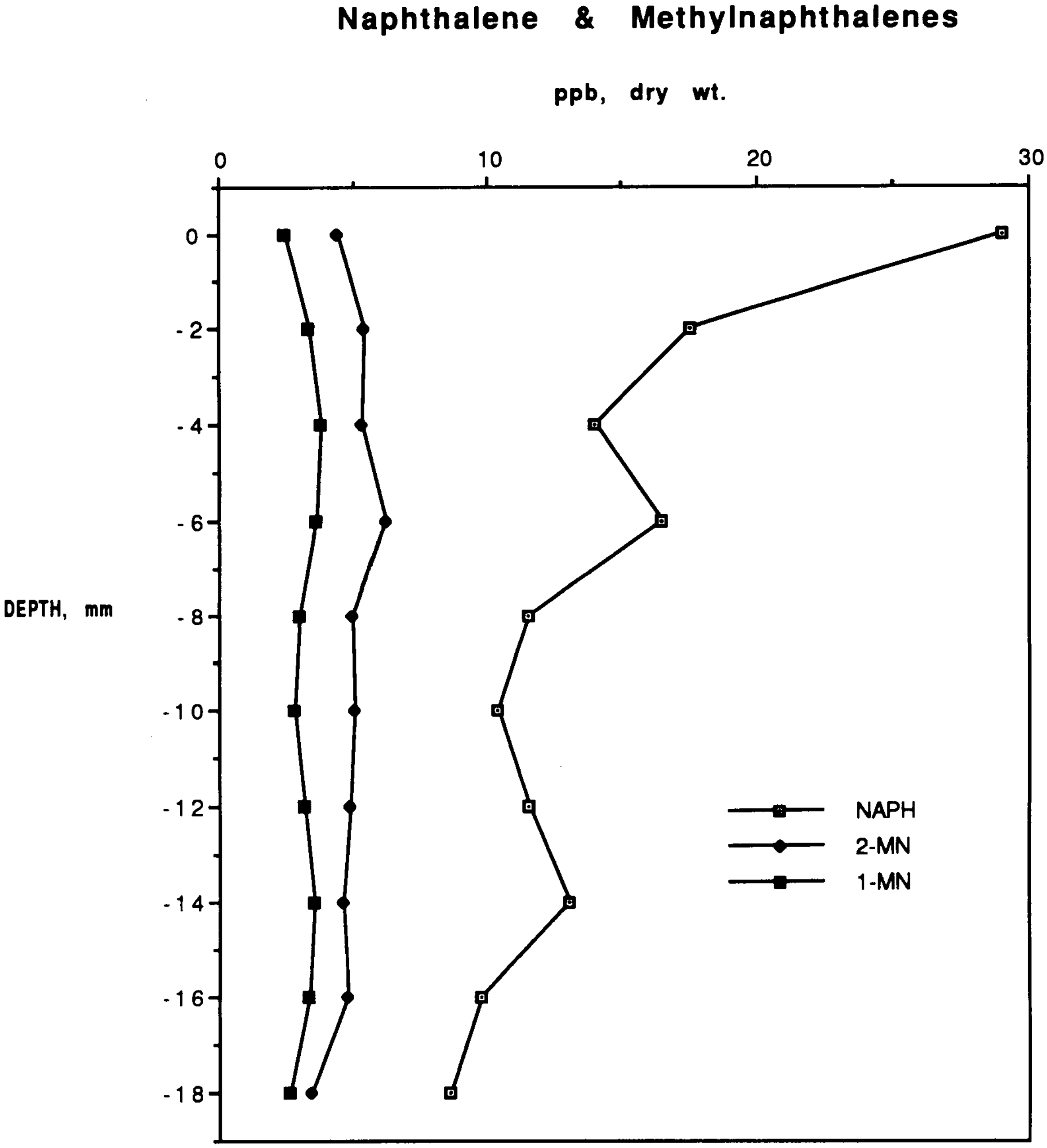


Figure 5.4.3. Depth profiles for naphthalenes and methylnaphthalene showing average concentrations in microcosm cores collected at 120 days.

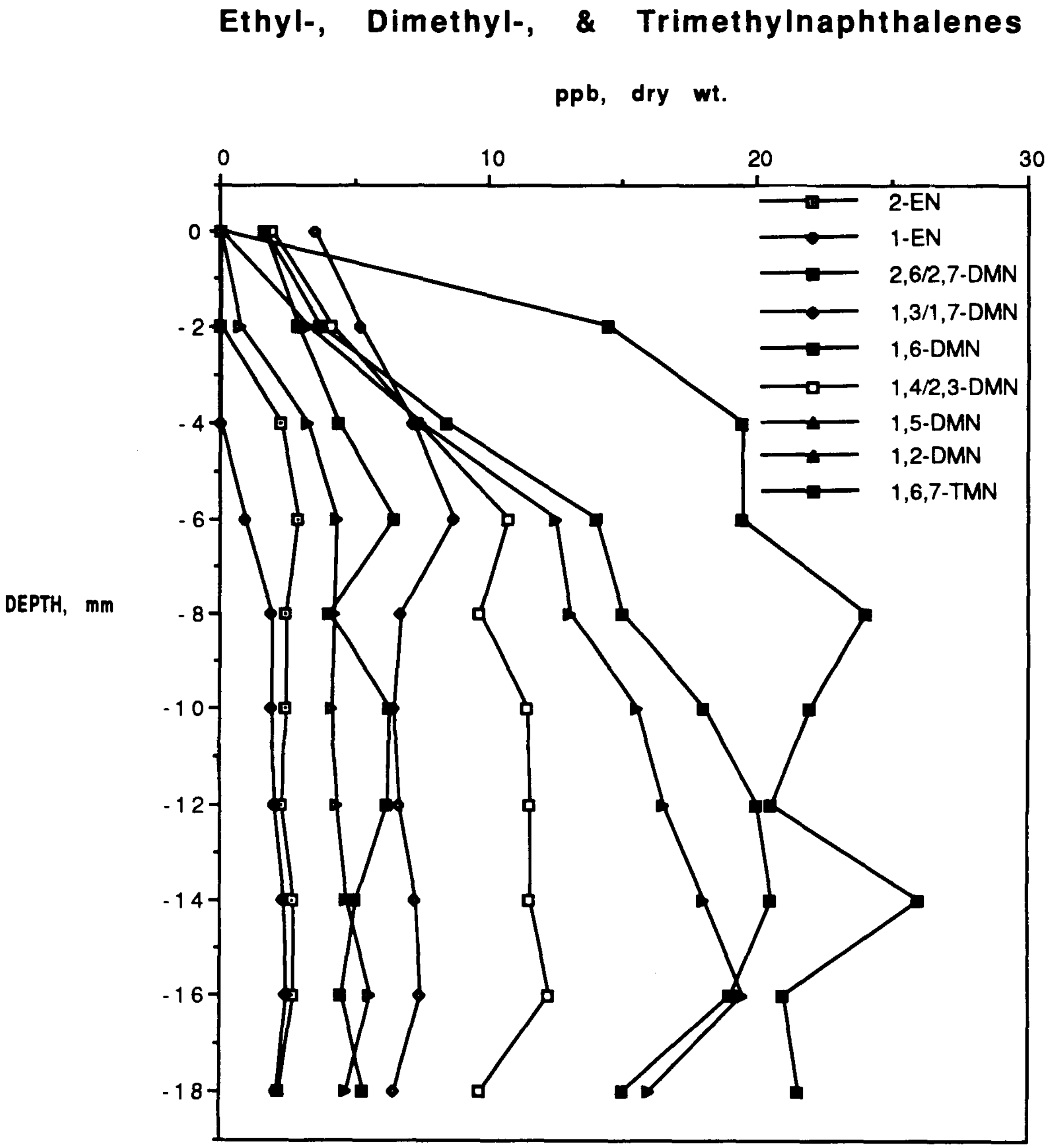


Figure 5.4.4. Depth profiles for C2- and C3-naphthalenes showing average concentrations in microcosm cores collected at 120 days.

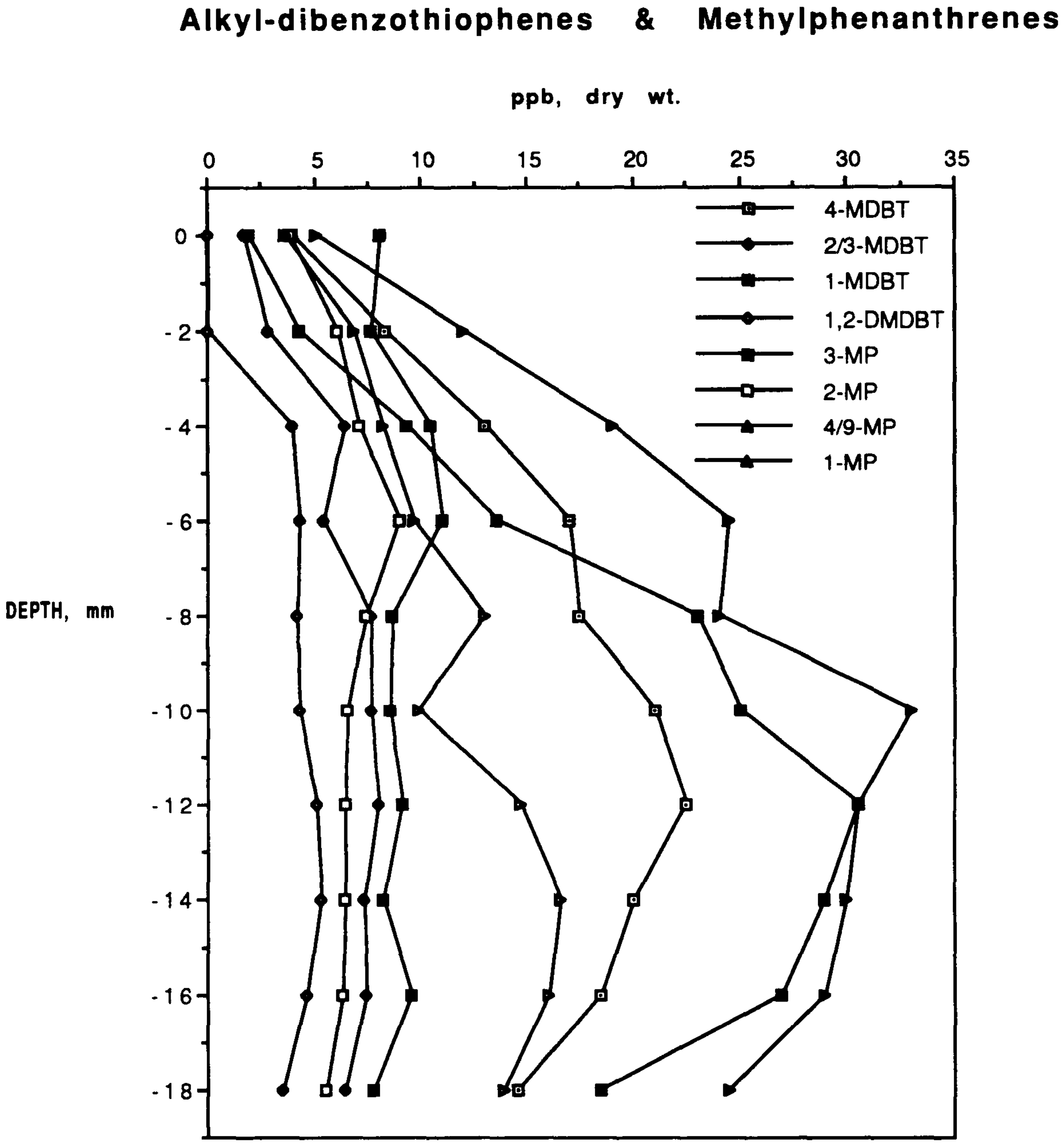


Figure 5.4.5. Depth profiles for methyl- and dimethyl-dibenzothiophenes and methylphenanthrenes showing average concentrations in microcosm cores collected at 120 days.

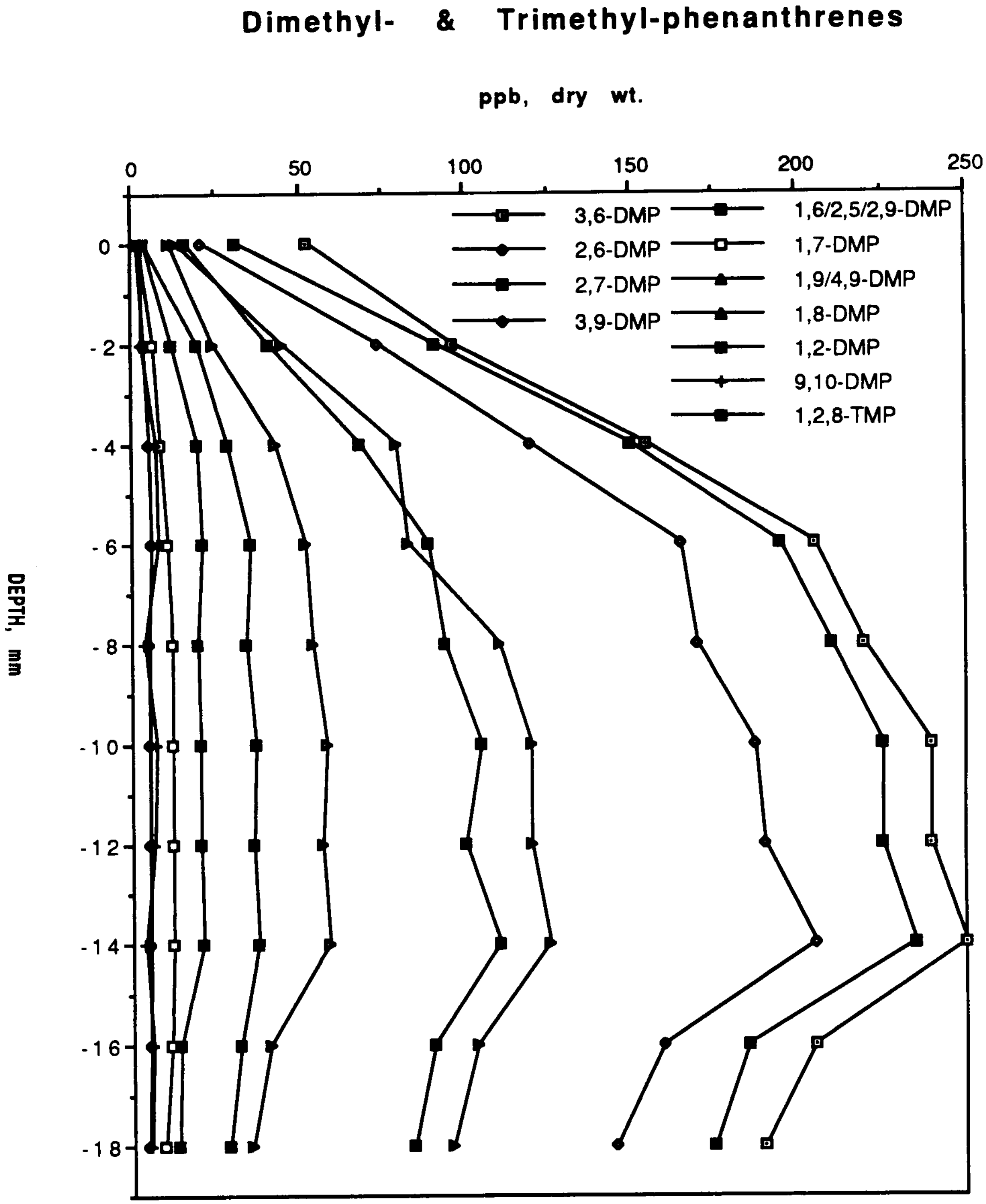


Figure 5.4.6. Depth profiles for dimethyl- and trimethyl-phenanthrenes showing average concentrations in microcosm cores collected at 120 days.

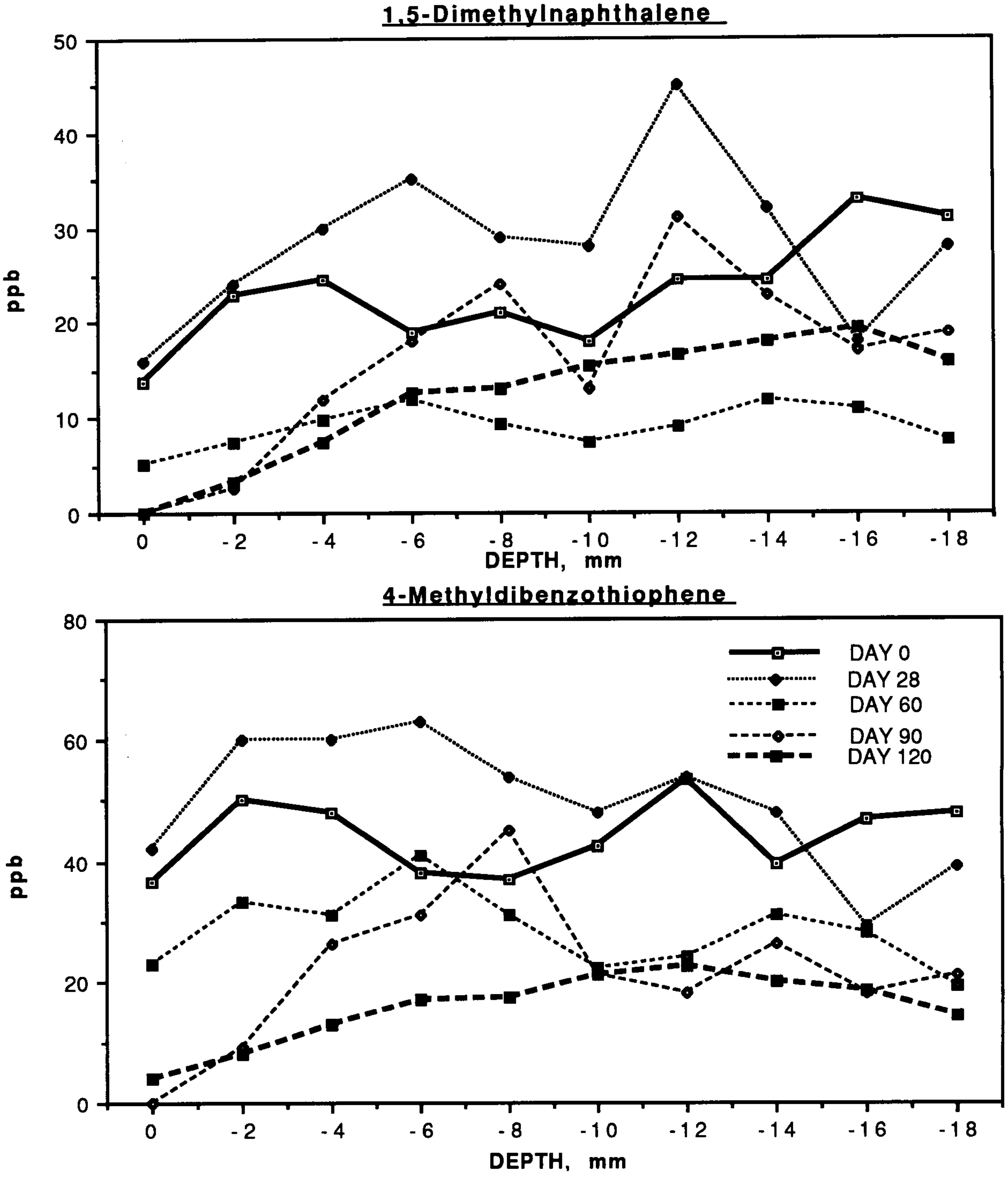


Figure 5.4.7. Changes in microcosm depth profiles over time for 1,5-dimethylnaphthalene and 4-methyldibenzothiophene.

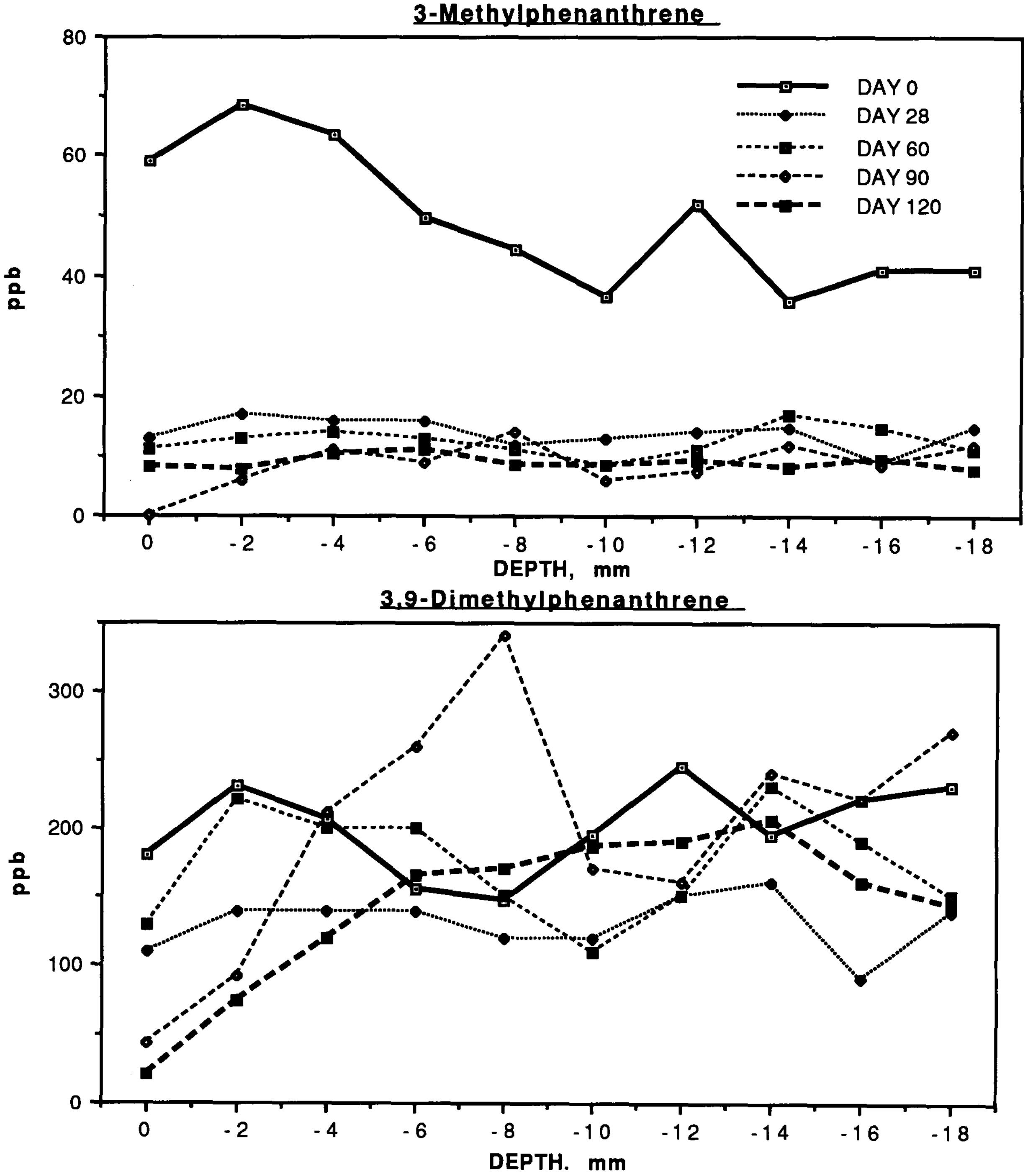


Figure 5.4.8. Changes in microcosm depth profiles over time for 3-methylphenanthrene and 3,9-dimethylphenanthrene.

In a system where the water column provides significant dilution (approaching infinity), aqueous concentrations will always be low enough such that a diffusion driven flux of sediment-bound contaminants to the water column will be maintained. In such systems, the diffusive process may be considered to follow Fick's second law of diffusion:

$$\frac{\delta C}{\delta t} = D_{eff} \frac{\delta^2 C}{\delta x^2}$$

where:

D_{eff} = effective diffusivity, cm^2/sec
C = concentration of contaminant
X = depth below sediment-water interface, cm
t = time, sec

In the field and in our laboratory microcosm, the aqueous concentrations of all of the contaminants diffusing from the sediment bed with time are low and can, for modeling purposes, be considered to approximately equal zero. The initial concentrations of the individual contaminants in the microcosm sediment beds, which were thoroughly homogenized prior to bedding, can all be assumed to be homogeneous with depth at the initial time point of the experiment. Further, it can be assumed that, at the sediment-water interface at the initiation of the experiment (depth=0 cm), the contaminant concentrations will also be zero.

Given these initial boundary conditions and also assuming that values of D_{eff} will be such that over the course of the experiment (~120 days) the maximum depth (X) at which diffusion is actively occurring will be less than the total depth of the experimental cores (L), then a semi-infinite solution to the Fickian diffusion model with respect to the concentrations of an individual contaminant can be written:

$$C_t = C_i * \mathrm{erf}\left[\frac{X}{[2*LD^{1/2}]}\right]*t$$

The experimental data from the depth profiles for individual compounds at various times in our study can be fitted to this equation to estimate values for D_{eff}. Alternatively, values of D_{eff} estimated from compound molecular parameters may be used to evaluate the "goodness of fit" of the Fickian diffusion model prediction to measured desorption profiles in the experimental microcosms (Thibodeaux, 1988). In this case D_{eff} is estimated in coupled diffusion/desorption model using the equation:

$$D_{eff} = \frac{Dp}{1 + \frac{\rho b * Kp}{\varepsilon}}$$

where:

D_p= the diffusivity in a non-absorbing porous medium, cm^2/sec
ρ_b= the bulk density, g/ml
K_p= the partition coefficient, ml/g
ε= the porosity of the sediment, ml/ml

One advantage of our data set is that because we have precise measurements of the concentrations of several isomers of the same compound (e.g., dimethylnaphthalenes), we are able to make multiple estimates of D_{eff} within a single core.

Modeling efforts are ongoing at this time and will be reported in the future.

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APPENDIX 1

Table A1.1. Hydrocarbon concentrations (ppb) in a core taken at Pass Fourchon, PF 600N, Feb. 1989.

Analyte	Depth in core:							
	0-2cm	2-5cm	5-10cm	10-15cm	15-20cm	20-25cm	25-30cm	30-33cm
Naphthalene	nd	tr	tr	tr	nd	tr	tr	nd
2-Methylnaph.	nd	tr	tr	tr	tr	tr	tr	tr
1-Methylnaph.	41	tr	tr	tr	42	28	nd	nd
2-Ethylnaph.	nd	tr	nd	nd	44	tr	tr	tr
1-Ethylnaph.	nd	tr	nd	nd	nd	tr	nd	nd
2,6/2,7-Dimethylnaph.	300	96	60	110	250	230	100	250
1,3/1,7-DMN	370	110	75	170	290	220	150	290
1,6-DMN	tr	nd	nd	nd	110	nd	nd	nd
1,4/2,3-DMN	200	89	57	82	140	190	79	180
1,5-DMN	72	20	nd	nd	73	78	nd	83
Acenaphthylene	nd	tr	nd	nd	nd	tr	nd	nd
1,2-DMN/2-IPN	trc	23	nd	nd	57	55	nd	50
2-IPN	trc	tr	nd	tr	32	41	nd	46
1,8-DMN.	nd	37	tr	33	48	29	32	47
Acenaphthene	nd	17	tr	tr	tr	tr	tr	tr
Fluorene	77	tr	nd	nd	42	tr	tr	34
Dibenzothiophene	27	tr	nd	tr	tr	30	nd	31
Phenanthrene	nd	19	tr	tr	93	35	tr	tr
Anthracene	nd	tr	tr	tr	tr	tr	tr	tr
4-MDBT	270	81	69	99	190	180	120	180
2/3-MDBT	120	nd	nd	tr	65	55	tr	52
3-MP	540	54	68	140	290	190	84	260
1-MDBT	72	30	32	tr	tr	54	45	69
2-MP	120	tr	tr	tr	180	55	tr	tr
4/9-MP	570	tr	75	160	300	220	89	260
1-MP	310	39	45	89	190	110	38	170
3,6-DMP	490	130	220	130	210	260	160	210
2,6-DMP	310	39	66	64	140	120	53	120
2,7-DMP	250	61	84	63	99	130	79	96
3,9-DMP	1,078	240	400	250	460	510	290	470
1,6/2,5/2,9-DMP	800	170	270	160	320	340	220	320
1,7-DMP	320	43	60	53	120	120	60	120
1,9/4,9-DMP	270	65	99	66	120	130	83	120
Fluoranthene	190	46	93	65	72	82	70	64
1,5-DMP	nd	nd	nd	nd	nd	nd	nd	nd
1,8-DMP	120	35	58	23	48	65	30	37
1,2-DMP	98	17	35	nd	38	40	32	25
9,10-DMP	nd	nd	nd	nd	tr	nd	nd	nd
Pyrene	190	tr	100	51	60	84	57	66
Benz(a)anthracene	94	27	nd	tr	tr	120	58	110
Chrysene	340	190	140	67	82	230	140	320
Benzo(b)fluoranthene	nd	56	nd	30	nd	100	nd	nd
Benzo(k)fluoranthene	nd	nd	nd	nd	nd	nd	nd	nd
Benzo(a)pyrene	nd	nd	nd	nd	nd	nd	nd	nd
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd	nd	nd	nd	nd
Dibenzo(a,h)anthracene	nd	nd	nd	nd	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd	nd	nd	nd	nd	nd
C1-Naphthalenes, total	41	tr	tr	tr	42	28	tr	tr
C2-Naphthalenes, total	942	375	192	395	1,012	802	361	900
C3-Naphthalenes, est.	6,400	3,700	2,800	3,200	5,400	5,600	3,100	5,900
C4-Naphthalenes, est.	5,000	4,500	4,300	4,300	5,200	6,100	3,800	6,100
C5-Naphthalenes, est.	tr	3,700	3,500	2,800	5,400	4,000	3,300	3,300
C1-Fluorenes	500	120	130	tr	130	200	150	180
C2-Fluorenes	1,600	650	660	480	870	600	610	760

Table A1.1. Hydrocarbon concentrations (ppb) in a core taken at Pass Fourchon, PF 600N, Feb. 1989 (continued).

Analyte	Depth in core:							
	0-2cm	2-5cm	5-10cm	10-15cm	15-20cm	20-25cm	25-30cm	30-33cm
C3-Fluorenes	1,400	580	720	480	1,000	840	380	810
C1-Dibenzothiophenes, total	462	111	101	99	255	289	165	301
C2-Dibenzothiophenes,est.	1,400	380	520	350	590	620	150	630
C3-Dibenzothiophenes,est.	1,500	390	620	300	460	520	360	590
C1-Phenanthrenes, total	1,540	93	188	389	960	575	211	690
C2-Phenanthrenes, total	3,736	800	1,292	809	1,555	1,715	1,007	1,518
C2-Phenanthrenes, est.	3,900	870	1,300	860	1,600	1,800	1,000	1,500
C3-Phenanthrenes, est.	3,400	770	1,100	430	800	1,000	760	1,000
Total Parent PAH	918	355	333	213	349	681	325	625
Total Alkylated PAH	28,085	16,239	16,131	14,083	23,719	22,974	14,347	22,661
Total PAH	29,003	16,594	16,464	14,296	24,068	23,655	14,672	23,286
FFPI	0.92	0.94	0.94	0.93	0.93	0.92	0.93	0.92
Saturated Hydrocarbons								
Resolved	57,000	31,000	25,000	21,000	67,000	51,000	30,000	51,000
Unresolved	523,000	289,000	305,000	179,000	373,000	489,000	270,000	479,000
Total	580,000	320,000	330,000	200,000	440,000	540,000	300,000	530,000
MDL	24	16	24	22	26	28	27	29

MDL: Minimum Detection Limit
nd: Not detected
tr: Trace; one ion present, but below detection limits
trc: Trace confirmed; two ions present, but below detection limits
n/a: not analyzed

Table A1.2. Hydrocarbon concentrations (ppb) in a core taken at Pass Fourchon, PF1000N, Feb. 1989.

Analyte	Depth in core:								
	0-2cm	2-5cm*	5-10cm	10-15cm	15-20cm	20-25cm	25-30cm	30-35cm	35-38cm
Naphthalene	5.1	tr	tr	tr	tr	tr	tr	tr	tr
2-Methylnaph.	8.4	tr	tr	tr	tr	nd	trc	tr	nd
1-Methylnaph.	6.6	tr	tr	trc	tr	nd	trc	tr	nd
2-Ethylnaph.	nd	nd	nd	nd	nd	nd	nd	nd	nd
1-Ethylnaph.	nd	nd	nd	nd	nd	nd	nd	nd	nd
2,6/2,7-Dimethylnaph.	trc	tr	tr	trc	tr	nd	trc	nd	nd
1,3/1,7-DMN	6.2	tr	tr	trc	nd	tr	trc	nd	nd
1,6-DMN	trc	tr	tr	nd	nd	nd	trc	nd	nd
1,4/2,3-DMN	trc	nd	nd	nd	nd	nd	nd	nd	nd
1,5-DMN	nd	nd	nd	nd	nd	nd	nd	nd	nd
Acenaphthylene	nd	nd	nd	nd	nd	nd	nd	nd	nd
1,2-DMN/2-IPN	nd	nd	nd	nd	nd	nd	nd	nd	nd
2-IPN	nd	nd	nd	nd	nd	nd	nd	nd	nd
1,8-DMN.	nd	nd	nd	nd	nd	nd	nd	nd	nd
Acenaphthene	trc	nd	nd	nd	nd	nd	nd	trc	nd
Fluorene	nd	tr	nd	nd	nd	nd	nd	nd	nd
Dibenzothiophene	nd	nd	nd	nd	nd	tr	nd	nd	nd
Phenanthrene	18	35	24	30	tr	130	11	nd	18
Anthracene	3.7	tr	13	tr	nd	tr	tr	nd	nd
4-MDBT	trc	nd	nd	nd	nd	nd	nd	nd	nd
2/3-MDBT	nd	tr	nd	nd	nd	nd	nd	nd	nd
3-MP	7.8	tr	tr	tr	nd	tr	nd	nd	nd
1-MDBT	nd	nd	nd	nd	nd	nd	nd	nd	nd
2-MP	6.0	tr	nd	nd	nd	tr	nd	nd	nd
4/9-MP	8.0	tr	nd	nd	nd	tr	nd	nd	nd
1-MP	tr	tr	nd	nd	nd	tr	nd	nd	nd
3,6-DMP	11	tr	31	tr	tr	nd	11	nd	nd
2,6-DMP	5	6	tr	nd	tr	tr	nd	nd	nd
2,7-DMP	5	tr	tr	nd	tr	tr	nd	nd	nd
3,9-DMP	15	17	21	15	tr	tr	7.6	tr	tr
1,6/2,5/2,9-DMP	12	15	25	18	tr	tr	11	nd	tr
1,7-DMP	5	7	nd	nd	nd	nd	nd	nd	tr
1,9/4,9-DMP	tr	tr	tr	tr	tr	nd	nd	nd	nd
Fluoranthene	54	98	110	54	79	530	39	34	44
1,5-DMP	nd	nd	nd	nd	nd	nd	nd	nd	nd
1,8-DMP	tr	nd	nd	nd	nd	nd	nd	nd	nd
1,2-DMP	tr	nd	nd	nd	nd	nd	nd	nd	nd
9,10-DMP	nd	nd	nd	nd	nd	nd	nd	nd	nd
Pyrene	56	87	96	50	61	350	43	33	35
Benz(a)anthracene	13	30	61	tr	17	37	11	tr	11
Chrysene	19	74	80	tr	29	130	25	tr	16
Benzo(b)fluoranthene	15	tr	130	nd	nd	120	nd	nd	nd
Benzo(k)fluoranthene	8.2	tr	nd	nd	nd	tr	nd	nd	nd
Benzo(a)pyrene	tr	tr	tr	nd	nd	tr	nd	nd	nd
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd	nd	nd	nd	nd	nd
Dibenzo(a,h)anthracene	nd	nd	nd	nd	nd	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd	nd	nd	nd	nd	nd	nd
C1-Naphthalenes, total	15	trc	tr	tr	tr	nd	trc	tr	nd
C2-Naphthalenes, total	6.2	trc	tr	tr	tr	nd	trc	nd	nd
C3-Naphthalenes, est.	33	nd	nd	nd	nd	nd	nd	nd	nd
C4-Naphthalenes, est.	tr	tr	tr	nd	tr	tr	tr	tr	tr
C5-Naphthalenes, est.	tr	tr	tr	tr	tr	tr	120	tr	tr
C1-Fluorenes	tr	tr	tr	nd	nd	nd	nd	nd	nd
C2-Fluorenes	tr	tr	59	tr	nd	tr	71	tr	tr

Table A1.2. Hydrocarbon concentrations (ppb) in a core taken at Pass Fourchon, PF1000N, Feb. 1989 (continued)

Analyte	Depth in core:								
	0-2cm	2-5cm*	5-10cm	10-15cm	15-20cm	20-25cm	25-30cm	30-35cm	35-38cm
C3-Fluorenes	36	tr	79	79	nd	130	tr	tr	tr
C1-Dibenzothiophenes, total	tr	tr	nd	nd	nd	nd	nd	nd	nd
C2-Dibenzothiophenes,est.	7.0	nd	nd	nd	nd	nd	nd	nd	nd
C3-Dibenzothiophenes,est.	11	nd	nd	nd	nd	nd	nd	nd	nd
C1-Phenanthrenes, total	22	tr	tr	tr	nd	tr	nd	nd	nd
C2-Phenanthrenes, total	53	45	77	33	0	0	30	0	0
C2-Phenanthrenes, est.	60	tr	65	tr	nd	nd	nd	nd	nd
C3-Phenanthrenes, est.	44	tr	tr	tr	76	nd	tr	nd	tr
Total Parent PAH	192	322	514	134	185	1,297	129	66	125
Total Alkylated PAH	234	tr	203	79	76	130	191	tr	tr
Total PAH	426	322	717	213	261	1,427	320	66	125
FFPI	0.52	0.05	0.13	0.11	0.29	0.05	0.04	na	0.07
Saturated Hydrocarbons									
Resolved	2,100	1,150	1,300	1,400	1,300	840	1,800	620	670
Unresolved	2,200	3,550	18,700	14,600	19,700	7,960	10,200	15,380	7,130
Total	4,300	4,700	20,000	16,000	21,000	8,800	12,000	16,000	7,800
MDL (ng/g)	3.6	7.0	9.7	8.0	11	16	6.6	12	8.4

MDL: Minimum Detection Limit
nd: Not detected
tr: Trace; one ion present, but below detection limits
trc: Trace confirmed; two ions present, but below detection limits
n/a: not analyzed

Table A1.3. Hydrocarbon concentrations (ppb) in a core taken at Bayou Rigaud, BR-9, Feb. 1989.

Analyte	Depth in core:							
	0-2cm	2-5cm	5-10cm	10-15cm	15-20cm	20-25cm	25-30cm	30-37cm*
Naphthalene	10	trc	17	12	12	12	17	190
2-Methylnaph.	10	nd	17	20	14	8.1	tr	170
1-Methylnaph.	trc	nd	17	28	12	8.6	tr	490
2-Ethylnaph.	nd	nd	nd	nd	nd	nd	nd	62
1-Ethylnaph.	nd	nd	nd	nd	nd	nd	nd	18
2,6/2,7-Dimethylnaph.	36	tr	29	38	28	18	18	170
1,3/1,7-DMN	16	tr	37	30	29	17	10	180
1,6-DMN	tr	nd	trc	tr	tr	tr	tr	73
1,4/2,3-DMN	16	tr	17	21	15	tr	tr	94
1,5-DMN	17	tr	38	46	29	30	19	59
Acenaphthylene	nd	nd	nd	nd	nd	nd	nd	nd
1,2-DMN/2-IPN	tr	nd	nd	nd	nd	nd	nd	49
2-IPN	nd	nd	nd	nd	nd	nd	nd	14
1,8-DMN	nd	nd	nd	nd	nd	nd	nd	nd
Acenaphthene	nd	nd	nd	22	9.0	nd	55	1600
Fluorene	17	nd	19	25	24	tr	10	1400
Dibenzothiophene	20	tr	13	16	17	tr	11	140
Phenanthrene	56	67	49	49	64	16	25	1800
Anthracene	16	tr	32	30	26	9.8	19	150
4-MDBT	76	110	86	100	56	49	76	88
2/3-MDBT	35	26	30	34	18	tr	22	22
3-MP	100	130	82	75	59	22	36	120
1-MDBT	21	trc	34	37	20	13	31	32
2-MP	51	57	30	41	34	13	tr	70
4/9-MP	98	140	100	100	60	27	34	100
1-MP	62	98	76	53	36	tr	14	60
3,6-DMP	120	160	130	150	97	140	160	140
3,5-DMP	nd	nd	nd	nd	nd	nd	nd	nd
2,6-DMP	63	100	46	54	29	17	22	43
2,7-DMP	56	97	63	78	43	54	63	67
3,9-DMP	200	290	220	220	130	120	160	190
1,6/2,5/2,9-DMP	130	210	150	170	110	120	150	140
1,7-DMP	52	88	48	49	33	22	28	38
1,9/4,9-DMP	50	86	73	76	44	64	88	63
Fluoranthene	99	140	120	170	120	100	130	310
1,5-DMP	nd	nd	nd	nd	nd	nd	nd	nd
1,8-DMP	21	29	30	39	29	32	28	26
1,2-DMP	24	23	16	20	18	18	17	22
9,10-DMP	nd	tr	nd	nd	tr	14	nd	37
Pyrene	89	130	94	140	95	80	92	190
Benzanthracene	30	46	52	45	27	37	48	67
Chrysene	42	67	74	71	49	47	81	120
Benzo(b)fluoranthene	tr	nd	tr	nd	tr	nd	47	140
Benzo(k)fluoranthene	tr	nd	nd	nd	tr	nd	nd	nd
Benzo(a)pyrene	tr	nd	nd	nd	nd	nd	nd	tr
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd	nd	nd	nd	nd
Dibenzo(a,h)anthracene	nd	nd	nd	nd	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd	nd	nd	nd	nd	nd
C1-Naphthalenes, total	10	nd	34	48	26	17	tr	660
C2-Naphthalenes, total	85	tr	121	135	101	65	47	706
C3-Naphthalenes, est.	1,100	900	1,300	1,400	710	830	1,500	2100
C4-Naphthalenes, est.	1,600	2,300	2,000	1,900	1,700	1,500	3,900	3000
C5-Naphthalenes, est.	1,500	1,600	1,600	1,400	1,000	1,800	tr	2300
C1-Fluorenes	120	120	120	140	90	96	100	190
C2-Fluorenes	140	350	380	390	130	220	420	450
C3-Fluorenes	270	500	330	390	230	390	270	380
C1-Dibenzothiophenes, total	130	140	150	170	94	62	130	140
C2-Dibenzothiophenes,est.	360	490	450	500	310	350	480	430

Table A1.3. Hydrocarbon concentrations (ppb) in a core taken at Bayou Rigaud, BR-9, Feb. 1989 (continued).

Analyte	Depth in core:							
	0-2cm	2-5cm	5-10cm	10-15cm	15-20cm	20-25cm	25-30cm	30-37cm*
C3-Dibenzothiophenes,est.	390	600	430	460	300	390	470	370
C1-Phenanthrenes, total	310	430	290	270	190	62	84	350
C2-Phenanthrenes, total	720	1,100	780	860	530	600	720	740
C2-Phenanthrenes, est.	690	1,200	840	890	550	650	800	790
C3-Phenanthrenes	630	1,100	760	830	520	830	670	650
Total Parent PAH	379	450	470	580	443	302	535	6,107
Total Alkylated PAH	7335	9730	8805	8923	5951	7261.7	8871	12515.7
Total PAH	7,714	10,180	9,275	9,503	6,394	7,564	9,406	18,623
FFPI	0.88	0.88	0.88	0.87	0.85	0.91	0.89	0.59
Saturated Hydrocarbons								
Resolved	19,000	25,000	31,000	24,000	13,000	22,000	30,000	29,000
Unresolved	101,000	140,000	179,000	156,000	85,000	158,000	210,000	161,000
Total	120,000	165,000	210,000	180,000	98,000	180,000	240,000	190,000
MDL	7.0	23	9.2	7.0	8.0	8.0	7.5	10

Table A1.4. Hydrocarbon concentrations (ppb) in a core taken at Bayou Rigaud, BR-11, Feb.1989.

Analyte	Depth in core:							
	0-2cm	2-5cm	5-10cm	10-15cm	15-20cm*	20-25cm	25-30cm	30-36cm
Naphthalene	14	tr	tr	tr	tr	tr	tr	tr
2-Methylnaph.	9.4	tr	tr	nd	tr	tr	nd	17
1-Methylnaph.	trc	tr	nd	nd	tr	tr	nd	trc
2-Ethylnaph.	nd	nd	nd	nd	nd	nd	nd	nd
1-Ethylnaph.	nd	nd	nd	nd	nd	nd	nd	nd
2,6/2,7-Dimethylnaph.	12	24	tr	nd	trc	19	tr	28
1,3/1,7-DMN	trc	trc	nd	nd	trc	tr	tr	15
1,6-DMN	trc	trc	nd	nd	nd	tr	nd	tr
1,4/2,3-DMN	tr	nd	nd	nd	tr	tr	nd	tr
1,5-DMN	nd	nd	nd	nd	tr	tr	nd	tr
Acenaphthylene	nd	nd	nd	nd	nd	nd	nd	nd
1,2-DMN/2-IPN	nd	nd	nd	nd	nd	nd	nd	nd
2-IPN	nd	nd	nd	nd	nd	nd	nd	nd
1,8-DMN.	nd	nd	nd	nd	nd	nd	nd	nd
Acenaphthene	nd	nd	nd	nd	73	12	nd	nd
Fluorene	nd	nd	nd	nd	89	16	38	nd
Dibenzothiophene	trc	nd	nd	45	tr	nd	tr	nd
Phenanthrene	18	22	23	16	120	53	41	23
Anthracene	8.6	15	nd	tr	27	27	58	tr
4-MDBT	27	16	nd	16	20	33	35	57
2/3-MDBT	tr	nd	nd	nd	nd	nd	nd	nd
3-MP	22	17	nd	16	tr	15	tr	tr
1-MDBT	nd	nd	nd	nd	nd	nd	nd	nd
2-MP	11	tr	nd	tr	tr	nd	tr	tr
4/9-MP	30	23	tr	tr	tr	tr	tr	28
1-MP	8.6	tr	tr	tr	tr	tr	tr	tr
3,6-DMP	30	32	38	65	54	70	46	88
2,6-DMP	17	14	13	tr	14.0	tr	tr	24
2,7-DMP	22	17	20	24	tr	30	13	40
3,9-DMP	69	44	43	46	39	68	53	72
1,6/2,5/2,9-DMP	53	36	52	39	47	63	55	61
1,7-DMP	18	tr	tr	nd	tr	nd	tr	tr
1,9/4,9-DMP	21	15	14	tr	26	35	25	13
Fluoranthene	54	44	64	69	87	100	93	61
1,5-DMP	nd	nd	nd	nd	nd	nd	nd	nd
1,8-DMP	tr	nd	tr	nd	13	16	nd	nd
1,2-DMP	tr	nd	tr	nd	nd	nd	nd	nd
9,10-DMP	tr	nd	nd	nd	nd	nd	nd	nd
Pyrene	47	43	35	61	66	88	83	43
Benz(a)anthracene	19	tr	tr	tr	43	tr	160	42
Chrysene	23	35	38	24	56	55	nd	75
Benzo(b)fluoranthene	nd	nd	nd	nd	tr	nd	nd	nd
Benzo(k)fluoranthene	nd	nd	nd	nd	tr	nd	nd	nd
Benzo(a)pyrene	nd	nd	nd	nd	tr	nd	nd	nd
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd	nd	nd	nd	nd
Dibenzo(a,h)anthracene	nd	nd	nd	nd	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd	nd	nd	nd	nd	nd
C1-Naphthalenes, total	9.4	tr	tr	nd	tr	tr	nd	17
C2-Naphthalenes, total	12	24	tr	nd	trc	19	tr	43
C3-Naphthalenes, est.	180	tr	nd	tr	tr	240	240	390
C4-Naphthalenes, est.	610	280	260	750	690	770	800	1,800
C5-Naphthalenes, est.	160	420	290	850	1,015	1,000	1,400	1,300
C1-Fluorenes	86	66	tr	tr	61	55	tr	92

Table A1.4. Hydrocarbon concentrations (ppb) in a core taken at Bayou Rigaud, BR-11, Feb.1989 (continued).

Analyte	Depth in core:							
	0-2cm	2-5cm	5-10cm	10-15cm	15-20cm*	20-25cm	25-30cm	30-36cm
C2-Fluorenes	110	50	69	130	84	240	200	160
C3-Fluorenes	210	tr	100	110	140	210	240	190
C1-Dibenzothiophenes, total	27	16	nd	16	20	33	35	57
C2-Dibenzothiophenes,est.	140	tr	tr	300	145	220	140	160
C3-Dibenzothiophenes,est.	180	tr	tr	270	180	230	tr	74
C1-Phenanthrenes, total	72	40	tr	16	tr	15	tr	28
C2-Phenanthrenes, total	230	158	180	174	193	282	192	298
C2-Phenanthrenes, est.	280	160	160	300	175	160	230	280
C3-Phenanthrenes, est.	340	130	130	290	165	220	tr	200
Total Parent PAH	184	159	160	215	560	351	473	244
Total Alkylated PAH	2,416	1,186	1,009	3,032	2,675	3,412	3,285	4,791
Total PAH	2,600	1,345	1,169	3,247	3,235	3,763	3,758	5,035
FFPI	0.86	0.68	0.67	0.88	0.60	0.78	0.60	0.83
Saturated Hydrocarbons								
Resolved	8,000	3,600	3,000	6,000	8,600	12,000	11,000	13,000
Unresolved	46,000	37,400	48,000	70,000	80,400	108,000	89,000	87,000
Total	54,000	41,000	51,000	76,000	89,000	120,000	100,000	100,000
MDL	6.8	9.8	12	11	7.9	12	17	15

MDL: Minimum Detection Limit

nd: Not detected

tr: Trace; one ion present, but below detection limits

trc: Trace confirmed; two ions present, but below detection limits

n/a: not analyzed

Table A1.5. Hydrocarbon concentrations (ppb) in a core taken at Eugene Island, EIA-0, Oct. 1989.

Analyte	Depth in core:							
	0-2cm	2-5cm	5-10cm	10-15cm	15-20cm	20-25cm	25-30cm	30-33cm
Naphthalene	43	53	36	36	43	36	38	16
2-Methylnaph.	67	91	29	68	50	44	99	18
1-Methylnaph.	62	76	93	290	120	75	84	12
2-Ethylnaph.	tr	trc	25	tr	21	tr	27	nd
1-Ethylnaph.	tr	trc	34	86	62	tr	trc	nd
2,6/2,7-Dimethylnaph.	160	160	250	830	280	180	150	34
1,3/1,7-DMN	94	110	190	770	260	140	130	22
1,6-DMN	69	96	110	300	67	74	78	18
1,4/2,3-DMN	52	75	110	420	190	82	70	23
1,5-DMN	tr	24	50	180	100	48	35	18
Acenaphthylene	nd	nd	nd	nd	15	nd	nd	nd
1,2-DMN/2-IPN	nd	47	46	250	140	60	46	tr
2-IPN	nd	nd	42	120	nd	nd	30	nd
1,8-DMN.	nd	nd	nd	nd	nd	nd	nd	nd
Acenaphthene	nd	nd	nd	nd	nd	nd	7.6	nd
Fluorene	nd	na	na	42	na	nd	20	30
Dibenzothiophene	nd	nd	nd	trc	nd	nd	tr	nd
Phenanthrene	53	55	49	55	61	46	45	29
Anthracene	nd	tr	nd	21	nd	nd	tr	nd
4-MDBT	nd	nd	nd	50	nd	nd	nd	nd
2/3-MDBT	nd	nd	nd	tr	nd	nd	nd	nd
3-MP	36	33	48	51	65	41	32	17
1-MDBT	nd	nd	nd	nd	nd	nd	nd	nd
2-MP	30	22	29	33	trc	20	23	tr
4/9-MP	36	29	33	43	50	28	21	12
1-MP	trc	19	14	25	31	10	11	tr
3,6-DMP	tr	11	23	30	44	30	30	13
2,6-DMP	23	8	15	17	30	16	9	tr
2,7-DMP	tr	tr	10	nd	18	13	7	tr
3,9-DMP	37	21	37	38	65	34	19	19
1,6/2,5/2,9-DMP	24	15	21	28	37	21	13	tr
1,7-DMP	tr	tr	16	15	22	tr	tr	tr
1,9/4,9-DMP	tr	nd	nd	tr	17	tr	nd	tr
Fluoranthene	48	32	30	16	34	22	19	26
1,5-DMP	nd	nd	nd	nd	nd	nd	nd	nd
1,8-DMP	nd	nd	nd	nd	nd	tr	nd	nd
1,2-DMP	nd	nd	nd	nd	nd	nd	nd	nd
9,10-DMP	nd	nd	nd	nd	nd	nd	nd	nd
Pyrene	47	24	24	24	28	16	17	16
Benz(a)anthracene	tr	trc	tr	tr	nd	nd	41	nd
Chrysene	tr	44	tr	110	97	nd	66	nd
Benzo(b)fluoranthene	nd	nd	nd	nd	nd	nd	nd	nd
Benzo(k)fluoranthene	nd	nd	nd	nd	nd	nd	nd	nd
Benzo(a)pyrene	nd	nd	nd	nd	nd	nd	nd	nd
Indeno(1,2,3-cd)pyrene	nd	na	na	nd	nd	na	na	na
Dibenz(a,h)anthracene	nd	na	na	nd	nd	na	na	na
Benzo(g,h,i)perylene	nd	na	na	nd	nd	na	na	na
C1-Naphthalenes, total	129	167	122	358	170	119	183	30
C2-Naphthalenes, total	375	512	815	2,836	1,120	584	536	115
C3-Naphthalenes, est.	890	1,200	2,200	10,000	4,400	1,700	1,300	580
C4-Naphthalenes, est.	tr	910	2,200	5,700	2,200	2,000	1,000	850
C5-Naphthalenes, est.	780	1,000	900	3,900	1,800	1,300	1,700	280
C1-Fluorenes	tr	tr	200	260	250	tr	85	150

Table A1.5. Hydrocarbon concentrations (ppb) in a core taken at Eugene Island, EIA-0, Oct. 1989 (continued).

Analyte	Depth in core:							
	0-2cm	2-5cm	5-10cm	10-15cm	15-20cm	20-25cm	25-30cm	30-33cm
C2-Fluorenes	370	90	100	530	75	tr	190	250
C3-Fluorenes	tr	nd	120	630	110	tr	100	120
C1-Dibenzothiophenes, total	nd	nd	nd	50	nd	nd	nd	nd
C2-Dibenzothiophenes,est.	nd	nd	tr	tr	nd	nd	nd	nd
C3-Dibenzothiophenes,est.	tr	tr	nd	tr	nd	nd	nd	nd
C1-Phenanthrenes, total	102	103	124	152	146	99	87	29
C2-Phenanthrenes, total	84	55	122	128	233	114	79	32
C2-Phenanthrenes, est.	83	78	120	120	240	130	60	tr
C3-Phenanthrenes, est.	tr	tr	tr	tr	130	tr	40	tr
Total Parent PAH	191	208	139	304	278	120	254	117
Total Alkylated PAH	2,729	4,060	6,901	24,536	10,641	5,932	5,281	2,404
Total PAH	2,920	4,268	7,040	24,840	10,919	6,052	5,535	2,521
FFPI	0.90	0.92	0.96	0.98	0.96	0.96	0.90	0.88
Saturated Hydrocarbons								
Resolved	100,000	89,000	130,000	98,000	160,000	78,000	69,000	25,000
Unresolved	110,000	81,000	150,000	272,000	300,000	112,000	131,000	95,000
Total	210,000	170,000	280,000	370,000	460,000	190,000	200,000	120,000
MDL	19	8.1	8.9	12	8.6	9.7	7.1	9.6

MDL: Minimum Detection Limit
nd: Not detected
tr: Trace; one ion present, but below detection limits
trc: Trace confirmed; two ions present, but below detection limits
n/a: not analyzed

Table A1.6. Hydrocarbon concentrations (ppb) in a core taken at Eugene Island, EIA-50, Oct. 1989.

Analyte	Depth in core:							
	0-2cm	2-5cm	5-10cm	10-15cm	15-20cm	20-25cm*	25-30cm	30-37cm
Naphthalene	9.9	tr	trc	9.5	13	tr	tr	tr
2-Methylnaph.	12	tr	trc	10	13	trc	trc	trc
1-Methylnaph.	8.5	nd	trc	trc	trc	trc	trc	trc
2-Ethylnaph.	nd	nd	nd	nd	nd	nd	nd	nd
1-Ethylnaph.	nd	nd	nd	nd	nd	nd	nd	nd
2,6/2,7-Dimethylnaph.	24	nd	tr	trc	tr	trc	tr	tr
1,3/1,7-DMN	12	tr	trc	trc	14	trc	trc	tr
1,6-DMN	trc	nd	nd	nd	tr	trc	tr	tr
1,4/2,3-DMN	trc	nd	nd	nd	tr	trc	nd	nd
1,5-DMN	trc	nd	nd	nd	tr	tr	nd	nd
Acenaphthylene	tr	nd	nd	nd	nd	nd	nd	nd
1,2-DMN/2-IPN	nd	nd	nd	nd	nd	nd	nd	nd
2-IPN	nd	nd	nd	nd	nd	nd	nd	nd
1,8-DMN.	nd	nd	nd	nd	nd	nd	nd	nd
Acenaphthene	nd	nd	nd	nd	nd	nd	nd	nd
Fluorene	trc	nd	nd	nd	nd	nd	nd	nd
Dibenzothiophene	nd	nd	nd	nd	nd	nd	nd	nd
Phenanthrene	24	tr	18	27	33	19	21	15
Anthracene	tr	nd	nd	nd	nd	nd	nd	nd
4-MDBT	nd	nd	nd	nd	nd	nd	nd	nd
2/3-MDBT	nd	nd	nd	nd	nd	nd	nd	nd
3-MP	trc	nd	nd	tr	16	trc	nd	nd
1-MDBT	nd	nd	nd	nd	nd	nd	nd	nd
2-MP	tr	nd	nd	tr	tr	trc	nd	nd
4/9-MP	tr	nd	tr	tr	16	trc	nd	nd
1-MP	tr	nd	tr	nd	tr	tr	nd	nd
3,6-DMP	tr	nd	nd	nd	tr	tr	nd	nd
2,6-DMP	nd	nd	nd	nd	9.0	4	nd	nd
2,7-DMP	tr	nd	nd	nd	tr	tr	nd	nd
3,9-DMP	4.0	tr	21	11	21	9.2	nd	tr
1,6/2,5/2,9-DMP	tr	nd	15	tr	13	7.9	nd	nd
1,7-DMP	tr	nd	nd	nd	6.8	5.2	nd	nd
1,9/4,9-DMP	nd	nd	nd	nd	nd	tr	nd	nd
Fluoranthene	22	53	35	31	35	21	28	21
1,5-DMP	nd	nd	nd	nd	nd	nd	nd	nd
1,8-DMP	nd	nd	nd	nd	nd	nd	nd	nd
1,2-DMP	nd	nd	nd	nd	nd	nd	nd	nd
9,10-DMP	nd	nd	nd	nd	nd	nd	nd	nd
Pyrene	20	44	29	36	37	20	31	27
Benz(a)anthracene	tr	tr	tr	tr	tr	tr	tr	nd
Chrysene	tr	tr	tr	27	57	tr	tr	tr
Benzo(b)fluoranthene	nd	nd	nd	nd	nd	nd	nd	nd
Benzo(k)fluoranthene	nd	nd	nd	nd	nd	nd	nd	nd
Benzo(a)pyrene	nd	nd	nd	nd	nd	nd	nd	nd
Indeno(1,2,3-cd)pyrene	nd	na	na	na	na	na	na	na
Dibenzo(a,h)anthracene	nd	na	na	na	na	na	na	na
Benzo(g,h,i)perylene	nd	na	na	na	na	na	na	na
C1-Naphthalenes, total	21	tr	trc	10	13	trc	trc	trc
C2-Naphthalenes, total	36	tr	tr	trc	14	trc	tr	tr
C3-Naphthalenes, est.	nd	nd	nd	nd	350	tr	nd	nd
C4-Naphthalenes, est.	tr	tr	tr	tr	340	tr	tr	nd
C5-Naphthalenes, est.	tr	tr	320	tr	nd	tr	tr	tr
C1-Fluorenes	tr	tr	tr	tr	nd	tr	nd	tr

Table A1.6. Hydrocarbon concentrations (ppb) in a core taken at Eugene Island, EIA-50, Oct. 1989 (continued).

Analyte	Depth in core:							
	0-2cm	2-5cm	5-10cm	10-15cm	15-20cm	20-25cm*	25-30cm	30-37cm
C2-Fluorenes	tr	tr	100	tr	nd	tr	nd	tr
C3-Fluorenes	tr	tr	nd	tr	100	tr	tr	nd
C1-Dibenzothiophenes, total	nd	nd	nd	nd	nd	nd	nd	nd
C2-Dibenzothiophenes,est.	nd	nd	nd	nd	nd	nd	nd	nd
C3-Dibenzothiophenes,est.	nd	nd	nd	nd	nd	nd	nd	nd
C1-Phenanthrenes, total	tr	nd	tr	tr	32	trc	nd	nd
C2-Phenanthrenes, total	4	0	36	11	50	27	0	0
C2-Phenanthrenes, est.	tr	nd	tr	tr	49	tr	nd	nd
C3-Phenanthrenes, est.	nd	nd	tr	nd	tr	tr	nd	nd
Total Parent PAH	76	97	82	131	175	59	80	63
Total Alkylated PAH	57	tr	420	10	898	tr	tr	tr
Total PAH	132	97	502	141	1,073	59	80	63
FFPI	0.59	na	0.11	0.23	0.74	0.16	0.13	0.12
Saturated Hydrocarbons								
Resolved	2,300	7,900	4,000	960	12,500	1,600	1,100	880
Unresolved	12,700	54,100	34,000	7,940	35,500	19,900	6,500	12,120
Total	15,000	62,000	38,000	8,900	48,000	21,500	7,600	13,000
MDL	6.6	22	9.8	8.8	6.8	7.7	13	11

MDL: Minimum Detection Limit
nd: Not detected
tr: Trace; one ion present, but below detection limits
trc: Trace confirmed; two ions present, but below detection limits
n/a: not analyzed

APPENDIX 2

Table A2.1. Seasonal Variations in hydrocarbon concentrations (ppb) at one location in Pass Fourchon, LA.

Analyte	PF600N-0-2 cm			
	Feb '89	May '89	Oct '89	Feb '90
Naphthalene	nd	trc	tr	76
2-Methylnaph.	nd	tr	trc	100
1-Methylnaph.	41	tr	tr	340
2-Ethylnaph.	nd	tr	nd	260
1-Ethylnaph.	nd	tr	nd	83
2,6/2,7-Dimethylnaph.	300	250	trc	1,100
1,3/1,7-DMN	370	240	nd	1,100
1,6-DMN	tr	49	nd	510
1,4/2,3-DMN	200	120	nd	560
1,5-DMN	72	56	nd	230
Acenaphthylene	nd	nd	nd	tr
1,2-DMN/2-IPN	trc	tr	nd	330
2-IPN	trc	nd	nd	160
1,8-DMN	nd	nd	nd	nd
Acenaphthene	nd	nd	nd	tr
Fluorene	77	nd	tr	na
Dibenzothiophene	27	26	nd	110
Phenanthrene	nd	130	tr	530
Anthracene	nd	nd	nd	tr
4-MDBT	270	190	nd	550
2/3-MDBT	120	78	nd	120
1-MDBT	72	56	nd	120
3-MP	540	420	nd	980
2-MP	120	240	nd	710
4/9-MP	570	460	nd	960
1-MP	310	280	nd	550
3,6-DMP	490	340	tr	540
3,5-DMP	nd	nd	nd	nd
2,6-DMP	310	180	nd	340
2,7-DMP	250	180	tr	220
3,9-DMP	1,078	760	49	1,100
1,6/2,5/2,9-DMP	800	570	43	740
1,7-DMP	320	210	nd	270
1,9/4,9-DMP	270	200	tr	240
Fluoranthene	190	140	51	120
1,5-DMP	nd	nd	nd	nd
1,8-DMP	120	110	nd	74
1,2-DMP	98	54	nd	55
9,10-DMP	nd	nd	nd	nd
Pyrene	190	130	52	140
Benzanthracene	94	47	tr	tr
Chrysene	340	130	tr	360
Benzo(b)fluoranthene	nd	nd	nd	nd
Benzo(k)fluoranthene	nd	nd	nd	nd
Benzo(a)pyrene	nd	nd	nd	nd
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd
Dibenzo(a,h)anthracene	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd	nd
C1-Naphthalenes, total	41	tr	tr	440
C2-Naphthalenes, total	940	715	tr	4,173
C3-Naphthalenes	6,400	3,700	nd	16,000
C4-Naphthalenes	5,000	2,900	580	7,000
C5-Naphthalenes	tr	tr	590	8,700
C1-Fluorenes	500	400	nd	1,200
C2-Fluorenes	1600	790	250	3,300
C3-Fluorenes	1400	1400	190	2,500
C1-Dibenzothiophenes, total	460	324	nd	790

Table A2.1. Seasonal Variations in hydrocarbon concentrations (ppb) at one location in Pass Fourchon, LA (continued).

Analyte	PF600N-0-2 cm Feb '89	May '89	Oct '89	Feb '90
C2-Dibenzothiophenes, est.	1,400	940	nd	1,900
C3-Dibenzothiophenes, est.	1,500	970	nd	1,500
C1-Phenanthrenes, total	1,500	1400	nd	3,200
C2-Phenanthrenes, total	3,700	2604	92	3,579
C2-Phenanthrenes, est.	3,900	2600	tr	3,700
C3-Phenanthrenes, est.	3,400	2300	130	2,300
Total Parent PAH	920	603	103	1,336
Total Alkylated PAH	28,041	18,439	1,740	56,703
Total PAH	29,000	19,042	1,843	58,039
FFPI	0.92	0.91	0.56	0.93
Saturated Hydrocarbons				
Resolved	57,000	57,000	9,500	380,000
Unresolved	523,000	313,000	82,500	920,000
Total	580,000	370,000	92,000	1,300,000
MDL (ng/g)	24	25	21	29

MDL: Minimum Detection Limit
nd: Not detected
tr: Trace; one ion present, but below detection limits
trc: Trace confirmed; two ions present, but below detection limits
n/a: not analyzed

Table A2.2. Hydrocarbon concentrations (ppb) in a core collected at PF600N, May 1989.

Analyte	PF-600 NORTH							
	0-2cm	2-5cm	5-10cm	10-15cm	15-20cm	20-25cm	25-30cm	30-33cm
Naphthalene	nd	tr	tr	tr	nd	tr	tr	nd
2-Methylnaph.	nd	tr	tr	tr	tr	tr	tr	tr
1-Methylnaph.	41	tr	tr	tr	42	28	nd	nd
2-Ethylnaph.	nd	tr	nd	nd	44	tr	tr	tr
1-Ethylnaph.	nd	tr	nd	nd	nd	tr	nd	nd
2,6/2,7-Dimethylnaph.	300	96	60	110	250	230	100	250
1,3/1,7-DMN	370	110	75	170	290	220	150	290
1,6-DMN	tr	nd	nd	nd	110	nd	nd	nd
1,4/2,3-DMN	200	89	57	82	140	190	79	180
1,5-DMN	72	20	nd	nd	73	78	nd	83
Acenaphthylene	nd	tr	nd	nd	nd	tr	nd	nd
1,2-DMN/2-IPN	trc	23	nd	nd	57	55	nd	50
2-IPN	trc	tr	nd	tr	32	41	nd	46
1,8-DMN.	nd	37	tr	33	48	29	32	47
Acenaphthene	nd	17	tr	tr	tr	tr	tr	tr
Fluorene	77	tr	nd	nd	42	tr	tr	34
Dibenzothiophene	27	tr	nd	tr	tr	30	nd	31
Phenanthrene	nd	19	tr	tr	93	35	tr	tr
Anthracene	nd	tr	tr	tr	tr	tr	tr	tr
4-MDBT	270	81	69	99	190	180	120	180
2/3-MDBT	120	nd	nd	tr	65	55	tr	52
3-MP	540	54	68	140	290	190	84	260
1-MDBT	72	30	32	tr	tr	54	45	69
2-MP	120	tr	tr	tr	180	55	tr	tr
4/9-MP	570	tr	75	160	300	220	89	260
1-MP	310	39	45	89	190	110	38	170
3,6-DMP	490	130	220	130	210	260	160	210
2,6-DMP	310	39	66	64	140	120	53	120
2,7-DMP	250	61	84	63	99	130	79	96
3,9-DMP	1,078	240	400	250	460	510	290	470
1,6/2,5/2,9-DMP	800	170	270	160	320	340	220	320
1,7-DMP	320	43	60	53	120	120	60	120
1,9/4,9-DMP	270	65	99	66	120	130	83	120
Fluoranthene	190	46	93	65	72	82	70	64
1,5-DMP	nd	nd	nd	nd	nd	nd	nd	nd
1,8-DMP	120	35	58	23	48	65	30	37
1,2-DMP	98	17	35	nd	38	40	32	25
9,10-DMP	nd	nd	nd	nd	tr	nd	nd	nd
Pyrene	190	tr	100	51	60	84	57	66
Benz(a)anthracene	94	27	nd	tr	tr	120	58	110
Chrysene	340	190	140	67	82	230	140	320
Benzo(b)fluoranthene	nd	56	nd	30	nd	100	nd	nd
Benzo(k)fluoranthene	nd	nd	nd	nd	nd	nd	nd	nd
Benzo(a)pyrene	nd	nd	nd	nd	nd	nd	nd	nd
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd	nd	nd	nd	nd
Dibenzo(a,h)anthracene	nd	nd	nd	nd	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd	nd	nd	nd	nd	nd
C1-Naphthalenes, total	41	tr	tr	tr	42	28	tr	tr
C2-Naphthalenes, total	942	375	192	395	1,012	802	361	900
C3-Naphthalenes, est.	6,400	3,700	2,800	3,200	5,400	5,600	3,100	5,900
C4-Naphthalenes, est.	5,000	4,500	4,300	4,300	5,200	6,100	3,800	6,100
C5-Naphthalenes, est.	tr	3,700	3,500	2,800	5,400	4,000	3,300	3,300
C1-Fluorenes	500	120	130	tr	130	200	150	180

Table A2.2. Hydrocarbon concentrations (ppb) in a core collected at PF600N, May 1989 (continued).

Analyte	PF-600 NORTH							
	0-2cm	2-5cm	5-10cm	10-15cm	15-20cm	20-25cm	25-30cm	30-33cm
C2-Fluorenes	1,600	650	660	480	870	600	610	760
C3-Fluorenes	1,400	580	720	480	1,000	840	380	810
C1-Dibenzothiophenes, total	462	111	101	99	255	289	165	301
C2-Dibenzothiophenes,est.	1,400	380	520	350	590	620	150	630
C3-Dibenzothiophenes,est.	1,500	390	620	300	460	520	360	590
C1-Phenanthrenes, total	1,540	93	188	389	960	575	211	690
C2-Phenanthrenes, total	3,736	800	1,292	809	1,555	1,715	1,007	1,518
C2-Phenanthrenes, est.	3,900	870	1,300	860	1,600	1,800	1,000	1,500
C3-Phenanthrenes, est.	3,400	770	1,100	430	800	1,000	760	1,000
Total Pyrogenic PAH	918	355	333	213	349	681	325	625
Total Petrogenic PAH	28,085	16,239	16,131	14,083	23,719	22,974	14,347	22,661
Total PAH	29,003	16,594	16,464	14,296	24,068	23,655	14,672	23,286
FFPI	0.92	0.94	0.94	0.93	0.93	0.92	0.93	0.92
Saturated Hydrocarbons								
Resolved	57,000	31,000	25,000	21,000	67,000	51,000	30,000	51,000
Unresolved	523,000	289,000	305,000	179,000	373,000	489,000	270,000	479,000
Total	580,000	320,000	330,000	200,000	440,000	540,000	300,000	530,000
MDL	24	16	24	22	26	28	27	29

MDL: Minimum Detection Limit
nd: Not detected
tr: Trace; one ion present, but below detection limits
trc: Trace confirmed; two ions present, but below detection limits
n/a: not analyzed

Table A2.3. Hydrocarbon concentrations (ppb) in a core collected at PF600N, Oct. 1989.

Analyte	Depth in core:							
	0-2 cm	2-5 cm	5-10 cm	10-15 cm	15-20 cm	20-25 cm	25-30 cm	30-35 cm*
Naphthalene	trc	trc	tr	trc	tr	tr	tr	nd
2-Methylnaph.	tr	tr	tr	tr	tr	tr	tr	nd
1-Methylnaph.	tr	tr	tr	nd	tr	tr	tr	nd
2-Ethylnaph.	tr	trc	tr	tr	tr	22	tr	nd
1-Ethylnaph.	tr	trc	16	nd	nd	19	tr	nd
2,6/2,7-Dimethylnaph.	250	90	150	48	17	170	120	250
1,3/1,7-DMN	240	150	220	70	17	250	170	305
1,6-DMN	49	nd	tr	nd	tr	nd	tr	tr
1,4/2,3-DMN	120	110	120	68	30	130	120	185
1,5-DMN	56	50	57	24	nd	43	38	83
Acenaphthylene	nd	nd	nd	nd	nd	nd	nd	nd
1,2-DMN/2-IPN	tr	38	43	tr	nd	53	26	50
2-IPN	nd	22	28	15	nd	26	15	43
1,8-DMN.	nd	nd	nd	nd	nd	nd	nd	nd
Acenaphthene	nd	nd	nd	nd	nd	nd	nd	nd
Fluorene	nd	47	33	nd	nd	18	nd	52
Dibenzothiophene	26	27	38	nd	tr	tr	15	tr
Phenanthrene	130	17	nd	nd	nd	nd	nd	nd
Anthracene	nd	tr	nd	nd	nd	nd	nd	nd
4-MDBT	190	100	160	53	39	150	84	215
2/3-MDBT	78	45	49	tr	nd	61	trc	94
3-MP	420	180	220	50	36	270	63	300
1-MDBT	56	34	36	38	43	56	47	104
2-MP	240	21	47	tr	tr	42	18	tr
4/9-MP	460	180	220	57	44	240	100	320
1-MP	280	120	130	32	13	150	45	190
3,6-DMP	340	120	200	110	110	170	150	350
2,6-DMP	180	63	99	32	21	110	34	145
2,7-DMP	180	50	100	61	54	84	66	180
3,9-DMP	760	220	400	200	160	350	240	730
1,6/2,5/2,9-DMP	570	150	310	180	150	260	210	590
1,7-DMP	210	63	110	46	24	95	52	180
1,9/4,9-DMP	200	68	130	84	60	100	100	240
Fluoranthene	140	46	74	49	55	61	51	104
1,5-DMP	nd	nd	nd	nd	nd	nd	nd	nd
1,8-DMP	110	22	52	49	19	46	27	102
1,2-DMP	54	24	33	33	30	18	tr	72
9,10-DMP	nd	nd	nd	nd	nd	nd	tr	tr
Pyrene	130	46	83	49	51	55	53	120
Benz(a)anthracene	47	24	55	42	35	45	46	102
Chrysene	130	120	180	140	110	180	190	460
Benzo(b)fluoranthene	nd	49	tr	tr	63	46	29	69
Benzo(k)fluoranthene	nd	tr	nd	nd	nd	nd	nd	nd
Benzo(a)pyrene	nd	nd	nd	nd	nd	nd	47	tr
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd	nd	nd	nd	nd
Dibenz(a,h)anthracene	nd	nd	nd	nd	nd	nd	nd	nd
Benzo(g,h,i)perylene	nd	nd	nd	nd	nd	nd	nd	nd
C1-Naphthalenes, total	tr	tr	tr	tr	tr	tr	tr	nd
C2-Naphthalenes, total	715	438	606	210	64	687	474	872
C3-Naphthalenes, est.	3700	2,600	2,900	2,100	1,400	3,700	2,900	5,050
C4-Naphthalenes, est.	2900	2,400	3,800	2,400	3,000	3,900	4,000	4,500
C5-Naphthalenes, est.	tr	1,500	1,700	1,300	1,200	1,900	1,700	2,500
C1-Fluorenes	400	210	63	30	tr	47	41	88

Table A2.3. Hydrocarbon concentrations (ppb) in a core collected at PF600N, Oct. 1989 (continued).

Analyte	Depth in core:							
	0-2 cm	2-5 cm	5-10 cm	10-15 cm	15-20 cm	20-25 cm	25-30 cm	30-35 cm*
C2-Fluorenes	790	250	210	75	120	370	240	760
C3-Fluorenes	1400	160	290	290	210	300	240	445
C1-Dibenzothiophenes, total	324	179	245	91	82	267	131	413
C2-Dibenzothiophenes,est.	940	350	560	300	300	480	360	1,100
C3-Dibenzothiophenes,est.	970	280	560	340	310	470	420	1,150
C1-Phenanthrenes, total	1,400	501	617	139	93	702	226	810
C2-Phenanthrenes, total	2,604	780	1,434	795	628	1,233	879	2,589
C2-Phenanthrenes, est.	2600	810	1,500	800	650	1,300	960	2,650
C3-Phenanthrenes, est.	2300	520	1,500	640	540	950	830	2,750
Total Parent PAH	603	376	463	280	314	405	431	906
Total Alkylated PAH	18,439	10,198	14,551	8,715	7,969	15,073	12,522	23,088
Total PAH	19,042	10,574	15,014	8,995	8,283	15,478	12,953	23,993
FFPI	0.91	0.90	0.92	0.93	0.90	0.92	0.92	0.92
Saturated Hydrocarbons								
Resolved	57,000	32,000	110,000	44,000	59,000	110,000	90,000	220,000
Unresolved	313,000	178,000	530,000	256,000	311,000	540,000	440,000	1,080,000
Total	370,000	210,000	640,000	300,000	370,000	650,000	530,000	1,300,000
MDL	25	11	15	9.9	9.1	14	14	25

MDL: Minimum Detection Limit
nd: Not detected
tr: Trace; one ion present, but below detection limits
trc: Trace confirmed; two ions present, but below detection limits
n/a: not analyzed

Table A2.4. Hydrocarbon concentrations (ppb) in a core collected at PF600N, Feb. 1989.

Analyte	Depth in core:							
	0-2 cm	2-5 cm	5-10 cm	10-15 cm	15-20 cm	20-25 cm	25-30 cm	30-36 cm
Naphthalene	tr	tr	tr	trc	trc	trc	tr	tr
2-Methylnaph.	trc	tr	tr	tr	tr	trc	tr	tr
1-Methylnaph.	tr	tr	nd	tr	nd	tr	nd	nd
2-Ethylnaph.	nd	nd	nd	nd	nd	nd	nd	nd
1-Ethylnaph.	nd	nd	nd	nd	nd	nd	nd	nd
2,6/2,7-Dimethylnaph.	trc	tr	tr	tr	tr	tr	tr	tr
1,3/1,7-DMN	nd	tr	tr	tr	tr	tr	tr	tr
1,6-DMN	nd	nd	tr	tr	nd	tr	nd	tr
1,4/2,3-DMN	nd	nd	nd	tr	tr	nd	nd	tr
1,5-DMN	nd	nd	nd	nd	nd	nd	nd	nd
Acenaphthylene	nd	nd	nd	nd	nd	nd	nd	nd
1,2-DMN/2-IPN	nd	nd	nd	nd	nd	nd	nd	nd
2-IPN	nd	nd	nd	nd	nd	nd	nd	nd
1,8-DMN.	nd	nd	nd	nd	nd	nd	nd	nd
Acenaphthene	nd	nd	nd	nd	nd	nd	nd	nd
Fluorene	tr	nd	nd	nd	tr	nd	nd	nd
Dibenzothiophene	nd	nd	nd	nd	nd	nd	nd	nd
Phenanthrene	tr	12	tr	13	8.3	11	9.6	14
Anthracene	nd	nd	nd	tr	nd	nd	nd	nd
4-MDBT	nd	nd	nd	nd	nd	nd	nd	nd
2/3-MDBT	nd	nd	nd	nd	nd	nd	nd	nd
3-MP	nd	trc	nd	nd	nd	nd	nd	nd
1-MDBT	nd	nd	nd	nd	nd	nd	nd	nd
2-MP	nd	tr	nd	nd	nd	nd	nd	nd
4/9-MP	nd	tr	nd	nd	nd	nd	nd	nd
1-MP	nd	tr	nd	nd	nd	nd	nd	nd
3,6-DMP	tr	23	nd	nd	nd	nd	nd	nd
2,6-DMP	nd	tr	nd	nd	nd	nd	nd	nd
2,7-DMP	tr	12	nd	nd	tr	nd	nd	nd
3,9-DMP	44	20	nd	nd	trc	nd	tr	nd
1,6/2,5/2,9-DMP	43	20	nd	nd	tr	nd	7.8	nd
1,7-DMP	nd	nd	nd	nd	nd	nd	nd	nd
1,9/4,9-DMP	tr	14	nd	nd	tr	nd	nd	nd
Fluoranthene	51	35	19	27	17	19	24	19
1,5-DMP	nd	nd	nd	nd	nd	nd	nd	nd
1,8-DMP	nd	tr	nd	nd	nd	nd	nd	nd
1,2-DMP	nd	nd	nd	nd	nd	nd	nd	nd
9,10-DMP	nd	nd	nd	nd	nd	nd	nd	nd
Pyrene	52	30	23	26	21	18	21	18
Benz(a)anthracene	tr	tr	tr	21	tr	18	30	32
Chrysene	tr	66	38	77	32	46	46	39
Benzo(b)fluoranthene	nd	nd	tr	tr	tr	tr	12	tr
Benzo(k)fluoranthene	nd	nd	tr	tr	tr	tr	12	tr
Benzo(a)pyrene	nd	nd	tr	tr	tr	tr	38	tr
Indeno(1,2,3-cd)pyrene	nd	nd	tr	tr	tr	nd	tr	nd
Dibenz(a,h)anthracene	nd	nd	nd	nd	nd	nd	nd	nd

Table A2.4. Hydrocarbon concentrations (ppb) in a core collected at PF600N, Feb. 1989 (continued).

Analyte	Depth in core:							
	0-2 cm	2-5 cm	5-10 cm	10-15 cm	15-20 cm	20-25 cm	25-30 cm	30-36 cm
Benzo(g,h,i)perylene	nd	nd	tr	nd	tr	nd	tr	tr
C1-Naphthalenes, total	tr	tr	tr	tr	tr	tr	tr	tr
C2-Naphthalenes, total	tr	tr	tr	tr	tr	tr	tr	tr
C3-Naphthalenes, est.	nd	trc	nd	tr	nd	tr	nd	tr
C4-Naphthalenes, est.	580	tr	nd	nd	nd	85	nd	nd
C5-Naphthalenes, est.	590	270	nd	nd	nd	180	nd	nd
C1-Fluorenes	nd	56	tr	tr	28	nd	tr	tr
C2-Fluorenes	250	72	tr	nd	nd	nd	nd	nd
C3-Fluorenes	190	tr	nd	nd	nd	nd	nd	nd
C1-Dibenzothiophenes, total	nd	nd	nd	nd	nd	nd	nd	nd
C2-Dibenzothiophenes,est.	nd	tr	nd	nd	nd	nd	nd	nd
C3-Dibenzothiophenes,est.	nd	tr	nd	tr	tr	nd	tr	nd
C1-Phenanthrenes, total	nd	tr	nd	nd	nd	nd	nd	nd
C2-Phenanthrenes, total	87	89	nd	nd	tr	nd	7.8	nd
C2-Phenanthrenes, est.	tr	71	nd	nd	tr	nd	tr	nd
C3-Phenanthrenes, est.	130	82	nd	tr	tr	nd	tr	nd
Total Parent PAH	103	143	80	164	78	112	193	122
Total Alkylated PAH	1,740	551	0	0	28	265	0	0
Total PAH	1,843	694	80	164	106	377	193	122
FFPI	0.56	0.54	0.00	0.04	0.05	0.05	0.02	0.06
Saturated Hydrocarbons								
Resolved	9,500	14,000	4,000	4,800	4,800	6,800	6,800	6,700
Unresolved	82,500	77,000	42,000	39,200	43,200	56,200	63,200	60,300
Total	92,000	91,000	46,000	44,000	48,000	63,000	70,000	67,000
MDL	21	8.6	7.3	6.8	6.4	7.1	7.7	7.7

MDL: Minimum Detection Limit
nd: Not detected
tr: Trace; one ion present, but below detection limits
trc: Trace confirmed; two ions present, but below detection limits
n/a: not analyzed

APPENDIX 3

Table A3.1. Hydrocarbon concentrations (ppb) in a microcosm core collected on day 0. Replicate 1, core A.

Analyte	Sect. 1 ppb	Sect. 2 ppb	Sect. 3 ppb	Sect. 4 ppb	Sect. 5 ppb	Sect. 6 ppb	Sect. 7 ppb	Sect. 8 ppb	Sect. 9 ppb	Sect. 10 ppb	MEAN ppb	S. D.	%RSD ppb
Naphthalene	9.2	19	16	11	8.9	8.0	13	8.9	9.3	11	11	3.6	31%
2-Methylnaph.	3.6	7.3	7.7	3.5	4.8	2.3	3.4	2.2	6.0	4.6	4.5	1.9	43%
1-Methylnaph.	3.0	4.2	4.4	2.4	3.5	2.2	2.4	1.8	3.1	2.9	3.0	0.8	28%
2-Ethylnaph.	1.6	2.9	3.3	2.0	2.8	tr	2.3	tr	2.2	2.3	2.4	0.5	22%
1-Ethylnaph.	1.1	2.3	3.2	2.1	3.1	1.9	tr	tr	2.7	3.1	2.4	0.7	30%
2,6/2,7-Dimethylnaph.	8.2	16	16	8.9	13	7.0	9.1	7.3	11	11	11	3.3	31%
1,3/1,7-DMN	5.9	13	13	7.8	12	7.6	8.4	7.0	12	11	9.8	2.7	28%
1,6-DMN	2.6	5.4	6.7	3.9	5.4	3.3	3.9	2.6	5.0	5.0	4.4	1.3	31%
1,4/2,3-DMN	8.3	23	27	19	26	18	20	17	27	26	21	5.9	28%
1,5-DMN	7.7	24	30	21	31	22	23	20	34	30	24	7.6	31%
1,2-DMN	4.1	13	16	12	17	11	12	10	17	15	13	3.9	31%
1,8-DMN.	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
1,6,7-TMN (not in totals)						57	60	53	85	81	67	15	22%
Fluorene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Phenanthrene	14	17	15	9.3	11	12	30	6.8	16	10	14	6.4	46%
Anthracene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
4-MDBT	23	59	64	40	53	49	49	43	58	61	50	12	25%
2/3-MDBT	5.3	12	12	8	11	11	11	9.2	12	12	10	2	21%
3-MP	27	67	71	42	56	34	36	29	40	42	44	15	34%
1-MDBT	13	26	29	18	23	26	27	23	30	30	25	5	22%
2-MP	3.8	6.8	7.1	4.0	5.9	6.0	8.8	4.5	7.0	7.2	6.1	1.6	26%
4/9-MP	25	67	67	41	52	48	51	46	59	67	52	13	26%
1-MP	15	37	38	22	30	29	31	25	35	38	30	7.6	25%
3,6-DMP	90	230	220	130	160	140	130	130	160	170	156	43	27%
2,6-DMP	19	51	48	29	34	35	33	30	40	43	36	9.6	26%
2,7-DMP	29	76	70	43	51	63	62	56	70	79	60	16	26%
3,9-DMP	110	300	270	160	200	220	220	200	250	280	221	58	26%
1,6/2,5/2,9-DMP	88	230	210	130	150	190	190	170	220	240	182	48	26%
1,7-DMP	21	59	52	31	37	47	45	41	53	58	44	12	27%
1,9/4,9-DMP	36	85	78	41	51	100	88	84	110	130	80	30	38%
Fluoranthene	19	47	40	22	27	59	63	45	65	79	47	20	43%
1,2-DMDBT (not in totals)						4.8	4.0	4.2	5.1	5.3	4.7	0.6	12%
1,5-DMP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA

Table A3.1. Hydrocarbon concentrations (ppb) in a microcosm core collected on day 0. Replicate 1, core A (continued).

Analyte	Sect. 1	Sect. 2	Sect. 3	Sect. 4	Sect. 5	Sect. 6	Sect. 7	Sect. 8	Sect. 9	Sect. 10	MEAN	S. D.	%RSD
	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb		ppb
1,8-DMP	14	40	35	20	25	33	31	26	36	40	30	8.6	29%
1,2-DMP	11	30	25	15	17	22	21	19	26	25	21	5.7	27%
9,10-DMP	3.3	5.0	4.1	2.3	2.9	5.2	5.5	5.1	5.4	5.9	4.5	1.2	28%
1,2,8-TMP (not in totals)						13	11	10	15	16	13	2.5	20%
Pyrene	27	55	45	25	31	50	54	44	55	64	45	13	30%
Benz(a)anthracene	18	45	49	33	40	16	15	16	18	20	27	13	50%
Chrysene	56	110	120	69	89	78	81	67	83	140	89	26	29%
Benzo(b)fluoranthene	12	21	20	16	19	13	13	14	14	17	16	3.2	20%
Benzo(a)pyrene	8.2	15	12	9.4	12	9.3	nd	nd	10	13	11	2.3	20%
Benzo(e)pyrene	12	23	24	15	19	20	20	17	21	23	19	3.8	20%
Perylene	40	73	69	33	57	39	44	38	56	65	51	14	28%
Indeno(1,2,3-cd)pyrene	tr	tr	tr	tr	tr	8.1	nd	tr	7.2	11	8.8	2.0	NA
Dibenz(a,h)anthracene	nd	tr	nd	tr	tr	tr	tr	nd	tr	tr	tr	NA	NA
Benzo(g,h,i)perylene	tr	tr	tr	tr	tr	11	14	9.6	13	13	12	1.8	NA
C1-Naphthalenes, total	6.6	12	12	5.9	8.3	4.5	5.8	4.0	9.1	7.5	7.5	2.7	36%
C2-Naphthalenes, total	40	100	115	77	110	71	79	64	111	103	87	25	29%
C1-Dibenzothiophenes, total	41	97	105	66	87	86	87	75	100	103	85	20	23%
C1-Phenanthrenes, total	71	178	183	109	144	117	127	105	141	154	133	34	26%
C2-Phenanthrenes, total	421	1,106	1,012	601	728	855	826	761	970	1,071	835	217	26%
Total Parent PAH	215	425	410	243	314	323	347	266	368	466	338	82	24%
Total Alkylated PAH	580	1,492	1,428	859	1,077	1,134	1,124	1,009	1,331	1,439	1,147	288	25%
Total PAH	795	1,917	1,838	1,102	1,391	1,457	1,471	1,275	1,699	1,905	1,485	367	25%
Saturated Hydrocarbons													
Resolved	17,000	38,000	41,000	31,000	38,000	21,000	36,000	19,000	29,000	26,000	29,600	8644	29%
Unresolved	153,000	272,000	279,000	189,000	242,000	189,000	264,000	191,000	221,000	234,000	223,400	42082	19%
Total	170,000	310,000	320,000	220,000	280,000	210,000	300,000	210,000	250,000	260,000	253,000	49900	20%
MDL	0.41	0.41	0.40	0.42	0.39	1.8	2.2	1.8	1.5	2.0	1.1	0.8	

Table A3.2. Hydrocarbon concentrations (ppb) in a microcosm core collected on day 0. Replicate 2, core B.

Analyte	Sect. 1 ppb	Sect. 2 ppb	Sect. 3 ppb	Sect. 4 ppb	Sect. 5 ppb	Sect. 6 ppb	Sect. 7 ppb	Sect. 8 ppb	Sect. 9 ppb	Sect. 10 ppb	**MEAN ppb**	**S. D.**
Naphthalene	8.8	9.5	6.0	7.4	5.7	7.1	11	7.9	10	9.3	**8.3**	**1.7**
2-Methylnaph.	4.5	4.3	2.8	3.2	1.8	tr	2.9	2.8	2.9	3.8	**3.2**	**0.8**
1-Methylnaph.	3.1	3.0	2.0	3.9	1.2	tr	3.0	2.3	2.6	2.7	**2.6**	**0.8**
2-Ethylnaph.	2.7	2.6	1.7	1.8	1.0	nd	2.2	nd	tr	nd	**2.0**	**0.6**
1-Ethylnaph.	3.0	2.9	2.4	2.2	1.3	tr	2.8	3.0	3.1	2.6	**2.6**	**0.6**
2,6/2,7-Dimethylnaph.	13	16	10	19	11	7.3	13	15	11	14	**13**	**3.4**
1,3/1,7-DMN	18	19	15	15	8.5	11	21	22	25	25	**18**	**5.6**
1,6-DMN	3.7	4.6	3.2	3.7	2.0	tr	4.3	5.1	5.6	5.1	**4.1**	**1.1**
1,4/2,3-DMN	23	24	20	20	12	15	28	30	33	33	**24**	**7.2**
1,5-DMN	20	22	19	17	11	14	26	29	32	32	**22**	**7.4**
1,2-DMN	10	12	10	9.8	5.9	7.0	14	14	16	16	**11**	**3.5**
1,8-DMN.	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	**nd**	**NA**
1,6,7-TMN (not in totals)						39	72	81	98	97	**77**	**24**
Fluorene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	**nd**	**NA**
Phenanthrene	12	9.5	6.5	7.6	5.1	7.2	29	10	8.7	12	**11**	**6.8**
Anthracene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	**nd**	**NA**
4-MDBT	640	530	410	460	270	36	58	36	36	35	**251**	**241**
2/3-MDBT	170	140	110	120	75	8.6	14	9.5	8.3	8.7	**66**	**64**
3-MP	91	70	56	57	33	39	68	43	42	40	**54**	**18**
1-MDBT	190	140	120	120	82	16	27	19	16	18	**75**	**64**
2-MP	11	7.9	5.9	6.3	3.3	6.2	14	7.1	7.3	6.2	**7.5**	**3.0**
4/9-MP	73	53	45	47	28	48	81	52	54	49	**53**	**15**
1-MP	42	31	25	26	16	30	49	30	32	29	**31**	**9.1**
3,6-DMP	190	132	110	120	72	96	160	100	100	98	**118**	**35**
2,6-DMP	50	46	29	40	19	31	50	34	33	32	**36**	**10**
2,7-DMP	61	29	35	26	23	45	71	47	48	45	**43**	**15**
3,9-DMP	250	160	140	150	95	170	270	190	190	180	**180**	**51**
1,6/2,5/2,9-DMP	190	120	110	110	70	140	220	150	150	150	**141**	**43**
1,7-DMP	52	33	29	30	19	38	61	41	41	39	**38**	**12**
1,9/4,9-DMP	77	54	36	41	22	78	120	82	60	66	**64**	**28**
Fluoranthene	39	29	18	21	13	40	100	45	35	46	**39**	**24**
1,2-DMDBT (not in totals)						3.2	5.1	3.1	3.1	3.0	**3.5**	**0.9**
1,5-DMP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	**nd**	**NA**

Table A3.2. Hydrocarbon concentrations (ppb) in a microcosm core collected on day 0. Replicate 2, core B (continued).

Analyte	Sect. 1 ppb	Sect. 2 ppb	Sect. 3 ppb	Sect. 4 ppb	Sect. 5 ppb	Sect. 6 ppb	Sect. 7 ppb	Sect. 8 ppb	Sect. 9 ppb	Sect. 10 ppb	MEAN ppb	S. D.
1,8-DMP	30	17	18	18	11	23	36	24	22	25	**22**	**7.1**
1,2-DMP	21	13	13	13	7.9	16	25	17	16	17	**16**	**4.7**
9,10-DMP	3.6	2.4	nd	2.2	1.6	4.6	5.6	3.4	4.4	nd	**3.5**	**1.4**
1,2,8-TMP (not in totals)						10	14	10	11	10	**11**	**1.7**
Pyrene	42	23	21	22	14	37	73	37	39	43	**35**	**17**
Benz(a)anthracene	36	26	21	20	12	9.3	33	11	tr	11	**20**	**10**
Chrysene	83	60	49	51	25	47	100	59	67	52	**59**	**21**
Benzo(b)fluoranthene	13	13	9.5	9.8	6.0	8.0	29	8.8	8.5	8.8	**11**	**6.5**
Benzo(a)pyrene	9.4	4.4	7.0	4.2	3.8	nd	23	tr	nd	tr	**8.6**	**7.4**
Benzo(e)pyrene	15	13	10	9.3	5.6	9.5	28	16	13	12	**13**	**6.0**
Perylene	57	47	29	32	15	32	63	39	33	28	**38**	**14**
Indeno(1,2,3-cd)pyrene	tr	tr	tr	tr	tr	nd	16	tr	nd	11	**14**	**3.5**
Dibenz(a,h)anthracene	nd	tr	nd	nd	nd	nd	tr	nd	nd	nd	**tr**	**NA**
Benzo(g,h,i)perylene	tr	tr	tr	tr	tr	tr	22	tr	tr	tr	**tr**	**NA**
C1-Naphthalenes, total	7.6	7.3	4.8	7.1	3.0	0.0	5.9	5.1	5.5	6.5	**5.3**	**2.3**
C2-Naphthalenes, total	93	103	81	89	53	54	111	118	126	128	**96**	**27**
C1-Dibenzothiophenes, t	1,000	810	640	700	427	61	99	65	60	62	**392**	**369**
C1-Phenanthrenes, total	217	162	132	136	80	123	212	132	135	124	**145**	**42**
C2-Phenanthrenes, total	925	606	520	550	341	642	1,019	688	664	652	**661**	**193**
Total Parent PAH	315	234	177	184	105	197	527	234	214	233	**242**	**113**
Total Alkylated PAH	2,243	1,689	1,378	1,482	904	880	1,447	1,008	991	972	**1,299**	**437**
Total PAH	2,558	1,923	1,555	1,666	1,009	1,077	1,974	1,242	1,205	1,205	**1,541**	**494**
Saturated Hydrocarbons												
Resolved	32,000	29,000	21,000	25,000	11,000	11,000	23,000	11,000	9,800	9,200	**18,200**	**8764**
Unresolved	228,000	191,000	139,000	145,000	89,000	149,000	207,000	159,000	150,200	140,800	**159,800**	**39563**
Total	260,000	220,000	160,000	170,000	100,000	160,000	230,000	170,000	160,000	150,000	**178,000**	**46140**
MDL	0.39	0.32	0.34	0.31	0.34	2.3	2.0	2.2	2.4	2.1	**1.3**	**1.0**
d8-Naph	130%	150%	125%	150%	150%	55%	68%	30%	25%	24%	**91%**	**55%**
d10-Ace						50%	65%	53%	50%	48%	**53%**	**7%**
d10-Phen	120%	150%	150%	150%	130%	53%	68%	58%	58%	58%	**100%**	**44%**
d12-Chrys	25%	30%	30%	25%	30%	33%	33%	33%	33%	38%	**31%**	**4%**

Table A3.3. Hydrocarbon concentrations (ppb) in a microcosm core collected on day 7. Core 18D.

Analyte	Sect. 1 ppb	Sect. 2 ppb	Sect. 3 ppb	Sect. 4 ppb	Sect. 5 ppb	Sect. 6 ppb	Sect. 7 ppb	Sect. 8 ppb	Sect. 9 ppb	Sect. 10 ppb	**MEAN ppb**	**S. D.**	**%RSD ppb**
Naphthalene	24	26	22	11	21	12	12	6.5	10	9.2	**15**	**7.1**	**46%**
2-Methylnaph.	6.6	6.7	5.5	3.8	7.2	4.5	3.4	3.9	4.6	3.1	**4.9**	**1.5**	**30%**
1-Methylnaph.	4.7	4.7	4.3	2.6	5.3	3.3	3.0	2.7	3.3	2.8	**3.7**	**1.0**	**27%**
2-Ethylnaph.	nd	nd	4.0	2.0	4.5	3.5	3.1	3.0	3.9	2.9	**3.4**	**0.8**	**23%**
1-Ethylnaph.	nd	nd	3.5	2.1	4.3	3.4	2.9	2.8	3.2	2.7	**3.1**	**0.7**	**21%**
2,6/2,7-Dimethylnaph.	41	37	27	18	32	21	20	18	40	19	**27**	**9.4**	**35%**
1,3/1,7-DMN	24	23	26	16	31	24	21	21	27	21	**23**	**4.1**	**17%**
1,6-DMN	4.7	7.1	5.6	4.8	8.9	6.8	5.6	5.3	6.6	5.0	**6.0**	**1.3**	**22%**
1,4/2,3-DMN	20	21	25	16	30	24	20	22	27	21	**23**	**4.0**	**18%**
1,5-DMN	13	14	18	11	19	17	13	14	18	14	**15**	**2.7**	**18%**
1,2-DMN	4.6	5.3	6.6	3.9	7.1	7.2	4.6	5.3	6.4	5.2	**5.6**	**1.1**	**20%**
1,8-DMN.	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	**nd**	**NA**	**NA**
1,6,7-TMN (not in totals)	79	87	99	63	120	92	82	82	100	81	**89**	**15**	**17%**
Fluorene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	**nd**	**NA**	**NA**
Phenanthrene	18	20	15	11	24	12	15	10	14	11	**15**	**4.5**	**30%**
Anthracene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	**nd**	**NA**	**NA**
4-MDBT	65	82	84	54	100	67	67	59	68	65	**71**	**14**	**19%**
2/3-MDBT	19	22	22	15	27	17	18	16	18	17	**19**	**3.6**	**19%**
3-MP	74	96	87	64	120	72	81	73	77	76	**82**	**16**	**19%**
1-MDBT	34	41	43	27	47	32	34	28	34	31	**35**	**6.5**	**19%**
2-MP	13	16	10	8.8	18	7.9	11	9.1	9.0	8.6	**11**	**3.4**	**31%**
4/9-MP	82	110	100	68	130	81	90	77	87	85	**91**	**18**	**20%**
1-MP	46	64	58	39	70	45	48	43	49	47	**51**	**10**	**19%**
3,6-DMP	250	340	310	210	370	220	260	210	240	340	**275**	**60**	**22%**
2,6-DMP	67	91	83	57	99	62	71	58	70	66	**72**	**14**	**20%**
2,7-DMP	100	140	120	81	140	86	99	83	91	94	**103**	**22**	**22%**
3,9-DMP	380	510	450	310	541	320	380	310	350	350	**390**	**83**	**21%**
1,6/2,5/2,9-DMP	290	390	340	230	410	240	280	230	270	260	**294**	**65**	**22%**
1,7-DMP	76	100	89	60	110	65	78	62	75	72	**79**	**16**	**21%**
1,9/4,9-DMP	110	150	130	85	150	91	110	86	98	98	**111**	**25**	**22%**
Fluoranthene	67	84	76	47	92	50	73	52	66	58	**67**	**15**	**23%**
1,2-DMDBT (not in totals)	6.7	9.0	8.0	4.2	8.6	4.8	5.5	4.8	6.0	5.6	**6.3**	**1.7**	**27%**
1,5-DMP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	**nd**	**NA**	**NA**
1,8-DMP	46	70	58	35	73	40	48	41	45	44	**50**	**13**	**26%**
1,2-DMP	36	52	44	29	52	31	37	28	34	35	**38**	**8.7**	**23%**
9,10-DMP	8.9	9.3	12	5.8	11	6.3	nd	nd	5.1	7.9	**8.3**	**2.5**	**30%**

Table A3.3. Hydrocarbon concentrations (ppb) in a microcosm core collected on day 7. Core 18D (continued).

Analyte	Sect. 1 ppb	Sect. 2 ppb	Sect. 3 ppb	Sect. 4 ppb	Sect. 5 ppb	Sect. 6 ppb	Sect. 7 ppb	Sect. 8 ppb	Sect. 9 ppb	Sect. 10 ppb	**MEAN ppb**	**S. D.**	**%RSD ppb**
1,2,8-TMP (not in totals)	28	35	26	18	30	16	22	16	18	19	**23**	**6.6**	**29%**
Pyrene	87	100	84	52	99	50	75	55	70	63	**74**	**19**	**25%**
Benz(a)anthracene	26	33	35	21	42	24	30	24	29	25	**29**	**6.3**	**22%**
Chrysene	130	150	160	88	170	110	110	120	110	98	**125**	**27**	**22%**
Benzo(b & k)fluoranthene	43	25	35	31	25	31	44	21	21	22	**30**	**8.6**	**29%**
Benzo(a)pyrene	tr	nd	tr	tr	tr	nd	tr	tr	14	tr	**14**	**NA**	**NA**
Benzo(e)pyrene	45	23	37	35	37	36	42	21	23	26	**33**	**8.6**	**26%**
Perylene	82	110	86	50	120	58	70	52	67	52	**75**	**25**	**33%**
Indeno(1,2,3-cd)pyrene	nd	nd	nd	nd	nd	tr	nd	nd	tr	nd	**nd**	**NA**	**NA**
Dibenz(a,h)anthracene	nd	nd	nd	nd	nd	tr	nd	nd	nd	nd	**nd**	**NA**	**NA**
Benzo(g,h,i)perylene	nd	nd	nd	nd	nd	tr	nd	tr	tr	nd	**nd**	**NA**	**NA**
C1-Naphthalenes, total	11	11	9.8	6.4	13	7.8	6.4	6.6	7.9	5.9	**8.6**	**2.4**	**28%**
C2-Naphthalenes, total	107	107	116	74	137	107	90	91	132	91	**105**	**20**	**19%**
C1-Dibenzothiophenes, total	118	145	149	96	174	116	119	103	120	113	**125**	**24**	**19%**
C1-Phenanthrenes, total	215	286	255	180	338	206	230	202	222	217	**235**	**47**	**20%**
C2-Phenanthrenes, total	1,364	1,852	1,636	1,103	1,956	1,161	1,363	1,108	1,278	1,367	**1,419**	**301**	**21%**
Total Parent PAH	522	571	550	346	630	383	471	362	424	364	**462**	**101**	**22%**
Total Alkylated PAH	1,816	2,402	2,166	1,459	2,617	1,598	1,809	1,511	1,760	1,793	**1,893**	**383**	**20%**
Total PAH	2,338	2,973	2,716	1,805	3,247	1,981	2,280	1,873	2,184	2,157	**2,355**	**478**	**20%**
Saturated Hydrocarbons													
Resolved	17,000	24,000	35,000	20,000	48,000	33,000	25,000	27,000	23,000	25,000	**27,700**	**8,932**	**32%**
Unresolved	283,000	336,000	305,000	220,000	382,000	237,000	235,000	193,000	197,000	205,000	**259,300**	**64,503**	**25%**
Total	300,000	360,000	340,000	240,000	430,000	270,000	260,000	220,000	220,000	230,000	**287,000**	**70,087**	**24%**
MDL	4.2	4.4	2.2	2.3	3.1	1.2	2.1	1.2	1.5	1.5	**2.4**	**1.2**	**49%**

Table A3.4. Hydrocarbon concentrations (ppb) in a microcosm core collected on day 14. Core 14C.

Analyte	Sect. 1 ppb	Sect. 2 ppb	Sect. 3 ppb	Sect. 4 ppb	Sect. 5 ppb	Sect. 6 ppb	Sect. 7 ppb	Sect. 8 ppb	Sect. 9 ppb	Sect. 10 ppb	MEAN ppb	S. D.	%RSD ppb
Naphthalene	51	21	24	15	12	15	13	15	10	10	19	12	66%
2-Methylnaph.	12	7.0	7.3	4.9	4.6	4.3	4.2	4.6	4.5	3.4	5.7	2.5	45%
1-Methylnaph.	9.2	3.9	5.6	4.0	3.7	4.4	3.3	3.5	3.4	3.2	4.4	1.8	41%
2-Ethylnaph.	nd	nd	nd	3.3	3.4	3.6	3.0	2.9	3.3	2.9	3.2	0.3	8%
1-Ethylnaph.	nd	nd	nd	3.1	3.0	3.6	3.3	3.1	3.4	3.0	3.2	0.2	7%
2,6/2,7-Dimethylnaph.	nd	12	21	23	17	21	18	18	18	16	18	3.2	18%
1,3/1,7-DMN	14	17	24	24	20	24	22	22	22	21	21	3.3	16%
1,6-DMN	tr	4.4	7.4	6.8	5.9	4.6	4.5	6.0	6.1	5.6	5.7	1.0	18%
1,4/2,3-DMN	10	15	23	22	20	23	22	23	23	22	20	4.4	22%
1,5-DMN	6.9	9.5	15	15	15	16	15	15	16	15	14	3.1	22%
1,2-DMN	nd	3.5	6.5	5.6	5.8	6.1	5.7	6.2	6.0	5.8	5.7	0.9	15%
1,8-DMN.	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
1,6,7-TMN (not in totals)	37	61	91	89	79	94	88	92	91	86	81	18	22%
Fluorene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Phenanthrene	30	18	62	19	13	18	11	14	12	11	21	16	75%
Anthracene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
4-MDBT	42	58	83	68	56	73	62	70	60	56	63	11	18%
2/3-MDBT	11	16	20	21	14	18	16	17	15	13	16	3.1	19%
3-MP	43	51	85	66	47	75	65	67	61	69	63	13	21%
1-MDBT	22	28	46	40	33	38	36	37	35	33	35	6.5	19%
2-MP	11	8.6	20	11	6.2	14	9.4	8.5	7.1	10	11	4.0	38%
4/9-MP	55	71	110	86	65	92	82	91	77	81	81	15	19%
1-MP	34	42	67	55	40	54	49	52	47	49	49	9.1	19%
3,6-DMP	180	240	350	290	210	290	250	280	230	230	255	49	19%
2,6-DMP	41	53	85	67	48	69	60	69	55	58	61	13	21%
2,7-DMP	79	100	150	130	90	130	100	120	99	100	110	22	20%
3,9-DMP	270	360	550	430	300	430	370	430	340	350	383	80	21%
1,6/2,5/2,9-DMP	230	290	450	360	250	360	310	350	270	280	315	66	21%
1,7-DMP	58	74	110	91	64	91	78	93	70	74	80	16	20%
1,9/4,9-DMP	86	110	170	140	92	140	120	130	100	110	120	26	21%
Fluoranthene	66	78	160	93	63	99	77	87	67	72	86	29	33%
1,2-DMDBT (not in totals)	tr	5.4	8.5	6.5	4.4	6.5	5.2	5.9	4.9	4.9	5.8	1.2	21%

Table A3.4. Hydrocarbon concentrations (ppb) in a microcosm core collected on day 14. Core 14C (continued).

Analyte	Sect. 1 ppb	Sect. 2 ppb	Sect. 3 ppb	Sect. 4 ppb	Sect. 5 ppb	Sect. 6 ppb	Sect. 7 ppb	Sect. 8 ppb	Sect. 9 ppb	Sect. 10 ppb	MEAN ppb	S. D.	%RSD ppb
1,5-DMP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
1,8-DMP	42	48	81	63	43	65	56	66	49	53	57	12	22%
1,2-DMP	34	35	56	43	31	43	37	44	34	34	39	7.5	19%
9,10-DMP	12	9.4	15	8.8	4.3	8.7	8.0	8.2	6.0	nd	8.9	3.1	35%
1,2,8-TMP (not in totals)	22	23	39	28	15	27	22	27	19	19	24	6.7	28%
Pyrene	90	89	170	100	62	100	80	90	66	71	92	31	33%
Benz(a)anthracene	20	27	56	34	23	36	29	31	25	26	31	10	33%
Chrysene	140	120	210	140	120	150	120	150	110	110	137	30	22%
Benzo(b & k)fluoranthene	tr	tr	61	33	23	31	23	30	25	26	32	12	40%
Benzo(a)pyrene	tr	tr	tr	tr	13	tr	tr	tr	14	tr	14	0.7	5%
Benzo(e)pyrene	tr	34	45	36	26	38	25	23	28	25	31	7.5	24%
Perylene	180	100	140	110	66	100	85	58	69	86	99	37	37%
Indeno(1,2,3-cd)pyrene	nd	nd	tr	tr	tr	tr	tr	tr	tr	nd	tr	NA	NA
Dibenz(a,h)anthracene	nd	nd	nd	tr	tr	nd	nd	tr	nd	nd	nd	NA	NA
Benzo(g,h,i)perylene	nd	nd	tr	tr	tr	tr	tr	tr	tr	19	tr	NA	NA
C1-Naphthalenes, total	21	11	13	8.9	8.3	8.7	7.5	8.1	7.9	6.6	10.1	4.3	43%
C2-Naphthalenes, total	31	61	97	103	90	102	94	96	98	91	86	23	26%
C1-Dibenzothiophenes, total	75	102	149	129	103	129	114	124	110	102	114	20	18%
C1-Phenanthrenes, total	143	173	282	218	158	235	205	219	192	209	203	40	20%
C2-Phenanthrenes, total	1,032	1,319	2,017	1,623	1,132	1,627	1,389	1,590	1,253	1,289	1,427	290	20%
Total Parent PAH	577	487	928	580	421	587	463	498	426	456	542	149	28%
Total Alkylated PAH	1,302	1,666	2,558	2,082	1,492	2,101	1,809	2,037	1,661	1,698	1,841	361	20%
Total PAH	1,879	2,153	3,486	2,662	1,913	2,688	2,272	2,535	2,087	2,154	2,383	482	20%
Saturated Hydrocarbons													
Resolved	7,700	16,000	24,000	23,000	27,000	26,000	25,000	24,000	28,000	23,000	22,370	6,102	27%
Unresolved	232,300	234,000	356,000	257,000	193,000	244,000	205,000	236,000	212,000	187,000	235,630	47,968	20%
Total	240,000	250,000	380,000	280,000	220,000	270,000	230,000	260,000	240,000	210,000	258,000	48,028	19%
MDL	5.4	2.6	3.9	1.9	0.7	1.5	1.0	1.5	0.81	0.93	2.0	1.5	76%

Table A3.5. Hydrocarbon concentrations (ppb) in a microcosm core collected on day 28. Core 15A.

Analyte	Sect. 1 ppb	Sect. 2 ppb	Sect. 3 ppb	Sect. 4 ppb	Sect. 5 ppb	Sect. 6 ppb	Sect. 7 ppb	Sect. 8 ppb	Sect. 9 ppb	Sect. 10 ppb	MEAN ppb	S. D.	%RSD ppb
Naphthalene	16	13	13	12	12	11	14	12	9.5	12	12	1.7	14%
2-Methylnaph.	5.6	6.4	6.8	6.3	5.6	5.3	9.3	7.4	4.2	6.6	6.4	1.4	22%
1-Methylnaph.	3.8	4.5	4.7	4.3	3.6	3.3	5.7	4.5	2.6	4.2	4.1	0.85	21%
2-Ethylnaph.	3.0	3.8	3.7	3.6	3.2	3.2	5.1	4.2	2.5	3.9	3.6	0.72	20%
1-Ethylnaph.	2.0	2.9	3.3	3.4	3.1	2.6	4.4	3.4	1.9	3.1	3.0	0.73	24%
2,6/2,7-Dimethylnaph.	15	17	48	14	12	32	62	41	21	16	28	17	62%
1,3/1,7-DMN	8.3	11	10	9.8	8.0	8.1	15	11	5.9	10	9.7	2.4	25%
1,6-DMN	4.8	5.0	7.7	6.6	5.7	6.1	11	7.2	4.6	6.3	6.5	1.9	29%
1,4/2,3-DMN	14	20	23	24	21	19	28	20	12	17	20	4.7	24%
1,5-DMN	16	24	30	35	29	28	45	32	18	28	29	8.3	29%
1,2-DMN	7.5	12	14	17	14	13	20	14	7.9	12	13	3.7	28%
1,8-DMN.	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Fluorene	ndi	ndi	ndi	ndi	ndi	ndi	ndi	ndi	ndi	ndi	ndi	NA	NA
Phenanthrene	54	35	27	23	20	20	26	24	17	21	27	11	40%
Anthracene	ndi	ndi	ndi	ndi	ndi	ndi	ndi	ndi	ndi	ndi	ndi	NA	NA
4-MDBT	42	60	60	63	54	48	54	48	29	39	50	11	22%
2/3-MDBT	14	16	16	16	13	12	12	12	8.8	10	13	2.5	19%
3-MP	13	17	16	16	12	13	14	15	9.0	15	14	2.4	17%
1-MDBT	33	42	43	44	37	38	43	45	29	41	40	5.2	13%
2-MP	3.3	4.5	3.9	4.0	3.1	3.2	4.7	4.7	2.8	3.8	3.8	0.7	18%
4/9-MP	28	36	35	36	29	28	32	33	21	34	31	4.7	15%
1-MP	13	17	15	16	12	10	12	13	8.2	13	13	2.6	20%
3,6-DMP	95	120	120	120	110	110	130	130	82	120	114	15	13%
2,6-DMP	13	16	17	16	13	13	17	17	9.6	15	15	2.4	17%
2,7-DMP	33	41	41	42	37	37	45	49	28	44	40	6.1	15%
3,9-DMP	110	140	140	140	120	120	150	160	91	140	131	21	16%
1,6/2,5/2,9-DMP	100	130	130	130	110	110	140	150	84	130	121	20	16%
1,7-DMP	19	23	22	23	19	19	25	25	14	22	21	3.4	16%
1,9/4,9-DMP	36	46	44	47	41	41	52	55	31	48	44	7.2	16%
Fluoranthene	25	30	30	33	27	27	37	38	20	33	30	5.5	18%

Table A3.5. Hydrocarbon concentrations (ppb) in a microcosm core collected on day 28. Core 15A (continued).

Analyte	Sect. 1 ppb	Sect. 2 ppb	Sect. 3 ppb	Sect. 4 ppb	Sect. 5 ppb	Sect. 6 ppb	Sect. 7 ppb	Sect. 8 ppb	Sect. 9 ppb	Sect. 10 ppb	MEAN ppb	S. D.	%RSD ppb
1,5-DMP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
1,8-DMP	15	21	18	17	16	18	25	26	13	22	19	4.3	22%
1,2-DMP	11	14	13	14	12	13	15	17	10	15	13	2.1	15%
9,10-DMP	4.7	5.3	3.9	6.8	4.5	6.8	6.2	5.5	3.9	4.7	5.2	1.1	21%
Pyrene	28	33	30	32	28	28	39	42	21	35	32	6.1	19%
Benz(a)anthracene	32	43	54	57	43	46	64	55	28	53	48	11	24%
Chrysene	96	130	120	130	110	130	150	130	72	130	120	22	18%
Benzo(b)fluoranthene	11	15	18	18	13	13	24	18	10	15	16	4.1	27%
Benzo(a)pyrene	9.7	4.4	18	11	8.4	9.6	20	15	6.0	9.5	11	5.0	45%
Benzo(e)pyrene	26	23	27	27	22	21	34	31	17	26	25	4.9	19%
Perylene	110	160	130	87	72	62	130	110	41	89	99	36	36%
Indeno(1,2,3-cd)pyrene	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	NA	NA
Dibenz(a,h)anthracene	nd	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	NA	NA
Benzo(g,h,i)perylene	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	NA	NA
C1-Naphthalenes, total	9.4	11	12	11	9.2	8.6	15	12	6.8	11	10	2.2	21%
C2-Naphthalenes, total	71	96	140	113	96	112	191	133	74	96	112	35	32%
C1-Dibenzothiophenes, total	89	118	119	123	104	98	109	105	67	90	102	17	17%
C1-Phenanthrenes, total	57	75	70	72	56	54	63	66	41	66	62	10	16%
C2-Phenanthrenes, total	437	556	549	556	483	488	605	635	367	561	523	80	15%
Total Parent PAH	408	486	467	430	355	368	538	475	242	424	419	83	20%
Total Alkylated PAH	663	855	889	875	748	761	982	950	555	824	810	131	16%
Total PAH	1,071	1,342	1,356	1,305	1,103	1,128	1,520	1,425	796	1,247	1,229	210	17%
Saturated Hydrocarbons													
Resolved	22,000	40,000	39,000	38,000	42,000	42,000	49,000	44,000	29,000	41,000	38,600	7,720	20%
Unresolved	168,000	260,000	251,000	252,000	268,000	278,000	321,000	266,000	181,000	269,000	251,400	45,137	18%
Total	190,000	300,000	290,000	290,000	310,000	320,000	370,000	310,000	210,000	310,000	290,000	52,705	18%
MDL	0.53	0.72	0.61	0.49	0.45	0.58	0.55	0.52	0.52	0.46	0.54	0.08	15%

Table A3.6. Hydrocarbon concentrations (ppb) in a microcosm core collected on day 60. Replicate 1, core 13B.

Analyte	Sect. 1 ppb	Sect. 2 ppb	Sect. 3 ppb	Sect. 4 ppb	Sect. 5 ppb	Sect. 6 ppb	Sect. 7 ppb	Sect. 8 ppb	Sect. 9 ppb	Sect. 10 ppb	MEAN ppb	S. D.	%RSD ppb
Naphthalene	16	8.1	7.3	6.1	6.2	6.7	6.1	6.5	5.4	8.0	7.6	3.1	40%
2-Methylnaph.	7.2	5.1	4.7	3.8	3.9	2.4	4.4	3.7	3.4	5.1	4.4	1.3	30%
1-Methylnaph.	3.6	3.5	3.0	2.4	2.5	1.3	2.9	2.1	1.9	3.1	2.6	0.7	28%
2-Ethylnaph.	2.9	2.8	2.7	2.1	2.3	1.2	2.7	2.3	2.1	2.7	2.4	0.5	21%
1-Ethylnaph.	1.7	2.2	2.3	2.1	2.2	1.3	2.7	2.0	1.8	2.5	2.1	0.4	19%
2,6/2,7-Dimethylnaph.	56	72	54	32	26	12	44	34	27	54	41	18	44%
1,3/1,7-DMN	8.5	7.8	6.5	5.1	5.4	2.7	6.8	5.8	5.1	7.9	6.2	1.7	28%
1,6-DMN	5.9	7.4	6.4	4.9	5.2	3.1	6.2	4.9	4.6	6.5	5.5	1.2	22%
1,4/2,3-DMN	10	11	12	11	11	6.2	11	8.2	6.9	9.8	9.7	2.0	20%
1,5-DMN	10	15	15	15	16	9.2	15	11	8.7	12	13	2.8	22%
1,2-DMN	4.1	5.5	5.9	6.1	6.5	3.8	6.0	4.7	3.6	4.8	5.1	1.0	20%
1,8-DMN.	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Fluorene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Phenanthrene	19	13	12	10	11	6.0	14	12	9.4	14	12	3.4	28%
Anthracene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
4-MDBT	26	29	30	30	29	13	19	15	13	18	22	7.3	33%
2/3-MDBT	7.4	7.1	6.5	5.6	6.0	3.4	5.7	4.6	4.4	6.4	5.7	1.3	22%
3-MP	13	7.5	7.5	6.4	8.2	1.9	7.3	6.8	6.3	7.7	7.3	2.7	37%
1-MDBT	27	26	25	22	25	15	26	23	21	32	24	4.4	18%
2-MP	6.1	4.1	4.2	2.8	3.7	1.7	3.8	3.6	3.5	4.7	3.8	1.1	30%
4/9-MP	29	25	24	22	25	11	23	20	22	32	23	5.6	24%
1-MP	13	9.5	8.9	7.7	7.9	7.0	15	13	6.6	10	9.9	2.9	29%
3,6-DMP	150	120	120	99	120	62	120	110	100	150	115	26	22%
2,6-DMP	11	9.4	9.2	6.7	8.3	4.2	8.0	7.6	7.2	11	8.3	2.0	25%
2,7-DMP	71	51	50	43	50	26	52	46	43	66	50	12	25%
3,9-DMP	170	120	120	100	120	60	120	110	99	150	117	30	25%
1,6/2,5/2,9-DMP	170	130	130	100	120	61	130	110	100	160	121	31	26%
1,7-DMP	24	17	18	14	16	7.5	15	14	13	20	16	4.4	28%
1,9/4,9-DMP	77	56	59	47	54	28	58	52	48	74	55	14	25%
Fluoranthene	64	41	42	41	40	18	50	49	34	55	43	12	29%

Table A3.6. Hydrocarbon concentrations (ppb) in a microcosm core collected on day 60. Replicate 1, core 13B (continued).

Analyte	Sect. 1 ppb	Sect. 2 ppb	Sect. 3 ppb	Sect. 4 ppb	Sect. 5 ppb	Sect. 6 ppb	Sect. 7 ppb	Sect. 8 ppb	Sect. 9 ppb	Sect. 10 ppb	MEAN ppb	S. D.	%RSD ppb
1,5-DMP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
1,8-DMP	31	23	23	16	18	10	25	23	21	33	22	6.8	30%
1,2-DMP	25	15	17	12	15	7.9	16	15	13	21	16	4.7	30%
9,10-DMP	6.0	3.4	2.8	nd	tr	tr	nd	tr	tr	2.9	3.8	1.5	40%
Pyrene	57	35	35	26	32	14	39	32	28	44	34	11	33%
Benz(a)anthracene	32	27	24	20	23	12	33	27	22	30	25	6.3	25%
Chrysene	170	130	120	100	110	59	150	120	110	160	123	32	26%
Benzo(b,k)fluoranthene	47	36	35	27	38	15	43	39	30	43	35	9.3	26%
Benzo(a)pyrene	30	20	13	14	19	6.3	18	17	14	16	17	6.1	36%
Benzo(e)pyrene	40	35	28	23	27	15	38	32	27	41	31	8.2	27%
Perylene	180	160	130	87	77	29	110	80	71	130	105	45	43%
Indeno(1,2,3-cd)pyrene	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	NA	NA
Dibenz(a,h)anthracene	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	NA	NA
Benzo(g,h,i)perylene	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	NA	NA
C1-Naphthalenes, total	11	8.6	7.7	6.2	6.4	3.7	7.3	5.8	5.3	8.2	7.0	2.0	28%
C2-Naphthalenes, total	99	124	105	78	75	40	94	73	60	100	85	24.5	29%
C1-Dibenzothiophenes, total	60.4	62.1	61.5	57.6	60.0	31.4	50.7	42.6	38.4	56.4	52.1	10.9	21%
C1-Phenanthrenes, total	61.1	46.1	44.6	38.9	44.8	21.6	49.1	43.4	38.4	54.4	44.2	10.5	24%
C2-Phenanthrenes, total	735.0	544.8	549.0	437.7	521.3	266.6	544.0	487.6	444.2	687.9	521.8	130.9	25%
Total Parent PAH	655	505	446	354	383	181	501	415	351	541	433	129	30%
Total Alkylated PAH	966	785	768	619	707	363	746	652	586	907	710	171	24%
Total PAH	1,621	1,290	1,214	973	1,090	544	1,247	1,067	937	1,448	1,143	298	26%
Saturated Hydrocarbons													
Resolved	23,000	31,000	28,000	29,000	29,000	19,000	36,000	24,000	25,000	34,000	27,800	5,181	19%
Unresolved	237,000	229,000	212,000	201,000	201,000	141,000	264,000	196,000	195,000	246,000	212,200	34,321	16%
Total	260,000	260,000	240,000	230,000	230,000	160,000	300,000	220,000	220,000	280,000	240,000	38,586	16%
MDL	0.91	0.45	0.37	0.35	0.34	0.23	0.37	0.33	0.32	0.45	0.41	0.19	45%

Table A3.7. Hydrocarbon concentrations (ppb) in a microcosm core collected on day 60. Replicate 2, core 5D.

Analyte	Sect. 1 ppb	Sect. 2 ppb	Sect. 3 ppb	Sect. 4 ppb	Sect. 5 ppb	Sect. 6 ppb	Sect. 7 ppb	Sect. 8 ppb	Sect. 9 ppb	Sect. 10 ppb	MEAN ppb	S. D.	%RSD
Naphthalene	18	19	10	11	7.2	5.6	6.9	9.5	9.0	5.2	10.1	4.8	47%
2-Methylnaph.	6.4	7.5	5.8	6.4	4.3	3.5	4.1	6.0	5.7	3.7	5.3	1.3	25%
1-Methylnaph.	6.1	5.5	6.3	6.8	2.9	2.3	2.8	3.8	6.6	2.4	4.6	1.9	41%
2-Ethylnaph.	nd	2.5	2.8	3.1	2.3	1.9	2.3	2.7	3.0	1.8	2.5	0.5	18%
1-Ethylnaph.	nd	2.3	2.1	2.4	2.1	1.8	2.3	2.5	2.7	1.8	2.2	0.3	14%
2,6/2,7-Dimethylnaph.	59	63	40	64	26	19	23	30	28	22	37	18	48%
1,3/1,7-DMN	8.1	8.5	9.1	9.9	7.0	5.4	7.0	9.6	9.2	5.6	7.9	1.6	20%
1,6-DMN	5.3	6.5	6.2	7.9	5.2	4.2	4.9	6.3	6.2	4.3	5.7	1.1	20%
1,4/2,3-DMN	6.6	10.0	12	14	10.0	8.4	10.0	14	13	8.1	11	2.6	24%
1,5-DMN	5.1	7.5	9.8	12	9.3	7.5	9.0	12	11	7.6	9.1	2.2	24%
1,2-DMN	2.2	2.7	4.0	4.9	4.0	3.1	4.1	5.0	5.1	3.2	3.8	1.0	26%
1,8-DMN.	nd	nd	nd	nd	nd	nd	6.3	9.2	9.7	nd	8.4	1.8	22%
Fluorene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Phenanthrene	19	15	10	16	10	8.4	10	15	14	8.9	13	3.6	29%
Anthracene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
4-MDBT	23	33	31	41	31	22	24	31	28	19	28	6	23%
2/3-MDBT	8.3	9.4	5.6	9.9	7.6	5.6	6.1	9.2	8.1	5.8	7.6	1.7	22%
3-MP	11	13	14	13	11	8.6	11	17	15	11	12	2.4	20%
1-MDBT	22	30	27	38	30	23	30	41	41	30	31	7	22%
2-MP	6.3	6.0	5.6	5.5	3.8	3.0	3.7	5.4	4.9	3.8	4.8	1.1	24%
4/9-MP	23	31	36	36	27	22	27	20	37	26	29	6.2	22%
1-MP	10	15	16	14	11	8.9	11	16	14	11	13	2.6	20%
3,6-DMP	110	180	160	180	130	100	130	190	170	130	148	32	22%
2,6-DMP	10	15	15	17	12	8.9	12	20	18	13	14	3.6	25%
2,7-DMP	50	81	73	76	55	43	54	83	71	55	64	14	22%
3,9-DMP	130	220	200	200	150	110	150	230	190	150	173	40	23%
1,6/2,5/2,9-DMP	130	220	200	200	150	110	140	230	190	150	172	41	24%
1,7-DMP	19	32	28	30	20	16	20	33	28	22	25	6.1	24%
1,9/4,9-DMP	67	120	88	91	51	50	63	99	84	64	78	23	29%
Fluoranthene	56	85	64	68	64	46	51	84	62	46	63	14	22%

Table A3.7. Hydrocarbon concentrations (ppb) in a microcosm core collected on day 60. Replicate 2, core 5D (continued).

Analyte	Sect. 1 ppb	Sect. 2 ppb	Sect. 3 ppb	Sect. 4 ppb	Sect. 5 ppb	Sect. 6 ppb	Sect. 7 ppb	Sect. 8 ppb	Sect. 9 ppb	Sect. 10 ppb	MEAN ppb	S. D.	%RSD
1,5-DMP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
1,8-DMP	27	45	39	37	23	19	25	41	37	25	32	9.0	28%
1,2-DMP	16	31	31	24	16	13	16	27	22	17	21	6.7	31%
9,10-DMP	4.4	6.7	11	4.5	3.7	2.4	3.3	5.3	4.3	3.2	4.9	2.5	50%
Pyrene	47	74	60	54	35	28	35	59	47	35	47	14	31%
Benz(a)anthracene	15	30	12	25	25	19	25	33	37	21	24	7.8	32%
Chrysene	89	130	110	150	110	88	120	150	170	98	122	28	23%
Benzo(b)fluoranthene	12	19	13	17	15	13	13	19	20	11	15	3.3	22%
Benzo(a)pyrene	10.0	9.5	11	15	15	7.1	9.0	17	12	7.7	11	3.4	30%
Benzo(e)pyrene	18	32	22	28	25	19	21	32	34	21	25	5.9	23%
Perylene	110	140	140	150	92	64	84	110	120	57	107	32	30%
Indeno(1,2,3-cd)pyrene	tr	tr	tr	18	tr	tr	tr	tr	tr	tr	tr	NA	NA
Dibenz(a,h)anthracene	nd	tr	tr	14	nd	nd	nd	nd	nd	nd	nd	NA	NA
Benzo(g,h,i)perylene	tr	tr	tr	27	tr	tr	tr	tr	tr	tr	tr	NA	NA
C1-Naphthalenes, total	13	13	12	13	7.2	5.8	6.9	9.8	12	6.1	9.9	3.1	31%
C2-Naphthalenes, total	86	103	86	118	66	51	69	91	88	54	81	21	26%
C1-Dibenzothiophenes, total	53	72	64	89	69	51	60	81	77	55	67	13	19%
C1-Phenanthrenes, total	50	65	72	69	53	43	53	58	71	52	58	10	17%
C2-Phenanthrenes, total	563	951	845	860	611	472	613	958	814	629	732	173	24%
Total Parent PAH	394	554	452	593	398	298	375	529	525	311	443	103	23%
Total Alkylated PAH	766	1,204	1,078	1,148	805	623	802	1,199	1,063	796	948	212	22%
Total PAH	1,160	1,758	1,530	1,741	1,203	921	1,177	1,728	1,588	1,107	1,391	310	22%
Saturated Hydrocarbons													
Resolved	7,200	9,200	19,000	30,000	24,000	22,000	28,000	31,000	34,000	22,000	22,640	8,924	39%
Unresolved	192,800	240,800	201,000	220,000	216,000	168,000	192,000	239,000	226,000	168,000	206,360	26,411	13%
Total	200,000	250,000	220,000	250,000	240,000	190,000	220,000	270,000	260,000	190,000	229,000	29,231	13%
MDL	1.3	1.3	0.56	0.50	0.44	0.32	0.39	0.63	0.44	0.32	0.62	0.37	60%

Table A3.8. Hydrocarbon concentrations (ppb) in a microcosm core collected on day 90. Core 9A.

Analyte	Sect. 1 ppb	Sect. 2 ppb	Sect. 3 ppb	Sect. 4 ppb	Sect. 5 ppb	Sect. 6 ppb	Sect. 7 ppb	Sect. 8 ppb	Sect. 9 ppb	Sect. 10 ppb	MEAN ppb	S. D.	%RSD ppb
Naphthalene	24	12	6.3	7.3	14	6.5	6.6	6.8	6.1	8.7	9.8	5.7	58%
2-Methylnaph.	5.7	4.0	3.9	3.4	6.6	2.5	4.5	4.3	3.9	4.4	4.3	1.1	26%
1-Methylnaph.	2.7	1.8	2.4	2.4	3.9	2.0	3.7	3.1	2.2	2.9	2.7	0.7	26%
2-Ethylnaph.	nd	nd	2.3	2.1	3.1	1.6	3.7	3.0	2.3	2.9	2.6	0.7	25%
1-Ethylnaph.	nd	nd	1.9	2.1	2.9	1.4	3.9	2.7	2.2	2.8	2.5	0.8	31%
2,6/2,7-Dimethylnaph.	nd	nd	16	18	25	13	34	17	15	16	19	6.9	36%
1,3/1,7-DMN	2.1	1.9	6.2	6.5	7.8	3.9	9.6	7.7	5.8	8.1	6.0	2.6	43%
1,6-DMN	tr	tr	4.8	4.3	7.5	2.7	8.6	6.4	5.1	6.6	5.8	1.9	33%
1,4/2,3-DMN	tr	2.7	9.0	11	14	7.8	19	13	9.7	11	11	4.5	42%
1,5-DMN	tr	2.6	12	18	24	13	31	23	17	19	18	8.1	46%
1,2-DMN	nd	nd	2.9	4.1	5.4	2.9	6.5	5.9	4.8	5.7	4.8	1.4	29%
1,8-DMN.	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
1,6,7-TMN (not in totals)	tr	2.8	14	21	25	14	33	21	14	15	18	8.5	48%
Fluorene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Phenanthrene	11	7.5	12	13	15	7.2	8.5	12	8.7	15	11	2.9	26%
Anthracene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
4-MDBT	nd	9.4	26	31	45	21	18	26	18	21	24	10	42%
2/3-MDBT	nd	tr	10	10	14	6.5	6.7	11	8.4	9.9	9.6	2.4	25%
3-MP	nd	5.8	11	8.8	14	6.1	7.4	12	8.6	12	9.5	2.9	30%
1-MDBT	nd	11	35	38	56	27	25	36	30	33	32	12	37%
2-MP	nd	5.3	6.0	4.3	8.7	3.6	3.9	5.8	6.0	6.4	5.6	1.6	28%
4/9-MP	7.8	12	27	34	43	21	22	36	29	36	27	11	42%
1-MP	nd	5.8	14	17	21	11	11	17	15	17	14	4.5	31%
3,6-DMP	64	100	240	300	390	200	190	290	270	330	237	101	43%
2,6-DMP	tr	4.3	7.9	8.3	11	6.1	5.5	7.6	7.2	9.5	7.5	2.0	27%
2,7-DMP	22	43	100	130	160	81	77	120	110	140	98	43	44%
3,9-DMP	44	92	210	260	340	170	160	240	220	270	201	87	44%
1,6/2,5/2,9-DMP	49	98	230	280	370	180	170	270	240	300	219	96	44%
1,7-DMP	tr	9.1	18	22	29	15	12	19	16	20	18	5.8	33%
1,9/4,9-DMP	27	52	110	140	180	93	87	140	130	160	112	48	43%
Fluoranthene	19	29	68	84	120	60	52	87	79	99	70	31	44%
1,2-DMDBT (not in totals)	tr	3.8	6.9	7.5	9.5	5.1	5.1	6.4	6.6	6.3	6.4	1.6	26%

Table A3.8. Hydrocarbon concentrations (ppb) in a microcosm core collected on day 90. Core 9A (continued).

Analyte	Sect. 1 ppb	Sect. 2 ppb	Sect. 3 ppb	Sect. 4 ppb	Sect. 5 ppb	Sect. 6 ppb	Sect. 7 ppb	Sect. 8 ppb	Sect. 9 ppb	Sect. 10 ppb	MEAN ppb	S. D.	%RSD ppb
1,5-DMP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
1,8-DMP	17	30	58	71	93	45	36	58	57	72	54	22	42%
1,2-DMP	10	23	41	49	63	34	30	48	45	53	40	16	39%
9,10-DMP	tr	tr	8.8	11	11	6.7	6.4	7.7	9.5	11	9.0	1.9	21%
1,2,8-TMP (not in totals)	8.2	15	24	30	37	17	15	24	24	29	22	8.6	38%
Pyrene	32	47	80	90	130	64	56	88	84	98	77	28	37%
Benz(a)anthracene	tr	11	31	30	44	21	18	33	27	36	28	10	36%
Chrysene	44	60	120	130	160	74	80	140	120	170	110	43	39%
Benzo(b & k)fluoranthene	tr	tr	32	32	50	22	22	34	24	28	31	9.2	30%
Benzo(a)pyrene	nd	nd	17	18	30	14	tr	21	17	tr	20	5.6	29%
Benzo(e)pyrene	tr	tr	40	43	64	28	28	50	30	38	40	12	31%
Perylene	94	75	220	230	280	120	89	160	89	120	148	72	49%
Indeno(1,2,3-cd)pyrene	nd	nd	7.6	7.5	tr	nd	nd	5.3	5.0	tr	6.4	1.4	22%
Dibenz(a,h)anthracene	nd	nd	tr	nd	tr	nd	nd	tr	nd	tr	tr	NA	NA
Benzo(g,h,i)perylene	nd	tr	5.5	8.4	15	8.3	4.7	8.7	7.1	6.7	8.1	3.1	39%
C1-Naphthalenes, total	8.4	5.8	6.3	5.8	11	4.5	8.2	7.4	6.1	7.3	7.0	1.7	24%
C2-Naphthalenes, total	2.1	7.2	55	66	90	46	116	79	62	72	60	35	59%
C1-Dibenzothiophenes, total	0.0	20	71	79	115	55	50	73	56	64	58	32	54%
C1-Phenanthrenes, total	7.8	29	58	64	87	42	44	71	59	71	53	23	43%
C2-Phenanthrenes, total	233	451	1,024	1,271	1,647	831	774	1,200	1,105	1,366	990	428	43%
Total Parent PAH	224	242	639	693	922	425	365	646	497	619	527	219	41%
Total Alkylated PAH	251	514	1,214	1,486	1,949	978	992	1,430	1,288	1,580	1,168	506	43%
Total PAH	475	755	1,854	2,180	2,871	1,403	1,357	2,076	1,785	2,200	1,695	717	42%
Saturated Hydrocarbons													
Resolved	nd	380	16,000	15,000	23,000	13,000	8,100	24,000	20,000	22,000	15,720	7,752	49%
Unresolved	91,000	119,620	214,000	225,000	287,000	157,000	141,900	246,000	190,000	248,000	191,952	63,095	33%
Total	91,000	120,000	230,000	240,000	310,000	170,000	150,000	270,000	210,000	270,000	206,100	71,343	35%
MDL	7.6	4.2	1.7	2.3	2.5	1.6	1.4	1.3	1.3	1.8	2.6	2.0	77%

Table A3.9. Hydrocarbon concentrations (ppb) in a microcosm core collected on day 120. Replicate 1, core 12A.

Analyte	Sect. 1 ppb	Sect. 2 ppb	Sect. 3 ppb	Sect. 4 ppb	Sect. 5 ppb	Sect. 6 ppb	Sect. 7 ppb	Sect. 8 ppb	Sect. 9 ppb	Sect. 10 ppb	MEAN ppb	S. D.	%RSD ppb
Naphthalene	23	14	13	17	10	9.6	11	15	7.4	7.2	13	4.8	38%
2-Methylnaph.	tr	4.3	4.8	7.1	5.1	4.5	5.0	5.4	3.4	3.1	4.7	1.2	25%
1-Methylnaph.	tr	3.0	3.4	4.1	2.9	2.6	3.2	3.9	2.6	1.9	3.1	0.7	22%
2-Ethylnaph.	tr	nd	2.4	3.5	2.3	2.1	2.2	2.8	2.1	1.4	2.4	0.6	26%
1-Ethylnaph.	tr	nd	tr	tr	1.8	1.6	2.1	2.5	1.9	1.3	1.9	0.4	22%
2,6/2,7-Dimethylnaph.	tr	18	17	26	16	16	14	20	10	10	16	4.9	30%
1,3/1,7-DMN	tr	4.7	7.6	11	6.8	6.0	6.7	7.8	6.2	4.6	6.8	1.9	28%
1,6-DMN	tr	2.4	4.6	7.1	4.6	5.0	5.4	5.7	4.9	3.1	4.8	1.4	29%
1,4/2,3-DMN	tr	3.5	8.2	13	9.2	9.9	11	11	9.4	6.2	9.0	2.8	31%
1,5-DMN	tr	2.8	8.4	14	11	13	15	17	15	10	12	4.4	37%
1,2-DMN	nd	nd	3.8	5.0	3.8	3.4	4.5	4.5	4.3	2.6	4.0	0.8	19%
1,8-DMN.	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
1,6,7-TMN (not in totals)	nd	2.6	9.6	17	15	16	19	21	16	10	14	5.7	40%
Fluorene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Phenanthrene	23	10.0	12	17	13	11	12	13	10	9.0	13	4.2	32%
Anthracene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
4-MDBT	nd	5.5	13	17	15	15	17	17	16	12	14	3.7	26%
2/3-MDBT	nd	nd	6.8	3.3	7.9	7.0	7.6	7.3	7.1	5.8	6.6	1.5	22%
3-MP	6.8	7.1	12	11	6.2	7.0	7.2	6.4	7.9	4.5	7.6	2.2	30%
1-MDBT	nd	tr	5.6	9.0	20	14	24	25	23	13	17	7.3	44%
2-MP	tr	4.6	5.7	7.0	5.3	4.1	4.4	5.4	4.5	3.3	4.9	1.1	22%
4/9-MP	tr	10.0	19	24	25	27	30	30	26	20	23	6.3	27%
1-MP	tr	6.6	7.6	10	10	11	8.4	13	11	8.7	9.6	2.0	21%
3,6-DMP	53	83	180	240	250	260	250	270	200	190	198	75	38%
2,6-DMP	tr	3.1	4.9	5.7	5.5	4.3	5.3	4.8	4.2	3.0	4.5	1.0	22%
2,7-DMP	15	33	76	100	100	111	100	120	86	83	82	34	41%
3,9-DMP	7.5	60	130	180	180	194	180	210	150	140	143	64	45%
1,6/2,5/2,9-DMP	23	72	160	210	220	230	220	240	170	170	172	72	42%
1,7-DMP	tr	5.0	8.3	11	11	11	10	12	9.6	7.7	9.5	2.2	23%
1,9/4,9-DMP	8.8	37	86	73	120	130	120	130	96	94	89	40	45%
Fluoranthene	25	28	56	120	72	78	72	82	62	57	65	27	42%
1,2-DMDBT (not in totals)	nd	tr	4.5	5.0	3.9	4.0	4.8	5.0	4.6	3.2	4.4	0.6	14%
1,5-DMP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA

Table A3.9. Hydrocarbon concentrations (ppb) in a microcosm core collected on day 120. Replicate 1, core 12A (continued).

Analyte	Sect. 1 ppb	Sect. 2 ppb	Sect. 3 ppb	Sect. 4 ppb	Sect. 5 ppb	Sect. 6 ppb	Sect. 7 ppb	Sect. 8 ppb	Sect. 9 ppb	Sect. 10 ppb	MEAN ppb	S. D.	%RSD ppb
1,8-DMP	12	20	47	62	58	62	56	63	42	37	46	18	40%
1,2-DMP	tr	17	32	42	37	40	38	41	30	30	34	7.9	23%
9,10-DMP	nd	nd	7.3	7.5	6.5	7.3	5.8	nd	4.9	5.2	6.4	1.1	17%
1,2,8-TMP (not in totals)	tr	11	21	25	23	23	21	24	14	15	20	5.0	26%
Pyrene	nd	39	70	86	75	84	79	87	65	63	72	15	21%
Benz(a)anthracene	nd	12	19	31	24	26	25	23	22	17	22	5.5	25%
Chrysene	42	60	97	140	100	120	110	120	99	89	98	29	30%
Benzo(b & k)fluoranthene	tr	tr	16	18	22	23	22	24	13	17	19	3.9	20%
Benzo(a)pyrene	nd	nd	nd	tr	tr	tr	16	nd	11	tr	14	3.5	26%
Benzo(e)pyrene	nd	tr	40	45	44	39	35	42	11	25	35	12	33%
Perylene	nd	81	150	190	160	160	160	180	130	86	144	38	27%
Indeno(1,2,3-cd)pyrene	nd	tr	24	tr	tr	tr	21	tr	20	nd	22	2.1	10%
Dibenz(a,h)anthracene	nd	nd	tr	nd	tr	tr	tr	nd	tr	nd	tr	NA	NA
Benzo(g,h,i)perylene	nd	tr	tr	33	tr	tr	19	tr	11	tr	21	11	53%
C1-Naphthalenes, total	0.0	7.3	8.2	11	8.0	7.1	8.2	9.3	6.0	5.0	7.0	3.0	43%
C2-Naphthalenes, total	0.0	31	52	80	56	57	61	71	54	39	50	22	45%
C1-Dibenzothiophenes, total	0.0	5.5	25	29	43	36	49	49	46	31	31	17	55%
C1-Phenanthrenes, total	6.8	28	44	52	47	49	50	55	49	37	42	15	35%
C2-Phenanthrenes, total	119	330	732	931	988	1,050	985	1,091	793	760	778	320	41%
Total Parent PAH	113	244	497	697	520	551	582	586	461	370	462	175	38%
Total Alkylated PAH	126	403	861	1,103	1,141	1,199	1,153	1,276	948	871	908	372	41%
Total PAH	239	647	1,358	1,800	1,661	1,749	1,735	1,862	1,409	1,241	1,370	538	39%
Saturated Hydrocarbons													
Resolved	2,200	780	5,000	8,500	9,200	13,000	11,000	9,100	16,000	8,800	8,358	4,655	56%
Unresolved	93,800	109,220	175,000	211,500	200,800	207,000	189,000	200,900	164,000	161,200	171,242	40,797	24%
Total	96,000	110,000	180,000	220,000	210,000	220,000	200,000	210,000	180,000	170,000	179,600	44,038	25%
MDL	6.5	2.6	1.8	1.9	1.7	1.6	1.4	1.8	0.82	1.4	2.2	1.6	74%

Table A3.10. Hydrocarbon concentrations (ppb) in a microcosm core collected on day 120. Replicate 2, core 3B.

Analyte	Sect. 1 ppb	Sect. 2 ppb	Sect. 3 ppb	Sect. 4 ppb	Sect. 5 ppb	Sect. 6 ppb	Sect. 7 ppb	Sect. 8 ppb	Sect. 9 ppb	Sect. 10 ppb	MEAN ppb	S. D.	%RSD
Naphthalene	35	21	15	16	13	11	12	11	12	9.9	16	7.6	48%
2-Methylnaph.	8.8	6.3	5.7	5.2	4.7	5.4	4.6	3.6	6.1	3.7	5.4	1.5	28%
1-Methylnaph.	4.8	3.6	4.0	3.1	2.9	2.9	3.1	3.0	3.9	3.2	3.5	0.6	18%
2-Ethylnaph.	nd	tr	2.0	2.3	2.5	2.7	2.3	2.6	3.3	2.8	2.6	0.4	15%
1-Ethylnaph.	nd	nd	nd	1.7	2.0	2.2	1.9	2.2	3.0	2.8	2.3	0.5	21%
2,6/2,7-Dimethylnaph.	nd	11	22	13	32	28	27	32	32	33	26	8.4	33%
1,3/1,7-DMN	6.9	5.7	6.7	6.3	6.6	6.9	6.6	6.6	8.6	8.2	6.9	0.9	12%
1,6-DMN	3.2	3.4	4.2	5.8	3.5	7.5	7.0	4.3	4.0	7.4	5.0	1.7	34%
1,4/2,3-DMN	3.8	4.8	6.5	8.5	10	13	12	12	15	13	10	3.8	39%
1,5-DMN	tr	3.7	6.4	11	15	18	18	19	24	22	15	6.9	45%
1,2-DMN	nd	1.5	2.6	3.6	4.6	4.9	4.1	4.7	6.7	6.6	4.4	1.7	39%
1,8-DMN.	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
1,6,7-TMN (not in totals)	3.2	4.7	7.1	11	15	20	21	20	22	20	14	7.3	51%
Fluorene	4.0	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
Phenanthrene	31	16	15	14	17	13	13	13	15	15	16	5.4	33%
Anthracene	15	11	9.1	nd	nd	13	nd	nd	nd	8.8	11	2.6	23%
4-MDBT	7.8	11	13	17	20	27	28	23	21	17	18	6.6	36%
2/3-MDBT	3.4	5.7	6.0	7.5	7.3	8.2	8.2	7.2	7.7	7.0	6.8	1.5	21%
3-MP	9.4	8.2	8.9	11	11	10	11	10	11	11	10	1.0	10%
1-MDBT	3.9	8.4	13	18	26	36	37	33	31	24	23	12	51%
2-MP	7.6	7.4	8.5	11	9.5	8.8	8.4	7.4	8.1	7.7	8.4	1.1	13%
4/9-MP	10	14	19	25	23	39	31	30	32	29	25	8.9	35%
1-MP	7.2	7.1	8.7	9.3	16	8.7	21	20	21	19	14	6.1	44%
3,6-DMP	52	110	130	170	190	220	230	230	210	190	173	59	34%
2,6-DMP	3.0	4.3	4.5	5.0	4.8	5.9	4.9	4.7	5.1	5.1	4.7	0.7	16%
2,7-DMP	16	48	61	78	88	99	100	100	94	85	77	28	36%
3,9-DMP	34	88	110	150	160	180	200	200	170	150	144	53	37%
1,6/2,5/2,9-DMP	39	110	140	180	200	220	230	230	200	180	173	61	35%
1,7-DMP	4.1	7.6	8.6	9.7	12	13	13	12	13	10	10	2.9	28%
1,9/4,9-DMP	17	52	72	92	100	110	120	120	110	97	89	33	37%
Fluoranthene	22	36	46	57	64	72	78	78	71	63	59	19	32%
1,2-DMDBT (not in totals)	tr	tr	3.3	3.6	4.4	4.4	5.3	5.4	4.6	3.8	4.4	0.8	17%

Table A3.10. Hydrocarbon concentrations (ppb) in a microcosm core collected on day 120. Replicate 2, core 3B (continued).

Analyte	Sect. 1 ppb	Sect. 2 ppb	Sect. 3 ppb	Sect. 4 ppb	Sect. 5 ppb	Sect. 6 ppb	Sect. 7 ppb	Sect. 8 ppb	Sect. 9 ppb	Sect. 10 ppb	MEAN ppb	S. D.	%RSD
1,5-DMP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	NA	NA
1,8-DMP	10	28	38	41	50	54	57	54	39	33	40	14	36%
1,2-DMP	6.9	22	25	28	31	33	34	34	33	27	27	8.3	30%
9,10-DMP	5.3	5.7	6.9	7.3	nd	6.1	6.7	6.7	5.9	4.6	6.1	0.9	14%
1,2,8-TMP (not in totals)	6.5	13	17	17	16	17	19	18	14	11	15	3.8	26%
Pyrene	29	46	55	62	68	71	76	79	70	60	62	15	25%
Benz(a)anthracene	14	18	20	24	30	33	35	32	35	29	27	7.5	28%
Chrysene	110	100	110	130	130	150	150	150	150	140	132	19	15%
Benzo(b & k)fluoranthene	tr	24	28	23	27	32	35	34	35	29	30	4.6	15%
Benzo(a)pyrene	nd	nd	tr	tr	14	25	20	18	22	16	19	4.0	21%
Benzo(e)pyrene	43	27	32	28	31	38	36	48	37	36	36	6.5	18%
Perylene	170	160	160	160	170	220	220	190	180	120	175	30	17%
Indeno(1,2,3-cd)pyrene	tr	tr	18	29	17	23	22	tr	20	24	22	4	19%
Dibenz(a,h)anthracene	nd	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	NA	NA
Benzo(g,h,i)perylene	tr	tr	26	24	28	28	25	28	24	35	27	3.6	13%
C1-Naphthalenes, total	14	9.9	9.7	8.3	7.6	8.3	7.7	6.6	10	6.9	8.9	2.1	23%
C2-Naphthalenes, total	14	30	50	52	76	83	79	83	97	96	66	28	43%
C1-Dibenzothiophenes, total	15	25	32	43	53	71	73	63	60	48	48	20	41%
C1-Phenanthrenes, total	34	37	45	56	60	67	71	67	72	67	58	14	25%
C2-Phenanthrenes, total	187	476	596	761	836	941	996	991	880	782	745	257	35%
Total Parent PAH	473	459	534	567	609	729	722	681	671	586	603	97	16%
Total Alkylated PAH	264	577	733	920	1,032	1,170	1,227	1,212	1,118	999	925	313	34%
Total PAH	737	1,036	1,267	1,487	1,641	1,899	1,949	1,893	1,789	1,585	1,528	404	26%
Saturated Hydrocarbons													
Resolved	2,700	2,700	5,900	9,800	12,000	16,000	13,000	14,000	20,000	18,000	11,410	6,079	53%
Unresolved	82,300	117,300	134,100	180,200	168,000	184,000	187,000	186,000	210,000	182,000	163,090	39,261	24%
Total	85,000	120,000	140,000	190,000	180,000	200,000	200,000	200,000	230,000	200,000	174,500	44,873	26%
MDL	2.0	1.0	0.92	0.94	0.69	0.71	0.90	0.94	0.75	0.59	0.94	0.39	42%

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.

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U.S. DEPARTMENT OF THE INTERIOR
MINERALS MANAGEMENT SERVICE