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MONITORING ENVIRONMENTAL RECOVERY AT TERMINATED PRODUCED WATER DISCHARGE SITES IN COASTAL LOUISIANA WATERS

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Continental Shelf Associates, Inc.
Jupiter, Florida

National Petroleum Technology Office
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Monitoring Environmental Recovery at Terminated Produced Water Discharge Sites in Coastal Louisiana Waters

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Work Performed Under Contract DE-AC22-91MT92001

Prepared for
U.S. Department of Energy
Assistant Secretary for Fossil Energy

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LIST OF ACRONYMS

AAS	atomic absorption spectrometry
ADL	Arthur D. Little, Inc.
BNL	Brookhaven National Laboratory
CORE	Core Laboratories, Inc.
CSA	Continental Shelf Associates, Inc.
DOE	U.S. Department of Energy
EPA	Environmental Protection Agency
ERL	effects range-low
ERM	effects range-median
FIT	Florida Institute of Technology
GC/FID	gas chromatography/flame ionization detection
GC/MS	gas chromatography/mass spectrometry
HPLC	high-performance liquid chromatography
LDEQ	Louisiana Department of Environmental Quality
LIMS	Laboratory Information Management System
LLD	lower limit of detection
MDL	method detection limit
MMS	Minerals Management Service
ND	not detected
NIST	National Institute for Standards and Technology
NRC	National Research Council
OOC	Offshore Operators Committee
PAH	polycyclic aromatic hydrocarbon
QA	quality assurance
QC	quality control
RPD	relative percent difference
RSD	relative standard deviation
S&A	Steimle & Associates, Inc.
SAP	Sampling and Analysis Plan
SHC	saturated hydrocarbon
SIM	selected ion monitoring
SOP	Standard Operating Procedure
SRC	Scientific Review Committee
SRM	Standard Reference Material
THC	total hydrocarbon
TOC	total organic carbon
UCM	unresolved complex mixture
VAH	volatile aromatic hydrocarbon

ABSTRACT

This report presents the results of a study of terminated produced water discharge sites in the coastal waters of Louisiana. Environmental recovery at the sites is documented by comparing pre-termination and post-termination (six months and one year) data. Produced water, sediments, and sediment interstitial water samples were analyzed for radionuclides, metals, and hydrocarbons. Benthic infauna were identified from samples collected in the vicinity of the discharge and reference sites. Radium isotope activities were determined in fish and crustacean samples. In addition, an environmental risk assessment is made on the basis of the concentrations of metals and hydrocarbons determined in the samples.

EXECUTIVE SUMMARY

Introduction

This study was completed as part of a U.S. Department of Energy sponsored project entitled "Environmental and Economic Assessment of Discharges from Gulf of Mexico Region Oil and Gas Operations" (Contract No. DE-AC22-92MT92001). The objective of this study was to determine the extent and rate of recovery of environmentally impacted produced water discharge sites in coastal waters of Louisiana by analyzing produced water, sediments, sediment interstitial water, and faunal samples collected during pre- and post-termination surveys. These data are used in environmental and human health risk assessments. Metal and hydrocarbon data are utilized in this report for an environmental risk assessment. Radionuclide, metal, and hydrocarbon data are incorporated into environmental (radionuclide data) and human health (radionuclide, metal, and hydrocarbon data) risk analysis being performed by Brookhaven National Laboratory.

Study Sites

Three oil production facilities were selected for sampling. They were located in coastal waters (tidal wetlands) of Louisiana in water depths of approximately 1 to 3 m and had produced water discharges ranging from approximately 850 to 3,800 barrels/day prior to produced water discharge termination.

Quality Assurance Program

This study was conducted under a Quality Assurance Program that encompassed all aspects of sample and data collection, processing, analysis, and management. The primary purpose of the Program was to document the sample and data collection and analysis process, provide statistically valid measures of uncertainty, maintain data integrity, and ensure that the QA Program was operating as required.

Sampling Program

Sampling was conducted at each of the three facilities before termination of the produced water discharges and at two of the facilities approximately six months after the termination, and again approximately one year after the first field survey. The termination of the produced water discharge was delayed approximately one year from the pre-termination sampling at the third facility which did not allow for post-termination sampling within the schedule of this study.

Produced water was collected from each facility prior to termination. Water quality and limited current data were collected at the discharge location and two reference sites for each facility on all surveys. Sediment samples (surficial sediments and deeper strata) were collected at the three discharge locations, several stations located at different distances along transects radiating from the discharges, and two reference stations away from the influence of each produced water discharge. One to three replicate samples were collected at each sampling station on each survey. Three replicate sediment interstitial water samples (surficial sediments and deeper layers) were collected at the discharge locations and reference sites. Six replicate benthic infauna samples also were collected at all the sediment sampling stations. Fish and invertebrates were also collected in the vicinity of the two facilities where multiple surveys were conducted.

Produced water, sediment, and sediment interstitial water samples were analyzed for radionuclides, several metals, and polycyclic aromatic hydrocarbons (PAHs). Volatile aromatic hydrocarbons (VAHs) and saturated hydrocarbons (SHCs) also were analyzed in produced water and sediments (VAHs in sediments from only the discharge and reference sites). The metals analyzed in all samples were arsenic, barium, cadmium, chromium, copper, iron, lead, manganese, mercury, molybdenum, nickel, vanadium, and zinc. Aluminum, calcium, and sulfate also were analyzed in sediment samples. Percent total organic carbon (TOC) and grain size were analyzed in sediments, and TOC, chlorinity, and sulfate were analyzed in sediment interstitial water. Four of the replicate benthic infauna samples were analyzed at two of the facilities and three analyzed at the facility where only pre-termination sampling was conducted. The fish and invertebrates were analyzed for radium isotopes.

Radionuclide Activities

The produced water sample mean radionuclide activities (163 to 253 pCi/L ^{226}Ra and 249 to 318 pCi/L ^{228}Ra) were within the range of previously published data. The activities of ^{210}Pb, ^{210}Po, and ^{228}Th in the produced water samples were substantially lower than those of the radium isotopes.

The mean activities in the surficial sediments (0 to 5 cm) in the vicinity of the discharge locations were generally low (approximately ≤11 and ≤3 pCi/g dry weight ^{226}Ra and ^{228}Ra, respectively) and similar to the reference sites (approximately ≤5 pCi/g dry weight for both ^{226}Ra and ^{228}Ra) during all surveys. The activities also decreased following the termination of the produced water discharges. The mean activities in the deeper strata (20 to 25 and 35 to 40 cm) were also low (approximately ≤10 pCi/g dry weight for both) with the exception of the samples from one of the discharge locations in the 35 to 40 cm strata (approximately 50 pCi/g dry weight for ^{228}Ra) prior to produced water discharge termination. No samples were collected at depth following termination in the vicinity of this facility though increases were observed at the other facility in the 20 to 25 cm stratum and decreases in the 35 to 40 cm stratum.

The pre-termination activities in the sediment interstitial water from surficial sediments (0 to 5 cm) at the discharge locations were generally low (approximately ≤10 pCi/L for both ^{226}Ra and ^{228}Ra) and similar to the reference sites at two of the facilities. The third facility had much higher activities (108 to 143 and 118 to 162 pCi/L ^{226}Ra and ^{228}Ra, respectively) which declined to reference site levels in post-termination samples. Slightly higher activities were found in some of the deeper strata samples collected during pre- and post-termination sampling in comparison with the reference sites at the single discharge location where post-termination samples were collected.

Radionuclide activities in crustacean and fish samples were very low in pre- and post-termination samples. Activities ranged from 0.004 to 0.063 and 0.01 to 0.27 pCi/g wet weight ^{226}Ra and ^{228}Ra, respectively.

Environmental Risk Assessment for Metals and Aromatic Hydrocarbons

Produced Water and Ambient Water

The discharged produced water sampled prior to termination contained elevated concentrations (compared to the estimated concentrations in local receiving waters) of several metals (barium, iron, and magnesium at 1,000 fold and lead and zinc at 100 fold) and hydrocarbons. Concentrations of all metals, except barium, in a 100-fold dilution of the produced waters (the maximum likely exposure concentration to local aquatic biota) were below concentrations equivalent to 1 toxic unit (ambient water concentration/water quality criterion value). Concentrations below 1 toxic unit are not expected to be toxic to estuarine and marine organisms. Barium probably precipitated as barite following discharge and so may have been present in a dissolved, bioavailable form in the receiving water at a concentration much lower than 1/100 the concentration in the produced water. VAHs and PAHs were present in 100-fold dilutions of the produced water at concentrations well below 1 toxic unit. Therefore, after initial dilution in the receiving waters, treated produced water from the three facilities was not expected to be toxic to local estuarine and marine organisms.

Sediment and Sediment Interstitial Water

Concentrations of several metals were elevated in sediments near the produced water discharges before and after termination of the discharges. For those metals for which estimates of the toxicity (screening concentrations) in sediments are available, none were present in sediment near the three discharges at concentrations higher than 1 toxic unit either before or after termination of the produced water discharges. Concentrations of most metals did not decrease in sediments near the production facilities following termination of the discharges. Most of the metals, except barium, were natural constituents of the local sediments and were not derived from the produced water discharges.

Sediment interstitial water near the three production facilities also contained elevated concentrations (compared to background concentrations in clean estuarine waters) of several metals. Concentrations of barium, iron, and manganese in most sediment interstitial water samples from the three discharge sites were well above those equivalent to 1 toxic unit. A few interstitial water samples also contained cadmium, copper, lead, or nickel concentrations equivalent to 1 toxic unit or slightly more. All metals, except manganese, were present in sediment interstitial samples collected from the discharge and reference sites at one of the facilities on a post-termination survey at concentrations equivalent to less than 1 toxic unit. The physical and chemical forms of barium, iron, and manganese in the sediment interstitial water are not known. They were most probably in microparticulate form or complexed with dissolved or colloidal organic matter in the sediment interstitial water. Thus, these interstitial water metals may not have been present in toxic forms. If they were bioavailable, they probably contributed to the toxicity of the sediments before termination of the produced water discharges. After termination of the produced water discharge at the single facility, where post-termination samples were collected, concentrations of metals in sediment interstitial water near the facility decreased, suggesting that they were derived at least in part from the produced water discharge.

Concentrations of chloride and salinity also were elevated in sediment interstitial water from the discharge sites before termination of the discharges. The salinity was high enough and ionic ratios in the interstitial waters probably were sufficiently different from those in the overlying brackish water that the sediments may have been unsuitable for habitation by benthic organisms.

Concentrations of VAHs were present in only a few sediment samples from the vicinity of two of the facilities. The concentrations were below those that might be expected to be toxic to benthic organisms. However, total PAH concentrations in surficial sediments from two of the three discharge sites before termination of the produced water discharges were equivalent to slightly more than 1 toxic unit. These sediment PAHs may have contributed to the toxicity of the sediments to benthic infauna. Sediments along one of the transects from one facility near a former fuel dock and pipe storage facility also contained potentially toxic concentrations of total PAHs. Sediments from this location were the only ones containing potentially toxic concentrations of PAHs at the time of the post-termination surveys. Most of the PAHs detected in sediments near the three production facilities were pyrogenic, probably derived from creosote from wood pilings at the facility. The contribution of produced water to the PAH concentrations in sediments at all sampling stations except the discharge sites probably was small.

Infauna

Benthic infauna were adversely affected at two of the discharge sites before termination of the produced water discharges. The evidence indicate that the adverse effects on the infauna probably were caused by a combination of elevated concentrations of chloride, barium, iron, manganese, and PAHs. The chloride and PAHs probably contributed the most to the unsuitability of the sediments near the discharges for habitation by several species of benthic infauna found at greater distances from the discharges. Concentrations of these chemicals in sediments returned to near background levels after termination of the produced water discharges. Concentrations of pyrogenic, creosote-derived PAHs still were high in sediments. There was strong evidence of some recovery of the benthic communities after termination of the discharges. The observed reductions in sediment contamination probably allowed benthic infauna to recolonize the affected substrates.

CHAPTER 1 - INTRODUCTION

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1.1 BACKGROUND

Hydrocarbon resource production operations result in the recovery of oil and/or natural gas as well as various by-products. By-products include produced water which is obtained from the formation as part of the oil and/or gas production stream. Produced water may contain varying concentrations of radionuclides, metals, and hydrocarbons. In addition, the volumes of produced water vary greatly depending on the hydrocarbon reservoir and production operations.

The discharge of produced water in coastal areas of Louisiana and Texas (U.S. Environmental Protection Agency [EPA] Coastal Subcategory of the Oil and Gas Extraction Point Source Category) was prohibited by EPA Region VI National Pollutant Discharge Elimination System as of 1 January 1997 (60 FR 2387, January 9, 1995). The EPA regulatory definition of "coastal" is any body of water landward of the territorial seas whose shoreward limit for this purpose is the line marking the seaward limit of inland water or any wetlands adjacent to such waters. The State of Louisiana began a phased prohibition of produced water discharges in coastal areas beginning on 1 January 1993 with completion on 1 January 1997.

1.2 OBJECTIVES OF THE PROJECT

This study (task) was completed as part of a U.S. Department of Energy (DOE) sponsored project entitled "Environmental and Economic Assessment of Discharges from Gulf of Mexico Region Oil and Gas Operations." A primary objective of the project was to increase the scientific knowledge of the environmental fate and effects of constituents found in produced water. This study of terminated produced water discharge sites in coastal Louisiana and a second study conducted under this project of active produced water discharge sites in offshore Gulf of Mexico waters (Continental Shelf Associates, Inc., 1997) address this objective. A third study by Steimle & Associates, Inc. was implemented to detail the catch, consumption, and human use patterns of seafood collected from coastal and offshore waters of the Gulf of Mexico (Continental Shelf Associates, Inc., 1996a). The data from these three studies were provided as input into an environmental risk assessment and a human health risk analysis. A second objective of this project was to evaluate and assess (i.e., predict) the economic impacts of proposed regulations on offshore oil and gas producers in the Gulf of Mexico region. This objective was addressed in a report by ICF Resources, Inc. (Continental Shelf Associates, Inc., 1996b).

1.3 OBJECTIVES OF THE STUDY

The overall objective of this study was to determine the extent and rate of recovery of environmentally impacted produced water discharge sites in coastal areas of Louisiana and Texas by collecting chemical, geological, and biological samples during pre- and post-termination surveys of the sites. Produced water, sediments, and interstitial water samples were to be collected and analyzed for radionuclides, metals, hydrocarbons, total organic carbon (TOC), (produced water and sediment), grain size (sediment), chlorinity (interstitial water), and sulfate (interstitial water). Bottom dwelling organisms (infauna) were also to be collected and identified.

Fish and larger invertebrates were to be collected and analyzed for radionuclide levels. Measurements of water quality and currents were also to be conducted. In addition to determining environmental recovery, a portion of these data were to be used in an environmental risk assessment for metals and hydrocarbons, which is part of this report. Brookhaven National Laboratory (BNL) was to use the radionuclide data for an environmental risk assessment of radionuclides and the radionuclide, metal, and hydrocarbon data for a human health risk assessment (Holtzman *et al.*, 1995; Meinhold *et al.*, 1996a,b).

1.4 REFERENCES

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1.5 ACKNOWLEDGEMENTS

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CHAPTER 2 - STUDY DESIGN AND OVERVIEW

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2.1 SELECTION OF SITES

A listing of Louisiana and Texas produced water discharge sites in coastal canals and bays was obtained along with produced water discharge termination schedules from the Louisiana Department of Environmental Quality and Texas Railroad Commission (sites only). The Operators in Texas were contacted to determine termination schedules. No suitable Texas sites had termination schedules which fit the schedule of this study. Only a few Louisiana sites had current discharges of greater than 500 barrels (bbl)/day in canals and bays, termination schedules which fit the schedule of this study, and were not in the direct path of Hurricane Andrew which impacted Louisiana at the time of the site selection process (August 1992). Sites in the direct path were avoided due to the potential sediment redistribution that might have occurred at those sites.

Three facilities were selected as study sites:

- Delacroix Island Tank Battery #1,
- Bay de Chene Tank Battery #5, and
- Four Isle Dome Central Production Facility.

Figure 2.1 shows the locations of these sites as well as the path of Hurricane Andrew. Delacroix Island and Bay de Chene are open water sites while Four Isle Dome is a canal site. The scheduled dates for termination of produced water discharges from these facilities at the time of selection were May 1993, July 1993, and January 1994, respectively.

2.2 SURVEYS AND SAMPLING ELEMENTS

The scope of the sampling and analysis effort was based on guidance and comments received from DOE representatives and a 24 member Scientific Review Committee (SRC). The members included representatives from the States of Louisiana and Texas (State of Louisiana Department of Environmental Quality, State of Texas Railroad Commission, and State of Texas Water Commission), U.S. government agencies (EPA, U.S. Fish and Wildlife Service, Minerals Management Service [MMS], and National Oceanic and Atmospheric Administration), BNL, and oil industry groups (American Petroleum Institute, Gas Research Institute, Louisiana Association of Independent Producers and Royalty Owners, Louisiana Mid-Continent Oil and Gas Association, Texas Mid-Continental Oil and Gas Association, and Offshore Operators Committee [OOC]).

Sampling was to include one survey prior to cessation of produced water discharges and two surveys after cessation. The survey schedule that was developed is presented in **Table 2.1**.

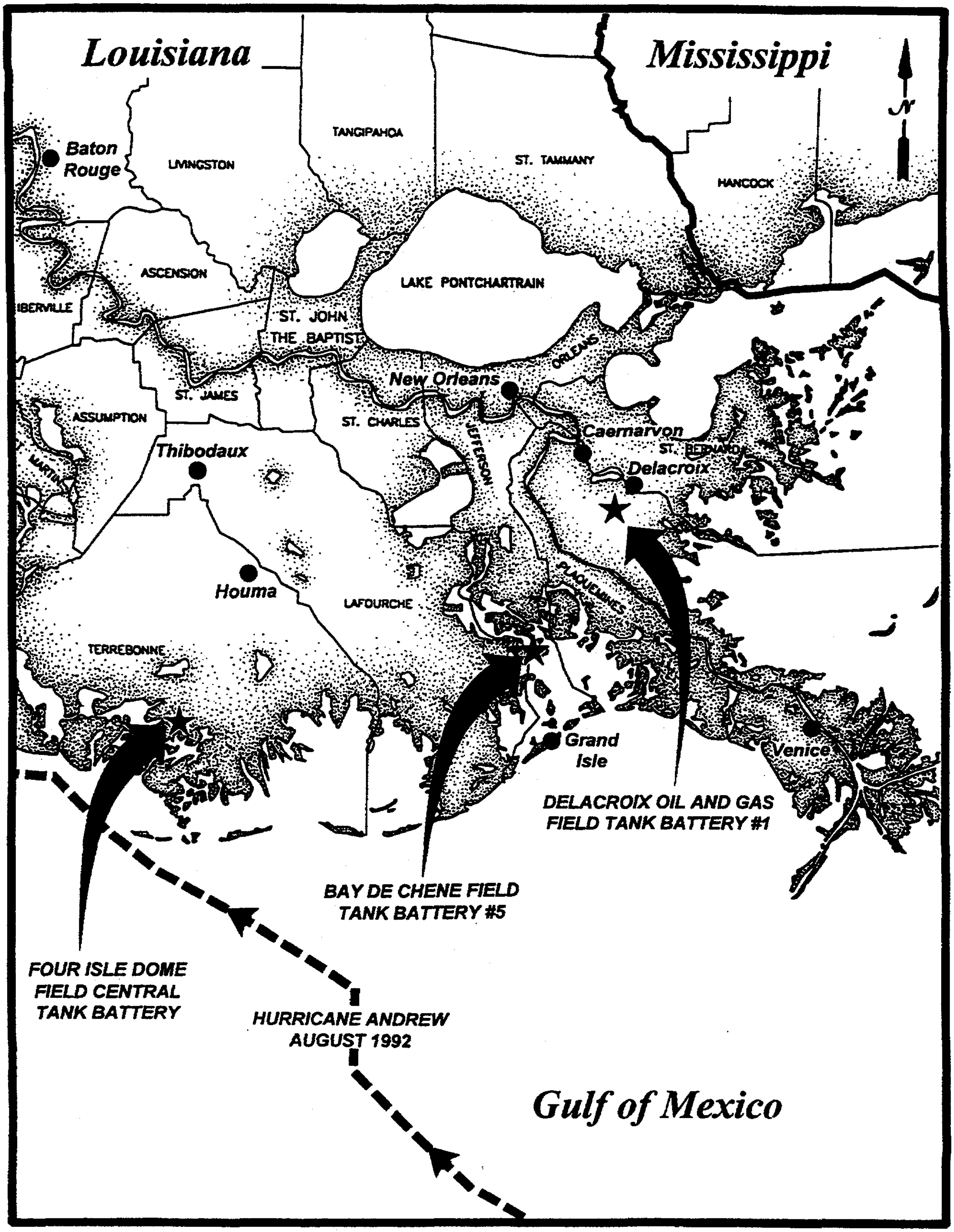

Figure 2.1. Location of sites in relation to path of Hurricane Andrew.

Table 2.1. Survey schedule.

Survey	Sites		
	Delacroix Island	Bay de Chene	Four Isle Dome
Pre-termination	Spring 1993	Spring 1993	Fall 1993
Estimated Termination Date	April 1993	August 1993	January 1994
First Post-termination	Fall 1993	Fall 1993	Spring 1994
Second Post-termination	Spring 1994	Spring 1994	Fall 1994

The sample collection effort at each site was to be comprised of two types of surveys. An expanded sampling effort was to be conducted during the Pre-termination Survey and Second Post-termination Survey. The Second Post-termination Survey was to be conducted in the same season as the Pre-termination Survey. Samples and data to be collected were to include the following elements:

- Water quality and currents;
- Surficial sediments to evaluate the temporal changes in spatial distributions of produced water constituents and to provide data to interpret the distributions of the infauna;
- Sediments at two depths in the surficial sediment column to evaluate the penetration of produced water into the sediments;
- Infauna to examine the biological effect of the discharges and recovery of the infauna after cessation of the discharges;
- Sediment interstitial water at three depths in the sediment column to evaluate the penetration of produced water into the sediments; and
- Biological tissues for risk assessment.

The marsh sediments in the vicinity of the discharge point were to be sampled on the Pre-termination Survey at Four Isle Dome. The data were to be evaluated and marsh sediments were to be collected during the Second Post-termination Survey if necessary.

A reduced sampling effort was to be conducted during the First Post-termination Survey. Sample collection for this survey was to include the following elements:

- Water quality;
- Surficial sediment; and
- Infauna.

2.3 SAMPLE AND DATA COLLECTION

Table 2.2 lists the sample and data types, type and number of sampling stations, number of samples to be collected per station, and analyses to be conducted at the three sites.

Table 2.2. Summary of sampling to be conducted.

Sample/Data Type	Station Location (number of stations) (number of samples per station)			Type of Laboratory Analysis
	Pre-termination Survey	First Post-termination Survey	Second Post-termination Survey	
Water Quality	Discharge (1) (2) Reference (2) (2)	Discharge (1) (2) Reference (2) (2)	Discharge (1) (2) Reference (2) (2)	--
Currents	Discharge (1) (1) Reference (2) (1)	-- --	-- --	--
Produced Water	Discharge (1) (8)	--	--	Radionuclides (^{226}Ra, ^{228}Ra, ^{210}Pb, ^{210}Po, ^{228}Th)
	Discharge (1) (8)	--	--	Metals (As, Ba, Cd, Cu, Fe, Hg, Mn, Mo, Ni, Pb, V, Zn)
	Discharge (1) (8)	--	--	Hydrocarbons (VAHs, SHCs, PAHs)
	Discharge (1) (8)	--	--	Total organic carbon
Surficial Sediments (0-5 cm)	Discharge (1) (3) Transect (4) (3) Transect (7) (1) Reference (2) (3)	Discharge (1) (3) Transect (4) (3) Transect (7) (1) Reference (2) (3)	Discharge (1) (3) Transect (4) (3) Transect (7) (1) Reference (2) (3)	Radionuclides (^{226}Ra and ^{228}Ra)
	Discharge (1) (3) Transect (4) (3) Transect (7) (1) Reference (2) (3)	Discharge (1) (3) Transect (4) (3) Transect (7) (1) Reference (2) (3)	Discharge (1) (3) Transect (4) (3) Transect (7) (1) Reference (2) (3)	Metals (Al, As, Ba, Cd, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, V, Zn)
	Discharge (1) (3) Transect (4) (3) Transect (7) (1) Reference (2) (3)	Discharge (1) (3) Transect (4) (3) Transect (7) (1) Reference (2) (3)	Discharge (1) (3) Transect (4) (3) Transect (7) (1) Reference (2) (3)	Hydrocarbons (SHCs/PAHs)
	Discharge (1) (1) Reference (2) (1)	--	Discharge (1) (1) Reference (2) (1)	Hydrocarbons (VAHs)
	Discharge (1) (3) Transect (4) (3) Transect (7) (1) Reference (2) (3)	Discharge (1) (3) Transect (4) (3) Transect (7) (1) Reference (2) (3)	Discharge (1) (3) Transect (4) (3) Transect (7) (1) Reference (2) (3)	Total organic carbon

Table 2.2. (Continued).

Sample/Data Type	Station Location (number of stations) (number of samples per station)			Type of Laboratory Analysis
	Pre-termination Survey	First Post-termination Survey	Second Post-termination Survey	
	Discharge (1) (3) Transect (4) (3) Transect (7) (1) Reference (2) (3)	Discharge (1) (3) Transect (4) (3) Transect (7) (1) Reference (2) (3)	Discharge (1) (3) Transect (4) (3) Transect (7) (1) Reference (2) (3)	Grain size
Deeper Sediments (25-30 and 50-55 cm)	Discharge (1) (3) Reference (2) (3)	--	Discharge (1) (3) Reference (2) (3)	Radionuclides (^{226}Ra and ^{228}Ra)
	Discharge (1) (3) Reference (2) (3)		Discharge (1) (3) Reference (2) (3)	Metals (Al, As, Ba, Cd, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, V, Zn)
	Discharge (1) (3) Reference (2) (3)		Discharge (1) (3) Reference (2) (3)	Hydrocarbons (SHCs/PAHs)
	Discharge (1) (3) Reference (2) (3)		Discharge (1) (3) Reference (2) (3)	Total organic carbon
	Discharge (1) (3) Reference (2) (3)		Discharge (1) (3) Reference (2) (3)	Grain size
Interstitial Water (0-5, 25-30, and 50-55 cm)	Discharge (1) (3) Reference (2) (3)	--	Discharge (1) (3) Reference (2) (3)	Radionuclides (^{226}Ra and ^{228}Ra)
	Discharge (1) (3) Reference (2) (3)	--	Discharge (1) (3) Reference (2) (3)	Metals (0-5 cm only) (As, Ba, Cd, Cu, Fe, Hg, Pb, Mn, Mo, Ni, V, Zn)
	Discharge (1) (3) Reference (2) (3)	--	Discharge (1) (3) Reference (2) (3)	Hydrocarbons (PAHs) (0-5 cm only)
	Discharge (1) (3) Reference (2) (3)	--	Discharge (1) (3) Reference (2) (3)	Total organic carbon
	Discharge (1) (3) Reference (2) (3)	--	Discharge (1) (3) Reference (2) (3)	Chlorinity (0-5 cm)
	Discharge (1) (3) Reference (2) (3)	--	Discharge (1) (3) Reference (2) (3)	Sulfate (0-5 cm)

Table 2.2. (Continued).

Sample/Data Type	Station Location (number of stations) (number of samples per station)			Type of Laboratory Analysis
	Pre-termination Survey	First Post-termination Survey	Second Post-termination Survey	
Infauna	Discharge (1) (6) Transect (11) (6) Reference (2) (6)	Discharge (1) (6) Transect (11) (6) Reference (2) (6)	Discharge (1) (6) Transect (11) (6) Reference (2) (6)	Community composition
Biological Tissue	Discharge (1) (1) Reference (2) (1)	–	Discharge (1) (1) Reference (2) (1)	Radionuclides (^{226}Ra and ^{228}Ra)
Marsh Sediments*	Two stations on three transects	–	Two stations on three transects	Radionuclides (^{226}Ra and ^{228}Ra)

* Four Isle Dome only.

2.3.1 Water Quality and Currents

Water quality sampling (temperature, salinity, conductivity, and dissolved oxygen) and measurements of current speed and direction were to be conducted at a station located at the produced water discharge (discharge station) and at two reference stations. Temperature, salinity, conductivity, and dissolved oxygen were to be measured at 0.3 m below the surface and 0.3 m above the bottom. Water current velocity data were to be collected at similar depths.

2.3.2 Produced Water

A produced water sample was to be collected at each site during the Pre-termination Survey. These samples were to be analyzed to determine concentrations of radionuclides, metals, hydrocarbons, and TOC. Radionuclides to be measured in produced water are ^{226}Ra, ^{228}Ra, ^{210}Pb, ^{210}Po, and ^{228}Th. Metals to be measured in produced water are arsenic, barium, cadmium, copper, iron, lead, manganese, mercury, molybdenum, nickel, vanadium, and zinc. Hydrocarbons to be measured are volatile aromatic hydrocarbons (VAHs), saturated hydrocarbons (SHCs), and polycyclic aromatic hydrocarbons (PAHs). The specific compounds are listed in **Table 2.3**.

2.3.3 Sediments

Surficial sediment (0 to 5 cm) samples were to be collected to evaluate the temporal changes in spatial distributions of produced water constituents and to provide data to interpret the distributions of the infauna. During each of the three surveys, surficial sediment samples were to be collected at 14 (1 discharge, 11 transect, and 2 reference) stations located at each site. Three replicate sediment samples were to be collected at the discharge station and four transect stations for analyses of radionuclides (^{226}Ra and ^{228}Ra), hydrocarbons (SHCs and PAHs), metals (aluminum, arsenic, barium, cadmium, chromium, copper, iron, lead, manganese, mercury, molybdenum, nickel, vanadium, and zinc), and TOC. The replicated transect stations were to be located along a gradient from the discharge point to span the range of variability of concentrations. Single samples for these sample types were to be collected at seven other transect stations. Three replicate samples were to be collected at the two reference stations. A single grain size sample was to be collected at each of the 14 stations. During the Pre-termination Surveys at each site, a single surficial sediment sample was also to be collected at the discharge and reference stations for analysis of sediment VAHs. Samples for VAHs were also to be collected during the Second Post-termination Survey if their VAH concentrations were relatively high in the Pre-termination Survey samples.

During the expanded surveys (Pre-termination and Second Post-termination Surveys), sediment samples were to be collected at two depths below the surface of the sediment column to evaluate the penetration of produced water into the sediments. Three replicate samples were to be collected at 25 to 30 and 50 to 55 cm at the discharge station and the two reference stations. These samples were to be analyzed to determine radionuclides (^{226}Ra and ^{228}Ra), metals (same as surficial sediments), hydrocarbons (SHCs/PAHs), and TOC. One of the three replicate samples was to be analyzed for grain size.

Table 2.3. Target compounds for volatile aromatic hydrocarbons (VAHs), saturated hydrocarbons (SHCs), and polycyclic aromatic hydrocarbons (PAHs).

VAH Target Compounds	Alkane and Isoprenoid (SHC) Target Compounds	PAH and alkyl PAH Target Compounds
Benzene	n-C_{10} Decane	Naphthalene
Toluene	n-C_{11} Undecane	1-Methylnaphthalene
Xylene	n-C_{12} Dodecane	2-Methylnaphthalene
C_3-benzene	n-C_{13} Tridecane	2,6-Dimethylnaphthalene
C_4-benzene	n-C_{14} Tetradecane	1,3,5-Trimethylnaphthalene
Naphthalene	n-C_{15} Pentadecane	C_1-Naphthalenes
	n-C_{16} Hexadecane	C_2-Naphthalenes
	n-C_{17} Heptadecane	C_3-Naphthalenes
	n-C_{18} Octadecane	C_4-Naphthalenes
	n-C_{19} Nonadecane	Biphenyl
	n-C_{20} Eicosane	Acenaphthylene
	n-C_{21} Heneicosane	Acenaphthene
	n-C_{22} Docosane	Fluorene
	n-C_{23} Tricosane	C_1-Fluorenes
	n-C_{24} Tetracosane	C_2-Fluorenes
	n-C_{25} Pentacosane	C_3-Fluorenes
	n-C_{26} Hexacosane	Dibenzothiophene
	n-C_{27} Heptacosane	C_1-Dibenzothiophenes
	n-C_{28} Octacosane	C_2-Dibenzothiophenes
	n-C_{29} Nonacosane	C_3-Dibenzothiophenes
	n-C_{30} Triacontane	Phenanthrene
	n-C_{31} Hentriacontane	Anthracene
	n-C_{32} Dotriacontane	1-Methylphenanthrene
	Pristane	C_1-Phenanthrenes/Anthracenes
	Phytane	C_2-Phenanthrenes/Anthracenes
		C_3-Phenanthrenes/Anthracenes
		C_4-Phenanthrenes/Anthracenes
		Fluoranthene
		Pyrene
		C_1-Fluoranthenes/Pyrenes
		Benzo[a]anthracene
		Chrysene
		C_1-Chrysenes
		C_2-Chrysenes
		C_3-Chrysenes
		C_4-Chrysenes
		Benzo[b]fluoranthene
		Benzo[k]fluoranthene (BKF)
		Benzo[e]pyrene (BEP)
		Benzo[a]pyrene (BAP)
		Perylene (PERY)
		Indeno[1,2,3-c,d]pyrene
		Dibenzo[a,h]anthracene
		Benzo[g,h,i]perylene

2.3.4 Sediment Interstitial Water

Samples of sediment interstitial water were to be collected at the discharge and two reference stations during the Pre-termination and Second Post-termination Surveys to evaluate the penetration of produced water into the sediments. Three replicate samples were to be collected at each station at three depths in the sediment column – 0 to 5, 25 to 30, and 50 to 55 cm. Samples from the 0 to 5 cm interval were to be analyzed to determine radionuclides (^{226}Ra and ^{228}Ra), hydrocarbons (PAHs), metals (arsenic, barium, cadmium, copper, iron, lead, manganese, mercury, molybdenum, nickel, vanadium, and zinc), TOC, chlorinity, and sulfate. Deep sediment samples (25 to 30 and 50 to 55 cm intervals) were to be analyzed to determine radionuclides and TOC.

2.3.5 Infauna

Infaunal core samples were to be collected at each site to examine the biological effect of the discharges and recovery of the infauna after cessation of the discharges. Six samples were to be collected at the discharge station, 11 transect stations, and two reference stations where sediment samples were to be collected. Three of the infaunal samples were to be analyzed for infaunal assemblage composition and the other three were to be archived.

2.3.6 Biological Tissue

Five species were to be collected to determine radionuclides in tissues for risk assessment during the Pre-termination and Second Post-termination Surveys. The same species were to be collected at the discharge station and at the corresponding reference stations to insure that comparisons could be made. Target species for collection were to be an oyster, two species of fish, a shrimp, and a crab. Samples of edible tissues from five specimens of each species, which would serve as individual replicates, were to be analyzed to determine concentrations of ^{226}Ra and ^{228}Ra.

2.3.7 Marsh Sediments

At the canal site (Four Isle Dome Central Production Facility), sediment cores were to be collected within the marsh habitat in the vicinity of the produced water discharge to determine the potential penetration of radionuclides into the marsh. The marsh stations were to be located on three transects. Two stations (50 and 100 m from the discharge) on each transect were to be sampled.

2.4 QUALITY ASSURANCE AND QUALITY CONTROL

This study was conducted under a Quality Assurance (QA) Program that encompassed all aspects of sample and data collection, processing, analysis, and management. This section describes the role, components, and characteristics of the QA Program. A description of the QA Program and guidance for study personnel was provided in a Sampling and Analysis Plan (SAP) that was prepared as a draft document, reviewed by the SRC, and revised.

It should be noted that due to budgetary constraints, the field and analytical program was reduced with the agreement of DOE and the SRC. These modifications to the original SAP and rationale are documented in CSA's project files. The data quality objectives (DQOs) were substantially achieved with the exception of meeting target detection limits for radionuclides in sediment samples. The QA Program ensured that the data quality was adequate to meet the study objectives.

2.4.1 Purpose

The primary purpose of the QA Program was to document the sample and data collection and analysis process, provide statistically valid measures of uncertainty, maintain data integrity, and ensure that the QA Program was operating as required.

2.4.2 Components and Characteristics

Integral to the QA Program are the definitions of specific parameters used to assess the quality of the data produced in the study. The parameters were to be quantified by documented methods and procedures, analysis of quality control (QC) samples, and conducting data reviews. The parameters used to specify the quality of the data were as follows:

- Accuracy - the degree of agreement between a measurement and an accepted reference or known (certified true) value. Accuracy is quantified and usually expressed as percent recovery, the difference between the mean and true value expressed as a percentage of the true value. Analytical instruments and methods are calibrated with known samples (standards) or reference materials for each sample run to ensure accuracy. Accuracy may be documented using procedural blanks, matrix spikes/matrix spike duplicates, surrogate compounds, internal standards, and Standard Reference Materials (SRMs). Consistent differences between a set of measurements and a reference standard due to instrumental or analytical problems or limitations is known as bias.

- Precision - a quantitative measure of the variability of two measurements taken under similar conditions and usually expressed in terms of either the relative standard deviation (RSD), the relative percent difference (RPD), or as a range. Analytical laboratory precision may be evaluated through the use of analytical duplicates. Comparison of matrix spike/matrix spike duplicates, and reference analyses/laboratory control values can also be calculated to provide an estimate of laboratory precision.

- Comparability - a qualitative characteristic expressing the confidence with which one set of data can be compared with another. Assurance of the comparability of two or more sets of data can be achieved through the use of standard techniques to collect and analyze representative samples, and by reporting analytical results in appropriate units. Comparability may be assessed through the use of matrix spike/matrix spike duplicates, surrogate compounds, duplicates, SRMs, equipment rinsate blanks, and field blanks. Interlaboratory calibration of methods also assure comparability of data and results.

- Representativeness - a qualitative expression of how well a sample or group of samples reflect the characteristics of the media at the sampling point.

Representativeness is ensured by following proper sample collection, preservation, and analytical procedures. Procedural blanks are used to evaluate representativeness by providing information on potential contamination introduced by analytical methodology, while field and equipment blanks provide information on potential contamination resulting from field collection and handling procedures.

- Completeness - a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected from the sampling design. Completeness is evaluated by comparing the number of valid measurements obtained with the number of measurements intended.

The QA Program was developed and implemented with documented methods and procedures through the SAP and laboratory QA Plans and Standard Operating Procedures (SOPs). Methods and techniques for sample collection, handling, storage, and processing were developed to minimize environmental and analytical contamination. Diligent care was taken by the field crew and laboratory personnel to ensure that samples were not compromised by contamination and contamination could be detected through preparation and subsequent analysis of relevant QC samples. All samples were collected in prescribed containers, properly labeled, stored, and tracked. A chain-of-custody record was maintained following sample collection through analysis. A complete sample log was maintained for the field and laboratory processing.

SOPs at each laboratory defined specific procedures for sample preparation and analysis. Samples were analyzed in batches along with standard QC samples such as procedural or method blanks and duplicates, matrix spikes/matrix spike duplicates, and SRMs to quantify and document accuracy and precision, and detect possible contamination and interferences. Specific detection limits were determined for each analyte and matrix. Data were reported in data packages or reports that were reviewed by the CSA Data Manager. At each participating laboratory, raw and processed data were backed-up and archived in electronic files and hardcopy. At CSA, a complete copy of submitted data packages was archived in electronic and/or hardcopy form.

The participating laboratories had QA Programs prior to this study and due to large differences in methodology and laboratory setups, no attempt was made to standardize QA Program procedures among the participating laboratories. General guidelines were observed which provided adequate documentation of the level of QA at each laboratory. Relevant details on the QA Program at each corresponding laboratory are presented in succeeding sections.

The CSA Program Manager coordinated the QA activities including ensuring that all activities and procedures adhered to documented plans and data quality was properly assessed and documented. Laboratory QA Officers ensured that deviations from the QA Plans and SOPs were documented, analytical problems resolved, corrective actions were documented, and that reported data were accurate, and if necessary, properly qualified. Case narratives submitted by the participating laboratories along with data packages and reports were the primary mode of reporting QA results to management.

2.5 ACKNOWLEDGEMENTS

Selection of sites in Louisiana was conducted by Steimle & Associates, Inc.

CHAPTER 3 - FIELD METHODS, LABORATORY SAMPLE PROCESSING, AND QUALITY ASSURANCE/QUALITY CONTROL

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3.1 FIELD METHODS AND LABORATORY SAMPLE PROCESSING

Table 3.1 shows the produced water termination and survey dates for the three sites. Due to delays in the produced water discharge termination schedule at Four Isle Dome, no post-termination sampling was performed.

Table 3.1. Produced water termination and surveys schedule.

	Delacroix Island	Bay de Chene	Four Isle Dome
Pre-termination Survey	April 1993	May 1993	November 1993
Termination	April 1993	October 1993	January 1995
First Post-termination Survey	October 1993	May 1994	–
Second Post-termination Survey	April 1994	October 1994	–

All water quality data collection and produced water, sediment, and infauna sampling was carried out aboard a 6.4 m Mon Ark boat with two 100 hp Evinrude outboard engines. Trawling and setting and recovering of gill nets for collection of biological tissue were done aboard a 5.5 m aluminum flat boat equipped with a 90 hp Evinrude outboard engine. Station locations were determined using a Raytheon Model 550 or Model 570 LORAN-C unit calibrated to known survey monuments. The calibration of the LORAN-C was checked daily during the surveys using the same monument each time.

All samples were labeled in the field with survey, station, sample type, sample media (e.g., sediment), analysis required, and replicate designation. Custody seals were placed on all samples upon return to the office. Custody sheets were sent with all sample sets to the laboratories.

3.1.1 Water Quality and Current Data Collection

Water quality data were collected at the stations shown in **Figures 3.1** through **3.3** during each survey. Water quality data were collected at all stations rather than only the planned discharge and reference stations. The number of transect stations varied from the

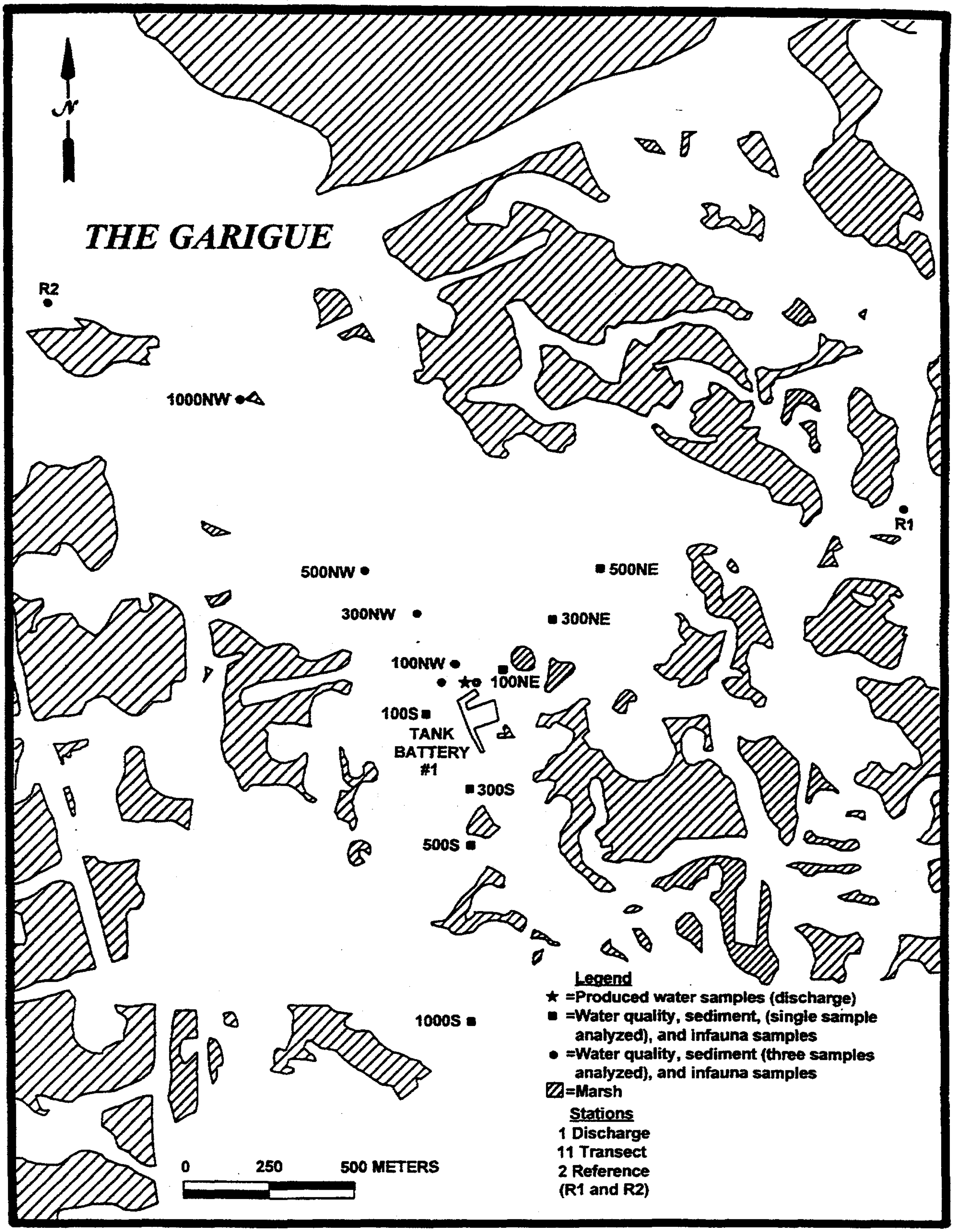

Figure 3.1. Delacroix Island Tank Battery #1 sample locations.

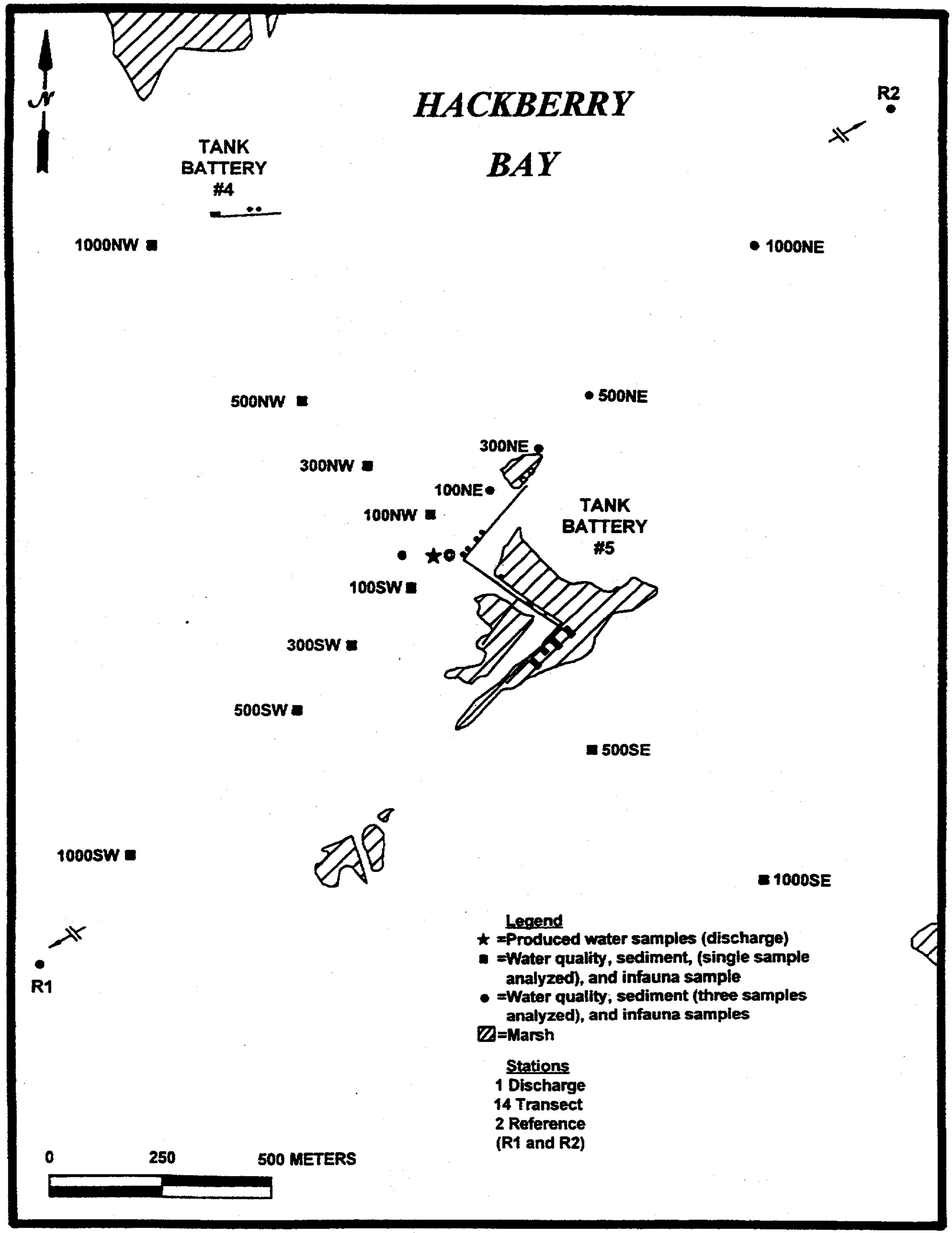

Figure 3.2. Bay de Chene Tank Battery #5 sample locations.

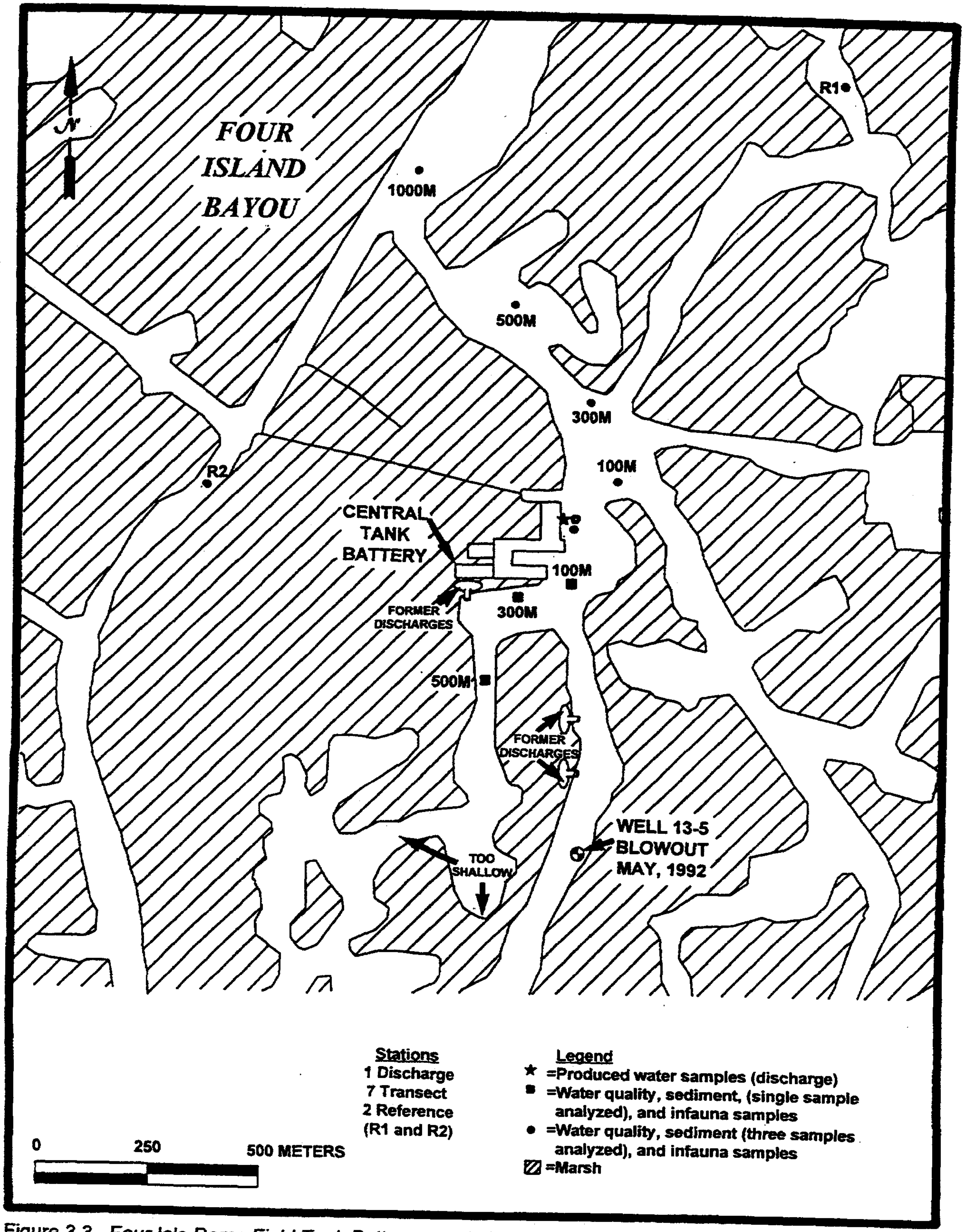

Figure 3.3. Four Isle Dome Field Tank Battery sample locations.

planned 11 with 11, 14, and 7 stations sampled at Delacroix Island, Bay de Chene, and Four Isle Dome, respectively. This variation was due to site specific open water and marsh distributions. Salinity, conductivity, temperature, and depth data were collected using a YSI Model 33 S-C-T meter. Dissolved oxygen and temperature were measured using a YSI Model 51B dissolved oxygen meter. Salinity, conductivity, water temperature, and dissolved oxygen were measured 0.3 m below the surface and 0.3 m above the bottom except in areas less than 1 m deep. In these areas, a single mid-depth reading was taken for all parameters. Both meters were calibrated daily by Analysis Laboratories in Metairie, Louisiana. Temperature readings were also checked using a thermometer calibrated according to National Institute for Standards and Technology (NIST) specifications.

Current direction and velocity data were collected using a Marsh-McBirney Model 201 flow meter calibrated according to manufacturer's directions.

3.1.2 Produced Water Sampling

Samples were taken of the discharge during the pre-termination sampling at all three sites. Both Bay de Chene and Delacroix Island discharges were into skimmer piles which prevented the escape of any oily sheen which may have accompanied the produced water. Discharge lines at Delacroix Island and Bay de Chene both had sample taps very close to the end of the line; samples were taken from the taps.

The discharge at Four Isle Dome had no sample tap and did not discharge into a skimmer pile. The discharge was simply a pipe which discharged directly into the bayou from several feet above the water line. Samples had to be taken from the end of the pipe.

3.1.2.1 Radionuclides

One-liter samples for radionuclides were collected from the discharge pipe hourly for 8 hours. These samples were preserved with nitric acid to a pH of 2 and stored at 4°C in 1-L polyethylene bottles. The samples were sent to Core Laboratories, Inc. (CORE) where they were composited to produce two, 4-hour composite samples.

3.1.2.2 Metals

One 250 mL sample for metals was collected from the discharge pipe in a polyethylene container each hour for 8 hours. These samples were frozen and shipped to Dr. Trefry's lab at Florida Institute of Technology (FIT) within 48 hours of collection to be composited into two, 4-hour composite samples.

3.1.2.3 Hydrocarbons

Triplicate samples for VAHs were collected from the discharge pipe at the first and fourth hour of the 8-hour sampling. Each of the two sets of triplicate samples was collected in 40 mL VOA vials, preserved with HCl to a pH of 2, and stored upside down at 4°C. Samples were shipped to Arthur D. Little, Inc. (ADL) within 48 hours of collection.

Samples for SHCs/PAHs were collected from the discharge pipe in pre-cleaned 1 L glass containers, preserved with 100 mL methylene chloride, and stored at 4°C. Samples were collected hourly for 8 hours and shipped to ADL for compositing into two, 4-hour composite samples.

3.1.2.4 Total Organic Carbon

One sample for TOC was collected from the discharge pipe in a 30 mL glass container each hour for 8 hours. Samples were frozen and shipped to FIT within 48 hours of collection to be composited as above.

3.1.3 Sediment and Interstitial Water Sampling

3.1.3.1 Discharge and Reference Stations

Sediment sampling stations at all three sites are shown in **Figures 3.1** through **3.3**.

3.1.3.1.1 Sediment Sampling

Long Sediment Cores

Collection

At the discharge and two reference stations during the Pre-termination and Second Post-termination Surveys at Delacroix Island and the Pre-termination Survey at Bay de Chene and Four Isle Dome, two sets of triplicate cores were taken to a depth of at least 40 cm. Cores could not be collected to the planned depth of 50 cm. Cores were not collected as planned at Bay de Chene on the Second Post-termination Survey due to re-allocation of project funds. Sediment cores were taken using a pole-mounted Barrett corer and a 10 cm nominal outer diameter acrylic core tube with a teflon lined lid.

The triplicate sediment samples of one set of long cores were shipped frozen to ADL for subsampling while the second set was retained at Steimle & Associates, Inc. (S&A).

Laboratory Processing

The three replicate samples from the discharge and reference stations were subsampled at ADL at the 0 to 5, 20 to 25, and 35 to 40 cm strata for PAHs, TOC, and grain size. Metals were not analyzed due to re-allocation of project funds. The subsampling process was as follows:

1) Frozen sediment cores were partially thawed to allow the sediment to be extruded while maintaining the integrity of the sediment within the core;
2) The top and bottom caps were removed and the core was secured on an inclined processing bracket;
3) The core was extruded using an appropriately sized pre-cleaned teflon-coated plunger;
4) The three strata were separated from the core using a pre-cleaned stainless steel spatula;
5) The intact and partially frozen sediment strata were placed on a pre-cleaned glass processing plate;

6) Approximately 0.5 cm of sediment was removed from the outer edge (i.e., portion in contact with the acrylic core) of the sediment strata and discarded; and
7) Remaining sediment was placed in pre-cleaned glass bowl and homogenized.

A pre-cleaned teflon spatula was used to put approximately 100 g of sediment for SHCs/PAHs analyses in a pre-cleaned 250-mL glass jar and 80 g for grain size/TOC analyses in a plastic bag. Sample containers were labeled according to analyses type and stored frozen. Frozen samples were shipped to the appropriate laboratory for analyses (Dr. Wayne Isphording at the University of Alabama for grain size/TOC and SHCs/PAHs retained at ADL). The remaining portion of the sediment cores were frozen and archived.

The second set of triplicate long sediment cores were thawed and cut at the 0 to 5, 20 to 25, and 35 to 40 cm strata by S&A. The core subsamples were packaged in 500 mL wide-mouth polypropylene jars and shipped to CORE for radionuclide analyses.

Short Sediment Cores

Collection

During the First Post-termination Survey at Delacroix Island and the two post-termination samplings at Bay de Chene, two triplicate sets of short acrylic cores were collected at the discharge and reference stations. The cores were kept on ice in the field, and frozen within 12 hours of collection. One set was shipped to ADL frozen while the second set was retained at S&A.

Samples were also taken at the discharge and reference stations for VAHs on the Pre-termination Survey at the three sites and Second Post-termination Survey at Delacroix Island. These samples, taken from the 0 to 5 cm stratum in the core, were poured from a clean acrylic core tube into a 120 mL glass container without leaving airspace. The container was kept on ice, frozen within 12 hours of collection, and shipped to ADL.

Laboratory Processing

The set of triplicate cores that was received at ADL was subsampled for metals, SHCs and PAHs, TOC, and grain size. The same procedure was followed as described for the long cores with the exception that only a 0 to 5 cm stratum was separated from the cores.

The second set of triplicate cores retained at S&A was thawed and the 0 to 5 cm stratum cut and shipped in 500 mL wide mouth polypropylene jars to CORE for radionuclides analysis.

3.1.3.1.2 Interstitial Water Sampling

Three replicate samples were collected at 0 to 5, 20 to 25, and 35 to 40 cm depths in the sediment column at the discharge and two reference stations at each site during the Pre-termination Surveys. Samples were also collected at Delacroix Island during the Second Post-termination Survey. Cores were not collected as planned at Bay de Chene on the Second Post-termination Survey due to re-allocation of project funds.

Collection

The surface sediment increment (0 to 5 cm) samples were collected with a stainless steel Eckman grab. It was necessary to collect 2 grab samples to provide sufficient sediment for each station replicate. The grab sample was visually inspected to determine that there was no forceful leakage of water and fine sediments from the sample. Each of the 2 grab samples were subsampled with 2 pre-cleaned teflon coring tubes (10-cm inside diameter). Coring tubes were inserted vertically into the sediment sample through the top access doors of the grab sampler. Both coring tubes were placed in the grab sample prior to removal to prevent the disturbance of the sediment surface for subsequent core samples. Each core tube was manually removed from the sediment grab sampler and temporarily capped with teflon-lined core lids.

The following procedure was used to collect the top 5 cm of sediment from each coring tube. The clear (i.e., sediment free) surface water overlying the subsample was decanted. Any fluid, flocculent layer was saved as part of the sample. The 0 to 5 cm sediment increment was removed from the subcore and placed into a pre-cleaned 5-cm high teflon ring (of the same diameter as the tube) using a pre-cleaned teflon-coated spatula. The sediment was transferred from the 5-cm teflon ring directly into pre-cleaned glass holding jars. The 0 to 5 cm sediment stratum from the 4 subcores was stored in a 1-L, a 500-mL, and a 250-mL pre-cleaned glass jars with teflon-lined lids. It was necessary to completely fill each jar and eliminate air space to prevent biodegradation. Sample holding jars were capped, labeled, and the samples stored at 4°C until extraction.

Deep sediment samples (20 to 25 and 35 to 40 cm increments) were collected with a pole-mounted Barrett sampler equipped with an acrylic core tube (approximate dimension of 100-cm long and 10-cm outside diameter). Three closely placed cores were collected to provide sufficient sediment for each station replicate. Acceptable samples contained a sediment core of ≥45 cm. The sediment increments (20 to 25 and 35 to 40 cm) were exuded by plunging from the bottom of the core. Sediment increments were placed on a channeling tray and funneled or placed directly into separate 2-L pre-cleaned glass holding jars. Sample holding jars were capped, labeled, and the samples stored at 4°C until extraction.

Laboratory Processing

Radionuclides

Three replicate samples of interstitial water for radionuclides analyses were extracted from three sediment strata (0 to 5, 20 to 25, and 35 to 40 cm) collected at the discharge and two reference stations. Interstitial water was extracted from the sediment using a "squeezer" device which had dual systems each comprised of a cylinder/piston unit and opposing pressure plates. The "squeezer" was equipped with a hand-crank hydraulic jack to apply pressure to sediment during interstitial water extraction.

A diagram of the cylinder/piston unit used to hold sediment during interstitial water extraction is presented in **Figure 3.4**. The cylinder/piston unit was comprised of thick-walled cylinder and a piston equipped with dual o-rings to provide an air-tight seal between the walls of the cylinder and the piston. Cylinder/piston units were constructed of both teflon and polyvinyl chloride (PVC). The base of the cylinder had a small centered opening for funneling extracted interstitial water into a sample container. The cylinder/piston unit was cleaned with Liquinox and distilled water and thoroughly rinsed with distilled water prior to the initial "squeezing" for each day of operations; the cylinder/piston unit was only thoroughly rinsed with distilled water following the initial "squeezing." The cylinder/piston unit was completely dried prior to use. The process for loading sediment into the cylinder/piston unit was performed as follows:

1) A 47-mm diameter nylon reinforcement screen was placed in a recessed area above and adjacent to the opening in the base of the cylinder;
2) A 47-mm diameter/ 0.4 micron pore size polycarbonate membrane was placed on top of the nylon reinforcement screen;
3) A 12.5-cm diameter ashless paper filter which covers the entire base of the cylinder was placed over the polycarbonate membrane;
4) A PVC ring was inserted into the cylinder to stabilize the entire series of filters;
5) Standing water present in the sample holding jar was decanted;
6) Approximately 500-mL of sediment was placed in the cylinder; and
7) The pre-cleaned piston is placed in the cylinder on top of the sediment to be squeezed.

A diagram of the "squeezer" device is presented in **Figure 3.5**. The sediment-filled cylinder/piston unit was placed on a PVC stand which was placed on a moveable pressure plate. The stand elevated the cylinder/piston unit during "squeezing" to accommodate the placement of a sample collection jar under the cylinder/piston unit. The pressure plate, stand, and sediment-filled cylinder/piston unit was raised with the hydraulic jack until the top of the piston was properly aligned and came in contact with an opposing pressure plate. Pressure was gradually applied to the cylinder/piston unit until the piston came in contact with the sediment within the cylinder and interstitial water began dripping from the opening at the base of the cylinder. The first few drops of interstitial water were discarded because they could potentially be contaminated with residue present in the opening. Extracted interstitial water was collected in a pre-cleaned 250-mL Nalgene bottle which was placed inside the stand and directly under the opening at the base of the cylinder. Continuous pressure was applied to the sediment until most of the interstitial water was extracted (i.e., rate of extraction decreased significantly).

Multiple "squeezes" were necessary to provide the minimum volume of 150 mL of interstitial water required for radionuclide analyses. Interstitial water samples for radionuclide analyses were preserved with nitric acid at a pH of ≤ 2. A plastic dropper bottle was used to add HNO_3 to the samples. Following acidification, the sample bottle was capped, a custody seal attached, and placed in a refrigeration unit for storage at a temperature of approximately 4°C.

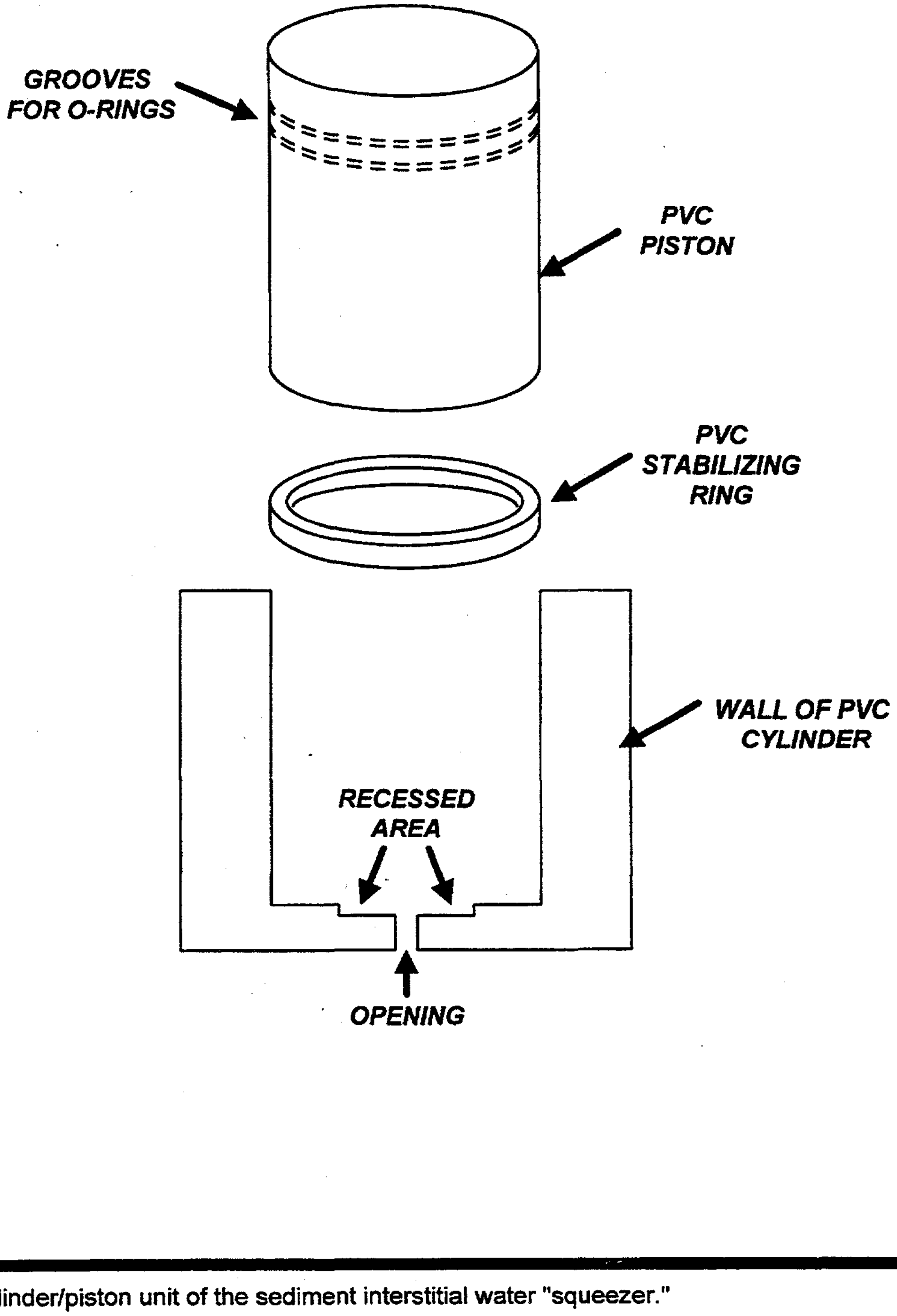

Figure 3.4. Cylinder/piston unit of the sediment interstitial water "squeezer."

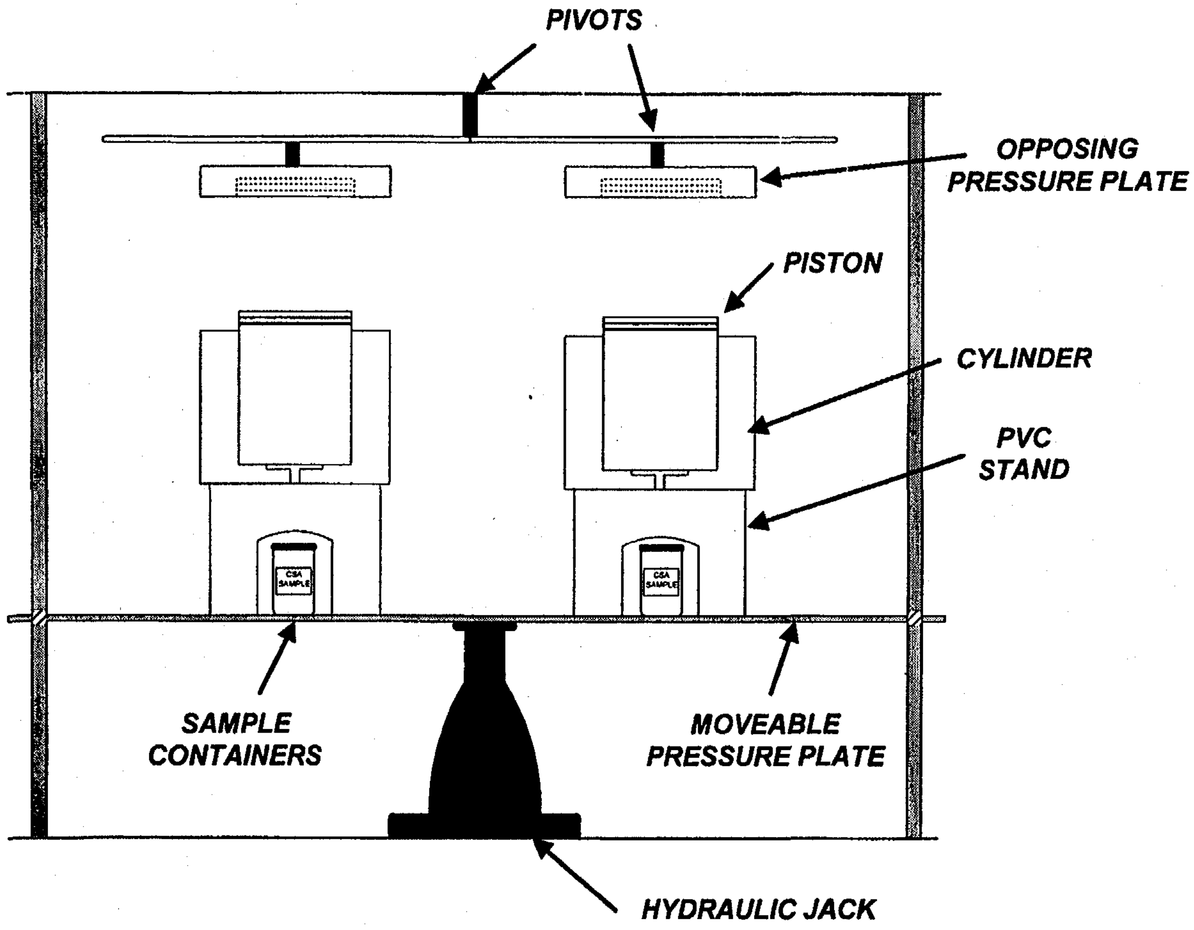

Figure 3.5. Diagram of "squeezer" device.

Interstitial water samples for radionuclide analyses had a recommended holding time of 6 months.

Metals

Three replicate samples of interstitial water for metal analyses were extracted from the 0 to 5 cm sediment increment. Interstitial water samples for metal analyses were extracted using the same method previously described for radionuclide samples. However, the cylinder/piston unit used for extracting metal interstitial water samples was additionally cleaned in 10% to 20% solution of HNO_3 prior to the initial "squeezing" for each day of operations.

A 25-mL interstitial water sample was required for metal analyses and the sample was collected directly in a pre-cleaned 30-mL Nalgene bottle. Samples were preserved with HNO_3 a pH of ≤ 2 and HNO_3 was added to the sample using a 1-mL calibrated pipette with disposable plastic volume tip. Before HNO_3 was added to the samples the plastic volume tip was filled with acid and the acid discarded to clean the volume tip and prevent possible contamination to the interstitial water samples. The volume tips were discarded following the preservation of the replicate samples. After the samples were preserved, the sample bottle was capped, a sample custody seal attached, and the samples stored at room temperature. Interstitial water samples for metal analyses had a recommended holding time of 6 months.

Hydrocarbons (PAHs)

Three replicate samples of interstitial water for PAH analyses were extracted from the 0 to 5 cm sediment increment. Interstitial water samples for hydrocarbon analyses were extracted using the same method previously described for radionuclides samples with the following exceptions:

- teflon cylinder/piston unit was used during extraction;
- teflon cylinder/piston unit was cleaned with methylene-chloride prior to each "squeezing"; and
- a 12.5-cm diameter teflon filter pre-cleaned with methylene-chloride was used instead of the ashless paper filter.

A 100-mL sample was collected directly in a 125-mL pre-cleaned glass jar. Samples were preserved with approximately 10 mL of methylene-chloride. After the samples were preserved, the sample bottle was capped, a custody seal attached, and the samples stored at 4°C. Interstitial water samples for hydrocarbon analyses had a recommended holding time of 40 days.

Total Organic Carbon

Three replicate samples of interstitial water for TOC analyses were extracted from three sediment increments (0 to 5, 20 to 25, and 35 to 40 cm) using the same method previously described for radionuclide samples. A 5-mL sample was collected directly in a 20-mL pre-cleaned glass vial, the sample vial was capped, a sample custody seal attached, and the sample stored frozen. Interstitial water samples for TOC analysis had a holding time of 28 days.

Chlorinity/Sulfate

Three replicate samples of interstitial water for chlorinity analysis were extracted from three sediment strata (0 to 5, 20 to 25, and 35 to 40 cm). Three replicate samples for sulfate analysis were extracted only from the surface (0 to 5 cm) sediment stratum. Samples for both parameters were extracted using the same method previously described for radionuclide samples. The combined chlorinity/sulfate samples required approximately 10 mL of interstitial water and were taken from the radionuclide collection bottles. Chlorinity/sulfate samples were stored in precleaned 10-mL plastic vials. Chlorinity samples required approximately 2 mL of interstitial water and were taken from the radionuclide collection bottles. Chlorinity samples were stored in pre-cleaned 10-mL plastic vials. Samples were capped, a custody seal attached, and stored at room temperature. Interstitial water samples for chlorinity and sulfate analyses had a holding time of 28 days.

3.1.3.2 Transect Stations - Sediment Sampling

3.1.3.2.1 Collection

The pole mounted Barrett corer was used to collect short cores at all transect sampling stations. During the pre-termination surveys, two triplicate sets of short cores were collected at all transect stations. From one of the sets of triplicate short cores, (A) replicates were shipped frozen to ADL for subsampling of the 0 to 5 cm stratum while the second set was processed at S&A and subsequently sent to CORE. Based on the results of the analysis of the single replicate for both radionuclides and PAHs, a single transect was chosen from which the other two replicates (B and C) were analyzed. The northwest transect at Delacroix, the northeast transect at Bay de Chene, and the north transect at Four Isle Dome were chosen. These sampling transects are distinguished on **Figures 3.1** through **3.3** by the circles representing replicate samples. On post-termination sampling trips to Delacroix and Bay de Chene, the selected transects were sampled in triplicate. At other transect stations, two cores were taken, with one shipped frozen to ADL for subsampling (0 to 5 cm) while the second was retained at S&A.

3.1.3.2.2 Laboratory Processing

The cores shipped to ADL were subsampled for metals, SHCs and PAHs, TOC, and grain size. The same procedure was followed as described for the long cores with the exception that only a 0 to 5 cm stratum was separated from the cores. The following samples were thawed and the 0 to 5 cm stratum removed, placed in clean 500 mL wide mouth polypropylene jars and shipped by S&A to CORE for radionuclides analysis: (1) one replicate (A) from the second set of triplicate pre-termination samples, (2) the other two replicates (B and C) from the pre-termination transects stations selected for analysis of triplicate samples, (3) the three replicates from the selected transects stations from the post-termination sampling, and (4) one replicate (B) from the post-termination, non-triplicate stations.

3.1.3.3 Marsh Stations

The marsh sampling which was planned at Four Isle Dome was not performed as there was a lack of marsh unobscured by dredged material that lined both banks of the canal.

3.1.4 Biological Sampling

3.1.4.1 Infauna Sampling

Infauna samples were collected at the stations shown in **Figures 3.1** through **3.3** during each survey. Two reference stations were designated at all sites to lessen the probability that a reference station had been affected by drilling and/or disposal activities in the past. Six replicate samples were collected by Ekman grab, 23 cm x 23 cm and sieved in the field using a WILDCO 0.5 mm screen. Samples were preserved in 10% buffered formalin which had added Rose Bengal stain and Borax in 500 mL wide mouth polypropylene jars.

Infauna sampling was conducted at Delacroix Island at the stations on the three transects designated in **Figure 3.1**. Because of the land formations around the discharge, the northeast transect had no 1,000 m station. Infauna samples were collected during the pre-termination and the two post-termination samplings.

At Bay de Chene, infauna samples were collected at all stations on the four transects shown in **Figure 3.2**. Because of the presence of the field facilities on the southeast transect, only a 500 and 1,000 m station were sampled. Infauna samples were collected during the pre-termination and the two post-termination samplings.

Sampling at Four Isle Dome was limited to two transects because of the constraints of sampling in a canal system. Infauna samples were collected at the stations shown in **Figure 3.3**.

3.1.4.2 Tissue Sampling

Tissue sampling was conducted for commercial species at the discharge and reference stations during the pre-termination survey at Delacroix Island, Bay de Chene, and Four Isle Dome and during the second post-termination surveys at Delacroix Island and Bay de Chene. Sampling was accomplished over a three day effort which included trawl samples using a 16 foot otter trawl dragged for 30 min twice daily at each sampling station. Fifteen meter long gill nets which had a mesh of 3.8 cm square and 7.6 cm stretched and a depth of 3 m were set at each station. The nets were checked twice a day at each station. Tissues were also collected by hook and line where appropriate.

Blue crabs were collected in commercial plastic coated chicken wire traps baited with turkey necks. Two traps per station were deployed and left out for the three days. The traps were checked and emptied daily and rebaited as necessary.

All specimens collected were identified, labeled and placed in 7.5 L (2 gal) plastic ziplock bags and placed on ice in the field. Specimens were frozen upon return to the office of S&A.

3.2 QUALITY ASSURANCE/QUALITY CONTROL

An SAP and checklists were used in the field program to ensure sample integrity, representativeness, completeness, and data quality as it related to field sampling. Prior to the field effort, the required sample matrices, types, volumes, collection techniques, containers, preservation type, storage, and handling requirements along with QC samples were determined and specified in a detailed field plan and instructions to the field team. Specific sampling stations at each site were identified and used to generate sample log templates and sample IDs.

To further ensure data quality in this study, the following field QA activities were implemented:

- Adherence of sample and data collection activities to SOPs, including calibration of instruments, cleaning of sample collection containers, use of prescribed sampling equipment and methods;
- Maintenance of a sample log and proper sample labeling;
- Strict observance of sample custody procedures; and
- Preparation and collection of QC samples.

The succeeding section describes the field QA activities. These activities and relevant records are documented in S&A and CSA's project files including field notes, data sheets, sample logs, and sample custody sheets. Project files are archived at S&A and CSA for at least five years before disposal.

3.2.1 Mobilization and Sample Collection

During the mobilization phase of the field effort, the S&A Manager met with the field team to review objectives, methods, and procedures to ensure that the study objectives would be met. In the field, specific sample collection procedures for each matrix and sample type as prescribed in S&A's SAP were observed. Particular attention was made to minimizing contamination of samples from environmental sources and cross-contamination among samples. Samplers were cleaned and field equipment was calibrated according to specifications prior to use. A Field Scientist supervised all sampling activities conducted by project personnel to ensure that study and data quality objectives would be met. Any difficulties and problems encountered during the field effort were noted in the Field Scientist's Field Log. Relevant ancillary information relating to the sampling conditions were also noted. Data on water quality parameters were collected on field instruments calibrated according to SOPs and manufacturer's specifications.

3.2.2 Sample Logging and Tracking

Logging of samples was accomplished through the use of prepared sample checklists and the sample custody forms described below. Because sampling locations, matrices, and types were pre-determined prior to the field effort, sample checklists were generated during mobilization and were available for use in the field. To minimize errors and confusion, S&A and CSA used a descriptive sample labeling protocol that identified the sample origin, matrix, analysis parameter, and replicate. As each sample was collected, the sample checklist was completed and ancillary information recorded. Replicates and QC samples were identified similarly.

Ancillary information was recorded and maintained in the sample log. Custody sheets were prepared for all samples to accurately and consistently track them following the field collection.

3.2.3 Sample Custody

From the time a sample was collected in the field, its custody was carefully documented such that the entire history of the sample and all who handled it were directly traceable. QC samples were documented similarly. Sample custody was documented from the time of collection to final disposal or archival by S&A (responsible for collection of all samples but interstitial water and sectioned sediment cores for radionuclides), CSA (extracted and prepared samples of interstitial water), University of New Orleans (analyzed infauna), University of South Alabama (analyzed sediment grain size and TOC), ADL (analyzed VAHs, SHCs, and PAHs), FIT (analyzed metals), and CORE (analyzed radionuclides). A chain-of-custody record served also as a sample logging mechanism for the analytical laboratory where the samples were delivered for analyses. Samples were properly packaged for shipment and delivered or shipped to the designated laboratory for analyses. The documentation included the sample date, site, station, sample type, time of collection, collection personnel, and a sequential identification number for that sampling effort. Signed custody sheets with this information accompanied all samples during collection, transportation, shipping, analyses, and final disposition. Upon receipt and logging of samples, copies of signed chain-of-custody sheets were sent to the originating laboratory and to CSA. This allowed the CSA Program Manager and Task Manager to track samples from collection to analysis.

3.2.4 Quality Control Samples

To detect and document possible sources of contamination in the field, QC samples with exception of the sediment matrix were collected along with actual field samples. Several types of QC samples were prepared and collected during the mobilization and field effort including trip blanks, field blanks, and equipment blanks or rinsates. The type of QC samples collected reflected the degree of significance of possible sources of contamination and requirements for quantifying data quality.

Trip, field, and equipment blanks were prepared in the appropriate matrix for produced water, ambient seawater, and interstitial water and analyzed for radionuclides, metals, VAHs, and PAHs. Trip blanks were collected to quantify possible contamination from sample containers. Field blanks can document environmental contamination sources in the field while equipment blanks can quantify contamination from sampling equipment including cross-contamination between samples. Accuracy, precision, and comparability of analyses for radionuclides was quantified through composite samples of produced water, ambient seawater, interstitial water, and tissues. Composite samples were prepared by collecting sufficient volumes of sample over time in single or multiple containers and then homogenizing the sample prior to splitting and shipping to the analytical laboratories.

3.2.5 Sample Summary and Shipping

Published sample collection, storage, and holding guidelines were observed for those sample types that had such guidelines. Volumes, preservatives, container types, and holding times for water, sediment, and tissue samples are provided in **Table 3.2**.

Table 3.2. Volumes, preservatives, container types, and holding times for water, sediment, and tissue samples collected during the field survey.

Matrix and Sample Type	Minimum Sample Volume	Preservative	Container	Holding Time
Produced Water, Ambient Seawater, Discharge Plume and Interstitial Water				
Radionuclides	2 L except 150 mL (interstitial water)	HNO_3 at a pH ≤ 2; stored at 4°C	polyethylene	6 months (recommended)[a]
Volatile Aromatic Hydrocarbons	40 mL	HCl at a pH ≤ 2; stored at 4°C	amber open top glass vial with teflon/silicone septa	14 days from collection to extraction[b]
Saturated Hydrocarbons and Polycyclic Aromatic Hydrocarbons	2.5 L (includes preservative)	200 ml of methylene chloride; stored at 4°C	amber glass with teflon-lined lid with insert of purified aluminum foil	40 days after extraction; addition of methylene chloride considered beginning of extraction process[b]
Metals	1 L (produced water); 2 L (ambient seawater)	HNO_3 at a pH ≤ 2; stored at 4°C	polyethylene	7 days from collection (laboratory specified)[c]
Total Organic Carbon	20 mL	frozen	glass vial with teflon-lined lid	28 days[b]
Sediment				
Radionuclides	100 g	frozen	pre-cleaned 500 mL plastic jar	6 months (recommended)[a]
Volatile Aromatic Hydrocarbons	150 g	4°C	120 mL glass	14 days (EPA)
Saturated Hydrocarbons and Polycyclic Aromatic Hydrocarbons	100 g	frozen	pre-cleaned 250 mL glass jar	Unspecified
Metals	30 g	frozen	pre-cleaned 100 mL plastic jars	Unspecified

Table 3.2. (Continued).

Matrix and Sample Type	Minimum Sample Volume	Preservative	Container	Holding Time
Grain Size	80 g	frozen	zip-loc plastic bag	Unspecified
Total Organic Carbon	same sample as grain size	frozen	glass vial with teflon-lined lid	28 days[b]
Tissues				
Radionuclides	100 g	frozen	double plastic bags	6 months (recommended)[a]

[a] Dr. David Demorest (Core Laboratories, Inc.).
[b] EPA, 1991.
[c] Dr. John Trefry (Florida Institute of Technology).

Produced water samples to be analyzed were kept at 4°C until shipment to the appropriate laboratory. Sediment cores were shipped and stored frozen until processed. Sediment and tissue composites, splits, and subsamples were also shipped and stored frozen until analyzed.

3.3 ACKNOWLEDGMENTS

We would like to acknowledge the cooperation and assistance of the field personnel at the Texaco Delacroix Island and Bay de Chene facilities. We would like to thank the field sampling team which included the authors and the following personnel: Raymond Albert, Floyd Belsome, Randall Poincot, and Frederick Schultz. We would also like to thank Dr. John Trefry of the Florida Institute of Technology for assistance during interstitial water sampling and laboratory processing.

CHAPTER 4 - DESCRIPTION OF THE STUDY SITES

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4.1 ENVIRONMENTAL DESCRIPTION

4.1.1 Delacroix Island

The Delacroix Island Oil and Gas Field which is located approximately 9 km southeast of Delacroix, Louisiana (**Figure 2.1**) has been in constant production since the first well was drilled in the field in 1940. The many oil field canals or remnants thereof in the field are visible in **Figure 3.1**. The area is part of a subsiding delta which results in broken marsh and numerous small water bodies with few large open bays.

Brackish marsh consisting of *Spartina patens* and *Scirpus* sp. dominates the area. Submerged aquatic vegetation which was abundant during the First Post-termination Survey in October 1993 was Eurasian watermilfoil (*Myriophyllum spicatum*). This species has become very abundant in Louisiana waters in the last decade, often replacing all other submerged vegetation.

Salinities in the Delacroix Island Field vary widely between seasons and years. Late summer/fall salinities are the most stable. During the First Post-termination Survey (October 1993), salinities were 5.0 to 6.5 ppt. Spring salinities are the lowest experienced during the year due to the influence of the Mississippi River. The Pre-termination and Second Post-termination Surveys were conducted during the spring and salinities varied from about 1.5 to 3 ppt. The length of time which the Mississippi River influences the area varies from year to year. Often the river is high during the late winter and high water continues into the spring.

The influence of the river is exaggerated in this area because of the proximity of the Caenarvon freshwater diversion located about 28 km northwest of the field. This diversion was built by the U.S. Army Corps of Engineers to bring the sediment rich Mississippi water to the subsiding delta. The method of operation of this diversion can effect lowered salinity over a large area and it can affect the period of time over which low salinity persists.

The bottom substrate in areas of subsiding marsh like the Delacroix Island Field varies from soft, fine grained sediments in open water areas to subsided marsh root mat which is firmer and may persist intact for many years. Some portions of the area also consist of shell bottom. Areas of root mat or shell may be encountered at any sampling station depending on which portions of the area were marsh in recent years.

The Delacroix Island Field is typical of many brackish habitats in the Louisiana inshore waters in that its inhabitants are eurytolerant, opportunistic species. Benthos species are those which occur commonly in oligohaline environments (0.5 to 5 ppt), including oligochaetes, polychaetes, several molluscs (*Rangia cuneata, Macoma mitchelli, Mulinia lateralis, Texadina sphinctostoma*), amphipods (*Mucrogammarus mucronatus, Corophium louisianum, Grandidirella bonnieroides, Cerapus benthophilus*), and the mud crab (*Rhithropanopeus harrisii*).

Commercially important species in this area include, brown shrimp (*Penaeus aztecus*) and white shrimp (*Penaeus setiferous*). Commercial and recreational shrimping is conducted extensively in this area. Brown shrimp are harvested during the period from about mid-May through about mid-July. White shrimp are harvested from about mid-August through about mid-December although harvesting effort falls off significantly toward the end of the white shrimp season. The dates of the inshore shrimp seasons are set yearly by the Louisiana Wildlife and Fisheries Commission and depend on several factors including shrimp size.

The area around the Delacroix Island Field is marginal for the American oyster (*Crassostrea virginica*) because of long periods of very low salinities. Blue crab (*Callinectes sapidus*), however, is harvested extensively in the area year round and are abundant and most desirable commercially in the summer/early fall.

Recreational and commercial finfishing is also popular in this area. Red drum or redfish (*Sciaenops ocellatus*) and speckled trout (*Cynoscion nebulosus*) are the most prized species inshore. Both are most available in the late fall and winter months. Flounder (*Paralicthys lethostigma*) are most abundant in the fall months and croaker (*Micropogonias undulatus*), spot (*Leiostomas xanthurus*), sand seatrout (*Cynoscion arenarius*), black drum (*Pogonias cromis*), and sheepshead (*Archosargus probatocephalus*) are fished inshore year round.

4.1.2 Bay de Chene

The Bay de Chene Field which is located approximately 21 km north-northwest of Grand Isle, Louisiana (**Figure 2.1**), is part of the Barataria Basin (**Figure 3.2**). The field has been in constant production since the first well was drilled in 1942. The tank battery chosen for study (Tank Battery # 5) is located in Hackberry Bay which is a large open bay typical of the Barataria system.

The shoreline area is characterized by saline marsh dominated by *Spartina alterniflora* and *Juncus romerianus*. Submerged aquatic vegetation is absent in the area. The shoreline areas are constantly eroding in the Barataria system creating more and more open water.

Salinities in the Bay de Chene Field also vary during the year with lowest salinities occurring when the high water from the Mississippi River influences the area. Unlike the Delacroix Island Field, there is no freshwater diversion structure in close proximity so the influence is dependent upon influx of freshwater from the mouth of the river. Surface salinities during the spring Pre-termination Survey (May 1993) ranged from 1 to 5 ppt with stratification occurring at most locations. Bottom salinities ranged from 3.5 to 9.5 ppt. Salinity measurements taken during the First Post-termination Survey (May 1994) were between 4.5 and 7 ppt with stratification much less evident. Fall salinities as evidenced by the Second Post-termination Survey (October 1994) were higher. Surface salinities encountered during this survey varied from 12.5 to 22 ppt.

The bottom substrate in most open water areas is soft, fine grained sediments although some areas of bay bottom have firm clay at the surface. Portions of the bay have been altered by the planting of *Rangia* shell by the Louisiana Department of Wildlife and Fisheries (LDWF) for oyster cultch. Clam shell was planted on firm bottom substrate so that the shell would not sink below the mud. One of these planted areas on the west side of the bay was chosen as a reference site virtually no drilling was allowed on shell plants by the LDWF.

The Bay de Chene Field habitat experiences higher salinities than the Delacroix Island Field. The area is mesohaline (5 to 18 ppt) most of the year. The organisms which characterize this habitat are also eurytolerant and opportunistic. Benthos species common at Bay de Chene are similar to those found at Delacroix Island with the addition of a few taxa, primarily polychaetes.

Commercially important species harvested at the Bay de Chene Field are identical to those harvested in the Delacroix Island Field with the possible exception of the American oyster which is cultivated on numerous leases in the area. Recreational and commercial finfishing are also conducted extensively in this area. Species and seasonal abundances are the same as at the Delacroix Island Field.

4.1.3 Four Isle Dome

The Four Isle Dome Oil Field is located approximately 40 km south-southwest of Houma, Louisiana (**Figure 2.1**). The field is located in a series of natural bayous and man made oil field canals as shown in **Figure 3.3**. Information regarding the age of the field and the number of wells in production was not made available to us.

The surrounding marsh is saline and characterized by *Spartina alterniflora* and *Juncus romerianus*. This area is less influenced by influx of Mississippi River water because of its distance from the mouth of the river. Local runoff from spring rains can, however, lower salinities in the spring.

The area was impacted by the 1992 passage of Hurricane Andrew (**Figure 2.1**). Canal and bayou bottom sediments were heavily laden with detritus. Large clay balls with marsh vegetation detached by the hurricane came up in trawls throughout the sampling area.

Benthos which normally dominate this habitat are the same as those found throughout the estuarine areas in Louisiana and listed above for Delacroix Island and Bay de Chene. Commercial species harvested are identical to those listed above for Delacroix Island and Bay de Chene. Recreational and commercial finfishing and shellfishing are common in the area, and oysters are cultivated on numerous leases throughout the area.

4.2 HISTORICAL RADIONUCLIDES AND DISCHARGE DATA

4.2.1 Delacroix Island Tank Battery #1

Information provided in the Louisiana Department of Environmental Quality (LDEQ) database from a one time sampling of produced water discharges in 1989 show a discharge of 222,081 L/day (1,397 bbl/day) with a Ra^{226} concentration of 273 pCi/L and a Ra^{228} concentration of 344 pCi/L. Updated discharge volume information provided in LDEQ files (Discharge Monitoring Reports) (1990 to 1992) averaged 276,767 L/day (1,741 bbl/day) for this discharge. The discharge terminated a week and a half prior to the 1 May 1993 scheduled termination date. At the time of termination, data were provided to us by Texaco field personnel which showed a volume of produced water which fluctuated between 312,217 L/day (1,964 bbl/day) and 314,442 L/day (1,978 bbl/day) for the period 26 March to 19 April 1993 during which time there were 11 wells in production. Prior to March 26, there were 12 wells in production. Discharge volumes during 19 to 25 March 1993 varied from 357,056 L/day (2,246 bbl/day) to 358,636 L/day (2,256 bbl/day).

4.2.2 Bay de Chene Tank Battery #5

Data provided in the LDEQ database recorded a 1989 volume of 582,784 L/day (3,666 bbl/day) with a Ra^{226} concentration of 71 pCi/L and a Ra^{228} concentration of 74 pCi/L. Updated 1990 to 1992 discharge volume data were not available in the LDEQ files. The discharge did not terminate on its scheduled 1 August 1993 termination date, but actually terminated about 15 October 1993. At the time we sampled the facility in May 1993 for the Pre-termination Survey, four wells were in production. Data provided by Texaco personnel showed a discharge volume of 608,060 L/day (3,825 bbl/day).

4.2.3 Four Isle Dome Central Production Facility

Data provided in the LDEQ database record a 1989 volume of 644,941 L/day (4,057 bbl/day) with a Ra^{226} concentration of 145 pCi/L and a Ra^{228} concentration of 158 pCi/L. Updated 1990 to 1992 discharge volume data available in the LDEQ files revealed a discharge rate of 135,442 L/day (852 bbl/day). Pre-termination sampling was conducted in November 1993. Termination of the discharge scheduled to be completed January 1994 was not effected until January 1995. Because the discharge was not terminated in a manner timely to this study, no post-termination sampling was conducted. At the time of the pre-termination sampling, no discharge data were made available to us by the operator.

CHAPTER 5 - SEDIMENT GRAIN SIZE AND TOTAL ORGANIC CARBON CONTENT

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5.1 INTRODUCTION

This chapter presents the results of the grain size and TOC analyses of sediment samples. Sediment grain size and TOC samples were collected at both Bay de Chene and Delacriox Island during the Pre-termination and First and Second Post-termination Surveys. Sediment grain size and TOC samples were collected at Four Isle Dome during the Pre-termination Survey. Samples were collected and analyzed from the 0 to 5 cm stratum at all stations and the 20 to 25 and 35 to 40 cm strata at selected stations. The data are used to characterize the sediment at each of the stations sampled for sediment chemistry (radionuclides, metals, and hydrocarbons).

5.2 LABORATORY METHODS

5.2.1 Grain Size

Grain size samples were washed in demineralized water, dried, and weighed. The coarse and fine fractions (sand/silt) were separated by sieving through a U.S. Standard Sieve Mesh No. 230 (62.5 μm). Sediment texture of the coarse fraction was determined at half-phi intervals by passing the sediment through nested sieves on a Ro-Tap apparatus. The weight of the material collected in each size was recorded. Boyocouse hydrometer analyses was used to determine the fine fraction (<62.5 μm). A computer algorithm was used to determine the complete size distribution and provide interpolated size information for the fine fraction at 0.25-phi intervals. A Sedigraph 5,000 ET Particle Size Analyzer was used to check the hydrometer analyzes. Median grain size and percentages of gravel, sand, silt, and clay were calculated for each sample.

5.2.2 Total Organic Carbon

TOC analysis was conducted using a LECO Induction Furnace. Sample combustion crucibles were cleaned by heating them in an induction furnace to 950°C. They were then removed, cooled to room temperature in a desiccator, and weighed to the nearest 0.1 mg. Five to 10 g of each sample were put in a cleaned crucible and dried to a constant weight at 70°C (±2°C) to avoid loss of semivolatile and volatile compounds. Each sample was then cooled to room temperature in a desiccator. The sample was then ground to a fine powder using an agate mortar and pestle. A 0.2 to 0.5 g aliquot of sample was transferred to a clean pre-weighed combustion crucible. Several drops of 10% HCl were added to the sample to remove any carbonates present. Acid was added until effervescing ceased (the acid was added slowly to prevent loss of sample by "overflow" during effervescence). The sample was then re-dried at 70°C to a constant weight and cooled to room temperature in a desiccator. A pre-measured scoop of copper was then added to the sample as a combustion aid. The sample was combusted in the induction furnace in the presence of oxygen and the evolved CO_2 was captured in a pre-weighted collection bulb.

The percent organic carbon was calculated by the following formula:

$$\text{Percent carbon} = \frac{A(0.2729)(100)}{B}$$

where A = weight, in grams, of CO_2 obtained by weighing the ascarite collection bulb before and after combustion of the sample;

B = the dry weight, in grams, of the unacidified sample in the combustion boat; and

0.2729 = the ratio of the molecular weight of carbon to the molecular weight of carbon dioxide.

5.2.3 Quality Assurance and Quality Control

5.2.3.1 Procedures

Data quality in the grain size and TOC analyses was ensured through the University of South Alabama, Department of Geology's Laboratory QA Program and SOPs. Prior notice to the laboratory was provided by CSA before samples were delivered to ensure that sample processing could proceed soon after delivery due to the extended processing time required. All samples received at the laboratory were checked against the accompanying sample custody sheets, entered into the laboratory's sample logbook, and placed in cold storage. A copy of the signed custody sheets was sent to ADL to complete the chain-of-custody and processing and analysis instructions and authorization were confirmed with the CSA Task Manager prior to proceeding with the analyses.

5.2.3.1.1 Grain Size Analysis

To the best extent possible, QA procedures were observed in the dry sieving and hydrometer methods used for the analysis of the coarse and fine fractions (<62.5 μm). Because grain size analysis involved primarily gravimetric procedures and there are no direct reproducible methods for assessing accuracy through the analysis of calibration standards and standard reference materials, accuracy is primarily ensured through continuing calibration of weighing equipment. ASTM-grade standard copper-mesh sieves were used. All sediment washing and sieving equipment were cleaned and checked daily for possible tears and major occlusions. The accuracy of all weighing equipment was checked daily or for each sample batch through the use of internal or NIST-traceable calibration-grade standard weights appropriate to the instrument being used and sample weights involved. Instrument accuracy ranges from 0.00001 g for analytical (Mettler) balances to 0.001 g for pan balances. Analytical balances were serviced and calibrated by factory service personnel twice a year. Maintenance and repair records for each balance were kept in logbooks at the laboratory.

NIST-traceable volumetric glassware, thermometers, and Bouyocous hydrometers were used to measure volumes, temperatures, and specific-gravity of sediment suspensions. Sediment samples were suspended in dilute solutions of sodium hexametaphosphate prepared according to SOPs. The Sedigraph 5,000 ET Particle Size Analyzer used to analyze the fine fraction as a QC check of the hydrometer method was calibrated according to the manufacturer's specifications using glass spherule standards of known particle size (microspheres). The QC check primarily involved comparison of the shape of the particle density distribution. A lower limit of detection of the hydrometer method cannot be measured because Brownian motion limits the particle size which will settle out. Median grain size and percentages of gravel, sand, silt, and clay were calculated for each sample.

5.2.3.1.2 Total Organic Carbon

For each sample batch, the LECO Induction Furnace carbon analyzer was initially calibrated by running at least three steel ring standards of known carbon content supplied by LECO, Inc. according to procedures specified by the manufacturer. Other than instrument standards, no standard reference materials were analyzed for carbon content to measure sample and analytical accuracy using the LECO carbon analyzer. Ten percent of all sediment samples were randomly selected and analyzed for TOC in duplicate to assure that precision was being maintained. Accuracy was checked through continuing calibrations using ring standards that were analyzed every 10 samples. The analysis was stopped and the instrument serviced or repaired if results from calibration standards varied from known values by more than 1%. However, records of these initial, continuing calibration, and other QC checks were not kept.

All analysts involved in the grain size and TOC analyses were extensively trained on the SOPs involved. All sample, fraction, and aliquot weights and analytical data were entered in ink in each analyst's data logbook. Each data set underwent internal reviews and audits prior to submission to CSA. Relevant project files and data will be archived at the University of South Alabama for at least five years before being destroyed.

5.2.3.2 Results

Due to limitations inherent to the sieving and hydrometer methods, no QA/QC results can be reported. Although QC steps were undertaken to check accuracy and precision in each analytical batch, records are not available. In addition, the parameters reported from grain size and TOC analyses are operationally defined, and therefore issues of accuracy and precision are difficult, if not impossible, to consistently quantify and resolve. Similarly, concern about contamination and interferences in the methods also cannot be addressed.

5.3 RESULTS AND DISCUSSION

5.3.1 Delacroix Island

Pre-termination Survey

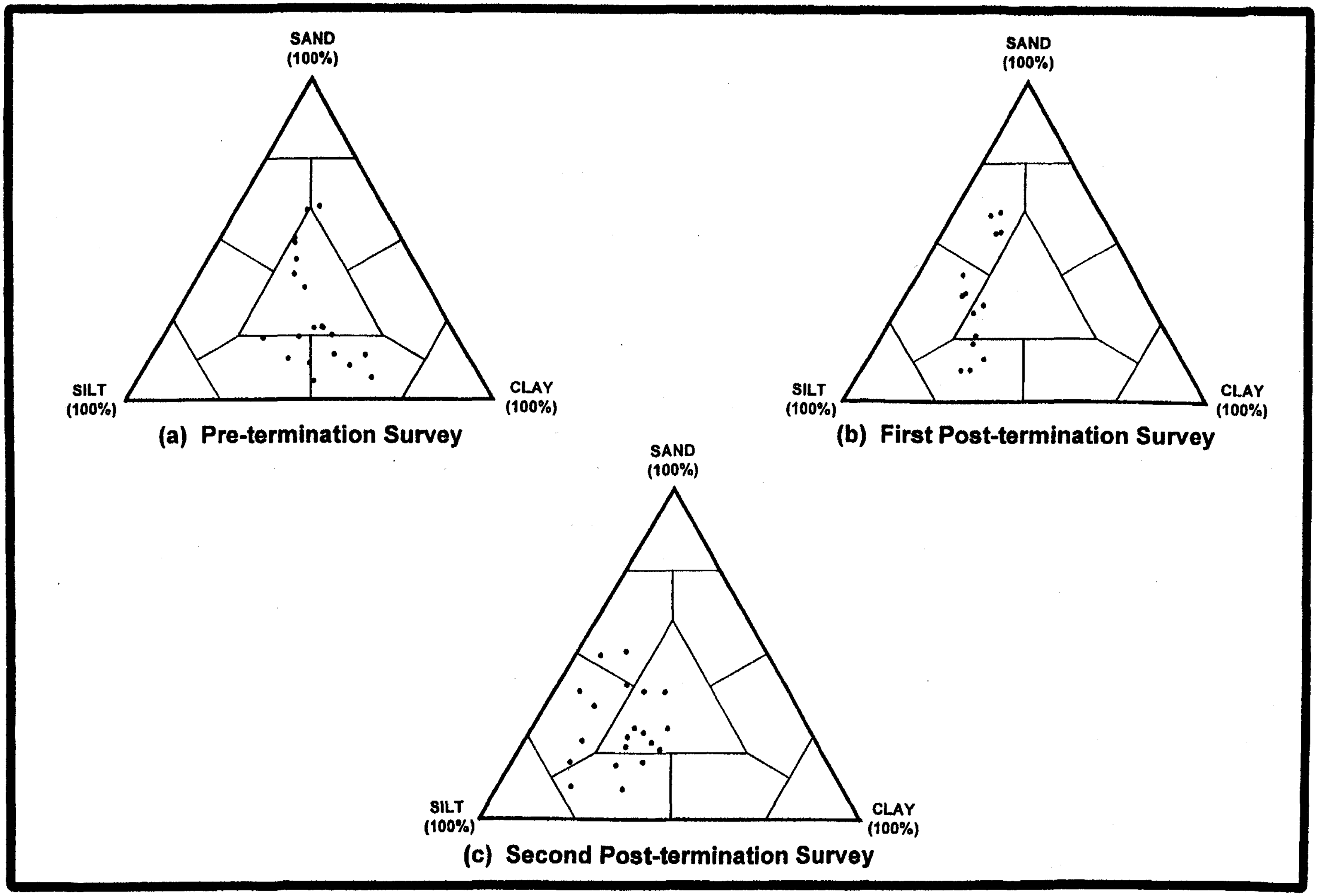
The percentage of gravel, sand, silt, clay, and TOC for sediment samples collected at Delacroix Island during the Pre-termination Survey are presented in **Table 5.1**. Three replicate grain size and TOC sediment samples were analyzed at three depth increments (0 to 5, 20 to 25, and 35 to 40 cm) at the discharge location and two reference stations located ≥2,000 m from the discharge. A single grain size and triplicate TOC surficial (0 to 5 cm) sediment samples were analyzed at each station along a northwest transect (**Figure 3.1**). Single grain size and TOC surficial sediment samples were analyzed at stations along the other transects. The sediment composition in the area of Delacroix Island is variable. The surficial sediments at 9 of the 14 stations are comprised of >60% mud (silt and clay components combined) and all deep sediments collected at the discharge and reference stations are comprised of >70% mud. Sand is the primary component in the surficial sediments at 6 of the 14 stations. The percent gravel at the sampled stations is low and ranges from 0 to 6.7 and surficial sediment composition did not exceed 2.4% gravel. All but three stations have a sediment composition that includes gravel. The grain size distributions for the sediment samples collected at Delacroix Island during the survey are presented in **Figure 5.1(a)**. The percentage of TOC in the sediments ranges from 2.16 to 17.52 with no obvious gradient associated with the produced water discharge. The high mean value and standard deviation compared to the other stations at the NW 1000 station may be due to vegetation.

First Post-termination Survey

The percentage of gravel, sand, silt, clay, and TOC for sediment samples collected at Delacroix Island during the First Post-termination Survey are presented in **Table 5.2**. Surficial (0 to 5 cm) sediment grain size (single) and TOC (single and triplicate) samples were analyzed at the same stations as during the Pre-termination Survey. The sediment composition in the area of Delacroix Island during this survey is quite similar to what was observed during the Pre-termination Survey. The surficial sediments at the same 9 of the 14 stations are comprised of >60% mud (silt and clay components combined). However, the percentage of sand at the discharge during this survey is 33.58% compared to a mean percentage of 4.83 during the first survey. The percent gravel, which is present at only 4 of the 14 stations, ranged from 0.00 to 2.12. The grain size distributions for the sediment samples collected at Delacroix Island during this survey are presented in **Figure 5.1(b)**. The percentage of TOC in the sediments ranged from 1.75 to 20.49. The high mean values and standard deviations compared to the other stations at the NW 1000 and R2 stations may be due to vegetation. The value at the NW 1000 station was similar during the Pre-termination Survey whereas the value at R2 was much lower. A slightly different geographic position may have been sampled on the First Post-termination Survey.

Table 5.1. Percentage (mean ± 1 standard deviation) of gravel, sand, silt, clay, and total organic carbon (TOC) for sediment samples (n=3) collected at Delacroix Island during the Pre-termination Survey (Spring 1993). All other values are percentages for a single sample (n=1). Stations are presented as discharge (DSC), transect compass heading, or reference (R), distance (m) along transect, and sediment increment (cm). Sediment textural descriptions based on Folk's (1954) classification are presented.

Station	Gravel	Sand	Silt	Clay	TOC	Textural Description
DSC 0-5	0.88 ±1.11	4.83 ±1.18	46.26 ±3.23	48.03 ±3.66	5.75 ±1.30	gravelly mud
DSC 20-25	0.48 ±0.80	13.66 ±7.77	36.42 ±5.66	49.44 ±4.66	4.49 ±0.60	gravelly sandy mud
DSC 35-40	0.06 ±0.09	11.36 ±5.73	44.63 ±5.92	43.95 ±3.89	3.31 ±1.59	gravelly sandy mud
NW 100 0-5	0.07	22.36	35.28	42.29	3.71 ±1.02	gravelly sandy mud
NW 300 0-5	0.07	20.12	33.96	45.85	6.28 ±5.66	gravelly sandy mud
NW 500 0-5	0.00	39.18	34.91	25.91	2.98 ±0.67	sandy mud
NW 1000 0-5	2.40	57.88	17.27	22.45	17.52 ±12.68	gravelly muddy sand
NE 100 0-5	0.36	12.50	49.70	37.44	3.63	gravelly sandy mud
NE 300 0-5	0.10	19.13	53.15	27.62	4.57	gravelly sandy mud
NE 500 0-5	0.13	19.54	43.38	36.95	4.28	gravelly sandy mud
S 100 0-5	0.00	59.17	21.32	19.51	2.60	muddy sand
S 300 0-5	0.17	50.30	29.12	20.41	2.38	gravelly muddy sand
S 500 0-5	0.00	48.93	29.85	21.22	2.36	sandy mud
S 1000 0-5	1.00	33.92	34.20	30.88	2.16	gravelly sandy mud
R1 0-5	0.12 ±0.15	22.63 ±7.42	35.42 ±0.71	41.84 ±7.96	3.67 ±0.49	gravelly sandy mud
R1 20-25	0.16 ±0.11	22.32 ±4.74	37.76 ±1.87	39.76 ±6.48	4.32 ±0.46	gravelly sandy mud
R1 35-40	1.10 ±1.17	12.90 ±7.25	28.01 ±10.50	57.99 ±18.70	5.79 ±0.79	gravelly sandy mud
R2 0-5	0.08 ±0.02	43.68 ±3.25	32.03 ±3.87	24.21 ±1.29	2.83 ±0.60	gravelly sandy mud
R2 20-25	2.26 ±3.84	6.28 ±3.62	27.18 ±1.16	44.28 ±7.86	5.80 ±1.13	gravelly sandy mud
R2 35-40	0.05 ±0.08	6.76 ±2.55	29.86 ±4.04	63.34 ±5.18	6.95 ±0.84	gravelly mud



(a) Pre-termination Survey

(b) First Post-termination Survey

(c) Second Post-termination Survey

Figure 5.1. Ternary diagrams for sediment grain size samples collected at Delacroix Island. Sediment textural descriptions are based on Shepard's (1954) classification. Sand sediment classification includes gravel component.

Table 5.2. Percentage of gravel, sand, silt, clay, and total organic carbon (TOC) for surficial (0-5 cm [0-2 in.]) sediment samples collected at Delacroix Island during the First Post-termination Survey (Spring 1994). Values for gravel, sand, silt, and clay are percentages for a single sample (n=1). Values for TOC are presented in percentage (mean ± 1 standard deviation, n=3). Stations are presented as discharge (DSC), transect compass heading, or reference (R) and distance (m) along transect. Sediment textural descriptions based on Folk's (1954) classification are presented.

Station	Gravel	Sand	Silt	Clay	TOC	Textural Description
DSC	0.00	33.58	50.82	15.60	3.54 ±0.47	sandy silt
NW 100	0.00	28.23	50.18	21.59	4.41 ±0.50	sandy silt
NW 300	0.00	20.97	53.13	25.90	4.85 ±1.30	sandy silt
NW 500	0.00	34.35	49.41	16.24	3.77 ±0.90	sandy silt
NW 1000	0.61	58.90	27.14	13.35	9.63 ±9.88	gravelly muddy sand
NE 100	0.00	18.48	55.13	26.39	1.75	sandy silt
NE 300	0.00	9.94	62.78	27.28	2.58	silt
NE 500	0.00	30.64	46.25	23.11	3.34	sandy silt
S 100	0.00	58.61	30.32	11.07	2.01	silty sand
S 300	0.00	52.94	31.74	15.32	2.12	silty sand
S 500	0.22	53.23	30.15	16.40	3.20	gravelly muddy sand
S 1000	0.00	10.08	60.08	29.84	5.26	sandy silt
R1	0.10	13.43	54.55	31.92	5.15 ±0.72	gravelly sandy mud
R2	2.12	37.96	47.38	12.54	20.49 ±7.64	gravelly sandy mud

Second Post-termination Survey

The percentage of gravel, sand, silt, clay, and TOC for sediment samples collected at Delacroix Island during the Second Post-termination Survey are presented in **Table 5.3**. Single and triplicate grain size and TOC sediment samples were analyzed from the Pre-termination Survey stations. The sediment composition in the area of Delacroix Island is relatively unchanged from the First Post-termination Survey. Gravel is present in the surficial sediments at only 5 of the 14 stations and ranges from 0.00% to 5.09%. The grain size distribution for the sediment samples collected at Delacroix Island during this survey are presented in **Figure 5.1(c)**. The percentage of TOC in the sediments ranges from 2.05 to 11.07.

5.3.2 Bay de Chene

Pre-termination Survey

The percentages of gravel, sand, silt, clay, and TOC for sediment samples collected at Bay de Chene during the Pre-termination Survey are presented in **Table 5.4**. Three replicate sediment grain size and TOC samples were analyzed at three depth increments (0 to 5, 20 to 25, and 35 to 40 cm) at the discharge location and two reference stations located ≥2,000 m from the discharge. A single grain size and triplicate TOC surficial (0 to 5 cm) sediment samples were analyzed at each station along a NE transect (**Figure 3.2**). Single grain size and TOC surficial sediment samples were analyzed at stations along the other transects. The sediment composition in the area of Bay de Chene is relatively homogeneous and can best be characterized as muddy with surficial sediments (0 to 5 cm) from 15 of the 17 stations comprised of ≥75% mud (silt and clay components combined) and all deep sediment increments (20 to 25 and 35 to 40 cm) comprised of ≥86% mud. Gravel is present in surficial sediments collected at each station. The percentage of gravel which is primarily of biogenic origin (mollusk shell) ranges from 0 to 9.11 (includes deep sediment increments). The grain size distribution for the sediment samples collected at Bay de Chene are presented in **Figure 5.2(a)**. The percentage of TOC in the sediments ranges from 1.36 to 7.76 with no obvious gradient associated with the produced water discharge.

First Post-Termination Survey

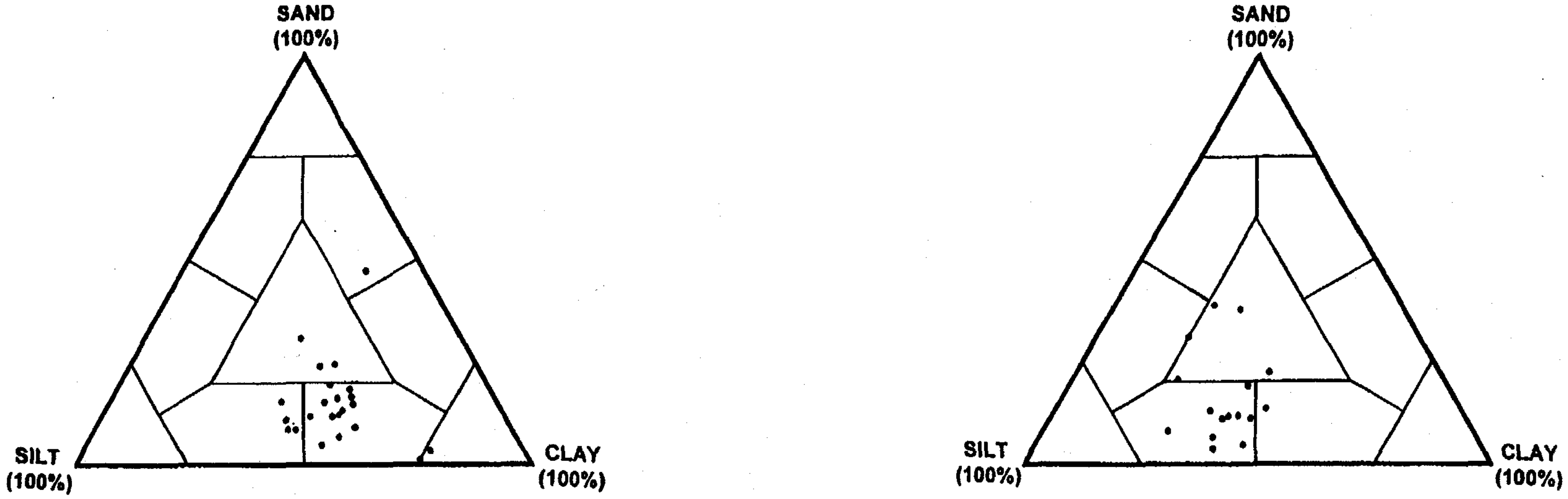
The percentages of gravel, sand, silt, clay, and TOC for sediment samples collected at Bay de Chene during the First Post-termination Survey are presented in **Table 5.5**. Surficial (0 to 5 cm) sediment grain size and TOC samples (single and triplicate) were analyzed at the same stations as during the Pre-termination Survey. The sediment composition in the area of Bay de Chene is similar to what was observed during the Pre-termination Survey, except during this survey surficial sediments at NW 1000 and R1 had a much higher percentage of gravel. Gravel was also present at only three of the stations, ranging from 0.13% to 26.75% ± 3.18% at these stations. Surficial sediments from 14 of the 17 stations are comprised of ≥75% mud (silt and clay components combined). The grain size distribution for the sediment samples collected at Bay de Chene during the First Post-termination Survey are presented in **Figure 5.2(b)**. The percentage of TOC in the sediments ranged from 2.63 to 6.59.

Table 5.3. Percentage (mean ± 1 standard deviation) of gravel, sand, silt, clay, and total organic carbon (TOC) for sediment samples (n=3) collected at Delacroix Island during the Second Post-termination Survey (Spring 1994). All other values are percentages for a single sample (n=1). Stations are presented as discharge (DSC), transect compass heading, or reference (R), distance (m) along transect, and sediment increment (cm). Sediment textural descriptions based on Folk's (1954) classification are presented.

Station	Gravel	Sand	Silt	Clay	TOC	Textural Description
DSC 0-5	0.00 ±0.00	24.76 ±13.40	49.18 ±7.17	26.06 ±8.68	4.10 ±0.71	sandy mud
DSC 20-25	0.23 ±0.39	23.04 ±6.43	43.68 ±3.08	33.05 ±9.75	4.95 ±0.50	gravelly sandy mud
DSC 35-40	0.84 ±1.45	25.90 ±11.76	43.95 ±8.32	29.31 ±3.77	4.00 ±0.92	gravelly sandy mud
NW 100 0-5	0.00 ±0.00	9.81 ±3.52	71.22 ±9.20	18.97 ±5.97	3.41 ±1.11	silt
NW 300 0-5	0.00 ±0.00	17.18 ±10.33	67.85 ±6.85	14.97 ±3.53	2.96 ±0.78	sandy silt
NW 500 0-5	0.26 ±0.23	33.84 ±8.26	53.23 ±8.22	12.67 ±2.75	3.20 ±1.24	gravelly sandy mud
NW 1000 0-5	0.16 ±0.27	50.45 ±7.10	36.84 ±4.71	12.55 ±2.63	3.43 ±0.86	gravelly sandy mud
NE 100 0-5 A	0.00	16.32	56.36	27.32	4.11	sandy silt
NE 300 0-5 A	0.00	9.02	58.22	32.76	3.87	mud
NE 500 0-5 A	0.98	22.67	61.51	14.84	2.44	gravelly sandy mud
S 100 0-5 A	5.09	33.38	54.93	6.60	2.69	gravelly mud
S 300 0-5 A	0.00	49.44	44.04	6.52	2.05	sandy silt
S 500 0-5 A	0.00	40.42	41.68	17.90	11.07	sandy silt
S 1000 0-5 A	0.00	21.89	51.04	27.07	9.15	sandy mud
R1 0-5	0.00 ±0.00	27.49 ±12.59	45.98 ±6.69	26.53 ±5.93	3.81 ±1.13	sandy mud
R1 20-25	0.00 ±0.00	17.22 ±11.80	48.91 ±9.56	33.87 ±2.30	6.05 ±0.99	sandy mud
R1 35-40	0.00 ±0.00	27.29 ±17.13	37.49 ±11.53	35.22 ±8.51	3.71 ±0.49	sandy mud
R2 0-5	1.70 ±1.82	36.63 ±13.07	38.19 ±9.55	23.48 ±6.94	3.79 ±1.28	gravelly sandy mud
R2 20-25	3.97 ±6.00	34.20 ±12.34	32.86 ±10.84	28.97 ±8.07	6.83 ±2.78	gravelly sandy mud
R2 35-40	1.32 ±1.21	19.69 ±2.73	42.64 ±3.79	36.35 ±2.94	9.75 ±3.00	gravelly sandy mud

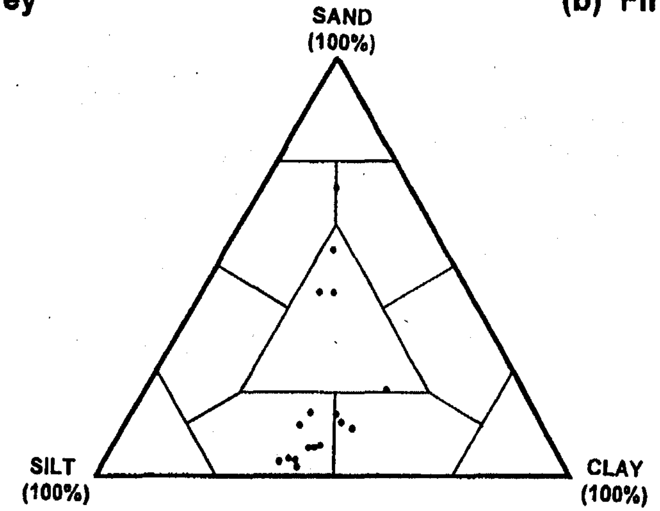
Table 5.4. Percentage (mean ± 1 standard deviation) of gravel, sand, silt, clay, and total organic carbon (TOC) for sediment samples (n=3) collected at Bay de Chene during the Pre-termination Survey (Spring 1993). All other values are percentages for a single sample (n=1). Stations are presented as discharge (DSC), transect compass heading, or reference (R), distance (m) along transect, and sediment increment (cm). Sediment textural descriptions based on Folk's (1954) classification are presented.

Station	Gravel	Sand	Silt	Clay	TOC	Textural Description
DSC 0-5	0.06 ±0.10	14.70 ±2.90	31.53 ±2.23	53.71 ±0.86	5.59 ±0.34	gravelly sandy mud
DSC 20-25	0.09 ±0.13	11.58 ±0.69	37.90 ±5.47	50.44 ±5.02	6.68 ±0.53	gravelly sandy mud
DSC 35-40	0.25 ±0.02	12.87 ±2.03	34.67 ±0.69	52.21 ±1.47	6.26 ±0.59	gravelly sandy mud
NE 100 0-5	0.18	8.35	49.11	42.36	6.05 ±2.63	gravelly mud
NE 300 0-5	0.53	15.64	34.44	49.39	5.39 ±2.09	gravelly sandy mud
NE 500 0-5	0.07	4.48	43.74	51.71	5.39 ±0.21	gravelly mud
NE 1000 0-5	0.25	18.12	30.37	51.26	3.44 ±0.32	gravelly sandy mud
NW 100 0-5	0.55	6.09	38.73	54.63	5.38	gravelly mud
NW 300 0-5	0.04	16.51	30.90	52.55	7.76	gravelly sandy mud
NW 500 0-5	0.03	10.89	48.37	40.71	4.69	gravelly sandy mud
NW 1000 0-5	0.20	15.27	47.08	37.45	3.08	gravelly sandy mud
SW 100 0-5	0.38	8.57	33.99	57.06	5.25	gravelly mud
SW 300 0-5	0.06	19.31	34.51	46.12	4.01	gravelly sandy mud
SW 500 0-5	0.22	30.46	35.03	34.29	1.36	gravelly sandy mud
SW 1000 0-5	0.03	12.08	36.11	51.78	2.28	gravelly sandy mud
SE 500 0-5	5.40	41.69	12.61	40.30	3.35	gravelly sandy mud
SE 1000 0-5	0.36	23.55	34.43	41.66	3.83	gravelly sandy mud
R1 0-5	5.68 ±2.98	18.75 ±3.79	30.86 ±6.02	44.71 ±6.81	5.15 ±0.84	gravelly sandy mud
R1 20-25	0.03 ±0.03	3.15 ±2.54	20.71 ±5.18	76.11 ±7.68	2.41 ±1.87	gravelly mud
R1 35-40	0.00 ±0.00	1.50 ±0.31	24.04 ±4.50	74.46 ±4.21	2.59 ±0.38	clay
R2 0-5	0.11 ±0.12	15.09 ±2.35	37.82 ±4.20	46.98 ±6.24	4.29 ±0.33	gravelly sandy mud
R2 20-25	0.07 ±0.08	11.62 ±4.39	42.65 ±2.47	45.65 ±6.47	4.77 ±0.74	gravelly sandy mud
R2 35-40	0.02 ±0.02	8.43 ±0.36	47.45 ±0.89	44.10 ±0.51	3.87 ±0.48	gravelly mud



(a) Pre-termination Survey

(b) First Post-termination Survey



(c) Second Post-termination Survey

Figure 5.2. Ternary diagrams for sediment grain size samples collected at Bay de Chene. Sediment textural descriptions are based on Shepard's (1954) classification. Sand sediment classification includes gravel component.

Table 5.5. Percentage (mean ± 1 standard deviation) of gravel, sand, silt, clay, and total organic carbon (TOC) for surficial (0-5 cm [0-2 in.]) sediment samples (n=3) collected at Bay de Chene during the First Post-termination Survey (Fall 1993). All other values are percentages for a single sample (n=1). Stations are presented as discharge (DSC), transect compass heading, or reference (R) and distance (m) along transect. Sediment textural descriptions based on Folk's (1954) classification are presented.

Station	Gravel	Sand	Silt	Clay	TOC	Textural Description
DSC	0.00 ±0.00	11.79 ±3.59	48.02 ±6.10	40.19 ±2.63	6.59 ±1.01	sandy mud
NE 100	0.00 ±0.00	11.16 ±2.48	45.58 ±3.80	43.26 ±5.45	3.62 ±1.33	sandy mud
NE 300	0.00 ±0.00	22.31 ±16.84	35.97 ±14.78	41.72 ±3.99	6.47 ±0.18	sandy mud
NE 500	0.00 ±0.00	13.41 ±2.71	41.11 ±2.78	45.48 ±2.09	5.66 ±1.38	sandy mud
NE 1000	0.00 ±0.00	19.00 ±4.52	42.24 ±3.56	38.76 ±2.03	4.80 ±1.02	sandy mud
NW 100	0.00	4.60	50.45	44.95	5.43	mud
NW 300	0.00	13.00	53.40	33.60	4.31	sandy mud
NW 500	0.00	5.49	62.59	31.92	5.12	mud
NW 1000	9.78	21.11	49.11	20.00	2.63	gravelly mud
SW 100	0.13	3.46	57.52	38.89	5.34	gravelly mud
SW 300	0.00	6.48	56.09	37.43	5.57	mud
SW 500	0.00	11.66	50.20	38.14	4.11	sandy mud
SW 1000	0.00	8.06	65.05	26.89	6.07	silt
SE 500	0.00	38.84	39.64	21.52	5.11	sandy mud
SE 1000	0.00	10.94	51.89	37.17	4.86	sandy mud
R1	26.75 ±3.18	10.96 ±3.78	34.50 ±3.77	27.79 ±1.60	5.64 ±0.42	gravelly mud
R2	0.00 ±0.00	20.63 ±1.31	56.67 ±1.69	22.69 ±2.18	4.85 ±0.37	sandy silt

Second Post-termination Survey

The percentages of gravel, sand, silt, clay, and TOC for sediment samples collected at Bay de Chene during the Second Post-termination Survey are presented in **Table 5.6**. Single and triplicate grain size and TOC surficial (0 to 5 cm) sediment samples were analyzed from the Pre-termination Survey stations. The sediment composition in the area of Bay de Chene was predominantly muddy and similar to what was observed during the previous surveys. Major differences in sediment composition between surveys was due primarily to large fluctuations in the percentage of gravel. The percentage of gravel, present at only four stations, ranged from 10.85% to 57.08% at these stations. Minor changes in the sediment composition at Bay de Chene between surveys is most probably due to spatial rather than temporal heterogeneity. The grain size distribution for the sediment samples collected at Bay de Chene during this survey are presented in **Figure 5.2(c)**. The percentage of TOC in the sediments ranged from 3.83 to 8.58.

5.3.3 Four Isle Dome

Pre-termination Survey

The percentages of gravel, sand, silt, clay, and TOC for sediment samples collected at Four Isle Dome during the Pre-termination Survey are presented in **Table 5.7**. Single grain size and triplicate TOC sediment samples were analyzed at three depth increments (0 to 5, 20 to 25, and 35 to 40 cm) at the discharge location and two reference stations located ≥2,000 m from the discharge. A single grain size and single TOC surficial sediment samples were analyzed at all the other stations (**Figure 3.3**). The sediment composition in the area of Four Isle Dome is muddy. The surficial sediments at all 10 stations were comprised of >85% mud (silt and clay components combined) and all deep sediments collected at the discharge and reference stations were comprised of >80% mud. Gravel was not present in the surficial sediments and surficial sand content ranged from 2.70% to 21.21%. The grain size distribution for the sediment samples collected at Four Isle Dome during this survey are presented in **Figure 5.3**. The percentage of TOC in the sediments was quite variable and ranged from 3.33 to 12.49.

5.4 REFERENCES

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5.5 ACKNOWLEDGEMENTS

Dr. Wayne Isphording was responsible for conducting the grain size and TOC analyses. Wayne also provided the computer program used to produce the ternary diagrams. His efforts and cooperation are greatly appreciated.

Table 5.6. Percentage of gravel, sand, silt, clay, and total organic carbon (TOC) for surficial (0-5 cm) sediment samples collected at Bay de Chene during the Second Post-termination Survey (Spring 1994). Values for gravel, sand, silt, and clay are percentages for a single sample (n=1). Values for TOC are presented in percentage (mean ± 1 standard deviation, n=3). Stations are presented as discharge (DSC), transect compass heading, or reference (R) and distance (m) along transect. Sediment textural descriptions based on Folk's (1954) classification are presented.

Station	Gravel	Sand	Silt	Clay	TOC	Textural Description
DSC	0.00	3.69	59.93	36.38	7.31 ±0.83	mud
NE 100	0.00	4.00	56.33	39.67	7.80 ±1.62	mud
NE 300	0.00	20.59	28.86	50.55	8.58 ±2.98	sandy mud
NE 500	50.38	3.45	23.64	22.53	5.35 ±0.39	muddy gravel
NE 1000	0.00	11.55	40.61	47.84	5.93 ±0.08	sandy mud
NW 100	0.00	7.00	50.83	42.17	6.15	mud
NW 300	0.00	4.34	57.56	38.10	6.05	mud
NW 500	0.00	15.28	47.56	37.16	4.98	sandy mud
NW 1000	35.17	8.38	28.75	27.70	5.51	muddy gravel
SW 100	0.00	14.87	42.33	42.80	5.93	sandy mud
SW 300	0.00	12.99	42.20	44.81	5.50	sandy mud
SW 500	0.00	2.34	56.83	40.83	5.75	mud
SW 1000	0.00	7.46	49.31	43.23	5.46	mud
SE 1000	0.00	6.90	52.12	40.98	5.30	mud
SE 500	10.85	32.81	31.64	24.70	3.83	gravelly mud
R1	57.08	11.62	15.65	15.65	7.14 ±1.27	muddy gravel
R2	0.00	12.39	51.26	36.35	5.76 ±0.57	sandy mud

Table 5.7. Percentage of gravel, sand, silt, clay, and total organic carbon (TOC) for sediment samples collected at Four Isle Dome during the Pre-termination Survey (Fall 1993). Values for gravel, sand, silt, and clay are percentages for a single sample (n=1). Values for TOC are presented in percentage (mean ± 1 standard deviation, n=3). Stations are presented as discharge (DSC), transect compass heading, or reference (R), distance (m) along transect, and sediment increment (cm). Sediment textural descriptions based on Folk's (1954) classification are presented.

Station	Gravel	Sand	Silt	Clay	TOC	Textural Description
DSC 0-5	0.00	12.21	36.25	51.54	5.24 ±0.98	sandy mud
DSC 20-25	0.00	10.93	45.47	43.60	4.99 ±0.42	sandy mud
DSC 35-40	0.74	18.92	42.57	37.77	10.76 ±11.17	gravelly sandy mud
N 100 0-5	0.00	7.53	44.83	47.64	9.56	mud
N 300 0-5	0.00	6.69	39.88	53.43	9.88	mud
N 500 0-5	0.00	3.71	47.49	48.80	10.77	mud
N 1000 0-5	0.00	9.08	44.78	46.14	12.49	mud
S 100 0-5	0.00	5.25	48.28	46.47	7.19	mud
S 300 0-5	0.00	3.09	47.93	48.98	9.06	mud
S 500 0-5	0.00	2.70	49.47	47.83	10.64	mud
R1 0-5	0.00	3.06	48.96	47.98	5.44 ±1.36	mud
R1 20-25	0.00	1.84	41.82	56.34	12.33 ±6.66	mud
R1 35-40	0.00	2.13	45.10	52.77	5.17 ±4.17	mud
R2 0-5	0.00	11.41	55.85	32.74	4.06 ±2.00	sandy mud
R2 20-25	0.00	13.26	45.79	40.95	3.33 ±0.73	sandy mud
R2 35-40	0.00	6.41	51.90	41.69	5.19 ±2.99	mud

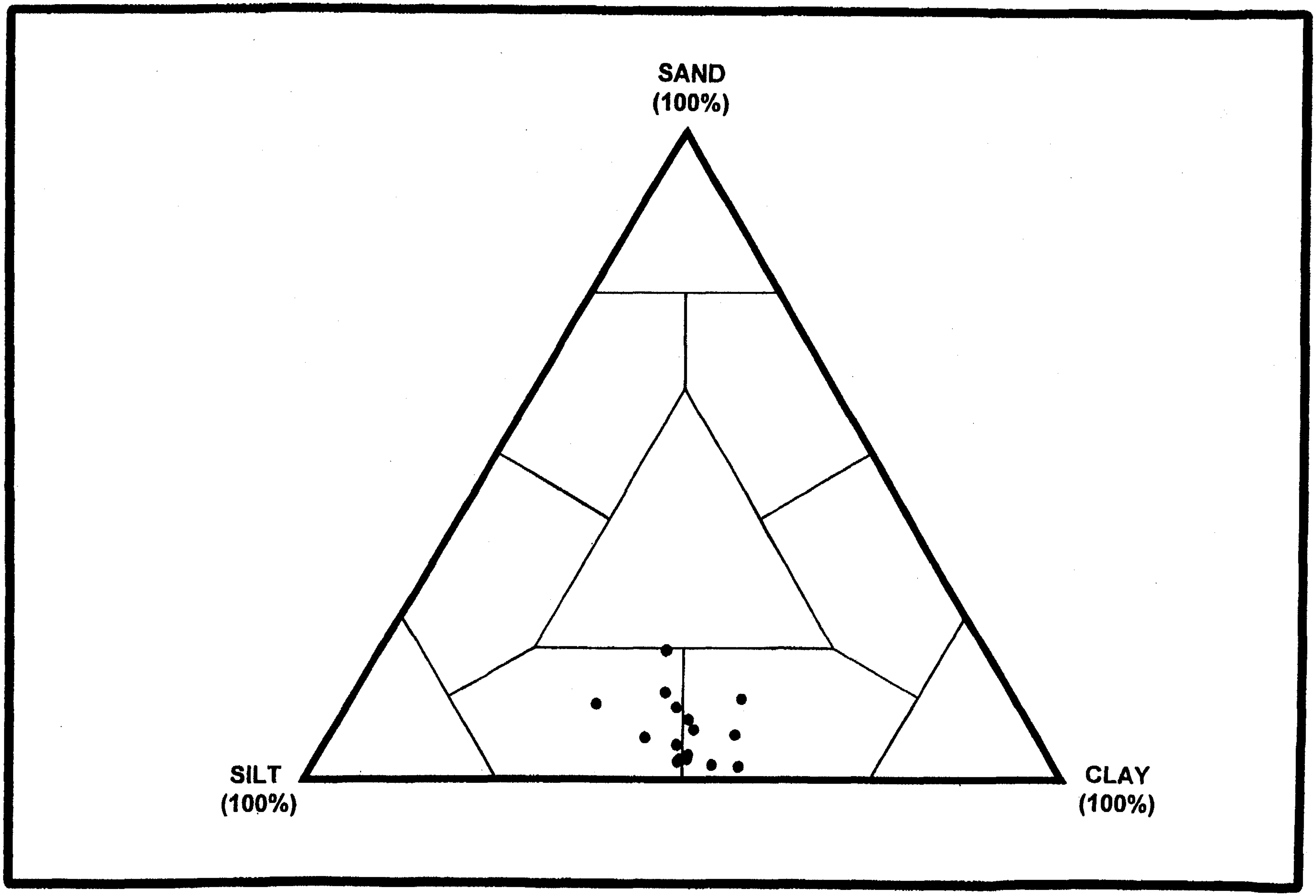

Figure 5.3. Ternary diagram for sediment grain size samples collected at Four Isle Dome during the Pre-termination Survey (Survey I). Sediment textural descriptions are based on Shepard's (1954) classification. Sand sediment classification includes gravel component.

CHAPTER 6 - DISTRIBUTION OF RADIONUCLIDES IN PRODUCED WATER, INTERSTITIAL WATER, SEDIMENTS, AND FAUNA IN AREAS WHERE PRODUCED WATER WAS DISCHARGED TO COASTAL LOUISIANA WATERS

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6.1 INTRODUCTION

Radionuclide analyses (^{226}Ra and ^{228}Ra) were conducted on samples of produced water, interstitial water, sediment, and biological tissues. Additional radionuclides (^{210}Pb, ^{210}Po, and ^{228}Th) were determined in produced water samples. The samples were collected during the surveys that are described in **Chapter 3**. The results of the analyses were used in environmental and human health risk assessments of radionuclides (Meinhold et al., 1996a,b).

6.2 LABORATORY METHODS

Upon delivery at the CORE laboratory in Casper, Wyoming, all samples were logged in and held in cold storage (water) or frozen (sediment and tissue) until specific analysis instructions and authorizations were received by the laboratory.

6.2.1 Water Samples

Each produced water sample consisted of four 1-L samples. The individual samples were mixed in the laboratory and a 1-L composite was used for the analysis. To measure the dissolved isotope concentrations, each sample was filtered to remove suspended particles. The interstitial water samples were filtered during the squeezing process (**Section 3.1.3.1.2**).

Radionuclide analyses of water samples were performed following standard protocols of Percival and Martin (1974) and EPA (1980) with slight modifications to remove interferences known to occur in specific sample types following Demorest and Wallace (1992).

Preparation of the samples for ^{226}Ra and ^{228}Ra analysis followed the sequential method of Percival and Martin (1974) with modification. Radium was initially co-precipitated on lead sulfate out of a hot solution of saturated potassium sulfate by multiple additions of lead nitrate with heating between each addition. In cases where there were elevated total dissolved solids levels (200,000 mg/L of chloride or 10,000 mg/L of calcium), the aliquot size was adjusted down and the materials were diluted 20 to 40 fold (100 mL sample diluted to 2 L with deionized water). This dilution, the principal modification of the Percival and Martin method, eliminates interferences from high chloride and calcium content. The sample was then precipitated with lead sulfate. This precipitate was dissolved in diethlenetriamininepentaacetic acid (DTPA) and the radium was re-precipitated with barium sulfate leaving thorium, lead, and actinide daughters in the solution.

The barium sulfate precipitate was then redissolved in DTPA. ^{226}Ra activity was then determined by alpha counting of the barium sulfate directly using a Ludlum scintillation counter. The DTPA solution containing the ^{228}Ra was set aside for a minimum of 36 h to allow equilibrium to be achieved. ^{228}Ra was then precipitated out of the DTPA using barium sulfate. ^{228}Ra activity was then determined by beta counting ^{228}Ac, the decay product of ^{228}Ra, precipitated on cerium oxalate using a Berthhold 770 10-channel low background proportional counter. Following the re-precipitation of radium using DTPA, ^{210}Pb remains in the solution. Thorium and lead ions were re-precipitated as lead sulfate for the produced water samples. The sulfate ion was removed via ammonium acetate and sodium carbonate double precipitation. The aqueous solution containing the ^{228}Th was then extracted with trioctylphosphinoxide (TOPO) in heptane, then co-precipitated with neodinium flouride and mounted for counting by alpha spectroscopy. The lead carbonate precipitate with the ^{210}Pb was then dissolved in acetic acid, added to a 10-ml of Packard Ultima Gold-XL scintillation cocktail solution, and counted in a Packard 2260XL Tri-carb Low Background Liquid Scintillation Counter with multi-channel analyzer window sets at 7 to 30 Kev and 30 to 250 Kev. For the ^{210}Po analysis of the produced water, a separate aliquot of the digested sample was purified by extraction with diethyldithiocarbamic acid-diethyl-ammonium salt (DDTC) in chloroform. The precipitate was redissolved in mild nitric acid and electro-deposited on a nickel disk. The disk was rinsed, dried, and counted using alpha spectroscopy.

6.2.2 Sediment Samples

To prepare the sediment samples for the chemical separation of the radium isotopes, the samples were dried, ground, homogenized, and digested using a nitric-hydrofluoric-perchloric acid digestion to destroy organic material. Two grams of sediment were used for analyses. Siliceous material was driven off by the nitric-hydrofluoric acid digestion and a potassium fluoride fusion. Finally a sodium sulfate fusion was utilized to destroy any residual organic material. The resulting lead sulfate precipitation was used following similar procedures to those described above for the analyses of ^{226}Ra and ^{228}Ra in water samples.

The sediment samples from Four Isle Dome were not analyzed using chemical separation and a proportional counter, but were analyzed using gamma spectroscopy (EPA Method 901.1). While gamma spectroscopy is a valid and accepted methodology for radionuclide analysis, the detection limits obtainable are one to three orders of magnitude higher than the chemical separation of radium methodology used on the samples from Delacroix Island and Bay de Chene. The gamma analyses were performed on a EG&G ADCAM System, multi-channel analyzer using EG&G ORTEC MINGAM software. The samples were counted for 18,000 seconds on a 20% high purity, high resolution germanium detector. The spectral output for ^{214}Bi was reported for ^{226}Ra and the spectral output for ^{228}Ac reported for ^{228}Ra. Experience has shown that radionuclide activities determined by both instruments (proportional counter and gamma spectrometer) are generally comparable (D. Demorest, pers. comm. 1997, Core Laboratories, Inc.).

Statistical analyses of the Delacroix Island and Bay de Chene sediment radionuclide data were conducted using analysis of variance procedures described by Sokal and Rohlf (1995). Tukey's post hoc test was used to identify significantly different means. Dependent variables were ^{226}Ra and ^{228}Ra activities. Independent variables for the sites were Sample Period (Pre-termination Survey, First Post-termination Survey, and Second Post-termination Survey) and Zone (discharge, 100, 300, 500, and 1,000 m stations on all transects, and the reference stations). Due to the station configurations at both Delacroix Island and Bay de Chene, the data sets were not completely balanced. At Delacroix Island there was not a 1,000 m station on the NE transect. At Bay de Chene, the SE transect did not have 100 and 300 m stations. The assumptions for analysis of variance were verified, including normality and homogeneous variances. Due to the difference in analytical methodology and the one time nature of the sampling at the Four Isle Dome site, the ^{226}Ra and ^{228}Ra data were not analyzed statistically.

6.2.3 Tissue Samples

Tissue material used for radionuclide analyses was exclusively the edible portion (flesh) of the organism. Approximately 50 to 60 g of tissue were used in the extraction, when available. The tissues were homogenized then digested with concentrated nitric acid and peroxide. This solution was extracted with an equal volume of heptane to remove the long-chain fat molecules. The nitric fraction was then solubilized with consecutive digestions using dilute nitric acid, then nitric acid-peroxide, and finally nitric-hydrofluoric-perchloric acid digestion. The digested material was then subjected to a sodium sulfate fusion to complete destruction of the organic material and to ensure the ionic state of the isotopes. A lead sulfate precipitation was then performed, followed by analyses for ^{226}Ra and ^{228}Ra.

6.2.4 Quality Assurance and Quality Control

6.2.4.1 Procedures

CORE provides radiochemistry analytical services through a comprehensive, rigorous corporate QA Program. The laboratory has been granted Region VIII EPA certification for radionuclide analysis and maintains certifications with a number of states for analysis of various radionuclides in different matrices. CORE is subject to and has passed EPA audits every 2 years. In addition, CORE was subjected to and passed audits by several DOE facilities (e.g., by Sandia, Oak Ridge National Laboratories) for site-specific projects.

Upon arrival, all samples received at the CORE Casper, Wyoming laboratory were examined with a gamma probe for high activity levels, checked for possible contamination from breakage/spillage, and inspected for acceptable shipping conditions. The samples were sorted and matched with the accompanying chain-of-custody forms and analysis instructions. A laboratory sample identification number was assigned to each sample as part of CORE's log-in process. At times when a hold order was placed on a batch of samples, CORE's standard log-in process was not completed until authorization was received from CSA. In these cases, samples were held in storage until specific analysis instructions and authorization was obtained from CSA prior to proceeding with the analyses.

According to CORE's SOP, each sample was assessed for adequate sample volume and the sample information was entered into the CORE Laboratory Information Management System (LIMS) including client, laboratory sample identification number, processing instructions, and count times. Upon completion of the log-in procedure, summary reports were generated with the LIMS for sample receipt verification and reviewed by the Radiochemistry Section Supervisor. Following review, copies of the log-in verification, chain-of-custody, and sample verification forms were sent to S&A or CSA.

Samples were prepared for analysis as described in **Section 6.2** and each analytical instrument was setup and initially calibrated according to the manufacturer's specifications and applicable SOPs. Instrument and analyst performance was monitored continuously using laboratory control charts. Calibration sources for each instrument and matrix were prepared from NIST-traceable materials. Stock solutions and method blanks were prepared with distilled-deionized water. Certified analytical grade acids and solvents for all solutions were used according to SOP. Records were kept of all standards and prepared solutions and sources, including certified analyses.

After initial instrument calibration was completed, each batch of field samples was analyzed with a complete set of QC samples including method blanks, method duplicates, a laboratory control standard, and matrix spikes to assess contamination, interferences, accuracy, and precision. Detection limits (minimum detectable activity) were determined and reported for each sample, analyte, sample type, and matrix. DQOs and acceptance criteria for radionuclide analysis are presented in **Table 6.1**.

All analytical results were reviewed and audited prior to submission to CSA. Along with a case narrative and a complete QC summary, each data package was submitted in hardcopy and spreadsheet format. According to laboratory SOP, data reports, working documents, and project files will be archived for at least 5 years before disposal.

6.2.4.2 Results

Two QA problems occurred in the radionuclide analyses. These problems involved a lack of consistency in the analysis methods and different reported lower limits of detection (LLDs) for the same method for sediment samples. A LLD is determined for each sample because the detection limit is a function of the quantity of sample, counting time, and the gross background counts. CSA did not notice these problems when the data were submitted by CORE. They were not discovered until all the data were sent to S&A for report writing and a comparison between data sets was made. Direct comparison of the pre-termination, first post-termination, and second post-termination data could have been problematic if there were major inconsistencies in the methodology and LLDs.

Although CSA provided analysis instructions which specified the target LLD for each sample delivered to CORE, a number of sediment samples were mistakenly analyzed by gamma spectroscopy rather than proportional counting following wet chemistry. The SAP specified wet-chemistry methods and proportional counting for ^{226}Ra and ^{228}Ra as these methods result in detection limits that are comparable to the target LLDs. Unfortunately, CORE did not use this method but instead used gamma spectroscopy for the Four Isle Dome samples. LLDs similar to those reported from wet-chemistry and proportional counting were not reported for the samples analyzed by gamma spectroscopy unless a value fell below the detection limit. The samples could not be re-analyzed as they had been disposed of by the time the problem was identified. However, the low radionuclide values and the lack of post-termination radionuclide data for Four Isle Dome precluded the need for re-analysis of the samples.

Table 6.1. General data quality objectives and criteria for radionuclide analyses.

Element or Sample Type	Minimum Frequency	Data Quality Objective/ Acceptance Criteria
Initial Calibration	Prior to every analytical batch	± 10% of calibration values
Laboratory Control Sample	1 per batch	Percent recovery within 80 to 120%
Matrix Spikes	1 per batch or 5% of field samples	Percent recovery target analytes 75% to 125%
Matrix Duplicate	1 per batch or 5% of field samples	Relative percent difference within 20%
Procedural Blank	1 per batch or 5% of field samples	Not to exceed 5 times target detection limit
Duplicate Sample Analysis	1 per batch or 5% of field samples	Absolute difference between duplicates less than detection limit
Target Detection Limit: ^{226}Ra*	Produced water Ambient seawater Produced sand and sediment Tissue	2.09 pCi/L 0.1 pCi/L 0.05 pCi/g 0.006 pCi/g
Target Detection Limit: ^{228}Ra*	Produced water Ambient seawater Produced sand and sediment Tissue	3.5 pCi/L 0.35 pCi/L 0.19 pCi/g 0.019 pCi/g
Target Detection Limit: ^{210}Pb*	Produced water Ambient seawater Produced sand and sediment Tissue	3.28 pCi/L 0.22 pCi/L 0.11 pCi/g 0.012 pCi/g
Target Detection Limit: ^{228}Th	Produced water	3 pCi/L
Target Detection Limit: ^{210}Po	Produced water	3 pCi/L

* Due to sample limitations, target detection limits were not specified for interstitial waters.

Several of the pre-termination sediment samples from Delacroix Island and Bay de Chene were also initially analyzed for ^{226}Ra and ^{228}Ra by gamma spectroscopy, but were later re-analyzed by wet chemistry and proportional counter methods. The re-analysis by wet chemistry and proportional counting of these samples resulted in higher LLDs and radionuclide values than the samples from the same surveys that were initially analyzed by wet chemistry and proportional counting. Although the specific basis for the higher detection limits is unclear, the target limits of detection may have not been achieved initially or consistently due to differences in the gross background counts, counting efficiency, and counting times.

Based on the results of the analyses of the QC samples, data quality for radionuclides in the relevant matrices was good. ^{226}Ra and ^{228}Ra activity in the equipment blanks were low. Except for a single instance (equipment blank from Delacroix Island Second Post-termination Survey), evidence that samples were contaminant-free can be found in the low radionuclide activities in the equipment blanks that were analyzed. Low radionuclide activities were also found in the produced water field blanks indicating contaminant-free samples.

The DQOs for accuracy, precision, detection limits (other than sediment), and comparability for radionuclide analyses of samples were met by CORE in most cases. Low background counts were found in method blanks used in each analytical sample batch. Quality control data from the matrix spikes and reference materials demonstrated that the accuracy and precision of the radionuclide measurements were mostly within the DQOs. Although the method duplicates in some cases were out of the stated acceptance criteria ranges for precision, these were due to the very low activity levels found in the majority of the samples.

In produced water, the reported LLD for ^{226}Ra was 0.3 pCi/L for Delacroix Island and Bay de Chene samples while in Four Isle Dome samples it was 1.7 pCi/L. The produced water samples from Four Isle Dome analyzed for ^{228}Ra had LLDs which slightly exceeded the target detection limit of 3.5 pCi/L ^{228}Ra LLDs for Delacroix Island and Bay de Chene did not exceed the target detection limit. In the samples whose reported LLDs exceeded the target detection limit, radionuclide concentrations were greater than the target detection limit by two orders of magnitude. The ^{210}Pb, ^{210}Po, and ^{228}Th target detection limits of 3.28, 3.0, and 3.0 pCi/L, respectively, were met in all of the produced water samples from all sites.

The other exceedances of the target detection limits were, as previously mentioned, for ^{226}Ra and ^{228}Ra in the Delacroix Island and Bay de Chene pre-termination sediment samples that were re-analyzed. In the tissues samples the LLDs in only 2 out of 80 tissue samples exceeded the target detection limits of 0.006 pCi/g for ^{226}Ra and 4 samples exceeded the target for ^{228}Ra of 0.019 pCi/g.

CSA specified target detection limits for ^{226}Ra and ^{228}Ra activity in all matrices except for interstitial waters as part of the analysis instructions. Target detection limits for interstitial water samples could not be specified because there was little experience in the analysis of this matrix upon which to base detection limits. In addition, detection limits could not be set *a priori* because of the uncertainty in the sample volume that could be extracted from each sediment sample as this is a function of the porosity of the sediment and the amount of sediment available for extraction (number of cores times volume of subcores or sections). The reported lower limits of detection for ^{226}Ra and ^{228}Ra activity in interstitial water samples from all sites and surveys were generally within the target limits for produced water.

6.3 RESULTS

Radionuclide data from the laboratory were reported as pCi/L for water, pCi/g dry weight for sediment, and pCi/g wet weight tissue samples. To convert the reported pCi/L or pCi/g units values to metric units (bequerels or Bq), multiply by 0.037.

6.3.1 Produced Water

Two, four-hour, composite radionuclide samples of produced water were collected during the Pre-termination Surveys at Delacroix Island (**Figure 3.1**) and Bay de Chene (**Figure 3.2**). At Four Isle Dome (**Figure 3.3**), a total of three, 4-hour, composite samples were collected. The results of the composite samples are shown in **Table 6.2.** The table presents the total ^{226}Ra or ^{228}Ra value, the counting error associated with the value (±2 standard deviations [95% confidence interval]), and the LLD reported for the value. **Figure 6.1** presents the average radionuclide activities of the produced water samples for these three sites.

6.3.1.1 Delacroix Island

The two composite samples from Delacroix Island contained ^{226}Ra activities of 194 ± 5.8 and 131 ± 4.7 pCi/L and ^{228}Ra activities of 383 ± 7.3 and 252 ± 6.0 pCi/L. The averages of the ^{226}Ra and ^{228}Ra activities were 162 and 318 pCi/L, respectively. ^{210}Pb produced water values at this site were 62.4 ± 2.6 and 58.1 ± 2.5 and averaged 60 pCi/L. ^{210}Po values for the composite produced water samples were below the LLD of 2.0 pCi/L. The ^{228}Th activities were 18.8 ± 5.3 and 11.1 ± 3.1 and averaged 15 pCi/L.

6.3.1.2 Bay de Chene

The Bay de Chene produced water discharge samples contained ^{226}Ra activities of 188 ± 5.9 and 249 ± 6.6 pCi/L. The ^{228}Ra activities of the produced water samples were 286 ± 7.7 and 243 ± 7.1 pCi/L. The averages of the ^{226}Ra and ^{228}Ra activities were 218 and 264 pCi/L, respectively. ^{210}Pb produced water values at this site were 84.9 ± 3.8 and 71.0 ± 3.8 and averaged 78 pCi/L. ^{210}Po values were below the LLD of 1.1 pCi/L. The ^{228}Th activities were 16.0 ± 5.6 and 24.1 ± 6.3 and averaged 20 pCi/L.

6.3.1.3 Four Isle Dome

The three composite produced water samples from Four Isle Dome contained ^{226}Ra activities of 213 ± 16.8, 322 ± 20.3 and 223 ± 17.2 pCi/L and ^{228}Ra activities of 202 ± 23.6, 279 ± 25.6, and 267 ± 25.3 pCi/L. The averages of the ^{226}Ra and ^{228}Ra activities, respectively, were 253 and 249 pCi/L. The average ^{210}Pb, ^{210}Po, and ^{228}Th produced water values at this site were 9.2, not detected (ND) (average LLD 4.3), and 24.1 pCi/L.

Table 6.2. Pre-termination produced water radionuclide data (pCi/L) for Delacroix Island (DI), Bay De Chene (BDC), and Four Isle Dome (FID).

Sample ID (Site-Replicate)	^{226}Ra			^{228}Ra			^{210}Pb			^{210}Po			^{228}Th		
	Value	+\-	LLD	Value	+\-	LLD	Value	+\-	LLD	Value	+\-	LLD	Value	+\-	LLD
DI-A	194	5.8	0.3	383.0	7.3	0.4	62.4	2.6	1.8	ND	1.1	2.0	18.8	5.3	1.0
DI-B	131	4.7	0.3	252.0	6.0	0.4	58.1	2.5	1.8	ND	1.3	2.0	11.1	3.1	0.7
BDC-A	188	5.9	0.3	286.0	7.7	0.5	84.9	3.8	0.5	ND	0.7	1.1	16.0	5.6	1.0
BDC-B	249	6.6	0.3	243.0	7.1	0.5	71.0	3.5	0.5	ND	0.7	1.1	24.9	6.3	0.6
FID-A	213	16.8	1.7	202.0	23.6	3.6	10.8	11.2	2.4	ND	1.6	3.7	26.3	9.1	6.1
FID-B	322	20.3	1.7	279.0	25.6	3.6	8.1	11.1	2.4	ND	0.1	4.2	30.8	10.3	9.8
FID-C	223	17.2	1.7	267.0	25.3	3.6	8.7	11.1	2.4	ND	0.1	5.0	15.2	6.0	5.0

+\- = Two standard deviations.
LLD = Lower limit of detection.
ND = Not detected, below LLD.

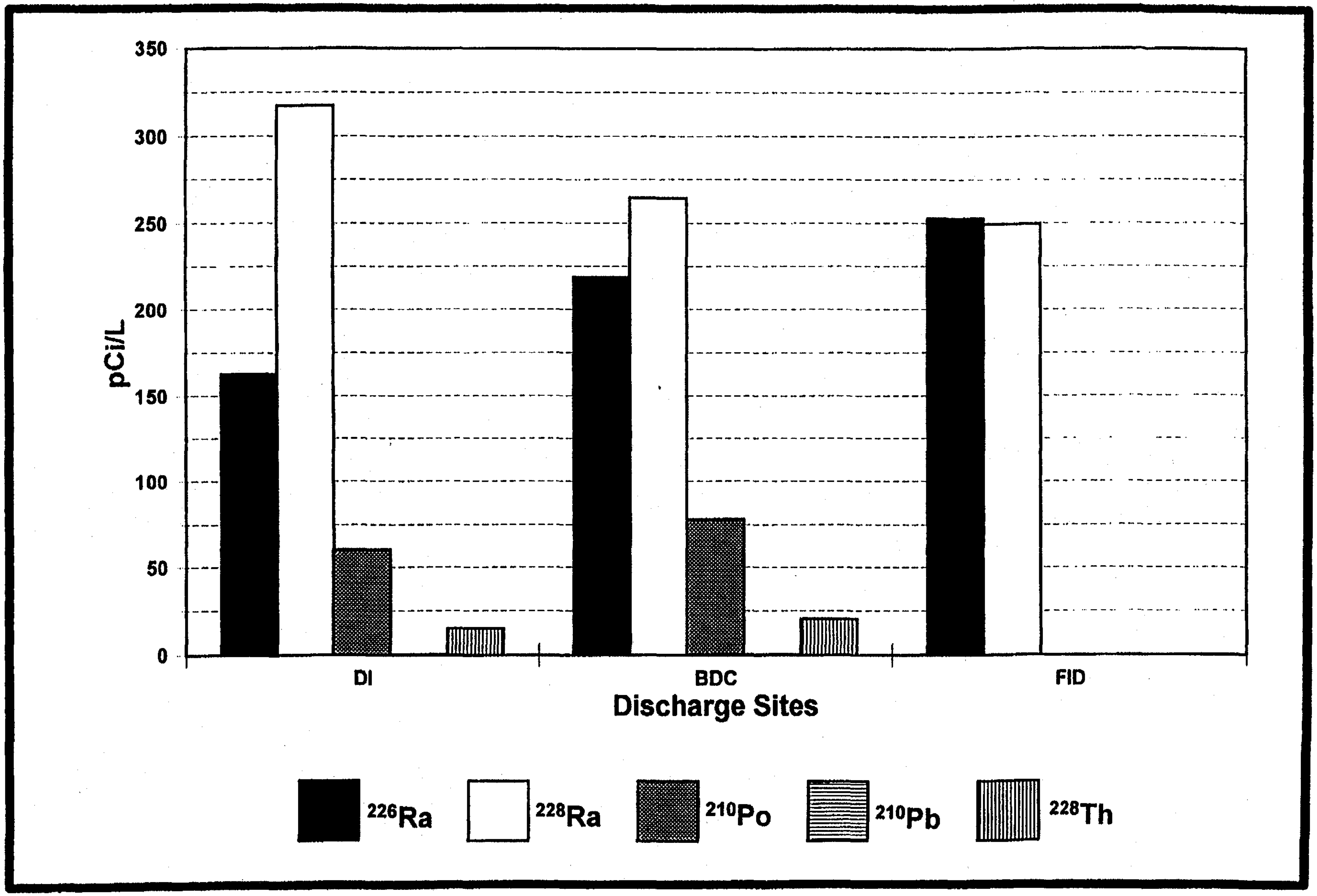

Figure 6.1. Average pre-termination produced water radionuclide data for Delacroix Island (DI), Bay de Chene (BDC), and Four Isle Dome (FID).

6.3.1.4 All Sites

The produced water ^{226}Ra and ^{228}Ra data showed wide variability from composite samples collected over a four hour time span. The Four Isle Dome discharge had the highest average produced water ^{226}Ra activity (253 pCi/L) in this study (**Figure 6.1**). The average ^{226}Ra activities at Bay de Chene (219 pCi/L) and Delacroix Island (163 pCi/L) were not significantly different from the Four Isle Dome discharge considering the wide variability of the data. Similarly, the Delacroix Island discharge had the highest average ^{228}Ra activity (318 pCi/L), but the Bay de Chene (265 pCi/L) and Four Isle Dome (249 pCi/L) discharges were not significantly different, considering the variability of the data.

The average produced water ^{210}Pb, ^{210}Po, and ^{228}Th activities in the Delacroix Island and Bay de Chene discharges were substantially lower than the ^{226}Ra and ^{228}Ra activities. ^{210}Pb activities averaged 60 pCi/L at the Delacroix Island discharge, 78 pCi/L at the Bay de Chene discharge, and 9 pCi/L at Four Isle Dome. All of the ^{210}Po activities were below the 1.1 to 5.0 pCi/L LLD. The ^{228}Th activities were less than the ^{210}Pb activities, but higher than the ^{210}Po activities.

6.3.2 Sediments

6.3.2.1 Delacroix Island

Sediment ^{226}Ra and ^{228}Ra data (dry weight basis) for the Pre-termination, First Post-termination, and Second Post-termination Surveys at Delacroix Island are presented in **Tables 6.3** through **6.5**, respectively. **Figure 6.2**, presents the average sediment ^{226}Ra data for all three surveys. Similarly, **Figure 6.3** presents the average ^{228}Ra data for all three surveys. **Figure 6.4** shows the average pre-termination and second post termination sediment radionuclide activities at differing depths for the discharge (@) and reference (R1, R2) stations. These data were collected from the 0 to 5, 20 to 25, and 35 to 40 cm strata of long cores collected at these stations.

Due to an error at the analytical laboratory, a total of eight replicate samples (the B and C replicates from the 100NW, 300NW, 500NW, and 1000NW sampling locations) from the Pre-termination Survey at Delacroix Island were analyzed with a LLD of 0.3 pCi/g for ^{226}Ra and a LLD of 1.4 to 1.5 pCi/g for ^{228}Ra. The remaining 36 samples were analyzed with a LLD of 0.03 pCi/g for ^{226}Ra and a LLD of 0.04 to 0.08 pCi/g for ^{228}Ra. Sample values for ^{226}Ra with the higher LLD were always substantially lower than the values from the same station analyzed at the lower LLD. This relationship did not hold for the ^{228}Ra data. The ^{228}Ra sample replicates analyzed at the higher LLD usually had higher values than the replicate samples from the same station analyzed at the lower LLD.

The differences in the pre-termination samples analyzed at the different LLDs precluded meaningful analysis of the unmodified data. For statistical analysis of the entire data set, samples analyzed at the higher LLD were adjusted. The adjustment factor was applied to the higher LLD sample replicates from the Pre-termination Survey. The individual radionuclide adjustment factor was the ratio of the mean of all the pre-termination samples for a given radionuclide analyzed at the higher LLD to the mean of all the pre-termination samples for that radionuclide analyzed at the lower LLD. Both the original laboratory analytical values and the adjusted values are presented in **Table 6.3**. In the results that follow for the pre-termination

Table 6.3. Delacroix Island Field sediment radionuclide Pre-termination Survey (April 1993) data (pCi/g dry weight).

Sample ID (Station-Depth-Replicate*)	^{226}Ra				^{228}Ra			
	Value	ADJ.	+\-	LLD	Value	ADJ.	+\-	LLD
@-0-A	1.3		0.2	0.03	0.6		0.2	0.04
@-0-B	3.3		0.3	0.03	1.9		0.2	0.04
@-0-C	1.5		0.2	0.03	0.6		0.2	0.04
@-20-A	2.2		0.2	0.03	1.4		0.2	0.04
@-20-B	2.3		0.2	0.03	0.9		0.3	0.07
@-20-C	3.9		0.3	0.03	1.1		0.3	0.07
@-35-A	2.5		0.2	0.03	0.9		0.3	0.08
@-35-C	2.7		0.2	0.03	1.1		0.3	0.07
100NE-0-A	3.1		0.3	0.03	1.4		0.2	0.04
100NW-0-A	2.7		0.2	0.03	1.0		0.2	0.06
100NW-0-B	1.8	3.0	0.5	0.3	1.8	0.8	1.0	1.5
100NW-0-C	1.6	2.7	0.4	0.3	ND		1.0	1.5
100S-0-A	2.1		0.2	0.03	0.7		0.2	0.06
300NE-0-A	2.3		0.2	0.03	0.9		0.2	0.04
300NW-0-A	2.5		0.2	0.03	0.4		0.2	0.06
300NW-0-B	1.9	3.2	0.5	0.3	ND		1.0	1.5
300NW-0-C	1.3	2.2	0.4	0.3	ND		0.9	1.5
300S-0-A	2.0		0.2	0.03	0.5		0.2	0.06
500NE-0-A	2.3		0.2	0.03	1.1		0.2	0.04
500NW-0-A	2.8		0.2	0.03	0.7		0.2	0.06
500NW-0-B	1.3	2.2	0.4	0.3	2.3	1.0	1.0	1.4
500NW-0-C	1.3	2.2	0.4	0.3	1.8	0.8	0.9	1.4
500S-0-A	2.1		0.2	0.03	0.3		0.2	0.06
1000NW-0-A	0.1		0.1	0.03	ND		0.2	0.04
1000NW-0-B	ND	0.3	0.2	0.3	3.0	1.3	1.0	1.4
1000NW-0-C	ND	0.0	0.2	0.3	2.9	1.2	1.0	1.4
1000S-0-A	0.3		0.1	0.03	ND		0.2	0.06
R1-0-A	1.2		0.2	0.03	0.1		0.2	0.07
R1-0-B	1.8		0.2	0.03	0.3		0.2	0.07
R1-20-A	2.2		0.2	0.03	0.6		0.3	0.07
R1-20-C	2.8		0.2	0.03	1.0		0.3	0.07
R1-35-A	1.2		0.2	0.03	0.4		0.2	0.07
R1-35-B	0.1		0.1	0.03	0.4		0.2	0.07
R1-35-C	0.7		0.1	0.03	0.4		0.2	0.07
R2-0-A	0.4		0.1	0.03	0.2		0.2	0.07
R2-0-B	0.4		0.1	0.03	0.3		0.2	0.07
R2-0-C	ND		0.1	0.03	0.2		0.2	0.07
R2-20-A	ND		0.1	0.03	ND		0.2	0.06
R2-20-B	1.8		0.2	0.03	0.9		0.2	0.06

Table 6.3. (Continued).

Sample ID (Station-Depth-Replicate*)	^{226}Ra				^{228}Ra			
	Value	ADJ.	+\-	LLD	Value	ADJ.	+\-	LLD
R2-20-C	1.2		0.2	0.03	0.5		0.2	0.06
R2-35-A	1.1		0.2	0.03	0.3		0.2	0.06
R2-35-B	1.0		0.2	0.03	0.3		0.2	0.06
R2-35-C	2.2		0.2	0.03	1.0		0.2	0.06

* = Shallowest depth of 5 cm sediment stratum.
+\- = Two standard deviations.
LLD = Lower limit of detection.
ND = Not detected, below LLD.
@ = Discharge station.

Table 6.4. Delacroix Island Field sediment radionuclide First Post-termination Survey (October 1993) data (pCi/g dry weight).

Sample ID (Station-Depth-Replicate*)	^{226}Ra			^{228}Ra		
	Value	+\-	LLD	Value	+\-	LLD
@-0-A	1.40	0.07	0.004	0.74	0.06	0.009
@-0-B	0.56	0.04	0.004	0.46	0.06	0.009
@-0-C	1.18	0.06	0.004	1.13	0.07	0.009
100NE-0-A	0.26	0.03	0.004	1.15	0.08	0.009
100NW-0-A	0.89	0.05	0.004	0.87	0.06	0.008
100NW-0-B	1.15	0.06	0.004	1.32	0.07	0.008
100NW-0-C	0.68	0.05	0.004	1.63	0.08	0.008
100S-0-A	0.98	0.06	0.004	0.63	0.06	0.008
300NE-0-A	0.70	0.05	0.004	1.62	0.09	0.009
300NW-0-A	1.13	0.06	0.004	1.03	0.07	0.008
300NW-0-B	1.28	0.06	0.004	0.87	0.06	0.008
300NW-0-C	1.05	0.06	0.004	0.83	0.06	0.009
300S-0-A	0.80	0.05	0.004	1.22	0.07	0.008
500NE-0-A	0.87	0.05	0.004	0.48	0.06	0.009
500NW-0-A	0.37	0.04	0.004	1.60	0.08	0.009
500NW-0-B	0.54	0.04	0.004	0.63	0.06	0.009
500NW-0-C	0.47	0.04	0.004	0.60	0.06	0.009
500S-0-A	0.97	0.06	0.004	1.07	0.07	0.008
1000NW-0-A	0.65	0.05	0.004	0.41	0.05	0.009
1000NW-0-B	0.29	0.03	0.004	ND	0.03	0.009
1000NW-0-C	0.85	0.05	0.004	0.80	0.07	0.009
1000S-0-A	0.57	0.04	0.004	1.05	0.07	0.009
R1-0-A	0.70	0.05	0.004	1.33	0.08	0.009
R1-0-B	1.14	0.06	0.004	1.13	0.07	0.009
R1-0-C	0.91	0.06	0.004	1.23	0.07	0.009
R2-0-A	0.57	0.04	0.004	0.88	0.06	0.009
R2-0-B	0.46	0.04	0.004	0.56	0.05	0.008
R2-0-C	0.73	0.05	0.004	0.59	0.06	0.008

* = Shallowest depth of 5 cm sediment stratum.
+\- = Two standard deviations.
LLD = Lower limit of detection.
ND = Not detected, below LLD.
@ = Discharge station.

Table 6.5. Delacroix Island Field sediment radionuclide Second Post-termination Survey (April 1994) data (pCi/g dry weight).

Sample ID (Station-Depth-Replicate)	^{226}Ra			^{228}Ra		
	Value	+\-	LLD	Value	+\-	LLD
@-0-A	2.21	0.29	0.04	0.48	0.40	0.12
@-0-B	3.57	0.36	0.04	0.79	0.42	0.12
@-0-C	2.44	0.30	0.04	0.59	0.41	0.12
@-20-A	5.44	0.45	0.04	2.15	0.50	0.12
@-20-B	8.88	0.56	0.04	3.80	0.58	0.12
@-20-C	7.92	0.54	0.04	3.11	0.54	0.12
@-35-A	2.56	0.31	0.04	0.83	0.40	0.12
@-35-B	1.50	0.24	0.04	ND	0.34	0.12
@-35-C	3.31	0.35	0.04	0.44	0.38	0.12
100NE-0-A	0.69	0.12	0.02	0.57	0.32	0.09
100NW-0-A	0.69	0.14	0.03	0.15	0.40	0.13
100NW-0-B	1.18	0.17	0.03	0.51	0.48	0.15
100NW-0-C	0.31	0.10	0.03	ND	0.39	0.13
100S-0-A	0.17	0.92	0.03	0.47	0.42	0.13
300NE-0-A	0.70	0.12	0.02	0.62	0.32	0.09
300NW-0-A	0.81	0.15	0.03	0.29	0.47	0.15
300NW-0-B	1.06	0.16	0.03	0.79	0.50	0.15
300NW-0-C	0.78	0.14	0.03	0.76	0.50	0.15
300S-0-A	0.73	0.14	0.03	0.40	0.42	0.13
500NE-0-A	1.60	0.18	0.02	0.41	0.43	0.13
500NW-0-A	0.61	0.11	0.02	0.56	0.32	0.09
500NW-0-B	0.42	0.10	0.02	0.18	0.29	0.09
500NW-0-C	0.49	0.10	0.02	0.26	0.30	0.09
500S-0-A	0.49	0.12	0.03	ND	0.39	0.13
1000NW-0-A	0.45	0.10	0.02	0.39	0.31	0.09
1000NW-0-B	0.37	0.09	0.02	0.16	0.39	0.13
1000NW-0-C	0.48	0.10	0.02	0.70	0.33	0.09
1000S-0-A	0.47	0.12	0.03	0.13	0.38	0.13
R1-0-A	1.30	0.18	0.03	0.33	0.37	0.12
R1-0-B	2.57	0.31	0.04	0.69	0.39	0.12
R1-0-C	2.05	0.28	0.04	0.79	0.40	0.12
R1-20-A	1.55	0.25	0.04	0.32	0.37	0.12
R1-20-B	1.67	0.25	0.04	0.40	0.44	0.14
R1-20-C	1.55	0.25	0.04	0.14	0.36	0.12
R1-35-A	1.12	0.21	0.04	0.50	0.44	0.14
R1-35-B	1.74	0.26	0.04	0.53	0.45	0.14
R1-35-C	0.98	0.20	0.04	0.48	0.44	0.14
R2-0-A	1.31	0.18	0.03	0.46	0.42	0.12
R2-0-B	1.37	0.18	0.03	0.35	0.41	0.12

Table 6.5. (Continued).

Sample ID (Station-Depth-Replicate)	^{226}Ra			^{228}Ra		
	Value	+\-	LLD	Value	+\-	LLD
R2-0-C	0.34	0.11	0.03	0.42	0.36	0.12
R2-20-A	0.27	0.10	0.03	0.59	0.35	0.12
R2-20-B	1.46	0.19	0.03	0.72	0.43	0.12
R2-20-C	0.66	0.14	0.03	0.18	0.40	0.12
R2-35-A	0.98	0.16	0.03	ND	0.39	0.12
R2-35-B	0.67	0.14	0.03	0.15	0.40	0.13
R2-35-C	0.30	0.11	0.03	0.00	0.39	0.13

* = Shallowest depth of 5 cm sediment stratum.
+\- = Two standard deviations.
LLD = Lower limit of detection.
ND = Not detected, below LLD.
@ = Discharge station.

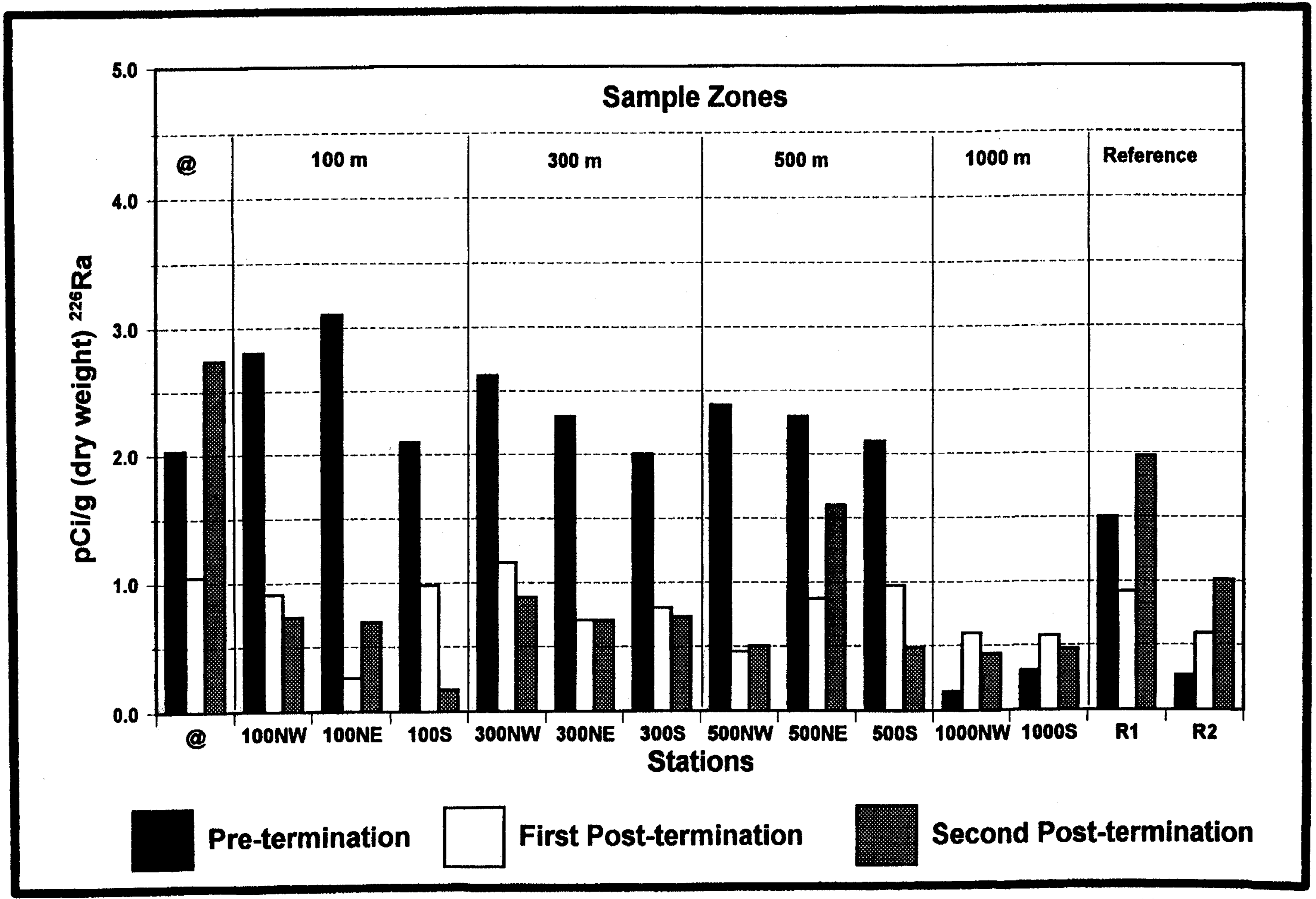

Figure 6.2. Average surface sediment ^{226}Ra data for the April 1993, October 1993, and April 1994 surveys at Delacroix Island Field.

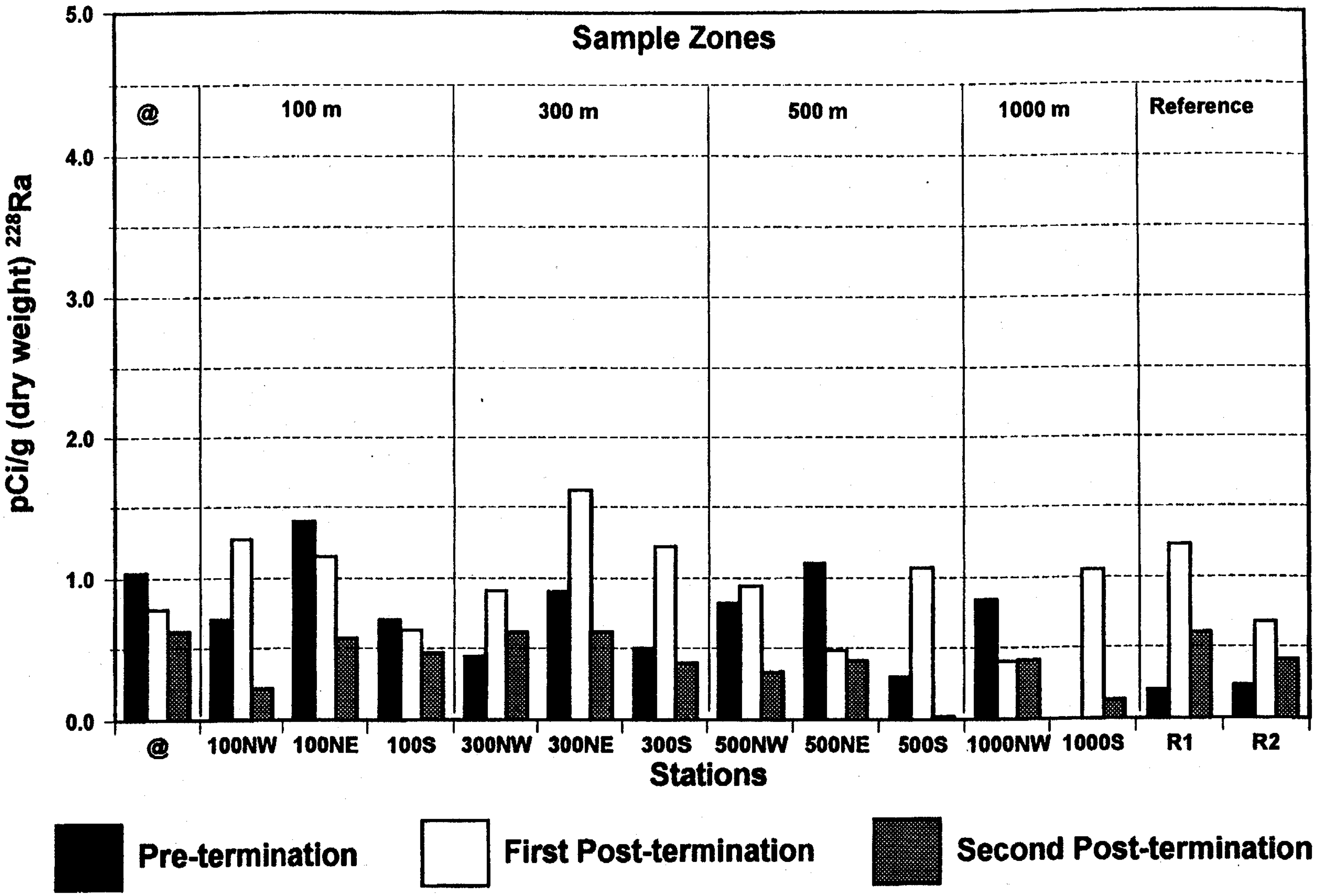

Figure 6.3. Average surface sediment ^{228}Ra data for the April 1993, October 1993, and April 1994 surveys at Delacroix Island Field.

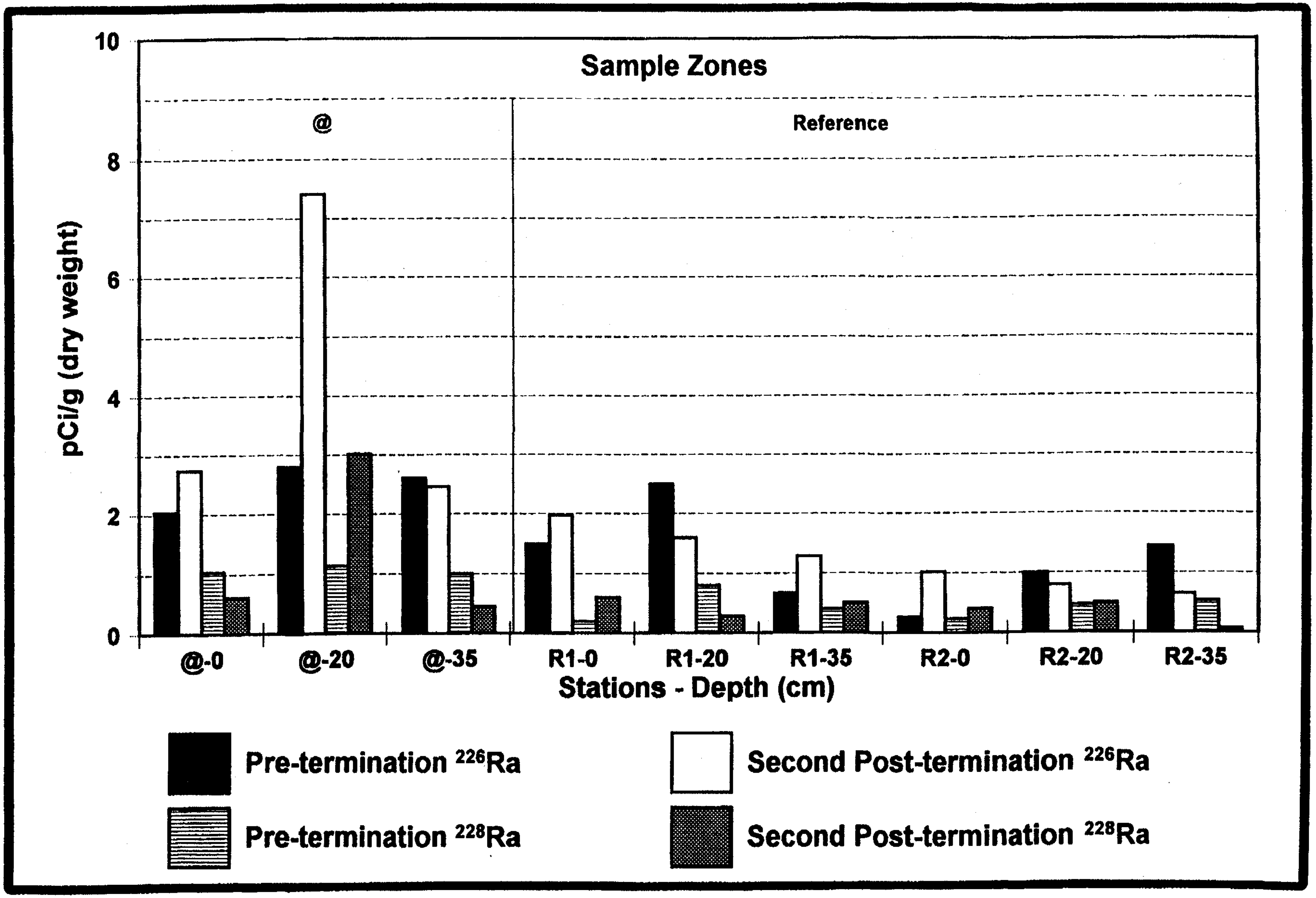

Figure 6.4. Average sediment ^{226}Ra and ^{228}Ra data with depth for the April 1993 Pre-termination and April 1994 Second Post-termination Surveys at Delacroix Island Field.

sediment radionuclide samples from Delacroix Island, the values presented will reflect the adjusted activity for those samples with the higher LLD. Similarly, **Figures 6.2** and **6.3** are based on averages calculated from the adjusted data.

Pre-discharge termination surface sediment (0 to 5 cm) ^{226}Ra activities at Delacroix Island (**Table 6.3**) ranged from ND in the 1000NW-0-C and R2-0-C samples to 3.3 ± 0.3 pCi/g in the @-0-B sample. The ^{228}Ra activities ranged from ND in the 1000NW-0-B and 1000S-0-A samples to 1.9 ± 0.2 pCi/g in the @-0-B sample.

The average surface sediment ^{226}Ra activity in the Pre-termination Survey samples at Delacroix Island (**Figure 6.2**) showed similar values for most of the stations. All stations except the 1000NW, 1000S, and the R2 reference fell within a narrow range (1.5 to 3.1 pCi/g) of values. The 1000NW, 1000S, and R2 reference had average values of less than 0.5 pCi/g.

The average surface sediment ^{228}Ra activities in the Pre-termination Survey (**Figure 6.3**) ranged from ND at 1000S to 1.4 pCi/g at 100NE. The @ station average activity was 1.0 pCi/g and the R1 and R2 stations had average ^{228}Ra activities of 0.2 pCi/g.

All of the Delacroix Island First Post-termination Survey samples (**Table 6.4**) analyzed for ^{226}Ra activity had a LLD of 0.004 pCi/g. Similarly, the ^{228}Ra data all had a LLD of 0.008 to 0.009 pCi/g. The surface sediment (0 to 5 cm) ^{226}Ra activities at Delacroix Island ranged from 0.26 ± 0.03 pCi/g in the 100NE-0-A sample to 1.40 ± 0.07 pCi/g in the @-0-A sample. The ^{228}Ra activities ranged from ND in the 1000NW-0-B sample to 1.63 ± 0.08 pCi/g in the 100NW-0-C sample. No subsurface samples were collected during this survey.

Average sediment ^{226}Ra activities (**Figure 6.2**) in the First Post-termination Survey were uniformly low at all stations and ranged from approximately 0.3 to 1.0 pCi/g. The 100NE station, which had the highest average surface sediment activity (3.1 pCi/g) in the Pre-termination Survey, had the lowest First Post-termination Survey activity (0.3 pCi/g). The R1 and R2 reference stations average ^{226}Ra activities were 0.6 and 0.9 pCi/g, respectively.

The average surface sediment ^{228}Ra activities (**Figure 6.3**) in the First Post-termination Survey ranged from 0.4 at 1000NW to 1.3 pCi/g at 100NW. The @ station average activity was 0.8 pCi/g and the R1 and R2 stations had average ^{228}Ra activities of 1.2 and 0.7 pCi/g, respectively.

The Second Post-discharge termination Survey radionuclide data (**Table 6.5**) from Delacroix Island had a ^{226}Ra LLD of 0.02 to 0.04 pCi/g and a ^{228}Ra LLD of 0.09 to 0.15. Surface sediment ^{226}Ra activities at Delacroix Island ranged from 0.31 ± 0.10 in the 100NW-0-C sample to 3.57 ± 0.36 pCi/g in the @-0-B sample. The surface sediment ^{228}Ra activities ranged from 0.01 ± 0.13 pCi/g in the 100NW-0-C sample to 0.79 ± 0.50 pCi/g in the 300NW-0-B samples.

The Second Post-termination Survey ^{226}Ra data from Delacroix Island (**Figure 6.2**) showed the highest average surface sediment values at the @ (2.74 pCi/g) and R1 (1.97 pCi/g) stations in any of the three surveys. Activities from this survey at the other stations were uniformly low and ranged between 0.4 to 1.6 pCi/g.

The average surface sediment ^{228}Ra activities in the Second Post-termination Survey (**Figure 6.3**) ranged from 0.02 pCi/g at the 500S station to 0.6 pCi/g at the @, 100NE, 300NW, 100NE, 300NE, and R1 stations. The average ^{228}Ra activity at the R2 station was 0.4 pCi/g.

Pre-termination ^{226}Ra activities from the subsurface samples at the discharge and reference stations (**Table 6.3**) ranged from ND in the R2-20-A sample to 3.9 ± 0.3 pCi/g in the @-20-C sample. Similarly, ^{228}Ra activities from the subsurface samples at the discharge and reference stations ranged from ND in the R2-20-A sample to 1.4 ± 0.2 pCi/g from the @-20-A sample.

^{226}Ra activities from the subsurface Second Post-termination Survey samples (**Table 6.5**) at the discharge and reference stations ranged from 0.30 ± 0.03 in the R2-35-C sample to 8.9 ± 0.04 pCi/g in the @-20-B sample. Similarly ^{228}Ra activities from the subsurface samples at the discharge and reference stations ranged from ND in the R2-35-C sample to 3.8 ± 0.12 pCi/g in the @-20-B sample.

Pre-discharge termination and second post-discharge termination average subsurface sediment ^{226}Ra data (**Figure 6.4**) from the @, R1, and R2 stations showed similar activities to the surface samples at those locations, with the exception of the replicates from the @ station, 20 cm strata in the Second Post-termination Survey. These samples had an average ^{226}Ra activity of 7.4 pCi/g. This was more than double the highest activity found in the pre-termination samples and was the highest activity found at Delacroix Island. Similarly, the ^{228}Ra subsurface sediment data showed the highest values in the Second Post-termination Survey @ station 20 cm strata and averaged 3.0 pCi/g.

In general, surface sediment ^{228}Ra activity in the Delacroix Island samples from all three surveys were generally lower than the corresponding ^{226}Ra activity in the same sample. The average ^{228}Ra activities in the samples from all three surveys ranged from 0.02 to 1.62 pCi/g. No clear trends of higher ^{228}Ra activities associated with the discharge station were found in the data. The highest average surface activity (1.62 pCi/g) was in the 300NE samples from the Pre-termination Survey. ^{228}Ra activities in the Second Post-termination Survey were generally lower than those from the previous two surveys.

The ^{226}Ra surface sediment data were analyzed using a two-way factorial analysis of variance. The independent variables used in the analysis were zone (discharge, 100, 300, 500, 1,000 m, and reference) and sample period (Pre-termination, First Post-termination, and Second Post-termination Surveys). The results of the analysis of variance for ^{226}Ra showed that the zone, sample period, and the interaction of the two factors were highly significant ($p<0.001$). Tukey's post hoc test showed that the mean discharge station sediment ^{226}Ra activity was significantly different ($p<0.05$) from all of the other zones. Additionally, the 100, 300, and 500 m zones were significantly different ($p<0.001$) from the 1,000 m and reference zones. The sampling period post hoc analysis showed that the Pre-termination Survey mean ^{226}Ra activities were significantly different ($p<0.001$) than the mean activities in the other two surveys. No significant differences were found between the two post termination surveys.

^{228}Ra surface sediment data were also analyzed using a two-way factorial analysis of variance. The independent variables used in the analysis were zone (discharge, 100, 300, 500, 1,000 m, and reference) and sample period (Pre-termination, First Post-termination, and Second Post-termination Surveys). The results of the analysis of variance for ^{228}Ra showed that zone effects were not significant, but the sample period was highly significant ($p<0.001$). The sampling period post hoc analysis showed that the Pre-termination Survey ^{228}Ra activities were not significantly different from the First Post-termination Survey, but were significantly different ($p<0.05$) from the Second Post-termination Survey data. Additionally, ^{228}Ra activities from the First Post-termination Survey were significantly different ($p<0.05$) from the Second Post-termination Survey.

6.3.2.2 Bay de Chene

Sediment ^{226}Ra and ^{228}Ra data for the Pre-termination, First Post-termination, and Second Post-termination Surveys at Bay de Chene are presented in **Tables 6.6** through **6.8**, respectively. **Figure 6.5** presents the average sediment ^{226}Ra data for all three surveys. Similarly, **Figure 6.6** presents the average ^{228}Ra data for all three surveys. **Figure 6.7** shows the average pre-termination sediment radionuclide activities with depth for the @, R1, and R2 stations. No post-termination sediment radionuclide samples at the 20 and 35 cm depth strata were collected.

The Bay de Chene pre-termination data set also contained sample replicates analyzed at different LLDs. A total of 60 individual sediment samples were analyzed in the Pre-termination Survey at Bay de Chene. Of this number, 40 were analyzed with a LLD of 0.1 pCi/g for ^{226}Ra and a LLD of 0.1 to 0.2 pCi/g for ^{228}Ra. The remaining 20 samples (the B and C replicates from the northwest, southwest, and southeast transects) were analyzed with a LLD of 0.004 pCi/g for ^{226}Ra and a LLD of 0.008 pCi/g for ^{228}Ra. Inspection of the data indicated that the B and C replicate sample values for ^{226}Ra with the lower LLD always had higher activities than the A replicate samples collected at the same location, but analyzed with the 0.1 pCi/g LLD. Similarly, the ^{228}Ra sample values analyzed with the 0.008 pCi/g LLD were always higher than the replicate samples collected at the same station and analyzed with the 0.1 pCi/g LLD. Radionuclide data from the two post-discharge termination surveys at Bay de Chene analyzed at 0.01 to 0.03 pCi/g LLD showed similar ^{226}Ra and ^{228}Ra values to the samples from the pre-termination samples analyzed at the 0.004 to 0.008 pCi/g LLD. The differences between the 0.004 pCi/g and 0.1 pCi/g LLD sample results for the Pre-termination Survey were most pronounced in the ^{226}Ra and ^{228}Ra samples that had 0.1 to 0.3 pCi/g sample values at the 0.1 pCi/g LLD.

For statistical analysis of the Bay de Chene data set, samples analyzed at the higher LLD and the lower LLD were adjusted. The adjustment factor was applied to the higher LLD sample replicates from the Pre-termination Survey. The adjustment factor was the ratio of the mean of all the pre-termination samples for a given radionuclide analyzed at the higher LLD to the mean of all the pre-termination samples analyzed at the lower LLD. Both the original laboratory analytical values and the adjusted values are presented in **Table 6.6**. In the results that follow for the pre-termination sediment radionuclide samples from the Bay de Chene site, the values presented will reflect the adjusted activity for those samples with the higher LLD. Similarly, **Figures 6.5** through **6.7** are based on averages calculated from the adjusted data.

Table 6.6. Bay de Chene Field sediment radionuclide Pre-termination Survey (May 1993) data (pCi/g dry weight).

Sample ID (Station-Depth-Replicate*)	^{226}Ra				^{228}Ra			
	Value	ADJ.	+\-	LLD	Value	ADJ.	+\-	LLD
@-0-A	1.2	11.0	0.2	0.1	0.3	1.5	0.3	0.1
@-0-B	1.2	11.0	0.2	0.1	0.5	2.4	0.2	0.1
@-20-A	0.8	7.4	0.1	0.1	0.4	2.0	0.2	0.1
@-20-B	0.6	5.5	0.1	0.1	0.3	1.5	0.2	0.1
@-20-C	1.2	11.0	0.2	0.1	0.6	2.9	0.3	0.1
@-35-A	1.6	14.7	0.2	0.1	18.1	88.3	1.3	0.2
@-35-B	0.8	7.4	0.1	0.1	13.5	65.9	0.8	0.1
@-35-C	0.9	8.3	0.1	0.1	0.2	1.0	0.3	0.1
100SW-0-A	0.3	2.8	0.1	0.1	0.2	1.0	0.2	0.1
100SW-0-B	2.76		0.10	0.004	1.46		0.08	0.008
100SW-0-C	4.22		0.13	0.004	2.25		0.09	0.008
100NW-0-A	0.3	2.8	0.1	0.1	ND	0.0	0.2	0.1
100NW-0-B	2.34		0.09	0.004	1.00		0.07	0.008
100NW-0-C	1.88		0.08	0.004	0.59		0.05	0.008
100NE-0-A	0.4	3.7	0.1	0.1	0.1	0.5	0.2	0.1
300SW-0-A	0.3	2.8	0.1	0.1	0.2	1.0	0.2	0.1
300SW-0-B	0.98		0.06	0.004	0.37		0.05	0.008
300SW-0-C	1.67		0.08	0.004	1.01		0.07	0.008
300NW-0-A	0.1	0.9	0.1	0.1	0.2	1.0	0.2	0.1
300NW-0-B	2.12		0.09	0.004	1.18		0.07	0.008
300NW-0-C	1.70		0.08	0.004	0.94		0.06	0.008
300NE-0-A	0.1	0.9	0.1	0.1	0.2	1.0	0.2	0.1
500SE-0-A	0.1	0.9	0.1	0.1	0.5	2.4	0.3	0.1
500SE-0-B	1.07		0.06	0.004	0.70		0.06	0.008
500SE-0-C	0.93		0.06	0.004	0.44		0.05	0.008
500SW-0-A	0.1	0.9	0.1	0.1	0.1	0.5	0.2	0.1
500SW-0-B	1.22		0.07	0.004	0.89		0.06	0.008
500SW-0-C	1.37		0.07	0.004	1.08		0.07	0.008
500NW-0-A	0.1	0.9	0.1	0.1	0.2	1.0	0.2	0.1
500NW-0-B	1.22		0.07	0.004	0.76		0.06	0.008
500NW-0-C	0.82		0.06	0.004	0.62		0.05	0.008
500NE-0-A	0.3	2.8	0.1	0.1	0.2	1.0	0.2	0.1
1000SE-0-A	0.3	2.8	0.1	0.1	0.2	1.0	0.2	0.1
1000SE-0-B	1.11		0.06	0.004	0.73		0.06	0.008
1000SE-0-C	1.32		0.07	0.004	1.02		0.07	0.008
1000SW-0-A	0.1	0.9	0.1	0.1	ND	0.0	0.2	0.1
1000SW-0-B	1.03		0.06	0.004	0.57		0.05	0.008
1000SW-0-C	1.17		0.07	0.004	0.56		0.05	0.008
1000NW-0-A	0.8	7.4	0.1	0.1	0.4	2.0	0.2	0.1

Table 6.6. (Continued).

Sample ID (Station-Depth-Replicate*)	^{226}Ra				^{228}Ra			
	Value	ADJ.	+\-	LLD	Value	ADJ.	+\-	LLD
1000NW-0-B	1.15		0.07	0.004	0.78		0.06	0.008
1000NW-0-C	1.28		0.07	0.004	0.97		0.06	0.008
1000NE-0-A	0.7	6.4	0.2	0.1	0.6	2.9	0.5	0.1
R1-0-A	0.1	0.9	0.1	0.1	0.6	2.9	0.6	0.2
R1-0-B	0.4	3.7	0.1	0.1	1.2	5.9	0.3	0.1
R1-0-C	0.4	3.7	0.1	0.1	1.4	6.8	0.4	0.1
R1-20-A	0.6	5.5	0.2	0.1	0.8	3.9	0.4	0.1
R1-20-B	0.7	6.4	0.1	0.1	0.5	2.4	0.2	0.1
R1-20-C	0.7	6.4	0.1	0.1	0.9	4.4	0.2	0.1
R1-35-A	0.6	5.5	0.1	0.1	0.8	3.9	0.2	0.1
R1-35-B	0.7	6.4	0.1	0.1	1.0	4.9	0.2	0.1
R1-35-C	0.9	8.3	0.1	0.1	1.1	5.4	0.2	0.1
R2-0-A	0.4	3.7	0.2	0.1	1.0	4.9	0.4	0.1
R2-0-B	0.3	2.8	0.1	0.1	0.4	1.9	0.2	0.1
R2-0-C	0.1	0.9	0.1	0.1	ND	0.0	0.2	0.1
R2-20-A	0.5	4.6	0.1	0.1	0.1	0.5	0.4	0.1
R2-20-B	0.6	5.5	0.1	0.1	0.4	2.0	0.2	0.1
R2-20-C	0.6	5.5	0.1	0.1	0.5	2.4	0.2	0.1
R2-35-A	0.6	5.5	0.1	0.1	0.3	1.5	0.4	0.1
R2-35-B	0.7	6.4	0.1	0.1	0.3	1.5	0.2	0.1
R2-35-C	0.4	3.7	0.1	0.1	0.3	1.5	0.2	0.1

* = Shallowest depth of 5 cm sediment stratum.
+\- = Two standard deviations.
LLD = Lower limit of detection.
ND = Not detected, below LLD.
@ = Discharge station.

Table 6.7. Bay de Chene Field sediment radionuclide First Post-termination Survey (May 1994) data (pCi/g dry weight).

Sample ID (Station-Depth-Replicate*)	^{226}Ra			^{228}Ra		
	Value	+\-	LLD	Value	+\-	LLD
@-0-A	3.16	0.15	0.01	1.00	0.13	0.02
@-0-B	2.56	0.13	0.01	0.61	0.12	0.02
@-0-C	3.92	0.16	0.01	0.86	0.15	0.03
100SW-0-A	2.81	0.14	0.01	0.92	0.12	0.02
100NW-0-A	5.01	0.18	0.01	1.85	0.16	0.02
100NE-0-A	3.47	0.17	0.01	0.84	0.10	0.02
100NE-0-B	3.17	0.17	0.01	0.88	0.10	0.02
100NE-0-C	4.54	0.20	0.01	1.16	0.11	0.02
300SW-0-A	1.96	0.11	0.01	0.67	0.11	0.02
300NW-0-A	1.71	0.11	0.01	0.74	0.12	0.02
300NE-0-A	2.55	0.15	0.01	0.87	0.10	0.02
300NE-0-B	1.80	0.13	0.01	0.69	0.11	0.02
300NE-0-C	4.22	0.19	0.01	1.24	0.12	0.02
500SW-0-A	0.74	0.07	0.01	0.31	0.09	0.02
500NW-0-A	1.36	0.10	0.01	0.82	0.12	0.02
500SE-0-A	1.72	0.11	0.01	0.73	0.11	0.02
500NE-0-A	1.36	0.11	0.01	0.26	0.08	0.02
500NE-0-B	2.89	0.16	0.01	0.77	0.11	0.02
500NE-0-C	2.63	0.15	0.01	0.77	0.11	0.02
1000SE-0-A	1.79	0.11	0.01	0.58	0.11	0.02
1000SW-0-A	1.80	0.11	0.01	0.74	0.12	0.02
1000NW-0-A	0.62	0.07	0.01	0.22	0.09	0.02
1000NE-0-A	2.33	0.14	0.01	0.75	0.11	0.02
1000NE-0-B	2.39	0.14	0.01	0.74	0.11	0.02
1000NE-0-C	2.49	0.15	0.01	1.04	0.12	0.02
R1-0-A	1.72	0.11	0.01	0.80	0.12	0.02
R1-0-B	0.96	0.08	0.01	0.48	0.11	0.02
R1-0-C	2.02	0.12	0.01	0.83	0.13	0.02
R2-0-A	1.89	0.11	0.01	0.86	0.12	0.02
R2-0-B	1.75	0.11	0.01	0.69	0.11	0.02
R2-0-C	2.18	0.12	0.01	0.79	0.12	0.02

* = Shallowest depth of 5 cm sediment stratum.
+\- = Two standard deviations.
LLD = Lower limit of detection.
ND = Not detected, below LLD.
@ = Discharge station.

Table 6.8. Bay de Chene Field sediment radionuclide Second Post-termination Survey (October 1994) data (pCi/g dry weight).

Sample ID (Station-Depth-Replicate*)	^{226}Ra			^{228}Ra		
	TOTAL	+\-	LLD	TOTAL	+\-	LLD
@-0-A	2.81	0.2	0.02	1.16	0.15	0.03
@-0-B	3.65	0.23	0.02	0.90	0.14	0.03
@-0-C	3.29	0.22	0.02	1.12	0.15	0.03
100SW-0-A	6.4	0.3	0.0	1.58	0.17	0.03
100NW-0-A	6.5	0.3	0.0	1.69	0.18	0.03
100NE-0-A	2.1	0.2	0.0	1.45	0.15	0.03
100NE-0-B	3.6	0.2	0.0	1.10	0.14	0.03
100NE-0-C	1.4	0.1	0.0	1.34	0.15	0.03
300SW-0-A	4.1	0.2	0.0	0.78	0.14	0.03
300NW-0-A	3.5	0.2	0.0	0.82	0.13	0.03
300NE-0-A	1.2	0.1	0.0	1.00	0.14	0.03
300NE-0-B	0.8	0.1	0.0	1.07	0.15	0.03
300NE-0-C	1.5	0.1	0.0	0.48	0.12	0.03
500SE-0-A	3.7	0.2	0.0	0.73	0.14	0.03
500SW-0-A	3.6	0.2	0.0	0.75	0.14	0.03
500NW-0-A	1.0	0.1	0.0	0.91	0.13	0.03
500NE-0-A	1.4	0.1	0.0	0.79	0.13	0.03
500NE-0-B	1.7	0.2	0.0	0.85	0.14	0.03
500NE-0-C	1.3	0.1	0.0	0.21	0.18	0.04
1000SE-0-A	2.9	0.2	0.0	0.57	0.13	0.03
1000SW-0-A	3.3	0.2	0.0	0.64	0.13	0.03
1000NW-0-A	1.1	0.1	0.0	0.73	0.13	0.03
1000NE-0-A	1.6	0.2	0.0	1.00	0.14	0.03
1000NE-0-B	2.0	0.2	0.0	0.99	0.14	0.03
1000NE-0-C	1.9	0.2	0.0	0.63	0.13	0.03
R1-0-A	2.3	0.2	0.0	0.47	0.12	0.03
R1-0-B	0.9	0.1	0.0	0.19	0.11	0.03
R1-0-C	1.9	0.2	0.0	0.43	0.12	0.03
R2-0-A	3.3	0.2	0.0	0.66	0.13	0.03
R2-0-B	3.5	0.2	0.0	0.77	0.14	0.03
R2-0-C	3.8	0.2	0.0	0.94	0.15	0.03

* = Shallowest depth of 5 cm sediment stratum.
+\- = Two standard deviations.
LLD = Lower limit of detection.
ND = Not detected, below LLD.
@ = Discharge station.

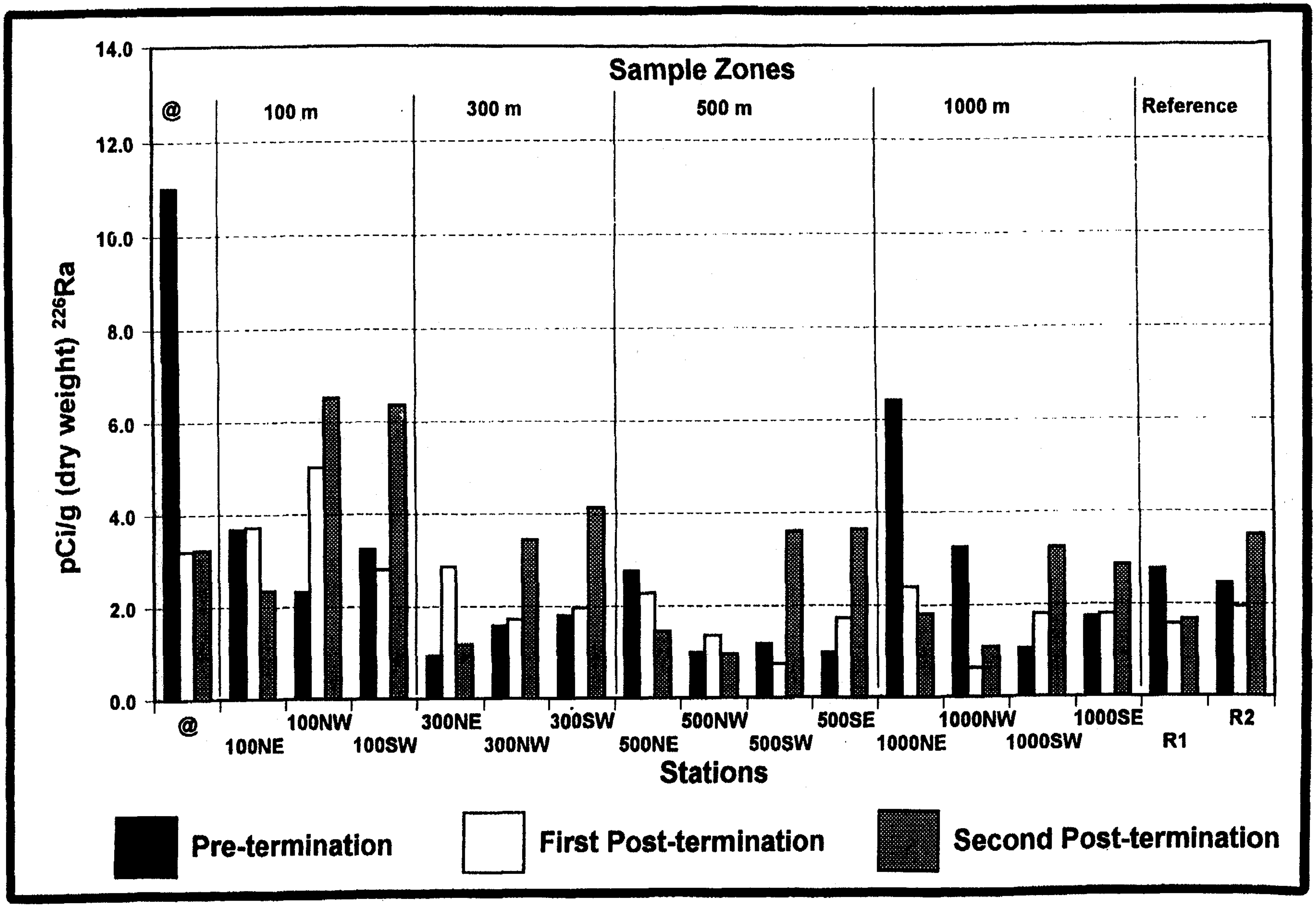

Figure 6.5. Average sediment ^{226}Ra data for the May 1993, May 1994, and October 1994 surveys at Bay de Chene Field.

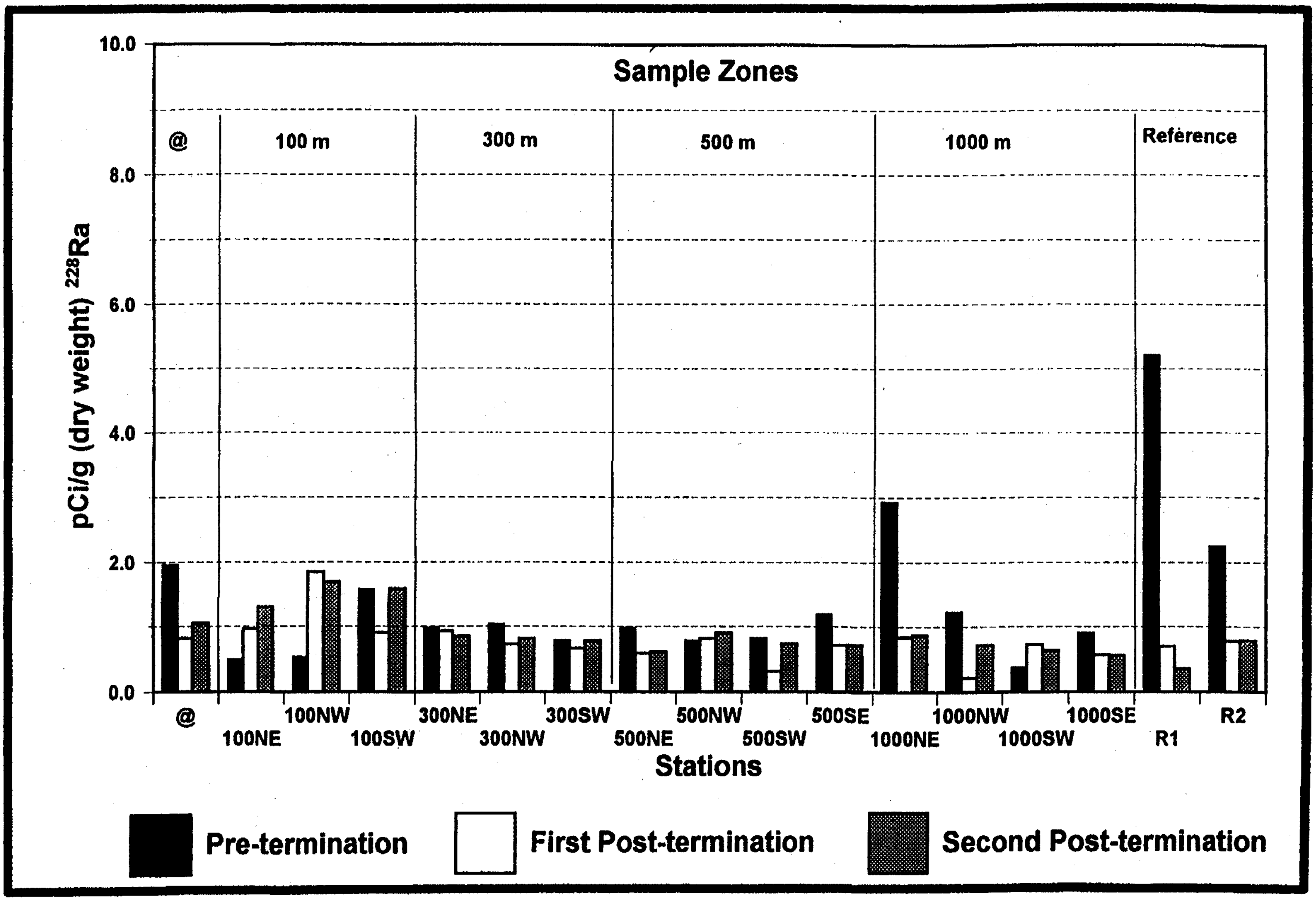

Figure 6.6. Average sediment ^{228}Ra data for the May 1993, May 1994 and October 1994 surveys at Bay de Chene Field.

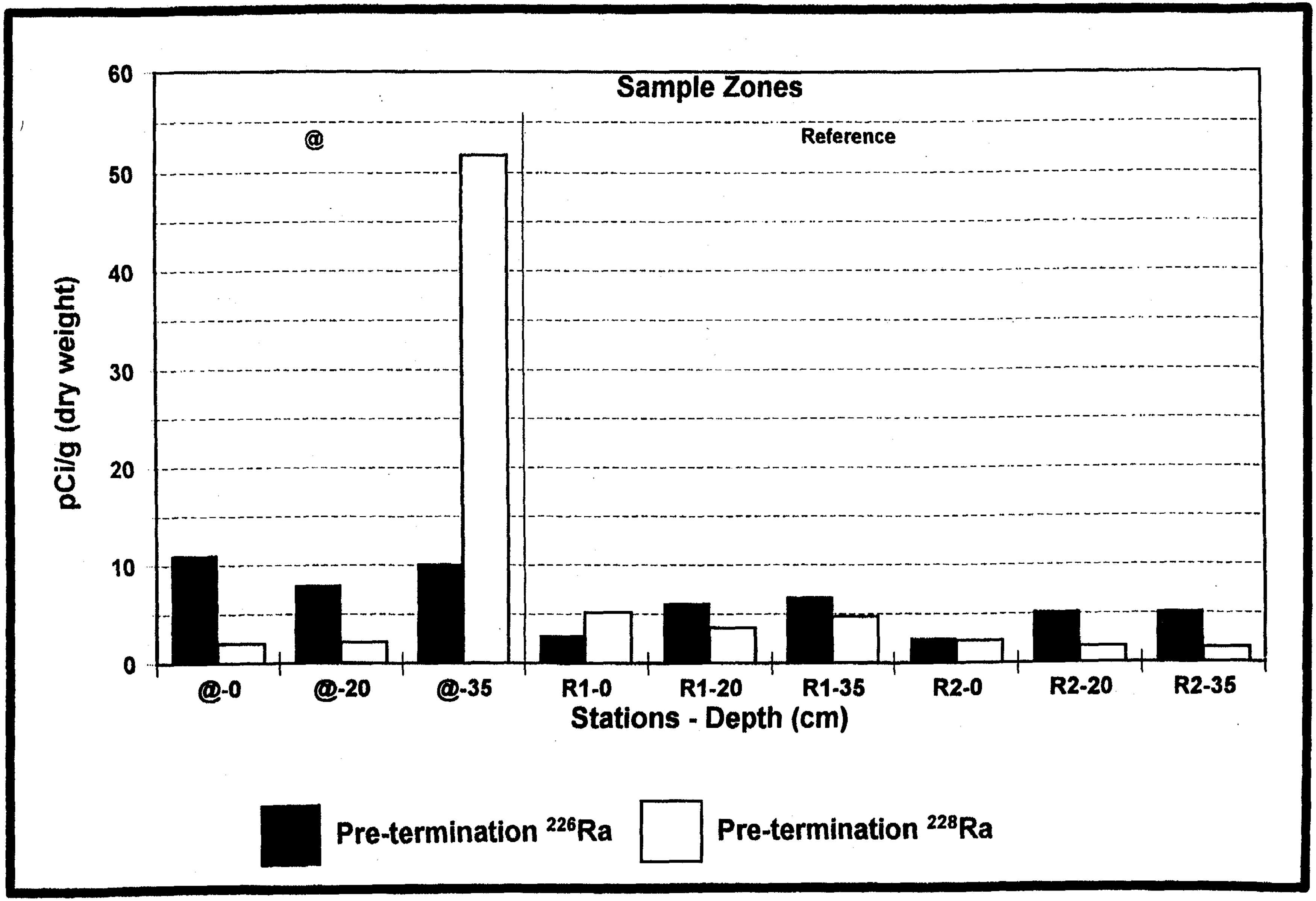

Figure 6.7. Average sediment ^{226}Ra and ^{228}Ra data with depth for the May 1993 Pre-termination Survey at Bay de Chene Field.

Pre-discharge termination surface sediment (0 to 5 cm) ^{226}Ra activities (**Table 6.6**) at Bay de Chene ranged from 0.82 ± 0.06 in the 500NW-0-C sample to 11.0 pCi/g in the @-0-A and @-0-B samples. The ^{228}Ra activities ranged from ND in the 100NW-0-A, 1,000SW-0-A, and R2-0-C samples to 6.8 pCi/g in the R1-0-C sample.

Average surface sediment ^{226}Ra activity (**Figure 6.5**) in the Pre-termination Survey samples at Bay de Chene showed a much higher value (11.0 pCi/g) for the @ station than any of the other transect (maximum 6.4 pCi/g at the 1000NE station) or reference stations (maximum 2.8 pCi/g at the R1 station).

Like the surface sediment ^{228}Ra activity in the Delacroix Island samples from all three surveys, the ^{228}Ra pre-termination activities at Bay de Chene (**Table 6.6**) were generally lower than the corresponding ^{226}Ra activity in the same sample. The average ^{228}Ra activities in the surface samples from the Pre-termination Survey ranged from 0.5 (100NE and 100NW) to 5.2 pCi/g (R1). The average activity was 2.0 pCi/g for the @ station and 2.2 pCi/g at the R2 station. With the highest activities at one of the reference stations, no clear trend of ^{228}Ra activity was present in the pre-termination data.

All of the Bay de Chene first post-termination samples analyzed for ^{226}Ra activity had a LLD of 0.01 pCi/g. Similarly, the ^{228}Ra data all had a LLD of 0.02 to 0.03 pCi/g. The surface sediment (0 to 5 cm) ^{226}Ra activities at Bay de Chene (**Table 6.7**) ranged from 0.62 ± 0.07 pCi/g in the 1000NW-0-A sample to 4.54 ± 0.20 pCi/g in the 100NE-0-C sample. The ^{228}Ra activities ranged from 0.31 pCi/g in the 500SW-0-A sample to 1.85 ± 0.16 pCi/g in the 100NW-0-A sample. No subsurface samples were collected in this survey.

The average surface sediment ^{226}Ra activities in the First Post-termination Survey (**Figure 6.5**) were substantially lower at the @ (3.2 pCi/g) and 1000NE (0.62 pCi/g) stations, compared to the Pre-termination Survey. In this survey, the maximum average ^{226}Ra activity (5.0 pCi/g) occurred at the 100NE station, not the discharge. The R1 and R2 reference station average ^{226}Ra activities ranged from 1.6 to 2.0 pCi/g.

^{228}Ra activities in the First and Second Post-termination Surveys were generally lower than those from the Pre-termination Survey. The First Post-termination Survey had average surface sediment ^{228}Ra activities (**Figure 6.6**) ranging from 0.31 (500SW) to 0.96 pCi/g (100NW). The @ station had an average ^{228}Ra activity of 0.82 pCi/g compared to the R1 and R2 stations activities of 0.70 and 0.72 pCi/g, respectively.

The Second Post-termination Survey radionuclide data (**Table 6.8**) from Bay de Chene had a ^{226}Ra LLD of 0.02 pCi/g and a ^{228}Ra LLD of 0.03. Surface sediment ^{226}Ra activities at Bay de Chene ranged from 0.85 ± 0.10 in the R1-0-B sample to 6.52 ± 0.30 pCi/g in the 100NW-0-A sample. The surface sediment ^{228}Ra activities ranged from 0.19 ± 0.11 in the R1-0-B sample to 1.69 ± 0.18 pCi/g in the 100NW-0-A sample. No subsurface samples were collected in this survey.

The Second Post-termination Survey ^{228}Ra surface sediment activities (**Table 6.8**) ranged from 0.36 pCi/g at R1 to 1.58 pCi/g at 100SW. The average for the @ and R2 stations were 1.06 and 0.79 pCi/g.

The Second Post-termination Survey ^{226}Ra data from Bay de Chene showed generally similar results to the First Post-termination Survey data. The highest average surface sediment values (**Figure 6.6**) occurred at the 100NW (6.5 pCi/g) and 100SW (6.4 pCi/g) stations. The discharge station average activity was similar to the previous survey (3.3 pCi/g). The R1 and R2 reference station average ^{226}Ra activities ranged from 1.7 to 3.5 pCi/g, similar to the values from the First Post-termination Survey.

^{226}Ra activities from the subsurface samples (**Table 6.6**) at the discharge and reference stations ranged from 3.7 pCi/g in the R2-35-C sample to 14.7 pCi/g in the @-35-A sample. Similarly ^{228}Ra activities from the subsurface samples at the discharge and reference stations ranged from 0.5 pCi/g in the R2-20-A sample to 88.3 pCi/g from the @-35-A sample. The 88.3 pCi/g activity was the highest ^{226}Ra or ^{228}Ra activity recorded in any of the samples from any of the study sites.

Pre-discharge termination subsurface sediment ^{226}Ra data from the discharge, R1, and R2 stations showed similar activities to the surface samples at those locations. The activities at the surface and at depth were approximately 1.5 to 3.0 times higher at the discharge than at the reference stations. With the exception of the @-35 strata, all of the pre-termination ^{228}Ra subsurface sediment data were similar to the surface activity. The average adjusted value for the ^{228}Ra @-35 strata was much higher than any of the values found in the unadjusted data.

The Bay de Chene ^{226}Ra surface sediment data were analyzed using a two-way factorial analysis of variance. The independent variables used in the analysis were Sampling Period (Pre-termination, First Post-termination, and Second Post-termination Surveys) and Zone (discharge, 100, 300, 500, 1,000 m, and reference), the same as those for Delacroix Island. The statistical analysis used the adjusted sample values for those samples from the Pre-termination Survey with the higher LLD. The results of the analysis of variance for ^{226}Ra showed that the zone, sample period, and the interaction of the two factors were highly significant ($p<0.005$). Tukey's post hoc test showed that the discharge station sediment mean ^{226}Ra activity was significantly different ($p<0.005$) from all of the other zones. Additionally, the 100-m zone was significantly different ($p\leq0.05$) from the 300, 500, 1,000 m, and reference zones. The sampling period post hoc analysis showed that the Pre-termination Survey ^{226}Ra activities were significantly different than the activities in the First Post-termination Survey ($p<0.005$) and the Second Post-termination Survey ($p<0.05$). No significant differences were found between the two post-termination surveys.

Similarly, the ^{228}Ra surface sediment data were statistically analyzed using the same methods and the same independent variables as in the ^{226}Ra analysis. The results of the analysis of variance for ^{228}Ra showed that statistically significant differences existed for zone ($p<0.005$), sample period ($p<0.001$), and the interaction between zone and sample period ($p<0.001$). The post hoc analysis of the zone effects showed that the discharge mean was not significantly different from the means of the other zones. The reference zone was significantly different from the 300 ($p<0.05$), 500 ($p<0.01$), and 1,000 m ($p<0.01$) zones. ^{228}Ra activities from the Pre-termination Survey were significantly different from the First Post-termination Survey ($p<0.005$) and the Second Post-termination Survey ($p<0.005$). The First Post-termination and Second Post-termination Surveys, ^{228}Ra activities were not significantly different.

6.3.2.3 Four Isle Dome

As described in the analytical methods section, the radionuclide sediment samples from Four Isle Dome were analyzed by a different methodology than those from Delacroix Island and Bay de Chene. A total of 34 sediment samples were analyzed for ^{226}Ra and ^{228}Ra by gamma spectroscopy (**Table 6.9**). Of these samples, 20 had ^{226}Ra activities of less than the 1.1 to 2.5 pCi/g LLD. The 16 surface sediment samples had ^{226}Ra activities ranging from <1.4 pCi/g in the 100N-0-A and R2-0-A samples to 5.7 ± 1.2 pCi/g in the R1-0-A replicate. Similarly, 14 of 34 samples analyzed for ^{228}Ra activity were below the 0.4 to 0.7 pCi/g LLD. The surface sediment samples had ^{228}Ra activities ranging from <0.5 pCi/g in the @-0-C replicate to 2.6 ± 0.3 pCi/g in the 500S-0-A sample.

^{226}Ra activities from the Four Isle Dome study site subsurface samples at the discharge and reference stations ranged from <1.1 pCi/g in the @-20-B replicate to 5.2 ± 1.1 and 5.2 ± 1.3 pCi/g in the @-35-C and R1-35-C replicates, respectively. Similarly ^{228}Ra activities from the subsurface samples at the discharge and reference stations ranged from <0.4 pCi/g in the R2-20-A sample to 2.2 ± 0.3 pCi/g from the R1-35-C replicate.

The Four Isle Dome sediment radionuclide data were not statistically analyzed. The large number of below the method detection limit values and the lack of post-termination comparison samples precluded a useful analysis.

6.3.3 Interstitial Water

Interstitial water was extracted from sediment samples that were collected at Delacroix Island during the Pre-termination and Second Post-termination Surveys and at Bay de Chene and Four Isle Dome during the Pre-termination Survey. The ^{226}Ra and ^{228}Ra activities were determined from three sediment increments (0 to 5, 20 to 25, and 35 to 40 cm) at the discharge location and two reference stations located $\geq$2,000 m from the discharge.

6.3.3.1 Delacroix Island

Pre-termination Survey

The ^{226}Ra and ^{228}Ra activities in interstitial water samples collected at Delacroix Island during the Pre-termination Survey are presented in **Table 6.10**. Radionuclide activity for the 0 to 5 and 20 to 25 cm sediment increments is highest at the discharge with a general pattern of decreased activity with increased sediment depth. Highest overall levels of activity for both ^{226}Ra and ^{228}Ra are in the surficial sediment (0 to 5 cm) from the discharge with ranges of 108 to 143 and 118 to 162 pCi/L, respectively. Activities in the surficial sediments at the discharge are 5-fold greater than lower increments. Radionuclide activities at the reference stations are much lower than at the discharge with the exception of the 35 to 40 cm sediment increment. Levels of activity for ^{226}Ra and ^{228}Ra in the surficial sediment from the reference stations range from 0.9 to 3.3 and 1.4 to 3.9 pCi/L, respectively. Many samples collected at the reference stations have levels of activity below the LLD.

Table 6.9. Four Isle Dome Field sediment radionuclide Pre-termination Survey (November 1993) data (pCi/g dry weight).

Sample ID (Station-Depth-Replicate*)	^{226}Ra		^{228}Ra	
	Value	+\-	Value	+\-
@-0-A	<2.5		2.4	0.3
@-0-B	1.6	1.6	1.4	0.3
@-0-C	<2.2		<0.5	
@-20-A	2.0	1.2	1.8	0.2
@-20-B	<1.1		1.4	0.4
@-20-C	<2.0		<0.5	
@-35-A	<1.7		1.9	0.2
@-35-B	<1.7		<0.6	
@-35-C	5.2	1.1	1.6	0.2
100N-0-A	<1.4		2.4	0.5
300N-0-A	<2.0		2.0	0.4
500N-0-A	2.1	1.0	<0.7	
1000N-0-A	<1.7		1.4	0.2
100S-0-A	<2.1		1.6	0.2
300S-0-A	<2.3		<0.7	
500S-0-A	4.6	1.2	2.6	0.3
R1-0-A	5.7	1.2	<0.6	
R1-0-B	<2.0		1.6	0.2
R1-0-C	1.8	1.4	<0.7	
R1-20-A	1.5	1.2	<0.7	
R1-20-B	<2.0		<0.7	
R1-20-C	<1.4		2.0	0.2
R1-35-A	<1.7		2.0	0.6
R1-35-B	1.5	1.6	1.8	0.2
R1-35-C	5.2	1.3	2.2	0.3
R2-0-A	<1.4		<0.7	
R2-0-B	<2.0		<0.6	
R2-0-C	<1.7		<0.5	
R2-20-A	<1.5		<0.4	
R2-20-B	<1.6		<0.7	
R2-20-C	5.0	1.4	1.9	0.2
R2-35-A	3.8	1.0	2.0	0.2
R2-35-B	1.4	1.6	2.0	0.3
R2-35-C	1.8	1.5	2.0	0.3

* = Shallowest depth of 5 cm sediment stratum.
+\- = Two standard deviations.
@ = Discharge station.

Table 6.10. Summary of radionuclide activities (pCi/L) in interstitial water collected at Delacroix Island. Values are presented as ranges for multiple sample replicates. The less than (<) symbol indicates the measured activity in the sample was less than the sample's lower limit of detection which is the value behind the symbol.

Survey	Station					
	Discharge		Reference 1		Reference 2	
Sediment Increment (cm)	^{226}Ra	^{228}Ra	^{226}Ra	^{228}Ra	^{226}Ra	^{228}Ra
Pre-termination						
0 to 5	108 - 143	118 - 162	0.9 - 2.4	1.4 - 3.9	1.3 - 3.3	<1.8
20 to 25	2.4 - 18.3	2.8 - 29.4	0.8 - 1.2	<1.2 - 10.1	1.1 - 6.7	<1.7
35 to 40	1.0 - 3.3	8.4 - 15.1	1.3 - 1.5	<1.1 - 10.3	2.3 - 3.6	<0.8 - 3.9
Second Post-termination						
0 to 5	<0.31 - 0.51	<1.54 - 2.28	<0.50 - 0.51	<1.32 - 5.05	<0.41 - 0.84	<1.72 - 3.58
20 to 25	5.55 - 6.51	5.44 - 19.4	<0.50 - 2.11	<1.28 - 5.70	<0.31 - 1.21	5.37 - 11.2
35 to 40	1.21 - 1.98	<1.72 - 2.11	<0.50 - 1.58	<1.28 - 3.50	0.83 - 2.34	5.82 - 9.85

Second Post-termination Survey

The ^{226}Ra and ^{228}Ra activities in interstitial water samples collected at Delacroix Island during the Second Post-termination Survey are presented in **Table 6.10**. Radionuclide activities are generally very low with the highest level of activity for both ^{226}Ra and ^{228}Ra in the 20 to 25 cm sediment increment at the discharge. ^{226}Ra activities are generally less than a few pCi/L with the low end of the range for 6 of 9 sampling increments below the LLD. Although ^{228}Ra activities are slightly higher than ^{226}Ra in most samples, many were below the LLD. There are no apparent patterns relative to strata and distance from the discharge.

6.3.3.2 Bay de Chene

Pre-termination Survey

The ^{226}Ra and ^{228}Ra activities in interstitial water samples collected at Bay de Chene during the Pre-termination Survey are presented in **Table 6.11**. ^{226}Ra activity is highest in the 35 to 40 and 20 to 25 cm sediment increments at the discharge with ranges of 24.6 to 37.8 and 14.8 to 26.7 pCi/L, respectively. Highest activities of ^{228}Ra are in the 35 to 40 cm sediment increment at each of the stations. There is a general pattern for increased activity of ^{226}Ra with increased sediment depth at the discharge. Activity of ^{228}Ra generally increased with increased sediment depth at all stations. Although radionuclide activities in the interstitial waters are generally similar at all stations, higher ^{226}Ra activities were measured in the 20 to 25 and 35 to 40 cm strata at the discharge station.

6.3.3.3 Four Isle Dome

Pre-termination Survey

The ^{226}Ra and ^{228}Ra activities in interstitial water samples collected at Four Isle Dome during the Pre-termination Survey are presented in **Table 6.12**. ^{226}Ra activity is generally very low at each of the nine sampling increments ranging from below LLD to 6.6 pCi/L. Highest activities of ^{226}Ra are in the 0 to 5 cm stratum at each station. Highest activities of ^{228}Ra are in the subsurface sediment increments at the discharge ranging from <3.0 to 35.4 pCi/L. Highest activities of ^{228}Ra at the reference stations is from the 35 to 40 cm sediment increment ranging from below the LLD to 14.1 pCi/L.

6.3.4 Biological Tissue

Biological tissue samples were collected at Delacroix Island during the Pre-termination and Second Post-termination Surveys and at Bay de Chene and Four Isle Dome during the Pre-termination Surveys. Samples were only analyzed from Delacroix Island and Bay de Chene as insufficient tissue quantities (no large individuals) were collected at Four Isle Dome. The ^{226}Ra and ^{228}Ra activities were determined for tissue samples collected at the discharge location and two reference stations located $\geq$2,000 m from the discharge.

Table 6.11. Summary of radionuclide activities (pCi/L) in interstitial water collected at Bay de Chene during the Pre-termination Survey. Values are presented as ranges for multiple sample replicates. The less than (<) symbol indicates the measured activity in the sample was less than the sample's lower limit of detection which is the value behind the symbol.

Sediment Increment (cm)	Station					
	Discharge		Reference 1		Reference 2	
	^{226}Ra	^{228}Ra	^{226}Ra	^{228}Ra	^{226}Ra	^{228}Ra
0 to 5	3.8 - 10.1	<2.1 - 7.4	3.3 - 5.7	<1.3 - 29.0	5.8 - 12.5	<1.0 - 3.1
20 to 25	14.8 - 26.7	11.9 - 19.5	1.6 - 5.3	10.2 - 39.4	2.0 - 3.6	7.7 - 17.0
35 to 40	24.6 - 37.8	10.0 - 39.2	3.1 - 6.1	2.9 - 56.8	2.7 - 3.3	17.0 - 33.5

Table 6.12. Summary of radionuclide activities (pCi/L) in interstitial water collected at Four Isle Dome during the Pre-termination Survey. Values are presented as ranges for multiple sample replicates. The less than (<) symbol indicates the measured activity in the sample was less than the sample's lower limit of detection which is the value behind the symbol.

Sediment Increment (cm)	Station					
	Discharge		Reference 1		Reference 2	
	^{226}Ra	^{228}Ra	^{226}Ra	^{228}Ra	^{226}Ra	^{228}Ra
0 to 5	2.9 - 5.3	<3.9	<1.2 - 5.1	<3.9	2.4 - 6.6	<4.4
20 to 25	<1.7 - 4.0	<3.0 - 35.4	<1.7	<4.1	<1.7	<4.1
35 to 40	<1.7 - 4.4	7.3 - 25.2	<1.7	3.4 - 14.1	<1.9	<3.6 - 5.9

6.3.4.1 Delacroix Island

One species of crustacean (blue crab [*Callinectes* sp.]) and two species of fish (croaker [*Micropogonias undulatus*] and spot [*Leiostomus xanthurus*]) were analyzed from samples collected at Delacroix Island. Single composite samples for each of the three species were analyzed from both surveys. Samples were composited because individual specimens did not provide sufficient tissue for analyses.

Pre-termination Survey

The ^{226}Ra and ^{228}Ra activities for tissue samples collected at Delacroix Island during the Pre-termination Survey are presented in **Table 6.13**. Activity levels for both ^{226}Ra and ^{228}Ra are generally low for all species collected at the stations. ^{228}Ra activities are higher than ^{226}Ra for each sample. There is no apparent difference in radionuclide activities between stations in these mobile animals.

Second Post-termination Survey

The ^{226}Ra and ^{228}Ra activities for tissue samples collected at Delacroix Island during the Second Post-termination Survey are presented in **Table 6.13**. Activity levels for both ^{226}Ra and ^{228}Ra are generally low for all species collected at the stations. ^{226}Ra and ^{228}Ra activities range from below the LLD to 0.063 and below the LLD to 0.266 pCi/g wet weight, respectively. There is no apparent difference in radionuclide activities between stations.

6.3.4.2 Bay de Chene

Two species of crustacean (blue crab and shrimp [*Penaeidae*]) and three species of fish (croaker, seatrout [*Cynoscion* sp.], and spot) collected at Bay de Chene were analyzed during the Pre-termination Survey. Composite samples for each of the species were analyzed because individual specimens did not provide sufficient tissue. The ^{226}Ra and ^{228}Ra activities are presented in **Table 6.14**. Activity levels for both ^{226}Ra and ^{228}Ra are similar and generally low for all species collected at the stations. ^{226}Ra and ^{228}Ra activities range from below the LLD to 0.034 and below the LLD to 0.159 pCi/g, respectively. There is no apparent pattern in radionuclide activities relative to station.

6.4 DISCUSSION

6.4.1 Produced Water

In comparing produced water radionuclide data from this study to literature values, it should be noted that many of the values reported in the literature are the results of single samples and may or may not reflect long term discharge radionuclide values. The wide variability in the composite samples collected for this study indicate that truly representative produced water radionuclide sampling may require numerous composite samples collected over days or longer to obtain representative samples. Additionally, analytical methods and techniques often differ from study to study, making comparisons of detection limits, counting errors, and determining the significance of differences between studies difficult. For the purpose of this portion of the study, the literature discussed will be limited to those studies with radionuclide data primarily from the onshore and nearshore coastal waters of Louisiana.

Table 6.13. Summary of radionuclide activities (pCi/g wet weight) in crustacean (blue crab) and fish (croaker and spot) tissues collected at Delacroix Island during the Pre-termination and Second Post-termination Surveys. Crustacean edible tissue and whole fish were analyzed. The less than (<) symbol indicates the measured activity in the sample was less than the sample's lower limit of detection which is the value behind the symbol.

Survey	Station					
	Discharge		Reference 1		Reference 2	
Species	^{226}Ra	^{228}Ra	^{226}Ra	^{228}Ra	^{226}Ra	^{228}Ra
Pre-termination						
Blue crab (*Callinectes* sp.)	0.013	0.032	0.025	0.090	0.023	0.013
Croaker (*Micropogonias undulatus*)	0.025	0.037	0.005	0.112	0.018	0.039
Spot (*Leiostomus xanthurus*)	0.005	0.027	<0.004	0.076	<0.003	0.017
Second Post-termination						
Blue crab (*Callinectes* sp.)	0.007	0.046	0.007	<0.008	0.012	0.041
Croaker (*Micropogonias undulatus*)	0.019	0.0159	0.028	0.266	0.063	<0.042
Spot (*Leiostomus xanthurus*)	<0.004	0.036	<0.004	0.025	<0.003	0.107

Table 6.14. Summary of radionuclide activities (pCi/g wet weight) in crustacean (blue crab and shrimp) and fish (croaker, seatrout, and spot) tissue collected at Bay de Chene during Survey I (discharge pre-termination). Crustacean edible tissue and whole fish were analyzed. Summary values for multiple sample replicates are presented as ranges. Any value proceeded by a less than (<) symbol is the method detection limit for that particular sample (e.g., <0.010 pCi/g for shrimp from the Discharge).

Species	Station					
	Discharge		Reference 1		Reference 2	
	^{226}Ra	^{228}Ra	^{226}Ra	^{228}Ra	^{226}Ra	^{228}Ra
Blue crab (*Callinectes* sp.)	0.009 - 0.023	0.041 - 0.059	0.012	<0.019	0.007 - 0.024	<0.018
Shrimp (*Penaeidae*)	0.006 - 0.011	<0.010 - 0.026	0.005 - 0.027	<0.018	0.006 - 0.021	<0.017 - 0.124
Croaker (*Micropogonias undulatus*)	0.004 - 0.024	0.029 - 0.094	0.010 - 0.027	<0.015 - 0.046	0.014 - 0.032	<0.012
Seatrout (*Cynoscion* sp.)	0.004 - 0.021	0.037 - 0.159	0.016	0.020	<0.004 - 0.012	<0.010 - 0.036
Spot (*Leiostomus xanthurus*)	0.019 - 0.034	0.018 - 0.086	0.020 - 0.029	<0.018	<0.004 - 0.023	<0.012 - 0.042

Kramer and Reid (1984) reported produced water ^{226}Ra and ^{228}Ra activities for 40 oil, gas, and geothermal wells in Louisiana and Texas with 30 from Louisiana. The ^{226}Ra and ^{228}Ra activities in the produced water ranged from <0.05 to 1,580 pCi/L and 8.3 to 1,523 pCi/L, respectively. Neff et al. (1989) reported produced water radionuclide activities for four discharges in central coastal Louisiana. The data were reported as the sum of the ^{226}Ra and ^{228}Ra activities in the samples. The total $^{226+228}$Ra values reported ranged from 605 to 1,215 pCi/L. St. Pé (1990) reported ^{226}Ra activities in four produced water discharges from coastal Louisiana ranging from 335 to 567 pCi/L.

In 1989, the LDEQ required a one time sampling of all produced water discharges into Louisiana waters for ^{226}Ra and ^{228}Ra activities. Stephenson (1992) presented the means, standard deviations, and ranges of activities for these samples. The ^{226}Ra activities in the LDEQ data ranged from 0 to 930, with a mean of 68 and a standard deviation of 144 pCi/L. The ^{228}Ra activities in the LDEQ data ranged from 0 to 928, with a mean of 165 and a standard deviation of 150 pCi/L.

Rabalais et al. (1991) reported ^{210}Pb and total $^{226+228}$Ra values in samples from seven coastal Louisiana produced water discharges. These sampling locations discharged produced water that originated, at least partly, in the Louisiana outer continental shelf waters. ^{210}Pb activities at the seven discharges ranged from 0.1 to 11.5 pCi/L. The total $^{226+228}$Ra activities at the seven discharges ranged from 138 to 1,051 pCi/L.

Mulino and Rayle (1992) reported produced water ^{226}Ra and ^{228}Ra activities for three discharges in coastal Louisiana. Two of the discharges were in the coastal marshes and one was in the Gulf of Mexico. The ^{226}Ra activities ranged from 143 to 477 pCi/L and the ^{228}Ra activities ranged from 149 to 198 pCi/L.

The total $^{226+228}$Ra activities for the three produced water discharges from this study averaged 481 to 503 pCi/L. This places them within the range reported by Rabalais et al. (1991) for total $^{226+228}$Ra activity and below the range reported by Neff et al. (1989). The individual ^{226}Ra and ^{228}Ra activities reported here fall within the wide range of values reported by both Kramer and Reid (1984) and Stephenson (1992). The ^{226}Ra activities in the produced water samples from this study generally fell below those reported by St. Pé (1990) and within the range reported by Mulino and Rayle (1992). The produced water ^{228}Ra activities in this study were higher than those reported by Mulino and Rayle.

Relatively little data exists in the literature on the typical range of produced water radionuclide activities for ^{210}Pb, ^{210}Po, and ^{228}Th in onshore or nearshore discharges. The ^{210}Pb activities in the Delacroix Island and Bay de Chene produced water samples (62.4 ± 2.6 to 84.9 ± 3.8 pCi/L) were higher than those reported by Rabalais et al. (1991). It is not known if this is an actual difference in the radionuclide activity between studies or a function of different analytical techniques used in the two surveys.

6.4.2 Sediment

While the surface sediment radionuclide activities were generally low at all of the stations, statistical analysis of the Delacroix Island data showed that ^{226}Ra activities were significantly higher at the discharge than at the other stations (zone effect). The post hoc analysis also showed that ^{226}Ra activities at the 100, 300, and 500 m stations were significantly different from the 1,000 m and reference stations. This produces a grouping of stations by decreasing ^{226}Ra activity with the discharge having the highest activity, the 100, 300, and 500 m stations having the next lower activity, and the 1,000 m and reference stations having the lowest activities. The post hoc analysis also showed a statistically significant ($p<0.001$) drop in sediment ^{226}Ra activity between the Pre-termination and both the First and Second Post-termination Surveys.

The statistical analysis of the Delacroix Island ^{228}Ra data showed a highly significant difference ($p<0.001$) for the sample period. The post hoc analysis of the surface sediment ^{228}Ra data showed significantly ($p<0.05$) higher activities in the Pre-termination and First Post-termination Surveys than in the Second Post-termination Survey.

The Bay de Chene surface sediment post hoc analysis showed that the discharge ^{226}Ra activities were significantly ($p\leq0.001$) higher than in all the other zones. The ^{226}Ra activities from the 100-m zone was significantly ($p\leq0.05$) higher than the 300, 500, 1,000 m, and reference zones. This produces a grouping of stations by decreasing ^{226}Ra activity with the discharge having the highest activity, the 100-m zone the next lower activity, and the 300, 500, 1,000 m, and reference stations having the lowest activities. The separation of the 100-m zone from the 300, 500, 1,000 m, and reference zones appears to be due to higher activities in the unadjusted second post-termination sediment data at two of the three 100-m zone stations. The analysis also showed a statistically significant ($p<0.005$) decrease in sediment ^{226}Ra activity between the Pre-termination and First Post-termination Surveys and between the Pre-termination and Second Post-termination Surveys ($p<0.05$).

Like the ^{226}Ra sediment data, the statistical analysis of ^{228}Ra data showed a highly significant difference ($p<0.001$) for the sample period. The post hoc statistical analysis of the data showed that ^{228}Ra activities were significantly higher in the Pre-termination Survey than in the First Post-termination Survey ($p<0.005$) and the Second Post-termination Survey ($p<0.005$). The post hoc zone effects analysis showed no significant differences between the discharge and the other zones, but, did show the 300-m zone had significantly lower ^{228}Ra activities than did the 500 m ($p<0.05$), 1,000 m ($p<0.01$), and reference zones ($p<0.01$). This is apparently due to the low ^{228}Ra activities found at all of the 300-m stations in all surveys.

Statistical analyses for Delacroix Island and Bay de Chene were performed on the entire data sets including the adjusted values. This procedure was employed to reduce the error mean square in the analysis of variance, thus making the analysis more sensitive to significant differences.

Subsurface sample replicates from the discharge site in both the Pre-termination and Second Post-termination Surveys at Delacroix Island and the Pre-termination Survey at Bay de Chene showed widely variable ^{226}Ra and ^{228}Ra activities. These variabilities may reflect the heterogeneous nature of the sediments at the discharge, differing radionuclide input rates or differing previous depositional regimes. In this study, at least one replicate at the Delacroix Island and Bay de Chene discharge stations had the highest radionuclide activities of the site. At Bay de Chene, the adjustment of the data set undoubtedly exaggerated the elevated ^{228}Ra values found at the 35 cm strata.

Hanan (1981) reported ^{226}Ra activities ranging from 1.00 ± 0.06 to 5.17 ± 0.15 pCi/g at surface (0 to 10 cm) sediment sampling locations within 20 m of a single produced water discharge located in the Mississippi River Delta. Surface sediment ^{226}Ra activities at Delacroix Island in all three survey periods were similar to this range. At Bay de Chene, the Pre-termination and Second Post-termination Surveys had slightly higher values than the range above, but the majority of the samples in all three surveys fell within the range. The background or control samples Hanan analyzed had activities ranging from 1.05 ± 0.04 to 1.46 ± pCi/g. This is a narrower range that the ND to 2.57 ± 0.31 pCi/g from the Delacroix Island reference stations and the 0.85 ± 0.11 to 3.78 ± 0.23 pCi/g from the Bay de Chene reference stations in all three surveys.

Hanan (1981) documented a significant (approximately double), but non-dramatic increase in sediment ^{226}Ra in the vicinity of the produced water discharge he sampled. He found a significant correlation between the ^{226}Ra activity and the cation exchange capacity of the sediment. Clay sized particles were found to provide the highest number of sorption surfaces for ^{226}Ra. Within station variances of sediment radionuclide activities at all three of the sites in the current study may be related to small differences in the sediment clay fraction.

St Pé (1990) sampled sediments in the vicinity of four produced water discharges in coastal Louisiana. Surface sediment ^{226}Ra data ranged from 2.7 ± 1.3 pCi/g to 533.0 ± 25.9 pCi/g. These sediment samples were collected from a reference station and at a discharge, respectively, in the Lirette Oil and Gas Field. At three of the four sites sampled, ^{226}Ra surface sediment activities were significantly elevated at the discharge when compared to reference station values. The reference station ^{226}Ra activities at all four study sites ranged from 2.7 ± 1.3 pCi/g to 8.2 ± 0.6 pCi/g. Surface sediment ^{226}Ra activities at all three sites in the current study were significantly lower than the levels found by St Pé.

Rayle and Mulino (1992) found sediment ^{226}Ra activities ranging from ND to 6.3 ± 0.6 pCi/g in surface (0 to 10 cm) sediment samples collected at 15 m from six produced water discharges in coastal Louisiana. ^{228}Ra activities in the same sediment samples ranged from 0.0 ± 0.7 to 3.9 ± 0.8, of which only three of the ten samples had activities above the LLD. The LLDs for the ^{226}Ra and ^{228}Ra data were 0.1 pCi/g and 0.9 to 1.2 pCi/g, respectively. The maximum sediment activities for both ^{226}Ra and ^{228}Ra in that study were found at the same Bay de Chene discharge sampled for this study.

6.4.3 Interstitial Water

Radionuclide activities in interstitial waters were generally very low (<0.31 to 12.5 pCi^{226}Ra/L and <0.08 to 19.4 pCi^{228}Ra/L) at survey locations with two exceptions. The sediment strata sampled at the Delacroix Island discharge during the Pre-termination Survey had radionuclide activities which were relatively high and had ranges of 108 to 143 pCi^{226}Ra/L and 118 to 162 pCi^{228}Ra/L in the 0 to 5 cm increment and 2.4 to 18.3 pCi^{226}Ra/L and 2.8 to 29.4 pCi^{228}Ra/L in the 20 to 25 cm increment. The deep sediment (20 to 25 and 35 to 40 cm) ^{226}Ra and ^{228}Ra activities from the discharge (range was 14.8 to 37.8 pCi^{226}Ra/L and 10.0 to 39.2 pCi^{228}Ra/L) and ^{228}Ra activity from the reference stations (range was 2.9 to 56.8 pCi/L) at Bay de Chene was also relatively high. There was a noticeable decline in radionuclide activities at the Delacroix Island discharge between the Pre-termination Survey and the Second Post-termination (see **Table 6.9**). Comparison of interstitial water radionuclide activities determined during this study with other studies is difficult because of lack of available data. Radionuclide activities in the interstitial waters excluding the aforementioned exceptions are similar to radionuclide activities reported for interstitial waters from stations located near offshore platforms discharging produced water (Lagera et al., 1997). ^{226}Ra and ^{228}Ra levels at these stations ranged from <0.6 to 3.3 and from <5.3 to 13.5 pCi/L, respectively. Cochran and Krishnaswami (1980) reported activities of 0.22 to 6.39 pCi^{226}Ra/L for deep-sea sediments from the eastern tropical Pacific Ocean.

6.4.4 Biological Tissue

Radionuclide activities in biological tissue (crustaceans and fish) samples collected during this study were very low. All the specimens analyzed during this study were motile and transient which would probably prevent extended exposure to the produced water discharge. ^{226}Ra and ^{228}Ra activities in the edible tissue of blue crab (*Callinectes* spp.) collected during this study ranged from 0.007 to 0.025 and <0.008 to 0.090 pCi/g wet weight, respectively. Hart et al. (1996) reported similar ^{226}Ra and ^{228}Ra activities in blue crab collected in close proximity to discharging oil and gas platforms from nearshore Louisiana with ranges of <0.003 to 0.015 and <0.011 to 0.047 pCi/g wet weight, respectively. Continental Shelf Associates, Inc. (1991) reported ^{226}Ra and ^{228}Ra activities of <0.002 to 0.132 and <0.035 to 0.065 pCi/g wet weight, respectively for blue crab collected at a produced water discharging structure located in a Louisiana bay area. Shrimp (Penaeidae) tissue collected at Bay de Chene during the Pre-termination Survey had low activities for both ^{226}Ra and ^{228}Ra with most values close to the LLD (<0.010 pCi/g wet weight) which is similar to what was reported by Hart et al. (1996) and Continental Shelf Associates, Inc. (1991). Fish tissue analyzed during this study also had low radionuclide activities comparable to previously reported analytical results for seatrout (*Cynoscion* sp.) (Continental Shelf Associates, Inc., 1991) and other fish species (Hart et al., 1996). Radionuclide activities in the tissues in this study were variable and usually close to the sample specific lower limits of detection.

6.5 SUMMARY

Produced water discharges sampled from the Delacroix Island, Bay de Chene, and Four Isle Dome oil and gas fields had ^{226}Ra and ^{228}Ra activities within the wide ranges published in the literature. Most of the radionuclide activity in the produced water samples was associated with the ^{226}Ra and ^{228}Ra isotopes.

At Delacroix Island, surface sediment ^{226}Ra and ^{228}Ra activities were generally low at all stations. The sediment ^{226}Ra activities at the discharge station were significantly higher than those from the transect and reference stations. The sediment ^{228}Ra activities at the discharge station were not significantly different from the transect or reference stations. Both ^{226}Ra and ^{228}Ra activities significantly decreased after the termination of the produced water discharge. For ^{226}Ra, the decrease occurred between the Pre-termination and First Post-termination Surveys (6 months post-termination). The ^{228}Ra activities decreased between the First and Second Post-termination Surveys (1 year post-termination).

The surface sediment ^{226}Ra and ^{228}Ra activities at Bay de Chene were generally higher than at Delacroix Island. The sediment ^{226}Ra activities at the discharge station were significantly higher than the those from the transect and reference stations. The sediment ^{228}Ra activities at the discharge station were not significantly different from the transect or reference stations. Both ^{226}Ra and ^{228}Ra activities significantly decreased after the termination of the produced water discharge. For both radionuclides, the decrease occurred between the Pre-termination and First Post-termination Surveys (9 months post-termination).

Interstitial water was extracted from sediment samples that were collected at Delacroix Island during the Pre-termination and Second Post-termination Surveys and at Bay de Chene and Four Isle Dome during the Pre-termination Survey. Radionuclide activities in interstitial waters were generally very low at survey locations with the exception of the sediment stratum sampled at the Delacroix Island discharge during the Pre-termination Survey and deep sediments from Bay de Chene during the Pre-termination Survey. Radionuclide activity for the 0 to 5 and 20 to 25 cm sediment increments were highest at the Delacroix Island discharge during the Pre-termination Survey. At the Delacroix Island discharge during the Pre-termination Survey, there was a general pattern of decreased radium activities with increased sediment depth. The activities of ^{226}Ra and ^{228}Ra in the surficial sediment (0 to 5 cm) from the discharge ranged from 108 to 143 and 118 to 162 pCi/L, respectively. These activities were 5-fold greater than activities at lower increments. There was a noticeable decline in radionuclide activities at the Delacroix Island discharge between the Pre-termination and the Second Post-termination Surveys.

Radionuclide activities in biological tissue (crustaceans and fish) samples collected during this study were very low. Radionuclide activities in tissues were variable and usually close to sample specific lower limits of detection.

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CHAPTER 7 - ASSESSMENT OF METALS IN PRODUCED WATER, INTERSTITIAL WATER, AND SEDIMENT IN AREAS WHERE PRODUCED WATER WAS DISCHARGED TO COASTAL LOUISIANA WATERS

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7.1 INTRODUCTION

This portion of the study of Louisiana coastal waters was designed to assess whether discharges of produced water lead to enhanced levels of metals in interstitial water and sediment at stations near discharging facilities relative to reference stations. Concentrations of metals in produced water can be enriched by factors of 10 to >10,000 relative to ambient water (Boesch and Rabalais, 1989; Ray and Engelhardt, 1992). In addition to presenting data that show the distribution of metals in areas around produced water discharges, this study also provided an opportunity to follow changes in metal concentrations of interstitial water and sediment after discharges of produced water were discontinued.

Concentrations of arsenic, barium, cadmium, chromium, copper, iron, mercury, manganese, molybdenum, nickel, lead, vanadium, and zinc are presented for produced water, interstitial water, and sediment samples collected at stations near discharging facilities and from non-discharging reference sites. Concentrations of aluminum and calcium are also presented for sediment samples. Our results are described within the context of the following: (1) concentrations of metals in produced water versus ambient water; (2) concentrations of dissolved metals in interstitial water from sediments at reference versus discharge stations; and (3) accumulation of metals in sediments at stations adjacent to oil and gas facilities relative to more distant reference stations.

7.2 LABORATORY METHODS

According to the study design described in **Chapter 2**, three locations were investigated for this study. They included Delacroix Island, Bay de Chene, and Four Isle Dome (**Figures 3.1** through **3.3**). For the metals portion of the study, interstitial water from Delacroix Island was analyzed on two occasions, once prior to termination of produced water discharges (Pre-termination Survey - April 1993) and once 12 months after discharges had been discontinued (Second Post-termination Survey - April 1994). Sediments were sampled at Delacroix Island on three occasions, the two periods mentioned above plus at 6 months following termination of discharges (First Post-termination Survey - October 1993). Interstitial water samples from Bay de Chene and Four Isle Dome were collected and analyzed once, prior to termination of discharges (Pre-termination Surveys), during May 1993 and November 1993, respectively. Sediments from Bay de Chene were collected and analyzed on three occasions, once prior to termination of discharges (Pre-termination Survey - May 1993) and twice following cessation of discharges (First and Second Post-termination Surveys - May 1994 and October 1994). Sediments from Four Isle Dome were collected and analyzed once (Pre-termination Survey - November 1993).

Produced and interstitial water samples were analyzed directly following appropriate dilution with distilled-deionized water. Sediment was completely digested using a mixture of HF-HNO_3-$HClO_4$ (Trefry and Metz, 1984). Instrumental analyses were carried out by one or more of the following techniques, depending on sample type and metal levels: (1) atomic absorption spectrometry (AAS), using either flame atomization with a Perkin-Elmer (PE) model 4000 instrument (aluminum, calcium, chromium, copper, iron, manganese, nickel, vanadium, zinc) or heated graphite atomization using a PE model 5100 or 4000 system (arsenic, cadmium, copper, manganese, nickel, lead, vanadium); (2) hydride generation in tandem with the PE model 4000 AAS using flame atomization (arsenic); (3) cold-vapor AAS using a Laboratory Data Control system (mercury); (4) inductively coupled plasma-mass spectrometry using a PE ELAN 5000 (barium, cadmium, molybdenum, and lead); and (5) instrumental neutron activation analysis (barium) using the research and training reactor at the University of Florida. Concentrations of TOC in interstitial water were determined with good agreement by both the wet digestion method of Fredericks and Sackett (1970) using an OI Corporation model 524C T.O.C. analyzer and by high-temperature combustion using a Shimadzu model TOC-500 instrument. Chlorinity levels in the interstitial water were determined by Mohr titration using silver nitrate that was standardized with IAPSO standard seawater. Sulfate levels in interstitial water (0 to 5 cm) were determined using EPA Method 9038-1 (turbidimetric).

7.2.1 Quality Assurance and Quality Control

7.2.1.1 Procedures

All field and QC samples received at the laboratory were examined for possible contamination from breakage, spillage, and for acceptable shipping conditions, assessed for adequate sample volume, and then checked against the accompanying sample custody sheets. It is standard practice in the FIT laboratory to use the client sample I.D. as the laboratory sample I.D. number which was entered into the laboratory's sample logbook, and the sample container placed in cold storage according to SOP. After accomplishing the required chain-of-custody procedures, including sending a copy of the signed custody sheets to S&A, ADL, or CSA, individual samples were evaluated, and specific storage, handling, and analytical instructions were specified. All applicable holding time requirements were met according to SOP. After assessing if the sample set was complete, specific analysis instructions and authorization were obtained from CSA prior to proceeding with the analyses.

Samples were prepared for analysis as described in the previous section with careful attention placed on minimizing contamination from environmental sources and sample carry-over (cross-contamination). Each analytical instrument was setup and underwent initial calibration according to manufacturer's directions and applicable SOPs. Calibration stock solutions for each instrument and matrix were prepared from U.S. NIST-traceable analytical-grade material. Stock solutions, and instrument, procedural, and method blanks were prepared with distilled-deionized water. Certified analytical grade acids for all solutions were used according to SOP.

After initial instrument calibration was completed, each batch of field samples was analyzed with a complete set of QC samples including procedural blanks, sample duplicates, matrix spikes/matrix spike duplicates to assess contamination, interferences, accuracy, and precision. Seawater and sediment SRMs were prepared and analyzed along with field samples to assess analytical accuracy. SRMs included the following: (1) CASS-2 seawater and SLRS-1 river water; and (2) BCSS-1 marine sediment from the National Research Council (NRC) of Canada.

Method detection limits (MDLs) were determined for each analyte, sample type, and matrix. Although general MDLs are presented below, in practice MDLs for metal analyses were sample specific because modifications of procedures (e.g., increased sample volume) were done to achieve the necessary detection limit to determine an actual concentration.

All analytical results were reviewed and audited prior to submission to CSA. Each data report was submitted as a hardcopy and in spreadsheet format. According to laboratory SOP, data reports, working documents, and project files will be archived for at least 5 years before disposal.

7.2.1.2 Results

Table 7.1 summarizes the DQOs for metal analysis. The general MDLs established for each metal are presented in **Table 7.2**. Based on the results of the analyses of the QC samples, data quality for metals in the relevant matrices was good. Many replicate samples were analyzed to determine analytical precision. Results for precision varied as a function of metal concentration and typically ranged from <1% to 5% with values as high as 20% for very low metal levels. Low analyte concentrations (below detection limits) were also found in the produced water field blank indicating contaminant-free samples. With the exception of copper and zinc, evidence that samples were contaminant-free can be found in the low analyte concentrations found in the equipment blanks (core tubes and squeezer apparatus) that were prepared and analyzed for sediments and interstitial water samples.

Analytical accuracy and precision was good based on results of sample duplicates and SRMs. **Table 7.3** summarizes the results of the water and sediment SRM analyses, respectively. All analyte values obtained were within acceptable limits for the particular SRM as established by the certifying agency.

7.3 RESULTS AND DISCUSSION

7.3.1 Metals in Produced and Ambient Water

The potential for enhanced bioaccumulation of metals from ambient water and interstitial water in an area around a facility that is discharging produced water is influenced by the concentration of the metal in produced water relative to ambient water, by the rates of discharge and mixing of the produced water with ambient water, and by the chemical forms of the metal in the produced water/ambient water mixture. Overall, dissolved metal levels in produced water are controlled by a complex interplay of metals with organic matter, chloride, sulfide, pH, temperature, redox state, and other variables (Barth, 1991; Helgeson et al., 1993). Concentrations of metals in produced water from the three sites sampled for this study were relatively uniform and generally much higher than in ambient water (**Table 7.4**). The highest metal levels found for produced water from the three sites were all from Four Isle Dome where the chlorinity of the discharge water (97 g dissolved solids/L) was about 15% higher than at the other sites (**Table 7.4**). Concentrations of barium and iron averaged about 15% and 40% higher, respectively, in produced water from the Four Isle Dome facility relative to the other sites (**Table 7.4**) and levels of lead and zinc averaged 5 and 100 times greater, respectively, for produced

Table 7.1. Data quality objectives and acceptance criteria for metals.

Element or Sample Type	Minimum Frequency	Data Quality Objective/ Acceptance Criteria
Initial Calibration	Prior to every analytical batch	3 to 5 point calibration curve over two orders of magnitude. Percent relative standard deviation ≤25%
Continuing Calibration	Every 5-10 samples	Percent relative standard deviation ≤30% for 90% of analytes
Matrix SRM	One per batch or 5% of field samples	Values must be within ±20% of true value on average for all analytes
Matrix Spikes	1 per batch or 5% of field samples	Percent recovery target analytes 80% to 120%
Matrix Duplicate	1 per batch or 5% of field samples	Relative percent difference within 20%
Procedural Blank	1 per batch or 5% of field samples	Not to exceed 5x target MDL
Duplicate SRM or Sample Analysis	1 per batch or 5% of field samples	Relative percent difference ≤20%

MDL = Method detection limit.
SRM = Standard reference material.

Table 7.2. Method detection limits for metals. Sediment values are reported on a dry weight basis.

Metal	Sample Matrix	Method Detection Limit
Aluminum	Sediment	6 µg/g
Arsenic	Produced Water	0.01 µg/L
	Interstitial Water	0.2 µg/L
	Sediment	0.1 µg/g
Barium	Produced Water	4.6 µg/L
	Interstitial Water	1.0 µg/L
	Sediment	0.1 µg/g
Cadmium	Produced Water	0.1 µg/L
	Interstitial Water	0.1 µg/L
	Sediment	0.002 µg/g
Chromium	Produced Water	0.01 µg/L
	Interstitial Water	0.10 µg/L
	Sediment	0.1 µg/g
Copper	Produced Water	0.2 µg/L
	Interstitial Water	0.06 µg/L
	Sediment	2.0 µg/g
Iron	Produced Water	0.09 mg/L
	Interstitial Water	0.05 mg/L
	Sediment	5 µg/g
Mercury	Produced Water	0.010 µg/L
	Interstitial Water	0.010 µg/L
	Sediment	0.001 µg/g
Manganese	Produced Water	0.1 µg/L
	Interstitial Water	0.05 µg/L
	Sediment	2.0 µg/g
Molybdenum	Produced Water	0.10 µg/L
	Interstitial Water	0.10 µg/L
	Sediment	0.1 µg/g
Nickel	Produced Water	1.0 mg/L
	Interstitial Water	0.10 µg/L
	Sediment	0.2 µg/g
Lead	Produced Water	0.2 µg/L
	Interstitial Water	0.10 µg/L
	Sediment	0.1 µg/g
Vanadium	Produced Water	1.2 µg/L
	Interstitial Water	0.1 µg/L
	Sediment	10 µg/g
Zinc	Produced Water	0.1 µg/L
	Interstitial Water	0.2 µg/L
	Sediment	1.0 µg/g

Table 7.3. Results (mean ± 1 standard deviation) from analyses of standard reference coastal seawater CASS-2 and riverine water SLRS-1 from the National Research Council (NRC) of Canada. All concentrations in μg/L.

	Al	As	Ba	Cd	Cr	Cu	Fe	Mn	Mo	Ni	Pb	V	Zn
CASS-2 This study (n=11)	--	1.02 ±0.03	7.85 ±0.44	0.024 ±0.009	0.12 ±0.01	0.67 ±0.02	1.19 ±0.16	1.99 ±0.10	9.12 ±0.12	0.31 ±0.04	0.025 ±0.008	1.11 ±0.04	2.0 ±0.1
CASS-2 Certified Value (NRC)	--	1.01 ±0.07	--	0.019 ±0.004	0.12 ±0.02	0.68 ±0.04	1.20 ±0.12	1.99 ±0.15	9.01 ±0.28	0.30 ±0.04	0.019 ±0.006	--	2.0 ±0.1
SLRS-1 This study (n=11)	--	0.51 ±0.04	21.0 ±0.6	0.016 ±0.001	0.37 ±0.01	3.58 ±0.10	30.7 ±0.8	1.87 --	0.79 ±0.02	1.05 ±0.03	0.107 ±0.006	0.66 ±0.03	1.2 ±0.1
SLRS-1 Certified Value (NRC)	--	0.55 ±0.08	22.2 ±1.7	0.015 ±0.002	0.36 ±0.04	3.58 ±0.30	31.5 ±2.1	1.77 ±0.23	0.78 ±0.04	1.07 ±0.06	0.106 ±0.011	0.66 ±0.09	1.3 ±0.2

Results (mean ± 1 standard deviation) from analyses of standard reference sediment BCSS-1 from the National Research Council (NRC) of Canada. All concentrations in μg/g unless specified.

	Al (%)	As	Ba	Cd	Cr	Cu	Fe (%)	Mn	Mo	Ni	Pb	V	Zn
BCSS-1 This study (n=19)	6.31 ±0.17	11.3 ±1.1	331 ±23	0.28 ±0.02	114 ±7	17.6 ±1.0	3.30 ±0.07	232 ±5	2.5 ±0.3	53.1 ±2.9	22.9 ±1.3	92.8 ±4.9	113 ±5
BCSS-1 Certified Value (NRC)	6.26 ±0.22	11.1 ±1.4	(330)[a]	0.25 ±0.04	123 ±14	18.5 ±2.7	3.29 ±0.10	229 ±15	(1.9)[a]	55.3 ±3.6	22.7 ±3.4	93.4 ±4.9	119 ±12

[a] Non-certified value.

Table 7.4. Metal concentrations in produced water (PW) and interstitial water (IW, 0-5 cm) from Delacroix Island (DI), Bay de Chene (BDC), and Four Isle Dome (FID). Data for discharge (DC) and reference stations (R1, R2) are shown. Data are listed for the Pre-termination (IW and IW-1) and Second Post-termination (IW-3) Surveys. Mean values are presented for produced water (n=2) and interstitial water (n=3).

Sample ID	Cl (g/kg)	SO_4 (g/kg)	As (µg/L)	Ba (mg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Fe (mg/L)	Hg (µg/L)	Mn (mg/L)	Mo (µg/L)	Ni (µg/L)	Pb (µg/L)	V (µg/L)	Zn (µg/L)
DI-PW	86.0	--	0.06	126	0.3	0.2	<0.2	19	0.03	0.7	0.5	1.5	0.8	<1.2	42
DI-DC-IW-1	43.2	0.1	6.6	54	0.5	0.5	2.2	12	0.03	24	2.3	2.2	1.1	<0.2	11
DI-R1-IW-1	2.5	0.3	2.3	0.4	<0.1	0.7	4.6	1	0.02	9	5.9	4.3	0.4	1.5	11
DI-R2-IW-1	2.0	0.2	4.7	0.4	<0.1	0.6	3.5	2	<0.01	10	1.6	4.5	0.3	2.4	17
DI-DC-IW-3	1.4	--	8.5	0.3	<0.1	0.4	0.9	0.6	--	0.4	3.0	1.7	0.6	2.9	9
DI-R1-IW-3	1.5	--	7.0	0.25	<0.1	0.8	0.5	0.2	0.01	0.1	1.4	1.4	0.6	2.6	5
DI-R2-IW-3	1.3	--	8.5	0.3	<0.1	0.7	0.6	0.1	<0.01	0.1	4.1	1.0	0.6	3.6	4
BDC-PW	85.3	--	0.05	120	0.2	0.2	0.5	18	<0.01	0.9	0.4	2.2	0.6	<1.2	9
BDC-DC-IW	7.3	0.3	32	1.6	<0.1	0.8	0.9	15	--	9	5.9	3.8	1.7	4.7	7
BDC-R1-IW	3.9	0.5	5.3	0.2	<0.1	0.4	1.2	0.1	<0.01	2	7.0	1.0	0.3	4.6	8
BDC-R2-IW	4.2	0.5	4.3	0.7	<0.1	0.4	0.8	1	<0.01	4	3.3	0.8	0.6	2.7	6
FID-PW	97.0	--	3.9	145	3.26	<0.1	2.1	30	0.05	6	0.8	<1	3.6	<1.2	1500
FID-DC-IW	3.6	--	4.3	0.2	<0.1	1.4	3.4	7	<0.01	6	1.9	5.0	0.2	2	3
FID-R1-IW	2.4	--	6.1	0.2	<0.1	0.9	2.0	0.05	<0.01	0.6	3.5	1.1	0.2	1.6	2
FID-R2-IW	3.1	--	5.1	0.2	<0.1	1.0	2.3	0.2	<0.01	1.0	2.3	1.6	0.2	2.1	2
PW[a]	--	--	5-300	0.1-2000	--	--	0.4-1500	--	0.05-2	--	--	0.4-1700	1.5-8800	--	0.1-69,000
AW[b]	--	--	0.6-1.5	0.01-0.09	--	--	0.2-1.7	<0.001	<0.01	<0.0005	3-10	0.2-1.6	0.02-0.05	1.1-1.7	5

[a] From Neff and Sauer (1995).

[b] Trefry *et al.* (1997) ambient water (AW).

water from Four Isle Dome. Levels of TOC were enhanced in all produced waters and were quite variable from site to site with 25 mg/L at Delacroix Island, 83 mg/L at Bay de Chene, and 500 mg/L at Four Isle Dome. The very high levels of TOC at Four Isle Dome are consistent with greatly enhanced levels of arsenic, lead, and zinc in produced water from that site and the tendency for TOC to complex metals.

Concentrations of metals in produced water from this study were all much less than the upper limit of values presented by Neff and Sauer (1995) in their summary of produced water composition. Maximum concentrations for arsenic, barium, mercury, and zinc determined for produced water from this study were 14 to 80 times lower than maximum values reported by Neff and Sauer (1995) (**Table 7.4**). In addition, our maximum values for copper, nickel, and lead in produced water from the three sites were 700 to 2,400 times lower than maximum levels from other studies. Our lowest levels of arsenic, copper, mercury, lead, and zinc were below minimum values presented by Neff and Sauer (1995) in **Table 7.4**. Finally, maximum levels of iron and manganese in produced water from this study were essentially the same as those found at offshore sites in the Gulf of Mexico. In contrast, levels of arsenic, barium, lead, and zinc were two- to six-fold lower in produced water from this study relative to produced water from the open Gulf of Mexico.

Concentrations of dissolved metals in ambient water from the three sites were not determined for this study; so, typical values for dissolved metals in coastal waters from the Gulf of Mexico are listed in **Table 7.4** to provide a general frame-of-reference for determining metal enrichment in produced water relative to the ambient, receiving coastal water. Highest enrichment factors for metal concentrations in produced water versus coastal seawater were found for barium, iron, and manganese with average values ≥1,000 (**Figure 7.1**). Maximum levels of lead and zinc in the produced water were about 100-fold enriched relative to ambient water. In contrast, produced water samples from this study were depleted with copper, molybdenum (not in **Figure 7.1**), and vanadium compared with ambient water (**Table 7.4**). Thus, only five metals (iron, manganese, barium, zinc, and lead) are present in the produced water at levels that are on the order of 100 times or greater than ambient water. However, the behavior and subsequent bioaccumulation of metals following mixing of produced water with ambient water is a function of both the concentration and chemical form of the metal of interest in ambient water. For example, metals complexed by organic matter may stay dissolved in seawater for longer periods of time. Additional studies are necessary to evaluate these reaction processes.

7.3.2 Chlorinity, Sulfate, and Metals in Interstitial Water from Delacroix Island

When dense, high salinity produced water (salinity ≥135 g/kg or ‰) is discharged into coastal embayments, it may settle to the bottom and pond near the discharge site until local currents mix the higher salinity produced water with lower salinity ambient water. Under such conditions, dissolved salts and potentially toxic contaminants in the produced water may diffuse or be advected into the interstitial water. In addition to changing the salinity environment for benthic infauna, contaminant levels in sediment interstitial water also may be increased. At Delacroix Island, we had the opportunity to analyze sediment interstitial water while produced water was being discharged as well as after discharges were terminated. This opportunity provided an ideal case study for tracing temporal shifts in the chemistry of the interstitial water following termination of produced water discharges.

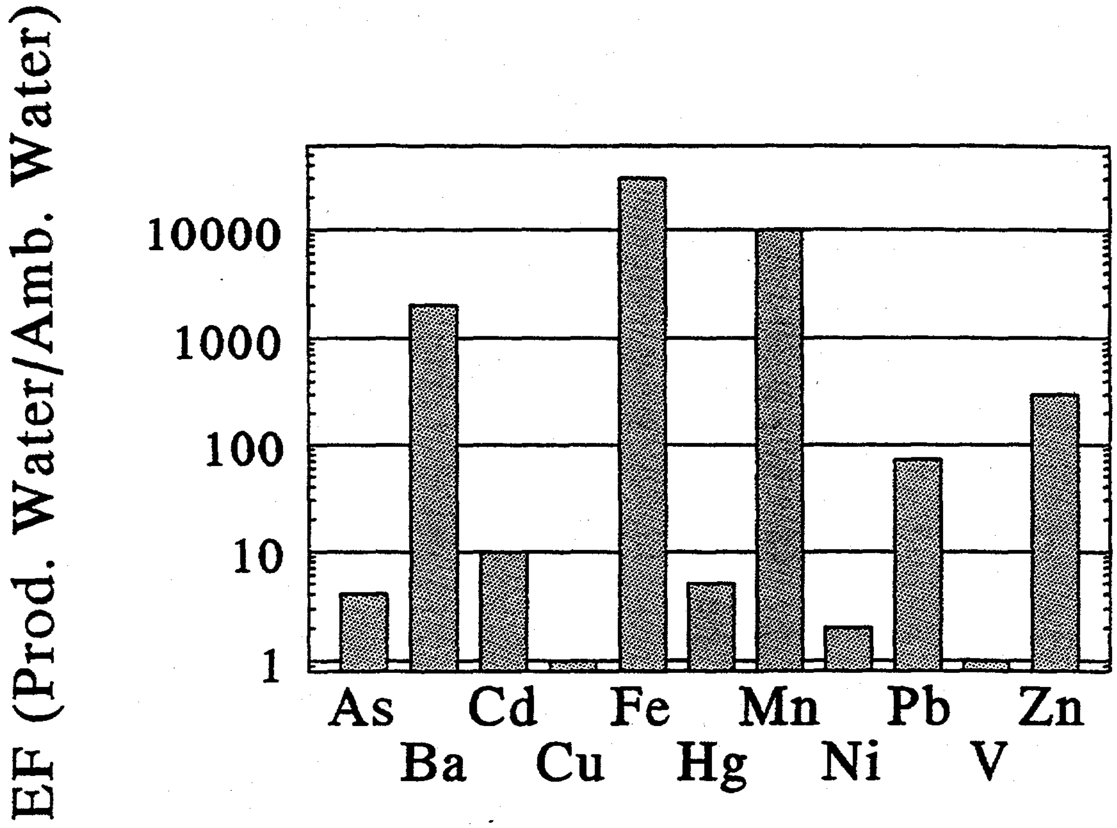

Figure 7.1. Graph showing the enrichment factor (EF) for selected metals in produced water relative to ambient water.

The NaCl-rich produced water discharged at Delacroix Island (salinity = 135 °/₀₀; chlorinity = 86 °/₀₀) had about 40 times greater salinity levels than ambient interstitial water, based on data from the reference stations (**Table 7.4**). During the Pre-termination Survey (April 1993), interstitial water in the top 5 cm at the Delacroix Island discharge station had chlorinity levels of 43 °/₀₀ (g/kg), about half the value of the produced water, but about 20 times higher than typical interstitial water in the Delacroix Island area as shown for the reference stations (**Figure 7.2**). However, after 12 months of no discharges, the Second Post-termination Survey (April 1994) data for interstitial water chlorinity at the Delacroix Island discharge station showed background chlorinity levels of 1 to 2 g/kg (**Figure 7.2**). This shift in chlorinity of the interstitial water can be traced over time by calculating Cl^- diffusion from the interstitial water to the overlying water. Initially, a first-order approximation of the diffusion time (t) for interstitial water chloride was made using the expression $t = l^2/D$, where l is the diffusion length in cm and D is the diffusion coefficient for the Cl^- ion (D_s = 1.06 cm^2/day for Cl^- at 25 °C; Li and Gregory, 1974). The calculation shows that a Cl^- ion can diffuse over a 5 cm interval in about two weeks. However, somewhat more rigorous calculations are required to estimate the time required for the enhanced chloride in the interstitial water to diffuse out of the sediment column and return the chlorinity of the interstitial water to estuarine levels.

We used a relatively simple model to determine the time required for chlorinity values to return to ambient levels by diffusion following inputs of produced water. First, the integrated amount of excess interstitial chloride in the sediment column to depths of 5, 10, and 20 cm was calculated. Then the flux of chloride from the interstitial water to the overlying water was calculated using Equation 1 shown below:

$$F=-D_s\frac{dCl^-}{dx} \tag{1}$$

where D_s = $\phi D_m/\Theta^2$, the molecular diffusion coefficient corrected for porosity and tortuosity (cm^2 sec^{-1});

ϕ = porosity (interstitial water volume fraction; dimensionless);

D_m = molecular diffusion coefficient (cm^2 sec^{-1}) (from Li and Gregory, 1974);

Θ = tortuosity (the extended path length for molecular diffusion in sediments; dimensionless);

$\frac{dCl^-}{dx}$ = concentration gradient with depth in the interstitial water (mg cm^{-4});

Cl- = concentration of interstitial chloride (mg cm^{-3}); and

x = thickness of sediment from surface to concentration maximum at depth.

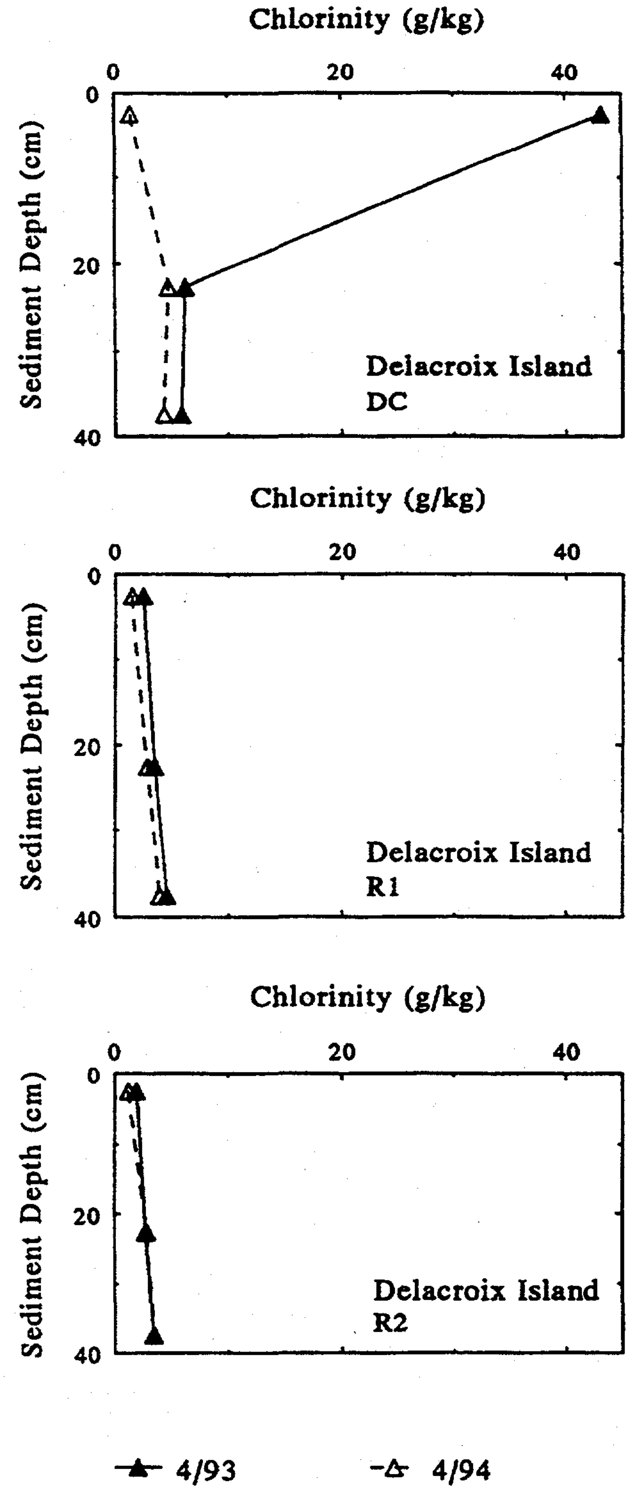

Figure 7.2. Vertical profiles showing values for chlorinity of interstitial water from the area surrounding Delacroix Island (DC = discharge station; R1 = reference station 1; R2 = reference station 2).

Values for D_m are corrected for temperature (T) and viscosity (η) according to Equation 2 shown below:

$$\left(\frac{D_m\eta}{T}\right)_{T_1} = \left(\frac{D_m\eta}{T}\right)_{T_2} \qquad \textbf{(2)}$$

where η = the viscosity of seawater (centipoise) at a given temperature, T(K), and salinity (S).

We are somewhat limited by available data, especially with respect to a detailed chlorinity profile from the bottom water down through the sediment column. If higher chlorinity water persists in the near-bottom water due to restricted mixing, the flux of chloride from the interstitial water to the overlying water will be lower. Thus, different values for (dCl^-/dx) have been used in separate runs of this simplified model. In all cases, the calculated flux over a 1 to 2 day period is subtracted from the integrated amount of chloride in the 5, 10, or 20-cm long column of sediment. Then, a new interstitial water chloride concentration is calculated and the flux calculation repeated at 1 to 2 day intervals, depending on the rate of change of (dCl^-/dx). The iteration was continued until interstitial water chlorinity approached ambient levels, depending on the chlorinity value chosen for near-bottom salinity (**Table 7.5**). The flux rate decreases as values for chlorinity decrease.

Results of two separate model runs are shown in **Figure 7.3** with salinity scales. The classic salinity/chlorinity ratio of 1.806 is lower in the produced water (1.570) due to the increased proportion of NaCl in produced water relative to normal seawater. Within the limits of the data and as a function of boundary conditions, about 1 to 6 months is required for diffusion to lower interstitial water salinities to about 10 °/.. Thus, salinities in the surficial interstitial water should have been reduced to levels that were tolerable to brackish water infauna 6 months after the April 1993 termination period. We did not sample interstitial water again until April 1994, 12 months after discharges were terminated. Extended runs of the simple model suggest a range of 2 to 12 months for salinities to return to background levels of about 5 °/... Observed shifts in interstitial water chloride and calculated times for reestablishing the ambient interstitial water chloride profile are consistent with observations for biological recolonization of sediments from the discharge station.

The sulfate values for the interstitial water samples (0 to 5 cm) ranged from 0.1 to 0.3 °/... Generally higher values were recorded at the reference stations than the discharge station.

Concentrations of metals in interstitial water in the area of Delacroix Island are the complex result of biogeochemical reactions in the sediments and inputs from produced water at the discharge site during April 1993. Overall, concentrations of metals in the interstitial water are comparable with or higher than those for the overlying water (**Table 7.4**). At the Delacroix Island discharge station (Delacroix Island-DC) during April 1993, concentrations of barium and iron are 2.3 and 1.6 times lower, respectively, in the interstitial water than values for the produced water. However, concentrations of barium and iron were 100 and 10 times greater, respectively, for interstitial water from the discharge station relative to the reference stations. These results are comparable with the two-fold dilution of produced water observed for chloride in the interstitial

Table 7.5. Sample calculation and partial output for determining changes in concentrations of chloride in interstitial water (IW) at the discharge station for Delacroix Island (Run 2, **Figure 7.3**). (Assumptions: start with uniform [Cl^-] in the IW to 10 cm, bottom water salinity = 4.5 g/kg, diffusion path = 5 cm, diffusion coefficient for Cl^- in sediment IW = 1.06 cm^2/day).

Time (days)	Initial $\sum Cl^-$ (mg)	$[Cl^-]_{IW}$ (mg/cm^3)	Flux (mg/cm^2)	New $\sum Cl^-$ (mg)	Initial Salinity (g/kg)
2	338.4	42.3	16.9	321.5	76.4
4	321.5	40.2	16.0	305.5	72.6
↓	↓	↓	↓	↓	↓
20	215.0	26.9	10.3	204.7	48.6
22	204.7	25.6	9.8	194.9	46.2
↓	↓	↓	↓	↓	↓
60	85.6	10.7	3.5	82.2	19.3
62	82.2	10.3	3.3	78.9	18.6
↓	↓	↓	↓	↓	↓
120	32.8	4.1	0.7	32.1	7.4
↓	↓	↓	↓	↓	↓
180	22.5	2.8	0.13	22.4	5.1

Where:

(1) Initial $\sum Cl^-$ = (10 cm) (1 cm^2) (0.8 fraction H_2O) (42.3 mg Cl/cm^3) = 338.4 mg Cl for first calculation.
(2) Flux (from Eq.1) = (1.06 cm^2/d) x [(42.3 - 2.5 mg Cl/cm^3)/(5-0cm)] x 2d = 16.9 mg/cm^2 (for 2 d).
(3) New $\sum Cl^-$ = (338.4 mg) - (16.9 mg) = 321.5 mg. This value becomes initial [Cl^-] for subsequent calculations.

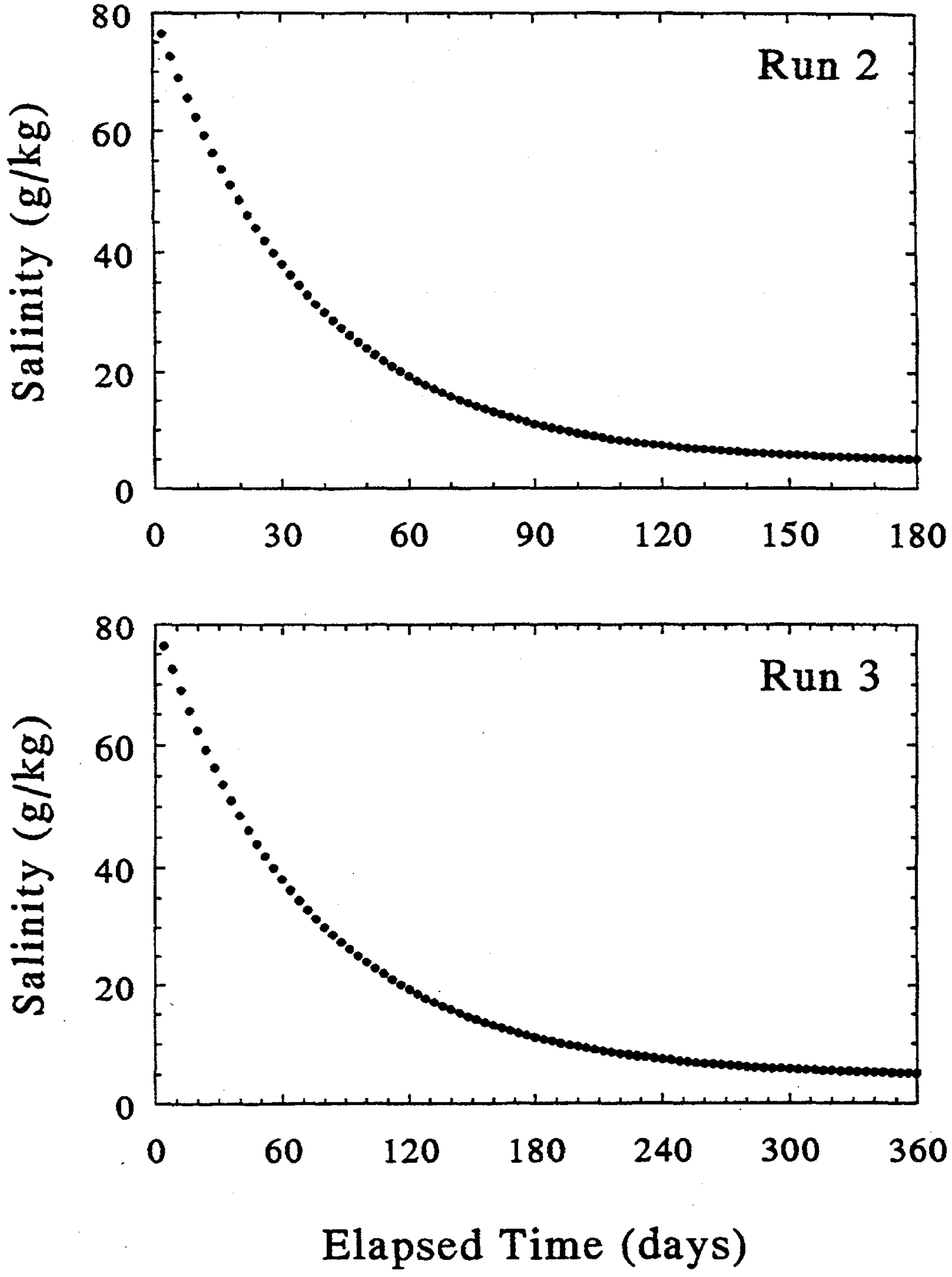

Figure 7.3. Results from model calculations showing interstitial water salinity (S) versus time after produced water discharges were terminated (April 1993). Run 2 used a uniform Cl^- level to 10 cm, bottom water S = 4.5 g/kg and a diffusion length (dx) of 5 cm. Run 3 used a uniform Cl^- level to 10 cm, bottom water S = 4.5 g/kg and a diffusion length (dx) of 10 cm.

water at Delacroix Island-DC (**Figure 7.4**), suggesting that the high metal levels have a produced water source and are behaving relatively conservatively. In contrast, manganese, a metal that is more soluble under reducing conditions is present at concentrations that are more than 30-fold enriched in interstitial water from the Delacroix Island discharge station than in the produced water and more than twice as enriched at the discharge station relative to the reference stations. This trend suggests that reducing conditions in sediments at the discharge station are more intense than at the reference stations, perhaps a function of the presence of the high TOC and anoxic produced water. Although concentrations of zinc are high for interstitial water from the Delacroix Island discharge station, they are similar to those for the reference stations (**Table 7.4**), suggesting that these are natural zinc levels for interstitial water at the station. Similarly, concentrations of arsenic, chromium, copper, manganese, molybdenum, nickel, and lead for interstitial water from the discharge station during the period of produced water discharges (April 1993) are comparable with those for the reference stations and higher than determined for the produced water (**Table 7.4**), showing that the produced water is not enhancing levels of these metals in the interstitial water. In fact, concentrations of copper, molybdenum, nickel, and vanadium were depleted in interstitial water from the discharge station, most likely due to the diluting effect of the produced water on the interstitial water.

When data for the April 1993 samples from the Delacroix Island discharge station are compared with data for the April 1994 samples, concentrations of each metal have returned to levels comparable with those from the reference stations. In the case of barium (**Figure 7.4**), the change is a sharp decrease, whereas for arsenic and zinc (**Figure 7.4**), concentrations are slightly increased. Thus, the entire system seems to have returned to background conditions during the one year between samplings. This trend is consistent with the calculations for chloride that show a return to ambient levels in the interstitial water over a period of 2 to 12 months, depending on boundary conditions chosen for the calculation.

7.3.3 Interstitial Water from Bay de Chene and Four Isle Dome

Interstitial water from Bay de Chene and Four Isle Dome was collected only during periods of produced water discharges. No differences in interstitial water profiles for chlorinity were observed for the discharge station versus the reference stations for Four Isle Dome (**Figure 7.5**), showing that the produced water was not infiltrating the sediments at this site. This observation suggests that discharge rates and mixing of produced water with ambient water at Four Isle Dome are sufficient enough to prevent accumulation of high salinity bottom water. Data for Bay de Chene are somewhat similar; however, the top 5-cm of interstitial water at the discharge site averages 1.7 times more chloride than in surficial interstitial water from the two reference stations (**Figure 7.5**). Furthermore, interstitial water from deeper depths (20 to 25 and 35 to 40 cm) at the discharge station (Bay de Chene-DC) is about three times higher than at the reference stations (**Figure 7.5**). This observation suggests that higher salinity, near-bottom water was present at the Bay de Chene discharge station at some time in the past and chloride may be diffusing from the interstitial water to the bottom water over time.

The sulfate levels for the interstitial water samples (0 to 5 cm) ranged from 0.3 to 0.5 °/.. at Bay de Chene. No analyses were made at Four Isle Dome. Higher values were recorded at the reference stations than the discharge station at Bay de Chene.

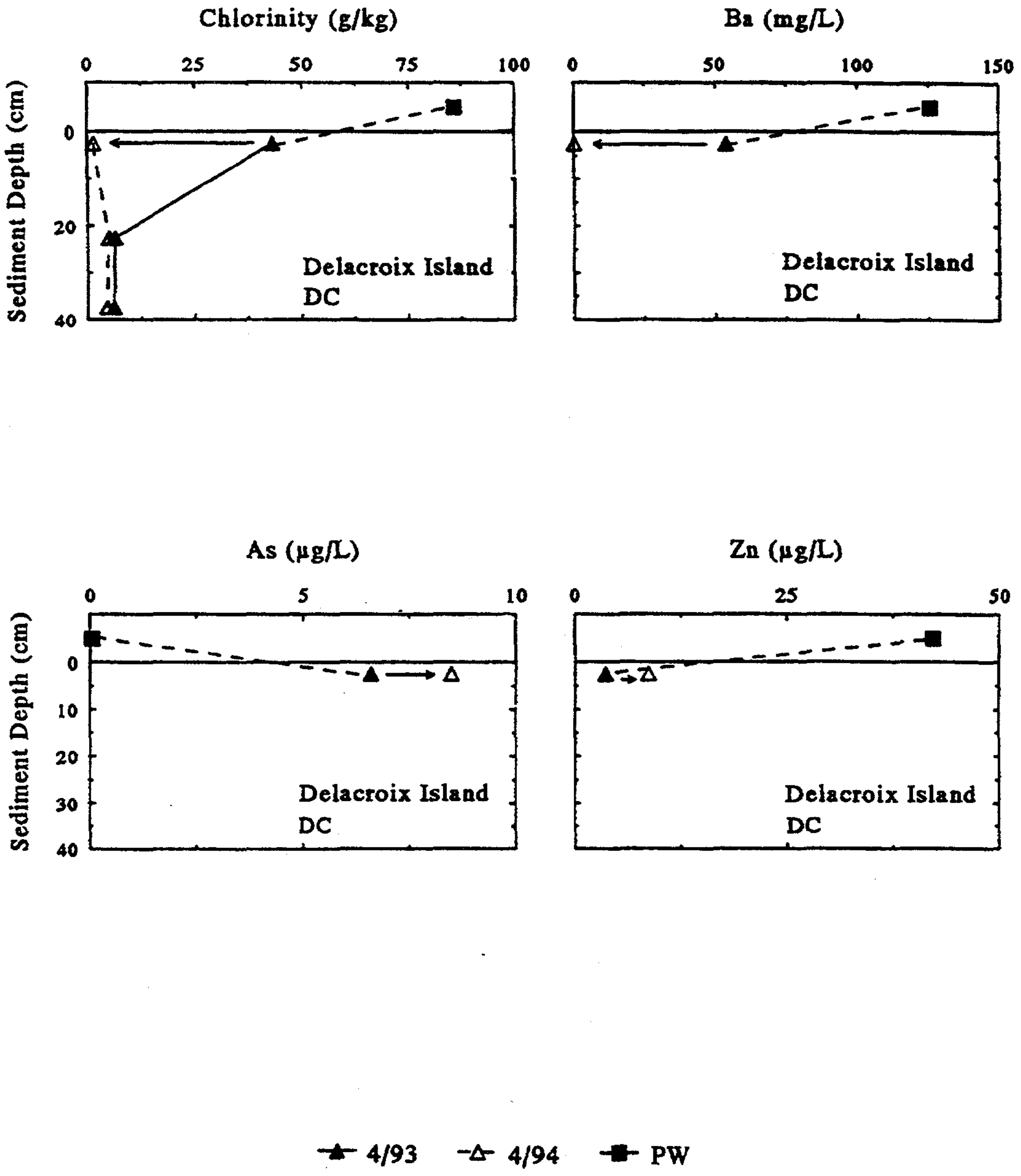

Figure 7.4. Vertical profiles showing values for chlorinity, Ba, As, and Zn in produced water and interstitial water from the discharge station (DC) at Delacroix Island for April 1993 (Pre-termination Survey) and April 1994 (Second Post-termination Survey).

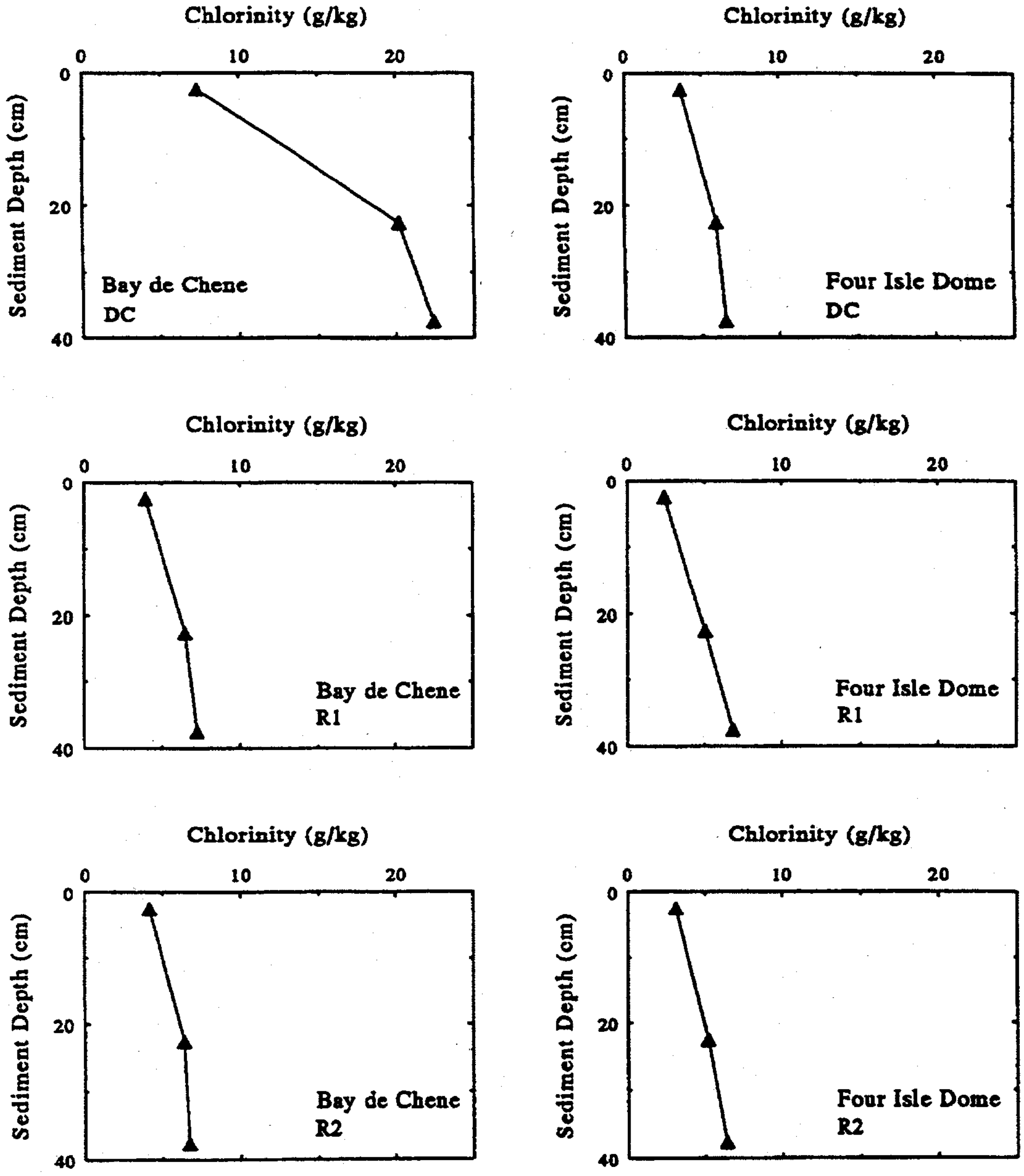

Figure 7.5. Vertical profiles showing values for chlorinity for interstitial water from the area surrounding Bay de Chene and Four Isle Dome during periods of produced water discharges (DC = discharge station; R1 = reference station 1; R2 = reference station 2).

With respect to metals in the interstitial water at the discharge station in Bay de Chene, concentrations of arsenic, barium, iron, and manganese are enriched relative to interstitial water from the reference stations (**Table 7.4**). Of these four metals, arsenic and manganese are in concentrations in the interstitial water that greatly exceed those in the produced water (**Table 7.4**) and are unlikely to have produced water as a source. Instead, the data for these metals, along with iron, suggest that more intense reducing conditions have been established at the discharge station, most likely due to a greater rate of deposition of organic matter at this location. Thus, only levels of chloride and barium in the top 5 cm of interstitial water at Bay de Chene show any likely, albeit minimal, impact from produced water.

In the top 5 cm of interstitial water at Four Isle Dome, only concentrations of iron and manganese are enriched relative to values determined for interstitial water from the reference stations. No significant differences in interstitial chloride or barium are observed at Four Isle Dome-DC and thus the enhanced iron and manganese levels are more likely due to more intense reducing conditions at the discharge station relative to the reference stations. At present, we have insufficient information to determine whether petroleum-related activities in the area of the discharge station or naturally higher accumulation rates of sediment and organic matter have led to more intense reducing conditions at Four Isle Dome-DC.

7.3.4 Metals in Sediments

7.3.4.1 Identifying Sediment Metal Contamination

Sediment samples were collected at each of the three discharge sites and at several distances away from the production facilities (**Figures 3.1** through **3.3**). To help confirm the presence of metal contamination in these sediments, concentrations of each metal were plotted versus aluminum (Trefry et al., 1985; Schropp et al., 1990). Fine-grained, clay-rich sediment naturally contains higher levels of aluminum and metals. As fine-grained sediment introduced from riverine sources is mixed with metal-poor carbonates and coarse-grained sediment, concentrations of aluminum and metals are diluted. Good linear fits for metal versus aluminum plots (r >0.8), along with a slope that is compatible with natural metal levels for the region, are generally observed for a suite of uncontaminated sediments with a mixture of grain sizes and mineralogy. Metal concentrations that show a positive deviation on the y-axis relative to aluminum and thus exceed the natural metal/aluminum relationship are identified as contaminated. On each metal versus aluminum graph for sediments from this study, we have drawn a dashed line to represent our estimate of the natural metal/aluminum relationship. This natural relationship was developed from our database for Mississippi River suspended sediment and data from Trefry et al. (1997).

7.3.4.2 Delacroix Island

Sediment samples were collected from the discharge station and 13 other stations in the Delacroix Island area on three occasions, once before termination of produced water discharges (April 1993) and at six months (October 1993) and 12 months (April 1994) following the termination of produced water discharges. Metal concentrations are summarized in **Table 7.6** with selected metal versus aluminum plots presented in **Figure 7.6**. The dashed lines on **Figure 7.6** show the metal/aluminum ratio for natural sediment from the northwestern Gulf of Mexico. Underlined numbers in **Table 7.6** identify metal values that exceed by more than 50%

Table 7.6. Metal concentrations in sediments from Delacroix Island. [DC = discharge station; R1 = reference station 1; R2 = reference station 2; other stations at 100, 300 and 500 m northeast (NE) or 100, 300, 500, and 1,000 m northwest (NW) or 100, 300, 500, and 1,000 south (S) of discharge station; final number in sample ID identifies sample period with 1 for April 1993 (Pre-termination Survey), 2 for October 1993 (First Post-termination Survey), and 3 for April 1994 (Second Post-termination Survey)]. Underlined numbers indicate values that exceed natural levels by >50%.

Sample ID	Al (%)	As (µg/g)	Ba (µg/g)	Ca (%)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	Fe (%)	Hg (µg/g)	Mn (µg/g)	Mo (µg/g)	Ni (µg/g)	Pb (µg/g)	V (µg/g)	Zn (µg/g)
DC-1	5.90	10.7	699	0.84	0.25	55.4	22.8	3.35	0.068	1100	1.4	34.1	24.4	98.7	99.0
DC-2	4.93	4.2	1310	1.04	0.27	44.8	13.0	1.95	0.038	433	0.6	22.3	16.4	58.8	56.2
DC-3	5.09	3.6	1190	1.29	0.30	46.0	14.1	2.22	0.041	583	1.0	21.6	16.6	62.0	69.2
100NE-1	5.70	4.6	278	0.91	0.23	50.3	17.2	2.44	0.043	380	1.1	21.7	14.2	75.2	77.2
100NE-2	5.29	4.8	949	0.93	0.39	51.0	17.3	2.48	0.046	536	0.8	26.3	17.0	102.0	69.6
100NE-3	5.56	3.7	1720	1.14	0.32	52.3	17.5	2.53	0.054	545	1.0	24.7	19.2	74.3	72.1
300NE-1	5.52	3.9	615	0.93	0.17	44.7	16.3	2.30	0.038	470	1.0	21.6	18.3	68.5	70.8
300NE-2	5.54	5.1	1140	0.86	0.41	53.2	18.9	2.72	0.050	841	0.9	27.8	19.5	115.0	75.1
300NE-3	5.75	3.7	473	1.00	0.29	50.6	16.2	2.40	0.038	525	1.0	23.3	15.8	70.1	68.8
500NE-1	5.47	4.7	1050	0.96	0.10	47.0	14.7	2.32	0.037	549	0.8	22.6	20.8	75.1	73.8
500NE-2	5.25	5.2	1050	0.95	0.35	46.4	13.6	2.21	0.036	469	0.7	24.1	17.3	107.0	62.7
500NE-3	5.82	3.3	1210	1.15	0.29	49.3	15.0	2.37	0.039	520	0.9	23.4	18.3	80.4	72.4
R1-1	5.56	4.7	1020	1.03	0.19	50.6	16.3	2.52	0.045	598	1.1	25.1	23.3	77.8	77.4
R1-2	5.71	5.2	924	0.75	0.32	55.9	17.3	2.58	0.049	538	0.8	28.5	21.2	87.4	76.6
R1-3	5.43	3.4	812	1.01	0.26	46.0	13.1	2.09	0.035	475	1.0	21.4	17.0	67.9	64.1
DC-1	5.90	10.7	699	0.84	0.25	55.4	22.8	3.35	0.068	1100	1.4	34.1	24.4	98.7	99.0
DC-2	4.93	4.2	1310	1.04	0.27	44.8	13.0	1.95	0.038	433	0.6	22.3	16.4	58.8	56.2
DC-3	5.09	3.6	1190	1.29	0.30	46.0	14.1	2.22	0.041	583	1.0	21.6	16.6	62.0	69.2
100NW-1	5.33	6.2	1300	1.08	0.47	44.7	13.5	2.15	0.044	749	0.7	23.7	17.8	61.3	61.8
100NW-2	5.48	5.5	1240	0.95	0.32	50.2	16.5	2.45	0.044	606	0.8	27.7	18.8	76.7	69.7
100NW-3	6.39	4.7	1410	0.87	0.39	58.7	21.4	3.08	0.052	1110	1.2	33.4	23.2	95.2	92.4
300NW-1	5.55	6.2	1120	2.00	0.29	50.2	15.2	2.15	0.032	424	0.9	25.2	16.7	74.0	64.2
300NW-2	5.73	5.4	1210	0.89	0.32	51.1	16.8	2.45	0.043	652	0.8	29.0	20.0	82.9	69.5

Table 7.6. (Continued).

Sample ID	Al (%)	As (µg/g)	Ba (µg/g)	Ca (%)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	Fe (%)	Hg (µg/g)	Mn (µg/g)	Mo (µg/g)	Ni (µg/g)	Pb (µg/g)	V (µg/g)	Zn (µg/g)
300NW-3	6.02	4.4	1510	1.00	0.36	53.5	18.9	2.75	0.051	1020	1.0	30.4	21.2	81.9	81.3
500NW-1	5.00	3.7	921	1.05	0.11	39.0	10.9	1.79	0.034	323	0.8	21.2	14.0	54.3	56.7
500NW-2	5.160	4.6	1980	1.03	0.25	47.0	12.4	1.99	0.035	420	0.8	23.6	17.1	68.2	56.2
500NW-3	5.22	3.0	1660	1.00	0.25	42.5	11.5	1.89	0.030	388	0.8	21.0	14.7	57.1	56.5
1000NW-1	3.31	4.8	1070	4.61	0.11	29.4	10.7	1.70	0.029	366	1.6	15.1	8.0	44.3	40.6
1000NW-2	4.04	4.5	967	3.37	0.26	36.0	10.5	1.60	0.028	517	0.8	17.4	11.0	72.8	46.3
1000NW-3	4.95	2.2	3410	1.04	0.19	36.5	9.2	1.68	0.026	359	0.6	18.4	14.7	47.2	53.6
R2-1	4.84	3.9	1360	1.04	0.11	40.7	11.1	1.88	0.031	452	0.9	20.0	18.7	55.9	57.2
R2-2	3.80	4.7	187	0.65	0.24	36.8	13.5	2.37	0.037	447	3.4	22.4	9.8	67.1	42.4
R2-3	4.86	2.8	1290	1.66	0.21	41.7	10.2	1.73	0.026	415	1.2	18.5	15.1	54.6	52.1
DC-1	5.90	10.7	699	0.84	0.25	55.4	22.8	3.35	0.068	1100	1.4	34.1	24.4	98.7	99.0
DC-2	4.93	4.2	1310	1.04	0.27	44.8	13.0	1.95	0.038	433	0.6	22.3	16.4	58.8	56.2
DC-3	5.09	3.6	1190	1.29	0.30	46.0	14.1	2.22	0.041	583	1.0	21.6	16.6	62.0	69.2
100S-1	4.46	3.7	1170	1.18	0.07	35.6	8.7	1.46	0.024	378	0.6	15.6	14.8	35.6	47.5
100S-2	4.71	4.5	1620	1.03	0.17	44.1	8.3	1.51	0.024	265	0.8	18.7	13.7	47.6	45.0
100S-3	4.20	2.7	1180	2.69	0.16	35.0	8.9	1.43	0.026	336	0.8	14.5	11.9	40.7	41.7
300S-1	4.73	3.5	933	1.13	0.07	36.5	9.2	1.54	0.029	274	0.7	15.3	13.8	42.4	52.4
300S-2	4.74	3.9	1310	1.05	0.19	40.9	11.9	1.54	0.039	280	0.5	18.0	13.9	50.8	45.5
300S-3	4.54	2.4	1260	1.05	0.17	37.9	8.9	1.41	0.022	274	0.7	15.4	13.0	43.6	42.5
500S-1	4.84	4.0	1220	1.04	0.07	36.0	9.8	1.70	0.031	340	0.7	17.6	16.1	55.9	51.8
500S-2	5.08	4.4	1310	0.90	0.24	43.8	11.0	1.81	0.035	303	0.8	20.8	16.3	59.7	53.0
500S-3	4.96	2.6	1400	1.05	0.20	39.7	9.8	1.69	0.034	292	0.7	19.4	14.1	53.6	49.8
1000S-1	4.79	3.2	283	3.96	0.17	41.2	11.0	1.80	0.028	430	0.8	17.7	12.7	56.6	57.9
1000S-2	5.40	5.3	243	0.72	0.37	53.6	18.4	2.65	0.049	883	0.8	30.7	14.0	83.3	75.2
1000S-3	5.40	3.5	1650	0.90	0.24	47.8	13.7	2.18	0.036	478	0.8	23.9	16.8	61.4	64.3

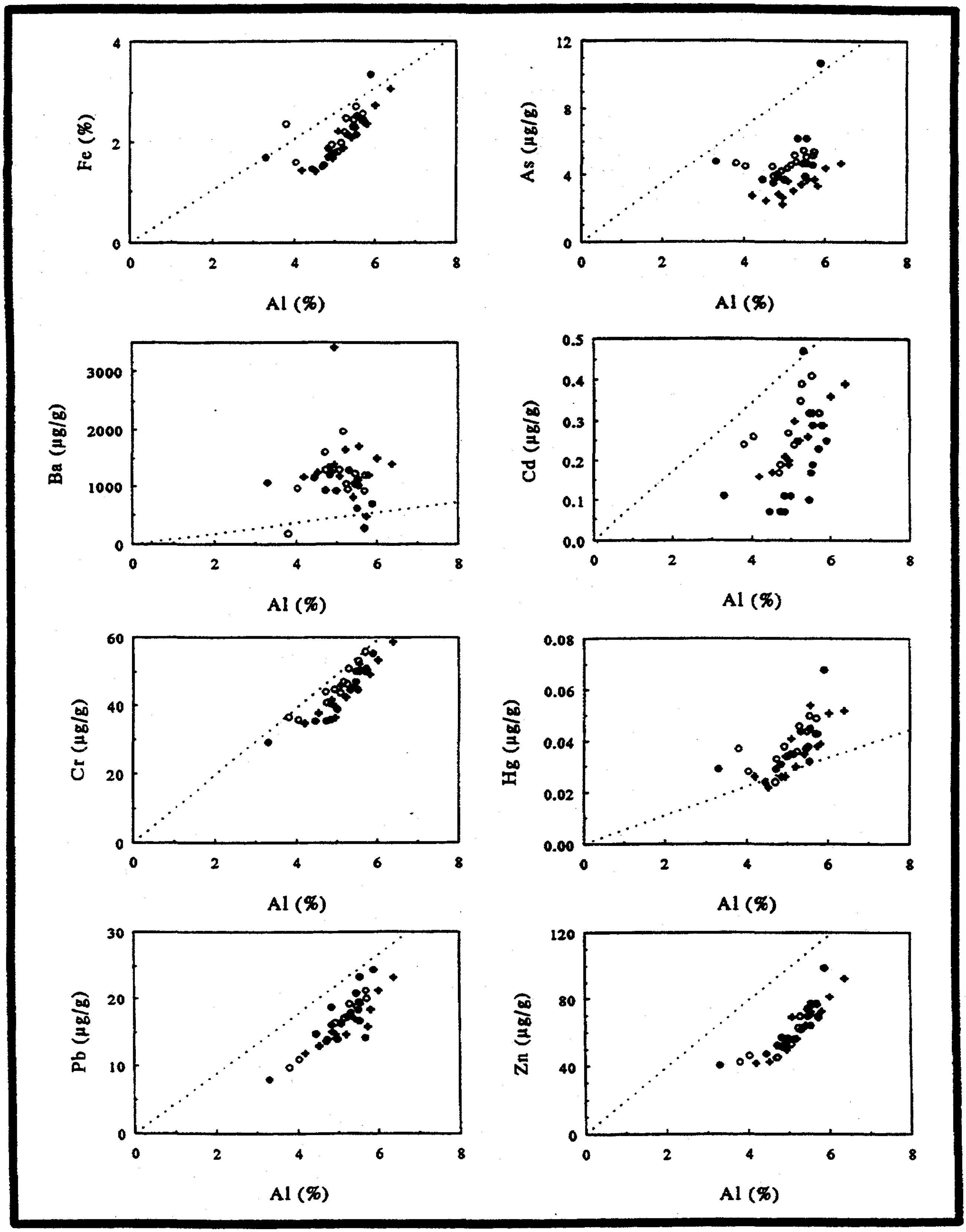

Figure 7.6. Scatter plots showing concentrations of Fe, As, Ba, Cd, Cr, Hg, Pb, and Zn versus Al in all surficial (0-5 cm) sediments from the Delacroix Island area. Dashed line on each graph identifies natural metal/Al relationship for the northwestern Gulf of Mexico.

expected natural levels for the northwestern Gulf of Mexico or natural sediments from the Delacroix Island area.

Most of the points on the graphs for iron, arsenic, barium, cadmium, chromium, mercury, lead, and zinc (**Figure 7.6**) and copper, manganese, molybdenum, and vanadium fall on or below the dashed line, suggesting that these samples are typical of uncontaminated sediment. Good linear relationships (r >0.8) were calculated for chromium, lead, and zinc versus aluminum (**Figure 7.6**) and similar, good correlations were found for nickel and vanadium versus aluminum. For elements such as arsenic and cadmium (**Figure 7.6**) and manganese, the points are more scattered and often significantly below the dashed line. This deviation may mean that the sediment from the Delacroix Island area has a somewhat different composition from typical sediment from the northwestern Gulf of Mexico or that diagenetic processes in the sediment column have led to the release of metal from the sediment to the overlying water. Such diagenetic activity is supported by the high levels of these metals observed in the interstitial water as previously discussed. In any case, there is no clear evidence for significant contamination of the sediments with arsenic, cadmium, chromium, copper, manganese, molybdenum, nickel, lead, vanadium, or zinc in the area of Delacroix Island.

In contrast with the other metals, a sizeable number of high barium/aluminum values were observed for sediments from Delacroix Island (**Figure 7.6**). These deviations indicate anthropogenic inputs of barium with values that are 2 to 4 times greater than natural levels. The influence of drilling and production on metals in sediments has been most noteworthy for barium (Trocine and Trefry, 1983; Boothe and Presley, 1987). Sources of barium include drilling fluids wherein $BaSO_4$ is used as a weighting agent for pressure control and from produced waters that have high barium concentrations naturally, due to its enhanced solubility at elevated chloride and low sulfate levels.

In addition to looking at sediment barium values relative to natural levels, temporal and spatial variations in barium concentrations can also be evaluated. Because sediment concentrations of aluminum and iron are relatively uniform throughout the Delacroix Island area (**Table 7.6**), barium levels can be compared relatively well using unnormalized data. As such, no simple temporal or spatial trends were observed. For example, the highest barium value in the Delacroix Island area of 3,410 µg barium/g was found 1,000 m northwest of the discharge station during the Second Post-termination Survey (April 1994, **Figure 7.7**). Furthermore, the grand average barium value (± 1 standard deviation) for the April 1994 period of 1,470 ± 780 µg/g (5.2 ± 0.7% aluminum) was higher than the mean of 940 ± 330 µg/g (5.5 ± 0.5% aluminum) observed for April 1993 (**Table 7.6**). Thus, **Figure 7.7** shows that barium values in surficial sediments were typically higher during the Second Post-termination Survey, April 1994, sample period and along the northwest transect relative to the northeast transect. Most likely, the ubiquitous and somewhat patchy distribution of barium in sediment from the Delacroix Island area reflects long-term input and dispersion of drilling fluid and produced water in the Delacroix Island area.

Besides barium, one arsenic value and several mercury values are enhanced relative to expected natural levels. The anomalous arsenic value was observed at the discharge station only during the Pre-termination Survey. Sediment mercury/aluminum ratios suggest that mercury levels were as much as 50% enhanced relative to natural levels at the discharge station during the Pre-termination Survey and during the First or Second Post-termination Surveys at distances

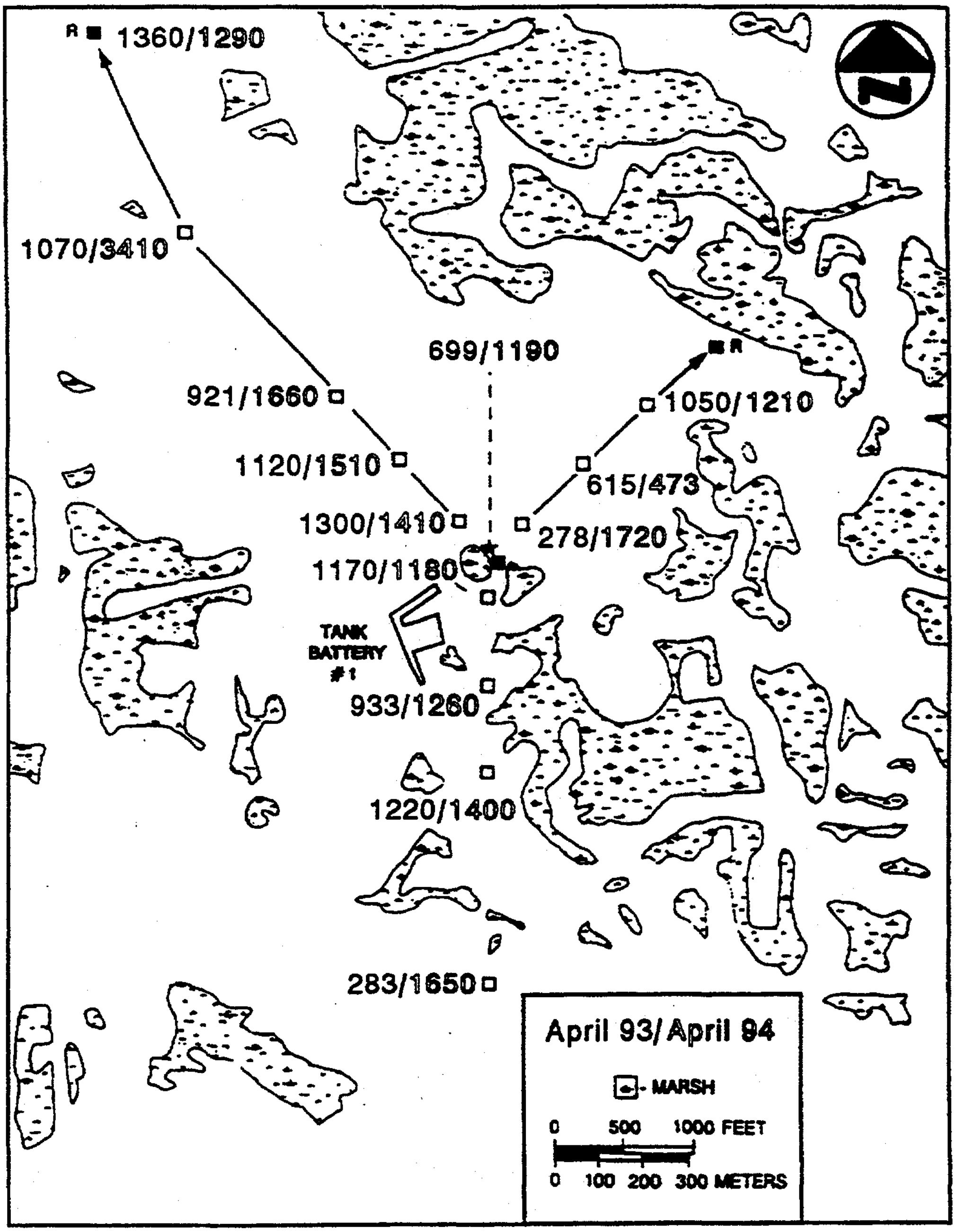

Figure 7.7. Map showing concentrations of Ba in surficial (0-5 cm) sediments from stations in the Delacroix Island area. Solid numbers are for samples collected during April 1993 (Pre-termination Survey) and open numbers are for samples collected during April 1994 (Second Post-termination Survey).

of 100 and 300 m away from the discharge station (**Table 7.6** and **Figure 7.6**). Concentrations of mercury are not greatly elevated in produced water samples that were collected (**Table 7.4**) and thus the identified mercury enhancement may be related to other facility activities or a different source.

7.3.4.3 Bay de Chene

Sediment samples were collected from the discharge station and 16 other stations in the Bay de Chene area on three occasions, once before termination of produced water discharges (Pre-termination Survey - May 1993) and at seven months (First Post-termination Survey - May 1994) and 12 months (Second Post-termination Survey - October 1994) following the end of discharges. Produced water discharges were terminated during October 1993. Overall, the trends observed for the Bay de Chene area were similar to those found for Delacroix Island, except that the variation in aluminum levels (6.0 ± 0.4%) was smaller and a greater number of samples from Bay de Chene were enriched above estimated natural levels for arsenic, barium, cadmium, mercury, lead, and zinc (**Figure 7.8**). Thus, when the complete Bay de Chene data set (**Table 7.7**) was used, none of the linear regression lines for metals versus aluminum had correlation coefficients >0.8. As previously presented for Delacroix Island, the dashed lines for Bay de Chene on **Figure 7.8** show the metal/aluminum ratio for natural sediment from the northwestern Gulf of Mexico. Most of the points on graphs for iron, arsenic, barium, cadmium, chromium, mercury, lead, and zinc (**Figure 7.8**) and copper, manganese, molybdenum, and vanadium fall below or within 10% to 20% of the values predicted by the dashed line, suggesting that these samples are comparable with uncontaminated sediment from the northwestern Gulf of Mexico. For elements such as arsenic and cadmium (**Figure 7.8**) and manganese and nickel, the points are more scattered and often significantly below the dashed line. This deviation also may be related to local sediment sources or diagenetic processes in the sediment column. Once again, with one or two minor exceptions, no clear evidence exists to support significant contamination of sediments in the area of Bay de Chene with arsenic, cadmium, chromium, copper, manganese, molybdenum, nickel, lead, vanadium, or zinc.

The primary exception among this group of stations was elevated concentrations of cadmium, chromium, mercury, lead, and zinc at the site 100 m northeast of the discharge station (**Table 7.7** and **Figure 7.8**). Concentrations of mercury were most enriched at this 100 m northeast station with values about 10 times above natural levels. This station at 100 m northeast of the discharge facility was once a fuel dock and pipe storage facility. Such activities have left a strong contaminant signal at the station.

Concentrations of barium are elevated above natural levels throughout the Bay de Chene area (**Table 7.7** and **Figure 7.8**). The pervasive spatial distribution of barium in sediments throughout the Bay de Chene area is shown in **Figure 7.9** and with the underlined numbers in **Table 7.7**. No simple spatial patterns are visible and once again a ubiquitous, patchwork occurrence of barium is discernible. No clear temporal pattern in sediment barium distribution is observed as demonstrated by no significant difference in the grand mean values for barium (± 1 standard deviation) for the three sampling periods: May 1993 (1,110 ± 220 µg barium/g), May 1994 (1,480 ± 530 µg barium/g), and October 1994 (1,140 ± 500 µg barium/g). Thus, Bay de Chene, like Delacroix Island, shows widespread barium contamination in the sediments.

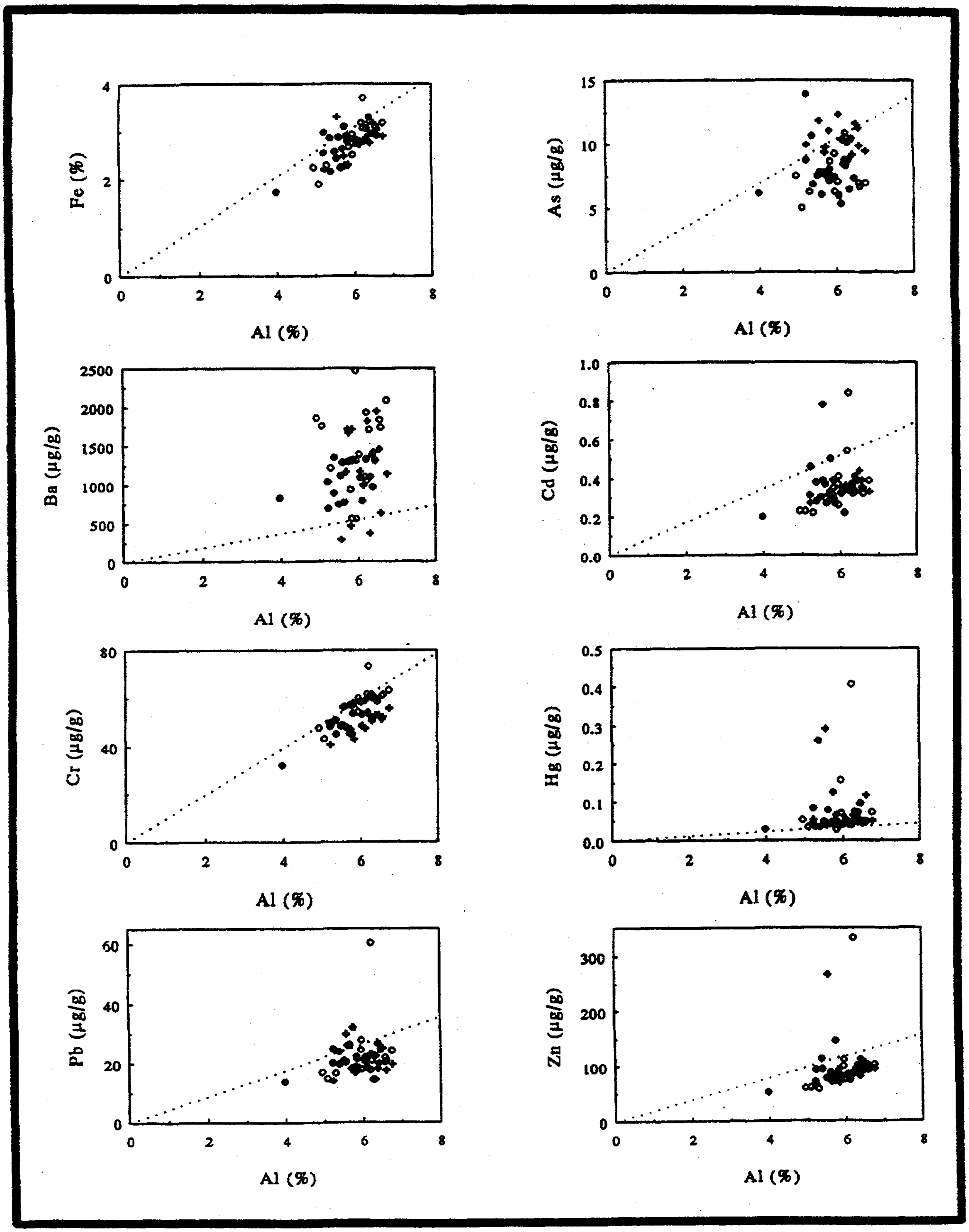

Figure 7.8. Scatter plots showing concentrations of Fe, As, Ba, Cd, Cr, Hg, Pb, and Zn versus Al in all surficial (0-5 cm) sediments from the Bay de Chene area. Dashed line on each graph identifies natural metal/Al relationship for the northwestern Gulf of Mexico.

Table 7.7. Metal concentrations in sediments from Bay de Chene. [DC = discharge station; R1 = reference station 1; R2 = reference station 2; other stations at 100, 300, 500, and 1,000 m northeast (NE), 500 and 1,000 m southeast (SE), or 100, 300, and 500 m northwest (NW) of discharge station; final number in sample ID identifies sample period with 1 for May 1993 (Pre-termination Survey), 2 for May 1994 (First Post-termination Survey) and 3 for October 1994 (Second Post-termination Survey)]. Underlined numbers show values that exceed natural levels.

Sample ID	Al (%)	As (µg/g)	Ba (µg/g)	Ca (%)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	Fe (%)	Hg (µg/g)	Mn (µg/g)	Mo (µg/g)	Ni (µg/g)	Pb (µg/g)	V (µg/g)	Zn (µg/g)
DC-1	5.37	10.6	892	0.86	0.38	50.9	21.8	2.8	0.261	496	1.2	23.3	24.0	85.8	113
DC-2	5.95	9.2	558	0.76	0.41	60.2	24.4	2.9	0.070	441	1.9	28.1	27.8	97.9	111
DC-3	6.60	9.8	632	0.66	0.35	52.3	23.4	3.0	0.117	363	1.4	25.8	17.6	110.8	100
100NE-1	5.74	7.5	1300	0.99	0.50	57.3	28.5	3.1	0.124	520	1.4	28.8	32.0	88.5	146
100NE-2	6.23	10.8	1930	0.95	0.84	73.3	46.1	3.7	0.407	522	2.4	32.4	60.3	100.2	332
100NE-3	5.56	11.8	287	1.63	0.78	56.2	34.5	3.3	0.292	384	1.8	25.0	29.8	92.3	266
300NE-1	5.60	6.0	1290	1.93	0.37	56.5	21.2	2.8	0.078	403	3.3	25.1	26.0	88.1	88.0
300NE-2	5.94	7.4	2470	0.89	0.37	58.7	19.5	2.7	0.156	381	1.7	23.0	24.5	85.9	99.0
300NE-3	6.26	10.1	1820	1.24	0.35	52.9	18.3	2.8	0.064	377	1.4	22.3	14.5	100.2	94.3
500NE-1	6.33	6.4	1110	0.68	0.32	60.2	21.5	3.0	0.069	441	1.1	28.3	22.5	97.4	95.3
500NE-2	6.57	6.9	1840	0.90	0.35	61.2	21.1	3.0	0.05	396	1.3	26.5	21.9	98.6	97
500NE-3	5.73	9.7	1710	1.51	0.33	45.4	15.2	2.4	0.043	321	0.8	19.5	17.8	85.6	82
1000NE-1	6.11	5.3	901	1.88	0.22	58.8	19.5	2.8	0.044	303	1.3	28.0	18.4	91.8	74.4
1000NE-2	5.95	6.2	1320	2.65	0.26	54.4	16.6	2.5	0.039	321	1.5	22.2	17.9	83.4	74.8
1000NE-3	6.76	9.4	1150	1.21	0.33	55.8	19.2	2.9	0.051	355	1.1	22.0	19.7	112.0	95
R1-1	5.21	8.7	1040	7.55	0.31	49.7	17.0	2.5	0.047	346	2.0	20.6	20.1	84.0	71.6
R1-2	6.19	8.4	1110	1.45	0.54	61.8	20.3	3.1	0.039	339	2.6	27.1	17.8	100.3	85.6
R1-3	6.38	10.3	1380	3.23	0.33	52.2	19.5	2.9	0.047	338	1.9	23.5	18.1	108.7	81.6

Table 7.7. (Continued).

Sample ID	Al (%)	As (µg/g)	Ba (µg/g)	Ca (%)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	Fe (%)	Hg (µg/g)	Mn (µg/g)	Mo (µg/g)	Ni (µg/g)	Pb (µg/g)	V (µg/g)	Zn (µg/g)
DC-1	5.37	10.6	892	0.86	0.38	50.9	21.8	2.8	0.261	496	1.2	23.3	24.0	85.8	113
DC-2	5.95	9.2	558	0.76	0.41	60.2	24.4	2.9	0.070	441	1.9	28.1	27.8	97.9	111
DC-3	6.60	9.8	632	0.66	0.35	52.3	23.4	3.0	0.117	363	1.4	25.8	17.6	110.8	100
500SE-1	3.97	6.1	832	12.3	0.20	32.2	10.8	1.7	0.029	387	0.9	14.0	14.0	53.40	51.8
500SE-2	6.23	8.3	1060	0.68	0.35	60.5	21.6	3.0	0.045	348	1.2	26.2	20.9	93.70	86.7
500SE-3	5.22	9.9	1040	5.17	0.27	40.8	13.4	2.2	0.053	290	1.6	17.8	14.0	77.00	67.1
1000SE-1	5.55	7.8	1120	1.50	0.39	49.0	15.5	2.4	0.040	440	1.1	20.3	20.5	77.40	77.5
1000SE-2	4.94	7.5	1860	1.09	0.23	48.0	14.6	2.2	0.053	285	2.2	18.5	16.9	69.60	60.0
1000SE-3	6.06	12.3	1180	0.71	0.35	48.7	22.4	2.8	0.057	373	1.0	22.5	20.2	88.80	83.3
DC-1	5.37	10.6	892	0.86	0.38	50.9	21.8	2.8	0.261	496	1.2	23.3	24.0	85.8	113
DC-2	5.95	9.2	558	0.76	0.41	60.2	24.4	2.9	0.070	441	1.9	28.1	27.8	97.9	111
DC-3	6.60	9.8	632	0.66	0.35	52.3	23.4	3.0	0.117	363	1.4	25.8	17.6	110.8	100
100NW-1	6.39	10.4	977	0.71	0.50	57.3	27.8	3.1	0.124	520	1.4	28.8	32.0	88.5	146.00
100NW-2	6.75	6.9	2090	0.65	0.39	63.3	23.7	3.1	0.073	388	1.2	27.5	24.3	98.7	102.00
100NW-3	6.50	11.6	1950	0.60	0.44	53.1	23.6	3.1	0.043	364	1.0	26.5	25.2	120.00	106.00
300NW-1	5.22	13.9	691	0.66	0.46	48.5	23.5	2.9	0.083	505	1.3	25.7	24.9	86.5	93.00
300NW-2	5.83	8.6	562	0.83	0.35	58.0	20.4	2.8	0.027	356	1.3	24.6	21.4	91.8	84.90
300NW-3	6.31	10.1	370	0.70	0.36	50.7	20.8	2.8	0.050	389	0.1	23.44	14.5	104.00	89.90
500NW-1	6.21	8.7	1330	0.99	0.34	54.1	18.6	2.7	0.052	357	1.4	23.9	23.1	86.4	88.40
500NW-2	5.86	7.7	1317	0.75	0.27	55.6	17.6	2.6	0.042	302	1.3	22.6	18.6	83.2	73.00
500NW-3	5.84	7.6	1710	0.83	0.29	43.1	15.0	2.3	0.043	297	1.6	16.8	17.6	84.8	69.50

Table 7.7. (Continued).

Sample ID	Al (%)	As (µg/g)	Ba (µg/g)	Ca (%)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	Fe (%)	Hg (µg/g)	Mn (µg/g)	Mo (µg/g)	Ni (µg/g)	Pb (µg/g)	V (µg/g)	Zn (µg/g)
1000NW-	5.64	7.7	771	1.22	0.27	48.0	15.3	2.2	0.046	312	1.4	18.6	26.3	77.9	70.80
1000NW-	5.08	5.0	1760	1.12	0.23	43.4	11.3	1.9	0.033	283	0.9	15.3	14.8	59.7	60.63
1000NW-	5.76	7.9	1670	1.56	0.29	47.2	14.4	2.2	0.041	361	0.8	19.7	17.0	81.1	72.80
DC-1	5.37	10.6	892	0.86	0.38	50.9	21.8	2.8	0.261	496	1.2	23.3	24.0	85.8	113
DC-2	5.95	9.2	558	0.76	0.41	60.2	24.4	2.9	0.070	441	1.9	28.1	27.8	97.9	111
DC-3	6.60	9.8	632	0.66	0.35	52.3	23.4	3.0	0.117	363	1.4	25.8	17.6	110.8	100
100SW-1	6.45	7.3	1320	0.76	0.39	58.9	20.9	2.9	0.096	380	1.1	25.3	24.6	101.0	102
100SW-2	6.30	8.7	1710	0.64	0.37	61.8	22.9	3.1	0.074	349	1.1	27.1	22.3	99.0	99.5
100SW-3	5.81	11.0	461	1.03	0.39	45.4	20.6	2.8	0.064	369	1.0	23.2	17.0	96.8	92.3
300SW-1	5.82	8.0	1310	1.80	0.29	53.7	18.5	2.7	0.050	386	2.0	22.8	22.2	84.0	82.3
300SW-2	6.60	6.6	1740	1.25	0.32	61.6	20.5	2.9	0.049	341	1.2	25.4	20.8	97.9	93.4
300SW-3	6.57	11.2	1460	0.67	0.39	51.4	21.3	2.9	0.046	329	0.8	24.4	20.4	102.0	93.2
500SW-1	5.38	6.8	1350	1.24	0.28	45.3	13.2	2.1	0.034	291	1.6	19.9	19.6	68.6	93.7
500SW-2	6.03	7.0	139	0.75	0.32	58.4	20.0	2.8	0.044	333	1.1	25.2	20.9	91.2	83.4
500SW-3	6.41	9.1	1420	0.68	0.33	53.1	19.1	2.7	0.056	312	0.9	21.5	19.9	97.2	88.4
1000SW-	6.06	5.9	1100	1.08	0.33	53.3	17.2	2.7	0.045	344	1.7	22.9	22.1	93.2	84.3
1000SW-	5.29	6.2	1220	1.41	0.22	50.1	13.7	2.2	0.035	283	0.9	18.6	16.6	68.0	57.8
1000SW-	5.69	9.3	1170	0.78	0.31	47.1	19.4	2.6	0.046	316	1.3	21.8	18.2	93.4	77.7
R2-1	5.50	7.5	741	1.10	0.30	48.6	17.1	2.5	0.048	451	1.5	21.5	20.9	81.4	77.3
R2-2	5.80	7.1	939	0.96	0.31	57.0	18.1	2.9	0.041	521	1.4	23.2	18.7	84.1	73.8
R2-3	6.14	10.3	996	0.90	0.36	47.7	19.0	2.7	0.047	431	1.0	23.3	18.4	95.4	82.2

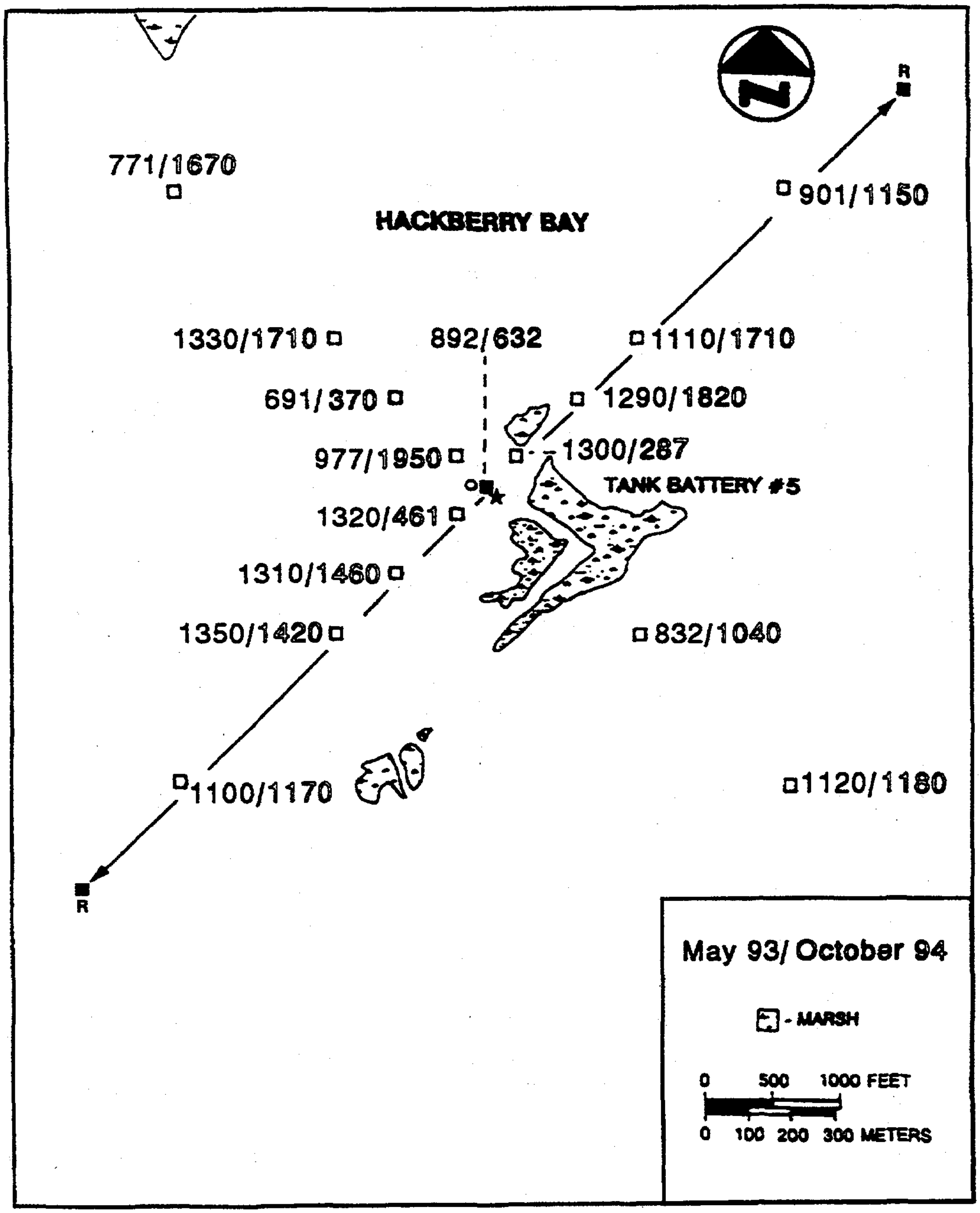

Figure 7.9. Map showing concentrations of Ba in surficial (0-5 cm) sediments from stations in the Bay de Chene area. Solid numbers are for samples collected during May 1993 (Pre-termination Survey) and open numbers are for samples collected during October 1994 (Second Post-termination Survey).

7.3.4.4 Four Isle Dome

Sediment samples were collected from 10 stations in the Four Isle Dome area only once, during the Pre-termination Survey (November 1993). Overall, the trends observed for the Four Isle Dome area were similar to those found for Delacroix Island and Bay de Chene (**Table 7.8**). Most of the points on the graphs for iron, arsenic, cadmium, chromium, lead, and zinc (**Figure 7.10**) and copper, manganese, molybdenum, and vanadium fall below or within 10% to 20% of the values predicted by the dashed line, suggesting that these samples are comparable with uncontaminated sediment from the northwestern Gulf of Mexico. For elements such as arsenic and cadmium (**Figure 7.10**) and manganese and nickel, the points are more scattered and often significantly below the dashed line. This deviation also may be related to local sediment sources or diagenetic processes in the sediment column. No clear evidence exists to support any contamination of the sediments with arsenic, cadmium, chromium, copper, manganese, molybdenum, nickel, lead, vanadium, or zinc in the area of Four Isle Dome.

Concentrations of barium in sediments are elevated above natural levels at the Four Isle Dome discharge station and along the northern, but not along the southern transect (**Table 7.8** and **Figure 7.11**). Evidently, transport of barium-rich particles follows a pathway to the north and not to the south of the facility site (**Figure 7.11**). Furthermore, concentrations of barium in sediments along the southern transect (**Table 7.8**, **Figures 7.10** and **7.11**) are actually lower than expected values. This observation may be due to differences in source material for these sediments or to benthic fluxes of barium from the sediment interstitial water to the overlying water column that deplete sediment barium levels.

Concentrations of mercury are above expected natural levels throughout the Four Isle Dome area (**Table 7.8** and **Figure 7.10**). However, no clear point source or spatial trends were observed for mercury from the available data. Concentrations of mercury in produced water from the Four Isle Dome platform were only about 10 times greater than values for ambient water; thus this sediment mercury contamination is most likely due to some other activity or source than produced water.

7.4 SUMMARY

Highest enrichment factors for metal concentrations in produced water versus coastal seawater were found for barium, iron, and manganese with average values >1,000. Maximum levels of lead and zinc in the produced water were about 100-fold enriched relative to ambient water. In contrast, produced water samples from this study were depleted with copper, molybdenum, and vanadium compared with ambient, receiving waters. To trace the dispersion of metals from produced water discharges, samples of sediment and sediment interstitial water were collected from three sites.

Interstitial water in the top 5 cm at the Delacroix Island discharge station had chlorinity levels of 43 g/kg during the Pre-termination Survey (April 1993), about half the value of the produced water, but at least 20 times higher than interstitial water chloride concentrations at the reference stations. After 12 months of no discharges at the Delacroix Island site (Second Post-termination Survey - April 1994), chlorinity levels in interstitial water samples had returned to background chlorinity levels of 1 to 2 g/kg. This time frame is consistent with results from a

Table 7.8. Metal concentrations in sediments from Four Isle Dome. [DC = discharge station; R1 = reference station 1; R2 = reference station 2; other stations at 100, 300, 500 and 1,000 m north (N) or 100, 300 and 500 m south (S) of discharge station; final numbers in sample ID identifies sample period 1 for November 1994 (Pre-termination Survey)]. Underlined numbers show values that exceed natural levels.

Sample ID	Al (%)	As (µg/g)	Ba (µg/g)	Ca (%)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	Fe (%)	Hg (µg/g)	Mn (µg/g)	Mo (µg/g)	Ni (µg/g)	Pb (µg/g)	V (µg/g)	Zn (µg/g)
DC	6.77	5.7	1435	0.66	0.50	66.3	25.1	3.44	0.112	619	1.4	32.1	16.8	135	150
100N	6.46	5.4	1760	0.81	0.45	67.3	25.1	3.36	0.096	597	1.4	32.9	23.0	147	123
300N	6.81	6.2	2260	0.66	0.44	68.2	26.7	3.52	0.070	673	1.3	35.2	21.5	161	115
500N	7.01	6.2	1600	0.87	0.52	67.6	25.3	3.45	0.053	650	1.0	35.8	20.2	158	109
1000N	6.60	6.6	903	1.20	0.45	67.8	26.0	3.53	0.062	908	1.5	32.1	18.6	158	114
R1	6.77	4.9	168	0.76	0.41	69.3	26.9	3.58	0.098	598	2.0	33.4	11.5	118	118
DC	6.77	5.7	1435	0.66	0.50	66.3	25.1	3.44	0.112	619	1.4	32.1	16.8	135	150
100S	6.69	5.5	189	0.68	0.43	66.1	24.4	3.35	0.080	488	1.2	32.2	11.5	121	116
300S	6.75	5.2	197	0.63	0.46	68.6	26.3	3.45	0.099	527	1.2	32.3	12.3	113	130
500S	6.69	4.9	164	0.64	0.48	69.9	25.9	3.37	0.123	569	1.2	31.9	11.3	112	131
R2	5.92	5.3	1110	0.88	0.34	56.3	18.5	2.65	0.046	423	1.1	26.1	15.3	85.7	76.8

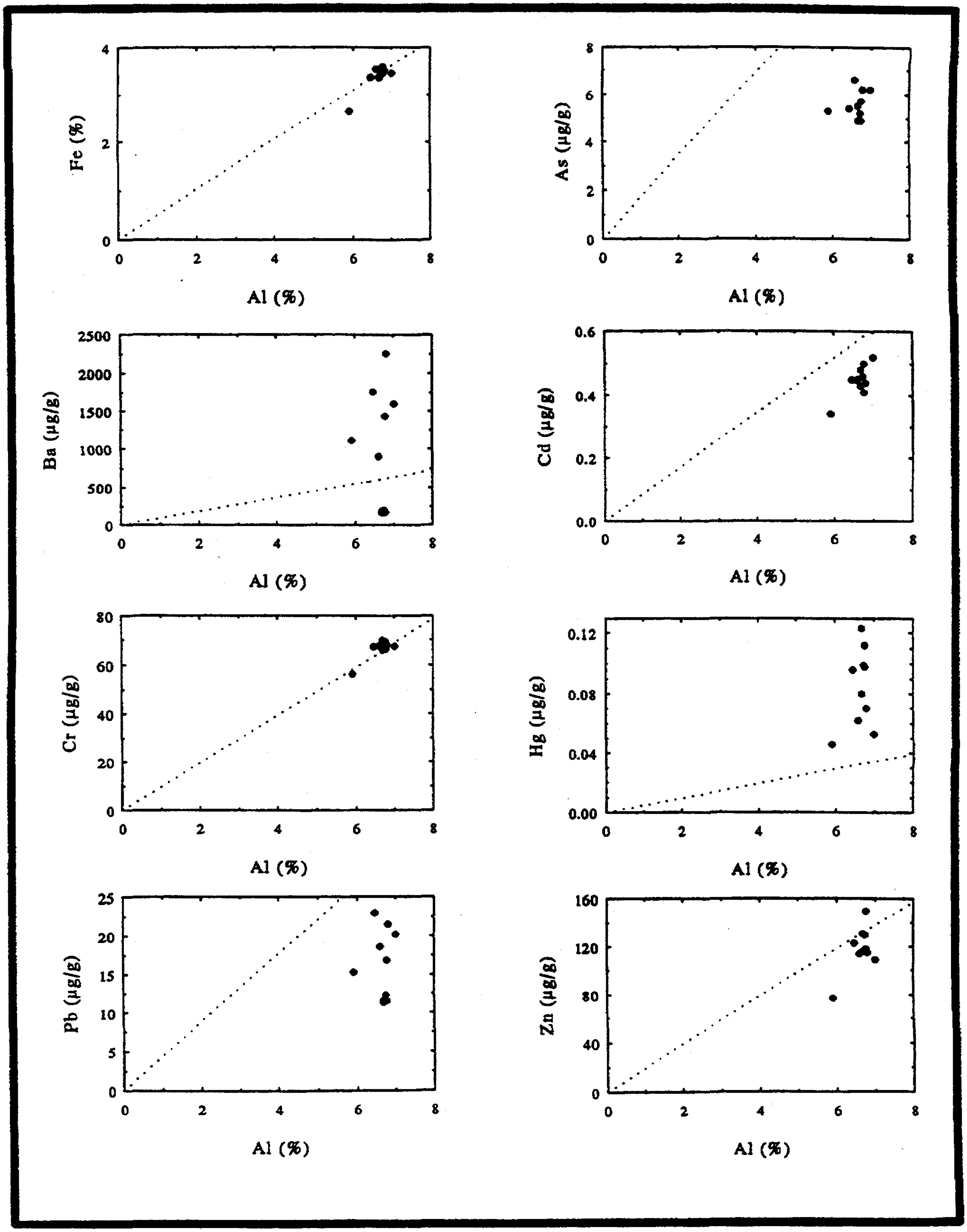

Figure 7.10. Scatter plots showing concentrations of Fe, As, Ba, Cd, Cr, Hg, Pb, and Zn versus Al in all surficial (0-5 cm) sediments from the Four Isle Dome area. Dashed line on each graph identifies natural metal/Al relationship for the northwestern Gulf of Mexico.

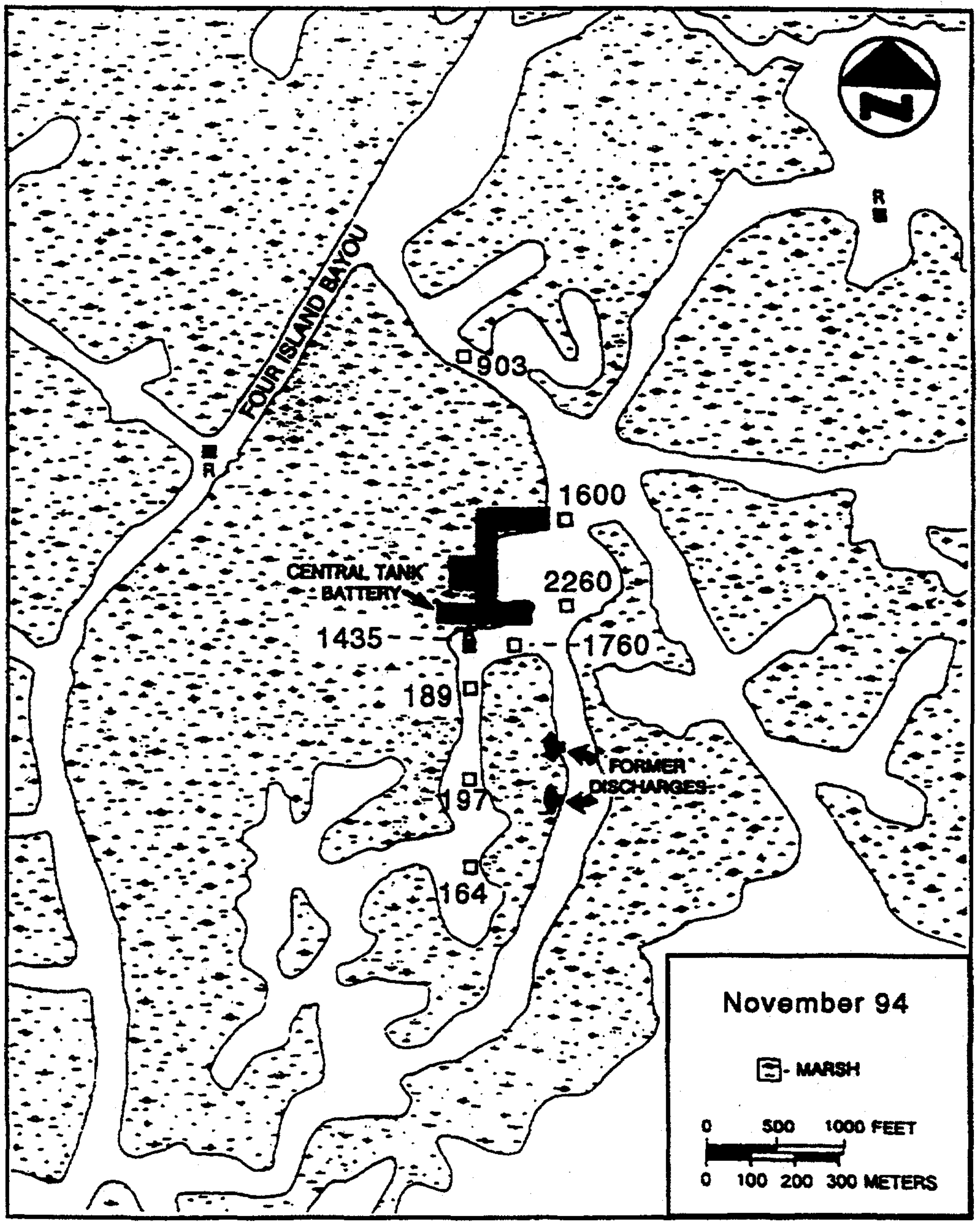

Figure 7.11. Map showing concentrations of Ba in surficial (0-5 cm) sediments from stations in the Four Isle Dome area. All numbers are for samples collected during November 1994 (Pre-termination Survey).

simple diffusion model which suggested that 2 to 12 months would be required for salinity values to return to background concentrations of about 5 ‰ following termination of produced water discharges, depending on boundary conditions chosen for the model. Concentrations of barium and iron in the interstitial water from Delacroix Island were enriched 100 and 10 fold, respectively, at the discharge station relative to the reference stations during the Pre-termination Survey (April 1993). During the Second Post-termination Survey (April 1994), concentrations of these metals, like chloride, had returned to levels comparable with those from the reference stations. In contrast, concentrations of arsenic, chromium, copper, manganese, nickel, and lead for interstitial water from the Delacroix Island area during the period of produced water discharges are comparable with those for the reference stations, showing that produced water is not enhancing levels of these metals.

Interstitial water from Bay de Chene and Four Island Dome was collected only during periods of produced water discharges. Profiles from Bay de Chene showed that the top 5 cm had 1.7 times higher chloride concentrations and 3 times greater chloride values at depths in the sediment column at the discharge station relative to the reference stations. This observation suggested that higher salinity, near bottom water was present at the Bay de Chene discharge station at some time in the past and chloride was diffusing out of the top layers of sediment to the bottom water. In contrast, interstitial water chloride values from the Four Isle Dome discharge station were similar to those of the reference stations, suggesting that produced water was not infiltrating the sediments at this location. With respect to metals in the interstitial water, only barium values in the top 5 cm at the Bay de Chene discharge station, show any impact, albeit minimal, influence of produced water discharges. At Four Isle Dome, no significant differences in the metal concentrations of interstitial water between the discharge station and the reference stations were observed.

Sediment samples from the Delacroix Island area show no clear evidence for significant contamination with arsenic, cadmium, chromium, copper, manganese, molybdenum, nickel, lead, vanadium, or zinc as a result of discharging produced water. However, high barium/aluminum values for sediment from the Delacroix Island station indicate significant anthropogenic inputs of barium with values that are two to four times greater than natural levels. Sources of barium include drilling fluid as well as produced water. No simple temporal and spatial trends were observed for barium at the Delacroix Island site and patterns reflect long-term inputs and dispersion of drilling fluid and produced water to the area. Trends observed for Bay de Chene and Four Isle Dome were similar to those found for Delacroix Island. Concentrations of mercury were also elevated in sediments at some stations at each of the three sites. This enhancement is unlikely to be related to discharges of produced water because mercury levels in produced water were not greatly elevated. Most of the points on metal/aluminum graphs for Bay de Chene and Four Isle Dome for iron, arsenic, cadmium, chromium, copper, manganese, molybdenum, lead, vanadium, and zinc fall below or within 10% to 20% of the values predicted for uncontaminated sediment from the northwestern Gulf of Mexico. One exception to this trend occurred for cadmium, chromium, mercury, lead, and zinc at 100 m northeast of the discharge station in Bay de Chene, the remnant of a previous fuel dock and pipe storage facility at that location.

The overall lack of contamination for most metals in sediments from the three sites is summarized in **Table 7.9**. With the exceptions of barium and mercury, average concentrations of arsenic, cadmium, chromium, copper, manganese, molybdenum, nickel, lead, vanadium, and zinc are within the typical range for natural sediments in the northwestern Gulf of Mexico.

Table 7.9. Metal concentrations (grand mean ± 1 standard deviation) for sediment from all stations at Delacroix Island (DI), Bay de Chene (BDC), and Four Isle Dome (FID) for all surveys along with average values for the northwestern Gulf of Mexico (NW GOM). Underlined numbers show values that exceed natural levels.

Sample ID	Al (%)	As (µg/g)	Ba (µg/g)	Ca (%)	Cd (µg/g)	Cr (µg/g)	Cu (µg/g)	Fe (%)	Hg (µg/g)	Mn (µg/g)	Mo (µg/g)	Pb (µg/g)	Zn (µg/g)
DI (n=30)	5.3 ±0.6	4.6 ±1.5	1170 ±580	1.2 ±0.8	0.27 ±0.09	47 ±7	15 ±3	2.3 ±0.4	0.040 ±0.009	560 ±210	1.0 ±0.5	17 ±4	66 ±13
BDC (n=33)	6.0 ±0.4	8.4 ±1.8	1240 ±460	1.4 ±1.2	0.37 ±0.13	55 ±6	21 ±6	2.8 ±0.3	0.084 ±0.083	380 ±70	1.5 ±0.5	22 ±8	100 ±50
FID (n=10)	6.6 ±0.3	5.6 ±0.6	980 ±780	0.8 ±0.2	0.45 ±0.05	67 ±4	25 ±2	3.4 ±0.3	0.084 ±0.026	600 ±130	1.3 ±0.3	16 ±4	120 ±20
Typical NW GOM[a]	7-8	7-12	500-800	1-7	0.1-0.7	40-80	10-30	3-4	0.02-0.06	400-1000	1-3	15-30	100-150

[a] Trefry *et al.* (1997).

Furthermore, the standard deviation for each mean value is small, showing the general uniformity of sediment metal levels. As previously discussed, concentrations of barium, and to a lesser degree mercury, are elevated above expected natural levels throughout much of each of the sites. The source for mercury is unlikely to be produced water based on low mercury levels found during this study. Inputs of barium may be from produced water and/or drilling fluids.

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CHAPTER 8 - ASSESSMENT AND FINGERPRINTING OF VOLATILE AND SEMIVOLATILE HYDROCARBONS IN PRODUCED WATER, INTERSTITIAL WATER, AND SEDIMENTS IN AREAS WHERE PRODUCED WATER WAS DISCHARGED TO COASTAL LOUISIANA WATERS

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8.1 INTRODUCTION

8.1.1 Background

Hydrocarbons, which are one of the major groups of chemicals associated with oil and gas production operations, were determined in produced water, interstitial water, and sediment as part of an assessment of environmental recovery from terminated discharges at oil and gas facilities in coastal waters of Louisiana. These environmental samples were collected before and after termination of produced water discharging activities at three production fields, Delacroix Island, Bay de Chene, and Four Isle Dome (**Figure 2.1**). In this chapter, spatial and temporal trends in hydrocarbon composition of impacted sediment and potential sources of hydrocarbons in the environment are evaluated. The hydrocarbon results are also used in environmental and human health risk assessments which are discussed in **Chapter 10**, Holtzman et al. (1995), and Meinhold et al. (1996a) (environmental risk) and Meinhold et al. (1996a) (human health risk).

Environmental samples were analyzed for total hydrocarbons (THCs), SHCs, PAHs, and VAHs. Specific target hydrocarbons determined in these samples are listed in **Table 2.3**.

8.1.2 Saturated Hydrocarbon and Polycyclic Aromatic Hydrocarbon Background Characteristics

SHCs are a group of semivolatile hydrocarbons that consist of n-alkanes with carbon numbers from C_{10} to usually C_{40} and selected isoprenoids (branched chain alkanes) such as pristane and phytane. They make up approximately 5% to 20% of the hydrocarbons in crude oils and are major hydrocarbon constituents in unpolluted aquatic environments. Although they are not of general biological or toxicological concern, these hydrocarbons are useful in assessing the sources of hydrocarbons in the environment. SHCs are used as tracers of spilled oil and used to monitor the extent of weathering in the environment. They are also used in distinguishing biogenic and petrogenic hydrocarbons in the environment (Blumer et al., 1971, 1973; Atlas, 1981; NRC, 1985).

The distribution of n-alkanes serves as an initial fingerprint of sources of hydrocarbons. The presence of petroleum hydrocarbons is usually indicated by a wide range of n-alkanes up to C_{40} with no predominance of odd or even carbon numbers. The branched alkanes, pristane and phytane, provide information of the effect of biodegradation on the loss of hydrocarbons in an oil impacted environment. Hydrocarbons that have a biogenic origin have a predominance of odd carbon number compounds over the even carbon number compounds in the n-alkane distribution. Natural (i.e., biogenic) hydrocarbons of marine origin have SHC compounds in the C_{15} to C_{22} n-alkane range, whereas hydrocarbons of terrestrial origin are represented by higher molecular weight SHCs in the C_{27} to C_{35} n-alkane range. There are some marine blue-green algae that have high-molecular-weight n-alkanes in the terrestrial n-alkane range. Terrestrial plant signatures may be evident as part of wetland environments and from land runoff or wind carrying plant debris or pollen.

In the analysis for n-alkanes and isoprenoids by gas chromatography/flame ionization detection (GC/FID), THC content is also determined. In this study, THC content is equal to the sum of the concentrations of the resolved compounds in the chromatogram from n-alkanes C_{10} to C_{40} plus the concentration of the unresolved complex mixture (UCM) between n-alkanes C_{10} and C_{40}. The UCM is the "hump" in the gas chromatogram (GC trace) and its presence is usually associated with anthropogenic inputs that include fossil fuels. Because of the complex mixture of compounds in fossil fuels, the GC technology does not resolve all compounds and as a result relatively large UCMs are almost always present in samples containing fossil fuels.

Probably the most essential set of hydrocarbons in environmental assessments are the two- through six-ring polycyclic aromatic and sulfur-heterocyclic hydrocarbons (PAHs), and including the alkyl homologues (C_1, C_2, C_3, C_4 alkyl carbon substituents on the parent compound) of the prominent two- through four-ring PAHs--naphthalene, fluorene, phenanthrene, dibenzothiophene, chrysene (i.e., families of PAHs). Besides being critical to assessing biological effects and toxicological relationships of dose and response (Neff, 1979; Neff and Anderson, 1981; Neff, 1987), PAHs are extremely valuable in identifying and differentiating sources of hydrocarbons in an impacted environment (Youngblood and Blumer, 1975; Laflamme and Hites, 1978; Wakeham et al., 1980; Requejo and Boehm, 1985; Sauer and Boehm, 1991; Sauer and Uhler, 1994; Page et al., 1995).

PAHs in the environment are prominently of pyrogenic or petrogenic origin. There are some PAHs that have also a diagenic origin such as retene (methyl, propyl phenanthrene) and perylene which are formed by chemical transformation of certain biological precursors during early diagenesis (Venkatesan, 1988). Pyrogenic PAHs distribution consists of relatively high amounts of the four- and six-ring PAHs such as fluoranthene, pyrene, benz(b)fluoranthene, benz(a)anthracene, and benzo(a)pyrene. PAHs of pyrogenic origin (fossil fuel pyrolytic or combustion products, natural combustion products) are characterized by the dominance of the parent PAH with decreasing abundance with increasing alkylation ($C_0 > C_1 > C_2 > C_3 > C_4$). Pyrogenic PAHs are associated with coal tar and its by-products such as creosote used in the preservation of lumber (**Figure 8.1**). Pyrogenic hydrocarbons can be transported to the marine environment through the atmosphere and on particulate material associated with coastal runoff and river discharge (Neff, 1979).

PAHs of petrogenic origin (e.g., crude oil, refined oils, natural seeps) have a characteristic "bell shape" in the homologous series distribution where the C_2 or C_3 alkyl PAH predominates within a PAH family (**Figure 8.1**). For fossil fuels, especially petroleum, the relative abundances of each family of PAH are highly influenced by the source of the hydrocarbons. For instance, crude oil from Saudi Arabia has two to three times more dibenzothiophenes than phenanthrenes whereas crude oil from the North Slope of Alaska has almost equal amounts of

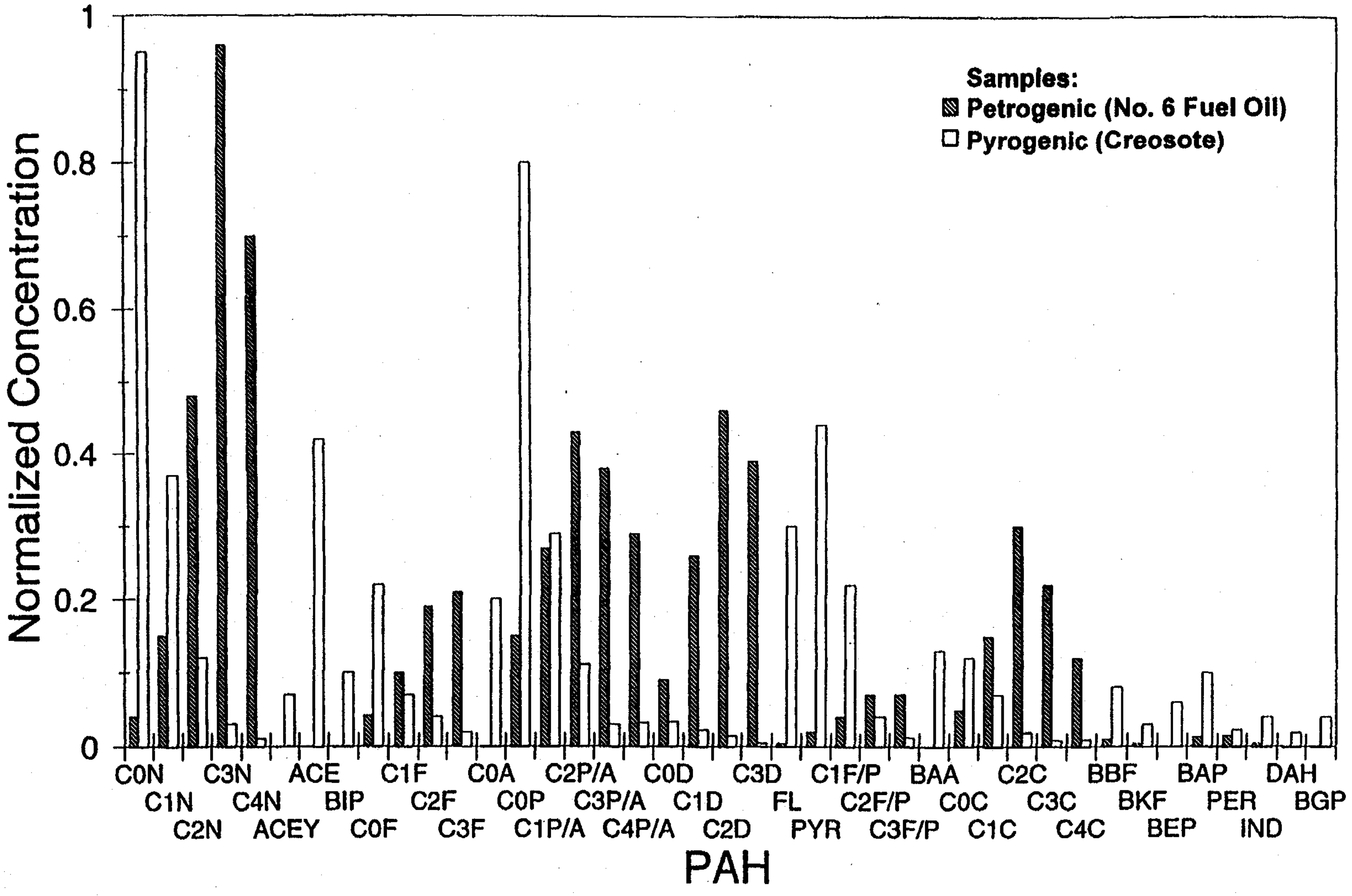

Figure 8.1. PAH distributions of example crude oil (petrogenic) and creosote (pyrogenic).

dibenzothiophenes and phenanthrenes. Also, petrogenic hydrocarbons usually contain relatively low amounts of five- and six-ring PAHs, such as benz(a)anthracene and benzo(a)pyrene, unlike pyrogenic hydrocarbons where the presence of these compounds is relatively high. The relative distributions in alkyl homologues provide the important distinguishing features to hydrocarbon source identification.

Over time, there are certain physical, chemical, and biological processes that contribute to the alteration of the composition of hydrocarbons in the environment. The term for these altering processes is 'weathering' and include evaporation, dissolution, photooxidation, and biodegradation (NRC, 1985; Neff, 1990). The resistance to alteration is based on a combination of hydrocarbon boiling point, solubility, and structure. Most of the alteration proclivities for hydrocarbons are based on the chemical structure.

In the case of petroleum releases, initial loss or change to hydrocarbon composition is generally associated with evaporation where the lower boiling point compounds are preferentially lost. The n-alkanes are generally the most susceptible to weathering of all the hydrocarbons. The isoprenoids are more resistant to biodegradation than the n-alkanes. With weathering of fossil fuels, the GC fingerprint of a weathered oil sample shows a loss in resolved compounds and an increase in the size of the UCM. PAHs are more resistant to weathering than non-cyclic hydrocarbons. Within an alkyl group (e.g., naphthalenes), the parent and lower alkyl groups will weather first (rate: $C_1 > C_2 > \ldots$). The C_2 and C_3-alkyl homologues of phenanthrenes, dibenzothiophenes, and chrysenes have been found to hold their signature except in the more highly weathered situations. In these situations, some of the chemical biomarkers (polycycloalkanes: steranes and triterpanes) are very useful in identifying hydrocarbon sources. Although weathering of the five- and six-ring PAHs has not been studied extensively, their high molecular weight affords a structure that would be recalcitrant to biodegradation.

8.1.3 Site Descriptions and Sampling Design

The three coastal oil and gas facilities selected for chemical characterization and assessment were the Delacroix Island Oil and Gas Field, the Bay De Chene Field, and Four Isle Dome Oil Field (**Figure 2.1**). They are located in the southern Louisiana delta region both east (Delacroix Island) and west (Bay de Chene and Four Isle Dome) of the confines of the Mississippi River. Surveys for collection of environmental samples were conducted before and after termination of produced water discharges at Delacroix Island (April 1993 termination) and Bay de Chene (October 1993 termination). Pre-termination Surveys were conducted in April 1993 at Delacroix Island and May 1993 at Bay de Chene. Two Post-termination Surveys (First and Second Post-termination Surveys) were conducted at both sites: October 1993 and April 1994 at Delacroix Island and May 1994 and October 1994 at Bay de Chene. Because of a change in the termination schedule at the Four Isle Dome site to January 1995, no post-termination surveys were conducted; only a Pre-termination Survey was performed in November 1993.

At Delacroix Island and Bay de Chene, produced water samples were collected from sample taps at the end of the discharge line. Unlike Four Isle Dome, these two sites had skimmer piles before the sample taps to remove oily sheen. The produced water at Four Isle Dome did not discharge into a skimmer pile nor did it have a sample tap; it was discharged directly into the bayou through a straight pipe. Four Isle Dome samples were collected from the end of the pipe. Two replicate produced water samples, each a composite of same day, four hourly samples, were collected during the Pre-termination Survey and analyzed for SHCs and

PAHs. VAHs were determined in two produced water samples, taken at the first and fourth hours during the sampling day.

At all sites, sediment surface (0 to 5 cm) and deeper strata (20 to 25 and 35 to 40 cm) samples were collected and analyzed for SHCs, THCs, and PAHs. VAHs were only determined in Pre-termination (all three sites) and Second Post-termination (Delacroix and Bay de Chene) Survey sediment (0 to 5 cm) samples at the discharge and reference locations for all three sites. At all three sites, interstitial water samples were analyzed from the discharge and reference locations during the Pre-termination Surveys. Interstitial water samples were also analyzed for PAH from the Second Post-termination Survey only at Delacroix Island.

8.1.3.1 Delacroix Island

The Delacroix Island Field, located approximately 9 km southeast of Delacroix, Louisiana and east of the Mississippi River, had been producing since 1940. The field is in an area of subsiding delta with broken marsh from oil field canals and numerous small water bodies. The influence of the Mississippi River is exacerbated by the Caenarvon freshwater diversion (constructed by the U.S. Army Corps of Engineers), 22 km northwest of the field. Salinities at the field are as low as 1 to 3 parts per thousand (ppt) in the spring. The bottom substrate in the area varies from soft, fine grained (muddy) sediments in open water areas to subsided firm marsh root mats. Because of the configuration of the field, environmental samples collection locations were positioned in the north, south, and east directions out to 1,000 m (**Figure 3.1**). Reference sample locations, R1 and R2, were established at distances greater than 1,000 m in the north and east direction. Recorded discharge rates varied from 200,000 to 360,000 L/day during 1989 to 1993.

8.1.3.2 Bay de Chene

The Bay de Chene Field situated approximately 21 km north-northwest of Grand Isle, Louisiana had been producing since 1942. The Tank Battery #5 site selected for study is located in Hackberry Bay within the Barataria Basin system. The Bay de Chene habitat experiences higher salinities (8 to 15 ppt) than the Delacroix Island field most of the year, except in the spring when the Mississippi River reduces the surface salinities to 1 to 5 ppt. The shoreline is characterized by saline marsh that constantly erodes and does not have submerged aquatic vegetation. The bottom substrate in most open water areas is soft, fine grained sediments although some areas of the bottom have firm clay at the surface. Being located in an open bay environment, Bay de Chene sample locations were positioned along transects from 100 to 1,000 m in the northeast, northwest, southeast, and southwest compass directions (**Figure 3.2**). Reference (R1 and R2) sample locations were positioned at distances greater than 1,000 m in the northeast and southwest directions. Recorded discharge rates ranged from 580,000 to 610,000 L/day.

8.1.3.3 Four Isle Dome

The Four Isle Dome Oil Field is located in a network of natural bayous and man-made oil field canals approximately 40 km south-southwest of Houma, Louisiana and 120 km from the mouth of the Mississippi River. The surrounding marsh is saline and not influenced appreciably by the Mississippi River. Salinity decreases occur in the spring from local runoff. In 1992, Hurricane Andrew passed through this area leaving bottom sediments heavily laden with detritus. The network of canals and bayous did not allow for conventional radial sampling of sediments (**Figure 3.3**). Sample transects were oriented approximately north and south from the central production facility with sample stations at 100 to 1,000 m from the discharge. Reference sample locations were positioned at distances greater than 1,000 m to the north and west. Records of recent produced water discharges indicated rates ranging from 135,000 to 650,000 L/day.

8.2 ANALYTICAL METHODS

Analyses for VAHs, SHCs, and PAHs listed in **Table 8.1** were conducted at ADL. The methods have already been established as SOPs at ADL, and are either modifications of EPA SW 846 methods or methods implemented from the literature (NRC, 1985; IOC/UNEP/IAEA, 1991; Sauer and Boehm, 1995). The methods for SHC and PAH determinations have been validated and subjected to intercalibration exercises with other laboratories.

8.2.1 Volatile Aromatic Hydrocarbons

The method used to determine the VAHs listed in **Table 8.1** is based upon a purge and trap isolation procedure and analysis by gas chromatography/mass spectrometry (GC/MS) in the full scan mode (a modified SW-846 Method 8240) as described by Sauer and Boehm (1995). The volatile hydrocarbons are introduced into the gas chromatograph by a purge-and-trap method. An inert gas is bubbled through the water sample at elevated temperature, and the volatile hydrocarbon components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are trapped. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The components are separated with a non-polar fused silica mega-bore capillary chromatographic column in a gas chromatograph and detected with a mass spectrophotometer, which provides both qualitative and quantitative information.

Prior to use for individual component analysis, a five-point calibration was established to demonstrate the linear range of the analysis. Check standards were analyzed with every analytical batch to validate the integrity of the initial calibration. Quantitation of the compounds was performed by the method of internal standards using the response factors established in the initial calibration. Surrogate internal standards (benzene-d_6, ethylbenzene-d_{10}, and naphthalene-d_8) and recovery internal standards (chlorobenzene-d_5) were spiked into the samples just before analysis.

Table 8.1. Target volatile aromatic, polycyclic aromatic, and heterocyclic compounds.

VAH[a]

*Benzene (BZ)
*Toluene (T)
*Ethylbenzene (E)
*m,p-Xylenes (m,p-X) and *o-Xylene (o-X)
C_3-benzenes (C3BZ)
C_4-benzenes (C4BZ)

Polycyclic Aromatic and Heterocyclic Compounds (PAHs)[a]

*Naphthalene (C0N)
C_1-Naphthalenes (C1N), plus individual PAH--1-methylnaphthalene and 2-methylnaphthalene
C_2-Naphthalenes (C2N), plus individual PAH--2,6-dimethylnaphthalene
C_3-Naphthalenes (C3N), plus individual PAH--1,3,5-trimethylnaphthalene
C_4-Naphthalenes (C4N)
*Acenaphthene (ACE)
*Acenaphthylene (ACEY)
Biphenyl (BIP)
*Fluorene (C0F)
C_1-Fluorenes (C1F)
C_2-Fluorenes (C2F)
C_3-Fluorenes (C3F)
*Anthracene (C0A)
*Phenanthrene (C0P)
C_1-Phenanthrenes/anthracenes (C1P/A), plus individual PAH--1-methylphenanthrene
C_2-Phenanthrenes/anthracenes (C2P/A)
C_3-Phenanthrenes/anthracenes (C3P/A)
C_4-Phenanthrenes/anthracenes (C4P/A)
Dibenzothiophene (C0D)
C_1-Dibenzothiophenes (C1D)
C_2-Dibenzothiophenes (C2D)
C_3-Dibenzothiophenes (C3D)
*Chrysene (C0C)
C_1-Chrysenes (C1C)
C_2-Chrysenes (C2C)
C_3-Chrysenes (C3C)
C_4-Chrysenes (C4C)
*Fluoranthene (FLU)
*Pyrene (PYR)
C_1-Fluoranthenes/pyrene (C1F/P)
C_2-Fluoranthenes/pyrene (C2F/P)
C_3-Fluoranthenes/pyrene (C3F/P)
*Benzo(a)anthracene (BAA)
*Benzo(b)fluoranthene (BBF)
*Benzo(k)fluoranthene (BKF)
*Benzo(a)pyrene (BAP)
Benzo(e)pyrene (BEP)
Perylene (PER)
*Indeno(1,2,3-cd)pyrene (INDP)
*Dibenzo(a,h)anthracene (DAHA)
*Benzo(g,h,i)perylene (BGP)

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* Priority pollutant compounds—listed in EPA SW-846 Methods.

[a] C_1, C_2, C_3, C_4 refer to number of alkyl (CH_2) substitutions on the parent compound.

The Purge and Trap conditions for the analysis were as follows:

Purge:	40 mL/min He 11 min at 40°C	Trap:	Tekmar Vocarb Trap 20°C
Desorb Conditions:	20 mL/min He 2 min	Desorb Temp:	260°C bake 8 min at 20°C
Line Temperature:	200°C	Valve Temp:	200°C

GC/MS conditions for this analysis were as follows:

Initial Column Temperature:	35°C	Initial Hold Time:	15 min
Program Rate:	2°C/min		
Final Column Temperature:	250°C	Final Hold Temperature:	5 min
Injector Temperature:	220°C	Detector Temperature:	280°C

8.2.2 Saturated Hydrocarbons and Polycyclic Aromatic Hydrocarbons

SHC and PAH analyses involved sample extraction, extract cleanup, extract fractionation, and instrumental analysis. The extraction procedures for water and sediment required different procedures. The extract cleanup, fractionation, and instrumental analysis were identical for the two matrices. The procedures for the SHC and PAH analyses are summarized in flow diagrams. As part of the SHC analysis, THC concentrations were determined.

8.2.2.1 Sample Extraction

8.2.2.1.1 Water

Water samples were extracted three times with a solvent mixture of 1:1 acetone:methylene chloride. Details of the extraction procedure are provided in **Figure 8.2.**

8.2.2.1.2 Sediment

Sediment samples were extracted three times with a solvent mixture of 1:1 acetone:methylene chloride utilizing an ambient temperature shaking method. Details of the sediment extraction procedure are provided in **Figure 8.3.**

8.2.2.2 Extract Cleanup

Before fractionation, sample extracts were passed through an alumina column to help remove potentially interfering lipid-type compounds. This cleanup column procedure is summarized in **Figure 8.4.**

8.2.2.3 Extract Fractionation

The extracts were fractionated by a high-performance liquid chromatography (HPLC) method into a saturate fraction (f1) containing the SHC compounds and an aromatic fraction (f2) containing the PAH compounds. The HPLC method, as summarized in **Figure 8.5**, produces f1 and f2 fractions similar to those generated by silica gel/alumina column chromatography

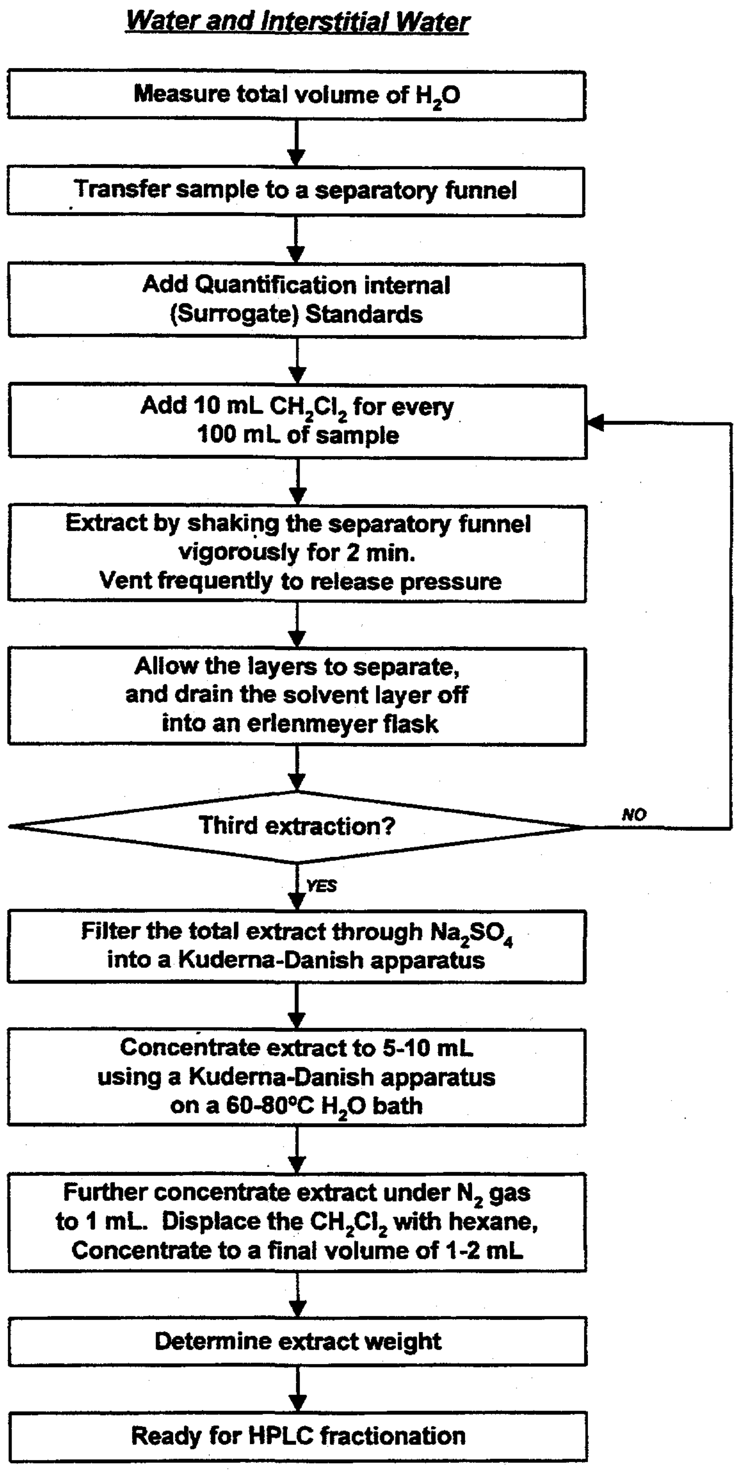

Figure 8.2. SHC/PAH extraction procedure for produced water and interstitial water samples.

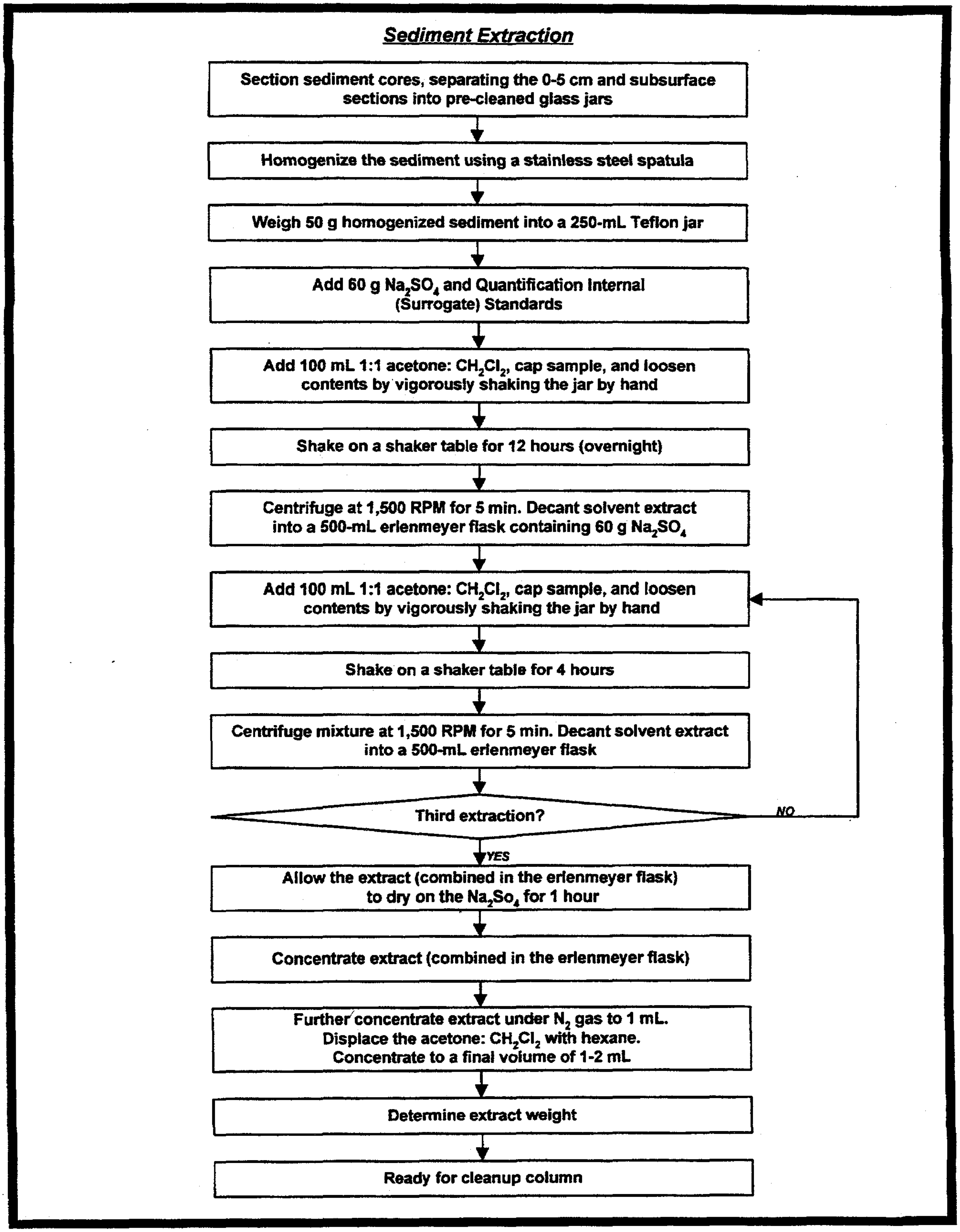

Figure 8.3. SHC/PAH extraction procedure for sediment samples.

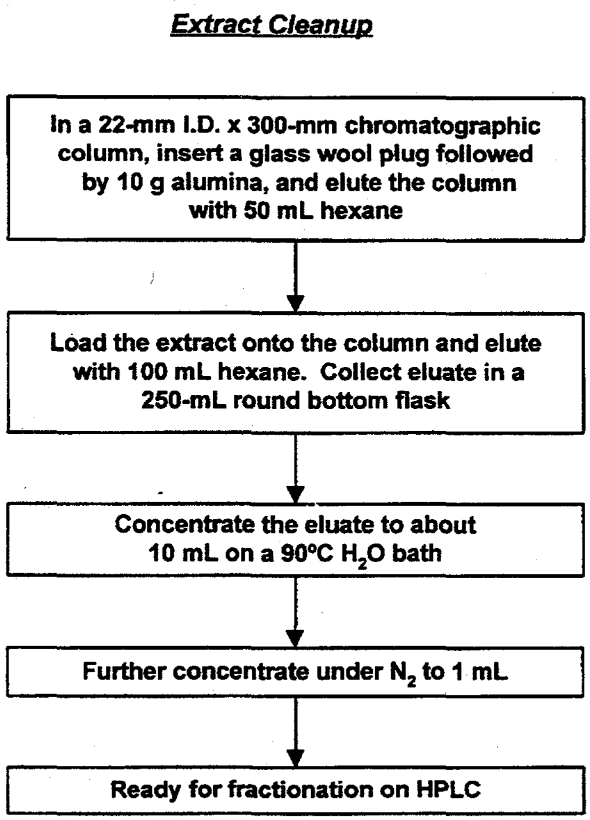

Figure 8.4. Extract cleanup column procedure.

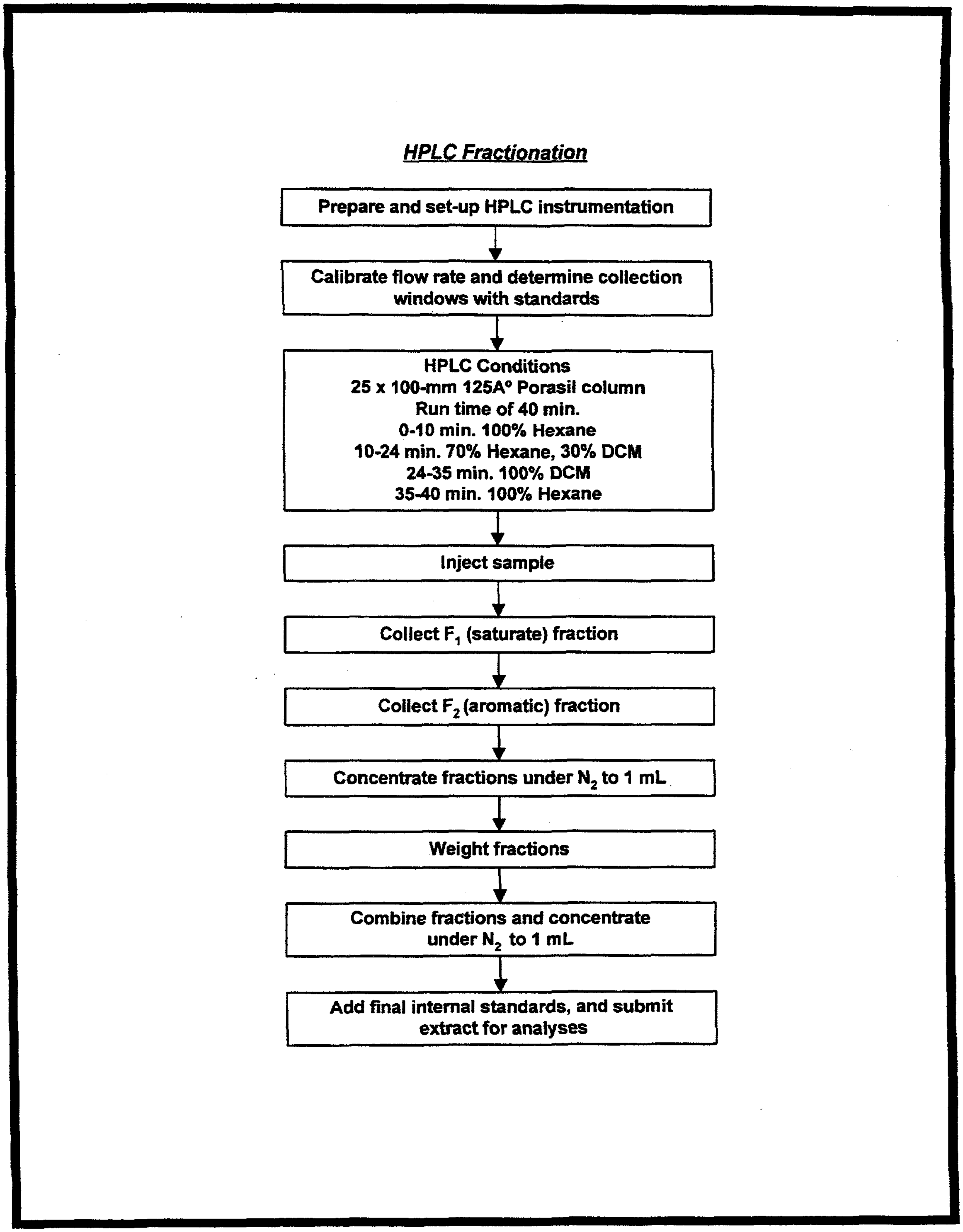

Figure 8.5. HPLC fractionation procedure.

methods, but with more consistent separation (i.e., reduces variability) of target analytes than the column chromatography procedure.

At the completion of the HPLC fractionation, the f1 and f2 fractions were weighed. To determine THCs (total resolved and total unresolved complex mixtures) as defined by the GC-FID analysis of the extract, the f1 and f2 fractions were combined before instrumental analyses. After combination of fractions and addition of recovery internal standards, the extracts were submitted for instrumental analysis for SHC and PAH target determinations.

8.2.2.4 Instrumental Analysis

The final processed extracts were analyzed for the target SHCs and THCs by GC/FID and the target PAHs by GC/MS. The GC/MS analysis of PAHs were performed in the selected ion monitoring (SIM) mode. This mode of operation for GC/MS improves (i.e., lowers) the instrumental detection limits for PAHs and allows for detection of PAHs at the parts per trillion concentrations (ng/L) for water samples and parts per billion concentrations (ng/g) for sediment samples. The lower MDLs for individual PAH analytes of approximately 10 ng/L in water samples and 10 ng/g in sediment samples are especially necessary for the interstitial water analyses. The procedures for analysis of SHCs and PAHs are provided in **Figures 8.6** and **8.7**, respectively.

8.2.3 Quality Assurance and Quality Control

8.2.3.1 Procedures

Data quality for hydrocarbon analyses was ensured through ADL's corporate QA Program that is extensively documented through a Corporate QA Plan and SOPs. As a matter of policy and practice, ADL requires that independent QA staff ensure that data quality objectives are met, QA issues are coordinated among project personnel, and an independent audit of each data package is conducted prior to submission.

Upon arrival at the laboratory, all field and QC samples for water and sediment were examined for possible contamination from breakage, spillage, and for acceptable shipping conditions, assessed for adequate sample volume, and then checked against the accompanying sample custody sheets. Each sample received was entered into the ADL sample logging system and assigned a laboratory sample I.D. and the sample container placed in storage according to SOP. The required chain-of-custody procedures, including sending a copy of the signed custody sheets to S&A or CSA, were accomplished and individual samples were evaluated for storage, handling, and analytical instructions. All applicable holding time requirements were met according to SOP. Explicit sample preparation and analysis instructions and authorization were obtained from CSA prior to proceeding with the analyses.

Prior to each analysis all instruments were initially calibrated according to manufacturer's specifications and SOPs. Similarly, SOPs for continuing calibration and other QC requirements were observed. With each batch of samples of similar matrix (20 samples to a batch), QC samples were processed that included a procedural blank, blank spikes, matrix spikes, sample duplicate, and SRM (NIST SRM-1941 for sediment analysis). Field blank samples were also processed. Data quality objectives for the PAH target analytes and SHCs are summarized in **Table 8.2**, and MDLs for all target analyte groups are provided in **Table 8.3.** Any values that were below the analyte and matrix specific MDL are reported as ND.

At ADL, well established specific QA/QC procedures and formal mechanisms for periodic QA review were implemented. QA/QC procedures were followed in all phases of data generation and analysis for the proposed project. The ADL Project Quality Assurance Officer is independent of the technical organizational and reporting structure. Audit reports and reviews were submitted to the Project Manager and any problems were resolved before the data or reports were released. Data packages were submitted to CSA with a complete QC report and case narratives relating any analytical problems. All project files, including electronic files such as GC/MS output files and laboratory records are archived at ADL for at least five years before being destroyed.

8.2.3.2 Results

Except for trace contamination of some PAHs in a procedural blank of one sample batch of interstitial water, all analyses met the data quality objectives presented in **Table 8.2**.

In some water samples, the qualifier "B" was applied to PAH target analytes, naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, C_1-naphthalenes, biphenyl, and phenanthrene. The "B" qualifier signifies that these particular PAH analytes were found at significantly high levels in the procedural blank of the analytical batch in which the qualified environmental samples were part. Any analyte labeled with a "B" qualifier was in the range of the procedural blank concentration and therefore the analyte was not used in the interpretation.

8.3 RESULTS AND DISCUSSION

8.3.1 Produced Waters

The VAH, SHC, and PAH distributions in produced water should reflect the respective solubilities of the individual hydrocarbon compounds and the composition of the produced crude oil in contact with the produced water. For PAHs, naphthalene or C_1-naphthalenes (depending on the hydrocarbon composition of the produced oil) will have the highest concentration in the produced water with decreasing alkyl concentrations as alkyl carbon number increases. Concentrations of the three-ring PAHs (fluorenes, phenanthrenes, and dibenzothiophenes) will be considerably lower in concentration compared to the naphthalenes, and the relative concentration differences between the alkyl groups in each of the families will be considerably smaller because the relative solubility differences of alkyl group compounds are lower. Of course, the composition of the produced crude oil with its characteristic 'bell shaped' distribution of the alkyl groups will also complicate the composition of the produced water. The concentrations of the four- through six-ring PAHs will be negligible or non-detectable because of the low-level presence of these compounds in produced oil and the low solubilities in water.

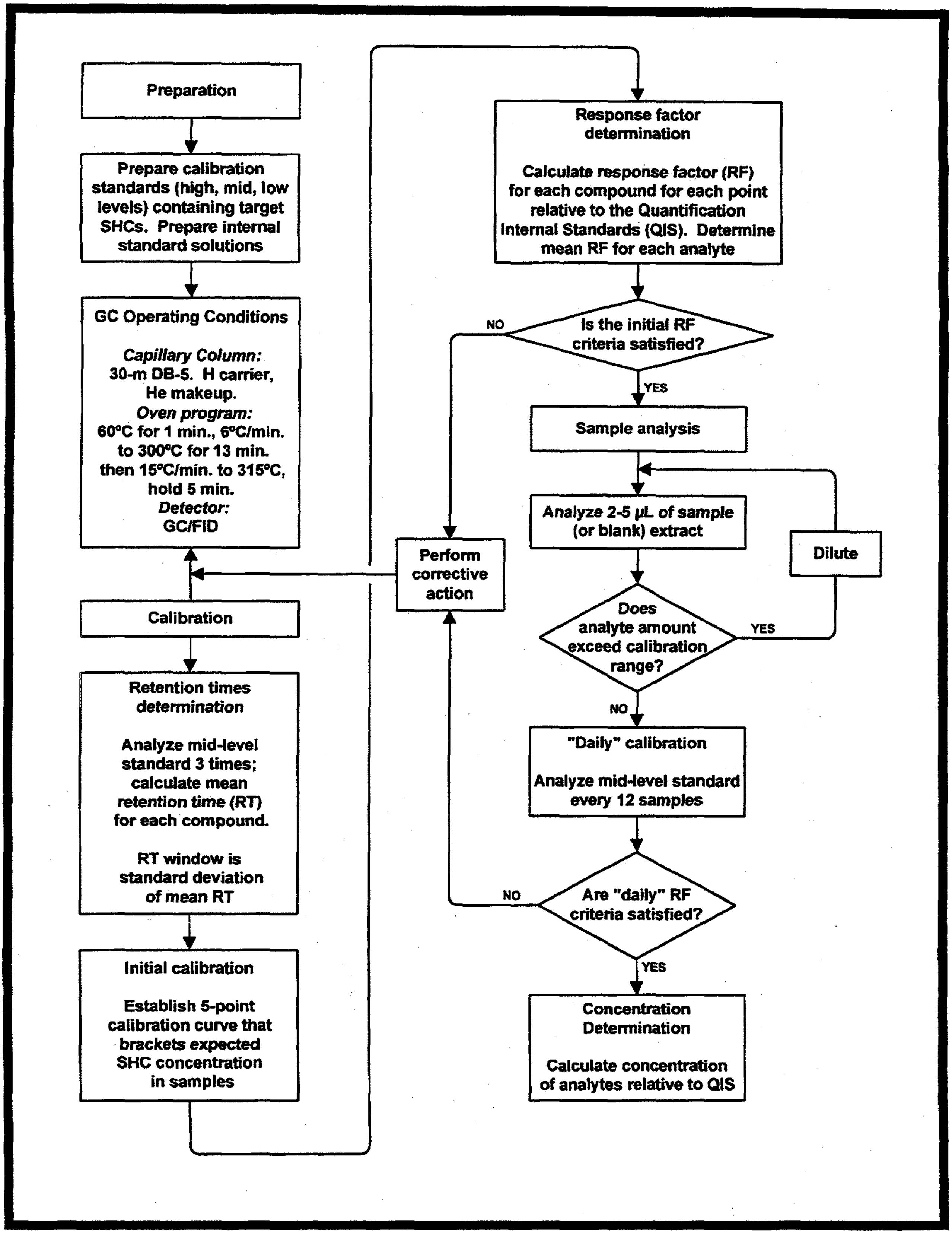

Figure 8.6. Instrumental procedures for SHC analysis by GC/FID.

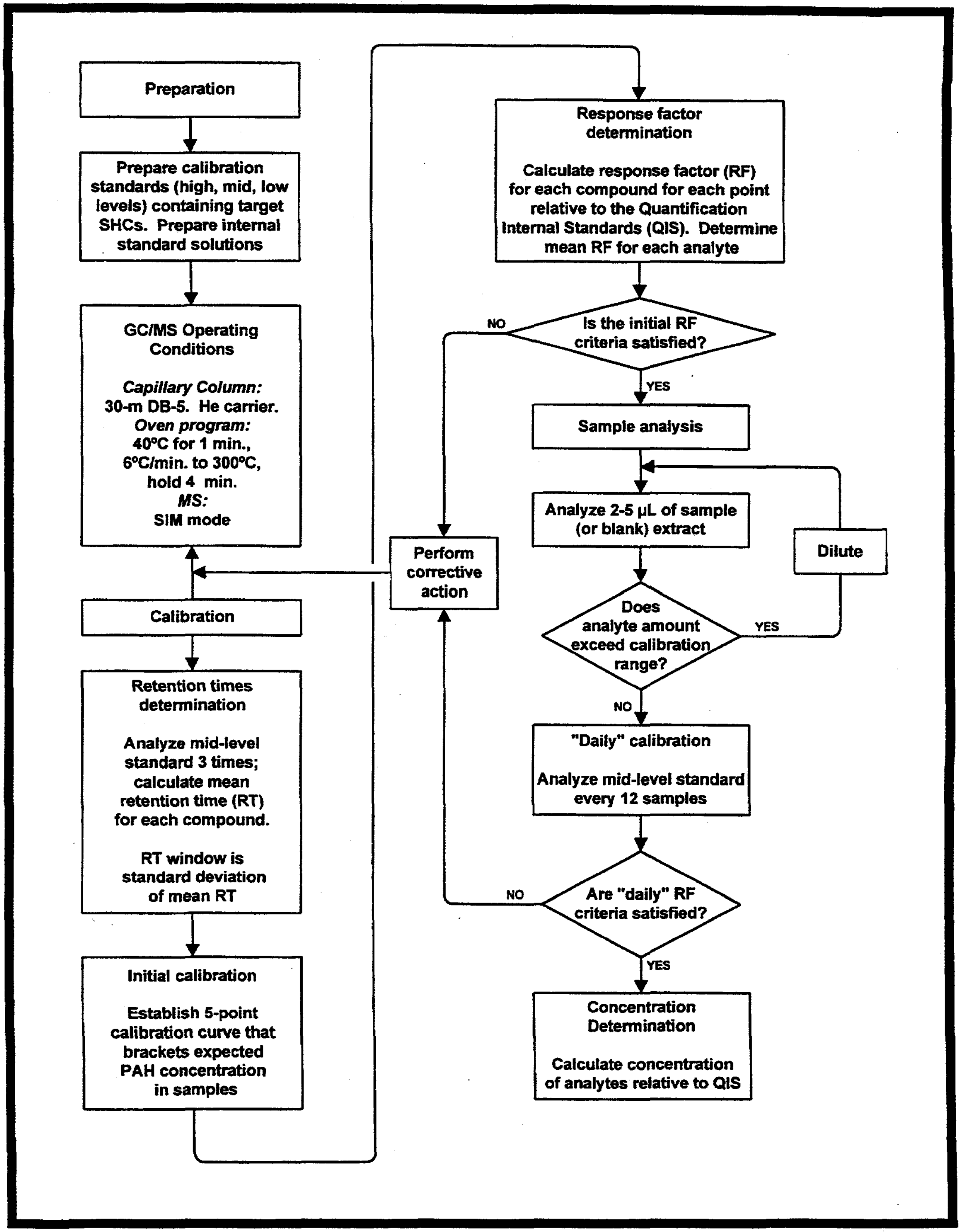

Figure 8.7. Instrumental procedures for PAH analysis by GC/MS.

Table 8.2. Data quality objectives and criteria for volatile aromatic hydrocarbons (VAHs), polycyclic aromatic hydrocarbons (PAHs), and saturated hydrocarbons (SHCs).

Element or Sample Type	Minimum Frequency	Data Quality Objective/ Acceptance Criteria
Initial Calibration (all parent PAHs and selected alkyl homologues; C_{10} -C_{32} n-alkanes, pristane, phytane)	Prior to every sequence	5 point calibration curve over two orders of magnitude; % RSD ≤25%
Continuing Calibration	Every 12 field samples or 16 hours, whichever is more frequent, and at end of analytical sequence with appropriate mid-level standard	% RSD ≤25% for 90% of analytes; % RSD ≤35% for 10% of analytes
Matrix SRM (#1941)	Two per batch/every 20 field samples	Values must be within ±20% of true value on average for all analytes >10x MDL, not to exceed ±25% of true value for more than 30% of individual analytes
Matrix Spikes	Two per batch/every 20 field samples	% recovery of target analytes 40%-125%
Oil Standard	One per batch/every 20 field samples	Values must be within ±10% of the mean of all previous values
Procedural Blank	One per batch/every 20 field samples	No more than 2 analytes to exceed 5x target MDL unless analyte not detected in associated sample(s) or analyte concentration >10x blank value
Duplicate SRM or Sample Analysis	One per batch/every 20 field samples	RPD ≤30%
Internal Standard/ Surrogates	Every sample	% recovery 40%-125%
Target MDLs	Sediment - VAHs Sediment - PAHs Sediment - SHCs Water - VAHs Water (2 liter) - PAH Oil - PAH	30-100 ng/g (dry weight) 1-5 ng/g (dry weight) 0.05-0.1 µg/g (dry weight) 0.2-0.5 µg/L 5-10 ng/L 0.5-2.5 ng/mg

MDL = Method detection limit.
RPD = Relative percent difference.
RSD = Relative standard deviation.
SRM = Standard reference material.

Table 8.3. Method detection limits of target compound groups.

Analytes	Sediment (dry weight)	Water
Polycyclic aromatic hydrocarbons	0.7-6 ng/g	5-20 ng/L
Total hydrocarbons	1-2 μg/g	10-20 μg/L
Saturated hydrocarbons	0.05-0.1 μg/g	0.5-1.0 μg/L
Volatile aromatic hydrocarbons	30-100 ng/g	0.2-0.5 μg/L

Table 8.4. Volatile aromatic hydrocarbon concentrations (μg/L) in produced water.

Study Site	Delacroix Island	Delacroix Island	Bay de Chene	Bay de Chene	Bay de Chene	Four Isle Dome	Four Isle Dome
Station	Discharge	Discharge	Discharge	Discharge	Discharge	Discharge	Discharge
Replicate	A	D	A	D	FB (BLANK)	B	D
Field ID	I-DI-EOP-A	I-DI-EOP-D	I-BDC-EOP-PW-A	I-BDC-EOP-PW-D	I-BDC-EOP-PW-FB	I-FID-EOP-PW-B	I-FID-EOP-PW-D
Analyte							
Benzene	230	470	630	590	ND	2700	2500
Toluene	610	780	560	550	ND	1600	1500
Ethylbenzene	41	48	52	54	ND	100	100
Total Xylenes	410	430	360	360	ND	750	780
m,p-Xylenes	NA	NA	NA	NA	NA	490	520
o-Xylene	NA	NA	NA	NA	NA	260	260
C_3-Benzenes	NA	NA	NA	NA	NA	200	220
C_4-Benzenes	NA	NA	NA	NA	NA	36	42

NA = Not analyzed.
ND = Not detected.

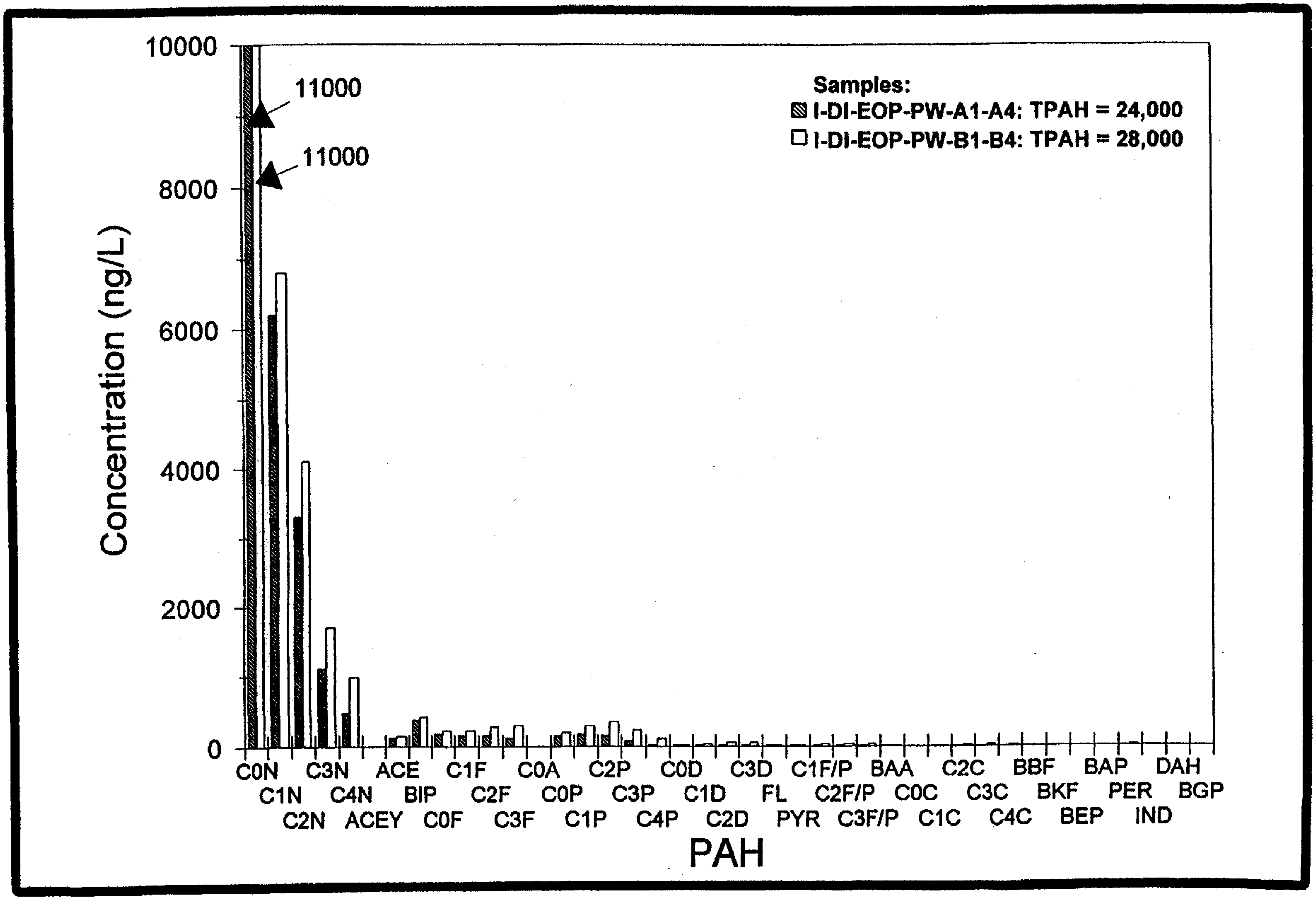

Figure 8.8. PAH distributions in replicate samples of produced water from Delacroix Island collected during the Pre-termination Survey (Survey I).

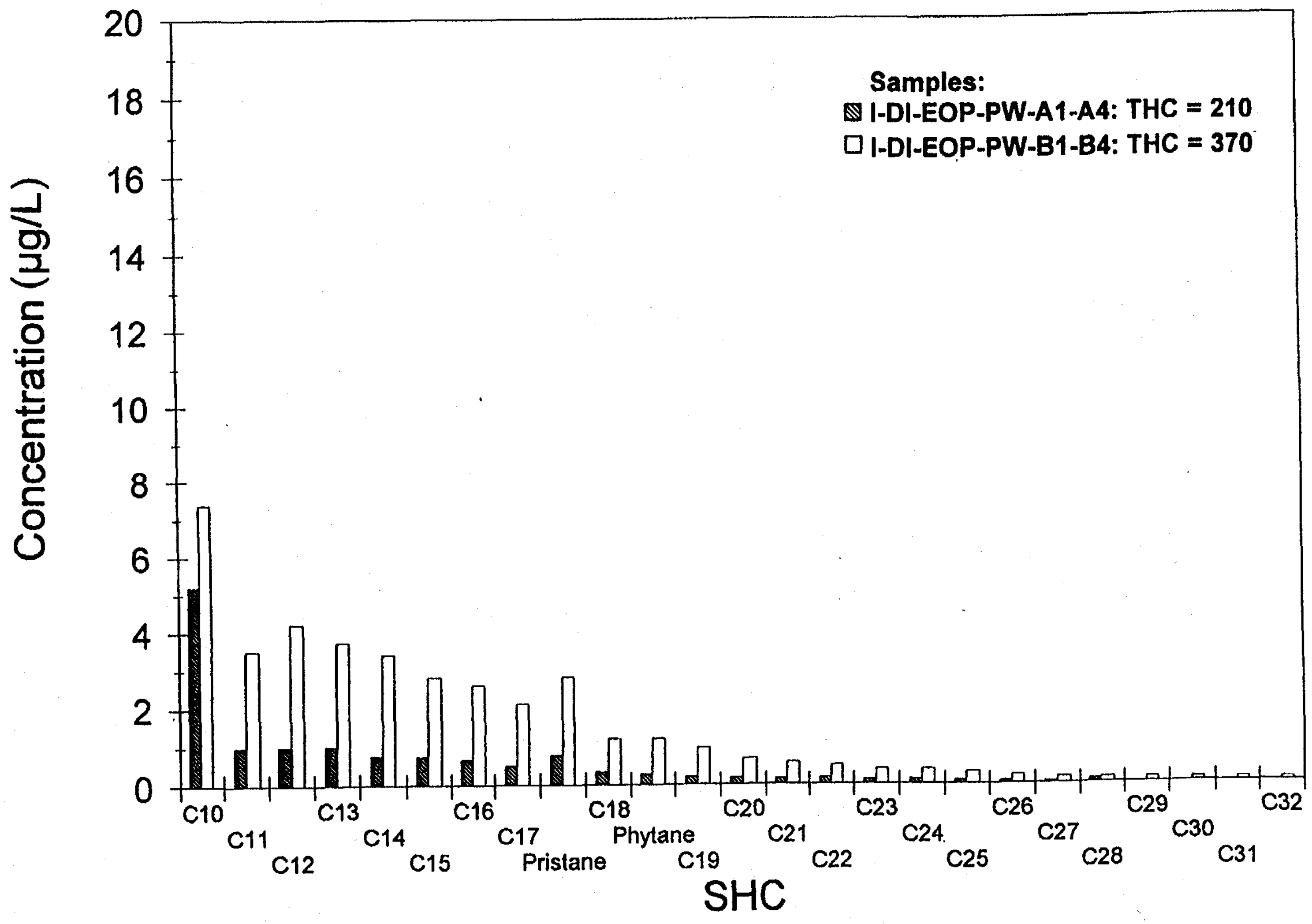

Figure 8.9. SHC distributions in replicate samples of produced water from Delacroix Island collected during the Pre-termination Survey (Survey I).

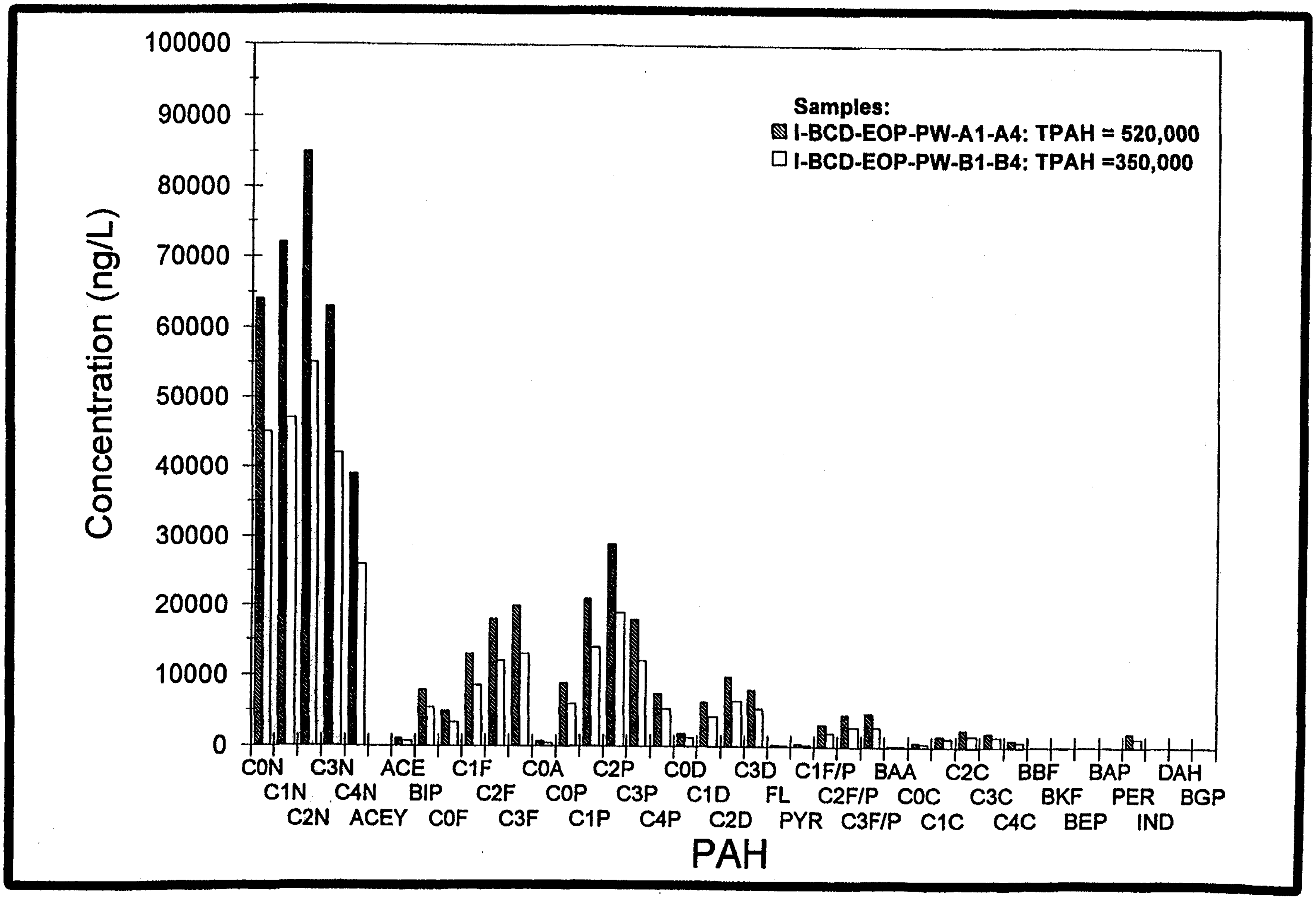

Figure 8.10. PAH distributions in replicate samples of produced water from Bay de Chene collected during the Pre-termination Survey (Survey I).

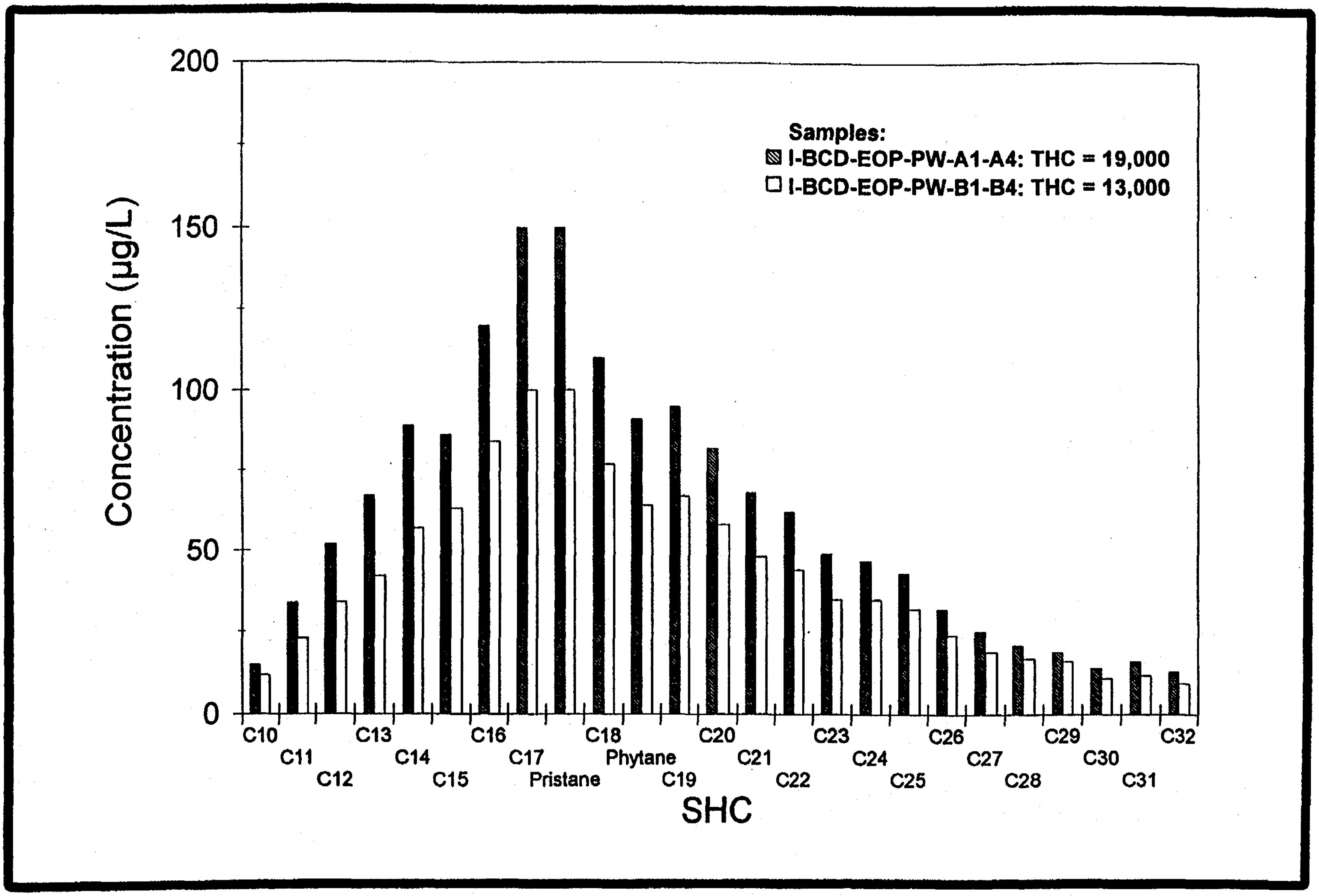

Figure 8.11. SHC distributions in replicate samples of produced water from Bay de Chene collected during the Pre-termination Survey (Survey I).

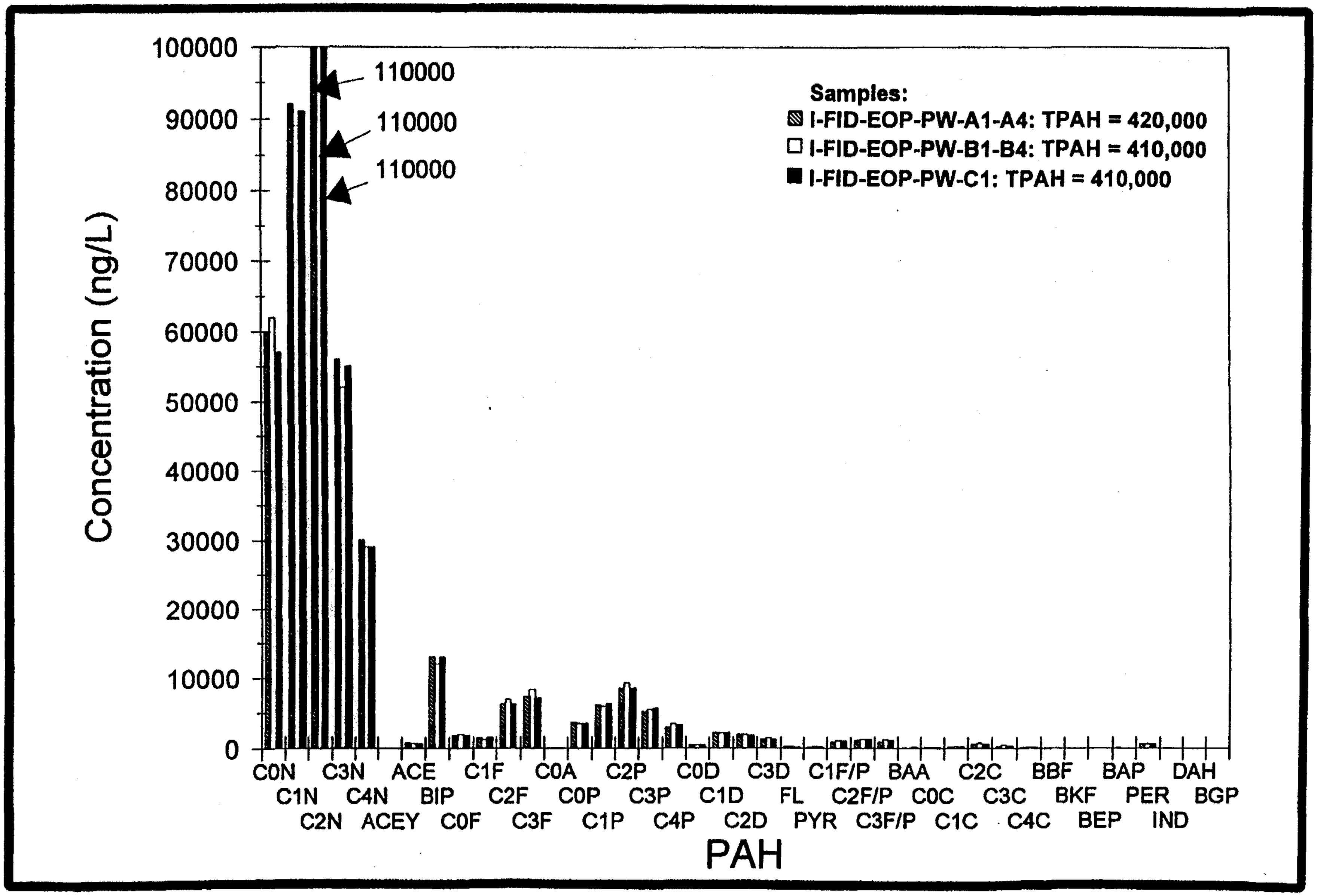

Figure 8.12. PAH distributions in replicate samples of produced water from Four Isle Dome collected during the Pre-termination Survey (Survey I).

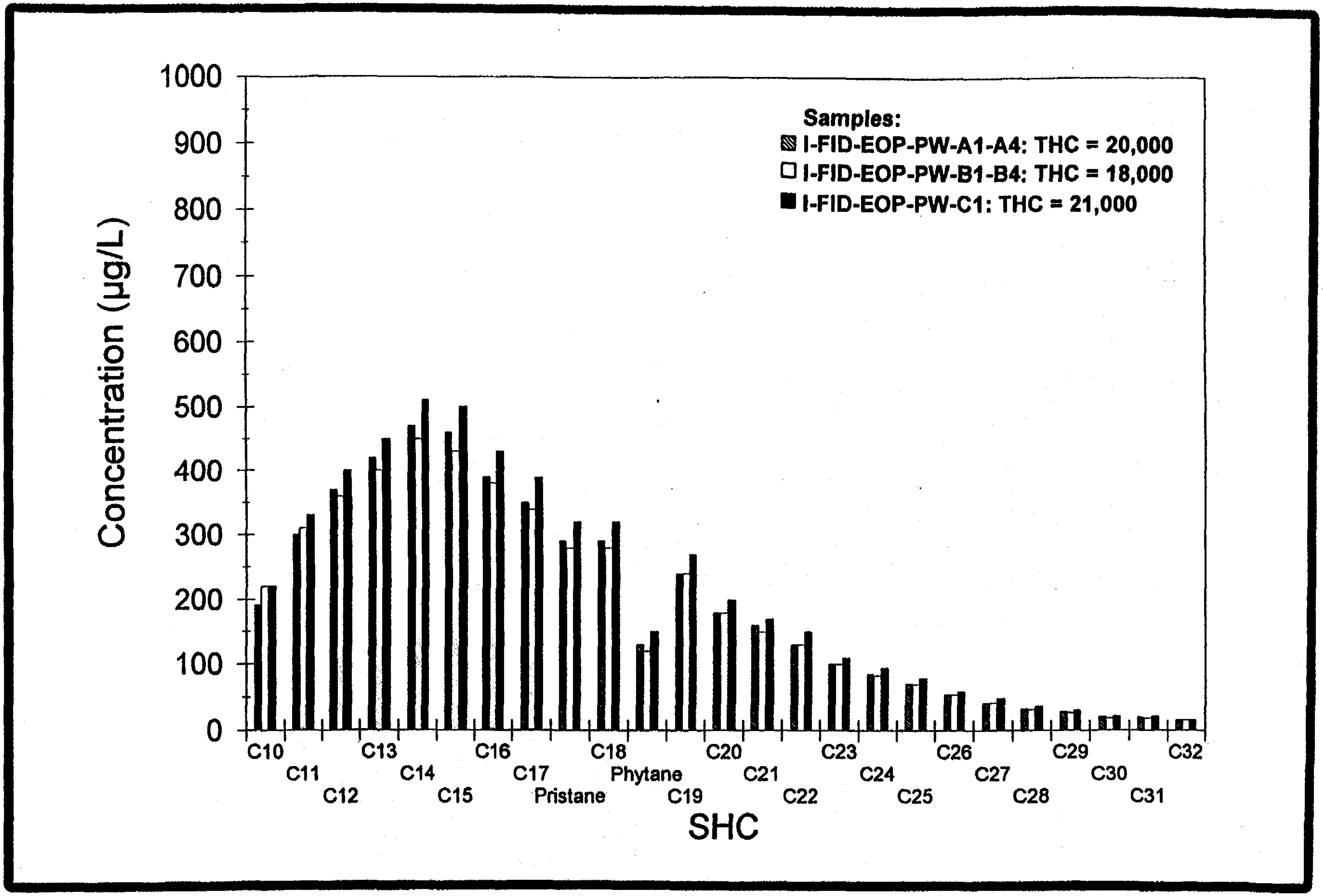

Figure 8.13. SHC distributions in replicate samples of produced water from Four Isle Dome collected during the Pre-termination Survey (Survey I).

Concentrations of the individual VAHs--benzene, toluene, ethylbenzene, the xylenes, C_3-benzenes, and C_4-benzenes--are summarized for the replicate produced water analyses in **Table 8.4**. PAH and SHC distributions are presented in **Figures 8.8** through **8.13**. THC and total PAH and THC concentrations are provided in the figures.

Mean concentrations for BTEX compounds (benzene, toluene, ethylbenzene, and xylenes), the most commonly measured VAHs (**Table 8.4**), ranged from 1,300 to 1,700 μg/L at Delacroix Island, 1,550 to 1,600 μg/L at Bay de Chene, and 4,900 to 5,200 μg/L at Four Isle Dome. These values fall within the range determined in other produced waters discharged into the central Gulf of Mexico from 68 to 38,000 μg/L (Neff, 1996). The relatively higher BTEX concentrations at Four Isle Dome were due to higher concentrations of benzene in the samples which may be a function of the lack of processing (just straight discharge) of the produced water before discharge.

Although BTEX concentrations in the Delacroix Island and Bay de Chene produced water samples were similar, PAH and THC concentrations at the two sites were considerably different by at least an order of magnitude. Total PAH and THC concentrations of Delacroix Island produced waters averaged 26,000 ng/L and 290 μg/L, respectively, whereas Bay de Chene concentrations averaged 440,000 ng/L and 16,000 μg/L, which were similar to the Four Isle Dome samples of 410,000 ng/L and 19,000 μg/L. Although Bay de Chene samples were subjected to some type of treatment (skimmer pile) before discharge, the effectiveness was not evident because hydrocarbon concentrations were similar to the Four Isle Dome samples which had no treatment.

The PAH distribution of the Delacroix Island samples (**Figure 8.8**) showed a relatively large amount of naphthalenes (greater than 95% of the total PAHs) with decreasing alkyl concentrations as alkyl carbon number increased, and very small amounts of the three-ring PAHs (non-detectable amounts of four- through six-ring PAHs) with generally constant alkyl concentrations. The PAH compositions of this produced water reflect the solubility properties for PAHs, as discussed previously. Relatively higher concentrations of the phenanthrene, fluorene, and dibenzothiophene alkyl groups were, however, evident in the Bay de Chene and Four Isle Dome produced waters (**Figures 8.10** and **8.12**). The relatively large amounts of the three- and four-ring PAHs and the characteristic 'bellshaped' distribution of the alkyl homologues reflects the composition of the produced crude oil. SHC concentrations decreased with increasing carbon number from C_{14} to C_{32} in all produced waters (**Figures 8.9**, **8.11**, and **8.13**), which reflected the solubilities and produced oil composition of the analytes. Due to the volatility of the C_{10} through C_{14}, the trend of lower concentrations in produced water samples from Bay de Chene and Four Isle Dome may be due to volatile compound loss during processing/analysis of the samples, not indicative of the actual distribution. The prominent presence and 'bellshaped' distribution of the alkyl PAHs and the higher hydrocarbon concentrations indicated that there were probably oil droplets in the Bay de Chene and Four Isle Dome samples.

As a tool in determining potential sources of hydrocarbons in environmental (sediment) samples, the PAH diagnostic ratios of C_2-phenanthrenes and C_2-dibenzothiophenes (C2P/C2D) and C_3-phenanthrenes and C_3-dibenzothiophenes (C3P/C3D) were calculated for the produced waters at each site (**Table 8.5**).

Table 8.5. PAH diagnostic ratios of produced waters collected during the Pre-termination Survey.

Site	C2P/C2D	C3P/C3D
Delacroix Island	6.8 - 6.9*	4.0 - 4.8*
Bay de Chene	3.0 - 3.1	2.2 - 2.3
Four Isle Dome	4.5 - 4.9	3.9 - 4.8*

These produced waters showed a dominance of the phenanthrenes relative to the dibenzothiophenes, especially the Delacroix Island and Four Isle Dome produced waters at approximately 5:1. Although the produced water C2P/C2D ratios were distinctively different at each site, the C3P/C3D ratios were similar at Delacroix Island and Four Isle Dome. Louisiana crude oils (e.g., South Louisiana) do not commonly have diagnostic ratios this high. Generally, these oils have ratios of approximately 3. The PAH concentrations in the Delacroix Island and Four Isle Dome produced waters probably reflect more the solubilities of the PAHs (* in **Table 8.5**) in the produced water and not necessarily the PAH distribution of the produced crude oil. The PAH distribution of Bay de Chene produced water is, however, very similar to that of the produced crude oil indicating that there were probably oil droplets in the water.

8.3.2 Sediments

The major focus of the organics analysis for this study was on PAHs and SHCs in sediment. However, there were two other supplemental organic analyses performed on sediment and sediment interstitial water. VAHs were determined in surface (0 to 5 cm) sediment samples from the discharge and reference sample locations collected during the Pre-termination Survey (Survey I) and the Second Post-termination Survey at Delacroix Island (Survey III). Also, PAHs were determined in interstitial water from the same sample locations analyzed for VAHs. Sediment VAH results are presented in **Table 8.6** and the interstitial water PAH results are summarized in **Table 8.7**. Because most of the interstitial water samples did not contain any detectable PAHs, only the samples that contained PAHs were provided in the table.

In the assessment of the hydrocarbon results, spatial and temporal trends of hydrocarbon concentrations are discussed separately for each site starting at the outer stations and moving to the stations nearest the discharge locations. The compositions of SHC and PAH target groups are then discussed and potential sources identified based on produced water and other hydrocarbon source signatures. In the final interpretative analysis, multivariate statistical analyses are applied to PAH data of the sediment and produced water samples to statistically confirm some of the observations made about PAH distribution and sources in the sediments. All PAHs except naphthalenes and fluorenes, which are most receptive to early weathering, and perylene, which has a diagenic source, were used in a principle component analysis. Each sample was normalized to its highest PAH concentration to remove the bias of concentration from the analysis.

Table 8.6. Volatile aromatic hydrocarbon concentrations (ng/g) in sediments collected during the Pre-termination (Survey I) and Second Post-termination (Survey III) Surveys.

Survey Number	I	I	I	I	I	I
Study Site	Delacroix Island	Delacroix Island	Delacroix Island	Bay de Chene	Bay de Chene	Bay de Chene
Station	Discharge	R1	R2	Discharge	Discharge	R1
Replicate	A	A	A	A	B	A
Field ID	I-DI-@-S-O-A	I-DI-R1-S-A	I-DI-R2-S-A	I-BDC-@-S-O-A	I-BDC-@-S-O-B	I-BDC-R1-S-O-A
Analyte						
Benzene	91	ND	ND	ND	ND	ND
Toluene	ND	ND	ND	ND	ND	ND
Ethylbenzene	69	ND	ND	ND	ND	ND
Total Xylenes	420	ND	ND	ND	ND	ND
m,*p*-Xylenes	NA	NA	NA	NA	NA	NA
o-Xylene	NA	NA	NA	NA	NA	NA
C_3-Benzenes	NA	NA	NA	NA	NA	NA
C_4-Benzenes	NA	NA	NA	NA	NA	NA

Table 8.6. (Continued).

Survey Number	I	I	I	I
Study Site	Bay de Chene	Four Isle Dome	Four Isle Dome	Four Island Dome
Station	R2	Discharge	R1	R2
Replicate	A	A	A	A
Field ID	I-BDC-R2-S-O-A	1-FID-@-S-O-A	1-FID-R1-S-O-A	1-FID-R2-S-O-A
Analyte				
Benzene	ND	13	ND	ND
Toluene	ND	45	0.56	0.25
Ethylbenzene	ND	19	0.1	ND
Total Xylenes	ND	163	0.45	ND
m,p-Xylenes	NA	120	0.31	ND
o-Xylene	NA	43	0.14	ND
C_3-Benzenes	NA	190	ND	ND
C_4-Benzenes	NA	152	ND	ND

Table 8.6. (Continued).

Survey Number	III	III	III	III	III
Study Site	Delacroix Island	Delacroix Island	Delacroix Island	Delacroix Island	Delacroix Island
Station	Discharge	Discharge	R1	R2	R2
Replicate	A	B	A	A	A (DUP)
Field ID	111-DI-@-S-A	111-DI-@-S-B	111-DI-R1-S-O-A	111-DI-R2-S-O-A	111-DI-R2-S-O-A
Analyte					
Benzene	ND	ND	ND	ND	ND
Toluene	ND	ND	ND	ND	ND
Ethylbenzene	ND	0.24	ND	ND	ND
Total Xylenes	ND	0.81	ND	ND	ND
m,p-Xylenes	ND	0.58	ND	ND	ND
o-Xylene	ND	0.23	ND	ND	ND
C_3-Benzenes	ND	ND	ND	ND	ND
C_4-Benzenes	ND	ND	ND	ND	ND

NA = Not analyzed.
ND = Not detected.

Table 8.7. PAH concentrations (ng/L) in interstitial water samples collected during the Pre-termination (Survey I) and Second Post-termination (Survey III) Surveys. Values are listed for only those samples containing PAHs.

Survey Number	I	I	I	III	III
Study Site	Delacroix Island	Delacroix Island	Delacroix Island	Delacroix Island	Delacroix Island
Station	Discharge	Discharge	R1	Discharge	Discharge
Replicate	A	B	A	A	B
Field ID	1-D1-DSC-1W-A	1-D1-DSC-1W-B	1-D1-R1-1W-A	DSC-1W-A	DSC-1W-B
Analyte					
Naphthalene	4000	2600	2700	110	120
2-Methylnaphthalene	530	510	480	32	34
1-Methylnaphthalene	660	410	610	17	23
C_1-Naphthalenes	810	730	1000	35	37
Acenaphthene	ND	190	360	ND	ND
Phenanthrene	ND	180	ND	44	51
Biphenyl	ND	ND	ND	ND	ND
Fluorene	ND	ND	ND	ND	ND
Benzo[g,h,i]perylene	ND	ND	ND	ND	ND

Table 8.7. (Continued).

Survey Number	III	III	III	III	III
Study Site	Delacroix Island	Delacroix Island	Delacroix Island	Delacroix Island	Delacroix Island
Station	Discharge	Discharge	R1	R1	R1
Replicate	C	D	A	B	C
Field ID	DSC-1W-C	DSC-1W-D	R1-1W-A	R1-1W-B	R1-1W-C
Analyte					
Naphthalene	180	98	93	78	130
2-Methylnaphthalene	29	ND	29	18	19
1-Methylnaphthalene	21	ND	9	8.7	18
C_1-Naphthalenes	41	ND	35	23	33
Acenaphthene	ND	ND	ND	ND	ND
Phenanthrene	55	22	55	52	31
Biphenyl	18	ND	ND	ND	ND
Fluorene	10	ND	ND	ND	ND
Benzo[g,h,i]perylene	ND	ND	ND	ND	ND

Table 8.7. (Continued).

Survey Number	III	III	III	III	III	I
Study Site	Delacroix Island	Delacroix Island	Delacroix Island	Delacroix Island	Delacroix Island	Bay de Chene
Station	R1	R1	R2	R2	R2	R1
Replicate	D	E	A	B	C	E
Field ID	R1-1W-D	R1-1W-E	R2-1W-A	R2-1W-B	R2-1W-C	1-BC-R1-1W-E
Analyte						
Naphthalene	66	71	78	100	100	300
2-Methylnaphthalene	ND	ND	ND	25	21	ND
1-Methylnaphthalene	ND	ND	ND	14	16	ND
C_1-Naphthalenes	ND	ND	ND	36	31	ND
Acenaphthene	ND	ND	ND	ND	ND	ND
Phenanthrene	ND	ND	49	48	40	ND
Biphenyl	ND	ND	ND	ND	ND	ND
Fluorene	ND	ND	ND	ND	17	ND
Benzo[g,h,i]perylene	13	ND	ND	ND	ND	ND

ND = Not detected.

8.3.2.1 Delacroix Island

The hydrocarbon content of the surface sediments at 500 and 1,000 m, which was consistent among surveys, ranged from 32 to 83 μg/g for THCs and from 270 to 550 ng/g for total PAHs (**Table 8.8**). Hydrocarbon concentrations of surface reference sediments were generally slightly lower than the outer station sediments and ranged from 25 to 47 μg/g for THCs and 220 to 280 ng/g for total PAHs. The reference sediment PAH values were similar to those found in nearshore sediments of Texas and Louisiana (10 to 200 ng/g total PAHs) by other investigators (Brooks et al., 1990; Neff et al., 1992; Kennicutt, 1995). Interestingly, total PAH concentrations in subsurface reference sediments (35 to 40 cm) were higher (480 to 830 ng/g PAHs) than the surface sediments at the outer stations, which were due not to increased overall PAH inputs, but to increased amounts of perylene only that made up to one-third of the total PAHs in these deeper sediments (**Figure 8.14**).

The sediments at the inner stations (100 and 300 m) had hydrocarbon concentrations that were generally higher, but more variable. THC concentrations ranged from 14 to 230 ng/g and PAH concentrations from 330 to 2,500 ng/g. There were no obvious temporal or spatial trends in concentrations of the pre-termination and post-termination sediments. The northeast sediments, however, showed higher THC and PAH concentrations than the northwest and south sediments at 300 m, but this trend was not evident at 100 m where the THC and PAH values were more variable among stations and surveys. Lower hydrocarbon concentrations in the south sediments may be due to the different hydrological conditions in the south transect evident by the lower percent silt/clay content of 40% to 50% compared to the other transects where silt/clay content was 70% to 80%.

Hydrocarbon concentrations in surface sediments at the discharge station were highest in the pre-termination sediments, 1,800 μg/g for THCs and 12,000 ng/g for PAHs, and decreased to 130 to 140 μg/g THCs and 2,800 to 7,700 ng/g PAHs in the post-termination sediments. Although PAH concentrations decreased with depth in the pre-termination sediments, relatively huge amounts of PAHs from 34,000 to 69,000 ng/g, the highest in all sediments analyzed, were found in the second post-termination (Survey III) subsurface sediments. As discussed later, the elevated PAH concentrations were not from petrogenic origin, but had principally a pyrogenic source.

The hydrocarbon compositions were dominated by the higher molecular weight SHCs from C_{23} to C_{32}. Example SHC distributions for Bay de Chene are presented in (**Figure 8.15**). The contribution of lower molecular weight SHCs, C_{16} to C_{22} n-alkanes, was significantly lower (<20% of total SHCs) except in those sediments at the discharge station sampled during the Pre-termination Survey. For this SHC group, the C_{17} n-alkane was the dominate compound, not the isoprenoids--pristane or phytane. The relatively higher concentrations of the C_{17} n-alkane compared to the other lower molecular weight SHCs, low concentrations of the isoprenoids, and the large odd/even n-alkane preference (4 to 1) indicated a biogenic source for the SHCs, probably of terrestrial and wetland origin.

Lower molecular weight SHCs (C_{10} to C_{20}), which were highly representative of a petrogenic input, dominated the SHC composition only at the discharge station (**Figure 8.16**). In later surveys, the content of these SHCs decreased considerably to levels similar to the other sediments (**Figure 8.17**) where the higher molecular weight SHCs greatly dominated. Since

Table 8.8. Summary of THC (μg/g) and TPAH (ng/g) concentrations in sediment collected during the Pre-termination (Survey I) and Second Post-termination (Survey III) Surveys from Delacroix Island.

Distance (m)	Direction	Analyte Group	Survey I	Survey II	Survey III
R1	0-5 cm	THC	25	47	31
		TPAH	270	280	280
	20-25 cm	THC	–	–	–
		TPAH	230	–	350
	35-40 cm	THC	–	–	–
		TPAH	480	–	370
R2	0-5 cm	THC	40	39	36
		TPAH	260	220	240
	20-25 cm	THC	–	–	–
		TPAH	400	–	450
	35-40 cm	THC	–	–	–
		TPAH	830	–	500
1000 m	NE	THC	–	–	–
		TPAH	–	–	–
	NW	THC	50	25	29
		TPAH	550	300	290
	S	THC	27	83	55
		TPAH	330	550	460
500 m	NE	THC	66	45	61
		TPAH	650	310	490
	NW	THC	35	38	37
		TPAH	370	270	370
	S	THC	32	36	32
		TPAH	410	470	570
300 m	NE	THC	170	180	140
		TPAH	1000	1000	740
	NW	THC	42	44	48
		TPAH	780	330	500
	S	THC	26	29	24
		TPAH	740	2100	350
100 m	NE	THC	230	130	120
		TPAH	1400	1200	1400
	NW	THC	96	210	64
		TPAH	2500	1500	840
	S	THC	22	14	27
		TPAH	1000	270	1500

Table 8.8. (Continued).

Distance (m)	Direction	Analyte Group	Survey I	Survey II	Survey III
Discharge	0-5 cm	THC TPAH	1800 12000	130 2800	140 7700
	20-25 cm	THC TPAH	– 8800	– –	– 34000
	35-40 cm	THC TPAH	– 3200	– –	– 69000

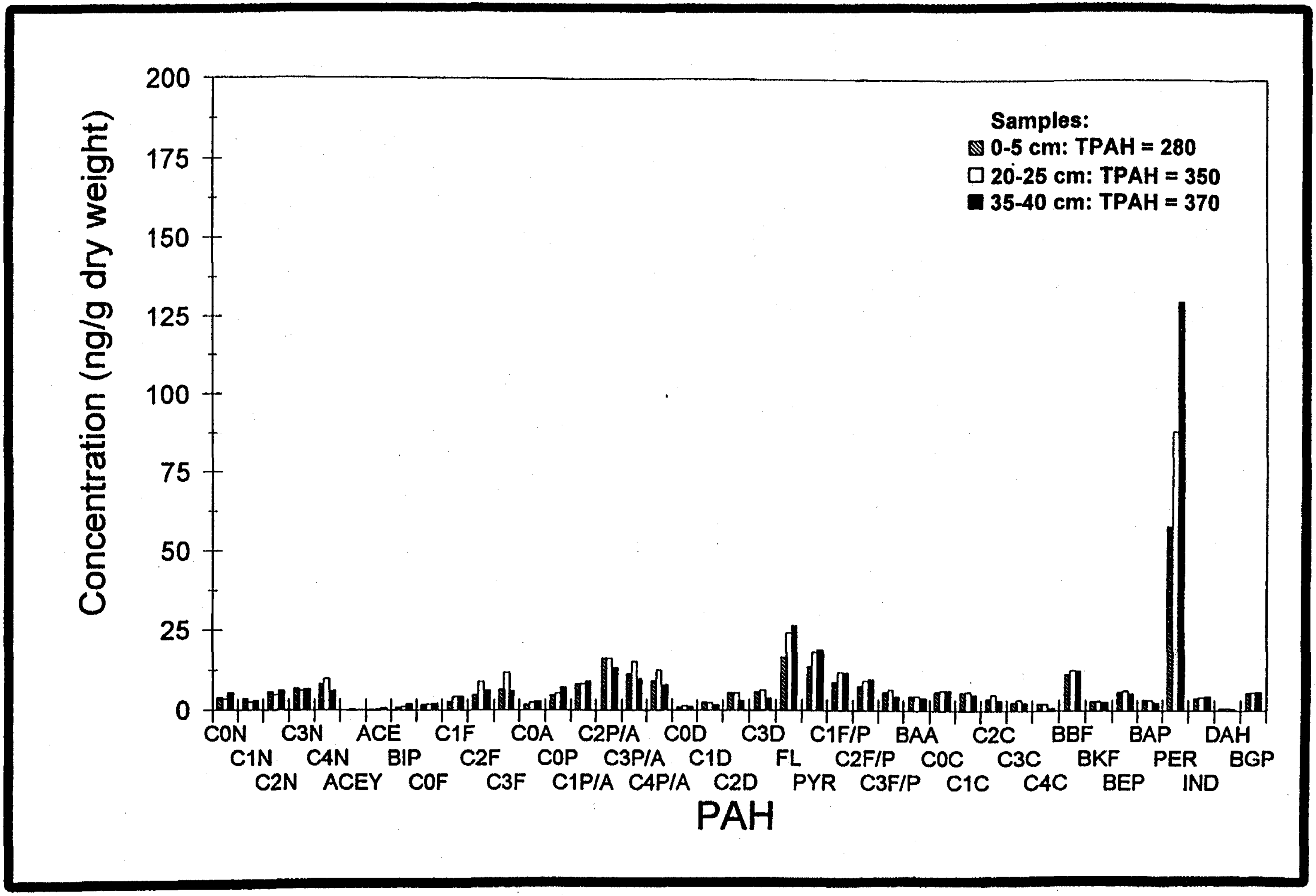

Figure 8.14. PAH distributions in sediments from the reference 1 station of Delacroix Island collected during the Second Post-termination Survey (Survey III).

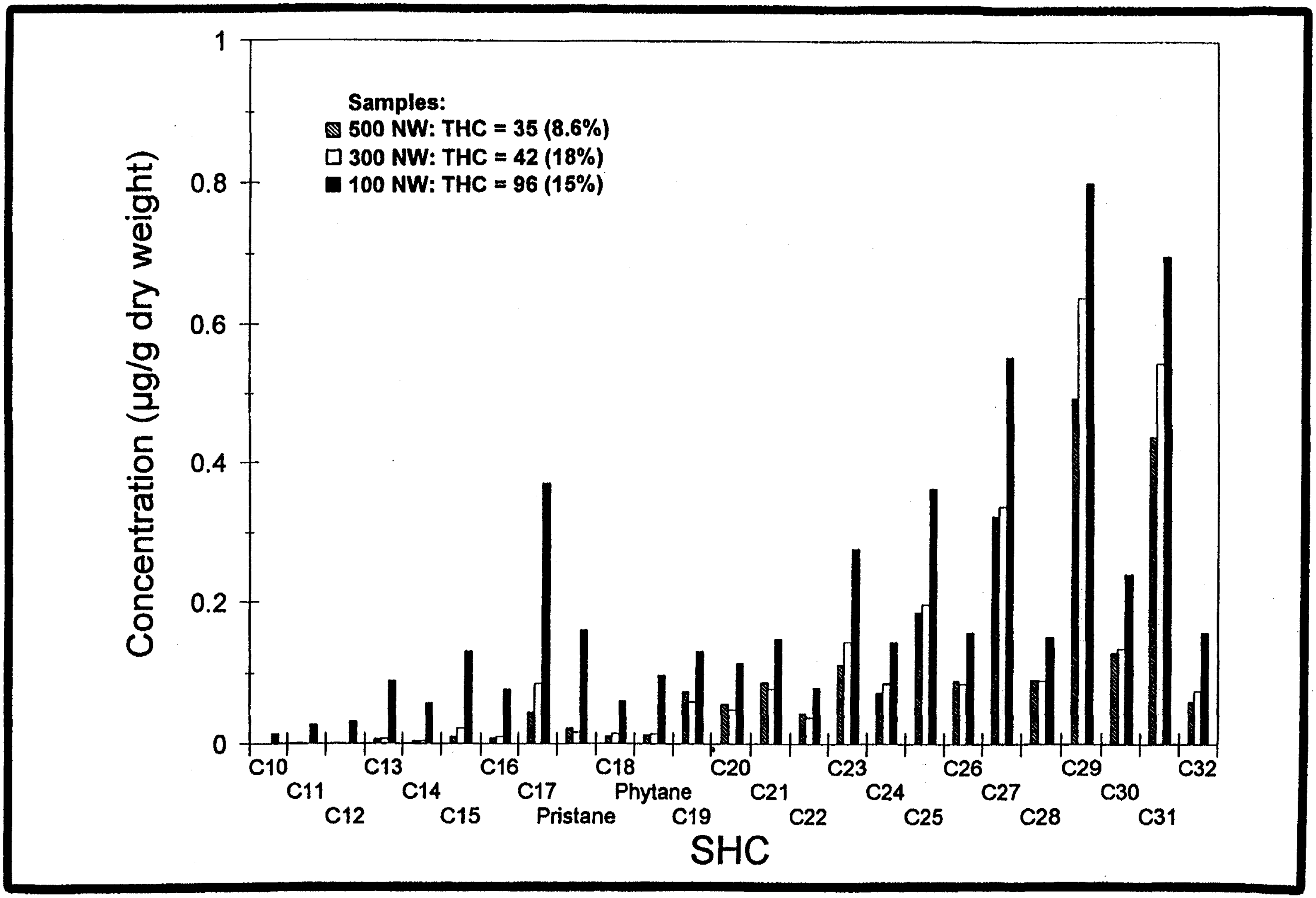

Figure 8.15. SHC distributions in sediments from the northwest transect of Delacroix Island collected during the Pre-termination Survey (Survey I).

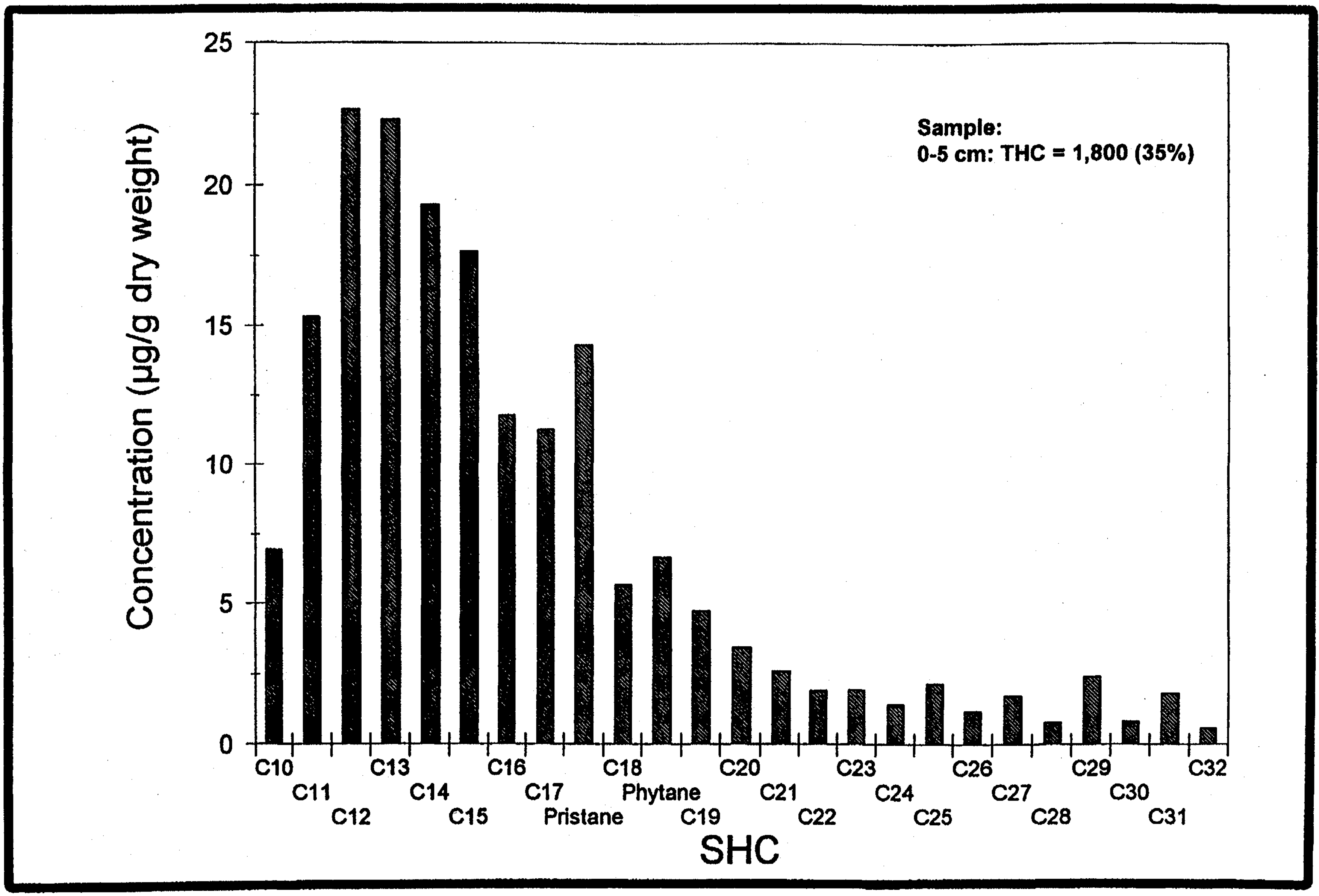

Figure 8.16. SHC distributions in sediments from the discharge station of Delacroix Island collected during the Pre-termination Survey (Survey I).

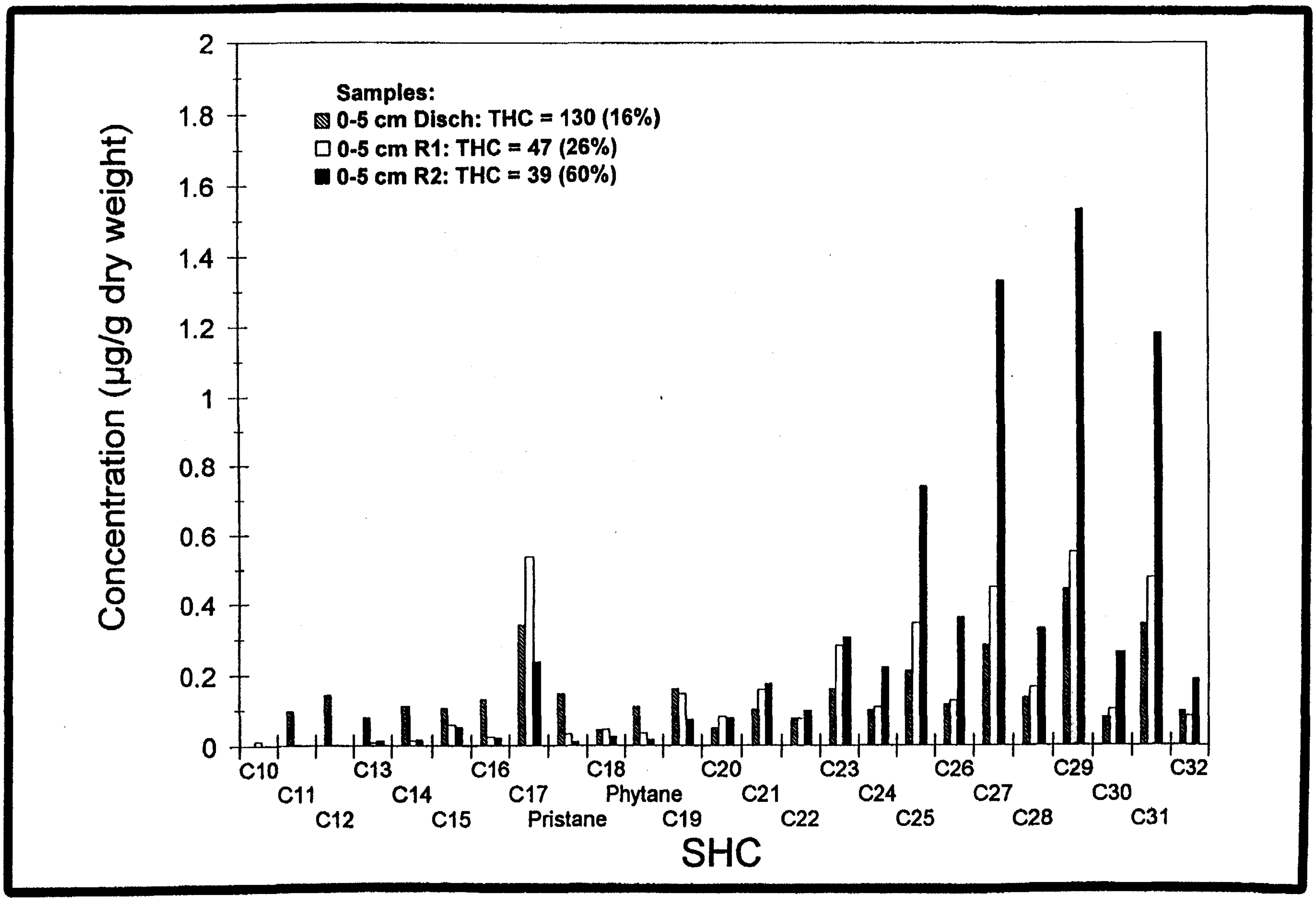

Figure 8.17. SHC distributions in sediments from the discharge and reference stations of Delacroix Island collected during the First Post-termination Survey (Survey II).

sediments in these Post-termination Surveys were collected from the same area as during the Pre-termination Survey, loss of the lower molecular weight SHCs including the isoprenoids indicates fairly rapid microbial degradation in this environment.

In all sediments, but to a lesser extent in the reference sediments, the UCM dominated total hydrocarbon content. UCM content in reference sediments ranged from 40% to 75% of the THCs, whereas at the other stations UCM made up 80% to 90% of the THCs. In most sediment environments large UCM are indicative of petroleum inputs (fresh and/or weathered residual oil); however in this environment where the biogenic load is very high, non-petroleum, humic-type material may be contributing to the UCM. The presence of UCM at the reference station provides some evidence of a natural and/or chronic contamination contribution of complex compound content in these coastal sediments.

In reviewing the hydrocarbon results, it was expected that the increased PAH concentrations at the stations close to the discharge at Delacroix Island would reflect increases in petrogenic PAHs. However, except for the sediments at the discharge station before discharge termination, the increased PAHs were due principally to inputs of pyrogenic PAHs, not petrogenic PAHs. Representative PAH distributions of this pyrogenic input are provided in **Figures 8.18** through **8.21**.

Characteristic of pyrogenic sources, the PAH distributions showed a dominance of the four- through six-ring PAHs, especially fluoranthene, pyrene, chrysene, benzo(a)anthracene, and benz(b)fluoranthene. Also, the alkyl homologues of the three- to six-ring PAHs had a dominant parent compound abundance with decreasing alkyl abundances as alkylation increased ($C_0 > C_1 > C_2 > C_3 > C_4$).

Except for surface sediments from the Pre-termination Survey (Survey I), sediment at the discharge location was dominated by pyrogenic PAHs (**Figures 8.22** through **8.24**). From 70% to 90% of the total PAHs were attributed to four- through six-ring pyrogenic PAHs. The deeper sediment, especially in Survey III (**Figure 8.24**), contained more of the less volatile two- and three-ring pyrogenic PAHs such as acenaphthene, anthracene, and phenanthrene. These distributions showed negligible amounts of the PAH characteristic of petrogenic PAHs, where alkyl group would dominate.

Significant amounts of petrogenic PAHs (>80% of total PAHs) were only evident in the pre-termination discharge sediments, but precipitously decreased with time. High naphthalenes concentrations (approximately 50% of total PAHs) indicated that the input was fresh and representative of the relatively high concentrations of naphthalenes in produced water. The diagnostic ratios of C2P/C2D and C3P/C3D were 3.6 and 2.5, not similar to produced water ratios (**Table 8.5**), but similar to Louisiana-type crude oils. These diagnostic ratios were maintained in the Survey II sediments but the contribution of the petrogenic PAHs were considered lower than the contribution from the pyrogenic PAHs (**Figure 8.23**). The petrogenic PAH signature was essentially lost in Survey III sediments (**Figure 8.24**) and similar to the other sediments 100 m from the facility (**Figure 8.25**).

VAH compounds, benzene, ethylbenzene, and xylenes, were found in sediments at the discharge station before termination of the discharge at concentrations of 91, 69, and 420 ng/g which all decreased to <1 ng/g a year later (**Table 8.6**). This concentration trend corresponded to the petrogenic PAHs in the discharge sediments. No VAHs were detected in the reference sediments.

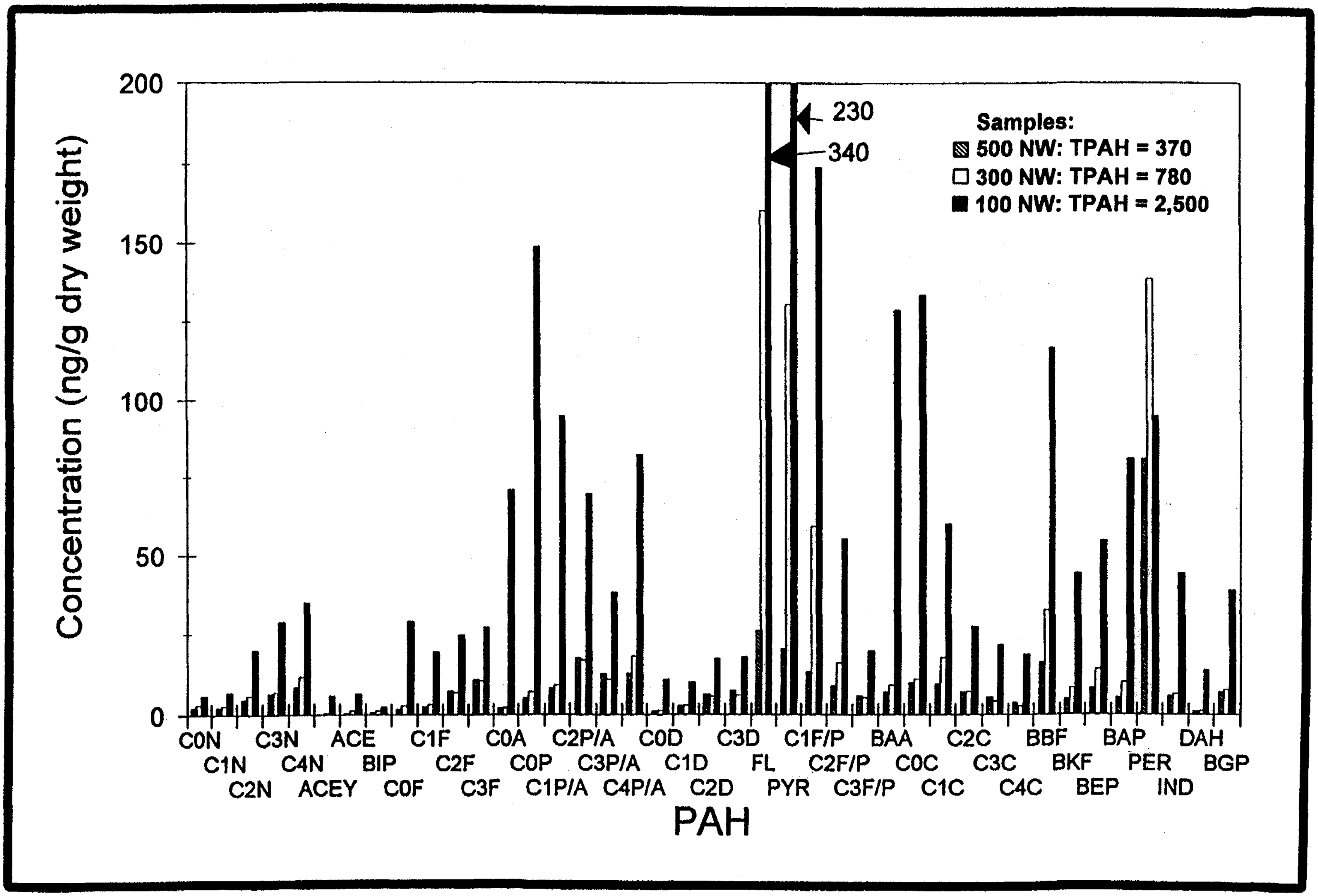

Figure 8.18. PAH distributions in sediments from the northwest transect of Delacroix Island collected during the Pre-termination Survey (Survey I).

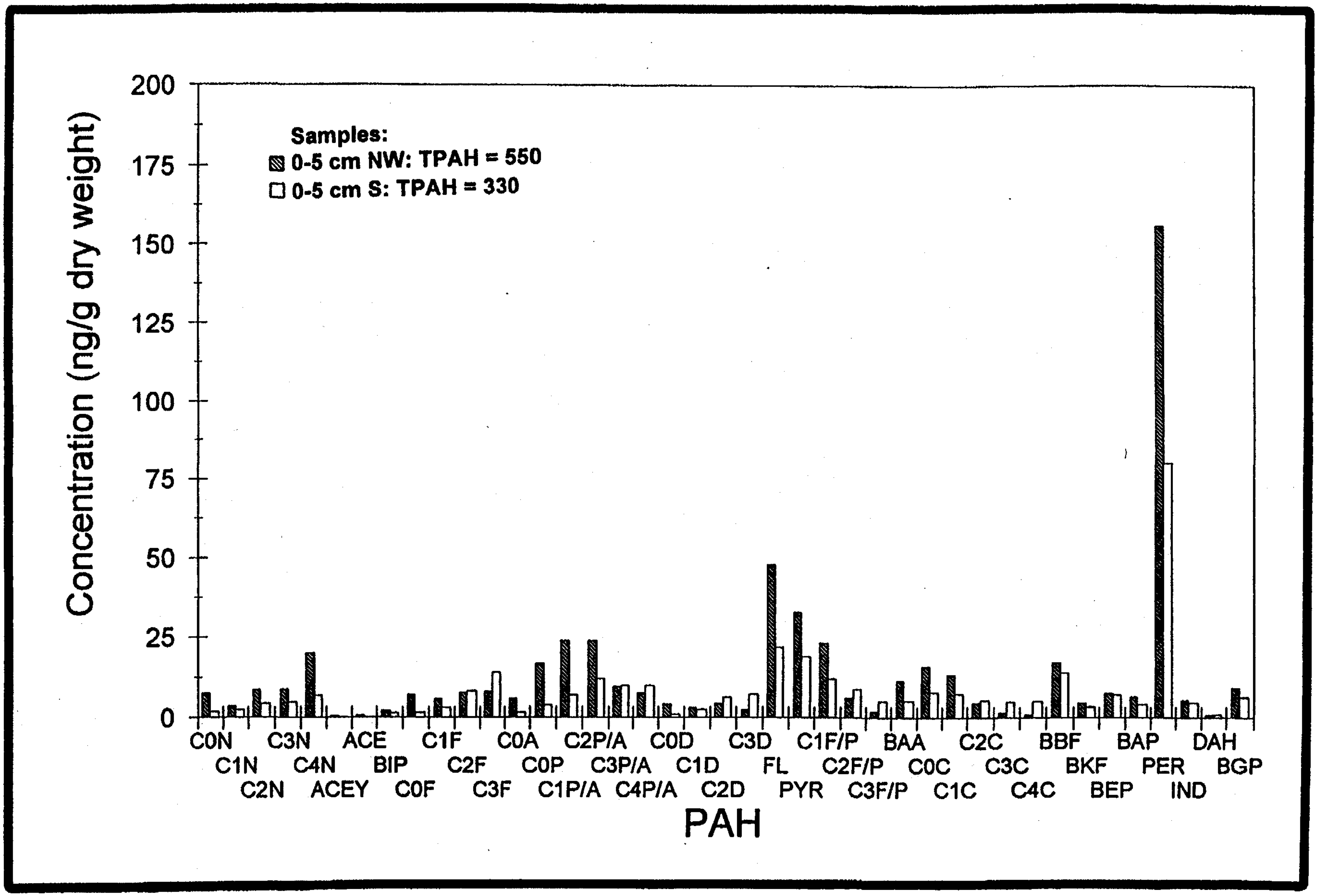

Figure 8.19. PAH distributions in sediments from the 1000 m northwest and south stations of Delacroix Island collected during the Pre-termination Survey (Survey I).

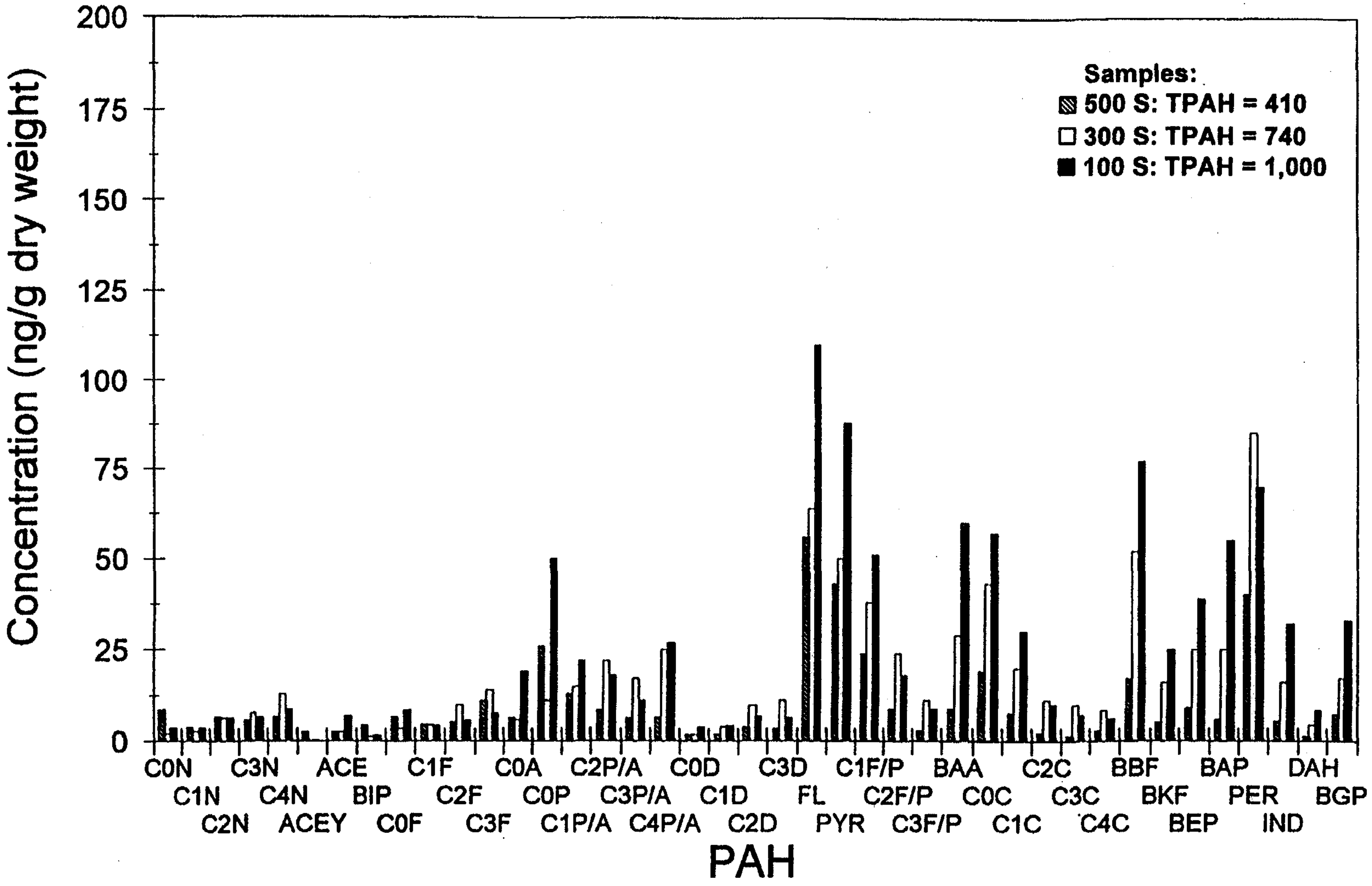

Figure 8.20. PAH distributions in sediments from the south transect of Delacroix Island collected during the Pre-termination Survey (Survey I).

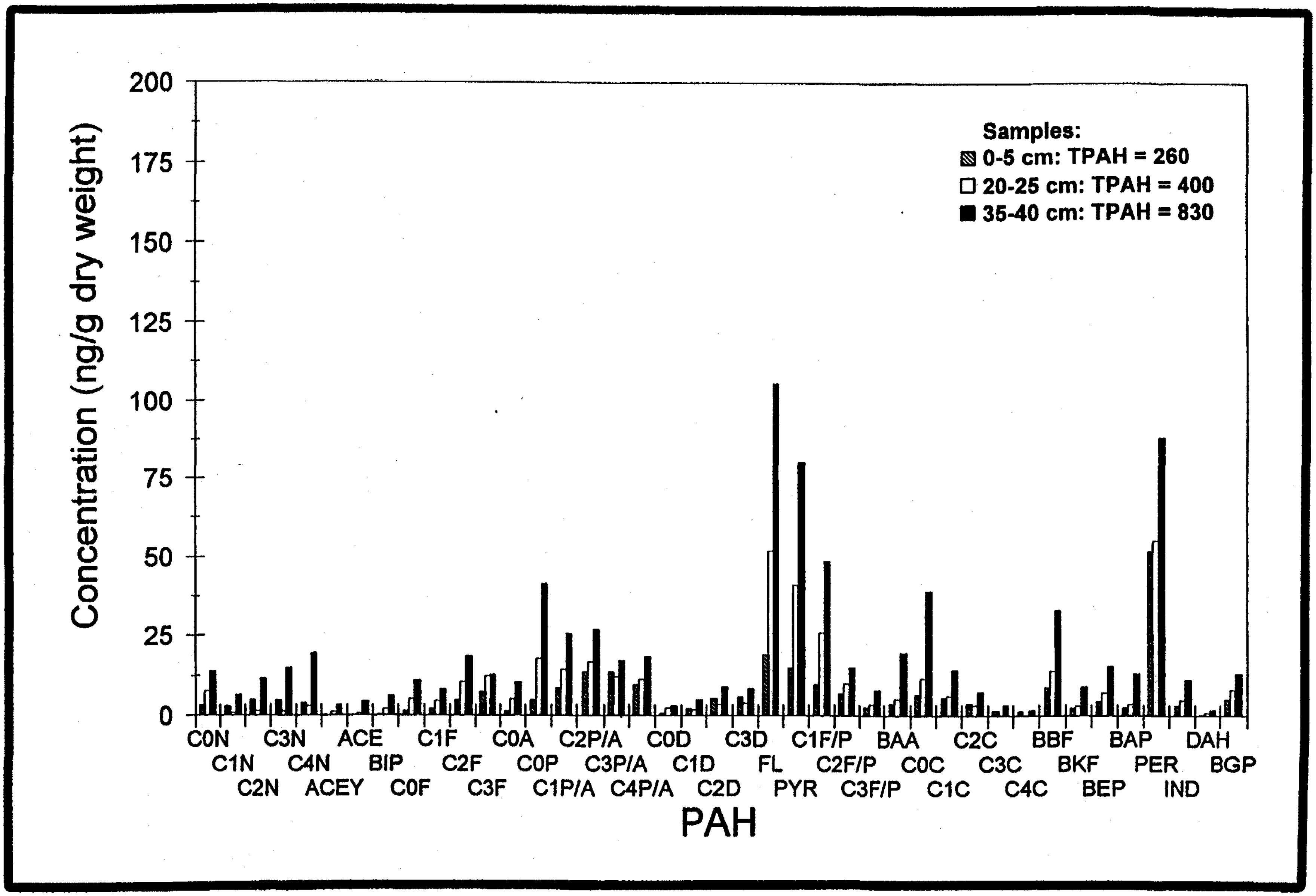

Figure 8.21. PAH distributions in sediments from the reference 2 station of Delacroix Island collected during the Pre-termination Survey (Survey I).

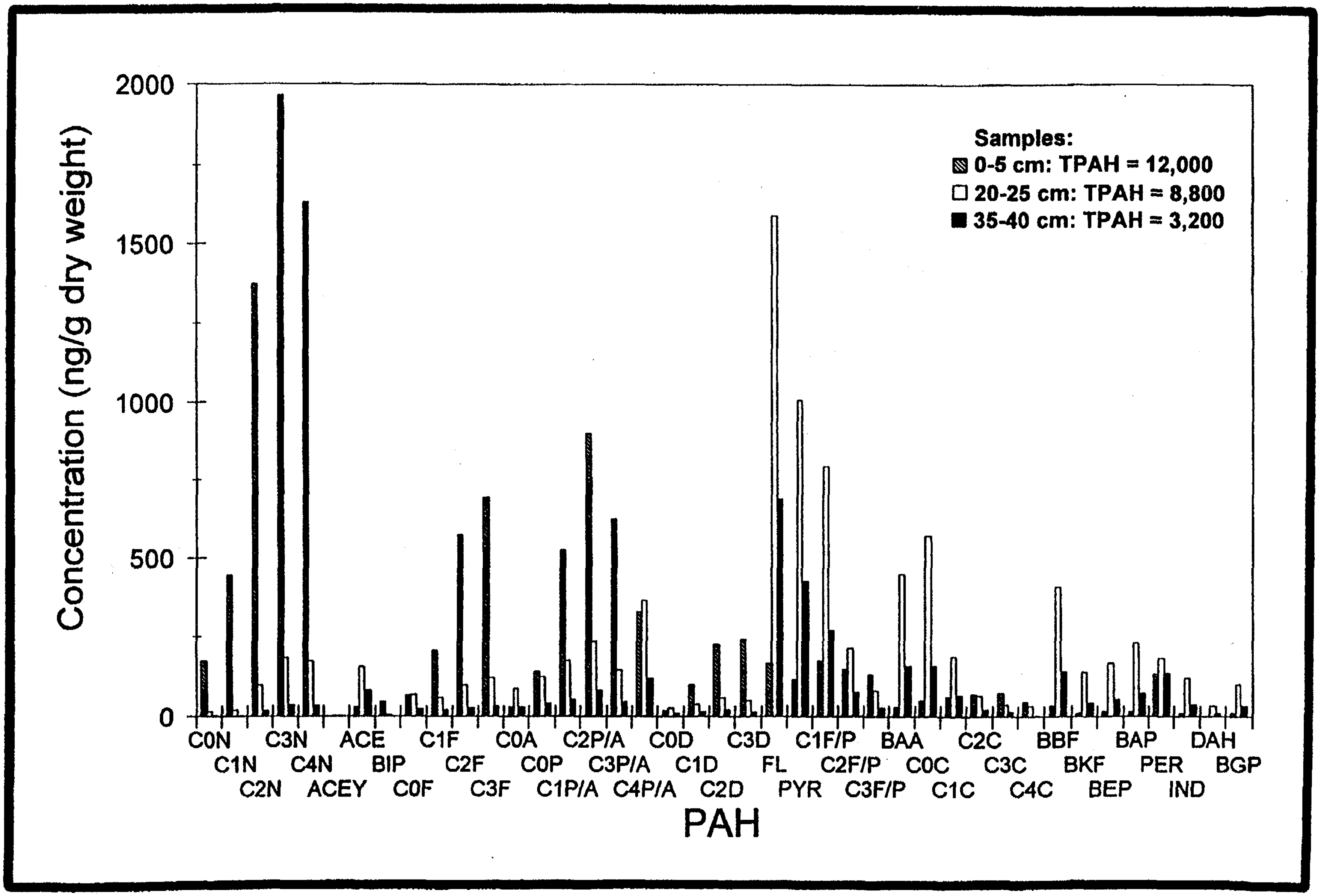

Figure 8.22. PAH distributions in sediments from the discharge station of Delacroix Island collected during the Pre-termination Survey (Survey I).

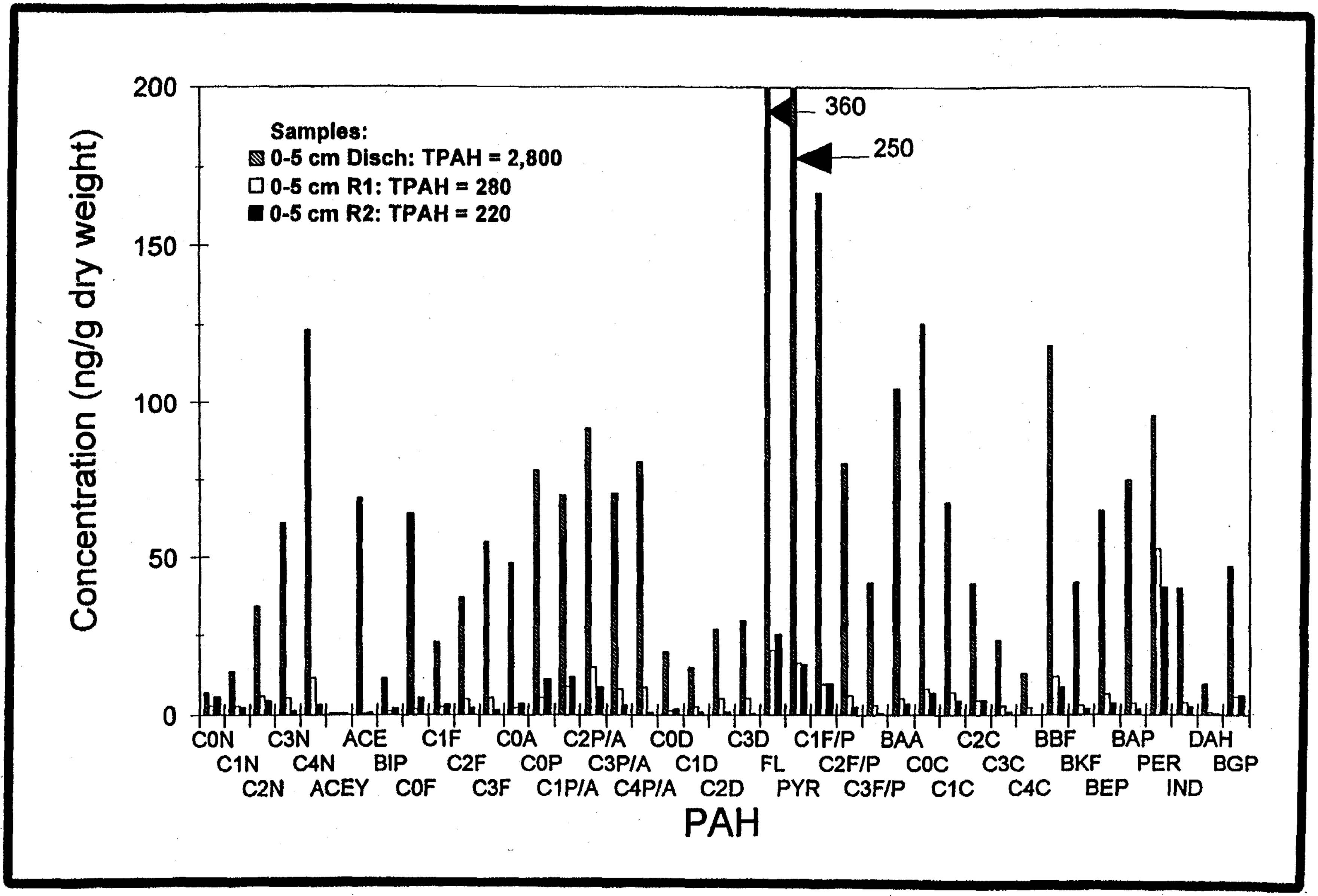

Figure 8.23. PAH distributions in sediments from the discharge and reference stations of Delacroix Island collected during the First Post-termination Survey (Survey II).

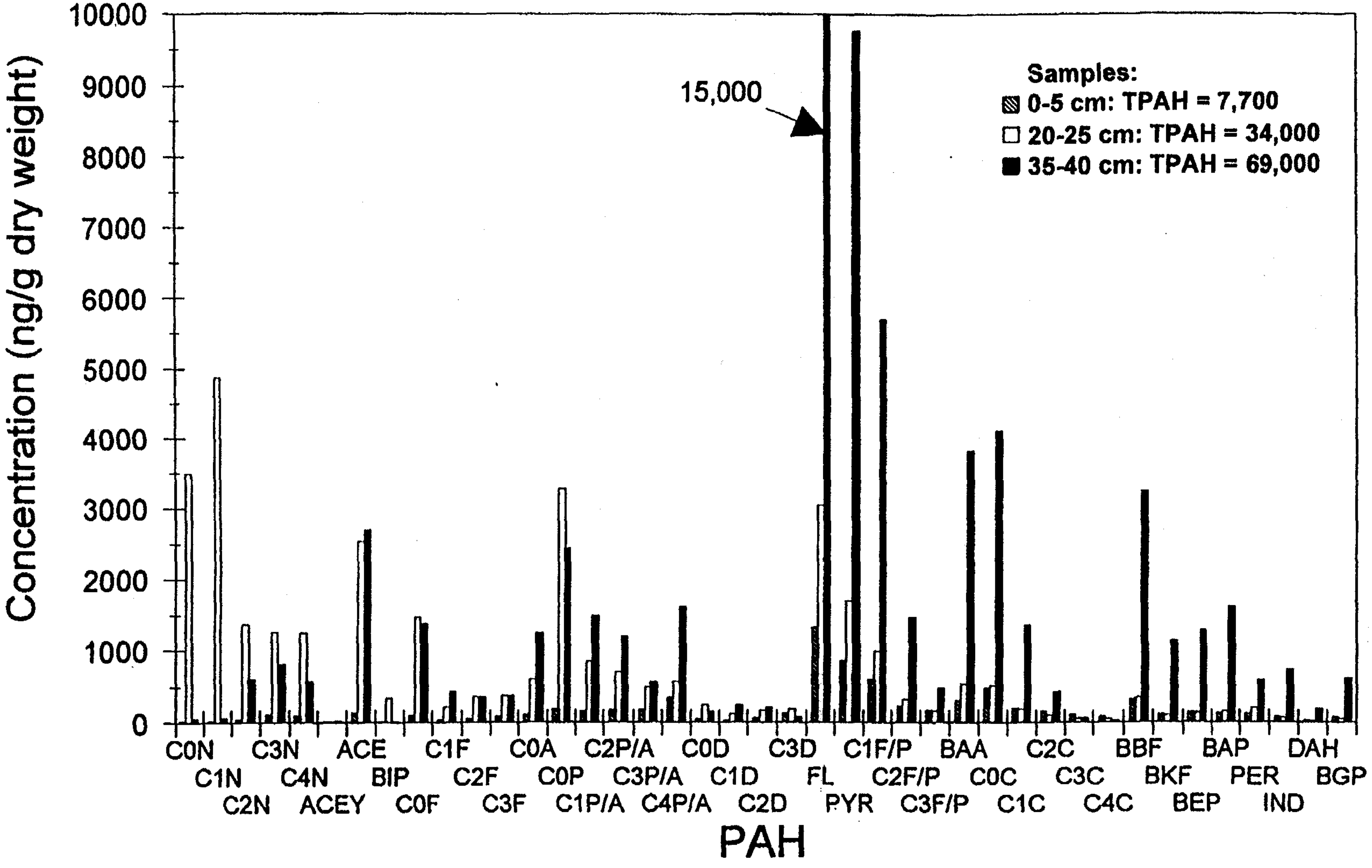

Figure 8.24. PAH distributions in sediments from the discharge station of Delacroix Island collected during the Second Post-termination Survey (Survey III).

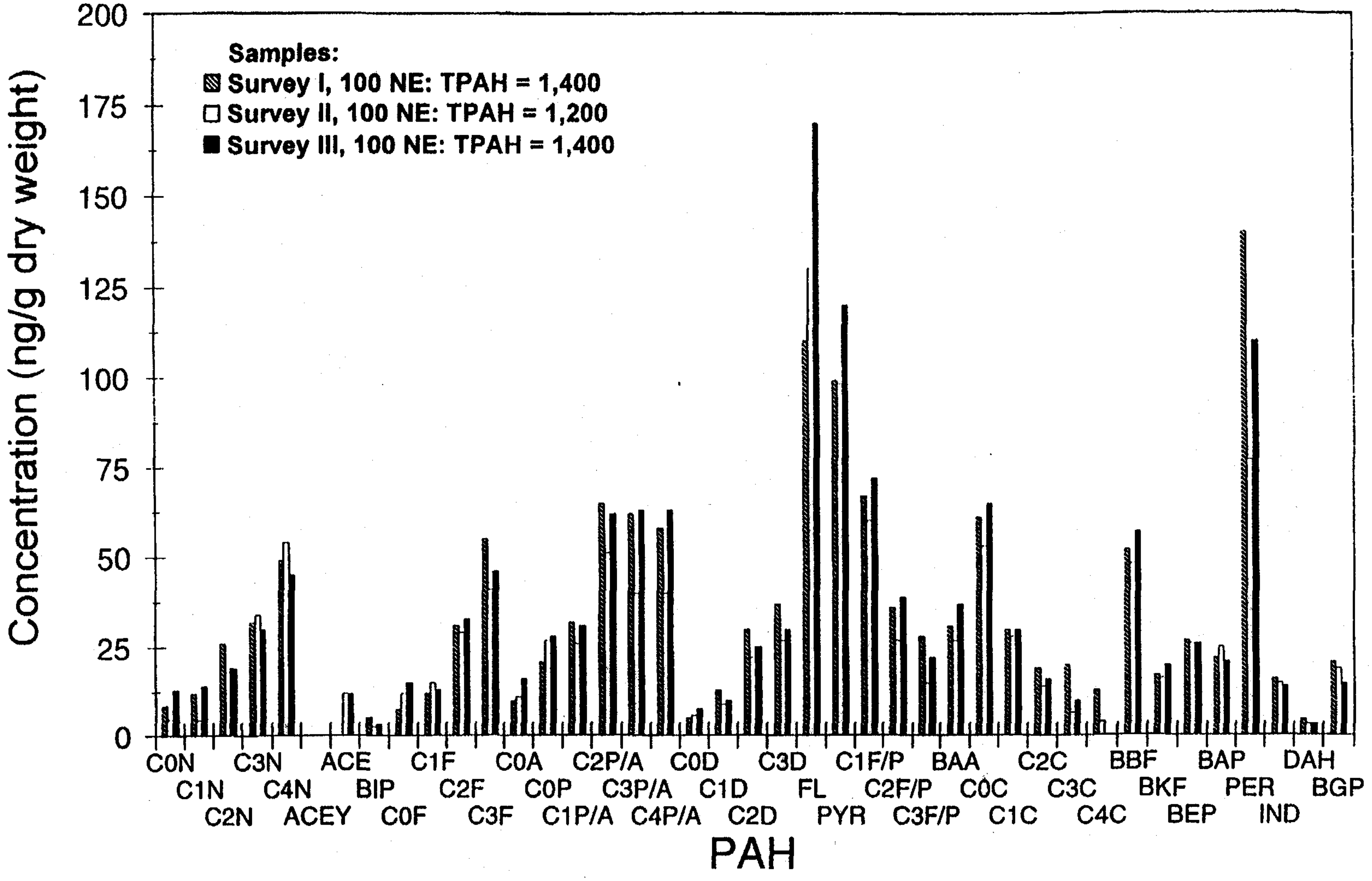

Figure 8.25. PAH distributions in sediments from the 100 m northeast station of Delacroix Island collected during all surveys (Surveys I to III).

Very few PAHs, mostly naphthalenes and C_1-naphthalenes, were detected in sediment interstitial waters of discharge and reference stations (**Table 8.7**). No samples were collected for interstitial water analysis at the other site locations. Concentrations were highest in the pre-termination interstitial waters at approximately 1,000 ng/L. Most replicates had non-detectable amounts of PAHs. Only one reference replicate contained PAHs and had concentrations of naphthalenes similar to the discharge sediments. A year after discharge termination (Survey III), PAH (naphthalenes and phenanthrene) concentrations decreased to approximately 20 to 100 ng/L. These PAHs were present in most replicates of both discharge and reference interstitial waters.

Only at the northeast transect of the 100 and 300 m stations was there a contribution of petrogenic PAHs (**Figures 8.25** and **8.26**). Concentrations of the alkyl groups of the two- and three-ring PAHs increased with increasing alkylation. Concentrations of the alkyl PAHs were higher (25 to 50 ng/g individual PAHs) compared to other more distant sediments (5 to 20 ng/g individual PAHs), and PAH diagnostic ratios C2P/C2D and C3P/C3D of the 100 m northeast sediments were consistently 2.3 and 1.8, respectively, for all Pre- and Post-termination Surveys. The diagnostic ratio values were similar to the sediment ratios at the discharge station.

Sediment at the 300 m station on the northeast transect, however, showed a consistent (Pre- and Post-termination Surveys) dominance of the alkyl groups of the three-ring PAHs relative to the pyrogenic PAHs (**Figures 8.26** through **8.28**), not evident in the other sediments. Similar three-ring PAH distributions and concentrations were evident at 100 m northeast and to a lesser degree in the discharge sediments, but, unlike 300 m northeast sediments, were dominated by the pyrogenic PAHs. This consistency in PAH composition from both Pre- to Post-termination Surveys indicated another possible source of petrogenic PAHs in this area of the study site.

The PAH signature of the pyrogenic PAHs resembles that of a weathered creosote or coal tar (**Figure 8.1**). Creosote, which is a distillation product of coal tar, is used as a preservative for wood pilings and timber. Oil field facilities in coastal regions such as the Delacroix Island field were often constructed of wood that was commonly treated with preservative (creosote and perhaps other wood preservatives). These pyrogenic PAHs also resemble signatures associated with products of fossil fuel combustion which should be considered as a potential source.

Because of larger concentrations of pyrogenic PAHs near the facility, the major source of PAHs in the study area was probably originating from the facility. The potential source is creosote. Although creosote itself does not contain a UCM or SHC compounds found in the sediments, fuel oil, such as No. 2 (diesel) fuel oil or No. 6 (Bunker C) fuel oil, which contains a UCM and SHC compounds is often mixed with creosote in its application to the lumber. However in most sediments, biogenic SHCs dominated the sediment hydrocarbon composition, not petrogenic SHCs; UCM was though clearly present in all samples.

Results of the principle component analysis for each of the surveys are shown in scores (sample station) plots in **Figures 8.29** through **8.31**. A representative load (PAH compound variables) plot for the three surveys, which were very similar, is shown as an insert in

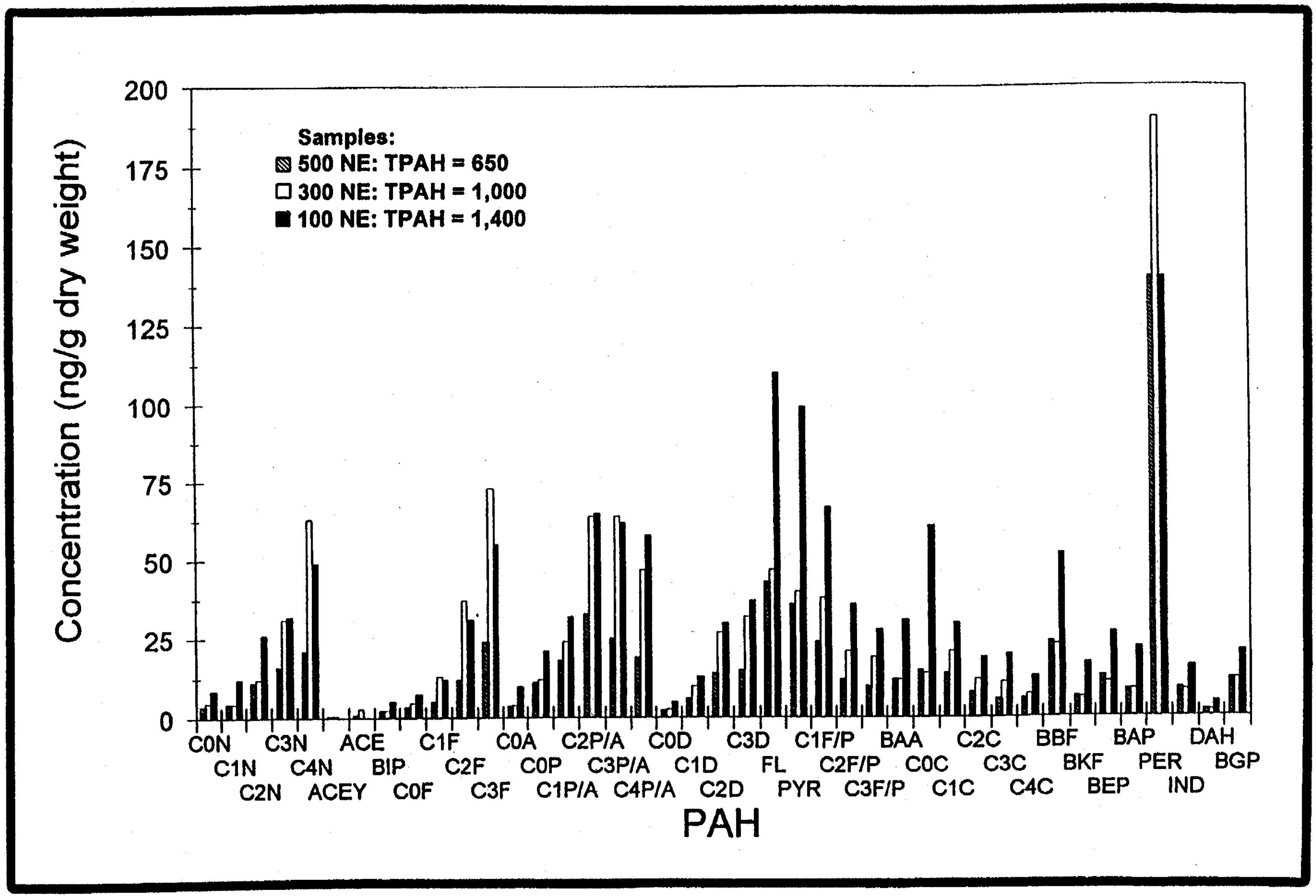

Figure 8.26. PAH distributions in sediments from the northeast transect of Delacroix Island collected during the Pre-termination Survey (Survey I).

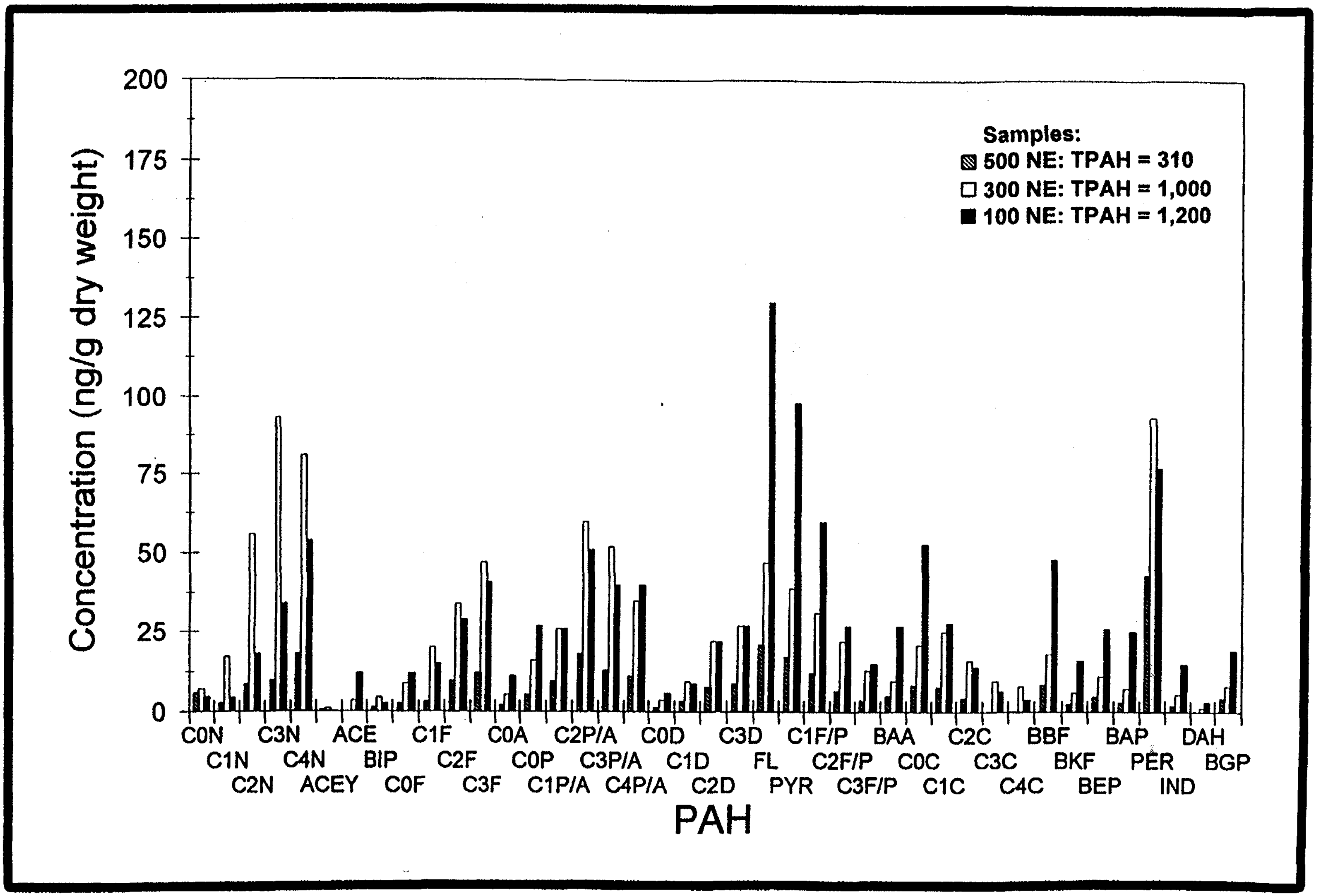

Figure 8.27. PAH distributions in sediments from the northeast transect of Delacroix Island collected during the First Post-termination Survey (Survey II).

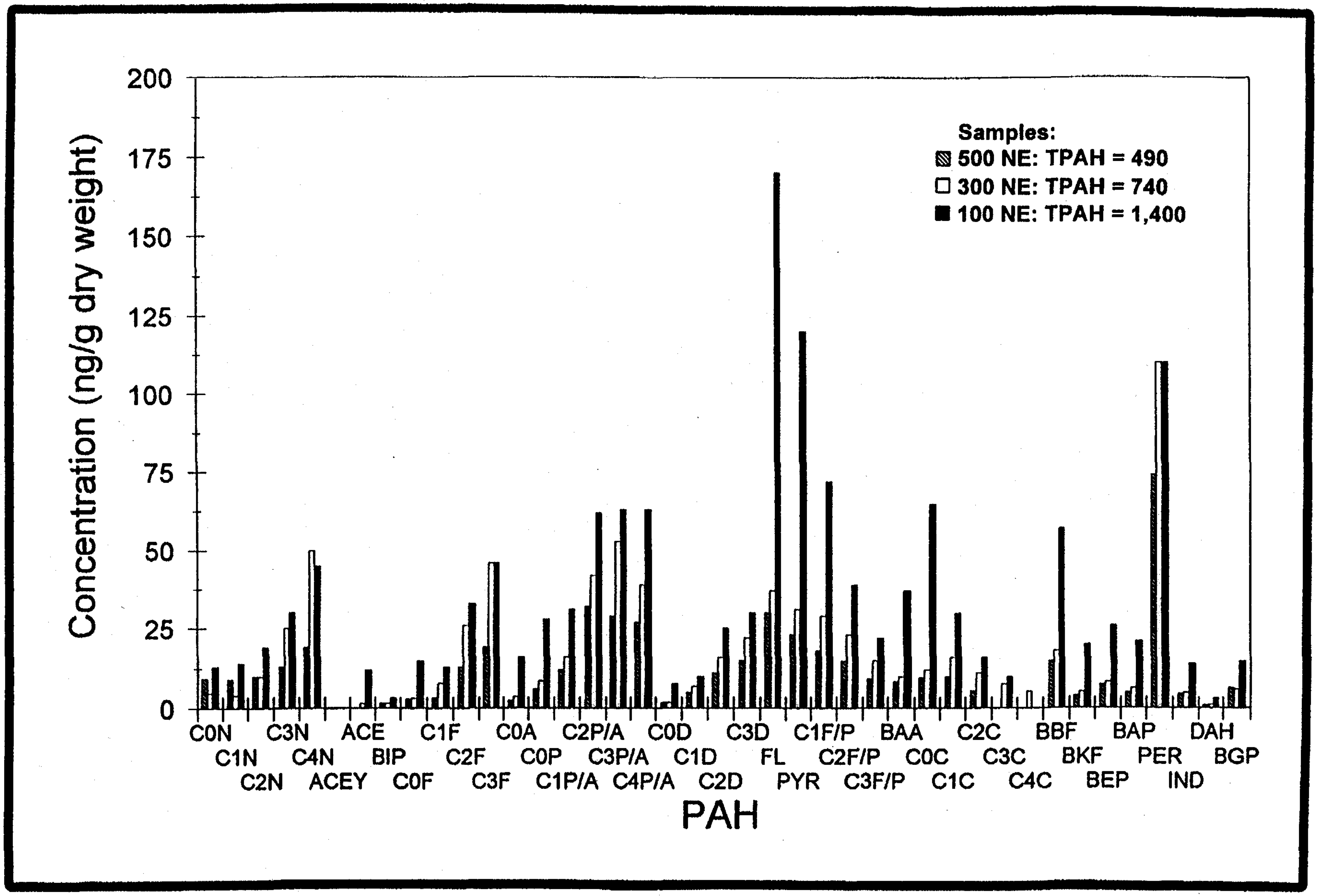

Figure 8.28. PAH distributions in sediments from the northeast transect of Delacroix Island collected during the Second Post-termination Survey (Survey III).

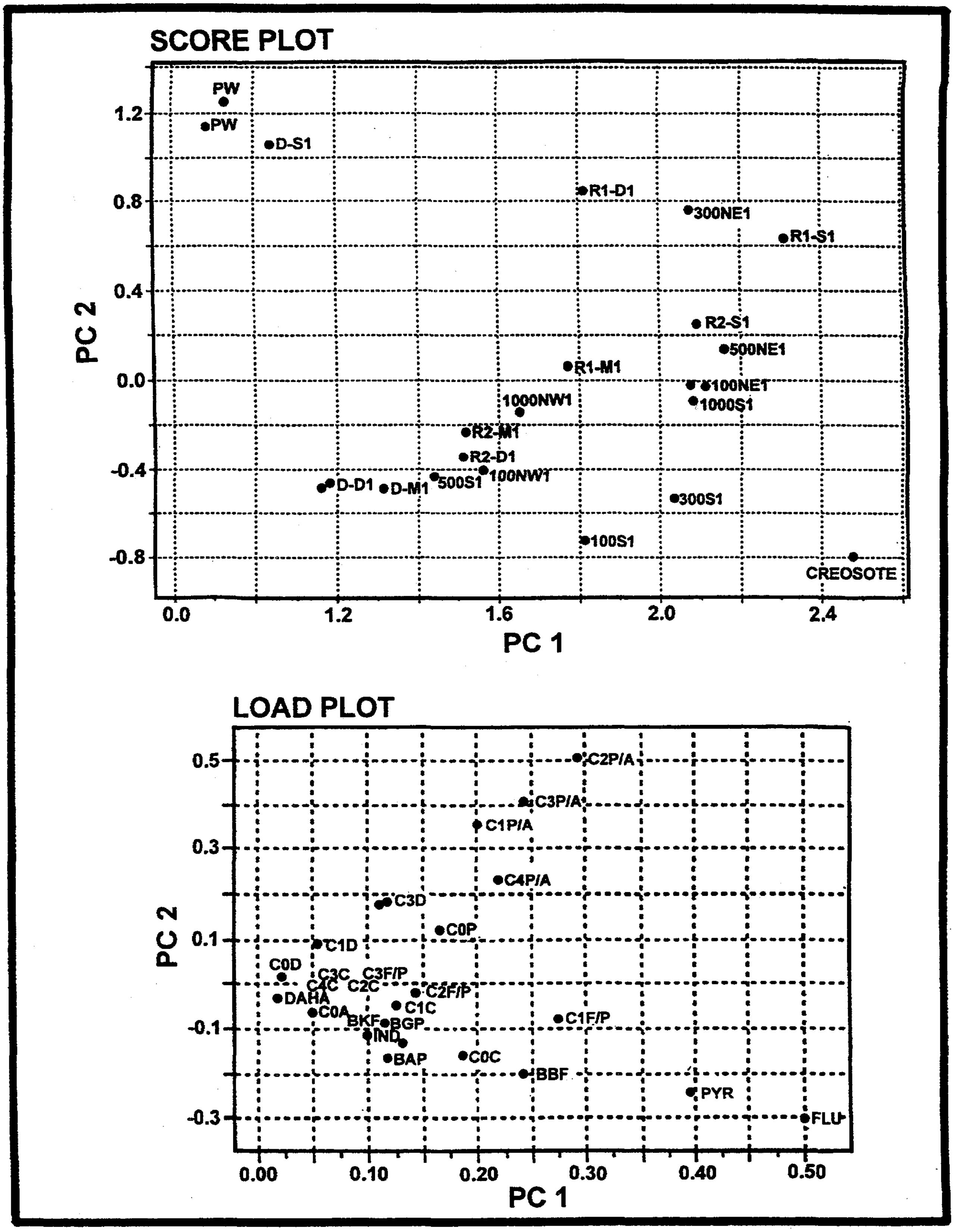

Figure 8.29. Principle component analysis plot of PAH data of produced water (PW) and sediments from Delacroix Island collected during the Pre-termination Survey (Survey I). PAHs (less naphthalenes, fluorenes, and perylene) were normalized by the highest concentration PAH in each sample. Score plot presents sediment stations (D - discharge, R - reference, and distance/compass heading), sediment increment (S - 0 to 5 cm, M - 20 to 25 cm, and D - 35 to 40 cm), and survey designation (1). Load plot presents PAH acronyms which are defined in **Table 8.1.**

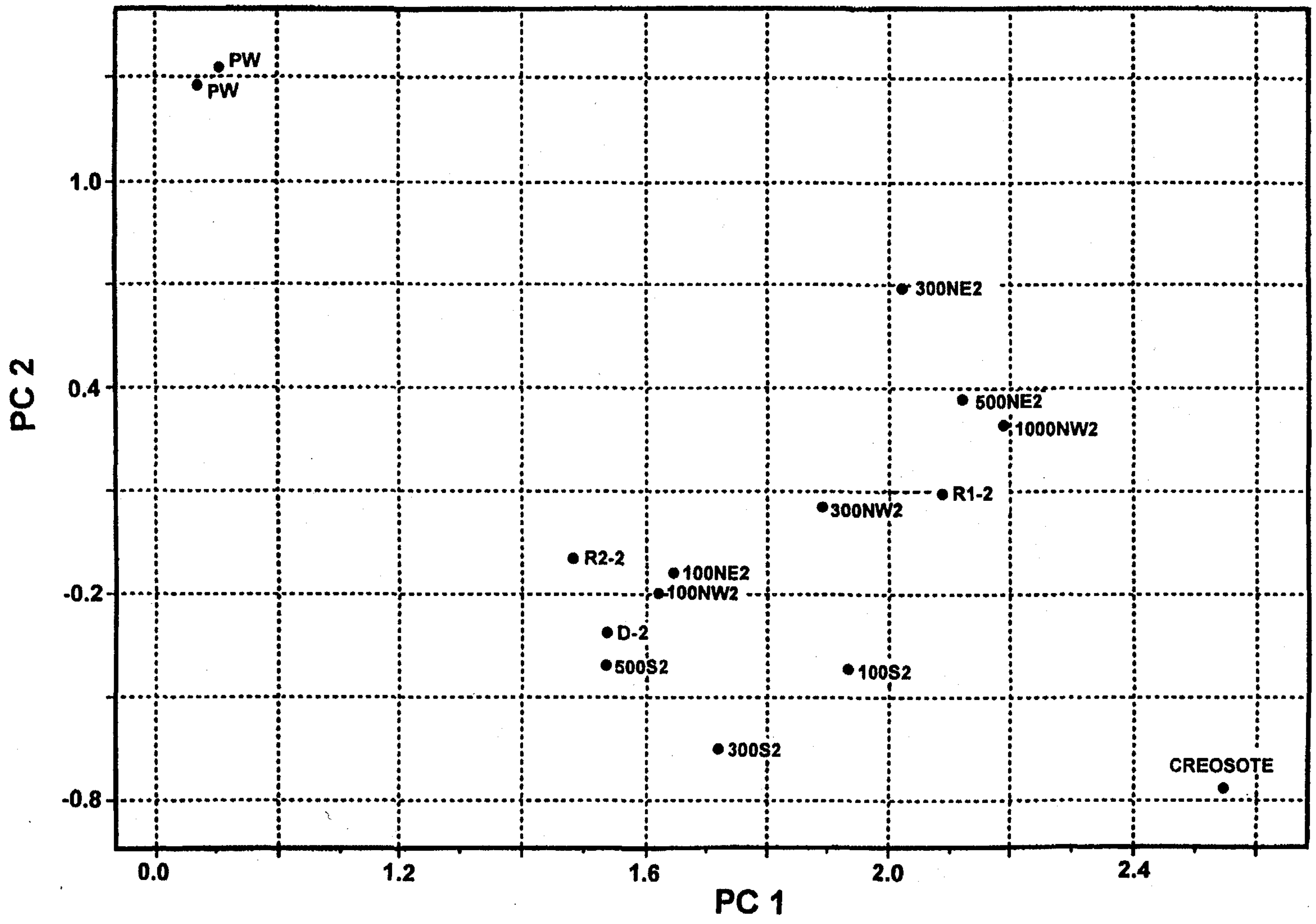

Figure 8.30. Principle component analysis plot of PAH data of produced water (PW) and sediments (0 to 5 cm) from Delacroix Island collected during the First Post-termination Survey (Survey II). PAHs (less naphthalenes, fluorenes, and perylene) were normalized by the highest concentration PAH in each sample. Plot presents sediment stations (D - discharge, R1 - reference 1, R2 - reference 2, and distance/compass heading) and survey designation (2).

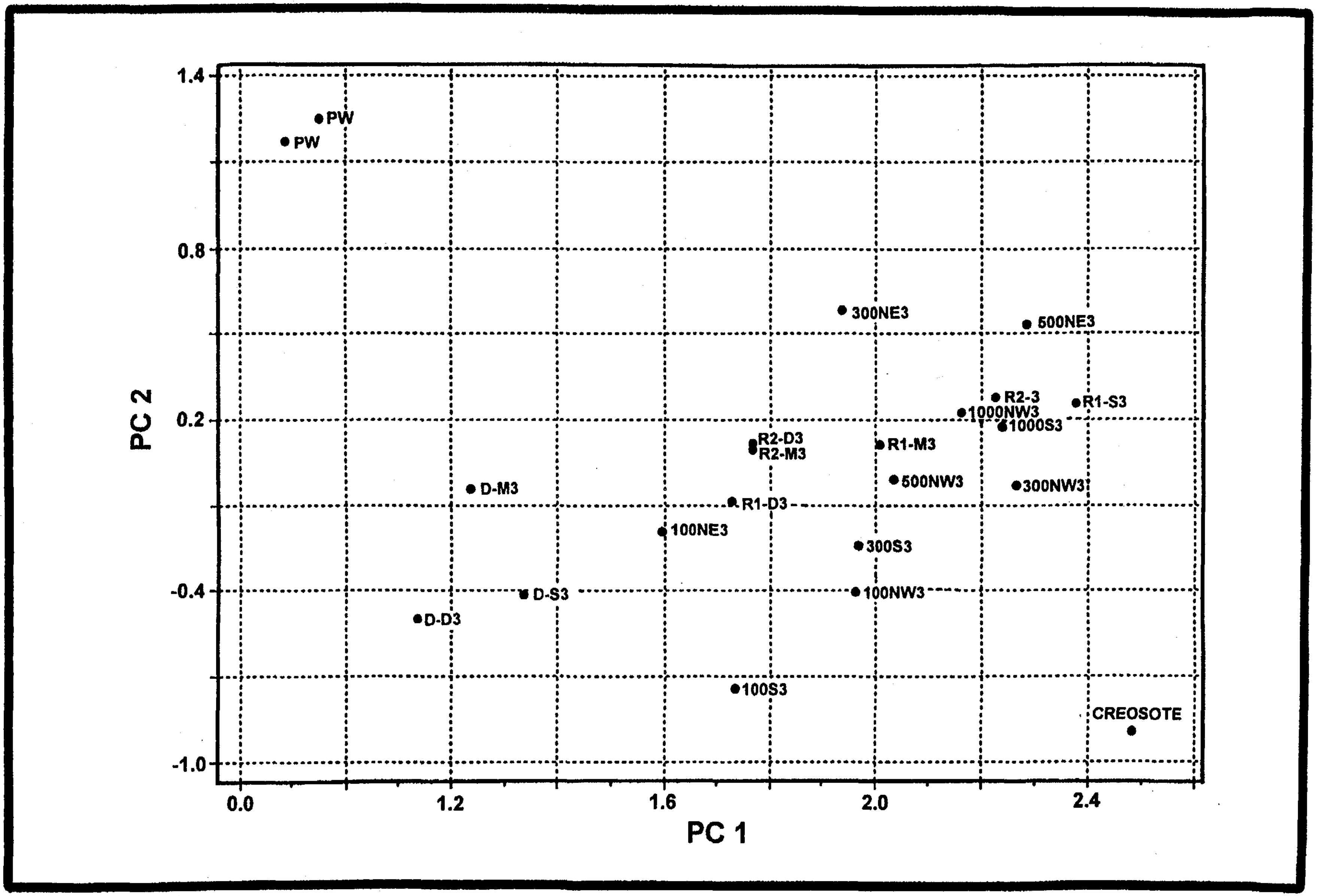

Figure 8.31. Principle component analysis plot of PAH data of produced water (PW) and sediments from Delacroix Island collected during the Second Post-termination Survey (Survey III). PAHs (less naphthalenes, fluorenes, and perylene) were normalized by the highest concentration in each sample. Plot presents sediment stations (D - discharge, R1 - reference 1, R2 - reference 2, and distance/compass heading), sediment increment (S - 0 to 5 cm), M - 20 to 25 cm, and D - 35 to 40 cm), and survey designation (3).

Figure 8.29. A PAH distribution representing a typical creosote sample was included in the analysis.

Except for surface sediments at the discharge location of the Pre-termination Survey, PAH distributions at each of the locations were generally similar from survey to survey. The only sediment positioned near the produced water (PW) samples was the surface sediment at the discharge station collected before discharge termination and this confirmed the observation of dominant petrogenic PAHs in that sample. The positions of the other sediment samples were different than the Survey I discharge station sediment, and generally reflected varying contributions of pyrogenic PAHs. Differences in PAH composition could be loosely grouped into four areas: discharge and 100 m sediments, northeast sediments, northwest sediments, and south sediments. Reference sediments did not cluster together nor were they part of one group as would be expected. None of the post-termination discharge sediments, both at the surface and subsurface, were similar to the surface discharge sediment of the Pre-termination Survey.

The load plot (**Figure 8.29**) that indicates the relative influence of the individual PAHs on the position of the samples in the scores plot showed the dominance of pyrogenic PAHs in samples below the zero axis of the PC2 component and the influence of petrogenic PAHs above the zero axis of the PC2 component. The positions of the produced water samples were driven by the alkyl groups of two- and 3-ring PAHs; the position of the creosote sample was driven by the four- and five-ring PAHs, especially of pyrene and fluoranthene. The sediments of Delacroix Island contained the attributes of both the petrogenic alkyl homologues and the pyrogenic four- through six-ring PAHs and as a result the positions in the PCA plot reflected differences in the relative amounts of the pyrogenic PAHs in the sediments similar to creosote. The relative amounts of pyrogenic PAH contributions in these sediments seemed to be the only major driving variables in the plots, even in the sediments nearest the discharge facility.

8.3.2.2 Bay de Chene

Unlike Delacroix Island, sediments at Bay de Chene had both spatial and temporal hydrocarbon concentration trends (**Table 8.9**). Although reference and 1,000 m stations surface sediments had similar hydrocarbon concentrations, which ranged from 32 to 93 ng/g for THCs and 230 to 390 ng/g for PAHs, hydrocarbon concentrations increased gradually as one approached the facility. Concentrations (THCs) were approximately 10 times higher at the 100 m stations than the outer 1,000 m stations. This trend was observed in all surveys.

The northeast transect had the highest hydrocarbon concentrations ranging from approximately 1,000 μg/g THCs and 50,000 ng/g total PAHs at 100 m to 100 μg/g THCs and 500 ng/g total PAHs at 1,000 m. The northeast hydrocarbon concentrations were generally 5 to 10 times higher than northwest or southwest sediment concentrations. Concentrations of THCs and PAHs decreased in northeast and northwest sediments from Pre- to Post-termination Surveys. Southwest sediments which contained lower pre-termination hydrocarbon concentrations than the other transects showed an increase in hydrocarbon concentration with time. By the time of the Second Post-termination Survey, southwest hydrocarbon concentrations were similar to northwest concentrations.

Table 8.9. Summary of THC (μg/g) and TPAH (ng/g) concentrations in sediments collected during the Pre-termination (Survey I), First Post-termination (Survey II), and Second Post-termination (Survey III) Surveys from Bay de Chene.

Distance (m)	Direction	Analyte Group	Survey I	Survey II	Survey III
R1	0-5 cm	THC	45	37	64
		TPAH	300	420	300
	20-25 cm	THC	–	–	–
		TPAH	570	–	–
	35-40 cm	THC	–	–	–
		TPAH	560	–	–
R2	0-5 cm	THC	56	32	93
		TPAH	490	230	350
	20-25 cm	THC	–	–	–
		TPAH	340	–	–
	35-40 cm	THC	–	–	–
		TPAH	290	–	–
1000 m	NE	THC	51	74	180
		TPAH	260	470	640
	NW	THC	58	33	160
		TPAH	260	290	270
	SE	THC	41	83	180
		TPAH	390	670	1,100
	SW	THC	75	43	170
		TPAH	560	340	390
500 m	NE	THC	120	140	150
		TPAH	920	1,300	610
	NW	THC	110	67	91
		TPAH	860	560	440
	SE	THC	24	44	51
		TPAH	320	150	370
	SW	THC	23	34	160
		TPAH	270	550	580
300 m	NE	THC	260	250	260
		TPAH	9,200	7,200	5,800
	NW	THC	180	110	240
		TPAH	4,000	2,300	1,100
	SE	THC	–	–	–
		TPAH	–	–	–
	SW	THC	66	110	220
		TPAH	440	990	930

Table 8.9. (Continued).

Distance (m)	Direction	Analyte Group	Survey I	Survey II	Survey III
100 m	NE	THC TPAH	510 35,000	930 80,000	1,800 66,000
	NW	THC TPAH	680 5,300	480 5,000	950 3,600
	SE	THC TPAH	– –	– –	– –
	SW	THC TPAH	270 2,100	230 2,400	440 3,900
Discharge	0-5 cm	THC TPAH	1,500 72,000	570 9,600	960 8,300
	20-25 cm	THC TPAH	– 26,000	– –	– –
	35-40 cm	THC TPAH	– 40,000	– –	– –

At the discharge station, the PAH concentrations were significantly higher in sediments before discharge termination (72,000 ng/g total PAHs), but decreased nearly an order of magnitude after termination. High PAH concentrations were maintained in the subsurface sediments at the discharge (26,000 to 40,000 ng/g).

In the outer stations (300, 500, and 1,000 m) of Bay de Chene, sediment SHC distribution and UCM content were very similar to those of Delacroix Island. Example SHC distributions are presented in **Figures 8.32** through **8.35**. Consistent in all surveys, the SHC signature was representative of hydrocarbons from a biogenic origin.

At the inner 100 m sample locations, petrogenic SHC signatures were more evident, especially in sediments from the northeast transect (**Figure 8.36**). The odd/even n-alkane preference ratios were near to one, the isoprenoids were more prevalent, and relatively higher concentrations of the low molecular weight SHCs were present. The petrogenic SHC signature was typical of a weathered petroleum and was superimposed on an approximately equal contribution of biogenic SHCs. These SHC distributions were consistent in sediments from all three surveys (**Figure 8.37**). The petrogenic low molecular weight SHCs in Survey III sediments were, however, slightly more weathered than those of the Survey I sediments (**Figure 8.36**).

Similar to Delacroix Island, sediment at the discharge station showed a dominance of a petrogenic hydrocarbon evident by the relatively high concentration of the low molecular weight SHCs (**Figure 8.38**). This signature was prevalent in all three survey sediments with a slight decrease in the post-termination sediments (**Figure 8.39**). This petrogenic SHC signature of low-molecular weight hydrocarbons was superimposed on the higher molecular weight biogenic background SHCs. Pristane and phytane were the dominant SHC compounds indicating the early stages of microbial degradation; n-alkanes had been preferentially degraded compared to the isoprenoids.

The pyrogenic PAHs were the dominant PAHs in the Bay de Chene sediments, similar to that in the Delacroix Island sediments. Pyrogenic type PAHs in which the abundances of parent and lower alkyl groups (C_1) dominate the distribution within each PAH family were apparent, especially for the phenanthrenes, fluoranthenes/pyrenes, and chrysenes. The relatively high concentrations of five- and six-ring PAHs (benz(a)anthracene, benzo(a)pyrene, and benzo(b)fluoranthene) are classical fingerprints of PAHs from a pyrogenic source. The concentration of the pyrogenic PAHs increased as one approached the facility. The dominance of pyrogenic PAHs was most exaggerated starting at the 300 m locations especially on the northeast transect where the influence of a petrogenic PAH input was not evident (**Figure 8.40**).

Reference station surface sediments (**Figure 8.41**) contained low levels of the pyrogenic PAHs (100 to 200 ng/g), but relatively large amounts of perylene (~80 μg/g). Concentrations of perylene were especially high in the subsurface sediments and made up from 35% to 80% of the total PAHs. Large increases in subsurface sediment PAHs compared to surface sediment PAHs was due to increased amounts of perylene. In the surface sediment of both reference stations, there were also low levels of petrogenic PAHs exemplified by the alkyl distribution of the three-ring PAHs. The contributions of the PAHs without perylene were relatively constant at low concentrations throughout the sediment core, and consistent in all surveys.

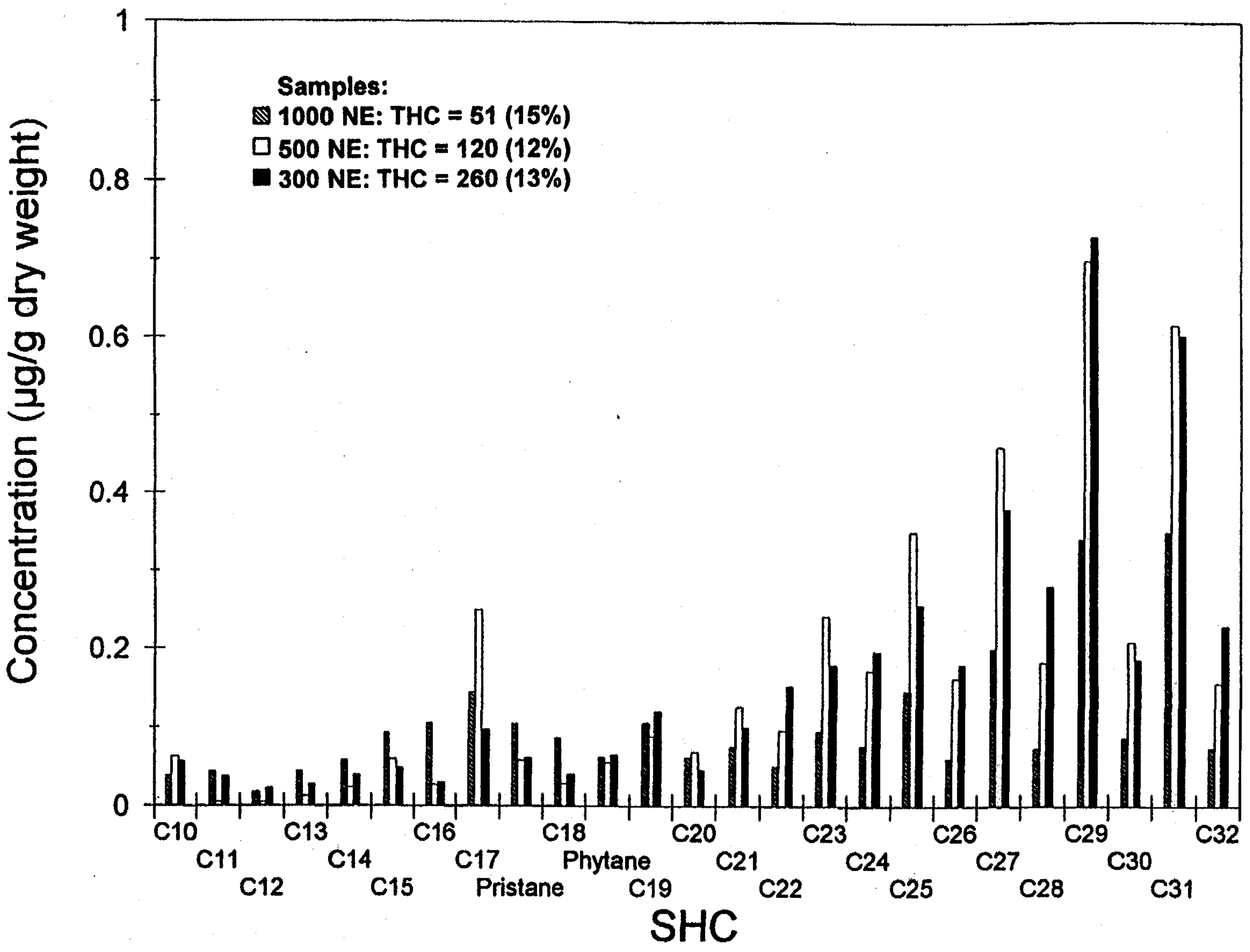

Figure 8.32. SHC distributions in sediments from the northeast transect of Bay de Chene collected during the Pre-termination Survey (Survey I).

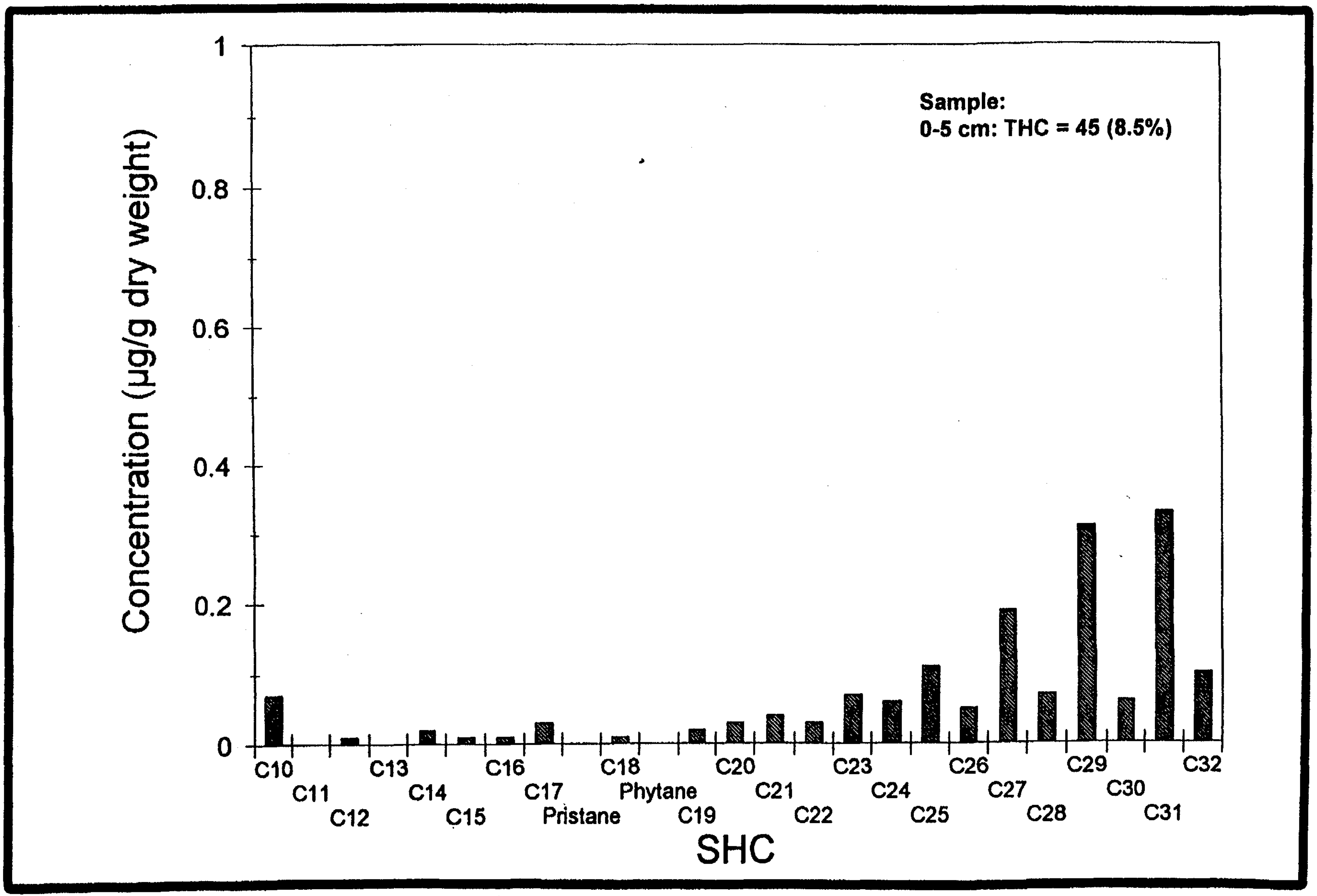

Figure 8.33. SHC distributions in sediments from the reference 1 station of Bay de Chene collected during the Pre-termination Survey (Survey I).

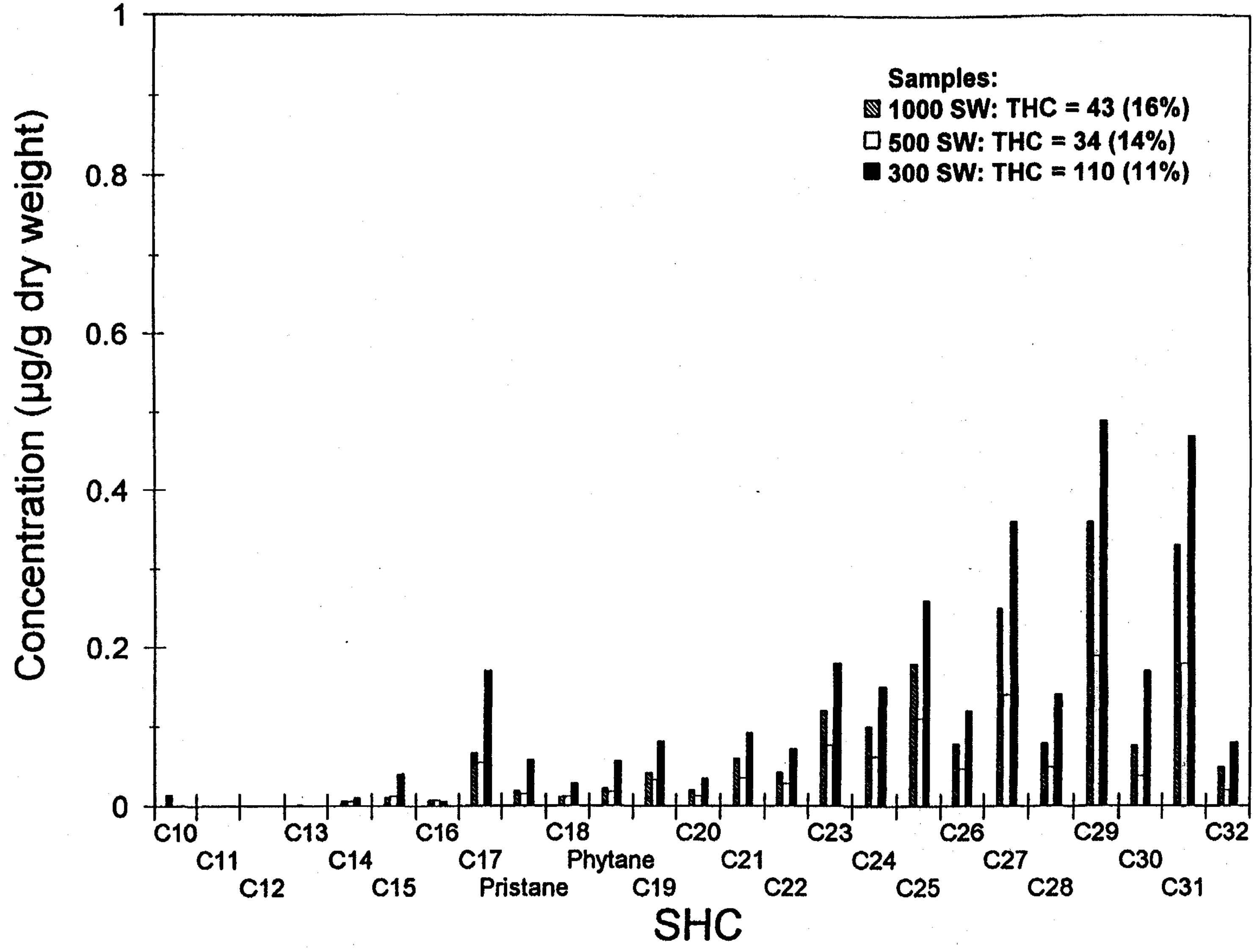

Figure 8.34. SHC distributions in sediments from the southwest transect of Bay de Chene collected during the First Post-termination Survey (Survey II).

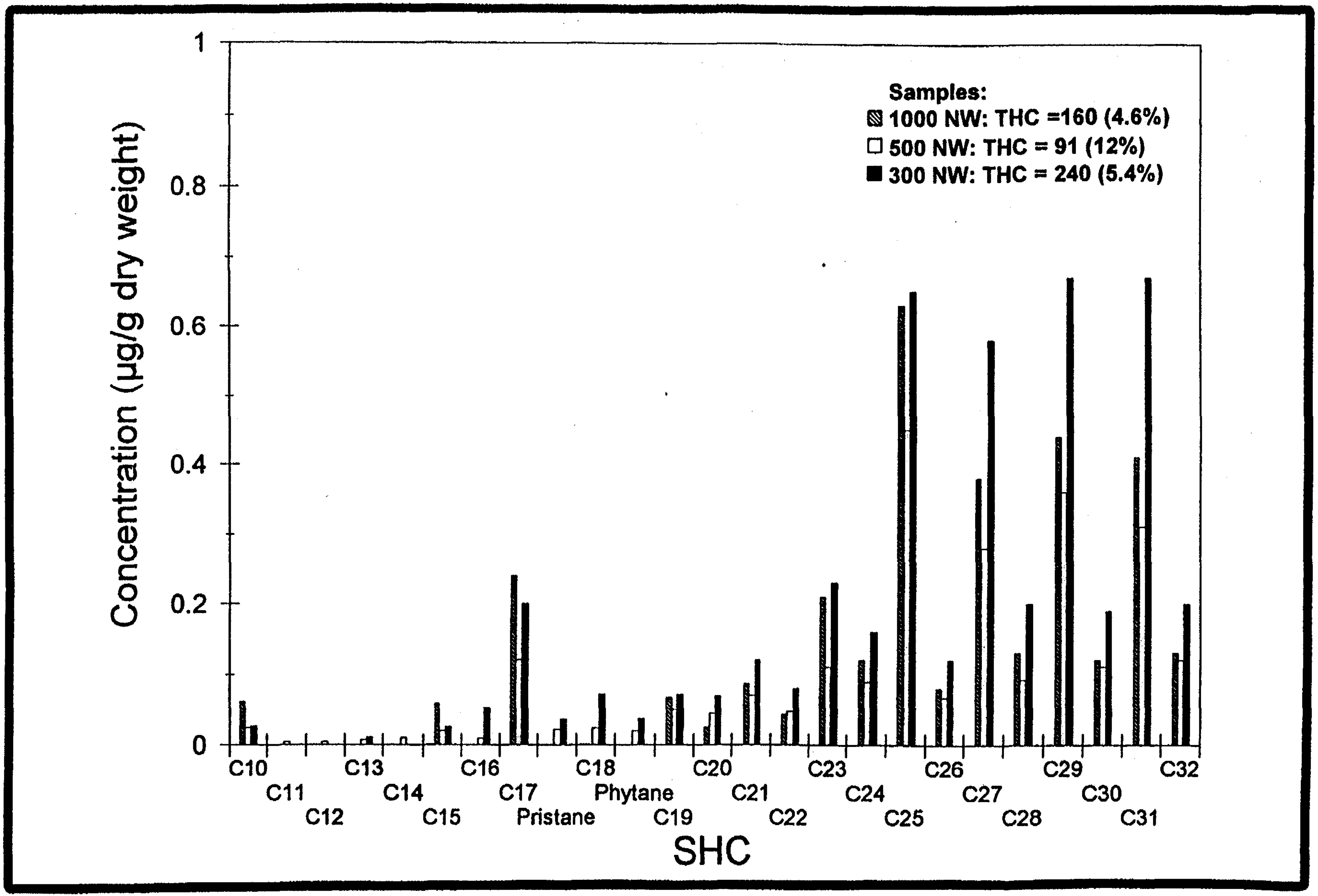

Figure 8.35. SHC distributions in sediments from the northwest transect of Bay de Chene collected during the Second Post-termination Survey (Survey III).

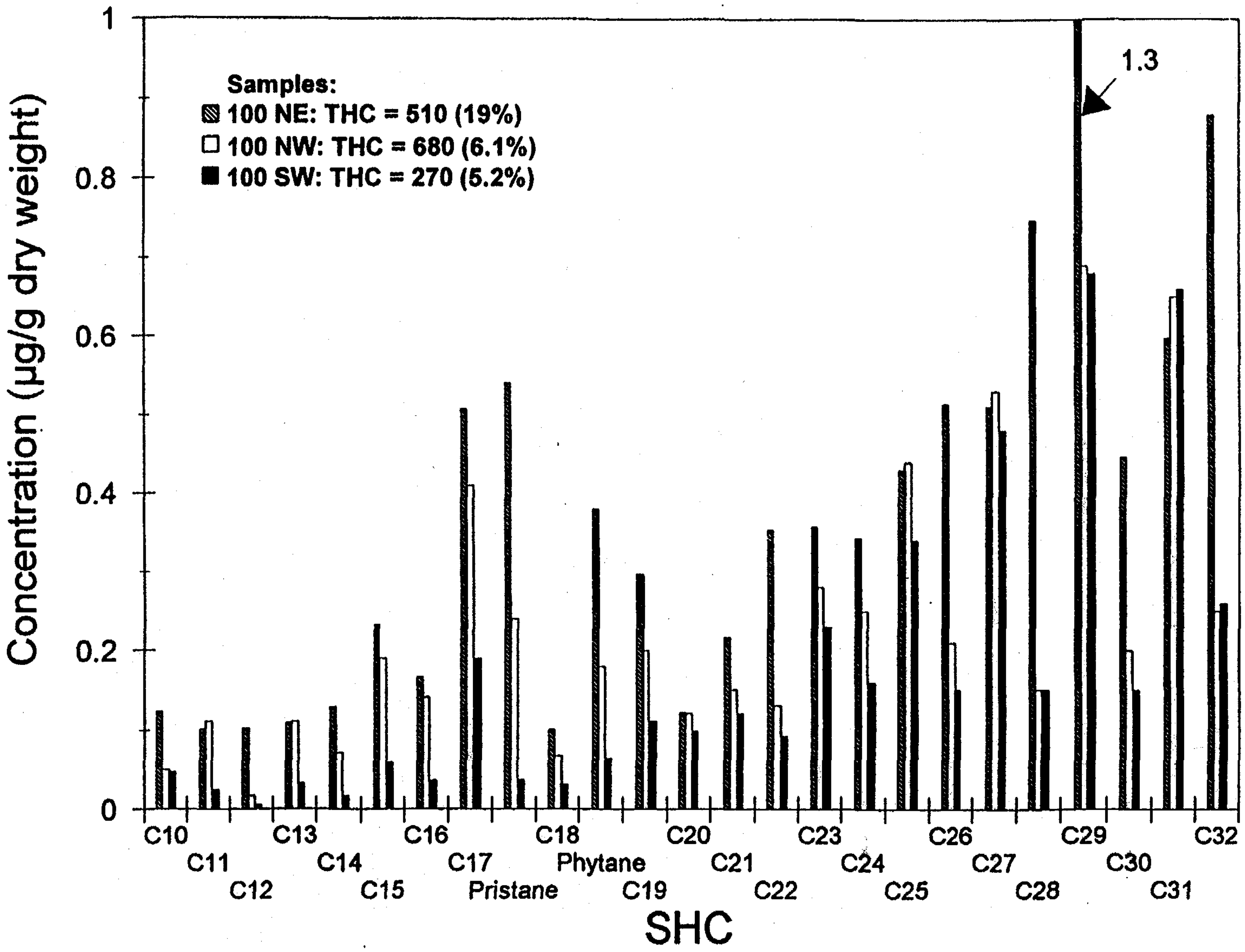

Figure 8.36. SHC distributions in sediments from the 100 m northeast, west, and southwest stations of Bay de Chene collected during the Pre-termination Survey (Survey I).

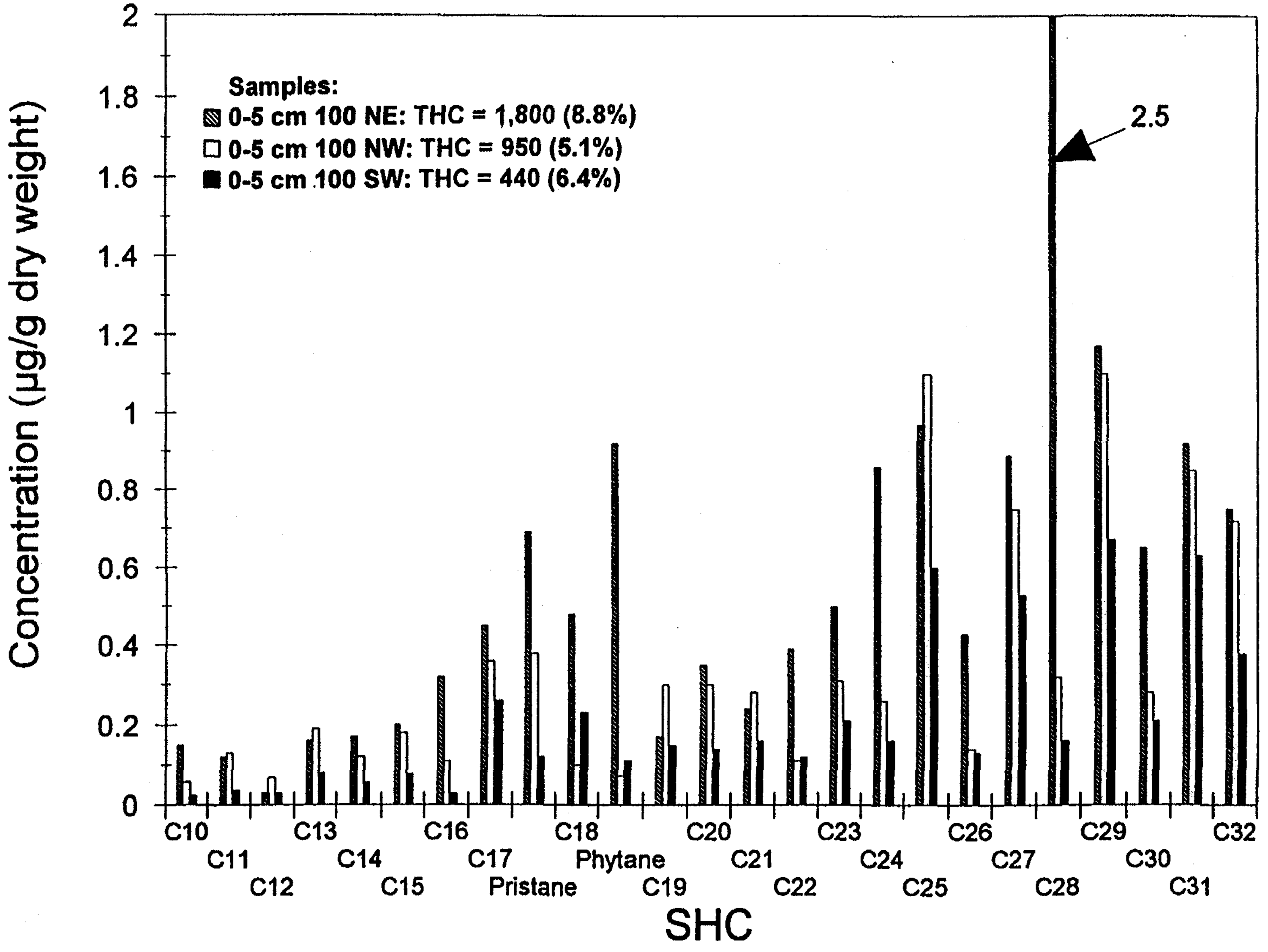

Figure 8.37. SHC distributions in sediments from the 100 m northeast, northwest, and southwest stations of Bay de Chene collected during the Second Post-termination Survey (Survey III).

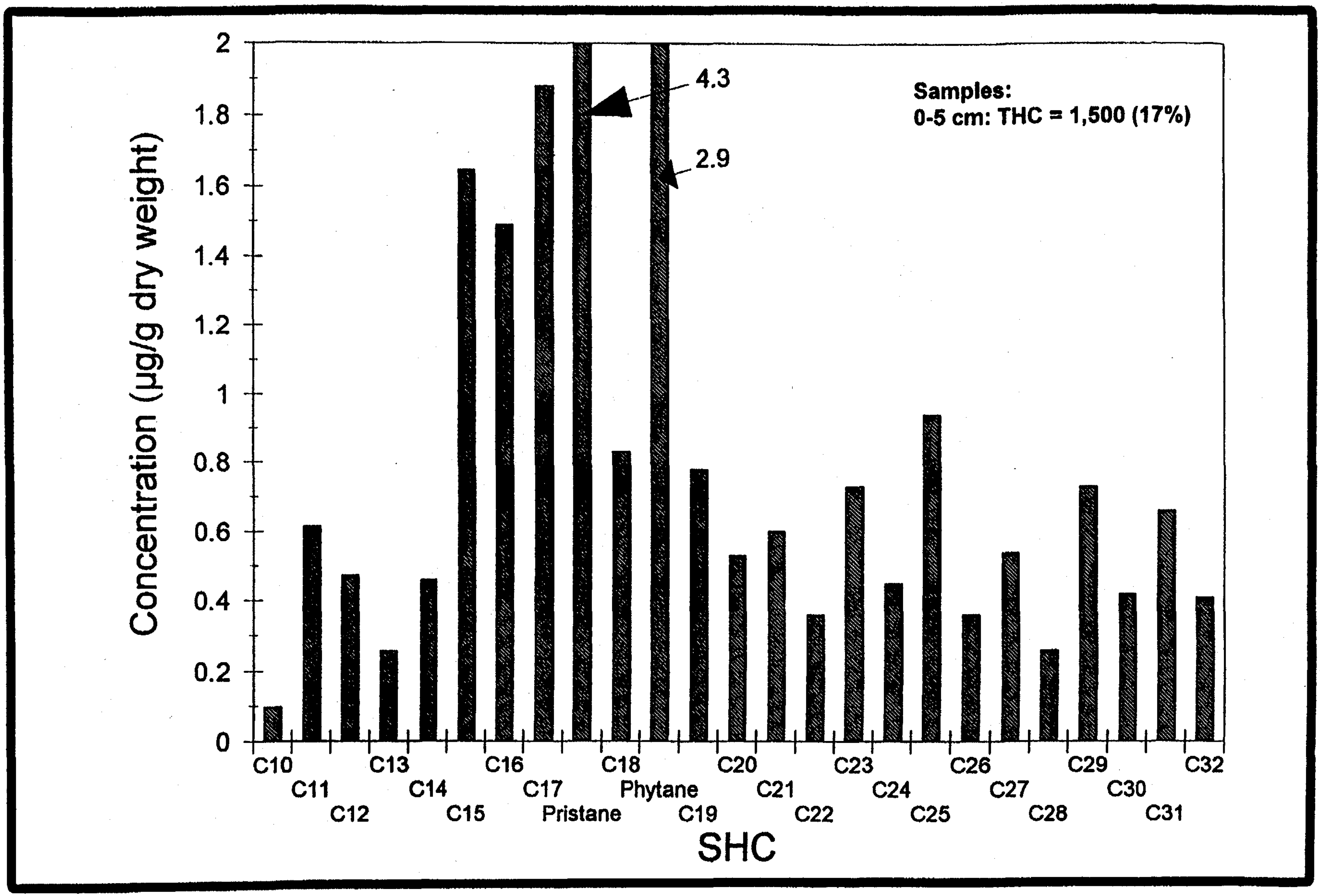

Figure 8.38. SHC distribution in sediments from the discharge station of Bay de Chene collected during the Pre-termination Survey (Survey I).

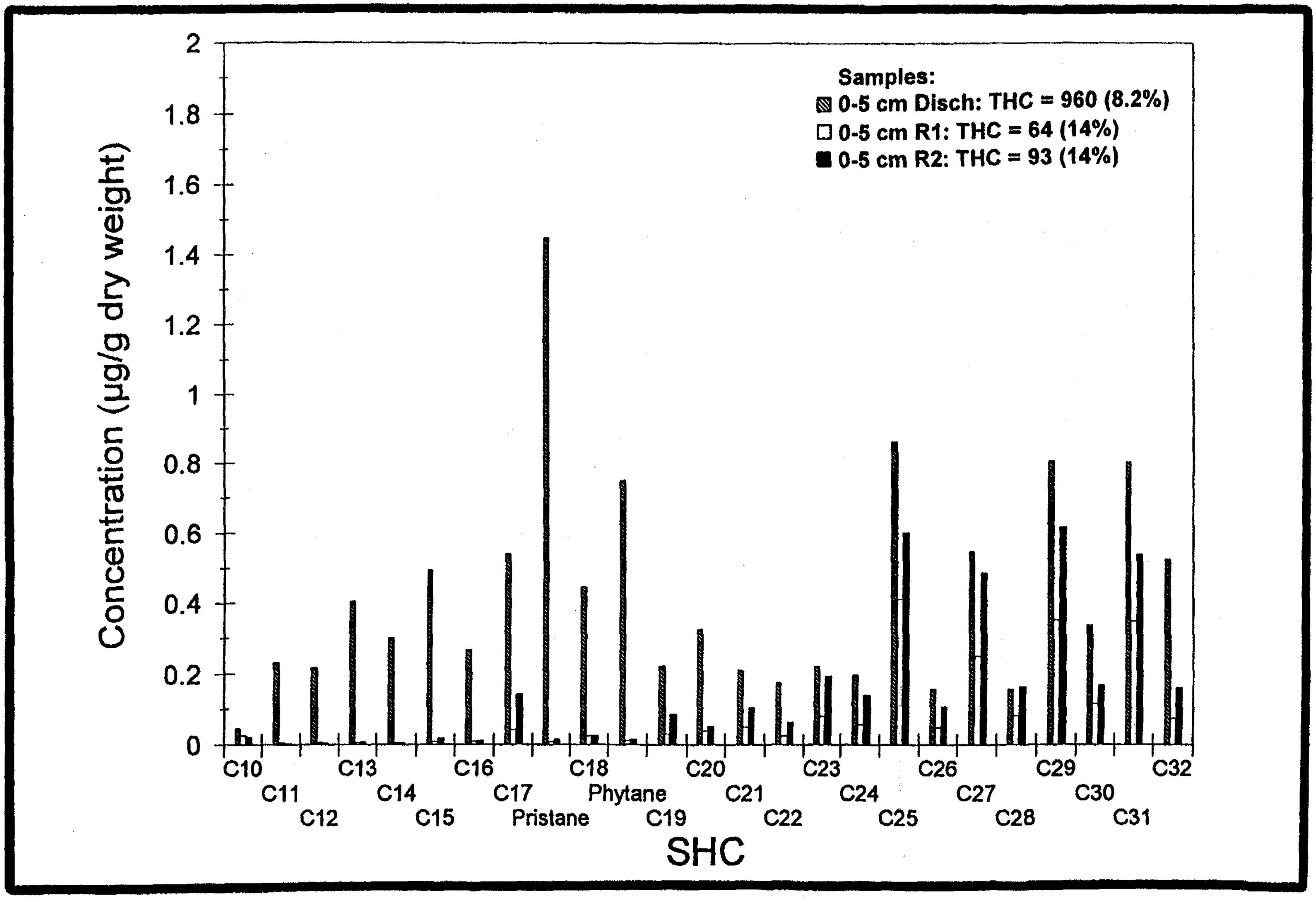

Figure 8.39. SHC distributions in sediments from the discharge station of Bay de Chene collected during the Second Post-termination Survey (Survey III).

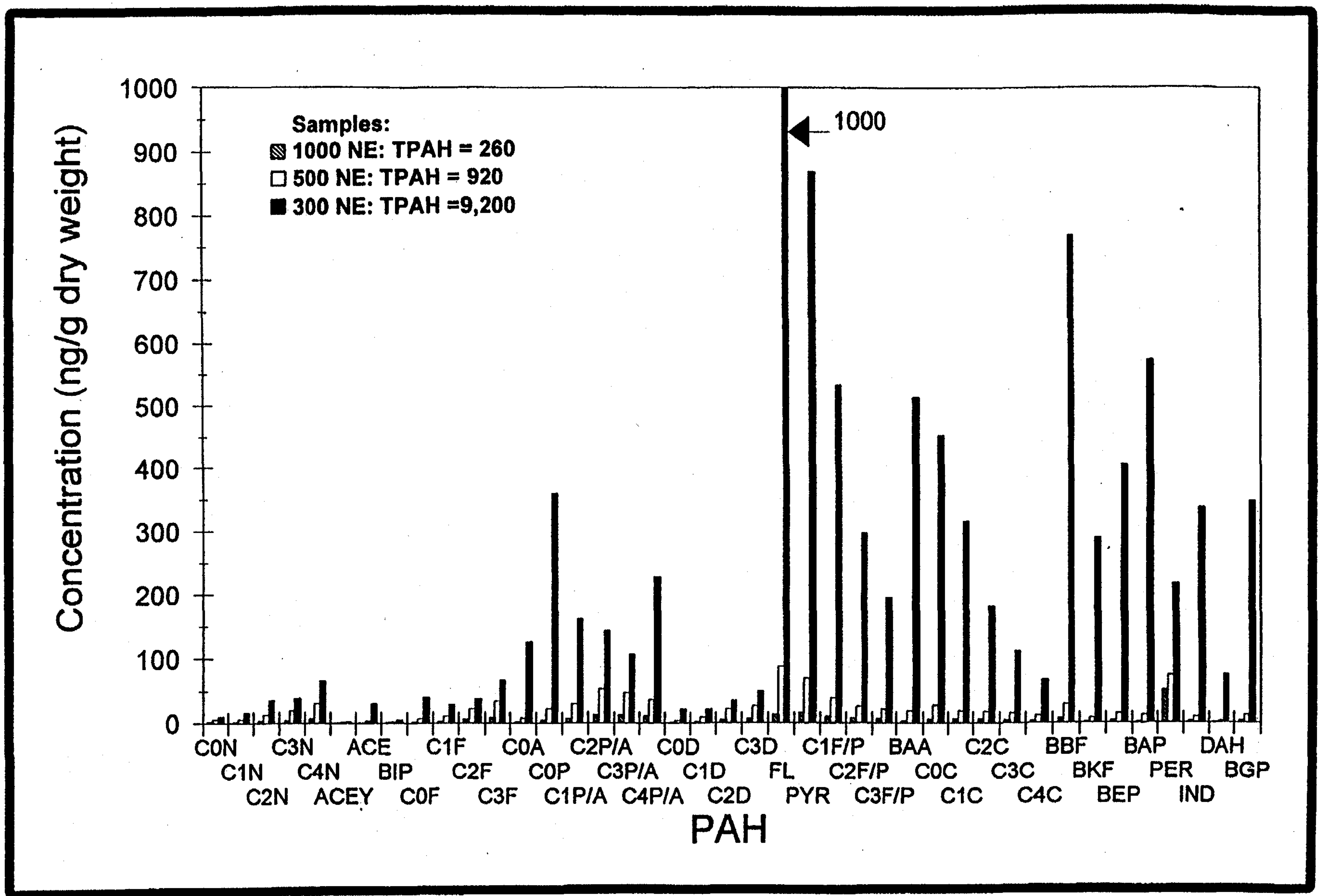

Figure 8.40. PAH distributions in sediments from the northeast transect of Bay de Chene collected during the Pre-termination Survey (Survey I).

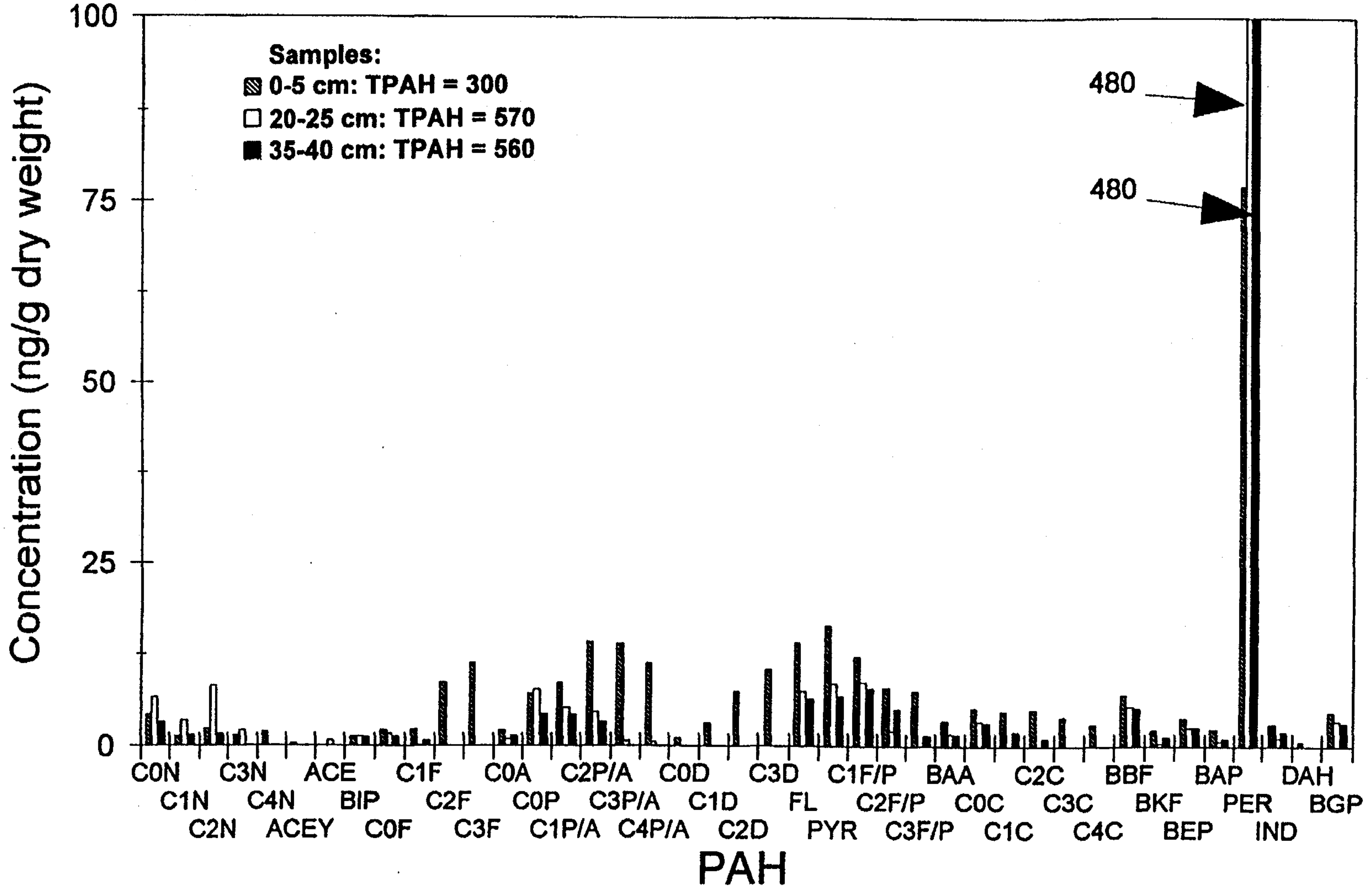

Figure 8.41. PAH distributions in sediments from the reference 1 station of Bay de Chene collected during the Pre-termination Survey (Survey I).

Unlike Delacroix Island, the presence of the petrogenic signature was noticeable as far out as 300 m (**Figure 8.42** and **8.43**). The alkyl groups of the three-ring PAHs showed the characteristic "bell-shape" distribution. The pyrogenic PAHs still dominated, however, at 50% to 70% of the total. The source diagnostic ratios of C2P/C2D and C3P/C3D for the 300 m Survey I sediments in the northwest and southwest transects were 2.5 to 2.6 and 2.2 to 2.3, respectively which were comparable to the produced water PAH diagnostic ratios of 3.0 to 3.1 for C2P/C2D and 2.2 to 2.3 for C3P/C3D (**Table 8.5**). Perylene, the diagenetic PAH, was especially evident in the southwest transect samples.

In post-termination 300 m sediments, the pre-termination PAH signatures were essentially retained (**Figure 8.44** through **8.46**). Sediments at the northwest 300 m station had almost exclusively pyrogenic PAHs. Similar to the pre-termination sediments, the 300 m northwest and southwest station sediments contained minor amounts of the petrogenic PAHs; however, the relative amounts of the pyrogenic PAHs increased (60% to 80% of total PAHs).

At the 100 m stations, total PAH concentrations in northeast sediments were 5 to 10 times higher than PAHs in northwest and southwest sediments. The northeast PAHs were dominated by 90% pyrogenic PAHs (**Figure 8.47**). By contrast in the northwest sediments, a petrogenic signature was especially evident and petroleum PAHs made up nearly 50% to 60% of the total PAHs (**Figure 8.48**). Southwest sediments showed less petrogenic PAHs, but did not contain the content of pyrogenic PAHs observed in the northeast sediments (**Figure 8.49**). PAH distributions in pre-termination sediments at the 100 m stations were essentially retained in post-termination sediments. Changes in total PAH concentrations in the northeast and southwest sediments were attributed to changes in the amounts of pyrogenic PAHs. Slight losses of the petrogenic PAHs (two- and three-ring PAHs) were, however, evident in northwest sediments (**Figure 8.48**).

Petrogenic PAHs were most prevalent in the sediments of the discharge station (**Figure 8.50**). The contribution of pyrogenic PAHs in the pre-termination surface sediments were especially large at concentrations of approximately 50,000 ng/g, but were in the range determined in northeast 100 m sediments (all surveys). Petrogenic PAH concentrations decreased rapidly in the post-termination sediments, but were accompanied by an overall decrease of pyrogenic PAHs. Post-termination PAH distributions and concentrations at the discharge station were similar to those of the 100 northwest sediments. The difference in the pre- and post-termination PAHs in discharge station sediments may be due to differences in the location of sample collection, not to alterations in environmental and discharge conditions.

Diagnostic values, C2P/C2D and C3P/C3D, for the petrogenic portions of the PAHs in these sediments were approximately 2.6 and 2.3, respectively, and similar to the produced water and the petrogenic PAHs in other sediments near the facility. Interestingly the highest concentration and freshest petroleum PAHs were observed in the subsurface sediments especially at 35 to 40 cm depth (**Figure 8.51**). Seventy percent of the 40,000 ng/g total PAHs were petrogenic PAHs. Historical produced water discharge practices or accidental petroleum releases may be possible causes of the unusually high concentrations of petroleum in the deeper sediments.

Principle component analysis of the Bay de Chene PAH data produced similar results as the Delacroix Island statistical analysis (**Figure 8.52** through **8.54**). The grouping of stations with similar chemical characteristics was less obvious in the Bay de Chene analysis, but the

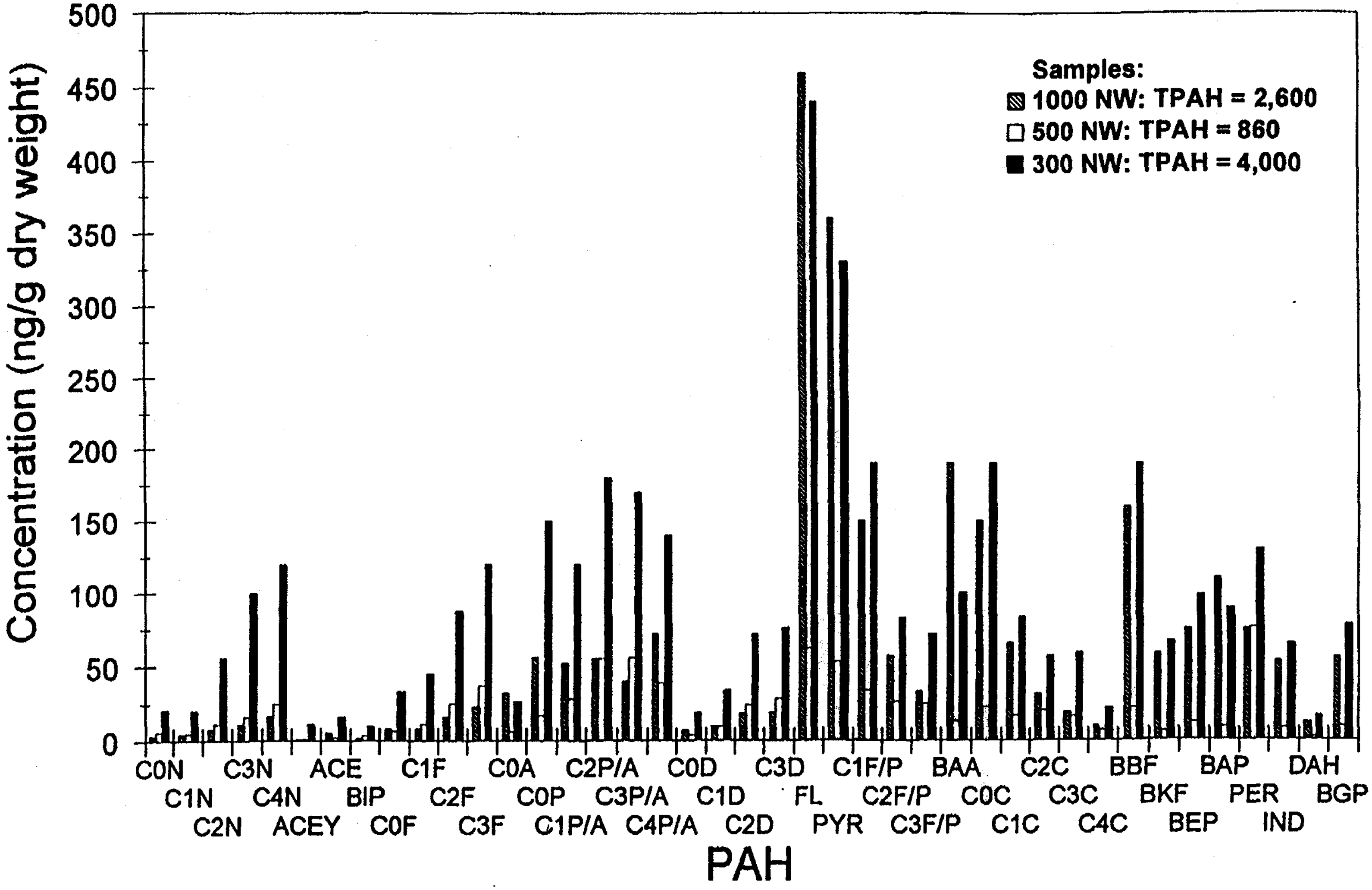

Figure 8.42. PAH distributions in sediments from the northwest transect of Bay de Chene collected during the Pre-termination Survey (Survey I).

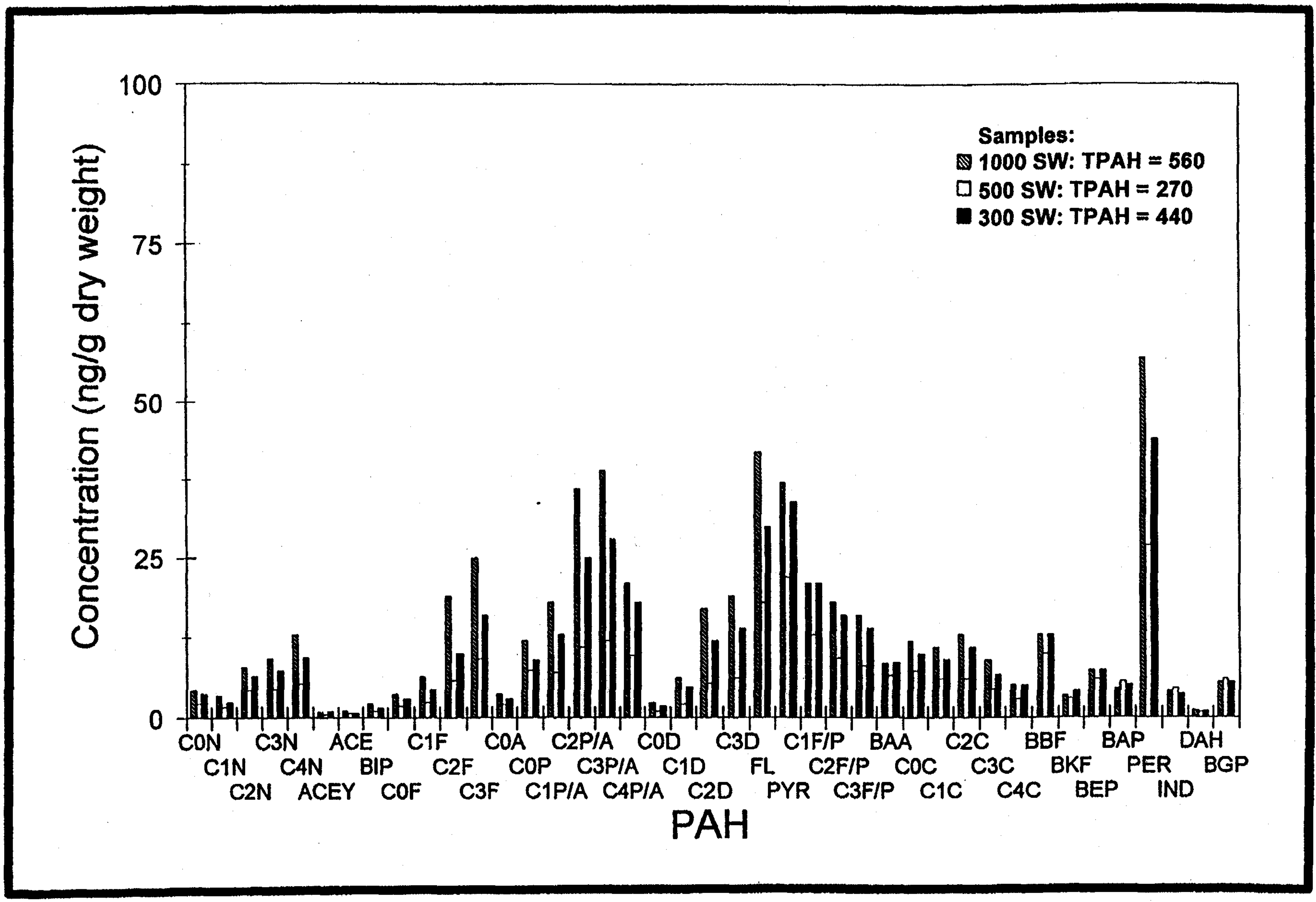

Figure 8.43. PAH distributions in sediments from the southwest transect of Bay de Chene collected during the Pre-termination Survey (Survey I).

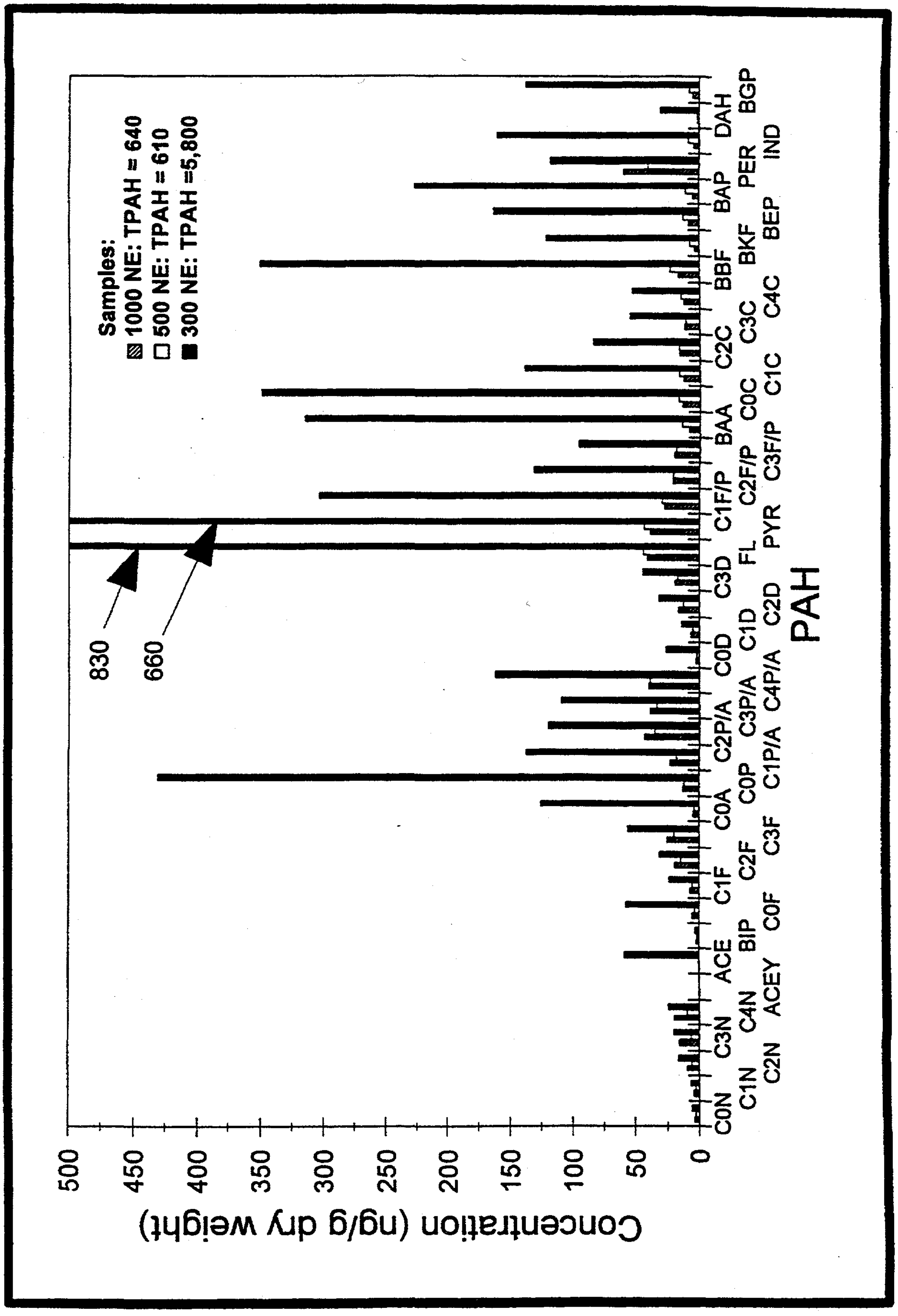

Figure 8.44. PAH distributions in sediments from the northeast transect of Bay de Chene collected during the Second Post-termination Survey (Survey III).

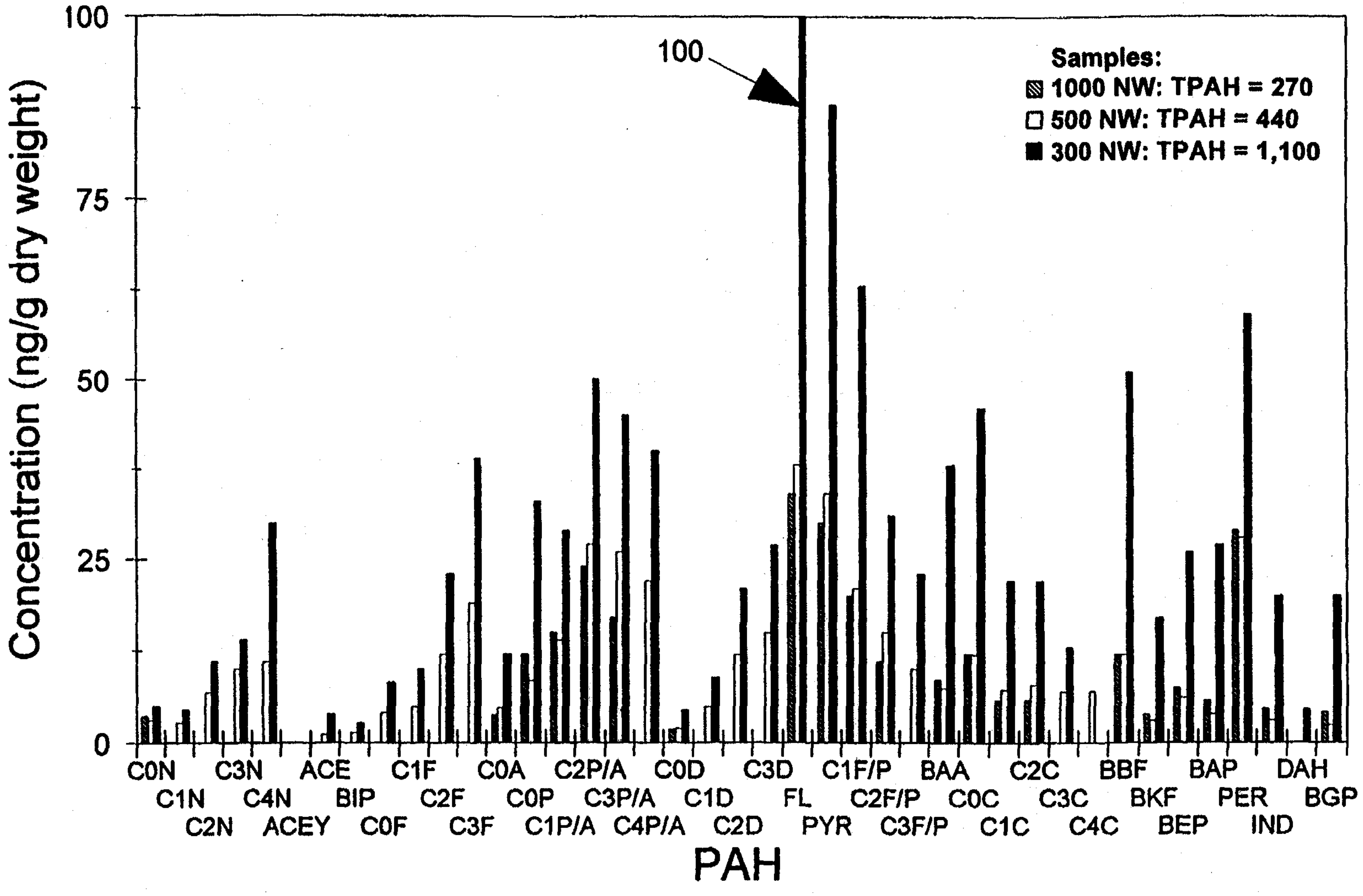

Figure 8.45. PAH distributions in sediments from the northwest transect of Bay de Chene collected during the Second Post-termination Survey (Survey III).

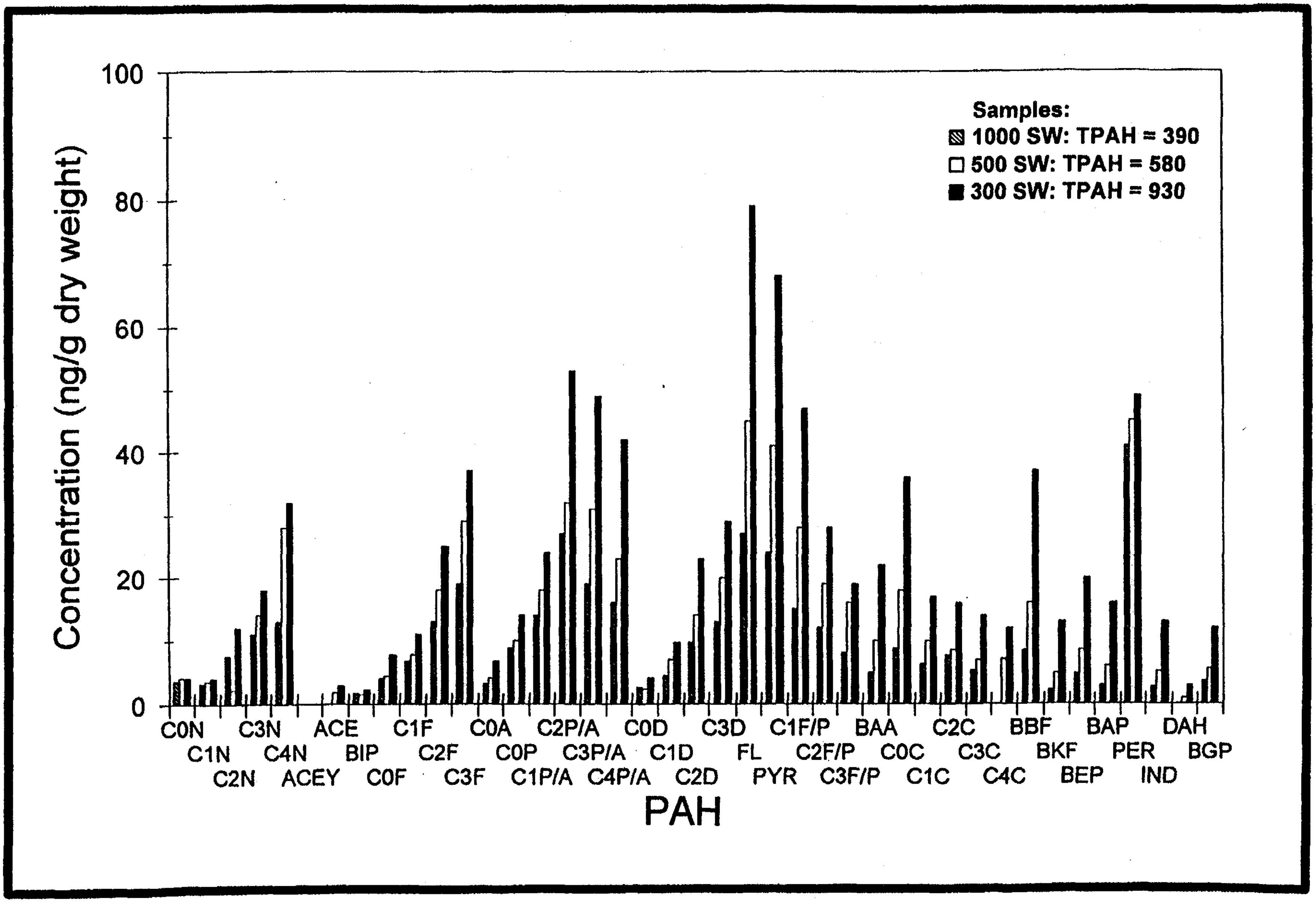

Figure 8.46. PAH distributions in sediments from the southwest transect of Bay de Chene collected during the Second Post-termination Survey (Survey III).

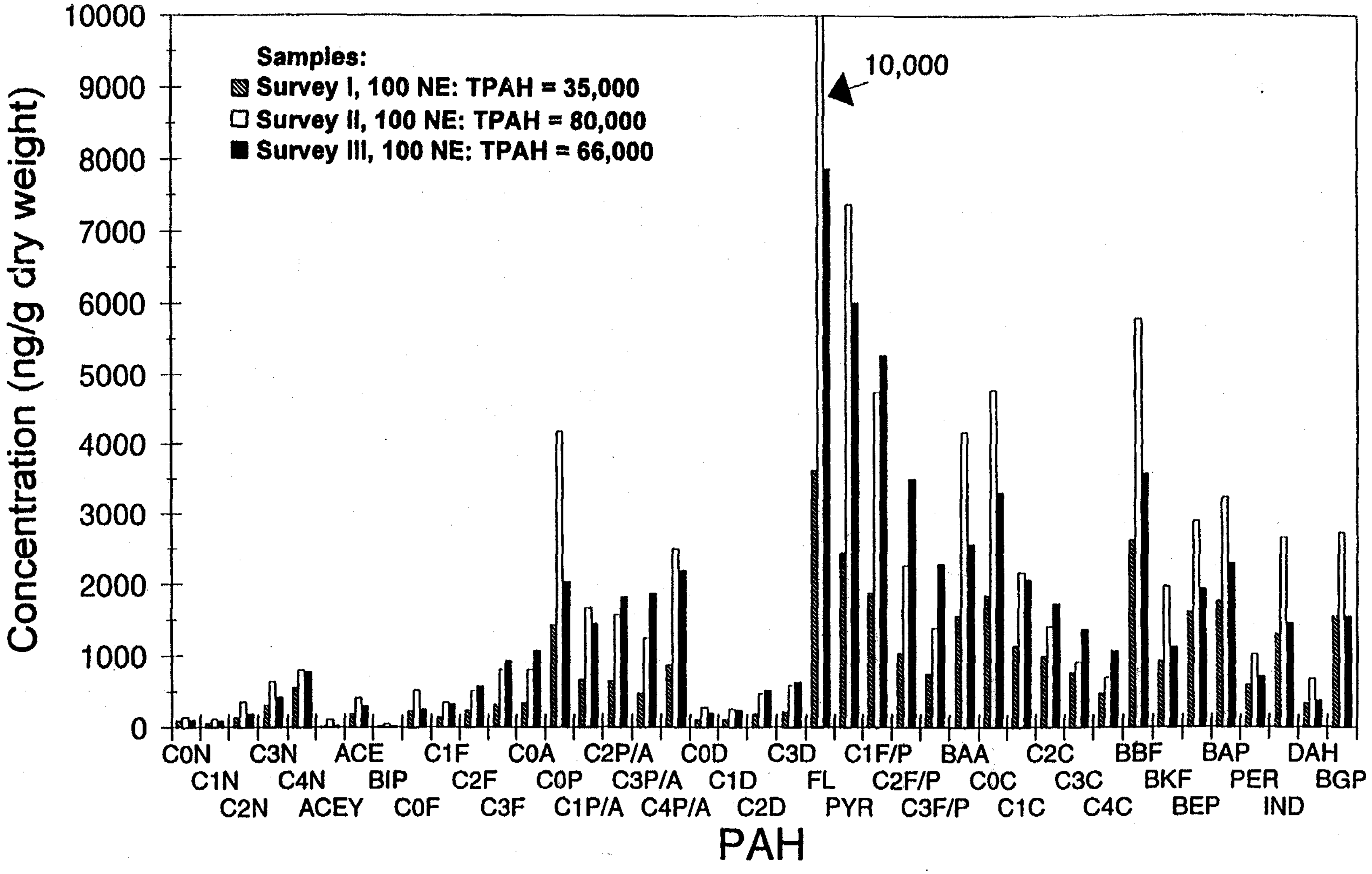

Figure 8.47. PAH distributions in sediments from the 100 m northeast station of Bay de Chene collected during all surveys (Surveys I to III).

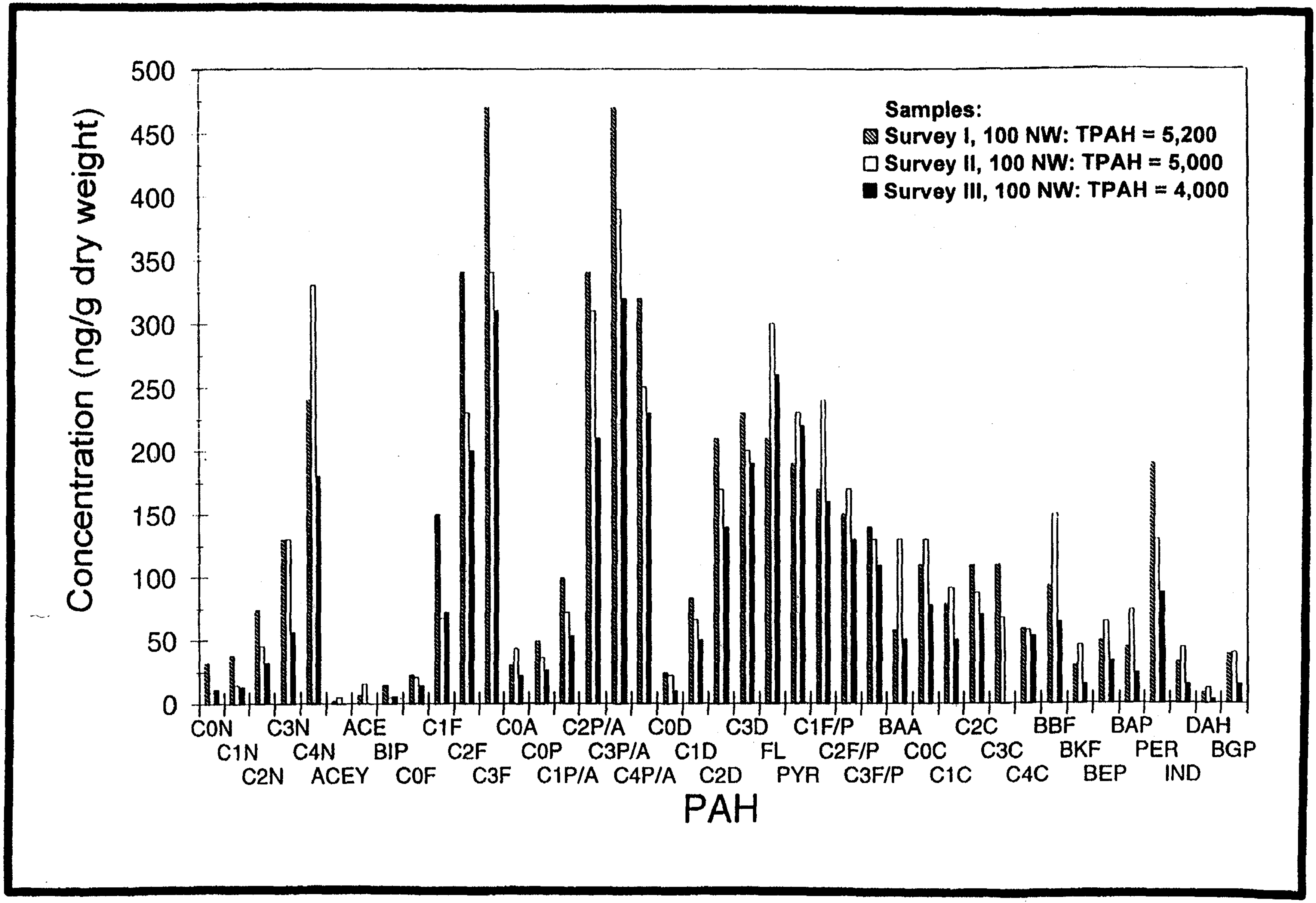

Figure 8.48. PAH distributions in sediments from the 100 m northwest station of Bay de Chene collected during all surveys (Surveys I to III).

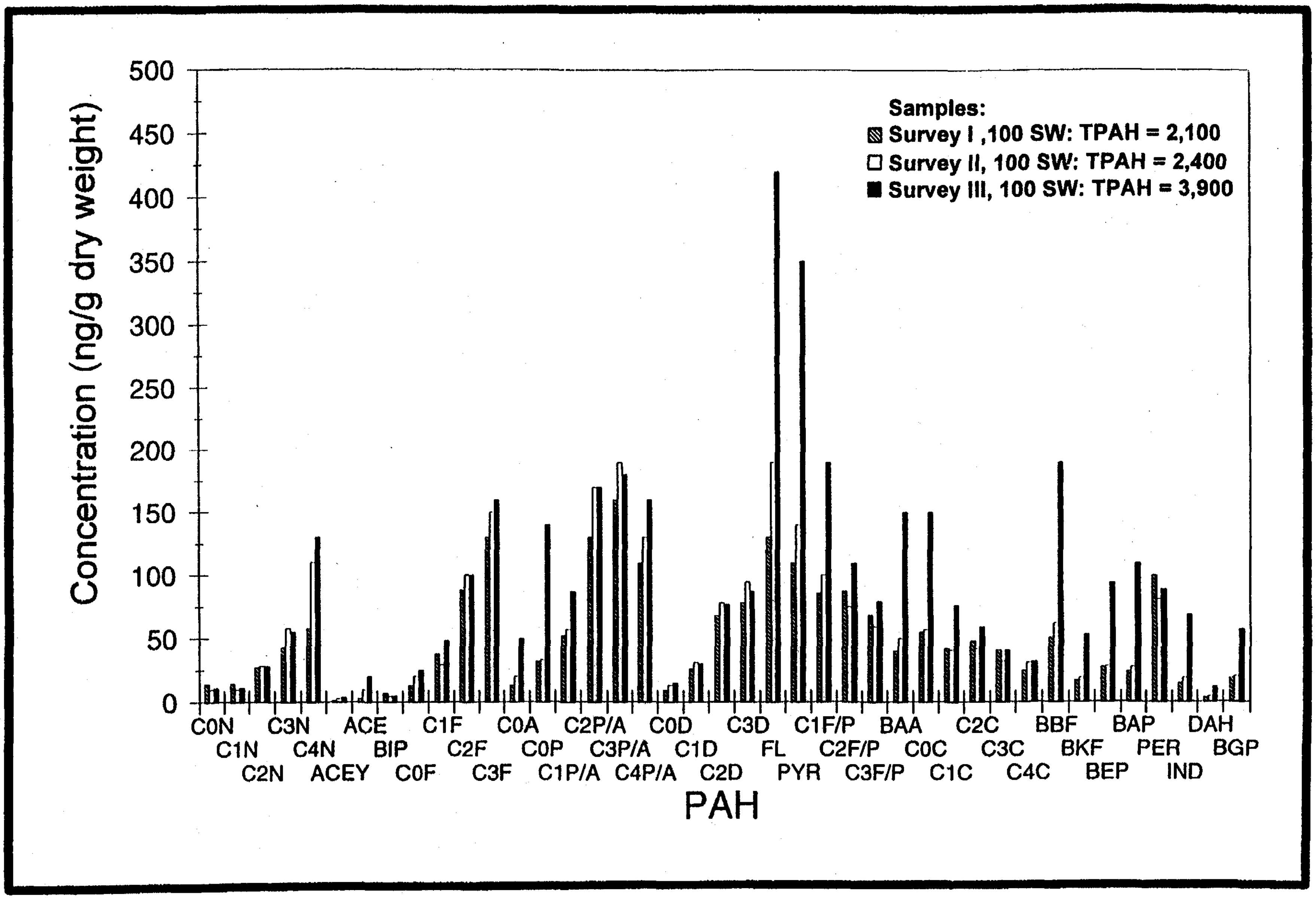

Figure 8.49. PAH distributions in sediments from the 100 m southwest station of Bay de Chene collected during all surveys (Surveys I to III).

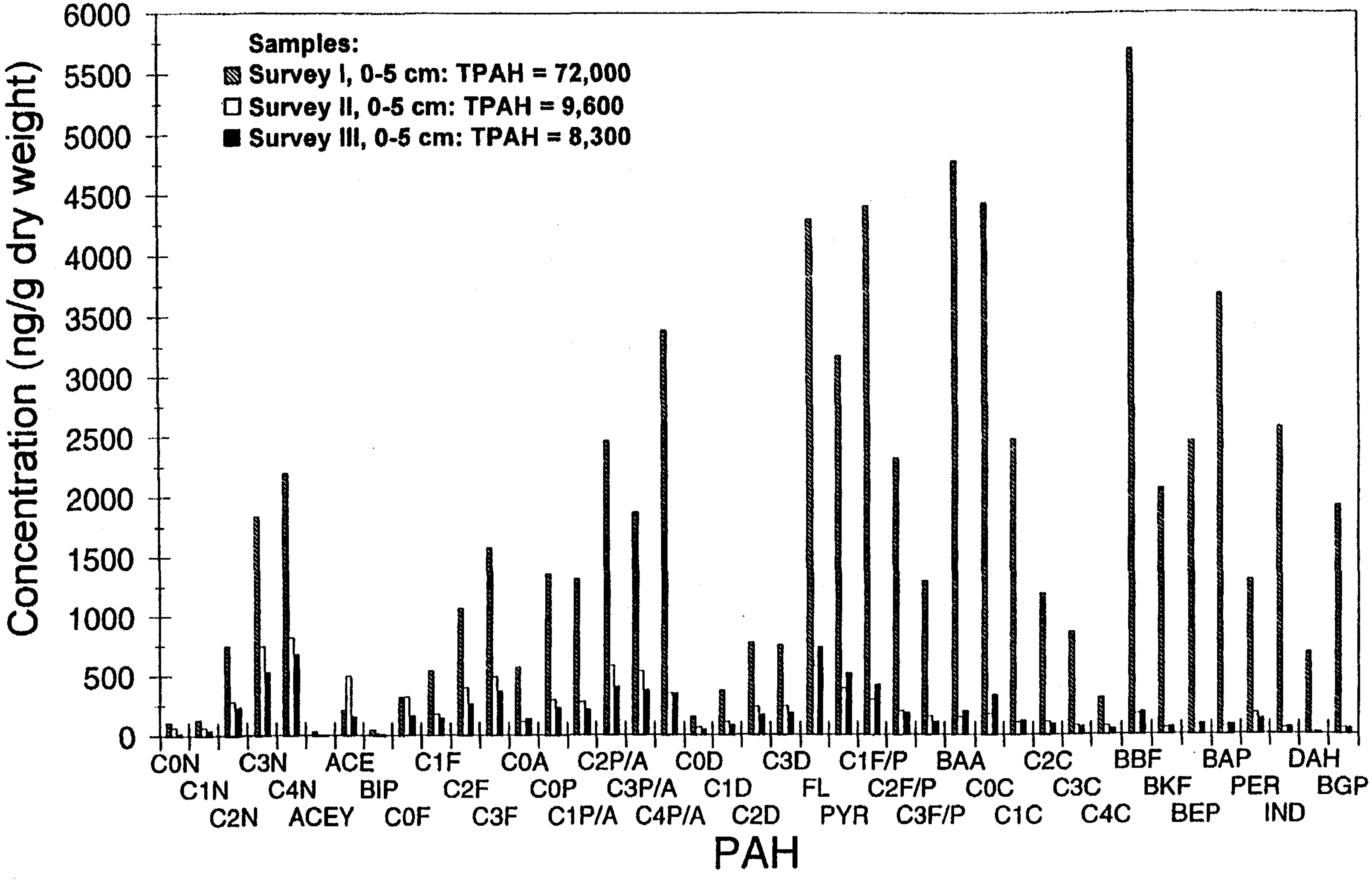

Figure 8.50. PAH distributions in sediments from the discharge station of Bay de Chene collected during all surveys (Surveys I to III).

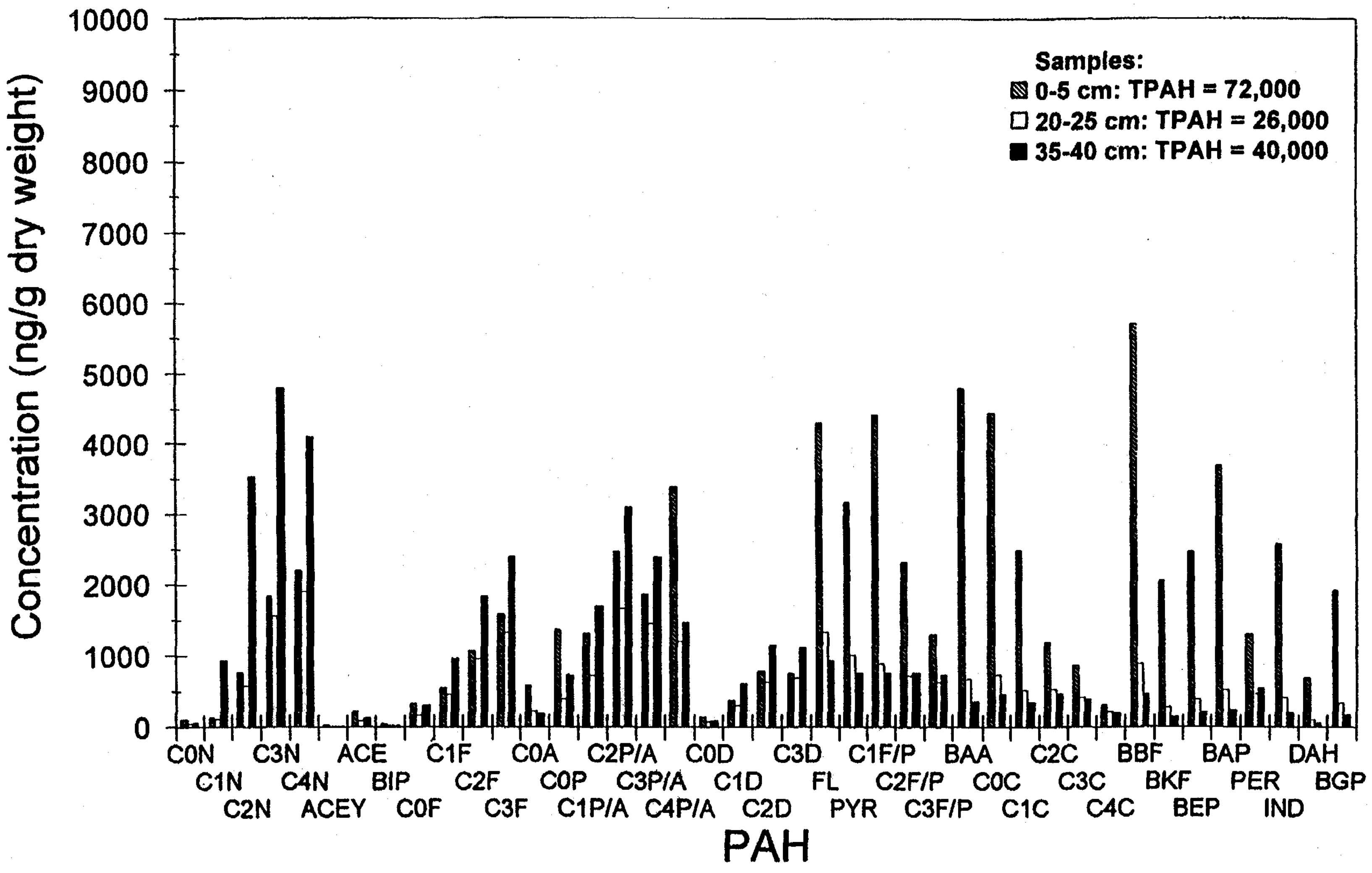

Figure 8.51. PAH distributions in sediments from the discharge station of Bay de Chene collected during the Pre-termination Survey (Survey I).

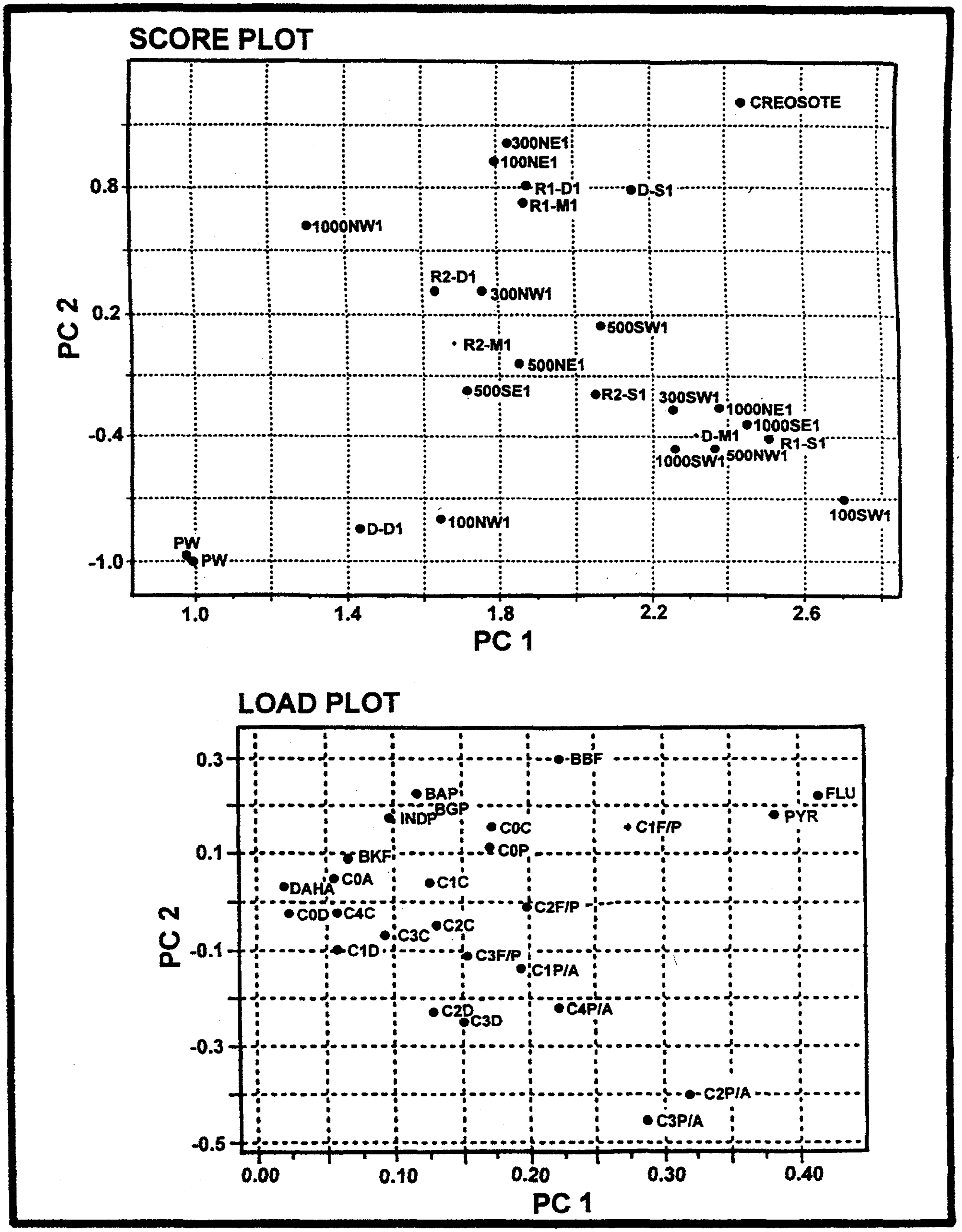

Figure 8.52. Principle component analysis plot of PAH data of produced water (PW) and sediments from Bay de Chene collected during the Pre-termination Survey (Survey I). PAHs (less naphthalenes, fluorenes, and perylene) were normalized by the highest concentration PAH in each sample. Score plot presents sediment stations (D - discharge, R1 - reference 1, R2 - reference 2, and distance/compass heading), sediment increment (S - 0 to 5 cm, M - 20 to 25 cm, and D - 35 to 40 cm), and survey designation (1). Load plot presents PAH acronyms which are defined in **Table 8.1**.

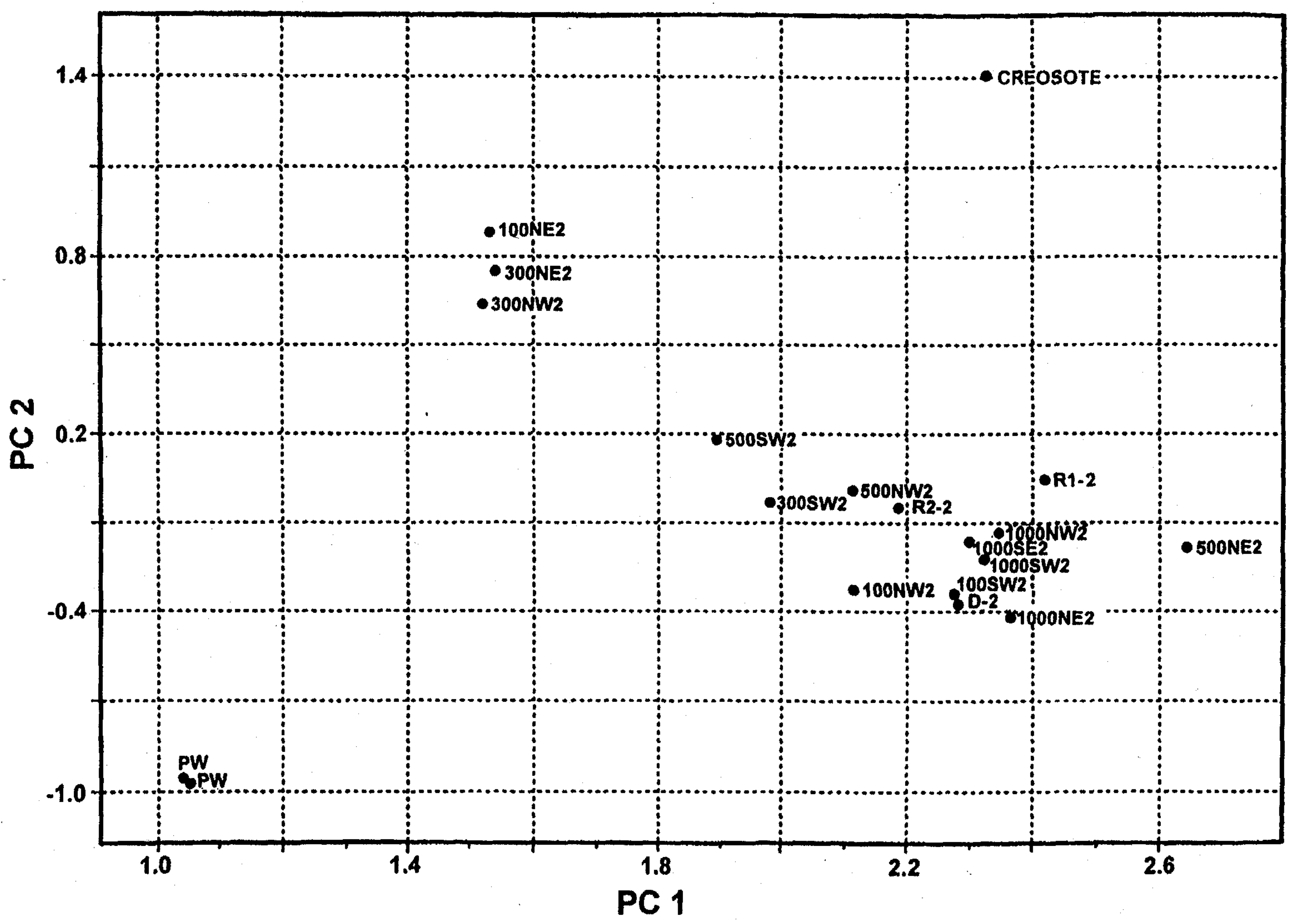

Figure 8.53. Principle component analysis plot of PAH data of produced water (PW) and sediments (0 to 5 cm) from Bay de Chene collected during the First Post-termination Survey (Survey II). PAHs (less naphthalenes, fluorenes, and perylene) were normalized by the highest concentration PAH in each sample. Plot presents sediment stations (D - discharge, R1 - reference 1, R2 - reference 2, and distance/compass heading) and survey designation (2).

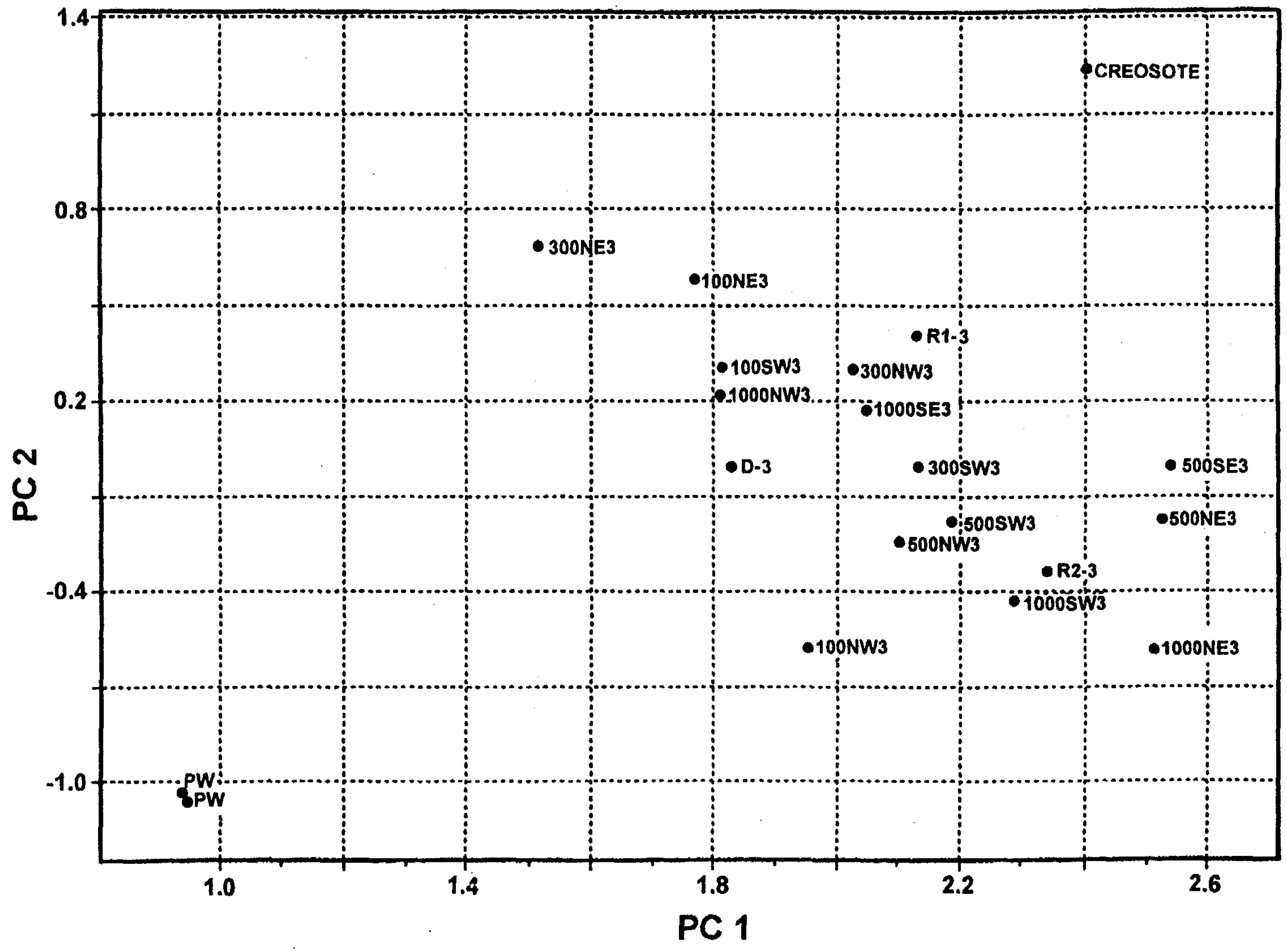

Figure 8.54. Principle component analysis plot of PAH data of produced water (PW) and sediments (0 to 5 cm) from Bay de Chene collected during the Second Post-termination Survey (Survey III). PAHs (less naphthalenes, fluorenes, and perylene) were normalized by the highest concentration in each sample. Plot presents sediment stations (D - discharge, R1 - reference 1, R2 - reference 2, and distance/compass heading) and survey designation (3).

differences in relative position in the principle component analysis plots confirmed the observations discussed above. The relative contribution of pyrogenic PAHs influenced the position of the stations in the plots.

8.3.2.3 Four Isle Dome

At Four Isle Dome, only a Pre-termination Survey was conducted. Because of the configuration of shallow canals in the Louisiana wetland, sediments in only the north and south direction were sampled. Site samples did not include a 1,000 m station on the south transect.

Each transect showed different hydrocarbon concentration trends (**Table 8.10**). The north transect THC and PAH sediment concentrations increased from outer stations to the discharge facility, from 67 μg/g THCs and 450 ng/g PAHs at 500 m to 310 μg/g THCs and 3,600 ng/g total PAHs at 100 m. On the south transect, hydrocarbon concentrations were consistently high at all stations (500, 300, and 100 m) at 300 to 460 μg/g for THCs and 3,200 to 3,600 ng/g total PAHs. At 100 m, hydrocarbon concentrations were the same on both transects.

Compared to the other sites, the reference station's hydrocarbon concentrations were high. Surface THC and PAH concentrations at both stations were approximately 100 μg/g THCs and 740 ng/g total PAHs. These concentrations were similar in subsurface sediments of R2, but in the R1 subsurface sediments, concentrations increased sharply to 16,000 ng/g total PAHs at 35 to 40 cm, higher than the subsurface sediments at the discharge station. THC and PAH concentrations were highest in the discharge surface sediments, 700 μg/g THCs and 49,000 ng/g total PAHs, which were comparable to discharge stations at the other sites.

Unlike Delacroix Island and Bay de Chene, increases in hydrocarbon concentrations in Four Isle Dome sediments were due to petroleum inputs not to pyrogenic (or biogenic) inputs. Petroleum hydrocarbons dominated SHC and PAH distributions at all stations on the south transect (**Figures 8.55** and **8.56**). The characteristic petrogenic SHCs and two- and three-ring PAH alkyl homologue distributions were present in equal amounts at the 100, 300, and 500 m stations. Pyrogenic PAHs were also present with the petrogenic PAH analytes at approximately 25% of the total PAHs. The type of petroleum in the sediments was probably produced water hydrocarbons or a light-end fuel oil (e.g., No. 2 Fuel Oil), because of the dominance of lower molecular weight SHCs and isoprenoids, the large amounts of naphthalenes, the two- and three-ring alkyl PAHs, and the absence of the ‘bell shaped’ alkyl distribution in chrysenes.

These petroleum signatures were also present at comparable concentrations in north sediments at the 100 m station, but not in the outer station north sediments (**Figure 8.57** and **8.58**) and distributions. Petrogenic concentrations and distributions decreased sharply, but were still evident at the 300 m station. The 500 m station resembled more of the characteristics of the reference stations.

At the discharge station, the dominant PAH distribution changed to pyrogenic PAHs, the distribution typical of the discharge stations at the other sites (**Figure 8.59**). Approximately 80% of the PAHs in these sediments, which are highly contaminated with hydrocarbons (49,000 ng/g total PAHs), were pyrogenic PAHs. The PAH signature resembled a weathered creosote.

Table 8.10. Summary of THC ($\mu g/g$) and TPAH (ng/g) concentrations in sediment collected during the Pre-termination Survey (Survey I) from Four Isle Dome.

Distance (m)	Direction	Analyte Group	Pre-termination Survey I
R1	0-5 cm	THC	120
		TPAH	730
	20-25 cm	THC	–
		TPAH	1300
	35-40 cm	THC	–
		TPAH	16000
R2	0-5 cm	THC	70
		TPAH	750
	20-25 cm	THC	–
		TPAH	680
	35-40 cm	THC	–
		TPAH	760
1000 m	N	THC	150
		TPAH	1300
500 m	N	THC	67
		TPAH	450
	S	THC	460
		TPAH	3600
300 m	N	THC	160
		TPAH	720
	S	THC	350
		TPAH	3200
100 m	N	THC	310
		TPAH	3600
	S	THC	300
		TPAH	3600
Discharge	0-5 cm	THC	700
		TPAH	49000
	20-25 cm	THC	–
		TPAH	11000
	35-40 cm	THC	–
		TPAH	5200

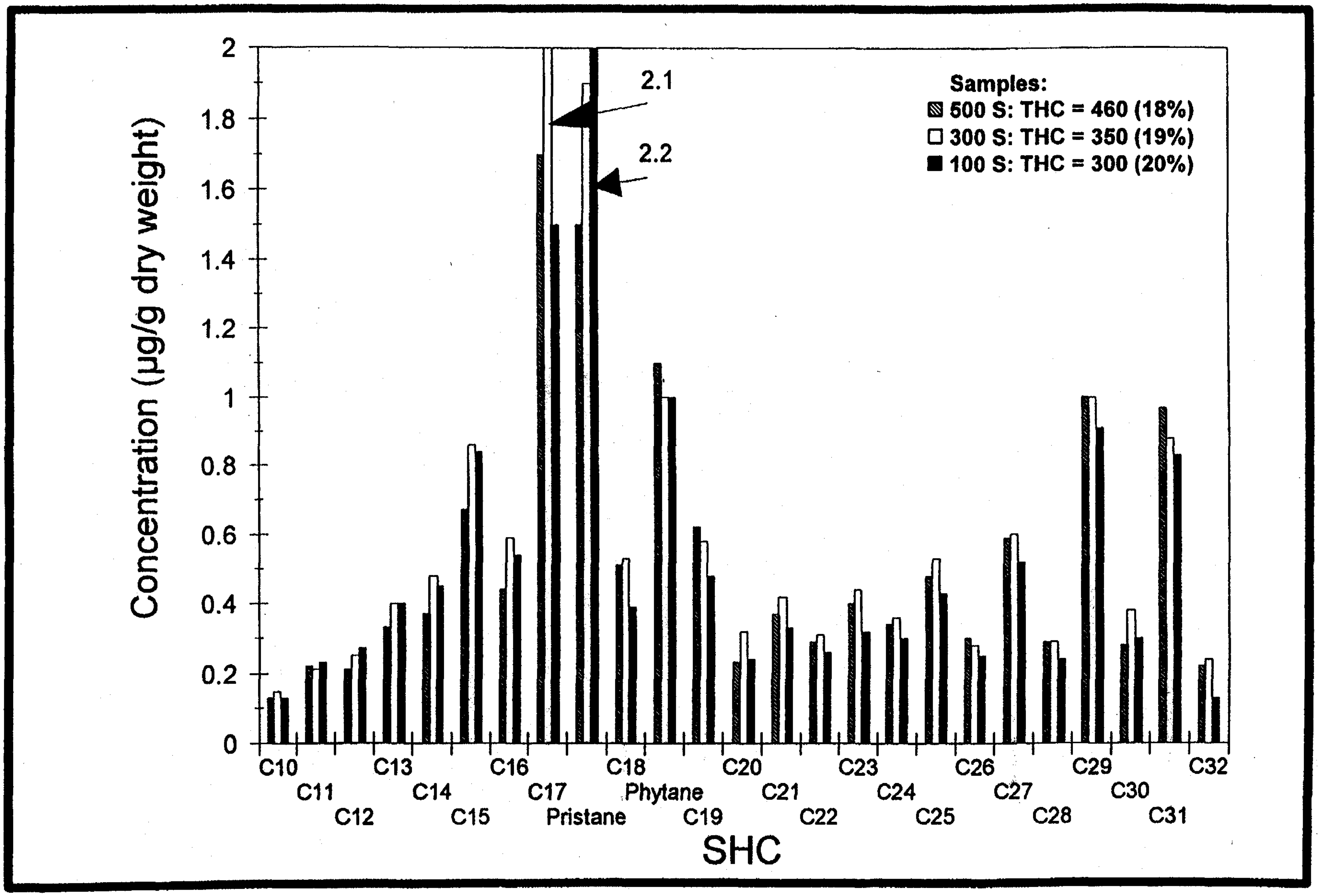

Figure 8.55. SHC distributions in sediments from the south transect of Four Isle Dome collected during the Pre-termination Survey (Survey I).

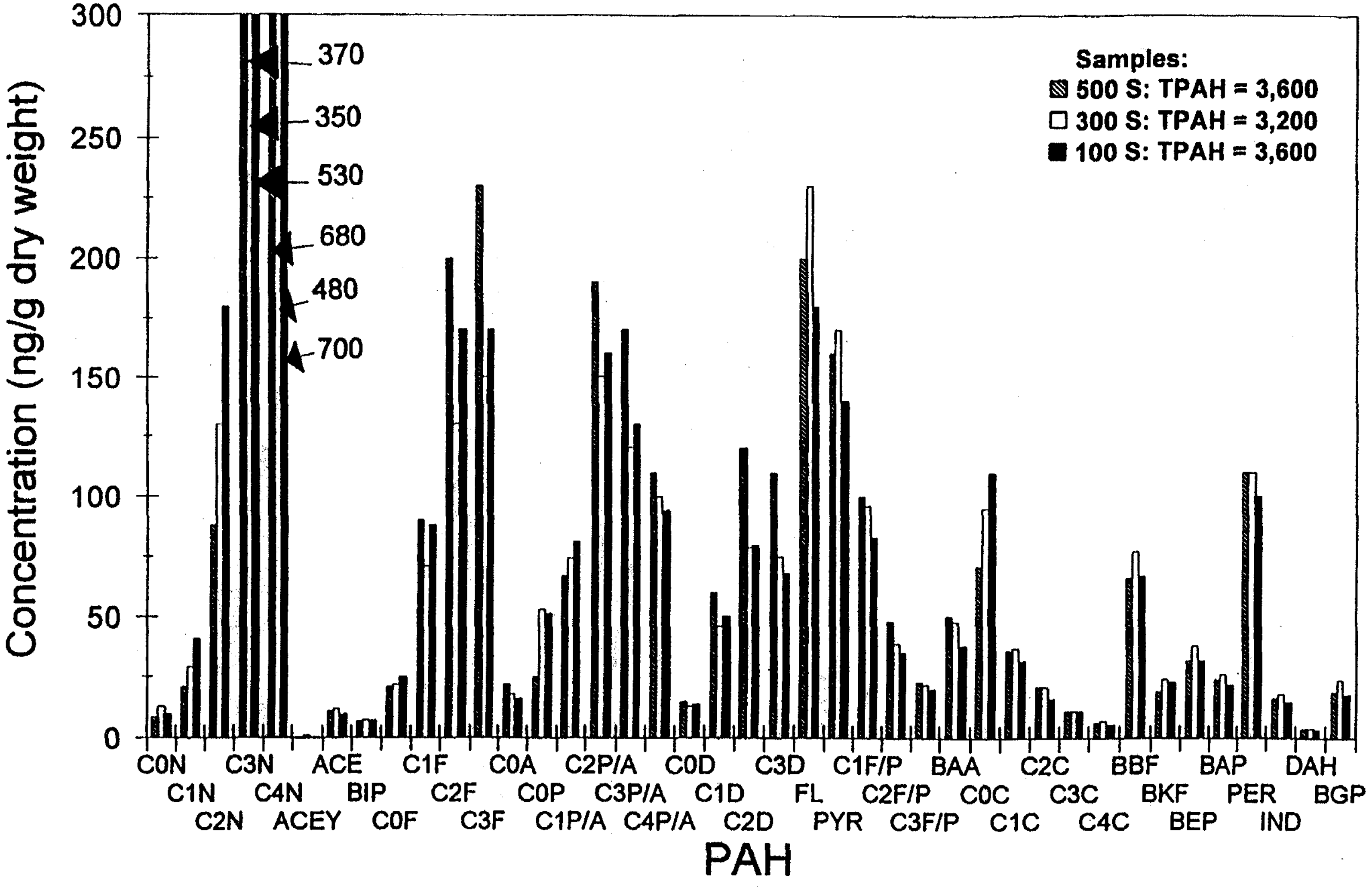

Figure 8.56. PAH distributions in sediments from the south transect of Four Isle Dome collected during the Pre-termination Survey (Survey I).

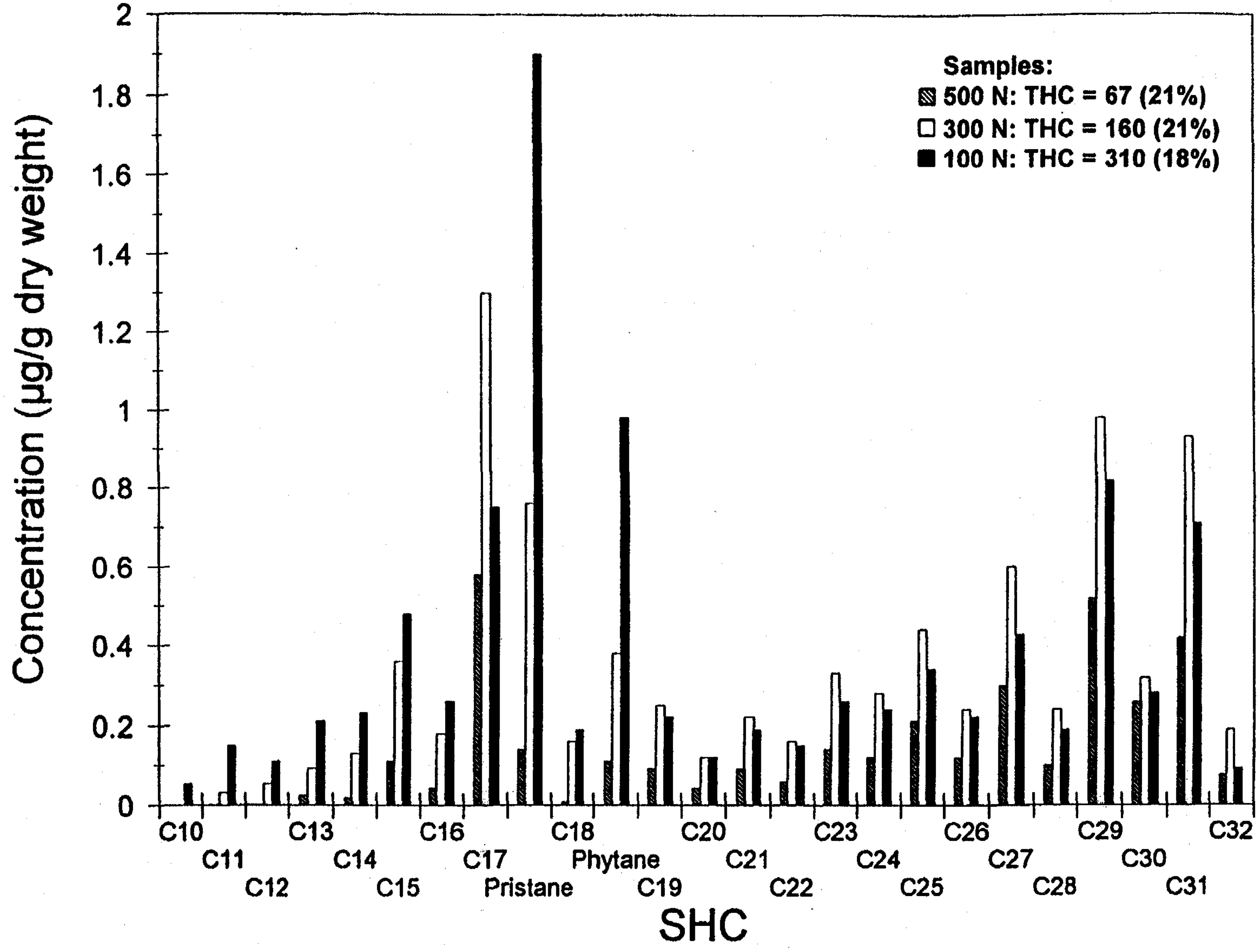

Figure 8.57. SHC distributions in sediments from the north transect of Four Isle Dome collected during the Pre-termination Survey (Survey I).

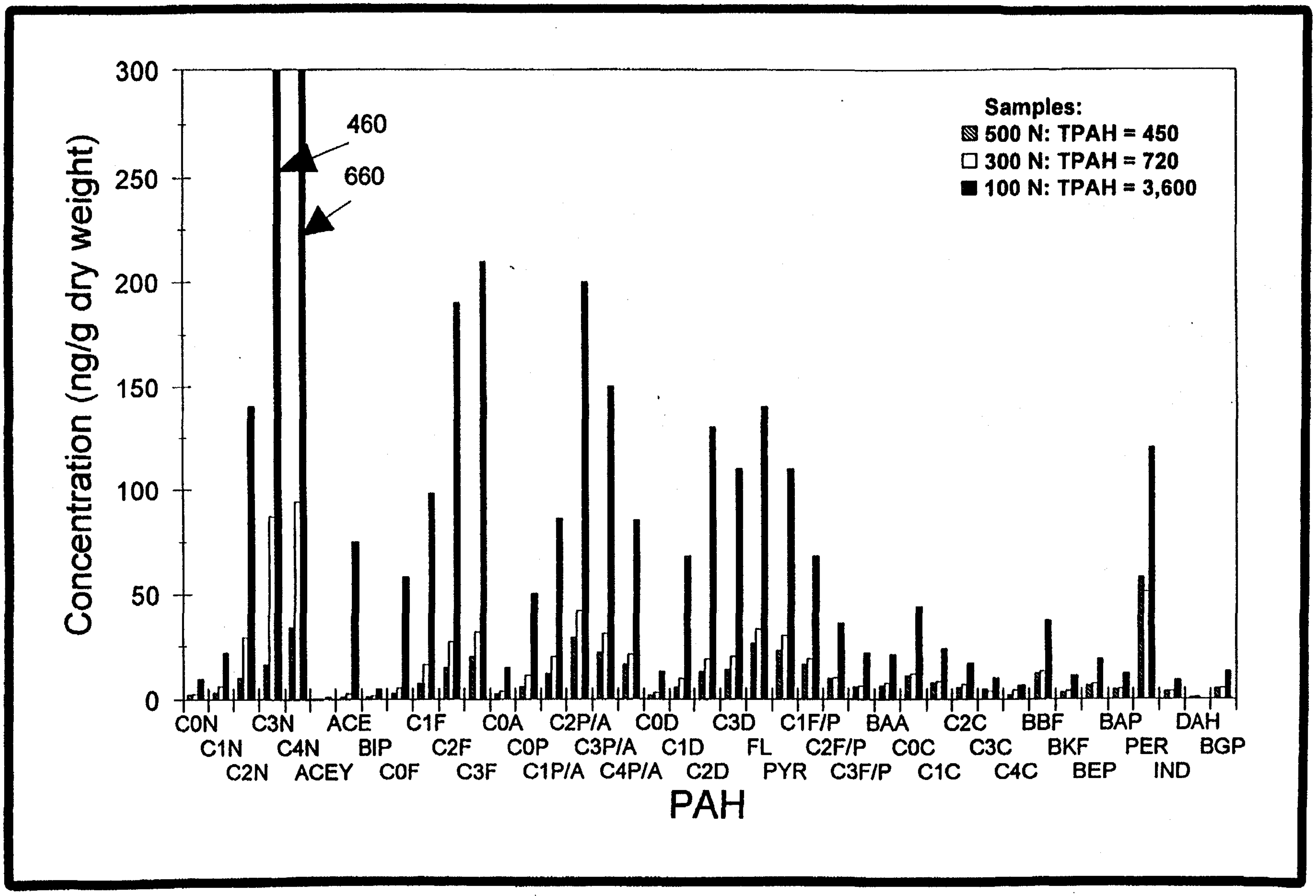

Figure 8.58. PAH distributions in sediments from the north transect of Four Isle Dome collected during the Pre-termination Survey (Survey I).

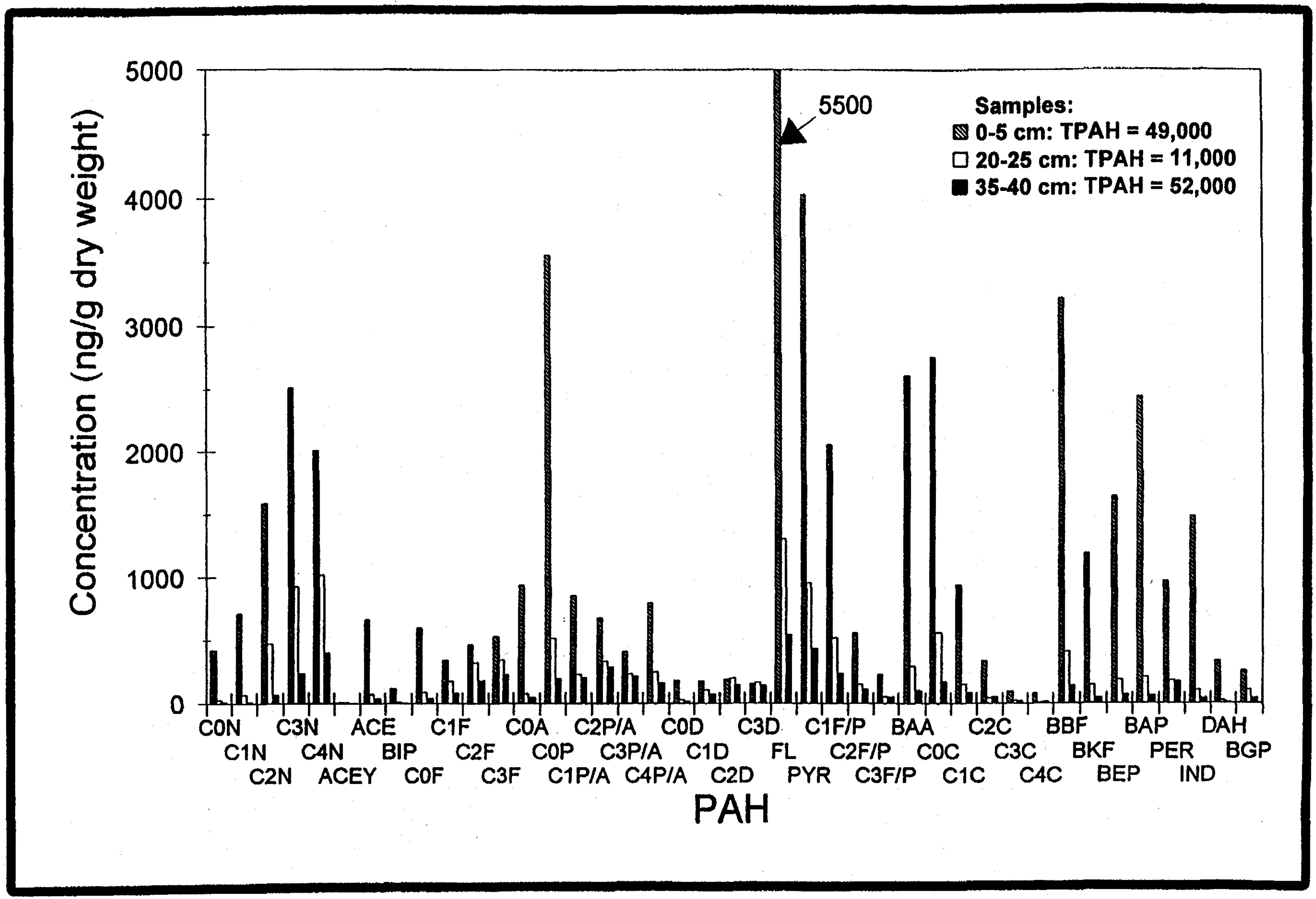

Figure 8.59. PAH distributions in sediments from the discharge station of Four Isle Dome collected during the Pre-termination Survey (Survey I).

The SHC distribution in the surface sediment, however, was characteristic of a weathered light-end fuel oil (**Figure 8.60**). The biogenic n-alkanes usually accompanying pyrogenic PAHs in the other site stations were not evident at the Four Isle Dome discharge stations.

The characteristic biogenic SHCs were present, however, in the reference station sediments (**Figure 8.61**), similar to all reference stations at the other sites. The PAH distributions at the Four Isle Dome reference stations contained relatively more of the two- and three-ring alkyl PAHs than reference stations at the other sites where the pyrogenic PAHs dominated the PAH distribution (**Figure 8.62**).

Unlike any sediment sample from any site in this study, an unusually large amount of fairly fresh petroleum (16,000 ng/g total PAHs), probably a light-end refined oil, was buried deep (35 to 40 cm) in the sediment at one of the reference stations (R1). Only a small amount had migrated to the upper sediment layers (20 to 25 cm). A past accidental spill that was quickly buried was the probable source of this oil.

The principle component analysis plot of the Four Isle Done sediments (**Figure 8.63**) showed that the deep reference station oil was most similar to a potential petroleum source (PW). This deep reference sediment was positioned near PW (produced water PAHs) because pyrogenic PAHs were almost absent in this sample, unlike other 'oiled' sediments which contained appreciable amounts of pyrogenic PAHs. Produced water was, however, not the cause of the large petroleum signature at this reference station. Ironically the separation of the discharge station sediment from the other sediments in the plot was due to the influence of large inputs of pyrogenic PAHs (probably creosote or perhaps fossil fuel combustion PAHs).

Although the petroleum PAH concentrations were relatively large in the Four Isle Dome sediments, a comparable amount of pyrogenic PAHs accompanied the petroleum input. The similarity in positions in the principle component analysis plot of most station sediments, even the reference sediments, suggested a common source for both pyrogenic and petrogenic PAHs.

8.4 SUMMARY AND CONCLUSIONS

In this chapter, spatial and temporal trends in hydrocarbon composition, and potential sources of hydrocarbons in impacted sediments were evaluated at three oil and gas production fields in coastal waters of Louisiana with different physical and hydrological characteristics. The three study sites were Delacroix Island Oil and Gas Field, Bay de Chene Field, and Four Isle Dome Oil Field. Sediment (mostly fine-grained, muddy substrate) samples were collected near and along transects away from the discharging facilities at the three sites just before termination, and twice after termination (within a year) of produced water discharge at Delacroix Island and Bay de Chene. The samples were analyzed for SHCs, THCs, and PAHs. SHCs, THCs, and PAHs were also determined in produced water from the three sites. Selected sediment interstitial water samples were also analyzed for PAHs. VAHs were determined in produced water samples and selected sediment samples.

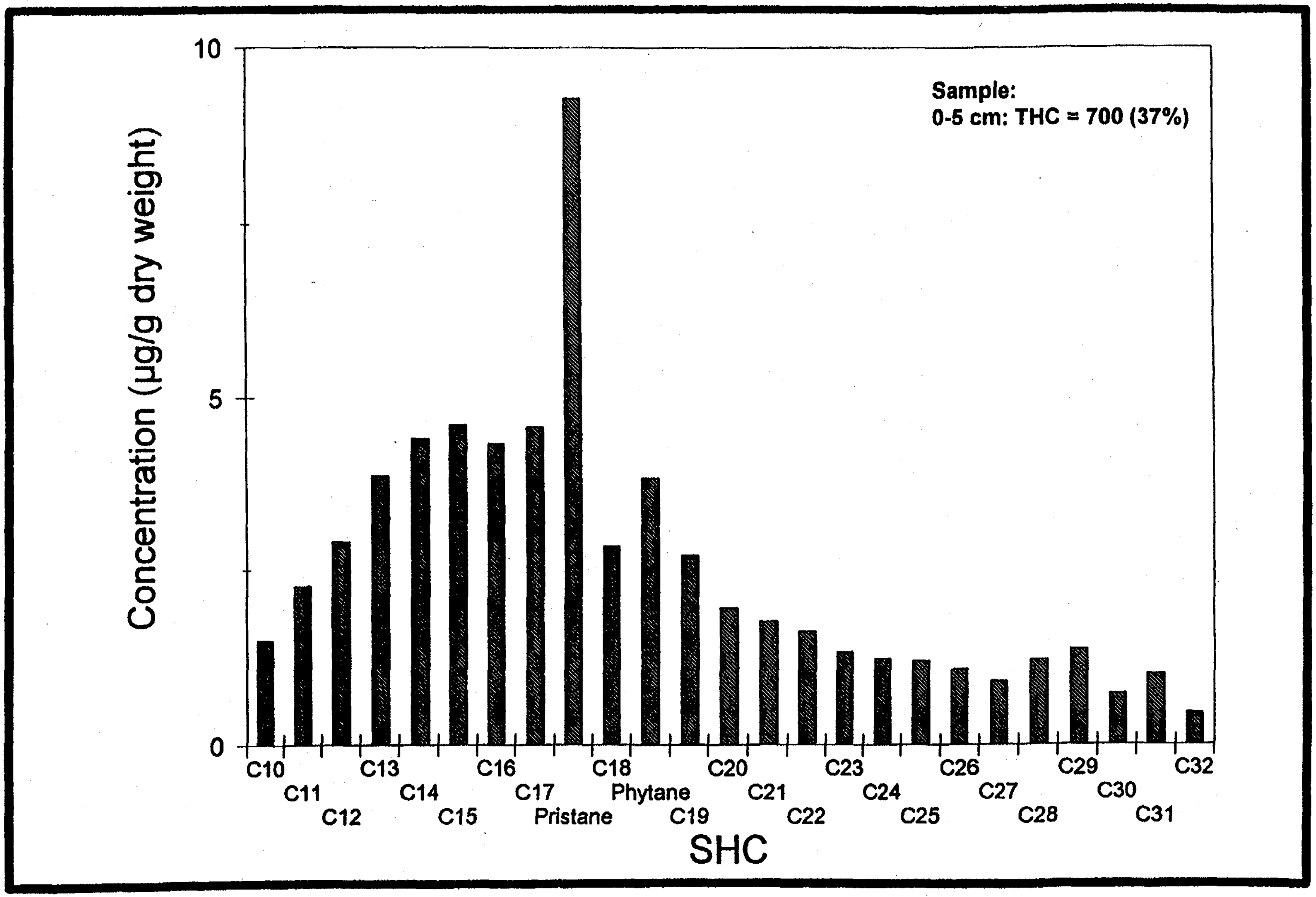

Figure 8.60. SHC distribution in sediments from the discharge station of Four Isle Dome collected during the Pre-termination Survey (Survey I).

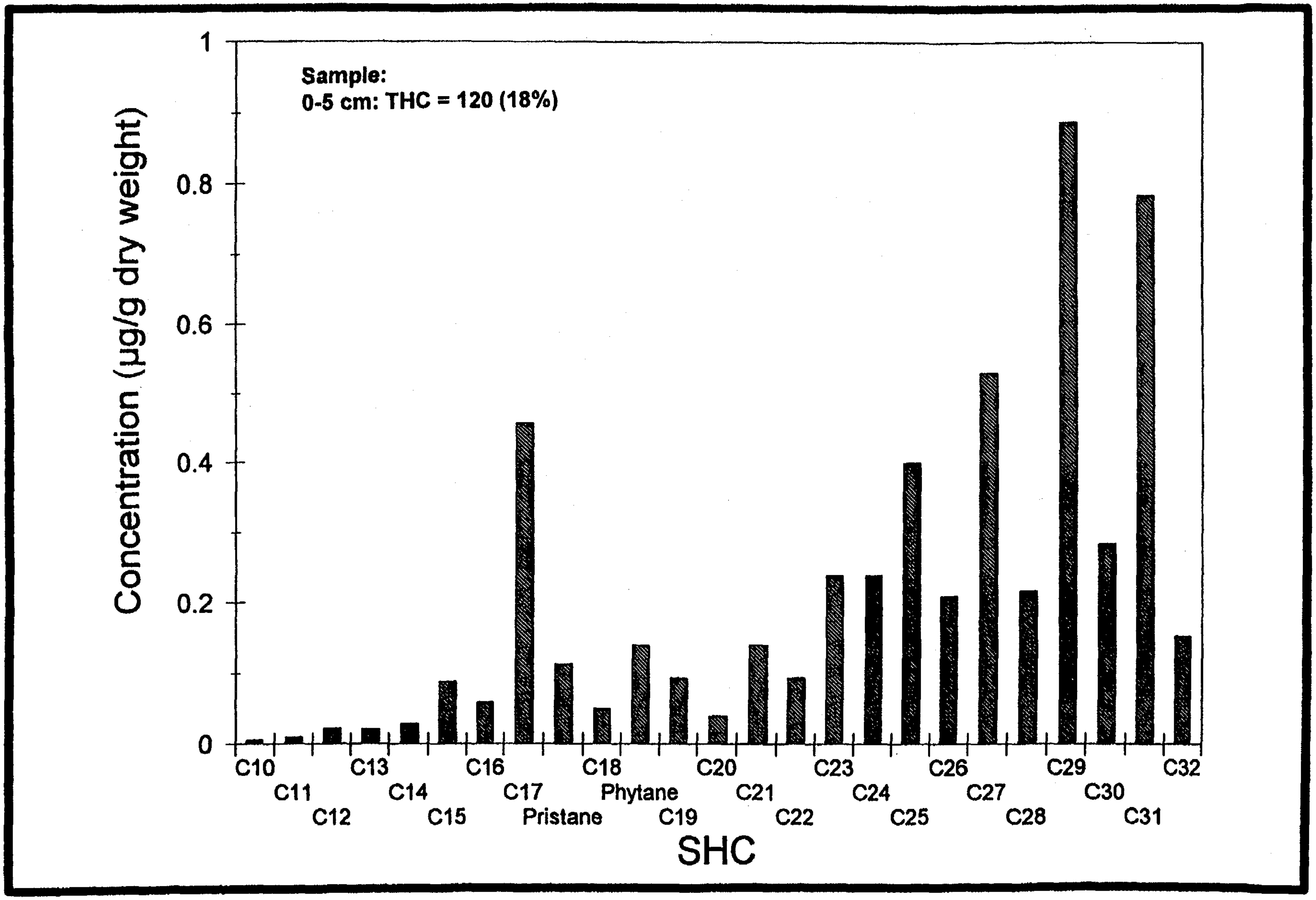

Figure 8.61. SHC distribution in sediments from the reference 1 station of Four Isle Dome collected during the Pre-termination Survey (Survey I).

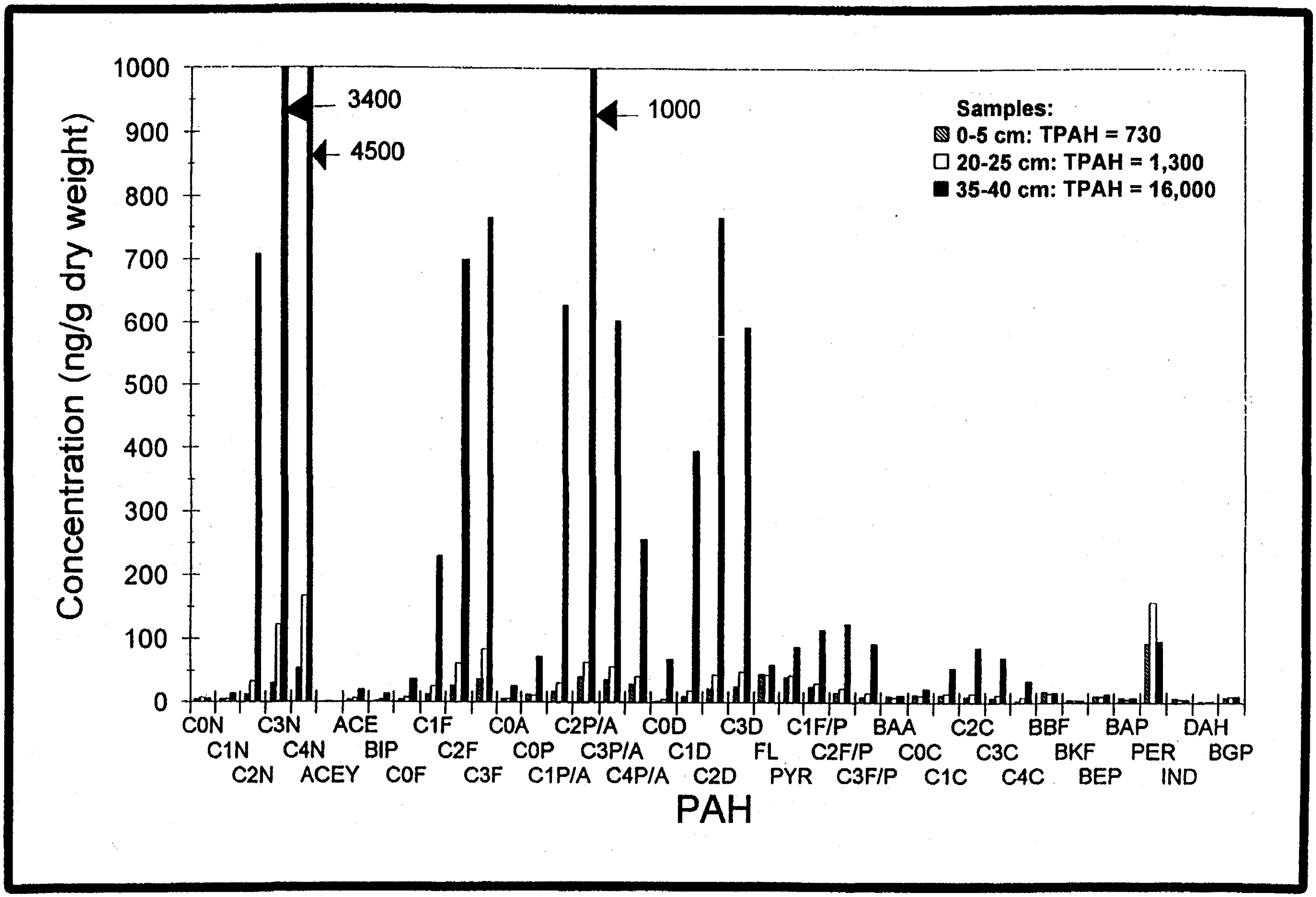

Figure 8.62. PAH distributions in sediments from the reference 1 station of Four Isle Dome collected during the Pre-termination Survey (Survey I).

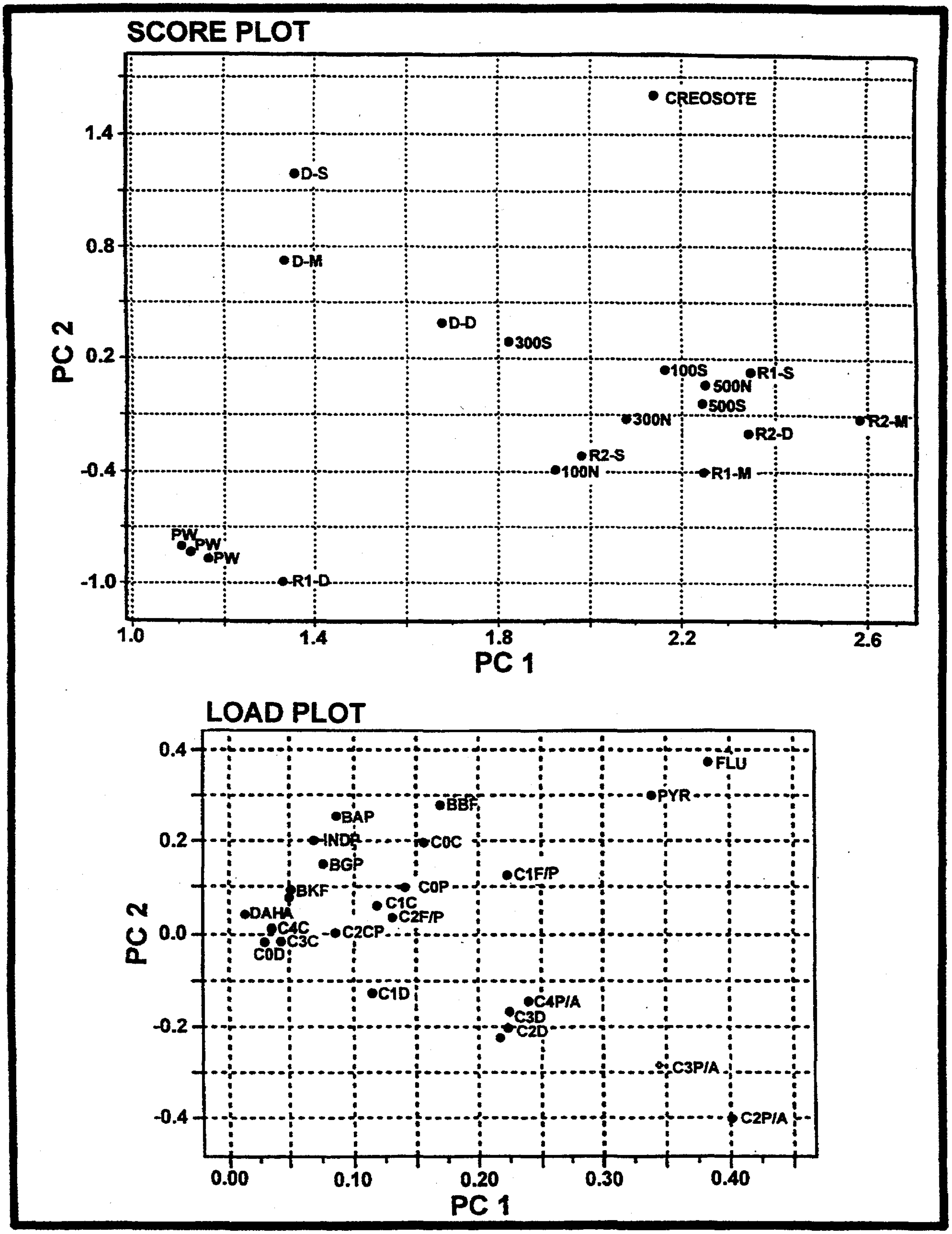

Figure 8.63. Principle component analysis plot of PAH data of produced water (PW) and sediments from Four Isle Dome collected during the Pre-termination Survey (Survey I). PAHs (less naphthalenes, fluorenes, and perylene) were normalized by the highest concentration PAH in each sample. Score plot presents sediment stations (D - discharge, R1 - reference 1, R2 - reference 2, and distance/compass heading), sediment increment (S - 0 to 5 cm, M - 20 to 25 cm, and D - 35 to 40 cm), and survey designation (1). Load plot presents PAH acronyms which are defined in **Table 8.1**.

Compositional distributions (fingerprints) of SHC and PAH target compounds were used to study hydrocarbon trends, and with PAH diagnostic ratios, to identify potential sources of hydrocarbons at the sites. Multivariate statistical analysis was also performed on the data to explain some of the differences and similarities in the hydrocarbon composition.

SHC and PAH concentrations in produced waters from the three sites were typical of produced waters in the region. Total PAH and THC concentrations of Delacroix Island produced waters averaged 26,000 ng/L and 290 μg/L, respectively, whereas the Bay de Chene concentrations averaged 440,000 ng/L and 16,000 μg/L, which were similar to the Four Isle Dome samples of 410,000 ng/L and 19,000 μg/L. PAH diagnostic ratios of C_2-phenanthrenes and C_2-dibenzothiophenes (C2P/C2D) and C_3-phenanthrenes and C_3-dibenzothiophenes (C3P/C3D) in Bay de Chene produced water were 3.0 and 2.2, respectively, similar to other Louisiana oils. Delacroix Island and Four Isle Dome PAH diagnostic ratios were higher and may reflect more of the solubility influence of oil in water than the composition of the oil.

At all sites, hydrocarbon concentrations in sediments generally decreased with increasing distance from the discharge station. Reference sediment concentrations were generally 25 to 100 μg/g for THCs and 250 to 750 ng/g for PAHs. The highest hydrocarbon concentrations, approximately 700 to 1,000 μg/g for THCs and 50,000 to 700,000 ng/g for PAHs, occurred in surface sediments at the discharge stations and were consistent among the three sites. Each site had different spatial and temporal trends.

> Delacroix Island sediments had consistent low concentrations of hydrocarbons in sediments from the outer (500 and 1,000 m) stations (25 to 50 μg/g THCs, 220 to 280 ng/g PAHs), slight increases in the inner (100 and 300 m) stations (140 to 230 μg/g THCs, 330 to 2,500 ng/g PAHs), and highest concentrations at the discharge station.
>
> Unlike Delacroix Island, the sediments at Bay de Chene had both spatial and temporal hydrocarbon concentration trends. Northeast transect hydrocarbon concentrations at the inner stations (1,000 μg/g THCs and 50,000 ng/g PAHs at 100 m) were generally 5 to 10 times higher than northwest or southwest transect sediment concentrations. Concentrations decreased in northeast and northwest transect sediments from Pre- to Post-termination Surveys.
>
> Sediments at Four Isle Dome had different hydrocarbon trends in each transect. North transect THC and PAH sediment concentrations increased from outer stations to the discharge facility. On the south transect hydrocarbon concentrations were consistently high at all stations (500, 300, and 100 m) at 300 to 460 μg/g for THCs and 3,200 to 3,600 ng/g total PAHs. At 100 m, hydrocarbon concentrations were the same on both transects.
>
> Only naphthalene and C_1-naphthalenes were detected in interstitial water samples from discharge and reference stations of Delacroix Island at concentrations less than 100 ng/L. Delacroix Island and Four Isle Dome (not Bay de Chene) sediments contained VAHs (15 to 160 mg/g VAH) at the discharge stations sampled during the Pre-termination Survey only.

At all sites except at the stations nearest the facility (discharge) the resolvable hydrocarbon composition in sediments was dominated by pyrogenic PAHs and high molecular weight biogenic SHCs (C_{23} to C_{32}). Sediments at stations nearest the facility and the discharge station had a petrogenic signature superimposed on the pyrogenic PAHs and biogenic SHCs. Petrogenic PAHs although present at the nearest stations (100 m) in most cases, dominated the PAH composition only in sediments at the discharge stations from the Pre-termination Survey (example: **Figure 8.64**).

Pyrogenic PAHs, such as creosote or fossil fuel combustion products, are characterized by relatively high amounts of the four- and six-ring PAHs such as fluoranthene, pyrene, benz(b)fluoranthene, benz(a)anthracene, and benzo(a)pyrene. PAHs of pyrogenic origin (fossil fuel pyrolytic or combustion products, natural combustion products) are characterized by the dominance of the parent PAHs with decreasing abundance with increasing alkylation ($C_0 > C_1 > C_2 > C_3 > C_4$). The PAHs of petrogenic origin (e.g., crude oil, refined oils, natural seeps) have a characteristic "bell shape" in the homologous series distribution where the C_2 or C_3-alkyl PAHs predominate within a PAH family for principally two- and three-ring PAHs.

At Delacroix Island and Bay de Chene, the SHC composition was dominated by the C_{23} to C_{32} n-alkanes with a 4:1 odd to even n-alkane preference, typical of SHCs of biogenic origin. In the lower molecular weight range (C_{14} to C_{22}), which was only 10% to 25% of the total SHCs, the C_{17} n-alkane was the dominant compound with relatively low concentrations of the isoprenoids, phytane and pristane. Consistent in all surveys, the SHC signature was representative of hydrocarbon from biogenic origin typical of a terrestrial/wetland environment. In the discharge station sediments of the Pre-termination Survey only, lower molecular weight SHCs (C_{10} to C_{20}) dominated the SHC distribution, which were highly representative of a petrogenic input. Unexpectedly in an environment which petrogenic inputs are envisioned, the large PAH concentrations were consistently due to the contribution of pyrogenic PAHs (80% to 90% of total PAHs), not petrogenic PAHs. Also, increases in PAH concentrations subsurface sediment at the discharge locations were due to increased pyrogenic PAHs, not petrogenic PAHs. The contribution of petrogenic hydrocarbons was relatively minor except very close to the facility and less persistent as evident by the loss of the petrogenic signature in post-termination sediments approximately a year later. Diagnostic ratios C2P/C2D and C3P/C3D in the petroleum contaminated sediments were approximately 2.6 and 2.2, comparable to the Bay de Chene produced water ratios.

The Four Isle Dome sediments showed more petrogenic PAH contribution, but these PAHs were accompanied and often were dominated by pyrogenic PAHs. Unlike Delacroix Island and Bay de Chene, increases in hydrocarbon concentrations in Four Isle Dome sediments were due to petroleum inputs not to pyrogenic (or biogenic) inputs. The characteristic petrogenic SHCs and two- and three-ring PAH alkyl homologue distributions were present in equal amounts at the 100, 300, and 500 m stations (south transect only). Pyrogenic PAHs were also present with the petrogenic PAH analytes at approximately 25% of the total PAHs.

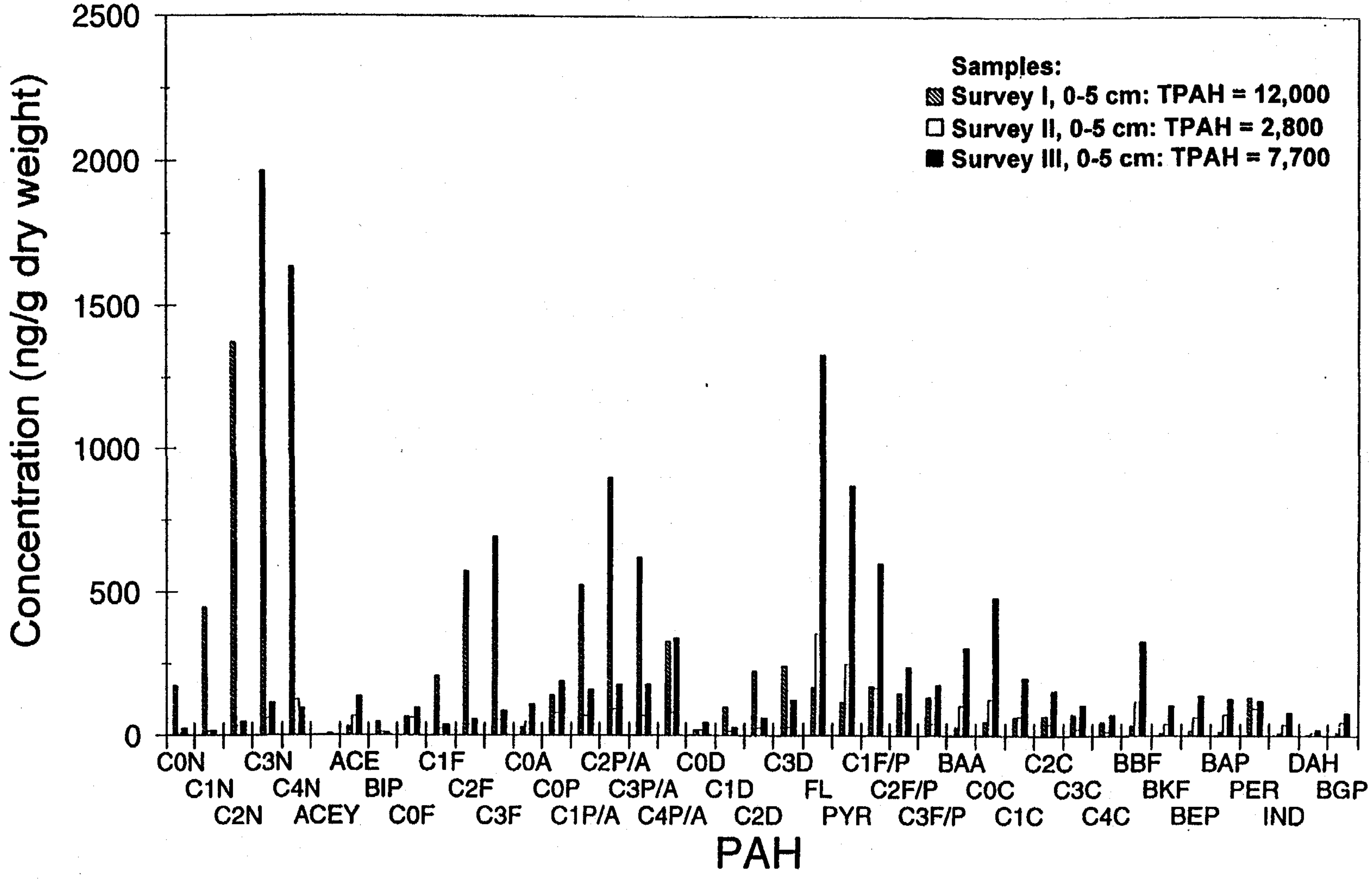

Figure 8.64. PAH distributions in sediments from the discharge station of Delacroix Island collected during all surveys (Surveys I to III).

The relative contributions of perylene, a diagenetic compound from natural biological precursors, increased with distance from the discharge, and made up approximately one-third of the total PAHs in sediments at the reference stations. Increases in PAH concentrations at the reference stations, reflected, however, increases only in perylene. The composition of PAHs without perylene in the reference stations sediments (**Figures 8.65** and **8.66**) remained constant in subsurface sediments and probably could be considered the 'background' composition for the region. Oil had been spilled and buried some time in the past near the location of one of the reference stations at Four Isle Dome.

The petrogenic hydrocarbons in the impacted sediment probably originated from the produced water discharges, and/or light-end refined oil (e.g., No. 2 Fuel Oil) releases based on the dominance of lower molecular weight SHCs and isoprenoids in the SHC distribution, the large amounts of naphthalenes, and the two- and three-ring 'bell-shaped' alkyl PAHs in the PAH distribution. Produced sand discharges could also be a possible source, however, the absence of the 'bell shaped' alkyl distribution in chrysenes, found in crude oil, indicates a light-end refined oil.

Because of the general spatial trend of decreasing hydrocarbon concentrations with increasing distance from the study facility, the source of the hydrocarbon contamination, both the pyrogenic and petrogenic hydrocarbons, in the sediments appears to be from the study facility. The pyrogenic PAHs found in the site sediments were very similar to those in creosote. Fuel oils (No. 2) are often mixed with creosote in application as a preservative in treating wood, which together could be considered a common hydrocarbon source to the sediment. Alternatively creosote, or less likely combustion PAHs from the facility (combustion of fossil fuel), could be accompanied by produced water petroleum PAHs, with both contributing to the hydrocarbon load in the sediments and the trend of simultaneous decreasing contamination away from the facility.

Any interpretation of PAH temporal and spatial trends at these sites require consideration of the composition of the PAHs and the relative amounts of the petrogenic PAHs in the samples. Assessing impact or recovery from petroleum input at these sites using just the total PAH or THC data will lead to inaccurate interpretation. High concentrations of PAHs in surface or deep sediments should not be inferred as originating from petroleum hydrocarbon sources. Most of the PAHs in these sediments are not petrogenic.

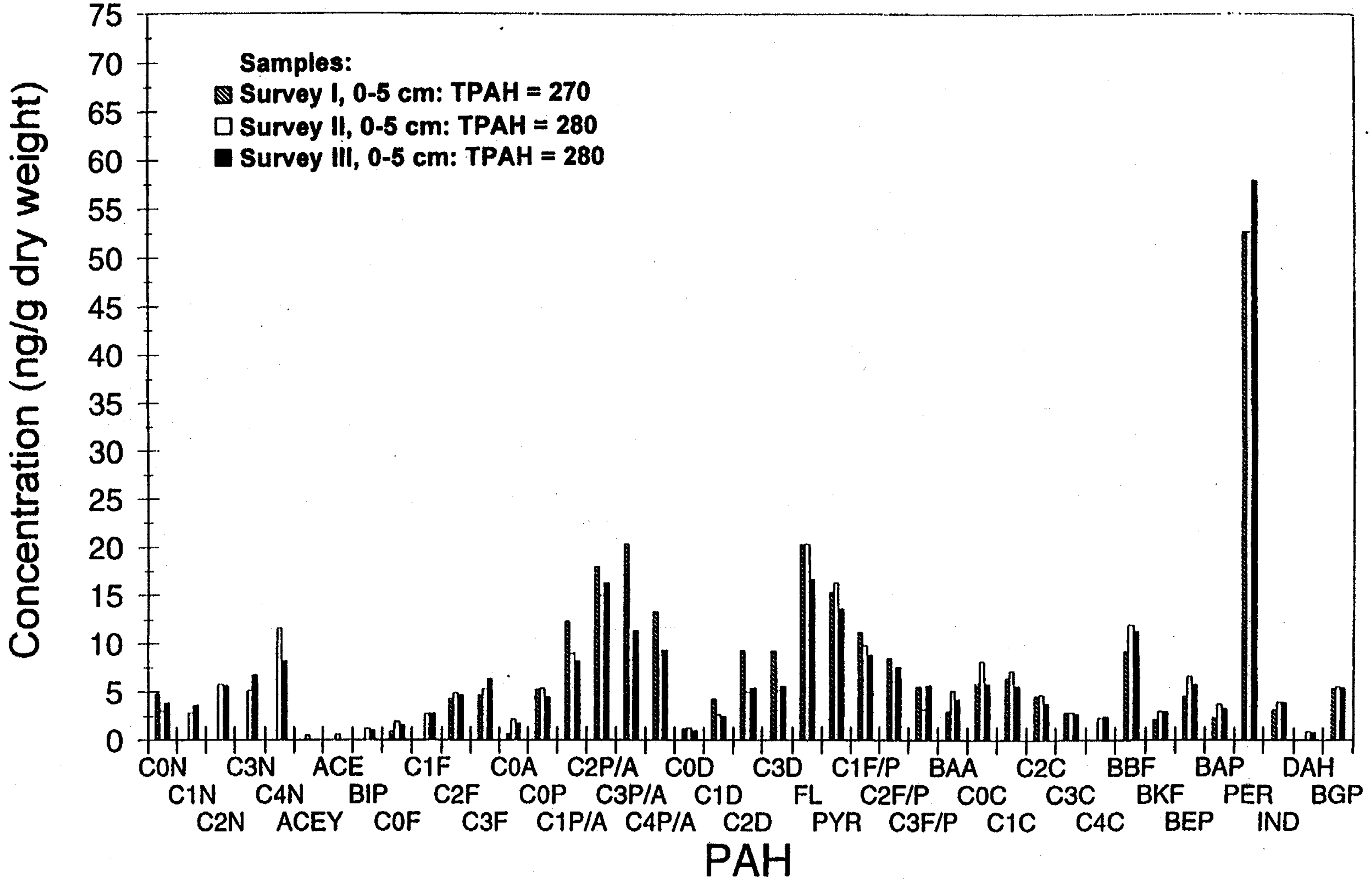

Figure 8.65. PAH distributions in sediments from the reference 1 station of Delacroix Island collected during all surveys (Surveys I to III).

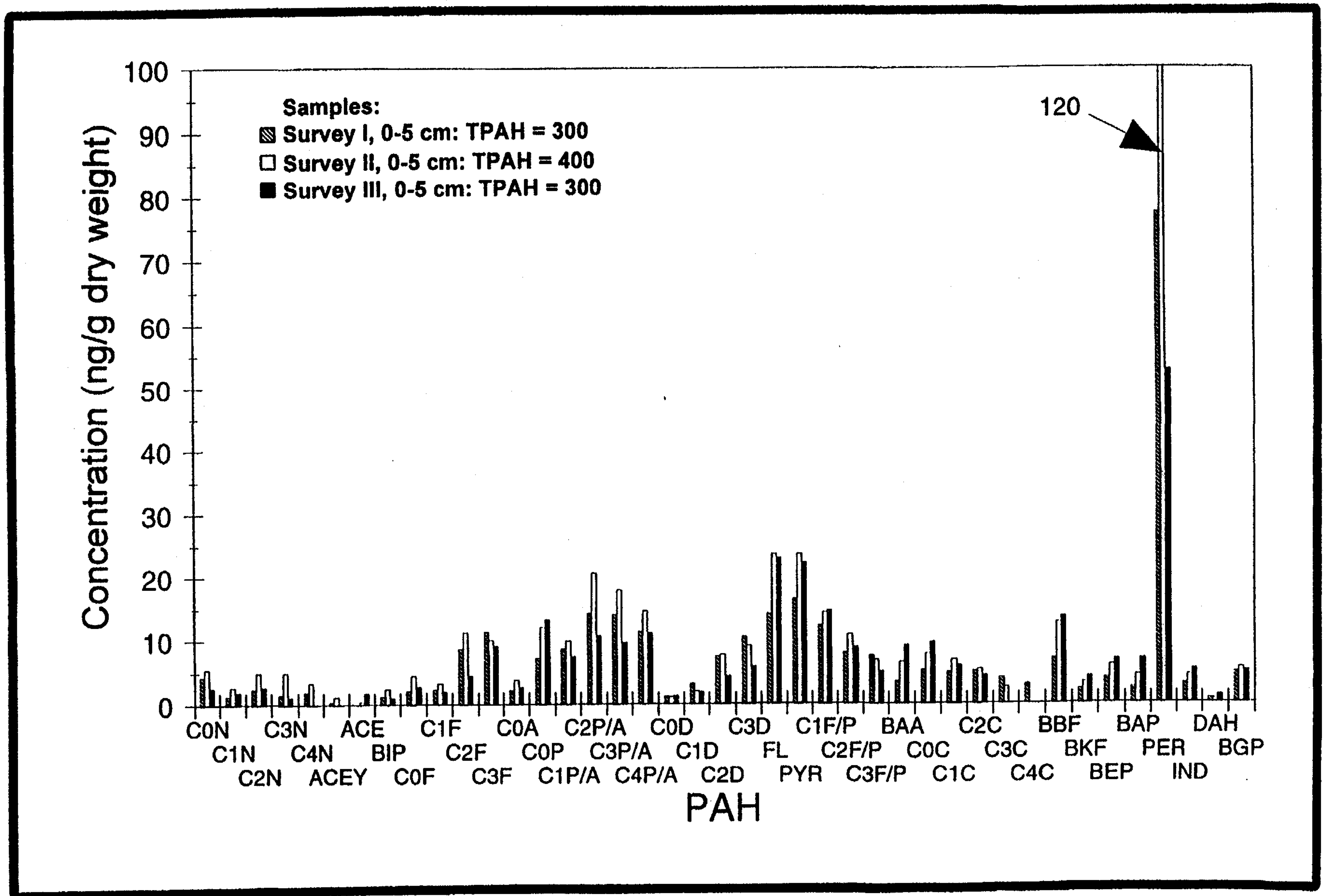

Figure 8.66. PAH distributions in sediments from the reference 1 station of Bay de Chene collected during all surveys (Surveys I to III).

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8.6 ACKNOWLEDGEMENTS

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CHAPTER 9 - BIOLOGICAL RECOVERY IN AREAS WHERE PRODUCED WATER WAS DISCHARGED TO COASTAL LOUISIANA WATERS

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9.1 INTRODUCTION

This chapter presents and discusses the infauna data from samples collected at Delacroix Island, Bay de Chene, and Four Isle Dome. The water quality data collected during each survey are also provided in this chapter.

9.2 LABORATORY METHODS

Four of the six replicate benthos samples from Delacroix Island and Bay de Chene and three of the six replicate benthos samples collected at Four Isle Dome were hand sorted by personnel at the University of New Orleans laboratory of Dr. Michael Poirrier. A decision was made to analyze four rather than the three planned replicate samples at each station to allow for a better estimate of the infauna at the stations. Many of the samples from Delacroix Island and Four Isle Dome were full of detritus which made accurate counts very difficult. No subsampling techniques were employed, and samples were randomly checked for accuracy of specimen identification and counts by Dr. Poirrier.

Infaunal data were analyzed using analysis of variance procedures described in Sokal and Rohlf (1994). Tukey's post hoc test was used to identify significantly different stations within a group. Dependent variables used in the analysis were number of species and number of individuals. Independent variables for each study site included Sample Period (Pre-termination Survey, First Post-termination Survey, and Second Post-termination Survey) and Zone (discharge site, 100 m, 300 m, 500 m, and 1,000 m stations on all transects, and reference stations). The data sets were not completely balanced. At the study locations, there was no transect designation for the discharge site or for the reference sites. At Delacroix Island, there was no 1,000 m station on the northeast transect. At Bay de Chene, there were only 500 and 1,000 m stations on the southeast transect. There was no 1,000 m station on the south transect at Four Isle Dome. The stations are shown on **Figures 3.1** to **3.3**.

The assumptions for analysis of variance were verified including normality and homogeneous variances. Both dependent variables (number of species and individuals) were transformed prior to analysis by taking the square root of all sample observations. This procedure was employed to ensure the variables were normally distributed. Analysis of residuals in analysis of variance confirmed that the dependent variables realize essentially the same variance at different levels of the independent variables.

Multiple regression analyses were used to relate the number of species and number of individuals at Delacroix Island and Bay de Chene to sediment parameters (TOC, grain size, naphthalenes, acenaphthylenes, fluorenes, dibenzothiophenes, anthracenes, fluoranthenes,benzo[a] anthracene, and chrysenes). The 100 m station on the northeast transect at Bay de Chene was excluded from the analysis because it was located at an abandoned fuel dock.

9.3 RESULTS

9.3.1 Water Quality Data

Results of field water quality testing for each station during each sampling are provided in **Appendix 1** (page 9-37).

9.3.2 Benthos

9.3.2.1 Delacroix Island

The list of lowest identified taxa from the Delacroix Island samples excluding epifauna is given in **Table 9.1**. The taxonomic composition (by major groups) of each station by transects and by years is shown in **Appendix 2** (page 9-40).

Average number of species at each station in the Delacroix Island study area (by zone) along the northwest transect, the northeast transect, and the south transect are given in **Figures 9.1** through **9.3**. Average number of individuals at each station along the northwest transect, the northeast transect, and the south transect are given in **Figures 9.4** through **9.6**. The discharge station was repeated on the figures for all transects as it was the origin of the transect. In these figures, reference station 1 was considered the termination of the northeast transect and reference station 2 was considered the termination of the northwest transect. Zone 5 which does not exist on the northeast transect was not represented in these figures.

The data were analyzed using a two-way factorial analysis of variance for both number of species and number of individuals. Independent variables used in the two-way analysis of variance included zone and sample period. Results of the analysis of variance for number of species showed that both zone and sample period and the interaction of the two were highly significant ($p<.01$). The post hoc test conducted to determine significant differences among zone means showed that the number of species at the discharge station and the number of species at the reference stations were significantly different from other zone means.

A second post hoc test was conducted to determine significant differences among sampling periods. Results of this test showed that the number of species collected in October 1993 was significantly different from the number of species collected in April 1993 ($p<.001$) and April 1994 ($p<.001$). The number of species collected in April 1993 was also significantly different from the number collected in April 1994 ($p=.057$).

Results of the two-way analysis of variance for number of individuals show that again the effects of zone and sampling period were highly significant ($p<.01$) and that the interaction of these two variables was highly significant ($p<.01$). A post hoc test was conducted to determine the significant differences among zone means. Results showed that the number of individuals at the reference stations was significantly different from the number of individuals in all other zones. The number of individuals in Zone 1, the discharge station, was not significantly different from those in Zones 2 (100 m), 3 (300 m), 4 (500 m), and 5 (1,000 m).

Table 9.1. Lowest taxon of organisms identified in samples from Delacroix Island stations.

- Phylum Platyhelminthes
  - Class Turbellaria
- Phylum Nemertea
- Phylum Nematoda
- Phylum Annelida
  - Class Polychaeta
    - Order Phyllodocidae
      - Family Phyllodocidae
        - *Eteone* sp.
      - Family Pilargidae
        - *Parandalia americana*
      - Family Nereidae
        - *Neanthes succina*
    - Order Capitellida
      - Family Capitellidae
    - Order Spionida
      - Family Spionidae
        - *Streblospio benedicti*
        - *Polydora* spp.
    - Order Terebellida
      - Family Ampharetidae
        - *Hobsonia florida*
  - Class Oligochaeta
  - Class Hirudinea
- Phylum Mollusca
  - Class Gastropoda
    - Subclass Prosobranchia
      - Order Mesogastropoda
        - Family Hydrobiidae
          - *Probythinellas louisanae*
          - *Texadina sphinctostoma*
    - Subclass Opisthobranchia
      - Order Nudibranchia
  - Class Bivavia
    - Subclass Pteriomorphia
      - Order Mytiloidea
        - Family Mytilidae
          - *Ischadium recurvum*
    - Subclass Heterdonta
      - Order Hippuritoidea
        - Family Mactridae
          - *Mulina lateralis*
          - *Rangia cuneata*
          - Clams <5mm
        - Family Tellinidae
          - *Macoma mitchell*
        - Family Dreissenidae
          - *Congeria leucopaeta*

Table 9.1 (Continued).

- Phylum Anthropoda
  - Subphylum Crustacea
    - Class Branchiopoda
      - Order Cladocera
    - Class Maxillopedia
      - Subclass Copopoda
        - Order Harpacticoida
          - Family Canuellidae
            - *Scottolana canadensis*
        - Order Calanoida
          - Family Acartiidae
            - *Acartia tonsa*
      - Subclass Cirripedia
        - Order Thoracica
          - *Balanus* spp.
    - Class Ostracoda
    - Class Malacostraca
      - Order Cumacea
      - Order Tanaidacea
        - Family Paratanaidae
          - *Hargeria rapax*
      - Order Isopoda
        - Family Idoteidae
          - *Edotea montosa*
        - Family Sphaeromatidae
          - *Cassidinedia ovalis*
        - Family Anthuridae
          - *Cyathura polita*
        - Family Munnidae
          - *Munna reynoldsi*
      - Order Amphipoda
        - Family Ampeliscidae
          - *Ampelisca* sp.
        - Family Aoridae
          - *Grandidierella bonnieroides*
        - Family Corophiidae
          - *Corophium louisianum*
          - *Ceraphus benthophilis*
        - Family Gammaridae
          - *Gammarus* sp.
          - *Murcogammarus mucronatus*
          - *Melita* sp.
        - Family Oedicerotidae
          - *Monoculodes* sp.
      - Order Mysidacea
        - Family Mysidae

Table 9.1. (Continued).

      - Order Decapoda
        - Family Palaemonidae
          - *Palaemonetes* spp.
        - Family Xanthidae
          - *Rhithropanopeus harrisii*
  - Subphylum Uniramia
    - Class Insecta
      - Order Diptera
        - Family Ceratopogonidae
        - Family Chironomidae
          - Subfamily Tanypodinae
          - Chironomid B
          - Subfamily Chironomidae
          - Chironomid A, C, and D
      - Order Coleoptera
      - Order Odonata
        - Suborder Zygoptera
- Phylum Chordata
  - Subphylum Vertebrata
    - Class Osteichthyes
      - Order Perciformes
        - Family Gobiidae
          - *Gobiosoma bosci*
        - Family Syngnathidae
          - *Syngnathus scovelli*

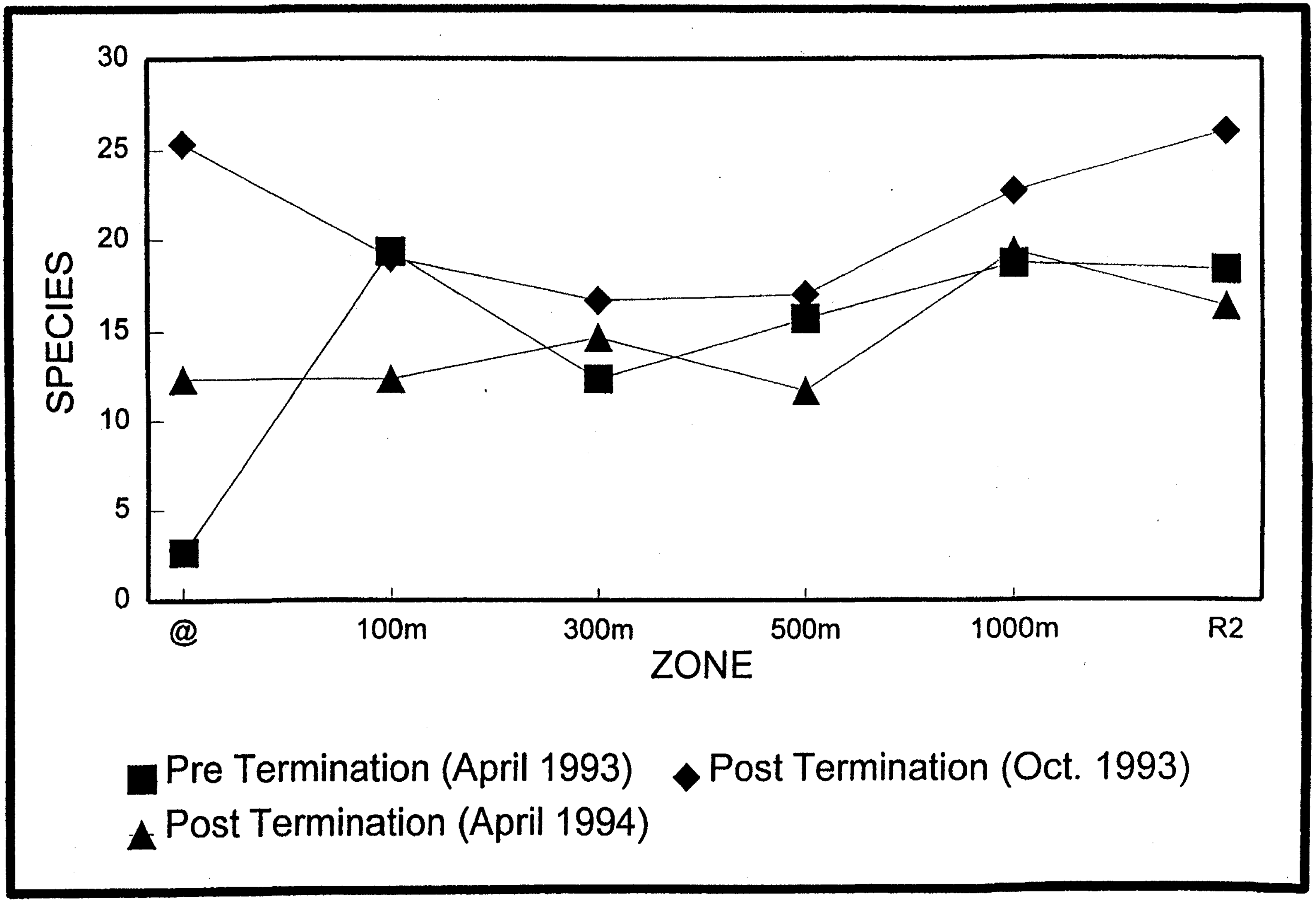

Figure 9.1. Average number of species collected at stations on the northwest transect at Delacroix Island for all sampling periods.

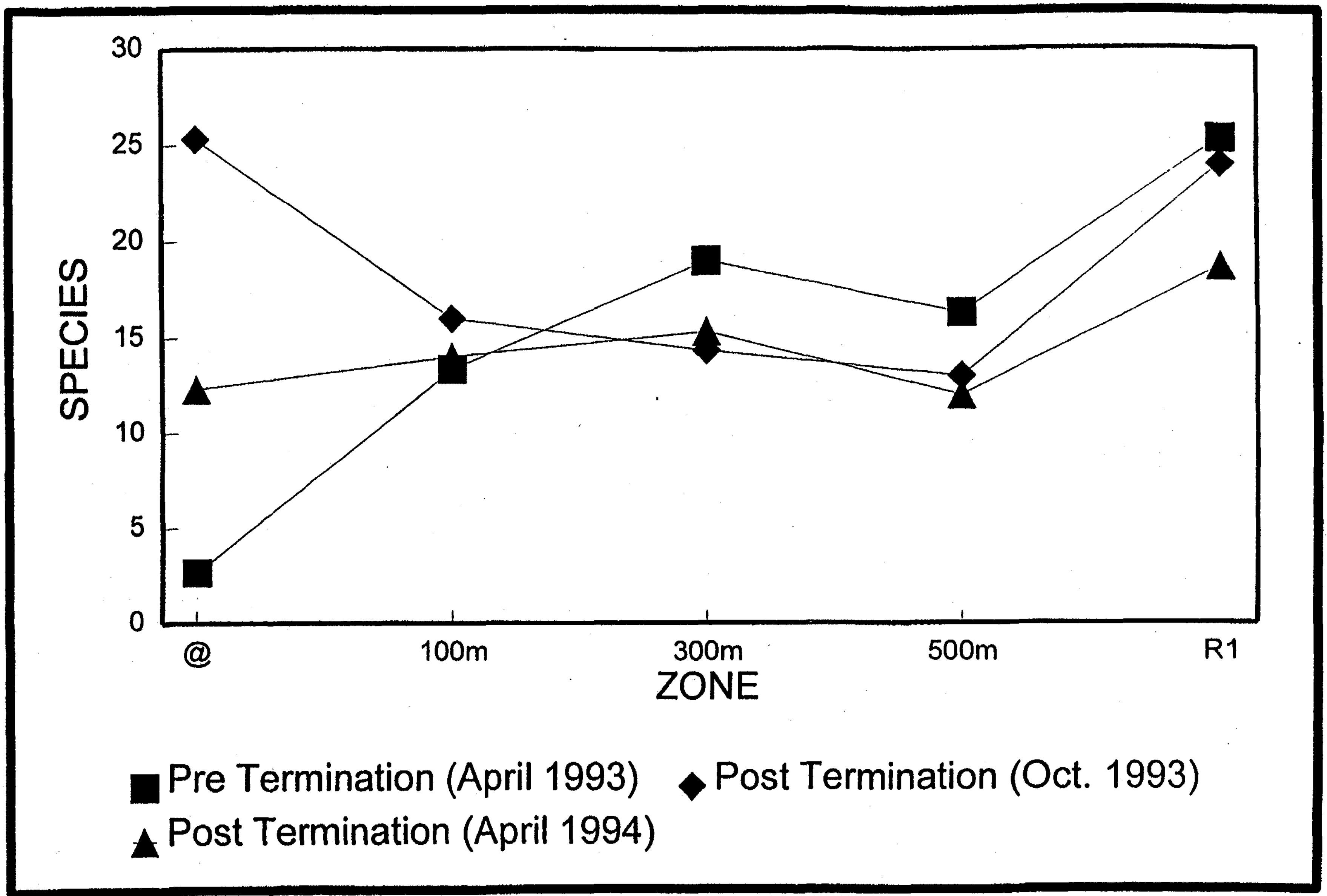

Figure 9.2. Average number of species collected at stations on the northeast transect at Delacroix Island for all sampling periods.

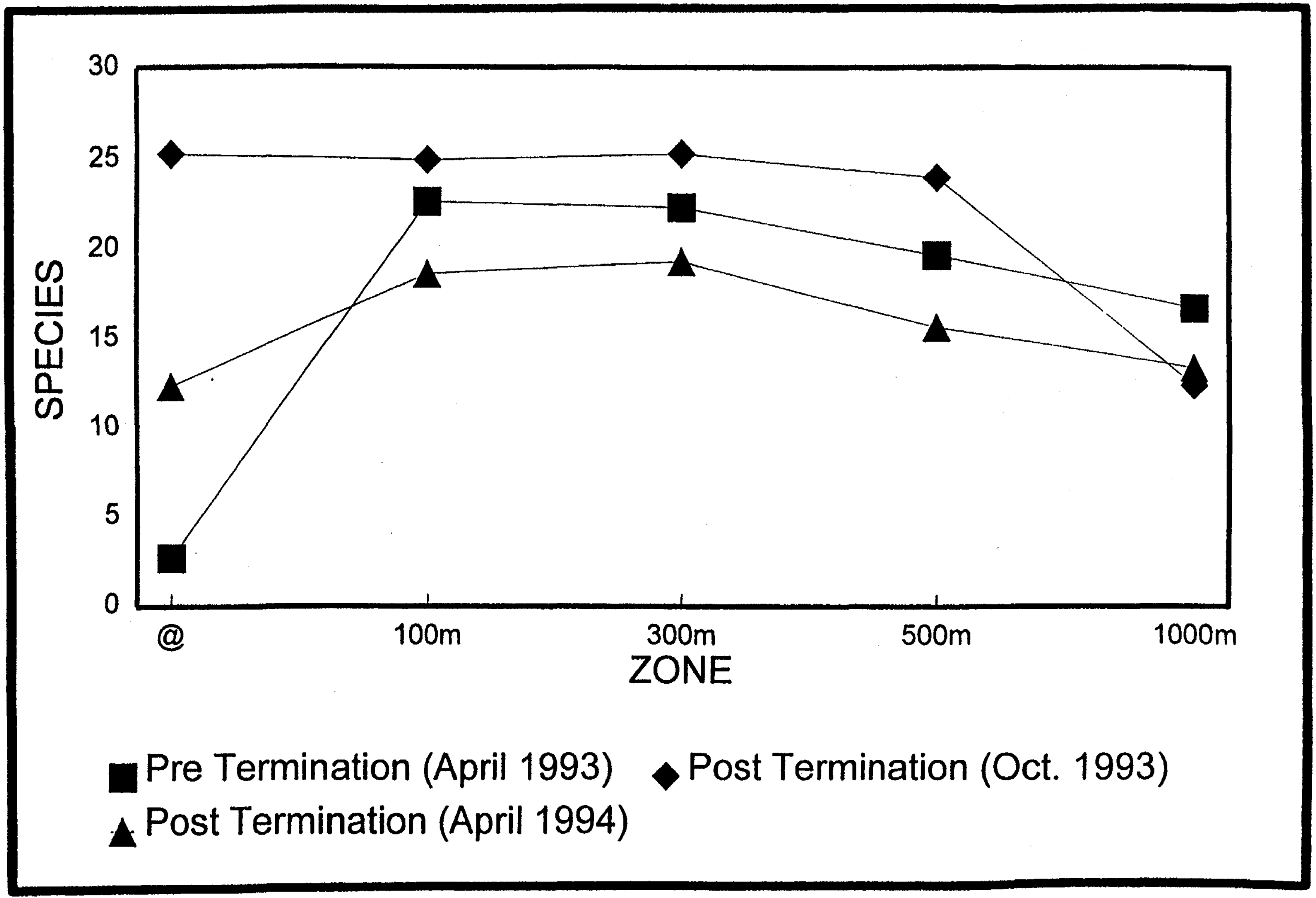

Figure 9.3. Average number of species collected at stations on the southern transect at Delacroix Island for all sampling periods.

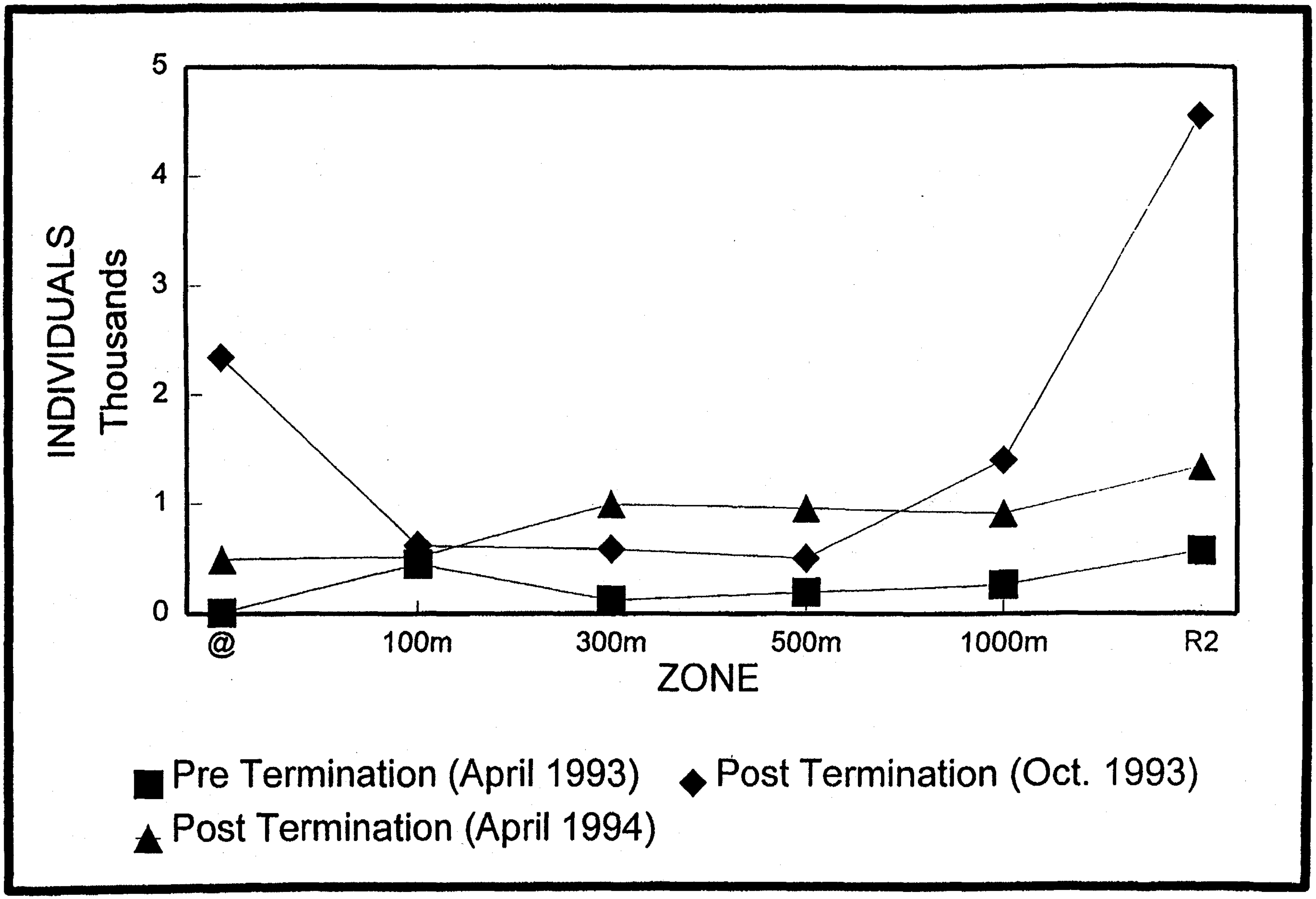

Figure 9.4. Average number of individuals collected at stations on the northwest transect at Delacroix Island for all sampling periods.

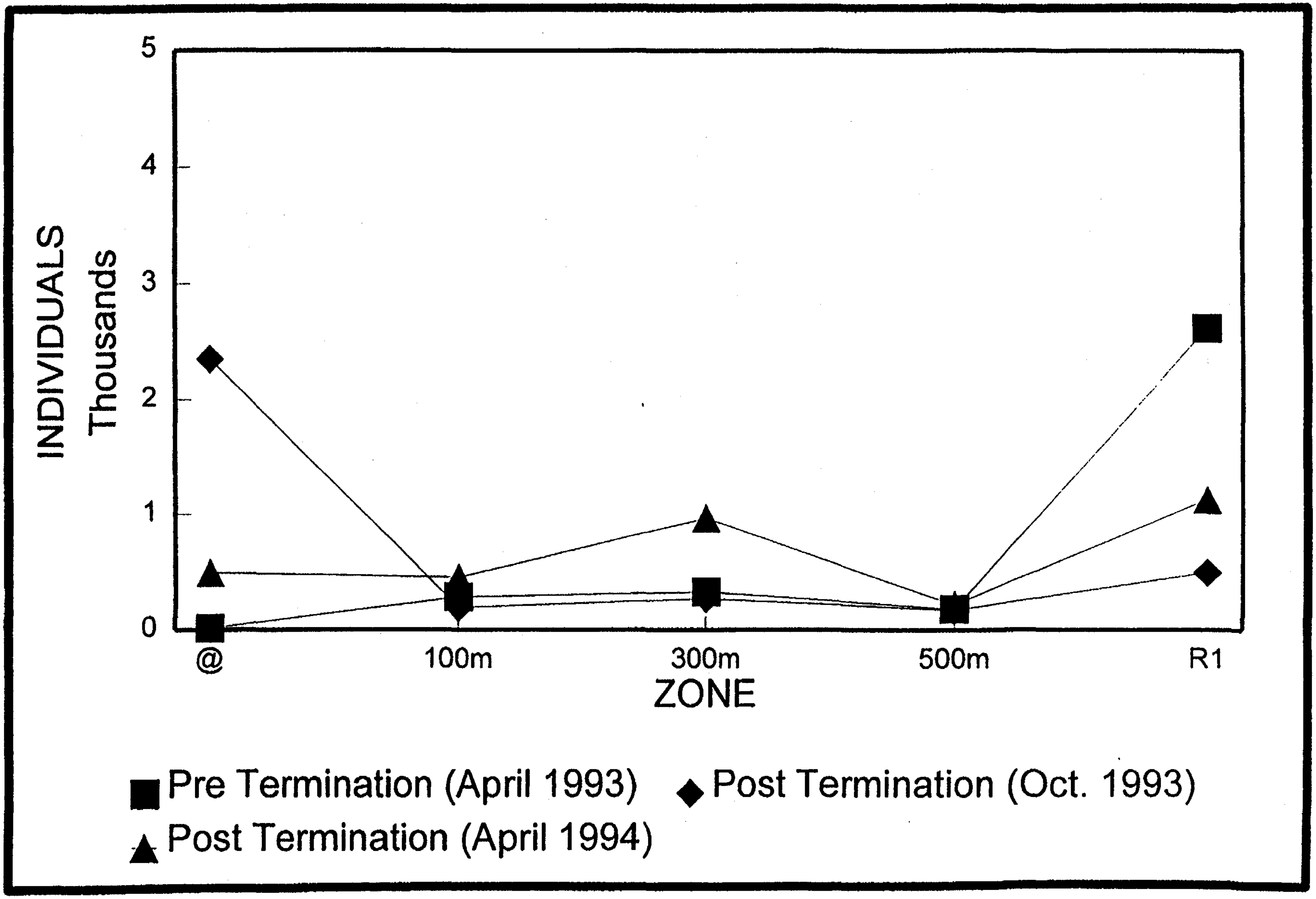

Figure 9.5. Average number of individuals collected at stations on the northeast transect at Delacroix Island for all sampling periods.

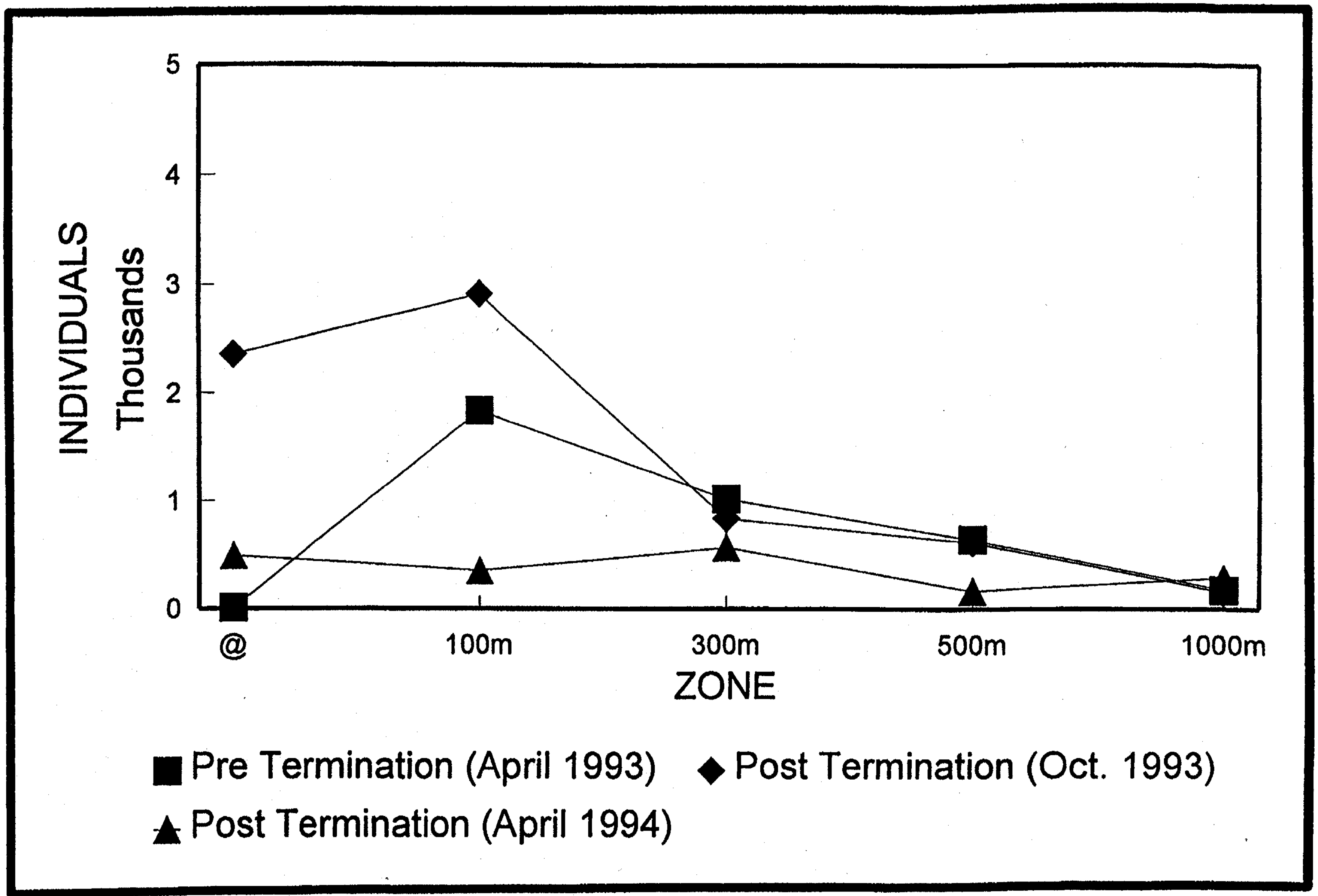

Figure 9.6. Average number of individuals collected at stations on the southern transect at Delacroix Island for all sampling periods.

A second post hoc test was conducted to determine significant differences among sampling periods. Results of this test showed that the number of individuals collected in October 1993 was significantly different from that collected in April 1993 (p<.01) and in April 1994 (p<.01).

The multiple regression analysis identified several factors which had a negative influence on the numbers of species and individuals at Delacroix Island. These factors included sample period, dibenzothiophenes, and flouranthene. Sediment grain size was positively correlated with numbers of species.

9.3.2.2 Bay de Chene

The list of lowest taxa identified in Bay de Chene samples excluding epifauna is given in **Table 9.2**. The taxonomic composition (by major groups) of each station by transects and by years is provided in **Appendix 3** (page 9-50).

Average number of individuals at each station in the Bay de Chene study area (by zone) along the northeast transect, the southeast transect, the northwest transect, and the southwest transect are given in **Figures 9.7** through **9.10**, respectively. As in the previous data, the discharge station was considered the origin of all transects. Reference Station 1 was considered the termination of the southwest transect and Reference Station 2 was considered the termination of the northeast transect. The southeast transect was missing the 100 and 300 m stations. These stations were not represented.

The data were analyzed using a two way factorial analysis of variance for both numbers of species and numbers of individuals. Results of this analysis using numbers of species showed that there were no significant differences among zones and there were no significant differences among sampling periods. Numbers of species are therefore not presented.

With respect to the numbers of individuals, the analysis of variance showed significant effects for zone (p=.001), sampling period (p<.001), and the zone/sampling period interaction (p<.001). The post hoc test for significant differences of numbers of individuals between zone means showed that the discharge station was significantly different from all other stations. No other significant differences were found between zones. The second post hoc test was conducted to determine significant differences in numbers of individuals between sampling periods. Results of this test showed that the October 1994 sampling was significantly different from both the May 1993 sampling (p<.001) and from the May 1994 sampling (p<.001) with respect to numbers of individuals.

The multiple regression analysis identified two factors which had negative correlations with the numbers of individuals in the Bay de Chene samples. These factors, sample period and dibenzothiophenes, were two of the factors negatively correlated with the Delacroix Island benthos numbers. Sediment grain size was positively correlated with numbers of species.

Table 9.2. Lowest taxon of organisms identified in samples from Bay de Chene stations.

- Phylum Platyhelminthes
  - Class Turbellaria
- Phylum Nemertea
  - Nemertine A
  - Nemertine B
- Phylum Nematoda
- Phylum Annelida
  - Class Polychaeta
    - Order Phyllodocida
      - Family Phyllodocidae
        - *Eteone* sp.
      - Family Sigalionidae
      - Family Goniadidae
      - Family Pilargidae
        - *Parandalia americana*
        - *Sigambra* sp.
      - Family Nereidae
        - *Neanthes succinea*
        - *Nereis occidentalis*
    - Order Capitellida
      - Family Capellidae
      - Family Arenicolidae
    - Order Spionida
      - Family Spionidae
        - *Streblospio benedicti*
        - *Polydora* spp.
        - *Boccardiella* sp.
    - Order Eunicida
      - Family Onuphidae
      - Family Eunicidae
        - *Marphysa* sp.
    - Order Magelonida
      - Family Magelonidae
    - Order Terebellida
      - Family Pectinaridae
      - Family Ampharetidae
        - *Hobsonia florida*
  - Class Oligochaeta
- Phylum Mollusca
  - Class Gastropoda
    - Subclass Prosobranchia
      - Order Mesogastropoda
        - Family Hydrobiidae
          - *Probythinella louisanae*
          - *Texadina sphinctostoma*
    - Subclass Opisthobranchia

Table 9.2. (Continued).

- Class Bivalvia
  - Subclass Pteriomorphia
    - Order Mytiloidea
      - Family Mytilidae
        - *Ischadium recurvum*
        - *Amygdalum papyria*
    - Order Pteroidea
      - Family Ostreidae
        - *Crassostrea virginica*
  - Subclass Heterodonta
    - Order Hippuritoidea
      - Family Mactridae
        - *Mulinia lateralis*
        - *Rangia cuneata*
        - Clams <5mm
      - Family Tellinidae
        - *Macoma mitchelli*
      - Family Dreissenidae
        - *Congeria leucophaeta*
- Phylum Arthropoda
  - Subphylum Crustacea
    - Class Maxillopoda
      - Subclass Copepoda
        - Order Harpacticoida
          - Family Canuellidae
            - *Scottolana canadensis*
        - Order Calanoida
          - Family Acartiidae
            - *Acartia tonsa*
      - Subclass Cirripedia
        - Order Thoracica
          - *Balanus* spp.
    - Class Ostracoda
    - Class Malacostraca
      - Order Cumacea
      - Order Tanaidacea
        - Family Paratanaidae
          - *Hargeria rapax*
      - Order Isopoda
        - Family Idoteidae
          - *Edotea montosa*
        - Family Anthuridae
          - *Cyathura polita*
        - Family Munnidae
          - *Munna reynoldsi*

Table 9.2. (Continued).

- Order Amphipoda
  - Family Ampeliscidae
    - *Ampelisca* sp.
  - Family Aoridae
    - *Grandidierella bonnieroides*
  - Family Corophiidae
    - *Corophium louisianum*
    - *Cerapus benthophilis*
  - Family Gammaridae
    - *Mucrogammarus mucronatus*
    - *Melita* sp.
  - Family Oedicerotidae
    - *Monoculodes* sp.
- Order Mysidacea
  - Family Mysidae
- Order Decapoda
  - Family Palaemonidae
    - *Palaemonetes* spp.
  - Family Ogyrididae
    - *Ogyrides* sp.
  - Family Callianasidae
  - Family Paguroidea
  - Family Portunidae
    - *Callinectes sapidus*
  - Family Xanthidae
    - *Rhithropanopeus harrisii*

- Subphylum Uniramia
  - Class Insecta
    - Order Diptera
      - Family Chironomidae
        - Subfamily Tanypodinae
        - Chironomid B
        - Subfamily Chironomidae
        - Chironomid A and C

- Phylum Chordata
  - Subphylum Vertebrata
    - Class Osteichthyes
      - Order Perciformes
        - Family Gobiidae
          - *Gobiosoma bosci*
      - Order Anguilliformes
        - Family Ophichthidae
          - *Myrophus punctatus*

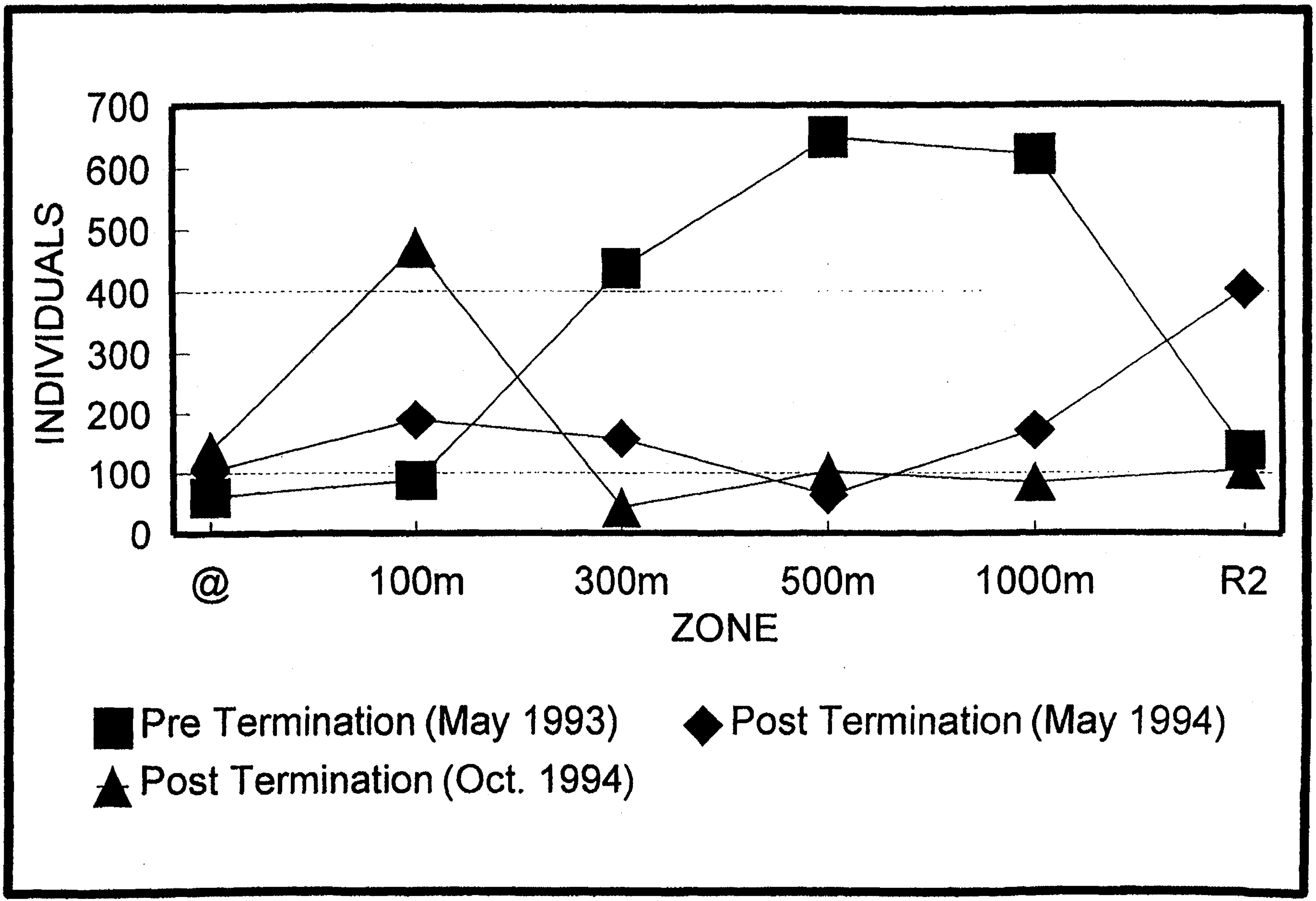

Figure 9.7. Average number of individuals collected at stations on the northeast transect at Bay de Chene for all sampling periods.

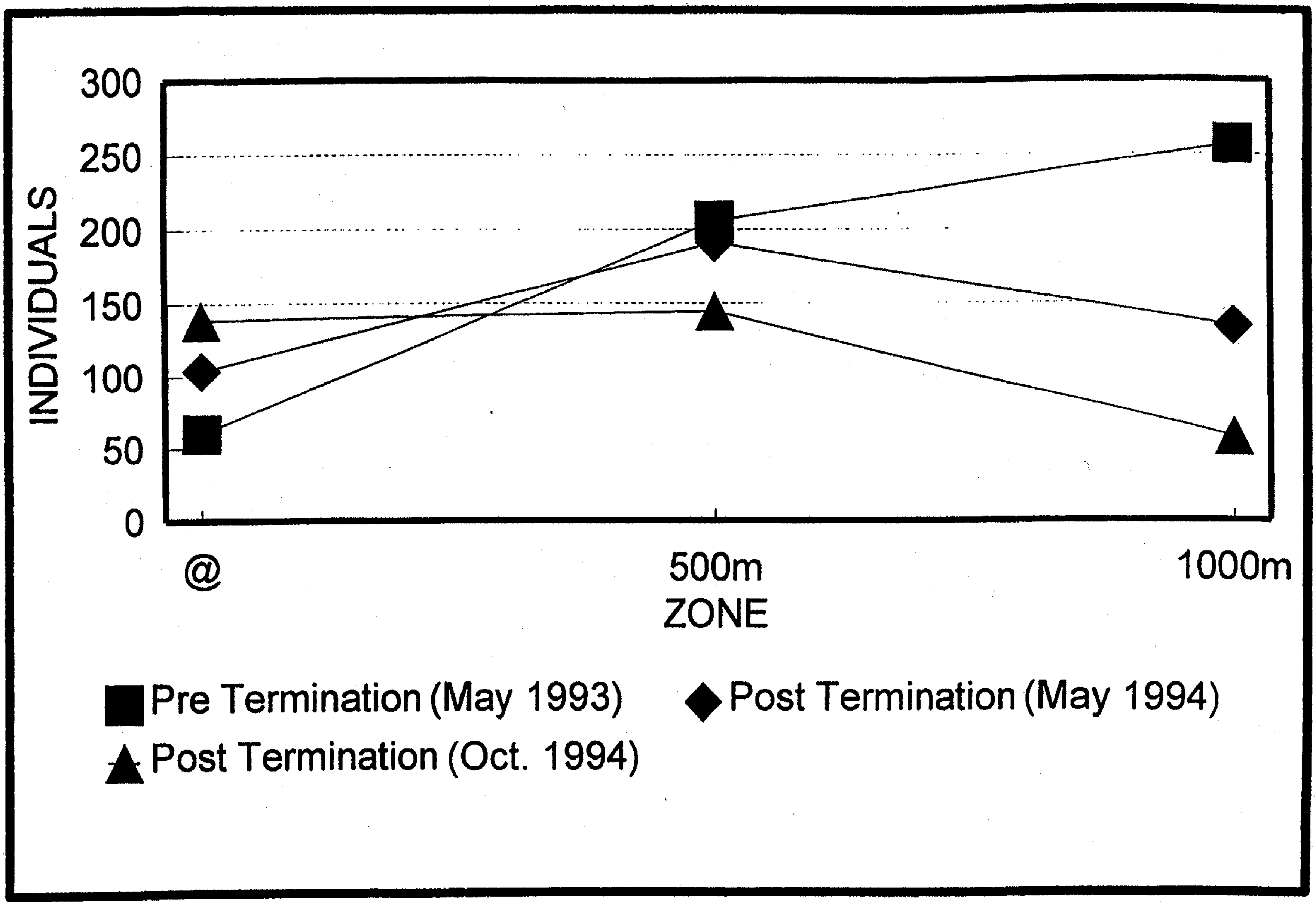

Figure 9.8. Average number of individuals collected at stations on the southeastern transect at Bay de Chene for all sampling periods.

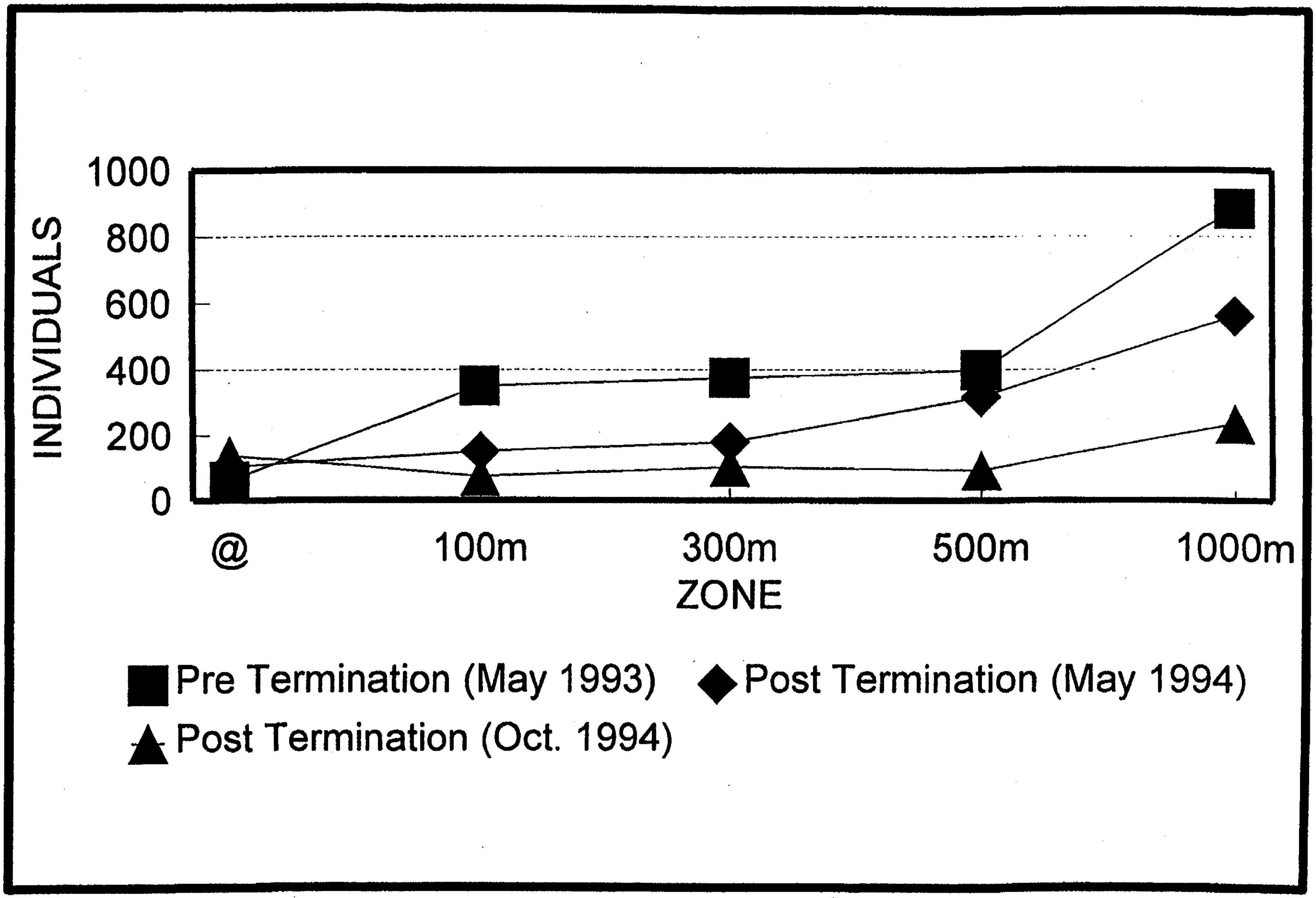

Figure 9.9. Average number of individuals collected at stations on the northwestern transect at Bay de Chene for all sampling periods.

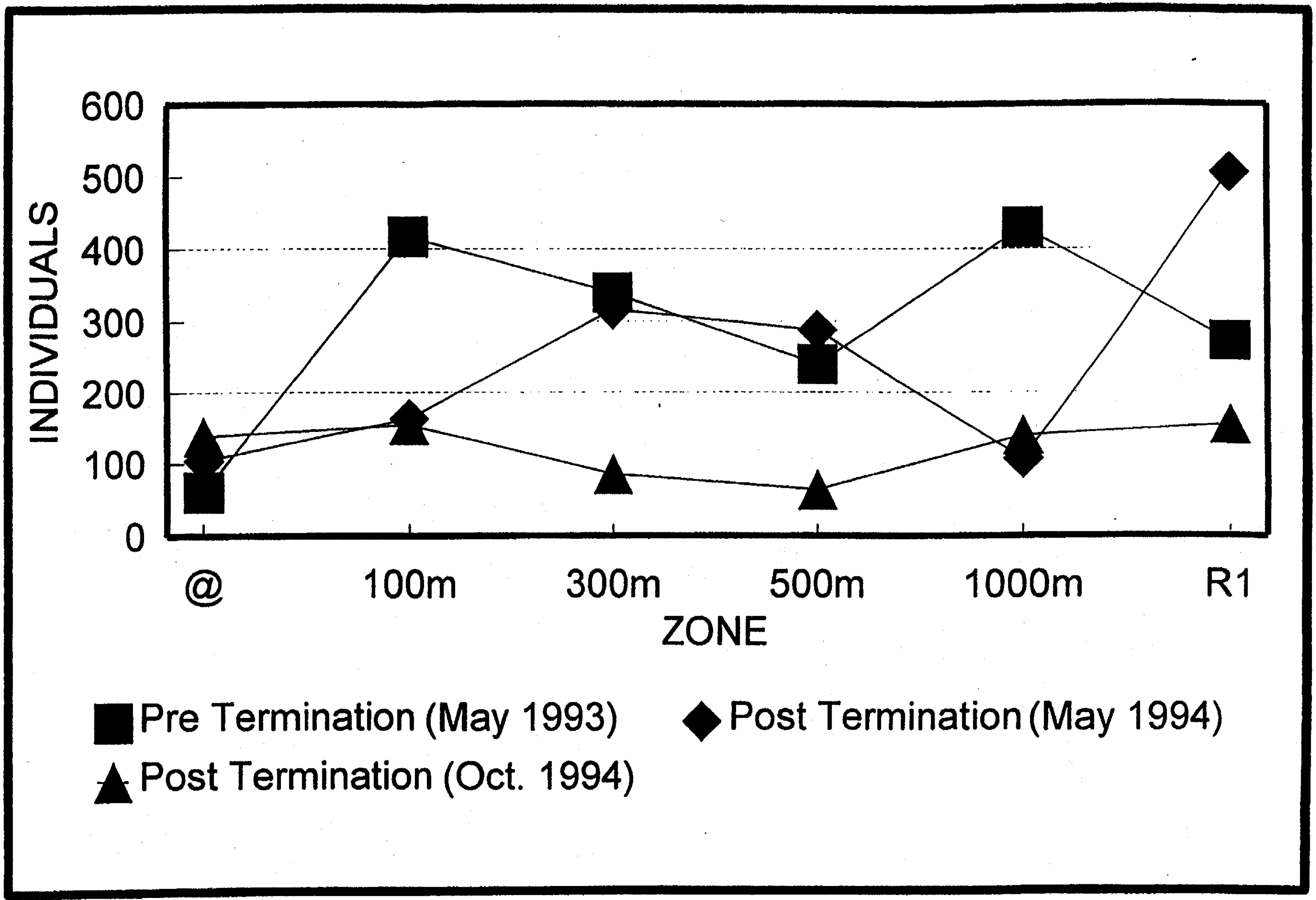

Figure 9.10. Average number of individuals collected at stations on the southwestern transect at Bay de Chene for all sampling periods.

9.3.2.3 Four Isle Dome

A list of the lowest taxa identified in the Four Isle Dome benthos samples excluding epifauna is presented in **Table 9.3**. The taxonomic composition (by major groups) of each station by transects and by years is provided in **Appendix 4** (page 9-63).

Average numbers of species per station for the north and south transects at Four Isle Dome for the Pre-termination Survey are given in **Figure 9.11**. Average numbers of individuals per station for the north and south transects at Four Isle Dome for the Pre-termination Survey are given in **Figure 9.12**.

Results of the randomized design analysis of variance based only on the zone effect show that significant differences are present among zones for both numbers of individuals ($p<.05$) and numbers of species ($p<.05$). Results of Tukey's post hoc test for both numbers of individuals and numbers of species showed significant differences ($p<.05$) between Zones 4 and 6 or between the 500 m stations and the reference stations.

9.3.3 Chloride Concentration of Interstitial Water

Chloride concentrations in interstitial water at the discharge and reference stations are provided in **Table 9.4**.

9.3.4 Sediment Contamination

Sediment concentrations of PAHs and their homologues are presented in **Figure 9.13** for the Delacroix Island Tank Battery #1 discharge site. Data presented in **Figure 9.13** indicate that the concentrations of most compounds at the discharge site decreased to approximately background levels by six months after discharge termination (October 1993). Background concentrations in this study were those realized at the reference stations. Other compounds - some chrysenes and some fluoranthenes/pyrenes - realized higher concentrations at both six months and one year post-termination (April 1994). For perspective, coefficients of variation (standard deviation as a percentage of the mean) for the compounds presented in **Figure 9.13** were approximately the same at 40% for all three sampling periods. This result indicates that the means presented in **Figure 9.13** probably are representative of actual concentrations and not the result of aberrant sample points.

Sediment concentrations of PAHs and their homologues are presented in **Figure 9.14** for the Bay de Chene discharge site. Data presented in **Figure 9.14** indicate that the concentrations of all compounds decreased dramatically by one year after discharge termination (May 1994) and that further decreases occurred by the October 1994 sampling although concentrations were still slightly above the background levels exhibited at the reference stations. For perspective, coefficients of variation (standard deviation as a percentage of the mean) for the compounds presented in **Figure 9.14** were approximately the same within sampling periods but were different for the three sampling periods: 74% for the May 1993 period, 25% for the May 1994 period, and 65% for the October 1994 period. The stable coefficients of variation within sampling periods indicate that the means presented in **Figure 9.14** probably are representative of actual concentrations and not the result of aberrant sample points. We do not have an explanation for the lower coefficients of variation for the May 1994 period.

Table 9.3. Lowest taxon of organisms identified in samples from Four Isle Dome stations.

- Phylum Nemertea
- Phylum Nematoda
- Phylum Annelida
  - Class Polychaeta
    - Order Phyllodocida
      - Family Phyllodocidae
        - *Eteone* sp.
      - Family Pilargidae
        - *Parandalia americana*
      - Family Nereidae
        - *Neanthes succinea*
        - *Leonereis culveri*
    - Order Capitellida
      - Family Capitellidae
    - Order Spionida
      - Family Spionidae
        - *Streblospio benedicti*
        - *Polydora* spp.
    - Order Terebellida
      - Family Ampharetidae
        - *Hobsonia florida*
  - Class Oligochaeta
- Phylum Mollusca
  - Class Gastropoda
    - Subclass Prosobranchia
      - Order Mesogastropoda
        - Family Hydrobiidae
          - *Texadina sphinctostoma*
    - Subclass Opisthobranchia
      - Order Nudibranchia
  - Class Bivalvia
    - Subclass Pteriomorphia
      - Order Mytiloidea
        - Family Mytilidae
          - *Ischadium recurvum*
    - Subclass Heterodonta
      - Order Hippuritoidea
        - Family Mactridae
          - *Rangia cuneata*
          - Clams <5 mm
        - Family Tellinida
          - *Macoma mitchelli*

Table 9.3. (Continued).

- Phylum Arthropoda
  - Subphylum Crustacea
    - Class Maxillopoda
      - Subclass Copepoda
        - Order Harpacticoida
          - Family Canuellidae
            - *Scottolana canadensis*
        - Order Calanoida
          - Family Acartiidae
            - *Acartia tonsa*
    - Class Malacostraca
      - Order Cumacea
      - Order Tanaidacea
        - Family Paratanaidae
          - *Hargeria rapax*
      - Order Isopoda
        - Family Idoteidae
          - *Edotea montosa*
        - Family Sphaeromatidae
          - *Cassidinedia ovalis*
        - Family Munnidae
          - *Munna reynoldsi*
      - Order Amphipoda
        - Family Ampeliscidae
          - *Ampelisca* sp.
        - Family Aoridae
          - *Grandidierella bonnieroides*
        - Family Corophiidae
          - *Corophium louisianum*
          - *Cerapus benthophilis*
        - Family Oedicerotidae
          - *Monoculodes* sp.
      - Order Mysidacea
        - Family Mysidae
      - Order Decapoda
        - Family Portunidae
          - *Callinectes sapidus*
  - Subphylum Uniramia
    - Class Insecta
      - Order Diptera
        - Family Ceratopogonidae
        - Family Chironomidae
          - Subfamily Tanypodinae
          - Chironomid B
          - Subfamily Chironominae
          - Chironomid A and C
- Phylum Chordata
  - Subphylum Vertebrata
    - Class Osteichthyes
      - Order Perciformes
        - Family Gobiidae
          - *Gobiosoma bosci*

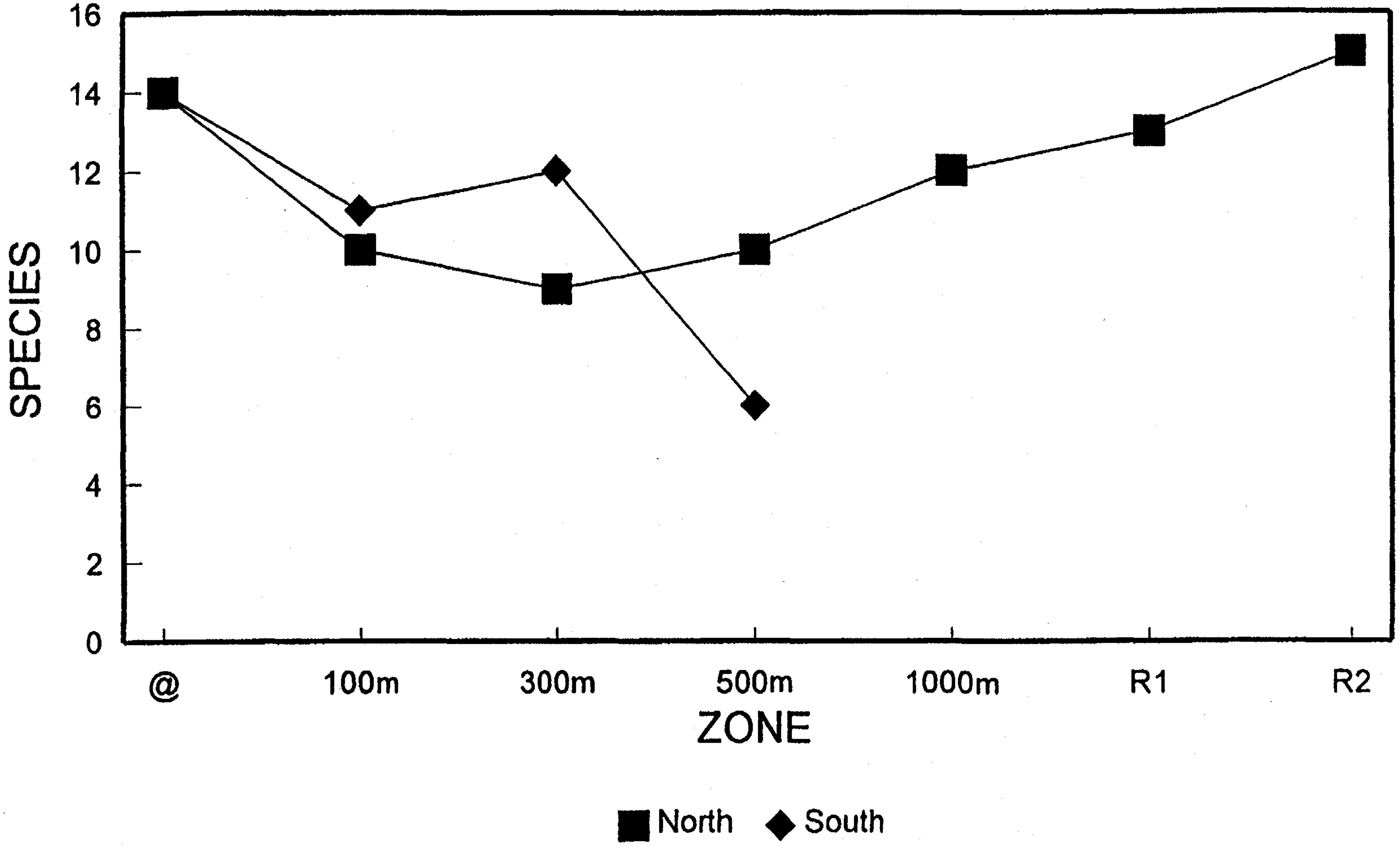

Figure 9.11. Average number of species per station for the north and south transects at Four Isle Dome for pre-termination sampling.

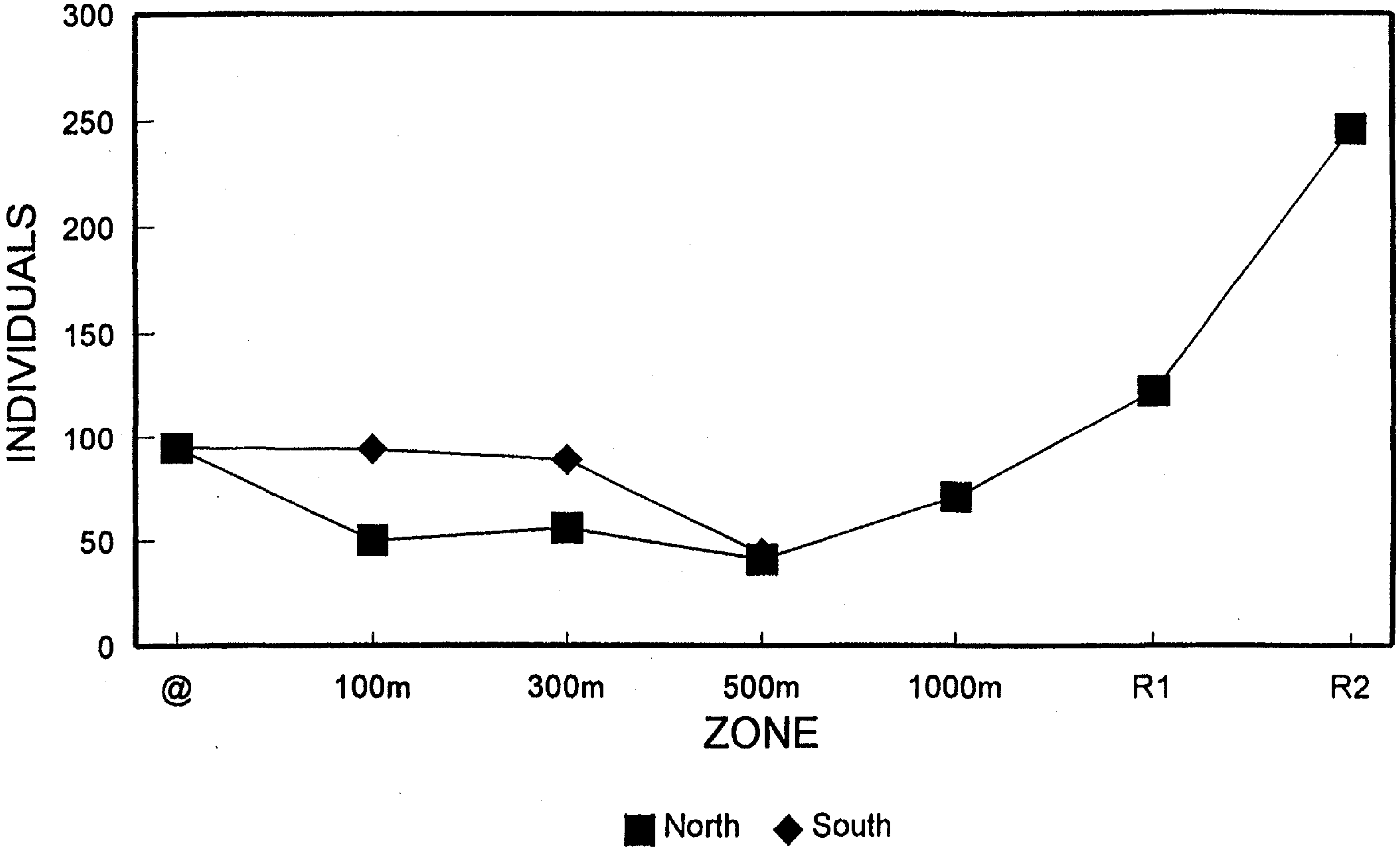

Figure 9.12. Average number of individuals per station for the north and south transects at Four Isle Dome for pre-termination sampling.

Table 9.4. Chloride concentrations in interstitial water (0 to 5 cm) at the discharge and reference stations.

Location	Pre-Termination Chloride (g/kg)	Second Post-Termination Chloride (g/kg)
Delacroix Island		
Produced Water	86.0	—
Discharge	43.2	1.4
Reference 1	2.5	1.5
Reference 2	2.0	1.3
Bay de Chene		
Produced Water	85.3	—
Discharge	7.3	—
Reference 1	3.9	—
Reference 2	4.2	—
Four Isle Dome		
Produced Water	97.0	—
Discharge	3.6	
Reference 1	2.4	—
Reference 2	3.1	—

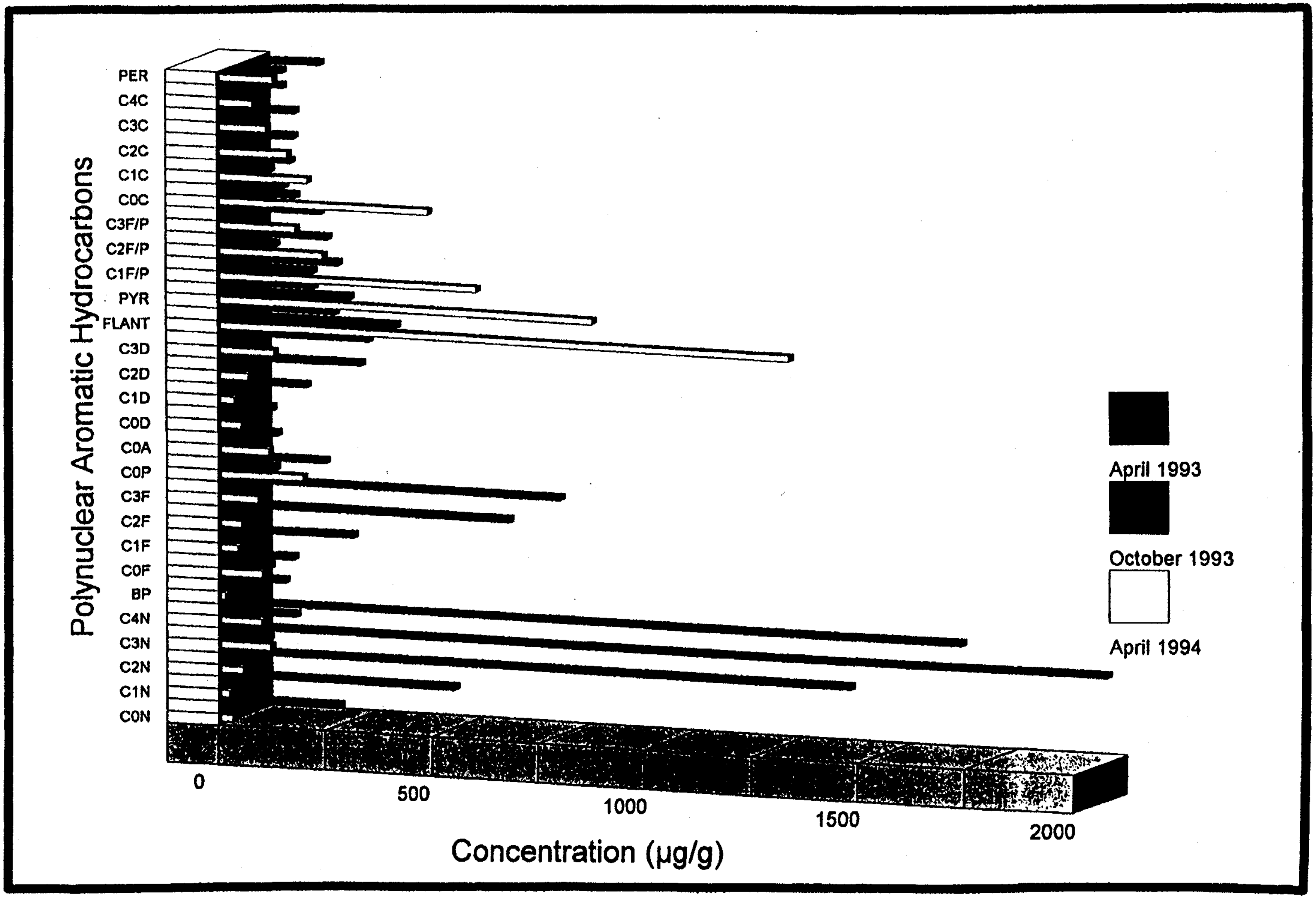

Figure 9.13. Sediment PAH concentrations at the discharge station at Delacroix Island during all sampling periods. C0N=Naphthalene; C1N=C_1-Naphthalenes; C2N=C_2-Naphthalenes; C3N=C_3-Naphthalenes; C4N=C_4-Naphthalenes; BP=Biphenyl; C0F=Fluorene; C1F=C_1-Fluorenes; C2F=C_2-Fluorenes; C3F=C_3-Fluorenes; C0D=Dibenzothiophene; C1D=C_1-Dibenzothiophenes; C2D=C_2-Dibenzothiophenes; C3D=C_3-Dibenzothiophenes; C0P=Phenanthrene; C0A=Anthracene; FLANT=Fluoranthene; PYR= Pyrenes; C1FP=C_1Floranthenes/Pyrenes; C2FP=C_2Fluoranthenes/Pyrenes; C3FP=C_3Fluoranthenes/Pyrenes; C0C=Chrysene; C1C=C_1-Chrysenes; C2C=C_2-Chrysenes; C3C=C_3-Chrysenes; C4C=C_4-Chrysenes; PER=Perylene.

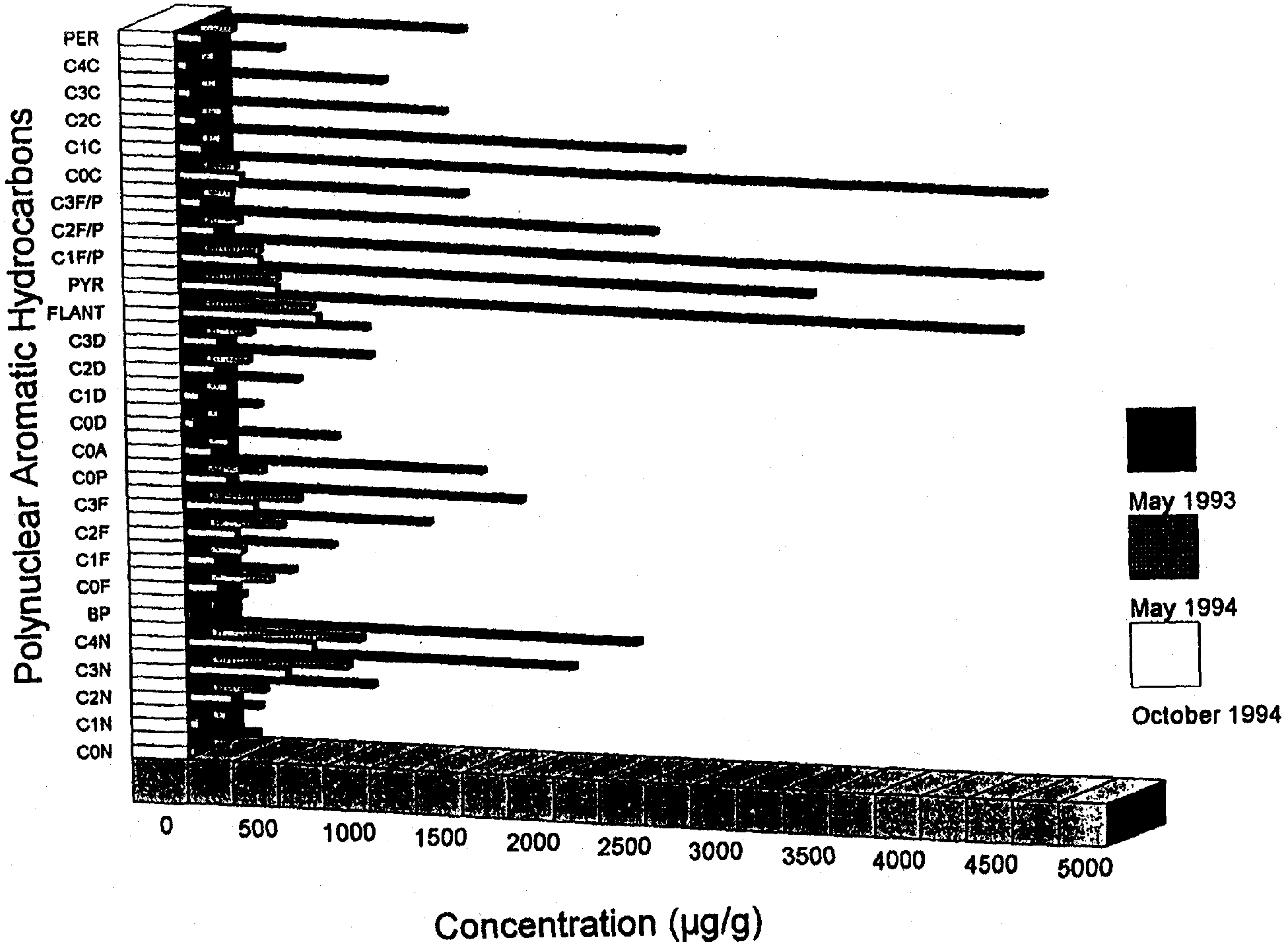

Figure 9.14. Sediment PAH concentrations at the discharge station at Bay de Chene during all sampling periods. C0N=Naphthalene; C1N=C_1-Naphthalenes; C2N=C_2-Naphthalenes; C3N=C_3-Naphthalenes; C4N=C_4-Naphthalenes; BP=Biphenyl; C0F=Fluorene; C1F=C_1-Fluorenes; C2F=C_2-Fluorenes; C3F=C_3-Fluorenes; C0D=Dibenzothiophene; C1D=C_1-Dibenzothiophenes; C2D=C_2-Dibenzothiophenes; C3D=C_3-Dibenzothiophenes; C0P=Phenanthrene; C0A=Anthracene; FLANT=Fluoranthene; PYR= Pyrenes; C1FP=C_1Floranthenes/Pyrenes; C2FP=C_2Fluoranthenes/Pyrenes; C3FP=C_3Fluoranthenes/Pyrenes; C0C=Chrysene; C1C=C_1-Chrysenes; C2C=C_2-Chrysenes; C3C=C_3-Chrysenes; C4C=C_4-Chrysenes; PER=Perylene.

The most heavily contaminated sediments at Bay de Chene were not at the discharge station, but were found at the Bay de Chene 100NE station located at an abandoned fuel dock. The data presented in **Figure 9.15** indicate that the 100NE station had PAH concentrations at least as high as those found at the discharge station, and that concentrations of most compounds did not decrease over the 18 month sampling period from May 1993 to October 1994.

Sediment concentrations of PAHs at the discharge site at Four Isle Dome are shown in **Figure 9.16**. These concentrations are given for the Pre-termination Survey only since no subsequent sampling was conducted.

9.4 DISCUSSION

Depressed numbers of species and individuals were evident at the discharge site at Delacroix Island Tank Battery #1 during the Pre-termination Survey. Statistically, over all three sampling periods, the number of species at the discharge was significantly lower than in all other zones. The infauna data from Delacroix Island appear to exhibit spatial recovery to a stable number of species on all transects by the 100 m station. **Figures 9.1** through **9.3** show graphically the similarity of the number of species for all sampling periods in Zones 2, 3, and 4 for all transects.

Recovery of the number of individuals from pre-termination levels at the discharge station on the northeast and northwest transects also appears graphically to have been realized by the 100 m stations. The similarity in the numbers of individuals at all sampling times in Zones 2, 3, and 4 are evident in **Figures 9.4** through **9.6**. The south transect, however, appears to exhibit highly variable recovery by the 100 m station. Recovery to a stable number of individuals appears to have been realized by the 300 m station for all discharge times.

In the Bay de Chene study area, numbers of species were relatively constant throughout the zones and no statistically significant differences were found. The discharge station samples exhibited depressed numbers of individuals during the Pre-termination Survey although numbers of individuals were much higher than those in the comparable Delacroix Island samples. Statistically, over all sampling periods, the numbers of individuals were different at the discharge station from those in all other zones. The number of individuals at the discharge station was also more stable than at other stations in the area although numbers of individuals increased slightly over time. Numbers of individuals were highly variable at the contaminated 100NE station, the site of an abandoned fuel dock, exhibiting a tolerance by some of the organisms such as the polychaete *Streblospio* for sediment hydrocarbon accumulations.

Average numbers of individuals in each zone on each transect are shown in **Figures 9.7** through **9.10**. These figures clearly show that beyond the discharge station numbers of individuals were extremely variable throughout the area. No differences are evident statistically between the reference stations and the other zones. One of the reference stations, R1, was even located in an old oyster seed ground area which has not recently been affected by oil field activities.

Data from Four Isle Dome are incomplete, but numbers of species and individuals at the discharge station are statistically not significantly different from those collected at the other stations on the transects. Depression is not evident in either numbers of individuals or numbers of species at the discharge station or the 100 m stations.

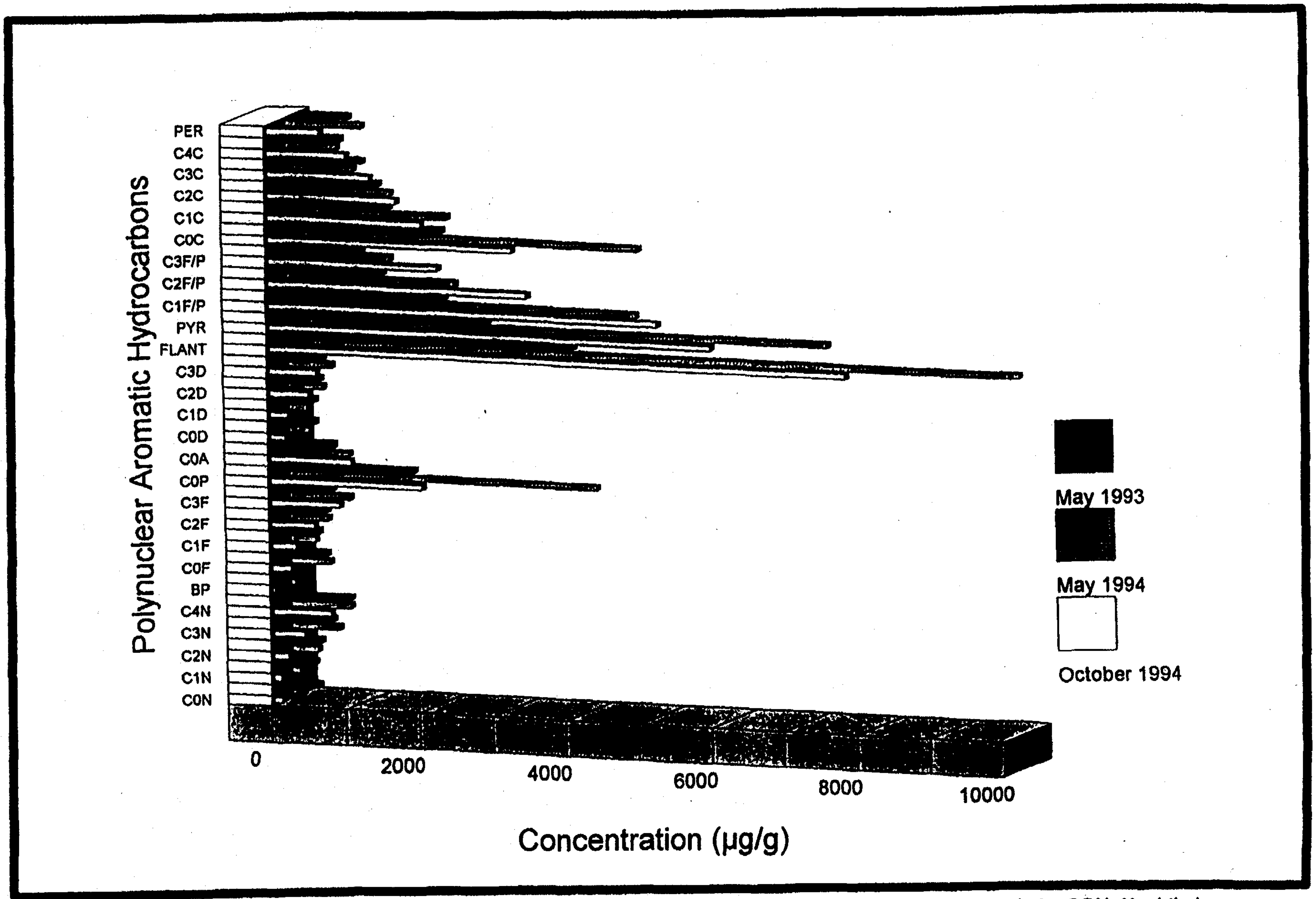

Figure 9.15. Sediment PAH concentrations at the discharge station at Bay de Chene 100NE during all sampling periods. C0N=Naphthalene; C1N=C_1-Naphthalenes; C2N=C_2-Naphthalenes; C3N=C_3-Naphthalenes; C4N=C_4-Naphthalenes; BP=Biphenyl; C0F=Fluorene; C1F=C_1-Fluorenes; C2F=C_2-Fluorenes; C3F=C_3-Fluorenes; C0D=Dibenzothiophene; C1D=C_1-Dibenzothiophenes; C2D=C_2-Dibenzothiophenes; C3D=C_3-Dibenzothiophenes; C0P=Phenanthrene; C0A=Anthracene; FLANT=Fluoranthene; PYR= Pyrenes; C1FP=C_1Floranthenes/Pyrenes; C2FP=C_2Fluoranthenes/Pyrenes; C3FP=C_3Fluoranthenes/Pyrenes; C0C=Chrysene; C1C=C_1-Chrysenes; C2C=C_2-Chrysenes; C3C=C_3-Chrysenes; C4C=C_4-Chrysenes; PER=Perylene.

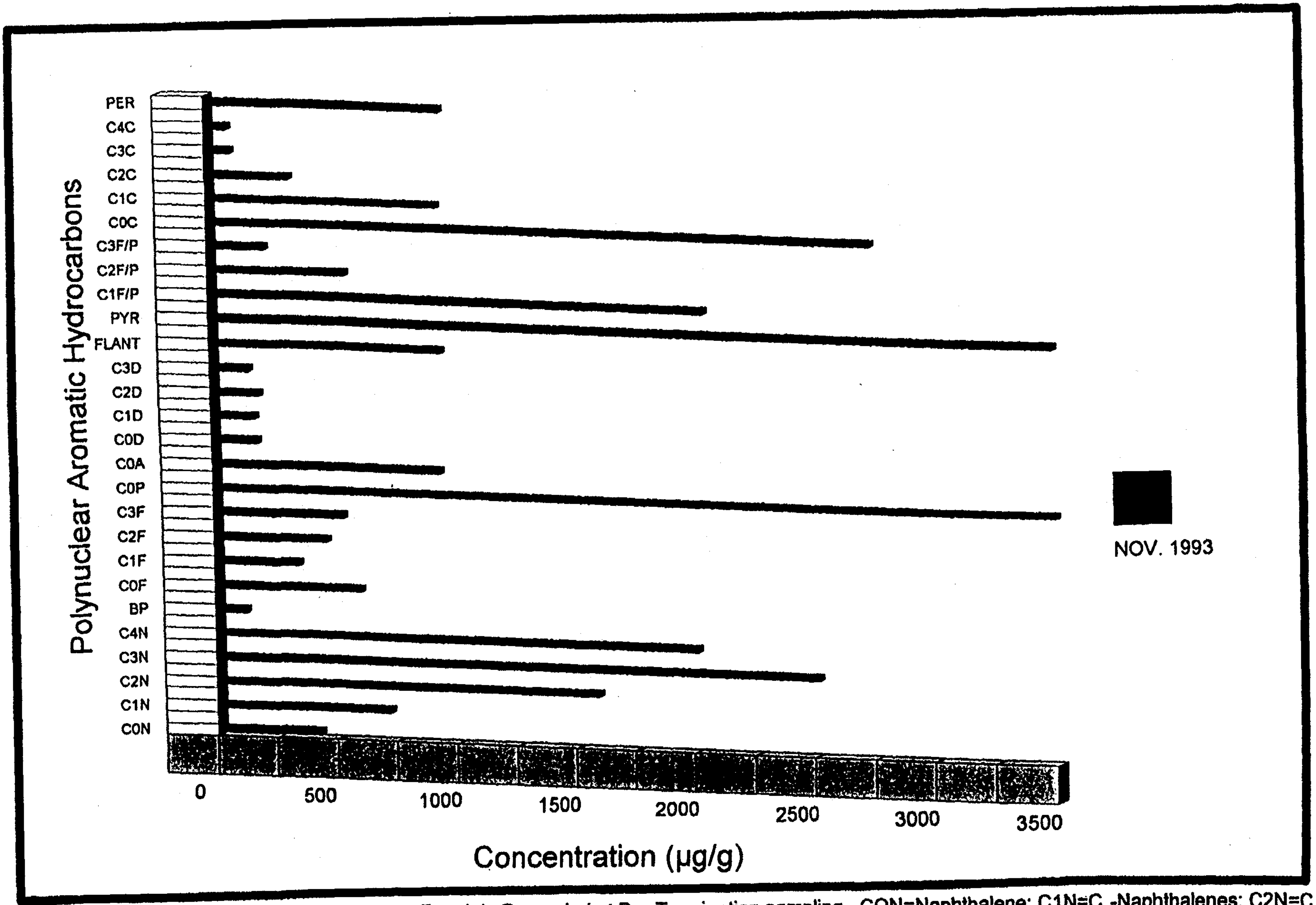

Figure 9.16. Sediment PAH concentrations at Four Isle Dome during Pre-Termination sampling. C0N=Naphthalene; C1N=C_1-Naphthalenes; C2N=C_2-Naphthalenes; C3N=C_3-Naphthalenes; C4N=C_4-Naphthalenes; BP=Biphenyl; C0F=Fluorene; C1F=C_1-Fluorenes; C2F=C_2-Fluorenes; C3F=C_3-Fluorenes; C0D=Dibenzothiophene; C1D=C_1-Dibenzothiophenes; C2D=C_2- Dibenzothiophenes; C3D=C_3-Dibenzothiophenes; C0P=Phenanthrene; C0A=Anthracene; FLANT=Fluoranthene; PYR= Pyrenes; C1FP=C_1Floranthenes/Pyrenes; C2FP=C_2Fluoranthenes Pyrenes; C3FP=C_3Fluoranthenes/Pyrenes; C0C=Chrysene; C1C=C_1-Chrysenes; C2C=C_2-Chrysenes; C3C=C_3-Chrysenes; C4C=C_4-Chrysenes; PER=Perylene.

The areas affected at Delacroix Island and Bay de Chene were less than 100 m in radius from the discharge. These were similar to the areas reported to be affected in previous studies of coastal environments. Armstrong et al. (1979) identified an area 150 m in radius around the discharge in which the fauna was severely depressed in Galveston Bay. In a summary of the Minerals Management Service studies of the outer continental shelf generated discharges into the coastal areas of Louisiana, Rabalais et al. (1992) reported the area of impacts to benthos varied from nothing in areas of high flow volume such as distributaries of the Mississippi River (Emeline and Romere Passes) and the Empire waterway to 800 m at Pass Fourchon, a dead end canal/dredged bayou environment. In a study of discharges at Eugene Island Block 105 and Lake Pelto Tank Battery #1, both large open coastal bays, Neff et al. (1992) concluded that the benthic fauna was affected up to 20 m from but not as far as 100 m from the discharges.

One of the major factors which was identified by Rabalais et al. (1992) as influencing the area affected by produced water discharge is the hydrology of the receiving environment. This factor may help to explain the differences in magnitude of effect at the discharge stations in this study. The benthic effects found in the Pre-termination Survey were much greater at the Delacroix Island discharge station than at the comparable Bay de Chene and Four Isle Dome stations even though the Delacroix Island discharge was approximately half the volume of the Bay de Chene discharge. The Four Isle Dome discharge was approximately one-fourth of the volume of the Bay de Chene discharge.

Both the Delacroix Island discharge and the Bay de Chene discharge were subsurface and the discharge was directed to the bottom. The Four Isle Dome discharge was elevated several feet above the water's surface so that dilution and mixing occurred at the surface. Delacroix was also a semi-enclosed hydrological environment which did not provide as much opportunity for turbulent mixing or dilution of the discharge as did the open water nature of Bay de Chene. It was therefore more likely that the saline, deoxygenated water of the discharge settled in a non-mixing layer on the bottom.

This was evident in the differences in the chloride concentrations of the interstitial water of the surface sediments at the three discharge stations. Average chloride concentration of the interstitial water at the Delacroix Island discharge station prior to its termination was equivalent to approximately 78 ppt salinity, a level toxic to most estuarine organisms. Chloride concentrations of the interstitial water at the Bay de Chene discharge station prior to discharge termination was equivalent to approximately 13 ppt salinity. Chloride concentrations in the two produced waters were nearly equal. Although chloride concentration of the Four Isle Dome produced water was higher than the other two discharges, approximate salinity in the interstitial water was 6.5 ppt.

In **Chapter 7**, the diffusion of chloride out of the surface sediments at Delacroix Island was modeled. Although there are a variety of potential variables which influence the diffusion of chloride from the interstitial water which were not quantified including the chloride profile of the interstitial water, the salinity of the near bottom water and sediment mixing, calculations indicated that the salinity would return to nearly 10 ppt between approximately 23 days and 6 months.

Hydrocarbons present in produced water also have the potential to impact benthos. Hydrocarbons adsorb preferentially onto fine grained clays (Boehm, 1987) which predominate in the bottom sediments of Louisiana estuaries. At the Delacroix Island discharge station, sediment PAH concentrations decreased (**Figure 9.13**) over time and between the discharge station and all 100 m stations. The number of benthic species and individuals increased dramatically at the discharge station after termination. Recovery was rapid with a large number of species and individuals inhabiting the former discharge station six months post-termination.

Although multiple regression analysis identified two hydrocarbon components, dibenzothiophenes and fluoranthenes, as being negatively correlated with the number of species and individuals, it is not possible to separate these effects from those of the low dissolved oxygen and high salt content of the ongoing discharge. The sediment PAH concentrations at Bay de Chene decreased greatly between the discharge station and the 100 m stations except the 100NE station. Concentrations at this station were similar to those found at the discharge station during the Pre-termination Survey. Sediment concentrations at the 100NE station did not decrease with time (**Figure 9.15**) although the number of individuals did vary with time (**Figure 9.7**).

At the Bay de Chene discharge station, sediment hydrocarbon concentrations did decrease with time with most of the decrease occurring in the first seven months after termination (**Figure 9.14**). The numbers of individuals increased slowly (**Figure 9.7**) through the October 1994 (1 year post-termination) sampling. Although the increase in number of individuals was not as dramatic as at Delacroix Island, by October 1994 the overall decrease in average number of individuals across the area and the slow increase in the number of individuals at the former discharge station make it indistinguishable from other stations. Little prior work is available on the time necessary for recovery of other coastal sites impacted by produced water. Rabalais et al. (1992) reported that an abandoned discharge studied in the Empire Waterway (Pelican Island Terminal) did not show benthic recovery three years after the discharge was abandoned probably because of accumulated contaminants in the sediments. The discharge into this dead-end, facility access canal which emptied into the Empire Waterway was 10,959 bbl/day (1,742,152 L/day), two to three times the volume of any discharge in this study.

Multiple regression analysis identified dibenzothiophene as one of the factors negatively correlated with the number of individuals. As with the Delacroix Island discharge station, however, it is not possible to separate the effects of hydrocarbon accumulation in the sediments from the low dissolved oxygen and high salt content on the initial sampling. The occurrence of infauna at the 100NE station does indicate a tolerance of at least some taxa to sediment hydrocarbon accumulation.

The infauna data from the Delacroix Island and Bay de Chene study areas show strong seasonal variability as reflected in the statistical differences in sampling periods. Results of the post hoc tests on the two-way analysis of variance for both species and individuals at the Delacroix Island study area clearly showed that the October 1993 sampling is significantly different from both the April 1993 and the April 1994 samplings. Multiple regression analysis identified sampling period as having a negative effect on species and individuals at Delacroix Island. Although sampling period was entered into the analysis to reflect length of time after discharge termination, seasonal element is present. It is not unusual to find higher diversity in coastal estuarine habitats in the fall since salinities are higher and more stable than those experienced in the spring.

The taxa which predominated in the Delacroix Island study area also varied seasonally. The October 1993 sampling (6 months post-termination) was characterized by a population explosion at most stations, including the former discharge station, of the amphipod *Grandidierella bonnieroides* and the tube-dwelling amphipods *Corophium louisianum* and *Cerapus benthophilus* (**Appendix 1**; page 9-37). The Pre-termination Survey sampling of the discharge station yielded only a few individuals of the gastropod *Texadina sphinctostoma* and a single isopod. The other organisms present during the Pre-termination Survey sampling were the epifaunal *Ischadium recurvum*, whose numbers were not included in infaunal counts. Throughout the area the October 1993 sampling was also characterized by an increase in the numbers of the polychaete *Streblospio benedicti* and the gastropod *Texadina sphinctostoma.*

The April 1994 sampling was characterized by the dominance of the gastropods *Texadina sphinctostoma* and *Probythinella louisianae* at all stations including the former discharge station. This is particularly evident in the plots of taxonomic composition in **Appendix 2** (page 9-40). These gastropods which are common inhabitants of low-salinity estuaries has been observed by one of the authors to undergo population explosions in Lake Pontchartrain following years of introduction of nutrient-enriched Mississippi River water into the lake through the Bonnet Carre' Spillway. The Caernarvon diversion inputs Mississippi River water into the Delacroix area during the spring which is probably related to the increase in numbers of these organisms.

Results of the post hoc tests on the two-way analysis of variance for numbers of individuals at Bay de Chene also show statistically significant differences between sampling periods which may be due to seasonal variability. Multiple regression also identified sampling period as having a negative effect on individuals at Bay de Chene. The May 1994 Post-termination Survey sampling was dominated by oligochaetes, and overall numbers of individuals of all species throughout the area were lower than in the previous May.

Seasonal trends in the taxonomic composition of the Bay de Chene transects are evident in the plots provided in **Appendix 3** (page 9-50). Dominant taxa during the Pre-termination Survey sampling included oligochaetes, the polychaete *Streblospio benedicti*, the bivalve *Mulinia lateralis* and the gastropod *Texadina sphinctostoma.* The October 1994 sampling was also dominated by *Streblospio benedicti.* The taxonomic composition of the discharge station remained relatively constant during the two spring Pre- and Post-termination Survey samplings (May 1993 and May 1994).

The taxa in the Delacroix and Bay de Chene study areas are those which are common in coastal Louisiana habitats. Two of these taxa, *Streblospio benedicti* and *Mulinia lateralis,* were also dominant in the sites studied by Neff et al. (1989) and Rabalais et al. (1991). These organisms as all the organisms of inshore Louisiana coastal bays and bayous are eurytolerant, short lived, and opportunistic. They have a high reproductive potential which allows them to succeed in the dynamic environment in which they live, the surface of the fine grained sediments which are constantly moved around by storms and currents. This provides a constant input of new colonizers to uncrowded substrate and, therefore, allows rapid recolonization of the areas affected by the discharge.

9.5 SUMMARY

Depressed numbers of species and individuals were evident at the discharge site at Delacroix Island Tank Battery #1 during the Pre-termination Survey. Statistically, over all three sampling periods, the number of species at the discharge was significantly lower than in all other zones. The infauna data from Delacroix Island appear to exhibit spatial recovery to a stable number of species on all transects by the 100 m station. Recovery to a stable number of individuals appears to have been realized by the 100 m station for all discharge times on the northeast and northwest transects. Recovery on the south transect appears to have been realized by the 300 m station for all sampling times.

In the Bay de Chene study area, numbers of species were relatively constant throughout the zones and no statistically significant differences were found. The discharge station samples exhibited depressed numbers of individuals during the Pre-termination Survey although numbers of individuals were much higher than those in the comparable Delacroix Island samples. Statistically, over all sampling periods, the numbers of individuals were different at the discharge station from those in all other zones.

Data from the Four Isle Dome are incomplete, but numbers of species and individuals at the discharge station are statistically not significantly different from those collected at the other stations on the transects. Depression is not evident in either numbers of individuals or numbers of species at the discharge station or the 100 m stations.

Differences in the hydrology and the discharge configuration of the three sites may account for the differences in benthic impact in the Pre-termination Survey samples. Bay de Chene is a more open environment than either Delacroix or Four Isle Dome. The Four Isle Dome discharge is not subsurface and not directed to the bottom as are the other two. Differences in interstitial chloride concentrations among the three sites support this conclusion.

9.6 REFERENCES

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9.7 ACKNOWLEDGMENTS

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APPENDIX I

Water Quality Data

Appendix 1. Delacroix Island, Bay De Chene and Four Isle Dome water quality data.

SURVEY /SITE	STATION	TEMP. (°C)		COND. (umhos/cm)		SALINITY (ppt)		D. O. (mg/l)		DEPTH (m)
		SURF.	BOTT.	SURF.	BOTT.	SURF.	BOTT.	SURF.	BOTT.	
I-DI	@	22.0	20.0	3,000	3,500	1.5	2.0	7.2	3.2	1.5
I-DI	R1	23.0	23.0	3,500	3,500	3.0	3.0	7.8	7.5	1.0
I-DI	R2	22.0	22.0	3,000	3,000	2.0	2.0	6.8	6.8	1.3
I-DI	1000S	21.0	21.0	2,500	2,500	1.8	1.8	8.2	8.0	1.2
I-DI	500S	21.0	n/a	3,000	n/a	2.0	n/a	8.8	n/a	0.9
I-DI	300S	21.0	n/a	3,000	n/a	2.0	n/a	8.8	n/a	0.9
I-DI	100S	21.0	21.0	3,000	3,000	2.0	2.0	9.0	8.8	1.5
I-DI	100NW	19.0	19.0	2,100	2,100	1.5	1.5	8.5	8.1	1.7
I-DI	300NW	19.0	19.0	2,500	2,500	1.5	1.5	8.6	7.7	2.0
I-DI	500NW	19.0	19.0	2,500	2,500	1.5	1.5	8.6	8.2	1.5
I-DI	1000NW	19.5	19.5	2,700	2,200	2.0	1.8	8.7	8.2	1.5
I-DI	100NE	20.0	20.0	3,000	3,000	2.0	2.0	9.6	9.4	1.5
I-DI	300NE	19.0	19.0	2,000	2,000	1.2	1.2	8.2	8.2	1.3
I-DI	500NE	19.3	19.3	2,000	2,000	1.2	1.2	8.8	8.8	1.3
I-BDC	@	25.0	25.5	8,000	18,000	5.0	9.5	5.5	5.8	2.3
I-BDC	R1	28.0	26.5	8,000	9,200	4.5	5.0	6.0	4.6	2.0
I-BDC	R2	27.5	27.0	9,000	9,000	5.0	5.0	7.7	7.0	1.5
I-BDC	1000SE	25.0	25.0	7,500	8,000	4.5	5.0	7.6	6.4	1.8
I-BDC	500SE	25.0	25.0	6,000	6,000	4.0	4.0	n/a	n/a	1.8
I-BDC	1000SW	23.5	25.0	3,000	7,000	2.0	4.0	7.5	6.0	1.8
I-BDC	500SW	23.5	25.0	4,000	9,000	3.0	5.0	7.5	5.4	1.8
I-BDC	300SW	24.0	25.0	3,000	9,000	2.0	5.0	8.0	5.4	1.8
I-BDC	100SW	25.0	25.0	4,500	6,000	3.0	3.5	n/a	n/a	1.8
I-BDC	100NW	25.0	24.5	2,500	6,000	1.5	3.5	7.5	6.0	1.6
I-BDC	300NW	27.0	25.0	2,000	8,000	1.0	4.5	8.0	5.4	1.8
I-BDC	500NW	27.0	25.0	2,000	9,000	1.0	5.0	9.0	4.8	1.8
I-BDC	1000NW	27.0	25.0	3,000	8,500	1.5	5.0	9.0	4.2	1.6
I-BDC	100NE	24.5	24.5	3,000	3,500	2.0	2.0	8.0	6.8	1.6
I-BDC	300NE	25.0	24.0	2,500	3,000	1.5	2.0	8.0	6.4	1.7
I-BDC	500NE	25.0	24.0	2,500	3,500	1.5	2.0	8.4	4.8	1.8
I-BDC	1000NE	26.0	24.0	2,000	4,000	1.0	2.5	8.6	5.4	1.8
I-FID	@	13.0	13.0	6,000	7,000	4.5	5.5	9.0	8.2	2.3
I-FID	R1	14.0	14.0	5,000	5,000	3.5	3.5	9.5	7.8	1.0
I-FID	R2	16.0	16.0	7,000	8,500	5.0	6.0	9.2	7.6	1.2
I-FID	100N	17.0	16.0	9,500	12,500	6.9	9.2	10.8	9.6	2.1
I-FID	300N	16.5	15.0	9,000	12,500	6.5	9.0	10.8	9.4	1.8
I-FID	500N	15.0	14.5	8,000	10,500	5.8	8.0	9.6	8.6	2.4
I-FID	1000N	14.0	14.0	6,500	9,000	5.0	6.0	9.2	8.6	1.8
I-FID	100S	17.0	16.5	8,500	10,000	5.0	6.0	8.4	5.4	2.1
I-FID	300S	17.0	17.0	9,000	9,000	5.0	5.0	8.5	7.8	1.8
I-FID	500S	19.0	18.0	9500	11000	6.5	7.0	9.0	8.2	2.1
II-DI	@	23.0	23.0	10,000	10,000	6.0	6.0	7.0	5.8	2.1
II-DI	R1	21.0	21.0	10,000	10,000	6.5	6.5	7.0	6.0	1.2
II-DI	R2	23.0	22.5	8,000	8,000	5.0	5.0	6.6	6.0	1.2
II-DI	1000S	23.0	23.0	10,000	10,000	6.0	6.2	6.8	6.6	1.8
II-DI	500S	23.0	23.0	10,000	10,000	6.0	6.0	7.0	6.0	1.4
II-DI	300S	23.0	23.0	10,000	10,000	6.0	6.0	5.6	5.8	1.5
II-DI	100S	23.0	23.0	10,000	10,000	6.0	6.0	7.2	7.0	1.5
II-DI	100NW	21.0	21.0	8,000	8,000	5.0	5.0	6.5	7.0	2.8
II-DI	300NW	21.0	23.0	8,000	8,000	5.0	5.0	6.5	6.8	2.4

Appendix 1.(cont.) Delacroix Island, Bay De Chene and Four Isle Dome water quality data .

SURVEY /SITE	STATION	TEMP. (°C)		COND. (umhos/cm)		SALINITY (ppt)		D. O. (mg/l)		DEPTH (m)
		SURF.	BOTT.	SURF.	BOTT.	SURF.	BOTT.	SURF.	BOTT.	
II-DI	500NW	23.0	24.0	8,000	8,000	5.0	5.0	6.6	6.6	1.7
II-DI	1000NW	22.0	22.0	8,000	8,000	5.0	5.0	6.4	6.0	1.5
II-DI	100NE	22.0	22.5	10,000	10,000	6.0	6.0	7.8	6.8	1.7
II-DI	300NE	21.0	21.0	10,000	10,000	6.5	6.5	7.4	7.0	1.8
II-DI	500NE	21.0	21.0	9,500	9,500	6.0	6.0	8.0	7.2	1.8
II-BDC	@	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
II-BDC	R1	28.0	26.5	10,000	12,000	6.0	7.0	7.4	4.8	2.1
II-BDC	R2	28.0	28.0	9,500	9,500	5.5	5.0	8.2	7.4	1.5
II-BDC	1000SE	27.0	27.0	11,000	11,000	6.0	6.0	7.4	5.4	1.5
II-BDC	500SE	27.0	27.0	12,000	12,000	6.5	6.5	6.6	6.5	1.5
II-BDC	1000SW	29.0	28.5	12,000	12,000	7.0	7.0	7.0	6.2	2.0
II-BDC	500SW	29.0	28.0	12,000	12,000	7.0	6.5	6.8	6.0	2.0
II-BDC	300SW	29.0	28.0	12,000	12,000	7.0	7.0	7.5	5.8	1.8
II-BDC	100SW	29.0	28.0	11,000	12,000	6.0	7.0	7.4	6.4	1.5
II-BDC	100NW	28.0	27.5	8,000	11,000	4.5	6.0	6.4	5.8	1.7
II-BDC	300NW	27.5	27.0	9,000	10,000	5.0	5.5	6.0	5.4	1.8
II-BDC	500NW	27.0	27.0	8,500	10,000	5.0	5.5	6.6	5.2	1.8
II-BDC	1000NW	27.0	27.0	8,000	8,500	4.5	5.0	6.2	5.5	1.5
II-BDC	100NE	26.5	26.5	9,000	12,000	5.0	6.5	6.6	6.0	1.7
II-BDC	300NE	26.5	26.0	9,000	10,000	5.0	6.0	7.0	6.0	2.0
II-BDC	500NE	26.5	26.0	9,000	9,000	5.0	5.0	6.9	6.2	1.8
II-BDC	1000NE	26.0	26.0	9,000	9,000	5.0	5.0	6.4	5.8	1.8
III-DI	@	20.0	20.0	4,000	4,000	3.0	3.0	8.2	7.0	2.1
III-DI	R1	20.0	20.0	5,000	5,500	3.5	3.5	8.2	7.8	1.2
III-DI	R2	21.0	21.0	3,500	4,000	2.5	2.5	8.0	7.8	1.5
III-DI	1000S	22.5	22.5	3,900	4,000	2.0	2.0	7.4	7.2	1.5
III-DI	500S	22.5	22.5	4,100	4,100	2.5	2.5	7.6	7.0	1.2
III-DI	300S	22.5	22.5	3,700	3,700	2.0	2.0	7.2	7.2	1.2
III-DI	100S	23.0	23.0	3,700	3,700	2.0	2.0	7.4	7.0	1.5
III-DI	100NW	21.5	22.0	3,300	3,300	2.0	2.0	7.4	7.0	2.1
III-DI	300NW	21.5	21.5	3,300	3,300	2.0	2.0	7.0	6.8	2.1
III-DI	500NW	22.0	21.5	4,000	4,100	2.5	2.5	8.3	7.4	1.5
III-DI	1000NW	22.0	21.5	3,900	3,900	2.5	2.5	7.8	7.8	1.2
III-DI	100NE	24.0	24.0	3,500	3,500	2.0	2.0	7.6	7.2	1.4
III-DI	300NE	24.5	24.5	3,500	3,600	2.0	2.0	8.8	8.4	1.2
III-DI	500NE	25.0	25.0	3,900	3,900	2.0	2.0	7.8	7.4	1.2
III-BDC	@	25.0	25.0	34,000	35,000	22.0	22.5	6.2	5.8	2.5
III-BDC	R1	26.0	25.0	23,000	28,000	14.0	18.0	3.8	5.0	1.8
III-BDC	R2	24.0	24.0	22,000	24,000	14.0	15.0	6.4	6.2	1.8
III-BDC	1000SE	28.5	27.0	32,000	32,000	20.0	20.0	6.6	6.4	1.2
III-BDC	500SE	27.5	27.5	30,000	32,000	19.0	20.0	5.6	5.8	1.4
III-BDC	1000SW	26.5	25.0	26,000	30,000	16.5	19.0	5.6	4.2	2.0
III-BDC	500SW	27.0	25.0	27,000	29,000	16.5	19.0	5.4	4.2	1.8
III-BDC	300SW	26.0	26.0	30,000	31,000	19.0	19.0	6.0	5.8	1.5
III-BDC	100SW	26.5	26.0	30,000	31,000	19.0	19.5	6.0	5.6	1.2
III-BDC	100NW	28.0	28.0	31,000	33,000	19.0	20.0	7.4	6.6	1.5
III-BDC	300NW	24.5	25.0	19,000	20,000	12.5	13.0	6.2	4.8	1.8
III-BDC	500NW	25.0	25.0	22,000	24,000	14.0	15.0	6.0	5.2	1.8
III-BDC	1000NW	25.0	25.0	22,500	23,000	14.5	15.0	5.8	5.6	1.8
III-BDC	100NE	26.0	26.0	32,000	35,000	21.0	23.0	6.0	5.6	1.5

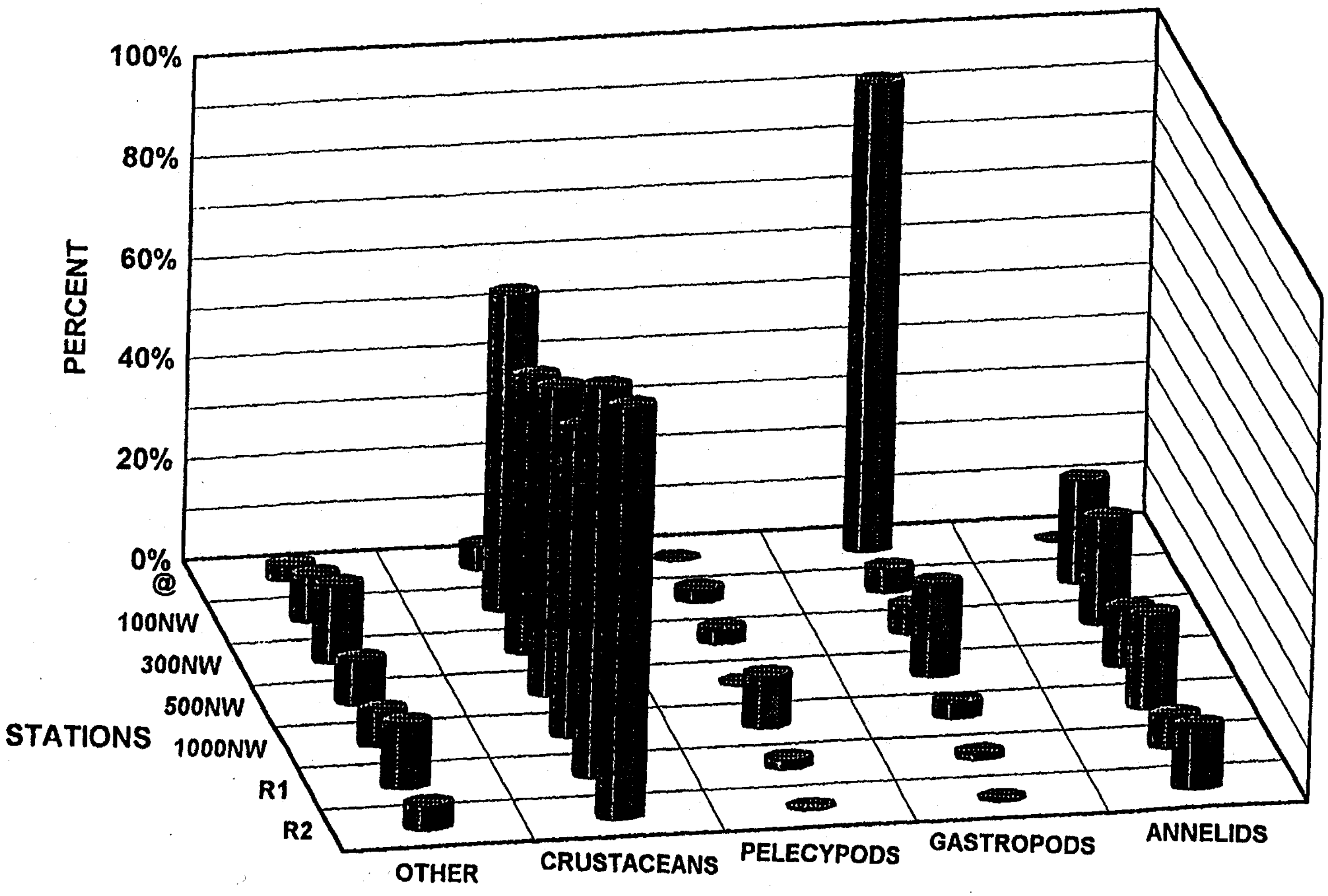
Appendix 1.(cont.) Delacroix Island, Bay De Chene and Four Isle Dome water quality data .

SURVEY /SITE	STATION	TEMP. (°C)		COND. (umhos/cm)		SALINITY (ppt)		D. O. (mg/l)		DEPTH (m)
		SURF.	BOTT.	SURF.	BOTT.	SURF.	BOTT.	SURF.	BOTT.	
III-BDC	300NE	27.0	26.0	31,000	35,000	21.0	22.5	7.0	7.0	1.8
III-BDC	500NE	26.0	26.0	34,000	35,000	22.0	23.0	7.8	7.5	2.0
III-BDC	1000NE	25.0	24.0	26,000	28,000	17.0	17.0	5.6	6.0	1.8

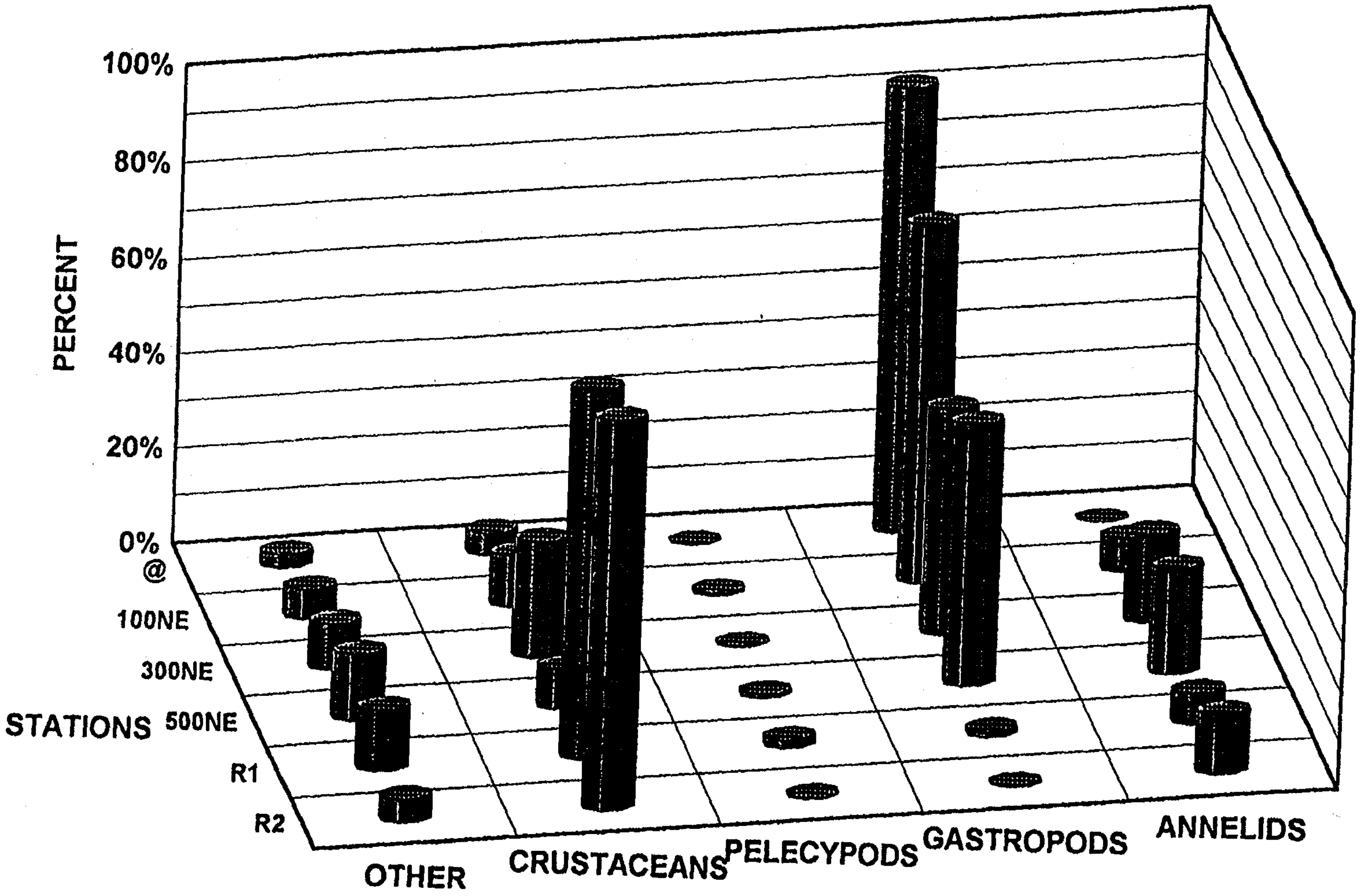
APPENDIX 2.

Taxonomic Composition (by major groups) of each station by transect and by years at Delacroix Island

TAXONOMIC COMPOSITION-DELACROIX ISLAND NORTHWEST TRANSECT - APRIL 1993



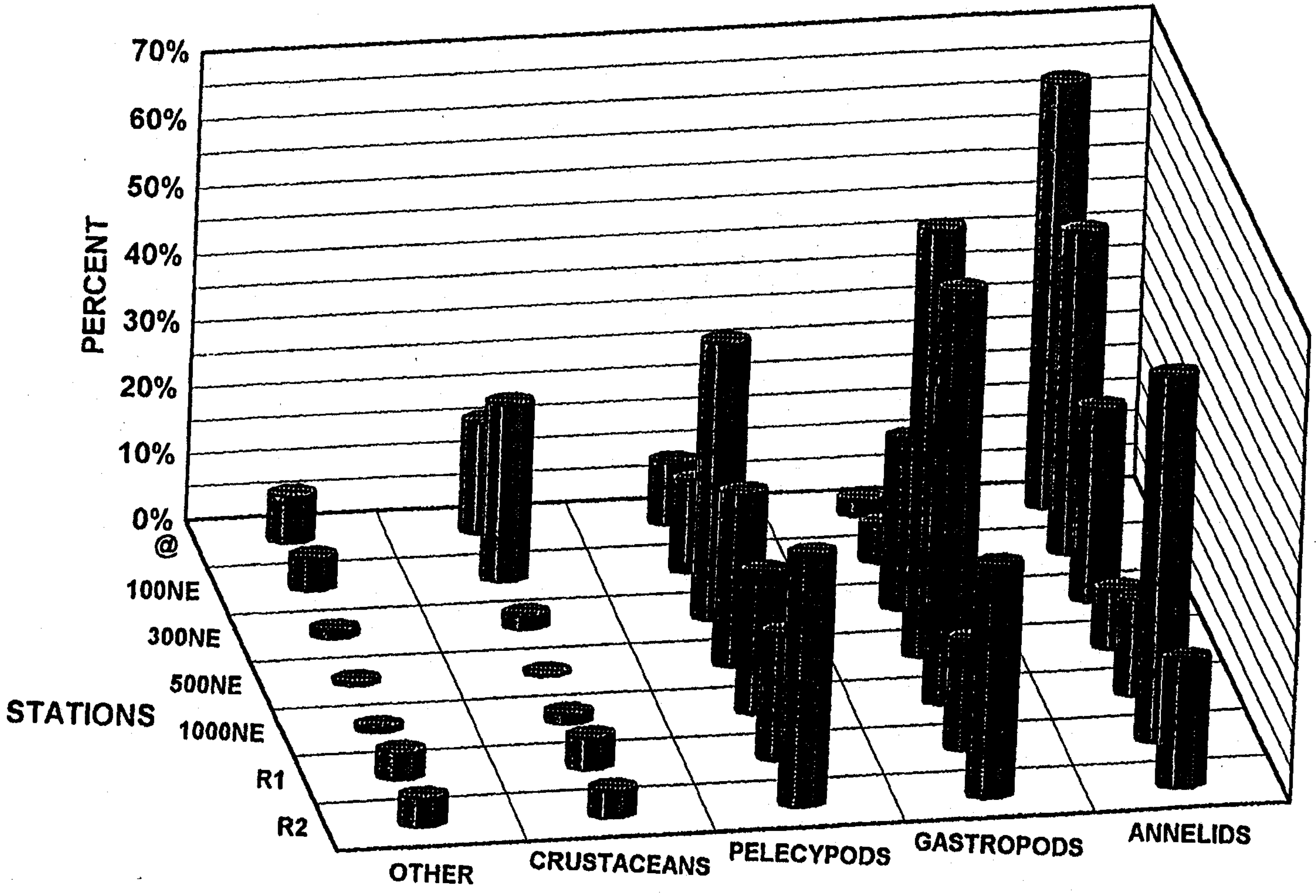
TAXONOMIC COMPOSITION-DELACROIX ISLAND NORTHEAST TRANSECT - APRIL 1993

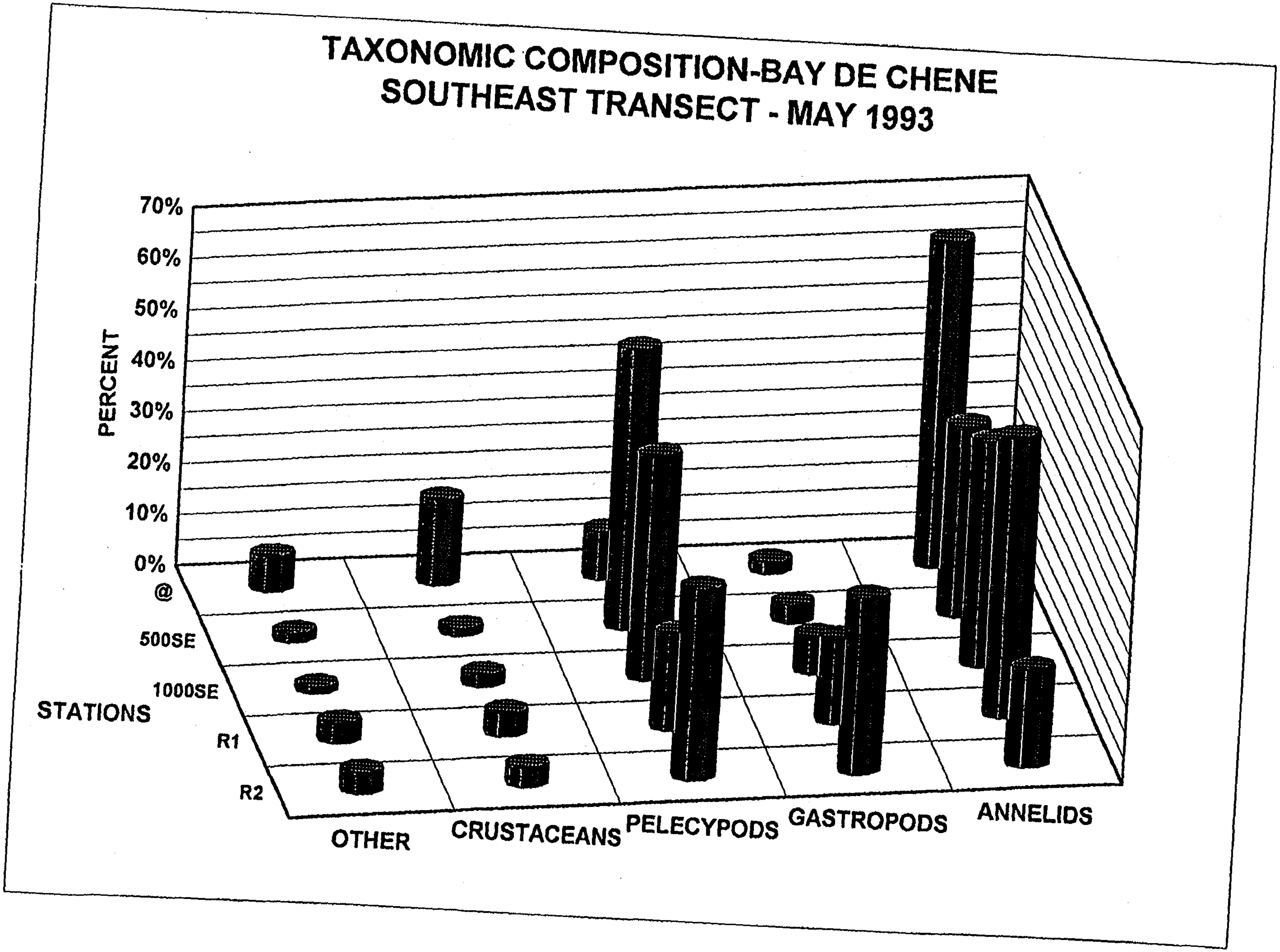


APPENDIX 3.

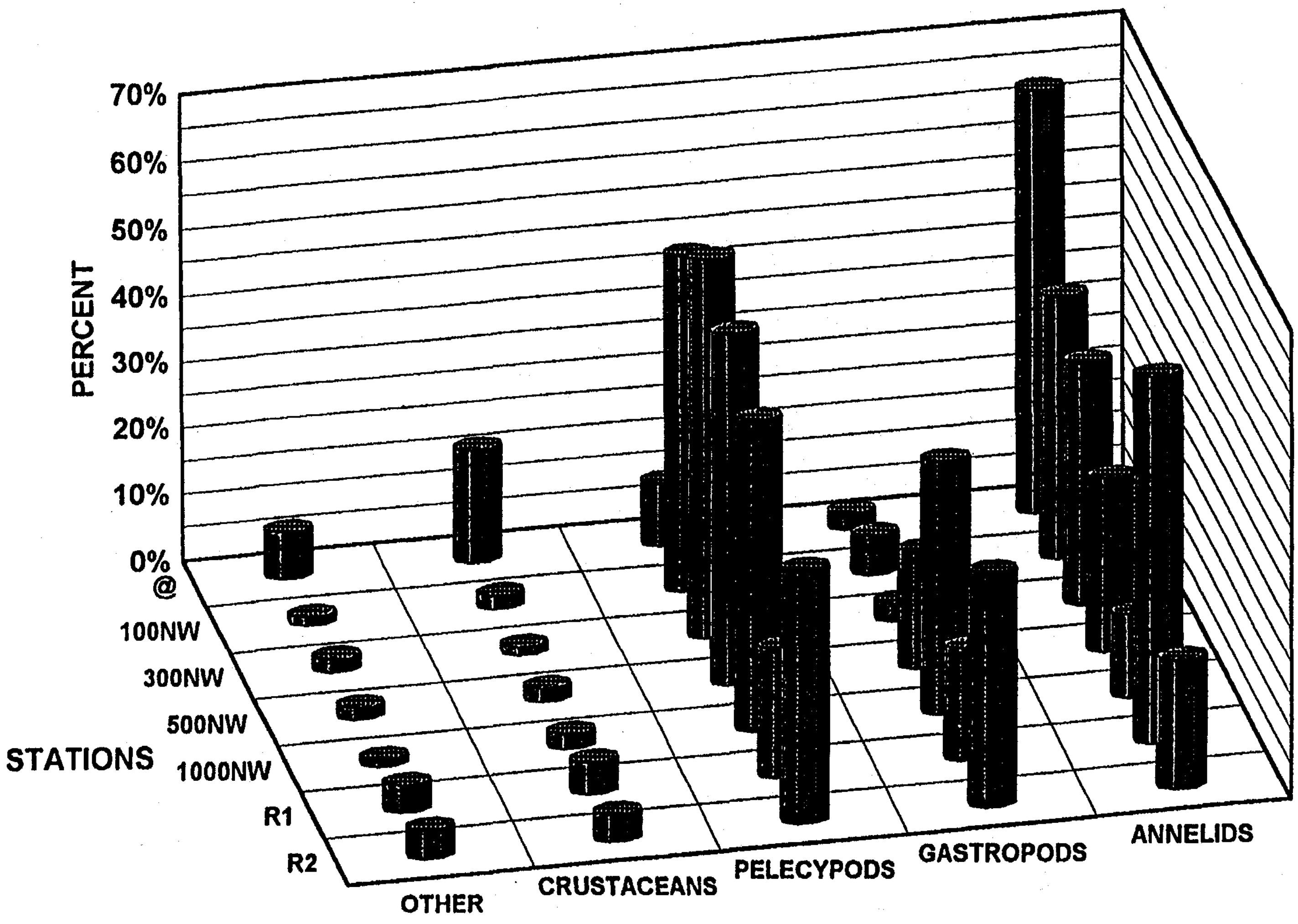
Taxonomic Composition (by major groups) of each station by transect and by years at Bay de Chene

TAXONOMIC COMPOSITION-BAY DE CHENE NORTHEAST TRANSECT - MAY 1993

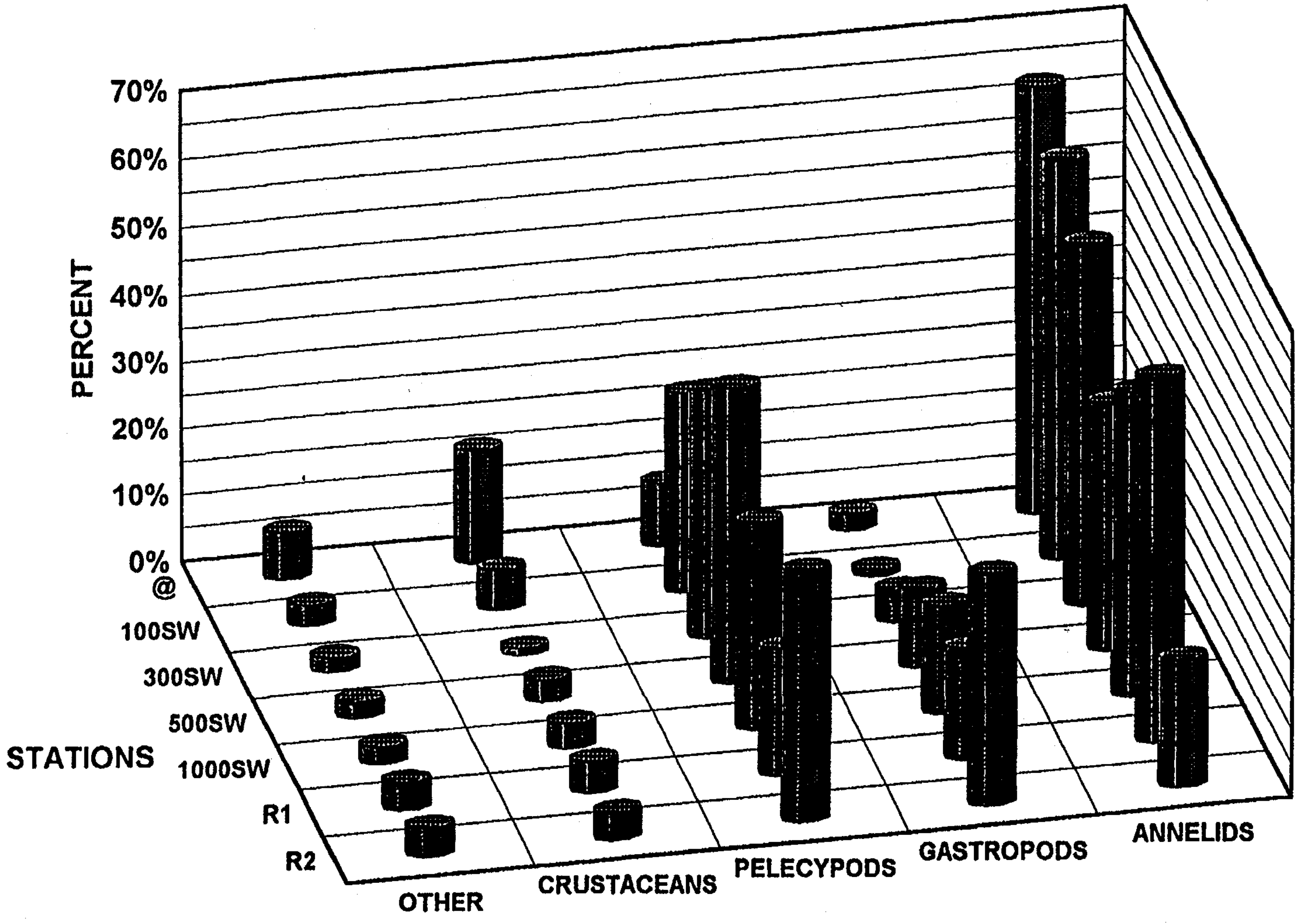



TAXONOMIC COMPOSITION-BAY DE CHENE
SOUTHEAST TRANSECT - MAY 1993
PERCENT
70%
60%
50%
40%
30%
20%
10%
0%
STATIONS
@
500SE
1000SE
R1
R2
OTHER
CRUSTACEANS
PELECYPODS
GASTROPODS
ANNELIDS

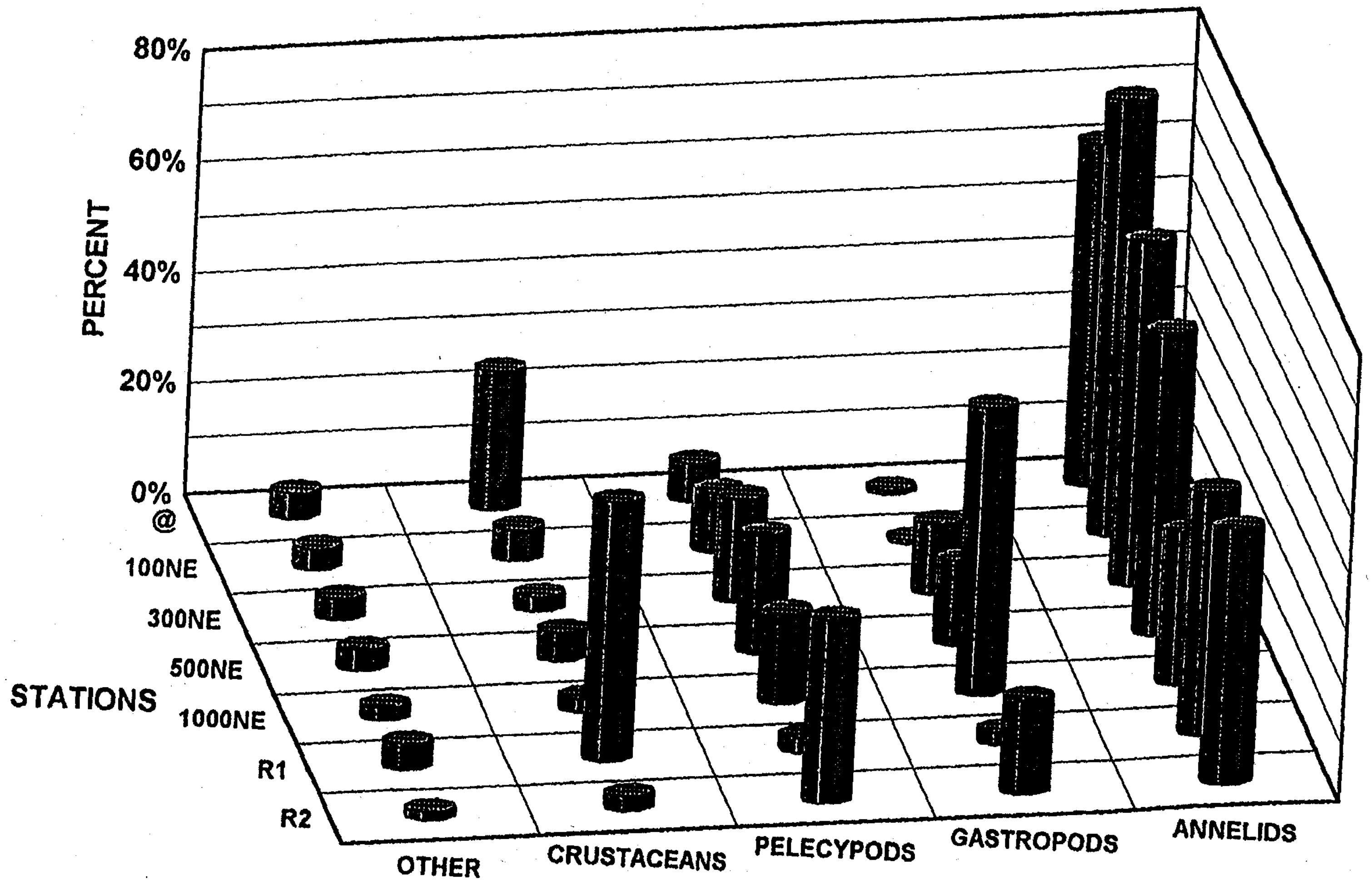
TAXONOMIC COMPOSITION-BAY DE CHENE
NORTHWEST TRANSECT - MAY 1993



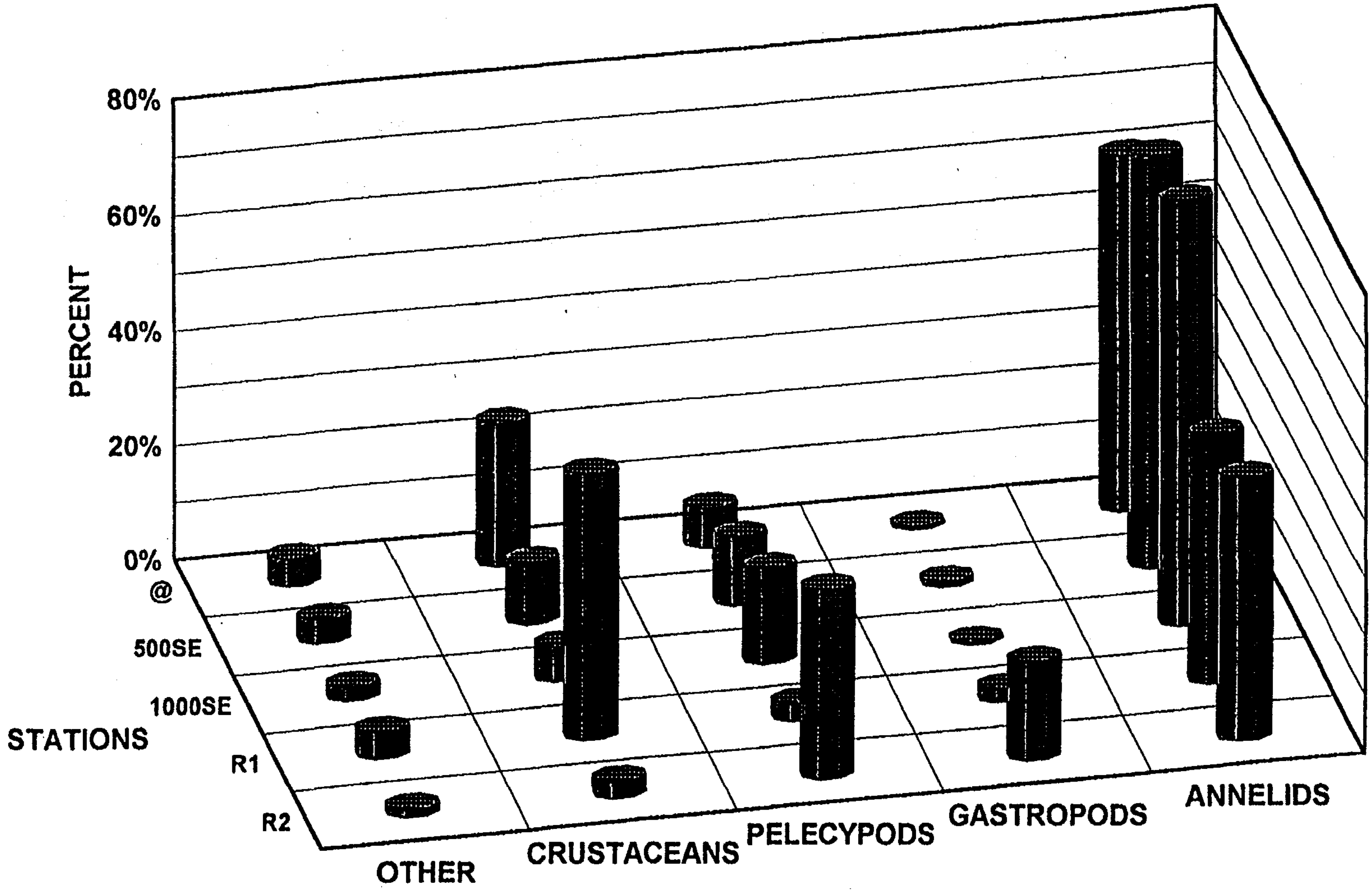
TAXONOMIC COMPOSITION-BAY DE CHENE
SOUTHWEST TRANSECT - MAY 1993



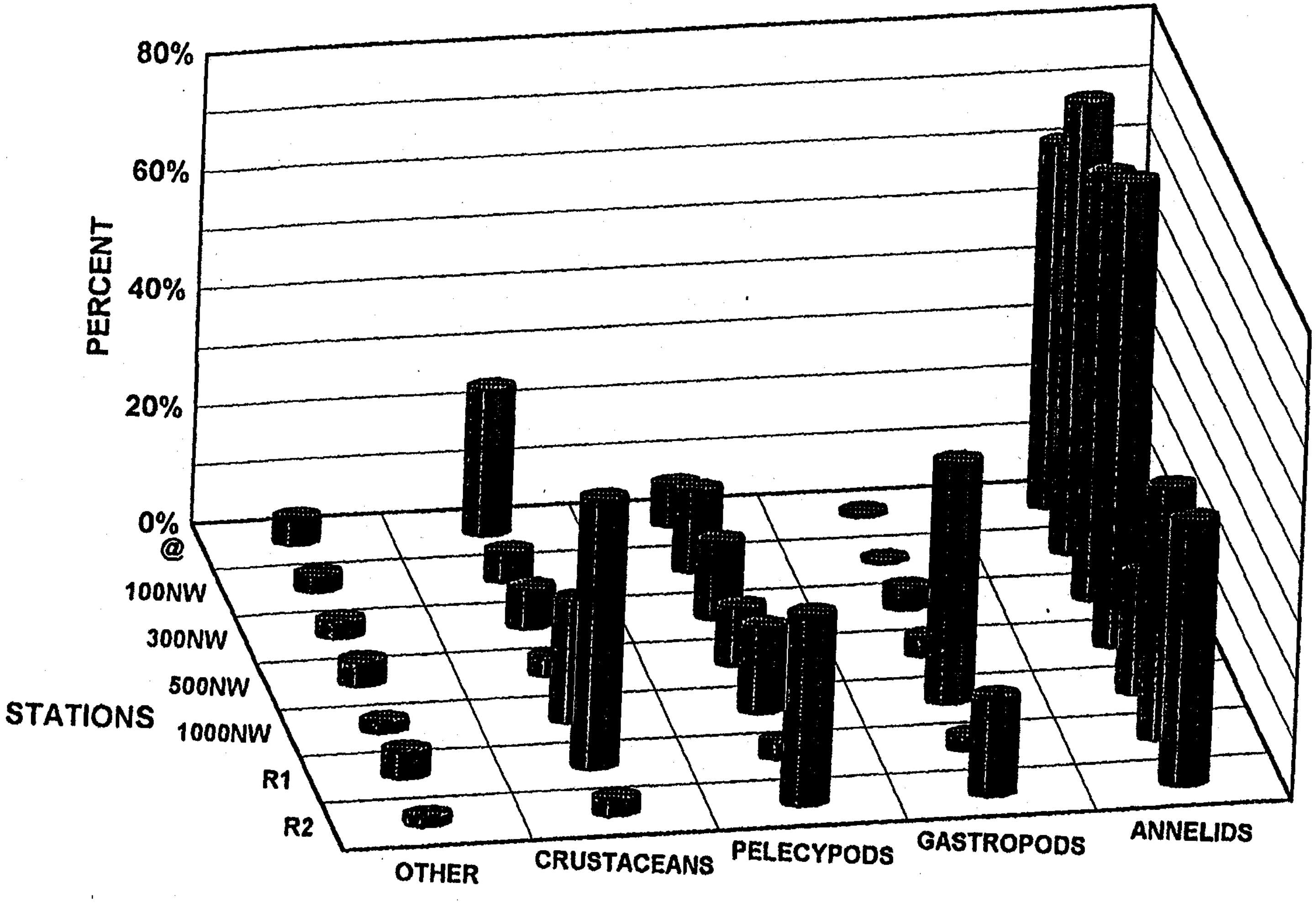
TAXONOMIC COMPOSITION-BAY DE CHENE
NORTHEAST TRANSECT - MAY 1994



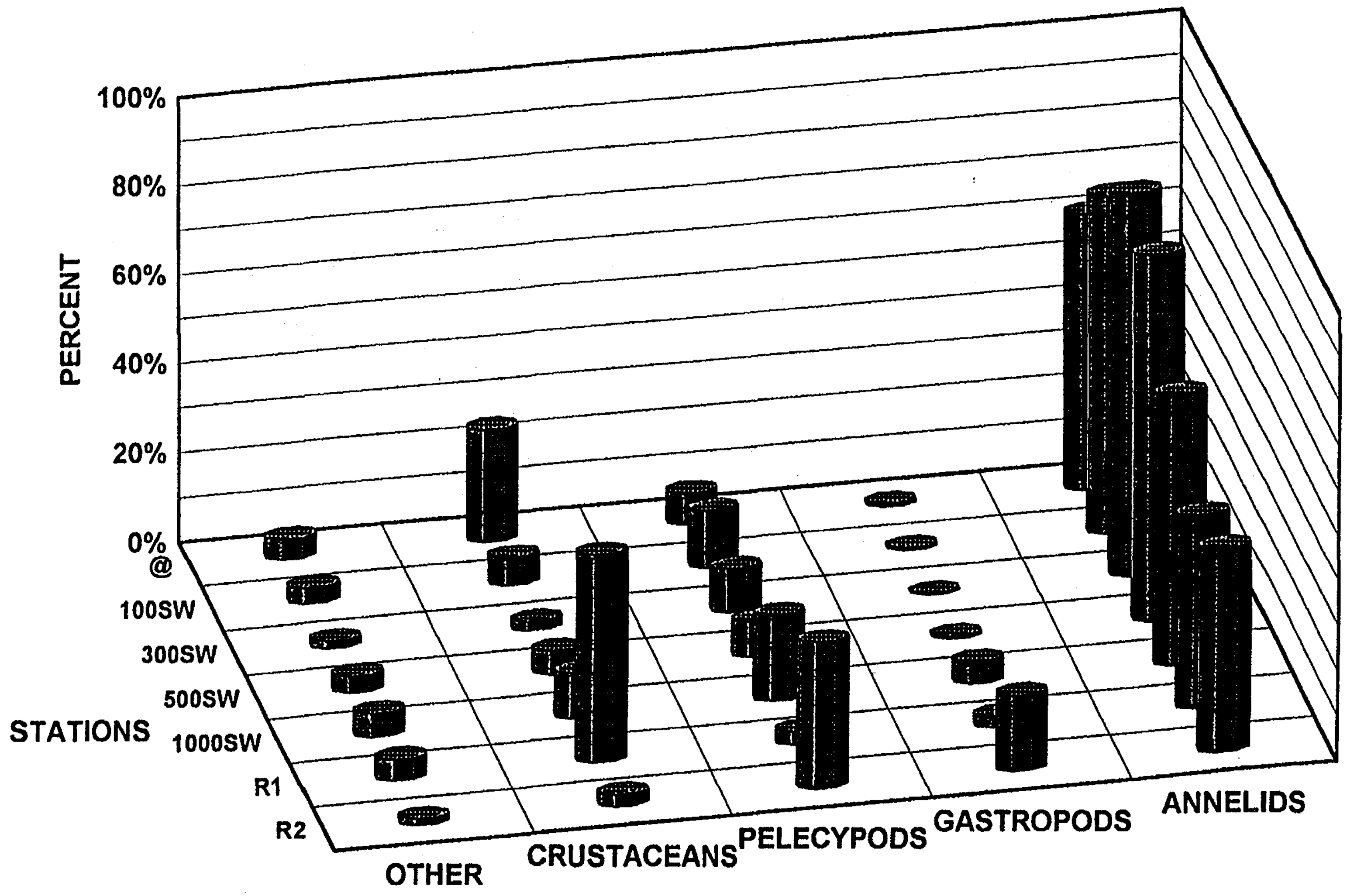
TAXONOMIC COMPOSITION-BAY DE CHENE SOUTHEAST TRANSECT - MAY 1994

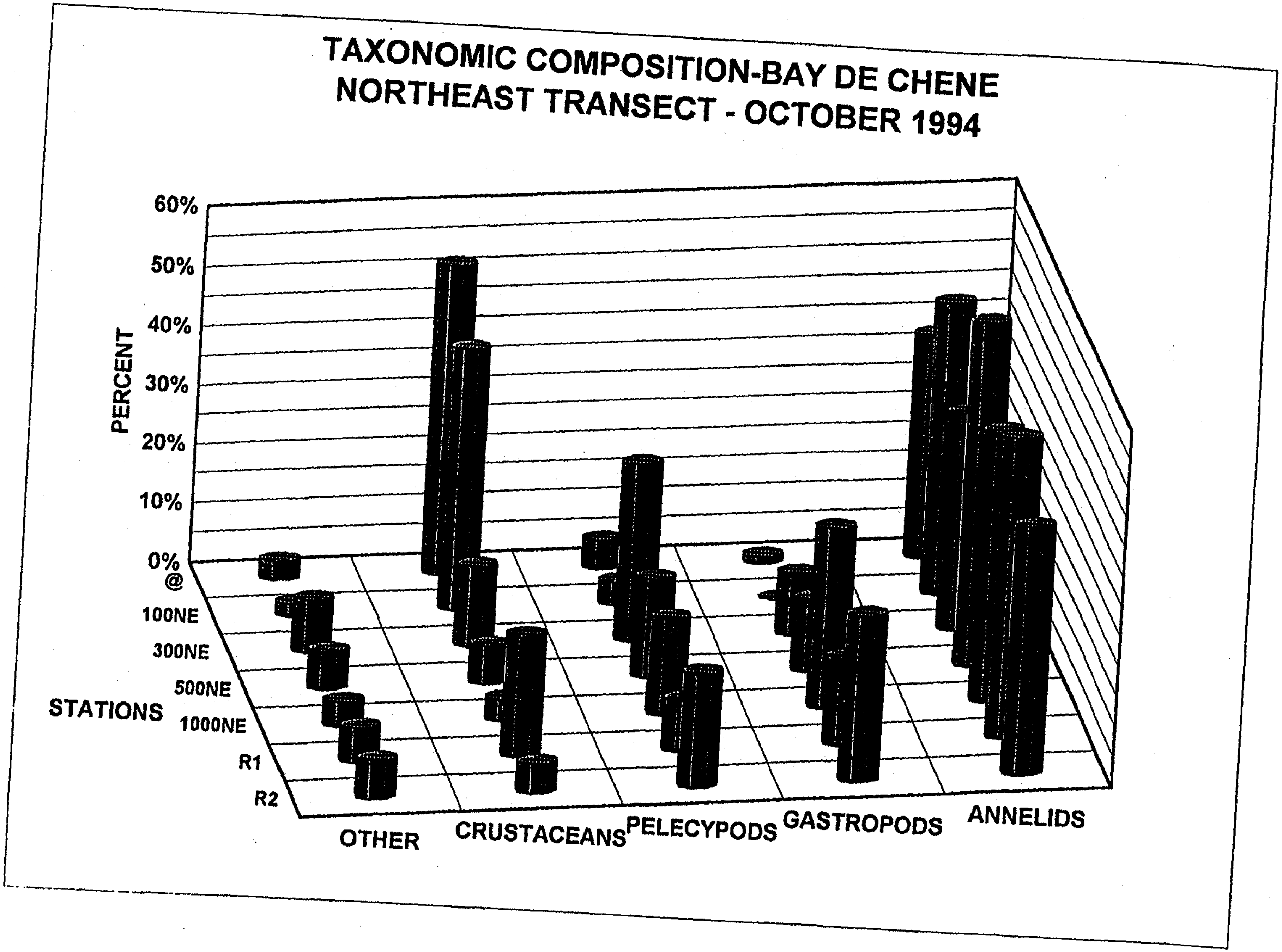


TAXONOMIC COMPOSITION-BAY DE CHENE
NORTHWEST TRANSECT - MAY 1994



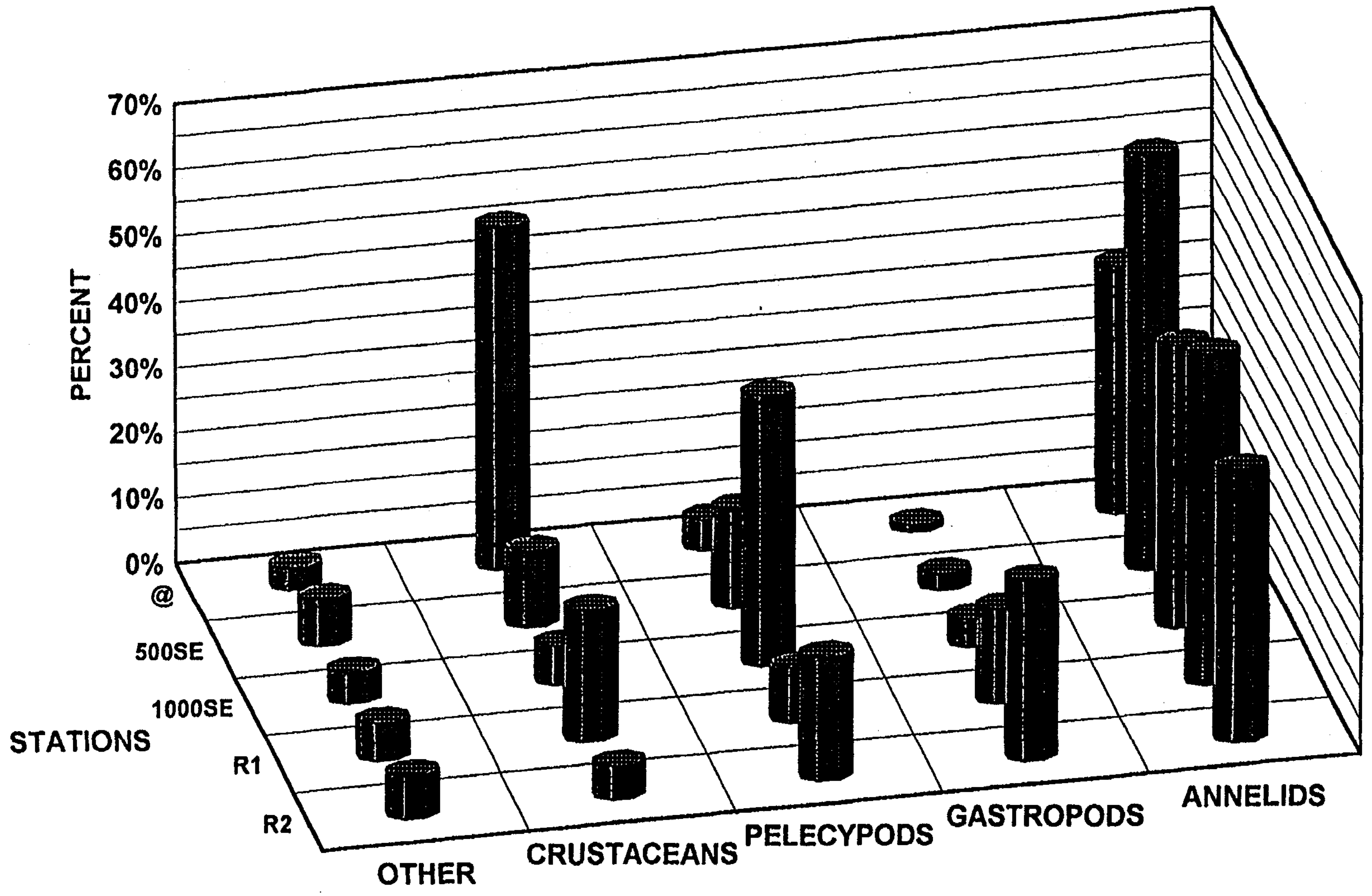
TAXONOMIC COMPOSITION-BAY DE CHENE
SOUTHWEST TRANSECT - MAY 1994



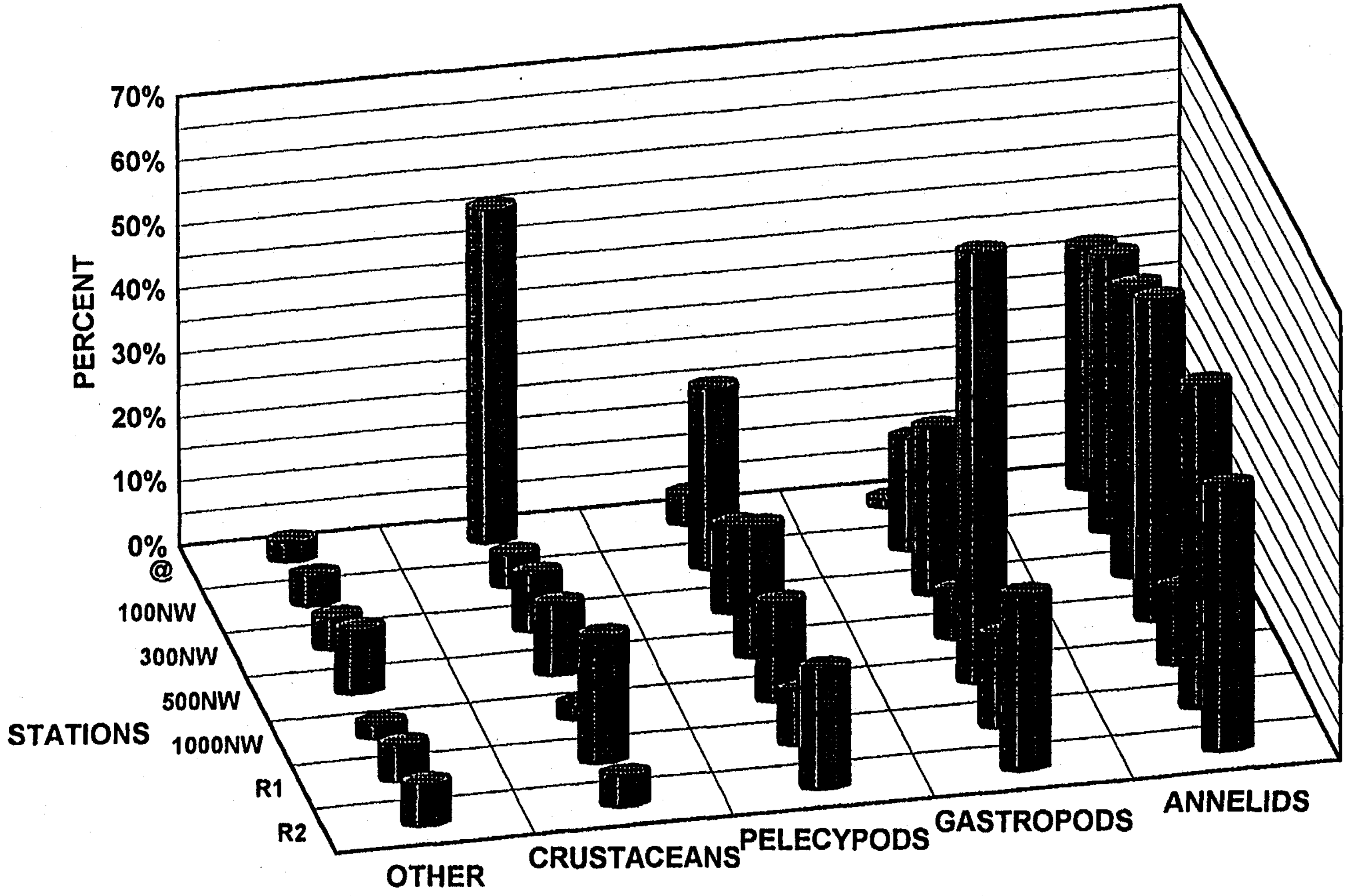


TAXONOMIC COMPOSITION-BAY DE CHENE
NORTHEAST TRANSECT - OCTOBER 1994

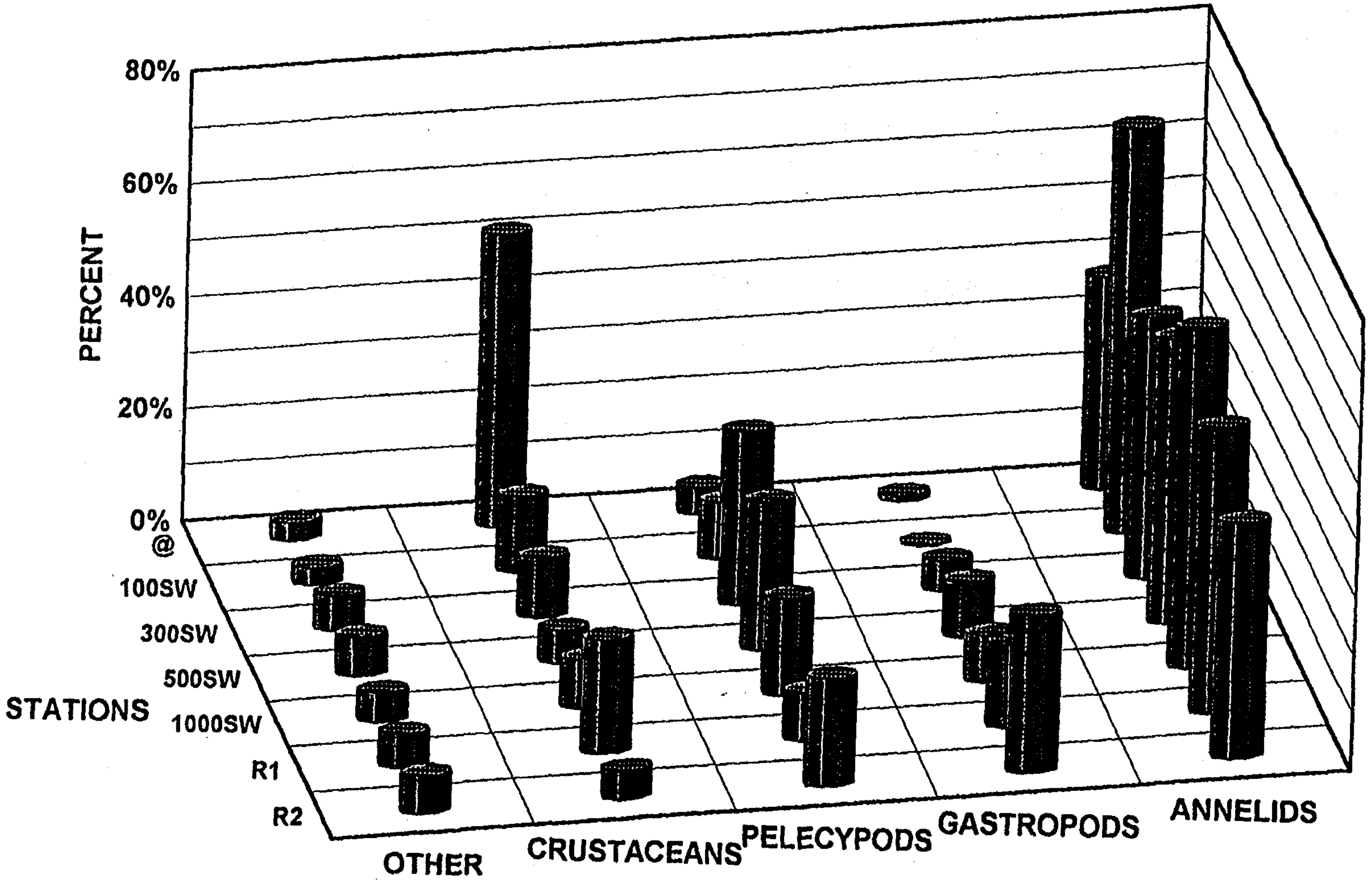
TAXONOMIC COMPOSITION-BAY DE CHENE
SOUTHEAST TRANSECT - OCTOBER 1994



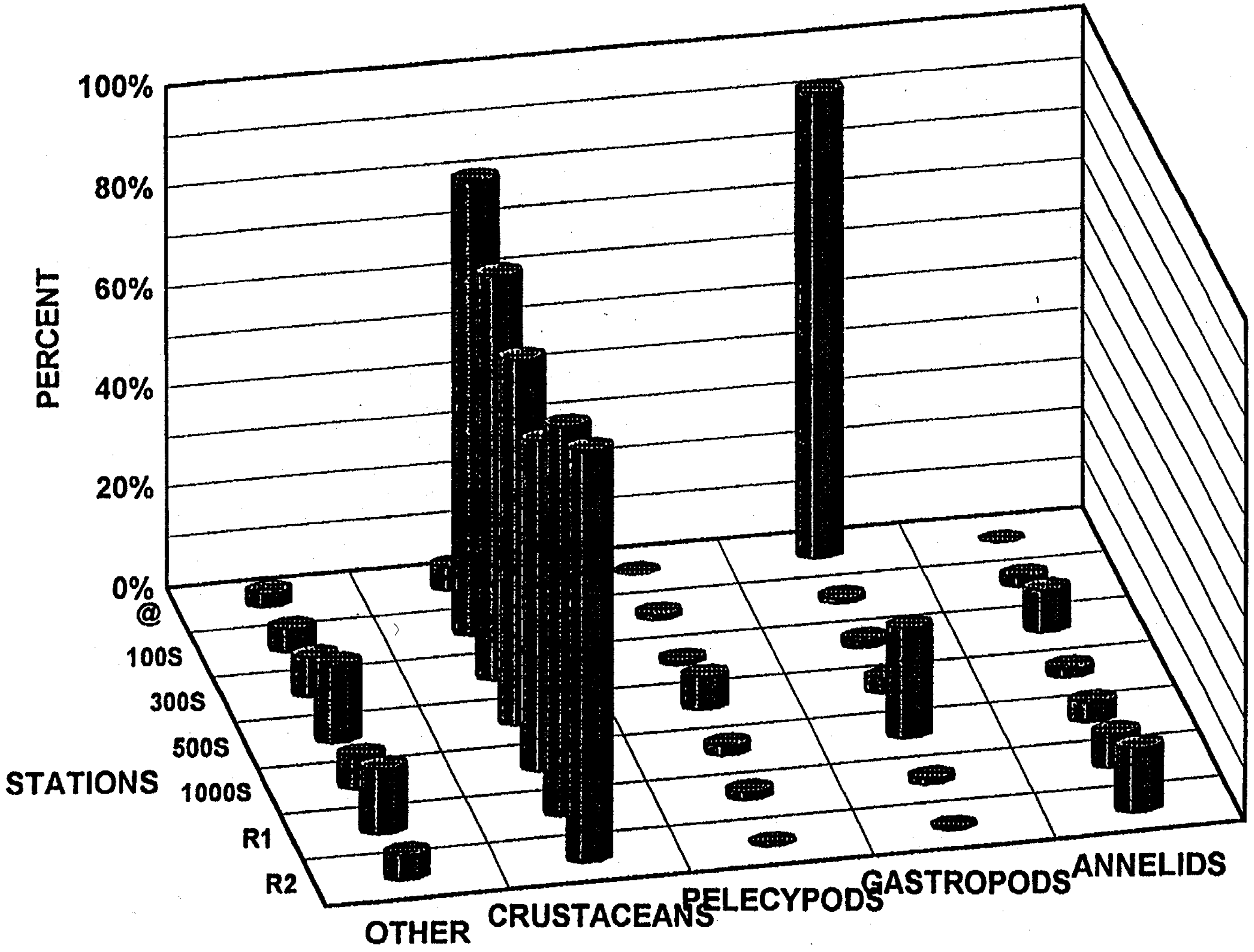
TAXONOMIC COMPOSITION-BAY DE CHENE
NORTHWEST TRANSECT - OCTOBER 1994



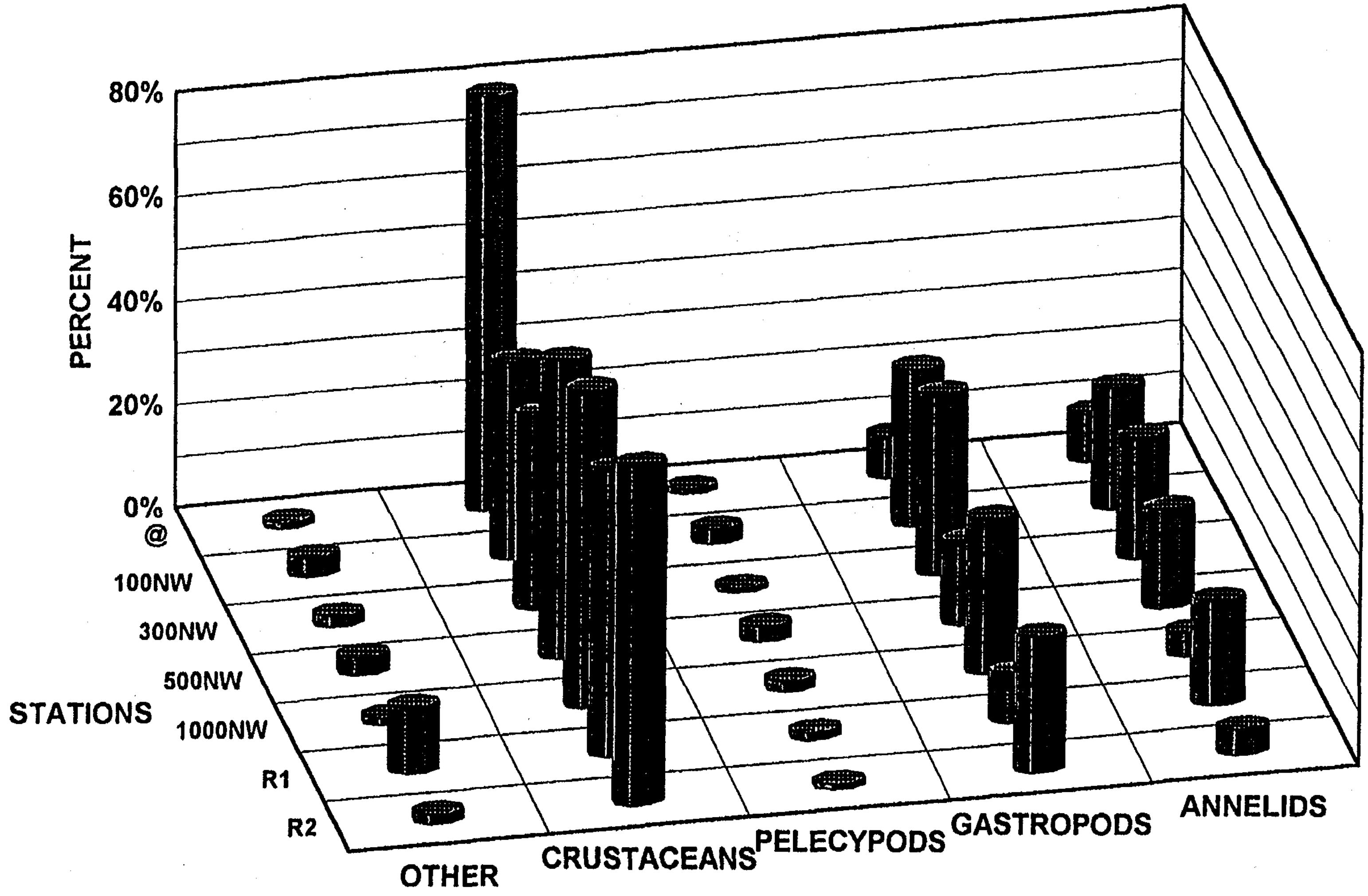
TAXONOMIC COMPOSITION-BAY DE CHENE SOUTHWEST TRANSECT - OCTOBER 1994



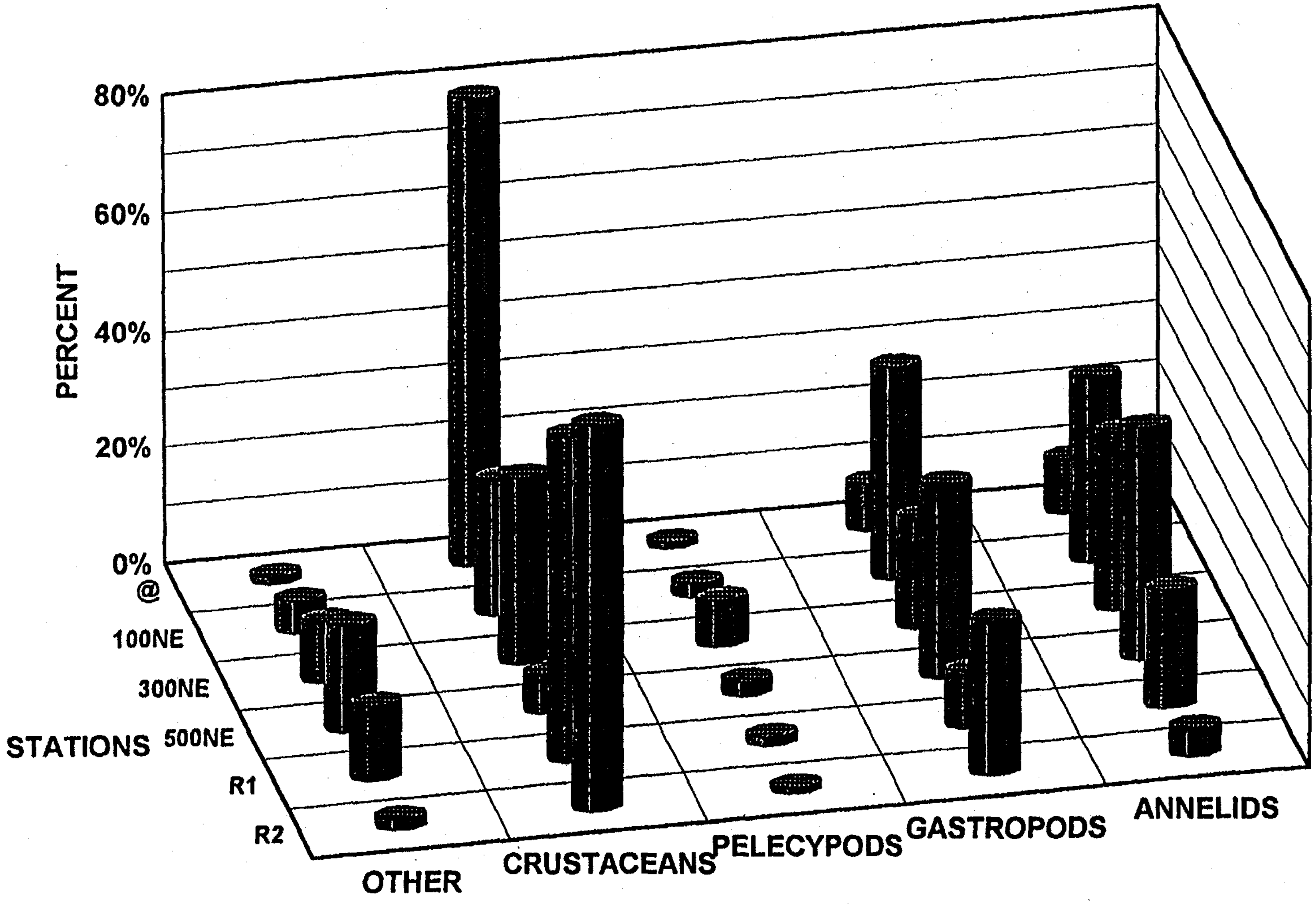
TAXONOMIC COMPOSITION-DELACROIX ISLAND
SOUTH TRANSECT - APRIL 1993



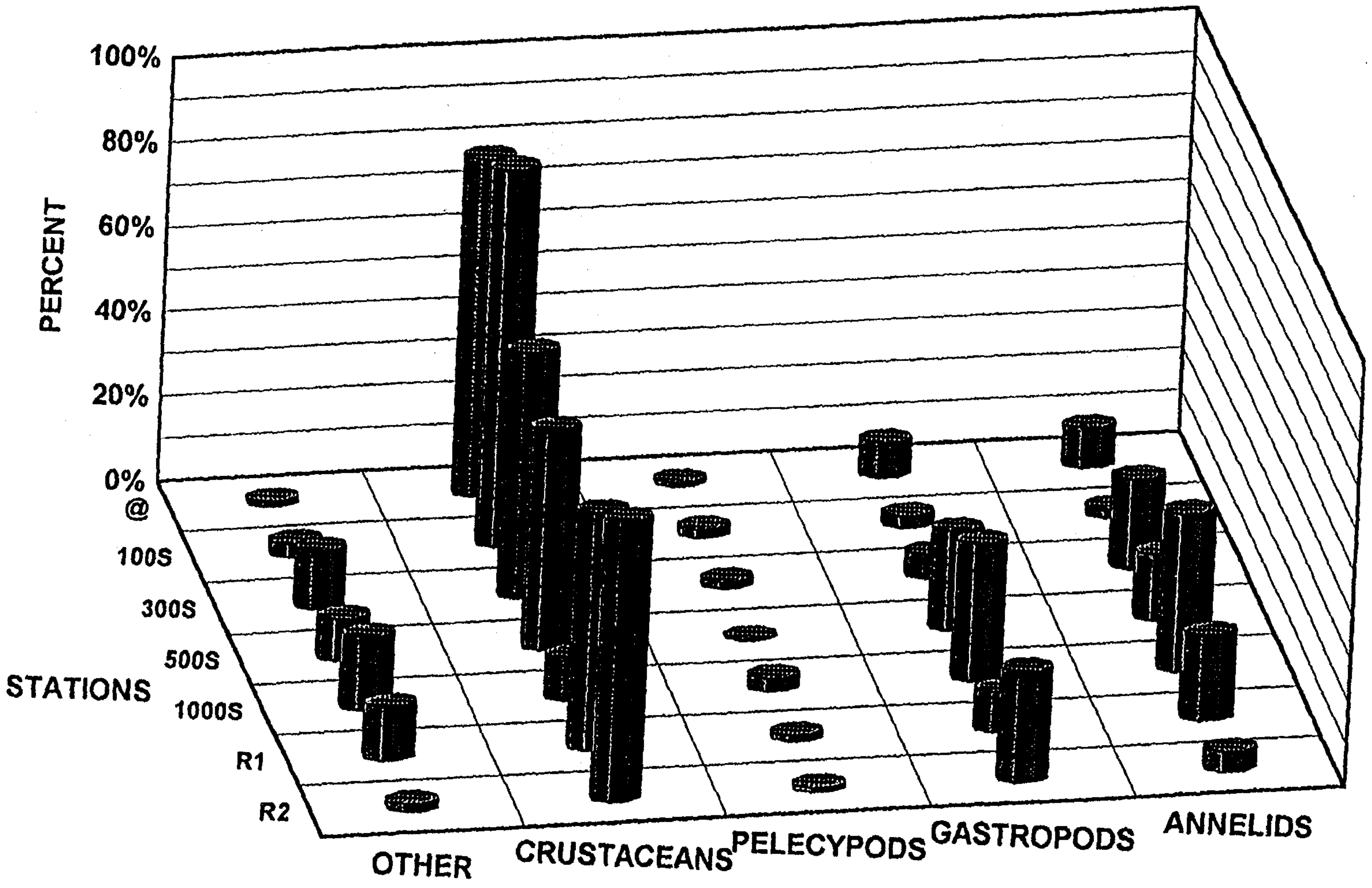
TAXONOMIC COMPOSITION-DELACROIX ISLAND
NORTHWEST TRANSECT - OCTOBER 1993



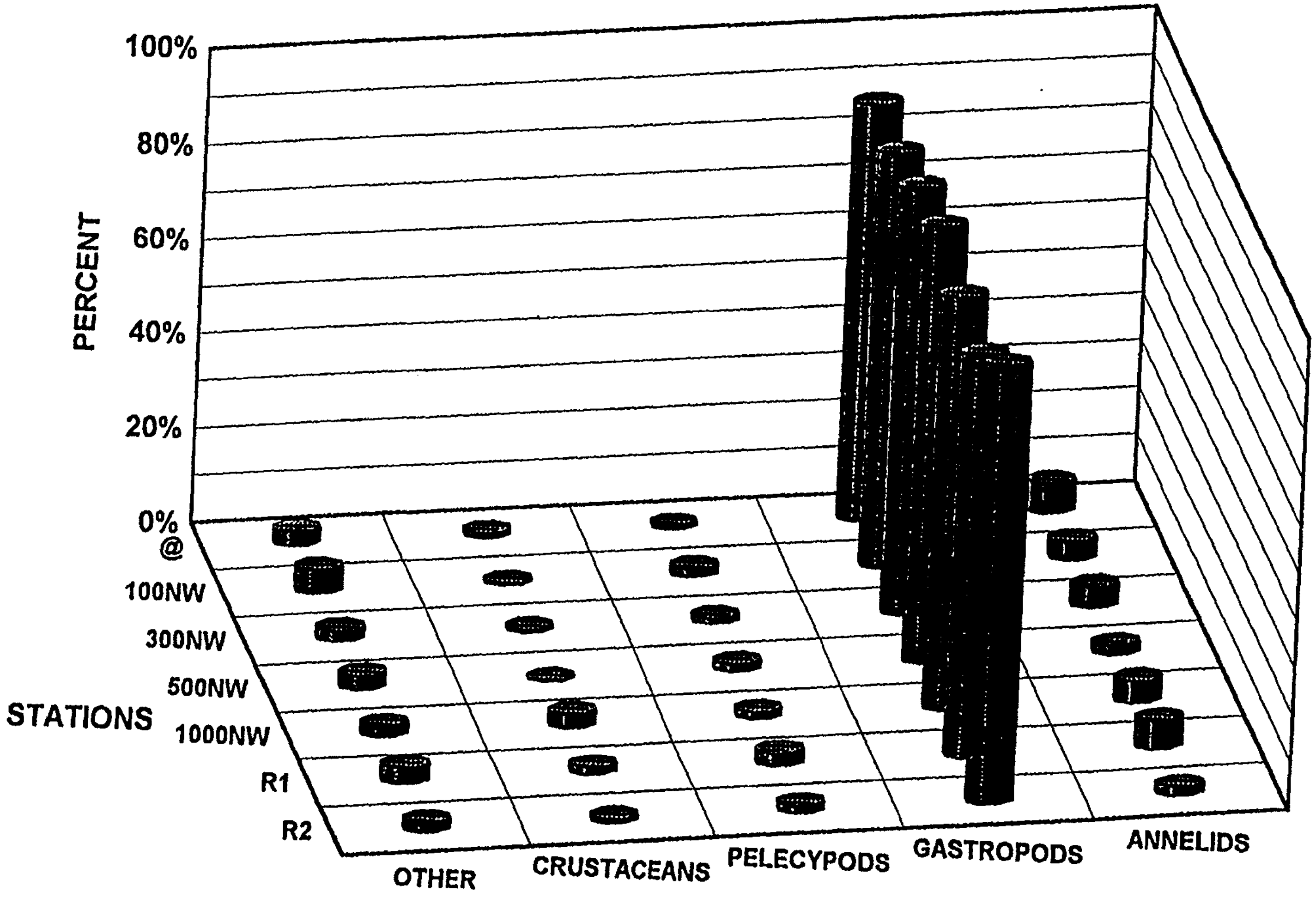
TAXONOMIC COMPOSITION-DELACROIX ISLAND
NORTHEAST TRANSECT - OCTOBER 1993



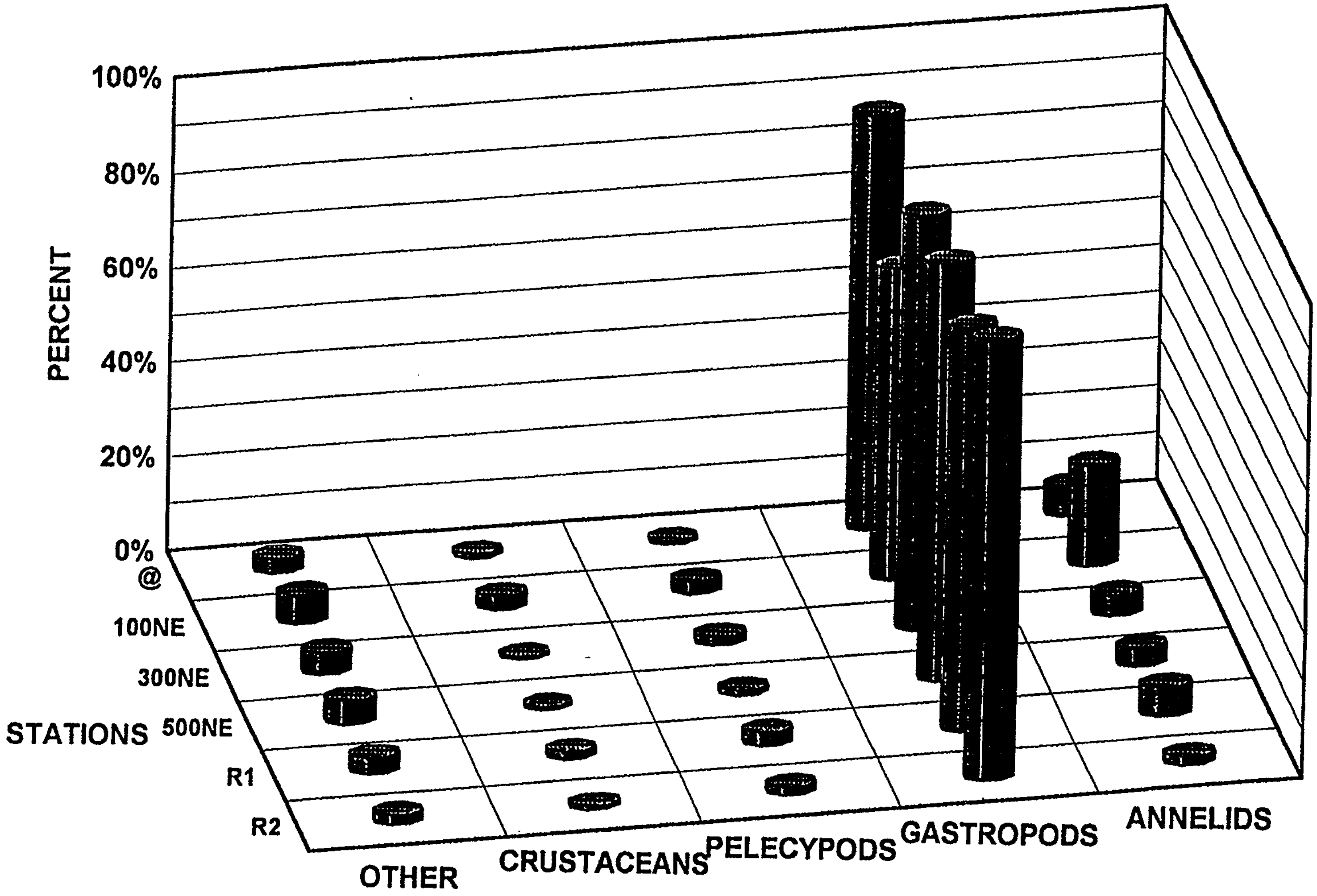
TAXONOMIC COMPOSITION-DELACROIX ISLAND SOUTH TRANSECT - OCTOBER 1993



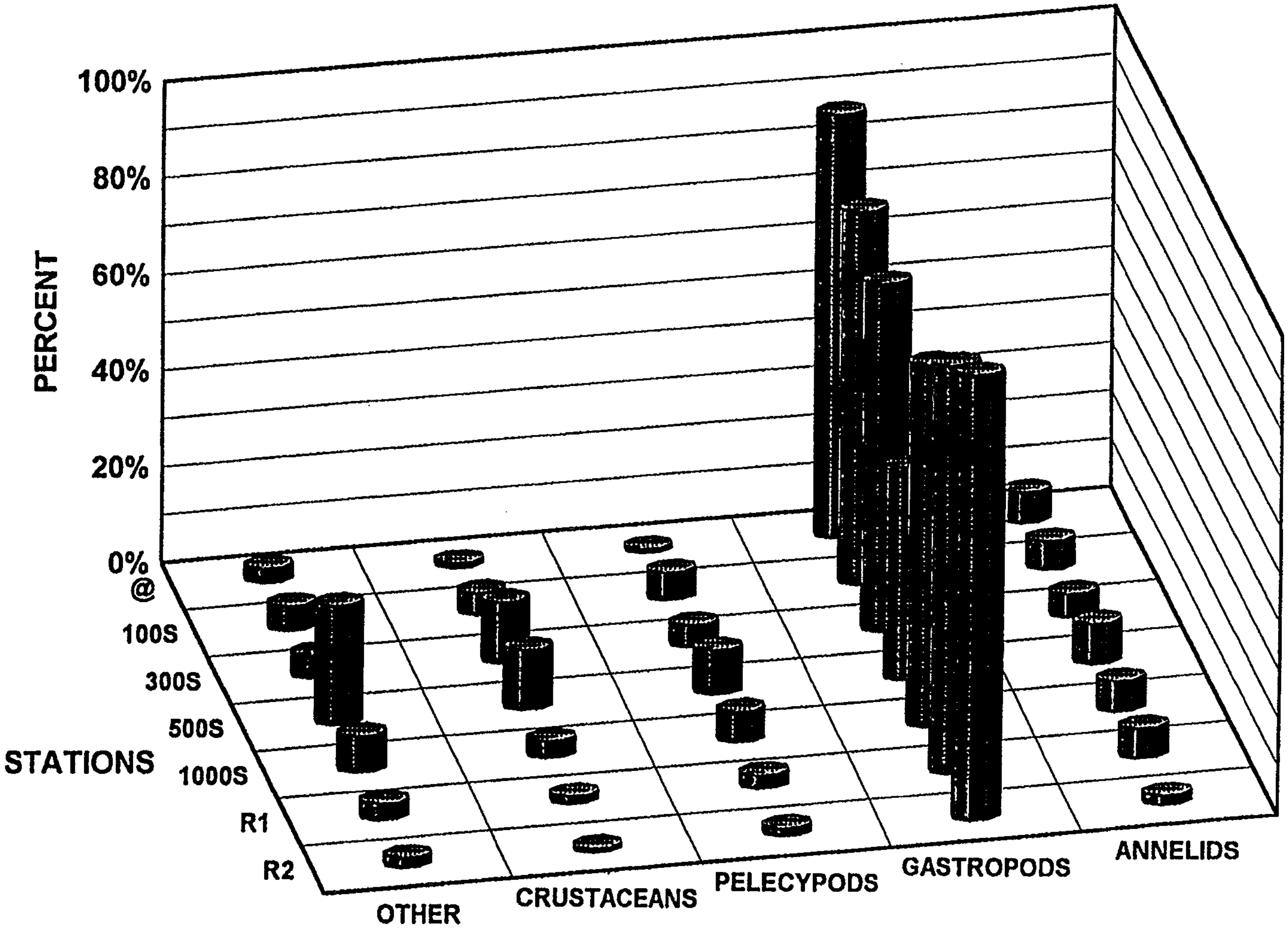
TAXONOMIC COMPOSITION-DELACROIX ISLAND
NORTHWEST TRANSECT - APRIL 1994



TAXONOMIC COMPOSITION-DELACROIX ISLAND NORTHEAST TRANSECT - APRIL 1994



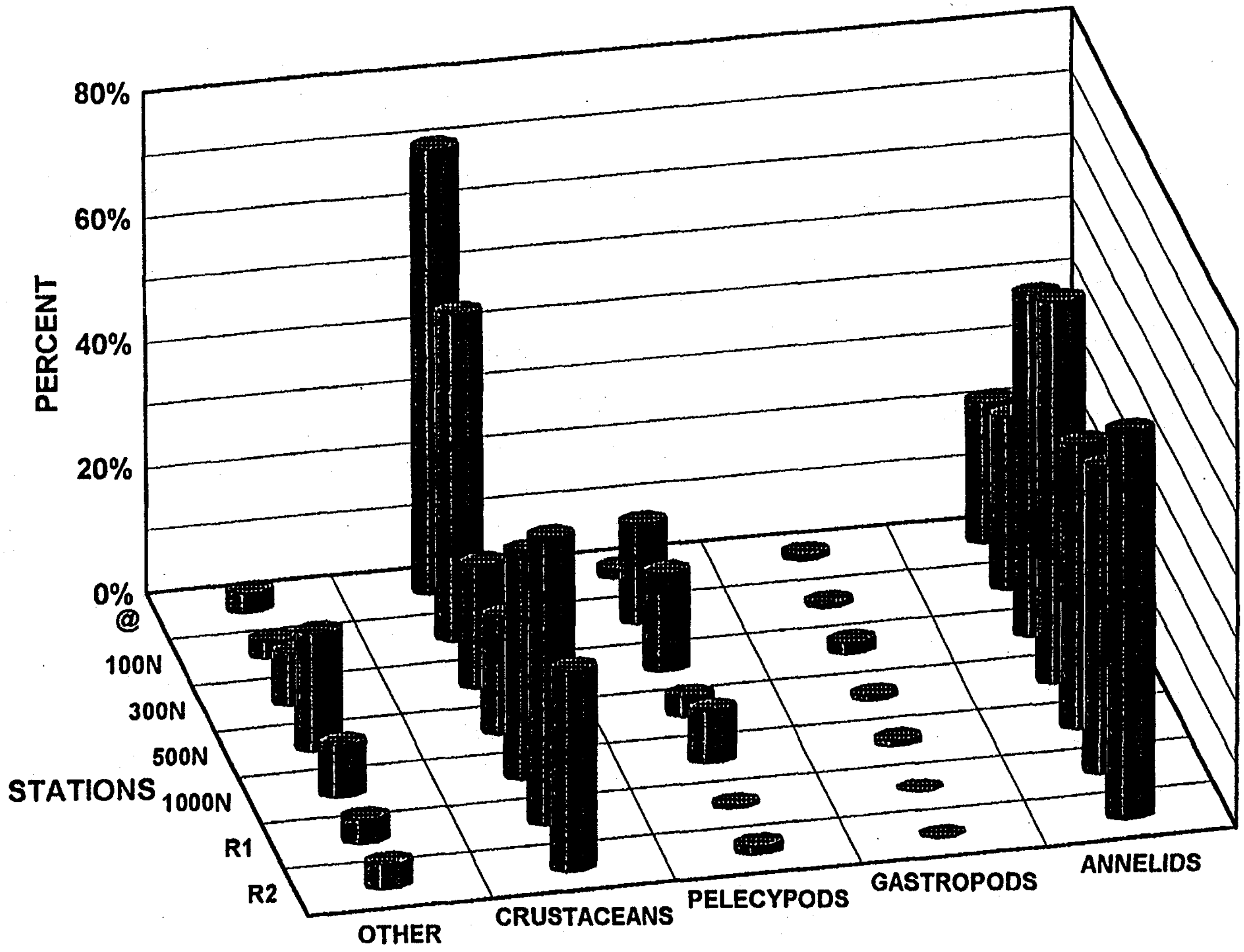
TAXONOMIC COMPOSITION-DELACROIX ISLAND
SOUTH TRANSECT - APRIL 1994



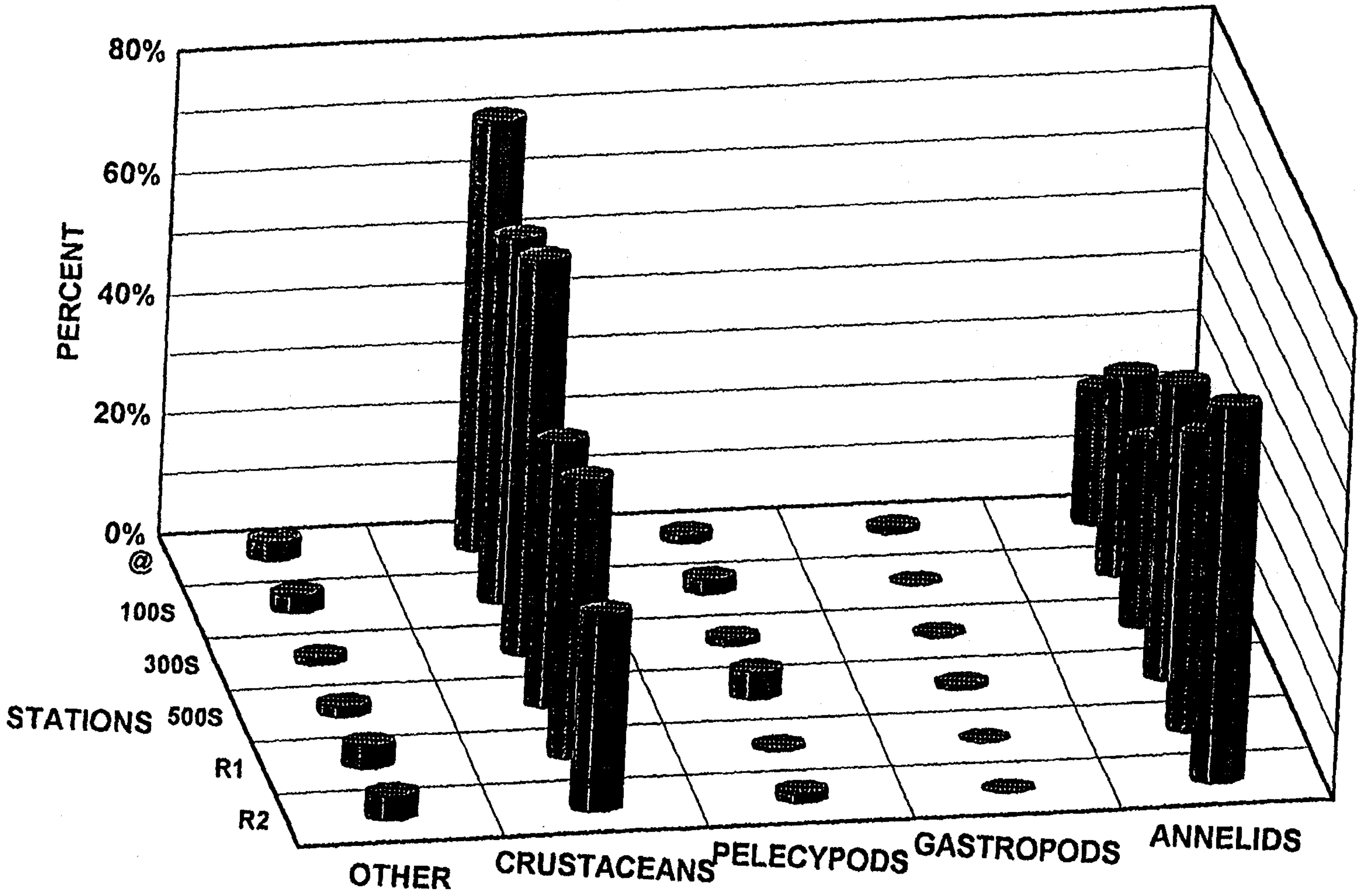
APPENDIX 4.

Taxonomic Composition (by major groups) of each station by transect and by years at Four Isle Dome

TAXONOMIC COMPOSITION-FOUR ISLE DOME
NORTH TRANSECT - NOVEMBER 1993



TAXONOMIC COMPOSITION-FOUR ISLE DOME
SOUTH TRANSECT - NOVEMBER 1993



CHAPTER 10 - AN ENVIRONMENTAL RISK ASSESSMENT OF METALS AND AROMATIC HYDROCARBONS IN AREAS WHERE PRODUCED WATER WAS DISCHARGED TO COASTAL LOUISIANA WATERS

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10.1 INTRODUCTION

The overall objective of this study was to determine the extent of contamination and impact from produced water discharges and the rate of recovery of coastal ecosystems following cessation of produced water discharges to shallow coastal waters of Louisiana. The objective of this chapter was to evaluate the environmental risk to shallow-water biological resources resulting from long-term produced water discharges to coastal waters of Louisiana and the reduction of environmental risk following cessation of the discharges. Three produced water discharge sites in different coastal habitats were evaluated. At two of the sites, field surveys were performed shortly before termination of produced water discharge, and six months and one year after termination of the discharge. At the other site, only the survey before discharge termination was completed.

In this study, produced water was collected from each platform site and analyzed for selected radionuclides, metals, and petroleum hydrocarbons. Sediment and sediment interstitial water samples were collected at stations located at different distances from the produced water discharges and at reference stations. Sediment and interstitial water samples were analyzed for selected radionuclides, metals, and petroleum hydrocarbons. Benthic infauna also were collected at all sediment sampling locations for evaluation of effects of the produced water discharges and cessation of discharges on community structure. These data will be used as the basis for this risk assessment for metals and aromatic hydrocarbons from produced water. The environmental risks of radioisotopes in produced water and sediments are discussed in a separate publication from the Brookhaven National Laboratory (Meinhold et al., 1996). Exposure to potentially toxic components of the produced water will be estimated based on concentrations of target chemicals in the produced water itself and in interstitial water and bulk sediments before and after cessation of produced water discharge.

Several studies have been performed in the Gulf of Mexico on the effects on the local ecosystems of produced water discharges to shallow coastal waters (Armstrong et al., 1979; Boesch and Rabalais, 1989; St. Pé, 1990; Rabalais et al., 1991; Neff et al., 1992). These studies have found that, in most cases, adverse effects are restricted to benthic communities in sediments within 20 to a few hundred meters of the produced water discharge where concentrations of petroleum hydrocarbons, particularly PAHs, are elevated. However, there have been no studies of recovery of benthic communities following cessation of a produced water discharge as sediment contamination decreases. An evaluation will be made in this chapter of the relationship between levels of sediment contamination and evidence of adverse effects in benthic communities at several locations near produced water discharges before and after termination of discharges.

10.2 METHODS

The study design and methods used for this project have been described in detail in **Chapters 2** and **3** of this report. They will be summarized briefly here.

Three produced water discharge facilities in tidal wetlands of southern Louisiana were chosen for this study. Produced water discharges at the three facilities were scheduled to cease shortly after the first field survey. The study design was to sample at each facility before termination of produced water discharge, approximately six months after the termination, and again approximately one year after the first field survey. The three facilities are:

Delacroix Island Tank Battery #1;
Bay de Chene Tank Battery #5; and
Four Isle Dome Central Production Facility.

The survey schedule is summarized in **Table 10.1.** Because cessation of produced water discharge at the Four Isle Dome Central Production Facility was delayed until January 1995, no post-termination surveys were performed at this facility.

Table 10.1. Pre-termination and Post-termination Survey schedules and dates of termination of produced water discharge at the three facilities monitored in this study.

Survey	Delacroix Island	Bay de Chene	Four Isle Dome
Pre-termination Survey	April 1993	May 1993	November 1993
Termination	April 1993	October 1993	January 1995
First Post-termination Survey	October 1993	May 1994	—
Second Post-termination Survey	April 1994	October 1994	—

Produced water was collected from each facility during the Pre-termination Surveys. Water quality data were collected at the discharge and two reference sites for each facility on all three surveys. Sediment and sediment interstitial water samples were collected at the three discharge locations, several stations located at different distances along transects radiating from the discharges, and two reference stations away from the influence of each produced water discharge. One to three replicate samples were collected at each sampling station on each survey. Six replicate benthic infauna samples also were collected at all the sediment sampling stations.

Produced water, sediment, and sediment interstitial water samples were analyzed for several metals, radionuclides, and PAHs. VAHs and SHCs also were analyzed in produced water and sediments (VAHs in sediments from only the discharge and reference sites). The metals analyzed in all samples are arsenic, barium, cadmium, chromium, copper, iron, lead, manganese, mercury, molybdenum, nickel, vanadium, and zinc. Aluminum, calcium, and sulfate also were analyzed in sediment samples. Percent TOC and grain size were analyzed in sediments, and TOC, chlorinity, and sulfate were analyzed in sediment interstitial water.

10.3 RESULTS AND DISCUSSION

10.3.1 Characteristics of Study Sites

The characteristics of the three study sites were described in detail in **Chapter 4** of this report. Characteristics relevant to the risk assessment will be summarized here.

Delacroix Island

The Delacroix Island Oil and Gas Field is located in tidal marsh lands adjacent to Black Bay east of the Mississippi River. Oil has been produced from the field since 1940. The area is characterized by subsiding tidal *Spartina* marshes interspersed with shallow waterways and man-made canals. Salinity of the ambient brackish water varies from 1.2 to 6.5 ‰ at the surface and 1.3 to 8.8 ‰ near the bottom (**Table 10.2**). Salinity usually is higher in the fall than in the spring. Water depth in the field ranges from 0.9 to 2.8 m. Sediments are predominantly gravely sandy mud with some sandy silt. The fine-grained sediments contain high concentrations of TOC, ranging from 1.75% to 26.16%. Tidal flushing in the natural waterways and artificial canals generally is sluggish. These local features influence the distribution and fate in the local environment of chemicals from produced water.

Benthic infauna in the area is depauperate and characteristic of bottom communities in disturbed oligohaline environments. The dominant benthic infauna include several species of oligochaetes, polychaetes, bivalve and gastropod mollusks, amphipods, and crabs (see **Chapter 9**). Because of the low and variable salinities at the facility, the habitat is marginal for the American oyster (*Crassostrea virginica*).

Several species of crustaceans and fish of commercial and recreational value frequent Black Bay and the waterways near the Delacroix facility on a seasonal basis. These include brown and white shrimp (*Penaeus aztecus* and *P. setiferus*), blue crab (*Calinectes sapidus*), red drum (*Sciaenops ocellatus*), speckled trout and sand seatrout (*Cynoscion nebulosus* and *C. arenarius*), flounder (*Paralichthys lethostigma*), Atlantic croaker, (*Micropogonias undulatus*), spot (*Leiostomus xanthurus*), black drum (*Pogonias cromis*), and sheepshead (*Archosargus probatocephalus*).

The Louisiana Department of Environmental Quality (LDEQ) reported that an average of 222,100 L/day (1,397 bbl/day) of produced water was discharged from Delacroix Island Tank Battery #1 in 1989. At the time of termination of the discharge, 312,250 to 314,475 L/day (1,964 to 1,978 bbl/day) were being discharged. The produced water had a salinity of 135 ‰, about 35 times the salinity of the receiving waters.

Bay de Chene

The Bay de Chene Field is in Hackberry Bay in the northern part of the Barataria Bay system about 21 km north-northwest of Grand Island, Louisiana, and west of the Mississippi River. The first well was drilled in the field in 1942 and the field has been in production since. The area is mostly open water with small tidal *Spartina* marsh areas. The water depth in the field is 1.2 to 2.3 m (**Table 10.2**). Ambient water salinities are low in the spring and high in the fall with seasonal ranges of 1 to 22 ‰ in surface water and 2 to 23 ‰ in bottom water. The predominant sediment type is sandy gravely mud containing 0.57% to 11.5% TOC.

Table 10.2. Characteristics of produced waters and the local discharging environments at the three oil production sites.

Parameter	Delacroix Island	Bay de Chene	Four Isle Dome
Produced water discharge rate	1,970 bbl/day	3,825 bbl/day	852 bbl/day
Produced water salinity	135 ‰	135 ‰	154 ‰
Ambient water salinity - surface	1.2 - 6.5 ‰	1.0 - 22.0 ‰	3.5 - 6.9 ‰
Ambient water salinity - bottom	1.3 - 8.8 ‰	2.0 - 23.0 ‰	3.5 - 9.2 ‰
Water depth	0.9 - 2.8 m	1.2 - 2.3 m	1.0 - 2.3 m
Dominant sediment texture	gravely sandy mud - sandy silt	gravely sandy mud	mud
Sediment total organic carbon	1.75 - 26.16 %	0.47 - 11.47 %	0.67 - 23.01 %

Benthic communities in the Bay de Chene Field are similar to those in the Delacroix Island Field, but are somewhat more diverse because of the higher average bottom water salinities. Oysters are cultivated commercially in several leased oyster grounds in the area of the field. Several species of commercially and recreationally important crustaceans and fish are common in the area. They include the same species as occur at Delacroix Island.

In 1989, the produced water discharge from Tank Battery #5 in the Bay de Chene Field averaged 582,850 L/day (3,666 bbl/day). At the time of the Pre-termination Survey, four wells were in production in the field and an average of 608,125 L/day (3,825 bbl/day) of produced water was discharged to local receiving waters. The produced water had a salinity of 135 ‰.

Four Island Dome

The Four Island Dome Field is located near the coast in a tidal marsh and bayou area about 40 km south of Houma, Louisiana, in the general vicinity of Caillou Lake. Little information is available about the history of the field. The area is predominantly tidal *Spartina* salt marsh interspersed with bayous and man-made canals.

The area is less influenced by the Mississippi River outflow than the other two fields. However, because of substantial freshwater runoff, salinities are low, ranging from 3.5 to 6.9 ‰ in surface waters and 3.5 to 9.2 ‰ in bottom waters in the fall. No salinity data are available for the spring. Water depth is similar to that in the other two fields, ranging from 1.0 to 2.3 m. The dominant sediment type is mud containing 0.67% to 23% TOC.

The estuarine fauna and flora of the field are similar to those at Delacroix Island and Bay de Chene. Oysters are cultivated on several local leases. Commercial and recreational harvesting of crustaceans and fish is common in the area.

Produced water discharges from the Four Isle Dome Central Production Facility decreased from an average of 645,000 L/day (4,057 bbl/day) in 1989 to 135,500 L/day (852 bbl/day) in 1990 to 1992. The produced water discharge rate at the time of the Pre-termination Survey is not available. The produced water discharged from the facility had a salinity of 152 ‰, about 30 times higher than the salinity of the receiving waters.

10.3.2 Environmental Risk of Metals in Produced Water

Metals in Produced Water

Two samples of produced water from each discharge site were collected during the Pre-termination Surveys and analyzed for metals. Concentrations of metals and chlorine in the three produced waters are variable (**Table 10.3**).

Table 10.3. Mean concentrations of metals in produced waters from three discharges to coastal waters of Louisiana and in ambient water from the northwest Gulf of Mexico. Concentrations are μg/L (parts per billion) except for chloride and salinity. Values for ambient water from J. Trefry, 1996, personal communication.

Metal	Delacroix Island	Bay de Chene	Four Isle Dome	Ambient Water
Chloride (g/kg)	86	85.3	97	—
Salinity (g/kg)	135	135	154	1.2 - 23
Arsenic	0.06	0.05	3.9	0.5 - 1.5
Barium	126,000	120,000	145,000	10 - 90
Cadmium	0.3	0.2	3.3	0.02
Chromium	0.2	0.2	<0.1	0.01 - 0.03
Copper	<0.2	0.5	2.1	0.2 - 1.7
Iron	19,000	18,000	30,000	0.05 - 1.5
Mercury	0.03	<0.01	0.05	<0.01 - 0.04
Manganese	700	900	6,000	0.25 - 1.1
Molybdenum	0.5	0.4	0.8	3 - 10
Nickel	1.5	2.2	<1.2	0.2 - 1.6
Lead	0.8	0.6	3.6	0.02 - 0.05
Vanadium	<1.2	<1.2	<1.2	1.1 - 1.7
Zinc	42	9	1,500	2.8 - 9.1

Chloride concentrations range from 85.3 to 97 g/kg, corresponding to salinities of approximately 135 to 154 ‰, based on a salinity/chlorinity ratio of 1.570 (see **Chapter 7**). These chlorinities and salinities are 30 times or more higher than the salinity of the ambient brackish water at the three discharge sites. Because the produced water is hypersaline in comparison to the receiving waters, the produced water plume tends to sink to the bottom following discharge. The hypersaline water may penetrate surface layers of bottom sediments near the discharges and persist there for the duration of discharge (St. Pé, 1990). In this investigation, the chlorine concentrations in the interstitial water of surficial sediments near the produced water discharges at the time of the Pre-termination Surveys were 43.2, 7.3, and 3.6 g/kg at Delacroix Island, Bay de Chene, and Four Isle Dome, respectively. Only the chloride concentration in surface sediment (0 to 5 cm) interstitial water at Delacroix Island was substantially elevated compared to the chloride concentrations at deeper levels in the sediment core. A chlorinity of 43.2 g/kg is equivalent to a salinity of 67.8 ‰, which is sufficiently high that it would be toxic to benthic organisms that might attempt to settle in sediments near the discharge. In addition, most produced waters have ratios of major ions different than the ratios in seawater. Altered ion ratios are suspected of contributing to the toxicity of some produced waters to marine and freshwater organisms.

Concentrations of arsenic, cadmium, copper, mercury, nickel, and vanadium in the three produced waters are comparable to or only slightly higher (less than 10-fold) than their concentrations in ambient seawater from coastal and offshore waters of the northwestern Gulf of Mexico (**Table 10.3**). The concentrations of these metals in Gulf of Mexico seawater is comparable to concentrations in other marine and coastal waters throughout the world (Neff, 1997). Concentrations of molybdenum in the produced waters are lower than those in ambient brackish water. Concentrations of lead and cadmium in one produced water and zinc in two produced waters are enriched (more than 10-fold) compared to typical concentrations in ambient brackish water and seawater. These three metals are present at elevated concentrations in the produced water from Four Isle Dome. Concentrations of barium, iron, and manganese are substantially enriched (more than 1,000-fold) in produced water compared to ambient water. Concentrations of all these metals in the three produced waters are in the same range as their concentrations in produced water from produced water discharges sampled from platforms offshore Louisiana and Texas (Continental Shelf Associates, Inc., 1997).

Dilution of Metals in Receiving Waters

Produced water is diluted rapidly following discharge to open coastal and oceanic waters (Brandsma and Smith, 1996). A 100-fold dilution of the chemicals in produced water can be expected within a few meters from discharges to open well-mixed waters. In less well-mixed shallow coastal waters, dilution is less rapid (Rabalais et al., 1991, 1992). The rate of dilution of produced water that is discharged to shallow, poorly mixed coastal waters depends primarily on the rate of discharge and differences in density (a function of salinity and temperature) of the produced water and the ambient receiving waters. High-volume saline water discharges to coastal waterways and canals monitored by Rabalais et al. (1991, 1992) generally were diluted by about 100-fold within 100 m or less of the discharges. The three discharges monitored here are considered relatively small (850 to 3,800 bbl/day) and probably were diluted by 100-fold within a few tens of meters of the discharges.

The three metals with the greatest enrichment in produced water, barium, iron, and manganese, all have a strong tendency to precipitate as barium sulfate and various oxyhydroxides of iron and manganese upon discharge and dilution of produced water with ambient brackish water and seawater. Iron and manganese oxyhydroxides, because of their small particle size and high charge densities, adsorb or coprecipitate dissolved metals (Schoer, 1985). Several metals, including in particular radium isotopes, may coprecipitate with barium.

The degree and speed of barium precipitation that occurs depends on the sulfate concentration of the ambient water. Brackish waters typical of the three discharge sites have lower sulfate concentrations than seawater, and barium precipitation may be slower than it is when barium-rich produced water is mixed with ocean water (Neff and Sauer, 1995). However, the barium does precipitate in these brackish waters, leaving in apparent solution concentrations of barium that may be several times higher than those in ocean waters. The concentration of barium in brackish receiving water near a platform discharge to coastal waters of Louisiana monitored in the offshore component of this investigation, was 90 μg/L, about six times higher than the normal concentration of barium in full-strength seawater. Much of the elevated dissolved barium concentration in coastal brackish water influenced by the Mississippi River outflow is derived from desorption of barium from suspended particles during estuarine mixing (Chan and Hanor, 1982). Most of the desorbed barium precipitates as river water is diluted with seawater. The net effect of precipitation of barium, iron, and manganese is to decrease the concentrations of dissolved metals from produced water in the receiving waters much more rapidly than can be accounted for by dilution alone.

Because of the rapid dilution and precipitation of metals from produced water during mixing of produced water with ambient water, estuarine organisms and ecosystems near produced water discharges to shallow coastal waterways are unlikely to encounter a dissolve, bioavailable metal concentration higher than that equivalent to the metal concentration in a 100-fold dilution of the produced water.

Environmental Risk of Metals in Produced Water

No measurements were made of metal concentrations in the produced water plume or in ambient water near the three produced water discharges before termination of discharges. Therefore, concentrations of metals in a 100-fold dilution will be used as the upper limit exposure concentrations of metals to aquatic organisms living near the three discharges before termination of the discharges. The concentrations of most of the metals in a 100-fold dilution of the three produced waters are lower than expected concentrations in clean ambient brackish waters (**Table 10.3**). The only exceptions are barium, iron, manganese, cadmium, and zinc (the last two at one site) (**Table 10.4**). The lead concentration in a 100-fold dilution of produced water from the Four Isle Dome facility approaches the expected concentration in ambient water. The actual concentrations of barium, iron, and manganese, and possibly also cadmium, lead, and zinc, in diluted produced water are lower than the estimated concentrations because of precipitation, as discussed above.

Table 10.4. Estimated concentrations of selected metals in a 100-fold dilution of produced waters from three production facilities in coastal waters of Louisiana, compared to expected concentrations in clean ambient brackish waters. Enrichments are given in parentheses. Concentrations are μg/L. Chronic criteria from Federal Register, Volume 60, Number 86 (Thursday, May 4, 1995), page 22229.

Metal	Delacroix Island	Bay de Chene	Four Isle Dome	Ambient Water
Barium	1,260 (84)	1,200 (80)	1,450 (97)	15
Cadmium	0.003 (0.15)	0.002 (0.1)	0.03 (1.5)	0.02
Iron	190 (190)	180 (180)	300 (300)	1.0
Manganese	7 (9)	9 (12)	60 (80)	0.75
Lead	0.008 (0.2)	0.006 (0.15)	0.036 (0.9)	0.04
Zinc	0.42 (0.09)	0.09 (0.02)	15 (3.3)	4.5

If it is assumed that all the metals were present before termination of produced water discharge in solution in ambient water near the produced water discharges at concentrations near their concentrations in a 100-fold dilution of the produced waters, only barium would be present at a concentration in excess of its freshwater quality criterion value of 1,000 μg/L (the drinking water criterion) (**Table 10.5**). Freshwater criteria, when available, were used in **Table 10.5** because the receiving waters at some sites were mostly fresh. The federal standard for barium concentration in effluents destined for discharge to fresh waters is 100,000 μg/L (Jackson et al., 1990). There are no water quality criteria for barium for protection of freshwater or marine life. As discussed above, barium probably precipitates as barite shortly after discharge of barium-rich produced water to brackish receiving waters. Barite is generally considered toxicologically inert (Neff and Sauer, 1995). Therefore, it is probable that the barium from produced water was producing little or no adverse biological effects in water column organisms near the three produced water discharge before termination of the discharges. Some marine invertebrate larvae appear to be sensitive to dissolved or organically complexed barium (Spangenberg and Cherr, 1996). These animals, if they were present for an extended period of time in ambient water near the discharges, could be adversely affected by the barium from the produced water. However, the most sensitive species are marine and would not be present in low salinity receiving waters where barium might persist in solution long enough to cause adverse effects. Iron and manganese also will precipitate <u>rapidly</u> in oxygenated receiving waters of any salinity and so are not likely to be present in potentially toxic forms.

The other metals that were present at elevated (relative to ambient water) concentrations in the produced water from the three produced water discharges were not present in a 100-fold dilution of the produced water at concentrations in excess of the most conservative water quality criteria (**Table 10.5**). Estimated toxic units for cadmium, iron, manganese, lead, and zinc in the diluted produced water range from <0.01 to 0.6. Given that the estimated concentration ranges are upper-bound estimates, because they do not consider precipitation, it is highly likely that these metals were not causing harm to water column aquatic organisms and ecosystems near the produced water discharges before termination of the discharges. All the other target metals in produced water were present in a 100-fold dilution of the produced water at estimated concentrations below expected ambient water concentrations and, therefore, are not likely to have caused any effects on local biota.

After termination of the produced water discharges, metal concentrations in the ambient water near the former discharges would be expected to be at concentrations similar to those at the reference stations. Quite frequently, surficial sediments near produced water discharges to shallow waters become enriched in organic matter, including petroleum hydrocarbons. Biodegradation of these organic chemicals may cause the local sediments to become anoxic (Kingston, 1992). Following termination of a produced water discharge, the organic contamination may decrease, allowing the sediments to become oxidized. Changes in the redox potential of surficial sediments may allow for the release of metals bound to sulfides and organic matter to the overlying water column. This may result in an increase in the concentrations of metals in the overlying water column (Salomons et al., 1987). This efflux of metals from sediments usually is of short duration and the resulting metal concentrations in the overlying water column are unlikely to exceed water column concentrations that occurred during produced water discharge.

Table 10.5. Comparison of the estimated concentrations of selected metals in 100-fold dilutions of produced water from three production facilities with the most conservative available water quality criterion values. Toxic units (ambient water concentration/criterion concentration) also are given for each metal. A toxic units value of 1.0 or greater indicates a potential for toxicity to aquatic organisms if all the metal is in a dissolved, bioavailable form. Concentrations are μg/L.

Metal	Estimated Concentration Range	Water Quality Criterion	Toxic Units
Barium	1,200 - 1,450	1,000	1.2 - 1.45
Cadmium	0.003 - 0.03	1.1	<0.01 - 0.03
Iron	180 - 300	1,000	0.18 - 0.3
Manganese	7 - 60	100	0.07 - 0.6
Lead	0.006 - 0.036	8.1	<0.01
Zinc	0.09 - 15	81	<0.01 - 0.19

10.3.3 Environmental Risk of Aromatic Hydrocarbons in Produced Water

Aromatic Hydrocarbons in Produced Water

Produced water destined for disposal in coastal and marine waters is treated at the production facility or at a separate treatment facility to remove petroleum hydrocarbons to a concentration below current regulatory requirements of 42 mg/L daily maximum and monthly average of 29 mg/L (Neff, 1997). Most modern treatment facilities can meet these regulatory requirements. However, produced water treatment systems remove mainly dispersed oil droplets from the water, leaving behind some hydrocarbons in solution or colloidal suspension in the treated produced water. Hydrocarbon solubility decreases with increasing molecular weight. Therefore, the most abundant hydrocarbons in properly treated produced water are low molecular weight saturated and aromatic hydrocarbons. High molecular weight resins, asphaltines, aliphatic hydrocarbons, and PAHs rarely are present at higher than trace concentrations.

The organic compounds of greatest concern in treated produced water destined for disposal in coastal and marine waters, because of their concentrations and toxicity, are aromatic hydrocarbons (Neff, 1987). Monocyclic aromatic hydrocarbons, including benzene and several alkylated benzenes, often are the most abundant hydrocarbons in produced water (Neff, 1997). Concentrations tend to decrease with increasing alkylation. PAHs also are present in most treated produced waters, but at concentrations much lower than the monocyclic aromatic hydrocarbons. The most abundant PAHs in produced water are the more soluble two- and three-ring aromatics and their alkylated homologs. Higher molecular weigh four- and higher-ring PAHs rarely are present at greater than trace (low parts per billion) concentrations. Upon discharge of produced water to the ocean, these aromatic hydrocarbons are diluted rapidly in the receiving waters. Dilution is enhanced by evaporation of the less alkylated monocyclic aromatic hydrocarbons and naphthalene, photooxidation and biodegradation of the higher molecular weight PAHs, and sorption to suspended particles and deposition of the PAHs (Neff, 1990). The concentrations, dilution, and toxicity of aromatic hydrocarbons from produced water are discussed below.

Produced water from the three facilities contained monocyclic aromatic hydrocarbons, PAHs, and total petroleum hydrocarbons at concentrations typical of produced waters from throughout the Gulf of Mexico (**Table 10.6**). Concentrations of monocyclic aromatic hydrocarbons, consisting primarily of benzene, toluene and total xylenes, ranged from 1,291 to 5,386 μg/L. Concentrations of total PAHs ranged from 24 to 520 μg/L. Total petroleum hydrocarbon concentrations in the three produced waters ranged from 210 to 21,000 μg/L. Thus, all the samples contained total petroleum hydrocarbon concentrations below the regulatory limit of 29,000 μg/L monthly average.

As is usual for treated produced water, the dominant PAHs in the three produced waters were naphthalene and mono- and di-methylnaphthalenes (see **Chapter 8**). Produced water from Bay de Chene also contained some fluorene, phenanthrene, and their alkyl homologues. Concentrations of four- through six-ring PAHs in the three produced waters were either below the MDLs (0.005 to 0.020 μg/L per analyte) or were just above the detection limits. The presence of alkanes with chain lengths greater than about 20 carbons in some of the produced water samples indicates that small amounts of particulate oil were present, possibly accounting for the traces of high molecular weight PAHs detected.

Table 10.6. Concentration ranges of volatile aromatic hydrocarbons, total polycyclic aromatic hydrocarbons (PAHs), and total petroleum hydrocarbons in produced water samples from three production facilities in coastal waters of Louisiana. Concentrations are μg/L.

Hydrocarbon	Delacroix Island	Bay de Chene	Four Isle Dome
Benzene	230 - 470	590 - 630	2,500 - 2,700
Toluene	610 - 789	550 - 560	1,500 - 1,600
Ethylbenzene	41 - 48	<0.5 - 41	100
Total Xylenes	410 - 430	360	750 - 780
C_3-Benzenes	NA	NA	200 - 220
C_4-Benzenes	NA	NA	36 - 42
Total Monocylic Aromatic Hydrocarbons	1,291 - 1,728	1,554 - 1,602	5,142 - 5,386
Total PAHs	24 - 28	350 - 520	410 - 420
Total Petroleum Hydrocarbons	210 - 370	13,000 - 19,000	18,000 - 21,000

NA = Not analyzed.

Dilution of Aromatic Hydrocarbons in Ambient Water

Monocyclic aromatic hydrocarbons and low molecular weight PAHs are diluted very rapidly following discharge of treated produced water to receiving waters. Monocyclic aromatic hydrocarbons, such as benzene, toluene, ethylbenzene, and xylenes (BTEX) are lost from receiving waters most rapidly, primarily through evaporation. Gschwend et al. (1982) estimated that under moderately calm conditions when BTEX concentrations in surface water are higher than those in the overlying atmosphere, the residence time of BTEX in the aqueous phase is approximately two days. Under more turbulent conditions with good vertical mixing, characteristic of offshore waters, residence time for BTEX in the water column may be as low as a few hours (Brooks et al., 1984).

Brooks et al. (1980) reported that concentrations of total gaseous and volatile hydrocarbons, including BTEX (75% of the total) decrease from 22,000 μg/L in the produced water effluent from the Buccaneer Platform off Galveston, TX, to 65 μg/L at the air/water interface below the outfall, to less than 2 μg/L in surface waters 50 m down-current from the discharge. This represents an 11,000-fold dilution of BTEX in the receiving water environment within 50 m of the discharge. In the Bass Strait off southeastern Australia, BTEX in a high-volume (69,000 bbl/day $\approx$ 1 million L/d) produced water discharge from an offshore platform is diluted from 6,410 μg/L in the effluent to 0.43 μg/L (14,900-fold) 20 m from the discharge (Terrens and Tait, 1996). This very rapid loss of BTEX in the receiving water probably is caused by the high temperature of the discharged produced water (95°C), which increases rates of dispersion and evaporation of the aromatic hydrocarbons.

PAHs in produced water discharged to ocean waters usually is diluted by more than 100-fold within a few meters of the discharge. For example, individual PAHs in produced water discharged from the Kingfish B platform to the Bass Strait, Australia, were diluted 2,000- to 18,000-fold at 20 m down-current of the produced water discharge (Terrens and Tait, 1996). The dilution rates of the individual PAHs were inversely related to their molecular weights. Brandsma and Smith (1996) predicted dilutions of several hundred-fold at 100 m from high-volume produced water discharges based on the Offshore Operators Committee model. Although dilution is not as rapid for produced water discharged to shallow, poorly mixed coastal waters, low-volume discharges usually are diluted by 100-fold or more within several tens of meters of the discharge. Therefore, it is unlikely that any marine organisms, except possibly some biofouling organisms on legs of the platform near the produced water discharge point or benthic organisms directly under the discharge, experience chronic exposure to concentrations of PAHs greater than those in a 100-fold dilution of the produced water. The 100-fold dilution of produced water was used in this risk assessment as an upper bound estimate of the exposure of marine organisms to BTEX and PAHs from produced water.

Environmental Risk of Aromatic Hydrocarbons in Produced Water

Concentrations of individual monocyclic aromatic hydrocarbons and total PAHs in 100-fold dilutions of the three produced waters are low (**Table 10.7**). None of the hydrocarbons approach the chronic marine water quality criterion values. Toxic units for individual aromatic hydrocarbons and total PAHs are in the range of <0.01 to 0.04 (benzene in produced water from Four Isle Dome). The total toxic units of all the aromatic hydrocarbons in the 100-fold dilutions of the produced waters ranges from <0.06 to 0.09.

Table 10.7. Comparison of the estimated concentrations of individual monocyclic aromatic hydrocarbons and total polycyclic aromatic hydrocarbons (PAHs) in 100-fold dilutions of produced water from three production facilities with marine chronic water quality criteria. Toxic units (ambient water concentration/criterion concentration) also are given. A toxic unit value of 1.0 or greater indicates a potential for toxicity to aquatic organisms. Concentrations in μg/L.

Aromatic Hydrocarbon	Estimated Concentration Range	Water Quality Criterion	Toxic Units
Benzene	2.3 - 27	700	<0.01 - 0.04
Toluene	5.5 - 16	5,000	<0.01
Ethylbenzene	<0.005 - 1.0	43	<0.01 - 0.02
Xylenes	3.6 - 7.8	600	<0.01 - 0.01
C_3-Benzenes	2.0 - 2.2	393	<0.01
C_4-Benzenes	0.36 - 0.42	173	<0.01
Total PAHs	0.24 - 5.2	300	<0.01 - 0.02
Total Toxic Units			<0.06 - 0.09

Even a 10-fold dilution of these three produced waters would not be toxic to aquatic organisms in the vicinity of the produced water discharges. Therefore, the aromatic hydrocarbons in produced water from the three production facilities did not pose a risk to local water column organisms and ecosystems before the produced water discharges were terminated.

Following termination of the discharges, the concentrations of petroleum hydrocarbons in the water column near the former discharges probably dropped rapidly to essentially background levels. However, there are other sources of aromatic hydrocarbons in the local coastal environment (runoff from land and the Mississippi River, aerial fallout, creosote from platform structures, and other releases from the platforms and vessels in the vicinity). Thus, hydrocarbons will not disappear completely from the local waterways following termination of produced water discharges.

10.3.4 Environmental Risk of Metals in Sediments

Concentrations of Metals in Sediments

A large fraction of the metals entering the ocean from natural and anthropogenic sources precipitates or becomes bound to suspended particles and colloidal and dissolved organic matter (Salomons and Förstner, 1984). These precipitated, adsorbed, or complexed metals tend to be deposited in more or less labile forms in surficial sediments. The sediment particles themselves may contain high concentrations of some metals. The metals that are part of the structure of the sediment particles are not readily mobilized and usually are termed residual metals.

Adsorbed, precipitated, and complexed metals may be mobilized under some conditions. In anoxic marine sediments, most of which contain high concentrations of sulfur, sulfides and to a lesser extent organic matter control metal speciation and the forms of metals present. Sulfur concentrations in some freshwater and estuarine sediments are low enough that speciation of metals in anoxic layers is controlled by other chemicals, particularly organic matter. In oxidized, fine-grained marine sediments, hydrous oxides of iron, aluminum, and manganese, clay minerals, carbonates, and organic matter all compete for binding of metals (Luoma and Bryan, 1981; Louma and Davis, 1983). Metals adsorbed to iron and manganese oxide phases, sediment organic matter, or present as solid sulfide salts may be released from the solid phase and be mixed into the overlying water column, particularly during periods of redox potential changes (up or down) in the sediments. Thus, marine sediments are not only a sink for metals, but also a source of dissolved, bioavailable metals in the overlying water column (Salomons et al., 1987).

The chemical species, complexes, adsorbed, and solid forms in which different metals occur in marine and estuarine sediments have a profound effect on their bioavailability and toxicity to marine organisms (Nelson and Donkin, 1985). Only bioavailable metals (dissolved or sometimes organically bound) in sediments are toxic to marine organisms if concentrations are high enough.

Concentrations of different metals in surficial sediments vary widely depending on the geochemistry of the sediments and proximity to natural and anthropogenic sources. All marine sediments contain measureable concentrations of most metals. Therefore, it often is difficult to determine with any certainty whether a sediment is contaminated with metals or reflects the natural concentrations. Normalization to aluminum (a major natural component of clay minerals) is used sometimes to identify the presence of some metals from anthropogenic sources (Windom et al., 1989; Trefry et al., 1996. See also **Chapter 7**). Aluminum normalization corrects for differences among sediments in grain size and mineralogy.

Trefry et al. (**Chapter 7**) concluded, based on aluminum normalization, that concentrations of arsenic, cadmium, chromium, copper, iron, manganese, nickel, lead, vanadium, and zinc in sediments near the three production facilities are at or near natural levels. On the other hand, concentrations of barium are in excess of expected values at most locations near the production facilities, probably as a result of discharges of drilling fluids and produced water from the platforms. Arsenic and mercury concentrations were elevated above expected concentrations in some sediments near the facilities. Concentrations of cadmium, chromium, mercury, lead, and zinc in sediments near a former fuel dock and pipe storage facility at the Bay de Chene facility were elevated. The metals probably were derived from the pipe storage facility and not from produced water.

Much of the metals in sediments is tightly bound to particles and are not readily bioavailable. Elevated concentrations of one or more metals in surficial sediments is not necessarily an indication that the local benthic plants and animals are being adversely affected.

Concentrations of metals in surface sediments at different distances from the three production facilities varied widely over spatial and temporal scales. There were not large differences in sediment metal concentrations among the three field surveys (**Table 10.8** through **10.10**). Metal concentrations in sediments near the two discharges for which post-termination data are available did not decrease substantially after termination of the discharges. As discussed by Trefry et al. (**Chapter 7**), most of the metals were present in sediments near the platforms at expected concentrations. The only metal that was consistently present at substantially elevated concentrations in sediments at all distances from the three discharges was barium. Barium undoubtedly was derived from produced water and water-base drilling mud discharges (both rich in barium). Somewhat elevated concentrations of a few other metals (arsenic and mercury) were observed at a few locations on one or more surveys. There is not evidence of significant accumulation of any metals other than barium in sediments from produced water.

Environmental Risk of Metals in Sediments

The sediment metals data summarized in **Tables 10.8** through **10.10** can be used to estimate the risk of sediment metals to benthic organisms living near the three production facilities. The measured concentrations can be compared to sediment threshold concentrations developed by Long et al. (1995) as indices of potentially toxic concentrations of chemical contaminants in sediments (**Table 10.11**).

A concerted effort has been made in the United States in recent years to develop sediment quality criteria to protect freshwater and marine life from contaminants associated with sediments (e.g., Di Toro et al., 1991; Ankley et al., 1996). Much of the data on the association between concentrations of different chemical contaminants in marine and estuarine sediments and biological responses in bottom-living marine and estuarine organisms has been evaluated to produce sediment quality guidelines that provide some indication of the concentrations of contaminants in sediments that may be associated with adverse biological effects (Long and

Table 10.8. Concentration ranges of potentially toxic metals in sediments near the Delacroix Island production facility before and after cessation of produced water discharges. Concentrations are μg/g dry weight.

Metal	Pre-termination Survey	First Post-termination Survey	Second Post-termination Survey
Arsenic	3.1 - 11.2	3.6 - 6.7	2.0 - 5.6
Barium	278 - 2,850	53.6 - 2,490	473 - 4,290
Cadmium	0.04 - 0.92	0.17 - 0.41	0.16 - 0.42
Chromium	28.9 - 56.1	27.2 - 59.6	34.7 - 61.9
Copper	8.7 - 23.4	8.3 - 19.6	8.4 - 22.4
Lead	4.1 - 27.4	6.2 - 22.9	11.9 - 24.1
Mercury	0.023 - 0.075	0.022 - 0.054	0.022 - 0.054
Molybdenum	0.5 - 2.2	0.6 - 4.9	0.5 - 1.6
Nickel	14.1 - 35.6	16.9 - 30.7	14.5 - 34.9
Vanadium	35.6 - 101	47.6 - 115	40.4 - 101
Zinc	30.0 - 101	27.0 - 82.5	41.7 - 95.6

Table 10.9. Concentration ranges of potentially toxic metals in sediments near the Bay de Chene production facility before and after cessation of produced water discharges. Concentrations are μg/g dry weight.

Metal	Pre-termination Survey	First Post-termination Survey	Second Post-termination Survey
Arsenic	4.6 - 13.9	4.5 - 11.4	7.6 - 13.1
Barium	466 - 1,670	143 - 3,740	41 - 2,170
Cadmium	0.20 - 0.55	0.22 - 1.0	0.27 - 0.81
Chromium	32.2 - 66.7	41.5 - 73.8	40.8 - 60.8
Copper	10.8 - 30.1	11.0 - 50.7	13.4 - 36.1
Lead	12.1 - 35.7	14.5 - 68.0	4.8 - 40.5
Mercury	0.029 - 0.423	0.027 - 0.462	0.036 - 0.314
Molybdenum	0.9 - 4.0	0.8 - 2.8	0.7 - 2.3
Nickel	14.0 - 32.1	14.1 - 33.6	16.8 - 29.5
Vanadium	53.4 - 115	58.0 - 111	77.0 - 132
Zinc	51.8 - 159	56.3 - 362	67.1 - 304

Table 10.10. Concentration ranges of potentially toxic metals in sediments near the Four Isle Dome production facility before temination of produced water discharge. Concentrations are μg/g dry weight.

Metal	Pre-termination Survey
Arsenic	4.5 - 7.2
Barium	78.6 - 3,880
Cadmium	0.28 - 0.54
Chromium	53.6 - 69.9
Copper	17.9 - 27.3
Lead	10.8 - 25.7
Mercury	0.045 - 0.139
Molybdenum	1.0 - 2.8
Nickel	24.7 - 35.8
Vanadium	84.1 - 161
Zinc	75.2 - 192

Table 10.11. Proposed sediment quality guidelines ($\mu g/g$ dry weight) and "high" concentrations (geometric mean plus one standard deviation) from the National Status and Trends database for metals in marine sediments. The effects range-low (ERL) is the lower 10th percentile effects concentration and the effects range-median (ERM) is the 50th percentile effects concentration. (From: Long et al., 1995; Daskalakis and O'Connor, 1995).

Chemical	ERL	ERM	High Concentration
Arsenic	8.2	70	13
Cadmium	1.2	9.6	0.54
Chromium	81	370	125
Copper	34	270	42
Lead	46.7	218	45
Mercury	0.15	0.71	0.22
Nickel	20.9	51.6	42
Zinc	150	410	135

Morgan, 1990; Long, 1992; Long et al., 1995). Two guideline values are generated from this analysis, an effects range-low (ERL) and an effects range-median (ERM). The ERL value represents the lower 10th percentile response concentration and the ERM value represents the median (50th percentile) response concentration (50% of recorded responses to the chemical are at lower concentrations and 50% are at higher concentrations). The two guideline values define concentrations of a particular chemical in sediments that are rarely (below the ERL), occasionally (between the ERL and ERM values), or frequently (above the ERM value) associated with adverse biological effects. Because most marine sediments that exhibit toxicity to benthic marine organisms contain several metals and potentially toxic organic chemicals at elevated concentrations, it often is difficult to identify the fraction of the total toxicity that can be attributed to a particular metal. Thus, the ERL and ERM values are conservative estimates of the toxicity of individual chemicals in sediments. Therefore, the ERM values (**Table 10.11**) were used in the present investigation as screening values for comparison with metal concentrations measured in sediments near the three sites.

Marine sediment screening concentrations are not available for aluminum, barium, calcium, iron, manganese, molybdenum, and vanadium. All but molybdenum and vanadium are abundant natural constituents of marine sediments and are unlikely to be present in solution in seawater or sediment interstitial water at toxic concentrations. Aluminum and calcium are matrix components of some of the sediment particles. Iron and manganese are present in oxidized sediment layers almost exclusively as various insoluble oxyhydroxides. In reduced sediment layers, the oxyhydroxides may dissolve, but much of the iron and manganese precipitates as sulfides. These reactions keep concentrations of dissolved, bioavailable iron and manganese low in sediment interstitial water (Schimmield and Pedersen, 1990; Thamdrup et al., 1994). Barium is present in sediments primarily as highly insoluble barite or as inclusions in clay particles (Neff and Sauer, 1995).

Daskalakis and O'Connor (1995) examined chemical residue data for large numbers of marine sediment samples collected as part of the National Status and Trends Program and several other monitoring programs in coastal marine environments of the U.S. They identified a "high" concentration of contaminants in sediments as the geometric mean plus one standard deviation of all National Status and Trend site means. "High" concentrations are included in **Table 10.11** for comparison.

Concentrations of several metals in sediments exceeded the National Status and Trends "high" concentrations at one or more stations or times. Most exceedences were in sediments near the Bay de Chene facility. One or more sediment samples at Bay de Chene contained elevated concentrations of arsenic, cadmium, copper, lead, mercury, or zinc. As discussed above, most of these elevated metal concentrations were in sediments near a former fuel and pipe storage facility in the Bay de Chene field and probably were not derived from produced water discharges.

Sediments collected at several platform and reference stations around the Delacroix Island production facility contained metal concentrations fairly typical of nearshore fine-grained sediments in the northwestern Gulf of Mexico. None of the metals was present in the bulk surficial sediments at concentrations in excess of their respective ERM values (**Table 10.12**). The highest values for toxic units (concentration in sediments/ERM value) were for nickel and zinc collected on both the Pre-termination and Post-termination Surveys.

Table 10.12. Estimated ranges of toxic units (concentration in sediment/effects range-median [ERM] value) of several metals in sediments from the vicinity of the Delacroix Island production facility before and after termination of produced water discharge. Concentrations are μg/g dry weight.

Metal	Pre-termination Concentration	Toxic Units	Post-termination Concentration	Toxic Units
Arsenic	3.1 - 11.2	0.04 - 0.16	2.0 - 6.7	0.03 - 0.10
Cadmium	0.04 - 0.92	<0.01 - 0.10	0.16 - 0.42	0.02 - 0.04
Chromium	28.9 - 56.1	0.08 - 0.15	27.2 - 61.9	0.07 - 0.17
Copper	8.7 - 23.4	0.03 - 0.09	8.3 - 22.4	0.03 - 0.08
Lead	4.1 - 27.4	0.02 - 0.13	6.2 - 24.1	0.03 - 0.11
Mercury	0.023 - 0.075	0.03 - 0.11	0.022 - 0.054	0.03 - 0.08
Molybdenum	0.5 - 2.2	NV	0.5 - 4.9	NV
Nickel	14.1 - 35.6	0.27 - 0.69	14.5 - 34.9	0.28 - 0.68
Vanadium	35.6 - 101	NV	47.6 - 115	NV
Zinc	30.0 - 101	0.07 - 0.25	27.0 - 95.6	0.07 - 0.23

NV = No ERM value available.

Highest concentrations of nickel and zinc at the time of the Pre-termination Survey were in sediments from the discharge site. After termination of the produced water discharge, the highest concentrations of nickel and zinc were in sediments from reference and transect stations. Nickel concentrations in produced water from Delacroix Island were not significantly higher than expected concentrations in ambient waters. Therefore, the source of nickel in the sediments near the discharge are unclear. Zinc was abundant in the produced water from the facility, so some of the zinc in the sediments may have come from produced water. Zinc in produced water may come from microcrystalline particles of zinc sulfide (spaeralite) or from metal chips from galvanized pipes, as well as from dissolved zinc.

Concentrations of all the metals evaluated in sediments from the vicinity of the Delacroix Island facility were below levels considered potentially toxic to benthic organisms. There was little or no change in toxic units for the different metals between the Pre-termination Survey and the two Post-termination Surveys. Most of the metals probably were natural and were not derived from the produced water discharge. Therefore, it is likely that the metals present in the sediments were not posing a significant risk to the local benthic communities.

Concentrations of most metals in sediments from the vicinity of the Bay de Chene facility were slightly higher than those in sediments from the vicinity of the Delacroix Island facility. However, none of the metals evaluated were present in sediments near the produced water discharge at a concentration greater than the ERM values (**Table 10.13**). Metal concentrations and the corresponding toxic units were not notably different for sediments collected before and after termination of the produced water discharge. Highest values for toxic units were for nickel, mercury, and zinc. Before termination of the produced water discharge, the highest mercury concentration was in sediments from the discharge site. Zinc and nickel concentrations in sediments collected during this survey were highest along the northeast transect. After termination of produced water discharge, most high concentrations of the three metals were in sediments from the northeast transect near the former fuel dock and pipe storage facility.

Toxic units for metals are not necessarily additive. However, it is possible that the presence of several metals in a sediment at concentrations below, but approaching their respective ERM values, could be toxic to local benthic organisms. These sediments contained toxic units of about 0.6 for nickel and mercury, and toxic units of 0.4 to 0.9 for zinc. Thus, sediments in the vicinity of the former fuel dock and pipe storage facility pose a moderate risk to the local benthic infauna. Metal concentrations, particularly of mercury, in sediments from the discharge site before termination of the produced water discharge also may have posed a risk to sensitive species and life stages of benthic organisms. Sediments from all other stations in the vicinity of the Bay de Chene facility before and after termination of the produced water discharge did not contain concentrations of metals high enough to represent a risk to the local benthic communities.

Concentrations of metals in sediments near the Four Isle Dome facility before termination of its produced water discharge were roughly similar to those in sediments from the vicinity of the other two production facilities. As with the other facilities no metals were present in sediments at concentrations higher than their ERM values (**Table 10.14**). The highest metal concentrations and toxic unit values were for nickel and zinc.

Table 10.13. Estimated ranges of toxic units (concentration in sediment/effects range-median [ERM] value) of several metals in sediments from the vicinity of the Bay de Chene production facility before and after termination of produced water discharge. Concentrations are μg/g dry weight.

Metal	Pre-termination Concentration	Toxic Units	Post-termination Concentration	Toxic Units
Arsenic	4.6 - 13.9	0.07 - 0.20	4.5 - 13.1	0.06 - 0.19
Cadmium	0.20 - 0.55	0.02 - 0.06	0.22 - 1.0	0.02 - 0.10
Chromium	32.2 - 66.7	0.09 - 0.18	40.8 - 73.8	0.11 - 0.20
Copper	10.8 - 30.1	0.04 - 0.11	11.0 - 50.7	0.04 - 0.19
Lead	12.1 - 35.7	0.06 - 0.16	4.8 - 68.0	0.02 - 0.31
Mercury	0.029 - 0.423	0.04 - 0.60	0.027 - 0.462	0.04 - 0.65
Molybdenum	0.9 - 4.0	NV	0.7 - 2.8	NV
Nickel	14.0 - 32.1	0.27 - 0.62	14.1 - 33.6	0.27 - 0.65
Vanadium	53.4 - 115	NV	58.0 - 132	NV
Zinc	51.8 - 159	0.13 - 0.39	56.3 - 362	0.14 - 0.88

NV = No ERM value available.

Table 10.14. Estimated ranges of toxic units (concentration in sediment/effects range-median [ERM] value) of several metals in sediments from the vicinity of the Four Isle Dome production facility before termination of produced water discharge. Concentrations are μg/g dry weight.

Metal	Pre-termination Concentration	Toxic Units
Arsenic	4.5 - 7.2	0.06 - 0.10
Cadmium	0.28 - 0.54	0.03 - 0.06
Chromium	53.6 - 69.9	0.14 - 0.19
Copper	17.9 - 27.3	0.07 - 0.10
Lead	10.8 - 25.7	0.05 - 0.12
Mercury	0.045 - 0.139	0.06 - 0.20
Molybdenum	1.0 - 2.8	NV
Nickel	24.7 - 35.8	0.48 - 0.69
Vanadium	84.1 - 161	NV
Zinc	75.2 - 192	0.18 - 0.47

NV = No ERM available.

Nickel concentrations in sediments actually were quite uniform throughout the area (range of concentrations from 24.7 to 35.8 μg/g) and were not higher in sediments near the discharge. Some sediment samples from the other two facilities contained lower nickel concentrations, in the range of 14 to 20 μg/g. It is possible that nickel concentrations up to about 35 μg/g are normal for sediments from the area. Apparently clean marine sediments often contain nickel concentrations up to 50 μg/g and even as high as 350 μg/g (Bowen, 1979; Loring and Asmund, 1996). Nickel concentrations usually are positively correlated with clay content of sediments; much of the nickel may be associated with the aluminosilicate lattice of the clay particles (Loring, 1982). Thus, the nickel concentrations in sediments near production facilities in coastal Louisiana probably are natural and not derived from produced water discharges.

10.3.5 Environmental Risk of Metals in Sediment Interstitial Water

Concentrations of Metals in Interstitial Water

Concentrations of dissolved or colloidal metals in sediment interstitial water collected from the vicinity of the three production facilities before termination of the produced water discharges generally were higher than expected concentrations in the overlying water column (**Tables 10.15** and **10.16**). This is typical for most freshwater and marine sediments, particularly where redox cycling is taking place (Gaillard et al., 1986). In most cases, interstitial water from reference stations contained lower concentrations of metals than interstitial water from the two discharge stations. Concentrations of copper, molybdenum, nickel, vanadium, and zinc were higher in interstitial water from some reference stations than in interstitial water from the corresponding discharge site. Sulfate concentrations usually were higher in reference site interstitial water than in discharge site interstitial water, reflecting the higher concentrations of this anion in seawater than in most produced waters. The elevated concentrations of iron and manganese in interstitial water from most sediment sampling sites, particularly the discharge sites, indicates that the sediments probably were hypoxic. These metals are insoluble in interstitial waters of oxidized sediments and tend to precipitate as sulfides in anoxic sediments. The high concentrations of barium and chloride and low concentrations of sulfate in interstitial water from the discharge sites indicate that produced water was penetrating into the sediments and mixing with the sediment interstitial water. Despite this contamination of interstitial water with produced water before termination of the produced water discharges, there was little difference in concentrations of toxic metals in interstitial water from discharge and reference sites. Concentrations of most metals were lower in sediment interstitial water from Four Isle Dome than in interstitial water from the other two facilities.

Post-termination samples of interstitial water were collected and analyzed for metals only at the discharge and reference sites at the Delacroix Island facility. Concentrations of most metals in the interstitial waters decreased between the Pre-termination and the Second Post-termination Surveys (**Table 10.15**). In particular there was a several-fold decrease in concentrations of barium, iron, and manganese in interstitial water samples from the discharge site. Concentrations of a few metals, arsenic and vanadium, actually increased in sediment interstitial water between the Pre-termination and Second Post-termination Surveys. This could be due to changes in sediment redox potential and a redistribution of metals adsorbed to dissolved organic matter in the sediments.

Table 10.15. Concentration ranges of metals in interstitial water from sediments collected from the discharge and reference sites at the Delecroix Island production facility during the Pre-termination and Second Post-termination Surveys. Concentrations are μg/L unless noted otherwise.

Metal	Pre-termination		Second Post-termination	
	Discharge	Reference	Discharge	Reference
Chloride (g/L)	37.6 - 53.0	1.8 - 2.8	---	---
Sulfate (g/L)	0.11 - 0.14	0.19 - 0.28	---	---
Arsenic	4.7 - 8.5	0.9 - 5.8	6.4 - 10.5	5.6 - 10.0
Barium	42,000 - 74,000	270 - 600	300 - 340	230 - 290
Cadmium	<0.25 - 1.25	<0.1 - 0.1	<0.1	<0.1
Chromium	0.42 - 0.56	0.56 - 0.72	0.75 - 1.1	0.61 - 0.93
Copper	1.6 - 2.7	2.9 - 5.9	0.75 - 1.0	0.40 - 0.80
Iron	7,360 - 13,550	140 - 3,440	480 - 550	80 - 260
Lead	0.8 - 1.6	0.3 - 0.5	0.49 - 0.80	0.40 - 0.71
Mercury	0.028 - 0034	<0.01 - 0.023	<0.01 - 0.43	<0.01 - 0.01
Manganese	21,900 - 25,250	5,870 - 14,990	210 - 330	60 - 130
Molybdenum	2.0 - 2.3	1.4 - 6.8	2.4 - 3.3	1.2 - 5.3
Nickel	1.1 - 3.8	3.3 - 4.9	1.3 - 2.1	0.90 - 1.9
Vanadium	<0.25	1.7 - 2.4	2.4 - 4.4	5.6 - 11.6
Zinc	2.5 - 4.5	3.4 - 16.1	5.6 - 11.6	2.6 - 7.6

Table 10.16. Concentration ranges of metals in interstitial water from sediments collected from the discharge and reference sites at the Four Isle Dome and Bay de Chene production facilities before termination of produced water discharge. Concentrations are μg/L unless noted otherwise.

Metal	Four Isle Dome Discharge	Four Isle Dome Reference	Bay de Chene Discharge	Bay de Chene Reference
Chloride (g/L)	3.6	2.4 - 3.1	6.8 - 7.6	3.8 - 4.3
Sulfate (g/L)	---	---	0.21 - 0.33	0.39 - 0.56
Arsenic	<0.20 - 8.6	<0.2 - 6.9	25.7 - 44.6	3.3 - 5.6
Barium	<1.0 - 370	<1.0 - 160	1,400 - 1,940	160 - 1,550
Cadmium	<0.10	<0.10	<0.1 - 0.27	<0.1 - 0.23
Chromium	<0.10 - 1.81	<0.10 - 1.3	0.87 - 0.95	0.38 - 0.46
Copper	0.20 - 3.7	0.48 - 3.0	0.4 - 1.9	0.4 - 2.1
Iron	<1.0 - 21,800	9.0 - 160	9,130 - 23,460	90 - 1,330
Lead	<0.1 - 0.27	<0.10	0.2 - 3.9	0.2 - 1.1
Mercury	<0.01	<0.01	0.031 - 1.57	<0.01
Manganese	<1.0 - 7,200	1.0 - 1,700	7,660 - 11,100	1,400 - 4,750
Molybdenum	<0.10 - 2.8	<0.10 - 4.4	5.0 - 6.9	2.3 - 8.5
Nickel	<0.10 - 8.7	0.11 - 1.9	3.1 - 4.9	0.2 - 1.7
Vanadium	<0.10 - 16.3	<0.10 - 2.8	4.0 - 5.1	1.7 - 4.9
Zinc	0.17 - 4.2	0.89 - 4.8	5.5 - 7.9	4.6 - 9.4

Environmental Risk of Metals in Interstitial Water

If it is assumed that all or most of the metals in interstitial water are present in a dissolved, bioavailable form (probably not true), the measured concentrations can be compared to water quality criterion values to derive values for toxic units (**Table 10.16**). The resulting toxic units range from less than 0.01 to more than 200 (**Tables 10.17** and **10.18**). Toxic units for chromium, nickel, and zinc are below 1.0 for all interstitial water samples. A few sediment interstitial water samples contain arsenic, cadmium, copper, lead, or mercury at a concentration equivalent to about 1.0 toxic units. These metals probably do not represent a significant risk to benthic marine animals in the vicinity of the production facilities.

Concentrations of barium in interstitial water from the discharge site at the Delacroix Island facility, iron and manganese in interstitial water from all three discharge sites, and manganese in interstitial water from the reference sites before termination of produced water discharges are considerably higher than 1 toxic unit. One year after termination of produced water discharges at the Delacroix Island facility, concentrations and toxic units of most metals had decreased substantially (**Table 10.17**). Only manganese was present at a concentration equivalent to more than 1 toxic unit.

One year after termination of the produced water discharge from the Delacroix Island facility, toxic units for metals in interstitial water generally were similar to or lower than toxic units in interstitial water samples collected during the Pre-termination Survey (**Table 10.17**). Largest decreases were for barium, iron, and manganese. Only manganese was still present at concentrations equivalent to more than 1 toxic unit.

Iron and manganese are abundant natural components of marine and estuarine sediments and it is doubtful that they are toxic to benthic organisms in the forms in which they occur in the sediment interstitial water. They probably are present in the interstitial water as amorphous particles of iron and manganese oxide or complexed with dissolved or colloidal organic matter in the sediment interstitial water. However, the barium, if it is present in the interstitial water at the discharge sites in a soluble, bioavailable form could be toxic to benthic organisms, particularly larval stages (Spangenberg and Cherr, 1996). Highest interstitial water barium concentrations were in sediments from Delacroix Island where sulfate concentrations were lower (0.11 to 0.14 g/kg) than in interstitial water of sediments from the other discharge site (0.21 to 0.33 g/kg). Water containing 0.11 g/L of sulfate and 0.074 g/L (74,000 μg/L) of barium would be substantially supersaturated with respect to barium sulfate (solubility product, 1.05×10^{-10} M). Therefore, most of the barium in the interstitial water at the discharge sites probably is complexed with organic matter or present as microcrystals, and may not be toxic.

10.3.6 Environmental Risk of Aromatic Hydrocarbons in Sediments

Concentrations of Aromatic Hydrocarbons in Sediments

As expected, concentrations of VAHs, BTEX, were low in sediments near the three produced water discharges before termination of the discharges (**Chapter 8**). Most sediment samples near the discharges did not contain quantifiable concentrations of any BTEX compounds. None of the sediment samples from the discharge and reference sites at Bay de Chene contained BTEX. A sediment sample from the discharge at Four Isle Dome contained

Table 10.17. Water quality criteria and toxic units (concentration in water/water quality criterion value) for metals in interstitial water of sediments collected from discharge and reference sites at the Delacroix Island facility on the Pre-termination and Second Post-termination Surveys. Concentrations are μg/L.

Metal	Water Quality Criteria	Toxic Units			
		Pre-termination		Second Post-termination	
		Delacroix Island Discharge	Delacroix Island Reference	Delacroix Island Discharge	Delacroix Island Reference
Arsenic	36	0.13 - 0.24	0.02 - 0.16	0.18 - 0.29	0.16 - 0.28
Barium	1,000	42 - 74	0.27 - 0.60	0.30 - 0.34	0.23 - 0.29
Cadmium	1.1	<0.23 - 1.14	<0.09 - 0.09	<0.09	<0.09
Chromium	11	0.04 - 0.05	0.05 - 0.07	0.07 - 0.10	0.06 - 0.08
Copper	2.9	0.55 - 0.93	1.0 - 2.03	0.26 - 0.34	0.14 - 0.28
Iron	1,000	7.36 - 13.55	0.14 - 3.44	0.48 - 0.55	0.08 - 0.26
Lead	3.2	0.25 - 0.50	0.09 - 0.16	0.15 - 0.25	0.12 - 0.22
Mercury	1.11*	0.03	<0.01 - 0.02	<0.01 - 0.38	<0.01 - 0.01
Manganese	100	219 - 252	58.7 - 150	2.1 - 3.3	0.60 - 1.3
Molybdenum	NV	---	---	---	---
Nickel	8.3	0.13 - 0.46	0.40 - 0.59	0.16 - 0.25	0.11 - 0.23
Vanadium	NV	---	---	---	---
Zinc	86	0.03 - 0.05	0.04 - 0.19	0.07 - 0.13	0.03 - 0.09

* Water quality criterion for inorganic mercury; criterion for methylmercury is 0.025 μg/L.
NV = No water quality criterion value available.

Table 10.18. Water quality criteria and toxic units (concentration in water/water quality criterion value) for metals in interstitial water of sediments collected from discharge and reference sites at the Four Isle Dome and Bay de Chene facilities during the Pretermination Survey. Concentrations are μg/L.

Metal	Water Quality Criteria	Toxic Units			
		Four Isle Dome Discharge	Four Isle Dome Reference	Bay de Chene Discharge	Bay de Chene Reference
Arsenic	36	<0.01 - 0.24	<0.01 - 0.19	0.71 - 1.24	0.09 - 0.16
Barium	1,000	<0.01 - 0.37	<0.01 - 0.16	1.40 - 1.94	0.16 - 1.55
Cadmium	1.1	<0.09	<0.09	<0.09 - 0.25	<0.09 - 0.21
Chromium	11	<0.01 - 0.16	<0.01 - 0.12	0.08 - 0.09	0.03 - 0.04
Copper	2.9	0.07 - 1.3	0.16 - 1.0	0.14 - 0.66	0.14 - 0.72
Iron	1,000	<0.01 - 21.8	0.01 - 0.16	9.13 - 23.46	0.09 - 1.33
Lead	3.2	<0.03 - 0.08	<0.03	0.06 - 1.22	0.06 - 0.34
Mercury	1.11*	<0.01	<0.01	0.03 - 1.41	<0.01
Manganese	100	<0.01 - 72	<0.01 - 17	76.6 - 111	14.0 - 47.5
Molybdenum	NV	—	—	—	—
Nickel	8.3	<0.01 - 1.0	0.01 - 0.22	0.37 - 0.59	0.02 - 0.20
Vanadium	NV	—	—	—	—
Zinc	86	<0.01 - 0.05	0.01 - 0.06	0.06 - 0.09	0.05 - 0.11

* Water quality criterion for inorganic mercury; criterion for methylmercury is 0.025 μg/L.
NV = No water quality criterion value available.

0.745 µg/g total monoaromatic hydrocarbons, compared to 0.0016 to 0.0002 µg/g in sediments from the reference sites. A sediment sample collected from the discharge site at Delacroix Island before termination of the discharge contained 0.58 µg/g total BTEX, mostly xylenes. A year later at the time of the Second Post-termination Survey, sediment from the same location contained 0.002 µg/g total monoaromatic hydrocarbons. The only monocyclic aromatic hydrocarbons remaining were the less volatile C_2- through C_4-benzenes. None of the sediments from reference stations at Delacroix Island contained detectable concentrations of monocyclic aromatic hydrocarbons.

Concentrations of PAHs in sediments near the three production facilities were highly variable in both space and time. Total PAH concentrations in sediments from different locations ranged from 0.22 to 80 µg/g dry weight (**Table 10.19**). Highest concentrations of total PAHs at the time of the Pre-termination Surveys were in sediments from the discharge from the Bay de Chene production facility (72 µg/g). However, highest PAH concentrations were observed in the two Post-termination Surveys at transect stations near the Bay de Chene facility. Most of the highest concentrations were in sediments near the former fuel dock and pipe storage facility. Sediments from the discharge site at the Four Isle Dome facility also contained an elevated concentration of total PAHs.

Sediments from reference stations near the three production facilities contained relatively uniform low concentrations ranging from 0.22 to 0.75 µg/g. Concentrations were highest in reference sediments in the vicinity of the Four Isle Dome facility. These concentrations of total PAHs in reference sediments can be considered background concentrations for coastal areas of Louisiana.

Advanced hydrocarbon fingerprinting methods were used (**Chapter 8**) to determine the sources of PAHs in sediments from the vicinity of the three production facilities. Most of the PAHs in sediments near the production facilities contained predominantly PAHs from a pyrogenic source, probably creosote. Most of the older shallow-water production facilities in coastal waters of Louisiana were built on wood pilings that had been treated with creosote to slow decay. Extensive use was made at many facilities of wooden walkways between wellheads and the different platform facilities. These wooden structures probably are the source of the creosote in the sediments near the three facilities. Some of the PAHs were derived from produced water and from refined petroleum products, primarily fuel oils. However, it is not possible to quantify the relative contributions of different sources to the total PAHs in sediments at different locations near the facilities. It is reasonable to assume that most of the PAHs in sediments under the discharges before termination of the produced water discharges were derived from the produced water discharges. However, after the termination of these discharges, concentrations of PAHs in sediments at the former discharge sites decreased rapidly (**Table 10.19**), indicating that the low molecular weight PAHs from produced water were not persistent in the sediments. The higher molecular weight PAHs characteristic of creosote and other pyrogenic sources were much more persistent in the site sediments. Their concentrations in sediments did not decrease rapidly following termination of the discharges.

Environmental Risk of Aromatic Hydrocarbons in Sediments

There are no screening values for VAHs in sediments. Because of their volatility and low sediment organic carbon/water partition coefficients (K_{oc}), they do not bind strongly

Table 10.19. Concentration ranges of total polycyclic aromatic hydrocarbons in surface sediments from the vicinity of three production facilities in coastal Louisiana. Concentrations are μg/g dry weight.

Site	Stations	Pre-termination Survey	First Post-termination Survey	Second Post-termination Survey
Delacroix Island	Discharge	12	2.8	7.7
	Transects	0.33 - 2.5	0.27 - 2.1	0.29 - 1.5
	Reference	0.26 - 0.27	0.22 - 0.28	0.24 - 0.28
Bay de Chene	Discharge	72	9.6	8.3
	Transects	0.26 - 35	0.15 - 80	0.27 - 66
	Reference	0.30 - 0.49	0.23 - 0.42	0.30 - 0.35
Four Isle Dome	Discharge	49	No Sampling	No Sampling
	Transects	0.45 - 3.6	---	---
	Reference	0.73 - 0.75	---	---

to sediments and rarely are found at greater than trace concentrations, even near point sources, such as waste-water effluents (Neff, 1997). The highest concentration in sediment was about 0.75 μg/g dry weight at the discharge from the Four Isle Dome facility. The VAHs in this sample undoubtedly were derived from the produced water discharge. Sediments from this location also contained 700 μg/g total petroleum hydrocarbons and 49 μg/g total PAHs. It is possible that the sediments contained small amounts of fresh oil droplets. Produced water from the Four Isle Dome facility contained the highest concentrations of monocyclic aromatic hydrocarbons, PAHs, and total petroleum hydrocarbons of the three discharges (**Table 10.6**), indicating that some dispersed oil droplets may have been present in the discharge.

The concentrations of monocyclic aromatic hydrocarbons in the sediments from the discharge sites probably were not sufficiently high to cause harm to local benthic organisms. Based on aquatic toxicity information for BTEX compounds, it is probable that toxic concentrations of BTEX in sediments are in the range of several parts per million, many times higher than measured concentrations.

Concentrations of total PAHs in some sediments were high enough that they posed a risk of harm to benthic organisms. Sediments collected during the Pre-termination Surveys from the discharge at the Bay de Chene and Four Isle Dome facilities contained total PAHs equivalent to slightly more than 1 toxic unit (**Table 10.20**). Sediments collected during the two Post-termination Surveys from a few transect stations near the Bay de Chene facility also contained PAHs equivalent to slightly more than 1 toxic unit. These stations were near the former fuel dock and pipe storage facility. The PAHs there probably did not come from the produced water discharges at Tank Battery #5.

Concentrations of total PAHs in sediments were high enough at a few locations before and after termination of the produced water discharge that they may pose a risk to benthic organisms living in sediments near the production facilities. The PAHs in the sediments under the discharge from the Bay de Chene and Four Isle Dome facilities probably were derived in large part from the produced water discharges. At the time of the First Post-termination Survey about six months after termination of the produced water discharge, concentrations of total PAHs in sediments under the Bay de Chene discharge had dropped from 72 μg/g to 9.6 μg/L, lending support to the hypothesis that the PAHs present in the sediments under the discharges when produced water was being discharged were from the produced water. Concentrations of total PAHs in discharge site sediments at the Delacroix Island facility also decreased between the Pre-termination Survey and the First Post-termination Survey from 12 to 2.8 μg/g. These results indicate that PAHs derived from produced water readily desorb from the sediments when concentrations in the overlying water decrease. They are not persistent.

However, PAHs in transect sediments near the Bay de Chene facility appear to be much more persistent. Alternatively, the sediments are being re-contaminated with PAHs from some source. The sediments from these transect locations contain PAHs from combined pyrogenic and petrogenic sources, possibly creosote and fuel oils (**Chapter 8**). PAHs associated with creosote are quite persistent in estuarine and marine sediments, particularly if the redox potential is low (Mueller et al., 1989).

Table 10.20. Estimated toxic units (concentration in sediment/effects range-median [ERM] value) for total polycyclic aromatic hydrocarbons (PAHs) in surface sediments from the vicinity of three production facilities in coastal Louisiana. The ERM value for total PAHs in sediments is 44.79 μg/g dry weight (Long et al., 1995).

Site	Stations	Pre-termination Survey	First Post-termination Survey	Second Post-termination Survey
Delacroix Island	Discharge	0.27	0.06	0.17
	Transects	0.01 - 0.06	0.01 - 0.05	0.01 - 0.03
	Reference	0.01	0.01	0.01
Bay de Chene	Discharge	1.61	0.21	0.19
	Transects	0.01 - 0.78	<0.01 - 1.79	0.01 - 1.47
	Reference	0.01	0.01	0.01
Four Isle Dome	Discharge	1.09	No Sampling	No Sampling
	Transects	0.01 - 0.08	---	---
	Reference	0.02	---	---

10.3.7 Environmental Risk of PAHs in Sediment Interstitial Water

Low concentrations of a few PAHs were detected in sediment interstitial water from discharge and reference sites at the Delacroix Island production facility before and after termination of the produced water discharge. The only other interstitial water sample containing a quantifiable concentration of PAHs was collected on the Pre-termination Survey from a reference site for the Bay de Chene facility. This sample contained 0.3 μg/L of naphthalene (see **Chapter 8**).

Two interstitial water samples collected during the Pre-termination Survey from the discharge site at the Delacroix Island facility contained 3.9 and 5.2 μg/L total PAHs, including naphthalene and alkyl-naphthalenes. One interstitial water sample collected at the same time from a reference station contained 4.2 μg/L total PAHs. Interstitial water samples collected during the Second Post-termination Survey from sediments at discharge and reference stations near the Delacroix Island production facility contained 0.10 to 0.31 μg/L total PAHs. There was no difference in concentrations between discharge and reference stations. The dominant PAHs in all samples were naphthalene and alkylnaphthalenes. These PAHs probably were derived primarily from produced water.

The chronic water quality criteria for naphthalene and alkylnaphthalenes estimated by the regression of McCarty et al. (1992) range from 8 to 214 μg/L. Thus, concentrations of total PAHs (consisting primarily of naphthalenes) in sediment interstitial water are well below potentially toxic concentrations. Therefore, PAHs in the interstitial waters of sediments near the produced water discharge from the three production facilities do not pose a significant risk to benthic marine organisms.

10.3.8 Impacts on Benthic Infauna

The composition and distribution of the benthic infauna in the vicinity of the three production facilities was investigated in **Chapter 9**. Benthic infaunal communities were significantly different from those at reference stations at locations within 100 m of the Delacroix Island and Bay de Chene production facilities. There was not a statistically significant difference in benthic community parameters at stations near the Four Isle Dome facility. There was apparent partial recovery of the benthic infauna near the discharges from the Delacroix Island and Bay de Chene facilities after termination of produced water discharges.

The risk assessment described earlier in this chapter provides evidence that the altered benthic infauna at stations near the platforms was caused by a combination of elevated concentrations of a few metals (barium, iron, and manganese) in sediment interstitial water, and total PAHs in bulk sediments. Elevated chloride concentrations, particularly in interstitial water at the Delacroix Island discharge site before termination of the produced water discharge, may have contributed substantially to alterations in benthic community structure near the platforms. Depressed redox potentials in surficial sediments near the platforms, as often occurs because of accumulation of biodegradable hydrocarbons in the sediments (Kingston, 1992), may also have contributed to benthic community alteration near the platforms.

10.4 CONCLUSIONS

Before produced water discharges were terminated in 1993 and 1995, shallow water production facilities at Delacroix Island, Bay de Chene, and Four Isle Dome discharged 852 to 3,825 bbl/day of produced water containing elevated concentrations (compared to the estimated concentrations in local receiving waters) of several metals and hydrocarbons to shallow coastal waterways of Louisiana. Concentrations of all metals, except barium, in a 100-fold dilution of the produced waters (the maximum likely exposure concentration to local aquatic biota) were below concentrations equivalent to 1 toxic unit. Concentrations below 1 toxic unit are not expected to be toxic to estuarine and marine organisms. Barium probably precipitated as barite following discharge and so may have been present in a dissolved, bioavailable form in the receiving water at a concentration much lower that 1/100 the concentration in the produced water. VAHs and PAHs were present in 100-fold dilutions of the produced water at concentrations well below 1 toxic unit. Therefore, after initial dilution in the receiving waters, treated produced water from the three facilities was not expected to be toxic to local estuarine and marine organisms.

Concentrations of several metals were elevated in bulk sediments near the produced water discharges from the three production facilities before and after termination of the produced water discharges. For those metals for which screening concentrations in sediments are available, none were present in sediment near the three discharges at concentrations higher than 1 toxic unit either before or after termination of the produced water discharges. Concentrations of most metals did not decrease in sediments near the production facilities following termination of the discharges. Most of the metals, except barium, were natural constituents of the local sediments and were not derived from the produced water discharges.

Interstitial water from sediments near the three production facilities also contained elevated concentrations (compared to background concentrations in clean estuarine waters) of several metals. Concentrations of barium, iron, and manganese in most sediment interstitial water samples from the three discharge sites were well above those equivalent to 1 toxic unit. A few interstitial water samples also contained cadmium, copper, lead, or nickel concentrations equivalent to 1 toxic unit or slightly more. All metals, except manganese, were present in sediment interstitial samples collected from the discharge and reference sites at Delacroix Island on the Second Post-termination Survey at concentrations equivalent to less than 1 toxic unit. The physical and chemical forms of barium, iron, and manganese in the sediment interstitial water are not known. They were most probably in microparticulate form or complexed with dissolved or colloidal organic matter in the sediment interstitial water. Thus, these interstitial water metals may not have been present in toxic forms. If they were bioavailable, they probably contributed to the toxicity of the sediments before termination of the produced water discharges. After termination of the produced water discharge at the Delacroix Island facility, concentrations of metals in sediment interstitial water near the facility decreased, suggesting that they were derived at least in part from the produced water discharge.

Concentrations of chloride and salinity also were elevated in sediment interstitial water from the discharge sites before termination of the discharges. The salinity was high enough and ionic ratios in the interstitial waters probably were sufficiently different from those in the overlying brackish water that the sediments may have been unsuitable for habitation by benthic organisms.

Concentrations of VAHs were present in a few sediment samples from the vicinity of two of the facilities at concentrations below those that might be expected to be toxic to benthic organisms. However, total PAH concentrations in surficial sediments from the discharge sites at Bay de Chene and Four Isle Dome before termination of the produced water discharges were equivalent to slightly more than 1 toxic unit. These sediment PAHs may have contributed to the toxicity of the sediments to benthic infauna. Sediments along one of the transects from the Bay de Chene facility near a former fuel dock and pipe storage facility also contained potentially toxic concentrations of total PAHs. Sediments from this location were the only ones containing potentially toxic concentrations of PAHs at the time of the First and Second Post-termination Surveys. Most of the PAHs detected in sediments near the three production facilities were pyrogenic, probably derived from creosote from wood pilings at the facility. The contribution of produced water to the PAH concentrations in sediments at all sampling stations except the discharge sites probably was small.

Benthic infauna were adversely affected at two of the discharge sites before termination of the produced water discharges. The evidence presented in this environmental risk assessment indicate that the adverse effects on the infauna probably were caused by a combination of elevated concentrations of barium, chloride, iron, manganese, and PAHs. The chloride and PAHs probably contributed the most to the unsuitability of the sediments near the discharges for habitation by several species of benthic infauna found at greater distances from the discharges. Concentrations of these chemicals in sediments returned to near background levels after termination of the produced water discharges. Concentrations of pyrogenic, creosote-derived PAHs remained high in sediments. There was strong evidence of some recovery of the benthic infauna communities after termination of the discharges. The observed reductions in sediment contamination probably allowed benthic infauna to recolonize the affected substrates.

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