FOSSIL ENERGY

DOE/MT/92001-23
OSTI ID: 9730

RADIONUCLIDES, METALS, AND HYDROCARBONS IN OIL AND GAS OPERATIONAL DISCHARGES AND ENVIRONMENTAL SAMPLES ASSOCIATED WITH OFFSHORE PRODUCTION FACILITIES ON THE TEXAS/LOUISIANA CONTINENTAL SHELF WITH AN ENVIRONMENTAL ASSESSMENT OF METALS AND HYDROCARBONS

Topical Report
June 1997

Date Published: July 1999

Work Performed Under Contract No. DE-AC22-91MT92001

Continental Shelf Associates, Inc.
Jupiter, Florida

National Petroleum Technology Office
U. S. DEPARTMENT OF ENERGY
Tulsa, Oklahoma

DOE/MT/92001-23
Distribution Category UC-122

Radionuclides, Metals, and Hydrocarbons in Oil and Gas Operational Discharges and Environmental Samples Associated With Offshore Production Facilities on the Texas/Louisiana Continental Shelf With an Environmental Assessment of Metals and Hydrocarbons

July 1999

Work Performed Under Contract DE-AC22-91MT92001

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

Rhonda Lindsey, Technology Manager
National Petroleum Technology Office
P.O. Box 3628
Tulsa, OK 74101

Prepared by
Continental Shelf Associates, Inc.
759 Parkway Street
Jupiter, Florida 33477

TABLE OF CONTENTS

TABLE OF CONTENTS
(Continued)

TABLE OF CONTENTS
(Continued)

TABLE OF CONTENTS
(Continued)

TABLE OF CONTENTS
(Continued)

Page

TABLE OF CONTENTS
(Continued)

TABLE OF CONTENTS
(Continued)

LIST OF FIGURES

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

LIST OF FIGURES
(Continued)

LIST OF TABLES

LIST OF TABLES
(Continued)

LIST OF TABLES
(Continued)

LIST OF TABLES
(Continued)

LIST OF TABLES
(Continued)

LIST OF TABLES
(Continued)

LIST OF TABLES
(Continued)

LIST OF TABLES
(Continued)

LIST OF TABLES
(Continued)

LIST OF TABLES
(Continued)

LIST OF ACRONYMS

AAS	atomic absorption spectrometry
ADL	Arthur D. Little, Inc.
ANOVA	Analysis of Variance
AVS	acid-volatile sulfide
BCF	bioconcentration factor
BNL	Brookhaven National Laboratory
CBR	critical body residue
COSED	Coastal Sediment Database
CSA	Continental Shelf Associates, Inc.
DDTC	diethylammoniumdiethyldithiocarbamate
DISCH	discharge
DMR	Discharge Monitoring Report
DOE	Department of Energy
DQO	data quality objective
DTPA	diethylenetriaminepentaacetic acid
EI	Eugene Island
EMAP	Environmental Monitoring and Assessment Program
EPA	Environmental Protection Agency
ERL	effects range-low
ERM	effects range-median
FIT	Florida Institute of Technology
GA	Galveston
GC trace	gas chromatogram
GC\FID	gas chromatography\flame ionization detection
GC\MS	gas chromatography\mass spectrometry
GOOMEX	Gulf of Mexico Offshore Operations Monitoring Experiment
GPS	Global Positioning System
HCl	hydrochloric acid
HI	High Island
HPLC	high-performance liquid chromatography
LIMS	Laboratory Information Management System
MDL	method detection limit
MI	Matagorda Island
MMS	Minerals Management Service
ND	non-detected
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
NPDES	National Pollutant Discharge Elimination System
NRC	National Research Council
OOC	Offshore Operators Committee
PAH	polycyclic aromatic hydrocarbon
PE	Perkin-Elmer
PVC	polyvinyl chloride
QA	Quality Assurance
QC	Quality Control
QSAR	quantitative structure activity relationship
RPD	relative percent difference

LIST OF ACRONYMS
(Continued)

RSD	relative standard deviation
SDU	Solids Decontamination Unit
SHC	saturated hydrocarbon
SIM	selected ion monitoring
SMI	South Marsh Island
SOP	Standard Operating Procedure
SRC	Scientific Review Committee
SRM	Standard Reference Material
SS	Ship Shoal
TDS	total dissolved solids
THC	total hydrocarbon
TOC	total organic carbon
TOPO	trioctyl phosphine oxide
TPH	total petroleum hydrocarbon
TSC	tissue screening concentrations
UCM	unresolved complex mixture
USA	University of South Alabama
VAH	volatile aromatic hydrocarbon
VOA	volatile organic analysis
VR	Vermilion
WC	West Cameron

ABSTRACT

This report presents concentrations of radionuclides, metals, and hydrocarbons in samples of produced water and produced sand from oil and gas production platforms located offshore Texas and Louisiana. Concentrations in produced water discharge plume/receiving water, ambient seawater, sediment, interstitial water, and marine animal tissue samples collected in the vicinity of discharging platforms and reference sites distant from discharges are also reported and discussed. 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 concentrations of selected radionuclides, metals, and hydrocarbons in produced water and produced sand discharges from Gulf of Mexico offshore platforms and to compare the concentrations with those in samples of ambient seawater, sediment, interstitial water, and marine animals collected in the vicinity of the discharges and from areas distant from the discharges. These data are used in environmental and human health risk assessments. The metal and hydrocarbon data are utilized in this report for an environmental risk assessment. The radionuclide, metal, and hydrocarbon data are incorporated into environmental (radionuclide data) and human health (radionuclide, metal, and hydrocarbon data) risk analyses being performed by Brookhaven National Laboratory.

Study Sites

Eight oil and gas production platforms were selected for sampling. They were located on the continental shelf offshore Texas and Louisiana in water depths of 6 to 122 m and had produced water discharges ranging from 250 to 22,880 barrels/day. Six reference sites also located on the continental shelf offshore Texas and Louisiana in water depths of 7 to 110 m and distant from production related discharges were also selected for sampling.

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

Produced water discharges from four of the eight platforms were sampled intensively over a 3-day period and once per month over a 5-month period. The other four platforms were sampled once. Produced sand, which is no longer discharged, was sampled at two of the eight platforms. Produced sand samples were also collected from three additional platforms. One of these produced sand samples was used in an evaluation of treatment equipment for removal of hydrocarbons through washing technologies. Water samples were collected within the produced water plumes following discharge, at stations located greater than 2,000 m from the discharge points, and at four of the seven reference sites. Sediment and interstitial water, which was squeezed from sediment samples, were sampled near four of the discharging platforms, at stations located greater than 2,000 m from the discharge points, and at four of the reference sites (sediment only). Biological tissue samples were collected at the eight discharging platforms and two of the reference sites, plus an additional site where the sampled biological specimens were believed not to be exposed to a near-bottom produced water discharge. Bivalve mollusks were removed by divers and fishes were collected by hook-and-line, trap, and spearing.

Shrimps, crabs, and fishes were also collected by trawl. The soft tissue of the mollusks; edible flesh, carcasses, and whole specimens of crustaceans; and edible flesh (fillet), carcasses, and whole specimens of fish were analyzed.

Produced Sand

Three of the five produced sand samples generally had higher radionuclide activities than the reference site sediments. Concentrations of cadmium, copper, mercury, and zinc were higher in two of the five produced sands than sediment samples from the reference sites. The produced sands had varying levels of petroleum hydrocarbons. The produced sand that was used in the evaluation of oil removal had 52% to 90% of the measured saturated and polycyclic aromatic hydrocarbons (PAHs) removed by the treatment equipment.

Radionuclide Activities

Produced water radionuclide activities varied among platforms and sampling times. The ^{226}Ra and ^{228}Ra activities (38 to 944 and 43 to 685 pCi/L, respectively) were within ranges previously reported for offshore Gulf of Mexico produced waters with the exception of eight samples (4% of the total samples). The high values were believed to be caused by solid residue (pipe scale) accidently entering the samples, which were unfiltered prior to analysis. Other mean radionuclide activities (^{210}Pb, 5 to 17; ^{228}Th, 29 to 121; and ^{210}Po, 1 to 2 pCi/L) were much lower. Produced water mean radionuclide activities rapidly decreased with distances from the discharges, with ^{226}Ra and ^{210}Pb activities less than 1.0 pCi/L and ^{228}Ra less than 4.0 pCi/L within 100 m of the discharge point. Ambient seawater mean ^{226}Ra, ^{228}Ra, and ^{210}Pb activities were less than 0.3, 3.2, and 0.5 pCi/L, respectively. There was little evidence of elevated radionuclide activities in sediments and interstitial water in the vicinity of sampled platforms. Radionuclides also do not appear to be accumulating in the sampled tissues of organisms living in the vicinity of the offshore produced water discharges.

Environmental Risk Assessment for Metals and Aromatic Hydrocarbons

Metals in Produced Water and Ambient Seawater

Concentrations of 13 metals (arsenic, barium, cadmium, chromium, copper, iron, lead, mercury, manganese, molybdenum, nickel, vanadium, and zinc) were determined in produced water and ambient seawater (except chromium). All the target metals except copper, nickel, and vanadium were detected in some of the samples. The metals with the greatest enrichment (≥10,000 times) in produced water from the four platforms compared to their concentrations in ambient seawater were barium, iron, and manganese. These three metals are expected to precipitate rapidly during mixing of the produced water plume with ambient seawater. Precipitation of these metals as barium sulfate (barite) and microparticulate oxyhydroxides of iron and manganese results in the co-precipitation or adsorption of most of the other metals in produced water, lowering their concentrations in solution in ambient seawater. Five metals (barium, copper, iron, mercury, and nickel) were present in ambient seawater at one or more discharge sites at higher concentrations (approximately two-fold) than in seawater from the four reference sites. In all but one case, the difference can be attributed to the influence of freshwater (higher concentration of some metals than seawater) dilution of seawater. The concentration of mercury in ambient seawater at the farthest offshore platform site was higher than in seawater from the reference sites. The source of the slightly elevated mercury was not produced water. Therefore, high volume discharges of produced water did not result in an increase in metal concentrations in ambient seawater at stations located 2,000 m from the platforms.

Comparison of measured and predicted concentrations of the metals in ambient seawater with chronic criterion values for protection of marine life indicates that none of the metals is likely to be present in solution in ambient seawater at a concentration high enough to represent a toxicological risk to marine animals.

Metals in Tissues

Several of the target metals analyzed in tissues (same metals analyzed in produced water) were present in tissues of marine bivalves, crustaceans, and fish from the vicinity of the produced water discharges and from one or more reference sites at concentrations that approach or exceed tissue screening concentrations or are in the upper part of the range of reported tissue residues, where screening concentrations are not available. These values might be toxic to marine animals. Arsenic was present in several species of marine animals from both reference and discharge sites at high (exceeding 20 μg/g dry weight) concentrations. However, nearly all the arsenic in tissues of marine organisms is present in non-toxic organic forms, particularly arsenobetaine. Barium was present in a few selected samples from the vicinity of the produced water discharges at elevated concentrations. The barium probably was present in the tissues as insoluble barite and is inert toxicologically.

Cadmium, chromium, copper, lead, mercury, and zinc concentrations in the sampled species of marine animals are within the expected natural ranges for the different species. Concentrations of essential micronutrients, such as copper, iron, manganese, and zinc in the marine animals collected near the produced water discharges are below potentially toxic concentrations.

There is little published information about the natural concentrations of molybdenum and vanadium (both essential micronutrients) in soft tissues of marine animals. Concentrations measured in tissues of marine animals from the produced water discharge and reference sites were similar and are within the range reported for marine animals from elsewhere in the world. Tissue residues of these metals probably do not pose a risk to marine animals in the vicinity of the platforms.

Aromatic Hydrocarbons in Produced Water and Ambient Seawater

Produced water from the four intensively sampled platforms contained an average of 1,754 to 5,183 μg/L total monocyclic aromatic hydrocarbons. The monocyclic aromatic hydrocarbons in the produced water are diluted rapidly in the ambient seawater following discharge of the produced water. These compounds are diluted by 50- to more than 100-fold within 5 m of the platforms. Dilutions in excess of 3,000-fold occur within 2,000 m of the platforms.

Estimated concentrations of total monocyclic aromatic hydrocarbons in a 100-fold dilution of produced water (the lowest dilution that might be encountered for an extended period of time by biofouling organisms on submerged platform structures) are less than one-tenth of the concentration that might be toxic to marine plants and animals. Therefore, monocyclic aromatic hydrocarbons in produced water do not represent a toxicological risk to marine animals near offshore produced water discharges.

The four sampled produced water discharges contained means of 58 to 596 μg/L total PAHs. Concentrations of a suite of 41 PAHs and PAH congener groups were determined. The most abundant PAHs in the produced water were the lower molecular weight naphthalenes, fluorenes, and phenanthrenes. High molecular weight four- through six-ring PAHs were present at trace concentrations (<0.1 μg/L) or at concentrations below the method detection limits. The concentrations of low molecular weight PAHs in produced water were much higher than those in ambient seawater.

Estimated concentrations of individual and total PAHs in a 100-fold dilution of produced water with seawater are well below concentrations that are considered potentially toxic to marine animals at three of the four platforms. At the fourth platform, the PAHs could be present in the 100-fold dilution at a potentially toxic concentration if all the PAHs were in solution. However, much of the predicted toxicity in this produced water is attributed to high molecular weight PAHs that probably were present in the produced water in oil droplets or adsorbed to particles. These forms of PAHs are less toxic than dissolved PAHs. Therefore, there is only a slight risk that marine organisms living in the immediate vicinity of the produced water discharges might be exposed to a harmful concentration of PAHs.

Metals in Sediments

Several of the metals analyzed in sediments (same metals analyzed in produced water plus aluminum and calcium) were present near the four produced water discharges and in some sediments from reference sites at concentrations higher than expected for clean offshore marine sediments. Arsenic, lead, mercury, nickel, and zinc concentrations near one or more of the discharges approached concentrations in sediments that could be toxic to some species of benthic marine animals. However, only lead and zinc were enriched in produced water compared to sea water and their elevated sediment concentrations are unlikely to be solely due to produced water. Also, most of these metals in the sediments probably are complexed with sulfides or sediment organic matter and are not bioavailable or toxic.

Aromatic Hydrocarbons in Sediments

PAHs were also observed in the sampled sediments near the four produced water discharges. Mean total PAH concentrations in sediments 60 m or closer to the four discharges ranged from 0.32 to 1.37 μg/g dry weight. Mean total PAH concentrations in sediments 2,000 m from the four produced water discharges and at the four reference sites were all less than 0.30 μg/g. Impacts of produced water discharges on benthic marine ecosystems, when they occur, usually are attributed to accumulation of hydrocarbons in sediments near the platform or to anoxia caused by biodegradation of hydrocarbons in the sediments. In this study, insufficient concentrations of PAHs have accumulated in the sediments around three of the four platforms to represent a toxicological risk to benthic marine organisms. In the fourth case, the concentrations of low molecular weight PAHs could be marginally toxic to sensitive marine organisms in sediments within about 20 m of the discharge.

Aromatic Hydrocarbons in Tissues

Marine invertebrates and fish collected near the four platform discharges contain concentrations of total PAHs in their soft or edible tissues ranging from less than 0.0001 to 11.68 μg/g dry weight. Most concentrations are below 1.0 μg/g. The most abundant PAHs in the soft tissues of marine animals collected near offshore produced water discharges were alkylnaphthalenes. These concentrations are well below tissue residues of individual and total PAHs that are associated with toxic effects in marine animals. Therefore, the health risk of measured tissue residues of PAHs in marine animals collected from the immediate vicinity of offshore produced water discharges is low.

Summary

Because of the rapid dilution of produced water from offshore platforms when it is discharged to the ocean, metals and aromatic hydrocarbons in the produced water do not pose a significant toxicological risk to marine animals in the immediate vicinity of the platforms. The most likely location where adverse effects might occur is in sediments within less than 100 m of the produced water discharge, particularly if water depth at the platform is shallow and discharge volume is high.

CHAPTER 1 - INTRODUCTION

David Gettleson and Brian Balcom
Continental Shelf Associates, Inc.
Jupiter, Florida and Issaquah, Washington

1.1 BACKGROUND

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

The processing and reduction or removal of specific constituents is typically needed to meet U.S. Environmental Protection Agency (EPA) National Pollutant Discharge Elimination System (NPDES) effluent limitations before these by-products can be discharged on site. Produced sand was no longer allowed to be discharged after 3 January 1994 as this was the effective date of the revised EPA Region VI NPDES General Permit. ICF Resources, Inc. (Continental Shelf Associates, Inc., 1996a) discusses discharge requirements for produced water.

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 in offshore Gulf of Mexico waters and a second study conducted under this project of terminated produced water discharge sites in coastal Louisiana (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., 1996b). 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., 1996a).

1.3 OBJECTIVES OF THE STUDY

The overall objective of this study was to determine concentrations of radionuclides, metals, and hydrocarbons in water, sediment, and biota collected in close proximity to oil and gas production operations in the offshore Gulf of Mexico. Further, ambient levels of these elements and compounds were also to be determined in reference areas that were distant from produced water discharges. Produced water, produced sand, produced water discharges/receiving water, ambient seawater, sediment, interstitial water, and biological tissue (i.e., biofouling, benthic soft substrate, and midwater fish assemblages) samples were to be collected and analyzed. Measurements of select physical oceanographic parameters (i.e., hydrography and currents) at representative sampling sites were also to be conducted. 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 (Meinhold and Holtzman, 1996).

1.4 REFERENCES

Continental Shelf Associates, Inc. 1996a. Assessment of Economic Impacts of Offshore and Coastal Discharge Requirements on Present and Future Operations in the Gulf of Mexico. Prepared by ICF Resources under subcontract to Continental Shelf Associates, Inc. Report for the U.S. Department of Energy, Bartlesville, Oklahoma.

Continental Shelf Associates, Inc. 1996b. Synthesis of Seafood Catch, Distribution, and Consumption Patterns in the Gulf of Mexico Region. Prepared by Steimle & Associates, Inc. under subcontract to Continental Shelf Associates, Inc. Report for the U.S. Department of Energy, Bartlesville, Oklahoma.

Continental Shelf Associates, Inc. 1997. Monitoring Environmental Recovery at Terminated Produced Water Discharge Sites in Coastal Louisiana Waters. Report for the U.S. Department of Energy, Bartlesville, Oklahoma.

Meinhold, A. F. and S. Holtzman. 1996. Human Health Risks of Metals and PAHs Discharged Offshore in Produced Water. Prepared by Brookhaven National Laboratory, Upton, New York. Draft report prepared for the U.S. Department of Energy, Bartlesville, Oklahoma.

1.5 ACKNOWLEDGEMENTS

This work was performed under contract to the U.S. Department of Energy (Contract No. DE-AC22-92MT92001). We would like to acknowledge the assistance and guidance of Dr. Brent W. Smith and Ms. Rhonda P. Lindsey, the U.S. Department of Energy Contracting Officer's Representatives and Mr. Keith R. Miles, the U.S. Department of Energy Contracting Officer. We would like to thank the facility operators for permission to incorporate their facilities into this study. We would like also to thank Pam Hudson (Contract Administration), Melody Powell (Report Editor), Pam Jones (Report Editor), Suzi Short (Report Graphic Artist), Debbie Cannon (Report Copying), Debbie Raffel (Report Word Processing), and Lynn Ugartemendia (Report Word Processing) of Continental Shelf Associates, Inc. (CSA) for their assistance. Finally, we wish to acknowledge the efforts by the subcontractors and consultants to CSA.

CHAPTER 2 - STUDY DESIGN AND OVERVIEW

Alan Hart, Bruce Graham, and Luis Lagera, Jr. (Section 2.4)
Continental Shelf Associates, Inc.
Jupiter, Florida

2.1 STUDY COMPONENTS

This study was divided into three components. The purpose of Component 1 was to sample platform sites that were representative of produced water discharging sites with much higher than average loadings for radionuclides. These sites were to be sampled more intensely than the sites for the other two components. The purpose of Component 2 was to sample sites representative of ambient seawater and sediment conditions in the western and central Gulf of Mexico; extensive efforts were to be made to insure that Component 2 sites were as unaffected by oil and gas activities as practical. The purpose of Component 3 was to sample sites that had produced water radionuclides loadings that were less than the higher than average cases sampled for Component 1, including sites where no produced water discharges had ever occurred.

The three components were as follows:

- **Component 1**

  Sampling was to involve collecting produced water, produced sand, discharge plume/receiving water, ambient seawater, sediments, and biological tissues for determination of concentrations of radionuclides, metals, and hydrocarbons and hydrographic and current data at four oil and gas platform sites located on the Texas/Louisiana continental shelf. In addition, produced water samples were to be collected monthly over a 6-month period to investigate temporal variability of produced water composition at the four Component 1 sites.

- **Component 2**

  The purpose of Component 2 sampling was to provide reference data for radionuclides, metals, and hydrocarbons at four sites far removed from oil and gas activities. Sampling was to consist of collecting ambient seawater and sediment samples.

- **Component 3**

  Sampling was to be conducted at four produced water-discharging platform sites, which had radionuclides loadings less than the Component 1 platform sites, and consist of collecting produced water and tissue samples. Radionuclide concentrations were to be determined in the produced water samples and radionuclides, metals, and hydrocarbons in the tissue samples. In addition, sampling was to be conducted at two platform sites where produced water discharges had never occurred; sampling at these sites was to consist of collecting ambient seawater and tissue samples. Radionuclide concentrations were to be determined in the ambient seawater samples and radionuclides, metals, and hydrocarbons in the tissue samples.

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, Fish and Wildlife Service, Minerals Management Service [MMS], and National Oceanic and Atmospheric Administration [NOAA]), Brookhaven National Laboratory, 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]).

2.2 SELECTION OF SITES

The basis for the selection of Components 1 and 3 sites was the level of radionuclides loadings in the produced water discharges. Component 1 sites were selected to be representative of platforms that had much greater than average radionuclides loadings (radionuclide concentrations × discharge volumes); and Component 3 sites were selected to represent platforms with radionuclides loadings ranging from zero to the loadings at Component 1 sites. Initially, potential candidate production platform sites were compiled from data sources received from the EPA and the OOC. Discharge Monitoring Reports (DMRs) for 1991 were received from EPA and tabulated to ascertain the upper quantile for discharge rates (**Figure 2.1**). This tabulation indicated that platforms discharging more than 4,000 bbl/d were in the upper quantile (i.e., platforms with produced water discharge volumes that were more than 75% of those reported for all the discharging platforms). It was recognized that this estimated volume for the 75th percentile is approximate because as many as 10% of the discharge volumes appear to have been misreported based on the number of platforms reported to have discharges exceeding 100,000 bbl/d.

A list of platforms where the OOC had measured ^{226}Ra and ^{228}Ra in produced water samples was examined to determine potential Components 1 and 3 sites. Other potential sites were identified by examining the EPA DMR database and conducting discussions with platform operators in the Gulf of Mexico. If radionuclide data were not available, then produced water samples were obtained from the platforms and analyzed for ^{226}Ra and ^{228}Ra. The platform operators were contacted and their willingness to participate in the study was determined; operators were asked to document monthly average discharge volumes. Based on the radium loading data and the operator responses, the study sites were selected. Three Component 1 sites were located offshore Louisiana in the South Marsh Island (SMI) and Vermilion (VR) lease block areas (SMI 130B; SMI 236A; VR 214A); and a fourth Component 1 site was located offshore Texas in the High Island (HI) lease block area (HI A-595CF). Platforms discharging produced water that were selected for Component 3 sites were Eugene Island (EI) 313A, HI A-382F, HI A-323A, and Matagorda Island (MI) 703A. Component 3 sites where produced water discharges had never occurred were SMI 229C and an offshore shallow-water bank (VR 298/305, Sonnier Bank). Loadings of ^{226}Ra and ^{228}Ra at the produced water-discharging platforms selected for Components 1 and 3 are shown in **Figure 2.2**.

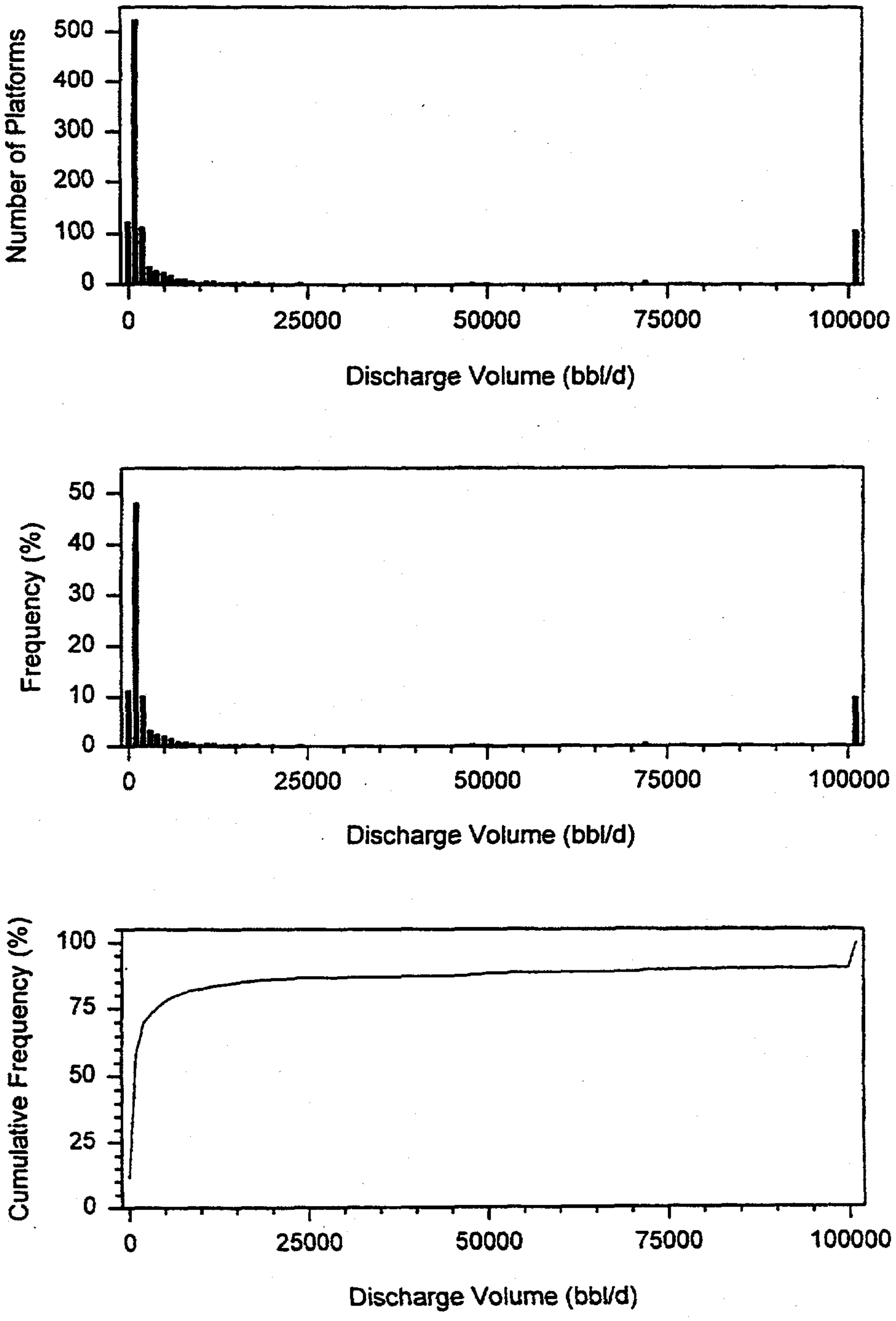


Figure 2.1. Produced water discharge volumes for Gulf of Mexico platforms based on discharge monitoring reports filed by platform operators with EPA.

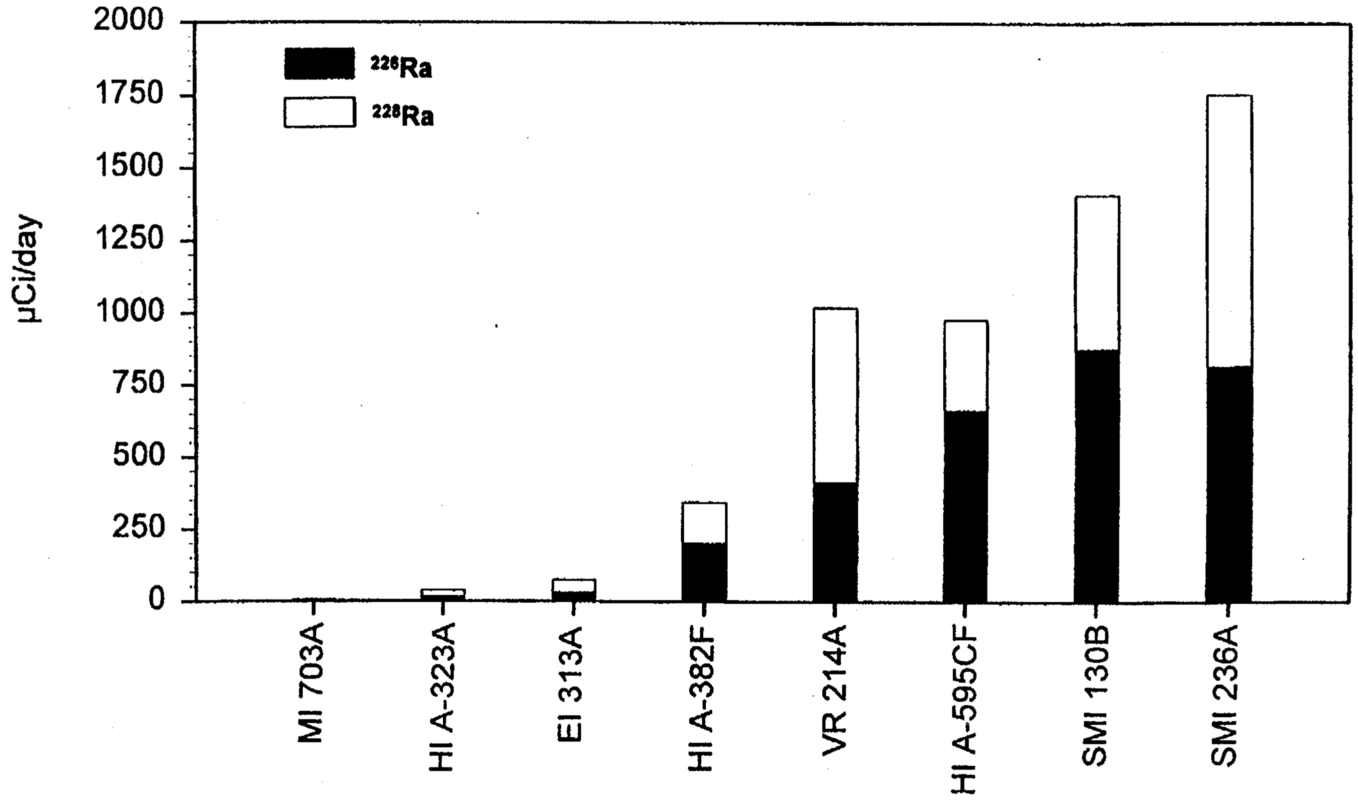


Figure 2.2. Radium loadings at Components 1 and 3 platform sites.

Component 2 sites were selected to be representative of ambient conditions in the central and western Gulf of Mexico. The original objective of Component 2 site selection was to identify potential sites that were located at least 15 km from any existing oil and gas structures discharging produced water. This was not possible in all cases and sites at least 10 km from discharging platforms were considered. Potential Component 2 sites were initially identified by examining recent navigational charts with existing oil and gas structures plotted. After a potential site was identified, MMS Public Records was contacted to obtain information pertaining to previous and existing oil and gas activities in the lease block where the potential site was located and in surrounding lease blocks. It was important that the site was distant from existing produced water discharges and also distant from previous drilling activities where drilling mud discharges could have altered the chemical composition of the sediments. A final evaluation of Component 2 sites was conducted on location using shipboard radar to verify the absence of oil and gas structures within the prescribed radius of the site (10 km). The Component 2 sites were in Galveston (GA) A-205, GA A-90, SMI 186/195, and West Cameron (WC) 448.

The geographic locations of the sites are presented in **Figure 2.3**. **Table 2.1** lists the latitudes/longitudes, water depths, produced water discharge rates (Components 1 and 3), and type of hydrocarbon production for the sites.

2.3 SAMPLING DESIGN

Table 2.2 presents a summary of data and samples that were designated for collection at each of the 14 sites. Produced water, produced sand, produced water discharge plume/receiving water, ambient seawater, sediment, interstitial water, and biological tissue samples were to be collected. **Table 2.2** lists the analyses that were to be performed on each sample type for each site. Radionuclides analytes were to include isotopes of radium (^{226}Ra and ^{228}Ra), lead (^{210}Pb), polonium (^{210}Po), and thorium (^{228}Th). Metals to be measured in the various sample matrices included arsenic, barium, cadmium, chromium, copper, iron, lead, manganese, mercury, molybdenum, nickel, vanadium, and zinc. Sediments (surficial and produced sand) were also to be analyzed for concentrations of aluminum and calcium. Hydrocarbon analytes included the volatile aromatic hydrocarbons (VAHs), saturated hydrocarbons (SHCs), and polycyclic aromatic hydrocarbons (PAHs) listed in **Table 2.3**.

2.3.1 Component 1

Produced water samples were to be collected at each of the Component 1 sites and analyzed for radionuclides, metals, hydrocarbons (VAHs, SHCs, and PAHs), and total organic carbon (TOC). Rhodamine WT dye was to be injected into the produced water discharge so that the discharge plume could be visually and flourometrically detected. Samples for radionuclides and VAHs were then to be collected to determine the dilution rate of the analytes within the plume. Ambient seawater samples were also designated for collection to determine background levels of radionuclides, metals, VAHs, PAHs, and TOC.

Produced sand was to be collected at each site for analysis of radionuclides, metals, SHCs, PAHs, and grain size.

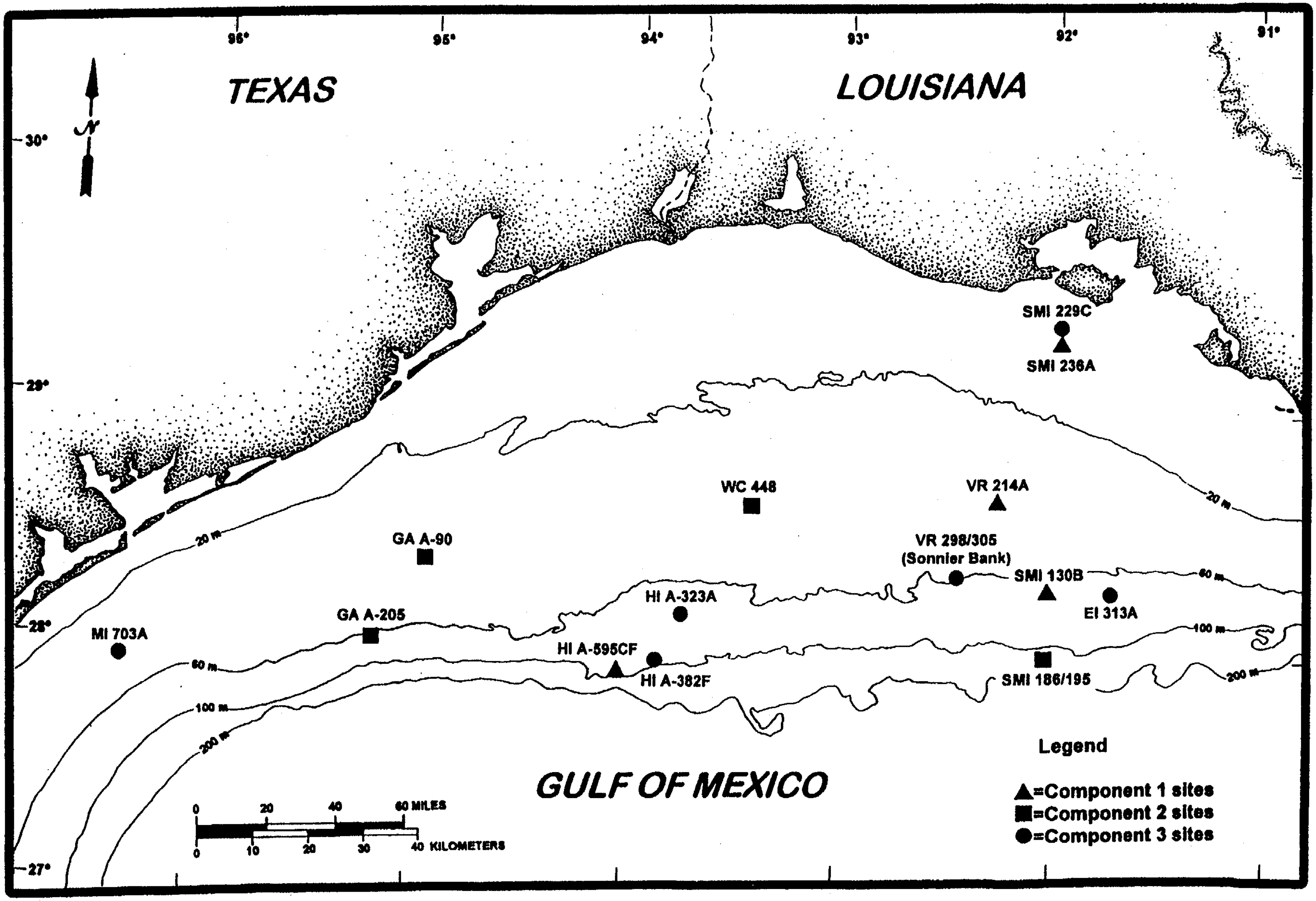


Figure 2.3. Geographic locations of the sites.

Table 2.1. Lease area and block designations, latitudes and longitudes, water depths, and produced water discharge rates of the selected sites.

Component	Lease Area and Block	Latitude/ Longitude	Water Depth (m)	Produced Water Discharge Rate (bbl/day)	Type of Hydrocarbon
Component 1	HI A-595CF	27° 52' 05" 93° 59' 30"	122	5,269	Oil/Gas
	SMI 130B	28° 17' 53" 92° 00' 43"	65	22,880	Oil/Gas
	SMI 236A	29° 20' 05" 92° 00' 44"	6	14,800	Oil/Gas
	VR 214A	28° 41' 50" 92° 15' 45"	39	8,500	Oil/Gas
Component 2	GA A-90	28° 20' 24" 94° 59' 00"	39	NA	
	GA A-205	28° 00' 05" 95° 14' 18"	66	NA	
	SMI 186/195	27° 59' 08" 92° 02' 53"	110	NA	
	WC 448	28° 36' 17" 93° 24' 58"	36	NA	
Component 3	EI 313A	28° 15' 27" 91° 46' 04"	72	883	Oil/Gas
	HI A-323A	28° 10' 03" 93° 46' 04"	72	621	Gas/Oil
	HI A-382F	27° 54' 48" 93° 56' 06"	104	8,818	Gas/Oil
	MI 703A	27° 53' 44" 96° 25' 41"	38	250	Gas/Oil
	SMI 229C	29° 20' 55" 91° 59' 19"	7	NA	
	VR 298/305 (Sonnier Bank)	28° 19' 51" 97° 27' 42"	25	NA	

Lease Areas:

EI - Eugene Island	SMI - South Marsh Island
GA - Galveston	VR - Vermilion
HI - High Island	WC - West Cameron
MI - Matagorda Island	

Table 2.2. Samples and data to be collected at each site.

SAMPLE TYPE	ANALYTE	STUDY SITES													
		Component 1				Component 2				Component 3					
		HI A-595CF	SMI 130B	SMI 236A	VR 214A	GA A-90	GA A-205	SMI 186/195	WC 448	EI 313A	HI A323A	HI A382F	MI 703A	SMI 229C	VR 298/305 (Sonnier Bank)
Produced Water	^{226}Ra, ^{228}Ra, ^{228}Th, ^{210}Po, ^{210}Pb	X	X	X	X					X	X	X	X		
	Metals	X	X	X	X										
	HCs	X	X	X	X										
	TOC	X	X	X	X					X	X	X	X		
Produced Sand	^{226}Ra, ^{228}Ra, ^{210}Pb	X	X	X	X										
	Metals	X	X	X	X										
	SHCs/PAHs	X	X	X	X										
	Grain Size	X	X	X	X										
Discharge Plume/Receiving Water	^{226}Ra, ^{228}Ra, ^{210}Pb	X	X	X	X										
	VAHs	X	X	X	X										
Ambient Seawater	^{226}Ra, ^{228}Ra, ^{210}Pb	X	X	X	X	X	X	X	X					X	X
	Metals	X	X	X	X	X	X	X	X						
	VAHs/PAHs	X	X	X	X	X	X	X	X						
	TOC	X	X	X	X	X	X	X	X					X	X
Sediment	^{226}Ra, ^{228}Ra, ^{210}Pb	X	X	X	X	X	X	X	X						
	Metals	X	X	X	X	X	X	X	X						
	SHCs/PAHs	X	X	X	X	X	X	X	X						
	Grain Size/TOC	X	X	X	X	X	X	X	X						
Interstitial Water	^{226}Ra, ^{228}Ra, ^{210}Pb	X	X	X	X										
Biological	^{226}Ra, ^{228}Ra, ^{210}Pb	X	X	X	X					X	X	X	X	X	X
	Metals	X	X	X	X										
	PAHs	X	X	X	X										
Hydrography (conductivity, temperature, dissolved oxygen, depth)		X	X	X	X										
Hydrography (dissolved oxygen, depth)													X	X	
Currents		X	X	X	X										

HCs = VAHs, SHCs (including total hydrocarbons), and PAHs.
PAHs = polycyclic aromatic hydrocarbons.
SHCs = saturated hydrocarbons (including THCs).
VAHs = volatile aromatic hydrocarbons.
TOC = total organic carbon.

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

VAHs	SHCs	PAHs
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

Sediment samples were to be collected at 25 stations with 24 stations distributed along four transects radiating from the point of produced water discharge and one station located at the discharge (**Figure 2.4**). Cores were to be taken to a depth of 20 cm, if possible, with levels of analytes to be initially determined from only the 0 to 2 cm sediment increment from each station. Levels of radionuclides were to be determined from single samples collected at 18 stations. At seven stations located on the down current transect, three replicate samples were to be collected at each station to provide estimates of the within-station variability for levels of radionuclides. Levels of metals, SHCs, and PAHs were to be determined in three samples collected at each of three stations located along the down current transect. Grain size and TOC were to be determined in single samples at each of the 25 stations. After review of the preliminary data for the 0 to 2 cm samples, deeper sediment increments from selected samples could be analyzed to determine the vertical distribution of selected analytes. Sediment cores were also to be collected at three stations (**Figure 2.4**), the interstitial water extracted from three sediment increments, and levels of radionuclides determined.

Collections were to be made and observations to be conducted of biological specimens at each Component 1 site. Specimens were to be collected from three biological assemblages (biofouling assemblage, benthic soft substrate assemblage, and platform and hardbottom associated fish assemblage) to determine the concentrations of radionuclides, metals, and PAHs in their tissues. Collection of tissues for radionuclides analyses were to be emphasized over metals and hydrocarbons. Sufficient amounts of tissues (individual specimens) were to be collected for analyses of radionuclides, metals, and hydrocarbons in a single species of bivalve mollusk, two crustaceans species (shrimp and crab), and two species of fish. Due to the expected small size of the candidate bivalve species and the large quantities of tissue necessary for analyses, it was anticipated that the collected individuals would be pooled at each site and one pooled sample analyzed per site. Five individual specimens of each target crustacean species were to be analyzed. Five individual specimens of each fish species were also to be analyzed. Various methods of collection (i.e., trawls, diver, and traps) and direct observations of specimens were to be conducted to assess the number of species of commercial and recreational value.

Water column profiles were to be performed at each site. For each profile, conductivity, temperature, dissolved oxygen, and depth was to be recorded from the sea surface to the seafloor (or a maximum water depth of 30 m) to characterize the water mass in the vicinity of the site. Vertical profiles of current speeds and directions were to be performed to provide data concerning changes in currents with depth. Continuous current meter data were also to be collected at a single depth during the occupation of each site.

2.3.2 Component 2

Ambient seawater and sediment samples were to be collected at each of the sites. The water samples were to be analyzed for radionuclides, metals, VAHs, PAHs, and TOC. The sediment samples were to be analyzed for radionuclides, metals, SHCs, PAHs, grain size, and TOC as listed in **Table 2.2**.

2.3.3 Component 3

Produced water samples were to be collected at four sites and analyzed for radionuclides and TOC as shown in **Table 2.2**. Tissue samples were also to be collected at these sites and analyzed for radionuclides, metals, and PAHs. Ambient seawater and tissue

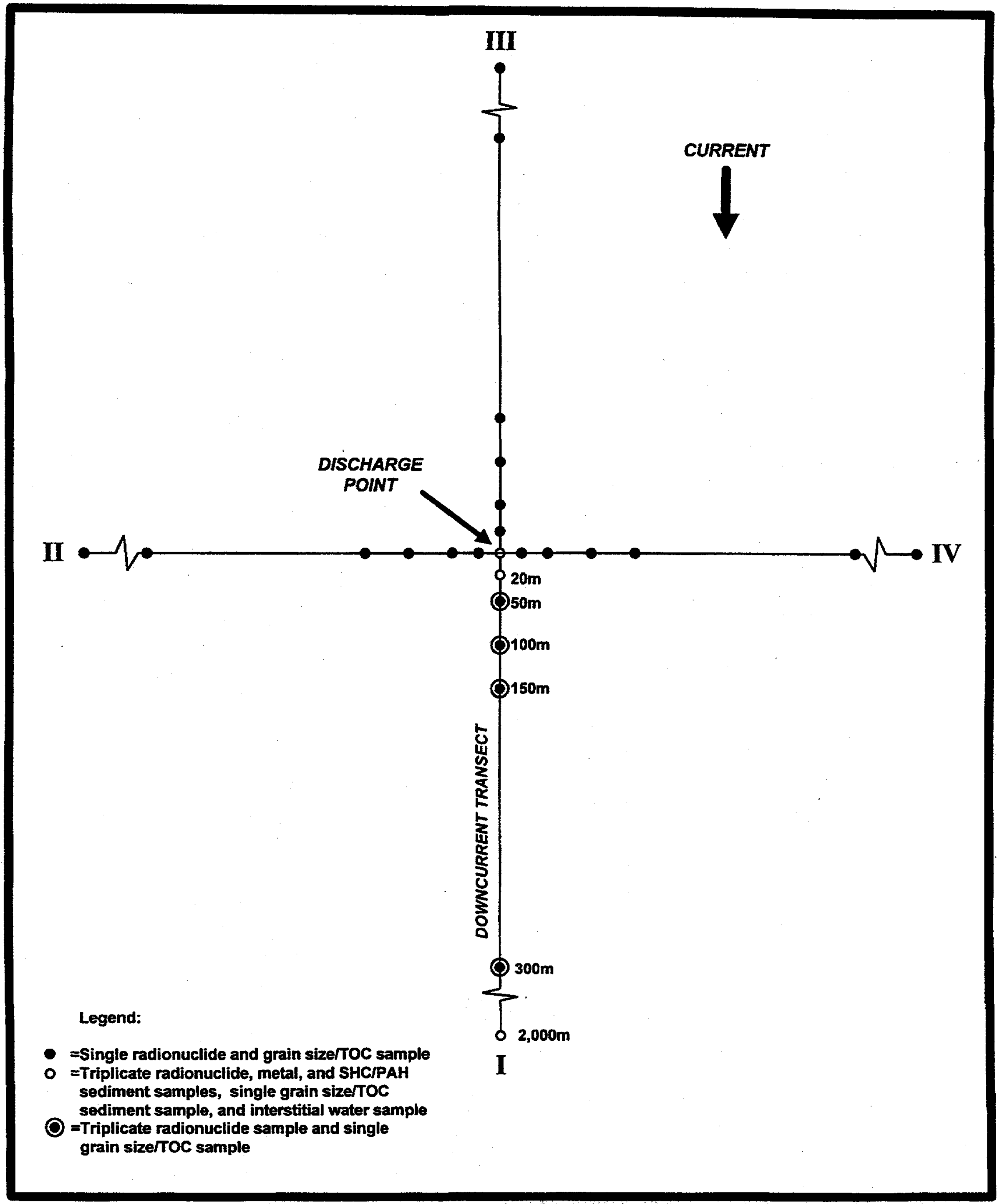


Figure 2.4. Sampling design for sediment and interstitial water sampling at Component 1 sites.

samples were to be collected at two additional sites. The water was to be analyzed for radionuclides and TOC and the tissues for radionuclides, metals, and PAHs. Dissolved oxygen profiles were to be made at sites shallower than 30 m. Specimens were to be collected from the same three biological assemblages sampled for Component 1.

2.4 QUALITY ASSURANCE PROGRAM

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 that was prepared as a draft document, reviewed by the SRC, and revised.

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 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 intended number of measurements.

The QA Program was developed and implemented with documented methods and procedures through the Sampling and Analysis Plan, 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 of relevant quality control (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 each field effort.

SOPs at each laboratory defined specific procedures for sample receipt, storage, and tracking. SOPs were also prepared for sample preparation and analysis. Samples were analyzed in batches along with 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. Data were reported in data packages that were reviewed by the Continental Shelf Associates, Inc. (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.

The 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 were the primary mode of reporting QA results to management.

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

Bruce Graham, David Snyder, and Luis Lagera, Jr.
Continental Shelf Associates, Inc.
Jupiter, Florida

3.1 FIELD METHODS AND LABORATORY SAMPLE PROCESSING

3.1.1 Field Survey Logistics

The offshore survey effort was conducted using two vessels. The M/V MR. OFFSHORE, a 145-ft utility/supply boat, was used from 4 to 29 June 1993 and the M/V WADE B, a 120-ft utility/supply boat, was employed between 29 June and 11 August 1993. Both vessels were equipped with sufficient freezer and cooler space for sample storage.

Navigation and long-range positioning were performed using a Global Positioning System (GPS) interfaced with a HYPACK Navigation System. GPS provided accuracies of ±15 m. A Measurement Devices Ltd, Lasertrak L5000 range/azimuth system installed and operated from Component 1 platforms was used for site-specific sediment, interstitial water, and ambient seawater station positioning and provided accuracies of ±1 m. The GPS receiver and Lasertrak system were interfaced to a computer for real-time shipboard tracking and positioning. Monitors placed on the ship's bridge and in the deck observation station were used to display the ship's position during operations. A calibrated line was used to accurately locate sediment/interstitial water stations that were under or very near the platform structure. A calibrated line was also used to accurately position produced water discharge plume/receiving water stations relative to the platform's produced water discharge location.

The Lasertrak system was only used during Component 1 site sampling. The Lasertrak system used the calculated geodetic position of the produced water discharge as a reference for determining range and bearing for selected stations within the survey area. Lasertrak system components included a laser rangefinder, theodolite, and a real-time data telemetry system. A technician on the platform tracked the vessel with a telescopic sight and real-time range and azimuth data were relayed, via telemetry, to the survey vessel at one second intervals. The navigation system enabled the survey team to pre-plot sediment, interstitial water, and ambient seawater stations and use the system for vessel guidance, data logging, and real time vessel track plotting via both a primary display on the navigator's computer and a secondary display monitor placed in front of the survey vessel's helmsman. On board the survey vessel, real-time range and azimuth data were converted to X and Y coordinates via an integrated navigation and data acquisition system. Navigation software was run by a battery-powered, portable, on-board computer. This system collected and printed the Lasertrak position data.

3.1.2 Water Sample Collection

3.1.2.1 Produced Water

Produced water samples were collected at Component 1 sites and at discharging (four of the six) Component 3 sites. Produced water samples collected at Component 1 sites were analyzed to determine levels of radionuclides, metals, hydrocarbons, and TOC. Produced water samples collected at Component 3 sites were analyzed to determine levels of radionuclides and TOC.

Produced water samples were collected six times at each Component 1 site during the field survey. Three replicate produced water samples (A,B, and C) were collected initially and single samples (D, E, F, G, and H) were collected five times at approximately 12-h intervals following the initial sampling. Following the field survey, platform operators collected three replicate produced water samples for determining levels of radionuclides at 1-month intervals for 5 months at Component 1 sites. Three replicate produced water samples were collected one time at discharging Component 3 sites during the field survey.

Produced water samples were collected directly from the platform in-line sampling spigot along the produced water discharge pipe. The in-line spigot was wiped clean of any loose particles using a lint-free laboratory towel. The spigot was turned on and the spigot line allowed to flush for approximately 1 minute prior to collecting water samples. Samples were collected directly into their respective storage containers. Separate sample containers were used for radionuclides, metals, VAHs, SHCs/PAHs, and TOC. The mouths of the sample containers did not contact the spigot during sample collection.

Produced water samples for determining levels of radionuclides were collected in 2-L pre-cleaned polyethylene bottles. The sample bottles were not completely filled with produced water; an air space was left for the addition of nitric acid (HNO_3) preservative. The partially filled sample bottles were capped, labeled, and placed in a plastic cooler with blue ice for transport to the survey vessel. On board the survey vessel, a plastic dropper bottle was used to add HNO_3 until the samples reached a pH ≤ 2. Following acidification, sample bottles were capped, custody seals were attached, and the bottles were placed in a refrigeration unit for storage at a temperature of approximately 4°C.

Platform operators were supplied with sampling kits and instructions for collecting produced water radionuclide samples at 1-month intervals for 5 months. Sample kits included 2-L pre-cleaned polyethylene bottles, each containing an appropriate amount of HNO_3 for sample preservation, an insulated cooler with form-fitted packing material, lint-free laboratory towels, sample and shipping labels, custody seals, and custody sheets. Operators collected produced water samples directly from the in-line spigot into the sample bottles, capped the sample bottles, attached custody seals, and placed the bottles in the insulated cooler. Samples were shipped in the insulated coolers to CSA. The pH of each sample was checked upon arrival at CSA to verify proper sample preservation.

Produced water samples for metals analyses were collected in 1-L pre-cleaned polyethylene bottles. Once the sample bottles were full, they were capped, labeled, and placed in a plastic cooler with blue ice for transport to the survey vessel. Duplicate samples for metal/analyses were collected to determine whether HNO_3 was necessary to preserve produced water samples. On board the survey vessel, HNO_3 was added to one of the duplicate samples until the pH was ≤ 2. HNO_3 was added to the samples 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 HNO_3 and the HNO_3 discarded to clean the volume tip and prevent possible contamination of the water samples. The volume tips were discarded following the preservation of the samples. The bottles of acidified and unacidified samples were capped, custody seals were attached, and the samples were stored at 4°C in a refrigeration unit. Based on the analytical results for acidified and unacidified duplicate produced water metal samples, it was determined it was not necessary to acidify in the field produced water samples for metals analyses provided the holding time did not exceed 7 days.

VAH samples were collected in triplicate; samples were collected in 40-mL pre-cleaned amber open top glass volatile organic analysis (VOA) vials with a teflon/silicone septa. All vials had a "Certificate of Analysis" for quality control of possible contaminant volatiles. Special precautions were taken when collecting VAH samples. The volume of produced water flowing from the spigot was reduced to prevent aeration of the sample and sample containers were completely filled to eliminate any air space. VAH samples were preserved immediately with hydrochloric acid (HCl) (approximately 37%) at a pH ≤2. A spare pre-cleaned VOA vial was used at each site to determine the amount of HCl to add to the VAH samples to reach a pH ≤2. The procedure for preservation of water samples to be analyzed for VAHs was as follows:

1) a spare VOA vial was filled with produced water;
2) HCl was added to the sample from a pre-cleaned teflon dropper bottle;
3) after each drop of HCl was added to the produced water, the pH of the water was determined with pH paper;
4) HCl was added and the pH determined until the water reached a pH ≤2;
5) after the amount of HCl needed to reach a pH ≤2 was determined for the test sample, it was assumed the same amount was sufficient for the actual sample and the proper amount of HCl was added to the VAH samples without introducing possible contamination from testing with pH paper; and
6) following acidification, the sample bottle was capped with the air space completely eliminated by applying pressure to the septa during closure, labeled, and placed in a plastic cooler with blue ice for transport to the survey vessel.

On board the survey vessel, a custody seal was attached to each of the VAH samples, and the samples were stored upside down at 4°C in a refrigeration unit.

SHC/PAH samples were collected in 2.5-L pre-cleaned amber glass jars with teflon-lined lids with inserts of purified aluminum foil. All jars had a "Certificate of Analysis" for quality control of possible organic contaminants. The sample jars were not completely filled with produced water to leave an air space for the addition of methylene chloride for preservation. The partially filled sample jars were capped, labeled, and placed in a plastic cooler with blue ice for transport to the survey vessel. On board the survey vessel, approximately 200 mL of laboratory-specified methylene chloride was added to the sample, the sample jars were capped, custody seals were attached, and the samples were stored at 4°C in a refrigeration unit.

TOC samples were collected in 20-mL pre-cleaned glass vials. The sample vials were not completely filled with produced water to leave an air space for expansion during freezing. The partially filled sample vials were capped, labeled, and placed in a plastic cooler with blue ice for transport to the survey vessel. On board the survey vessel, custody seals were attached to the vials and the samples were stored frozen.

3.1.2.2 Discharge Plume/Receiving Water

Discharge plume/receiving water samples were collected at Component 1 sites. Rhodamine WT dye was injected into the produced water just prior to overboard discharge from the platform which allowed the plume to be detected via visual and fluorometric methods. A calibrated and buoyed line attached to the produced water discharge pipe was deployed and held in position by a sub-surface parachute drogue. The positions of sampling stations along the discharge plume were marked by buoys attached to the calibrated line at five distances (5, 10, 30, 50, and 100 m) from the discharge. The center line of the discharge plume at each of the five sampling stations was determined by fluorometric measurement using a Turner Design flow-through fluorometer. Three replicate samples for radionuclide analyses were collected at each of the five distances in the plume. Discharge plume water samples for radionuclide analyses were collected from an inflatable rubber boat using an in-line water pump attached to the fluorometer. If the platform structure precluded sampling and use of the fluorometer from the inflatable rubber boat, a 5-L teflon-lined Go-Flo water bottle deployed from the platform "catwalk" into the visually detected plume was used to collect radionuclide samples at the 5 m distance. Three replicate VAH samples were collected at 5 and 100 m using a 5-L teflon-lined Go-Flo water bottle.

The sample containers and preservation methods were the same as those described for the produced water samples (**Section 3.1.2.1**).

3.1.2.3 Ambient Seawater

Ambient seawater samples were collected at three stations located ≥2,000 m from the produced water discharge at each Component 1 site. The stations were located on three of the four transects (**Figure 2.4**) that were most isolated from other oil and gas operations. Ambient seawater samples collected at Component 1 sites were analyzed to determine levels of radionuclides, metals, VAHs, PAHs, and TOC. Three replicate samples (A, B, and C) of ambient seawater for radionuclide analyses and single samples (A) of the other parameters were collected at each station.

Ambient seawater samples were collected at Components 2 and 3 (two non-discharging sites only) sites. Three replicate ambient seawater samples (A, B, and C) for radionuclides, metals, VAHs, PAHs, and TOC analyses were collected at each Component 2 site. Three replicate ambient seawater samples for radionuclides and TOC analyses were collected at the two reference Component 3 sites.

Ambient seawater samples were collected at a water depth of approximately 5 m using a clean 5-L teflon-lined Go-Flo water bottle suspended from ¼-in. braided dacron line and weighted with a lead anchor. Ambient seawater sampling was conducted from an inflatable rubber boat to avoid possible contamination from the survey vessel. Samples were collected directly from the water bottle into their respective storage containers. Separate storage/sample containers were used for radionuclides, metals, VAHs, PAHs, and TOC. Sample containers and preservation methods were the same as those described for the produced water samples (**Section 3.1.2.1**) with one exception. Ambient seawater samples for metals analyses were collected and stored in pre-cleaned 2-L polyethylene bottles instead of the 1-L bottles used for produced water because a larger sample quantity was needed.

3.1.3 Produced Sand Collection

Produced sand samples were collected at five locations as part of Component 1 sampling. Sampling locations included two of the four designated Component 1 sites (SMI 130B and SMI 236A). The two other Component 1 sites did not have an accumulation of produced sand. Three other sites [Eugene Island (EI) 189B and Ship Shoal (SS) 149 and 274C] were selected. Produced sand samples were analyzed to determine levels of radionuclides, metals, SHCs, PAHs, and grain size. For each sample parameter, three samples of produced sand were collected at SMI 130B and 236A, two samples at EI 189B and SS 274C, and one sample at SS 149. These samples were taken before treatment to remove free oil.

Produced sand samples from SMI 130B and 236A were collected (24 June and 12 September 1993, respectively) directly from a holding tank following their removal from the produced water discharge system. Samples from EI 189B and SS 274C were collected on 15 and 16 December 1993 from drums of produced sand that were stored on a platform in Mississippi Canyon Block 194. The compositing scheme for the produced sand samples collected from EI 189B and SS 274C is presented in **Figure 3.1**. Two storage drums of produced sand were sampled from each platform site (EI 189B and SS 274C). Three samples for each sample parameter were collected from each storage drum and the three samples were composited. The composite samples from each storage drum were used as replicate samples (A and B). The produced sand sample from SS 149 was collected in January and February 1994 from a small batch from nearly 2,000 barrels that were stored in Grand Chenier, Louisiana after removal from the wet and dry oil tanks on the SS 149 platform. The produced sand from EI 189B and SS 149 and 274C was used in an evaluation of produced sand treatment equipment (**Chapter 10**). This evaluation was added during conduct of the study.

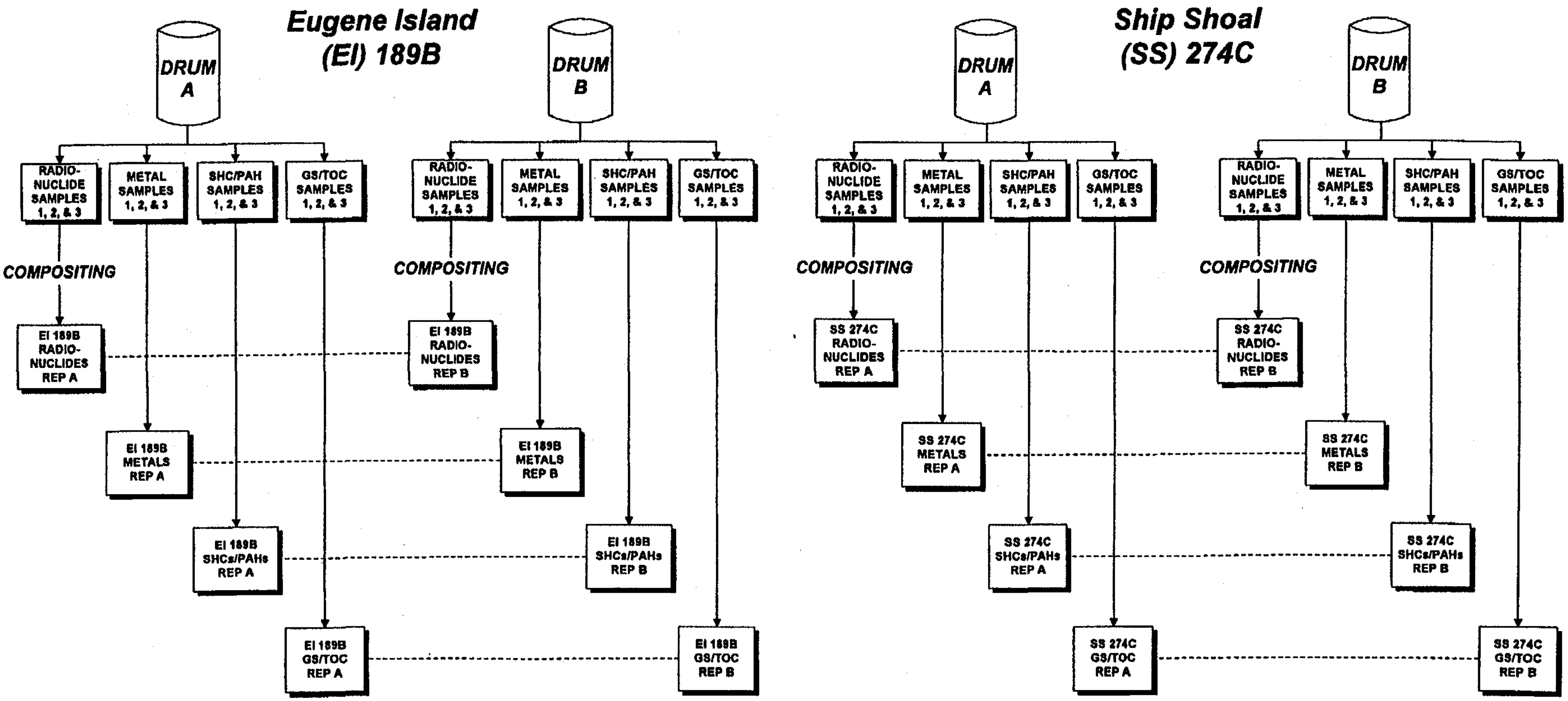
Produced sand samples were collected using a pre-cleaned teflon coated spatula. Separate sample containers were used for radionuclides, metals, SHCs/PAHs, and grain size. Radionuclide samples required approximately 200 g of produced sand and were stored in pre-cleaned 250-mL glass jars. Metal samples required approximately 50 g of produced sand and were stored in pre-cleaned 40-mL plastic or 60-mL glass jars. SHC/PAH samples required approximately 200 g of produced sand and were stored in pre-cleaned 250-mL glass jars. Grain size samples required approximately 200 g of produced sand and were stored in pint-size, sealable plastic bags. Sample containers were not completely filled with produced sand so that an air space was left for expansion. Samples jars were capped, custody seals were attached, and samples were stored frozen.

3.1.4 Sediment Samples

3.1.4.1 Sediment Chemistry

3.1.4.1.1 Field Collection

Sediment chemistry samples were collected at Components 1 and 2 sites. Samples were collected primarily with a stainless steel Gray O'Hara box core. Samples were also collected with a teflon-coated Van Veen grab or by divers with hand held cores when sediment conditions or physical obstructions precluded sufficient penetration by the box core. Samples were collected by divers only when the water depth was less than 33 m (100 ft).



SHCs/PAHs = Saturated hydrocarbons/polycyclic aromatic hydrocarbons
GS/TOC = Grain size/total organic carbon

Figure 3.1. Compositing scheme for produced sand samples collected from Eugene Island (EI 189B) and Ship Shoal (SS 274C) sites.

There were 25 sediment chemistry stations at each Component 1 site. One sediment chemistry station was located directly below the produced water discharge. Stations were located on four transects at distances of 20, 50, 100, 150, 300, and 2,000 m. The transect located along the predominant downcurrent direction relative to the produced water discharge was identified based on discussion with the platform operator. The four 2,000-m stations served as reference stations. Some minor deviations from pre-plotted station locations (**Figure 2.1**) were made in-field because of platform obstruction and/or difficulty in obtaining a sample due to anthropogenic debris. These deviations are noted in Chapter 4.

Single samples for radionuclide analyses were collected at 18 stations (**Figure 2.1**). Three samples for radionuclide analyses were collected at the station located at the discharge and at the six stations located on the downcurrent transect. Three samples for metals and SHC/PAH analyses were collected at the station located at the discharge and the 20 and 2,000-m stations along the downcurrent transect. Single discrete samples for grain size/TOC were collected at all stations except the three stations where samples were taken from one of the three metals and SHC/PAH samples. In addition, duplicate surficial sediment samples for grain size/TOC were collected at approximately 5% of the stations. Duplicate samples were collected by taking an additional core from the grab sample. The duplicate samples were analyzed separately to identify within-station variability for grain size and TOC. A 9.5-cm diameter acrylic tube was used to subcore the box core/grab or was used by divers as the primary sampling device. If possible, sediment cores were collected to a depth of 20 cm, with 4 cm being the minimal acceptable depth of penetration. Several attempts were made at each station to obtain a suitable sample (i.e., with sufficient sediment penetration). A single core was used to obtain each radionuclide sample. A single core was also used to obtain each discrete grain size/TOC sample. Two additional cores were used to provide sufficient sediment for metals and SHC/PAH samples. The grain size/TOC sample was also taken from the two cores collected for one of the three metals and SHC/PAH samples. Cores were capped and frozen until they were processed (**Section 3.1.4.1.2**) for laboratory analyses. All cores used to collect sediment for metals and SHC/PAH analyses had teflon-lined caps.

Three sediment samples for radionuclide, metal, and SHC/PAH analyses and a single sample for grain size/TOC analyses were collected at each Component 2 site. Methods for collection and storage of Component 2 site sediment samples were the same as those previously described for the Component 1 sites.

3.1.4.1.2 Laboratory Processing

The 0-2 cm sediment increment of the cores was processed in the laboratory prior to analyses. Sediment cores designated for radionuclide and grain size/TOC analyses were processed at CSA 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 subcore;
2) The top and bottom caps were removed and the core was secured on an inclined processing bracket;
3) The 0-2 cm sediment increment from the core was extruded using an appropriately sized plunger;

4) The increment was separated from the sediment core using a pre-cleaned stainless steel spatula;
5) Sediment was placed in a pre-cleaned glass bowl and homogenized with distilled water; and
6) Sediment was poured into a pre-cleaned 500-mL plastic jar.

Sample jars were labeled according to the sediment core designation (radionuclides or grain size/TOC) and stored frozen. Frozen samples were shipped to the University of South Alabama (Dr. Wayne Isphording's laboratory) and the remaining portion of the sediment cores were frozen and archived at CSA.

Frozen sediment cores designated for metals/SHC/PAH and metals/SHC/PAH/grain size/TOC analyses were sent to Arthur D. Little Inc. (ADL) for subsampling and processing prior to analyses. Sediment cores designated for either metals/SHC/PAH or metals/SHC/PAH/grain size/TOC analyses were processed 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 0-2 cm sediment increment from the core was extruded using an appropriately sized pre-cleaned teflon-coated plunger;
4) The increment was separated from the sediment core using a pre-cleaned stainless steel spatula;
5) The intact and partially frozen sediment increment was 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 increment and discarded; and
7) Remaining sediment was placed in pre-cleaned glass bowl, combined with other sediment from the same station, and homogenized.

The 0-2 cm sediment increment from the two cores collected at each station was combined and homogenized. The homogenized sediment was divided into aliquots and stored frozen prior to analyses. A pre-cleaned teflon spatula was used to put approximately 30 g of sediment for metals analyses in pre-cleaned 100-mL plastic jars, 100 g of sediment for SHC/PAH 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. The remaining portion of the sediment cores were frozen and archived.

3.1.4.2 Interstitial Water

3.1.4.2.1 Field Collection

Sediment samples for interstitial water extraction were collected at the station located at the discharge and the 20 and 2,000-m stations on the down current transect at each Component 1 site. Sediment for interstitial water extraction was collected in the same manner as described for sediment chemistry samples (see **Section 3.1.4.1.1**). Twelve sediment cores were needed to provide sufficient interstitial water for radionuclide analyses. Radionuclide levels were determined at three sediment depth intervals (0-2, 2-4, and 18-20 cm) in the sediment column. Identical sediment increments from each of the twelve cores were extruded using an appropriately sized plunger and were placed in a pre-cleaned 2-L glass holding jar. Samples of sediment for interstitial water extraction were stored at 4°C in a refrigeration unit while onboard and shipped to CSA.

3.1.4.2.2 Laboratory Extraction

Interstitial water was extracted at the CSA laboratory 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 the sediment during interstitial water extraction.

A diagram of the cylinder/piston unit used to hold the sediment during interstitial water extraction is presented in **Figure 3.2**. The cylinder/piston unit was comprised of a thick-walled polyvinyl chloride (PVC) cylinder and a PVC piston equipped with dual o-rings to provide an air-tight seal between the walls of the cylinder and the piston. 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 phosphate-free soap (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 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 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 interstitial size polycarbonate membrane was placed on top of the nylon reinforcement screen;
3) A 12.5-cm diameter ashless paper filter which covered the entire base of the cylinder was then 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 was placed in the cylinder on top of the sediment to be squeezed.

A diagram of the "squeezer" device is presented in **Figure 3.3**. The sediment-filled cylinder/piston unit was placed on a PVC stand which was then 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

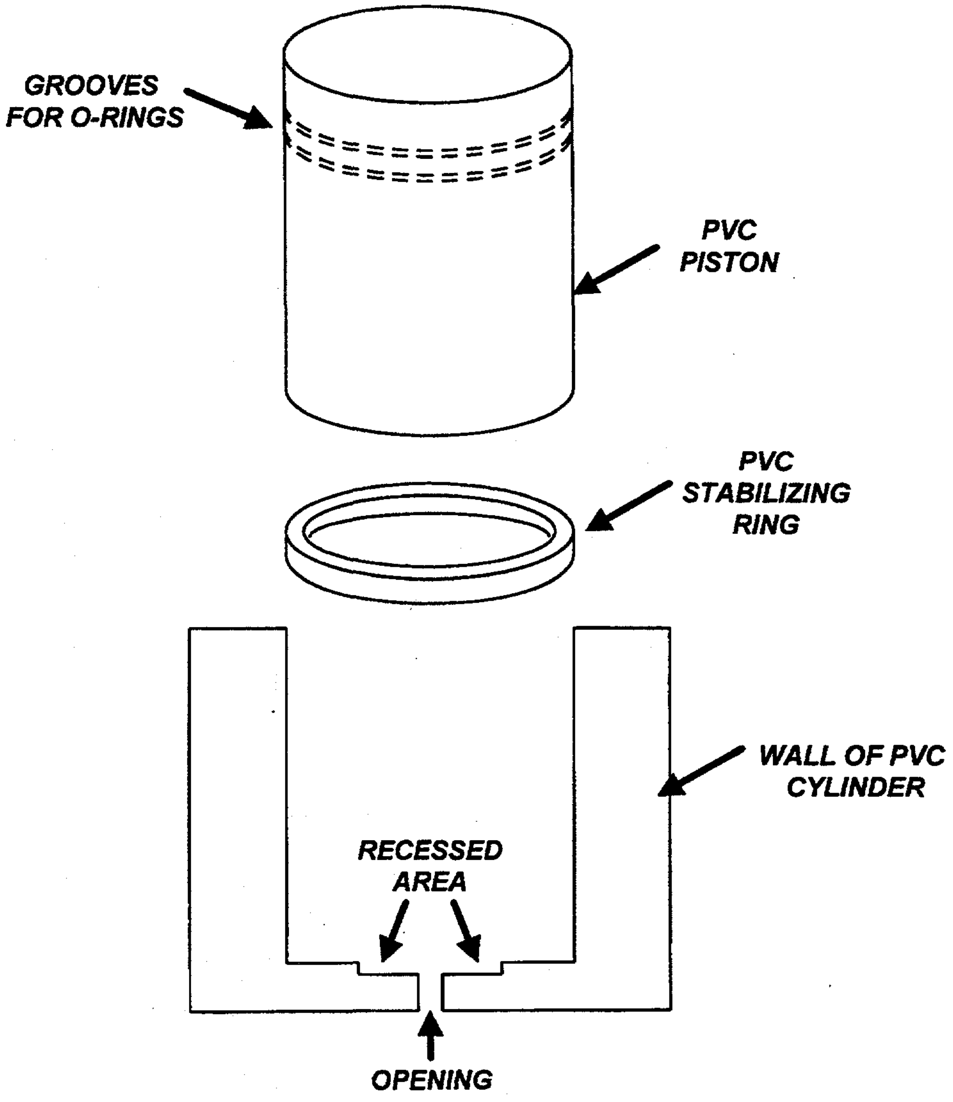


Figure 3.2. Cylinder/piston unit of the sediment interstitial water "squeezer."

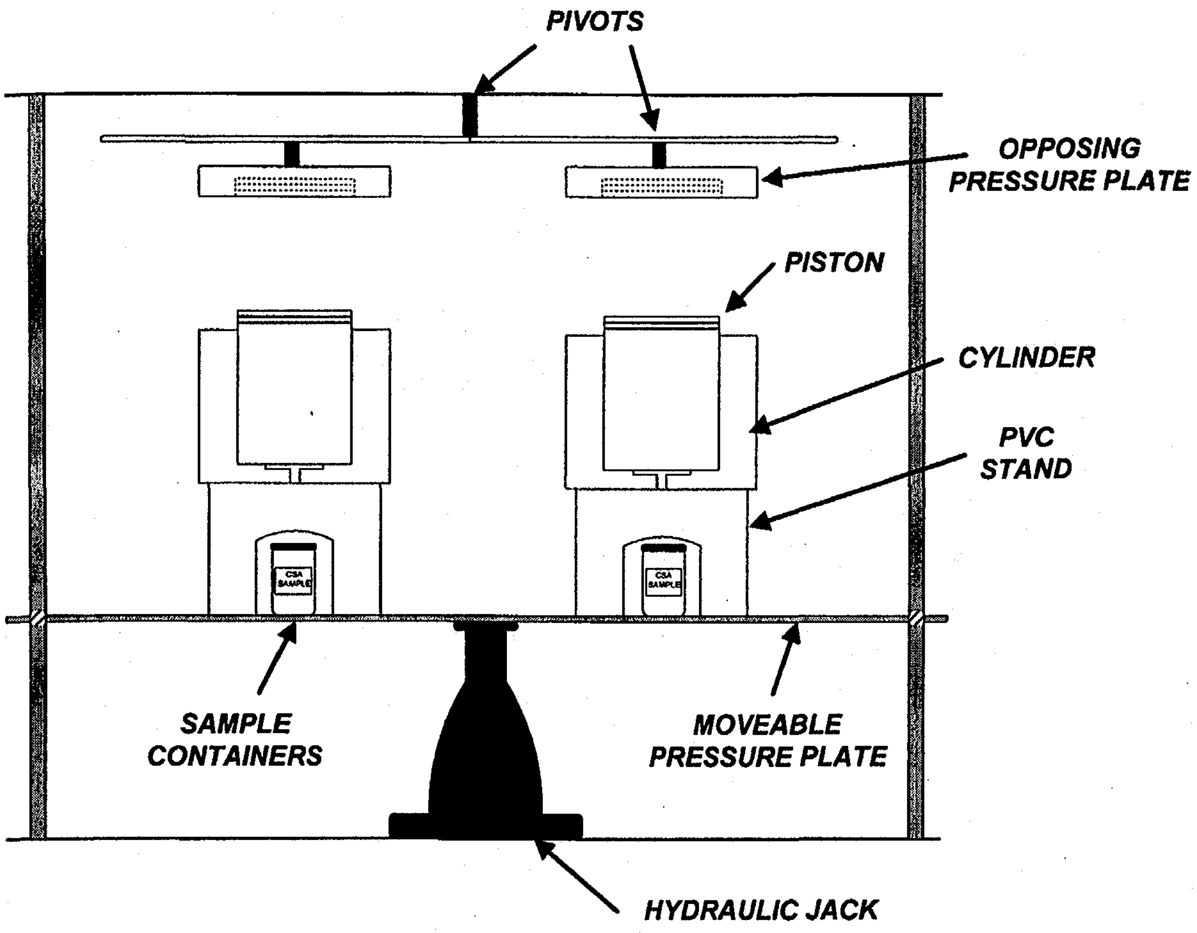


Figure 3.3. Diagram of "squeezer" device.

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 have potentially been contaminated with residue present in the opening. Extracted interstitial water was collected in a pre-cleaned 250-mL glass jar 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. A plastic dropper bottle was used to add HNO_3 to interstitial water samples until the samples were at a pH ≤ 2. Following acidification, the sample bottles were capped, custody seals attached, and placed in a refrigeration unit for storage at a temperature of approximately 4°C. Interstitial water samples for radionuclide analyses had a recommended holding time of 6 months and were shipped and analyzed prior to exceeding the holding time.

3.1.5 Biological Samples

3.1.5.1 Field Collection

Specimens for tissue analyses were collected at Components 1 and 3 sites. Biological samples collected at Component 1 sites were analyzed to determine levels of radionuclides, metals, and PAHs. Biological samples collected at Component 3 sites were analyzed to determine levels of radionuclides only. Insufficient bivalve mollusks were present at VR 298/305 (Sonnier Bank) for tissue collection. There were no other known hard bottom areas or non-discharging platforms in the central Gulf of Mexico that were 10 km from existing produced water discharges, had sufficient quantities of bivalve mollusks, and had either a portion of the hardbottom or platform in less than 30 m water depths. One platform was identified in HI A-389 in a water depth of 102 m that had a produced water discharge below a water depth of 90 m. Due to density differences between the produced water and seawater, the produced water is believed to remain near the depth of discharge and not affect bivalves collected on the upper 15 m of the platform. This platform was selected for collection of bivalves as a substitution of bivalve tissue from VR 298/305.

3.1.5.1.1 Biofouling Assemblage

A single sample of multiple bivalve specimens was collected for radionuclides, metals, and PAHs. Bivalve specimens were collected by divers from the platform-support and platform-associated structures (pilings) in water depths of less than 20 m and within a 100-m horizontal radius of the produced water discharge, if present. Divers collected bivalves by removing the whole specimen from the platform structure by use of a metal pry-bar. Specimens were taken intact to prevent incidental contamination during collection and subsequent processing. Once removed from the platform structure, specimens were placed in a nylon-mesh dive bag and brought to the vessel for processing. Bivalve specimens were placed in a clean glass sorting tray which was cleaned with Liquinox phosphate-free soap and seawater and rinsed with seawater. The extraneous biofouling material was removed from specimens prior to storage.

3.1.5.1.2 Benthic Soft Substrate Biological Assemblage

Up to five samples (A, B, C, D, and E) of various fish and crustacean taxa of the benthic soft substrate assemblage were collected for each sample parameter. Specimens were collected in close proximity (within 0.5 nmi) to the platforms using bottom trawls and traps. A "mongoose" style net with an 8 m head rope, 6 cm stretch mesh body, and 1 cm stretch mesh cod-end bag was used for trawling. Trawling time was approximately 30 min and once brought aboard, contents of the trawl were placed on a plywood sorting tray. Specimens retained for analyses were placed in clean plastic tubs during on-deck rough sorting. Fish and crab traps constructed of wire mesh with 3-cm opening and baited with dead fish were deployed on the bottom and marked with buoys. Traps soaked at least overnight before they were retrieved. Contents of the traps were emptied onto a plywood sorting tray, rough sorted, and stored frozen.

3.1.5.1.3 Platform and Hard Bottom Associated Fish Assemblage

Up to five tissue samples (A, B, C, D, and E) of various platform and hard bottom associated fish taxa were collected for each sample parameter. Specimens were caught by hook-and-line, fish trap, and spearing. Hook-and-line fishing was conducted from the survey vessel in close proximity to the platform. Fish caught by hook-and-line from the survey vessel had the hook removed and were immediately placed in a clean fish holding box until immobile. Fish traps constructed of wire mesh with 3-cm opening and baited with dead fish were deployed on the bottom and marked with buoys. Traps soaked at least overnight before they were retrieved. Contents of the traps were emptied onto a plywood sorting tray, rough sorted, and stored. Spearfishing with pole spears and spear guns was conducted by two-man dive teams. Spear shafts were equipped with stainless steel tips to reduce the possibility of tissue contamination. Fish caught by spearing were placed in a nylon dive bag, brought back to the vessel, then placed in the clean fish holding box until immobile.

3.1.5.1.4 Biota Available for Harvest

Observations concerning the availability of harvestable species (e.g., shrimp) were conducted concurrently with collection of biological samples for tissue analyses at Component 1 sites.

Harvestable biological species collected and/or observed within 1,000 m of the platform during sampling were identified. Specimens were collected by trawls, traps, hook-and-line, and spearfishing and observed during on-deck and diving operations. The proximity of collection/observation site of the specimen to the platform was noted, if possible.

3.1.5.2 Tissue Sample Storage and Shipping

Tissue samples for radionuclide and metals analyses were placed in separate, sealable, pre-labeled plastic bags and "double bagged." Samples for PAH analyses were placed in either a pre-cleaned glass jar with teflon-lined lids or triple wrapped in pre-cleaned aluminum foil, depending on size. Aluminum foil was cleaned with methylene-chloride. Labeled samples were stored frozen in chest freezers. All efforts were made to minimize time between collection and storage.

All tissue samples have unspecified holding times (Environmental Protection Agency [EPA], 1991) and were retained frozen in chest freezers on board until the vessel entered port. Frozen samples were transported by truck to CSA's laboratory for further processing. Sample shipments were conducted following personnel shift changes and the completion of the survey. Tissue samples were stored frozen in chest freezers at CSA prior to processing.

All tissue samples were stored frozen in chest freezers at CSA while decisions were made concerning which tissue sample were to be analyzed (see **Chapter 4**). Tissue samples were shipped frozen to the appropriate laboratory for processing and analyses.

3.1.5.3 Laboratory Processing

Mollusks, crustaceans, and fish specimens were collected to provide tissue samples for analyses of radionuclides, metals, and hydrocarbons (PAHs). Specimens were processed to provide the following tissue types:

- Soft tissue of bivalve mollusks;
- Edible flesh, carcasses, and whole specimens of crustaceans; and
- Edible flesh (i.e., fillet), carcasses, and whole specimens of fish.

Tissue sample processing was conducted at several laboratories, including CSA (radionuclides), Florida Institute of Technology (FIT) (metals), and ADL (hydrocarbons). The minimum required wet weight of tissue for radionuclide, metal, and PAH analyses was 100, 30, and 40 g, respectively. All processed tissue samples were stored frozen prior to analyses.

Mollusk soft tissues were removed and stored for analyses and the shell was discarded. The procedure for the removal of soft tissue was as follows:

1) The whole mollusk was thawed until the valves of the shell were partially separated;
2) The blade of a pre-cleaned stainless steel knife was inserted between the valves to cut the adductor muscles at their point of attachment on the dorsal valve; and
3) With the shell completely opened, the soft tissue was completely separated from the shell valves by cutting the adductor muscles at the point of attachment on the ventral valve.

The soft tissue of each specimen was weighed and recorded. Soft tissues from multiple individuals were composited to provide sufficient tissue for radionuclide and PAH analyses; the number of individuals per composite sample were recorded. Individual mollusk specimens provided sufficient soft tissue for metals analyses.

Crustacean tissue types included edible flesh, carcasses, and whole specimens. Edible flesh was removed from relatively large crabs and shrimp. Pre-cleaned stainless-steel instruments (e.g., scissors and forceps) were used to remove the edible tissue from the clawed chelipeds, walking/swimming legs, and peripheral body cavity of crabs and the tail (abdomen) of shrimp. The edible tissue of each crab specimen was weighed and recorded. Shrimp carcasses were processed for analyses and were comprised of the remaining portion of the shrimp following the removal of the edible tail flesh; crab carcasses were not processed for analyses. It was necessary to process whole specimens of crabs and shrimp from some sites because individuals were too small to efficiently remove the edible flesh. Edible tissue, carcasses, and whole specimens from multiple individuals were composited, by tissue type, to provide sufficient tissue for radionuclide and PAH analyses. Each composite sample replicate contained the same number of specimens with the number of specimens per composite sample replicate recorded. Individual specimens provided sufficient tissue for metals analyses.

Fish tissue types included edible flesh (i.e., fillets), carcasses, and whole specimens. The standard length and weight of each specimen was recorded prior to processing. A pre-cleaned stainless-steel knife with a flexible blade was used to remove the two lateral fillets from individual specimens. The fillet did not include skin with scales and bone. Filleting was conducted on a pre-cleaned glass or plastic cutting board. The weight of the two fillets from each specimen was recorded. Fish carcasses processed for analyses were comprised of the remaining portion of the fish following the removal of the fillets. It was necessary to process whole fish collected at some sites because individuals were too small for filleting. Edible tissue, carcasses, and whole specimens from multiple individuals were composited, by tissue type, to provide sufficient tissue for radionuclide and PAHs analyses. The number of individuals per composite sample was recorded. Individual specimens provided sufficient tissue for metals analyses.

3.1.6 Hydrographic and Current Data Collection

3.1.6.1 Hydrography

Hydrographic profiles for conductivity, temperature, dissolved oxygen, and depth were conducted at Component 1 sites to characterize the vertical structure of the water column. Profiles for dissolved oxygen and depth were conducted at Component 3 sites that were located in a water depth of less than 30 m (98 ft) to detect possible hypoxic conditions prior to tissue sample collections. Measurements for each parameter were recorded from the sea surface to the sea floor (or a maximum water depth of 30 m) at 5-m intervals. Profiles were conducted with a Hydrolab Surveyor III Water Quality Analyzer. An InterOcean Model S-4 electromagnetic current meter equipped with sensor probes also collected conductivity, temperature, and depth data concurrently with current profiles. These data were recorded to cross-check the Hydrolab data. Hydrographic profiles were conducted in close proximity (within approximately 2,000 m) to the study site.

3.1.6.2 Currents

Vertical profiles of current speed and direction were performed to provide data concerning changes in currents with depth and were conducted in conjunction with the hydrographic profiling previously described (see **Section 3.1.6.1**). Current measurements taken with an InterOcean Model S-4 electromagnetic current meter were collected at 5-m intervals from the sea surface to the seafloor (or a maximum water depth of 30 m).

Measurements for current speed and direction were collected continuously during sampling at each Component 1 site. Current data was collected using an InterOcean Model S-4 electromagnetic current meter and an Endeco Type 105 current meter was used as backup. The current meters were deployed on a taut-wire mooring array which was located upcurrent and in close proximity (within approximately 200 m) of the platform structure. The mooring array had a subsurface buoy positioned at a water depth of approximately 5 m to prevent the array from being hit by on-site vessel traffic. Current meters were positioned below the subsurface buoy at a water depth of approximately 6 m. The current meters and mooring array were deployed during the first day of site-specific operations and recovered when sampling was completed. Current meter data were transferred onto magnetic disk immediately after the recovery of each meter.

3.2 QUALITY ASSURANCE AND QUALITY CONTROL

A concern for data quality as it related to field sampling resulted in the incorporation of detailed sampling plans and comprehensive QA field checklists into the field sampling program. 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.

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

- Adherence of sample and data collection activities to SOPs;
- 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 CSA's project files including field notes, sample logs, and sample custody sheets.

3.2.1 Mobilization and Sample Collection

As a integral part of the mobilization phase of the field effort, the Task Manager met with the field team to review objectives, methods, and procedures to ensure that the study objectives would be met. An equipment and materials list and logistics plan was prepared and reviewed to ensure completeness, practicality, and workability. In the field, specific sample collection procedures for each matrix and sample type as prescribed in the Sample and Analysis Plan were observed. Particular attention was made to minimizing contamination of samples from vessel exhaust 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 (DQOs) 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.

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, CSA used a descriptive sample labeling protocol which identified the sample origin, matrix, and analysis parameter. 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. A Chain-of-Custody Record served 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.

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 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 3.1**.

Processed water samples to be analyzed for radionuclides, PAHs, and TOC were kept on board the survey vessel until samples could be shipped when the survey vessel reached the dock. These samples were shipped to the appropriate laboratory during weather delays, repairs, personnel shift changes, or demobilization. Water samples to be analyzed for metals and VAHs were shipped to the appropriate laboratory within one week of sample collection and were transported via helicopter to shore for shipping when necessary to meet a one-week time frame.

3.3 ACKNOWLEDGEMENTS

We would like to acknowledge the cooperation and assistance of participating oil and gas operators with special thanks to their field personnel. We would like to thank the field sampling team which included the authors (Bruce Graham and David Snyder) and the following personnel: Brock Stanaland, Lynwood Powell, Terry Stevens, Robert Berry, Norman Hammer, Frank Johnson, Richard Hanley, and Dr. Alan Hart. We would also like to thank the captains and crews of the MR. OFFSHORE and the WADE B.

Table 3.1. 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]
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
Grain Size	80 g	frozen	zip-loc plastic bag	Unspecified

Table 3.1. (Continued).

Matrix and Sample Type	Minimum Sample Volume	Preservative	Container	Holding Time
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]
Polycyclic Aromatic Hydrocarbons	40 g	frozen until extraction	pre-cleaned glass jars or triple-wrapped in CH3Cl-cleaned aluminium foil	Unspecified until extraction
Metals	30 g	frozen	double plastic bags	None

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

CHAPTER 4 - DESCRIPTION OF STUDY SITES

Bruce Graham
Continental Shelf Associates, Inc.
Jupiter, Florida

The description of the eight platform sites with produced water discharges and seven reference sites are presented in this section. The descriptions include the physical characteristics of the platforms and produced water discharges, the associated biological assemblages with emphasis on biota available for commercial and recreational harvest, and additional site-specific data. Site-specific deviations from the study design (see **Chapter 2**) are also presented.

A summary of biological taxa collected at each site and taxa selected for chemical analyses are presented in **Table 4.1**. Selection of taxa for analyses was based on the taxa being represented at multiple sites and important from an environmental risk and human health perspective. A preliminary list of selected taxa was reviewed with representatives of DOE, BNL, and several of the oil industry SRC members and a final list (**Table 4.1**) was developed. Although no tissue samples were collected at Component 3 sites specifically for metal analyses, extra samples were analyzed in some cases.

Hydrographic and current meter data collected during the study are not presented. These data may be used by BNL for produced water discharge plume modeling. Dissolved oxygen profiles did not indicate hypoxic conditions at any Components 1 and 3 sites located in a water depth of ≤30 m. Current speed and direction vertical profile data were determined to be unreliable and no moored current meter data were collected at SMI 236A as the meters were struck by a vessel and destroyed.

4.1 COMPONENT 1

The following site descriptions are presented alphabetically by area designation.

4.1.1 High Island A-595CF

HI A-595CF is an eight-pile platform located offshore of Texas in a water depth of approximately 122 m. The platform had been in place for 12 years at the time of the field survey. HI A-595CF is part of a two-platform structure. It is used for oil and gas production and discharges approximately 5,269 bbl/day of produced water. Produced water was discharged through a 15 cm diameter pipe at a water depth of 38 m below the sea surface.

The marine environment associated with HI A-595CF is characterized by clear water and a sand/mud substrate. The platform is located approximately 9 nmi west of the West Flower Garden Bank in the "Bluewater" zone as described by Gallaway and Lewbel (1982). The zones described by Gallaway and Lewbel (1982) are based on water depth and are characterized by distinct assemblages of biota (biofouling and ichthyofauna). The "Bluewater" zone is located in a water depth of greater than 60 m. The biofouling assemblage associated with the "Bluewater" zone is characterized by relatively low biomass and is dominated by algae, stalked barnacles, and bivalve mollusks (Gallaway and Lewbel, 1982). The ichthyofauna associated with the "Bluewater" zone is dominated by Caribbean reef forms (Gallaway *et al.*, 1981). The biofouling

Table 4.1. Biological samples collected at each site and samples selected for analyses.

Scientific Name	Common Name	STUDY SITES										
		Component 1				Component 3						
		HI A-595CF	SMI 130B	SMI 236A	VR 214A	EI 313A	HI A-323A	HI A-382F	HI A-389	MI 703A	SMI 229C	VR 298/305
INVERTEBRATES												
Arca zebra	turkey wing				x	x	x	x		x		
Barbatia spp.	ark	x	x		x	x	x	x		x		
Chama macerophylla	jewelbox	RMP	RMP		RMP	RM	RM	RM	RM	RM		
Crassostrea virginica	eastern oyster			RMP							RM	
Isognomon spp.	purse-oyster	x	x		x	x	x	x		x		
Pinctada imbricata	Atlantic pearl-oyster				x							
Spondylus americanus	thorny oyster	x	x					x				
Calappa sp.	box crab		x									
Callinectes spp.	blue crab			RMP	RMP					R	R	R
Hepatus sp.	calico box crab		x									
Libinia sp.	spider crab				x							
Menippe adina	stone crab			x							x	
Penaeidae	shrimp	x				x		x				x
Penaeus spp.	shrimp		R	RMP	x	R	R	R		R	R	R
Portunus spp.	swimming crab	x	RMP			R	R	R		R		R
Sicyonia brevirostris	rock shrimp		RP		RMP	R	x			x		R
Trachypenaeus sp.	roughneck shrimp				P					x		
FISH												
Arius felis	hardhead catfish			RMP							R	
Balistes capriscus	gray triggerfish	R	RMP		RMP	R	R	R		R		RM
Caranx crysos	blue runner						x					
Caulolatilus cyanops	blackline tilefish		x									
Centropristis spp.	sea bass	R	RP		R	R	R	R		R		R
Chaetodipterus faber	spadefish			x							x	
Cynoscion arenarius	sand seatrout					x						x
Cynoscion nebulosus	spotted seatrout			x							x	
Cynoscion nothus	silver seatrout			RMP							R	
Diplectrum bivittatum	dwarf sand perch				x							
Equetus umbrosus	cubbyu	x	x		x	x	x	x				x
Etrumeus teres	round herring				x							
Gymnachirus texae	fringed sole					x						
Hemanthias leptus	longtail bass	RP										
Lagodon rhomboides	pinfish	R	RP		R	R	R	R		R		
Leiostomus xanthurus	spot											x
Lutjanus campechanus	red snapper		RMP		RMP	R	R			R		RM

Table 4.1. (Continued).

Scientific Name	Common Name	STUDY SITES										
		Component 1				Component 3						
		HI A-595CF	SMI 130B	SMI 236A	VR 214A	EI 313A	HI A-323A	HI A-382F	HI A-389	MI 703A	SMI 229C	VR 298/305
Lutjanus synagris	lane snapper				R							
Micropogonias undulatus	Atlantic croaker		x	RMP							R	R
Mycteroperca phenax	scamp				x							
Orthopristis chrysoptera	pigfish			x							x	
Paralichthys spp.	flounder	x								R		
Peprilus burti	gulf butterfish		x	x	x	x						x
Pogonias cromis	black drum			R								
Priacanthus cruentatus	glasseye snapper					x						
Pristipomoides aquilonaris	wenchman	RP	x					R				R
Rhomboplites aurorubens	vermilion snapper	RMP	RM				R					
Sciaenops ocellatus	red drum			R								
Seriola dumerili	greater amberjack		R		R		R	R				
Sphyraena barracuda	great barracuda							R				
Stenotomus caprinus	longspine porgy	RMP	RMP		RP	R	R	R		x		R
Syacium spp.	dusky flounder				P							
Symphurus spp.	tonguefish			x							x	
Trachurus lathami	rough scad				x							
Trichiurus lepturus	Atlantic cutlassfish			RMP							R	
Trinectes maculatus	hogchoker			x							x	
Bothidae (multiple species)	lefteye flounder	P	x		x	x	x	x		x		x
Clupeidae	herring			x							x	
Haemulidae	grunts				R		R					R
Scorpaenidae	scorpionfish					x						
Serranidae	sea bass		x		x	x						
Synodontidae	lizardfish				x	x						
Triglidae	searobins		x			x						

Analyses:
X - collected, but not analyzed
R - radionuclides
M - metals
P - polycyclic aromatic hydrocarbons (PAHs)

Lease Area:
SMI 130 - South Marsh Island 130B
SMI 236 - South Marsh Island 236A
VR 214 - Vermilion 214A
EI 313 - Eugene Island 313A
HI 323 - High Island A-323A
HI 382 - High Island A-382F
HI 389 - High Island A-389
MI 703 - Mustang Island 703A
SMI 229 - South Marsh Island 229C
VR 298/305 - Vermilion 298/305; Sonnier Bank

assemblage associated with HI A-595CF covered a large percent of the available substrate with a relatively low biomass. The biofouling assemblage included numerous species of bivalves, none of which are commercially important. Gallaway *et al.* (1981) reported observing the commercially and recreationally important spiny lobster (*Panulirus argus*) on the platform support structure. No commercially important soft bottom-associated invertebrates were collected during this study. Commercially and recreationally important species as identified by Fischer (1978) of the demersal fish assemblage observed and/or caught during the field survey at HI A-595CF are presented in **Table 4.2**.

Deviations from the study design for HI A-595CF included in-field modifications concerning sediment sampling, insufficient biomass of invertebrate target species, and availability of produced sand. The platform structure precluded the collection of sediment samples at the exact locations for the 20-m stations along each transect and the 50-m station along the down current transect, so the stations were moved approximately 40 and 20 m, respectively, to avoid the obstructions. Sediment and interstitial water samples were not collected below the produced water discharge as metal plates for platform stabilization were present on the seafloor. Sufficient biomass of crustacean taxa were not available from the benthic soft bottom biological assemblage in the area of the platform. A total of 24 trawl samples were taken at HI A-595CF in the attempt to collect sufficient tissue sample biomass. Produced sand was not available at HI A-595CF.

4.1.2 South Marsh Island 130B

SMI 130B is an 8-pile platform located offshore of Louisiana in a water depth of approximately 65 m. The platform had been in place for 19 years at the time of the field survey. SMI 130B is part of a 3-platform structure used for oil and gas production and discharges approximately 22,880 bbl/day of produced water. Produced water was discharged from a 30 cm diameter pipe approximately 1 m above the sea surface.

The SMI 130B marine environment was characterized by clear water and a muddy sand bottom substrate. It is located at the boundary of the "Offshore" and "Bluewater" zones as described by Gallaway and Lewbel (1982). The "Offshore" zone is located in a water depth range of 30 to 60 m. The biofouling assemblage associated with the "Offshore" zone is dominated by bivalve mollusks and includes an abundant growth of octocorals and near-surface algae (Gallaway and Lewbel, 1982). The ichthyofauna associated with the "Offshore" zone is dominated by bluefish, spadefish, and mixed schools of moonfish and lookdowns (Gallaway and Lewbel, 1982). Other common ichthyofauna include blue runner, jacks, gray triggerfish, and snapper. Caribbean reef forms are neither diverse nor abundant in the "Offshore" zone (Gallaway and Lewbel, 1982). The biofouling assemblage associated with SMI 130B was representative of the "Offshore" assemblage. It included numerous species of bivalves and dense biotic coverage. Although the biofouling assemblage supported many species of bivalve mollusks, none of the species are commercially important. Juvenile stone crab (*Menippe adina*), which as an adult is commercially important and more closely associated with the bottom, was commonly observed within the dense biotic cover attached to the platform structure. Commercially important motile epifaunal invertebrates associated with the soft-bottom in the area of the platform included rock shrimp (*Sicyonia brevirostis*), penaeid shrimps (*Penaeus* spp.), and swimming crabs (*Portunus* spp.). No adult stone crab (*Menippe adina*) were collected during the field survey. The commercially and recreationally important species of the demersal fish assemblage observed and/or caught during the field survey at SMI 130B are presented in **Table 4.2**.

Table 4.2. Commercially and recreationally important species of the demersal fish assemblage observed and/or caught at Component 1 sites.

Scientific Name	Common Name	STUDY SITES			
		Component 1			
		HI A-595CF	SMI 130B	SMI 236A	VR 214A
Archosargus probatocephalus	sheepshead			x	
Balistes capriscus	gray triggerfish	x	x		x
Caranx crysos	blue runner				
Caranx latus	horse-eye jack	x	x		
Caulolatilus cyanops	blackline tilefish		x		
Centropristis spp.	sea bass	x	x		x
Cynoscion spp.	seatrout			x	
Elagatis bipinnulata	rainbow runner	x			
Epinephelus nigritus	warsaw grouper	x	x		
Epinephelus niveatus	snowy grouper	x	x		
Haemulon spp.	grunts				x
Lagodon rhomboides	pinfish	x	x		x
Leiostomus xanthurus	spot				
Lutjanus campechanus	red snapper		x		x
Lutjanus griseus	gray snapper				x
Lutjanus jocu	dog snapper		x		
Lutjanus synagris	lane snapper				x
Micropogonias undulatus	Atlantic croaker		x	x	
Mycteroperca phenax	scamp				x
Paralichthys spp.	flounder	x			
Peprilus burti	gulf butterfish		x	x	x
Pogonias cromis	black drum			x	
Rhomboplites aurorubens	vermilion snapper	x	x		
Sciaenops ocellatus	red drum			x	
Scomberomorus cavalla	king mackerel				x
Seriola dumerili	greater amberjack		x		x
Seriola rivoliana	almaco jack		x		
Sphyraena barracuda	great barracuda				
Thunnus atlanticus	blackfin tuna	x			
Clupeidae	herring			x	

It was necessary to make in-field modifications to the sampling design to facilitate the collection of complete data sets. A complete suite of sediment samples, with the exception of radionuclides, was collected at an additional 2,000-m reference station (along Transect IV, but designated as station V-2000) because the 2,000-m station along the down current transect (I) was located within 1,000 m of an adjacent platform. Sediment samples were not collected below the produced water discharge due to a platform obstruction nor closer than 30 m on any transect. Sediment interstitial water samples, proposed to be collected at the discharge location and 20-m station were collected approximately 50 m from the discharge location on both the down current transect and on Transect III. Anthropogenic debris on the seabed precluded the collection of interstitial water samples in closer than 50 m to the discharge along the down current transect.

4.1.3 South Marsh Island 236A

SMI 236A, an 8-pile platform, is part of a 2-platform complex which is located in the nearshore coastal environment of Louisiana in a water depth of approximately 6 m. The platform had been in place 10 years at the time of the field survey. SMI 236A is used for oil and gas production and discharges approximately 14,800 bbl/day of produced water. Produced water is discharged 1 m below the surface from a 15 cm diameter pipe.

The SMI 236A nearshore environment was characterized by murky, low salinity water, strong tidal currents, and a soft sediment substrate. The platform is in the "Coastal" zone (0 to 30 m) described by Gallaway and Lewbel (1982). The biofouling assemblage associated with the "Coastal" zone is typically dominated by one or more species of barnacle whose shells are covered by hydroids, bryozoans, and sponges (Gallaway and Lewbel, 1982). The ichthyofauna associated with the "Coastal" zone is dominated by sheepshead, spadefish, and schools of bluefish and blue runners (Gallaway and Lewbel, 1982). Vertical zonation of fishes is typically not observed at platforms in the "Coastal" zone (Gallaway and Lewbel, 1982). The commercially important Eastern oyster (*Crassostrea virginica*) was a common component of the biofouling assemblage at SMI 236A. Commercially important motile epifaunal invertebrates associated with the soft-bottom substrate in the area of the platform included penaeid shrimps (*Penaeus* spp.), blue crabs (*Callinectes* spp.), and the stone crab (*Menippe adina*). The commercially and recreationally important species of the demersal fish assemblage observed and/or caught during the field survey at SMI 236A are presented in **Table 4.2**.

4.1.4 Vermilion 214A

VR 214A is a 4-pile platform located offshore of Louisiana in a water depth of approximately 39 m. The platform had been in place for 18 years at the time of the field survey. VR 214A is used for oil and gas production and discharges approximately 8,500 bbl/day of produced water. Produced water was discharged approximately 1 m above the sea surface from a 15 cm diameter pipe.

The marine environment in the area of VR 214A was characterized by variable water clarity and a muddy substrate. The biological assemblages associated with the platform was similar to the "Offshore" assemblages described by Gallaway and Lewbel (1982). The biofouling assemblage observed in the upper 25 m of the water column at VR 214A had relatively dense coverage and was visually dominated by the octocoral *Carijoa riisei* and various species of bivalve mollusks. None of the bivalve species are commercially important. Juvenile stone crab (*Menippe adina*) was observed among the biofouling assemblage. No adults were observed or captured during the survey. Commercially important motile invertebrates collected in the area of the platform included rock shrimp (*Sicyonia brevirostis*), penaeid shrimps (*Penaeus* spp. and *Trachypenaeus* sp.), and blue crabs (*Callinectes* spp.). The commercially and recreationally important species of the demersal fish assemblage observed and/or caught during the field survey at VR 214A are presented in **Table 4.2**.

It was necessary to make in-field modifications to the sampling design at VR 214A. Sediment and interstitial water samples were not collected at the station directly below the produced water discharge because the platform had a shell-mud mat which precluded penetration of the box core. Produced sand was not available from VR 214A.

4.2 COMPONENT 2

Two of the non-platform reference sites (GA A-90 and GA A-205) were located offshore of Texas and two (SMI 186/195 and WC 448) were located offshore Louisiana. Both of the offshore Texas sites were located at a distance of greater than 10 nmi from other oil and gas platforms. The Louisiana platforms were located 9.2 (SMI 186/195) and 7.4 (WC 448) nmi from other oil and gas platforms.

4.3 COMPONENT 3

The sites included six platforms, four which discharged produced water near the surface (EI 313A, HI A-323A, HI A-382F, and MI 703A), one near-bottom discharging platform (HI A-389) used as a reference site for bivalve tissue samples, and a non-discharging platform (SMI 229C). A natural hardbottom bank feature (Vermilion 298/305, Sonnier Bank) also served as a reference site for collection of water and tissue samples.

4.3.1 Eugene Island 313A

EI 313A is located offshore of Louisiana in a water depth of approximately 72 m. EI 313A is used for oil and gas production and discharges approximately 833 bbl/day of produced water. The biological assemblages associated with the platform were similar to the "Bluewater" assemblages described by Gallaway and Lewbel (1982). The biofouling assemblage at EI 313A was characterized by broad coverage, relatively low biomass, and supported numerous species of bivalves, most confined to the upper 30 m of the platform substrate. The soft bottom-associated invertebrates included rock shrimp (*Sicyonia brevirostris*), swimming crabs (*Portunus* spp.), and penaeid shrimps (*Penaeus* spp.).

4.3.2 High Island A-323A

HI A-323A is an 8-pile platform located in a water depth of approximately 72 m. HI A-323A is used for oil and gas production and discharges approximately 621 bbl/day of produced water. The biological assemblages associated with the platform were similar to the "Bluewater" assemblages described by Gallaway and Lewbel (1982). The soft bottom-associated invertebrates included rock shrimp (*Sicyonia brevirostris*), swimming crabs (*Portunus* spp.), and penaeid shrimps (*Penaeus* spp.).

4.3.3 High Island A-382F

HI A-382F is an 8-pile platform located in a water depth of approximately 104 m. HI A-382F is used for oil and gas production and discharges approximately 8,818 bbl/day of produced water. The biological assemblages associated with the platform were similar to the "Bluewater" assemblages described by Gallaway and Lewbel (1982). The soft bottom-associated invertebrates included swimming crabs (*Portunus* spp.) and penaeid shrimps (*Penaeus* spp.). The observed ichthyofauna associated with the platform was relatively depauperate at the time of the field survey.

4.3.4 High Island A-389

HI A-389 is an 8-pile platform located in a water depth of approximately 102 m. The produced water is discharged at a water depth of approximately 92 m due to the proximity (<1 nmi) of the East Flower Garden Bank. The biological assemblages associated with the platform were similar to the "Bluewater" assemblages described by Gallaway and Lewbel (1982) with the exception that the biofouling assemblage exhibited dense coverage and high biomass. Biofouling tissue samples were collected in the upper 15 m and were considered not to be exposed to the discharged produced water.

4.3.5 Matagorda Island 703A

MI 703A is located offshore of Texas in a water depth of approximately 38 m. MI 703A has a produced water discharge rate of 250 bbl/day. The biological assemblages associated with the platform were similar to the "Offshore" assemblages described by Gallaway and Lewbel (1982). The soft bottom-associated invertebrates included blue crabs (*Callinectes* spp.), swimming crabs (*Portunus* spp.), rock shrimp (*Sicyonia brevirostris*), and penaeid shrimps (*Penaeus* spp. and *Trachypenaeus* sp.).

4.3.6 South Marsh Island 229C

SMI 229C, an 4-pile platform, is part of a 2-platform complex which is located in the nearshore coastal environment of Louisiana in a water depth of approximately 7 m. It is a non-discharging platform and had been in place 8 years at the time of the field survey. The platform is in the "Coastal" zone described by Gallaway and Lewbel (1982) and the platform-associated assemblages were similar to those described for SMI 236A (see **Section 4.1.1**). The soft bottom-associated invertebrates included blue crabs (*Callinectes* spp.) and penaeid shrimps (*Penaeus* spp.). Stone crabs (*Menippe adina*) were collected in traps.

4.3.7 Vermilion 298/305 (Sonnier Bank)

Sonnier Bank is located in Vermilion 298/305 in a water depth range of 18 to 61 m. The biological assemblages associated with the hardbottom formation were similar to those described by Putt *et al.* (1986) with macroepibiota dominated by fire corals and various species of sponge. Putt *et al.* (1986) identified 28 species of fish at Sonnier Bank. The surrounding soft bottom-associated invertebrates included swimming crabs (*Portunus* spp.), rock shrimp (*Sicyonia brevirostris*), penaeid shrimps (*Penaeus* spp.), and blue crabs (*Callinectes* spp.).

4.4 REFERENCES

Fischer, W. (ed.) 1978. FAO Species identification sheets for fishery purposes. Western Central Atlantic (fishing area 31). Volumes I-VII, FAO Rome, Italy.

Gallaway, B.J., M.F. Johnson, L.R. Martin, F.J. Margraf, G.S. Lewbel, R.L. Howard, and G.S. Boland. 1981. The artificial reef studies. Volume 2 in C.A. Bedinger, Jr., and L.Z. Kirby, eds. Ecological investigations of petroleum production platforms in the central Gulf of Mexico. SWRI Project 01-5245. Bureau of Land Management, New Orleans OCS, LA. 199 pp.

Gallaway, B.J. and G.S. Lewbel. 1982. The ecology of petroleum platforms in the northwest Gulf of Mexico: a community profile. U.S. Fish and Wildlife Services, Office of Biological Services, Washington, D.C. FWS/OBS-82/27. Bureau of Land Management, Gulf of Mexico OCS Regional Office, Open-File Report 82-03. XIV + 92 pp.

Putt, R.E., D.A. Gettleson, and N.W. Phillips. 1986. Fish assemblages and benthic biota associated with natural hard-bottom areas in the northwest Gulf of Mexico. Northeast Gulf Sciences 8(1):51-63.

CHAPTER 5 - SURFICIAL SEDIMENT GRAIN SIZE AND TOTAL ORGANIC CARBON CONTENT AND PRODUCED SAND GRAIN SIZE

Bruce Graham
Continental Shelf Associates, Inc.
Jupiter, Florida

5.1 INTRODUCTION

This chapter presents the results of the grain size and TOC analyses of surficial sediment samples and grain size analysis of produced sand samples. Surficial sediment grain size and TOC samples were collected at Components 1 and 2 sites. Produced sand grain size samples were collected at two of the four Component 1 sites. 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 heated and then washed with organic solvents to remove any heavy coating of hydrocarbons. Samples were then 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 analyses. 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 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-weighed 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.

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 (USA) 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 CSA 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 National Institute of Standards and Technology (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 quality control check of the hydrometer method was calibrated according to the manufacturer's specifications using glass spherule standards of known particle size (microspheres). The quality control 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 Surficial Sediments

5.3.1.1 Component 1

SMI 236A

The percentage of gravel, sand, silt, clay, and TOC for surficial (0-2 cm) sediment samples collected at SMI 236A are presented in **Table 5.1**. The surficial sediment composition in the area of SMI 236A is variable, but can best be characterized as muddy since 18 of the 23 stations sampled have sediments comprised of ≥50% mud (silt and clay components combined). The percentage of gravel ranges from 0 to 35.30 with only half of the stations having gravel present in the sediments. The grain size of the samples plotted on a ternary diagram is shown in **Figure 5.1(a)**. The percentage of TOC in the surficial sediments ranges from 0.79 at the discharge to 4.17 at the 300 m station along Transect IV. The grain size and TOC values of the duplicate samples (A and B) are similar.

VR 214A

The percentage of gravel, sand, silt and clay and TOC for surficial (0-2 cm) sediment samples collected at VR 214A are presented in **Table 5.2**. The surficial sediments in the area of VR 214A are best characterized as muddy with all stations outside of 100 m having sediments comprised of ≥50% mud (silt and clay components combined). All 20 and 50-m stations, except the 50-m stations along Transects I and IV (I-50 and IV-50) have sediments containing gravel. This is probably due to the shell mat which was placed on the sediments directly under the platform prior to the placement of the platform. Sediments at all 20 and 50-m stations are comprised of >70% sand. Grain size distribution for samples collected at VR 214A is shown in **Figure 5.1(b)**. The percentage of TOC in the surficial sediments ranges from 0.51 at the 2,000-m station along Transect I to 12.11 at the 20-m station along Transect II. Sediments with the highest TOC content are within 50 m of the produced water discharge location. The grain size and TOC of the duplicate sample (A and B) are similar.

HI A-595CF

The percentage of gravel, sand, silt, clay, and TOC for surficial (0-2 cm) sediment samples collected at HI A-595CF are presented in **Table 5.3**. The surficial sediments in the area of HI A-595CF are best characterized as sandy with 17 of the 24 stations having sediments comprised of ≥40% sand. Gravel is present at only 3 stations which were within 70 m of the discharge location. Grain size distribution for samples collected at HI A-595CF is shown in **Figure 5.1(c)**. Percentage of TOC ranged from 1.07 to 3.88.

SMI 130B

The percentage of gravel, sand, silt, clay, and TOC for surficial (0-2 cm) sediment samples collected at SMI 130B are presented in **Table 5.4**. The surficial sediments in the area of SMI 130B are highly variable. However, approximately half of the stations have sediments comprised of ≥50% mud (silt and clay components combined). The sediments along the primary

Table 5.1. Percentage of gravel, sand, silt, clay, and total organic carbon (TOC) for surficial (0-2 cm) sediment samples collected at SMI 236A. Sediment textural descriptions based on Folk's (1954) classification are presented.

Station [transect - distance (m)]	Gravel	Sand	Silt	Clay	TOC	Textural Description
Discharge	4.60	64.80	11.51	19.09	0.79	gravelly muddy sand
I-20	0.00	24.24	18.78	56.98	0.92	sandy clay
I-100	35.30	34.98	11.75	17.97	3.10	muddy sandy gravel
I-150	17.04	53.47	15.00	14.49	2.99	gravelly muddy sand
I-300	5.08	35.03	36.02	23.87	3.13	gravelly mud
I-2000	0.00	13.98	32.91	53.11	1.40	sandy mud
II-20	0.00	16.32	32.12	51.56	2.15	sandy mud
II-50 A	4.04	21.83	35.55	38.58	3.56	gravelly sandy mud
II-50 B	1.93	18.09	45.20	34.78	3.01	gravelly sandy mud
II-100	8.95	17.21	34.07	39.77	3.15	gravelly mud
II-150	3.28	24.59	29.73	42.40	3.12	gravelly sandy mud
II-300	0.00	16.98	39.04	43.98	3.61	sandy mud
II-2000	0.00	2.29	37.78	59.93	2.98	mud
III-20	0.00	25.85	28.90	45.25	2.94	sandy mud
III-50	0.00	26.91	28.09	45.00	3.67	sandy mud
III-100	0.00	35.98	23.87	40.15	3.12	sandy mud
III-150	0.00	1.07	29.83	69.10	3.18	clay
III-300	6.59	38.57	28.18	26.66	2.99	gravelly mud
III-2000 A	0.00	1.55	28.32	70.13	3.51	clay
III-2000 B	0.00	3.35	30.92	65.73	3.12	clay
IV-20	16.15	59.40	7.09	17.36	3.16	gravelly muddy sand
IV-50	12.79	10.63	33.01	43.57	2.09	gravelly mud
IV-100	9.12	17.62	36.35	36.91	2.12	gravelly mud
IV-150	0.00	3.19	36.04	60.77	2.98	mud
IV-300	11.77	42.19	21.45	24.59	4.17	gravelly mud

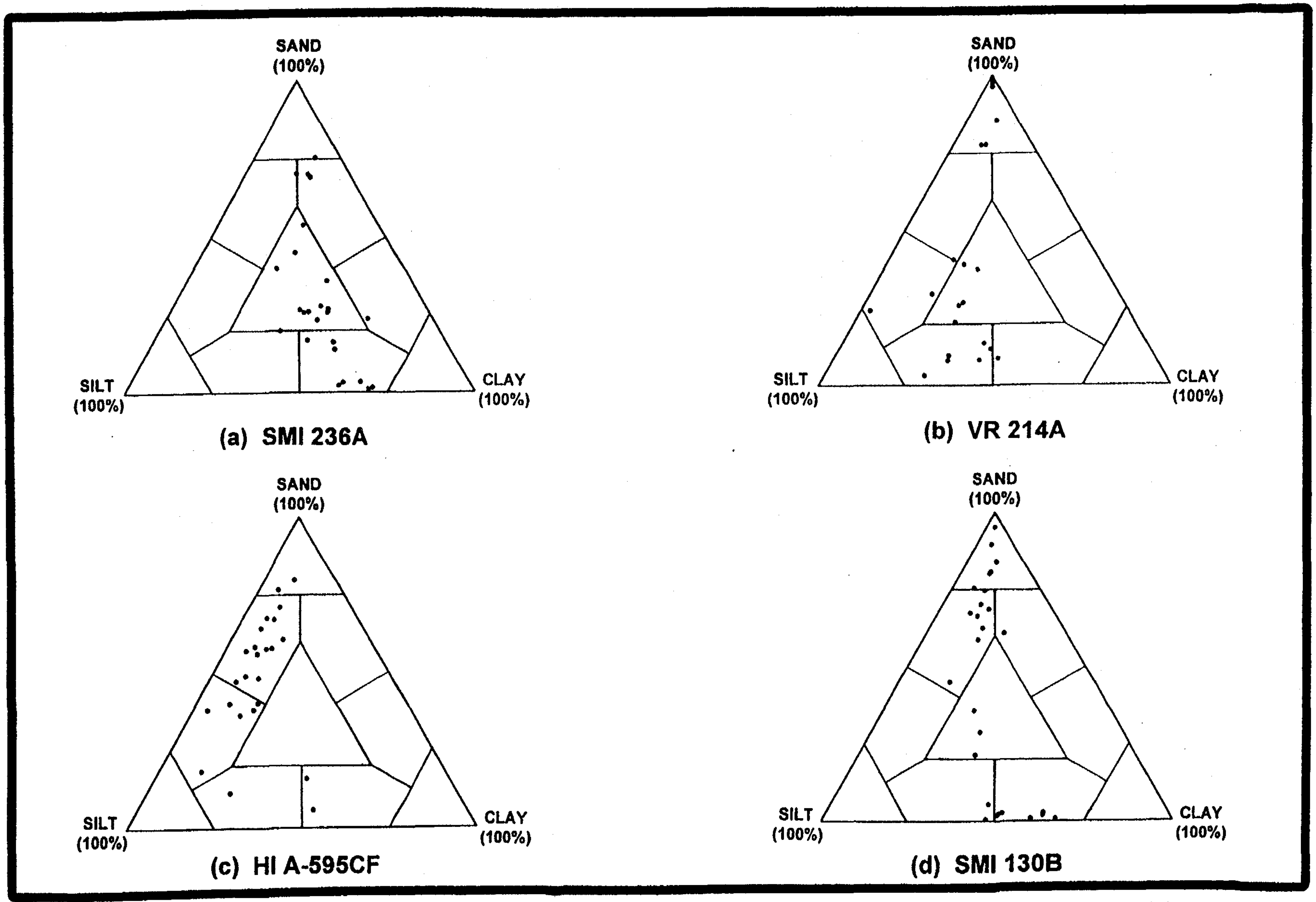


Figure 5.1. Ternary diagrams for surficial (0-2 cm) sediment grain size samples collected at Component 1 sites. Sediment textural descriptions are based on Shepard's (1954) classification. Sand sediment classification includes gravel component.

Table 5.2. Percentage of gravel, sand, silt, clay, and total organic carbon (TOC) for surficial (0-2 cm) sediment samples collected at VR 214A. Sediment textural descriptions based on Folk's (1954) classification are presented.

Station [transect-distance (m)]	Gravel	Sand	Silt	Clay	TOC	Textural Description
I-20	12.10	73.40	6.03	8.47	1.63	gravelly muddy sand
I-50	0.00	77.81	12.98	9.21	5.81	muddy sand
I-100 A	0.00	29.80	52.41	17.79	1.81	sandy silt
I-100 B	0.00	26.88	45.05	28.07	2.20	sandy mud
I-150	0.00	37.65	35.50	26.85	2.01	sandy mud
I-300	0.00	8.07	58.80	33.13	1.98	mud
I-2000	0.00	11.86	44.81	43.33	0.51	sandy mud
II-20	3.26	96.16	0.58[a]		12.11	gravelly sand
II-50	3.85	92.64	3.51[a]		7.18	gravelly sand
II-100	0.00	13.73	45.66	40.61	2.94	sandy mud
II-150	0.00	25.95	46.76	27.29	2.81	sandy mud
II-300	0.00	8.23	49.82	41.95	2.44	mud
II-2000	0.00	8.74	44.25	47.01	2.51	mud
III-20	11.76	85.96	2.28[a]		8.12	gravelly sand
III-50	10.12	88.99	0.89[a]		6.21	gravelly sand
III-100	0.00	96.35	3.65[a]		2.43	sand
III-150	0.00	40.88	40.62	18.50	2.77	sandy silt
III-300	0.00	19.46	58.22	22.32	2.15	sandy silt
III-2000	0.00	9.72	57.69	32.59	1.93	mud
IV-20	9.66	87.42	2.92[a]		7.18	gravelly sand
IV-50	0.00	77.72	14.28	8.00	4.91	muddy sand
IV-100	0.00	39.30	38.40	22.30	1.71	sandy mud
IV-150	0.00	20.58	50.45	28.97	2.38	sandy mud
IV-300	0.00	3.23	67.86	28.91	2.51	silt
IV-2000	0.00	5.77	48.51	45.72	2.38	mud

[a] Combined total for silt and clay components.

Table 5.3. Percentage of gravel, sand, silt, clay, and total organic carbon (TOC) for surficial (0-2 cm) sediment samples collected at HI A-595CF. Sediment textural descriptions based on Folk's (1954) classification are presented.

Station [transect-distance (m)]	Gravel	Sand	Silt	Clay	TOC	Textural Description
I-60	2.69	68.41	20.17	8.73	1.12	gravelly muddy sand
I-70	1.63	45.67	44.74	7.96	2.58	gravelly sandy mud
I-100	0.00	64.19	29.03	6.78	2.91	silty sand
I-150	0.00	40.17	50.15	9.68	3.75	sandy silt
I-300	0.00	11.28	64.76	23.96	3.88	sandy silt
I-2000	0.00	15.79	40.66	43.55	1.07	sandy mud
II-50	0.00	57.09	36.78	6.13	1.79	silty sand
II-50	0.00	18.38	69.38	12.24	1.99	sandy silt
II-100	0.00	48.96	41.06	9.98	2.68	sandy silt
II-150	0.00	57.81	29.21	12.98	2.22	silty sand
II-300	0.00	40.15	42.19	17.66	2.15	sandy silt
II-2000	0.00	5.71	43.77	50.52	2.59	mud
III-50	0.00	76.69	17.84	5.47	2.44	silty sand
III-50	2.37	57.36	32.18	8.09	2.46	gravelly muddy sand
III-100	0.00	57.74	30.78	11.48	2.63	silty sand
III-150	0.00	56.08	34.24	9.68	3.01	silty sand
III-300	0.00	79.84	11.68	8.48	2.73	muddy sand
III-2000	0.00	36.37	49.27	14.36	2.11	sandy silt
IV-50	0.00	38.18	57.63	4.19	1.61	sandy silt
IV-50	0.00	67.63	25.61	6.76	2.12	silty sand
IV-100	0.00	58.33	33.73	7.94	1.54	silty sand
IV-150	0.00	60.62	24.52	14.86	1.94	muddy sand
IV-300	0.00	38.02	44.61	17.37	2.50	sandy silt
IV-2000	0.00	48.24	37.86	13.90	2.75	sandy silt

Table 5.4. Percentage of gravel, sand, silt, clay, and total organic carbon (TOC) for surficial (0-2 cm) sediment samples collected at SMI 130B. Sediment textural descriptions based on Folk's (1954) classification are presented.

Station [transect-distance (m)]	Gravel	Sand	Silt	Clay	TOC	Textural Description
I-50	2.76	81.22	7.63	8.39	0.95	gravelly muddy sand
I-50	0.99	88.69	6.15	4.17	1.21	gravelly muddy sand
I-100	0.00	67.40	23.46	9.14	2.50	silty sand
I-150	0.00	70.22	18.94	10.84	1.41	muddy sand
I-300	0.00	1.82	48.56	49.62	1.97	mud
I-2000	0	1.91	35.79	62.3	1.59	mud
II-40	0.00	68.65	17.44	13.91	0.83	muddy sand
II-50	0.00	66.38	21.92	11.70	1.53	muddy sand
II-100	0.00	45.06	40.36	14.58	2.16	sandy silt
II-150	0.00	21.34	45.12	33.54	2.50	sandy mud
II-300 A	0.00	2.72	35.21	62.07	2.01	mud
II-300 B	0.00	2.60	46.65	50.75	1.99	mud
II-2000	0.00	2.30	47.85	49.85	1.89	mud
III-50	0.00	95.28	4.72[a]		0.70	sand
III-50	0.00	75.54	18.32	6.14	1.92	silty sand
III-100	5.74	55.10	17.07	22.09	1.83	gravelly muddy sand
III-150	0.00	28.68	40.07	31.25	1.54	sandy mud
III-300	0.00	5.33	49.16	45.51	1.74	mud
III-2000	0.00	0.87	39.61	59.52	1.97	mud
IV-30 A	0.00	80.19	11.56	8.25	2.91	muddy sand
IV-30 B	0.00	80.72	10.82	8.46	2.83	muddy sand
IV-50	0.00	74.71	15.68	9.61	2.14	muddy sand
IV-100	16.01	42.64	25.69	15.66	1.98	gravelly muddy sand
IV-150	0.00	35.79	38.32	25.89	2.18	sandy mud
IV-300	0.00	62.47	22.33	15.20	2.12	muddy sand
IV-2000	0.00	0.57	52.32	47.11	1.98	mud
V-2000	0	0.81	32.86	66.33	0.75	clay

[a] Combined total for silt and clay components.

transect (I) out to 150 m are predominantly sand as are sediments along the other transects out to 100 m. Gravel is present at only four stations. Sediments at all the 2,000-m stations are comprised of ≥97% fine particles (silt and clay). Grain size distribution for samples collected at SMI 130B is shown in **Figure 5.1(d)**. Percentage of TOC ranges from 0.70 to 2.91. The grain size and TOC of the duplicate samples (A and B) are similar.

5.3.1.2 Component 2

The percentage of gravel, sand, silt, clay, and TOC for surficial (0-2 cm) sediment samples collected at Component 2 sites are presented in **Table 5.5**. The two sites, WC 448 (36 m) and GA A-90 (39 m), with similar water depths are characterized as sandy mud based on Folk's (1954) classification. Overall, the sediment composition at the Component 2 sites are quite variable and should provide an adequate reference for comparing analytical results for sediment samples collected at Component 1 sites. Grain size distribution for samples collected at Component 2 sites is shown in **Figure 5.2**. Percentages of TOC are relatively low and range from 1.00 to 1.71.

Table 5.5. Percentage of gravel, sand, silt, clay, and total organic carbon (TOC) for surficial (0-2 cm) sediment samples collected at Component 2 sites. Sediment textural descriptions based on Folk's (1954) classification are presented.

Site	Gravel	Sand	Silt	Clay	TOC	Textural Description
WC 448	0.00	28.56	29.75	41.69	1.71	sandy mud
SMI 186/195	0.00	43.11	15.11	41.78	1.00	sandy clay
GA A-205	0.81	62.00	13.52	23.65	1.09	gravelly muddy sand
GA A-90	0.00	47.78	20.46	31.76	1.21	sandy mud

5.3.2 Produced Sand

The percentage of sand, silt, and clay for produced sand samples collected at SMI 130B and SMI 236A are presented in **Table 5.6**. The samples from both sites are predominantly sand with approximately 20% fine particles (silt and clay). Produced sand settles out in the oil/water separator, but the majority of fine particles probably remain in suspension and are discharged in the produced water.

5.4 ACKNOWLEDGEMENTS

Dr. Wayne Isphording was responsible for conducting the grain size and TOC analyses. Wayne put forth a diligent effort in specially treating the produced sand samples in order to conduct the grain size analysis.

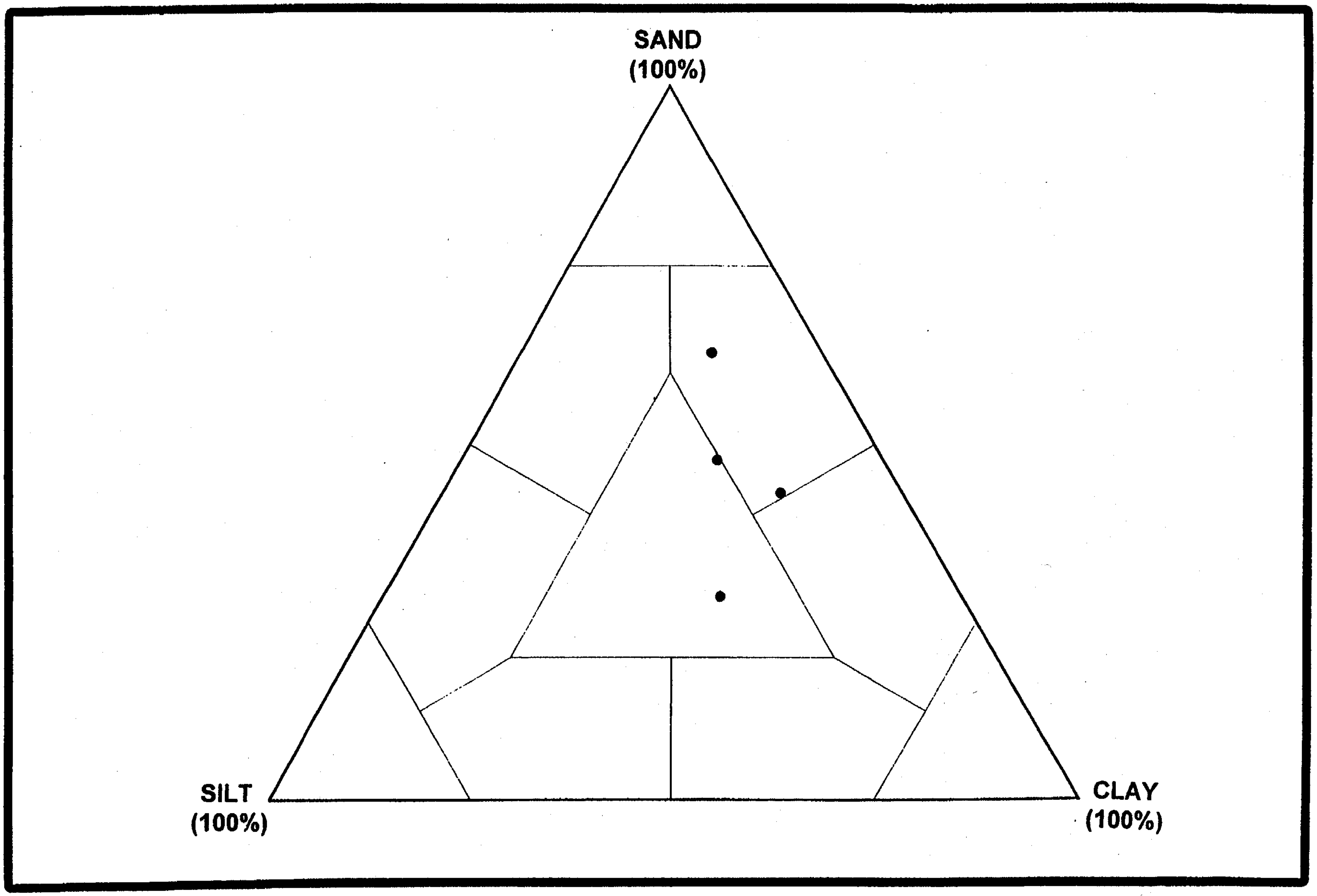


Figure 5.2. Ternary diagrams for surficial (0-2 cm) sediment grain size samples collected at Component 2 sites. Sediment textural descriptions are based on Shepard's (1954) classification. Sand sediment classification includes gravel component.

Table 5.6. Percentage (mean ± 1 standard deviation) of sand, silt, and clay for produced sand samples collected at Component 1 sites (n=3). Sediment textural descriptions based on Folk's (1954) classification are presented.

Sediment Component	Site	
	SMI 130B	SMI 236A
Sand	81.33 ± 1.74	79.48 ± 5.69
Silt	7.84 ± 1.36	20.52 ± 5.69[a]
Clay	10.96 ± 0.54	
Textural Description	muddy sand	muddy sand

[a] Combined total for silt and clay components.

CHAPTER 6 - RADIONUCLIDES IN OIL AND GAS OPERATIONAL DISCHARGES AND ENVIRONMENTAL SAMPLES ASSOCIATED WITH OFFSHORE OIL AND GAS PRODUCTION FACILITIES

Luis Lagera, Jr., Alan Hart, and Bruce Graham
Continental Shelf Associates, Inc.
Jupiter, Florida

6.1 INTRODUCTION

Produced water is commonly discharged from platforms located on the outer continental shelf of the Gulf of Mexico during production of oil and gas. Gulf of Mexico produced waters characteristically have elevated salinities and often contain elevated concentrations of inorganic and organic constituents compared to the receiving ambient seawater. Among the constituents of some Gulf of Mexico produced waters are radionuclides. Produced sand, which also contains radionuclides, was also commonly discharged prior to January 1994. There is a potential for marine organisms living around produced water discharges to bioaccumulate radionuclides.

The objective of this portion of the study was to gather data on the levels of selected radionuclides in produced water, produced sand, ambient seawater, sediment, interstitial water, and tissues of selected organisms. Radionuclide data collected during this study are being used by Brookhaven National Laboratory (BNL) in an environmental and human-health risk assessments of radionuclides from produced water discharges.

The primary focus of this chapter is to report levels of selected radionuclides (^{226}Ra, ^{228}Ra, and ^{210}Pb) in produced water, produced sand, ambient seawater, discharge plume/receiving water, sediment, interstitial water, and biological tissue samples collected from and in the vicinity of Gulf of Mexico discharging platforms (Components 1 and 3 sites) and reference sites (Components 2 and 3 sites). In addition, ^{228}Th and ^{210}Po levels were determined in the produced water samples.

Laboratory methods and QA issues specific to analyses for radionuclides are described in this chapter. Results and a brief discussion of the radionuclide analyses are also presented. The data show very clearcut differences between radionuclide activities in produced waters and ambient seawater, and very low radionuclide levels were found in almost all tissue samples.

Sampling was conducted at 15 sites classified into Component 1 discharging sites (4), Component 3 discharging sites (4), and non-discharging reference sites (2), and Component 2 reference sites (4). A supplemental site was also included as a reference site where bivalve collections were made. As described in detail in **Chapters 2** and **4**, the study sites were distributed over a range of water depths and oceanographic conditions (**Table 2.1**).

6.2 LABORATORY METHODS

6.2.1 Sample Preparation

6.2.1.1 Produced Water, Ambient Seawater, Discharge Plume/Receiving Water, and Interstitial Water Samples

Upon delivery at the Core Laboratories, Inc. laboratory in Casper, Wyoming, all water samples were logged in and held in cold storage until specific analysis instructions and authorizations were received by the laboratory. One liter of unfiltered water was used for each analysis of radionuclide activities.

6.2.1.2 Produced Sand and Sediment Samples

The produced sand and sediment samples were received and stored frozen until analysis. The samples were dried and weighed. The produced sand samples were then analyzed following the procedures similar to those used for water samples as described in **Section 6.2.2**. Whole sediment samples were analyzed by gamma spectroscopy.

6.2.1.3 Tissue Samples

Biological tissue samples (bivalve tissues, fish fillets, shrimp tails, and crab muscle tissues) were received and stored frozen until analysis. Each sample was thoroughly homogenized and then dissolved in concentrated HNO_3. The resulting 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 HNO_3, then HNO_3-H_2O_2, and finally HNO_3-$HClO_4$-HF digestion. After a Na_2SO_4 fusion to complete the destruction of the organic material, the samples were analyzed following the procedures in **Section 6.2.2.**

6.2.2 Radium-226 and 228 Analysis

Preparation of samples for radionuclide analyses was 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).

With the exception of the sediment samples which were analyzed using gamma spectrometry, ^{226}Ra and ^{228}Ra activities in produced water, ambient seawater, discharge plume/receiving water, interstitial water, produced sand, and tissues were determined using alpha and beta low background proportional counters. A new procedure was developed and employed in order to achieve low detection limits for the radium isotopes in ambient seawater and tissue samples and to reduce the error range of the numbers generated at these lower detection limits. The basic premise of the method was to increase the efficiency in counting of both ^{226}Ra and ^{228}Ra. Both of these isotopes decay to shorter lived alpha and beta emitters, and the classic methodologies often utilize these higher specific activity isotopes to identify and quantify the parent isotopes. In the past, it has been difficult to separate the many different decay products and identify them relative to the parent responsible for their production. In this method, the approach to this problem was simplified by making an assumption that at low levels of activity there would be a relatively constant contribution from both ^{226}Ra and ^{228}Ra if the materials were allowed to reach equilibrium. This assumption was tested by running a series of low level standards for ^{226}Ra and ^{228}Ra separately and combined. A very accurate estimate of percentage contribution to both alpha and beta was developed when the samples were allowed to equilibrate for 3 weeks.

This approach allowed the ^{228}Ra activity to be estimated utilizing an unlimited counting time without the need to consider the ^{228}Ac (6 h half-life) decay product. The classic method utilizes the isolation of this decay product and immediate counting. The rate of decay is so rapid that extended counting times are not feasible. The results of these calibration experiments demonstrated that there is a very constant contribution of decay products from each isotope at low activity levels.

Following the initial preparation previously described, all radium samples were analyzed identically using this method. A $PbSO_4$ precipitation was performed by the addition of $Pb(NO_3)_2$ to a solution that contained a high concentration of sulfate. This precipitate was dissolved in diethylenetriaminepentaacetic acid (DTPA) and the radium was coprecipitated with $BaSO_4$. The resulting barium precipitate was isolated on a planchet, and the planchet was set aside for a 3-week period to allow the in-growth and equilibration of the decay products from both ^{226}Ra and ^{228}Ra on the same planchet. A Berthold LB-7702 10 Detector Low-Background Gas Flow Proportional Counter was used for counting alpha and beta activity in the samples. The samples were counted for up to 600 min and the activity of the ^{226}Ra and ^{228}Ra determined by a calibration curve, which was developed by utilizing low level standards. The resulting data demonstrated much lower detection limits, as well as reduced uncertainty in the counting error. Radionuclide activity in produced water, ambient seawater, and interstitial water samples are expressed in pCi/L while tissues are in pCi/g wet weight.

Sediment samples were analyzed for ^{226}Ra and ^{228}Ra activity using 2-channel high-purity germanium co-axial detector gamma spectroscopy systems (GEM or GMX series). Experience has shown that radionuclide activities determined by both instruments (proportional counters and gamma spectrometer) are generally comparable. Radionuclide activity in sediment and produced sand samples are expressed as pCi/g on a dry weight basis.

6.2.3 Lead-210 Analysis

Following methods modified from Percival and Martin (1974), ^{210}Pb was determined by purification of the $PbSO_4$ precipitate (which contains the radium, lead, and thorium isotopes) through a series of precipitations and then isolated and counted by low background liquid scintillation analysis. After dissolution in DTPA, the radium isotopes were extracted from the $PbSO_4$ through $BaSO_4$ precipitation and the remaining thorium and lead isotopes were then re-precipitated as $PbSO_4$. The sulfate ion was removed via ammonium acetate and sodium carbonate double precipitation and the $PbCO_3$ precipitate was dissolved in acetic acid, added to a cocktail solution and counted using a Packard Instruments Corporation 2260 XL Low Background Liquid Scintillation Counting System. The method is specific for ^{210}Pb which is a low energy beta emitter. All sample batches were analyzed with the required QC samples according to SOP.

6.2.4 Thorium-228 Analysis

The analytical method for ^{228}Th, an alpha emitter, is also based on the sequential precipitation method for radium, thorium, and actinium described in **Section 6.2.3** (Percival and Martin, 1974). The thorium was purified by precipitation and liquid-liquid extraction with cerium fluoride and filtration and activity was counted by alpha spectrometry. The $PbCO_3$ generated by double precipitation was dissolved in nitric acid and the thorium extracted into trioctyl phosphine oxide (TOPO). The thorium was back extracted, the organic material removed by an acid digest, and the thorium isolated on cerium fluoride precipitate, filtered, and mounted on an aluminum disk for alpha spectrometry using a Canberra Nuclear Products 7404 Quad Alpha Spectrometer. All sample batches were analyzed with the required QC samples according to SOP.

6.2.5 Polonium-210 Analysis

^{210}Po is an alpha emitter and was determined by isolating the element by precipitation with iron hydroxide followed by isolation on diethylammoniumdiethyldithiocarbamate (DDTC) and counting via alpha spectroscopy. Water samples or digests from sediment or tissues were spiked with ^{208}Po tracer and ferric nitrate carrier, acidified, boiled, and precipitated using ammonium hydroxide. The precipitate was centrifuged out, acidified with hydrochloric acid, treated with ascorbic acid, then extracted with freshly prepared DDTC in chloroform. The organic extract was decomposed, then the polonium was plated out from solution onto nickel disks. Sample disks were then counted via alpha spectrometry using a Canberra Nuclear Products 7404 Quad Alpha Spectrometer. In addition to the internal ^{208}Po tracer to document chemical and counter efficiency, all sample batches were analyzed with the required QC samples according to SOP.

6.2.6 Quality Assurance and Quality Control

6.2.6.1 Procedures

Core Laboratories 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 Laboratories is subject to and has passed EPA audits every 2 years. In addition, Core Laboratories 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 Laboratories' 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 Laboratories' log-in process. At times when a hold order was placed on a batch of samples, Core Laboratories' 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 Laboratories SOP, each sample was assessed for adequate sample volume and the sample information was entered into Core Laboratories' 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 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 was 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 five years before disposal.

6.2.6.2 Results

Detection limits determined during the analysis for the radionuclides are presented in **Table 6.2**. Detection limits for the radium isotopes were determined for each analysis because the detection limit is a function of the quantity of sample and the gross background counts. Based on the results of the analyses of the QC samples, data quality for radionuclides in the relevant matrices was good. Low radionuclide activities were also found in field blanks indicating contaminant-free samples. Similarly, evidence that samples were contaminant-free can be found in the low radionuclide activities found in the equipment blanks that were analyzed. Low background counts were found in procedural blanks used in each analytical sample batch.

The DQOs for accuracy, precision, detection limits, and comparability for radionuclide analyses of samples were met by Core Laboratories in most cases. Quality control data from the matrix spikes and reference materials demonstrated that the accuracy and precision of the radionuclide measurements generally 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.

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[a]	Produced water Ambient seawater Produced sand and sediment Tissue	2.09 pCi/L 0.1 pCi/L 0.05 pCi/g dry weight 0.006 pCi/g dry weight
Target Detection Limit: ^{228}Ra[a]	Produced water Ambient seawater Produced sand and sediment Tissue	3.5 pCi/L 0.35 pCi/L 0.19 pCi/g dry weight 0.019 pCi/g dry weight
Target Detection Limit: ^{210}Pb[a]	Produced water Ambient seawater Produced sand and sediment Tissue	3.28 pCi/L 0.22 pCi/L 0.11 pCi/g dry weight 0.012 pCi/g dry weight
Target Detection Limit: ^{228}Th	Produced water	3 pCi/L
Target Detection Limit: ^{210}Po	Produced water	3 pCi/L

[a] Due to sample limitations, target detection limits were not specified for interstitial waters.

Table 6.2. Lower limits of detection achieved during radionuclide analysis of various matrices.

Radionuclide	Produced Water and Interstitial Water (pCi/L)	Ambient Seawater (pCi/L)	Produced Sand and Sediment (pCi/g dry weight)	Tissue (pCi/g wet weight)
^{226}Ra	0.10 to 0.80	0.02 to 0.40	0.03 to 3.70	0.001 to 0.006
^{228}Ra	0.20 to 2.3	0.10 to 2.40	0.1 to 1.0	0.002 to 0.020
^{210}Pb	0.10 to 2.3	0.10 to 2.30	0.05 to 0.2	0.002 to 0.011
^{210}Po[a]	0.10 to 10.90	--	--	--
^{228}Th[a]	0.30 to 16.60	--	--	--

[a] Produced water only.

Due to the nature of the material and the analytical methods, method detection limits (MDLs) comparable to the organics and metals were not developed for radionuclides. As defined by the methodology, a lower limit of detection (minimum detectable activity) was determined for each sample *a priori* as a function of the matrix, sample volume, background activity, and counting time. Core Laboratories was generally able to achieve detection limits at very low levels of activity and produced reliable and reproducible results at these low levels, particularly for tissue samples.

In produced water, the reported lower limit of detection for ^{226}Ra was higher than the target detection limit of 2.09 pCi/L in 131 of the 162 produced water samples analyzed. About 50% of the produced water samples analyzed for ^{228}Ra had reported detection limits that were greater than the target detection limit. The ^{228}Th target detection limit was not achieved in 13 of the 50 samples analyzed while the target detection limit for ^{210}Po was not achieved in 12 of the 50 produced water samples analyzed. For the majority of the samples whose reported detection limits exceeded the target, radionuclide concentrations were generally greater than the target detection limit by 2 times or more. Only 5 of 61 ambient seawater samples analyzed for ^{226}Ra, ^{228}Ra, and ^{210}Pb had reported lower detection limits that were higher than the target detection limits of 0.1, 0.35, and 0.22 pCi/L, respectively.

CSA specified target detection limits for all matrices except for interstitial waters as part of the analysis instructions provided to Core Laboratories. 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).

In the case of sediment samples, these were mostly analyzed by gamma spectroscopy without digestion which does not allow the lower limits of detection achievable through the wet chemistry method using proportional counters. Lower detection limits reported for ^{226}Ra and ^{228}Ra in sediment samples were therefore much higher than the target detection limits set for these radionuclides. Reported detection limits for ^{210}Pb analyses were below the target detection limit of 0.11 pCi/g for all the 162 sediment samples analyzed with the exception of six samples.

The target detection limits for ^{226}Ra and ^{228} Ra in tissues of 0.006 and 0.019 pCi/g, respectively, were met in the 550 samples analyzed with the exception of two samples analyzed for ^{228}Ra (reported lower detection limit was 0.020 vs. target of 0.019 pCi/g). Similarly, detection limits for ^{210}Pb in all tissue samples were below the target detection limit of 0.012 pCi/g.

6.3 RESULTS AND DISCUSSION

The field effort was conducted in the summer of 1993. At the four Component 1 discharging sites, samples of produced water, produced sand (two sites only, SMI 130B and SMI 236A), ambient seawater, discharge plume/receiving water, and biological tissues were collected. Sediment and interstitial water samples were also collected at the Component 1 sites. At the four Component 3 discharging sites, produced water and biological tissue samples were collected. Ambient seawater and biological tissue samples were also collected at two of the Component 2 non-discharging sites and biological tissue samples only at the third site. Ambient seawater and sediment samples were collected at the four Component 2 reference sites. When values were reported to be below the sample specific detection limit, the detection limit is reported (e.g., <2.09 pCi/L or <0.3 pCi/g).

6.3.1 Produced Water, Discharge Plume/Receiving Water, and Ambient Seawater

Three replicate produced water samples were collected at each of the Components 1 and 3 discharging platform sites (**Table 6.3**). With the exception of HI A-595CF, the ^{226}Ra and ^{228}Ra activities were within the range reported by Stephenson and Supernaw (1990) for 42 Gulf of Mexico offshore produced water discharges (4 to 584 pCi/L and 18 to 586 pCi/L, respectively). Continental Shelf Associates, Inc. (1993) reported ^{226}Ra and ^{228}Ra activities for two offshore Louisiana produced water discharges in Eugene Island Area Block 189 and Ship Shoal Area Block 169, where ^{226}Ra activities were 225 and 111 pCi/L, and ^{228}Ra activities were 260 and 240 pCi/L, respectively. The elevated mean ^{226}Ra activity reported in produced water from HI A-595CF includes a single outlier (showing an activity an order of magnitude higher than the two other samples) which is likely due to produced water scale entrained into the sample. Scale typically contains high radionuclide activities. There were no apparent differences in the activities of the three radionuclides between the Components 1 and 3 sites.

^{228}Th and ^{210}Po activities in produced water collected from the Components 1 and 3 sites were generally within an order of magnitude of the radium (^{228}Th) or lead (^{210}Po) radioisotopes. ^{228}Th activity ranged from 11 to 121 pCi/L while mean activity of ^{210}Po in produced water samples was less than 2.3 pCi/L.

Seawater samples collected at the ambient reference sites (**Table 6.3**) showed mean ^{226}Ra, ^{228}Ra, and ^{210}Pb activities that were several orders of magnitude lesser than the activities measured for the produced water samples. ^{228}Th and ^{210}Pb activities were not measured in the ambient seawater samples from the reference sites.

Additional produced water sampling was performed at the four Component 1 discharging sites to investigate the variability of radionuclide activities of produced water at two time scales. After the initial produced water sampling, five additional produced water samples were collected sequentially at 12-h intervals to investigate short-term variability of radionuclides in produced water. Up to five additional sets of replicate samples were also collected by the platform operators at monthly intervals to investigate longer term variability of radionuclides. With the exception of HI A-595CF, ^{226}Ra activities in the produced water collected at 12-h intervals were generally more consistent than samples collected at monthly intervals (**Table 6.4**). At HI A-595CF, the ^{226}Ra activities were variable at both time scales. ^{228}Ra and ^{210}Pb activities were not as variable as the ^{226}Ra activities at either time scale (**Table 6.4**). These data indicate that a single sampling of produced water at a platform may not be entirely representative of radionuclide levels over longer periods of time, which has implications for relating produced water activities to activities in organisms living in the vicinity of the discharge.

Table 6.3. Mean (± standard deviation) activities (pCi/L) of ^{226}Ra, ^{228}Ra, ^{210}Pb, ^{228}Th, and ^{210}Po in produced water samples from Components 1 and 3 sites. Mean (± standard deviation) activities (pCi/L)of ^{226}Ra, ^{228}Ra, and ^{210}Pb are also shown for ambient seawater samples from Component 2 reference sites.

Platform/Reference Site Location	^{226}Ra	^{228}Ra	^{210}Pb	^{228}Th	^{210}Po
Component 1 Sites					
South Marsh Island 236A	91 ± 13	239 ± 67	12.3 ± 4.3	81.7 ± 10.1	1.3 ± 0.7
Vermilion 214A	300 ± 157	228 ± 29	7.7 ± 4.7	77.6 ± 12.3	1.3 ± 0.7
South Marsh Island 130B	362 ± 43	164 ± 146	5.6 ± 5.5	43.1 ± 17.3	2 ± 1.1
High Island A-595CF	1,494 ± 1,989	356 ± 19	12.5 ± 2.6	79 ± 6.7	1 ± 0.6
Component 3 Sites					
Matagorda Island 703A	56 ± 3	69 ± 7	2.6 ± 0.5	11.4 ± 4.9	0.7 ± 0.5
High Island A-323A	112 ± 6	162 ± 12	5.2 ± 2.5	29 ± 4.4	0.6 ± 0.2
Eugene Island 313A	270 ± 16	388 ± 15	13.8 ± 1.9	62.6 ± 9	2.3 ± 1.4
High Island A-382F	255 ± 43	600 ± 107	16.7 ± 4.1	120.7 ± 7.4	1.9 ± 0.6
Component 2 Sites					
West Cameron 448	0.3 ± 0.17	<0.30	0.37 ± 0.15	-----	-----
Galveston A-90	0.07 ± 0.06	0.7 ± 0.66	0.23 ± 0.21	-----	-----
South Marsh Island 186/195	0.13 ± 0.06	0.6 ± 0.53	0.03 ± 0.06	-----	-----
Galveston A-205	0.13 ± 0.06	0.93 ± 1.21	0.3 ± 0.26	-----	-----

Table 6.4. Summary of activities (pCi/L) of ^{226}Ra, ^{228}Ra, and ^{210}Pb in produced water samples over time.

Analyte	Time of Sampling	SMI 236A	VR 214A	SMI 130B	HI A-595CF
^{226}Ra	Initial sampling	91 ± 13	300 ± 157	362 ± 43	1,494 ± 1,989
	12 h after initial sampling	70	400	261	490
	24 h after initial sampling	66	347	317	470
	36 h after initial sampling	47	441	110	83
	48 h after initial sampling	175	373	373	944
	60 h after initial sampling	68	344	229	734
	1 mo after initial sampling	39 ± 1	60 ± 8	196 ± 97	
	2 mo after initial sampling	65 ± 2	77 ± 11	315 ± 7	101 ± 11
	3 mo after initial sampling	38 ± 6	90 ± 25	265 ± 26	165 ± 259
	4 mo after initial sampling	292 ± 11	238 ± 71	287 ± 18	434 ± 13
	5 mo after initial sampling	321 ± 33		286 ± 12	
^{228}Ra	Initial sampling	239 ± 67	228 ± 29	164 ± 147	356 ± 19
	12 h after initial sampling	138	214	130	409
	24 h after initial sampling	307	193	113	362
	36 h after initial sampling	126	241	43	291
	48 h after initial sampling	187	263	187	220
	60 h after initial sampling	166	217 ±	279	257
	1 mo after initial sampling	119 ± 14	242 ± 6	193 ± 17	
	2 mo after initial sampling	277 ± 52	318 ± 11	188 ± 5	276 ± 30
	3 mo after initial sampling	126 ± 3	278 ± 26	156 ± 57	190 ± 297
	4 mo after initial sampling	274 ± 17	228 ± 63	196 ± 27	470 ± 55
	5 mo after initial sampling	306 ± 16		196 ± 23	

Table 6.4. (Continued).

Analyte	Time of Sampling	SMI 236A	VR 214A	SMI 130B	HI A-595CF
^{210}Pb	Initial sampling	12 ± 4	8 ± 5	6 ± 5	13 ± 3
	12 h after initial sampling	13	8	13	11
	24 h after initial sampling	16	5	4	15
	36 h after initial sampling	12	7	2	20
	48 h after initial sampling	16	11	5	23
	60 h after initial sampling	15	14	11	12
	1 mo after initial sampling	4 ± 1	6 ± 2	5 ± 2	
	2 mo after initial sampling	8 ± 2	7 ± 1	7 ± 0	4 ± 0
	3 mo after initial sampling	4 ± 1	6 ± 2	5 ± 1	8 ± 3
	4 mo after initial sampling	2 ± 3	4 ± 1	<2.1	9 ± 5
	5 mo after initial sampling	11 ± 9		<2.1	

Radionuclides were determined in water samples collected in the discharge plume/receiving waters at the four Component 1 platforms. Samples were collected at distances of 5, 10, 30, 50, and 100 m from the discharge point. In addition, ambient seawater samples were collected at three stations located greater than 2,000 m from each platform. All discharges were above the sea surface. The values are compared to those for the produced water and the Component 2 reference sites in **Tables 6.5** to **6.7**.

The activities of the radionuclides are quickly reduced after discharge of the produced water, generally approaching levels comparable to ambient conditions within short distances from the discharge point. At 5 m from the discharge point, ratios of produced water activity to plume water activity for ^{226}Ra and ^{228}Ra were 228:1 to 1668:1 and 162:1 to 759:1, respectively. The radium ratios observed at these four platforms were similar to those observed by Continental Shelf Associates, Inc. (1993) at Eugene Island Area Block 189 and Ship Shoal Area Block 169. Produced water-to-plume water activity ratios were lower for ^{210}Pb, ranging from 24:1 to 80:1. The difference in produced water-to-plume water activity ratios between the radium isotopes and the lead isotope indicated that they may be behaving differently in the plume. Lead is commonly associated with fine-grained particles. When the radium isotopes enter the sulfate-rich seawater, they may form particles of radium sulfate just as barium does. White (1992) suggested that 90% of the radium in discharged produced water could be coprecipitated with barium.

6.3.2 Produced Sand

Table 6.8 summarizes the results of the analyses of radionuclides in produced sand from Component 1 sites SMI 236A and 130B. Produced sand radionuclide activities were in the same order of magnitude as activities in sediment samples from Component 1 sites. ^{226}Ra activity in produced sand samples ranged from 1.49 to 2.34 pCi/g dry weight while ^{228}Ra activity ranged from 0.8 to 1.18 pCi/g dry weight. ^{210}Pb activity was least, ranging from 0.68 to 0.91 pCi/g dry weight.

6.3.3 Sediments and Interstitial Water

^{226}Ra, ^{228}Ra, and ^{210}Pb radionuclides were determined in surficial sediment samples collected at the four Component 1 sites. Sediment samples were also collected at the Component 2 reference sites. Sediment samples could not be collected directly below the discharge point at three of the platforms. The ^{226}Ra and ^{228}Ra activities in sediment samples from the vicinity of SMI 236A and VR 214A were slightly greater than those observed at the Component 2 reference sites. However, distinct gradients with distance from the discharge point were not evident (**Tables 6.9** and **6.10**). ^{210}Pb activities were similar to those observed at the Component 2 reference sites (**Table 6.11**). Radionuclide activities were generally less than 3 pCi/g dry weight with most samples below the lower limit of detection.

Interstitial water was extracted from sediment samples that were collected at the Component 1 platforms. The ^{226}Ra, ^{228}Ra, and ^{210}Pb activities were determined in several strata. The results are presented in **Tables 6.12** to **6.14**. ^{226}Ra activities were generally less than a few pCi/L with no apparent patterns relative to strata and distance from the platforms. Although slightly higher ^{228}Ra and ^{210}Pb activities were observed in interstitial water from some samples, most samples were below the lower limit of detection and no evident spatial patterns were observed.

Table 6.5. Mean ^{226}Ra activities (pCi/L) (± standard deviation) in water samples from Components 1 and 2 sites.

Component 1 Platform					
Water Sample Type		SMI 236A	VR 214A	SMI 130B	HI A-595CF
Produced Water		91.17 ± 12.61	300.33 ± 156.87	362.33 ± 43.02	1494.00 ± 1988.78
Discharge Plume/ Receiving Water	5 m	0.40 ± 0.17	0.18 ± 0.13	0.53 ± 0.21	0.93 ± 0.31
	10 m	0.30 ± 0.10	0.70 ± 0.35	0.97 ± 0.32	0.87 ± 0.32
	30 m	0.53 ± 0.12	0.45 ± 0.24	0.57 ± 0.31	0.47 ± 0.12
	50 m	0.50 ± 0.20	0.33 ± 0.60	0.90 ± 0.26	0.45 ± 0.23
	100 m	0.57 ± 0.15	0.33 ± 0.06	0.07 ± 0.06	0.23 ± 0.06
Ambient Seawater >2,000 m		0.20 ± 0.00 0.23 ± 0.12 0.07 ± 0.16	0.07 ± 0.06 0.07 ± 0.06 0.10 ± 0.00	0.10 ± 0.00 0.07 ± 0.06 0.10 ± 0.00	0.03 ± 0.06 0.03 ± 0.06 0.03 ± 0.06

Component 2 Lease Block				
Water Sample Type	WC 448	SMI 186/195	GA A-205	GA A-90
Ambient Seawater	0.30 ± 0.17	0.13 ± 0.06	0.13 ± 0.06	0.07 ± 0.06

Table 6.6. Mean ^{228}Ra activities (pCi/L) (± standard deviation) in water samples from Components 1 and 2 sites.

Water Sample Type		Component 1 Platform			
		SMI 236A	VR 214A	SMI 130B	HI A-595CF
Produced Water		238.67 ± 67.47	227.67 ± 28.54	164.00 ± 146.50	356.00 ± 19.31
Discharge Plume/ Receiving Water	5 m	0.83 ± 0.49	0.30 ± 0.35	0.63 ± 0.60	2.20 ± 0.52
	10 m	0.60 ± 0.56	1.87 ± 0.21	0.90 ± 0.66	1.93 ± 0.75
	30 m	1.07 ± 1.22	0.93 ± 0.85	0.33 ± 0.29	2.03 ± 1.10
	50 m	3.60 ± 4.94	0.50 ± 0.10	1.30 ± 0.20	1.93 ± 0.21
	100 m	3.87 ± 2.25	1.60 ± 0.20	1.23 ± 0.40	1.07 ± 0.72
Ambient Seawater >2,000 m		3.20 ± 2.31 0.10 ± 0.17 1.60 ± 0.70	0.30 ± 0.52 0.60 ± 0.52 1.03 ± 0.95	1.67 ± 0.65 1.27 ± 1.22 0.13 ± 0.23	0.63 ± 0.45 0.53 ± 0.35 1.20 ± 1.32

Component 2 Lease Block				
Water Sample Type	WC 448	SMI 186/195	GA A-205	GA A-90
Ambient Seawater	<0.30	0.60 ± 0.53	0.93 ± 1.21	0.70 ± 0.66

< = Below lower limit of detection.

Table 6.7. Mean ^{210}Pb activities (pCi/L) (± standard deviation) in water samples from Components 1 and 2 sites.

Component 1 Platform					
Water Sample Type		SMI 236A	VR 214A	SMI 130B	HI A-595CF
Produced Water		12.27 ± 4.31	7.70 ± 4.70	5.60 ± 5.50	12.50 ± 2.60
Discharge Plume/ Receiving Water	5 m	0.17 ± 0.15	0.10 ± 0.14	0.07 ± 0.12	0.53 ± 0.12
	10 m	0.17 ± 0.15	0.23 ± 0.06	0.13 ± 0.12	0.80 ± 0.10
	30 m	0.03 ± 0.06	0.10 ± 0.14	0.07 ± 0.06	0.70 ± 0.20
	50 m	0.13 ± 0.12	0.33 ± 0.35	0.03 ± 0.06	0.53 ± 0.35
	100 m	<0.10	0.80 ± 0.20	0.13 ± 0.12	0.17 ± 0.29
Ambient Seawater >2,000 m		0.33 ± 0.29 0.13 ± 0.15 0.30 ± 0.10	0.50 ± 0.10 0.13 ± 0.15 0.53 ± 0.21	0.13 ± 0.06 0.03 ± 0.06 0.07 ± 0.06	<0.20 <0.20 <0.20

Component 2 Lease Block				
Water Sample Type	WC 448	SMI 186/195	GA A-205	GA A-90
Ambient Seawater	0.37 ± 0.15	0.03 ± 0.06	0.30 ± 0.26	0.23 ± 0.21

< = Below lower limit of detection.

Table 6.8. Means and standard deviations (±) of ^{226}Ra, ^{228}Ra, ^{210}Pb activities (pCi/g dry weight) in three replicate samples of produced sand from SMI 236A and 130B.

Radionuclide	Platform	
	SMI 236A	SMI 130B
^{226}Ra	1.49 ± 0.12	2.34 ± 0.23
^{228}Ra	0.80 ± 0.19	1.18 ± 0.07
^{210}Pb	0.91 ± 0.14	0.68 ± 0.14

Table 6.9. Mean ^{226}Ra activities (pCi/g dry weight) (± standard deviation) in sediment samples collected along the four radial transects from four Component 1 platforms compared to the Component 2 reference sites.

Distance (m)	Component 1 Platform			
	SMI 236A	VR 214A	SMI 130B	HI A-595CF
0	3.10 ± 2.79	NS	NS	NS
20[a]	<1.50	<1.70	0.90 ± 1.56	0.44 ± 0.76
50[a]	<1.60	<1.30	1.03 ± 1.79	0.31 ± 0.54
100	<1.50	1.90 ± 3.29	0.16 ± 0.28	<2.50
150	<1.80	<1.80	0.93 ± 1.62	2.97 ± 2.71
300	0.50 ± 0.87	1.86 ± 3.23	<1.60	<2.00
2,000	<2.00	<2.60	1.32 ± 2.29	<1.70
	Component 2 Lease Block			
	WC 448	SMI 186/195	GA A-205	GA A-90
	<1.70	<1.60	<1.40	<1.20

NS = Not sampled.

[a] Station distance from the discharge point varied according to the transect and platform. See **Tables 5.1** to **5.4** for specific locations.

< = Below lower limit of detection.

Table 6.10. Mean ^{228}Ra activities (pCi/g dry weight) (± standard deviation) in sediment samples collected along the four radial transects from four Component 1 platforms compared to the Component 2 reference sites.

Distance (m)	Component 1 Platform			
	SMI 236A	VR 214A	SMI 130B	HI A-595CF
0	2.30 ± 2.01	NS	NS	NS
20[a]	1.17 ± 1.01	2.10 ± 0.44	0.83 ± 0.76	0.14 ± 0.25
50[a]	0.63 ± 1.10	0.43 ± 0.75	0.67 ± 0.58	0.10 ± 0.18
100	0.43 ± 0.75	0.60 ± 1.04	<0.11	<0.30
150	<0.60	0.83 ± 1.44	0.37 ± 0.64	1.03 ± 0.91
300	<0.60	0.30 ± 0.53	1.37 ± 0.25	<0.60
2,000	<0.70	0.37 ± 0.98	1.40 ± 1.21	1.43 ± 0.55
Component 2 Lease Block				
	WC 448	SMI 186/195	GA A-205	GA A-90
	0.77 ± 0.68	1.00 ± 1.41	0.93 ± 0.81	<0.60

NS = Not sampled.

[a] Station distance from the discharge point varied according to the transect and platform. See **Tables 5.1** and **5.4** for specific locations.

< = below lower limit of detection.

Table 6.11. Mean ^{210}Pb activities (pCi/g dry weight) (± standard deviation) in sediment samples collected along the fourradial transects from four Component 1 platforms compared to the Component 2 reference sites.

Distance (m)	Component 1 Platform			
	SMI 236A	VR 214A	SMI 130B	HI A-595CF
0	1.77 ± 0.81	NS	NS	NS
20[a]	1.30 ± 0.87	2.27 ± 0.65	1.23 ± 0.85	1.49 ± 0.18
50[a]	0.73 ± 0.42	1.57 ± 0.06	1.40 ± 0.10	1.81 ± 0.43
100	0.50 ± 0.10	2.17 ± 0.47	1.61 ± 0.29	1.87 ± 0.29
150	0.70 ± 0.10	2.57 ± 0.72	1.37 ± 0.12	2.17 ± 0.32
300	0.93 ± 0.25	2.70 ± 0.26	3.67 ± 0.06	3.27 ± 0.59
2,000	1.53 ± 0.21	3.23 ± 0.21	3.78 ± 0.20	3.97 ± 0.80
Component 2 Lease Block				
	WC 448	SMI 186/195	GA A-205	GA A-90
	2.27 ± 0.55	3.15 ± 0.21	2.40 ± 0.26	4.53 ± 0.55

NS = Not sampled.

[a] Station distance from the discharge point varied according to the transect and platform. See **Tables 5.1** and **5.4** for specific locations.

< = below lower limit of detection.

Table 6.12. ^{226}Ra activity in interstitial water samples from Component 1 sites.

Platform	Transect-Station	Stratum (cm below sediment surface)	Activity (pCi/L)
South Marsh Island 236A	Discharge	0 to 2	<1.6
		2 to 4	<0.9
		4 to 6	1.7
		6 to 88	2.1
		18 to 20	<0.9
	I-20	0 to 2	<0.9
		4 to 6	2.2
		6 to 8	1.5
		8 to 10	1.9
		18 to 20	3.3
	I-2,000	0 to 2	<0.9
		2 to 4	<0.9
		18 to 20	<1.2
Vermilion 214A	I-20	0 to 2	1.7
		2 to 4	<1.5
		18 to 20	2.4
	I-2,000	0 to 2	<0.9
		2 to 4	<0.9
		18 to 20	<2
South Marsh Island 130B	III-50	0 to 2	<0.8
		2 to 4	1.4
		18 to 20	1.4
	I-50	0 to 2	1.2
		2 to 4	2.7
		18 to 20	1.3
	I-2,000	0 to 2	1.8
		2 to 4	1.5
		18 to 20	1.1
	V-2,000	0 to 2	0.9
		2 to 4	<0.6
		18 to 20	0.8
High Island 595CF	I-60	0 to 2	<0.9
		2 to 4	<1.2
		18 to 20	<0.9
	I-2,000	0 to 2	<1.3
		2 to 4	0.7
		18 to 20	2.3

< = Below lower limit of detection.

Table 6.13. ^{228}Ra activity in interstitial water samples from Component 1 sites.

Platform	Transect-Station	Stratum (cm below sediment surface)	Activity (pCi/L)
South Marsh Island 236A	Discharge	0 to 2	<10
		2 to 4	<10
		4 to 6	<7
		6 to 8	<6.8
		18 to 20	<5.5
	I-20	0 to 2	7
		4 to 6	<13.6
		6 to 8	17.5
		8 to 10	<6.8
		18 to 20	7.4
	I-2,000	0 to 2	6.1
		2 to 4	<5.3
		18 to 20	7
Vermilion 214A	I-20	0 to 2	13.5
		2 to 4	15
		18 to 20	11.2
	I-2,000	0 to 2	<5.3
		2 to 4	6.1
		18 to 20	<13.2
South Marsh Island 130B	III-50	0 to 2	<7.7
		2 to 4	<13.5
		18 to 20	<6.1
	I-50	0 to 2	<8.8
		2 to 4	<11.6
		18 to 20	<8
	I-2,000	0 to 2	12.3
		2 to 4	12.2
		18 to 20	<6.6
	V-2,000	0 to 2	<5.6
		2 to 4	<6.3
		18 to 20	<7
High Island A-595CF	I-60	0 to 2	<5.9
		2 to 4	<7.9
		18 to 20	<5.9
	I-2,000	0 to 2	<12.3
		2 to 4	<5.9
		18 to 20	<15

< = Below lower limit of detection.

Table 6.14. ^{210}Pb activity in interstitial water samples from Component 1 sites.

Platform	Transect-Station	Stratum (cm below sediment surface)	Activity (pCi/L)
South Marsh Island 236A	Discharge	0 to 2	<6.1
		2 to 4	<3.3
		4 to 6	4.1
		6 to 8	4.6
		18 to 20	<3.3
	I-20	0 to 2	<3.3
		4 to 6	9.7
		6 to 8	<3.8
		8 to 10	4.4
		18 to 20	<4.5
	I-2,000	0 to 2	<3.3
		2 to 4	<3.3
		18 to 20	<4.5
Vermilion 214A	I-20	0 to 2	<4.5
		2 to 4	<4.5
		18 to 20	<3.3
	I-2,000	0 to 2	<3.3
		2 to 4	<3.3
		18 to 20	<7.4
South Marsh Island 130B	III-50	0 to 2	6.8
		2 to 4	13.4
		18 to 20	6.9
	I-50	0 to 2	9.5
		2 to 4	12.3
		18 to 20	9.6
	I-2,000	0 to 2	7.3
		2 to 4	8.3
		18 to 20	4.9
	V-2,000	0 to 2	4.7
		2 to 4	6.4
		18 to 20	4.5
High Island A-595CF	I-60	0 to 2	<3.3
		2 to 4	<4.5
		18 to 20	<3.3
	I-2,000	0 to 2	10.3
		2 to 4	6.2
		18 to 20	<8.2

< = Below lower limit of detection.

6.3.4 Tissues/Biota - Bivalves, Crustaceans, and Fish

As reported in Chapter 4, due to differences in water depth and site location the same species could not be collected from all sites. Selection of taxa for chemical analyses was based on the taxa being represented at multiple sites and important from an ecological risk and human health perspective.

The oyster (*Crassostrea virginica*) was collected from the legs and supporting structure of Component 1 platform (SMI 236A - 6 m water depth) and a Component 3 non-discharging platform (SMI 229C - 7 m water depth). The jewelbox (*Chama macerophylla*) was collected from seven Components 1 and 3 sites. Bivalves are excellent biological monitors of exposure to produced water discharges because they are sessile (they remain attached to the platform structures for extended periods and do not move), filter feeders with life histories extending over several years. The jewelbox was also collected at one other Component 3 site (HI A-389) in addition to the discharging platforms. The jewelbox was collected at HI A-389 because sufficient quantities of this bivalve were not available at VR 298/305 (Sonnier Bank). Although produced water is discharged at the HI A-389 site, the discharge is shunted to within 10 m of the seafloor. The water depth at this platform is 122 m; therefore, the bivalves were not thought to be exposed to produced water discharges because of this shunting and density differences between the produced water and seawater.

Several species (blue crab [*Callinectes* spp.], penaeid shrimp [*Penaeus* spp.], swimming crab [*Portunus* spp.], and rock shrimp [*Sicyonia brevirostris*]) were collected and analyzed from several Components 1 and 3 sites as shown in **Tables 4.1** and **6.15**.

The range in radionuclide activities among replicate analyses of bivalve and crustacean samples are presented in **Table 6.15**. Mean activities in bivalve tissues were very low with most levels close to or below the lower limits of detection.

Radionuclide activities were low in the edible tissue of the blue crabs and the data did not indicate greater levels in specimens collected around the discharging platforms compared to the reference sites. Radionuclide activities in the penaeid shrimps were low; activities at the discharging platforms were comparable with those observed at the shallow water and offshore reference sites (**Table 6.15**). Similar results were observed for edible tissue from rock shrimp, which were collected at the deeper study sites (**Table 6.15**). The swimming crabs also showed low radionuclide activities in whole individuals.

Radionuclide activities were also determined in the flesh of several fish species living around the platforms. Red snapper (*Lutjanus campechanus*) and gray triggerfish (*Balistes capriscus*) are associated with platform structures, living among the legs, pilings, and cross-members of platforms. Pinfish (*Lagodon rhomboides*) was collected in trawls over the seafloor in the vicinity of the platforms. The activities of the three radionuclides were consistently low at all sites (**Table 6.16**). For red snapper and gray triggerfish, activities at discharging sites were comparable to those at VR 298/305, which was an offshore reference site. Although pinfish was not collected at VR 298/305, activities in the fillets of this species were similar to those of the other two species.

Table 6.15. Summary of radionuclide activities (pCi/g wet weight) in bivalve (soft tissue) and crustacean tissues (blue crab, rock shrimp, and shrimp [E-edible, N-nonedible, W-whole]). Swimming crabs (*Portunus* spp.) were analyzed as whole individuals. South Marsh Island 229C, High Island A-389, and Vermilion 298/305 are reference sites.

Radionuclide	Site	Jewelbox	Eastern Oyster	Blue Crabs	Shrimp	Swimming Crabs	Rock Shrimp
^{226}Ra	South Marsh Island 229C		0.013	<0.003 -0.060 (W/E)	<0.003 - 0.093 (E/N)		
	South Marsh Island 236A		<0.004	<0.004 -0.015 (E)	<0.004 - 0.023 (E/N)		
	High Island A-389	0.365					
	Vermilion 298/305			0.007-0.027 (W)	<0.005 -0.010 (E/N)	0.011 - 0.031	<0.004 - 0.007 (E/N)
	Vermilion 214A	0.033		0.013 -0.037 (W)			<0.005 - 0.040 (E,N)
	South Marsh Island 130B	0.048			<0.004 - 0.008 (E/N)	<0.005 - 0.019	<0.003 - 0.021 (E/N)
	High Island A-595CF	0.118					
	Matagorda Island 703A	0.021		0.010 -0.058 (W)	<0.003 - 0.008 (E/N)		
	High Island A-323A	0.076			<0.004 - 0.005 (E/N)	0.020 - 0.061	
	Eugene Island 313A	0.167			<0.004 (E/N)	<0.005 - 0.016	<0.005-0.0063 (E/N)
	High Island A-382F	0.175			0.005 (E/N)	0.012 - 0.034	
^{228}Ra	South Marsh Island 229C		0.047	<0.011 - 0.065 (W/E)	<0.008 - 0.047 (E/N)		
	South Marsh Island 236A		<0.011	<0.011 - 0.037 (E)	<0.013-0.037 (E/N)		
	High Island 389A	<0.013					
	Vermilion 298/305			<0.011 - 0.033 (W)	<0.018-0.046 (E/N)	<0.017 - 0.158	<0.014 - 0.051(E/N)
	Vermilion 214A	<0.014		<0.011 - 0.115 (W)			<0.017 - 0.047 (E/N)
	South Marsh Island 130B	<0.009			<0.015 (E/N)	0.025 - 0.069	<0.01 7- 0.105 (E/N)
	High Island 595CF	0.061					
	Matagorda Island 703A	<0.016		0.017 - 0.070 (W)	<0.008 - 0.159 (E/N)		
	High Island 323A	<0.066			0.027-0.099 (E/N)	0.010 - 0.122	
	Eugene Island 313A	<0.003			0.093 (E)	<0.016 - 0.052	<0.015 - <0.017 (E/N)
	High Island 382F	0.081			<0.019 - 0.174	<0.013 - 0.032	
^{210}Pb	South Marsh Island 229C		0.035	<0.011 - 0.017 (E/W)	<0.011 - 0.033		
	South Marsh Island 236A		0.024	<0.010 - 0.022	<0.009 - 0.014	<0.008 -<0.010	
	High Island 389A	0.211					
	Vermilion 298/305			0.008 - 0.048 (W)	<0.009 - 0.034 (E/N)		0.041 - 0.104 (E/N)
	Vermilion 214A	0.075		<0.081 - 0.035 (W)			<0.009 - .075 (E/N)
	South Marsh Island 130B	0.281			<0.009 - 0.055 (E/N)	<0.028 - 0.053	<0.010 (E/N)
	High Island 595CF	0.416					
	Matagorda Island 703A	0.043		0.010 - 0.058	<0.010 (E/N)		
	High Island 323A	0.188			0.029 -0.041 (E/N)	<0.033-0.059	
	Eugene Island 313A	0.308			0.015 (E/N)	0.015-0.048	<0.009 - 0.0 58 (E/N)
	High Island 382F	0.454			0.018 - 0.046 (E/N)	<0.009-0.057	

< = Below method detection limit.

Table 6.16. Summary of radionuclide activities (pCi/g wet weight) in tissues of fish species. Letters in parenthesis indicate the tissues analyzed as follows: W-whole; F-fillets, and C-carcass. South Marsh Island 229C, High Island A-389, and Vermillion 298/305 are reference sites.

Radio-nuclide	Site	Atlantic Croaker	Atlantic Cutlassfish	Black Drum	Flounders	Gray Triggerfish
^{226}Ra	Vermilion 298/305	<0.004 - 0.021 (W)				<0.004 - 0.080 (F/C)
	South Marsh Island 229C	0.013 - 0.026 (W)	<0.006 - 0.016 (W)			
	South Marsh Island 236A	<0.003 - 0.011 (W)	<0.004 - 0.011 (W)	<0.005 - 0.071(F/C)		
	Vermilion 214A					<0.005 - 0.024 (F/C)
	South Marsh Island 130B					<0.004 - 0.080 (F/C)
	High Island A-595CF					<0.004 - 0.123 (F/C)
	Matagorda Island 703A				0.005 (F)	<0.004 - 0.032 (F/C)
	High Island 323A					0.006 - 0.129 (F/C)
	Eugene Island 313A					<0.005 - 0.088 (F/C)
	High Island 382F					<0.006 - 0.100 (F/C)
^{228}Ra	Vermilion 298/305	<0.018 - 0.017 (W)				<0.020 - 0.154 (F/C)
	South Marsh Island 229C	<0.017 - 0.036 (W)	<0.011 - 0.013 (W)			
	South Marsh Island 236A	<0.011 - 0.039 (W)	0.016 - 0.092 (W)	<0.008 - 0.035 (F/C)		
	Vermilion 214A					0.009 - 0.055 (F/C)
	South Marsh Island 130B					<0.015 - 0.082 (F/C)
	High Island A-595CF					<0.014 - 0.058 (F/C)
	Matagorda Island 703A				<0.014 (F)	0.045 - 0.137 (F/C)
	High Island 323A					<0.014 - 0.096 (F/C)
	Eugene Island 313A					<0.018 - 0.087 (F/C)
	High Island 382F					0.049 - 0.084 (F/C)
^{210}Pb	Vermilion 298/305	<0.005 - 0.030 (W)				<0.009 - 0.109 (F/C)
	South Marsh Island 229C	<0.009 - 0.018 (W)	<0.008 - <0.010 (W)			
	South Marsh Island 236A	<0.010 - 0.015 (W)	<0.008 -0.036 (W)	<0.009 - 0.023 (F/C)		
	Vermilion 214A					<0.010 - 0.112 (F/C)
	South Marsh Island 130B					0.009 - 0.140 (F/C)
	High Island A-595CF					<0.009 - 0.089 (F/C)
	Matagorda Island 703A				<0.008 (F)	<0.011 - 0.025 (F/C)
	High Island 323A					<0.009 - 0.033 (F/C)
	Eugene Island 313A					<0.010 - 0.115 (F/C)
	High Island 382F					<0.009 (F/C)

Table 6.16. (Continued).

Radio-nuclide	Site	Greater Amberjack	Great Barracuda	Grunts	Hardhead Catfish	Lane Snapper
^{226}Ra	Vermilion 298/305			<0.005 - 0.012 (F)		
	South Marsh Island 229C				<0.003 (W)	
	South Marsh Island 236A				<0.004 - 0.005 (W)	
	Vermilion 214A	<0.004 - 0.007 (C)		0.002 - 0.012 (F)		<0.015 - 0.015 (F/C)
	South Marsh Island 130B	<0.002 - 0.008 (F/C)				
	High Island A-595CF					
	Matagorda Island 703A					
	High Island 323A	<0.004 - 0.004 (F/C)		< 0.002 - 0.003 (F)		
	Eugene Island 313A					
	High Island 382F	<0.004 (F/C)	<0.004 - 0.035 (F/C)			
^{228}Ra	Vermilion 298/305			<0.012 (F)		
	South Marsh Island 229C				0.017 (W)	
	South Marsh Island 236A				<0.014 - 0.017 (W)	
	Vermilion 214A	<0.017 - 0.039 (C)		<0.013 - 0.119 (F)		<0.017 - 0.048 (F/C)
	South Marsh Island 130B	<0.018 - 0.124 (F/C)				
	High Island A-595CF					
	Matagorda Island 703A					
	High Island 323A	<0.015-0.040 (F/C)		<0.015 - 0.044 (F)		
	Eugene Island 313A					
	High Island 382F	<0.010 - 0.021 (F/C)	<0.009 -0.121 (F/C)			
^{210}Pb	Vermilion 298/305			<0.007 - 0.019 (F)		
	South Marsh Island 229C				<0.010 (W)	
	South Marsh Island 236A				<0.010 (W)	
	Vermilion 214A	<0.009 - 0.016 (C)		0.011 - 0.035 (F)		<0.009 - 0.036 (F/C)
	South Marsh Island 130B	<0.004 - 0.022 (F/C)				
	High Island A-595CF					
	Matagorda Island 703A					
	High Island 323A	<0.004 - 0.036 (F/C)		<0.010 - 0.020 (F)		
	Eugene Island 313A					
	High Island 382F	<0.004 - 0.021 (F/C)	<0.010 - 0.026 (F/C)			

Table 6.16. (Continued).

Radio-nuclide	Site	Longspine Porgy	Longtail Bass	Pinfish	Red Snapper	Sea Bass
^{226}Ra	Vermilion 298/305	0.023 - 0.046 (W)			<0.004 - 0.005 (F/C)	<0.005 - 0.017 (F/W)
	South Marsh Island 229C					
	South Marsh Island 236A					
	Vermilion 214A	0.015 (W)		<0.002 (F)	<0.005 - 0.014 (F/C)	<0.008 (W)
	South Marsh Island 130B	0.016 - 0.021 (W)		<0.005 - 0.008 (F)	<0.005 - 0.010 (F/C)	<0.005 - 0.010 (F/W)
	High Island A-595CF	0.027 - 0.042 (W)	<0.005 - 0.009 (F)	<0.002 (F)		<0.006 - 0.020 (F/W)
	Matagorda Island 703A			0.005 - 0.008 (F)	<0.003 - 0.009 (F/C)	<0.005 - 0.016 (W)
	High Island 323A	<0.005 - 0.004 (W)		<0.003 (F)	<0.005 - 0.033 (F/C)	<0.005 (W/F)
	Eugene Island 313A	0.012 - 0.067 (W)		<0.005 (F)	<0.003 - 0.012 (F/C)	<0.0004 - 0.013 (W/F)
	High Island 382F	<0.003 - 0.028 (W)		<0.003 (F)		<0.006 - 0.017 (W)
^{228}Ra	Vermilion 298/305	<0.018 - 0.080 (W)			<0.019 - 0.068 (F/C)	<0.013 - <0.014 (F/W)
	South Marsh Island 229C	0.030 - 0.090 (W)	<0.010 - 0.507 (F)			<0.020 (F/W)
	South Marsh Island 236A					
	Vermilion 214A	0.036 (W)		<0.014 (F)	<0.017 - 0.041 (F/C)	0.030 (W)
	South Marsh Island 130B	<0.013 - 0.140 (W)		0.037 - 0.045 (F)	<0.017 - 0.140 (F/C)	<0.019 - 0.076 (W)
	High Island A-595CF	0.025 - 0.089 (W)		0.039 (F)		<0.015 - <0.017 (F/W)
	Matagorda Island 703A			<0.010 - 0.020 (F)	<0.019 - 0.022 (F/C)	<0.090 - 0.173 (W)
	High Island 323A	0.010 - 0.085 (W)		<0.015 (F)	<0.015 - 0.146 (F/C)	<0.017 - 0.061 (F/W)
	Eugene Island 313A	<0.018 - 0.058 (W)		0.017 - 0.094 (F)	<0.014 - 0.047 (F/C)	<0.015 - 0.054 (F/W)
	High Island 382F	<0.009 - 0.163 (W)		<0.018 - 0.068 (F)		< 0.018 - 0.116 (F/W)
^{210}Pb	Vermilion 298/305	0.029 - 0.126 (W)			<0.006 - 0.042 (F/C)	<0.010 - 0.028 (F/W))
	South Marsh Island 229C					
	South Marsh Island 236A					
	Vermilion 214A	0.024 (W)		<0.010 (F)	<0.010 - 0.027 (F/C)	0.040 (W)
	South Marsh Island 130B	0.096 - 0.160 (W)		<0.008 - 0.025 (F)	<0.010 - 0.008 (F/C)	<0.011 - 0.011 (F/W)
	High Island A-595CF	0.122 - 0.162 (W)	<0.005 - 0.017 (F)	<0.010 (F)		<0.009 - 0.066 (F/W)
	Matagorda Island 703A			<0.007 - 0.008 (F)	<0.010 (F)	<0.010 - 0.030 (W)
	High Island 323A	0.195 - 0.303 (W)		<0.010 (F)	<0.011 - 0.030 (F)	<0.010 - 0.032 (F/W)
	Eugene Island 313A	0.016 - 0.134 (W)		<0.010 - 0.010 (F)	0.010 - 0.050 (F/C)	<0.009 - 0.027 (F/W)
	High Island 382F	0.129 - 0.261 (W)		<0.010 - 0.018 (F)		<0.009 - 0.021 (F/W)

Table 6.16. (Continued).

Radio-nuclide	Site	Spotted Trout	Trouts	Vermilion Snapper	Wenchman
^{226}Ra	Vermilion 298/305		0.004 (W)		0.005 - 0.020 (W)
	South Marsh Island 229C	<0.004 - 0.019 (F/C)	<0.005 - 0.011 (W)		
	South Marsh Island 236A	<0.005 - 0.013 (F/C)	<0.003 - < 0.005 (W)		
	Vermilion 214A				
	South Marsh Island 130B			0.005 - 0.020 (F/C)	
	High Island A-595CF			<0.005 - 0.016 (F)	<0.003 (W)
	Matagorda Island 703A				
	High Island 323A			<0.005 - 0.035 (F/C)	
	Eugene Island 313A				
	High Island 382F				0.006 - 0.009 (W)
^{228}Ra	Vermilion 298/305		< 0.019 (w)		0.017 - 0.029 (W)
	South Marsh Island 229C	<0.009 - 0.011 (F/C)	<0.013 - 0.023 (W)		
	South Marsh Island 236A	<0.013 - 0.014 (F/C)	<0.015 - <0.006 (W)		
	Vermilion 214A				
	South Marsh Island 130B			<0.017 - 0.067 (F/C)	
	High Island A-595CF			<0.093 - 0.171 (F)	0.022 - 0.051 (W)
	Matagorda Island 703A				
	High Island 323A			<0.018 - 0.107 (F/C)	
	Eugene Island 313A				
	High Island 382F				<0.013 - 0.046 (W)
^{210}Pb	Vermilion 298/305		<0.004 (W)		0.010 - 0.042 (W)
	South Marsh Island 229C	<0.002 - <0.006(F)	<0.006 - <0.009 (W)		
	South Marsh Island 236A	0.011 - 0.012 (F/C)	<0.009 - 0.016 (W)		
	Vermilion 214A				
	South Marsh Island 130B			0.016 - 0.048 (F/C)	
	High Island A-595CF			<0.005 - <0.006 (F)	0.020 - 0.045 (W)
	Matagorda Island 703A				
	High Island 323A			<0.001 - 0.040 (F/C)	
	Eugene Island 313A				
	High Island 382F				<0.011 - 0.018 (W)

< = Below limit of detection.

Radionuclide activities as listed in **Table 6.16** were also consistently low (most values were below the lower limits of detection) in replicate samples (whole individuals) of other fish species which were collected from the sites listed in **Table 4.1**. These fish species included Atlantic croaker, Atlantic cutlassfish, black drum, flounders, great barracuda, greater amberjack, grunts, hardhead catfish, lane snapper, longspine porgy, longtail bass, red drum, sea bass, spotted trout, trouts, vermilion snapper, and wenchman. In samples where enough material was available for radionuclide analyses, slightly higher radionuclide activities were measured in the whole individual or the carcass compared to the edible tissues (fillets).

6.3.5 Loadings vs. Body Burdens

Relationships between mean radionuclide activities in produced water or ambient seawater and bivalve tissues were not apparent (**Figure 6.1**). Similarly, mean radionuclide loadings from produced water discharges were not related to radionuclide activities in bivalve tissues (**Figure 6.2**). These comparative data provide evidence that there is no bioaccumulation of radionuclides in these species.

6.4 SUMMARY

Produced water and produced sand discharges are a potential source of radionuclides in offshore regions of the Gulf of Mexico. Radionuclide activities in produced water varied among platforms and over time. Produced water radionuclide levels are rapidly reduced after entering receiving waters. Based on sediment and interstitial water samples, there was little evidence radionuclide activities were elevated in areas where produced waters were discharged. Radionuclides do not appear to be accumulating in the tissues of organisms living in the vicinity of offshore produced water discharges above background concentrations. The organisms that were most likely to bioaccumulate radionuclides, the sessile filter-feeding bivalves, showed activities in edible tissues that were close to the lower limits of detection at both discharging and non-discharging sites. Pelagic fish, including some that are commonly eaten by humans, captured near the discharging and reference sites were similar in their levels of radionuclides.

6.5 REFERENCES

Continental Shelf Associates, Inc. 1993. Measurements of naturally occurring radioactive materials at two offshore production platforms in the northern Gulf of Mexico. A final report prepared for the American Petroleum Institute, Washington, DC.

Demorest, D.L. and E.S. Wallace. 1992. Radiochemical determination of NORM in produced water utilizing wet chemistry separation followed by radiochemical analysis. In: J.P. Ray and F.R. Engelhardt (eds.), Produced Water: Technological/Environmental Issues. Plenum Press, New York, NY.

Meinhold, A.F. and L.D. Hamilton. 1992. Radium concentration factors and their use in health and environmental risk assessment. In: J.P. Ray and F.R. Engelhardt (eds.), Produced Water: Technological/Environmental Issues. Plenum Press, New York, NY.

Percival, D.R. and D.B. Martin. 1974. Sequential determination of radium-226, radium-228, actinium-227, and thorium isotopes in environmental and process waste samples. Anal. Chem. 46.

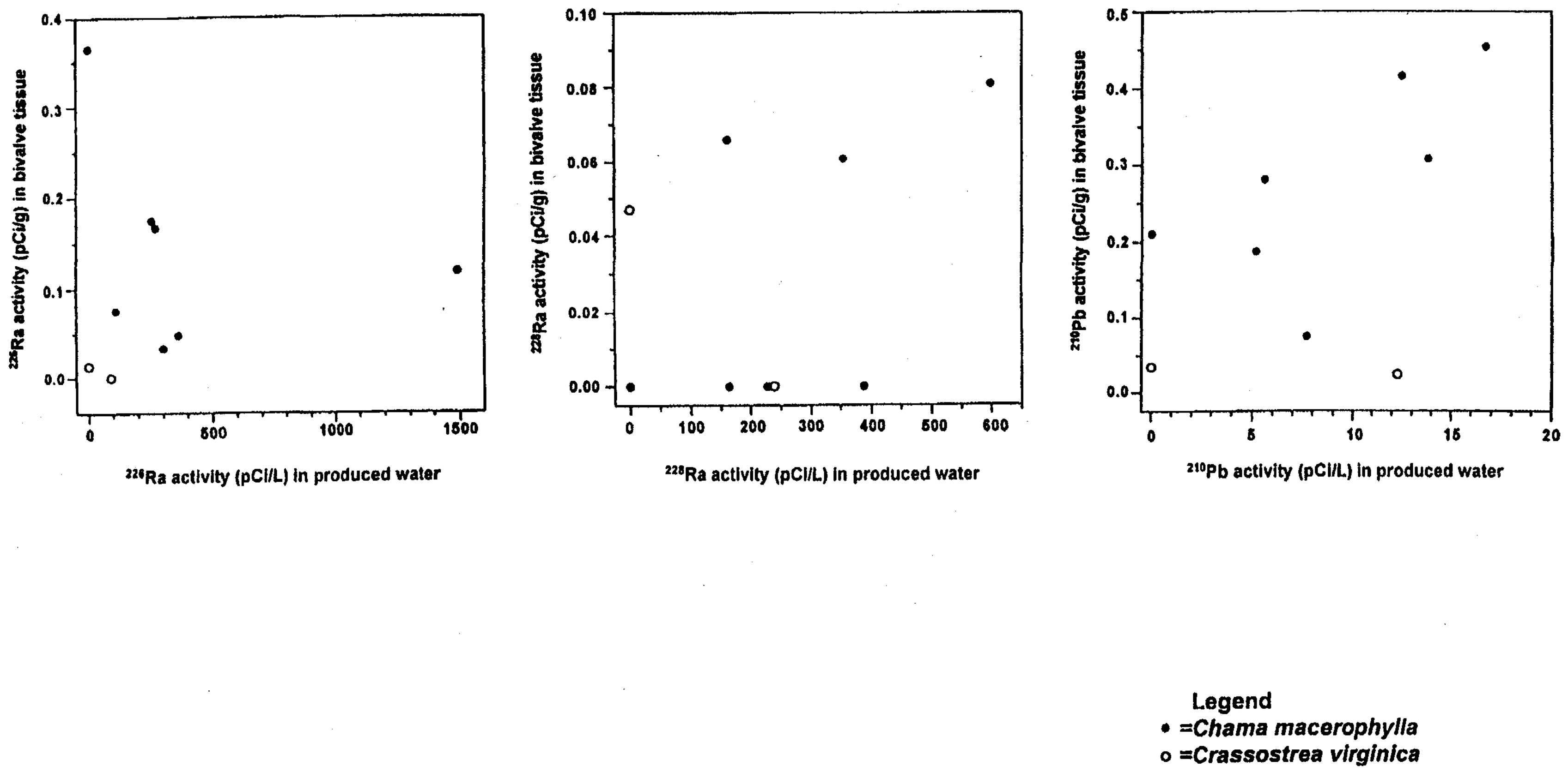


Figure 6.1. Comparison of ^{226}Ra, ^{228}Ra, and ^{210}Pb activities in produced water and edible tissues of the jewelbox (*Chama macerophylla)* and oyster (*Crassostrea virginica)*.

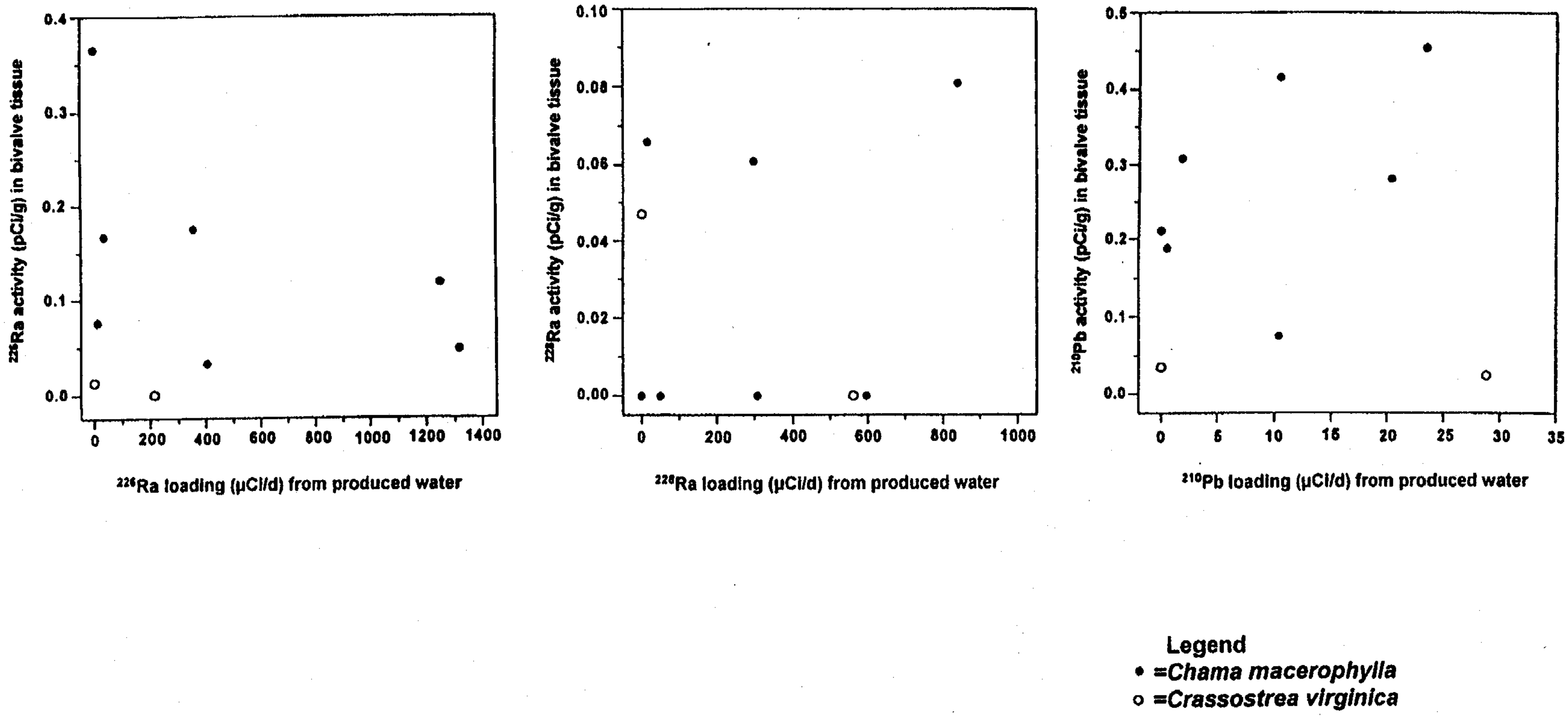


Figure 6.2. Comparison of ^{226}Ra, ^{228}Ra, and ^{210}Pb produced water loadings (activity × discharge rate) and ^{226}Ra, ^{228}Ra, and ^{210}Pb activities in edible tissues of the jewelbox (*Chama macerophylla)* and oyster (*Crassostrea virginica)*.

Smith, B.W. 1995. U. S. Department of Energy oil and gas environmental research programs. The La. Envir. Prof. 12(1):1-39.

Stephenson, M.T. and I.R. Supernaw. 1990. Offshore Operators Committee 44 platform study radionuclide analysis results. Offshore Operators Committee, New Orleans, LA.

U.S. Environmental Protection Agency. 1980. Prescribed methods for measurement of radioactivity in drinking water. EPA 600/4-80-032.

White, G.J. 1992. Naturally occurring radioactive materials (NORM) in oil and gas industry equipment and wastes, A literature review. A report to the U.S. Department of Energy. Contract No. DE-AC07-76ID01570.

6.6 ACKNOWLEDGEMENTS

This work was performed under contract to the U.S. Department of Energy (Contract No. DE-AC22-92MT92001). The assistance of David Demorest and Ronni Mull of Core Laboratories, Inc. is greatly appreciated.

CHAPTER 7 - ASSESSMENT OF METALS IN OIL AND GAS OPERATIONAL DISCHARGES AND ENVIRONMENTAL SAMPLES ASSOCIATED WITH OFFSHORE OIL AND GAS PRODUCTION FACILITIES

John H. Trefry, Robert P. Trocine, Kelly L. Naito, Anita L. Contreras, and Simone Metz
Florida Institute of Technology
Melbourne, Florida

7.1 INTRODUCTION

Concentrations of metals in produced water can be enriched by factors of 10 to greater than 10,000 relative to ambient seawater (Boesch and Rabalais, 1989; Ray and Engelhardt, 1992). This study was designed in part to assess whether organisms inhabiting areas adjacent to platforms that discharge produced water show enhanced bioaccumulation of metals compared with organisms from non-discharging sites. Such studies are limited in number because research efforts have focused more on laboratory toxicity studies to test the effects of produced water on organisms (Jacobs *et al.*, 1992; Schiff *et al.*, 1992). For example, Jacobs *et al.* (1992) showed that 50% of the populations of brine shrimp (*Artemia salina*) and rainbow trout (*Salmo gairdneri*) survived exposure to mixtures of 5:1 and 9:1 produced water:freshwater, respectively. In acute toxicity tests that concentrated on single elements, Jacobs *et al.* (1992) determined EC_{50} levels of 24,000 μg arsenic/L, 11,600 μg cadmium/L and 3,000 μg lead/L. However, direct comparison of these acute toxicity results with data obtained in the field are difficult because concentrations in water surrounding the platform are rarely as high as encountered in laboratory studies. Furthermore, such elevated metal concentrations would persist for only a brief time at discharging sites because dispersion models predict a 1,000-fold dilution of produced water within 20 to 30 m of the discharge point (Brandsma and Smith, 1996). To complement laboratory studies, field measurements of metal accumulation by organisms provide a longer-term integrator of metal uptake and facilitate more detailed environmental risk assessment.

In this chapter, we present concentrations of arsenic, barium, cadmium, chromium, copper, iron, lead, mercury, manganese, molybdenum, nickel, vanadium, and zinc in produced water, produced sand (aluminum and calcium also measured), ambient seawater (except chromium), bivalves - jewelbox (*Chama macerophylla*) and eastern oyster (*Crassostrea virginica*), red snapper (*Lutjanus campechanus*), gray triggerfish (*Balistes capriscus*), and sediments (aluminum and calcium also measured) collected from and near discharging platforms and from reference, non-discharging sites. Results are described within the context of the following: (1) concentrations of metals in produced water discharges versus ambient seawater; (2) concentrations of metals in organisms from reference versus discharging sites; and (3) accumulation of metals in sediments adjacent to oil and gas platforms versus reference sites. Concentrations of the metals in three additional invertebrates [blue crab (*Callinectes spp.*), shrimp (*Penaeus spp.*), and swimming crab (*Portunus spp.*)] from single discharging sites, five fish from single discharging sites [hardhead catfish (*Arius felis*), silver seatrout (*Cynoscion nothus*), Atlantic croaker (*Micropogonias undulatus*), vermilion snapper (*Rhomboplites aurorubens*), and Atlantic cutlassfish (*Trichiurus lepturus*)], and one fish [longspine porgy (*Stenotomus caprinus*)] from two discharging sites are also presented. The main use of metal data for these additional organisms was for risk assessment (**Chapter 9**), rather than for direct comparison of bioaccumulation between discharging and non-discharging sites. Thus, the data are only briefly introduced in this chapter.

7.2 LABORATORY METHODS

Metal concentrations were determined 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 (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. Produced water samples were analyzed directly following appropriate dilution with distilled-deionized water. Ambient seawater samples were analyzed directly for barium and mercury, and following preconcentration on Chelex-100 resin for cadmium, copper, iron, nickel, lead, vanadium, and zinc (Sturgeon *et al.*, 1980) and after preconcentration by reductive precipitation for manganese (Nakashima *et al.*, 1988).

Soft tissue from the bivalves was digested using concentrated HNO_3. Muscle tissue (fillet) was carefully excised from fish specimens and digested in concentrated HNO_3. The carcass remaining after removal of muscle tissue from some fish was homogenized and an aliquot digested with HNO_3. Sediment and produced sand samples were completely digested using a mixture of HF-HNO_3-$HClO_4$. Levels of TOC 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. The concentration of total dissolved solids (TDS) was determined to ±1 g/L in each water sample using a hand-held optical salinometer (Cambridge Instruments, Inc. Model 10419), thereby providing an approximate salt content.

Statistical treatment of the metals data for organisms was carried out, using the Jandel Sigma Stat software program. All metals data for a given species were placed in a common pool and both parametric and non-parametric tests were performed as appropriate. A t-test was used for groups of two and consisted of a normality test and an equal variance test with a 95% confidence level using two degrees of freedom. Analysis of Variance (ANOVA) was used for data sets of three or more. Non-parametric tests used included the Kruskal-Wallis One Way ANOVA on Ranks to identify statistical differences between two or more groups, and the Mann-Whitney Rank Sum test for statistical differences between two groups. The Student-Newman-Keuls Method was used for multiple correlations between several groups.

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 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 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. Records of all prepared solutions and source, including certified analyses, were kept.

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, tissue, 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 from the National Research Council (NRC) of Canada; and (2) TORT-1 lobster hepatopancreas from the NRC, oyster tissue (SRM-1566a) from the NIST and (3) BCSS-1 and BEST-1 marine sediment from the NRC.

MDLs were determined for each analyte, sample type, and matrix. Although general MDLs are presented below, in practice MDLs for metals analyses were sample specific because modifications of procedures (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. Low analyte concentrations

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. Tissues and sediment values are dry weight.

Metal	Sample Matrix	Method Detection Limit
Aluminum	Sediment and Produced Sands	6 µg/g
Arsenic	Produced Water	0.3 µg/L
	Ambient Seawater	0.3 µg/L
	Tissue	0.011 µg/g
	Sediment and Produced Sands	0.1 µg/g
Barium	Produced Water	4.6 µg/L
	Ambient Seawater	0.5 µg/L
	Tissue	0.013 µg/g
	Sediment and Produced Sands	0.1 µg/g
Cadmium	Produced Water	0.1 µg/L
	Ambient Seawater	0.001 µg/L
	Tissue	0.002 µg/g
	Sediment and Produced Sands	0.002 µg/g
Chromium	Produced Water	0.2 µg/L
	Tissue	0.001 µg/g
	Sediment and Produced Sands	0.1 µg/g
Copper	Produced Water	0.2 µg/L
	Ambient Seawater	0.001 µg/L
	Tissue	0.005 µg/g
	Sediment and Produced Sands	2.0 µg/g
Iron	Produced Water	0.9 mg/L
	Ambient Seawater	0.004 µg/L
	Tissue	1.0 µg/g
	Sediment and Produced Sands	5 µg/g
Lead	Produced Water	0.2 µg/L
	Ambient Seawater	0.001 µg/L
	Tissue	0.004 µg/g
	Sediment and Produced Sands	0.1 µg/g
Mercury	Produced Water	0.01 µg/L
	Ambient Seawater	0.01 µg/L
	Tissue	0.001 µg/g
	Sediment and Produced Sands	0.001 µg/g
Manganese	Produced Water	0.1 µg/L
	Ambient Seawater	0.001 µg/L
	Tissue	0.40 µg/g
	Sediment and Produced Sands	2.0 µg/g

Table 7.2. (Continued).

Metal	Sample Matrix	Method Detection Limit
Molybdenum	Produced Water	0.1 μg/L
	Ambient Seawater	0.1 μg/L
	Tissue	0.007 μg/g
	Sediment and Produced Sands	0.1 μg/g
Nickel	Produced Water	1.0 mg/L
	Ambient Seawater	0.003 μg/L
	Tissue	0.006 μg/g
	Sediment and Produced Sands	0.2 μg/g
Vanadium	Produced Water	1.2 μg/L
	Ambient Seawater	0.005 μg/L
	Tissue	0.009 μg/g
	Sediment and Produced Sands	10 μg/g
Zinc	Produced Water	0.1 μg/L
	Ambient Seawater	0.2 μg/L
	Tissue	0.2 μg/g
	Sediment and Produced Sands	1.0 μg/g

were found in procedural blanks used in each analytical sample batch. Low analyte concentrations were also found in field blanks and trip blanks indicating contaminant-free samples. Similarly, evidence that samples were contaminant-free can be found in the low analyte concentrations found in the equipment blanks that were analyzed.

Analytical accuracy and precision was good based on results of the sample duplicates and SRMs. **Tables 7.3** and **Table 7.4** summarize the results of the SRM analyses. All values obtained were within acceptable limits for the particular SRM as established by the certifying agency. Replicate samples analyzed throughout the study to determine analytical and sample precision show that 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.

7.3 RESULTS AND DISCUSSION

7.3.1 Produced Water and Ambient Seawater

The potential for enhanced bioaccumulation of metals from seawater surrounding a platform that is discharging produced water is influenced by the concentration of the metal in the produced water relative to the ambient seawater, the rates of discharge and mixing of the produced water with seawater, and the chemical forms of the metal in the produced water/seawater mixture. Concentrations of metals in produced water from this study were variable and generally much higher than in ambient seawater (**Table 7.5**). 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). In the suite of produced water samples analyzed for this study, a general trend of higher metal levels in samples with higher TDSs was observed (**Table 7.5**). For example, the highest metal levels found for produced water in this study were all from the high salinity discharges (175 g/L TDS) at HI A-595CF (**Table 7.5**). Concentrations of barium and iron were as much as 3 to 4 times higher in produced water from HI A-595CF relative to the other sites (**Table 7.5**) and levels of lead and zinc were 100 to 150 times greater for the HI A-595CF produced water. Considering all produced water samples from this study, the best trend for TDS versus metal concentrations was observed for iron ($r^2 = 0.85$) and most likely reflects the stabilizing effect of chloride ion complexation on dissolved iron (Templeton, 1960; Heinrich and Seward, 1990). Levels of TOC were enhanced in all produced water samples at 120 to 800 mg/L relative to 1 to 2 mg/L in ambient seawater. Although no direct, strong correlations were observed between concentrations of metals and TOC, organic matter complexation of metals certainly helps sustain elevated metal levels in produced water.

Although considerable variability in metal values for produced water was observed from site to site, metal concentrations in samples from the same discharge, collected over the 60-hour period, were very uniform with a coefficient of variance ([standard deviation]/[mean] x 100%) that was generally <10% (**Table 7.5**). The summary data for the produced water samples in **Table 7.5** show the overall uniformity in metal levels over a 60-hour period, thereby providing a reasonable estimate of metal levels during the sampling program.

Table 7.3. Results (mean ± 1 standard deviation) from analyses of standard reference materials (SRMs) for coastal seawater (CASS-2) and river water (SLRS-1). Both SRMs were obtained from the National Research Council (NRC) of Canada. All concentrations in μg/L. Mercury (Hg) is not presented because it is not certified for either SRM.

Reference	As	Ba	Cd	Cr	Cu	Fe	Mn	Mo	Ni	Pb	V	Zn
CASS-2[a] (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
Certified (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[a] (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 ±0.03	0.79 ±0.02	1.05 ±0.03	0.107 ±0.006	0.66 ±0.03	1.2 ±0.1
Certified (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

[a] This study.

Table 7.4. Results (mean ± 1 standard deviation) from analyses of standard reference materials (SRMs) for lobster hepatopancreas (TORT-1), oyster tissue (1566a), and marine sediment (BCSS-1 and BEST-1). The SRMs identified as TORT-1, BCSS-1 and BEST-1 (Hg) were obtained from the National Research Council (NRC) of Canada and SRM 1566a was obtained from the U.S. National Institute for Standards and Technology (NIST). All concentrations in μg/g unless specified.

Reference	Al (%)	As	Ba	Ca (%)	Cd	Cr	Cu	Fe (%)	Hg	Mn	Mo	Ni	Pb	V	Zn
TORT-1[a] (n=18)	--	24.9 ±0.9	3.8 ±1.0	--	26.0 ±0.9	2.3 ±0.3	435 ±10	182 ±4	0.32 ±0.03	23.3 ±0.4	1.4 ±0.1	2.2 ±0.2	10.8 ±0.9	1.3 ±0.2	175 ±4
Certified (NRC)	--	24.6 ±2.2	--	--	26.3 ±2.1	2.4 ±0.6	439 ±22	186 ±11	0.33 ±0.06	23.4 ±1.0	1.5 ±0.3	2.3 ±0.3	10.4 ±2.0	1.4 ±0.3	177 ±10
Oyster 1566a[a] (n=4)	--	13.3 ±0.3	3.2 ±0.4	--	4.29 ±0.19	1.41 ±0.29	67.9 ±1.7	542 ±6	0.061 ±0.002	12.2 ±0.8	0.17 ±0.06	2.2 ±0.2	0.378 ±0.004	4.70 ±0.09	850 ±7
Certified (NIST)	--	14.0 ±1.2	--	--	4.15 ±0.38	1.43 ±0.46	66.3 ±4.3	539 ±15	0.064 ±0.006	12.3 ±1.5	--	2.2 ±0.4	0.371 ±0.014	4.68 ±0.15	830 ±57
BCSS-1[a] (n=19)	6.31 ±0.17	11.3 ±1.1	331 ±23	0.56 ±0.01	0.28 ±0.02	114 ±7	17.6 ±1.0	3.30 ±0.07	0.087[b] ±0.002	232 ±5	2.5 ±0.3	53.1 ±2.9	22.9 ±1.3	92.8 ±4.9	113 ±5
Certified (NRC)	6.26 ±0.22	11.1 ±1.4	(330)[c]	0.54 ±0.05	0.25 ±0.04	123 ±14	18.5 ±2.7	3.29 ±0.10	0.092[b] ±0.009	229 ±15	(1.9)[c]	55.3 ±3.6	22.7 ±3.4	93.4 ±4.9	119 ±12

[a] This study.

[b] Marine sediment SRM BEST-1 from NRC.

[c] Reference value (not certified).

Table 7.5. Concentrations of total dissolved solids (TDS), total organic carbon (TOC), and metals in produced water (PW) and ambient seawater (AS). Values for individual (Component 1) sites are reported as a mean (± 1 standard deviation). Summary values for PW and AS at the bottom of the table are given as ranges or means when the range is small. Any number from this study shown as less than (<) a given value (e.g., <0.1 μg cadmium/L for PW from SMI 236A) is the method detection limit (MDL) for that particular sample. The MDLs differ for the same element in some cases because of the following variations in the method: the original volume of water analyzed, the dilution factor required to minimize the effects of salt matrices, and variations in instrumental and procedural blanks at the time a given sample was analyzed.

Reference	TDS (g/L)	TOC (mg/L)	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 (mg/L)
SMI 236A PW (n=12)	90±1	700 ±40	0.78 ±0.18	162 ±3	<0.1	0.4 ±0.2	<0.2	12±1	0.08 ±0.07	1.2 ±0.03	1.4 ±0.3	<2	0.3 ±0.2	<1.2	0.02 ±0.01
VR 214A PW (n=8)	97±1	440 ±20	5.9 ±0.5	215 ±2	0.3 ±0.3	<0.2	<0.2	12±1	0.04 ±0.02	4.5 ±0.1	1.7 ±0.2	<1	<0.2	<1.2	0.09 ±0.01
SMI 130B PW (n=9)	129±1	140 ±10	0.74 ±0.10	87 ±4	<0.3	0.3 ±0.2	<0.2	29±4	<0.02	1.4 ±0.1	0.8 ±0.4	3±2	0.7 ±0.3	<1.2	0.02 ±0.01
HI A-595CF PW (n=8)	175±3	760 ±50	25 ±4	320 ±14	0.6 ±0.3	<0.1	<0.2	35±2	0.04 ±0.02	7.1 ±0.3	1.4 ±0.3	<1	20 ±6	<1.2	3.0 ±0.4
SMI 236A AS (n=4)	7±1	(2)[a]	1.1 ±0.1	0.088 ±0.002	0.04 ±0.03	ND	1.5 ±0.2	<0.002	<0.01	<0.0002	3	1.3 ±0.2	0.04	1.5 ±0.2	0.005
VR 214A AS (n=3)	26±2	(1)[a]	0.6 ±0.1	0.023 ±0.002	0.01	ND	0.5	<0.0001	<0.01	<0.0003	8	0.5	0.06	1.2 ±0.1	0.005
SMI 130B AS (n=3)	33±1	(1)[a]	1.1 ±0.1	0.015	0.01	ND	0.2	<0.001	--	0.001	10	0.3	--	1.2 ±0.1	0.005
HI A-595CF AS (n=3)	34±1	(1)[a]	1.6 ±0.1	0.015	0.01	ND	0.2	<0.0001	--	<0.0003	10	0.3	0.03	1.2 ±0.1	0.005
PW (n=37)	90-176	120-800	0.5-31	81-342	<0.05-1.0	<0.1-0.8	<0.2	10-37	<0.01-0.2	1-7	0.3-2.2	<1-7	<0.1-28	<1.2	0.01-3.6
AS (n=25)[b]	7-35	1-2	1-2	0.01-0.09	0.020	ND	0.2-1.7	<0.001	<0.01	0.0005	3-10	0.25-1.6	0.02-0.05	1.1-1.7	0.005
PW[c]	--	<0.1-1500	5-300	0.1-2000	0.1-200	--	0.4-1500	--	0.05-2	--	--	0.4-1700	1.5-8800	--	0.1-69

[a] Data from nearby continental shelf locations (Benner *et al.*, 1992).
[b] Includes results from Component 2 sites.
[c] Neff and Sauer (1995).
n = Number of samples analyzed; includes individual samples collected during the field study and intra-laboratory quality control replicates.
ND = Not determined.

Lease Areas:
HI - High Island SMI - South Marsh Island VR - Vermilion

Concentrations of metals in produced water from this study were all 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 6 to 19 times lower than maximum values reported by Neff and Sauer (1995) (**Table 7.5**). In even sharper contrast, the maximum values for cadmium, nickel, and lead in produced water from this study were 200 to 300 times lower than maximum levels from other studies (Neff and Sauer, (1995) (**Table 7.5**). Furthermore, the lowest levels of arsenic, copper, mercury, lead, and zinc in this study were below minimum values presented by Neff and Sauer (1995) in (**Table 7.5**).

Concentrations of dissolved metals in ambient seawater are generally within the ranges expected for nearshore and continental shelf water in the Gulf of Mexico. The four Component 1 sites for which ambient seawater metal data are shown in **Table 7.5** traverse a range of salinities from 7‰ nearshore to about 34‰. Concentrations of barium, copper, and nickel show clear trends of decreasing values with increasing salinities relative to molybdenum which shows the expected opposite relationship. These trends are related to differences in river water versus seawater levels of these metals and the lower reactivities (i.e., longer residence times) of these metals in seawater. In contrast, concentrations of the more reactive metals such as iron, manganese, lead, and zinc show no clear trends with salinity or location and result from a variety of local particle and biogeochemical reactions. Concentrations of dissolved metals in ambient seawater collected at Component 2 reference sites are presented in **Table 7.6** and are included in the summary for ambient seawater in **Table 7.5**. Overall, the dissolved metal data provide a general frame-of-reference for determining metal enrichment in produced water relative to the ambient seawater.

Highest enrichment factors for metal concentrations in produced water versus ambient seawater were found for barium, iron, and manganese with average values ≥10,000 (**Figure 7.1**). Levels of lead and zinc in the produced water were >100-fold enriched relative to ambient seawater. In contrast, produced water samples from this study were depleted with copper, molybdenum, and vanadium compared with ambient seawater (**Table 7.5** and **Figure 7.1**). For mercury, cadmium, and lead, three metals of particular environmental concern, enrichment factors averaged about 10, 30, and 200, respectively. Dispersion models predict a 1,000-fold dilution of produced water within 20 to 30 m of the discharge point (Brandsma and Smith, 1996). Under this model scenario, only concentrations of dissolved barium, iron, and manganese would be above levels for receiving seawater at distances of >30 m from the discharge. Closer to the discharge site, mixing processes may be more complicated and concentrations of other metals such as lead and zinc may be elevated above values for receiving seawater.

Discharge rates for produced water also influence local metal loadings and the dose to which organisms in the area of a specific platform are exposed. Daily discharge rates were 838 m^3 (5,269 bbl/day) at HI A-595CF and 2,353 m^3 (14,800 bbl/day) at SMI 236A. This difference in discharge rates for these two sites yielded calculated metal loadings from each site that agreed within a factor of 3, despite much higher metal concentrations for produced water from HI A-595CF (**Table 7.5**). One notable exception to this similarity was a 47 times higher loading of lead from the HI A-595CF platform versus the SMI 236A platform.

Table 7.6. Concentrations of metals in ambient seawater samples collected at Component 2 reference sites. Values are expressed as a mean ±1 standard deviation (when present). Any number from this study shown as less than (<) a given value is the method detection limit (MDL) for that particular sample.

Site/Metal	As (µg/L)	Ba (mg/L)	Cd (µg/L)	Cu (µg/L)	Fe (µg/L)	Hg (µg/L)	Mn (µg/L)	Mo (µg/L)	Ni (µg/L)	Pb (µg/L)	V (µg/L)	Zn (mg/L)
WC 448	1.0 ±0.1	0.020 ±0.001	0.02	0.4 ±0.05	<0.001	<0.01	0.001	10	0.4	0.61 ±0.35	<1.2	0.009
SMI 186/195	0.8 ±0.1	0.017 ±0.001	0.01	0.3 ±0.04	<0.001	<0.01	<0.003	10	0.3	0.23 ±0.11	<1.2	0.005 ± 0.003
GA A-205	1.2 ±0.1	0.013 ±0.001	0.01	0.2	<0.001	<0.01	<0.003	10 ±1	0.2	0.09	1.3 ±0.1	0.003 ± 0.001
GA A-90	1.0 ±0.1	.014 ±0.001	0.01	0.3 ±0.1	<0.001	<0.01	<0.003	10	0.3	0.12 ±0.08	<1.2	0.003 ± 0.001

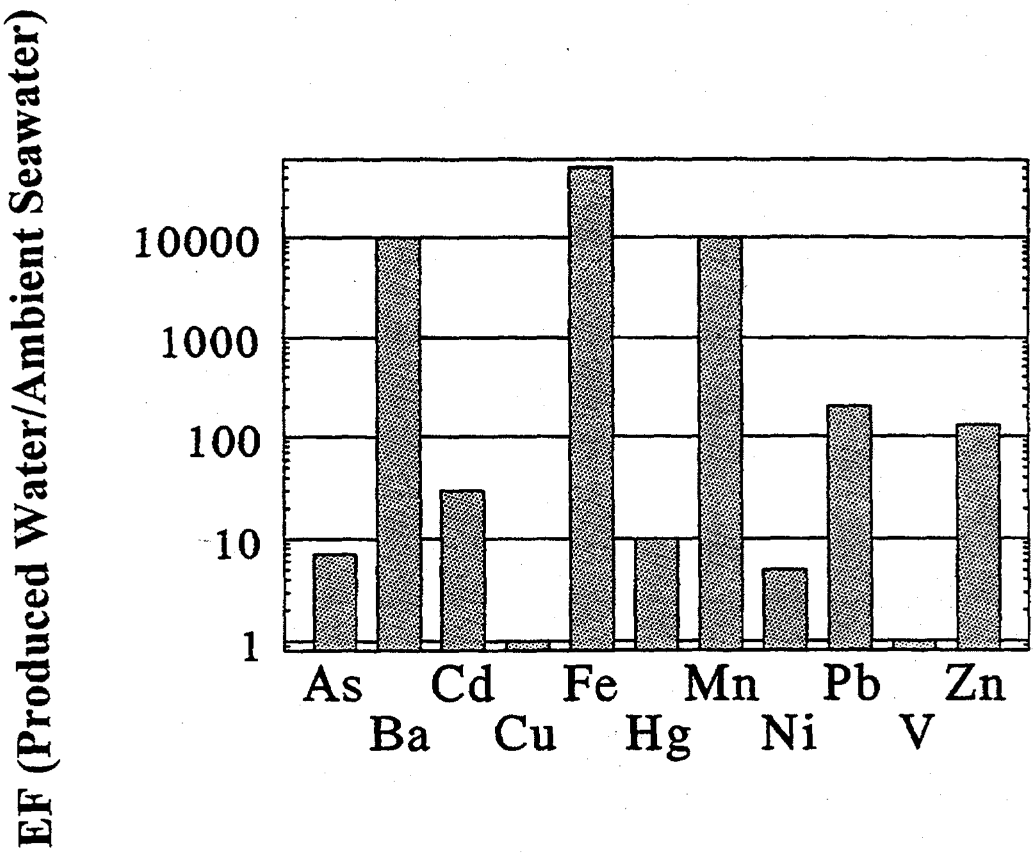


Figure 7.1. Enrichment factor (EF) for metals in produced water relative to ambient seawater.

The behavior and subsequent bioaccumulation of metals following mixing of produced water with seawater is a function of both the concentration and chemical form of the metal of interest in seawater. Once discharged, iron and barium in the produced water most likely precipitate rapidly as oxide and sulfate phases, respectively, and perhaps co-precipitate other metals. However, if barium, iron and other metals are complexed by organic matter, they may stay dissolved in seawater for longer periods of time. Additional studies are necessary to evaluate these processes as they relate to high TOC produced water discharges. The kinetics of manganese oxide precipitation are slower, and manganese generally stays in solution for a longer period of time than barium or iron. Although some of these more complex questions were beyond the scope of this study, the database developed for metals in organisms will help address the more direct question of whether enhanced bioaccumulation of metals occurs near produced water discharges in the Gulf of Mexico.

7.3.2 Mollusks

Metal concentrations were determined in three separate samples of the jewelbox from each of six discharging sites and one reference site (**Table 7.7** and **Figure 7.2**). No statistically significant differences ($\alpha = 0.05$) were observed among the sites for concentrations of barium, iron, lead, vanadium, or zinc. This statistical result is influenced by similar median values, some large standard deviations, and a small sample population. However, the data suggest that produced water discharges are not significantly enhancing bioaccumulation of these metals in jewelbox from the Gulf of Mexico.

Differences in arsenic levels observed for jewelbox from different sites seem to be more dependent on local concentrations of dissolved arsenic in ambient seawater than on discharges of produced water. Jewelbox from three offshore sites, including HI A-389 at 102 m, HI A-595CF at 122 m, and EI 313A at 72 m (**Figure 7.2**) averaged 43 ± 9 μg arsenic/g (dry weight) relative to values of 26 ± 6 μg arsenic/g (dry weight) for jewelbox from three sites in shallower water (MI 703A at 38 m, SMI 130B at 65 m, and VR 214A at 39 m, **Figure 7.2**). Dissolved arsenic values for ambient seawater from HI A-595CF averaged 1.6 ± 0.1 μg/L relative to 1.1 ± 0.1 μg/L for SMI 130B (**Table 7.5**). Using data from sites HI A-595CF and SMI 130B, tissue enrichment factors (EF_{tissue}) relative to seawater were calculated using the following equation:

$$EF_{tissue} = [\mu g \text{ metal/g tissue wet weight}] / [\mu g \text{ metal/g water}]$$

Despite some of the potential variability in water content for tissue samples, wet tissue weights are used in Equation 1 to provide a more direct relationship between seawater and a normal wet tissue sample. Collectively, the jewelbox samples averaged 83.0 ± 2.7% water (n = 21). Using the specific water content for each sample and ambient dissolved arsenic concentration for each site, the EF_{tissue} values for HI A-595CF and SMI 130B were $10^{3.59}$ and $10^{3.70}$, respectively. Using tissue data from the three offshore sites versus the three shallower sites, combined with available water data (**Table 7.5**), values for EF_{tissue} are $10^{3.72}$ and $10^{3.65}$, respectively. Within the limits of the data set, the results suggest that arsenic uptake by the jewelbox is influenced by arsenic levels in ambient seawater and not produced water. This observation is supported by a maximum arsenic enrichment of <20 in produced water (for HI A-595CF) relative to ambient seawater.

Table 7.7. Concentrations (dry weight; mean ± 1 standard deviation) of metals in jewelbox (*Chama macerophylla*) and eastern oyster (*Crassostrea virginica*) from reference and discharging sites. Dry weight concentrations are reported in µg/g. Reference sites are indicated in **bold**.

Bivalve/Site	As	Ba	Cd	Cr	Cu	Fe	Hg	Mn	Mo	Ni	Pb	V	Zn
Jewelbox													
HI A-389	43±11	22±13	7±2	0.8±0.2	4.8±0.4	60±10	0.051[a]	7±2	5±1	9±1	0.2±0.1	1.6±0.3	170±50
HI A-323A	58[a]	79±74	11±1	2.4±0.3	6.6±1.7	290±330	0.125[a]	12±2	47±13	12±1	0.3±0.2	3.5±1.3	151±42
EI 313A	47±8	13±1	14±6	2.5±0.6	5.2±1.1	80±30	0.065[a]	11±3	32±24	8±1	0.3±0.1	2.8±0.6	200±95
HI A-595CF	41±9	43±24	7±3	1.4±0.8	6.0±0.6	210±100	0.046[a]	9±3	6±3	6±2	0.7±0.5	2.2±0.6	145±70
MI 703A	29±3	14±15	4±1	4±3	6.8±1.3	110±60	0.110[a]	9±3	34±11	11±5	0.2±0.1	2.3±0.2	100±30
SMI 130B	26±8	14±2	5±1	1.3±0.5	11±3	180±40	0.054[a]	19±10	6±4	4±2	0.2±0.04	3.0±2.5	90±10
VN 214A	24±6	20±20	5±1	2.0±0.3	6.2±0.4	70±20	0.051[a]	15±2	47±13	5±1	0.2±0.1	4.1±1.1	180±90
Eastern oyster													
SMI 229C	10±1	12±6	5±1	0.7±0.1	98±90	320±170	0.13[a]	28±13	0.24[a]	1.0±0.3	0.4±0.2	1.4±0.1	1760±90
SMI 236A	11±1	11±4	7±2	1.3±0.2	140±30	480±210	0.06[a]	18±5	0.22[a]	1.0±0.1	0.6±0.02	1.6±0.3	1810±300
GOM[b]	8±3	--	6±2	0.6±0.3	250±120	370±140	0.05[a]	18±8	--	2.2±0.6	0.6±0.5	--	1880±730
GOM[c]	10±7	--	4±2	0.6±0.4	150±100	290±160	0.13[a]	14±7	--	1.8±1.6	0.6±0.9	--	2150±1580

[a] single sample (n=1)

[b] Gulf of Mexico oysters from Presley *et al.* (1990) for 3 comparable Louisiana locations (n=27): Joseph Harbor Bayou, Vermilion Bay, and Atchafalaya Bay.

[c] Gulf of Mexico oysters from Presley *et al.* (1990) for 50-69 locations (n=485).

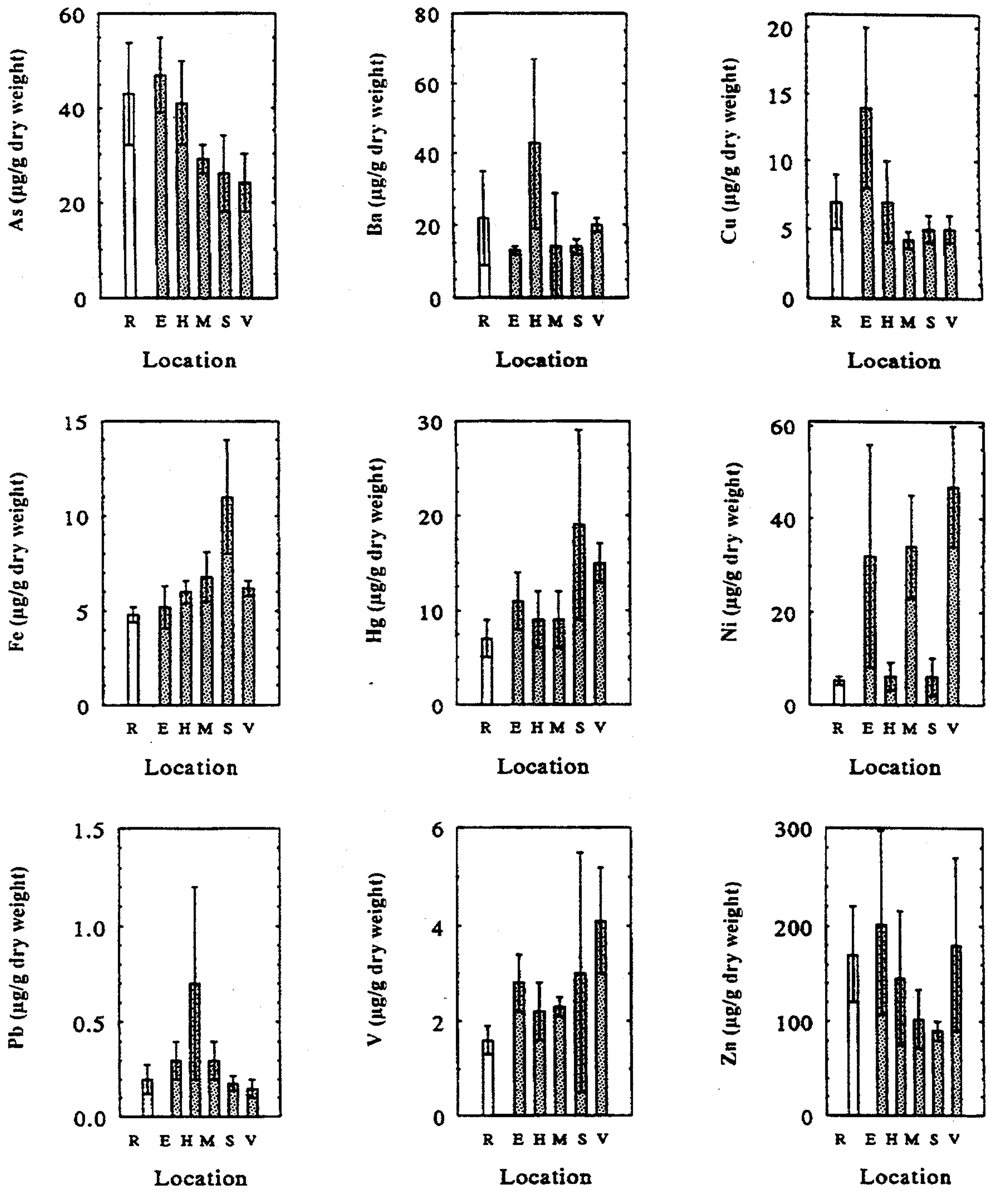


Figure 7.2. Concentrations of As, Ba, Cd, Cu, Mn, Mo, Pb, V, and Zn in jewelbox (*Chama macerophylla*). Locations include a reference site (R) (High Island A-389) and five discharge sites (E = Eugene Island 313A, H = High Island A-595CF, M = Matagorda Island 703A, S = South Marsh Island 130B, and V = Vermilion 214A).

Concentrations of molybdenum in jewelbox show an even stronger bi-modal distribution with samples from HI A-323A, EI 313A, MI 703A, and VR 214A averaging about 40 μg molybdenum/g (dry weight) relative to 6 μg molybdenum/g (dry weight) for samples from HI A-389, HI A-595CF, and SMI 130B (**Table 7.7**). Data for molybdenum in receiving water for VR 214A, SMI 130B, and HI A-595CF show minor differences in concentrations of this relatively conservative and abundant metal among the three sites where jewelbox were collected (**Table 7.5**). Thus, we can draw no simple explanation for the molybdenum distribution in jewelbox from this study. However, because all produced water samples had less molybdenum than ambient seawater, the differences are unlikely to be related to produced water discharges.

For cadmium and copper in jewelbox, concentrations were notably higher at a single site (EI 313A and SMI 130B, respectively) and concentrations of nickel were higher at two locations (HI A-323A and MI 703A) (**Table 7.7**). Similarly, concentrations of mercury averaged 0.053 ± 0.007 μg/g dry weight for five sites with higher values of 0.110 and 0.125 μg mercury/g at MI 703A and HI A-323A, respectively. The iron values for jewelbox were variable but low enough to ensure that these platform-associated bivalves did not contain any significant amount of sediment within their gut that could account for higher metal levels. Such sediment distortion of tissue metal levels would be most conspicuous for nickel and vanadium in these samples because of naturally low tissue levels of these metals, and none is observed (**Table 7.7**). Thus, we have no clear explanation for the above deviations, but note that such variations have been previously reported for bivalves (e.g., Presley *et al.*, 1990). Furthermore, all produced water samples had levels of copper, mercury and nickel that were below or comparable with those for ambient seawater, thereby minimizing the role of produced water discharges in the observed single site anomalies.

Our mean values for lead show that jewelbox from HI A-595CF contained 2 to almost 5 times more lead than those from the other sites (**Figure 7.2**). Although this result is not statistically significant and also may be due to natural variability, we should note that lead loading from HI A-595CF at 16.8 g lead/day is approximately 7 times higher than at SMI 130B (2.5 g lead/day). In a similar fashion, barium concentrations for jewelbox from HI A-595CF are also the highest for this study (**Figure 7.2**). However, this trend for barium is not consistent with loadings as about 268 kg barium/day are released from HI A-595CF, relative to a barium discharge at SMI 130B of 316 kg barium/day. Nevertheless, samples of organisms from platforms discharging produced water with high metal levels and high discharge rates may help to better identify worse-case scenarios for enhanced metal bioaccumulation.

Manganese is one metal with a potential for enhanced bioaccumulation in jewelbox because of its high enrichment factor (≥10,000) in produced water relative to ambient seawater and because the slower kinetics of manganese precipitation in seawater favor survival of the dissolved form in the platform area. However, manganese values of 15±2 μg/g for jewelbox from only one site (VR 214A) are statistically higher than in jewelbox from the reference site (**Table 7.7**). Thus, either the jewelbox is regulating manganese concentrations internally or the influence of high manganese in produced water is not easily discernible.

At the two nearshore sites (SMI 229C and SMI 236A), eastern oyster rather than jewelbox was the available bivalve. No significant differences ($\alpha = 0.05$) were observed for any metals in samples of eastern oyster from SMI 229C versus SMI 236A (**Table 7.7**, **Figure 7.3**). Furthermore, metal levels from this study were in good agreement with results obtained by Presley *et al.* (1990) for eastern oysters from coastal Louisiana and throughout the Gulf of Mexico (**Table 7.7**).

In addition to showing similarities in metal levels between the reference and discharge sites, **Figure 7.3** also shows a greater than three order-of-magnitude range in actual concentrations of the various metals in oyster tissue. The absolute metal concentrations also can be viewed from the perspective of their enrichment relative to seawater. When the tissue data are converted to EF_{tissue} using Equation 1, values greater than 10,000 are calculated for manganese, copper, cadmium, iron and zinc relative to levels of about 100 or less for nickel, vanadium, and barium (**Figure 7.3**). Essential micronutrients such as copper, manganese, iron and zinc can be very efficiently removed from seawater by marine organisms relative to non-essential elements such as arsenic, lead and barium. These data provide a frame of reference for comparing metal concentrations in eastern oysters for future monitoring efforts as well as for establishing universal trends in values for EF_{tissue}.

7.3.3 Red Snapper and Gray Triggerfish

Metal concentrations also were determined for five individuals of red snapper and gray triggerfish from each of two discharging sites (SMI 130B and VR 214A) and one reference site (VR 298/305). No statistical differences ($\alpha = 0.05$) were observed among the sites for concentrations of barium, cadmium, chromium, copper, iron, manganese, molybdenum, nickel, lead, vanadium or zinc for both species of fish (**Table 7.8**). Although this statistical result is influenced by similar median values, some large standard deviations and a small sample population, the results in **Table 7.8** and on **Figures 7.4** and **7.5** certainly support similarities in metal levels for these reference and discharging sites.

Higher levels of arsenic are observed in red snapper and gray triggerfish from the reference site on Sonnier Bank (VR 298/305 at a water depth of 25 m) relative to adjacent, platform sites SMI 130B (water depth of 65 m) and VR 214A (water depth of 39 m) (**Figures 7.4** and **7.5**). Observed arsenic enrichment in fish collected from VR 298/305 (Sonnier Bank) may be related to different food sources or even to movement of outer continental shelf waters into this area via advection or upwelling (Naito, 1994). Whatever the cause for this difference, the results once again show that local environmental conditions may have a greater influence on arsenic levels in biota than produced water discharges. A similar trend to that found for arsenic was observed for mercury in red snapper with the highest average values for samples from the reference site (**Figure 7.4**). In contrast, mercury levels in gray triggerfish from VR 214A average 1.1 μg/g relative to 0.5 μg/g at VR 298/305 (Sonnier Bank) and SMI 130B.

Metal concentrations in fish fillet (**Table 7.8**) are consistently lower than those found for bivalves (**Table 7.7**). Thus, tissue enrichment factors for red snapper fillet (**Figure 7.6**) are 10 to 20 times lower for arsenic, barium, lead, copper and iron, 100 times lower for zinc, and 300 times lower for manganese relative to values calculated for whole samples of eastern oysters (**Figure 7.3**). The micronutrient elements (especially copper, iron and zinc) are actively regulated in fish tissue, leading to the very uniform values shown in **Table 7.8**, and lower tissue enrichment

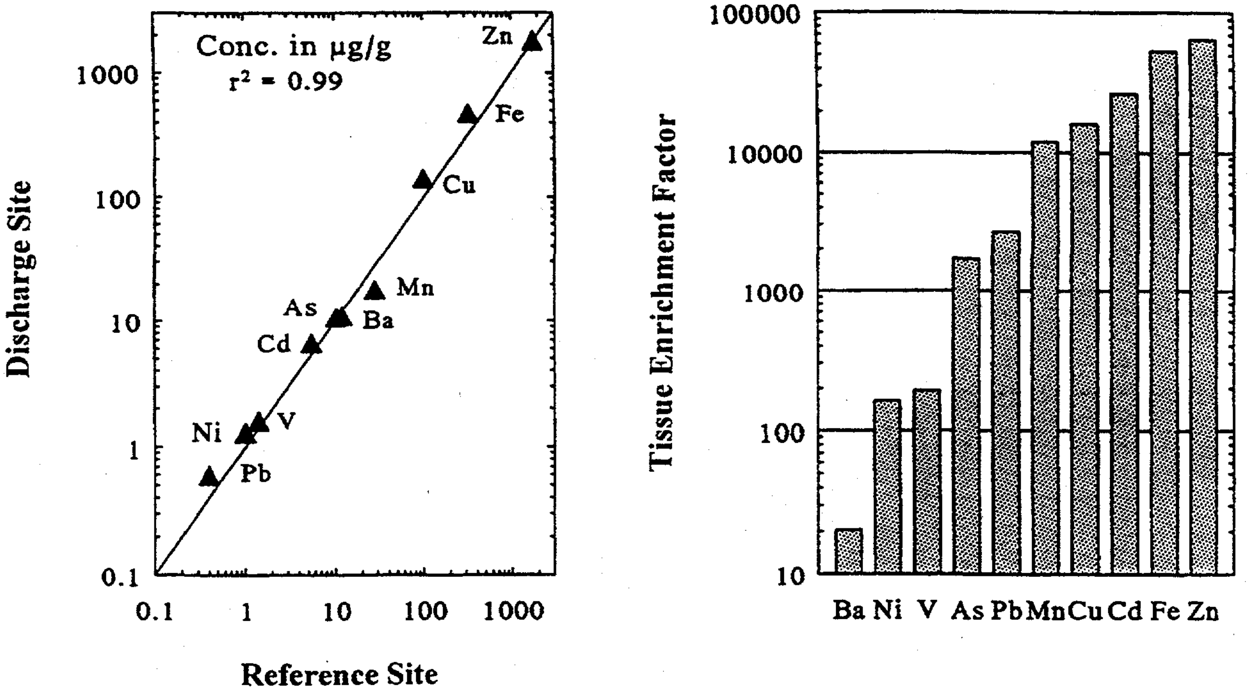


Figure 7.3. Metal concentrations in eastern oyster from discharge (SMI 236A) versus reference (SMI 229C) sites and tissue enrichment factors (relative to seawater) for metals in eastern oyster.

Table 7.8. Concentrations (dry weight; mean ± 1 standard deviation) of metals in muscle tissue (fillet) for red snapper (*Lutjanus campechanus*) and gray triggerfish (*Balistes capriscus*) from reference (non-discharging) and discharging sites (n = 5 for each site). Dry weight concentrations are reported in μg/g. Reference sites are indicated in **bold**. Any number from this study shown as less than (<) a given value (e.g., <0.01 μg Cd/g for red snapper from VR 298/305) is the method detection limit (MDL) for that particular sample. The MDLs differ for the same element in some cases because of the following variations in the method: the original mass of tissue analyzed, the dilution factor required to minimize the effects of organic/salt matrices, and variations in instrumental and procedural blanks at the time a given sample was analyzed.

Biota/Site	As	Ba	Cd	Cr	Cu	Fe	Hg	Mn	Mo	Ni	Pb	V	Zn
Red Snapper													
VR 298/305	3.1±1.8	0.06±0.03	<0.01	0.03±0.02	0.8±0.1	9±2	0.72±0.19	--	<0.04	1.4±0.1	0.1 ±0.05	0.86±0.23	13.3±0.7
VR 214A	1.1±0.6	0.1±0.1	0.03±0.01	0.10±0.14	0.8±0.1	12±5	0.37±0.20	0.4±0.1	2.4±3.5	1.2±0.1	<0.1	0.52±0.03	14.6±0.4
SMI 130B	0.8±0.4	0.05±0.05	--	0.04±0.02	0.8±0.1	7±1	0.28±0.03	0.2	0.08±0.07	1.4±0.1	<0.1	0.70±0.07	13.2±0.7
Gray Triggerfish													
VR 298/305	83±26	0.07±0.02	<0.01	0.10±0.08	1.2±0.3	8±2	0.47±0.31	--	<0.06	1.6±0.1	0.13±0.07	1.0±0.3	24±8
VR 214A	24±9	0.06±0.04	<0.03	0.05±0.05	1.0±0.1	8±1	1.1±0.3	1.1±0.4	0.25±0.50	1.5±0.1	0.07±0.05	0.7±0.1	19±1
SMI 130B	33±13	0.6±0.5	<0.10	0.11±0.16	1.2±0.2	9±3	0.44±0.52	1.1±0.7	<0.03	1.6±0.1	0.09±0.06	0.8±0.1	23±3

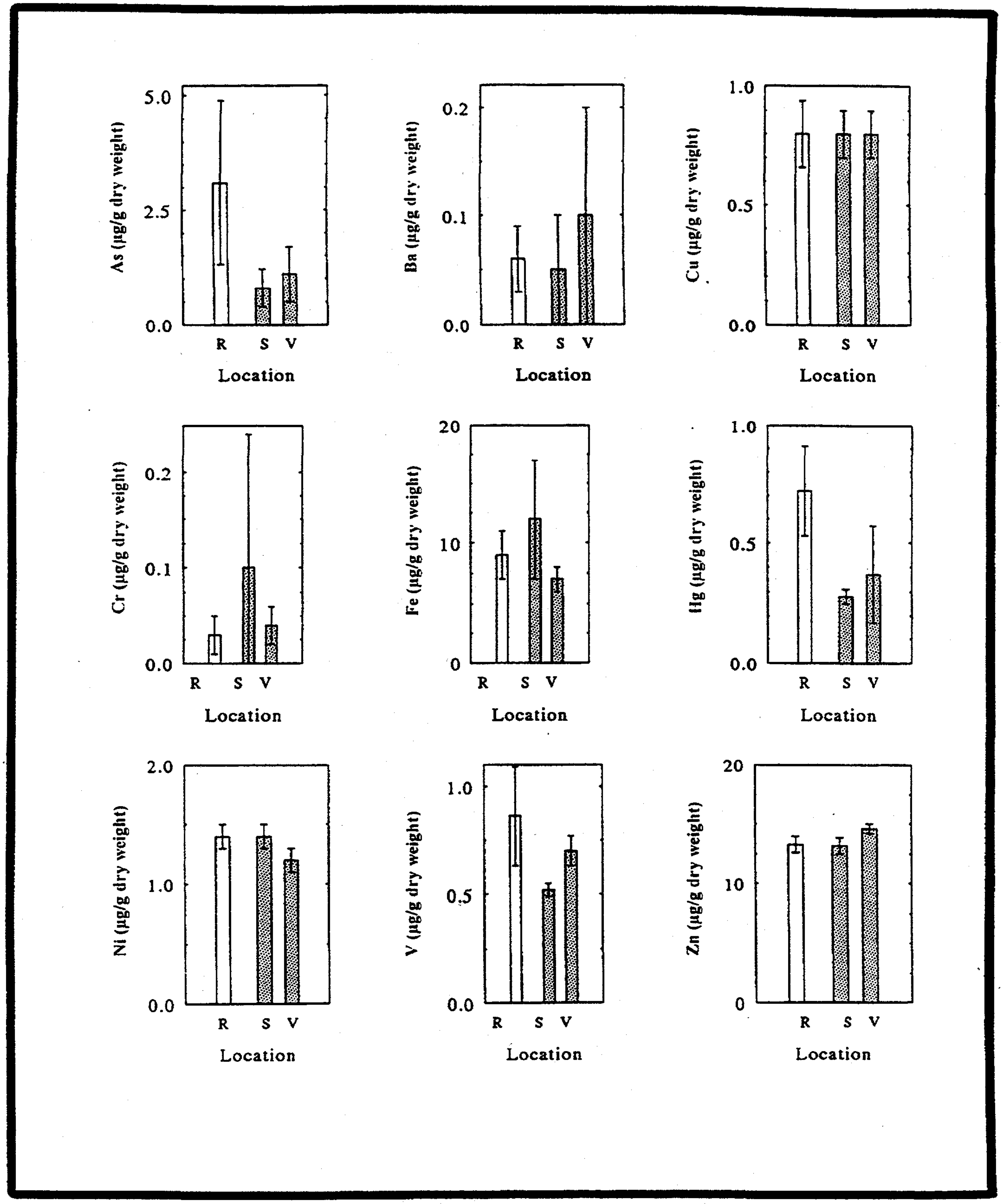


Figure 7.4. Concentrations of As, Ba, Cu, Cr, Fe, Hg, Ni, V, and Zn in red snapper. Locations include a reference site (R) (High Island A-389) and two discharge sites (S = South Marsh Island 130B and V = Vermilion 214A).

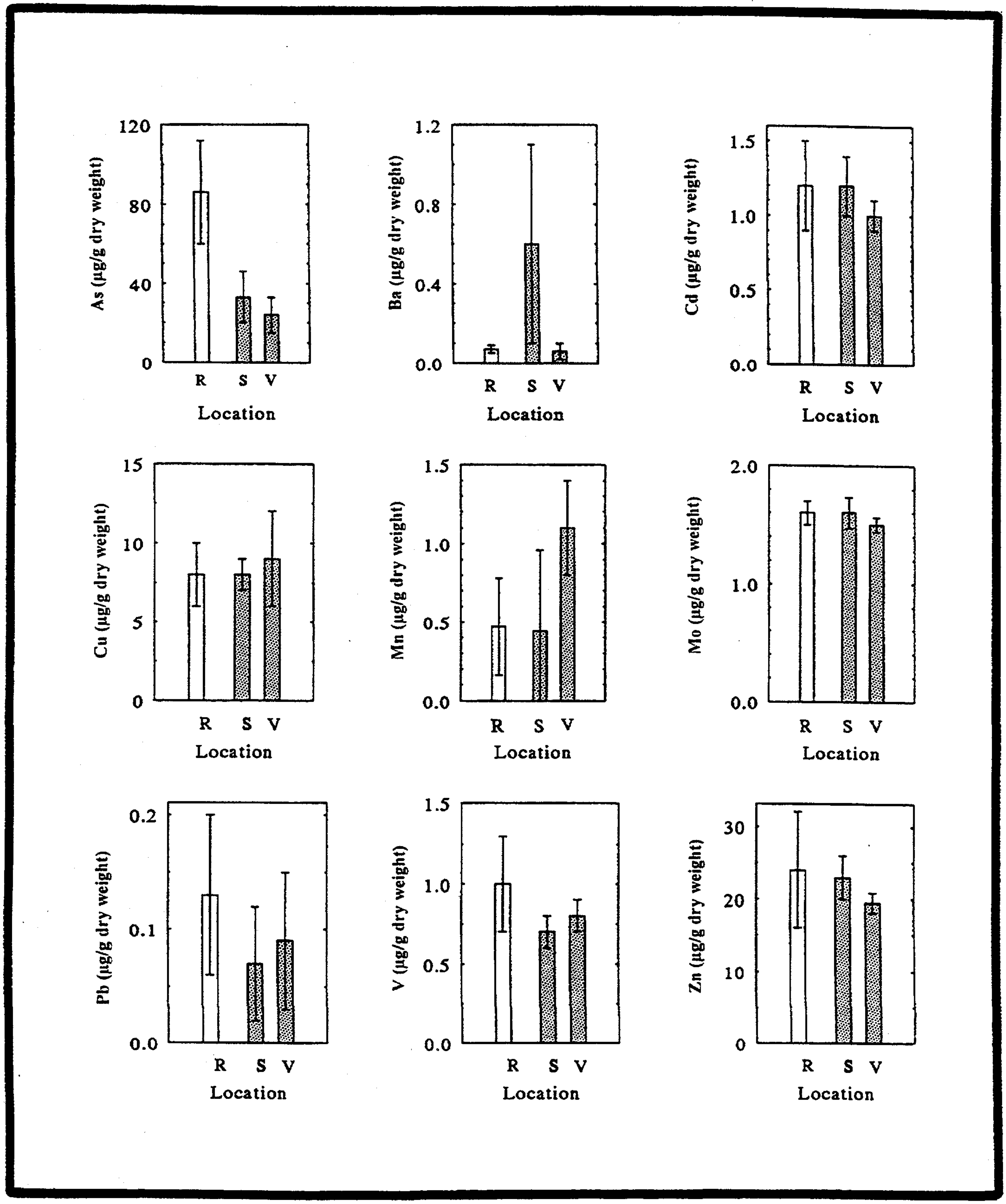


Figure 7.5. Concentrations of As, Ba, Cu, Fe, Hg, Ni, Pb, V, and Zn in gray triggerfish. Locations include a reference site (R) (High Island A-389) and two discharge sites (S = South Marsh Island 130B, and V = Vermilion 214A).

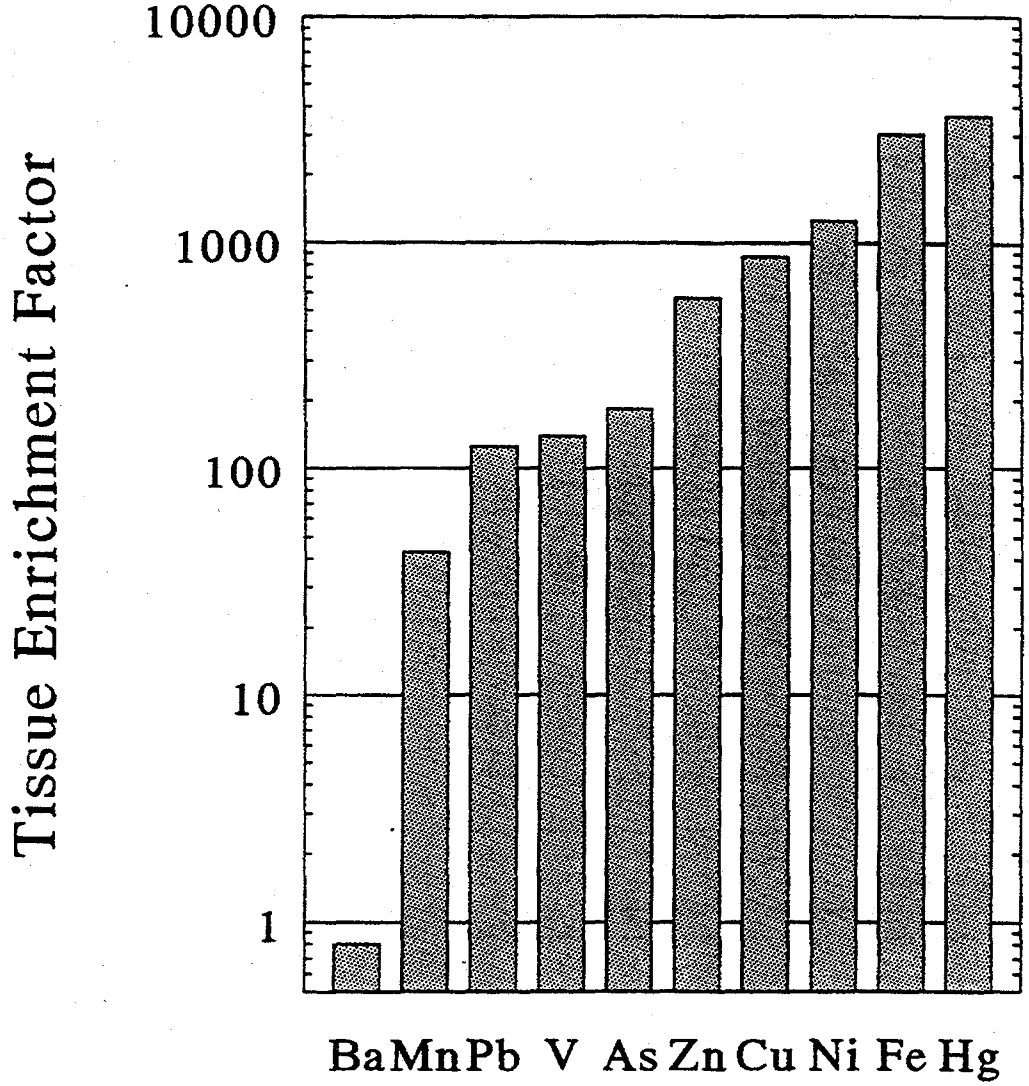


Figure 7.6. Tissue enrichment factors (relative to seawater) for metals in red snapper from the South Marsh Island 130B site.

factors in fish fillet. In sharp contrast, the degree of mercury bioaccumulation was >3,000 in red snapper (**Figure 7.6**) and almost 20 times higher than in the eastern oyster. Bioaccumulation of mercury in fish is favored because most of the mercury stored by fish is in the form of methylmercury (Fergusson, 1990). Once again, both concentrations and tissue enrichment factors provide a frame of reference for comparing metal concentrations in fish for future monitoring efforts as well as for establishing universal trends in values for EF_{tissue}.

Overall, barium levels in fish fillets from this study were low with mean concentrations of <0.1 μg/g (dry weight). In fact, samples of red snapper from SMI 130B averaged 0.012 μg barium/g, wet weight (wet tissue = 77±1 % water) and had EF_{tissue} values of about 1 (**Figure 7.6**). This observation suggests that no bioaccumulation of barium above seawater levels occurs in red snapper. In contrast, about 25% of the gray triggerfish fillets had >0.025 μg barium/g wet weight; and four samples of gray triggerfish from SMI 130B had >0.070 μg barium/g wet weight. The randomness of values in the barium-enriched tissues may be related to incorporation of minute particles of barite as has been noted by Jenkins *et al.* (1989); and it would be valuable to identify the mode of tissue incorporation when enhanced barium levels are determined.

In addition to analysis of muscle tissue (fillet), the remaining carcasses of red snapper and gray triggerfish from two discharging sites (VR 214A and SMI 130B) were homogenized, digested, and analyzed. Metal data for carcasses have been included in this study because many people consume other portions of the fish besides the fillet and because large marine carnivores at the upper end of the food chain eat the entire fish. In general, concentrations of the metals from this study are significantly enriched in the carcass relative to the fillet (**Figure 7.7**; **Tables 7.8** and **7.9**). Barium and manganese show the greatest enrichment (>10 fold) in carcass relative to fillet for both red snapper and gray triggerfish and lead and zinc in gray triggerfish (**Figure 7.7**). Intermediate enrichment in carcass relative to fillet (2 to 10 fold) was observed for chromium, copper, and iron in both fish species and lead and zinc in red snapper. Finally, carcass and fillet concentrations of arsenic, mercury, and nickel were similar (**Figure 7.7**).

7.3.4 Shrimp, Crab, and Additional Fish

Concentrations of arsenic, cadmium, chromium, iron, molybdenum, and nickel samples of shrimp and crabs, each from one discharging location (**Table 7.10**), were lower than found in jewelbox. However, the shrimp and crabs had consistently higher levels of copper, yet similar concentrations of mercury, manganese, lead, vanadium, and zinc to the jewelbox samples. No reference samples of shrimp or crabs were collected from non-discharging platforms. The metal data obtained for these other invertebrates are used in risk assessment (**Chapter 9**).

Metal levels in the vermilion snapper from the two discharging sites (**Table 7.10**) are markedly similar to those reported for the red snapper in **Table 7.8** and, as such, seem to show no evidence of enhanced metal levels relative to the reference site used for red snapper. Metal levels in the other five species of fish (**Table 7.10**) are generally within the range of metal concentrations found for fish with the exceptions of elevated barium and mercury in longspine porgy and iron in silver seatrout, Atlantic croaker, and longspine porgy. Samples of longspine porgy from both SMI 130B and HI A-595CF had very similar metal levels. The fish data presented in **Table 7.10** are used in risk assessment (**Chapter 9**).

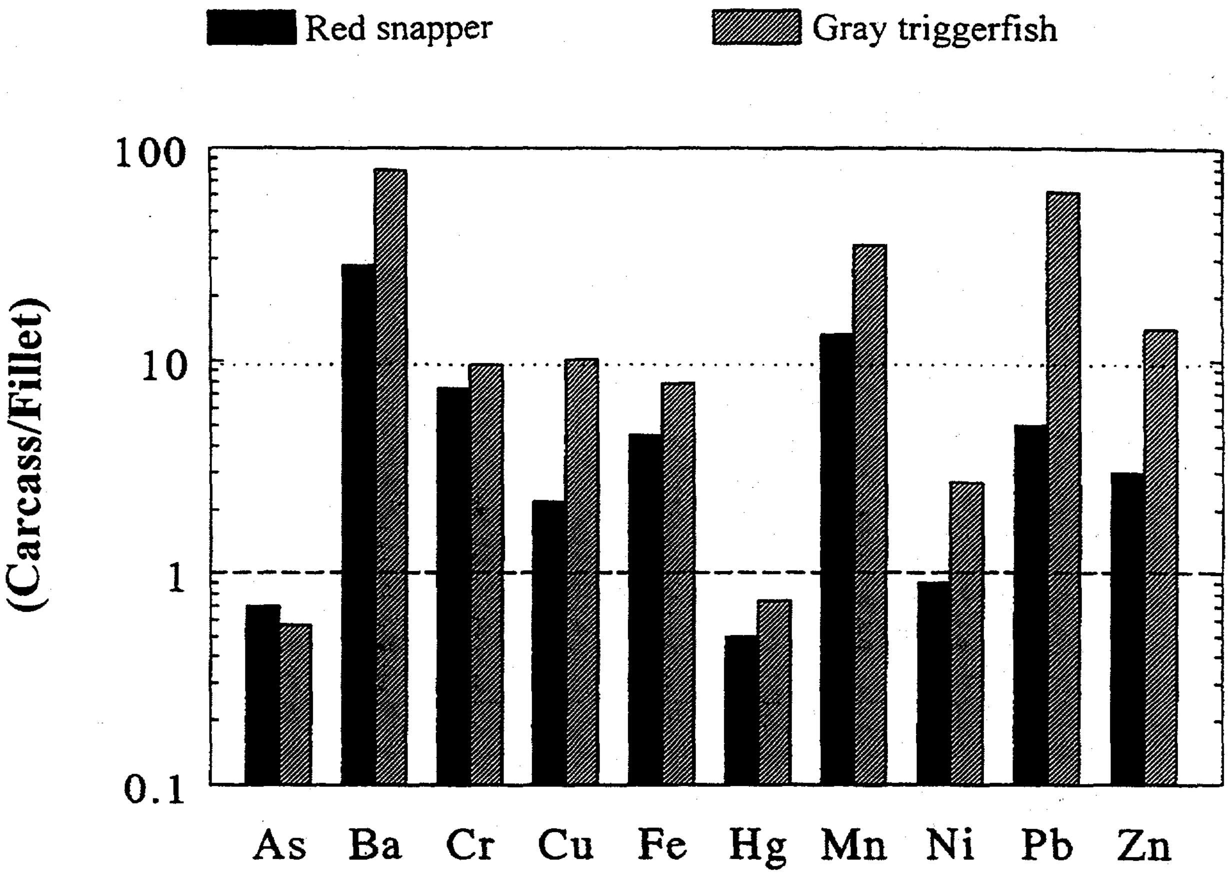


Figure 7.7. Concentrations of metals in carcass/fillet for red snapper and gray triggerfish from discharge sites at Vermilion 214A and South Marsh Island 130B.

Table 7.9. Concentrations (dry weight; mean ± 1 standard deviation) of metals in fish carcass (excluding fillet) for red snapper (*Lutjanus campechanus*) and gray triggerfish (*Balistes capriscus*) from discharging sites (n = 5 for each site). Dry weight concentrations are reported in μg/g.

Site/Metal	As	Ba	Cd	Cr	Cu	Fe	Hg	Mn	Mo	Ni	Pb	V	Zn
Red Snapper													
VR 214A	0.77±0.25	1.6±0.4	0.05±0.01	0.5±0.4	1.9±0.2	48±10	0.16±0.03	4.2±1.0	0.56±0.18	1.5±0.3	0.2±0.1	1.9±0.5	48±6
SMI 130B	0.60±0.31	2.0±0.7	0.17±0.16	0.4±0.1	1.5±0.3	35±8	0.16±0.02	3.3±1.0	0.45±0.17	1.4±0.3	0.8±0.8	1.4±0.4	34±8
Gray Triggerfish													
VR 214A	13±8	8±4	0.6±0.2	0.6±0.4	3.6±0.1	68±3	0.62±0.03	54±2	0.75±0.04	1.6±0.1	7.5±0.0	2.1±0.1	280±4
SMI 130B	20±14	15±10	0.6±0.3	0.8±0.1	20±34	67±9	0.41±0.61	24±6	0.47±0.16	7±13	1.5±1.6	1.7±0.8	320±100

Lease Areas:
VR - Vermilion
SMI- South Marsh Island

Table 7.10. Concentrations (dry weight; mean ± 1 standard deviation) of metals in invertebrates and fish from discharging platforms.

Biota/Metal	As (μg/g)	Ba (μg/g)	Cd (μg/g)	Cr (μg/g)	Cu (μg/g)	Fe (μg/g)	Hg (μg/g)	Mn (μg/g)	Mo (μg/g)	Ni (μg/g)	Pb (μg/g)	V (μg/g)	Zn (μg/g)
Invertebrates													
Shrimp[a]	4.1 ±0.7	4.6 ±1.3	0.14 ±0.02	0.36 ±0.12	32 ± 3	44 ±21	0.04 ±0.01	5.1 ±0.9	0.11 ±0.05	1.0 ±0.1	0.11 ±0.02	0.44 ±0.07	54 ± 3
Blue Crab[a]	10 ± 3	7.4 ±5.8	0.50 ±0.49	0.16 ±0.03	55 ±21	30 ±10	0.29 ±0.14	5.4 ±1.2	0.27 ±0.18	1.3 ±0.1	0.14 ±0.05	1.0 ±0.1	194 ±11
Swimming Crab[b]	35 ± 3	117 ±38	0.88 ±0.22	2.7 ±0.7	26 ± 2	458 ±279	0.09 ±0.02	90 ±15	0.31 ±0.10	7.1 ±1.9	0.93 ±0.83	8.0 ±1.2	78 ±10
Fish													
Silver Seatrout[a]	0.12 ±0.06	5.9 ±1.8	0.18 ±0.23	2.6 ±0.4	5.2 ±4.9	278 ± 51	0.04 ±0.01	15 ±3	0.18 ±0.03	1.3 ±0.2	0.21 ±0.09	0.54 ±0.21	72 ±4
Atlantic Croaker[a]	1.5 ±0.3	8.4 ±2.6	0.06 ±0.02	1.9 ±2.0	2.6 ±0.4	243 ± 92	0.03 ±0.01	29 ±12	0.58 ±0.25	2.4 ±0.8	0.23 ±0.09	2.0 ±0.7	54 ±5
Hardhead Catfish[a]	0.48 ±0.37	1.4 ±0.3	0.04 ±0.03	0.54 ±0.06	2.4 ±0.2	38 ± 6	0.36 ±0.14	1.5 ±0.3	0.02 ±0.00	0.11 ±0.03	0.06 ±0.06	0.11 ±0.06	54 ±17
Atlantic Cutlassfish[a]	0.20 ±0.03	1.3 ±1.1	0.16 ±0.09	2.5 ±2.0	6.9 ±5.3	131 ± 52	0.05 ±0.02	7.0 ±3.3	0.12 ±0.06	1.6 ±0.5	0.12 ±0.02	0.20 ±0.18	42 ±3
Longspine Porgy[b]	0.24 ±0.08	32 ± 22	0.13 ±0.02	5.4 ±2.8	1.5 ±0.3	247 ±118	0.42 ±0.42	23 ±3	0.22 ±0.15	1.8 ±0.9	0.90 ±0.25	2.4 ±0.5	45 ± 3
Vermilion Snapper[b]	3.2 ±0.6	0.06 ±0.01	0.02 ±0.01	0.13 ±0.03	1.4 ±0.0	11 ± 3	0.13 ±0.00	0.3 ±0.1	1.12 ±1.54	1.5 ±0.3	0.08 ±0.03	0.75 ±0.04	13 ± 1
Longspine Porgy[c]	0.40 ±0.17	26 ± 11	0.25 ±0.05	13.3 ±6.7	1.8 ±0.2	309 ±155	0.65 ±0.69	25 ±5	0.21 ±0.05	5.3 ±3.0	0.56 ±0.13	2.8 ±0.5	56 ±4
Vermilion Snapper[c]	3.3 ±0.2	0.24 ±0.26	0.02 ±0.01	0.25 ±0.30	1.6 ±0.0	9 ±1	0.37 ±0.05	0.3 ±0.1	0.05 ±0.04	1.3 ±0.1	0.19 ±0.09	0.69 ±0.04	13 ±0

[a] Samples from discharging site SMI 236A.
[b] Samples from discharging site SMI 130B.
[c] Samples from discharging site HIA 595CF.

7.3.5 Produced Sand

Concentrations of metals in the produced sand samples from SMI 130B and 236A are listed in **Table 7.11**. Concentrations of aluminum and iron are lower in samples of produced sand (**Table 7.11**) than in surficial sediments from the area (**Table 7.12**) because of lower amounts of clay and metal-bearing minerals in the produced sand. Consistent with the observations for aluminum and iron, concentrations of the metals in the produced sand are comparable with or slightly lower than found in area sediments. Higher metal levels in the produced sand sample from SMI 130B, relative to the sample from SMI 236A (**Table 7.11**), are related to the higher amounts of aluminum and iron in the former sample and the increased amounts of clays and metal-bearing phases associated with iron-bearing aluminosilicates.

7.3.6 Sediments

Three sediment samples were collected along the downcurrent transect at distances of 20 and 2,000 m from the Component 1 discharging sites (SMI 236A and VR 214A). At SMI 130B and HI A-595CF, the 20-m stations were moved approximately 30 m. Three sediment samples were also collected at the station located at the discharge for SMI 236A and at each of the Component 2 sites. To assess the presence of contaminant levels of metals in these sediments, concentrations of each metal were plotted versus aluminum to normalize metal values and thereby correct for differences in grain size and mineralogy. Fine-grained, clay-rich sediments naturally contain higher levels of aluminum and metals. As fine-grained sediments introduced from riverine sources are mixed with metal-poor carbonates and coarse-grained sediments, concentrations of aluminum and metals are diluted. Thus, for a suite of uncontaminated sediments with a mixture of grain sizes and mineralogy, a simple straight line, such as shown for nickel versus aluminum in **Figure 7.8** is observed. This trend suggests that no significant enhancement of nickel was observed in sediments from these sites due to platform activities. Similar good correlations were observed for vanadium, iron, manganese, chromium and copper indicating that these metals are generally present at close to natural levels near the sites.

Plots of lead and barium versus aluminum (**Figure 7.9**) show some large deviations from the natural metal/aluminum ratio represented by the straight line on each graph. These anomalies indicate significant anthropogenic inputs of lead and especially barium. The influence of offshore drilling on metals in sediments has been most notable 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 produced waters that have high barium concentrations naturally, due to its enhanced solubility at elevated chloride and low sulfate levels. Elevated barium levels were especially noteworthy (>4,000 μg/g) in sediments from SMI 130B and HI A-595CF. Lead tends to be a more ubiquitous contaminant related to a variety of platform activities (**Figure 7.9**). Concentrations of lead in sediments from SMI 236A are comparable with values of about 30 μg/g for incoming Mississippi River suspended sediment; however, an excess was identified for the 20 m distances from VR 214A and 50/60 m distances from HI A-595CF (**Table 7.12** and **Figure 7.9**). HI A-595CF also has the highest lead loading from produced water; however, the sediment lead enhancement is unlikely to be solely related to produced water.

Table 7.11. Metals concentrations (dry weight; mean ± 1 standard deviation) for produced sand samples collected at SMI 130B and SMI 236A. The MDLs differ for the same element in some cases because of the following variations in the method: the original volume of water analyzed, the dilution factor required to minimize the effects of salt matrices, and variations in instrumental and procedural blanks at the time a given sample was analyzed.

Site/Metal	Al (%)	As (μ/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)
SMI 130B	3.9 ± 0.1	3.7 ± 0.3	1,181 ±832	0.79 ± 0.10	0.43 ± 0.06	28 ± 3	18.7 ± 2.7	1.6 ± 0.3	0.003 ± 0.001	99.5 ± 2.6	3.4 ± 0.3	12.9 ± 0.5	14.5 ± 1.6	16.3 ± 0.2	140 ± 27
SMI 236A	2.0 ± 0.1	2.1 ± 0.2	816 ± 57	0.24 ± 0.03	0.1 ± 0.00	8 ± 1	7.4 ± 6.2	0.5 ± 0.1	0.005 ± 0.001	32.6 ± 2.9	0.8 ± 0.2	< 5.0	8.5 ± 0.0	10.7 ± 0.9	25 ± 2

Table 7.12. Concentrations of metals (dry weight; mean ± 1 standard deviation) in surficial sediments.

Site (m)[a]	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)
SMI 130B (50)	1.6 ±0.4	4.6 ±0.7	695 ±344	2.9 ±0.2	0.72 ±0.22	58 ±33	10.1 ±1.0	1.2 ±0.1	0.35 ±0.16	134 ±24	2.8 ±1.6	6 ±1	7.8 ±2.8	23 ±4	796 ±212
SMI 130B (2,000)	7.7 ±0.3	15.4 ±1.6	3,820 ±1,560	2.7 ±0.2	0.09 ±0.01	75 ±2	15.1 ±1.0	3.5 ±1.0	0.045 ±0.002	956 ±61	2.9 ±1.9	26 ±1	29.3 ±2.3	130 ±16	103±36
SMI 236A (DISCH)	1.2 ±0.6	1.6 ±0.9	605 ±31	1.7 ±0.6	0.19 ±0.06	13 ±4	6.2 ±0.6	1.0 ±0.1	0.017 ±0.021	103 ±37	0.7 ±0.1	6 ±1	12.9 ±0.8	15 ±9	467 ±255
SMI 236A (20)	7.4 ±0.7	7.7 ±0.4	963 ±243	1.1 ±0.4	0.24 ±0.10	77 ±15	19.7 ±3.7	3.6 ±0.4	0.044 ±0.004	772 ±119	1.5 ±0.8	27 ±3	36.1 ±8.1	115 ±12	268 ±24
SMI 236A (2,000)	7.7 ±0.9	8.4 ±0.3	738 ±71	1.7 ±1.0	0.16 ±0.02	83 ±11	18.3 ±2.6	3.7 ±0.5	0.046 ±0.011	781 ±81	0.8 ±0.2	28 ±4	24.4 ±2.3	112 ±13	112 ±9
VR 214A (20)	5.2 ±0.7	4.4 ±0.2	3,010 ±1,750	5.8 ±1.8	0.73 ±0.50	96 ±9	24.8 ±8.5	6.5 ±1.7	0.063 ±0.025	407 ±42	5.7 ±1.0	30 ±6	110±67	91 ±17	275±108
VR 214A (2,000)	7.1 ±0.1	7.7 ±0.6	1,080 ±15	1.7 ±0.1	0.42 ±0.47	79 ±1	11.6 ±0.6	3.1 ±0.02	0.033 ±0.001	940 ±24	0.8 ±0.1	21 ±1	22.8 ±0.1	118 ±10	99 ±4
HI A-595CF (60)	3.2 ±0.2	4.4 ±0.4	6,460 ±4,550	7.0 ±1.7	0.8 ±0.11	41 ±4	9.7 ±1.4	1.7 ±0.1	0.125 ±0.023	241 ±12	0.9 ±0.3	9 ±2	78 ±104	31 ±3	281 ±66
HI A-595CF (2,000)	5.8 ±0.1	8.0 ±0.8	6,350 ±586	8.3 ±3.0	0.12 ±0.03	58 ±3	12.6 ±0.6	2.6 ±0.1	0.054 ±0.008	653 ±124	0.7 ±0.1	21 ±2	24±1	87 ±4	96±5
WC 448	5.82 ±0.33	20.9 ±1.7	546 ±27	6.45 ±1.93	0.08 ±0.0	54.5 ±4.4	11.4 ±0.7	2.96 ±0.08	0.023 ±0.001	599 ±42	4.4 ±0.6	18 ±1	19.9 ±0.8	96 ±15	84.9 ±4.9
SMI 186/195	4.55 ±1.16	13.2 ±5.4	658 ±91	18.3 ±4.7	0.13 ±0.01	47.7 ±8.7	12.1 ±2.9	2.68 ±0.13	0.036 ±0.004	817 ±48	2.1 ±1.9	19 ±3	17.7 ±0.9	88 ±14	74.4 ±9.3
GA A-205	2.66 ±0.15	3.1 ±0.8	327 ±9	4.03 ±0.49	0.06 ±0.01	27.5 ±2.7	4.4 ±0.2	1.08 ±0.10	0.011 ±0.001	221 ±30	1.9 ±2.1	7 ±1	11.3 ±0.4	29 ±1	35.3 ±4.8
GA A-90	4.10 ±0.14	4.7 ±0.3	398 ±7	2.81 ±0.67	0.05 ±0.01	38.5 ±2.7	6.2 ±0.6	1.75 ±0.05	0.014 ±0.001	313 ±15	0.7 ±0.1	12 ±1	14.3 ±0.4	59 ±3	49.4 ±2.7

[a] Distance from platform in meters.
R = Reference (no dishcarge of produced water).

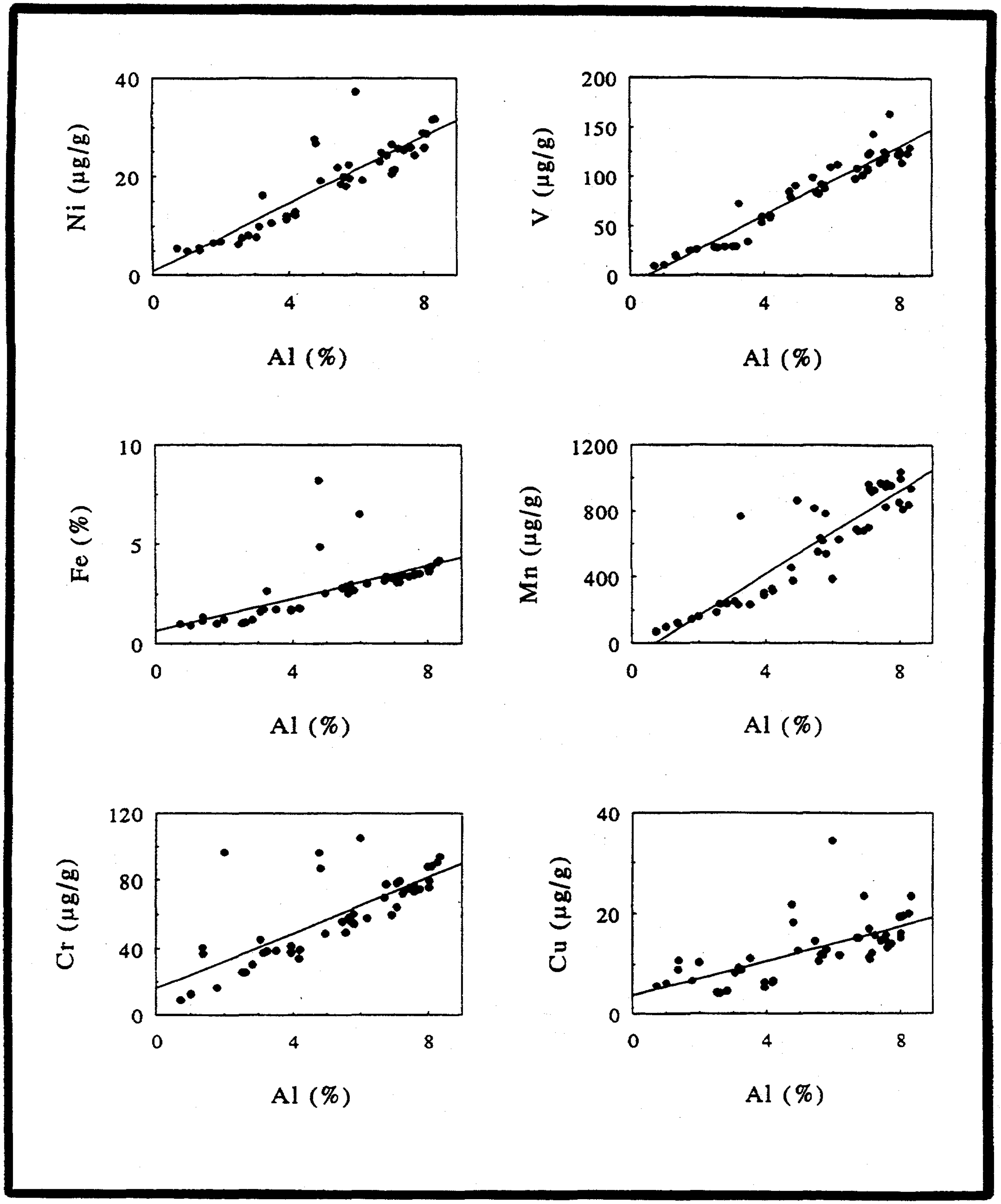


Figure 7.8. Sediment concentrations of Ni, V, Fe, Mn, Cr, and Cu plotted versus Al. The line identifies the natural metal/Al relationship for the northwestern Gulf of Mexico.

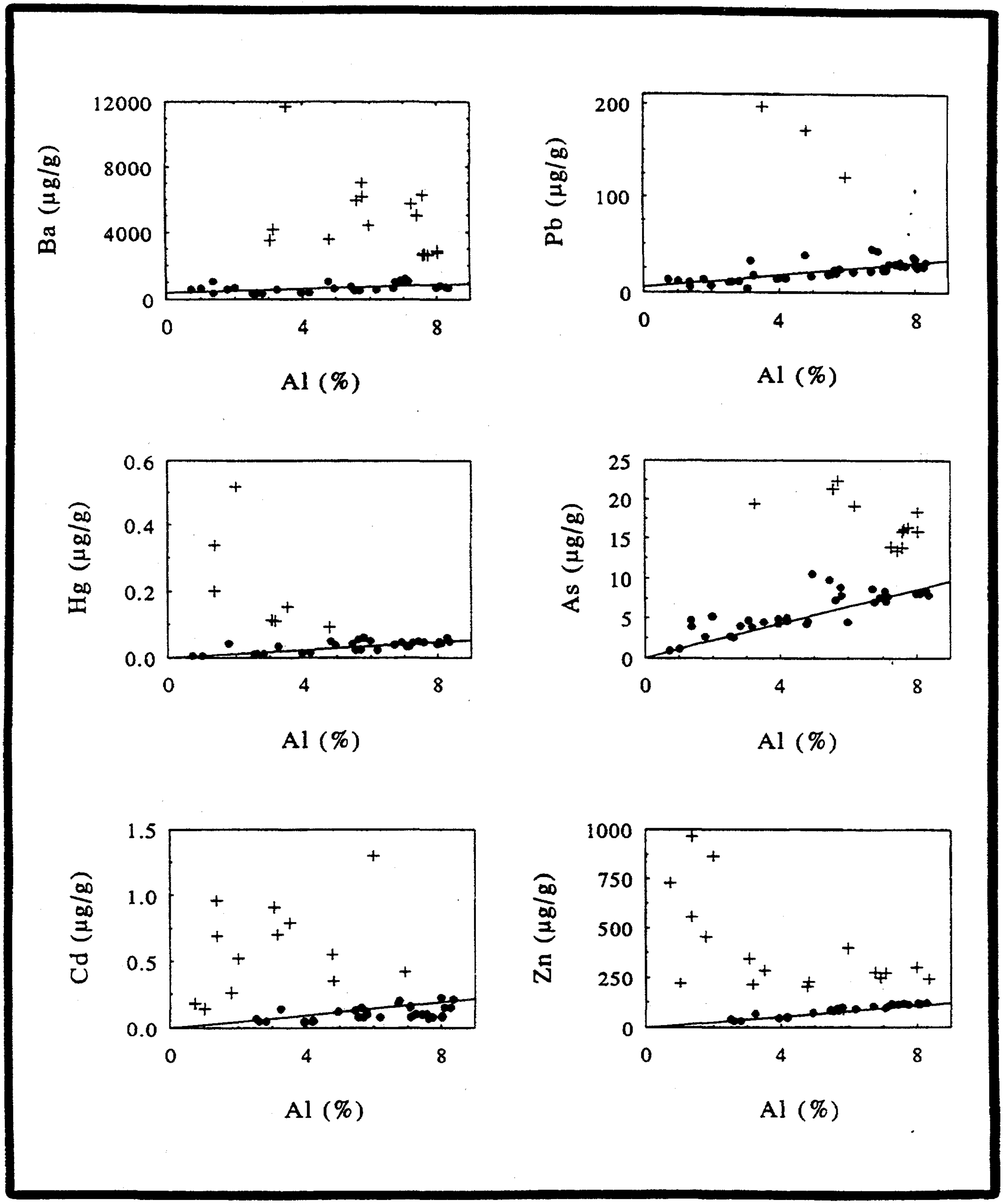


Figure 7.9. Sediment concentrations of Ba, Pb, Hg, As, Cd, and Zn versus Al. The line identifies the natural metal/Al relationship for the northwest Gulf of Mexico. Points marked with a (+) symbol are most likely influenced by anthropogenic inputs.

Elevated levels of mercury, arsenic, cadmium and especially zinc were observed at the near-platform locations (20, 50, and 60 m stations) for SMI 130B, HI A-595CF, and VR 214A. Zinc also is an ubiquitous contaminant and one of the first to be detected in many settings. The instances of contamination from these metals that were observed in this study are most likely related to platform activities, but not necessarily to produced water. This lack of association with produced water is especially pertinent in the instances of arsenic, cadmium, and mercury which have low enrichment factors (<50) for produced water relative to ambient seawater.

7.4 SUMMARY

The highest enrichment factors for metal concentrations in produced water versus ambient seawater samples were found for barium, iron, and manganese with average values ≥10,000. Levels of lead and zinc in the produced water samples were >100-fold enriched relative to ambient seawater samples; and enrichment factors of 5 to 30 were found for arsenic, cadmium, mercury and nickel. In contrast, produced water samples were depleted with copper, molybdenum, and vanadium compared with ambient seawater samples. Dispersion models predict a 1,000-fold dilution of produced water within 20 to 30 m of the discharge point at release rates of ≤4,000 m^3/day (Brandsma and Smith, 1996). Under this model scenario, only concentrations of dissolved barium, iron, and manganese would be above levels for ambient seawater at a distance of >30 m from the discharge. Closer to the discharge site, mixing processes may be more complicated; and concentrations of other metals, such as lead and zinc, may be elevated above values for ambient seawater. Thus, the produced waters sampled in this study most likely have a relatively limited opportunity for enhancing normal bioaccumulation of metals in resident organisms.

No statistically significant differences ($\alpha = 0.05$) in concentrations of barium, iron, lead, vanadium, or zinc were observed in jewelbox (*Chama macerophylla*) between reference and discharging sites; and only one unexplained exception in jewelbox levels was observed for cadmium, copper, nickel, and mercury. However, absolute values for barium and lead in jewelbox were 2 to 5 times higher near one platform, with much higher daily loadings of lead, but not barium, than at other sites. Differences in levels of arsenic observed for jewelbox from different sites seem to be more dependent on local concentrations of dissolved arsenic in ambient seawater than on discharges of produced water. No significant differences were observed for any metals in samples of eastern oyster (*Crassostrea virginica*) from a reference versus the discharging site. Furthermore, metal levels from this study were in good agreement with results obtained by Presley *et al.* (1990) for eastern oysters from coastal Louisiana and throughout the Gulf of Mexico.

No statistical differences ($\alpha = 0.05$) were observed among the sites for concentrations of barium, cadmium, chromium, copper, iron, manganese, molybdenum, nickel, lead, vanadium, or zinc for red snapper (*Lutjanus campechanus*) and gray triggerfish (*Balistes capriscus*). Higher levels of arsenic and mercury were found in fish from the reference site on Sonnier Bank (VR 298/305) than from discharging sites. The observed trends for arsenic and mercury may be related to different food sources or water mass movement.

Sediments from the platform sites often had elevated levels of lead, mercury, arsenic, cadmium and especially barium and zinc relative to aluminum. The level of metal contamination is greatest at stations nearest the platform (20, 50, and 60 m) relative to the 2,000-m station. This enhancement is unlikely to be solely related to produced water; however, additional work would be required to fingerprint metal inputs from produced water.

7.5 REFERENCES

Barth, T. 1991. Organic acids and inorganic ions in waters from petroleum reservoirs, Norwegian continental shelf: a multivariate statistical analysis and comparison with American reservoir formation waters. Appl. Geochem. 6:1-15.

Benner, R., G. Chin-Leo, W. Gardner, B. Eadie, and J. Cotner. 1992. The fates and effects of riverine and shelf-derived DOM on Mississippi River plume/Gulf Shelf processes. Nutrient Enhanced Coastal Ocean Productivity, Pub. #TAMU-SG-92-109, Texas Sea Grant Program, Galveston, Texas; 84-94.

Boesch, D.F. and N.N. Rabalais. 1989. Produced waters in sensitive coastal habitats: an analysis of impacts, Central Coastal Gulf of Mexico. U.S. Department of the Interior, Minerals Management Service, Gulf of Mexico Outer Continental Shelf Region, New Orleans, Louisiana. OCS Report/MMS 89-0031.

Boothe, P.N. and B.J. Presley. 1987. The effects of exploratory petroleum drilling in the Northwest Gulf of Mexico on trace metal concentrations in near rig sediments and organisms. Environ. Geol. Water Sci. 9:173-182.

Brandsma, M.G. and J.P. Smith. 1996. Dispersion modeling perspectives on the environmental fate of produced water discharges, pp. 339-354. In: M. Reed and S. Johnsen (eds.), Produced Water 2: Environmental Issues and Mitigation Technologies. Plenum Press, New York.

Fergusson, J.E. 1990. The Heavy Elements: Chemistry, Environmental Impact and Health Effects. Pergamon Press, Oxford. 614 pp.

Fredericks, A.D. and W.M. Sackett. 1970. Organic carbon in the Gulf of Mexico. J. Geophys. Res. 75:2,199-2,206.

Heinrich, C.A. and T.M. Seward. 1990. A spectrophotometric study of aqueous iron (II) chloride complexing from 25 to 200°C. Geochim. Cosmochim. Acta 54:2,207-2,221.

Helgeson, H.C., A.M. Know, C.E. Owens, and E.L. Shock. 1993. Petroleum oil field waters and authigenic mineral assemblages: Are they in metastable equilibrium in hydrocarbon reservoirs? Geochim. Cosmochim. Acta 57:3,295-3,339.

Jacobs, R.P.W.M, R.O.H. Grant, J. Kwant, J.M. Marquenie, and E. Mentzer. 1992. The composition of produced water from Shell operated oil and gas production in the North Sea, pp. 13-22. In: Ray, J.P. and F.R. Engelhardt (eds.), Produced Water. Plenum Press, New York.

Jenkins, K.D., Ball, J.W., Burchard, J.M., Vivit, D.V., and Barks, J.H. 1989. Sediment deposition, biological accumulation and subcellular distribution of barium following the drilling of an exploratory well, pp. 587-608. In: Engelhardt, F.R., J.P. Ray and A.H. Gillam (eds.), Drilling Wastes. Elsevier Applied Science, London.

Naito, K.L. 1994. Bioaccumulation of As, Ba, Cu and Zn in fish and bivalves collected near produced water outfalls in the Gulf of Mexico. M.S. thesis, Florida Institute of Technology, Melbourne.

Nakashima, S., R.E. Sturgeon, S.N. Willie, and S.S. Berman. 1988. Determination of trace elements in sea water by graphite-furnace atomic absorption spectrometry after preconcentration by tetrahydroborate reductive precipitation. Anal. Chim. Acta 207:291-299.

Neff, J.M. and T.C. Sauer, Jr. 1995. Barium in Produced Water: Fate and Effects in the Marine Environment. API Publication 4633. American Petroleum Institute, Washington, DC.

Presley, B.J., R.J. Taylor, and P.N. Boothe. 1990. Trace metals in Gulf of Mexico oysters. Sci. Total Environ. 97/98:551-593.

Ray, J.P. and F.R. Engelhardt (eds.). 1992. Produced Water. Plenum Press, New York. 616 pp.

Schiff, K.C., D.J. Reish, J.W. Anderson, and S.M. Bay. 1992. A comparative evaluation of produced water toxicity, pp. 199-208. In: Ray, J.P. and F.R. Engelhardt (eds.), Produced Water. Plenum Press, New York.

Sturgeon, R.E., S.S. Berman, A. Desaulniers, and D.S. Russell. 1980. Pre-concentration of trace metals from sea-water for determination by graphite furnace atomic-absorption spectrometry. Talanta 27:85-94.

Templeton, C.C. 1960. Solubility of barium sulfate in sodium chloride solutions from 25° to 95°C. J. Chem. Eng. Data. 5:514-516.

Trocine, R.P. and J.H. Trefry. 1983. Particulate metal tracers of petroleum drilling mud dispersions in the marine environment. Environ. Sci. Tech. 17:507-512.

7.6 ACKNOWLEDGMENTS

We thank our collaborators at Continental Shelf Associates, Inc. for their assistance during this study with special appreciation for the efforts of and discussions with Bruce Graham and Al Hart. We also thank Annette Bernard of Florida Institute of Technology for her efforts in preparing the manuscript. This study was supported by the U.S. Department of Energy, Contract Number DE-AC22-92MT92001.

CHAPTER 8 - ASSESSMENT AND FINGERPRINTING OF VOLATILE AND SEMIVOLATILE HYDROCARBONS IN DISCHARGES AND ENVIRONMENTAL SAMPLES ASSOCIATED WITH OFFSHORE OIL AND GAS PRODUCTION FACILITIES

Ted Sauer
Woods Hole Group
Cataumet, Massachusetts

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, produced sand, discharge plume/receiving water, ambient seawater, sediment, and biota as part of an environmental assessment of production related discharges from offshore oil and gas facilities in the U.S. Gulf of Mexico. This assessment included characterization of total hydrocarbons (THCs), SHCs, VAHs, and PAHs in representative environmental samples near producing oil and gas operations. 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. The specific VAH and PAH target hydrocarbons determined in these samples are listed in **Table 8.1**. These hydrocarbon results are used in the environmental risk assessments (including bioaccumulation) in **Chapter 9**.

In this chapter, hydrocarbon composition and concentrations are evaluated in environmental samples near produced water discharging platforms and from reference sites in the central and western part of the Gulf of Mexico. This evaluation includes assessment of hydrocarbon spatial trends, interrelationships of hydrocarbon composition among the different types of samples, and potential sources of the hydrocarbons in the environment. Analyte distributions and summary data tables were produced to assist in the interpretation of the data.

8.1.2 Saturated Hydrocarbons and Polycyclic Aromatic Hydrocarbons Background Information

SHCs 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 *et al.*, 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

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

VAHs[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)
*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 (BGHI)

*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 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 in offshore environments due to 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 concentration is also determined. In this study THC concentration 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 2- through 6-ringed polycyclic aromatic and sulfur-heterocyclic hydrocarbons (PAHs), and include the alkyl homologues (C_1, C_2, C_3, C_4 alkyl carbon substituents on the parent compound) of the prominent 2- through 4-ringed 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, 1987; Neff and Anderson, 1981), 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.*, 1995b).

PAHs in the environment are prominently of pyrogenic or petrogenic origin. There are some PAHs that have a diagenic origin, such as perylene and retene (methyl, propyl phenanthrene) which are formed by chemical transformation of certain biological precursors during early diagenesis (Venkatesan, 1988). Pyrogenic PAH distributions consist of relatively high amounts of the 4- through 6- 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 alkyl groups ($C_0 > C_1 > C_2 > C_3 > C_4$). 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).

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 PAH abundance predominates within a PAH family. For fossil fuels, especially petroleum, the relative abundances of each family of PAHs 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 dibenzothiophenes and phenanthrenes. Also, petrogenic hydrocarbons usually contain relatively low amounts of 5- and 6-ringed 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 UCM in the GC trace changes and the concentration of the UCM initially increases. 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: $C_1 > C_2 > ...$). 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 5- and 6-ringed PAHs has not been studied extensively, their high molecular weight affords a structure that would be recalcitrant to biodegradation.

8.2 LABORATORY METHODS

Analyses for VAHs, SHCs (C_{10}-C_{32} n-alkanes, pristane and phytane), and PAHs listed in **Table 8.1** were conducted at ADL. Produced water was analyzed for VAHs, SHCs, and PAHs; ambient seawater for VAHs and PAHs; sediment and produced sand for SHCs and PAHs; and biota tissue for PAHs. 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 GC 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 GC and detected with a MS, 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.

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 270°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 each of the matrices, water, sediment, and tissue, required different procedures. The extract cleanup, fractionation, and instrumental analysis were identical for all 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

Produced Water and Ambient Seawater. Water samples were extracted three times with a solvent mixture of 1:1 acetone:methylene chloride utilizing an ambient temperature shaking method. Details of the extraction procedure are provided in **Figure 8.1.**

Sediment and Produced Sands. 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 8.2.**

Tissue. Each of the tissue samples were extracted by an established extraction procedure (Sauer and Boehm, 1995). The extraction method for tissue samples is provided in **Figure 8.3.** As indicated in the figure, preparation of the sample for extraction involved slightly different procedures for each type of tissue sample.

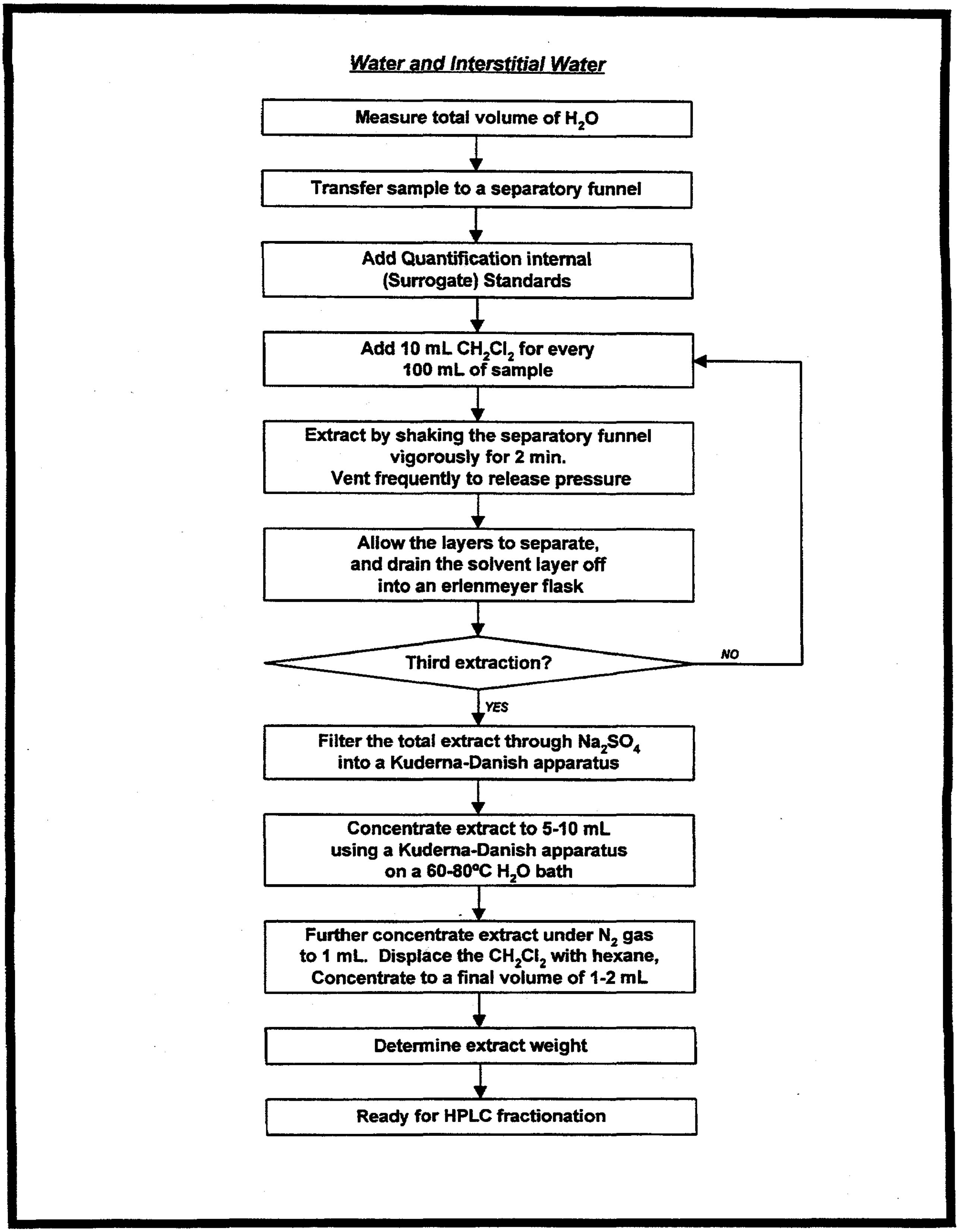


Figure 8.1. SHC/PAH extraction procedure for produced water and ambient seawater samples.

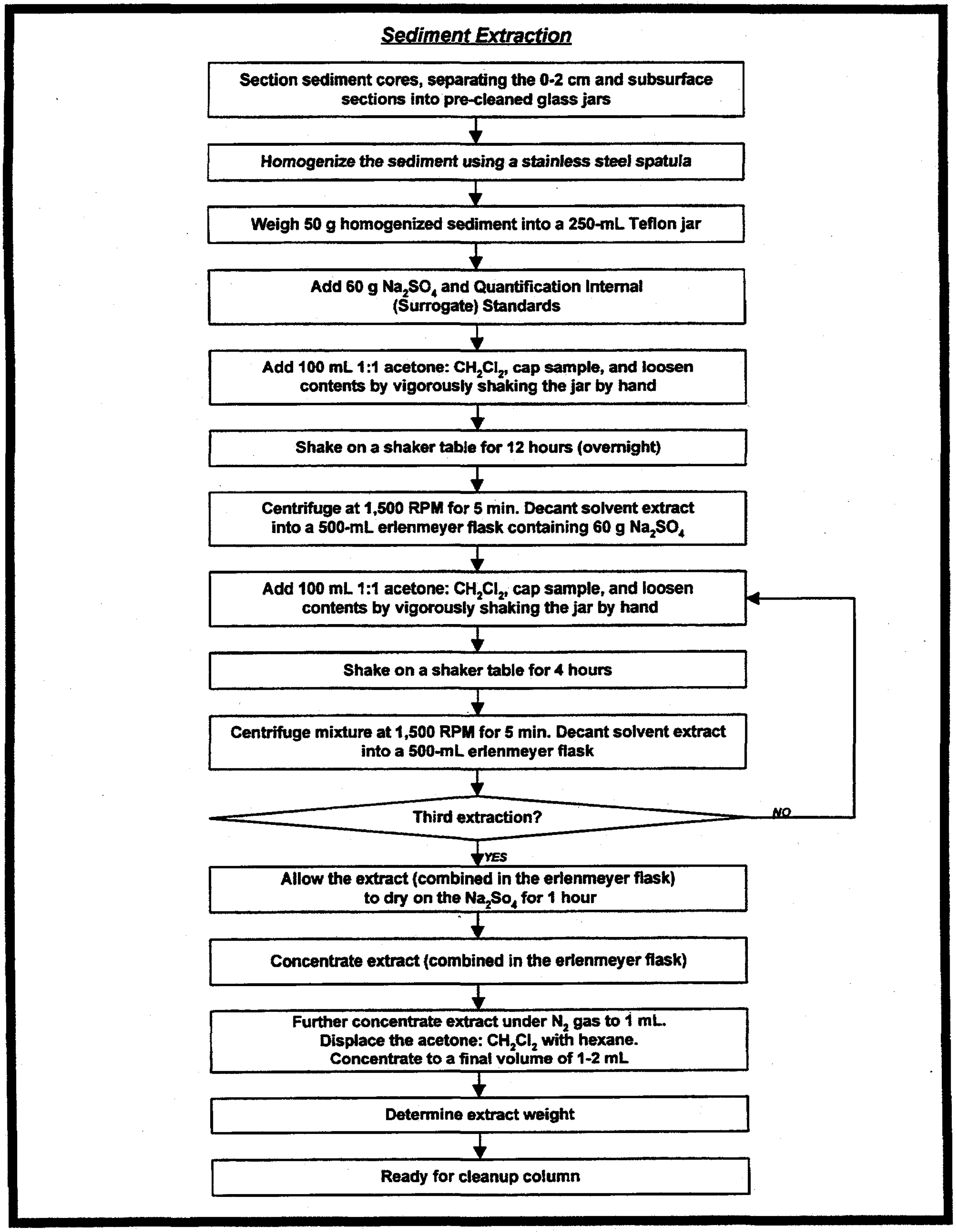


Figure 8.2. SHC/PAH extraction procedure for sediment and produced sand samples.

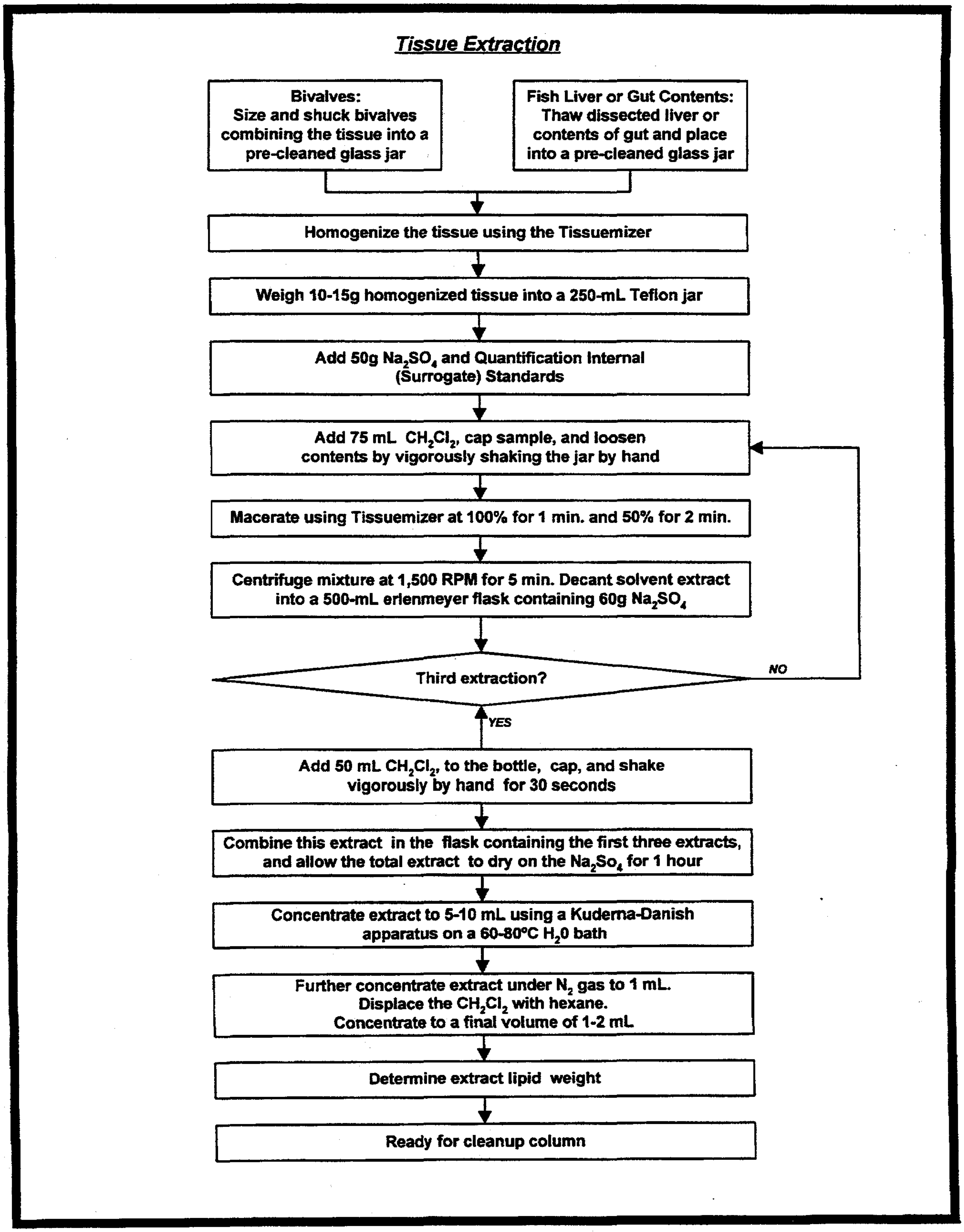


Figure 8.3. SHC/PAH extraction procedure for tissue samples.

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 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 analytes.

8.2.2.4 Instrumental Analysis

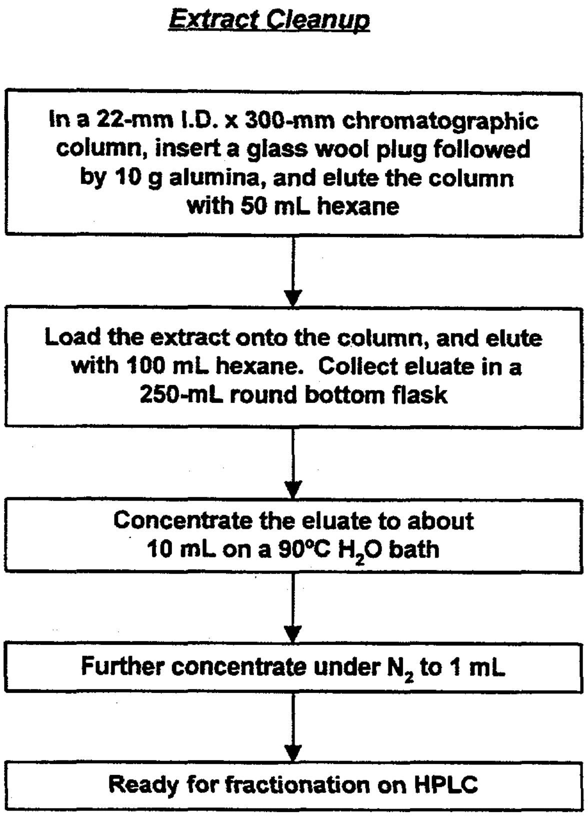
The final processed extracts were analyzed for the target SHCs and THCs by GC/FID and the target PAHs by GC/MS. The GC/MS analysis of PAHs was performed in the selected ion monitoring (SIM) mode. This mode of operation for GC/MS improves (i.e., lowers) the instrumental detection limits for PAHs and allows for detection of PAHs at the parts per trillion concentrations (ng/L) for water samples and parts per billion concentrations (μg/kg) for sediment and tissue samples. The lower method detection limits for individual PAH analytes of approximately 10 ng/L in water samples and 10 ng/g in sediment and tissue samples are especially necessary for the tissue 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 DQOs 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 including water, sediment, and tissue samples, 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 CSA, were accomplished and individual samples



In a 22-mm I.D. x 300-mm chromatographic column, insert a glass wool plug followed by 10 g alumina, and elute the column with 50 mL hexane

Load the extract onto the column, and elute with 100 mL hexane. Collect eluate in a 250-mL round bottom flask

Concentrate the eluate to about 10 mL on a 90°C H_2O bath

Further concentrate under N_2 to 1 mL

Ready for fractionation on HPLC

Figure 8.4. Extract cleanup column procedure.

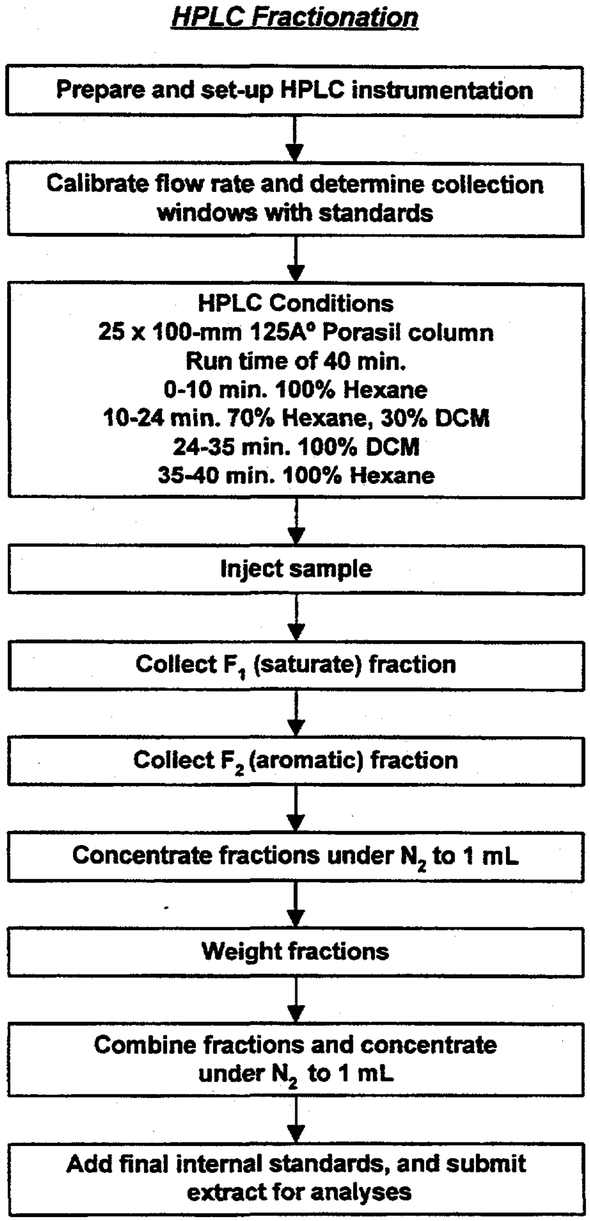


Figure 8.5. High-performance liquid chromatography (HPLC) fractionation procedure.

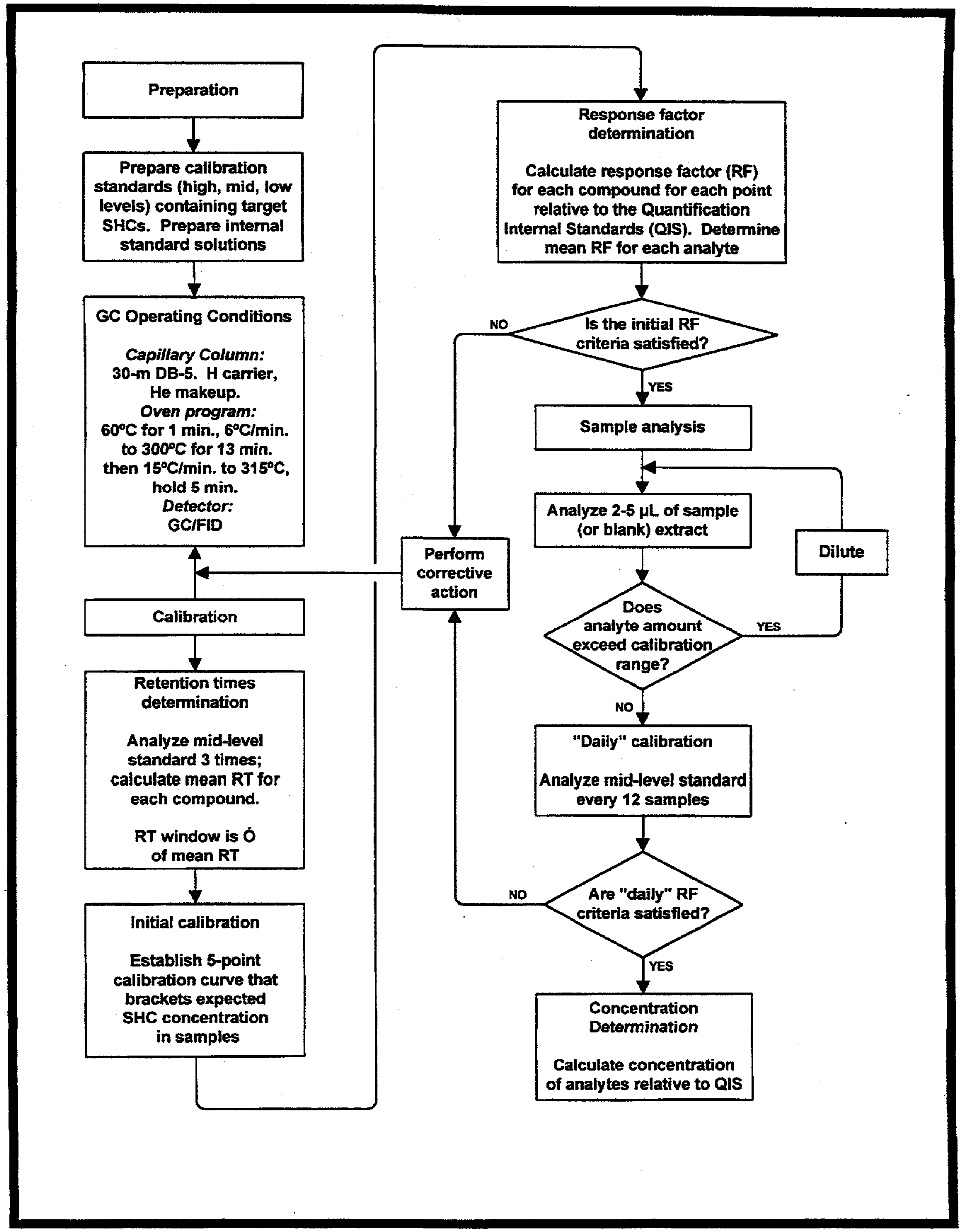


Figure 8.6. Instrumental procedures for SHC analysis by GC/FID.

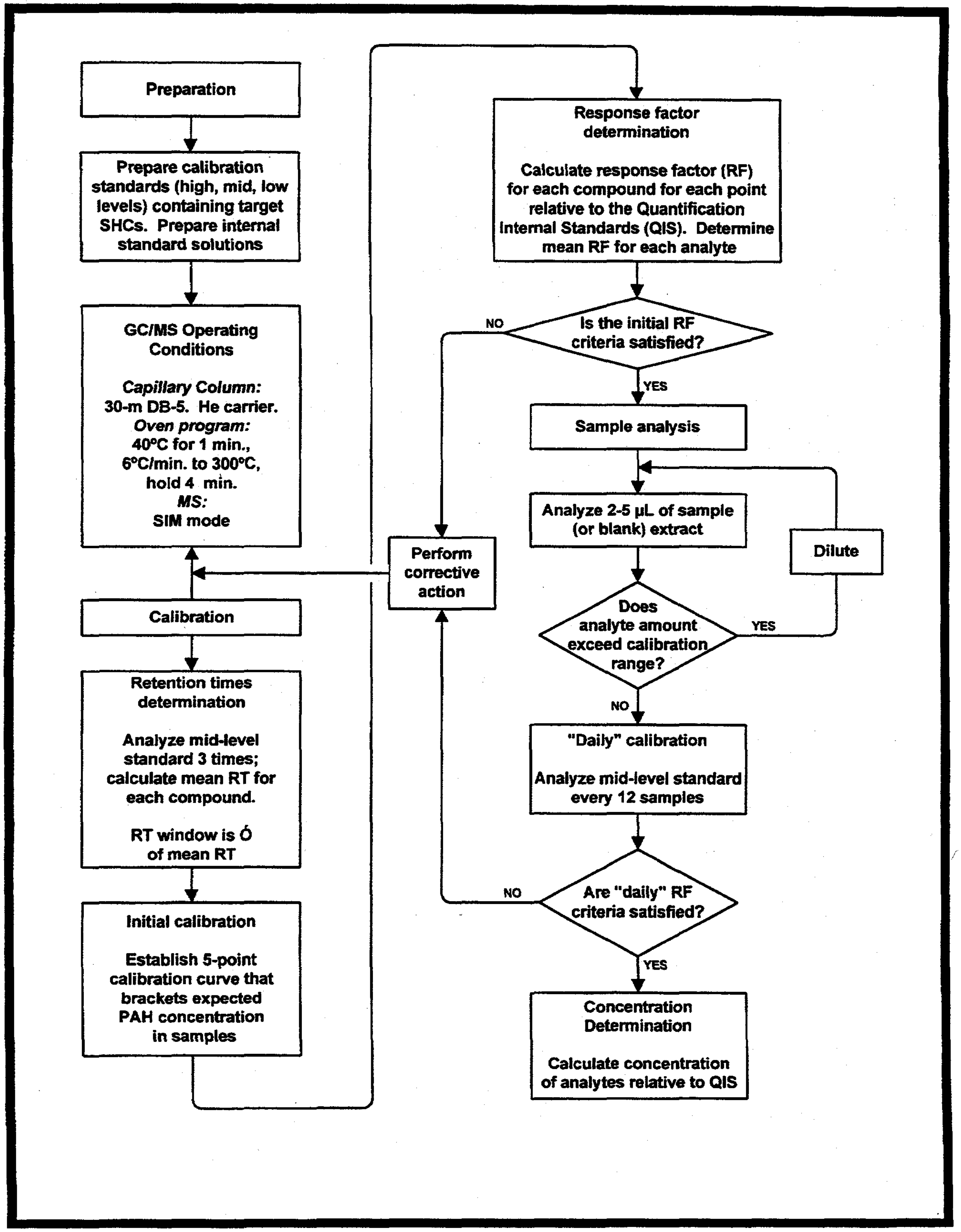


Figure 8.7. Instrumental procedures for PAH analysis by GC/MS.

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 procedural blanks, blank spikes, matrix spikes, sample duplicates, and standard reference materials (NIST SRM-1941 for sediment analysis). Field blank samples were also processed. The DQOs 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 non-detected (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 tissues, all analyses met the DQOs presented in **Table 8.2**.

In approximately 15 tissue 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 PAHs were found at significantly high levels in the procedural blank of the analytical batch of which the qualified tissue samples were part. Any analyte labeled with a "B" qualifier should be discounted in the interpretation of the data. Generally, the analyte procedural blank concentration was in the range of the sample concentration; and, therefore, the analyte was not used in the interpretation.

8.3 RESULTS AND DISCUSSION

8.3.1 Produced Water, Discharge Plume/Receiving Water, and Ambient Seawater

Eight samples of produced water, three samples initially and one sample five times at approximately 12-h intervals, were collected at the four Component 1 sites (SMI 236A, VR 214A, SMI 130B, and HI A-595CF). Each of these samples was analyzed for VAHs, SHCs, and PAHs. At the time of the produced water collection, water samples were collected in the plume of the produced water discharge as part of the discharge plume sampling and analyzed for VAHs only. Ambient seawater samples were collected at three different locations approximately 2,000 m from the discharge platform and analyzed for VAHs and PAHs. Three replicate ambient seawater samples were also collected at the four Component 2 reference sites (SMI 186/195, WC 448, GA 205, and GA 90) and analyzed for VAHs and PAHs.

Table 8.2. Data quality objectives and criteria - PAHs and 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[a] ≤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[b] (#1941)	Two per batch/every 20 field samples	Values must be within ±20% of true value on average for all analytes >10x MDL[c], not to exceed ±25% of true value for more than 30% of individual analytes.
Matrix Spikes	Two per batch/every 20 field samples	%R 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[d] ≤30%
Internal Standard/Surrogates	Every sample	%R 40%-125%
Target MDLs (PAHs and SHCs)	Sediment, tissue - PAHs Sediment - SHCs Water (2 liter) - PAHs Oil - PAHs	1-5 ng/g (dry weight) 0.05-0.1 µg/g (dry weight) 5-10 ng/L 0.5-2.5 ng/mg

[a] RSD = Relative standard deviation.
[b] SRM = Standard reference material.
[c] MDL = Method detection limit.
[d] RPD = Relative percent difference.

Table 8.3. Method detection limits of target compound groups.

Analytes	Sediment (dry weight)	Tissue (dry weight)	Water
PAH	0.7-6 μg/kg	1-7 μg/kg	5-20 ng/L
THC	1-2 μg/g	--	10-20 μg/L
SHC	0.05-0.1 μg/g	--	0.5-1.0 μg/L
VAH	--	--	0.2-0.5 μg/L

8.3.1.1 Produced Water

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 the alkyl carbon number increases. Concentrations of the 3-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 smaller. 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 4- through 6-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.

The concentrations of the individual concentrations of the 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**. THC and total PAH concentrations of the produced water samples are provided in **Table 8.5**.

Concentrations of individual VAHs generally varied around ±25% from the mean. SMI 236A produced water had the highest individual and total VAH concentrations at 5,200 μg/L mean total VAHs; and HI A-595CF produced water had the lowest at 1,800 μg/L mean total VAHs. Mean concentrations for BTEX compounds (benzene, toluene, ethylbenzene, and xylenes), the most commonly measured VAHs, ranged from 1,700 to 4,900 μg/L. BTEX concentrations in produced water discharged into the central Gulf of Mexico ranged from 68 to 38,000 μg/L (Neff, 1996). Among the four sites, mean concentrations of each analyte were not different by more than two times, and the concentrations were below their respective solubilities. The compositional (means) distributions of the four produced waters are shown in **Figure 8.8.**

Unlike the VAH results where concentrations were fairly consistent among platform produced waters, THC and total PAH concentrations were four times higher in the SMI 130B produced water than those of the other platform produced waters (**Table 8.4**). SHC distributions for the four produced waters showed decreasing concentration with increasing carbon number from C_{10} to C_{32} (**Figures 8.9** through **8.12**). The SHC distribution reflects the solubilities and produced oil composition of the analytes. Due to the volatility of C_{10} through C_{14}, the trend of lower concentrations in two of the produced water samples may be due to the limitations (volatile compound loss) of the analysis for semivolatile hydrocarbons for these compounds, not indicative of a general trend.

Table 8.4. VAH concentrations (mean, range; μg/L) in produced water samples.

VAH	SMI 236A (n=8)	VR 214A (n=8)	SMI 130B (n=8)	HI A-595CF (n=8)
Benzene (BZ)	2,500 (7,000-2,800)	850 (790-950)	1,200 (900-1,700)	820 (610-1,100)
Toluene (T)	1,500 (1,300-1,700)	800 (730-910)	1,100 (820-1,300)	490 (370-660)
Ethylbenzene (E)	100 (92-110)	100 (94-110)	76 (61-89)	52 (36-66)
m,p-Xylenes (m,p-X)	460 (430-480)	210 (200-230)	360 (280-410)	180 (130-240)
o-Xylene (o-X)	230 (220-240)	150 (140-170)	180 (150-200)	110 (82-130)
C_3-Benzenes (C_3 BZ)	260 (190-290)	280 (270-300)	140 (120-170)	100 (80-130)
C_4-Benzenes (C_4 BZ)	70 (50-110)	110 (100-120)	ND	ND

ND = Not detected.

Table 8.5. THC and total PAH concentrations (mean, range) in produced water samples.

Site	THC (μg/L)	Total PAH (μg/L)
SMI 236A (n=8)	3,900 (1,900-4,900)	270 (220-350)
VR 214A (n=8)	3,300 (1,500-4,700)	130 (122-134)
SMI 130B (n=8)	16,000 (12,000-19,000)	600 (460-690)
HI A-595CF (n=8)	1,300 (1,100-1,700)	58 (52-61)

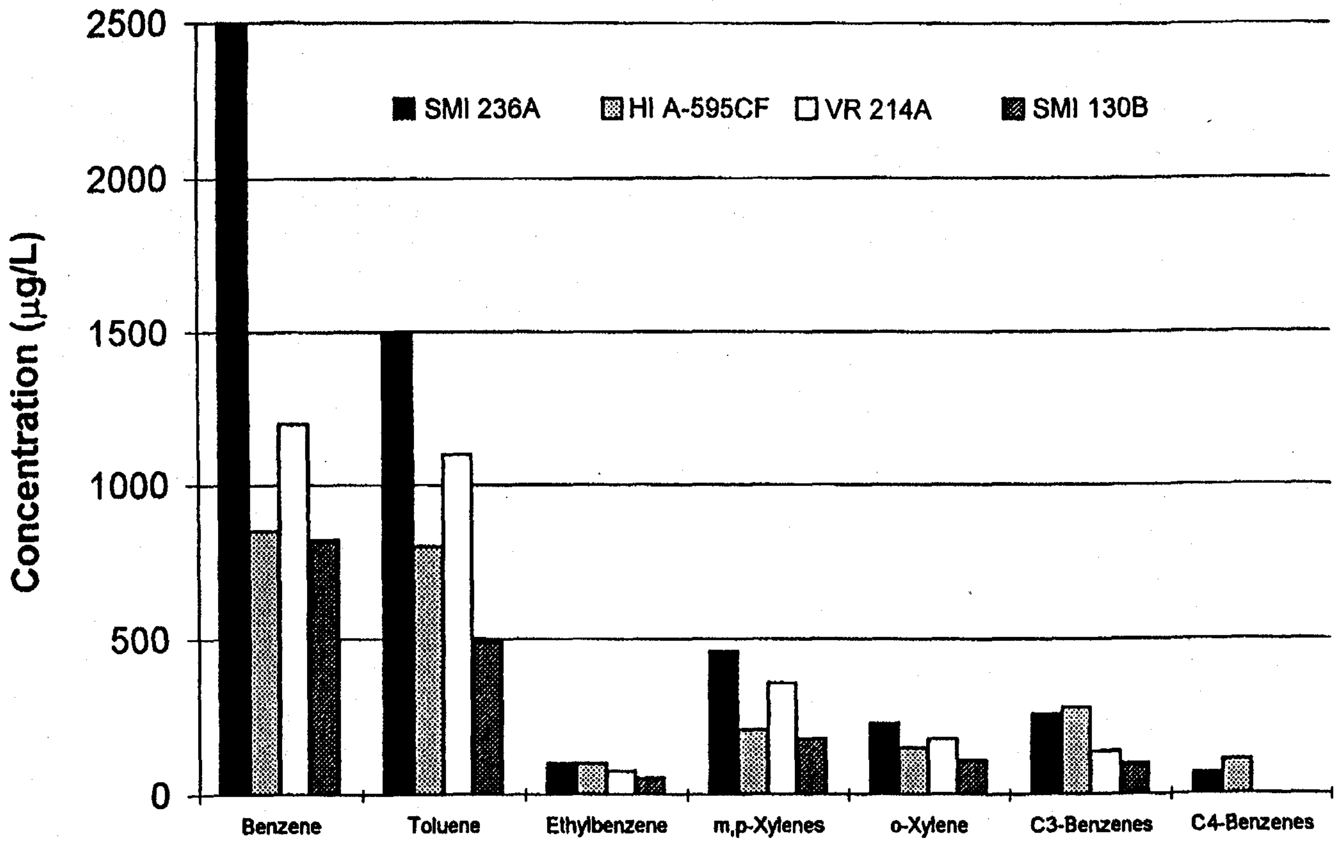


Figure 8.8. VAH distribution (mean concentrations) in produced waters at the four discharging sites.

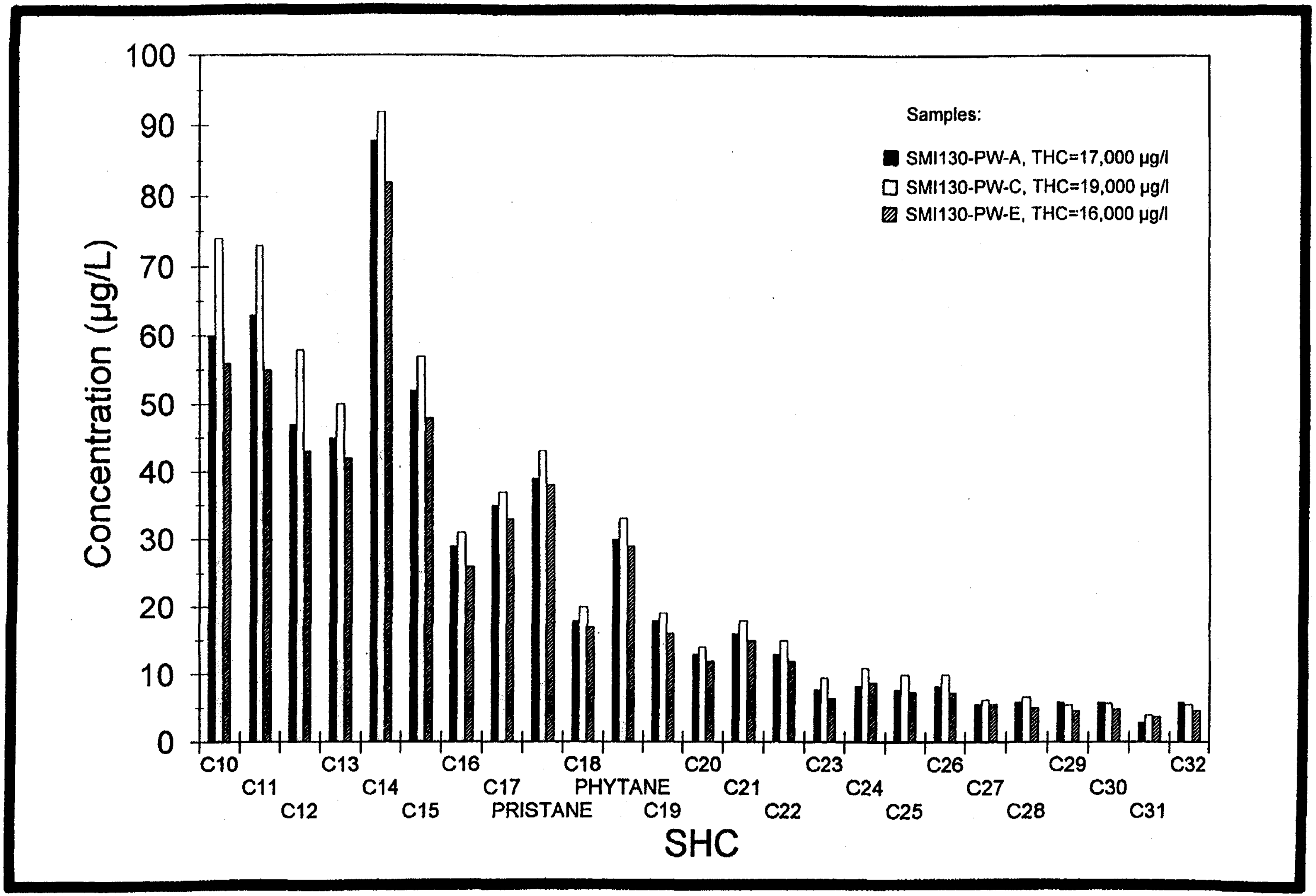


Figure 8.9. SHC distribution in Produced Water Replicates A, C, and E at SMI 130B.

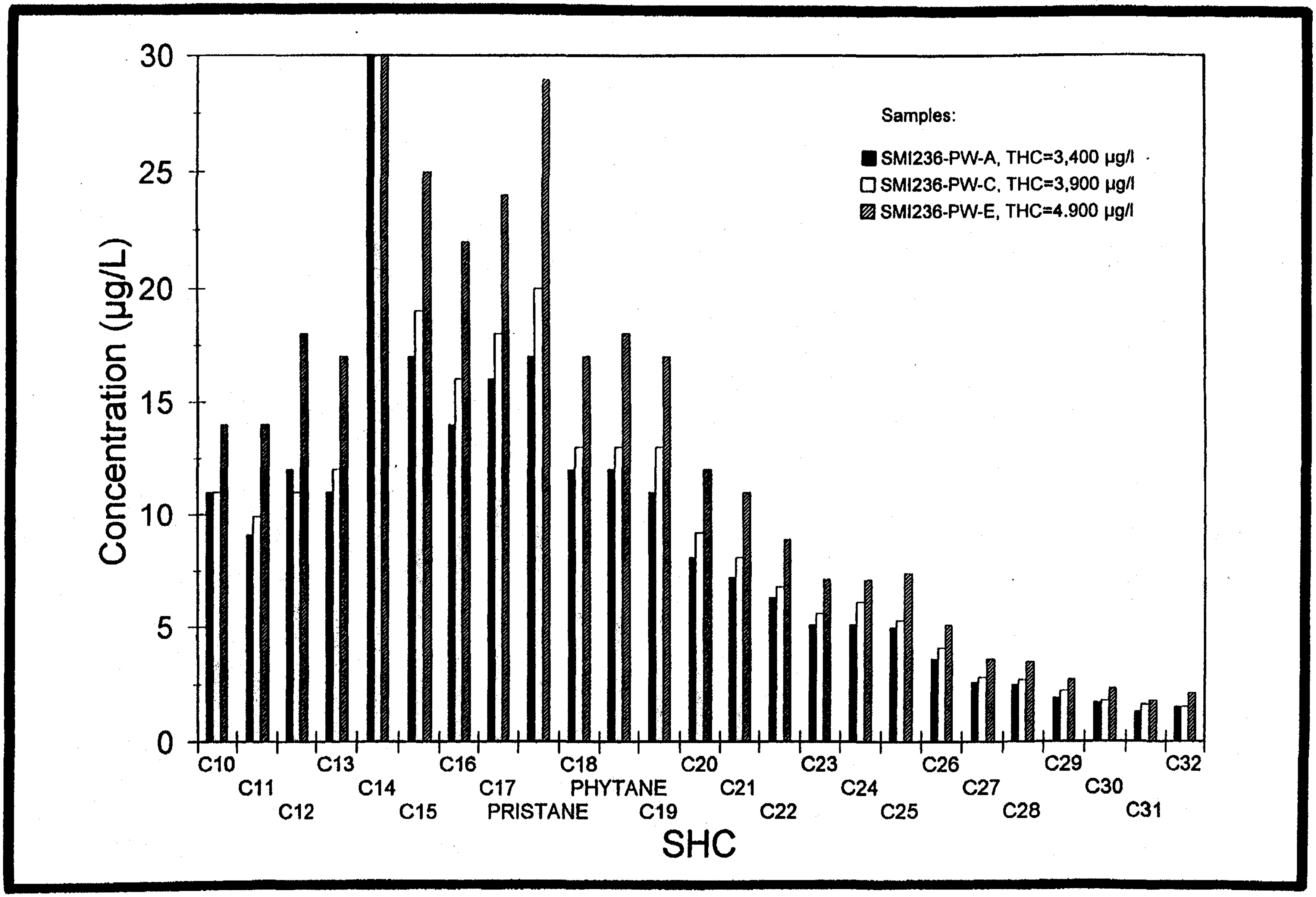


Figure 8.10. SHC distribution in Produced Water Replicates A, C, and E at SMI 236A.

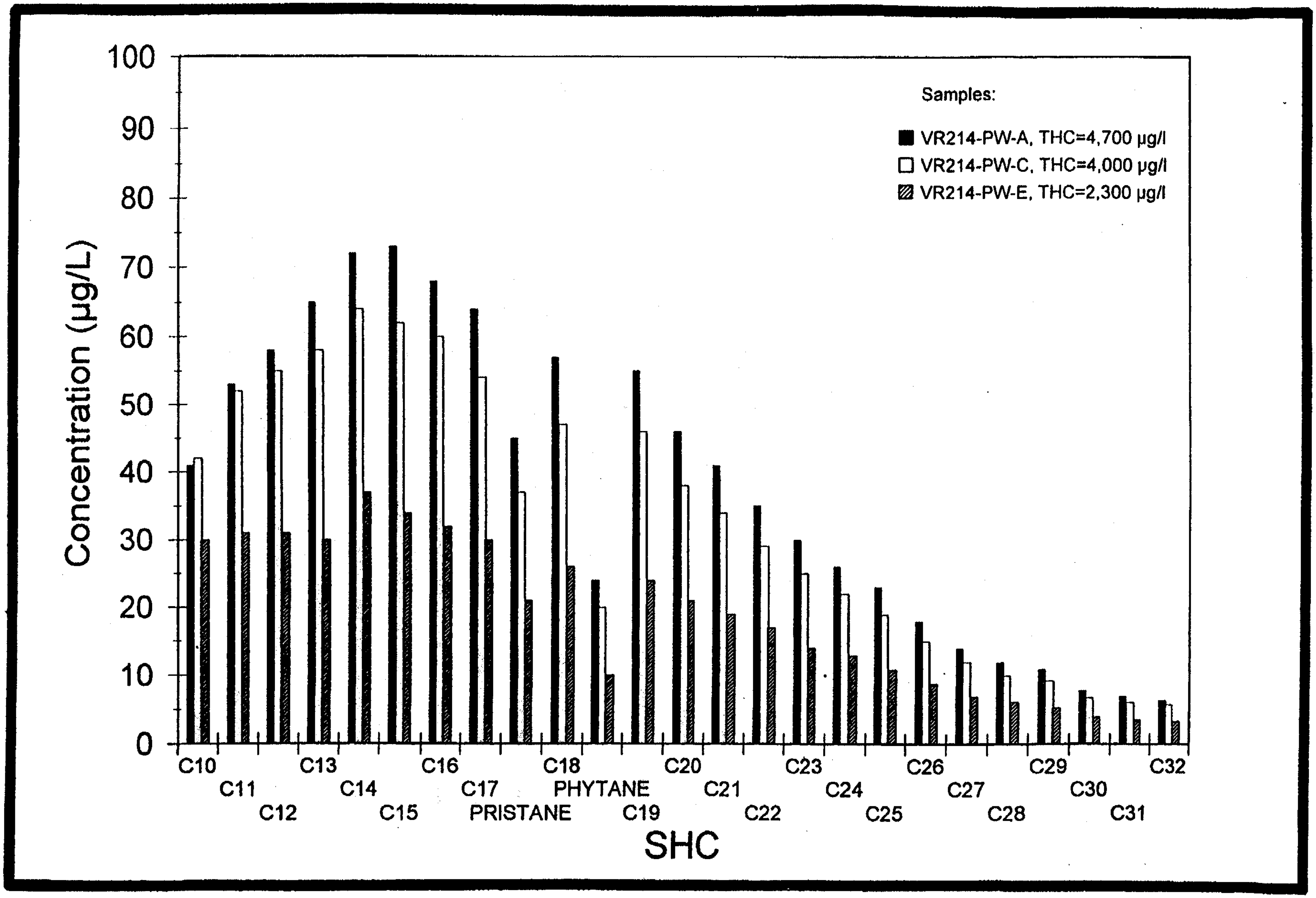


Figure 8.11. SHC distribution in Produced Water Replicates A, C, and E at VR 214A.

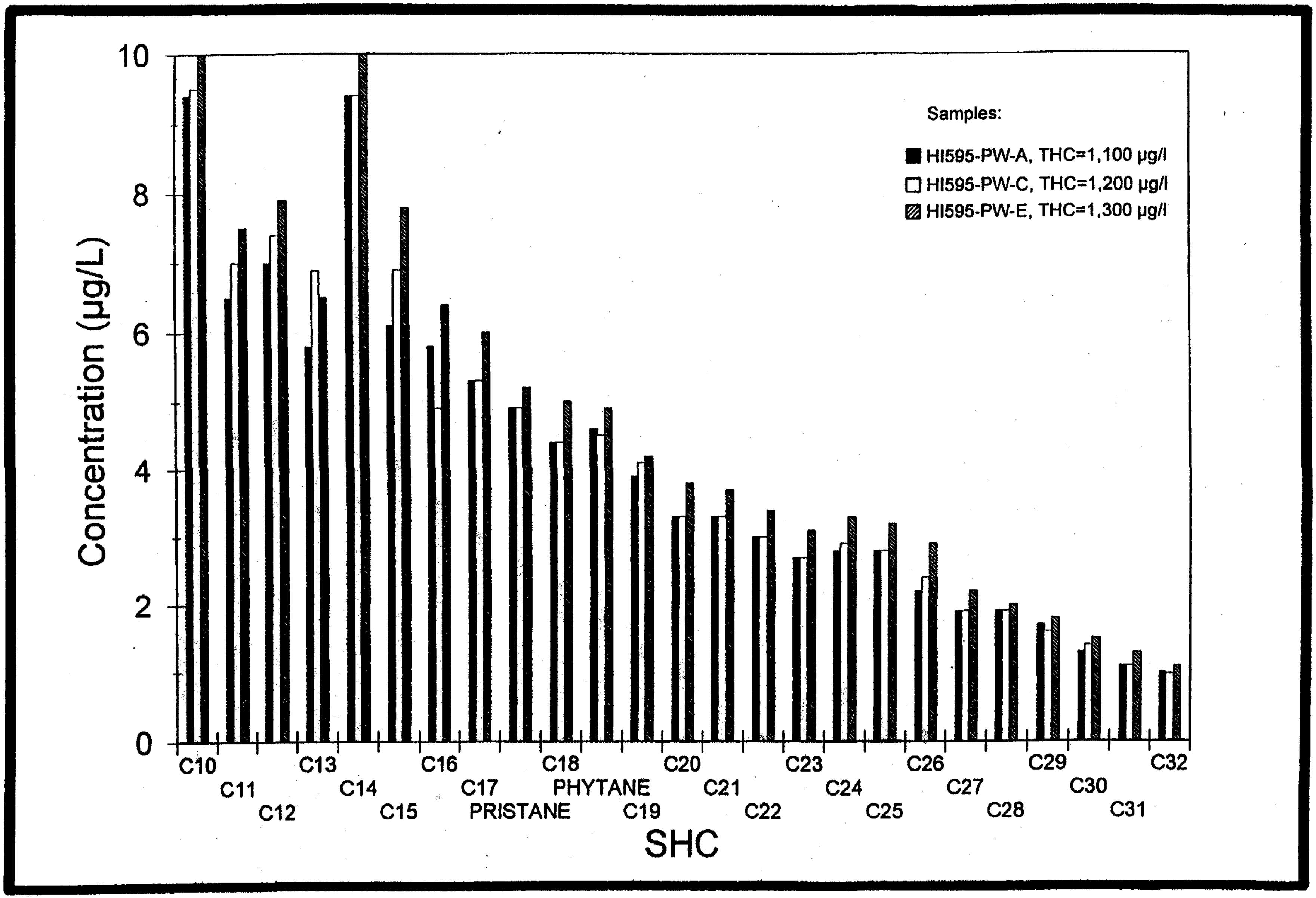


Figure 8.12. SHC distribution in Produced Water Replicates A, C, and E at HI A-595CF.

Comparison of the PAH distribution of SMI 130B and the distributions of the other three platforms (**Figures 8.13** through **8.16**) indicated that the SMI 130B produced water contained oil droplets of produced crude oil. Different than the other three platform PAH distributions, the SMI 130B PAH distribution showed relatively large amounts of the 3- and 4-ring PAHs and the characteristic 'bellshaped' distribution of the alkyl homologues. Each of the other three PAH distributions 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 3-ring PAHs (non detectable amounts of 4- through 6-ring PAHs) with generally constant alkyl concentrations. The PAH compositions of these three produced waters reflect the solubility properties for PAHs, as discussed previously. The PAH composition of SMI 130B, however, reflects the composition of the produced crude oil. Interestingly, the higher concentrations of THCs and PAHs in SMI 130B produced water compared to the other three produced waters were not similarly mimicked in the concentrations of VAHs. SMI 236A contained the highest amounts of VAHs (**Figure 8.8**).

Used in determining potential sources of hydrocarbons in environmental 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.

Site	C2P/C2D	C3P/C3D
SMI 236A	3.2	2.5
VR 214A	2.0	1.25
SMI 130B	1.25	0.9
HI A-595CF	0.8	0.7

8.3.1.2 Discharge Plume/Receiving Water and Ambient Seawater

Plume water samples collected near the discharge pipe were only analyzed for VAHs (and rhodamine WT dye). Samples at 5 m from the discharge pipe showed only trace amounts of VAHs in the water column, less than 10 μg/L benzenes and less than 1 μg/L of the other VAHs. The VAH concentrations at the 100 m distance were non-detectable for almost all VAHs; occasionally there were detectable amounts (0.1 to 1.0 μg/L) of toluene. These VAH concentrations are typical for open ocean water in the Gulf of Mexico (Sauer, 1981).

Ambient seawater samples collected approximately 2,000 m from the Component 1 discharging platforms and at the Component 2 reference sites generally contained non-detectable amounts of VAHs and PAHs (MDLs for VAHs were approximately 0.2 μg/L and for PAHs range from 1 to 5 ng/L). Mean total PAH concentrations at 2,000 m for each of the four platforms were 74, 60, 170, and 58 ng/L for SMI 236A, VR 214A, SMI 130B, and HI A-595CF, respectively. Although slightly higher than that observed in pristine environments (15 to 25 ng/L in Prince William Sound; Neff and Burns, 1996), a multitude of sources of PAHs besides produced water, such as tanker traffic, coastal and river runoff (Mississippi River), natural seeps, and aerial deposition of anthropogenic pollutants, contribute to the PAH loading in the Gulf of Mexico.

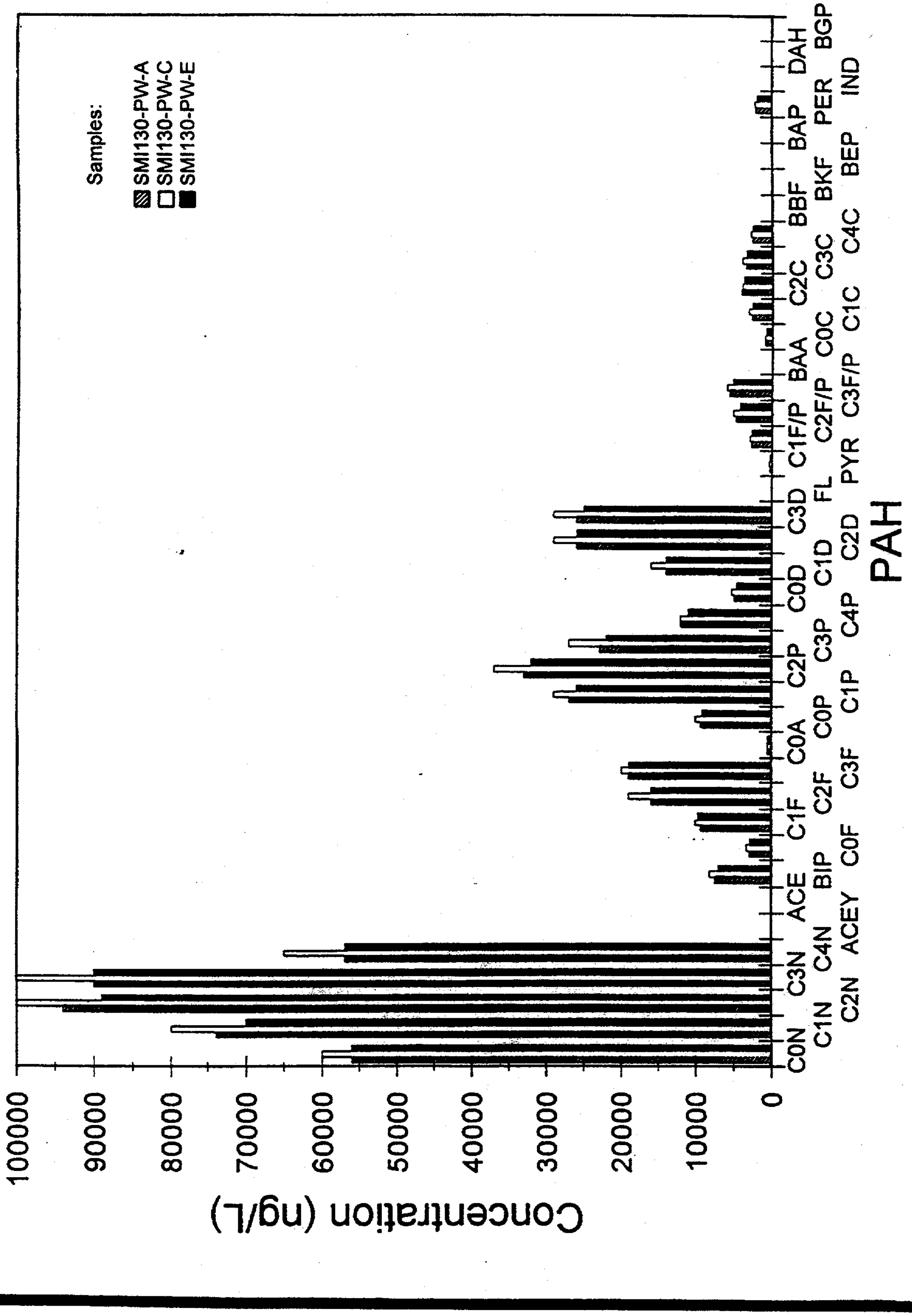


Figure 8.13. PAH distribution in Produced Water Replicates A, C, and E at SMI 130B.

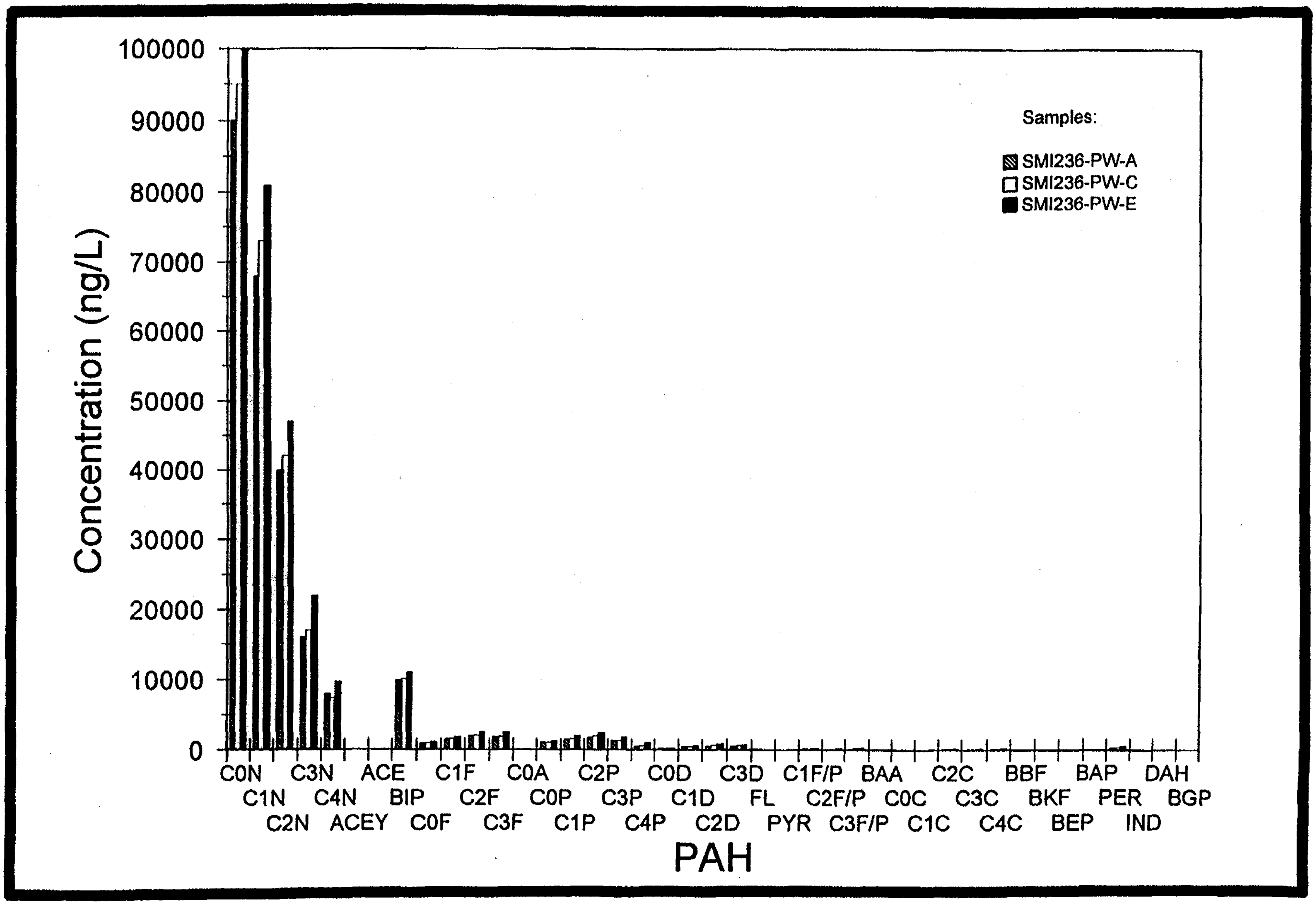


Figure 8.14. PAH distribution in Produced Water Replicates A, C, and E at SMI 236A.

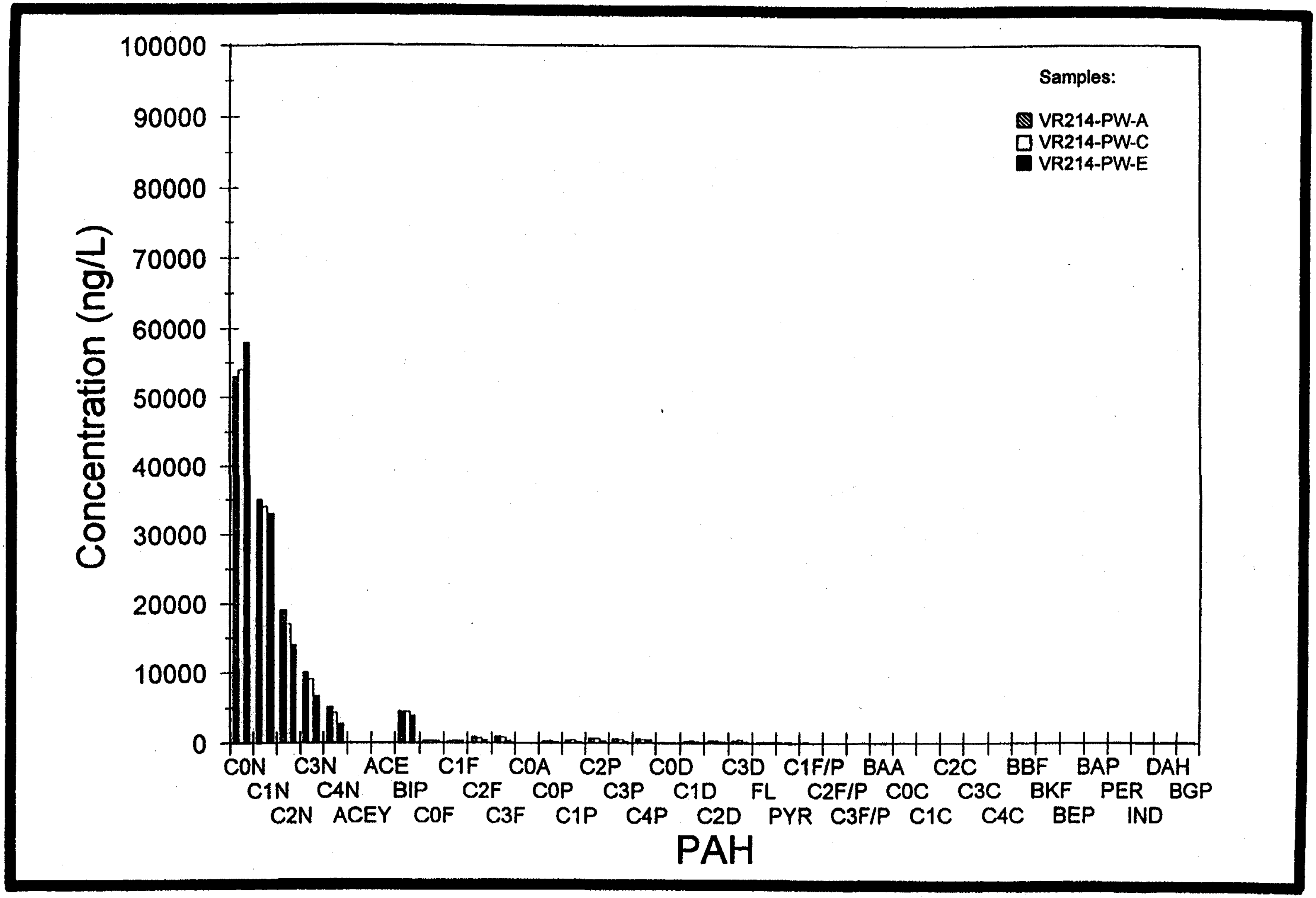


Figure 8.15. PAH distribution in Produced Water Replicates A, C, and E at VR 214A.

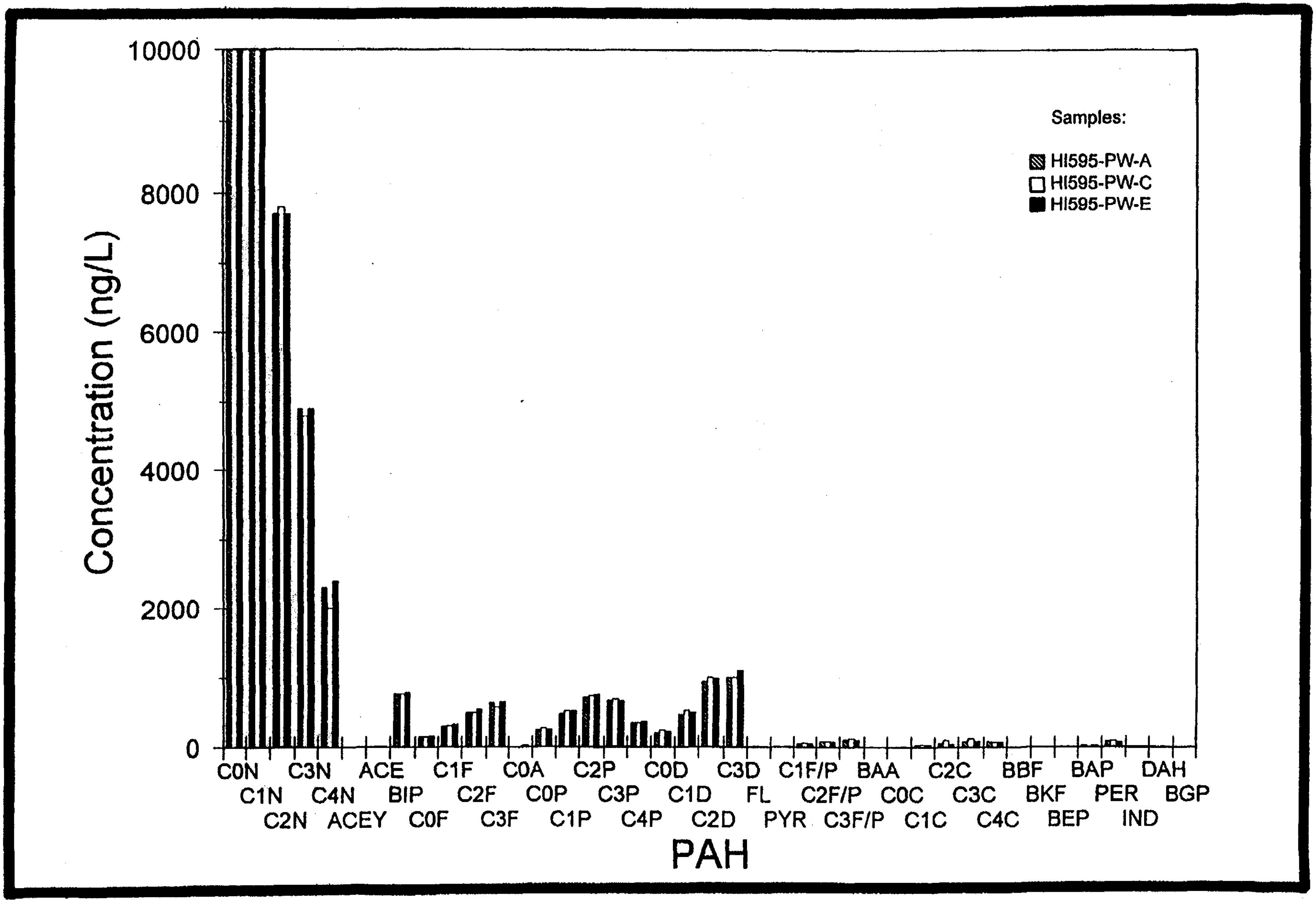


Figure 8.16. PAH distribution in Produced Water Replicates A, C, and E at HI A-595CF.

In some samples, a low-level (approximately 10 ng/L) pyrogenic PAH signature was evident. In these samples (e.g., WC 448 and GA A-205; **Figure 8.17**), the parent PAHs--fluorene, phenanthrene, fluoranthene, pyrene--and the 5- and 6-ring PAHs (e.g., benzo(a)pyrene) were the major PAHs present. These PAHs are probably associated with particulate matter (not tarballs) in these unfiltered samples and would not have originated from a petrogenic source. This type of PAH distribution would be typical of anthropogenic or natural combustion sources.

In a couple of replicate samples at 2,000 m or reference sites not evident in other replicate samples from the same location, PAHs of a petrogenic origin were detected. A replicate sample at reference site SMI 186/195 contained a full suite of petroleum PAHs (**Figure 8.18**) at concentrations no greater than 100 ng/L and VAHs from benzene to C_3-benzenes at concentrations less than 1 μg/L. The presence of these compounds may be due to contamination of the sample in the field, or most likely, due to either natural seeps that are abundant in the area (MacDonald *et al.*, 1996) or a very recent release of oil from a passing vessel. The presence of both VAHs and PAHs at the same location (collected in different vials from the sampler) suggested that the water was probably not contaminated during sampling. There was also a petrogenic PAH distribution in a GA A-90 replicate sample with PAH concentrations less than 25 ng/L (**Figure 8.19**), but this sample did not contain detectable VAHs. The hydrocarbons in this sample probably originated from a natural seep, weathered released oil or a minute tarball.

8.3.2 Produced Sand

SHC and PAH distributions of the replicate analysis of produced sand samples collected at SMI 236A and SMI 130B are presented in **Figures 8.20** through **8.23**. The petrogenic SHC and PAH signatures represent the hydrocarbon composition of crude oil (slightly weathered from water washing) produced at these platform facilities. THC and total PAH concentrations were the highest at SMI 130B, averaging 30,000 mg/kg dry weight and 922,000 μg/kg dry weight, respectively at SMI 130B and 7,000 mg/kg dry weight and 103,000 μg/kg dry weight, respectively at SMI 236A. The produced sand oils from the two platforms are of different sources, evident by the differences in the relative amounts of the phenanthrenes and dibenzothiophenes in the PAH composition. At SMI 130B, the ratio of C_2-phenanthrenes and C_2-dibenzothiophenes (C2P/C2D) is 1.25 and the ratio of C_3-phenanthrenes and C_3-dibenzothiophenes (C3P/C3D) is 0.91, similar to the produced water ratios. On the other hand at SMI 236A, the C2P/C2D ratio is 3.4 and the C3P/C3D ratio is 2.8, also similar to produced water ratios. As will be discussed later, there is some evidence, especially at SMI 130, that one of the sources of the hydrocarbons in the near platform sediments is from crude oil probably associated with the discharged produced sands.

8.3.3 Sediments

Surface sediment samples were collected at the four Component 1 platform sites, SMI 236A, VR 214A, SMI 130B, and HI A-595CF, and at four Component 2 reference sites in the lease blocks, SMI 186/195, WC 448, GA A-205, and GA A-90, and analyzed for SHCs and PAHs. At SMI 236A and VR 214A, samples were collected on the down current transect at 20 m and 2,000 m from the platform. At SMI 130B and HI A-595CF, the 20-m stations were moved 30 m. Only at SMI 236A were samples collected at the discharge (DISCH). At SMI 130B, two sets of

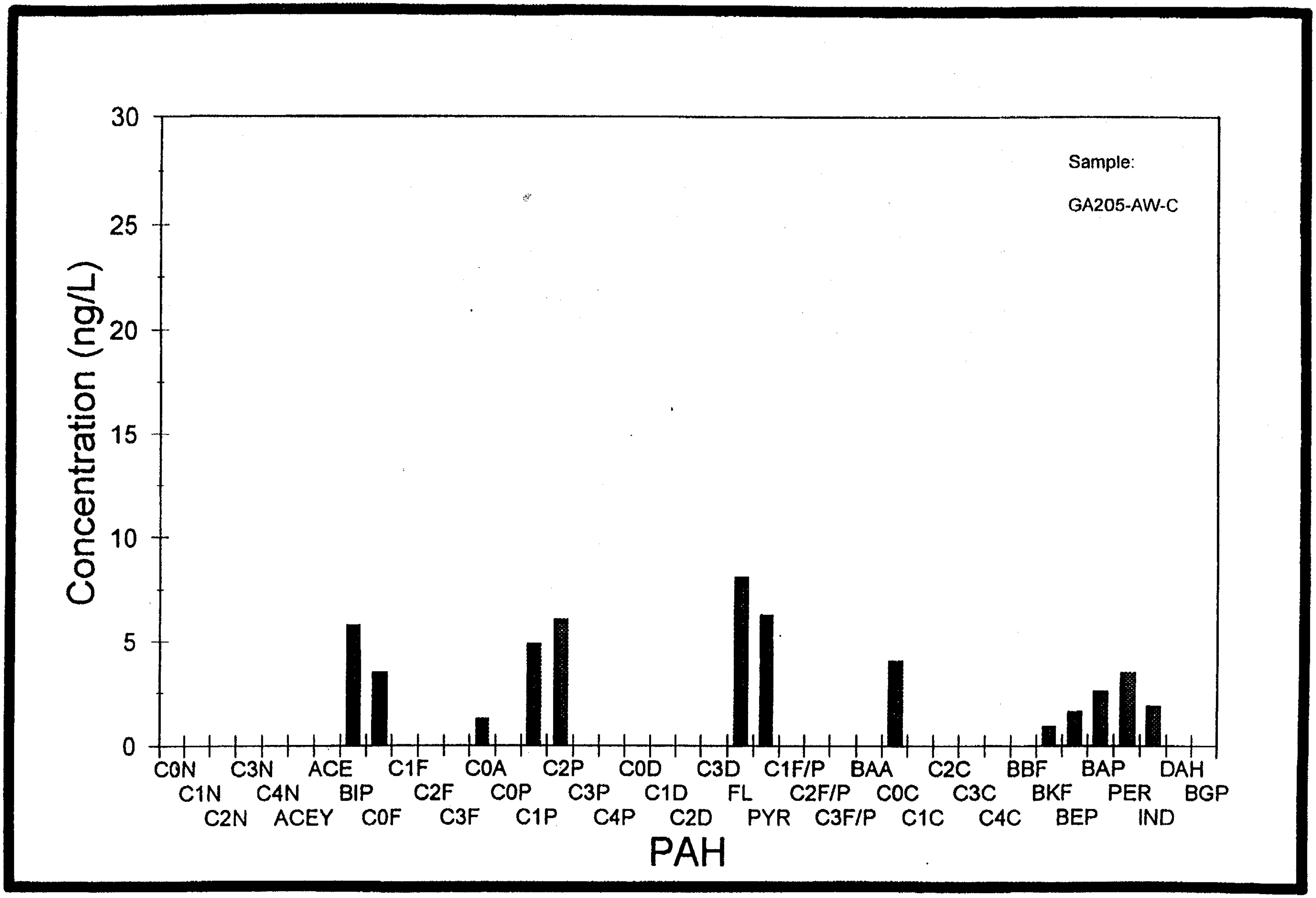


Figure 8.17. PAH distribution in Ambient Seawater Replicate C at GA A-205 reference site.

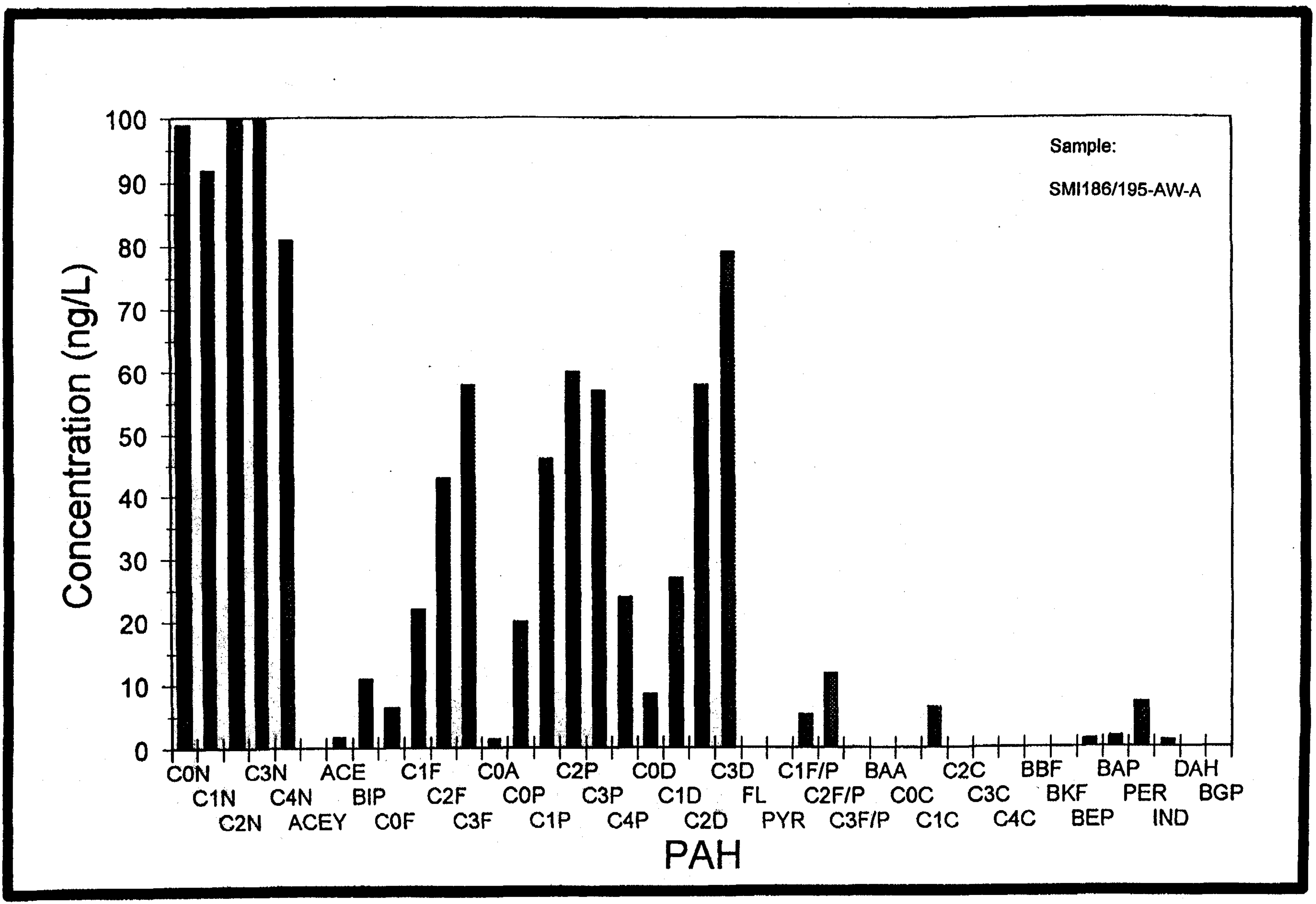


Figure 8.18. PAH distribution in Ambient Seawater Replicate A at SMI 186/195 reference site.

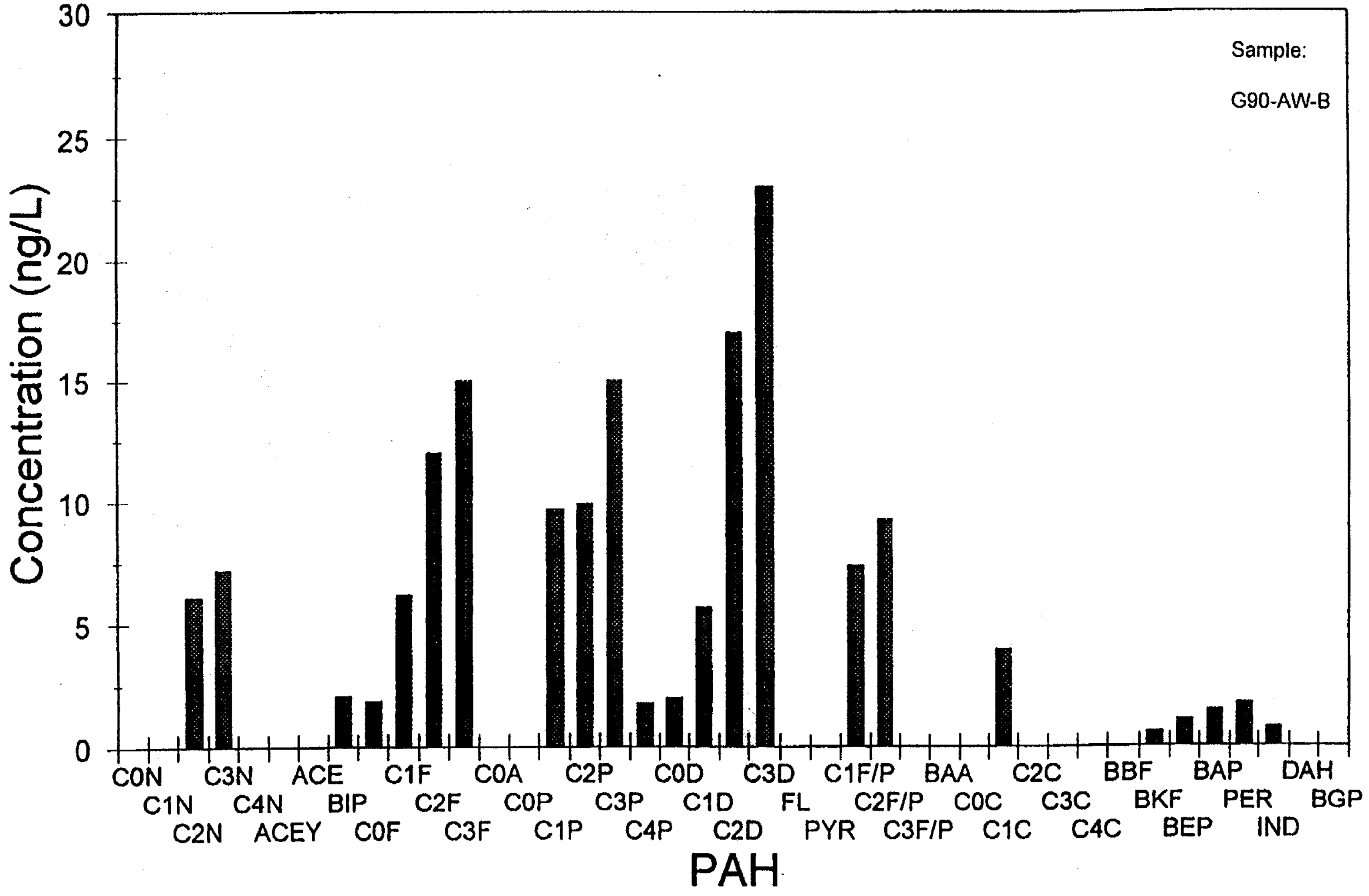


Figure 8.19. PAH distribution in Ambient Seawater Replicate B at GA A-90 reference site.

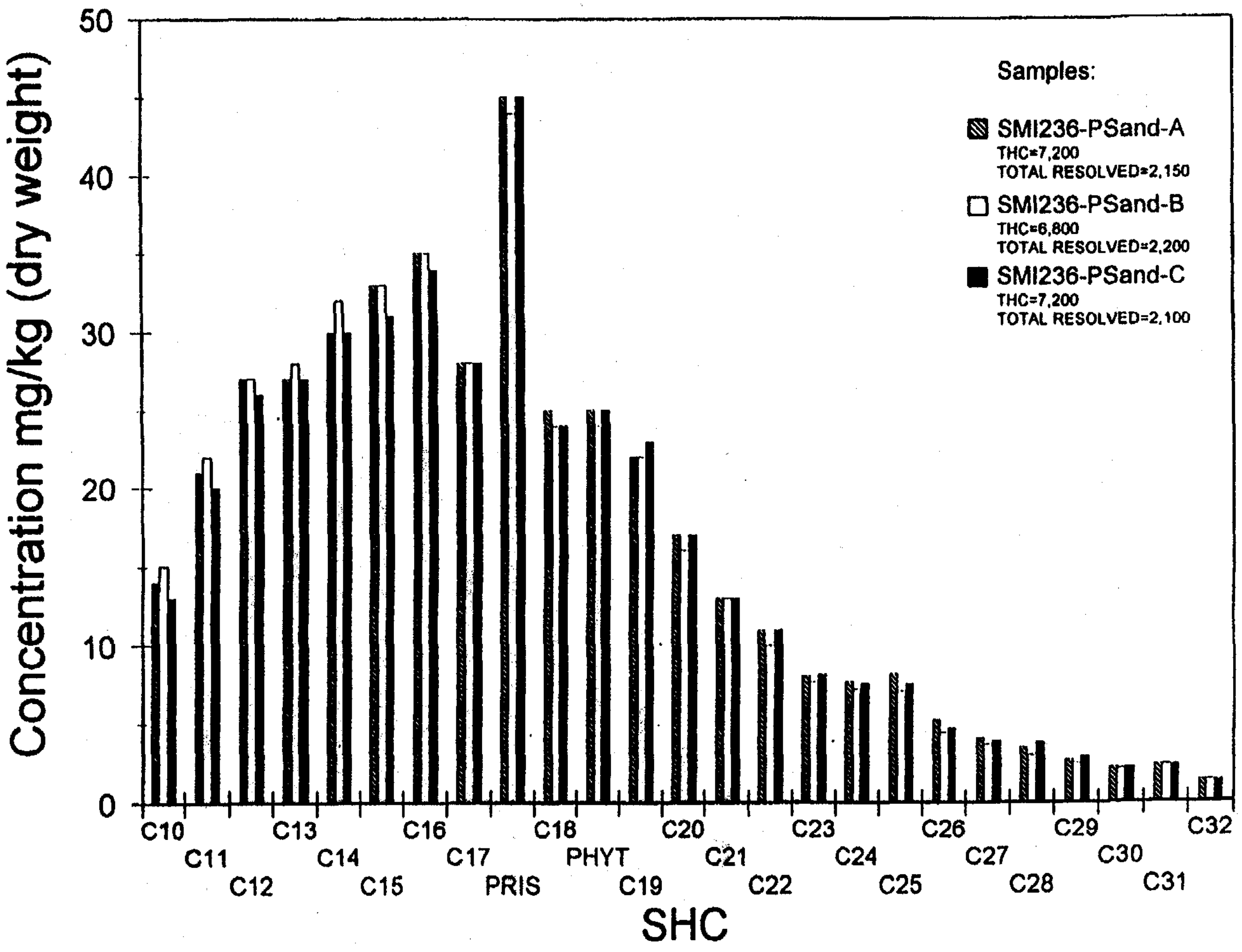


Figure 8.20. SHC distribution in Produced Sand Replicates A, B, and C at SMI 236A.

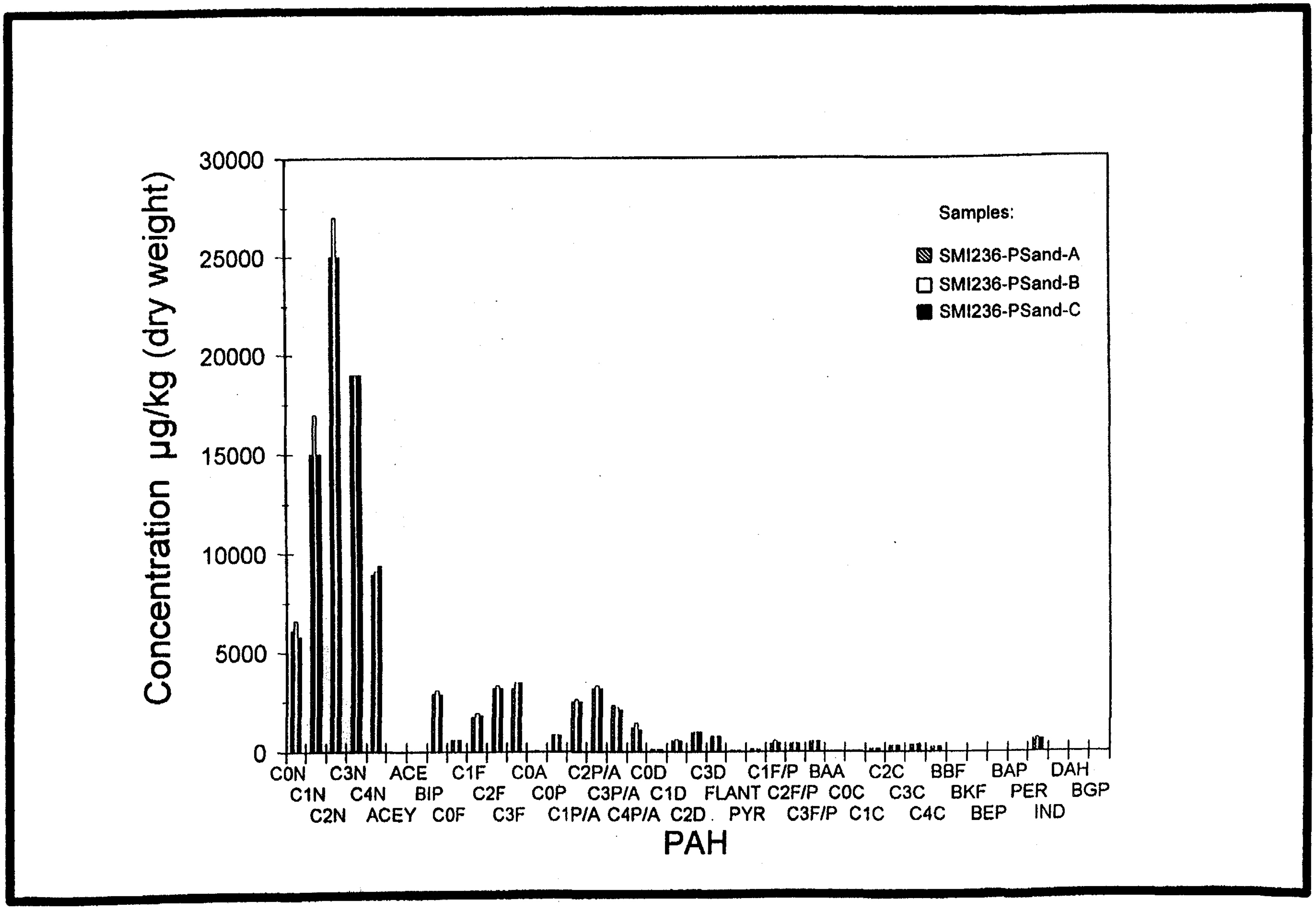


Figure 8.21. PAH distribution in Produced Sand Replicates A, B, and C at SMI 236A.

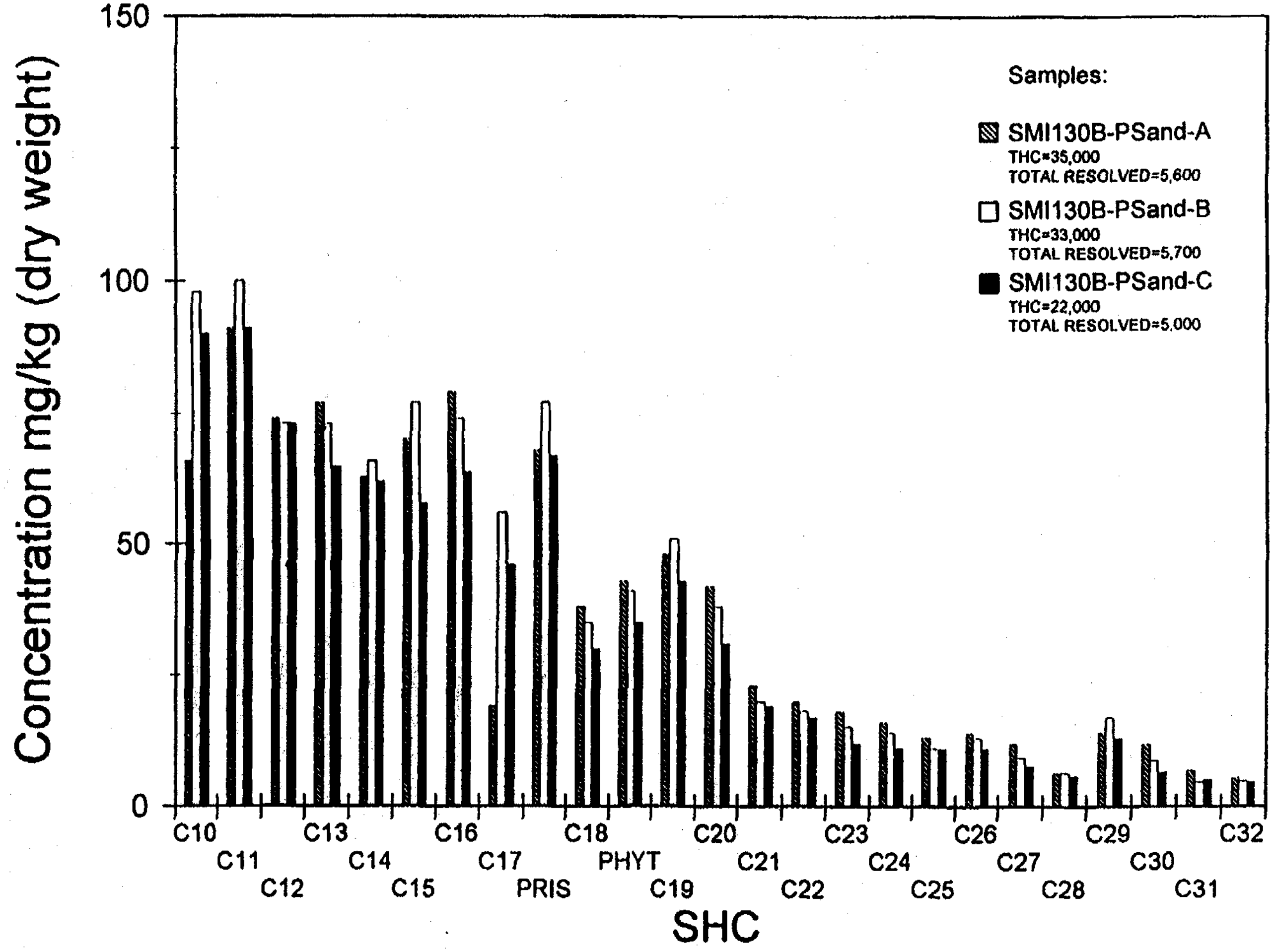


Figure 8.22. SHC distribution in Produced Sand Replicates A, B, and C at SMI 130B.

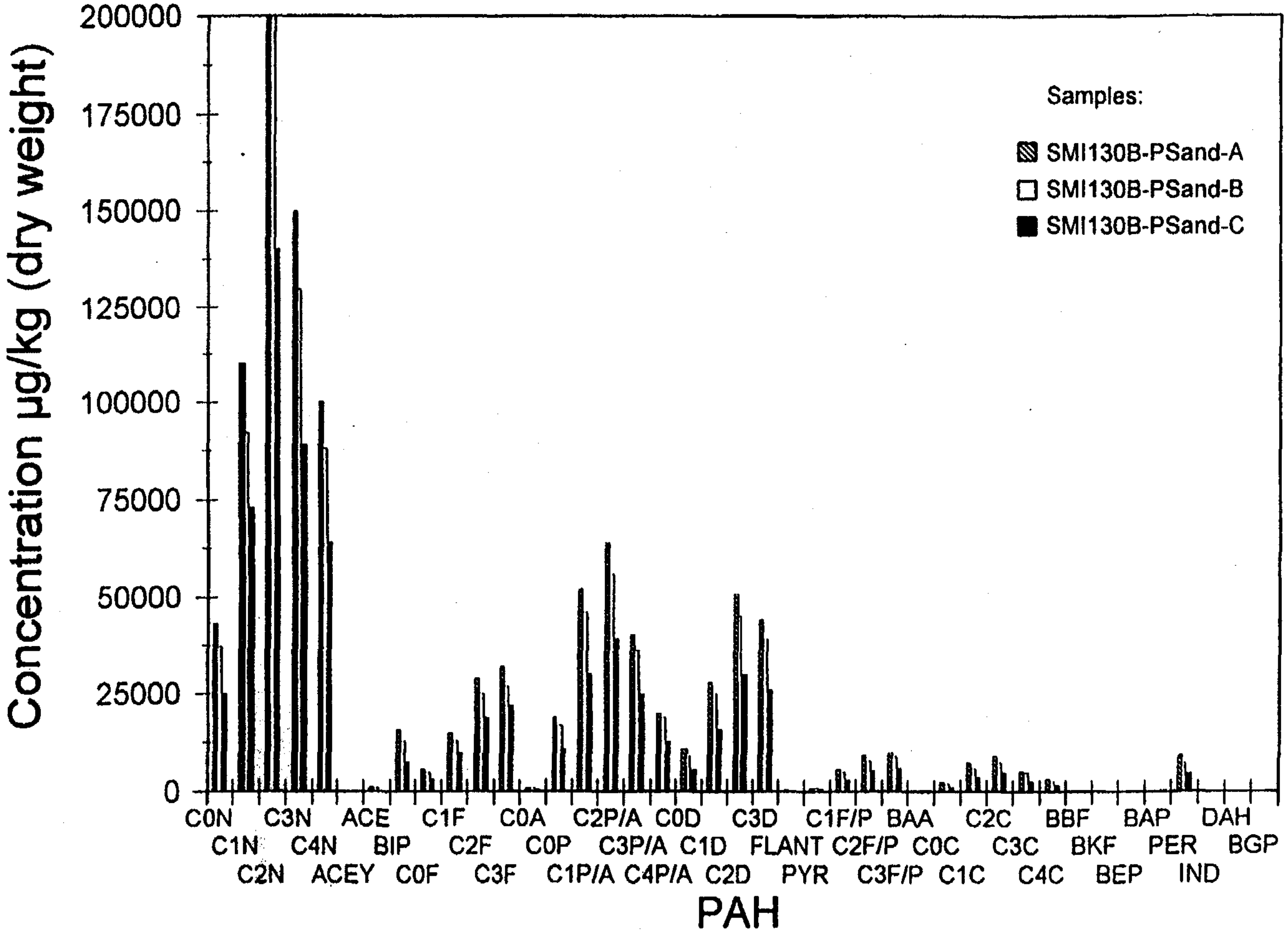


Figure 8.23. PAH distribution in Produced Sand Replicates A, B, and C at SMI 130B.

2,000 m samples ("I2000" and "V2000") were collected because the "I2000" samples were located within 1000 m of another platform. Three replicate samples were collected at one location in each reference lease block site and at each of the platform site stations. Sediment hydrocarbon results for all sites are summarized in **Table 8.6**.

8.3.3.1 South Marsh Island 236A

At the discharge station (DISCH) near the SMI 236A platform, THC concentration was not very high ranging from 62 to 110 mg/kg for the three replicates. The UCM made up 50% to 65% of the THC concentration. The SHC distribution (**Figure 8.24**) indicated hydrocarbons of petrogenic origin with a maximum abundance at n-alkanes C_{16} and C_{17}. The predominance of the isoprenoids pristane and phytane in this SHC distribution suggested that these hydrocarbons had been influenced by microbial degradation; n-alkanes had been preferentially biodegraded compared to the isoprenoids. The input of SHCs from biogenic sources (marine and terrestrial plant material) was only slightly evident.

The signature of a predominantly petrogenic source by the SHC data was not as evident in the PAH distribution (**Figure 8.25**). Pyrogenic type PAHs, in which the abundances of parent and lower alkyl groups (C_1) dominate the distribution within each family of PAHs, were apparent especially for the phenanthrenes, fluoranthenes/pyrenes, and chrysenes. The relatively high concentrations of 5- and 6-ringed PAHs (benz(a)anthracene, benzo(a)pyrene, and benzo(b)fluoranthene) are classical fingerprints of PAHs from a pyrogenic source. Total PAH concentrations ranged from 330 to 1,800 μg/kg for the three replicates. These concentrations were higher than typical for nearshore sediment of 10 to 200 μg/kg total PAHs in Texas and Louisiana (Brooks *et al.*, 1990; Neff *et al.*, 1992; Kennicutt, 1995).

At this discharge station, both pyrogenic and petrogenic hydrocarbons were evident. There were parts of the PAH distribution, however, that indicated the presence of petrogenic hydrocarbons. The high abundance of the alkyl naphthalenes and the relative distribution of the alkyl fluorenes and to a lesser extent the phenanthrenes were signatures of weathered petroleum. These petrogenic 2- and 3-ring alkyl PAHs from the oil and gas operations or nearshore sources were superimposed on 4- through 6-ring pyrogenic PAHs originating from coastal runoff, the Mississippi River, and/or atmospheric deposition. The SHC distribution with a maximum near the C_{16} and C_{17} alkanes and lacking an odd/even carbon preference for the n-alkanes confirmed the presence of petrogenic hydrocarbons in these samples. The potential source of the petroleum contribution to the DISCH sediment was probably the discharged produced sands. The diagnostic ratios C2P/C2D and C3P/C3D of the sediments were 3.3 and 2.8, respectively, which were nearly identical to the ratios of the produced sands, 3.4 and 3.0, respectively.

At the 20-m station, THC concentrations were higher than at the discharge station and ranged from 80 to 240 mg/kg. Only 10% of the THC content was, however, associated with the n-alkanes and isoprenoids, the remaining was UCM. The SHC distribution (**Figure 8.26**) indicated a combination of weathered petroleum (pristane and phytane dominance) and terrestrial biogenic (or blue-green algae) n-alkanes (C_{29} and C_{31}). The significant presence of the 2- and 3-ring alkyl PAHs and relatively low concentrations of the 4-and 5-ringed parent compounds suggested a dominant contribution of petrogenic hydrocarbons (**Figure 8.26**). The large perylene concentration was due to the diagenesis of natural biological precursors in the sediment (Venkatesan, 1988). Because of the large UCM and these alkyl PAHs, the hydrocarbons in these 20-m samples were mostly of petroleum origin of moderate concentration

Table 8.6. Concentration ranges of THC and total PAHs in sediment from discharge platform and reference sites.

Site	THC (mg/kg)	Total PAH (μg/kg)
Discharge Platforms		
SMI 236A		
DISCH	62-110	330-1,800
20 m	80-240	480-1,200
2,000 m	50-87	200-350
VR 214A		
20 m	130-160	450-2,300
2,000 m	33-39	140-300
SMI 130B		
50 m	130-200	720-1,000
2,000 m	10-21	140-150
HI A-595CF		
60 m	60-72	280-320
2,000 m	1.1-1.3	70-80
Reference Sites		
SMI 186/195	0.8-1.0	40-70
WC 448	5.4-9.5	180-220
GA A-205	0.5-0.6	10-17
GA A-90	0.5-0.7	15-40

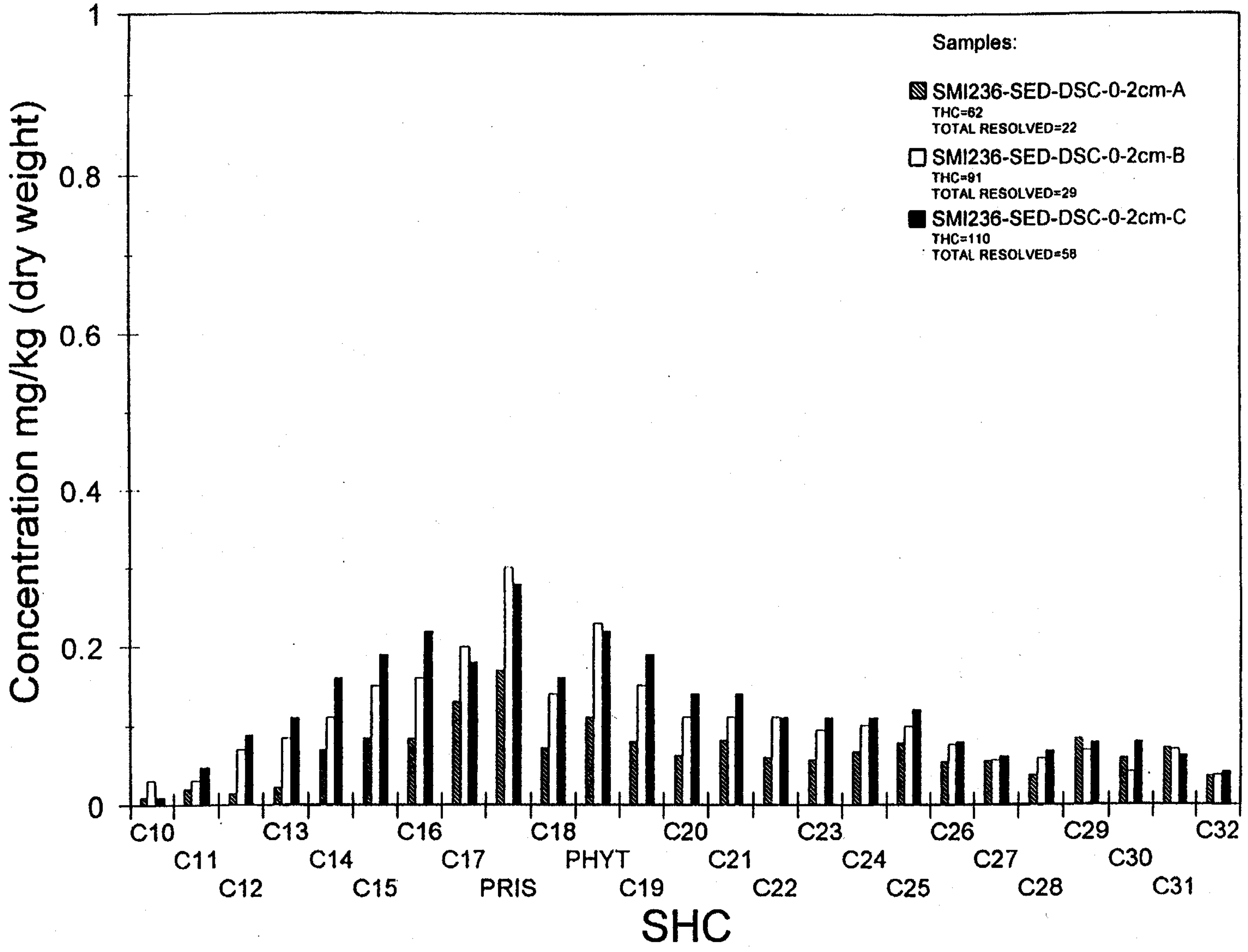


Figure 8.24. SHC distribution in Sediment Repicates A, B, and C at SMI 236A, discharge.

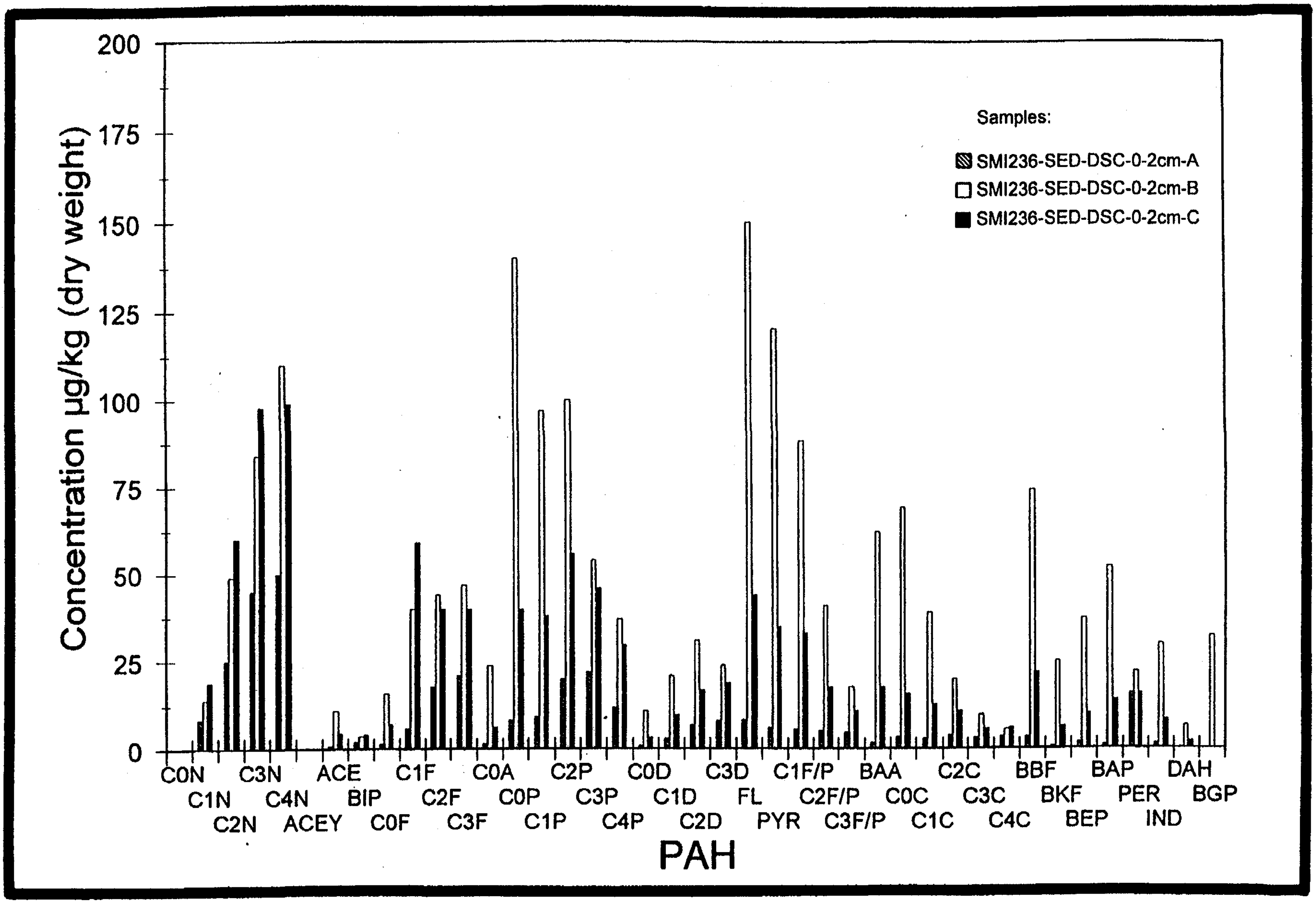


Figure 8.25. PAH distribution in Sediment Replicates A, B, and C at SMI 236A, discharge.

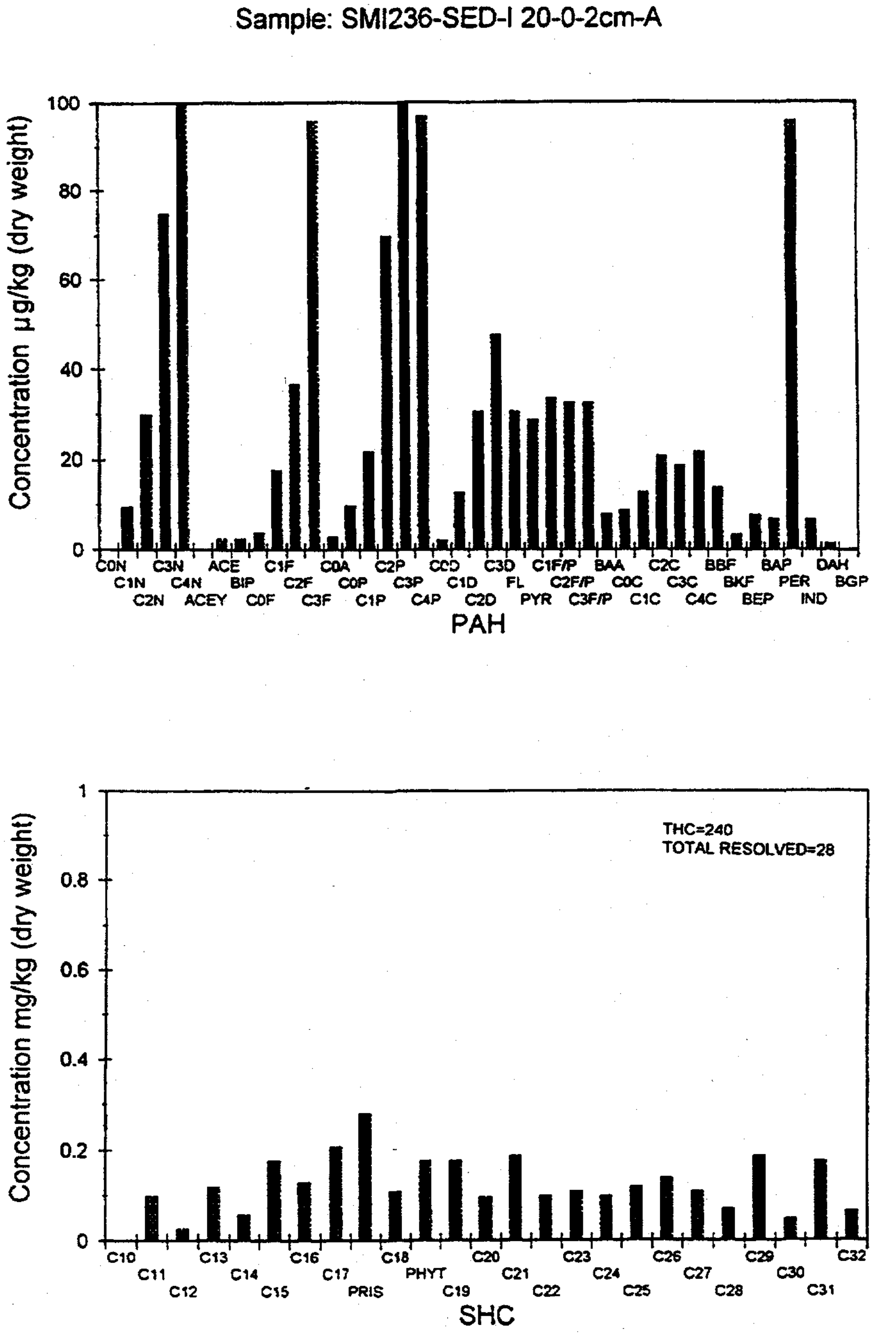


Figure 8.26. SHC and PAH distributions in Sediment Replicate A at SMI 236A, 20 m.

with total PAH concentration, ranging from 480 to 1,200 μg/kg. Using the diagnostic ratios C2P/C2D and C3P/C3D, the source of the petrogenic hydrocarbons in the 20-m sediments looked to be a combination of the produced sands and produced water discharges. The C2P/C2D and C3P/C3D ratios for the sediment were 2.4 and 2.4, respectively. The produced sands ratios were 3.4 and 2.8 and the produced water ratios were 3.2 and 2.5, respectively. The lower C2P/C2D in the sediments may be due to preferential weathering (loss) of the C_2-phenanthrenes relative to the C_2-dibenzothiophenes at this site which has been observed in some marine environments (Sauer *et al.*, 1993).

At the 2,000-m station, the SHC and PAH distributions changed dramatically compared to the other samples closer to SMI 236A. THC concentrations were lower, from 50 to 87 mg/kg. The SHCs were dominated by marine (C_{21}) and terrestrial (C_{29} and C_{31}) biogenic alkanes with an odd/even n-alkane preference in the SHC distribution (**Figure 8.27**). The UCM contributed 90% of the THC concentration. The PAH distribution (**Figure 8.27**) shows low-level presence of almost all the PAHs (approximately 10 ng/g individual PAH compounds; total PAH concentrations ranged from 200 to 350 μg/kg), probably typical of chronic hydrocarbon inputs from a variety of anthropogenic and natural sources in nearshore environments off of Louisiana or from the Mississippi River. The presence of a UCM and the PAH distribution are not, however, typical signatures of unpolluted, pristine environments, which are illustrated by open ocean sites GA A-205 and SMI 186/195 discussed later.

8.3.3.2 Vermilion 214A

The THC concentrations at the 20-m station (there were no samples collected at the discharge location) ranged from 130 to 160 mg/kg, comparable to the 20-m station at SMI 236A except that at VR 214A, the resolvable compounds made up 20% of the total hydrocarbon values instead of 10%. The SHC distribution (**Figure 8.28**) showed a fingerprint of a weathered petroleum with a gradual trend to a maximum at C_{18} n-alkane and no odd/even preference. Pristane and phytane were the most prevalent compounds indicating that the petroleum was experiencing some biodegradation.

Concentrations of total PAHs at the 20-m station ranged from 450 to 2,300 μg/kg, similar to those at SMI 236A. Both petrogenic and pyrogenic signatures were evident in the samples (**Figure 8.28**). The pyrogenic contribution was at least 70% of the total PAHs. Unlike SMI 236A and most other discharge platforms, the individual 5- and 6-ring PAHs equaled or exceeded the 2- through 4-ring alkyl PAHs indicating that the pyrogenic PAH source was a significant contributor to the overall PAH concentration. Fluoranthene, pyrene, and chrysene concentrations were equivalent to the 5- and 6-ring PAH concentration, and their alkyl groups decreased in concentrations with increasing alkyl carbon number, also an indicator of a pyrogenic PAH source. The relatively high napthalenes suggested a petrogenic input, which was confirmed by the SHC distribution; however, the petrogenic contribution was considerably less than that at SMI 236A. Although it has been on location longer, the reduced impact of petroleum hydrocarbons at VR 214A was probably due to the deeper water depth and lower discharge volume compared to SMI 236A.

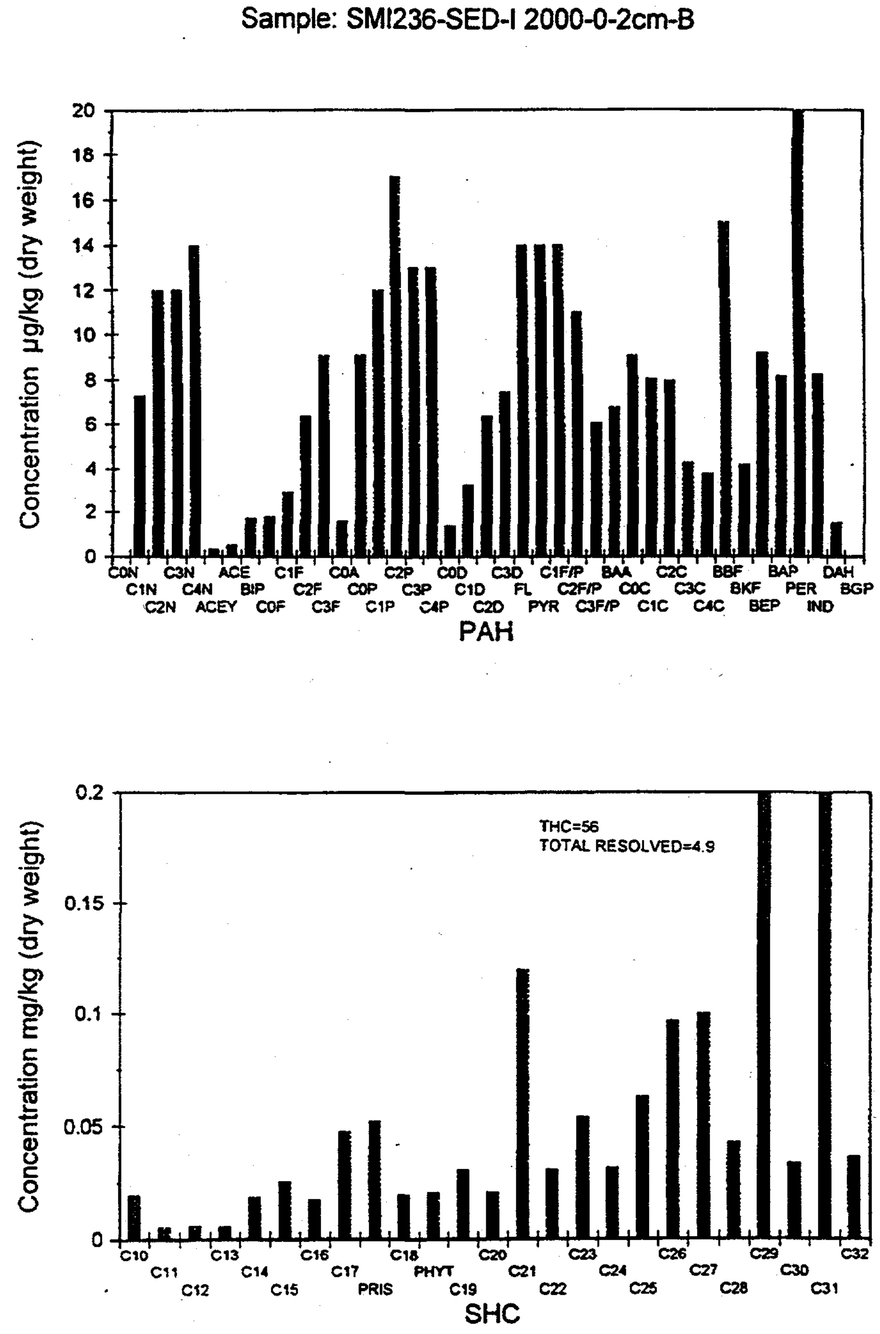


Figure 8.27. SHC and PAH distributions in Sediment Replicate B at SMI 236A, 2,000 m.

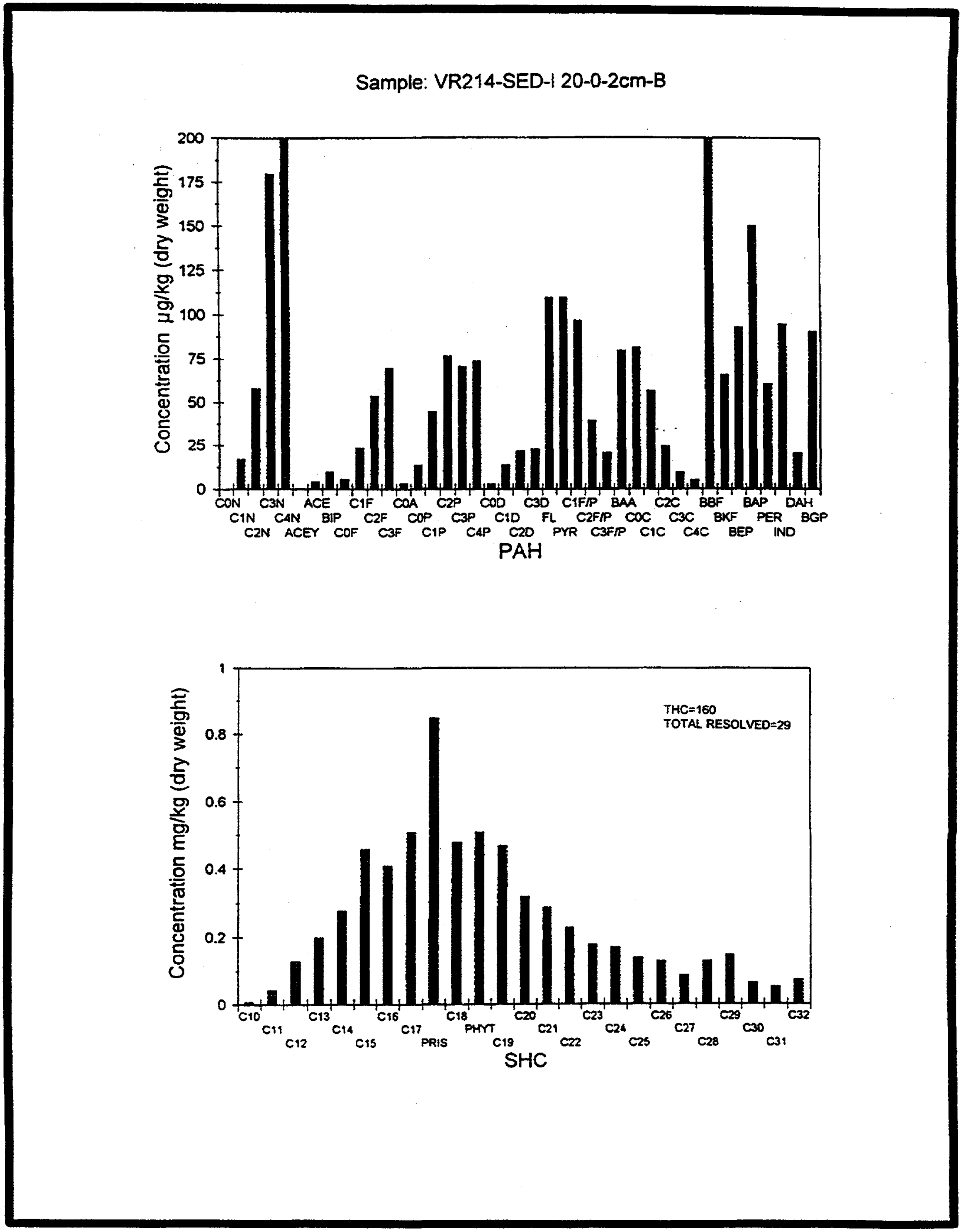


Figure 8.28. SHC and PAH distributions in Sediment Replicate B at VR 214A, 20 m.

At the 2,000-m station, the THC concentrations ranged from 33 to 39 mg/kg. The individual concentrations of SHCs were low, near the detection limits of the method; and the SHC distribution (**Figure 8.29**) showed a biogenic source with no preference in terrestrial or marine inputs. The pyrogenic PAHs were the overwhelming contributors to the total PAH concentration by evidence of the 4- through 6-ring distribution (**Figure 8.29**). Total PAH concentrations (ranging from 140 to 300 μg/kg) were lower than those from SMI 236A, 2,000-m station; however, in some samples, fluoranthene, pyrene, benzo(b)flouranthene, and benzo(a)pyrene concentrations at VR 214A were higher at values greater than 20 ng/g. As with the SMI 236A, this 2,000 m sediment is receiving hydrocarbons from a variety of anthropogenic and natural sources off the coast of Louisiana and/or most likely, from the Mississippi River. These signatures are not typical of unpolluted, pristine environments.

8.3.3.3 South Marsh Island 130B

Even at the water depth of 65 m, petrogenic hydrocarbons were the major contributors to the hydrocarbon composition at the 50-m station at SMI 130B. THC concentrations ranged from 130 to 200 mg/kg with only 10% of the THC content containing resolvable SHCs. The SHC distribution was similar to that of VR 214A showing a petroleum contribution in the n-alkane distribution and UCM content (**Figure 8.30**). The PAH distribution showed a preponderance of petroleum PAHs in the PAH assemblage (**Figure 8.31**). The petrogenic alkyl distributions ("bell-shaped") were not only evident in the naphthalenes and phenanthrenes but also in the chrysenes. The presence of a petrogenic signature in the higher molecular weight, 4-ring chrysenes indicated a crude oil/heavy refined oil source, not usually evident if the source of the PAHs was treated produced water.

Because of the water depth (65 m), the source of the petrogenic hydrocarbons in these sediments was probably the produced sands, although another source may be potentially contributing to the hydrocarbons because the diagnostic ratios of the sediment are not as similar to the produced sands or produced water of SMI 130B as in other sites. The diagnostic ratios C2P/C2D and C3P/C3D in the produced sands and produced waters at SMI 130B, which were nearly identical at 1.25 and 0.9 respectively, were slightly different than the sediment ratios ranging from 1.6 to 1.9 for the C2P/C2D and from 1.0 to 1.4 for C3P/C3D. One sediment replicate had ratios of 1.6 and 1.0 for C2P/C2D and C3P/C3D, values more similar to the produced sand values. Higher concentrations of the phenanthrenes seem to be the cause of the higher diagnostic ratios.

The contribution of pyrogenic PAHs was very low in the SMI 130B sediment, only 10% of the total PAH content (total PAH concentration: 720-1,000 μg/kg). The pyrogenic distribution in the alkyl groups was not evident even in the fluoranthenes/pyrenes and except for perylene, the 5- and 6-ring PAHs were relatively low. This lack of pyrogenic PAHs at SMI 130B was contrary to that from either VR 214A or SMI 236A where pyrogenic PAHs were most prevalent. The coastal anthropogenic and/or the Mississippi River sources of hydrocarbons were not as influential in these sediments as the 20-m station.

THC, SHC, and PAH concentrations were low at both 2,000-m stations (I and V). THC concentrations ranged from 10 to 21 mg/kg of which only 20% of the THC was SHC compounds. SHC distributions were similar at both stations (**Figures 8.32** through **8.34**) with individual SHC concentrations at usually less than 0.02 mg/kg and no predominance of either

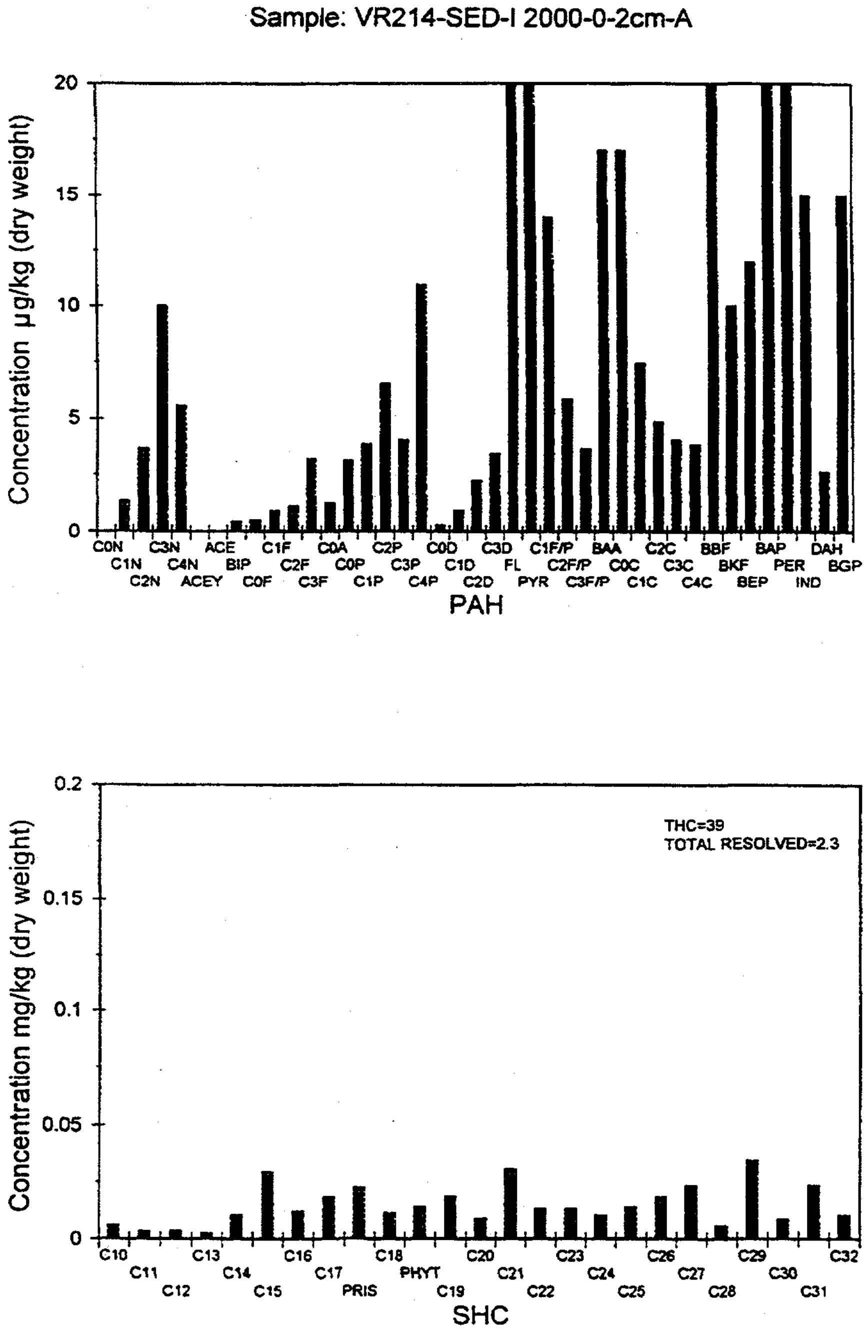

Sample: VR214-SED-I 2000-0-2cm-A

Figure 8.29. SHC and PAH distributions in Sediment Replicate A at VR 214A, 2,000 m.

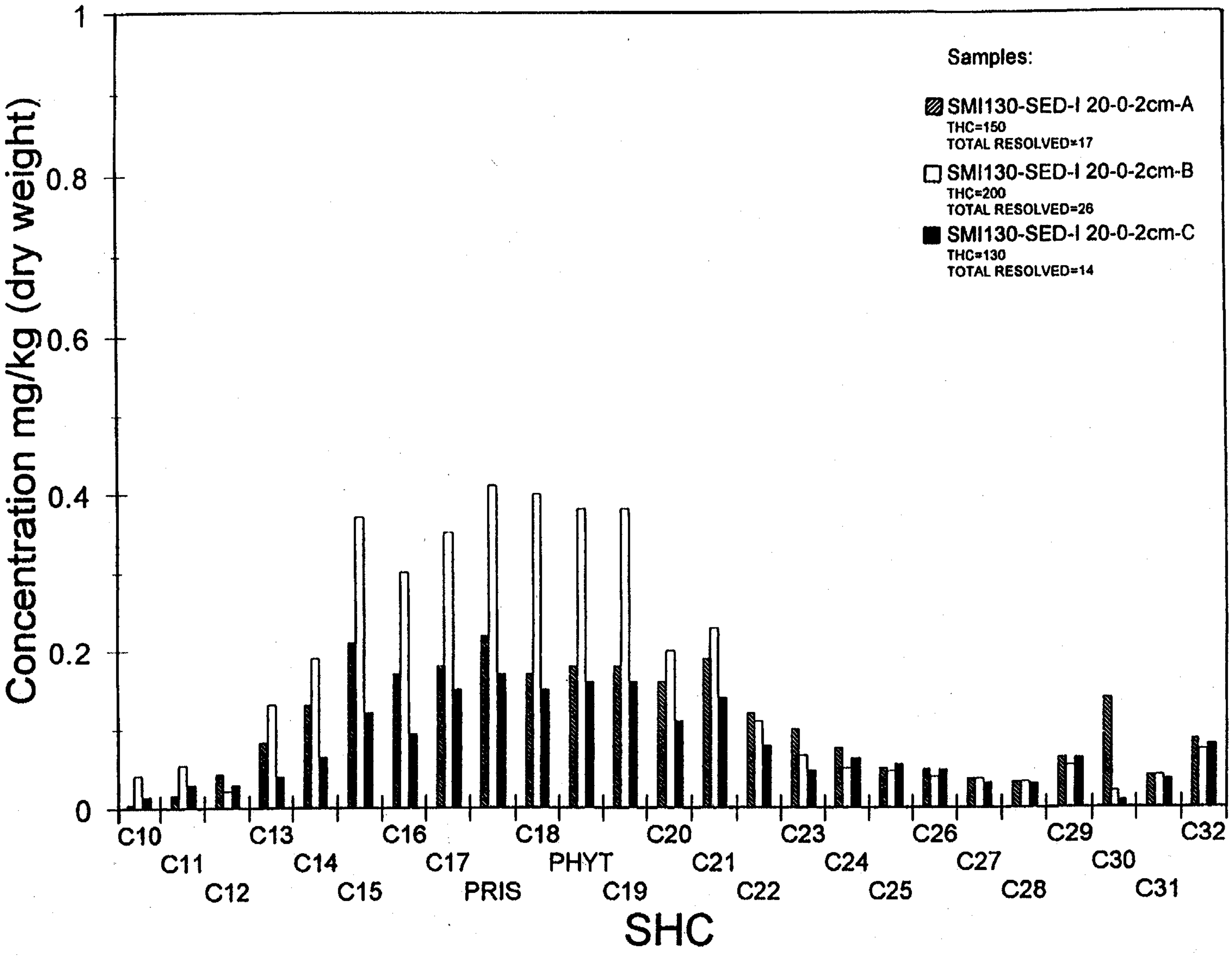


Figure 8.30. SHC distribution in Sediment Replicates A, B, and C at SMI 130B, 20 m.

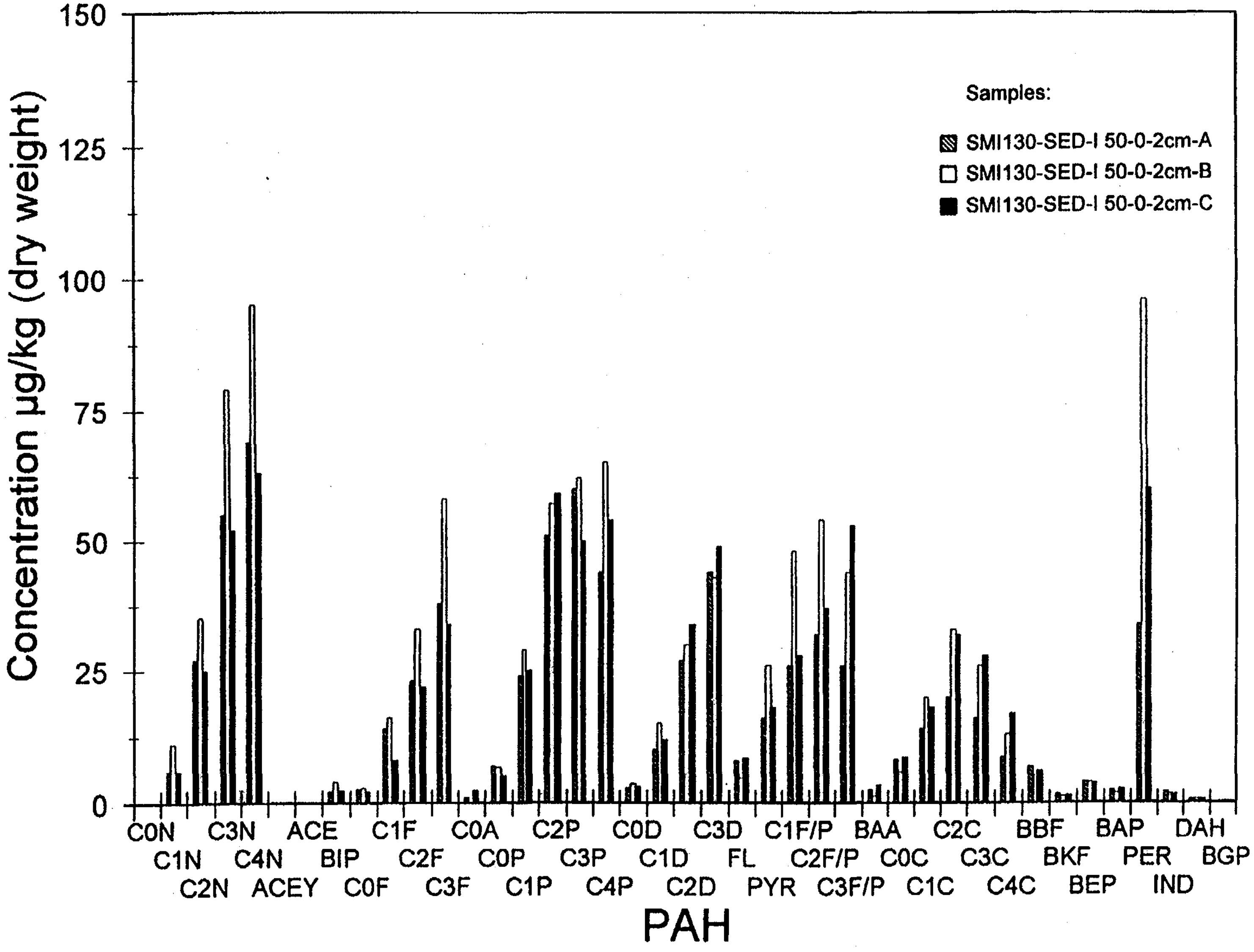


Figure 8.31. PAH distribution in Sediment Replicates A, B, and C at SMI 130B, 20 m.

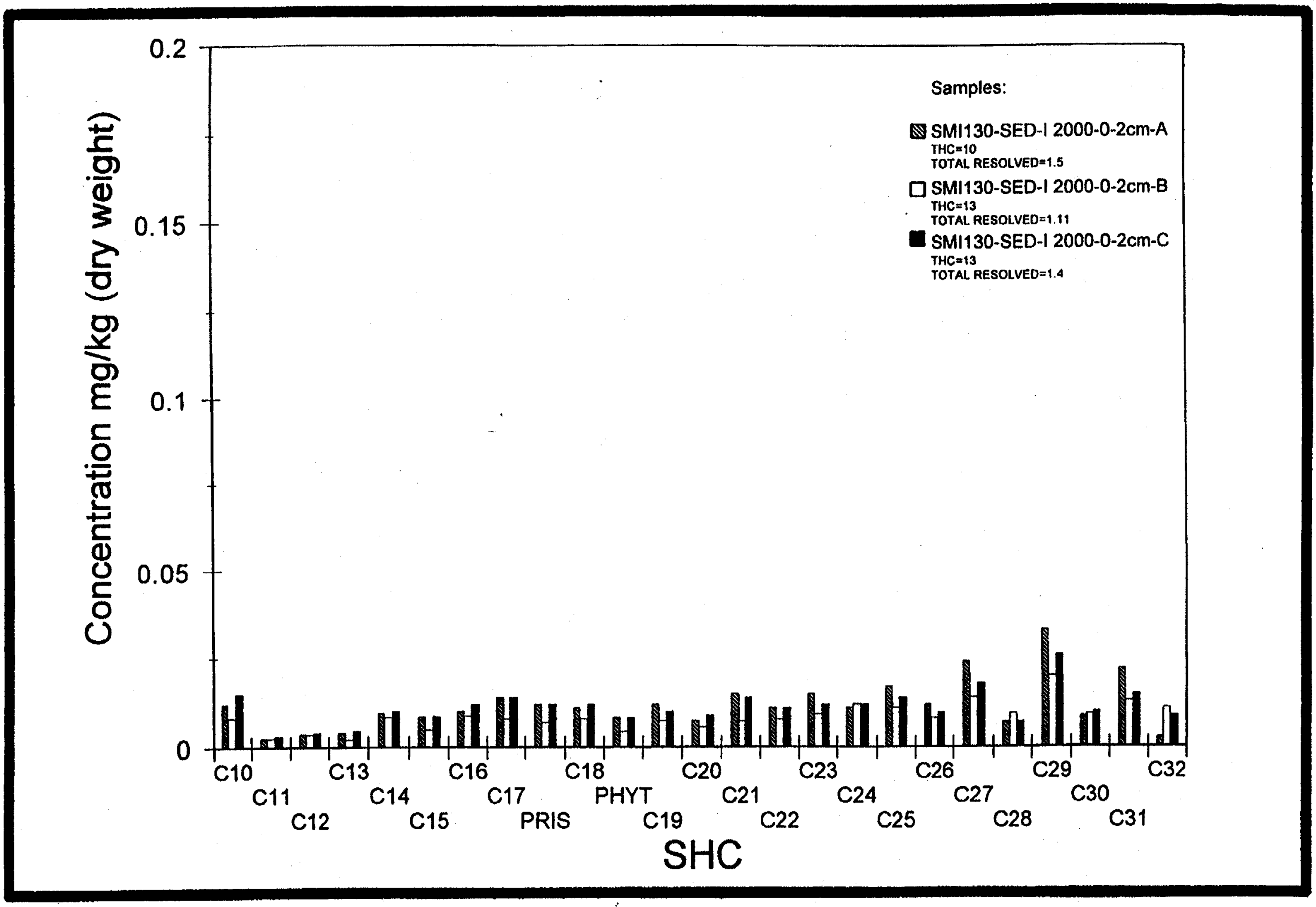


Figure 8.32. SHC distribution in Sediment Replicates A, B, and C at SMI 130B, 2,000 m.

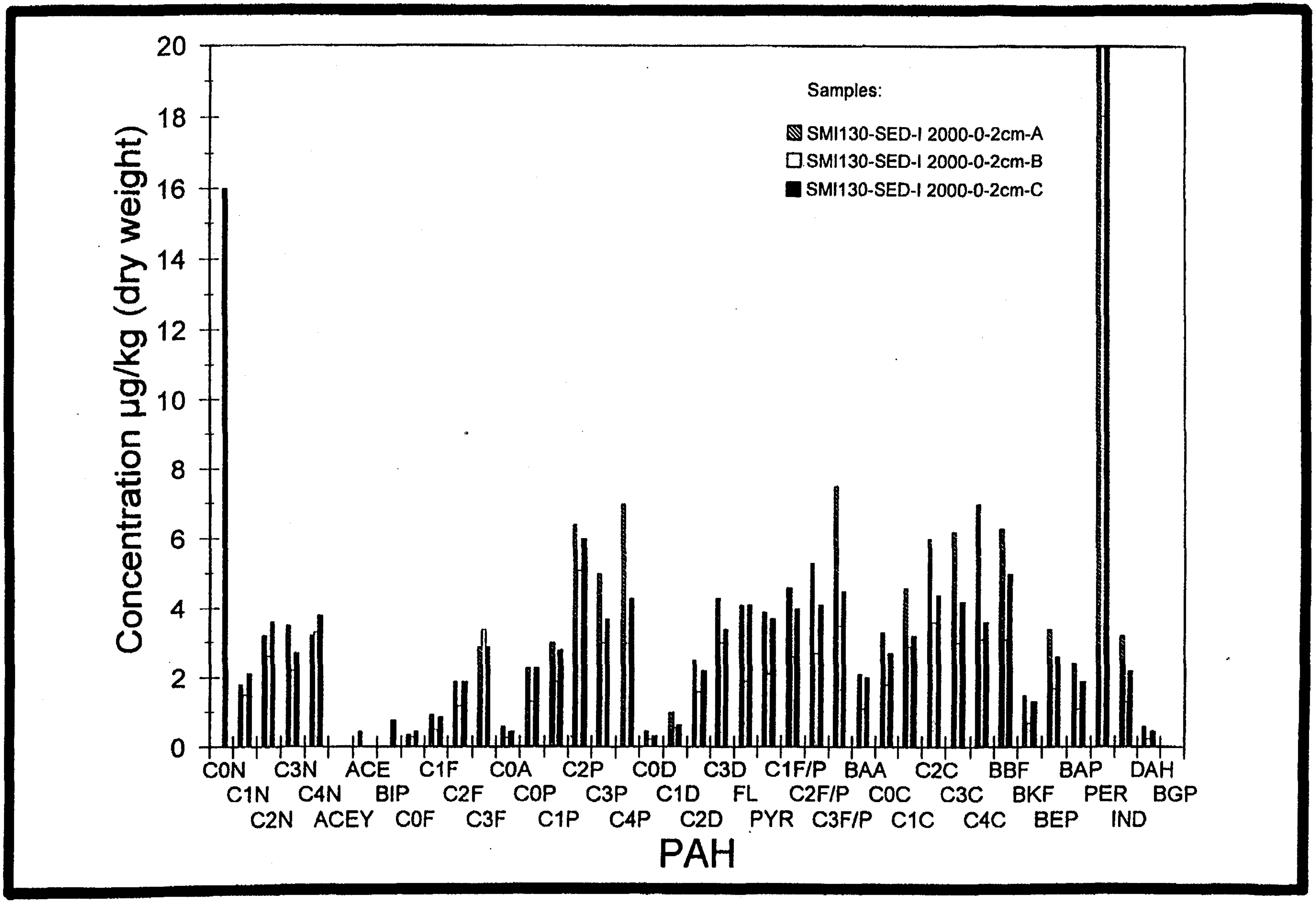


Figure 8.33. PAH distribution in Sediment Replicates A, B, and C at SMI 130B, 2,000 m.

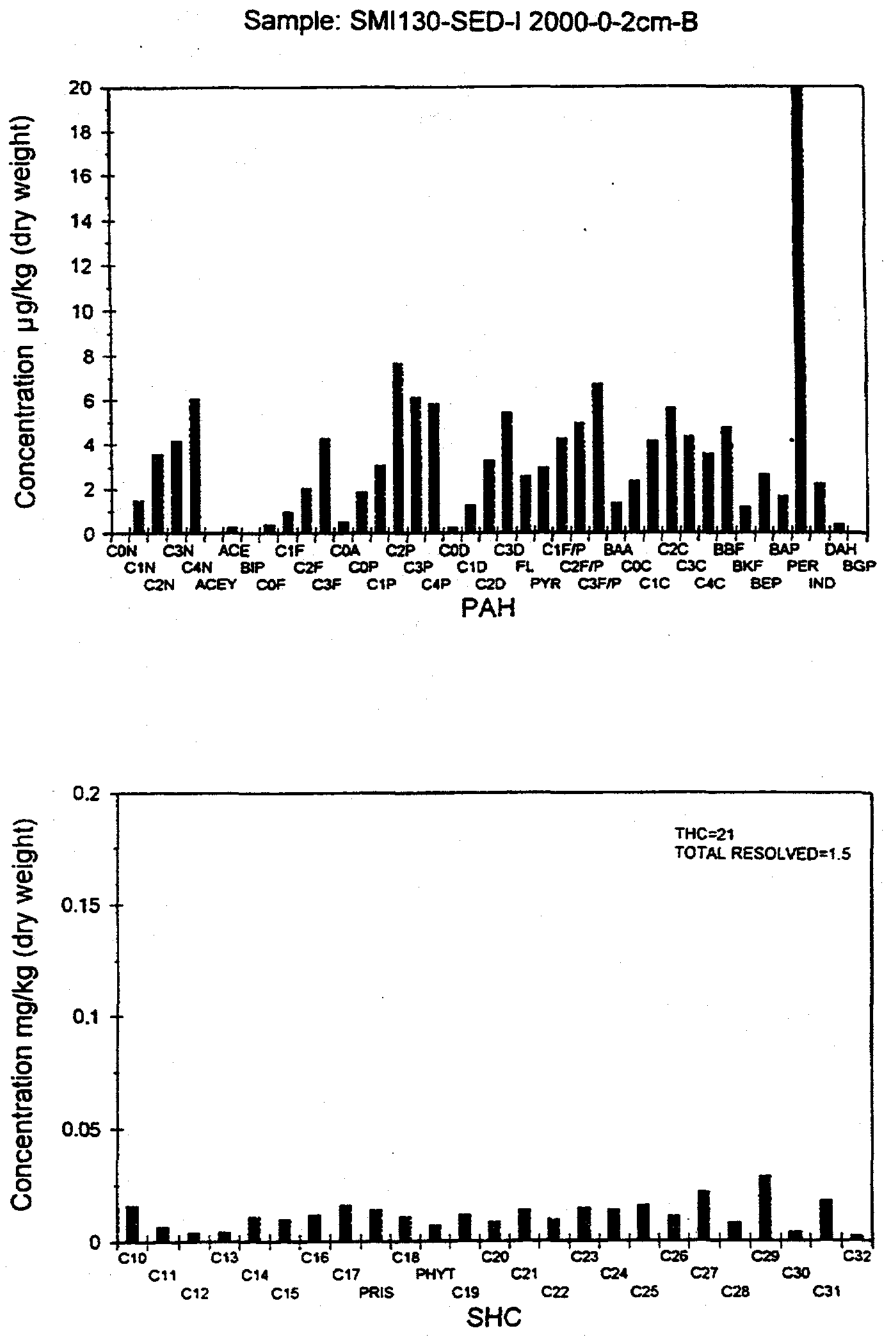


Figure 8.34. SHC and PAH distributions in Sediment Replicate A at SMI 130B, 2,000 m.

terrestrial or marine biogenic inputs. Total PAH concentrations ranged from 140 to 150 μg/kg. Except for perylene which was approximately 30 μg/kg, individual and alkyl group PAH concentrations were low, generally less than 6 μg/kg, and consistent among the 3- through 6-ring PAHs. Although both pyrogenic or petrogenic PAH signatures were present, neither signature predominated (**Figures 8.33** and **8.34**). The SHC and PAH distributions at the 2,000-m stations may be representative of the types of low-level ("background") hydrocarbons in outer shelf sediments partially influenced by the discharge of the Mississippi River in the central Gulf of Mexico.

8.3.3.4 High Island A-595CF

At the 60-m station at HI A-595CF, THC concentrations ranged from 60 to 72 mg/kg, 10% of which were resolved compounds. The odd/even preference of the n-alkanes was greater than 1 indicating a biogenic dominance (**Figure 8.35**). Except for pristane and phytane which were between 0.05 and 0.1 mg/kg, individual SHC concentrations were no higher than 0.05 mg/kg. The PAHs in this sediment at 60 m showed a negligible influence from petroleum sources. The 4- through 6-ring PAHs almost completely dominated the PAH distribution. Individual concentrations of these pyrogenic PAHs were generally between 10 and 20 μg/kg (total PAH concentrations ranged from 280 to 320 mg/kg). Although the station was close to the platform, the residual hydrocarbon concentrations at HI A-595CF were considerably lower and had negligible amounts of petrogenic hydrocarbons compared to the other platform sites. The shunting of the produced water to a depth of 38 m was offset by the deep water (122 m).

Sediment THC concentrations at the 2,000-m station were the lowest of all the discharge platform sites that ranged from 1.1 to 1.3 mg/kg. Greater than 90% of the THC content was resolved SHCs. The SHC distribution showed consistent low-level concentrations of less than 0.02 mg/kg from C_{14} to C_{32} (**Figure 8.36**). Total PAH concentrations ranged from 70 to 80 μg/kg with individual concentrations usually less than 3 μg/kg, near the detection limits of the method. The PAH distribution showed a consistent composition for the 3- to 6-ring PAHs, similar to the other deep water site (SMI 130B), but at concentrations considerably lower. This sediment seemed to represent "background" hydrocarbons for bottom sediments in the Gulf of Mexico (not influenced by the Mississippi River).

8.3.3.5 Component 2 Reference Sites

The hydrocarbon concentrations and SHC and PAH distributions of the deep water (110 m) reference site SMI 186/195 were very similar to the 2,000-m station of the deep water (122 m) discharge platform, HI A-595CF, even though the SMI 186/195 site is 80 miles due east of HI A-595CF and closer to the influence of the Mississippi River. THC and total PAH concentrations were similar at approximately 1 mg/kg and 40-70 μg/kg, respectively, with no UCM. SHC and PAH distributions showed the same low-level, consistent composition for C_{14} to C_{32} n-alkanes and 3- to 6-ring PAHs in both locations (compare **Figure 8.37** and **Figures 8.32** and **8.33**). These similarities suggest that these distributions are representative of "background" hydrocarbons in clay/silt sediments of the central Gulf of Mexico.

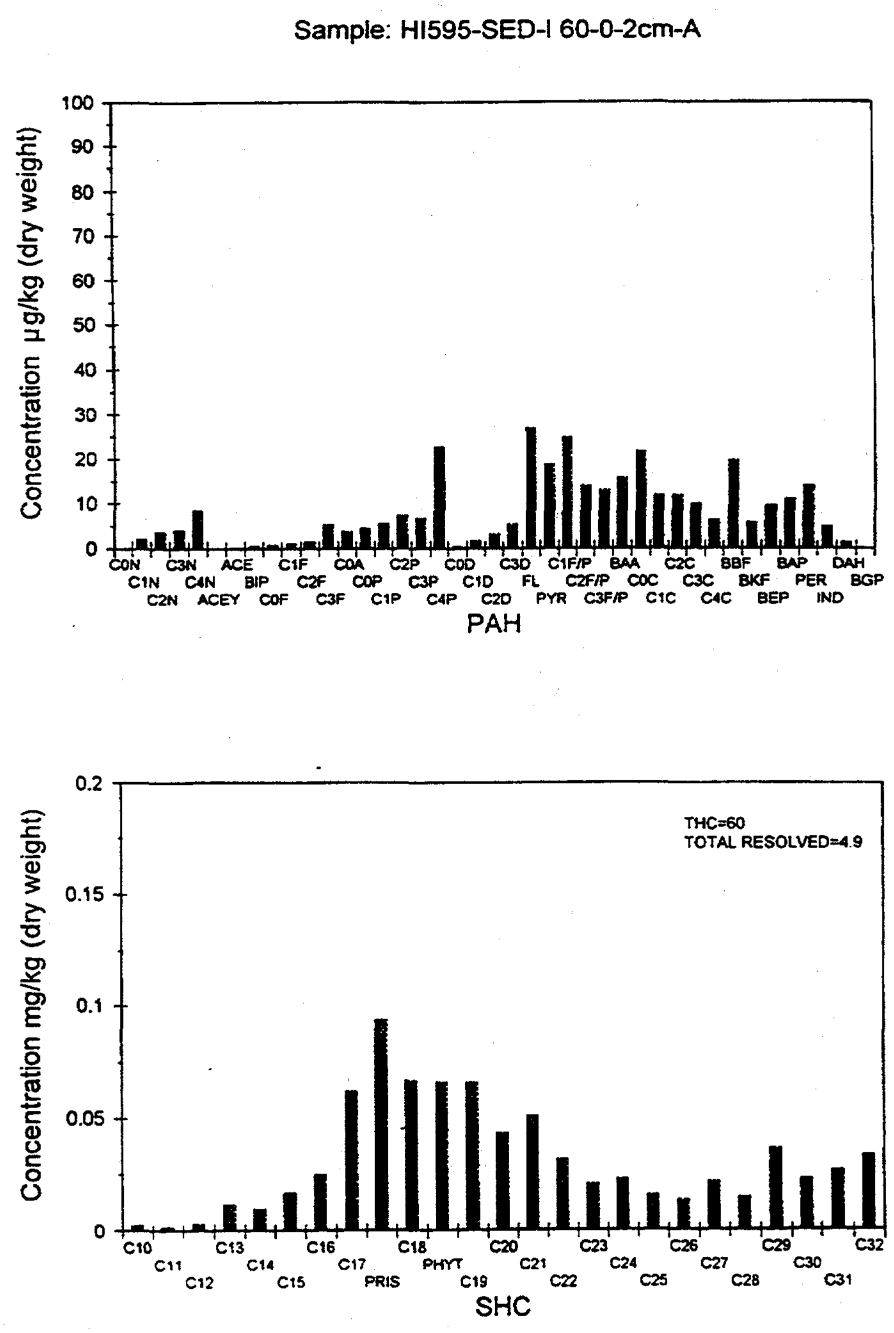


Figure 8.35. SHC and PAH distributions in Sediment Replicate A at HI A-595CF, 20 m.

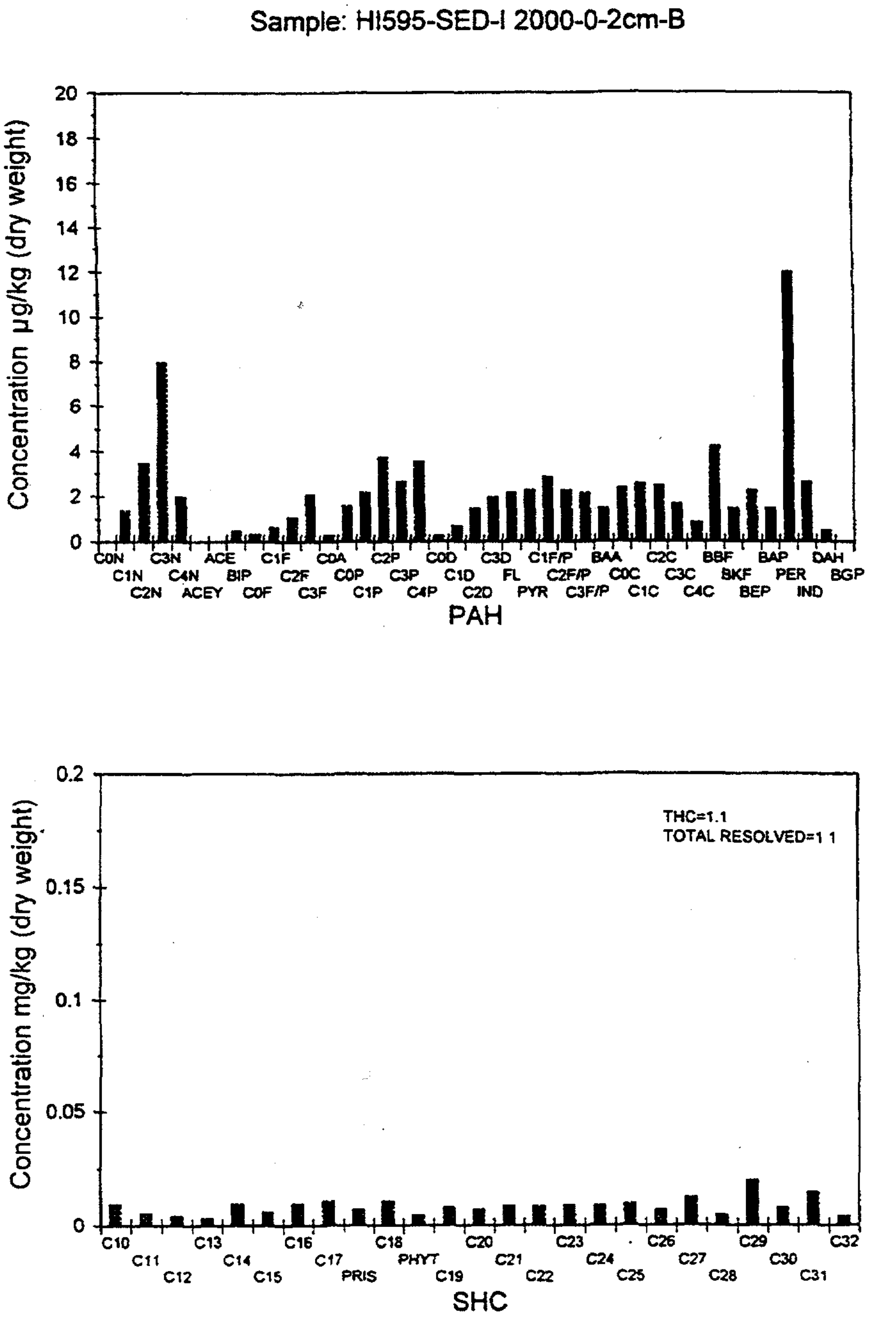


Figure 8.36. SHC and PAH Distribution in Sediment Replicate A at HI A-595CF, 2,000 m.

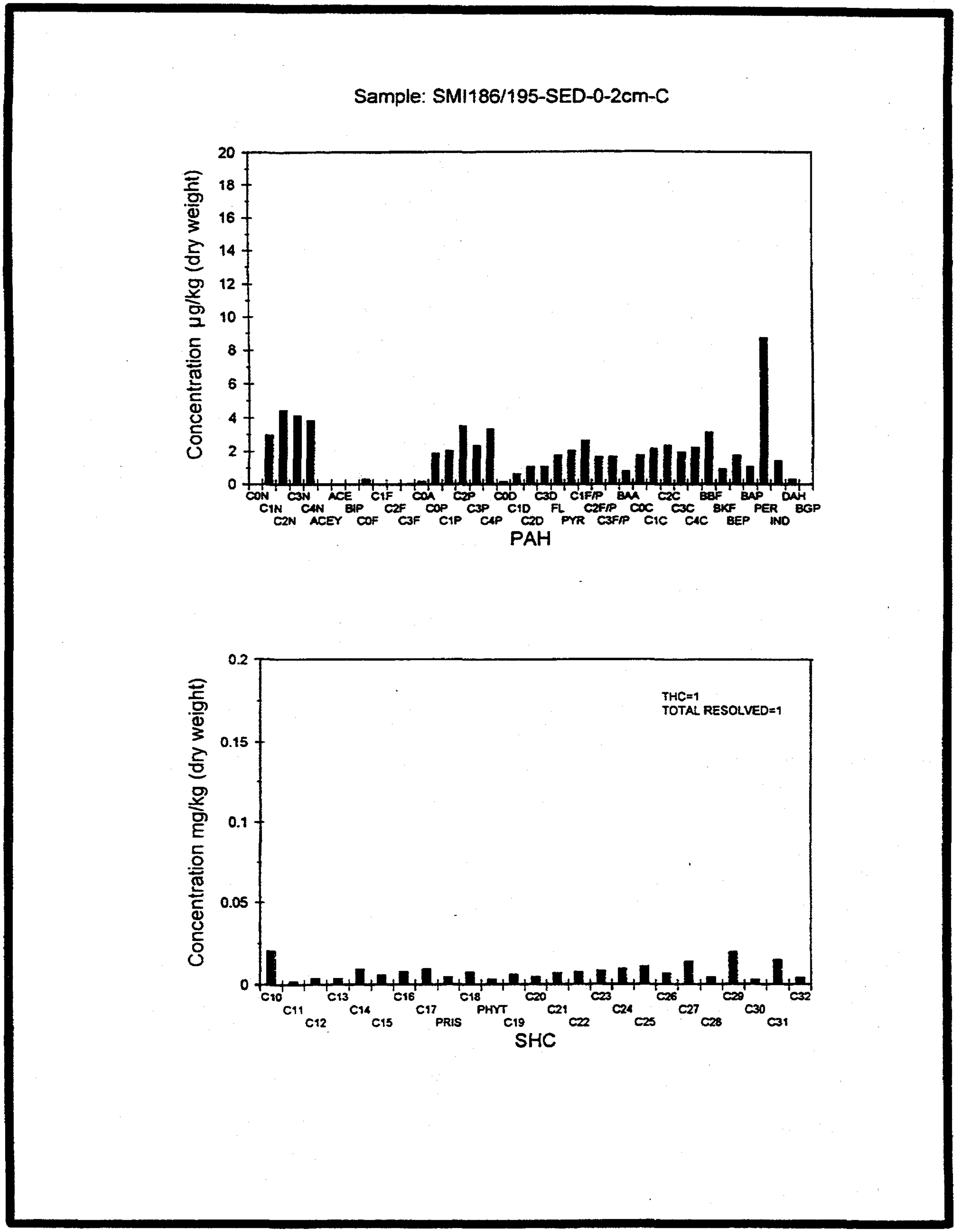


Figure 8.37. SHC and PAH distributions in Sediment Replicate C at SMI 186/195 reference site.

In the western Gulf at GA A-205 in 66 m of water and GA A-90 in 39 m of water, the hydrocarbon concentrations were even lower than those at SMI 186/195. THC concentrations were less than 1 mg/kg, and total PAH concentrations ranged from 10 to 40 μg/kg. The SHC and PAH concentrations were at trace levels generally below the detection limits of the methods (<0.01 mg/kg SHCs and <2 μg/kg PAHs). SHC and PAH distributions (represented in **Figure 8.38**) showed the consistent compositional representations as SMI 186/195 except the GA A-205 and A-90 distributions were at lower concentrations. The large sediment grain size--more sand content--may be the reason for the lower hydrocarbon concentrations at GA A-205 and GA A-90.

The hydrocarbon composition in sediment at WC 448 was, however, different from the other three reference sites. Its characteristics resembled more the composition of the SMI 130B, 2,000 m station, which has a water depth twice as deep as WC 448 (compare **Figures 8.32** and **8.33** with **Figures 8.39** and **8.40**). At WC 448, THC concentrations were 5 to 10 mg/kg with a UCM that made up 80% of the THC content. The SHC distribution (**Figure 8.39**) showed a small odd/even preference with elevated concentrations of C_{19}, C_{27}, C_{29}, and C_{31} at 0.025 to 0.05 mg/kg, similar to the SHC distribution in the sediment at SMI 130B, 2,000 m. Except for perylene which was approximately 30 μg/kg and represented nearly half of the total PAHs, individual and alkyl group PAHs were consistent among the 3- through 6-ring PAHs (**Figure 8.40**) and at concentrations less than 6 μg/kg (total PAH concentrations ranged from 180 to 220 μg/kg). Similar to SMI 130B, both pyrogenic and petrogenic PAH signatures were present. Although SMI 130B is in deeper water and 50 miles east of WC 448, the sources and accumulation of SHCs and PAHs at both sites were similar.

The similarity in hydrocarbon composition of a remotely located reference site and at SMI 130B suggested that the hydrocarbon composition in sediment 2,000 m from SMI 130B is representative of unimpacted oil and gas operation sediment and is typical sediment for many parts of the shelf in 30 to 60 m of water. The discharge of the Mississippi River and possibly other coastal inputs contribute to this consistent hydrocarbon composition in a region-wide basis. As the water depth becomes deeper, the sediment hydrocarbon concentrations decrease but with only a small change in composition. The combination PAH petrogenic and pyrogenic signatures in the deeper water sediments of SMI 186/195 and HI A-595CF are still present, but at lower concentrations.

8.3.3.6 Hydrocarbon Source Differentiation

The hydrocarbon composition in the sediments from the discharge and reference sites reflected the nearfield and regional petrogenic, biogenic, and pyrogenic hydrocarbon inputs. To determine the sources of hydrocarbon in sediments at these sites, a multivariate statistical analysis was performed on PAH data of the sediment, produced water, and produced sand samples. 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 concentration PAH to remove the bias of concentration from the analysis. The results of the analysis are presented in **Figure 8.41**. To reduce the clutter of too many samples on the graphics, mean PAH values for replicate samples were used for the reference sites [R] and the farfield (2,000 m [F]) discharge site locations. Mean values were also used for the produced water [PW] and produced sands (PS) samples. Unlike the nearfield (DISCH [D] and 20 m [N]) discharge site samples, the replicate variability of these samples was small enough to sufficiently be represented by mean values. Presentation of individual replicate samples (A, B, and C) at the nearfield locations was necessary because of the relatively large differences among sample replicates.

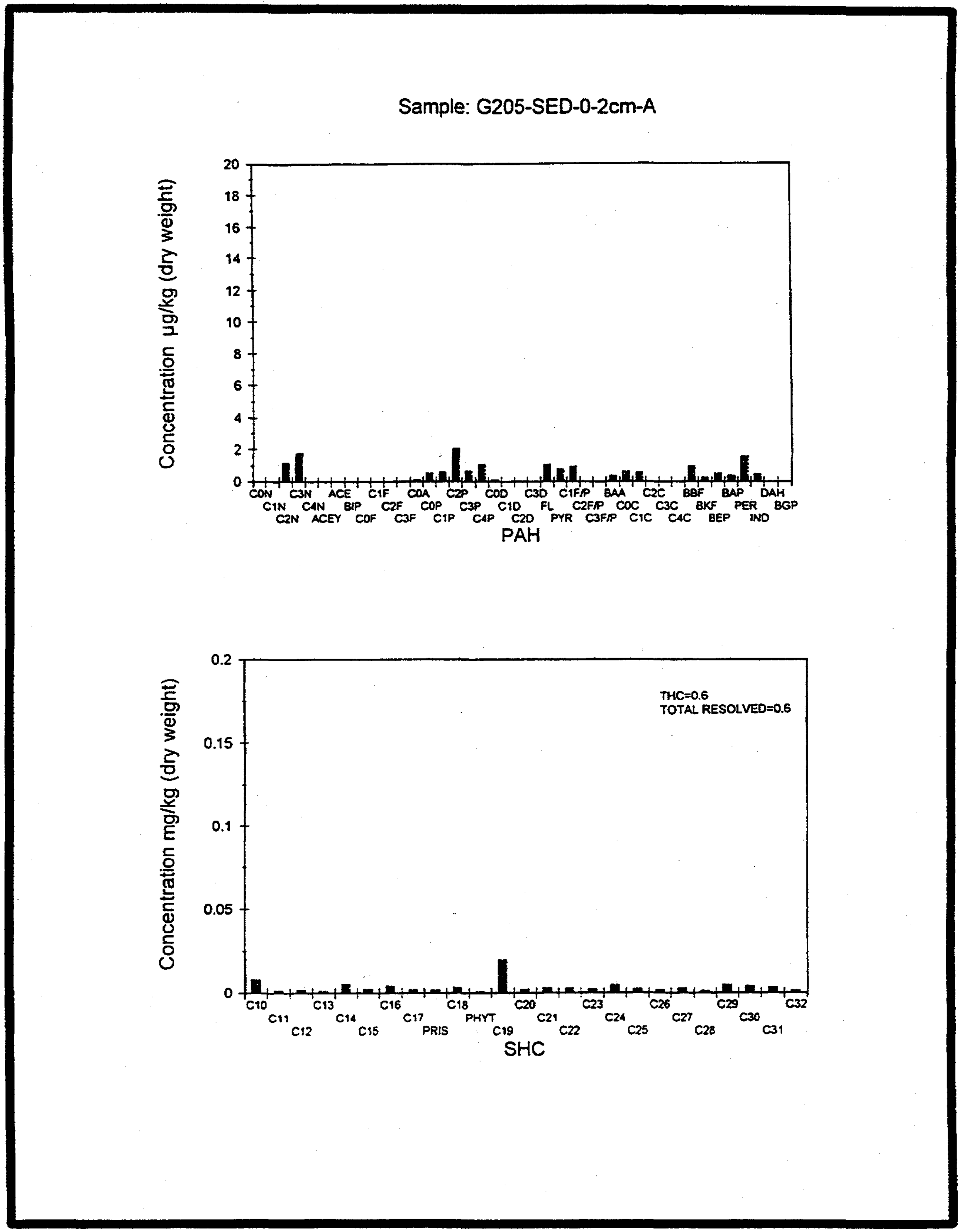


Figure 8.38. SHC and PAH distributions in Sediment Replicate A at GA A-205 reference site.

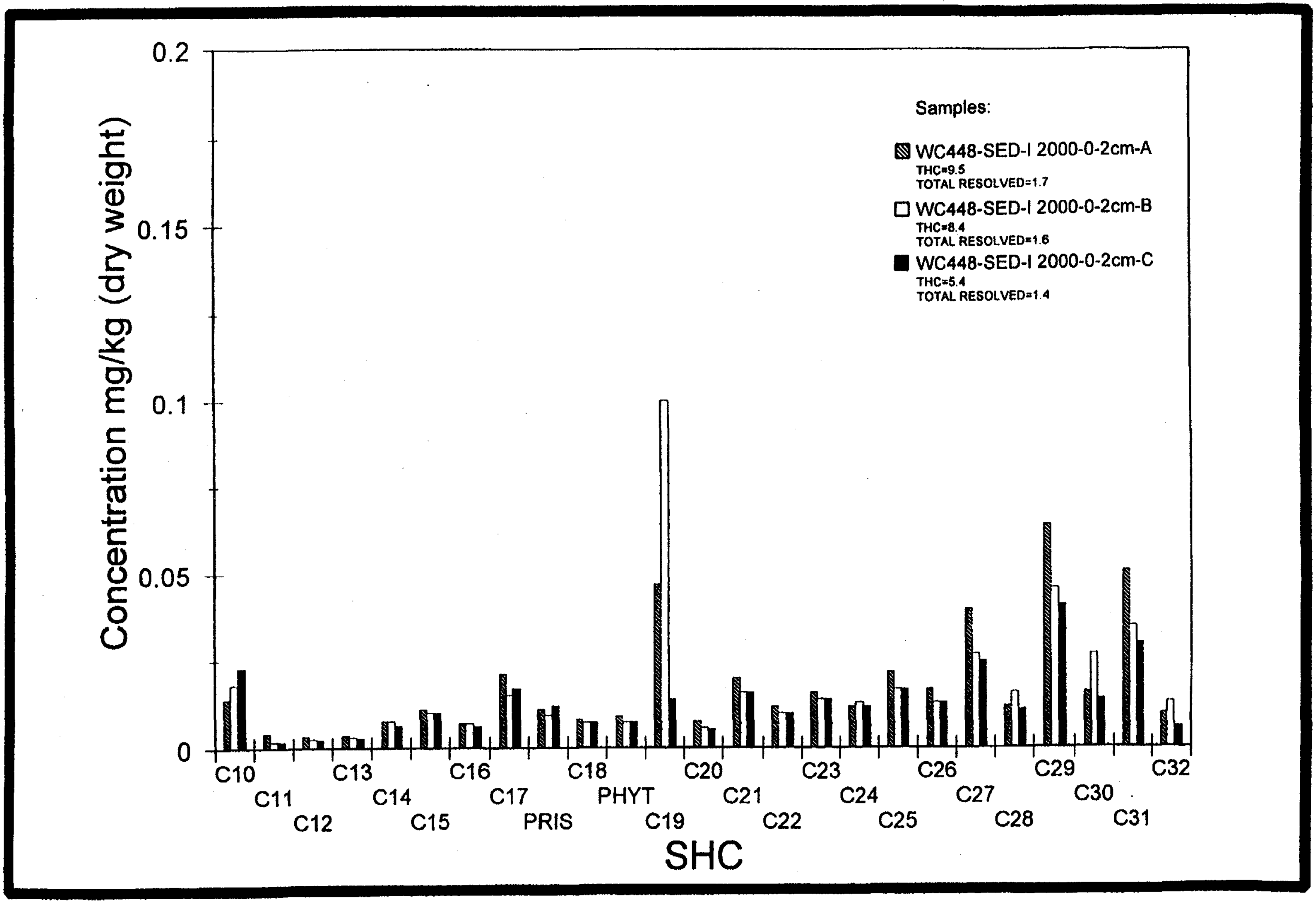


Figure 8.39. SHC distribution in Sediment Replicates A, B, and C at WC 448 reference site.

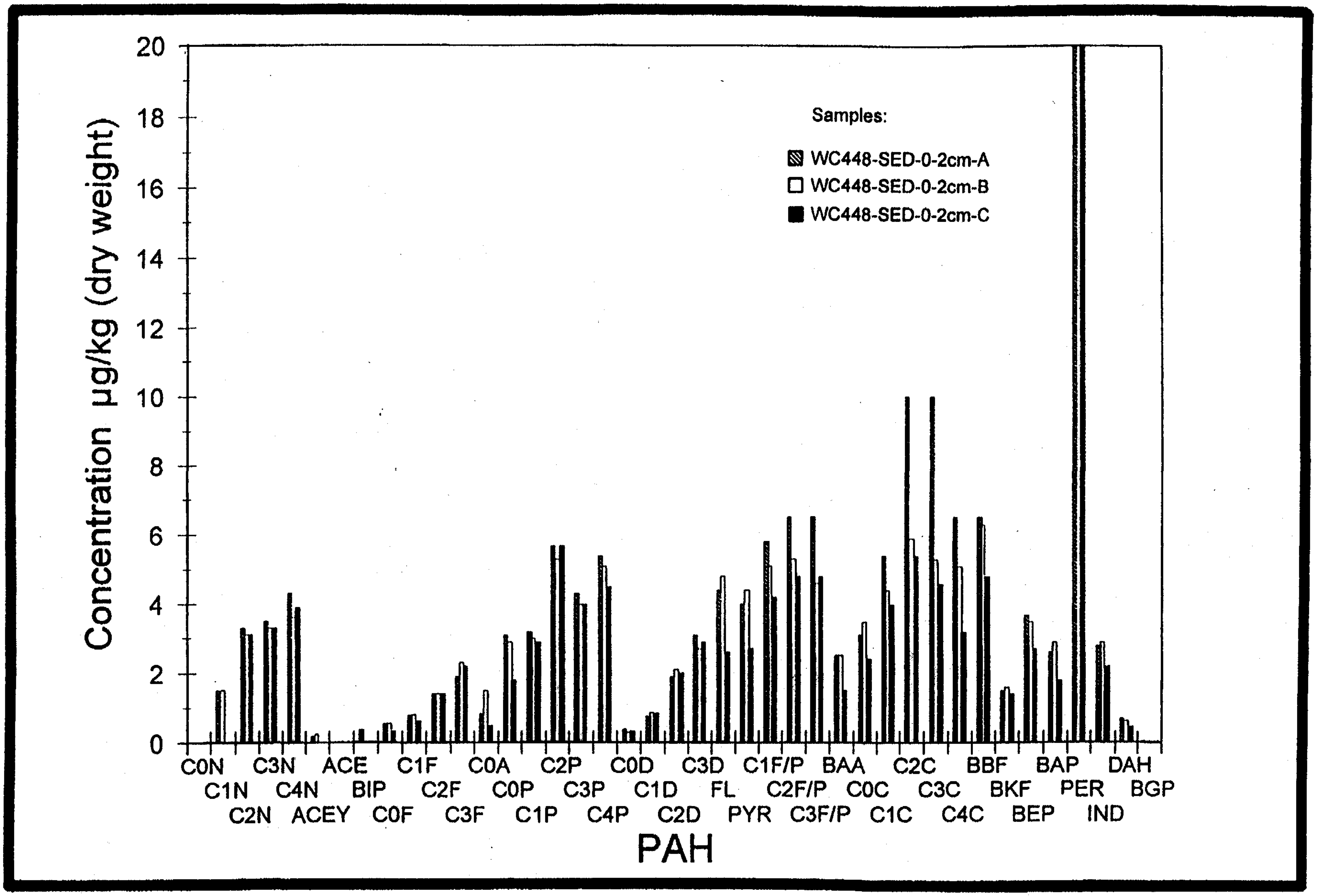


Figure 8.40. PAH distribution in Sediment Replicates A, B, and C at WC 448 reference site.

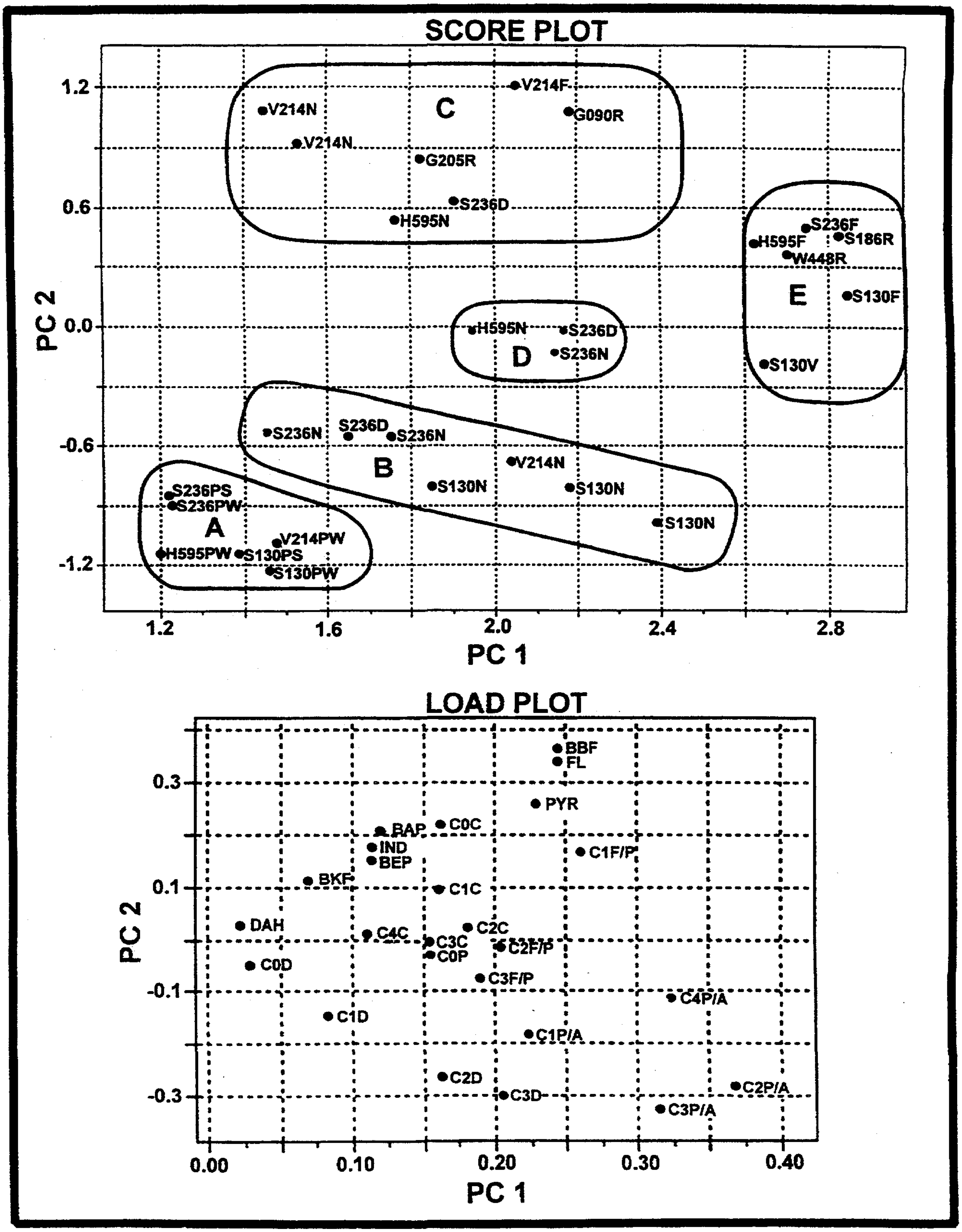


Figure 8.41. Principle component analysis plot of PAH data of produced water (PW), produced sand (PS), and sediment samples (discharge location [D] in triplicate; 20 m location [N] in triplicate; 2,000 m location [F or V]; reference location [R]). PAH (less naphthalenes, fluorenes, and perylene) were normalized by highest concentration in each sample.

In the PCA plot, five groups were identified that represented different hydrocarbon characteristics of the samples.

A: Petrogenic signature - oil and gas operational discharges (produced water [PW] and produced sands [PS]);
B: Dominance of a petrogenic signature - discharge [D] and nearfield [N] sediment samples only;
C: Dominance of a pyrogenic signature - mixture of nearfield [N], farfield [F], discharge [D], and reference [R] sediment samples;
D: Mixture of petrogenic and pyrogenic signatures - discharge [D] and nearfield [N] sediment samples only; and
E: No signature, but low-level combination of petrogenic and pyrogenic PAHs - farfield [F or V], and reference [R] sediment samples only.

Samples in Group A have the petrogenic signature characteristic of petroleum in produced water and produced sands (example: any of the produced sands PAH distributions). These samples have the "bell shaped" alkyl PAH distribution for the 3- and 4-ring PAHs (phenanthrenes, dibenzothiophenes, and chrysenes), and negligible amounts of the 5- and 6-ring PAHs. In the PCA plot, the Group A sample PAHs look to be very similar to each other compared to the PAHs of the sediment samples; however, they are compositionally different among themselves as evident by their different PAH diagnostic ratios (**Table 8.7**). The produced oils have their own signature that differentiates one oil from another.

The Group B nearfield discharge samples contain an overwhelming amount of the petrogenic alkyl homologues the 3- and 4-ring PAHs compared to the pyrogenic 4- through 6-ring PAHs. The closeness of the group to Group A indicates that Group A sources are a probable source of PAHs to these nearfield sediments. Also, the diagnostic ratios of the nearfield sediments in this group are in the same range as the discharges (**Table 8.7**), indicating a platform discharge contribution to the sediments. Differences between the groups could be for a variety of reasons. PAH compositions could vary dependent upon weathering (relative loss) of some key petrogenic PAHs or input of PAHs from other sources. The contribution of pyrogenic PAHs will also influence the overall sediment composition. The SHC distribution of these Group B samples usually suggested a major petrogenic signature, no or small odd/even n-alkane preference, enhanced amounts of pristane and phytane relative the biodegraded n-alkanes, and a large UCM. The biogenic signature was usually not present.

In Group C, the samples are dominated by pyrogenic PAHs (example: **Figure 8.28**). Pyrogenic PAHs are characterized by relatively high amounts of the 4- through 6-ring PAHs, such as fluoranthene, pyrene, benz(a)anthracene, and benzo(a)pyrene, and dominance of the parent PAHs with decreasing abundance with increasing alkyl groups ($C_0 > C_1 > C_2 > C_3 > C_4$). Concentrations of these type PAHs are usually low (individual concentrations are <50 ng/g). Samples away from oil and gas operations would be expected to have more of a pyrogenic signature because the ubiquitous of pyrogenic sources (e.g., fossil fuel combustion, natural fires). In this study, dominating pyrogenic signatures were present in nearfield samples (e.g., VR214A 20 m) as well as farfield and reference samples indicating the variability of sediment near producing platform. Local current conditions, induced at least partially by the platform structure, change the substrate by resuspending sediment or transporting away inputs from the platform operations. Two of the nearfield VR 214A samples have low amounts of petrogenic PAHs, whereas the third VR 214A sample has a dominating petrogenic signature. Often the pyrogenic PAHs are the only detectable PAHs when the hydrocarbon input is very low, illustrated

Table 8.7. Diagnostic ratios for produced water, produced sands, nearfield sediments, and jewelbox.

Sample Type	SMI 236A	VR 214A	SMI 130B	HI A-595CF
Produced Water				
C2P/C2D	3.2	2.0	1.25	0.8
C3P/C3D	2.5	1.25	0.9	0.7
Produced Sands				
C2P/C2D	3.4	--	1.25	--
C3P/C3D	2.8	--	0.9	--
Sediment				
C2P/C2D	3.0-3.3 (Disch) 2.3-2.9 (20 m)	2.7-3.5	1.8-1.9	1.6-2.6
C3P/C3D	2.3-2.7 (Disch) 2.0-2.5 (20 m)	2.2-3.1	1.0-1.4	1.3-1.6
Jewelbox				
C2P/C2D	--	1.5	2.5	2.0
C3P/C3D	--	1.0	1.9	1.3

by both reference sites in the middle of the Gulf (GA 90 and GA 205) where PAH concentrations are near the detection limits of the method (<5 ng/g). Pyrogenic PAHs in the marine sediments are generally accompanied by biogenic SHCs, terrestrial and/or marine alkanes depending on proximity to terrestrial sources.

The samples in Group D contained a mixture of petrogenic and pyrogenic PAHs. Both PAH-type distributions would be evident in the sample distribution, in relatively equal amounts. The 2- and 3-ring alkyl PAHs with the bell-shaped distribution are present in conjunction with 4- through 6-ring PAHs (e.g., **Figure 8.25**, Replicate B). The relative location of the samples in the group on the plot correspond to the relative amounts of the pyrogenic and petrogenic PAHs. Besides the PAHs, these samples have an UCM and n-alkane distribution that indicate a petrogenic source, but with some biogenic influence.

The pyrogenic and petrogenic PAH influences in the sediment samples are illustrated by the "Load" plot (see insert in **Figure 8.41**). Samples consisting of mostly pyrogenic PAHs are above 0.0. on the PC 2 axis and samples consisting of mostly petrogenic PAHs are below 0.0. In the Load plot, the pyrogenic PAHs (4-, 5-, and 6-ring PAHs) are above 0.0 and the petrogenic PAHs (alkyl groups) are below 0.0. Samples containing a mixture of the two types of PAHs lie along the 0.0 origin. Sediment at SMI 236A (DISCH) illustrates the cross-section of the PAH types (**Figure 8.25**) that correspond to different areas above and below the origin of the PCA plot (Groups B, C, and D).

All the samples in Group E are farfield (2,000 m) discharge site or reference site sediments. Remember these samples represent the mean of three replicates. Except for VR 214A 2,000-m samples, all farfield samples and samples from the two reference sites closest to the Mississippi River are represented in this Group E. The PAH distribution of this group is characterized by a consistent (constant) low-level concentration of most of the PAHs, both pyrogenic and petrogenic PAHs. There is no distinguishing form to the distribution (e.g., **Figure 8.36**). In this study, individual PAH concentrations were usually no higher than 10 ng/g except for perylene which is a diagenic PAH. Total PAH concentrations ranged from 70 to 250 μg/kg. Brooks *et al.* (1990) determined total PAHs in nearshore sediments at a mean concentration of 96 ± 112 μg/kg and offshore sediments (Texas shelf) at a mean concentration of 29 ± 28 μg/kg, comparable to the results in this study. SHC concentrations were very low (<0.03 μg/g) with little to no UCM and THC concentrations no higher than 10 μg/g. SHC distribution would be represented by biogenic source hydrocarbons, marine (C_{15} to C_{22} n-alkanes, odd preference) and/or terrestrial (C_{27} to C_{35} n-alkanes, odd preference).

8.3.4 Biota - Fish, Molluscs, and Crustaceans

As summarized in **Table 8.8**, fish and invertebrates were analyzed for PAHs only from the Component 1 discharge platform sites, SMI 236A, VR 214A, SMI 130B, and HI A-595CF; no tissue samples were analyzed for PAHs from Component 2 reference sites. For most fish and mollusc species, five replicate samples were analyzed. Each replicate sample of molluscs (edible tissue) was a composite of several individuals that were needed to achieve the desired biomass for analysis. A replicate sample for fish was composed of several individuals, analyzed as whole fish, muscle (fillet), or carcass.

Table 8.8. Mean and range of concentrations of total PAHs in tissues and non-edible tissues of fish and invertebrates collected near Component 1 produced water discharging platform sites.

Species	Tissue	Total PAHs (μg/kg dry weight)	Range (μg/kg dry weight)
SMI 236A			
Atlantic croaker	whole	480	22-1,900
Hardhead catfish	whole	110	51-130
Silver seatrout	whole	40	23-53
Atlantic cutlassfish	whole	62	49-72
Shrimp	edible flesh	9	3-11
Blue crab	edible flesh	450	31-970
Eastern oyster	soft tissue	26	26*
VR 214A			
Red snapper	muscle/carcass	12/110	7-20/34-110
Gray triggerfish	muscle/carcass	25/33	2-78/14-70
Longspine porgy	whole	6	ND-9
Dusky flounder	whole	0.2	ND-1
Rock shrimp	edible flesh	51	1-240
Roughneck shrimp	edible flesh	3	ND-11
Blue crab	whole	52	14-180
Jewelbox	soft tissue	12,000	12,000*
SMI 130B			
Red snapper	muscle/carcass	15/76	7-26/35-120
Gray triggerfish	muscle/carcass	11/92	2-21/10-270
Seabass	muscle	9	2-37
Pinfish	muscle	10	3-12
Longspine porgy	whole	9	4-13
Rock shrimp	edible flesh	0.7	ND-1
Swimming crab	whole	54	24-87
Jewelbox	soft tissue	1,700	1,700*
HI A-595CF			
Vermillion snapper	muscle/carcass	25/98	2-58/60-210
Longspine porgy	whole	2	1-8
Flatfish (Bothidae)	whole	14	5-23
Wenchman	muscle	51	4-190
Longtail bass	muscle	15	3-23
Jewelbox	soft tissue	310	310*

*Only one composite sample analyzed.
ND - Not detected.

Each of the sites had different species assemblages present, depending upon the water depth of the platform. In the shallower water environments, more molluscs and crustaceas were collected at the shallow water platform sites, SMI 236A and VR214A, than at the deeper sites, SMI 130B and HI A-595CF. Fish dominated the species collection at the deeper water sites. A list of the species analyzed for PAHs at each platform site is presented in **Table 8.8**.

Because of the analyte sensitivity of the analytical method, PAH concentrations in tissues were determined in the low parts per billion (as low as 1 μg/kg dry weight). Traces of C0, C1-naphthalenes, biphenyl, and phenanthrene (<2 μg/kg) consistently found in the samples are probably due to sample analysis contamination often found in the procedural blanks. The presence of these analytes at these levels should be considered qualified data.

For those species in which concentrations were near the detection limits of the method (1 to 5 μg/kg dry weight), the results of replicate samples were highly variable. For fish especially, some replicate samples of a species contained non-detectable amounts of particular PAHs while other replicates contained small amounts of PAHs. This presence/absence of PAHs in samples presents some difficulties in discussing bioacculumation and exposure potential of PAHs to organisms, especially when mean values are used in the assessments. As a result, environmental interpretations require explanation of the variability in the replicate samples. In this chapter, the composition of PAHs in replicate samples are discussed and related to potential sources of PAHs in tissue. PAH distributions of representative replicate tissue samples are presented to illustrate the variability in PAH composition. The significance of bioaccumulation of PAHs and impact of PAHs on the biota are discussed in **Chapter 9**.

8.3.4.1 South Marsh Island 236A

The nearshore SMI 236A platform had faunal groupings represented by "Coastal" assemblages (Gallaway and Lewbel, 1982). The biofouling community and epifauna associated with the soft sediment substrate near the platform included commercially important species of blue crab, white shrimp, and eastern oyster (1 replicate) which were analyzed. The demersal fish on which PAH analyses were conducted included the Atlantic croaker, hardhead catfish, Atlantic cutlassfish, and silver seatrout. The mean and range concentrations of total PAHs for these species are listed in **Table 8.8**.

PAH concentrations in fish and invertebrate species were highest at SMI 236A than the other discharging platform sites (**Table 8.8**). Mean total PAH concentrations in the fish ranged from 480 μg/kg for Atlantic croaker to 40 μg/kg for the silver seatrout. The high mean concentration for croaker was due, however, to one abnormally high replicate that had a total PAH concentration of 1,900 μg/kg. Without this replicate, the croaker mean total PAH concentration would be approximately 120 μg/kg, similar to the catfish. The blue crab mean total PAH concentration was also relatively high at 450 μg/kg, but this value reflected a more consistent contribution of PAHs from most of the replicates.

For most of the fish at the site, the representative PAH composition in replicate tissue samples were similar to the PAH distribution of the hardhead catfish (**Figure 8.42**). Trace levels of the C_0- through C_2-phenanthrenes and dibenzothiophenes (<5 μg/kg) were detected in most replicates and were accompanied with larger amounts of all the alkyl naphthalenes (10-50 μg/kg). The presence of these PAHs suggested a petrogenic origin to the PAHs in the tissue.

Fluoranthene and pyrene was also present at the low levels of the 3-ring PAHs indicating that some of the PAH bioaccumulation has a pyrogenic source. This pattern (with comparable concentrations) of relatively higher concentrations of naphthalenes and trace levels of the phenanthrenes and dibenzothiophenes was duplicated in the edible tissue of the blue crab (**Figure 8.43**), but not in the shrimp (**Figure 8.44**). Shrimp PAHs were almost all non-detectable.

Although the relative concentrations of naphthalenes were not as high, similar petrogenic signatures were observed in sediment near the platform (**Figure 8.26**). Organisms such as the catfish and blue crab which forage on the sea bottom would be most susceptible to the hydrocarbons in the sediment, and have the tendency to accumulate PAHs that reflect the composition of the benthic environment. The produced water was probably a major contributor to the tissue PAHs of these organisms at the site. The relatively higher accumulation of naphthalenes compared to the other PAHs in these tissues and consideration of the lower K_{ow} of naphthalenes compared to the 3-ring PAHs suggests that the produced water itself is a contributor to the PAHs in the fish and blue crabs. Naphthalenes comprised more than 95% of the PAHs in the produced water discharged at SMI 236A (**Figure 8.14**).

8.3.4.2 Vermilion 214A

The faunal communities associated with VR 214A represented the "Offshore" assemblages (Gallaway and Lewbel, 1982). The sea bottom was generally sandy. The crustacean species analyzed for PAHs included the rock shrimp, the penaeid shrimp, and the blue crab. No commercially important bivalves were present at this site, although one jewelbox sample was analyzed. A more pelagic variety of fish was collected at this site compared to those fish species at the SMI 236A site. They were red snapper, gray triggerfish, longspine porgy, and lefteye flounder. The mean and range concentrations of total PAHs for these organisms are listed in **Table 8.8**.

Mean total PAH concentrations in most fish tissues were 3 to 8 times lower than the fish and crustaceans at SMI 236A. Except for one replicate in the gray triggerfish, the fillets of red snapper, longspine porgy, lefteye flounder, and gray triggerfish were almost devoid of PAHs (**Figure 8.45**). The carcass of the red snapper, however, showed low levels (<10 μg/kg individual PAHs) of the 2- and 3-ring PAHs in all replicates (**Figure 8.46**), a distinct petroleum signature of a mid-distillate type (e.g., No. 2 fuel oil) because of the absence of chrysenes in the distribution. Since the fillet of the red snapper lacked these PAHs, the skin of the fish was probably slightly contaminated during field collection or processing. Except for one replicate rock shrimp which had 245 μg/kg total PAHs, the two shrimp species were also essentially devoid of PAHs. The blue crab had only traces of the lower molecular weight alkyl phenanthrenes and dibenzothiophenes in most replicates (mean total PAHs ~ 20 μg/kg) with one high total PAH replicate at 180 μg/kg (**Figure 8.47**).

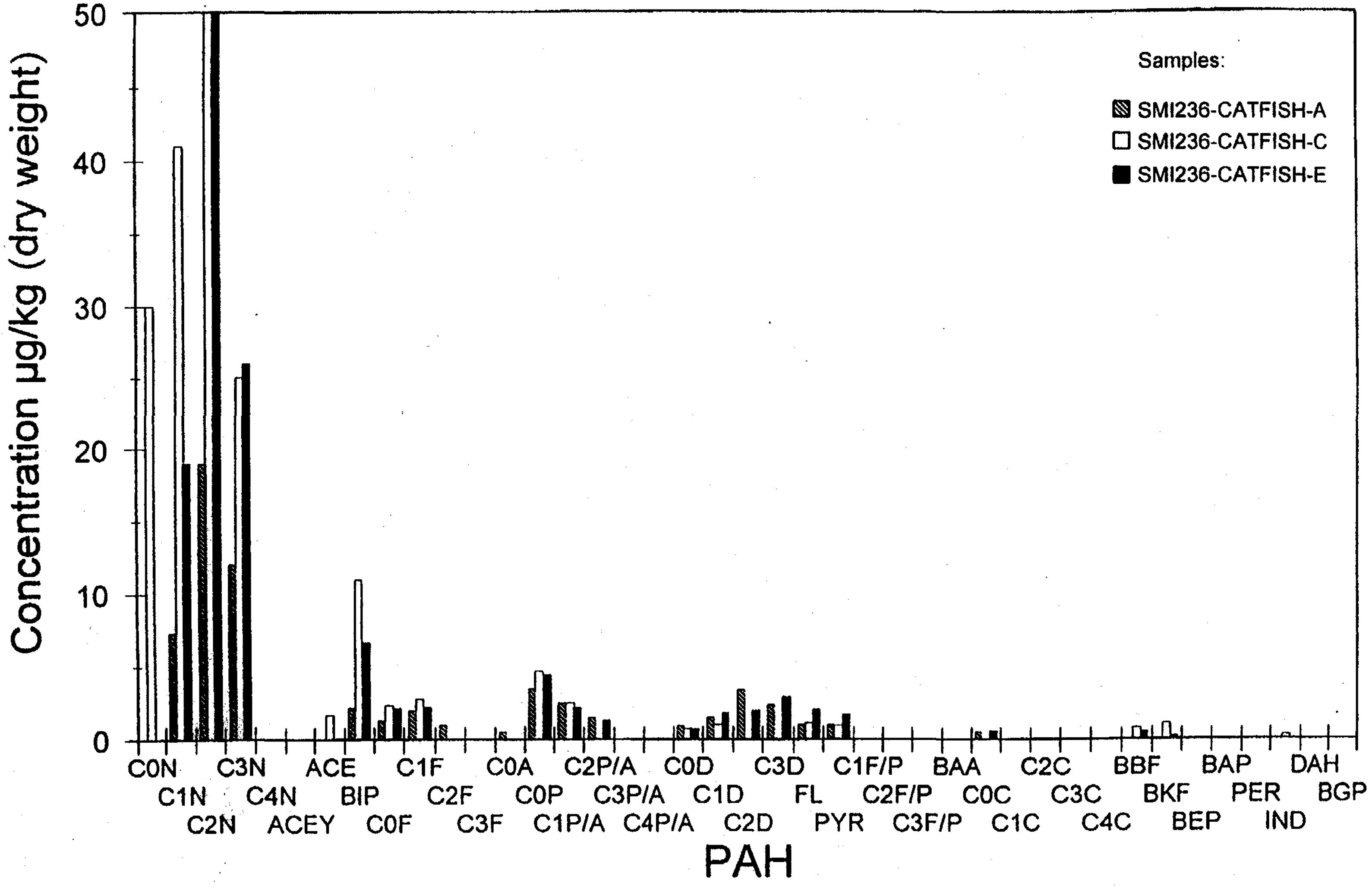


Figure 8.42. PAH distribution in Catfish Tissue Replicates A, C, and E at SMI 236A.

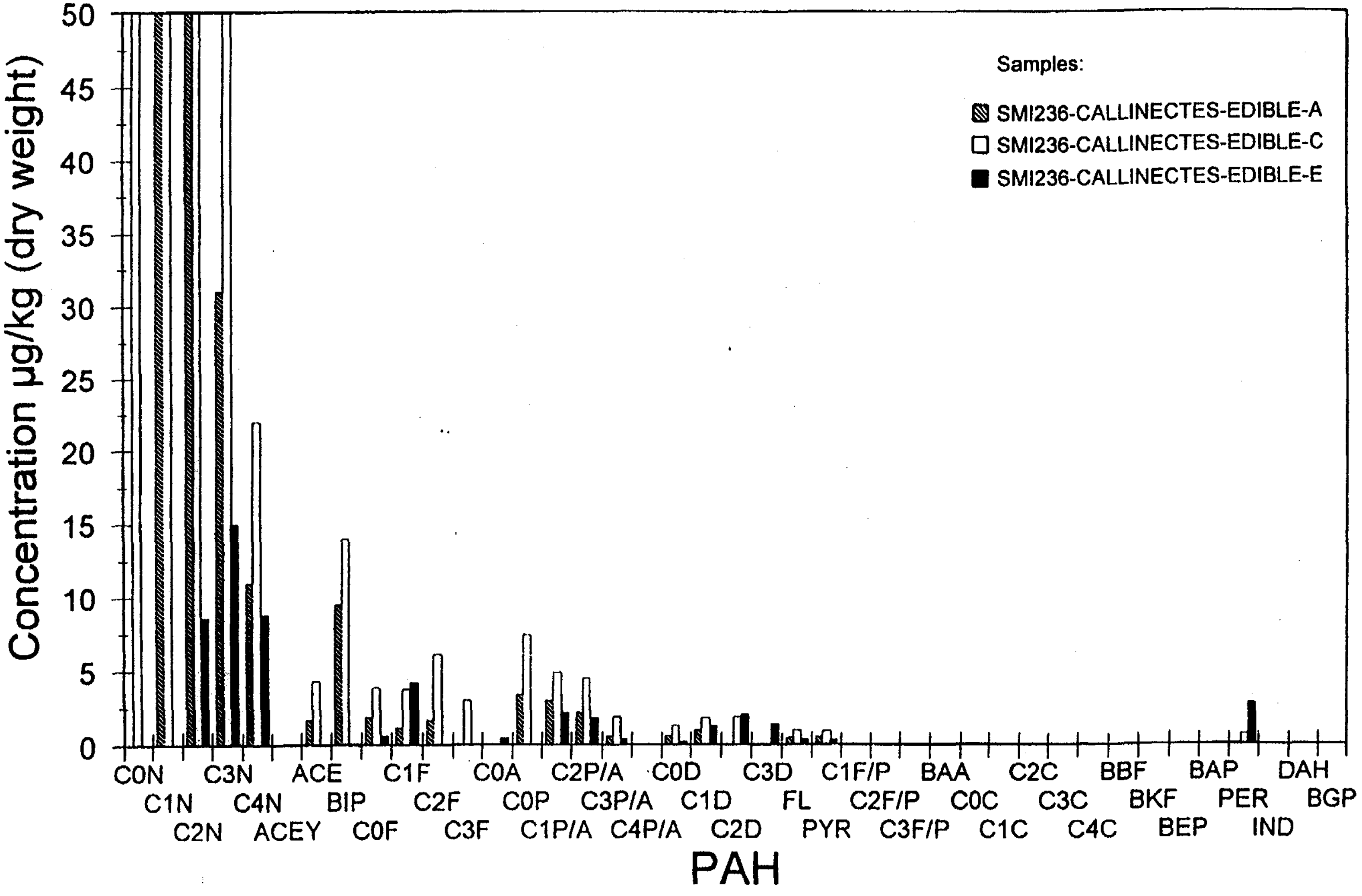


Figure 8.43. PAH distribution in Blue Crab Tissue Replicates A, C, and E at SMI 236A.

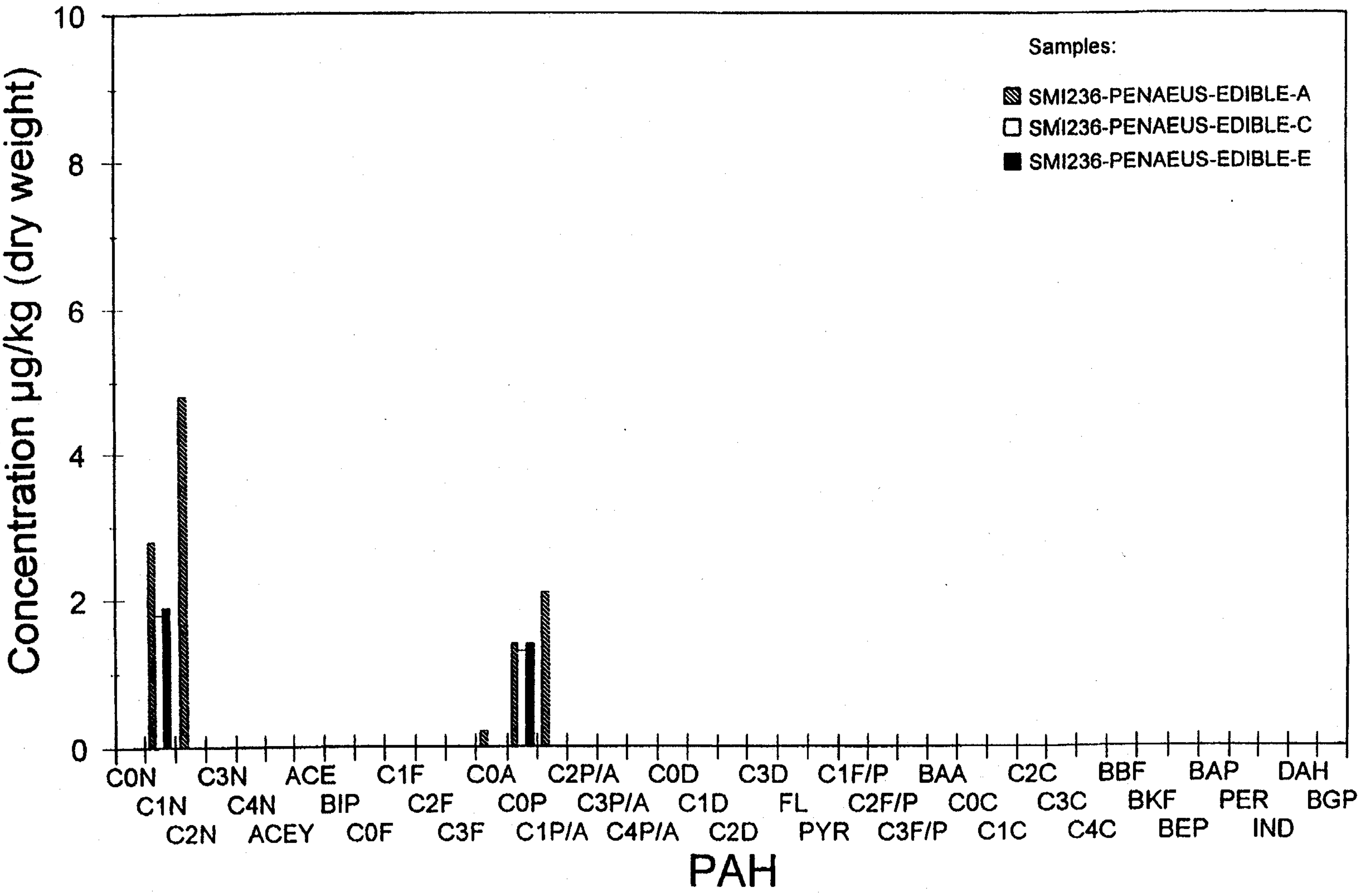


Figure 8.44. PAH distribution in Shrimp Tissue Replicates A, C, and E at SMI 236A.

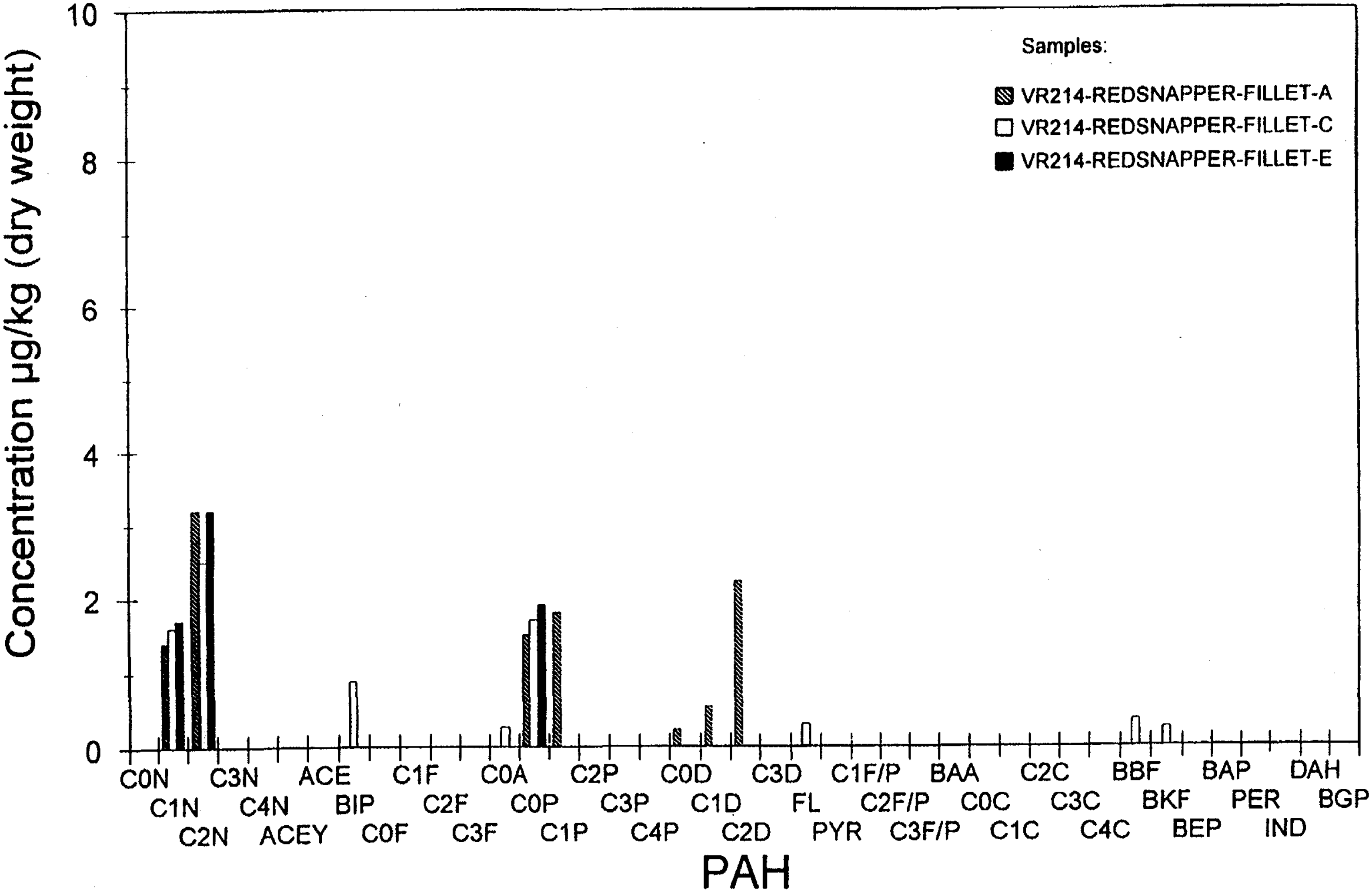


Figure 8.45. PAH distribution in Red Snapper Fillet Tissue Replicates A, C, and E at VR 214A.

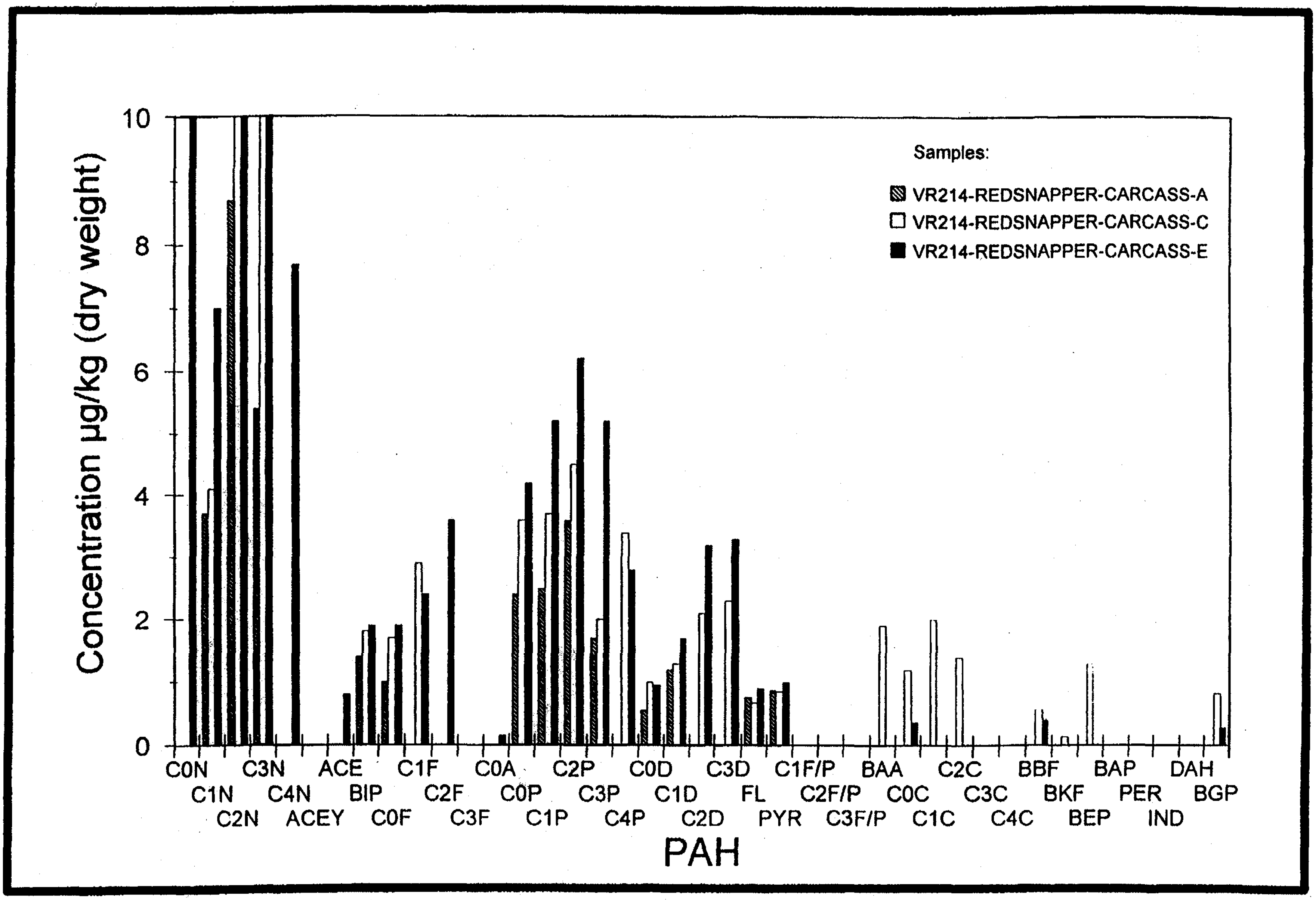


Figure 8.46. PAH distribution in Red Snapper Carcass Replicates A, C, and E at VR 214A.

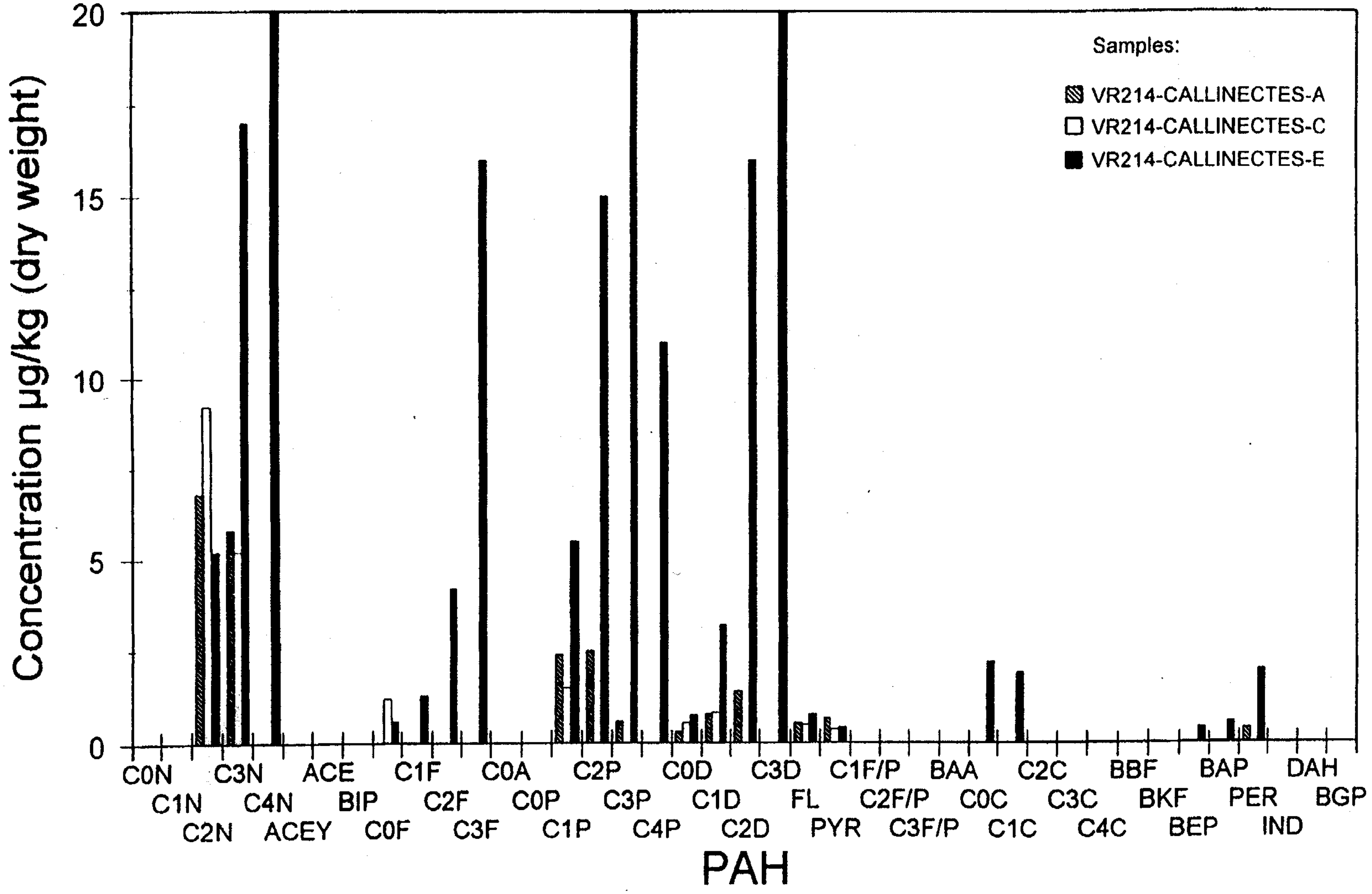


Figure 8. 47. PAH distribution in Blue Crab Tissue Replicates A, C, and E at VR 214A.

Only one sample of the jewelbox was analyzed and found to contain seemingly uncharacteristically high amount of PAHs, nearly 12,000 μg/kg total PAHs. The PAH signature (**Figure 8.48**) was characteristic of a weathered crude or heavy end distillate, not diesel, because of the presence of the chrysenes. Although the jewelbox contained petrogenic PAHs, the jewelbox PAH signature was not similar to the produced water distribution which had high naphthalenes concentrations (>95% of total PAHs) relative to the 3-ring alkyl PAHs. As shown later, the jewelbox consistently contained the highest PAH concentrations of any species at any platform.

The PAHs in the fish and crustacea from VR 214A were considerably different than the PAHs in organisms from SMI 236A. The target organisms at VR 214A were essentially clean of PAHs. Only an occasional replicate contained trace levels of petrogenic PAHs. The low-level petroleum PAHs found in the carcass samples were probably on the skin of the fish and originated from contamination during sample collection or processing.

8.3.4.3 South Marsh Island 130B

The clear water, sandy substrate environment at SMI 130B contained faunal assemblages representative of the "Offshore" assemblages (Gallaway and Lewbel, 1982). Commercially important fish--red snapper, gray triggerfish, seabass, longspine porgy, and pinfish--and epifaunal invertebrates--rock shrimp and swimming crab were analyzed for PAHs. Only one sample of jewelbox was also analyzed. Results of the PAH analyses are summarized in **Table 8.8**.

PAH concentrations of the fillets (muscle) of nearly all the fish and invertebrates were very low, ranging from ND to 37 μg/kg total PAHs. Four out of five replicates of each of the fish species and rock shrimp contained no more than 10 μg/kg total PAHs. A representative PAH distribution is presented in **Figure 8.49**. The occasional replicate with elevated PAH concentrations still contained less than 40 μg/kg total PAHs.

Carcass samples, however, contained higher concentrations of PAHs than fillets with compositions that usually resembled those of petroleum. The carcass samples of the red snapper and gray triggerfish illustrated two different types of PAH compositions (**Figures 8.50** and **8.51**). The red snapper PAH distribution had higher naphthalenes relative to the other 3-ring PAHs and negligible amounts of the 4- through 6-ring PAHs. This distribution was similar to the distribution found in produced water. The gray triggerfish, on the otherhand, had equal amounts of the 2- and 3-ring PAHs, and comparable amounts of the 4- through 6-ring PAHs indicating not only a petroleum origin to the PAHs but also a pyrogenic origin to the PAHs. The significance of these two different PAH distributions in the carcasses of these two species is not known, but may be due to a combination of the handling of the samples and the activities (e.g., eating behavior) of the species.

Besides the jewelbox in which only one composite sample was analyzed, the swimming crab was the only species containing a consistent petroleum signature in its edible tissue (**Figure 8.52**). The mean total PAH concentration was low at 54 μg/kg, and the range for the replicates was consistent from 24 to 87 μg/kg. The petrogenic signature in the tissue was representative of the produced water and bottom sediment. The occasional presence of pyrogenic PAHs in the tissue replicate indicated that the source of the PAHs is from the bottom sediment.

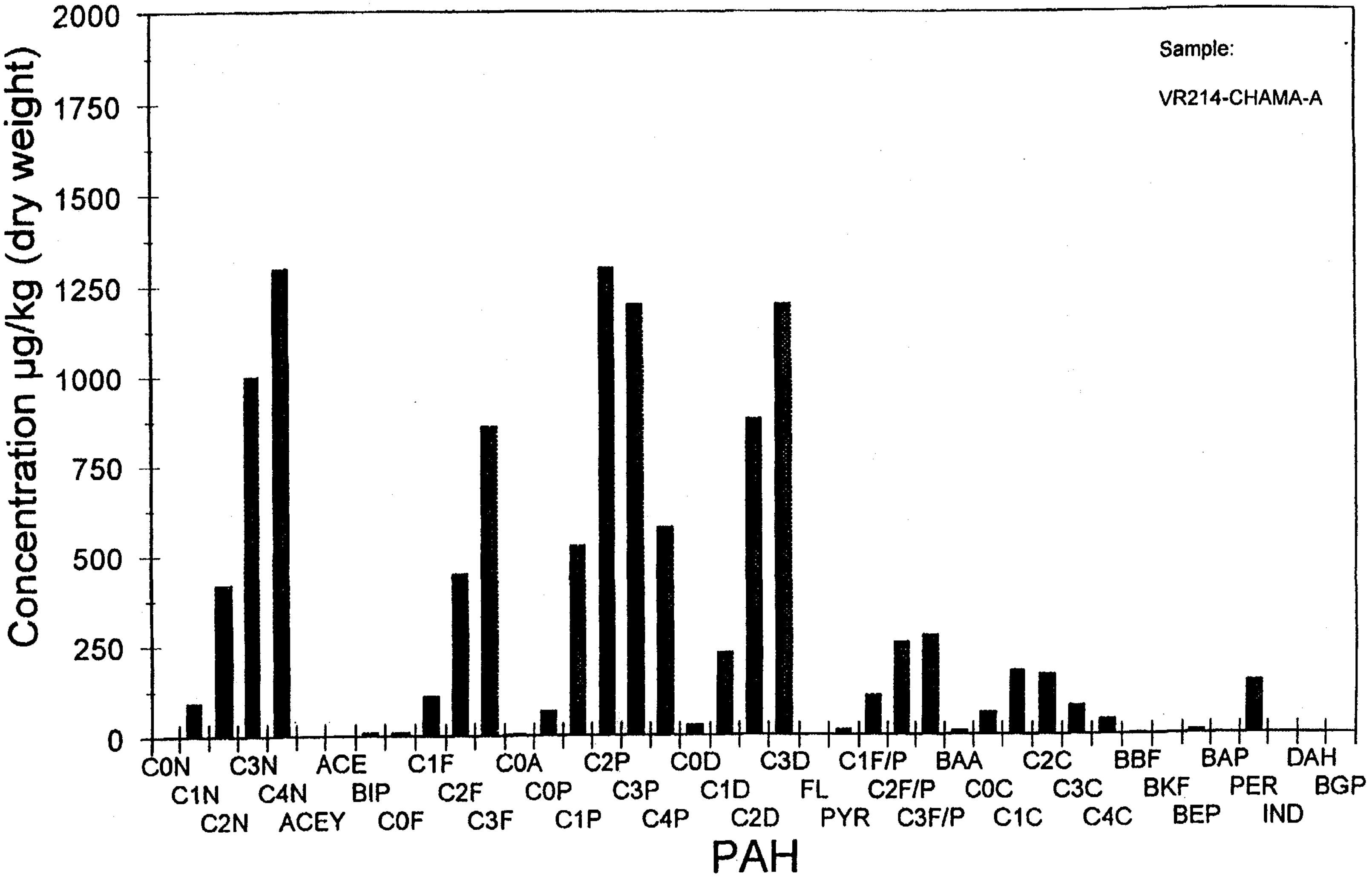


Figure 8.48. PAH distribution in Jewelbox Tissue Replicates A, C, and E at VR 214A.

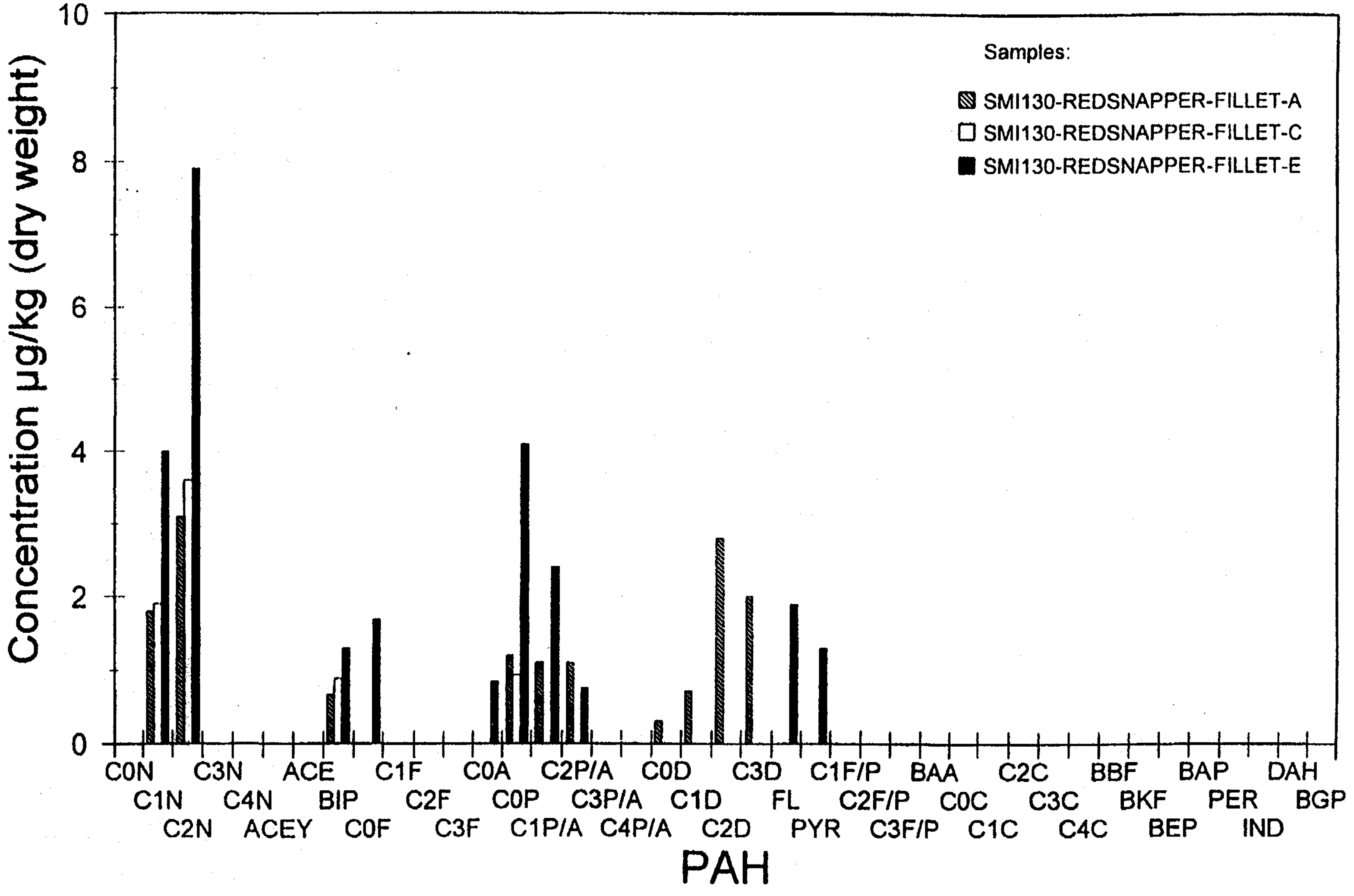


Figure 8.49. PAH distribution in Red Snapper Fillet Tissue Replicates A, C, and E at SMI 130B.

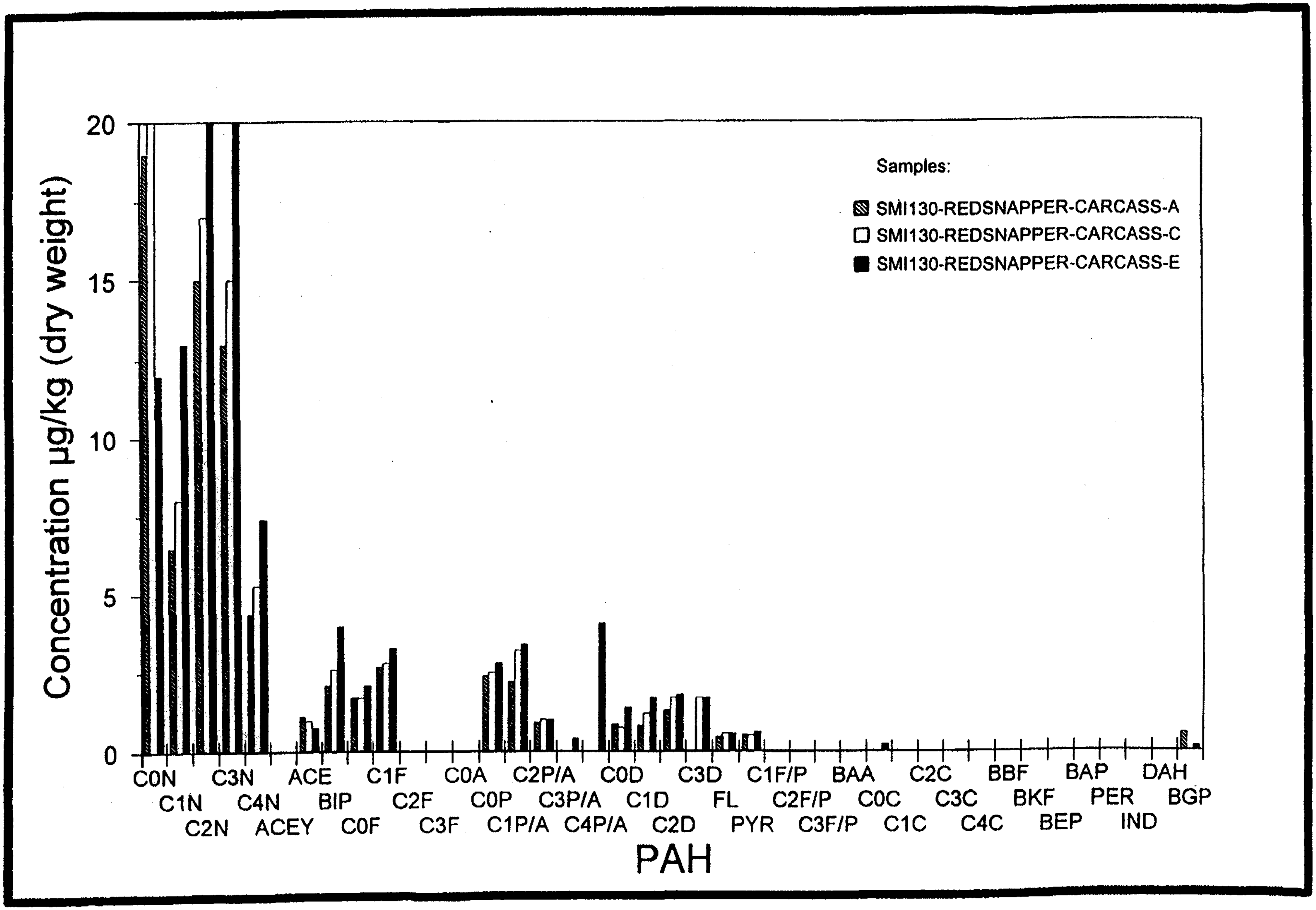


Figure 8.50. PAH distribution in Red Snapper Carcass Tissue Replicates A, C, and E at SMI 130B.

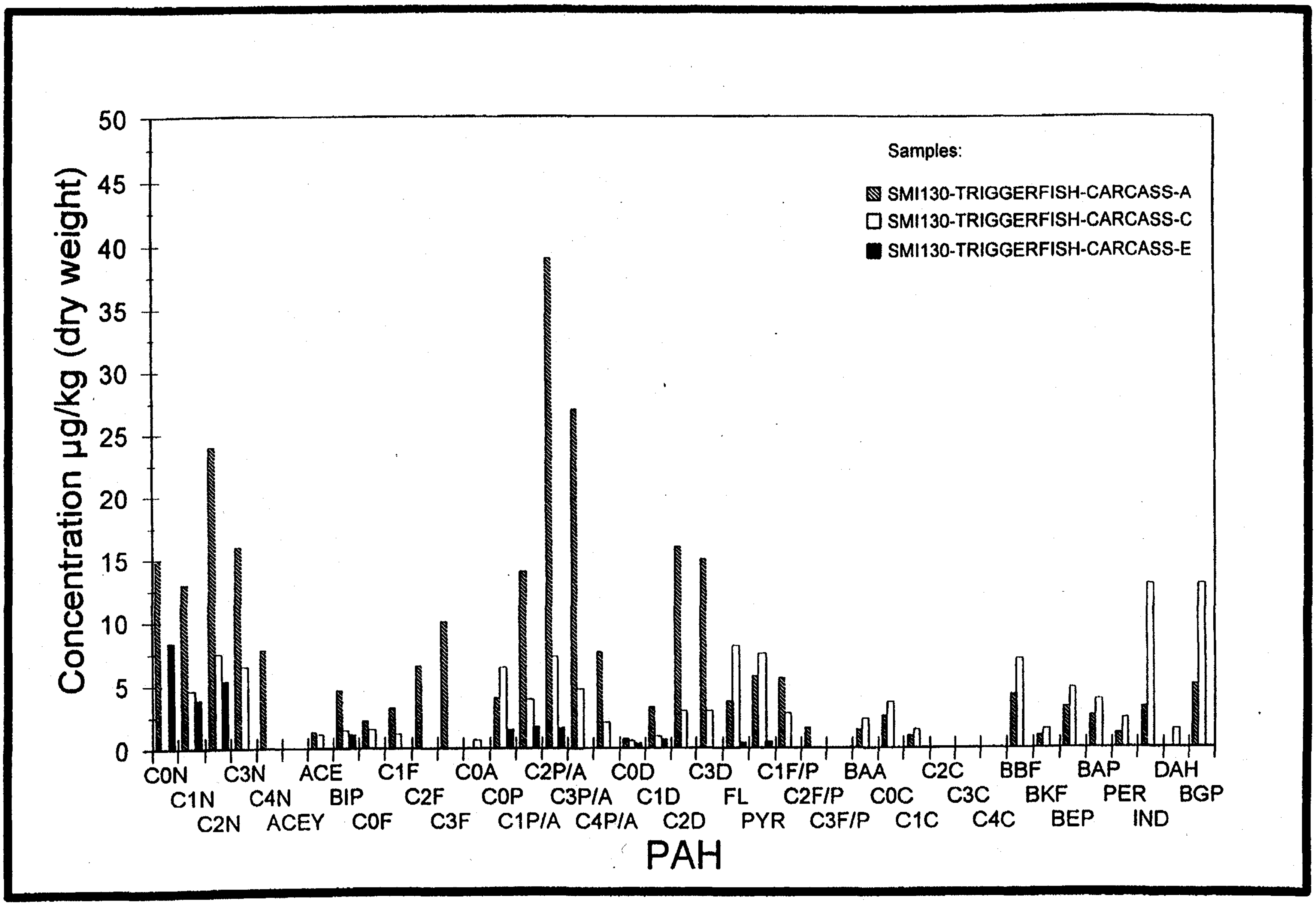


Figure 8.51. PAH distribution in Gray Triggerfish Carcass Tissue Replicates A, C, and E at SMI 130B.

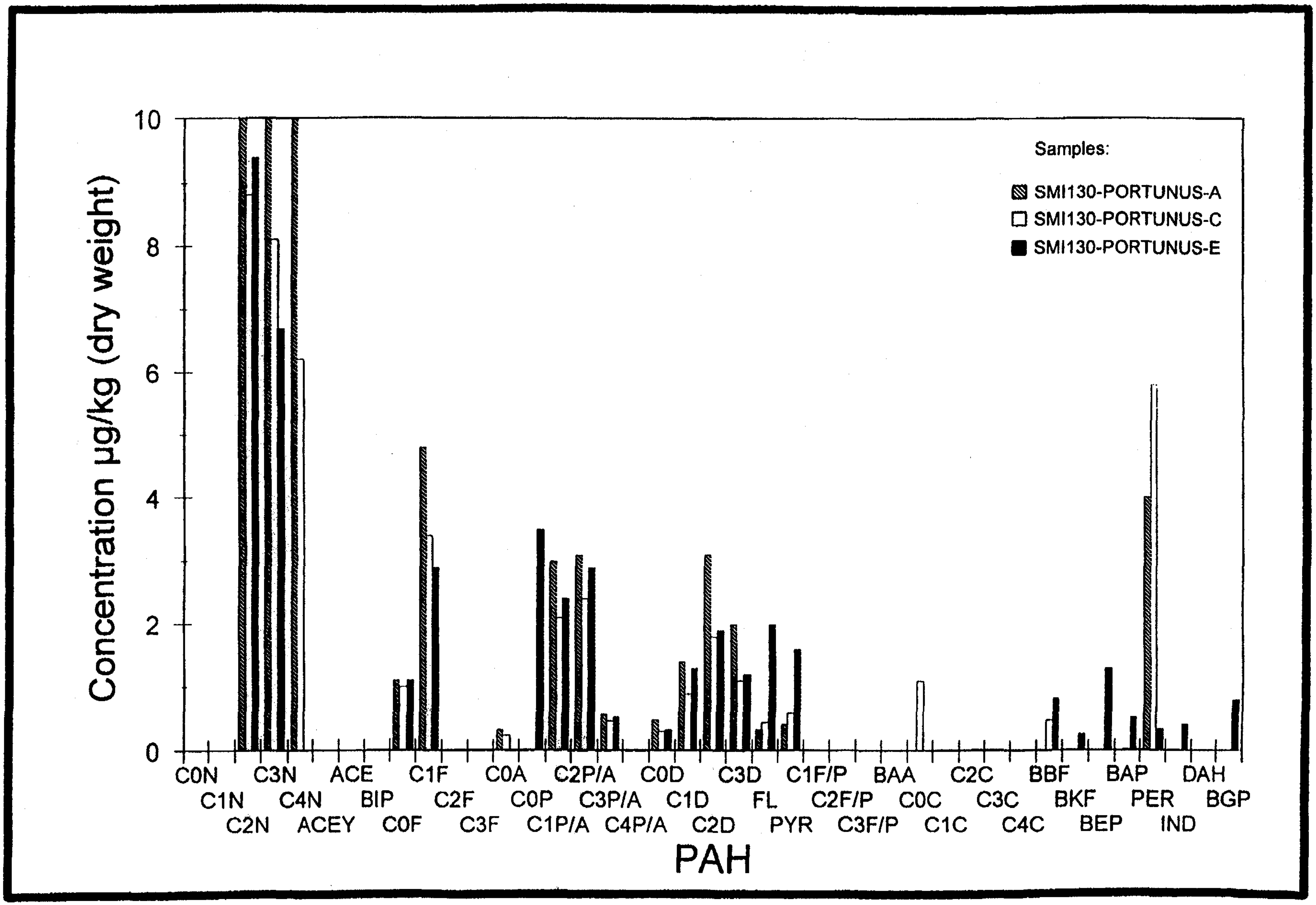


Figure 8.52. PAH distribution in Swimming Crab Tissue Replicates A, C, and E at SMI 130B.

The noncommercial jewelbox (single sample) contained about 1,700 μg/kg total PAHs, two to three orders of magnitude higher than any of the other organisms. The PAH signature included the full suite of petrogenic PAHs and almost equal amounts of pyrogenic PAHs (**Figure 8.53**). This same high concentration of PAHs was observed at VR 214A.

The PAH composition and concentrations in these organisms at SMI 130B were very similar to those at VR 214A. The fillets are essentially clean of PAHs, and the crabs (edible tissue) accumulate very low levels of petrogenic type PAHs. The distinct PAH distribution of the carcass of the gray triggerfish was not observed previously. The jewelbox single replicate again contained the highest concentration of PAHs in the platform environment.

8.3.4.4 High Island A-595CF

The HI A-595CF platform is located in the "Bluewater" depth zone (Gallaway and Lewbel, 1982), nine miles west of the West Flower Garden Bank. The biofouling assemblage associated with this "Bluewater" zone at this platform is characterized by high coverage and low biomass. The invertebrate species found at this platform are not commercially important. There are, however, commercial important species of fish. Five fish species, vermilion snapper, longspine porgy, flatfish (Bothidae), wenchman, and longtail bass, and one invertebrate species, jewelbox, were analyzed for PAHs at this platform. Total PAH concentrations for the target species are summarized in **Table 8.8**.

Similar to the other deep water platform, SMI 130B, 4 out of the 5 replicate fillet samples of the fish species contained very few detectable PAHs, and those PAHs that were detected in the tissues were at very low concentrations (<10 μg/kg). Except for one replicate of the wenchman, total PAH concentrations of fillets and whole tissue ranged from 2 to 23 μg/kg for all fish species. The longtail bass (**Figure 8.54**) represents the higher PAH concentration in the fish species. As observed at VRN 214A and SMI 130B, the longspine porgies were especially devoid of PAHs (**Figure 8.55**).

The carcass of the vermilion snapper had elevated concentrations of PAHs in the range of 60 to 200 μg/kg total PAHs (**Figure 8.56**), similar to the red snapper fish carcass at SMI 130B. In these carcass samples, the naphthalenes comprised 90% of the total PAHs. The 3-ring PAHs were not present as consistently in these samples as in other carcass samples. The presence of the full suite of naphthalenes, however, at elevated concentrations in most of the replicates indicated either a possible impact on the fish from the produced water discharge or contamination of the skin during collection handling.

The jewelbox (single composite) again had the highest concentration of PAHs than all the other species. The total PAH concentration was 310 μg/kg. The PAH distribution (**Figure 8.57**) showed a distinct weathered petroleum signature with equal amounts of the naphthalenes and 3-ring PAHs. This jewelbox sample did not contain the pyrogenic PAHs observed at the SMI 130B platform, but the PAH signature looked similar to the jewelbox sample at VR 214A which also did not contain pyrogenic PAHs. At all platform sites in which jewelbox species were collected, the concentrations of PAHs were highest of all species. In each case, the jewelbox PAH signature did not have the relatively high naphthalenes concentrations (>95% of total PAHs) characteristic of each produced water analyzed. The source of the PAHs in jewelbox, however, could be the produced water and/or produced sand because of the presence of petrogenic PAHs.

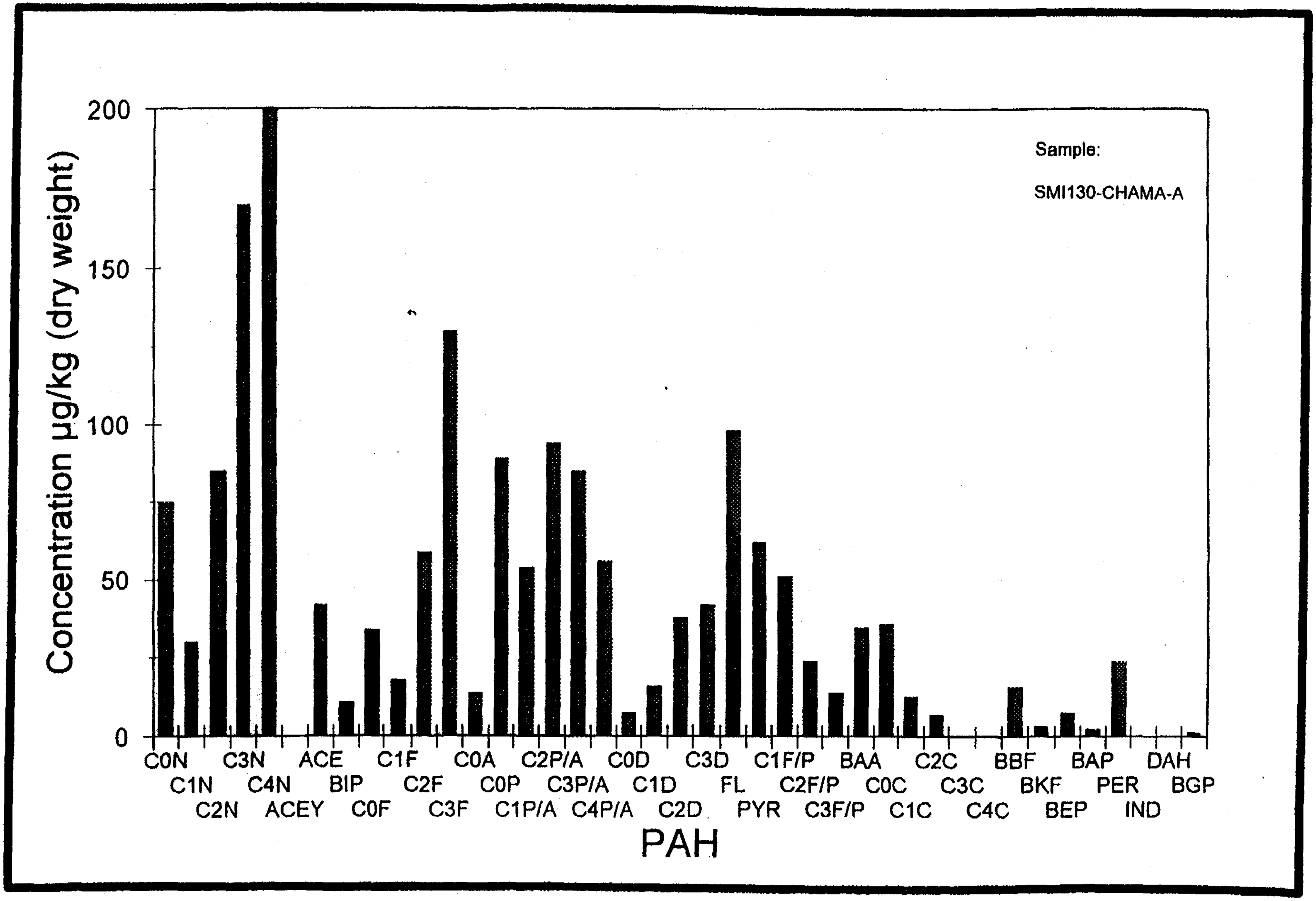


Figure 8.53. PAH distribution in Jewelbox Tissue Replicates A, C, and E at SMI 130B.

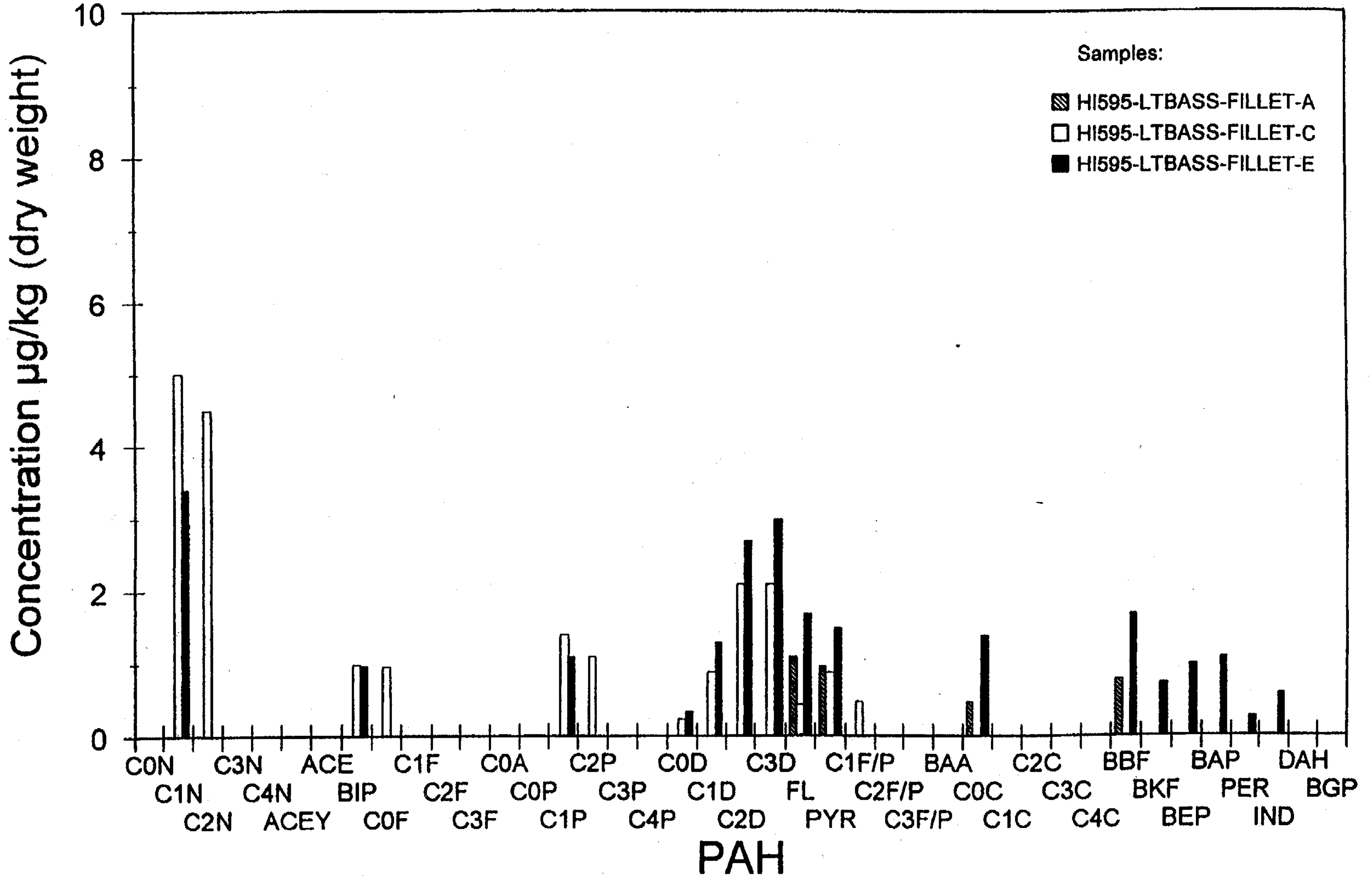


Figure 8.54. PAH distribution in Longtail Bass Tissue Replicates A, C, and E at HI A-595CF.

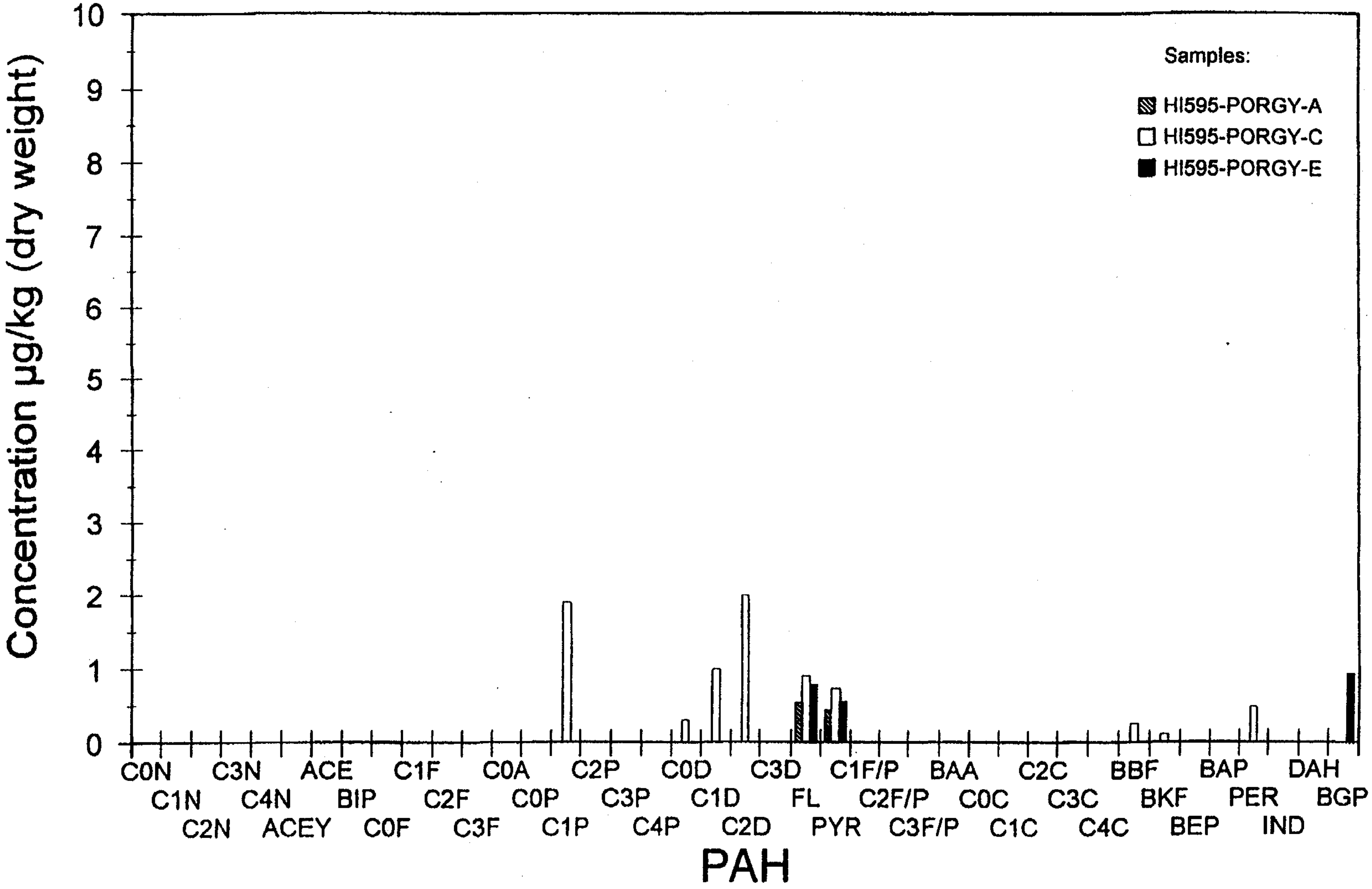


Figure 8.55. PAH distribution in Longspine Porgy Tissue Replicates A, C, and E at HI A-595CF.

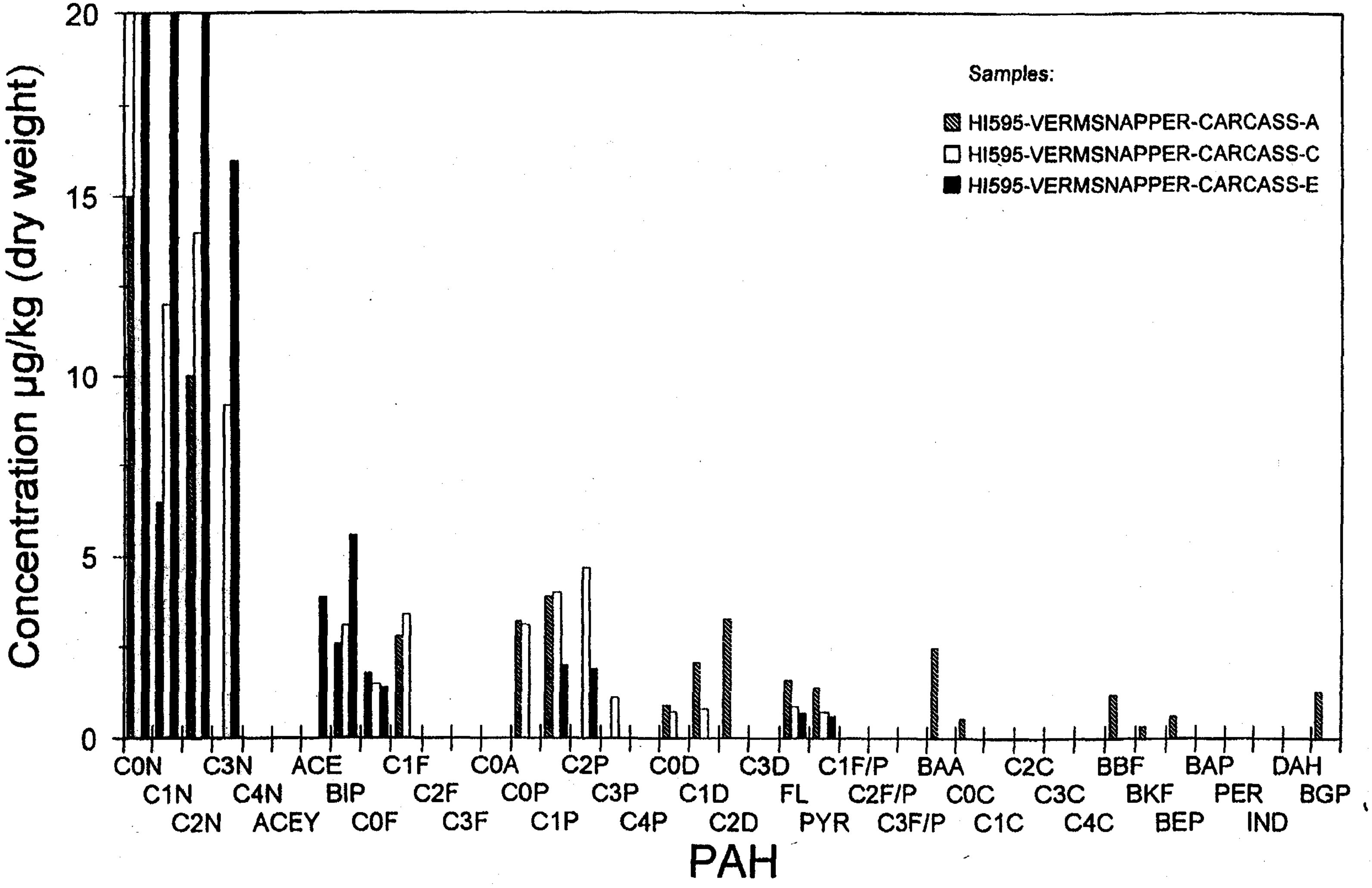


Figure 8.56. PAH distribution in Vermilion Snapper Tissue Replicates A, C, and E at HI A-595CF.

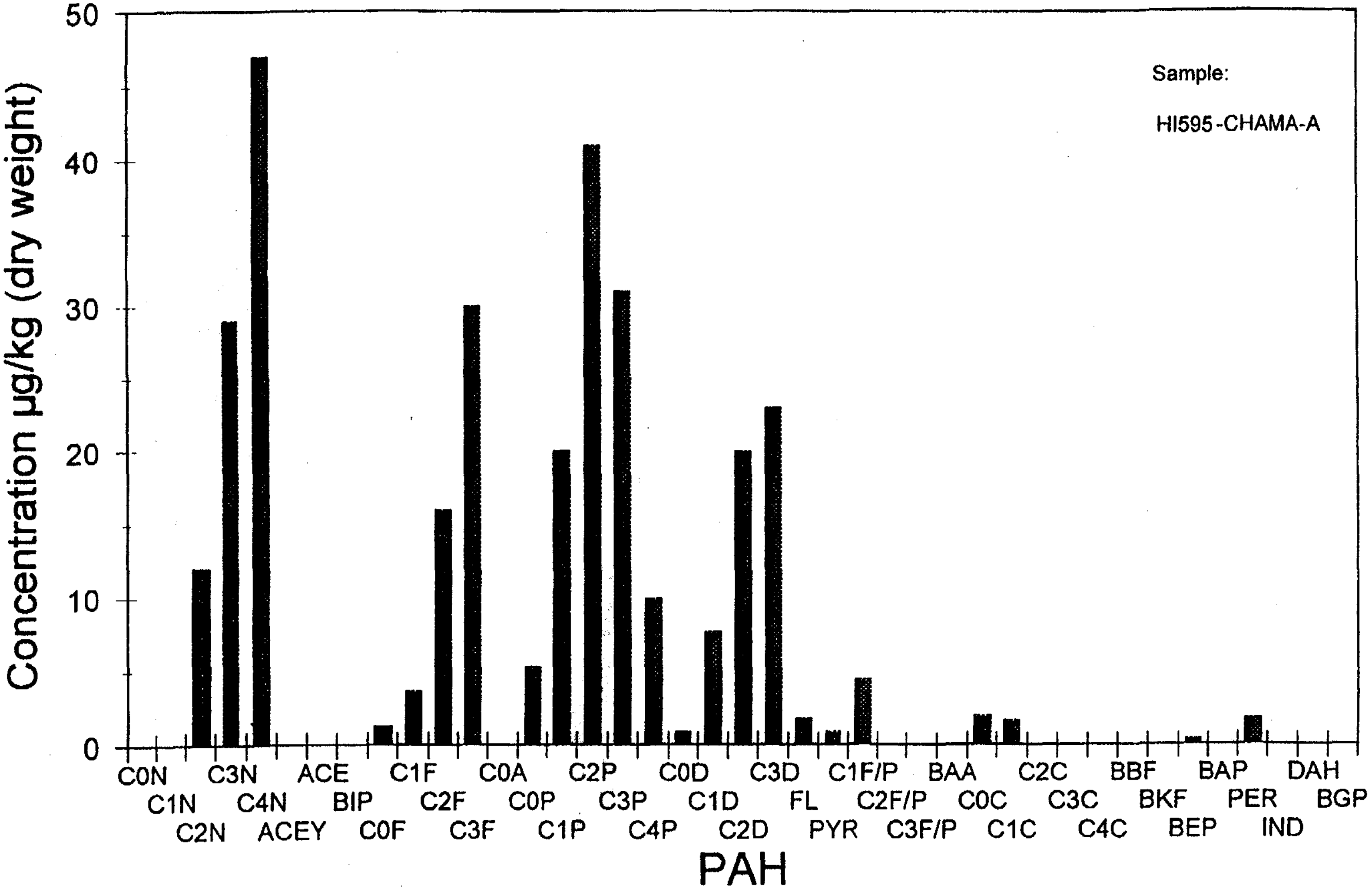


Figure 8.57. PAH distribution in Jewelbox Tissue Replicates A, C, and E at HI A-595CF.

8.4 Summary

As part of the environmental study of offshore oil and gas operational discharges to the Gulf of Mexico, representative discharge and environmental samples were collected at discharging platforms and reference sites and analyzed for hydrocarbon constituents typical of oil and gas discharges. The objective of this component of the study was to determine the composition, concentration, and potential sources of hydrocarbons in representative environmental samples near offshore oil and gas production facilities in the Gulf of Mexico. The hydrocarbons included THCs, SHCs, VAHs, and PAHs that include the alkyl homologues, which were analyzed in produced water, produced sands, discharge plume/receiving water, ambient seawater, sediment, and biota. The sites selected were four discharging platform sites, SMI 236A, VR 214A, SMI 130B, and HI A-595CF, and four open water sites in the lease blocks, SMI 186/195, WC 448, GA 205, and GA 90 that represented a cross-section of offshore environments in the Gulf from 6 to 100 m water depths.

Produced waters were analyzed for VAHs, SHCs, and PAHs. Total VAH concentrations ranged from 1,800 μg/L at HI A-595CF to 5,200 μg/L at SMI 236A with compositions typical of other Gulf discharges (Neff, 1996). The SHC distribution of n-alkanes from C_{10} to C_{32} and isoprenoids pristane and phytane reflected the solubilities of the compounds of decreasing concentration with increasing carbon number. THC (and total PAH) concentrations were four times higher in the SMI 130B produced water, 16,000 μg/L THCs (60 μg/L total PAHs) than the other produced waters. For the three produced water sites except SMI 130B, over 95% of the PAHs were naphthalenes with decreasing alkyl concentrations as alkyl carbon number increased. At the SMI 130B site, the PAH distribution indicated that whole oil (droplets) was present in the samples, relatively higher amounts of the 3-ring phenanthrenes and dibenzothiophenes and the 4-ring chrysenes were present.

Produced sands were collected only from SMI 236A and SMI 130B. PAH distributions showed the characteristic petrogenic (petroleum) signatures of the corresponding produced crude oil which are represented in the PAH diagnostic ratios, C_2-phenanthrenes and C_2-dibenzothiophenes (C2P/C2D) and C_3-phenanthrenes and C_3-dibenzothiophenes (C3P/C3D) shown in **Table 8.7**. The nearly identical diagnostic ratios of the produced water and produce sands suggest that the produced water has crude oil droplets. These sands were considered contributing sources of petrogenic hydrocarbons in the nearfield sediments at the discharge sites.

The sediments in the study area were represented by one of five characteristic hydrocarbon distributions (**Figure 8.41**).

A: Petrogenic signature - oil and gas operational discharges (produced water [PW] and produced sands [PS]);
B: Dominance of a petrogenic signature - discharge [D] and nearfield [N] sediment samples only;
C: Dominance of a pyrogenic signature - mixture of nearfield [N], farfield [F], discharge [D], and reference [R] sediment samples;
D: Mixture of petrogenic and pyrogenic signatures - discharge [D] and nearfield [N] sediment samples only; and
E: No signature, but low-level combination of petrogenic and pyrogenic PAHs - farfield [F or V], and reference [R] sediment samples only.

The PAH and SHC distributions that defines Group E could be considered "background" hydrocarbons of shelf sediment in the central Gulf of Mexico. The PAH signature of this group is a diluted version of a PAH distribution of chronic industrial polluted sediments (Costa *et al.*, 1996). Because of the spatial extent of this type PAH distribution as defined by the group, the origin of these PAHs is probably the Mississippi River discharge which has considerable regional influence in the Gulf. For the nearfield areas around production platforms, any petrogenic source to the sediments would be superimposed on this background distribution. Differences in the hydrocarbon signatures of production operation discharges near the Mississippi River (Group A) and the signatures of sediments around production facilities (Group B and D) will be influenced, depending upon the amount of petrogenic input, by the contribution from the pyrogenic (Group C) or "background" (Group E) signatures.

Evidence of petrogenic PAHs in edible tissue samples, defined by the combined presence of the alkyl homologues of the phenanthrenes and dibenzothiophenes, was limited principally to the molluscs and the crabs. Shrimp and most of the fish did not contain petrogenic PAHs (<2 ng/g dry weight).

Petrogenic PAHs were most apparent in biota at the shallow (6 m) platform, SMI 236A. Alkyl naphthalenes (10-50 μg/kg) and trace levels of alkyl phenanthrenes and dibenzothiophenes (<5 μg/kg) were found in catfish and blue crab. The PAHs in the fish and crustacea from VR 214A, SMI 130B, and HI A-595CF were considerably different than the PAHs in organisms from SMI 236A. The target organisms were essentially devoid of PAHs. Crabs and an occasional fish replicate contained trace levels of petrogenic PAHs. Petrogenic PAHs were often present on fish carcasses, but not in fish fillets. The presence of PAHs in fish carcass (includes skin) at total PAH concentrations ranging from 40 to 200 ng/g dry weight, mostly naphthalenes, may be the result of contamination in the field.

The jewelbox, which has limited ability to metabolize PAHs compared to fish, contained two to three orders of magnitude higher concentrations of PAHs than the other species of all sites. For this study only one composite sample was analyzed from each site except SMI 236A. At VR 214A, the PAH signature was characteristic of a weathered crude oil, not diesel, because of the presence of chrysenes. Total PAH concentration was 12,000 μg/kg. At SMI 130B, the full suite of petrogenic PAHs was accompanied by equal amounts of pyrogenic PAHs at 1,700 μg/kg total PAHs. The PAHs in the jewelbox at HI A-595CF were similar to VR 214A, not SMI 130B, but at a considerably lower concentrations (310 μg/kg total PAHs).

Although the jewelbox did not have the same PAH distribution of the produced water of predominately naphthalenes (>95% of total PAHs), the strong petrogenic signatures of the phenanthrenes and dibenzothiophenes suggest a strong and consistent petroleum input in the areas of the platforms. Diagnostic PAH ratios of the jewelbox (**Table 8.7**) were not generally similar to those of the corresponding discharge and sediment samples, except for HI A-595CF. Jewelbox PAH ratios at the HI site were similar to those of the sediment. The extent to which jewelbox PAHs should correlate to potential sources is dependent on the biological processes of bioaccumulation and depreation influencing the PAH distribution in the organism. The effect of these processes in this organism presently is not well known.

8.5 REFERENCES

Atlas, R.M. 1981. Microbial degradation of petroleum hydrocarbons; an environmental perspective. Microbio. Rev. 45:180-209.

Blumer, M., M. Ehrhardt, and J.H. Jones. 1973. The environmental fate of stranded crude oil. Deep-Sea Res. 20:239-259.

Blumer, M., R.R.L. Guillard, and T. Chase. 1971. Hydrocarbons of marine phytoplankton. Mar. Biol. 8:183-189.

Blumer, M. and J. Sass. 1972. Oil pollution: persistence and degradation of spilled fuel oil. Science 176:1,120-1,122.

Brooks, J.M., M.C. Kennicutt, T.L. Wade, A.D. Hart, G.J. Denoux, and T.J. McDonald. 1990. Hydrocarbon distributions around a shallow water multiwell platform. Environ. Sci. Technol. 24:1,079-1,085.

Costa, H.J. and T.C. Sauer. 1994. Distributions of chemical contaminants and acute toxicity in Delaware Estuary sediments. Final Report to U.S. EPA and Delaware River Basin Commission, Trenton, NJ.

Gallaway, B.J. and G.S. Lewbel. 1982. The ecology of petroleum platforms in the northwest Gulf of Mexico: a community profile. U.S. Fish and Wildlife Services, Office of Biological Services, Washington, D.C. FWS/OBS-82/27. Bureau of Land Management, Gulf of Mexico OCS Regional Office, Open-File Report 82-03.

IOC/UNEP/IAEA. 1991. Determination of Petroleum Hydrocarbons in Sediment. Manual and Guides. International Laboratory of Marine Radioactivity. IAEA, Monaco. No. 20.

Kennicutt, M.C., II. 1995. Gulf of Mexico Offshore Operations Monitoring Experiment, Final Report. Phase 1: Sublethal Responses to Contaminant Exposure. OCS Study MMS 95-0045. U.S. Dept. of the Interior, Minerals Management Service, Gulf of Mexico Region, New Orleans, LA.

Kingston, P.F. 1992. The impact of offshore oil production installations on the benthos of the North Sea. ICES J. Mar. Sci. 49:127-143.

LaFlamme, R.E. and R.A. Hites. 1978. The global distribution of polycyclic aromatic hydrocarbons in recent sediments. Geochimica et Cosmochimica Acta 42:289-303.

MacDonald, I.R., S.E. Best, R. Venkataramaiah, S. Sassen, N.L. Guinasso, Jr., J.E. Reilly, Jr., and J. Amos. 1996. Remote sensing inventory of active oil seeps and chemosynthetic communities in the northern Gulf of Mexico, pp. 27-37. In: D. Schumacher and M.S. Abrams (eds.), Hydrocarbon Migration and Its Near-Surface Expression. AAPA Memoir 66. American Association of Petroleum Engineers, Houston, TX.

National Research Council. 1985. Oil in the Sea: Inputs, Fates and Effects. National Academy Press, Washington, DC. 601 pp.

Neff, J.M. 1979. Polycyclic Aromatic Hydrocarbons in the Aquatic Environment. Sources, Fates and Biological Effects. Applied Science Publishers, Barking, Essex, England. 262 pp.

Neff, J.M. and J.W. Anderson, 1981. Response of Marine Animals to Petroleum and Specific Petroleum Hydrocarbons. Applied Sciences Publishers, London. 177 pp.

Neff, J.M. 1987. Biological effects of drilling fluids, drill cuttings and produced waters, pp. 469-538. In: D.F. Boesch and N.N. Rabalais (eds.), Long-Term Environmental Effects of Offshore Oil and Gas Development. Elsevier Applied Science Publishers, London.

Neff, J.M. 1990. Composition and fate of petroleum and spill-treating agents in the marine environment, pp. 1-33. In: J.R. Geraci and D.J. St. Aubin (eds.), Sea Mammals and Oil: Confronting the Risks. Acacemic Press, San Diego.

Neff, J.M. 1996. Metals and Organic Chemicals Associated with Oil a Gas Well Producted Water: Bioaccumulation, Fates, and Effects in the Marine Environment. Report to the U.S. Gulf of Mexico, Offshore Operators Committee, New Orleans, LA.

Neff, J.M. and W.A. Burns. 1996. Estimation of polycyclic aromatic hydrocarbon concentrations in the water column based on tissue residues in mussels and salmon: an equilibrium partitioning approach. Environ. Toxicol. Chem. 15:2,240-2,253.

Neff, J.M., T.C. Sauer, Jr., and N. Maciolek. 1992. Composition, fate and effects of produced water discharges to nearshore marine waters, pp. 371-385. In: J.P. Ray and F.R. Engelhardt (eds.), Produced Water: Technological/Environmental Issues and Solutions. Plenum Press, New York.

Page, D.S., P.D. Boehm, G.S. Douglas, and A.E. Bence. 1995b. Identification of Hydrocarbon Sources in the Benthic Sediments of Prince William Sound and the Gulf of Alaska Following the *Exxon Valdez* Oil Spill, pp. 41-83. In: P.G. Wells, J.N. Butler, and J.S. Hughes (eds.), *Exxon Valdez* Oil Spill: Fate and Effects in Alaskan Waters. ASTM STP 1219, American Society for Testing and Materials, Philadelphia, PA.

Requejo, A.G. and P.D. Boehm. 1985. Characterization of hydrocarbons in a subsurface oil-rich layer in the Sargasso Sea. Mar. Environ. Res. 17:45-64.

Sauer, T.C. Jr. 1981. Volatile organic compounds in open ocean and coastal surface waters. Org. Geochem. 3:91-101.

Sauer, T.C. and P.D. Boehm. 1991. The Use of Defensible Analytical Chemical Measurements for Oil Spill Natural Resource Damage Assessment, pp. 363-369. In: Proceedings of the 1991 International Oil Spill Conference, March 4-7, San Diego, CA. USCG, API, and EPA.

Sauer, T.C. and P.D Boehm. 1995. Hydrocarbon Chemistry for Oil Spill Assessments. Technical Report Series 95-032. Marine Spill Response Corporation, Washington, DC.

Sauer, T.C. and A.D. Uhler. 1994. Pollutant source identification and allocation: advances in hydrocarbon fingerprinting. Remediation 4(4):25-50.

Sauer, T.C., J.S. Brown, P.D. Boehm, D.V. Aurand, J. Michel, and M.O. Hayes. 1993. Hydrocarbon source identification and weathering characterization of intertidal and subtidal sediments along the Saudi Arabian coast impacted by the Gulf War oil spill. Mar. Pollut. Bull. 27:117-134.

Stegeman, J.J. 1981. Polynuclear aromatic hydrocarbons and their metabolism in the marine environment, pp. 1-60. In: HV Gelboin and P.O.P. T'so (eds.), Polycyclic Aromatic Hydrocarbons and Cancer. Vol. 3. Academic Press, New York.

Terrens, G.W. and R.D. Tait. 1996. Monitoring ocean concentrations of aromatic hydrocarbons from produced formation water discharges to Bass Strait, Australia, pp. 739-747. SPE 36033. Proc. International Conference on Health, Safety & Environment, New Orleans, Society of Petroleum Engineers, Richardson, TX.

Venkatesan, M.I. 1988. Occurrence and possible sources of perylene in marine sediments - a review. Mar. Chem. 25:1-27.

Wakeham, S.G., C. Schaffner, and W. Giger. 1980. Polycyclic aromatic hydrocarbons in recent lake sediments-I. Compounds having anthropogenic origins. Geochimica et Cosmochimica Acta 44:403-413.

Youngblood, W.W. and M. Blumer. 1975. Polycyclic aromatic hydrocarbons in the environment. Homologous series in soils and recent marine sediments. Geochimica et Cosmochimica Acta 39:1303-1314.

8.6 ACKNOWLEDGMENTS

The author would like to thank Mr. John Brown and Ms. Melissa Rigatti of Arthur D. Little, Inc. Cambridge, Massachusetts for their efforts in producing these hydrocarbon data for this study.

CHAPTER 9 - AN ENVIRONMENTAL RISK ASSESSMENT FOR METALS AND AROMATIC HYDROCARBONS IN PRODUCED WATER DISCHARGES TO OFFSHORE WATERS OF THE NORTHWESTERN GULF OF MEXICO

Jerry M. Neff
Battelle Ocean Sciences
Duxbury, Massachusetts

9.1 INTRODUCTION

Produced water represents the largest volume waste stream in the entire exploration and production process on most offshore platforms (Stephenson, 1991). Produced water usually is fossil water that has been trapped with oil and gas in geologic formations for millions of years (Collins, 1975). It is pumped to the surface with the oil and gas and must be separated from the fossil fuels before they can be processed further.

The amount of treated produced water discharged from a single platform usually is less than 1.5 million L/day (≈ 400,000 bbl/day), whereas discharges from large treatment facilities that process produced water from several platforms may be as high as 25 million L/day (Menzie, 1982). The total volume of treated produced water discharged to U.S. waters of the Gulf of Mexico in 1991 was approximately 549 million L/day (Rabalais *et al.*, 1991), approximately 65% of which was generated in and discharged to coastal (state) waters of Louisiana and Texas (Boesch and Rabalais, 1989). These discharges were from more than 3,000 offshore platforms and several on-shore treatment facilities (LeBlanc, 1994). Discharges of produced water generated offshore from shore-based treatment facilities is being phased out in the Gulf of Mexico.

In most oil and gas fields, relatively little water is produced in the initial phases of production, but the total fraction of production accounted for by produced water increases as production continues until, in an old, nearly depleted field, production may be as high as 95% water and 5% fossil fuels (Read, 1978). Some oil or gas wells may produce little or no water at all. However, over the economic life of most producing fields, the volume of produced water may exceed the volume of fossil fuel produced by a factor of ten (Stephenson, 1991). Injection of fresh water or seawater into the fossil fuel-bearing formation (water flooding) to enhance production may increase the yield of produced water. Most of the oil and gas fields in the Gulf of Mexico are mature or declining; produced water production is increasing as fossil fuel production decreases.

Produced water contains a large number of inorganic and organic chemicals that have been dissolved or dispersed from the geologic formations in which the produced water resided for millions of years. Petroleum hydrocarbons usually represent 10% to 65% of the total organic matter in produced water. Much of the remainder of the organic chemicals in produced water is low molecular weight organic acids, such as acetic, propionic, and butyric acids, which are thought to have been derived from hydrous pyrolysis of hydrocarbons in the hydrocarbon-bearing formation (Borgund and Barth, 1994). Low molecular weight organic acids are readily biodegraded and are not considered toxic. Phenols also may be present at relatively high concentrations in some produced waters. Concentrations of total phenols in produced water from platforms discharging to northwestern Gulf of Mexico are in the range of 675 to 4,510 μg/L (Neff, 1996a).

Monocyclic aromatic hydrocarbons, including benzene, toluene, ethylbenzene, and xylenes (BTEX), and more highly alkylated benzenes, are the most abundant hydrocarbons in produced water. Concentrations of BTEX in produced water from platforms discharging to the Gulf of Mexico are in the range of 68 to 38,000 μg/L (Neff, 1996a). Monocyclic aromatic hydrocarbons are moderately toxic to marine organisms, but quite volatile. They evaporate very rapidly from solution in seawater. Therefore, they are unlikely to contribute substantially to any environmental effects of produced water in the marine environment, except possibly in the immediate vicinity of the produced water discharge.

Polycyclic aromatic hydrocarbons (PAHs; also called polynuclear aromatic hydrocarbons) are the organic chemicals of greatest environmental concern in produced water, because of their toxicity and persistence in the marine environment (Neff, 1987). Concentrations of total PAHs in treated produced water discharged to the northwestern Gulf of Mexico are in the range of 80 to 1,860 μg/L (Neff, 1996a). The most abundant PAHs in produced water are the more water-soluble 2- and 3-ring PAHs (naphthalene, fluorene, phenanthrene, and dibenzothiophene) and their alkylated homologues (Neff *et al.*, 1987). High molecular weight PAHs, such as the carcinogen, benzo(a)pyrene, almost never are present at greater than ultratrace (<1 μg/L) concentrations.

Several metals and metalloids are present in produced water at concentrations higher than their concentrations in clean ocean waters. Metal concentrations in produced water from different platforms are highly variable, depending on the age and geology of the formation from which the oil and gas were produced (Collins, 1975). Deck drainage and other waste-water streams may be passed through the oil/water separator on the platform and could contribute to elevated concentrations of some metals in the treated produced water. The metals most frequently present in produced water at concentrations substantially higher (1,000-fold or more) than their concentrations in clean natural seawater include barium, cadmium, chromium, copper, iron, lead, nickel, and zinc (Neff *et al.*, 1987). Several of these metals, when present in seawater in dissolved, ionic forms, are toxic to marine organisms and could contribute to the toxicity of produced water.

The objective of this chapter is to evaluate the environmental risk of metals and aromatic hydrocarbons discharged to open ocean waters in treated oil well produced water. Concentrations of aromatic hydrocarbons and metals in ambient seawater, sediments, and whole tissues of marine animals are compared to published marine criteria or effects concentrations for these media. The evaluation of the radionuclide data collected during this study will be evaluated separately by Brookhaven National Laboratory.

9.2 RESULTS AND DISCUSSION

9.2.1 Characteristics of the Produced Water Discharges

9.2.1.1 Discharge and Reference Site Characteristics

Produced water, produced sand, and environmental samples (ambient seawater, discharge plume/receiving water sediments, and marine animals) were collected during the summer of 1993 from four oil production platforms (Component 1 sites) that discharge treated produced water to the continental shelf off Louisiana and Texas. The platforms are SMI 130B, SMI 236A, VR 214A, and HI A-595CF. Ambient seawater and sediment samples were collected at four sites (Component 2 reference sites) without platforms or produced water discharges. The four Component 2 reference sites are located in oil and gas lease blocks WC 448, SMI 195, GA

A-90, and GA A-204. Produced water samples and marine animals were collected at four additional near surface produced water discharge sites (EI 313A, HI A-323A, HI A-382F, and MI 703A) and marine animals at three reference sites (HI A-389, SMI 229C, and VR 298/305). One of the produced water discharge sites (SMI 236A) is located in shallow coastal waters strongly influenced by discharges from the Atchafalaya/Mississippi River system. Two of the reference sites, GA A-90 and GA A-204, are located farther west than all other sites, on the outer shelf south of Galveston Bay, TX (**Figure 2.3**).

Concentrations of metals and aromatic hydrocarbons in the water column and sediments of the outer continental shelf of the northwestern Gulf of Mexico are profoundly affected by freshwater runoff from the Mississippi River system and, to a lesser extent by runoff from smaller rivers, such as the Trinity River and the Nechez River. This makes it extremely difficult to distinguish between chemical signals coming from offshore produced water discharges and those coming from freshwater discharges from nearby river systems (Carney, 1987). Because discharge and reference sites used in this study are located over a wide area of the northwestern Gulf, it is probable that concentrations of metals and aromatic hydrocarbons in the ambient seawater and sediments vary widely due to the variable and heterogeneous influence of produced water discharges and freshwater runoff from rivers.

Water depth at the four Component 1 production platforms ranges from 6 to 122 m (**Table 9.1**). Water depths at the four Component 2 reference sites range from 36 to 110 m. There is no Component 2 reference site comparable in water depth to the shallowest produced water discharge site (SMI 236A). The extent to which chemicals in produced water are deposited in sediments near discharges is strongly influenced by water depth at the discharge site. Water depth may also affect the rates of vertical and horizontal dilution and dispersion of the produced water plume.

At the time water and biota samples were collected (summer 1993), the average salinity of ambient seawater at the produced water sites and reference sites ranged from 7.6 to 33.7 ‰. There is no reference site ambient seawater salinity comparable to that at produced water discharge site SMI 236A (7.6 ‰). This platform is in shallow water about 10 km south of Atchafalaya Bay, an area strongly influenced by the freshwater outflow of the Mississippi/Atchafalaya River system, particularly during high river flow periods (Dinnel and Wiseman, 1986). Therefore, at this site, concentrations of metals and aromatic hydrocarbons in ambient seawater, sediments, and tissues of marine animals may be influenced more by fluxes from the Mississippi River system than from produced water discharges from the platform. Produced water discharge site VR 214A also is influenced by the Atchafalaya/Mississippi River outflow, as indicated by an ambient salinity slightly lower than that at the other two produced water discharge sites and at the four reference sites. Ambient seawater at the other two produced water discharge sites is less influenced by freshwater intrusion from the Mississippi/Atchafalaya River system, as evidenced by mean ambient seawater salinities of 32.6 and 33.3‰, comparable to seawater salinities at the reference sites and throughout the inner and middle shelf off Louisiana (Temple *et al.*, 1977).

Table 9.1. Some characteristics of the produced water Components 1 and 2 discharge and reference sites in the northwestern Gulf of Mexico.

Platform/ Site	Water Depth (m)	Produced Water Discharge (L/day)	Produced Water Salinity (‰)	Ambient Seawater Salinity (‰)
Component 1 Discharge Sites				
SMI 236A	6	2,353,000	90.5	7.6
VR 214A	39	1,351,000	97.1	26.5
SMI 130B	65	3,600,000	129.0	32.6
HI A-595CF	122	838,000	174.9	33.3
Component 2 Reference Sites				
WC 448	36	no discharge	—	30.4
GA A90	39	no discharge	—	32.8
GA A205	66	no discharge	—	33.7
SMI 186/195	110	no discharge	—	32.3

Because Components 1 and 2 could not be closely matched with respect to water depth, ambient seawater salinity, and proximity to major natural freshwater discharges, particularly those from the Mississippi/Atchafalaya River system, it is difficult to make comparisons of concentrations of chemicals in ambient seawater from reference and produced water discharge sites. Proximity to a produced water discharge is only one of several factors that might influence the concentrations of chemicals in the ambient seawater near the produced water discharge sites. Therefore, statistical comparisons of concentrations of metals and organic contaminants in ambient seawater from reference and produced water discharge sites were not attempted in the environmental risk assessment.

9.2.1.2 Volumes and Salinities of Produced Waters

The four Component 1 platforms produce large-volume discharges, ranging from 838,000 to 3,600,000 L/day (5,270 to 22,500 bbl/day) (**Table 9.1**). The combined discharges from these four platforms (8,142,000 L/day) represent about 1.5% of the total volume of produced water discharged to U.S. Federal outer continental shelf waters of the western Gulf of Mexico (Rabalais *et al.*, 1991).

The produced waters discharged from these platforms are all hypersaline brines with salinities of 90.5 ‰ to 174.9 ‰, 2.75 to 5.3 times the salinity of natural seawater (**Table 9.1**). These salinities are fairly typical for produced water from platforms discharging to coastal and outer continental shelf waters of Louisiana and Texas. Although some Gulf coast produced waters have salinities as low as 10 ‰ or as high as 250 ‰, most have salinities in the range of 50 ‰ to 150 ‰ (Hanor *et al.*, 1986; Louisiana DEQ, 1990). Because the produced waters examined in this study have salinities substantially higher than the ambient salinities of the seawater at the discharge sites, they are denser than the ambient seawater and the produced water plumes sink initially if the produced water had a temperature near that of the ambient seawater at the time of discharge (Brandsma and Smith, 1996).

9.2.2 Metals and Metalloids in Produced Water and Ambient Seawater

Produced water samples from the four platform discharges and ambient seawater samples collected in this study were analyzed for arsenic, barium, cadmium, copper, chromium (but not ambient seawater), iron, lead, manganese, mercury, molybdenum, nickel, vanadium, and zinc. Several of these metals are found frequently at elevated concentrations in produced water (Neff, 1987, 1996a). Most produced waters are evaporates of ancient seawater and so contain the same metals and metalloids as found in seawater. The metals in produced water probably are in equilibrium with elements in the feldspars, plagioclase, biotite, and sandstones in the fossil fuel-bearing formation (Bloch and Key, 1981; Macpherson, 1989). However, if seawater is used for water flooding and seeps into the production stream, some metals may precipitate with the sulfate and carbonate that are abundant in seawater but rare in most produced waters (Stephenson *et al.*, 1994).

9.2.2.1 Arsenic

Arsenic is present in the produced water samples from the four platforms at average concentrations of 0.74 to 25 μg/L (parts per billion) (**Table 9.2**). The range of arsenic concentrations in individual samples is 0.53 to 31 μg/L. Arsenic concentrations in produced waters from the Gulf of Mexico have been reported in the range of less than 0.11 to 320 μg/L (Neff, 1996a). Highest concentrations are in produced water samples from coastal Louisiana

Table 9.2. Mean concentrations of arsenic, barium, cadmium, and mercury in produced water and ambient seawater 2,000 m from offshore platforms in the northwestern Gulf of Mexico. Concentrations are in μg/L.

Platform	Sample	Arsenic	Barium	Cadmium	Mercury
Discharge Sites					
SMI 236A	Produced Water Ambient Seawater	0.78 1.0	160,000 88	<0.10 0.03	0.08 <0.01
SMI 130B	Produced Water Ambient Seawater	0.74 1.1	87,000 15	<0.3 0.01	<0.02 0.02
VR 214A	Produced Water Ambient Seawater	5.9 0.64	220,000 23	0.31 0.01	0.04 <0.01
HI A-595CF	Produced Water Ambient Seawater	25 1.6	320,000 15	0.62 0.01	0.04 0.04
Reference Sites					
WC 448	Ambient Seawater	0.97	20	0.02	0.02
SMI 186/195	Ambient Seawater	0.81	17	0.02	0.01
GA A-205	Ambient Seawater	1.2	13	0.01	<0.01
GA A-90	Ambient Seawater	1.0	14	0.01	0.01

analyzed by Means *et al.* (1989). The highest values may have been anomalous because the investigators had problems with matrix interference. Produced water from North Sea platforms contains 0.004 to 100 μg/L arsenic; concentrations usually are higher in produced water from gas platforms than in produced water from oil platforms (Stephenson *et al.*, 1994). Thus, arsenic concentrations observed in produced water from the four discharges evaluated in this study are typical of arsenic concentrations in produced water elsewhere.

By comparison, the concentration of total arsenic in open ocean seawater is in the range of 1 to 3 μg/L, with an average of about 1.7 μg/L (Andreae and Andreae, 1989; Li, 1991). Coastal waters influenced by freshwater runoff from land may have higher or, more often, lower concentrations depending on the concentration of arsenic in the runoff. Metals were analyzed in surface ambient seawater from 2,000 m from the four produced water sites and from the four reference sites. Ambient seawater from the surface 2,000 m from the four produced water discharge sites contains mean concentrations of 0.64 to 1.6 μg/L total arsenic (overall mean, 1.1 μg/L) (**Table 9.2**). Seawater from reference stations contains mean concentrations of 0.81 to 1.2 μg/L arsenic (overall mean, 1.0 μg/L) (**Table 9.2**). These concentrations are all in the range of natural concentrations in coastal seawater influenced by runoff of fresh water low in arsenic. Differences in arsenic concentrations at the different sampling stations are caused mainly by dilution of oceanic seawater with freshwater runoff from land. There is no evidence that surface waters near produced water discharges contain higher than normal arsenic concentrations derived from the produced water discharges.

The produced water samples are enriched with arsenic compared to the average for local ambient seawater by factors of 0.68 to 16 (**Table 9.3**). Only one produced water, that from HI A-595CF, has an arsenic concentration that is substantially higher than that in clean natural seawater. A 10-fold dilution of this produced water would reduce the concentration of arsenic to ambient seawater concentrations. Although arsenic concentrations are highest in produced water and ambient seawater from platform HI A-595CF, the mean ambient seawater concentration is in the lower range of natural oceanic concentrations and probably reflects the more oceanic environment of this sampling location than the other sampling locations in this study. There is no apparent influence of the produced water discharges on concentrations of arsenic in ambient seawater 2,000 m from the produced water discharges.

9.2.2.2 Barium

Barium is extremely abundant in produced waters from many sources. Average barium concentrations in the four produced water samples are in the range of 87,000 μg/L to 320,000 μg/L (**Table 9.2**). Produced waters from throughout the Gulf of Mexico contain 1.0 to as high as 650,000 μg/L barium (Neff and Sauer, 1995). Barium concentrations as high as 2,000,000 μg/L have been reported (Barth *et al.*, 1989; Macpherson, 1989). Water flooding with seawater may increase the concentration of sulfate (present in seawater at a concentration of about 900,000 μg/L) in the formation water, causing barium to precipitate as barite ($BaSO_4$), lowering its concentration in the produced water (Stephenson *et al.*, 1994). Fouling of production equipment with barite scale is a serious problem in many oil and gas fields.

Table 9.3. Enrichment factors (concentration in produced water/concentration in ambient seawater 2,000 m from discharges) for several metals and metalloids in produced water from four production platforms in the northwestern Gulf of Mexico.

Metal	SMI 236A	SMI 130B	VR 214A	HI A-595CF
Arsenic	0.75	0.68	9.2	16
Barium	1,800	5,800	9,500	22,000
Cadmium	<3.9	<18	<22	<52
Mercury	<4.7	<0.74	<3.8	0.97
Copper	<0.85	<0.86	<0.41	<0.90
Nickel	<1.3	<11	<2.6	<4.7
Lead	<6.2	1.9	<1.9	600
Zinc	4.8	4.9	15	510
Iron	7,700	52,000	170,000	710,000
Manganese	4,900	1,200	15,000	20,000
Molybdenum	0.44	0.08	0.21	0.14
Vanadium	<0.85	<0.98	<1.0	<0.98

Concentrations of barium in surface waters of the western Gulf of Mexico are in the range of 11 to 12 μg/L (Chan and Hanor, 1982) and are higher in coastal waters influenced by freshwater runoff from land. Thus, barium concentrations in produced water nearly always are orders of magnitude higher than concentrations in seawater. The mean concentrations of barium in seawater from the four reference sites are in the range of 13 to 20 μg/L (overall mean, 16 μg/L) (**Table 9.2**). Mean concentrations of barium in ambient seawater 2,000 m from the four produced water discharges is in the range of 15 to 88 μg/L (overall mean, 35 μg/L). The highest value is for water from the brackish water location (SMI 236A) and undoubtedly reflects desorption of barium from suspended particles in the estuarine mixing zone of the Mississippi/Atchafalaya River system (Chan and Hanor, 1982). Other concentrations in ambient seawater at the produced water discharge sites are comparable to those in water samples from the reference sites. Variations of barium concentrations in ambient seawater near produced water discharges appear to be dependent more on the salinity of the ambient seawater (inflow of barium-rich water from the Mississippi River system) than the presence of high concentrations of barium in produced water.

Barium in the four produced waters in this study is enriched relative to its concentration in Gulf of Mexico seawater by factors of 1,800 to 22,000 (**Table 9.3**). Because of the high concentration of sulfate in seawater and the low solubility product of barium sulfate (1.05×10^{-10} M), barium is expected to precipitate almost immediately as barite upon discharge of barium-laden produced water to the ocean (Neff and Sauer, 1995). This rapid precipitation may explain the absence of barium enrichment in ambient seawater near discharges of barium-rich produced water.

9.2.2.3 Cadmium

Cadmium concentrations in the four produced water samples are in the range of 0.10 to 0.62μg/L (**Table 9.2**). Produced waters from elsewhere in the Gulf of Mexico contain 0.06 to 98 μg/L cadmium (Neff, 1996a). Concentrations of cadmium in produced water from the North Sea range from less than 0.0005 μg/L to 490 μg/L (Stephenson *et al.*, 1994). Produced water from gas wells usually has a higher cadmium concentration than produced water from oil wells.

The mean concentration of cadmium in surface waters of the northwestern Gulf of Mexico is in the range of 1 to 20 ng/L (0.001 to 0.02 μg/L) (**Chapter 7** and Trefry *et al.*, 1995). Cadmium concentrations may be as high as 0.2 μg/L in clean coastal waters (Neff, 1996a), and in the nutrient maximum layer (about 900 to 1,000 m below the surface) of the open ocean, natural cadmium concentrations may be as high as 0.15 μg/L (Yeats *et al.*, 1995). Surface water samples from the four reference locations contain 0.01 to 0.02 μg/L cadmium (overall mean, 0.02 μg/L) (**Table 9.2**). Average cadmium concentrations in ambient seawater 2,000 m from the four produced water discharges are in the range of 0.01 to 0.03 μg/L (overall mean, 0.02 μg/L). Thus, cadmium concentrations in seawater from reference and produced water discharge sites are comparable and are in the range typically found in clean coastal waters.

Concentrations of cadmium in the four produced water samples in this study are enriched relative to the average concentration in ambient seawater by factors of <3.9 to <52 (**Table 9.3**). The enrichments are all maximum values because at least one sample of produced water from all four discharges contained a cadmium concentration below the MDL. Mean concentrations of cadmium in produced water from the two South Marsh Island platforms actually are within the range frequently found in clean coastal waters influenced by freshwater runoff from land. Because of the small enrichment of cadmium in produced water compared to its concentration in ambient seawater, this metal is diluted rapidly to natural background concentrations and elevated concentrations of dissolved cadmium would not be expected near offshore produced water discharge sites.

9.2.2.4 Mercury

Mercury rarely is present in produced water at high concentrations. The four produced water samples in this study contain 0.01 to 0.08 μg/L total mercury (**Table 9.2**). These concentrations are typical of those reported for mercury in produced water from throughout the western Gulf of Mexico; the range of reported concentrations of mercury in Gulf produced water is 0.06 to 0.19 μg/L (Neff, 1996a). Mercury concentrations as high as 33 μg/L have been reported in produced water from other sources (Neff, 1996a).

Because it is volatile and highly mobile in the atmosphere, mercury is difficult to measure accurately at the ultra-trace concentrations at which it occurs in seawater. Many of the older reported concentrations of mercury in ocean waters are anomalously high because of laboratory contamination. Reported concentrations of total dissolved mercury in ocean waters, measured with appropriate precautions since 1990, usually are in the range of 0.07 to about 6 ng/L (0.00007 to 0.006 μg/L). Concentrations of total mercury in uncontaminated coastal and estuarine waters may be as high as 0.02 μg/L (Neff, 1996a). In turbid coastal and estuarine waters containing high concentrations of suspended particulate matter, a large fraction of the total mercury may be adsorbed to suspended particles. Suspended particulate matter in U.S. rivers and estuaries may contain 150 to 11,8000 μg/kg total adsorbed mercury (Lindberg *et al.*, 1975).

Surface water from the four reference locations contains <0.01 to 0.02 μg/L total mercury (overall mean, 0.01 μg/L) (**Table 9.2**). Mercury in surface water 2,000 m from the four produced water discharges contain averages of <0.01 to 0.04 μg/L (overall mean, 0.02 μg/L). Thus, the four produced waters evaluated in this study are enriched in mercury by factors of <0.74 to <4.7 (**Table 9.3**).

The highest mean mercury concentration in ambient seawater (mean 0.04 μg/L, range 0.03 to 0.04 μg/L) is near produced water discharge HI A-595CF; the produced water from this platform contains a mean of 0.04 μg/L (range 0.02 μg/L to 0.06 μg/L) total mercury. The concentration of mercury in surface seawater near this produced water discharge located about 76 km south of the Texas coast is higher than expected for clean ocean water. The apparently elevated mercury concentration in seawater in this area cannot be attributed to inputs of mercury from the produced water (mean produced water/ambient seawater enrichment factor 0.97). The slightly elevated concentration of total mercury may be caused in part by high suspended particulate concentrations in coastal waters off Texas and Louisiana, caused by a massive influx of suspended particulate matter from the Mississippi, Nachez, and Trinity River systems.

9.2.2.5 Copper

All but two produced water samples from the four production platforms in this study contain less than 0.2 µg/L copper (**Table 9.4**). The two samples are among 12 analyses conducted on eight samples collected from SMI 236A; they contain 6.9 and 7.1 µg/L. All other produced water samples from this platform contain less than 0.20 µg/L copper. The two samples probably are anomalous. Copper concentrations usually are low in produced water from the Gulf of Mexico; however, concentrations as high as 210 µg/L have been reported from a coastal treatment facility treating produced water from a large number of offshore facilities (Boesch *et al.*, 1989). Very high concentrations of copper, up to 55,000 µg/L, have been reported in produced waters from other sources (Neff, 1996a). Most produced waters contain less than 500 µg/L dissolved copper.

Mean copper concentrations in surface water samples from the four reference locations are in the range of 0.20 to 0.40 µg/L (overall mean, 0.30 µg/L). Mean copper concentrations in surface waters 2,000 m from the four produced water discharges range from 0.22 to 1.4 µg/L (overall mean, 0.58 µg/L) (**Table 9.4**). These concentrations are in reasonable agreement with reported concentrations of copper in clean oceanic water of 0.03 to 0.35 µg/L (Neff, 1996a). Estuarine and coastal waters usually have higher concentrations of copper, reflecting the importance of freshwater runoff as a source of copper in the ocean. The highest copper concentration in an ambient seawater sample is from platform SMI 236A, a short distance south of the Mississippi/Atchafalaya River system. Mississippi River water at Head of Passes, LA, contains about 8 µg/L copper (DeLeon *et al.*, 1986). Coastal waters and bays in Louisiana and Texas contain 0.13 to 1.70 µg/L copper (Morse *et al.*, 1993; **Chapter 7** and Trefry *et al.*, 1995a,b). Thus, copper concentrations are not higher than expected in the vicinity of the four produced water discharges.

Because most produced water samples contained less than the MDL (0.20 µg/L) of copper, maximum possible enrichment factors all were less than 1.0 (**Table 9.3**). Thus, these produced water discharges to offshore water are not expected to affect the concentration of total copper in surface waters of the northwestern Gulf of Mexico.

9.2.2.6 Nickel

Nickel is present in the four produced waters at concentrations of less than 1.2 to 3.1 µg/L (**Table 9.4**). These concentrations are lower than some nickel concentrations reported for produced waters discharged elsewhere in the Gulf of Mexico. For example, Rabalais *et al.* (1991) reported nickel concentrations of 3,700 to 8,800 µg/L in produced water from 15 discharges to coastal waters of Louisiana. These concentrations seem to be high by a factor of at least 10^3; an earlier report by Boesch *et al.* (1989) of metal concentrations in produced waters from some of the same treatment facilities indicated nickel concentrations of 36 to 41 µg/L. Produced water from two coastal platforms analyzed by Neff *et al.* (1992) contains 0.40 and 1.27 µg/L nickel. Produced water from oil and gas platforms discharging to the North Sea contain 10 to 170 µg/L nickel (Stephenson *et al.*, 1994).

Mean concentrations of nickel in surface seawater from the four reference sites are 0.24 to 0.35 µg/L (overall mean, 0.29 µg/L) (**Table 9.4**). Nickel concentrations in surface seawater 2,000 m from the four produced water discharges are in the range of 0.25 to 1.2 µg/L

Table 9.4. Mean concentrations of copper, nickel, lead, and zinc in produced water and ambient seawater 2,000 m from offshore platforms in the northwestern Gulf of Mexico. Concentrations are in μg/L.

Platform	Sample	Copper	Nickel	Lead	Zinc
Component 1 Discharge Sites					
SMI 236A	Produced Water	<0.20*	<2	0.24	22
	Ambient Seawater	1.4	1.2	0.04	4.6
SMI 130B	Produced Water	<0.20	3.1	0.66	28
	Ambient Seawater	0.23	0.27	0.34	5.7
VR 214A	Produced Water	<0.20	<1	0.13	86
	Ambient Seawater	0.48	0.46	0.07	5.6
HI A-595CF	Produced Water	<0.20	<1	20	3,000
	Ambient Seawater	0.22	0.25	0.03	5.8
Component 2 Reference Sites					
WC 448	Ambient Seawater	0.40	0.35	0.61	9.1
SMI 186/195	Ambient Seawater	0.30	0.30	0.23	5.0
GA A-205	Ambient Seawater	0.20	0.24	0.09	3.2
GA A-90	Ambient Seawater	0.28	0.26	0.12	2.8

* Two analyses resulted in more than 6 μg/L copper; ten analyses resulted in <0.20 μg/L copper.

(overall mean, 0.55 μg/L). These concentrations, with the exception of that for ambient seawater from the low-salinity location (SMI 236A), are comparable to nickel concentrations (0.10 to 1.0 μg/L) in offshore waters around Great Britain, including the North Sea (Hydes and Kremling, 1993; Laslett, 1995). The highest mean concentration is in brackish water from an area strongly influenced by freshwater runoff from the Mississippi/Atchafalaya River system. Thus, nickel concentrations are not elevated above expected levels in ambient seawater near produced water discharges.

Produced water from the four discharges investigated here is enriched by factors of <1.3 to <11 compared to concentrations in ambient seawater near the platforms (**Table 9.3**). Thus, nickel in produced water discharges to the ocean is diluted rapidly to background concentrations.

9.2.2.7 Lead

Concentrations of lead in produced water are highly variable. Mean concentrations in produced waters from the four platforms in this study range from 0.13 μg/L to 20 μg/L (**Table 9.4**). Highest concentrations are in produced water from HI A-595CF where lead concentrations in produced water collected at different times ranged from 10 to 28 μg/L. All but one replicate sample of produced water from the other three platforms contain less than 1 μg/L lead. Produced water from discharges to Louisiana coastal waters analyzed by Rabalais *et al.* (1991) contain ND to 29 μg/L lead. Lead concentrations as high as 18,000 μg/L have been reported in produced water from elsewhere in the world (Neff, 1996a). Lead is a difficult metal to analyze accurately in concentrated salt solutions, such as many produced waters; therefore, many of the reported high concentrations may be anomalous.

Mean lead concentrations in surface seawater from the four reference sites are in the range of 0.09 to 0.61 μg/L (overall mean, 0.26 μg/L) (**Table 9.4**). Similar concentrations (0.03 to 0.34 μg/L; overall mean, 0.12 μg/L) are present in surface seawater samples 2,000 m from the four produced water discharges. The concentration of lead in clean open ocean waters, measured by ultra-clean laboratory methods to avoid contamination, are in the range of 0.001 to 0.1 μg/L (Neff, 1996a). In coastal waters and estuaries, concentrations of dissolved lead may increase to more than 1.0 μg/L. Concentrations of particulate lead may be as high as or higher than those of dissolved lead. Waters of Galveston Bay, TX, contain 0.022 to 0.133 μg/L dissolved lead and 0.026 to 0.53 μg/L particulate lead (Morse *et al.*, 1993). Thus, lead concentrations in water from the reference and produced water discharge stations, particularly from WC 448 and SMI 130B, are in the upper part of the range of expected concentrations in the ocean. There is no relationship between produced water discharges and concentrations of lead in surface waters of the western Gulf of Mexico.

Enrichment of lead in produced water compared to ambient seawater is in the range of 1.9 to 600 fold (**Table 9.3**). The concentration of lead in ambient seawater is lowest at a location near the platform discharging produced water with the highest lead concentration (HI A-595CF). Thus, produced water discharges do not seem to be causing an increase in lead concentrations in ambient seawater in the northwestern Gulf of Mexico.

9.2.2.8 Zinc

Concentrations of zinc in produced water are highly variable from one sample to another, even from the same platform. This may reflect leaching or flaking of zinc from galvanized structures on the platform or occasional presence of microcrystalline zinc sulfide (sphalerite) in the produced water. The four platforms in this study discharge produced water containing means of 22 to 3,000 μg/L zinc. Individual samples contain 0.3 to 3,600 μg/L zinc. High and variable concentrations of zinc have been reported in produced waters from elsewhere in the Gulf of Mexico. Rabalais *et al.* (1991) report zinc concentrations ranging from 220 to 5,500 μg/L in 15 produced waters from coastal Louisiana. Zinc concentrations in produced waters discharged from oil and gas platforms to the North Sea range from 5 μg/L to 150,000 μg/L (Stephenson *et al.*, 1994), and usually are higher in produced water from gas than from oil platforms.

Mean concentrations of zinc in surface seawater from the four reference locations are in the range of 2.8 to 9.1 μg/L (overall mean, 5.1 μg/L) (**Table 9.4**). Mean zinc concentrations in surface seawater 2,000 m from the four produced water discharges are 4.6 to 5.8 μg/L (overall mean, 5.4 μg/L). Concentrations in the ambient seawater near the produced water discharges are not related to zinc concentrations in the produced waters.

These concentrations are high for ocean waters. Zinc is a difficult metal to analyze at the concentrations normally found in seawater. Zinc and iron often seem to co-occur in seawater samples as a result of contamination from metal surfaces in the field and laboratory (Bruland *et al.*, 1994). Recently-reported concentrations of zinc in surface waters of the Atlantic and Pacific Oceans are in the range of 0.006 to 0.12 μg/L (Pohl *et al.*, 1993; Bruland *et al.*, 1994). Concentrations in estuaries and coastal waters frequently are much higher than those in the open ocean with concentrations as high as 4 to occasionally 25 μg/L having been reported (Morse *et al.*, 1993; Law *et al.*, 1994). The waters of Galveston Bay contain 0.3 to 4.5 μg/L zinc. Influxes of zinc from rivers and surface runoff from land are important sources of zinc in coastal waters. Water from near the mouth of the Mississippi River contains about 7 μg/L zinc (DeLeon *et al.*, 1986). **Chapter 7** and Trefry *et al.* (1996) reported a mean zinc concentration of 5 μg/L in seawater in the vicinity of oil platforms in the northwestern Gulf of Mexico. Concentrations of dissolved zinc in seawater below about 0.8 μg/L may cause deficiency for this essential trace element in marine organisms (vanTilborg and van Assche, 1995); concentrations above about 100 μg/L may be toxic to some marine organisms. Therefore, concentrations of zinc in surface waters near offshore produced water discharges do not appear to be elevated above expected background levels for coastal waters influenced by river runoff.

Zinc is enriched in the four produced waters in this study compared to its concentration in surface waters near the four produced water discharges by factors of 4.8 to 510 (**Table 9.3**). The highest enrichment factor is for produced water from HI A-595CF where the produced water contains 2,600 to 3,600 μg/L zinc. Despite the high zinc concentrations in produced water from this platform, concentrations of zinc in ambient seawater near the platform (5.2 to 6.9 μg/L) are only slightly higher than concentrations in surface water near the other three produced water discharges (3.0 to 9.8 μg/L, overall mean 5.3 μg/L), and roughly comparable to zinc concentrations in surface water from most of the reference stations (2.1 to 9.5 μg/L, overall mean 5.1 μg/L). Zinc in produced water discharged to the northwestern Gulf of Mexico has, at most, a minimal effect on the concentration of zinc in surface waters near produced water discharges.

9.2.2.9 Iron

Iron has not been analyzed frequently in produced water. In those samples that have been analyzed, iron concentrations are high, compared to concentrations of dissolved iron in ambient seawater. The average concentrations of iron in the four produced waters discussed here are 12,000 to 35,000 µg/L (**Table 9.5**). Concentrations of iron in produced waters discharged to the North Sea are in the range of less than 10 µg/L to 32,000 µg/L (Stephenson *et al.*, 1994). The concentration of iron in produced water is directly correlated with the concentration of total dissolved solids (salinity) in the produced water (**Chapter 7** and Trefry *et al.*, 1995). Under the reducing conditions that prevail in produced water in the geologic formation, iron is quite soluble in waters with a high ionic strength. However, upon discharge of produced water to the ocean, the produced water plume rapidly becomes oxygenated and iron precipitates as various highly insoluble iron oxy-hydroxides (Kuma *et al.*, 1996).

The mean concentrations of iron in surface seawater from the four reference sites are 0.10 to 0.82 µg/L (overall mean, 0.29 µg/L) (**Table 9.5**). Mean iron concentrations in seawater 2,000 m from the four produced water discharges is in the range of 0.05 to 1.5 µg/L (overall mean, 0.55 µg/L). The highest concentration is in brackish water influenced by river runoff high in suspended iron. Concentrations of iron and zinc in the ambient seawater samples are highly correlated, suggesting possible contamination of the samples in the field or laboratory. Iron concentrations in surface waters of the English Channel and the eastern North Atlantic Ocean off Great Britain decrease from 4.29 µg/L in the channel to about 0.06 µg/L in the open ocean (Muller *et al.*, 1994). The concentration of dissolved iron in the open central North Pacific Ocean increases from a mean of about 0.008 µg/L at the surface to 0.02 µg/L at depths greater than 500 m (Bruland *et al.*, 1994). Concentrations of dissolve and particulate iron are about the same in open ocean water samples. Despite the presence of particulate iron in the ocean, concentrations of dissolved iron often are sufficiently low to limit growth of phytoplankton (Cullen, 1995). This indicates that the particulate iron (mostly microparticulate iron oxides and hydroxides) is not readily exchangeable with the dissolved fraction in oxygenated seawater and is not bioavailable. Much of the iron in coastal waters is derived from freshwater runoff from land (Sunda, 1994).

Enrichment of iron in produced water from the four discharges sampled here compared to concentrations in ambient seawater from 2,000 m from the four produced water discharges is in the range of 7,700 to 710,000 fold. Despite this substantial enrichment, iron concentrations in surface waters near produced water discharges are not elevated. This undoubtedly reflects the rapid precipitation of iron in the receiving water of the produced water discharges.

9.2.2.10 Manganese

Manganese, like iron, is more soluble in anoxic water than in oxygenated seawater, where it precipitates as various oxy-hydroxides (Schimmield and Pedersen, 1990). The four produced waters in this study contain 1,200 to 7,000 µg/L manganese. North Sea produced water contains 100 to 22,000 µg/L manganese (Stephenson *et al.*, 1994). Upon discharge of produced water to the ocean, the reduced Mn (+II) is oxidized slowly to insoluble Mn (+IV), which precipitates as manganese oxides and hydroxides. Because of these oxidation/reduction reactions, oxidized layers of marine sediments are naturally rich in iron and manganese.

Table 9.5. Mean concentrations of iron, manganese, molybdenum, and vanadium in produced water and ambient seawater 2,000 m from offshore platforms in the northwestern Gulf of Mexico. Concentrations are in μg/L.

Platform	Sample	Iron	Manganese	Molybdenum	Vanadium
Component 1 Discharge Sites					
SMI 236A	Produced Water	12,000	1,200	1.4	<1.2
	Ambient Seawater	1.5	0.25	3.2	1.4
SMI 130B	Produced Water	29,000	1,400	0.79	<1.2
	Ambient Seawater	0.56	1.1	10	1.2
VR 214A	Produced Water	12,000	4,500	1.7	<1.2
	Ambient Seawater	0.07	0.31	8.3	1.2
HI A-595CF	Produced Water	35,000	7,100	1.4	<1.2
	Ambient Seawater	0.05	0.36	10	1.2
Component 2 Reference Sites					
WC 448	Ambient Seawater	0.82	0.65	9.5	1.2
SMI 186/195	Ambient Seawater	0.13	0.61	10	1.1
GA A-205	Ambient Seawater	0.11	0.28	10	1.3
GA A-90	Ambient Seawater	0.10	0.25	9.7	1.2

Mean concentrations of manganese in seawater from the four reference locations are 0.25 to 0.65 µg/L (overall mean, 0.45) (**Table 9.5**). Mean manganese concentrations in surface waters 2,000 m from the four produced water discharges are in the range of 0.25 to 1.1 µg/L (overall mean, 0.51 µg/L). These concentrations are within the range expected in coastal and continental shelf waters influenced by riverine inputs and periodic episodes of anoxic bottom water. Manganese concentrations in surface waters decrease from about 1.6 µg/L in the English Channel to 0.03 µg/L in the open eastern North Atlantic Ocean (Muller *et al.*, 1994). Advection of hypoxic bottom water to the surface will tend to increase the concentration in surface waters of metals, such as iron and manganese, that are more soluble in the reduced than in the oxidized state (Morris *et al.*, 1982; Stone and Morgan, 1987).

Enrichment of manganese in produced water from the four sampled discharges compared to concentrations in ambient seawater from 2,000 m from the four produced water discharge sites ranges from 1,200 to 20,000 (**Table 9.3**). Despite the large enrichment factors, concentrations of manganese in ambient seawaters near the produced water discharges are not elevated above concentrations expected in coastal and offshore waters of the northwestern Gulf of Mexico. Manganese in produced water undoubtedly precipitates upon discharge of the produced water to oxidized surface waters. The rate of precipitation depends on the dissolved oxygen concentration, salinity, and suspended particulate matter (particularly clay) concentration in the diluting plume of produced water in the receiving waters (Morris *et al.*, 1982). Precipitation is slower at high than at low salinities. Receiving waters near offshore produced water discharges probably contain a mixture of dissolved and particulate manganese. Particulate manganese is not bioavailable or toxic to marine organisms.

9.2.2.11 Molybdenum

Molybdenum is quite abundant in seawater. The mean concentration in oceanic waters is 10 µg/L (Li, 1991). In the North Atlantic Ocean and adjacent seas, including the Gulf of Mexico, the concentration of dissolved molybdenum in surface waters ranges from 8.6 to 13 µg/L (Burton and Statham, 1982); the average concentration in surface waters of the eastern North Pacific Ocean is 10.3 µg/L (Collier, 1985). Typically, molybdenum concentrations increase from 0.5 µg/L or less in the freshwater portion of river estuaries to about 10 µg/L in the open ocean (van den Berg, 1993). Lower concentrations frequently are found in coastal waters influenced by riverine inputs of fresh water low in molybdenum. Its concentration in surface water from the four reference stations is 9.5 to 10 µg/L (overall mean, 9.9 µg/L) (**Table 9.5**). The mean molybdenum concentration in surface waters 2,000 m from the four produced water discharges are in the range of 3.2 to 10 µg/L (overall mean, 8.0 µg/L). Lowest concentrations are at platform sites SMI 236A and VR 214A, where salinities are lowest.

Mean molybdenum concentrations in the produced water samples from the four platforms range from 0.79 to 1.7 µg/L (**Table 9.5**). Molybdenum concentrations in produced water discharges to the North Sea were reported to be in the range of less than 50 to 140 µg/L (Tibbetts *et al.*, 1992). These concentrations may be anomalously high due to poor MDLs.

Molybdenum is depleted in the four produced waters investigated here compared to its average concentration in surface water from the reference locations. Enrichment factors range from 0.08 to 0.44 (**Table 9.3**). Thus, produced water discharges to offshore waters of the Gulf are unlikely to affect the concentration of molybdenum in the receiving waters.

9.2.2.12 Vanadium

Mean concentrations of vanadium in produced water from the four platforms is below the MDL for saline brines (1.2 μg/L) (**Table 9.5**). Means *et al.* (1990) reported concentrations of 1.2 to 60 μg/L in produced water from four platforms discharging to coastal wetlands of Louisiana. These concentrations are low compared to concentrations reported by Means *et al.* (1989) and Rabalais *et al.* (1991) in produced waters discharged to coastal Louisiana (310 to 22,000 μg/L). Vanadium is difficult to analyze in saline brines; the latter analyses could have suffered from matrix interference. Vanadium has been analyzed but rarely detected in produced water from the North Sea (Tibbetts *et al.*, 1992; Jacobs *et al.*, 1992; Stephenson *et al.*, 1994). Highest measured concentrations are 20 to 100 μg/L and may be anomalously high because of poor detection limits.

Vanadium is moderately abundant in oceanic waters. Jeandel *et al.* (1987) reported an average vanadium concentration in ocean water of 2.15 μg/L. However, surface waters of the North Atlantic Ocean contain 1.62 to 1.72 μg/L vanadium (Middleburg *et al.*, 1988); in the North Pacific Ocean, average vanadium concentration increases from 1.67 μg/L at the surface to 1.85 μg/L in deep water (Collier, 1984). Vanadium concentrations in surface water at the four reference sites in this study are in the range of 1.1 to 1.3 μg/L (overall mean, 1.2 μg/L) (**Table 9.5**). Mean vanadium concentrations in surface water 2,000 m from the four produced water discharges are in the range of 1.2 to 1.4 μg/L (overall mean, 1.3 μg/L). These concentrations are in the range of expected values for clean coastal and offshore marine waters.

True enrichment factors for vanadium in produced water could not be estimated because vanadium was not detected at a concentration above the MDL in any of the samples. However, the maximum enrichment factor for vanadium in produced water from the four platforms, assuming that vanadium was present at the MDL, are <0.85 to <1.0 (**Table 9.3**).

9.2.2.13 Summary of Metal Enrichment in Produced Water and Receiving Waters

The metals/metalloids with the greatest enrichment in produced water from the four platforms compared to their concentrations in local surface seawater are barium, iron, and manganese (**Table 9.3**). These three metals are expected to precipitate rapidly during mixing of the produced water plume with ambient seawater. Barium will precipitate as barium sulfate in the presence of the high natural concentration of sulfate in seawater (Neff and Sauer, 1995). Iron and manganese, which probably are present in produced water as reduced species, will be oxidized to insoluble oxy-hydroxides when the produced water mixes with oxygen-rich surface waters at the offshore discharge sites (Schindler and Stumm, 1987; Kuma *et al.*, 1996). Because the grain size of these precipitated metals is very small, the particulate metals tend to settle slowly out of the water column and accumulate to slightly elevated concentrations in surficial sediments over a large area around the produced water discharge, keeping their concentrations in the water column low.

Rapid precipitation of barium, iron, and manganese has the effect of reducing the concentrations of other dissolved metals and metalloids in seawater. Iron and manganese oxy-hydroxides, because of their small particle size and high charge densities, adsorb or coprecipitate dissolved metals (Schoer, 1985). The adsorbed or coprecipitated metals settle out of the water column with the particulate iron and manganese oxy-hydroxides. Some metals and metalloids may also be coprecipitated with barium sulfate. Thus, despite the fact that produced water is enriched compared to seawater in concentrations of several metals (**Table 9.3**), concentrations of the metals in seawater near the offshore produced water discharges rarely are substantially higher than their natural concentrations (**Table 9.6**).

Five of the 12 metals or metalloids examined in this study are present at elevated concentrations (approximately two-fold) in ambient seawater 2,000 m from the four produced water discharges compared to their concentrations in seawater from the four reference sites (**Table 9.6**). For four of the five metals, the difference can be attributed to differences in salinity between the produced water sites and the reference sites. The average seawater salinity at the platform sites is 25 ‰, compared to a mean salinity of 32 ‰ at the reference sites (platform/reference ratio, 0.77) (**Table 9.6**). Highest concentrations of barium, copper, iron, and nickel are at the low salinity produced water discharge sites. These metals tend to be present at higher concentrations in fresh water than in seawater. Therefore, their natural concentrations usually are higher in brackish than in full strength seawater. The overall average concentration of mercury is higher in seawater near produced water discharge sites than in water from the reference sites. In this case, the difference is due to a high mean concentration of mercury in seawater near the most oceanic produced water discharge, HI A-595CF. The mean concentration of mercury in the produced water from this platform is comparable to the concentration of mercury in the ambient seawater. Thus, the excess mercury probably is not coming from the produced water. The source of the slightly elevated mercury concentration in the ambient seawater near platform HI A-595CF is not known.

Therefore, high-volume discharges from four offshore platforms of produced water containing elevated concentrations of several metals and metalloids is not resulting in an increase in the concentrations of these metals in surface seawater 2,000 m from the platforms. It is possible that there are elevated concentrations of some of these metals, particularly barium, iron, and manganese, and also possibly lead and zinc, in seawater within a few hundred meters of the platform discharges. However, most, if not all, the metals from the produced water probably would be present in the ambient seawater in adsorbed or coprecipitated particulate forms that have a limited bioavailability to marine organisms.

9.2.2.14 Ecorisk of Metals in Ambient Seawater Near Offshore Produced Water Discharges

If it is assumed that all the metals measured in ambient surface seawaters 2,000 m from the produced water discharge sites are present in a dissolved, bioavailable form, it is possible to estimate the relative toxicity of the metals to marine organisms. The risk of each metal causing toxic responses in sensitive marine organisms in the receiving water environment of the produced water discharges can be estimated as toxic units, the ratio of the concentration of the metal in ambient seawater to its chronic water quality criterion value. A value for toxic units equal to or greater than 1 indicates that, if the chemical is present in the water in a bioavailable, toxic form, it could be causing harm to sensitive species and life stages of marine organisms. Concentrations below 1 toxic unit probably are safe for periodic or chronic exposure to all marine organisms.

Table 9.6. Ratio between mean concentrations of metals in all water samples from 2,000 m from four Component 1 offshore produced water discharges and mean concentrations of metals in all water samples from the four Component 2 reference sites. Concentrations are in μg/L.

Metal	Platform Water	Reference Water	Platform/Reference
Arsenic	1.1	1.0	1.1
Barium	35	16	2.2
Cadmium	0.02	0.02	1.0
Copper	0.58	0.30	2.0
Iron	0.55	0.29	1.9
Mercury	0.02	0.01	1.8
Manganese	0.51	0.45	1.2
Molybdenum	8.0	9.9	0.81
Nickel	0.55	0.29	1.9
Lead	0.12	0.26	0.46
Vanadium	1.3	1.2	1.1
Zinc	5.4	5.1	1.1
Salinity	25	32	0.77

Concentrations of the metals and metalloids analyzed in this study in surface seawater 2,000 m from the four produced water discharge sites are for the most part in the range of expected natural concentrations for marine waters influenced by riverine influxes of fresh water. Toxic units for the different metals range from less than 0.001 to 1.7 (**Table 9.7**). The only metals present at concentrations approaching 1 toxic unit are mercury and copper. All other metals are present at toxic units generally less than 0.1.

Mercury is present at a slightly elevated concentration in surface water near produced water discharge platform HI A-595CF. Three replicate water samples from this location contain 0.03 to 0.04 μg/L total mercury, equivalent to 1.1 to 1.7 toxic units. The relatively high toxic units for mercury in these offshore waters is due primarily to the low chronic value of 0.025 μg/L for total mercury in seawater. This marine chronic value was based on an estimated bioconcentration factor of 40,000 for methyl mercury in the American oyster *Crassostrea virginica* (Kopfler, 1974). The oysters were exposed to 1 μg/L methyl mercury and, after 60 days, had accumulated 40 mg/kg wet weight total mercury in tissues. This bioconcentration test is not a suitable basis for derivation of a chronic value for total mercury in seawater. Inorganic mercury is bioaccumulated much less efficiently than methyl mercury in marine food chains (Mason *et al.*, 1995). In addition, methyl mercury usually represents less than 10% of total mercury in ocean waters and freshwater lakes (Mason and Fitzgerald, 1993; Kelly *et al.*, 1995). Transformation of inorganic mercury to methyl mercury can occur in hypoxic seawater and sediments, but does not occur in oxygenated surface waters (Rolfus and Fitzgerald, 1995; Gagnon *et al.*, 1996). The traces of mercury in produced water probably are reduced, inorganic species. These forms of mercury would not be transformed to methyl mercury in oxygenated surface waters and would be transformed only very slowly in hypoxic water or sediment layers.

The Canadian water quality guideline for protection of aquatic life is 0.1 μg/L total mercury (Gaudet *et al.*, 1995). The U.S. EPA chronic value for mercury (II) in seawater, based on toxicity tests with marine organisms, is 1.106 μg/L (EPA, 1985a). If this value is used for estimating toxic units of mercury in the receiving water environment of the produced water discharge sites, the resulting toxicity units are in the range of less than 0.009 to 0.038. These values indicate that concentrations of dissolved inorganic mercury in the receiving water environment of the four produced water discharges are well below potentially toxic concentrations.

Marine water quality criteria for copper are based on several acute tests with embryos of bivalve molluscs and fish (EPA, 1985b). Only a few acute/chronic ratios are available, mostly for insensitive species. The resulting chronic value (2.4 μg/L) probably is overly conservative for total dissolved copper in seawater. Typical concentrations of total dissolved copper in coastal waters of the northwestern Gulf of Mexico influenced by freshwater runoff are in the range of 0.1 to 1.7 μg/L (Morse *et al.*, 1993; **Chapter 7** and Trefry *et al.*, 1995a,b), close to the chronic value for copper. Only a small fraction, usually less than 1% of copper in seawater is present in the toxic, reactive ionic state (Sunda and Huntsman, 1991; Shine and Wallace, 1995). Thus, the marine chronic criteria for copper are overly conservative. Concentrations of copper encountered in surface waters near the four produced water discharges probably are natural and are well below concentrations that would be toxic to marine organisms.

Table 9.7. Comparison of USEPA marine acute and chronic water quality criteria and ranges of concentrations and toxic units ([ambient seawater]/[chronic value]) of metals in ambient seawater near four Component 1 produced water discharges to offshore waters of the northwestern Gulf of Mexico. Chronic criteria for metals are from Federal Register, Vol. 60, No. 86, Thursday, May 4, 1995, 22229. Concentrations are μg/L.

Compound	Chronic Criterion	Concentration Range, Ambient Sea Water	Range, Toxic Units
Arsenic	36	0.59 - 1.6	0.05 - 0.02
Cadmium	9.3	0.01 - 0.02	0.001 - 0.002
Copper	2.4	0.21 - 1.5	0.09 - 0.52
Mercury	0.025[a]	<0.01 - 0.04	<0.4 - 1.7
Molybdenum	NV	2.7 - 11	—
Nickel	8.1	0.25 - 1.4	0.03 - 0.18
Lead	8.1	0.029 - 0.52	0.003 - 0.064
Vanadium	NV	1.1 - 1.5	—
Zinc	81	3.0 - 9.8	0.037 - 0.12

NV = no published marine water quality criterion value is available.

[a] Chronic value based on bioaccumulation of methyl mercury by marine mollusks.

These results indicate that metals and metalloids are present in ambient seawater near the four produced water discharges at concentrations well below potentially toxic concentrations. However, these samples were collected 2,000 m from the produced water discharges and reflect a substantial dilution of the produced water with ambient seawater. Produced water is diluted very rapidly following discharge to ocean waters (Brandsma and Smith, 1996). A 100-fold dilution usually is obtained within a few meters of the discharge and probably is the lowest dilution a marine organism might encounter for more than a few minutes near a produced water discharge. The only metals and metalloids present in one or more of the four produced waters at a concentration 100 times or more greater than their concentrations in clean natural seawater are barium, lead, zinc, iron, and manganese. Lead and zinc were present in only one produced water (HI A-595CF) at an elevated concentration. Dilution of lead (mean 20 μg/L) and zinc (mean 3,000 μg/L) in this produced water by 100-fold would yield ambient concentrations of 0.2 and 30 μg/L, respectively, representing 0.02 and 0.37 toxic units, respectively. Thus, these metals would not be toxic to marine organisms in a 100 to 1 dilution of produced water from HI A-595CF.

As discussed above, barium, iron, and manganese are likely to precipitate rapidly upon dilution of produced water in seawater rich in sulfate and oxygen. Thus, dissolved concentrations will be much lower than predicted based on dilution alone. There are no marine water quality criteria for barium and iron. The freshwater chronic value for iron (1,000 μg/L) would yield 0.012 to 0.35 toxic units for the 100-fold dilutions of produced water from the four discharges. The chronic value for manganese, based on bioaccumulation in marine shellfish, is 100 μg/L (**Table 9.7**). Based on this value, the 100-fold dilution of the four produced waters contain 1.2 to 7.1 toxic units of manganese. The chronic criterion probably is invalid. Marine sediments are rich in oxidized (solid) manganese. The bivalve molluscs used in the bioaccumulation experiments probably contained particulate manganese in their guts from ingesting of suspended sediment material. It is highly doubtful that manganese from produced water is toxic to marine organisms.

9.2.3 Aromatic Hydrocarbons in Produced Water and Ambient Seawater

The organic compounds of greatest concern in treated produced water destined for disposal in the ocean, 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. 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 2- and 3-ring aromatics and their alkylated homologs. Higher molecular weight 4- 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.

9.2.3.1 Monocyclic Aromatic Hydrocarbons

Produced water from the four discharges sampled in this study contain means of 1,800 to 5,200 μg/L total monocyclic aromatic hydrocarbons (total benzenes) (**Table 9.8**). Mean concentrations of the sum of benzene, toluene, ethylbenzene, and xylenes (BTEX) are in the range of 1,600 to 4,900 μg/l. C_3- and C_4-benzenes rarely are measured in produced waters. Concentrations of BTEX in produced waters discharged to the northwestern Gulf of Mexico are in the range of 68 to 38,000 μg/L (Neff, 1996a). BTEX concentrations as high as 578,000 μg/L have been reported for produced waters from elsewhere in the world. Therefore, the produced waters evaluated here contain BTEX concentrations in the middle of the range found in produced waters from throughout the northwestern Gulf of Mexico. Concentrations of total monocyclic aromatic hydrocarbons, which usually represent a majority of the total hydrocarbons in produced water, measured in the four produced water samples are below the regulatory limit of 42 mg/L daily maximum and 29 mg/L monthly average total oil and grease.

All four produced waters have a similar monocyclic aromatic hydrocarbon composition (**Table 9.9**). Benzene is most abundant, followed by toluene. These two aromatic hydrocarbons represent more than 50% of the total monocyclic aromatic hydrocarbons in the produced water samples. C_4-benzenes always are the least abundant monocyclic aromatic hydrocarbons in the produced waters.

Concentrations of individual and total monocyclic aromatic hydrocarbons were also measured in surface water samples collected 5, 100, and 2,000 m from the four produced water discharges. In all but one case, total benzenes concentrations in the ambient seawater decrease with distance from the discharges (**Table 9.8**). At VR 214A, the mean total benzenes concentration is higher at 100 than at 5 m from the discharge. It is difficult to prevent contamination of water samples with BTEX from exogenous sources (e.g., exhaust gas from the boat motor). Therefore, the 100 m samples could have been contaminated with a trace of BTEX.

In three of four cases, the concentration of BTEX in the produced water plume is diluted by more than 100-fold within 5 m of the discharge (**Table 9.8**). At SMI 130B, the dilution of total benzenes in surface water 5 m from the discharge is 41-fold. Dilutions at 2,000 m are in excess of 3,000-fold in all four cases. The rapid decrease in concentrations of total benzenes in the receiving water environment is due to a combination of physical dilution and evaporation.

In most cases, dilution is most rapid for benzene and decreases with increasing molecular weight of monocyclic aromatic hydrocarbons (**Tables 9.10** through **9.13**). This probably is due to the decreasing volatility with increasing molecular weight for aromatic hydrocarbons. Near three of the four platform discharges, dilutions of the individual monocyclic aromatic hydrocarbons are in excess of 100-fold at 5 m. At SMI 130B, dilutions of monocyclic aromatic hydrocarbons 5 m from the discharge are in the range of 20 to 50-fold.

At all three distances from the four produced water discharges, benzene and toluene are the most abundant monocyclic aromatic hydrocarbons in surface waters. The three xylene isomers usually are the next most abundant monocyclic aromatic hydrocarbons in the ambient seawaters near the discharges. Concentrations of C_3-benzenes and C_4-benzenes are below the MDLs at most distances from the produced water discharges. These alkylbenzenes, as well as the other monocyclic aromatic hydrocarbons, are present at higher concentrations in surface water 100 m from VR 214A than at 5 m. Ambient seawater 5 m from the discharge at SMI 130B contains 3.6 μg/L C_4-benzenes; C_4-benzenes were not detected in any of the produced water samples from this platform.

Table 9.8. Dilution of total benzenes in the receiving water from offshore produced water facilities. Mean concentrations are in μg/L.

Platform	Sample/Distance	Benzenes (Mean Concentration)	Dilution
HI A-595CF	Produced Water	1,800	0
	5 m	6.7	260
	100 m	0.59	3,000
	2,000 m	0.36	4,900
SMI 130B	Produced Water	3,000	0
	5 m	74	41
	100 m	0.90	3,400
	2,000 m	0	∞
SMI 236A	Produced Water	5,200	0
	5 m	36	140
	100 m	6.9	750
	2,000 m	0.68	7,600
VR 214A	Produced Water	3,600	0
	5 m	2.3	1,600
	100 m	24	150
	2,000 m	0.34*	11,000

* One of three replicate water samples contained an anomalously high concentration of total benzenes (9.9 μg/L) and was not included in the mean.

Table 9.9. Mean concentrations of individual and total monocyclic aromatic hydrocarbons in produced water from four Component 1 site discharges to the northwestern Gulf of Mexico. Concentrations are in μg/L.

Compound	HI A-595CF	SMI 130B	SMI 236A	VR 214A
Benzene	820	1,200	2,500	1,400
Toluene	490	1,100	1,500	1,100
Ethylbenzene	52	76	100	110
m-,p-Xylenes	180	360	460	350
o-Xylene	110	180	230	230
C_3-Benzenes	100	140	260	290
C_4-Benzenes	27	ND	70	110
Total Target Benzenes	1,800	3,000	5,200	3,600

Table 9.10. Mean concentrations of monocyclic aromatic hydrocarbons in ambient surface seawater 5, 100, and 2,000 m from the produced water discharge at HI A-595CF and dilution of each compound at 5 m compared to concentrations in produced water. Concentrations are μg/L.

Compound	5 m	100 m	2,000 m	Dilution at 5 m
Benzene	2.7	0.28	0.10	300
Toluene	1.8	0.27	0.32	270
Ethylbenzene	0.21	0.04	0.02	240
m-,p-Xylenes	0.86	0.16	0.11	210
o-Xylenes	0.45	0.07	ND	240
C_3-Benzenes	0.96	ND	ND	28
C_4-Benzenes	ND	ND	ND	∞

Table 9.11. Mean concentrations of monocyclic aromatic hydrocarbons in ambient surface seawater 5, 100, and 2,000 m from the produced water discharge at SMI 130A and dilution of each compound at 5 m compared to concentrations in produced water. Concentrations are μg/L.

Compound	5 m	100 m	2,000 m	Dilution at 5 m
Benzene	24	0.53	ND	50
Toluene	23	0.41	ND	46
Ethylbenzene	1.9	ND	ND	39
m-,p-Xylenes	9.4	0.20	ND	38
o-Xylenes	4.8	ND	ND	37
C_3-Benzenes	7.1	ND	ND	20
C_4-Benzenes	3.6	ND	ND	+

\+ Concentration in ambient seawater higher than that in produced water.

Table 9.12. Mean concentrations of monocyclic aromatic hydrocarbons in ambient surface seawater 5, 100, and 2,000 m from the produced water discharge at SMI 236A and dilution of each compound at 5 m compared to concentrations in produced water. Concentrations are μg/L.

Compound	5 m	100 m	2,000 m	Dilution at 5 m
Benzene	17	3.3	1.5	150
Toluene	10	2.0	0.66	150
Ethylbenzene	0.68	0.13	0.06	150
m-,p-Xylenes	3.3	0.67	0.32	140
o-Xylenes	1.6	0.33	0.15	140
C_3-Benzenes	2.6	0.45	0.28	100
C_4-Benzenes	1.0	ND	ND	69

Table 9.13. Mean concentrations of monoaromatic hydrocarbons in ambient surface seawater 5, 100, and 2,000 m from the produced water discharge at VR 214A and dilution of each compound at 5 m compared to concentrations in produced water. Concentrations are μg/L.

Compound	5 m	100 m	2,000 m	Dilution at 5 m
Benzene	1.0	13	1.1	1,400
Toluene	0.79	8.6	1.0	1,400
Ethylbenzene	0.05	0.62	0.20	2,300
m-,p-Xylenes	0.30	3.3	0.83	1,200
o-Xylenes	0.16	2.0	1.5	1,400
C_3-Benzenes	ND	4.6	0.96	∞
C_4-Benzenes	ND	3.4	ND	∞

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 = 2.9 million gal/day) 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.

Only traces of benzenes are present in surface seawater at the four reference locations (**Table 9.14**). Most concentrations of individual and total benzenes are below the MDL. Most measurable concentrations are below 1.0 μg/L. One sample contains 2.9 μg/L and may have been contaminated from an exogenous source. The presence of 0.35 μg/L benzene in this seawater sample indicates that the monocyclic aromatic hydrocarbons in the sample were of very recent origin (the half life of benzene in surface waters is a few hours), lending support to the theory that the hydrocarbons in the sample are from sampling or laboratory contamination.

Concentrations of BTEX in open waters of the Gulf of Mexico away from produced water discharges and other point sources usually are less than 0.1 μg/L, though concentrations up to about 0.5 μg/L frequently are encountered in clean coastal waters of the Gulf (Sauer *et al.*, 1978; Sauer, 1981). The most abundant monocyclic aromatic hydrocarbons detected in surface water from the reference stations are toluene, followed by xylenes. Background concentrations of toluene in waters of the open Gulf of Mexico are in the range of 0.003 to 0.03 μg/L; in coastal waters of the Gulf, background concentrations of toluene are in the range of 0.01 to 0.06 μg/L (Sauer, 1981). Surface water from the mouth of the Brazos River, TX contains up to 0.11 μg/L toluene and 0.23 μg/L benzene (McDonald *et al.*, 1988). The surface water sample from SMI 186/195 contains 0.88 μg/L toluene.

Table 9.14. Range of concentrations of total monocyclic aromatic hydrocarbons in surface waters from the four reference sites. Concentrations are μg/l.

Reference Site	Concentration Range	Benzenes Present
WC 448	ND	---
GA A-90	ND - 0.07	toluene
GA A-205	ND - 0.81	toluene, xylenes
SMI 186/195	ND - 2.9	benzene, toluene, elthybenzene, xylenes, C_3-benzenes

9.2.3.2 Ecorisk of Monocyclic Aromatic Hydrocarbons in Ambient Seawater Near Offshore Produced Water Discharges

Monocyclic aromatic hydrocarbons in produced water are diluted rapidly following discharge of produced water to the ocean. In the present study, dilutions of individual and total monocyclic aromatic hydrocarbons usually are in excess of 100-fold within 5 m of the discharge. Similar or even greater dilutions of BTEX compounds have been documented by others in receiving waters elsewhere (Brooks *et al.*, 1980; Terrens and Tait, 1996). It is highly unlikely that marine plants and animals will be exposed for more than a very brief time to less than 100-fold dilutions, relative to concentrations in the treated produced water, of monocyclic aromatic hydrocarbons in receiving waters near offshore produced water discharges. Therefore, concentrations of individual monocyclic aromatic hydrocarbons equivalent to 100-fold dilutions of produced water from the four offshore discharges were used to estimate potential risks to marine animals from water-column exposure to these chemicals.

An estimate can be made of the contribution of individual and total monocyclic aromatic hydrocarbons to the toxicity to marine organisms of a 100 to 1 dilution of produced water by dividing the estimated ambient concentrations of each aromatic hydrocarbon by its marine chronic water quality criterion to produce a measure of toxic units contributed to the mixture by each chemical (**Tables 9.15** through **9.18**). EPA (1992) has published marine chronic values for several monocyclic aromatic hydrocarbons; chronic values for the other monocyclic aromatic hydrocarbons were estimated (Parametrix, Inc., 1995).

Total monocyclic aromatic hydrocarbons in 100-fold dilutions of the four produced waters contribute 0.034 to 0.083 toxic units to the mixtures in the receiving water environment. Benzene and ethylbenzene contribute the most to the toxic units of the four diluted produced waters. The low values for total toxic units of monocyclic aromatic hydrocarbons in the diluted produced waters indicate that these compounds, representing the most abundant aromatic hydrocarbons in most produced waters, would be completely nontoxic to plants and animals in the receiving water environment of an offshore produced water discharge.

The only plants and animals that might be exposed to less than a 100-fold dilution of produced water are biofouling organisms attached to various platform structures located near the produced water discharge pipe. If these organisms are exposed continuously to an average dose of a 10-fold dilution of the produced water, the highest potential toxicity would be at SMI 236A where the organisms would be exposed to up to 0.83 toxic units of monocyclic aromatic hydrocarbons (**Table 9.17**). Most species of marine biofouling organisms would not be harmed by chronic exposure to these concentrations of total monocyclic aromatic hydrocarbons.

Table 9.15. Marine chronic values (marine chronic water quality criteria), concentrations in 100-fold diluted produced water (PW), and toxic units (ambient concentration/chronic value) for monocyclic aromatic hydrocarbons in produced water from HI A-595CF. Chronic Values are from EPA (1992) and Parametrix, Inc. (1995). Concentrations are μg/L.

Compound	Chronic Value	Concentration in 1/100 PW	Toxic Units
Benzene	700	8.2	0.012
Toluene	5,000	4.9	0.0009
Ethylbenzene	43	0.52	0.012
m-,p-Xylenes	730	1.8	0.002
o-Xylenes	600	1.1	0.002
C_3-Benzenes	393	1.0	0.003
C_4-Benzenes	173	0.27	0.002
Total Monoaromatics	---	18	0.034

Table 9.16. Marine chronic toxicity values (marine chronic water quality criteria), concentrations in 100-fold diluted produced water (PW), and toxic units (ambient concentration/chronic value) for monocyclic aromatic hydrocarbons in produced water from SMI 130B. Chronic Values are from EPA (1992) and Parametrix, Inc. (1995). Concentrations are μg/L.

Compound	Chronic Value	Concentration in 1/100 PW	Toxic Units
Benzene	700	12	0.017
Toluene	5,000	11	0.002
Ethylbenzene	43	0.76	0.018
m-,p-Xylenes	730	3.6	0.005
o-Xylenes	600	1.8	0.003
C_3-Benzenes	393	1.4	0.004
C_4-Benzenes	173	ND	---
Total Monoaromatics	---	30	0.049

Table 9.17. Marine chronic toxicity values (marine chronic water quality criteria), concentrations in 100-fold diluted produced water (PW), and toxic units (ambient concentration/chronic value) for monocyclic aromatic hydrocarbons in produced water from SMI 236A. Chronic Values are from EPA (1992) and Parametrix, Inc. (1995). Concentrations are μg/L.

Compound	Chronic Value	Concentration in 1/100 PW	Toxic Units
Benzene	700	25	0.036
Toluene	5,000	15	0.003
Ethylbenzene	43	1.0	0.023
m-,p-Xylenes	730	4.6	0.006
o-Xylenes	600	2.3	0.004
C_3-Benzenes	393	2.6	0.007
C_4-Benzenes	173	0.70	0.004
Total Monoaromatics	—	52	0.083

Table 9.18. Marine chronic toxicity values (marine chronic water quality criteria), concentrations in 100-fold diluted produced water (PW), and toxic units (ambient concentration/chronic value) for monocyclic aromatic hydrocarbons in produced water from VR 214A. Chronic Values are from EPA (1992) and Parametrix, Inc. (1995). Concentrations are μg/L.

Compound	Chronic Value	Concentration in 1/100 PW	Toxic Units
Benzene	700	14	0.02
Toluene	5,000	11	0.002
Ethylbenzene	43	1.1	0.03
m-,p-Xylenes	730	3.5	0.005
o-Xylenes	600	3.5	0.005
C_3-Benzenes	393	2.3	0.004
C_4-Benzenes	173	2.9	0.007
Total Monoaromatics	—	37	0.074

EPA (1991) has defined nonpolar organic chemicals with log K_{ow} greater than 3.5 as bioconcentratable. Therefore, the BTEX compounds, which have values for log K_{ow} between 2.13 and 3.2, are not expected to bioconcentrate to a significant degree in tissues of marine organisms in the immediate vicinity of the produced water discharges. C_3- and C_4-benzenes have log K_{ow}s of about 4.0 and might bioconcentrate to some extent. The 100-fold dilutions of produced water contain up to about 2 μg/L of these more highly alkylated benzenes. Bivalves attached to platform structures near the produced water outfall could bioconcentrate these compounds to concentrations as high as 20 mg/kg (parts per million). This concentration probably would not seriously harm the bivalves themselves (McCarty *et al.*, 1992); however, consumers, such as fish, of the bivalves may bioaccumulate the hydrocarbons in their tissues. Nonpolar organic chemicals with log K_{ow} below about 6 do not biomagnify in marine food webs (Thomann, 1989). Fish and most other marine animals have an active mixed function oxygenase system that rapidly converts aromatic hydrocarbons to polar metabolites that are excreted rapidly, preventing accumulation of these compounds to high concentrations in the tissues (Stegeman, 1981; Van Veld, 1990). Therefore, it is unlikely that bioconcentration of highly alkylated benzenes by marine animals near the produced water outfall will have adverse effects on the local food web.

9.2.3.3 Polycyclic Aromatic Hydrocarbons

The mean concentration of total PAHs in the four produced water discharges ranges from 58 to 600 μg/L (**Table 9.19**). These concentrations are in the low to middle part of the range of PAH concentrations (80 to 1,860 μg/L) reported previously for produced waters discharged to the western Gulf of Mexico (Neff, 1996a).

Most of the PAHs in the produced waters are the low molecular weight PAHs naphthalenes, fluorenes, phenanthrenes, and dibenzothiophenes. They represent 95% to more than 99% of the total PAHs in the four produced waters (**Table 9.19**).

The PAHs in produced water from the four offshore production platforms are dominated by naphthalene and alkyl naphthalenes, with lower concentrations of other 2- and 3-ring PAHs and their alkyl homologues (**Table 9.19**). Only trace amounts of 4-, 5-, and 6-ring PAHs are present. The most abundant of these higher molecular weight PAHs are alkyl fluoranthenes and pyrenes, chrysenes, and perylene. Acenaphthylene, acenaphthene, benz[a]anthracene, indeno[1,2,3-cd]pyrene, and dibenz[a,h]anthracene are present in three or four of the produced water samples at concentrations below the detection limit of the analytical method ($\approx$ 0.001 μg/L). Produced water from SMI 130B contains the highest concentrations of total PAHs and most individual PAHs. Mean concentrations above about 1 μg/L of alkylchrysenes and perylene (in excess of their aqueous solubilities) in these samples indicates that produced water from this platform contains some dispersed or particulate oil.

This PAH composition of the other samples is typical of produced water that has been treated effectively to remove dispersed oil droplets (Neff, 1987). As is typical of oil, alkyl PAHs usually are more abundant than the parent compounds and phenanthrene is much more abundant than anthracene (Neff, 1979) (**Table 9.19**). The most abundant PAH in three of the four samples is naphthalene. This preference of naphthalene over alkyl naphthalenes is attributable to the much greater solubility of the parent compound than the alkyl homologs, lending support to the suggestion that these three produced waters contain PAHs mainly in solution: little or no dispersed or particulate oil is present.

Table 9.19. Mean concentrations of individual and total PAHs in produced water from four discharges to the northwestern Gulf of Mexico. Concentrations are in μg/L.

Compound	HI A-595CF	SMI 130B	SMI 236A	VR 214A
Naphthalene	20	58	90	57
C_1-Naphthalene	14	69	73	34
C_2-Naphthalene	8.0	88	45	16
C_3-Naphthalene	5.2	83	20	8.1
C_4-Naphthalene	2.6	52	9.0	3.7
Acenaphthylene	0.00	0.00	0.00	0.00
Acenaphthene	0.06	0.00	0.00	0.00
Biphenyl	0.78	6.8	11	4.2
Fluorene	0.16	2.8	0.96	0.31
C_1-Fluorenes	0.32	8.7	1.6	0.38
C_2-Fluorenes	0.56	16	2.4	0.56
C_3-Fluorenes	0.68	18	2.3	0.60
Anthracene	0.01	0.45	0.07	0.04
Phenanthrene	0.26	8.8	1.2	0.32
C_1-Phenanthrenes*	0.54	25	1.9	0.37
C_2-Phenanthrenes*	0.82	31	2.3	0.52
C_3-Phenanthrenes*	0.72	22	1.7	0.40
C_4-Phenanthrenes	0.41	11	0.80	0.39
Dibenzothiophene	0.22	4.6	0.24	0.10
C_1-Dibenzothiophenes	0.52	13	0.57	0.25
C_2-Dibenzothiophenes	1.0	25	0.76	0.27
C_3Dibenzothiophenes	1.1	25	0.70	0.29
Fluoranthene	0.01	0.12	0.05	0.02
Pyrene	0.01	0.29	0.05	0.02
C_1-Fluoranthenes/Pyrenes	0.06	2.4	0.30	0.08
C_2-Fluoranthenes/Pyrenes	0.08	4.4	0.26	0.05
C_3-Fluoranthenes/Pyrenes	0.12	5.3	0.31	0.06
Benz(a)anthracene	0.00	0.20	0.00	0.00
Chrysene	0.00	0.85	0.02	0.00
C_1-Chrysenes	0.03	2.4	0.11	0.01

Table 9.19. (Continued).

Compound	HI A-595CF	SMI 130B	SMI 236A	VR 214A
C_2-Chrysenes	0.06	3.5	0.20	0.03
C_3-Chrysenes	0.09	3.3	0.21	0.05
C_4-Chrysenes	0.09	2.6	0.21	0.04
Benzo(b)fluoranthene	0.00	0.03	0.02	0.00
Benzo(k)fluoranthene	0.00	0.07	0.00	0.00
Benzo(e)pyrene	0.00	0.10	0.00	0.00
Benzo(a)pyrene	0.02	0.09	0.01	0.01
Perylene	0.08	2.0	0.36	0.09
Indeno(1,2,3-cd)pyrene	0.00	0.00	0.01	0.00
Dibenz(a,h)anthracene	0.00	0.02	0.00	0.00
Benzo(ghi)perylene	0.00	0.03	0.01	0.00
Total PAHs	58	600	270	130
Total Low MW PAHs	58	570	270	130

* May include alkylanthracenes.

PAHs are diluted rapidly when produced water is discharged to the ocean. Total PAH concentrations in surface water collected approximately 2,000 m down-current from the four produced water discharges are diluted by factors of 1,000 to 3,600 compared to concentrations in the undiluted produced water (**Table 9.20**). The low molecular weight fraction of the PAH assemblage is diluted even more. Concentrations of low molecular weight PAHs in the surface waters near the four produced water discharges are 62% to 80% of the concentrations of total PAHs; in the produced water, more than 95% of the total PAHs in the undiluted produced waters are low molecular weight compounds. The greater dilution of low molecular weight than high molecular weight PAHs is because ambient surface water near the produced water discharges and at the reference sites contains some high molecular weight, pyrogenic PAHs not derived from the produced water, and low molecular weight PAHs tend to be less persistent in the environment than high molecular weight PAHs. The lowest dilution is for the lowest volume, lowest concentration produced water discharge (from HI A-595CF). The reason for this is that the concentrations of total PAHs in this produced water are closer to the background concentration of total PAHs in surface waters of the northwestern Gulf of Mexico.

The composition of the PAH assemblage in surface water samples near the four produced water discharges is reasonably consistent (**Table 9.21**). The only low molecular weight PAHs present in surface water at three or four of the sites are C_2-naphthalenes, biphenyl, fluorene, and C_1-phenanthrenes. Dibenzothionene and alkyldibenzothionenes are present in water near HI A-595CF and VR 214A. These PAHs are strongly indicative of a petroleum source, possibly produced water. The water samples also contain small amounts of fluoranthene, pyrene, benzo(a)pyrene and perylene, all strongly indicative of a pyrogenic source. Thus, the PAHs in surface waters 2,000 m down-current from four offshore produced water discharges probably are derived from a combination of petrogenic sources, such as produced water discharges and releases of refined oil products from vessels, and pyrogenic sources, such as deposition of exhaust and combustion soot from the atmosphere.

Surface water samples from four reference sites in the northwestern Gulf of Mexico away from produced water discharges contain 0.05 to 0.38 μg/L total PAHs (**Table 9.20**). Thus, concentrations of PAHs in ambient surface waters of the northwestern Gulf of Mexico are not notably higher near offshore produced water discharges than elsewhere in the offshore environment. Concentrations of low molecular weight PAHs in the surface waters at the reference sites are 32% to 92% of the concentrations of total PAHs, similar to the relative abundance of low molecular weight PAHs in surface waters near the produced water discharges. High-volume produced water discharges do not seem to contribute measurably to the concentrations of total PAHs in surface waters at least 2,000 m from offshore platforms.

The highest mean concentration of total PAHs in surface water at a reference site (SMI 186/195) is 0.38 μg/L. One of the three replicate samples from this site contains 1.1 μg/L total PAHs, 97% of which are low molecular weight compounds. The other two samples contain 0.06 and 0.02 μg/L (mean 0.04 μg/L) total PAHs, 32% to 40% of which are low molecular weight compounds. It is probable that the one high value sample contains a droplet of a fairly fresh crude or refined petroleum product (higher concentrations of alkyl than parent naphthalenes, fluorenes, phenanthrenes, and dibenzothiophenes). The other two samples contain mainly high molecular weight unalkylated PAHs characteristic of a pyrogenic source. One of the three replicate samples from GA A-90 (reference site) also contains a slightly elevated concentration of total PAHs (0.161 μg/L), compared to the other two replicates (0.05 and 0.11 μg/L, average 0.08 μg/L). If these few, possibly anomalous samples are excluded, typical background concentrations of total PAHs in surface waters of the northwestern Gulf of Mexico are in the range of about 0.05 to 0.1 μg/L.

Table 9.20. Mean concentrations of total PAHs and low molecular weight PAHs in produced water from four offshore platforms and in ambient seawater 2,000 m from the four platforms and from four reference sites. Dilution of PAH from produced water in ambient seawater is also given. Concentrations are μg/L.

Site	PAH Fraction	Produced Water	Ambient Seawater	Dilution
HI A-595CF	Total	58	0.06	1000
	LMW PAHs	58	0.04	1400
SMI 130B	Total	600	0.17	3600
	LMW PAHs	570	0.10	5400
SMI 236A	Total	270	0.07	3600
	LMW PAHs	270	0.06	4700
VR 214A	Total	130	0.06	2100
	LMW PAHs	130	0.05	2700
GA A-205	Total	No Discharge	0.05	---
	LMW PAHs		0.02	---
GA A-90	Total	No Discharge	0.10	---
	LMW PAHs		0.09	---
SMI 186/195	Total	No Discharge	0.38	---
	LMW PAHs		0.35	---
WC 448	Total	No Discharge	0.14	---
	LMW PAHs		0.10	---

LMW PAHs = low molecular weight polycyclic aromatic hydrocarbons.

Table 9.21. Mean concentrations of individual and total PAHs in ambient water 2,000 m from four offshore produced water discharges. Concentrations are μg/L.

Compound	HI A-595CF	SMI 130B	SMI 236A	VR 214A
Naphthalene	ND	0.038	ND	ND
C_1-Naphthalene	ND	0.019	0.006	ND
C_2-Naphthalene	0.004	0.020	0.023	0.008
C_3-Naphthalene	ND	ND	0.004	ND
C_4-Naphthalene	ND	ND	ND	ND
Acenaphthylene	ND	ND	ND	ND
Acenaphthene	ND	ND	ND	ND
Biphenyl	0.002	0.004	0.008	0.003
Fluorene	ND	0.001	0.002	0.011
C_1-Fluorenes	ND	ND	ND	ND
C_2-Fluorenes	ND	ND	ND	ND
C_3-Fluorenes	ND	ND	ND	ND
Anthracene	ND	0.012	0.003	ND
Phenanthrene	ND	0.004	0.001	ND
C_1-Phenanthrenes*	ND	0.004	0.006	0.002
C_2-Phenanthrenes*	ND	0.003	0.004	ND
C_3-Phenanthrenes*	ND	ND	ND	ND
C_4-Phenanthrenes	ND	ND	ND	ND
Dibenzothiophene	0.001	ND	ND	0.001
C_1-Dibenzothiophenes	0.004	ND	ND	0.002
C_2-Dibenzothiophenes	0.011	ND	ND	0.007
C_3Dibenzothiophenes	0.022	ND	ND	0.015
Fluoranthene	0.002	0.011	0.002	0.001
Pyrene	0.001	0.008	0.002	ND
C_1-Fluoranthenes/Pyrenes	ND	ND	ND	ND
C_2-Fluoranthenes/Pyrenes	ND	ND	ND	ND
C_3-Fluoranthenes/Pyrenes	ND	ND	ND	ND
Benz(a)anthracene	ND	ND	ND	ND
2Chrysene	ND	0.004	ND	ND
C_1-Chrysenes	ND	ND	ND	ND

Table 9.21. (Continued).

Compound	HI A-595CF	SMI 130B	SMI 236A	VR 214A
C_2-Chrysenes	ND	ND	ND	ND
C_3-Chrysenes	ND	ND	ND	ND
C_4-Chrysenes	ND	ND	ND	ND
Benzo(b)fluoranthene	ND	0.006	ND	ND
Benzo(k)fluoranthene	ND	0.003	ND	ND
Benzo(e)pyrene	ND	0.004	ND	ND
Benzo(a)pyrene	0.012	0.006	0.013	0.010
Perylene	0.002	0.004	0.002	ND
Indeno(1,2,3-cd)pyrene	ND	0.002	ND	ND
Dibenz(a,h)anthracene	ND	ND	ND	ND
Benzo(ghi)perylene	ND	0.014	ND	ND
Total PAHs	0.058	0.17	0.074	0.060
Total Low MW PAHs	0.042	0.10	0.056	0.049

ND = Concentration less than about 0.0004 μg/L.

Concentrations of total PAHs (sum of 14 parent PAHs) in waters of Chesapeake Bay, USA are in the range of 0.0025 to 0.034 μg/L (Ko and Baker, 1994; Dickhut and Gustafson, 1995). By comparison, the total concentration of these 14 PAHs in the most heavily contaminated reference water sample in this study is 0.069 μg/L. The concentration of total PAHs (the same analytes as listed in **Table 9.19**) in surface waters of areas of Prince William Sound not affected by the *Exxon Valdez* oil spill of 1989 was in the range of 0.015 to 0.025 μg/L (Neff and Burns, 1996). Thus, outer continental shelf waters of the northwestern Gulf of Mexico are slightly contaminated with PAHs. Undoubtedly, produced water discharges are just one of several sources of these aqueous PAHs. The PAH assemblages in surface waters often are dominated by the higher molecular weight PAHs that are rare in produced water but abundant in pyrogenic PAH sources. Thus, other sources of these PAHs include emissions of fuel and exhaust from motor vessel traffic, coastal and river runoff, natural oil seeps, and aerial deposition of PAHs from combustion sources (Neff, 1979).

More individual PAHs were identified and quantified in the PAH assemblages in surface water from the four reference sites than in water from the four produced water discharge sites (**Table 9.22**). Sixteen PAHs were quantified in water samples from three or four of the reference sites. As at the produced water discharge sites, the surface water samples from the four reference sites contain a mixture of PAHs of petrogenic and pyrogenic origin. At all but one of the four reference sites, low molecular weight PAHs are more abundant than high molecular weight PAHs, suggesting that crude and refined petroleum are the main source of PAHs in these reference areas. The petroleum PAHs may be from small oil or oily water discharges from commercial vessels, including oil tankers.

9.2.3.4 Ecorisk of Polycyclic Aromatic Hydrocarbons in Ambient Seawater Near Offshore Produced Water Discharges

The U.S. EPA has published acute and chronic water quality criteria for protection of marine life for only five individual PAHs and for total PAHs. The published or estimated chronic criterion values, which range from 4.6 μg/L for phenanthrene to 710 μg/L for acenaphthene, are orders of magnitude higher than concentrations of individual and total PAHs measured in ambient seawater samples approximately 2,000 m down current from the produced water discharges (**Table 9.21**).

Produced water discharged to open ocean waters usually is diluted by more than 100-fold within 100 m 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. Therefore, it is unlikely that any marine organisms, except possibly some biofouling organisms on legs of the platform near the produced water discharge point, 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 as an upper end estimate of the exposure of marine organisms to PAHs from produced water.

Table 9.22. Mean concentrations of individual and total PAHs in surface water from four offshore reference sites in the northwestern Gulf of Mexico. Concentrations are in µg/L.

Compound	GA A-205	GA A-90	SMI 186	WC 448
Naphthalene	ND	ND	0.033	0.038
C_1-Naphthalene	ND	ND	0.031	0.024
C_2-Naphthalene	ND	0.009	0.037	0.008
C_3-Naphthalene	ND	0.002	0.037	ND
C_4-Naphthalene	ND	ND	0.027	ND
Acenaphthylene	ND	ND	ND	ND
Acenaphthene	ND	ND	0.001	ND
Biphenyl	0.003	0.003	0.007	0.006
Fluorene	0.001	0.002	0.002	0.003
C_1-Fluorenes	ND	0.004	0.007	ND
C_2-Fluorenes	ND	0.009	0.014	ND
C_3-Fluorenes	ND	0.009	0.019	ND
Anthracene	ND	ND	0.007	0.011
Phenanthrene	0.003	0.001	0.003	0.004
C_1-Phenanthrenes*	0.004	0.007	0.017	0.002
C_2-Phenanthrenes*	0.002	0.008	0.022	0.003
C_3-Phenanthrenes*	ND	0.008	0.019	ND
C_4-Phenanthrenes	ND	0.001	0.008	ND
Dibenzothiophene	ND	0.001	0.003	ND
C_1-Dibenzothiophenes	ND	0.003	0.009	ND
C_2-Dibenzothiophenes	0.002	0.009	0.019	ND
C_3Dibenzothiophenes	ND	0.014	0.026	ND
Fluoranthene	0.009	ND	0.004	0.008
Pyrene	0.007	ND	0.002	0.005
C_1-Fluoranthenes/Pyrenes	ND	0.004	0.002	ND
C_2-Fluoranthenes/Pyrenes	ND	0.005	0.004	ND
C_3-Fluoranthenes/Pyrenes	ND	ND	ND	ND
Benz(a)anthracene	ND	ND	ND	ND
Chrysene	0.003	ND	0.002	0.004

Table 9.22. (Continued).

Compound	GA A-205	GA A-90	SMI 186	WC 448
C_1-Chrysenes	ND	ND	ND	ND
C_2-Chrysenes	ND	0.001	ND	ND
C_3-Chrysenes	ND	ND	ND	ND
C_4-Chrysenes	ND	ND	ND	ND
Benzo(b)fluoranthene	0.001	ND	ND	0.004
Benzo(k)fluoranthene	0.001	0.001	0.001	0.002
Benzo(e)pyrene	0.002	0.001	0.002	0.003
Benzo(a)pyrene	0.004	0.001	0.003	0.004
Perylene	0.004	0.001	0.004	0.003
Indeno(1,2,3-cd)pyrene	0.002	ND	0.001	0.003
Dibenz(a,h)anthracene	ND	ND	ND	ND
Benzo(ghi)perylene	0.002	ND	0.005	0.004
Total PAHs	0.050	0.10	0.38	0.14
Total Low MW PAHs	0.016	0.090	0.35	0.10

ND = Concentration less than about 0.0004 μg/L.

The concentrations of PAHs in 100-fold dilutions of produced water from the four offshore produced water discharges are well below EPA chronic criterion values and chronic values that were modeled or interpolated (where no published value exists) (**Tables 9.23** through **9.26**). The fractional chronic toxicity of each PAH in the dilute produced water can be estimated as toxic units (observed concentration/chronic value). Assuming that the toxicity of different individual PAHs is additive, the toxicity of all the target PAHs in the diluted produced water (total PAHs) is equal to the sum of the toxicities of all the individual PAHs.

The estimated 100-fold dilutions of the four produced water samples have mean total toxic units attributable to PAHs ranging from 0.041 to 1.0 toxic units. The highest value is for diluted produced water from SMI 130B. It is possible that some sensitive species of marine organisms would suffer adverse sublethal effects during chronic exposure to a 100-fold or less dilution of produced water from this platform. The dilute produced water from the other three platforms contains total PAH concentrations well below concentrations that might lead to chronic sublethal effects.

The PAHs contributing most to the estimated toxicity of produced water from SMI 130B are C_2-naphthalenes, C_3-chrysenes, and C_4-chrysenes. C_4-naphthalenes, C_3-phenanthrenes, and C_4-phenanthrenes also contribute significantly to the estimated toxicity of the PAH mixture in the dilute produced water. There are no data on the aquatic toxicity of these alkylated PAHs, except C_2-naphthalenes. The chronic values were modeled based on their estimated log octanol/water partition coefficients (log K_{ow}) (McCarty *et al.*, 1992) and may be overestimates. These alkyl PAHs, particularly the alkylchrysenes, have very low aqueous solubilities, particularly in seawater. It may not be possible to get enough of these chemicals into true solution (the most bioavailable form) to cause toxic effects (Neff *et al.*, 1994). Therefore, the total PAHs in produced water from SMI 130B probably represent substantially less than 1 toxic unit, indicating that they are not toxic at the expected concentrations in the receiving water environment.

The few PAHs for which water quality criteria are available are representative of the toxicity range of low molecular weight PAHs of the types found in produced water. For low molecular weight PAHs, the toxic concentration in water appears to lie between 20% and 70% of the saturated concentration (Abernethy *et al.*, 1986). The toxic concentration for less soluble, higher molecular weight PAHs is at or in excess of the saturation concentration. Thus, the only PAHs from produced water that can reach lethal concentrations in receiving waters are the 2- and 3-ring PAHs. These PAHs have aqueous solubilities in the range of about 30 mg/L (naphthalene) to about 0.3 mg/L (methylphenanthrene) (Mackay *et al.*, 1992b). Chronically toxic concentrations will range from about 6 to 600 μg/L. Therefore, individual and total PAHs are not likely to reach concentrations that are potentially harmful to marine organisms in the near-field and far-field of these four high volume produced water discharges to the open ocean.

9.2.3.5 Summary of Ecorisk of Metals and Aromatic Hydrocarbons in Ambient Seawater

The chemicals considered most likely to contribute to the toxicity of produced water to marine organisms are metals and aromatic hydrocarbons. Very low or high salinity, ionic ratios different from those in natural seawater, ammonia, and hydrogen sulfide often contribute to the toxicity of produced water in laboratory toxicity tests. Some of these toxicants are artifacts generated during storage of the produced water in the laboratory. Others of these parameters are likely to be diluted to safe levels even more rapidly than metals and hydrocarbons when treated produced water is discharged to the ocean. Thus, they probably do not contribute

Table 9.23. Marine chronic toxicity values, concentrations in the 100-fold diluted produced water (PW), and toxic units for PAHs in produced water from HI A-595CF. Chronic values are from Parametrix, Inc. (1995) or are one-tenth of the acute toxicities estimated with the regression of McCarty *et al.* (1992). Concentrations are in μg/L.

Compound	Chronic Value	Concentration in 1/100 PW	Toxic Units
Naphthalene	214	0.2	0.0009
C_1-Naphthalenes	170	0.14	0.0008
C_2-Naphthalenes	8	0.08	0.01
C_3-Naphthalenes	32	0.05	0.002
C_4-Naphthalenes	10	0.03	0.003
Biphenyl	460	0.008	<0.0001
Fluorene	4.6	0.002	0.0004
C_1-Fluorenes	31	0.003	<0.0001
C_2-Fluorenes	21	0.006	0.0003
C_3-Fluorenes	12	0.007	0.0006
Anthracene	2.9	0.0001	<0.0001
Phenanthrene	4.6	0.003	0.0007
C_1-Phenanthrenes	45	0.005	0.0001
C_2-Phenanthrenes	12	0.008	0.0007
C_3-Phenanthrenes	4	0.007	0.002
C_4-Phenanthrenes	2	0.004	0.002
Dibenzothiophene	42	0.002	<0.0001
C_1-Dibenzothiophenes	43	0.005	0.0001
C_2-Dibenzothiophenes	12	0.01	0.0008
C_3-Dibenzothiophenes	8	0.01	0.001
Fluoranthene	16	0.0001	<0.0001
Pyrene	9	0.0001	<0.0001
C_1-Fluoranthenes/pyrenes	8	0.0006	<0.0001
C_2-Fluoranthenes/pyrenes	3	0.0008	0.0003
C_3-Fluoranthenes/pyrenes	1	0.001	0.001
Benz(a)anthracene	20	ND	---
Chrysene	20	<0.0001	<0.0001
C_1-Chrysenes	2	0.0003	0.0002

Table 9.23. (Continued).

Compound	Chronic Value	Concentration in 1/100 PW	Toxic Units
C_2-Chrysenes	0.8	0.0006	0.0008
C_3-Chrysenes	0.3	0.0009	0.003
C_4-Chrysenes	0.09	0.0009	0.01
Benzo(b)fluoranthene	8	ND	—
Benzo(k)fluoranthene	6	ND	—
Benzo(e)pyrene	13	ND	—
Benzo(a)pyrene	0.5	0.0002	0.0004
Perylene	3	0.0008	0.0003
Indeno(1,2,3-cd)pyrene	2.4	ND	—
Dibenz(a,h)anthracene	7	ND	—
Benzo(ghi)perylene	3	ND	—
Total		0.58	0.041

Table 9.24. Marine chronic toxicity values, concentrations in the 100-fold diluted produced water (PW), and toxic units for PAHs in produced water from SMI 130B. Chronic values are from Parametrix, Inc. (1995) or are one-tenth of the acute toxicities estimated with the regression of McCarty *et al.* (1992). Concentrations are in μg/L.

Compound	Chronic Value	Concentration in 1/100 PW	Toxic Units
Naphthalene	214	0.58	0.003
C_1-Naphthalenes	170	0.69	0.004
C_2-Naphthalenes	8	0.88	0.11
C_3-Naphthalenes	32	0.83	0.026
C_4-Naphthalenes	10	0.52	0.052
Biphenyl	460	0.07	0.0002
Fluorene	4.6	0.03	0.007
C_1-Fluorenes	31	0.09	0.003
C_2-Fluorenes	21	0.16	0.008
C_3-Fluorenes	12	0.18	0.015
Anthracene	2.9	0.004	0.001
Phenanthrene	4.6	0.09	0.019
C_1-Phenanthrenes	45	0.25	0.006
C_2-Phenanthrenes	12	0.31	0.026
C_3-Phenanthrenes	4	0.22	0.055
C_4-Phenanthrenes	2	0.11	0.055
Dibenzothiophene	42	0.05	0.001
C_1-Dibenzothiophenes	43	0.13	0.003
C_2-Dibenzothiophenes	12	0.25	0.021
C_3-Dibenzothiophenes	8	0.25	0.031
Fluoranthene	16	0.001	0.0001
Pyrene	9	0.003	0.0003
C_1-Fluoranthenes/pyrenes	8	0.02	0.0025
C_2-Fluoranthenes/pyrenes	3	0.04	0.013
C_3-Fluoranthenes/pyrenes	1	0.05	0.04
Benz(a)anthracene	20	0.002	0.0001
Chrysene	20	0.008	0.0004
C_1-Chrysenes	2	0.02	0.01

Table 9.24. (Continued).

Compound	Chronic Value	Concentration in 1/100 PW	Toxic Units
C_2-Chrysenes	0.8	0.04	0.05
C_3-Chrysenes	0.3	0.03	0.1
C_4-Chrysenes	0.09	0.03	0.33
Benzo(b)fluoranthene	8	0.0003	<0.0001
Benzo(k)fluoranthene	6	0.0007	0.0001
Benzo(e)pyrene	13	0.001	<0.0001
Benzo(a)pyrene	0.5	0.0009	0.002
Perylene	3	0.02	0.007
Indeno(1,2,3-cd)pyrene	2.4	ND	---
Dibenz(a,h)anthracene	7	0.0002	<0.0001
Benzo(ghi)perylene	3	0.0003	0.0001
Total	---	6.1	1.0

Table 9.25. Marine chronic toxicity values, concentrations in the 100-fold diluted produced water (PW), and toxic units for PAHs in produced water from SMI 236A. Chronic values are from Parametrix, Inc. (1995) or are one-tenth of the acute toxicities estimated with the regression of McCarty *et al.* (1992). Concentrations are in μg/L.

Compound	Chronic Value	Concentration in 1/100 PW	Toxic Units
Naphthalene	214	0.9	0.004
C_1-Naphthalenes	170	0.73	0.004
C_2-Naphthalenes	8	0.45	0.056
C_3-Naphthalenes	32	0.2	0.006
C_4-Naphthalenes	10	0.09	0.009
Biphenyl	460	0.11	0.0002
Fluorene	4.6	0.01	0.002
C_1-Fluorenes	31	0.02	0.0006
C_2-Fluorenes	21	0.02	0.001
C_3-Fluorenes	12	0.02	0.002
Anthracene	2.9	0.0007	0.0002
Phenanthrene	4.6	0.01	0.002
C_1-Phenanthrenes	45	0.02	0.0004
C_2-Phenanthrenes	12	0.02	0.002
C_3-Phenanthrenes	4	0.02	0.005
C_4-Phenanthrenes	2	0.008	0.004
Dibenzothiophene	42	0.002	<0.0001
C_1-Dibenzothiophenes	43	0.006	0.0001
C_2-Dibenzothiophenes	12	0.008	0.0007
C_3-Dibenzothiophenes	8	0.007	0.0008
Fluoranthene	16	0.0005	<0.0001
Pyrene	9	0.0005	<0.0001
C_1-Fluoranthenes/pyrenes	8	0.003	0.0003
C_2-Fluoranthenes/pyrenes	3	0.003	0.001
C_3-Fluoranthenes/pyrenes	1	0.003	0.003
Benz(a)anthracene	20	ND	—
Chrysene	20	0.0002	<0.0001
C_1-Chrysenes	2	0.001	0.0005

Table 9.25. (Continued).

Compound	Chronic Value	Concentration in 1/100 PW	Toxic Units
C_2-Chrysenes	0.8	0.002	0.002
C_3-Chrysenes	0.3	0.002	0.007
C_4-Chrysenes	0.09	0.002	0.022
Benzo(b)fluoranthene	8	0.0002	<0.0001
Benzo(k)fluoranthene	6	<0.0001	<0.0001
Benzo(e)pyrene	13	ND	---
Benzo(a)pyrene	0.5	0.0001	0.0002
Perylene	3	0.004	0.001
Indeno(1,2,3-cd)pyrene	2.4	0.0001	<0.0001
Dibenz(a,h)anthracene	7	ND	---
Benzo(ghi)perylene	3	0.0001	<0.0001
Total	---	27	0.14

Table 9.26. Marine chronic toxicity values, concentrations in the 100-fold diluted produced water (PW), and toxic units for PAHs in produced water from VR 214A. Chronic values are from Parametrix, Inc. (1995) or are one-tenth of the acute toxicities estimated with the regression of McCarty *et al.* (1992). Concentrations are in μg/L.

Compound	Chronic Value	Concentration in 1/100 PW	Toxic Units
Naphthalene	214	0.57	0.003
C_1-Naphthalenes	170	0.34	0.002
C_2-Naphthalenes	8	0.16	0.02
C_3-Naphthalenes	32	0.08	0.0025
C_4-Naphthalenes	10	0.04	0.004
Biphenyl	460	0.04	<0.0001
Fluorene	4.6	0.003	0.0006
C_1-Fluorenes	31	0.004	0.0001
C_2-Fluorenes	21	0.006	0.0003
C_3-Fluorenes	12	0.006	0.0005
Anthracene	2.9	0.0004	0.0001
Phenanthrene	4.6	0.003	0.0006
C_1-Phenanthrenes	45	0.004	<0.0001
C_2-Phenanthrenes	12	0.005	0.0004
C_3-Phenanthrenes	4	0.004	0.001
C_4-Phenanthrenes	2	0.004	0.002
Dibenzothiophene	42	0.001	<0.0001
C_1-Dibenzothiophenes	43	0.002	<0.0001
C_2-Dibenzothiophenes	12	0.003	0.0002
C_3-Dibenzothiophenes	8	0.003	0.0004
Fluoranthene	16	0.0002	<0.0001
Pyrene	9	0.0002	<0.0001
C_1-Fluoranthenes/pyrenes	8	0.0008	0.0001
C_2-Fluoranthenes/pyrenes	3	0.0005	0.0002
C_3-Fluoranthenes/pyrenes	1	0.0006	0.0006
Benz(a)anthracene	20	ND	—
Chrysene	20	<0.0001	<0.0001
C_1-Chrysenes	2	0.0001	<0.0001

Table 9.26. (Continued).

Compound	Chronic Value	Concentration in 1/100 PW	Toxic Units
C_2-Chrysenes	0.8	0.0003	0.0004
C_3-Chrysenes	0.3	0.0005	0.002
C_4-Chrysenes	0.09	0.0004	0.004
Benzo(b)fluoranthene	8	<0.0001	<0.0001
Benzo(k)fluoranthene	6	<0.0001	<0.0001
Benzo(e)pyrene	13	<0.0001	<0.0001
Benzo(a)pyrene	0.5	<0.0001	<0.0002
Perylene	3	0.0009	0.0003
Indeno(1,2,3-cd)pyrene	2.4	ND	---
Dibenz(a,h)anthracene	7	ND	---
Benzo(ghi)perylene	3	ND	ND
Total	---	1.3	0.046

significantly to the toxicity of produced water following its discharge to the offshore marine waters where dilution is rapid.

The toxicity, measured as estimated toxic units, of total monocyclic aromatic hydrocarbons plus total PAHs plus total metals in 100-fold dilutions of the four produced water are in the range of 0.15 to 1.1 (**Table 9.27**). As discussed above, much of the estimated toxicity of the produced water containing the highest concentration of toxic units is attributable to highly alkylated medium and high molecular weight PAHs that may not be in true solution in the diluted produced water. The colloidal or particulate alkyl-PAHs are less bioavailable and toxic than PAHs in solution. Thus, the actual toxic units in this produced water probably are less than 1.0 (the aromatic hydrocarbons are present at a concentration below the chronic toxicity concentration).

It is more difficult to estimate the contribution of metals and metalloids to the toxicity of a 100-fold dilution of the four produced waters. The only metals present in the undiluted produced waters at more than 100 times their natural concentrations in ambient seawater are barium, iron, and manganese (**Table 9.3**). All three of these metals have a very low solubility in oxygenated natural seawater. These solubilities are below acutely lethal or chronic toxicity concentrations. Therefore, they cannot reach concentrations in solution high enough or long enough to cause harm to marine organisms.

Produced water from HI A-595CF contains the highest concentration (of the four produced waters analyzed) of most of the other metals analyzed in this study. The sum of the mean toxic units of all the metals, except barium, iron, and manganese, in a 100-fold dilution of produced water from this platform is 0.42 toxic units. Most of the metal toxicity (0.37 toxic units) in this produced water is attributable to zinc which is present in the produced water at a mean concentration of 3,000 μg/L. The total estimated toxicity (metals plus aromatic hydrocarbons) for a 100-fold dilution of this produced water is 0.49 toxic units, well below a value likely to cause harm to marine animals in the receiving waters of the discharge.

The 100-fold dilution of produced water containing the highest estimated toxic units (SMI 130B) attributable to aromatic hydrocarbons also contains 0.015 toxic units of metals. This brings the total estimated toxic units for this diluted produced water to 1.1 toxic units. The produced water discharge from SMI 130B is the highest volume of those monitored (3,600,000 L/d). It is possible that produced water concentrations up to the 100-fold dilution modeled here could persist over a small area (~ 20 to 30 m radius around the platform) long enough to cause adverse chronic or sublethal effects in some sensitive organisms. However, it is highly probable that the diluting plume of produced water will be moved over a wide area by tidal and longer-term water currents, so that concentrations of chemicals from produced water at any one location will vary widely over time, with most concentrations below the chronic toxicity concentrations. Thus, few attached or motile organisms will be exposed continuously for long periods of time to potentially toxic concentrations of the diluting produced water. At the other offshore produced water discharges, it is highly unlikely that concentrations of metals and aromatic hydrocarbons will ever reach concentrations that could be toxic to local marine organisms.

Table 9.27. Mean total toxic units for total monoaromatic hydrocarbons and total PAHs in 100-fold dilutions of produced water from the four offshore platforms.

Compound Class	HI A-595CF	SMI 130B	SMI 236A	VR 214A
Monocyclic Aromatics	0.034	0.049	0.083	0.074
PAHs	0.041	1.0	0.14	0.046
Total Metals	0.42	0.015	0.042	0.033
Total Toxic Units	0.49	1.1	0.26	0.15

9.2.4 Metals and Metalloids 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. 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 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.

Metals dissolved in the interstitial water of sediments are considered to be the most bioavailable and toxic. Concentrations in solution in interstitial water of some metals (cadmium, copper, nickel, lead, and zinc) are thought to be controlled by concentrations of labile sulfides and organic matter in the sediments (Ankley *et al.*, 1996; Hansen *et al.*, 1996; Mahoney *et al.*, 1996). Labile metal sulfides in sediment, called acid-volatile sulfide (AVS) and operationally defined as the sulfides extracted from sediment with cold 1N hydrochloric acid, are primarily solid-phase iron and manganese monosulfides (DeWitt *et al.*, 1996). Metals whose solubility products with sulfide are lower than those of iron and manganese monosulfides will substitute for iron and manganese and precipitate from the interstitial water when they co-occur in sediments with the iron and manganese sulfides. If the sediment contains more AVS than the metals, concentrations of the metals in sediment interstitial water will be low and the metals are unlikely to be toxic to benthic organisms. Thus, the potential for a metal or group of metals in sediment to be toxic can be estimated from the ratio of the molar concentration of total metals ($\sum$SEM) to the molar concentration of AVS in the 1N hydrochloric acid extract of the sediments. If $[\sum \text{SEM}] \leq [\text{AVS}]$, the metals are unlikely to be toxic to benthic organisms.

Most marine sediments contain high concentrations of sulfur, iron, and manganese. Seawater contains about 0.029 M sulfate (2,760 mg/L). Interstitial water of oxidized marine sediments may contain similar or higher concentrations of sulfate. Marine sediments also contain high concentrations of iron and manganese. Sediments collected in this study from the vicinity of produced water discharges contain 1% to 6.5% iron and 100 to 960 mg/kg manganese; sediments from reference sites contain 1.1% to 3% iron and 220 to 600 mg/kg manganese.

Therefore, these sediments are likely to contain high concentrations of AVS. The high AVS probably keeps the concentrations of metals that form stable sulfides low in sediment interstitial water. Leonard *et al.* (1996) reported that 71% of 131 marine sediments collected from the US Atlantic coast in the Environmental Monitoring and Assessment Program (EMAP) contained $[\sum SEM] < [AVS]$. None of the sediment interstitial waters contained toxic concentrations of the five metals examined, cadmium, copper, lead, nickel, and zinc.

Concentrations of different metals and metalloids 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 and metalloids. 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: **Chapter 7** and Trefry *et al.*, 1996). Aluminum normalization corrects for differences among sediments in grain size and mineralogy. Trefry *et al.* (1996) and **Chapter 7** concluded, based on aluminum normalization, that concentrations of cadmium, iron, nickel, and mercury in sediments near SMI 236A and HI A-595CF are at or near natural levels. On the other hand, concentrations of barium and lead are in excess of expected values at some locations near the platforms, probably as a result of discharges of drilling fluids and produced water from the platforms. However, much of the metals in sediments are 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 bottom plants and animals are being adversely affected.

9.2.4.1 Aluminum, Iron, Calcium, and Manganese

Aluminum and calcium can be considered matrix chemicals in marine sediments. Most of the aluminum is part of the matrix of aluminosilicate minerals that are the dominant clay minerals in sediments. Most clays are hydrous aluminosilicates; in most marine sediments, there is a direct correlation between the percent clay and the concentration of aluminum. Clay particles, because of their large surface area to mass ratios and electrical charges, readily adsorb iron and manganese oxide coatings on their surfaces. These coatings, in turn, adsorb many metals (Jenne, 1977; Schoer, 1985). Thus, clay sediments sometimes contain high concentrations of several metals. In sediments with mixed grain sizes, most of the metals are associated with the clay fraction. Thus, normalization of metal concentrations to the aluminum in the sediments corrects for variances in sediment grain size.

Surficial sediments from the four reference locations contain 2.7% to 5.8% aluminum (**Table 9.28**). Sediments from the vicinity of the four offshore produced water discharges contain 1.2 to 7.7% aluminum (**Tables 9.29** through **9.32**). These concentrations are fairly typical of muddy sand sediments. Nearly all the aluminum in marine sediments is tightly bound to the matrix of the sediment particles and is not bioavailable or toxic to marine organisms. The aluminum data suggest that the range of grain sizes in sediments from the reference sites is wider than but includes the range found in surficial sediments from the vicinity of the four produced water discharge sites. This is not completely true as some of the discharge site stations have higher percentages of gravel/sand and other stations higher percentages of silt/clay (**Chapter 5**).

Table 9.28. Mean concentrations of selected metals and metallloids in surficial sediments (0-2 cm) from the four Component 2 reference sites in the northwest Gulf of Mexico. Concentrations, except where noted, are μg/g dry weight of sediment.

Metal/Metalloid	GA A-90	GA A-205	SMI 186/195	WC 448
Aluminum (%)	4.1	2.7	4.6	5.8
Iron (%)	1.8	1.1	2.7	3.0
Calcium (%)	2.8	4.0	18	6.4
Arsenic	4.7	3.1	13	21
Barium	400	330	660	550
Cadmium	0.05	0.06	0.13	0.08
Chromium	38	28	48	54
Copper	6.2	4.4	12	11
Mercury	0.01	0.01	0.04	0.02
Manganese	310	221	820	600
Molybdenum	0.74	1.9	2.1	4.4
Nickel	12	7.4	19	18
Lead	14	11	18	20
Vanadium	59	29	88	96
Zinc	49	35	74	85

Table 9.29. Mean concentrations of selected metals and metalloids in produced water and in surficial sediments at different distances from the produced water discharge from SMI 236A. Concentrations, except where noted, are in mg/L produced water and μg/g dry weight sediment.

Metal/Metalloid	Produced Water	Discharge Station	20 m	2,000 m
Aluminum (%)	—	1.2	7.4	7.7
Iron (%)	0.0012	0.97	3.6	3.7
Calcium (%)	—	1.7	1.0	1.7
Arsenic	0.0008	1.5	7.7	8.4
Barium	160	600	960	740
Cadmium	0.0001	0.19	0.24	0.16
Chromium	0.0004	13	77	83
Copper	0.002	6.2	20	18
Mercury	0.00008	0.02	0.04	0.05
Manganese	1.2	103	770	780
Molybdenum	0.001	0.70	1.5	0.77
Nickel	0.002	5.8	27	28
Lead	0.0002	13	36	24
Vanadium	<0.001	15	115	110
Zinc	0.022	470	268	110

Table 9.30. Mean concentrations of selected metals and metalloids in produced water and in surficial sediments at different distances from the produced water discharge from SMI 130B. Concentrations, except where noted, are in mg/L produced water and μg/g dry weight sediment.

Metal/Metalloid	Produced Water	60 m	2,000 m
Aluminum (%)	—	1.6	7.7
Iron (%)	0.003	1.2	3.5
Calcium (%)	—	2.9	2.7
Arsenic	0.0007	4.6	15
Barium	87	700	3,800
Cadmium	0.0002	0.72	0.09
Chromium	0.0003	58	75
Copper	<0.0002	10	15
Mercury	0.00001	0.35	0.05
Manganese	1.4	130	960
Molybdenum	0.0008	2.8	2.9
Nickel	0.0031	6.0	26
Lead	0.0007	7.8	29
Vanadium	<0.0012	22	130
Zinc	0.028	800	120

Table 9.31. Mean concentrations of selected metals and metalloids in produced water and *in* surficial sediments at different distances from the produced water discharge from VR 214A. Concentrations, except where noted, are in mg/L produced water and μg/g dry weight sediment.

Metal/Metalloid	Produced Water	20 m	2,000 m
Aluminum (%)	---	5.2	7.1
Iron (%)	0.0012	6.6	3.1
Calcium (%)	---	5.8	1.7
Arsenic	0.006	4.4	7.7
Barium	220	3,000	1,100
Cadmium	0.0003	0.73	0.11
Chromium	0.0001	96	79
Copper	<0.0002	25	12
Mercury	0.00004	0.06	0.03
Manganese	4.5	407	940
Molybdenum	0.0017	5.7	0.80
Nickel	<0.0012	31	21
Lead	0.0001	110	23
Vanadium	<0.0012	91	118
Zinc	0.086	280	99

Table 9.32. Mean concentrations of selected metals and metalloids in produced water and in surficial sediments at different distances from the produced water discharge from HI A-595CF. Concentrations, except where noted, are in mg/L produced water and μg/g dry weight sediment.

Metal/Metalloid	Produced Water	50 m	2,000 m
Aluminum (%)	—	3.2	5.8
Iron (%)	0.0035	1.7	2.6
Calcium (%)	—	7.0	8.26
Arsenic	0.025	4.4	8.0
Barium	320	6,500	6,300
Cadmium	0.0006	0.80	0.12
Chromium	0.00002	41	58
Copper	<0.0002	9.7	13
Mercury	0.00004	0.12	0.06
Manganese	7.1	240	650
Molybdenum	0.0014	0.93	0.70
Nickel	<0.0012	9.4	21
Lead	0.020	78	24
Vanadium	<0.0012	31	87
Zinc	3.0	280	96

Most of the calcium in marine sediments is associated with biogenic calcium carbonate (calcite, aragonite, and vaterite). It represents the weathered skeletal remains of marine plants, bacteria, and invertebrates. Thus, the concentration of calcium is an indication of the carbonate minerals in the sediments. Most carbonate sediments are coarse-grained, consisting of eroded skeletal fragments. Because only small amounts of most metals are included in the matrix of calcite and aragonite crystals or are adsorbed to the surface of calcium carbonate particles, carbonate sediments usually contain lower concentrations of most metals than do clay sediments.

Surficial sediments from the four reference sites contain 2.8% to 18% calcium (**Table 9.28**). Sediment from reference site SMI 186/195 may contain as much as 38% calcium carbonate and so would be classified as a carbonate sediment. Sediments from the vicinity of the four offshore produced water discharges contain 1.0% to 8.6% calcium (**Tables 9.29** through **9.32**). The calcium in these sediments is associated primarily with crystalline calcium carbonate and is not bioavailable or toxic to marine organisms. With the exception of sediments from reference site SMI 186/195, sediments from reference and produced water discharge sites have similar calcium concentrations and, thus, similar concentrations of calcium carbonate sediments.

Iron and manganese are present in marine sediments primarily as insoluble hydrous oxides. Fe(III) and Mn(III, IV) hydrous oxides tend to form colloidal precipitates in the water column and are deposited as coatings on suspended inorganic particles (Burns and Burns, 1981; Schoer, 1985). Hydrous oxides include oxides, hydroxides, and oxide hydroxides (Schindler and Stumm, 1987). Weathering and erosion of terrestrial rocks introduces several forms of colloidal Fe(III) to the ocean in runoff from land. Manganese probably enters the ocean primarily as amorphous or poorly crystalline vernadite (δ-MnO_2) and manganite (τ-MnOOH). These suspended iron and manganese hydrous oxide particles have diameters of only tens of angstrom units. Iron hydrous oxides, and to a lesser extent, manganese hydrous oxides tend to adsorb to and form coatings on inorganic sediment particles, particularly clays. Manganese hydrous oxides tend to persist as discrete microparticles.

The solid iron and manganese in sediments are not bioavailable or toxic to marine organisms. However, the Fe/Mn-oxide coatings and particles have a strong affinity for binding dissolved metals in the water column and sediments. Much of several metals (arsenic, cadmium, chromium, copper, lead, molybdenum, nickel, vanadium, and zinc) in oxidized marine sediments is associated with iron and manganese hydrous oxide coatings and particles (Shieh and Duedall, 1988; Schimmield and Pedersen, 1990; Brown and Neff, 1993). In this form, the metals are not readily bioavailable to marine organisms. However, if the sediments become anoxic, the iron and manganese oxides dissolve, releasing the adsorbed metals into the sediment interstitial water, from which they can be mixed up into the overlying oxidized sediment layers or water column in potentially bioavailable forms (Förstner and Wittmann, 1981; Ridgeway and Price, 1987). However, much of the iron released by dissolution of iron hydrous oxides in anoxic layers of sediments is reduced rapidly in the presence of sulfide to mackinawite (FeS), pyrite (FeS_2), and possibly greigite (Fe_3S_4) (Schimmield and Pedersen, 1990). Many metals and metalloids may coprecipitate with the iron sulfides.

9.2.4.2 Arsenic

Mean concentrations of arsenic in surficial sediments collected at different distances from the four produced water discharges range from 1.5 μg/g dry weight (discharge station at SMI 236A) to 15 μg/g (2,000 m station at SMI 130A) (**Tables 9.29** through **9.32**). At all four platforms, arsenic concentrations in sediments are lower in sediments 20, 50, and 60 m from the platform discharge than in sediments 2,000 m away. Sediments near the shallowest site (SMI 236A) contain the lowest mean concentrations of arsenic. Mean concentrations of arsenic in sediments near the produced water discharge containing the highest mean concentration of arsenic are not elevated compared to sediments from the vicinity of the other produced water discharges or the reference sites. Therefore, produced water discharges from the four offshore platforms do not appear to have an effect on concentrations of arsenic in nearby surficial sediments.

Surficial sediments from the four reference sites contain mean concentrations of 3.1 μg/g to 21 μg/g arsenic (**Table 9.28**). These concentrations are within the range or slightly higher than concentrations of arsenic in surficial sediments near the four produced water discharges.

Concentrations of total arsenic in uncontaminated nearshore marine and estuarine sediments usually fall in the range of 5 to 15 μg/g (Moore and Ramamoorthy, 1984). However, the average concentration of arsenic in deep sea sediments is about 40 μg/g (Bostrom and Valdes, 1969). 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. The "high" concentration for arsenic in U.S. coastal marine sediments is 13 μg/g (**Table 9.33**). This concentration is exceeded frequently near natural and anthropogenic sources of this metalloid. Eighteen percent of the 13,500 sediment samples in the Coastal Sediment Database (COSED) contain an arsenic concentration equal to or higher than the "high" value. Three of the 13 site mean concentrations of arsenic (23%) in this study are in excess of the "high" concentration for arsenic. Two of the sites are reference sites and one is 2,000 m from a produced water discharge. It is highly probable that the three high mean concentrations of arsenic are either natural or derived from a source other than the produced water discharges.

9.2.4.3 Barium

Concentrations of barium are highly variable in sediments near the four produced water discharges. The range of mean concentrations in sediments at different distances from the produced water discharges is from 60 μg/L (station at the produced water discharge at SMI 236A) to 6,500 μg/g (60-m station at HI A-595CF) (**Tables 9.29** through **9.32**). Mean barium concentrations in sediments are above 1,000 μg/L at five of the nine sampling stations near produced water discharges. At a sixth station, the mean concentration is 960 μg/L. The two highest barium concentrations in sediments are from the vicinity of the HI A-595CF, which is the farthest offshore in the deepest water. By comparison, mean concentrations of barium in surficial sediments at the four reference sites range from 400 to 660 μg/g (**Table 9.28**).

Table 9.33. Proposed sediment quality guidelines (μg/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) and 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	120
Copper	34	270	42
Lead	47	220	45
Mercury	0.15	0.71	0.22
Nickel	21	52	42
Zinc	150	410	140

Barium is the fourteenth most abundant element in the continental crust of the earth, with an average concentration of about 400 μg/g and a range in marine sediments from less than 1 μg/g to at least 2,000 μg/g (Trefry, 1982). Barium concentrations vary widely in marine and estuarine sediments not obviously contaminated with discharged oil well drilling fluids (rich in barite) and produced water (rich in dissolved barium). Coarse-grained carbonate and silicate sediments often contain less than 100 μg/g barium, whereas, fine grained sediments, rich in clay minerals, may contain more than 1,000 μg/g barium (Neff, 1996a). Boothe and James (1985) reported barium concentrations ranging from 245 to 1,000 μg/g in sediments from several regions of the Texas/Louisiana outer continental shelf and slope. Both drilling fluids, used during rotary drilling of oil and gas wells, and produced water often contain high concentrations of barium. Discharge of these wastes from offshore platforms to the ocean results in the deposition of dense, insoluble barium sulfate (barite) in sediments over a large area around the platform (Neff *et al.*, 1987; Boothe and Presley, 1989). This often results in gradients of steeply decreasing barium concentrations in sediments with distance from oil platforms (API, 1989; Boothe and Presley, 1989; Jenkins *et al.*, 1989). Barium from drilling fluids and produced water remains in marine sediments as relatively inert barite; however, some of the barite may dissolve, releasing small amounts of barium into the overlying water column. However, barium concentrations in the sediment interstitial water and in the overlying water column remain below the saturation concentration (~50 μg/L) of barium in seawater (Neff and Sauer, 1995). This concentration of dissolved barium is well below toxic concentrations to marine organisms (Spangenberg and Cherr, 1996).

The mass loadings of barium from the four produced water discharges to the ocean range from 98 metric tons/year at VR 214A to 140 metric tons/year at SMI 236A. During drilling of an offshore well with a water-base drilling mud, approximately 600 to 2,200 metric tons of drilling fluid solids containing 250 to 400 metric tons of barium are discharged to the ocean (National Research Council, 1983). From one to a dozen or more wells may be drilled from a single production platform. Thus, both produced water and drilling mud discharges may contribute to the total amounts of barite in sediments near the platforms.

Boothe and Presley (1989) reported that background concentrations of barium in sediments of the northwestern Gulf of Mexico are in the range of 200 to 800 μg/g dry weight. If, based on mean concentrations of barium in sediments from the four reference sites, it is assumed that the "typical background" concentration of barium in outer continental shelf sediments of the northwestern Gulf of Mexico is about 500 μg/g, sediments near the four produced water discharges contain excess barium ranging from 200 to 6,000 μg/g at stations 20, 50, and 60 m from the discharges and 240 to 5,800 μg/g at stations 2,000 m from the discharges. The excess inventories of barium in sediments are greatest near the deepest water, lowest volume produced water discharge (HI A-595CF). Barium concentrations are essentially the same in sediments 60 and 2,000 m from the discharge. One would expect a gradient of barium concentrations in sediments if the barium was coming from drilling fluid or produced water discharges. Barium deposition from produced water might produce a wider more uniform distribution of barium in the vicinity of the platform. Offshore sediments often contain higher natural concentrations of barium than nearshore sediments (Goldberg and Arrhenius, 1958; Turekian and Wedepohl, 1961). The true background concentration in sediments from this site is not known, but may be higher than about 500 μg/g. However, it is probable that it is substantially less than 6,000 μg/L. Therefore, it is highly probable that sediments near HI A-595CF are contaminated with barium, probably as barite, from platform discharges.

9.2.4.4 Cadmium

Mean concentrations of cadmium in surficial sediments near the four offshore produced water discharges are in the range of 0.09 to 0.80 μg/g (**Tables 9.29** through **9.32**). The "high" concentration of cadmium in marine sediments is 0.54 μg/g (**Table 9.33**). However, 31% of sediments in COSED contained higher concentrations of cadmium. Mean concentrations of cadmium in sediments 20, 50, and 60 m from three of the produced water discharges are greater than 0.54 μg/g. Mean concentrations in sediments at the discharge station and the 20-m station at SMI 236A and at all 2,000-m stations are below the "high' value (**Table 9.29**). In all cases, mean cadmium concentrations in sediments 20, 50, and 60 m from all four platforms are higher than concentrations 2,000 m from the platforms. These results suggest that sediments *near* the four offshore produced water discharges may be slightly contaminated with cadmium from platform discharges, possibly from produced water.

Mean cadmium concentrations in sediments from the four reference stations are in the range of 0.05 to 0.13 μg/g, well below the "high" concentration (**Table 9.28**). These observations suggest that background concentrations of cadmium in sediments from the northwestern Gulf of Mexico are generally below 0.15 μg/g. Cadmium concentrations in uncontaminated marine sediments usually fall in the range of 0.1 to 0.6 μg/g (Warren, 1981). Sediments from uncontaminated estuaries along the Atlantic and Gulf coasts of Florida contain 0.01 μg/g to about 0.3 μg/g cadmium; and there is a direct correlation between concentrations of cadmium and aluminum in the sediments (Schropp *et al.*, 1990). Wetland sediments from coastal Louisiana contain 0.5 to 10 μg/g cadmium; for all but the highest concentrations, there is a good correlation between aluminum and cadmium concentrations (Pardue *et al.*, 1992). Generally, there is a good correlation between cadmium and aluminum concentrations in sediments near the produced water discharges (**Chapter 7** and Trefry *et al.*, 1996), indicating minimal contamination of the sediments by platform discharges. Mississippi River suspended matter contains an average of 0.7 μg/g cadmium (**Chapter 7** and Trefry *et al.*, 1996) and could contribute to the slightly elevated concentrations of cadmium in some sediments in areas influenced by the outflow of the Mississippi River.

9.2.4.5 Chromium

Chromium is abundant in marine sediments. Concentrations in clean marine and estuarine sediments usually range from 50 to 100 μg/g (Salomons and Förstner, 1984; Mayer, 1988). The "high" concentration of chromium in U.S. coastal marine sediments is 125 μg/g (**Table 9.33**). Sediments from the coastal zone of Louisiana contain 17 to 66 μg/g chromium. Galveston Bay, Texas, sediments contain 4 to 102 μg/g chromium (Morse *et al.*, 1993). Sediments from the Calccasieu River estuary, Louisiana, contain 10 to 150 μg/g chromium. Most of the chromium in marine sediments is associated with iron and manganese oxides and with organic matter (Loring, 1982). Concentrations usually correlate well with concentrations of aluminum (Windom *et al.*, 1989; Schropp *et al.*, 1990).

Concentrations of chromium in surficial sediments tend to increase with distance from the four produced water discharges (**Tables 9.29** through **9.32**). Mean concentrations range from 13 μg/g at the produced water discharge station at SMI 236A to 96 μg/g at the 20-m station at VR 214A. The mean concentrations of chromium in sediments in the vicinity of the four produced water discharges are similar to or slightly higher than concentrations in sediments from the four reference sites (**Table 9.28**). Mean concentrations of chromium in sediments from the four reference sites range from 28 to 54 μg/g.

The chromium concentrations for the four produced waters examined in this study ranged from <0.1 to 0.4 μg/L, but chromium was not determined in ambient seawater so relative enrichment of chromium in produced water compared to ambient seawater is not known. Produced water from other locations in the Gulf of Mexico contains less than 0.01 μg/L to approximately 390 μg/L chromium. By comparison, concentrations of chromium in clean oceanic water usually fall in the range of 0.10 to 0.55 μg/L (Burton and Statham, 1982; Murray *et al.*, 1983; Ciceri *et al.*, 1992). Thus, chromium in the four produced waters in this study was not enriched compared to concentrations in ambient seawater.

Chromium concentrations in sediments near produced water discharges are not substantially higher than concentrations in clean marine sediments or sediments from reference sites. Therefore, it is probable that chromium from produced water is not accumulating in sediments near offshore produced water discharges.

9.2.4.6 Copper

Copper concentrations in clean marine and estuarine sediments usually are in the range of 10 to 50 μg/g (Salomons and Förester, 1984; Ridgway and Price, 1987). Sediments from Galveston Bay, Texas, and coastal Louisiana contain 2 to 30.3 μg/g copper. The "high" concentration of copper in National Status and Trends coastal marine sediments is 42 μg/g (**Table 9.33**).

Copper concentrations in surficial sediments from the four reference sites and the four produced water discharge sites all fall within the lower part of the range or natural sediment copper concentrations (**Tables 9.28** through **9.32**). Sediments from the reference sites contain 4.3 to 12 μg/g copper; sediments collected at different distances from the four produced water discharges contain means of 6.2 to 25 μg/g copper. At three of the four discharging platforms, copper concentrations in sediments increase with distance from the discharge. Concentrations of copper are lower in the four produced waters than they are in ambient seawater near the platforms. Therefore, there is no evidence that copper from produced water is accumulating in sediments near the produced water discharges.

9.2.4.7 Mercury

Mercury usually is present in uncontaminated marine and estuarine sediments at a concentration of 0.2 μg/g dry weight or lower (Crecelius *et al.*, 1975; Salmons and Förstner, 1984) except in areas, such as the East Pacific Rise and the Mid-Atlantic Ridge, where there are natural mercury-containing heavy minerals, such as cinnabar (Jonasson and Boyle, 1972). The "high" concentration of mercury in coastal sediments sampled in the National Status and Trends Program is 0.22 μg/g (**Table 9.33**). Surficial sediments from the four reference sites in this study contain 0.01 to 0.04 μg/g total mercury. These concentrations are typical of natural levels in marine sediments.

Surficial sediments near the four produced water discharges contain 0.02 to 0.35 μg/g total mercury (**Tables 9.29** through **9.32**). The only sediment containing mercury at a mean concentration higher than the "high" value is from the 50-m station at SMI 130B, where the produced water contains an average of 0.01 μg/L total mercury (**Table 9.30**). Sediments 2,000 m from this discharge contain 0.05 μg/g mercury. The source of the mercury in sediments near SMI 130A is unknown; it probably did not come from the produced water discharge which was not greatly enriched in mercury compared to ambient seawater.

9.2.4.8 Molybdenum

There is little published information about molybdenum in marine sediments. The average concentration in deep-sea clays is 27 μg/g (Turekian and Wedepohl, 1961). Molybdenum in sediments from a eutrophic area of the continental shelf off west Africa contained 0.74 to 2.62 μg/g; molybdenum concentration increased with depth in sediment cores, reflecting trapping of the molybdenum in hypoxic sediment layers (Legeleux *et al.*, 1995). Other marine sediments typically contain 0.2 to 8 μg/g molybdenum (Bowen, 1979). Mean molybdenum concentrations in sediments near the four reference sites are in the range of 0.74 to 4.4 μg/g (**Table 9.28**). These concentrations are similar to those in sediments collected at different distances from the four produced water discharges (**Tables 9.29** through **9.32**). Mean concentrations of molybdenum in surficial sediments near the produced water discharges range from 0.70 to 5.7 μg/g. The highest mean concentration is in sediment at the 20 m station at VR 214A in approximately 39 m of water. This is the only platform site where molybdenum concentration in sediments decreases significantly with distance from the platform. Produced water from the four platforms sampled in this study contain lower concentrations of molybdenum than is present in ambient seawater near the platforms. Therefore, it is highly unlikely that molybdenum from produced water is accumulating in sediments near the produced water discharges.

Molybdenum in seawater and oxidized marine sediments has a strong affinity for manganese oxyhydroxides and tends to coprecipitate with them (Schimmield and Pederson, 1990). Most of the molybdenum in oxidized layers is tightly bound to the solid manganese oxide phase of the sediments and is not readily bioavailable. In anoxic sediment layers, molybdenum co-precipitates with iron mono-sulfides, decreasing its mobility and bioavailability.

9.2.4.9 Nickel

Nickel often is relatively abundant in marine sediments. Clean marine sediments usually contain 50 g/g or less of nickel, the concentration often being positively correlated with the clay content of the sediments (Bowen, 1979). Sediments from Galveston Bay, Texas, contain 0.6 to 50 μg/g nickel. The "high" concentration of nickel in sediments from National Status and Trends monitoring sites is 42 μg/g (**Table 9.33**). However, much higher concentrations of nickel are reported frequently for apparently uncontaminated marine sediments. For example, Loring and Asmund (1996) reported 18 to 388 μg/g nickel in sediments from coastal waters of east and west Greenland. Offshore surficial sediments from the Tyrrhenian Sea (west of Italy) contain 35 to 457 μg/g nickel (Leoni *et al.*, 1991).

Most of the nickel in uncontaminated sediments is associated with oxide and silicate mineral matrix of the sediment and is inert (Loring, 1982). Nickel and aluminum concentrations are highly correlated in clean marine sediments (Schropp *et al.*, 1990; Schimmield and Pedersen, 1990).

Nickel concentrations in surficial sediments from the four reference sites range from 7.4 to 19 μg/g (**Table 9.28**). Surficial sediments near the four produced water discharges contain means of 5.8 to 31 μg/g (**Tables 9.29** through **9.32**). At three of the four platforms, nickel concentrations in sediments increase with distance from the platform. At VR 214A, mean sediment nickel concentration is 31 μg/g (the highest mean concentration measured) at the 20-m station and 21 μg/g at the 2,000-m station. All these concentration are in the expected range for clean marine sediments. The produced water is only slightly enriched in nickel compared to concentrations in ambient seawater. Therefore, it is doubtful that nickel from produced water is accumulating in sediments near the produced water discharges.

9.2.4.10 Lead

Concentrations of lead in uncontaminated marine and estuarine sediments usually are in the range of 5 to about 30 μg/g (Salomons and Förstner, 1984). Lead concentrations usually are inversely correlated to sediment grain size and directly correlated with aluminum concentrations (Schropp *et al.*, 1990; Krumgalz *et al.*, 1992). The "high" concentration of lead in sediments sampled during the National Status and Trends Program is 45 μg/g (**Table 9.33**). Sediments from Galveston Bay, Texas, contain 12 to 46 μg/g total lead (Morse *et al.*, 1993). Much of the lead in clean marine sediments is in residual forms, associated primarily with sulfide minerals, and is not bioavailable (Loring, 1982).

Mean concentrations of lead in sediments from the four reference sites are in the range of 11 to 20 μg/g (**Table 9.28**). Mean concentrations of lead in sediments from different distances from the four produced water discharges are more variable, ranging from 7.8 μg/g at the 50-m station at SMI 130A to 78 μg/g at the 60-m station at HI A-595CF and 110 μg/g at the 20-m station at VR 214A. Lead concentrations in sediments from the stations with the highest mean lead concentrations were higher than predicted from the correlation between lead and aluminum concentrations from most sediments, indicating that some of the excess lead in these sediments probably is of anthropogenic origin. Produced water from HI A-595CF contains 10 to 28 μg/L lead and may be a source of some of the excess lead in sediments near the platform. However, produced water from VR 214A contains a mean of only 0.13 μg/L lead, a concentration only about twice as high as the lead concentration in ambient seawater from the vicinity of that platform. The excess lead in sediments near this platform probably did not come from produced water. It may have been derived from other platform discharges (e.g., drilling fluids).

9.2.4.11 Vanadium

Vanadium is abundant in seawater and marine sediments. Mean concentrations in marine sediments of different mineralogy are in the range of 20 to 130 μg/g (Bowen, 1979). Vanadium concentrations in sediments near three oil platforms off Texas monitored in the Gulf of Mexico Offshore Operations Monitoring Experiment (GOOMEX) are in the range of 3.41 to 208.5 μg/g (Kennicutt, 1995).

Mean concentrations in surficial sediments near the four reference sites are in the range of 29 to 96 µg/g (**Table 9.28**). Mean concentrations of vanadium in sediments from the vicinity of the four produced water discharges are more variable and range from 15 µg/g at the discharge station at SMI 236A to 130 µg/g at the 2,000-m station at SMI 130A (**Tables 9.29** through **9.32**). Vanadium concentrations in sediments at the reference and discharge sites are tightly correlated with aluminum concentrations in the same sediments, indicating that all or most of the vanadium in the sediments is natural. Mean vanadium concentrations in sediments increase with distance from all four produced water discharges. Vanadium concentrations in produced water from the four platforms are lower than concentrations in ambient seawater. Therefore, vanadium from produced water is not accumulating in surficial sediments near the four produced water discharges.

9.2.4.12 Zinc

Concentrations of zinc in marine and estuarine sediments vary widely. Surficial sediments from Galveston Bay, Texas, contain 6 to 116 µg/g zinc (Morse *et al.*, 1993). Sediments from the coastal zone of Louisiana contain 52 to 133 µg/g zinc (Pardue *et al.*, 1988). Sediments in areas influenced by the outflow of the Mississippi River may contain elevated concentrations of zinc. Suspended particulate matter in the Mississippi River contains a mean of about 160 µg/g zinc (**Chapter 7** and Trefry *et al.*, 1996). The "high" concentration of zinc in sediments from the National Status and Trends Program is 135 µg/g (**Table 9.33**). Much of the zinc in uncontaminated marine sediments is in the non-bioavailable residual fraction, associated with clay or heavy minerals (Warren, 1981; Loring, 1982).

Surficial sediments from the four reference sites contain means of 35 to 85 µg/g zinc (**Table 9.28**). Zinc concentrations in sediments near the four produced water discharges are higher; mean concentrations range from 96 µg/g at the 2,000-m station at HI A-595CF to 800 µg/g at the 50-m station at SMI 130B. Although there does not seem to be a correlation between concentrations of zinc in produced water and in nearby sediments, there is a gradient of decreasing zinc concentrations in sediments with distance from all four produced water discharges. The zinc enrichment in sediments near platforms discharging produced water may have been derived, at least in part, from the produced water discharges.

9.2.4.13 Ecorisk of Metals in Sediments Near Produced Water Discharges

A fraction of the chemical contaminants associated with marine sediments may be mobile and bioavailable. However, it is difficult to estimate the fraction of total sediment metal that is bioavailable and extrapolate from that estimate, a prediction of the environmental risk of metal-contaminated marine sediments. Much of the metals in marine sediments may be tightly bound to sediments organic carbon or precipitated as metal sulfides. These metals are not readily bioavailable or toxic. One approach that has been taken is to develop estimates of the concentrations of individual metals in sediments that may be associated with adverse effects in benthic marine animals.

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 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 Morgan, 1990; Long, 1992; Long *et al.*, 1995). Two guidelines 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 guidelines 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. The ERLs and ERMs published by Long *et al.* (1995) are for estuarine and marine sediments. Marine sediments are likely to contain a larger fraction of the total of most metals in residual, non-bioavailable forms than are estuarine and freshwater sediments. Therefore, the ERM values (**Table 9.33**) were used in the present study as screening values for comparison with metal concentrations measured in marine sediments near offshore reference and produced water discharge 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 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 Pederson, 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).

Molybdenum is present in sediments from the vicinity of the four produced water discharges and four reference sites at concentrations comparable to those reported for clean marine sediments. Most of the molybdenum is trapped in relatively immobile forms in the reduced layers of the sediment or tightly bound to manganese oxyhydroxides in oxidized layers. Therefore, molybdenum at the concentrations present in sediments near produced water discharges, is not likely to be toxic to marine organisms residing in the sediments.

Vanadium in sediments near the produced water discharges also is in the range of concentrations expected for clean marine sediments. Concentrations of vanadium in the bioavailable dissolved form in sediment interstitial waters are controlled by the strong affinity of vanadium for amorphous ferric oxyhydroxides (Shieh and Duedall, 1988). Some of the vanadium in the sediments may also be associated with various heavy minerals, such as magnetite and various ferromagnesium minerals, in the sediments (Leoni *et al.* 1991; Loring and Asmund, 1996). The low concentrations of vanadium in produced water from the four discharge sites is suggestive that the vanadium in sediments near the discharges is from natural sources. Therefore, it is likely that vanadium in sediments near the produced water discharges does not pose a health risk to benthic organisms in the area.

Concentration ranges in reference and discharge site sediments of the eight metals for which sediment threshold concentrations are available are summarized in **Table 9.34**. Toxic risk of the metals in the sediments is estimated as the range of toxic units (concentration in sediment/ERM value) for sediments from near the discharges (60 m or less), 2,000 m from the discharges, and at reference sites.

Total toxic units for arsenic in sediments range from 0.013 to 0.32 and tend to increase with distance from the platform discharges (**Table 9.34**). These low values for toxic units indicate that marine animals in sediments would not be adversely affected by arsenic concentrations in the sediments. Toxic units of cadmium, chromium, copper, and mercury all are well below values that would indicate a possible toxic risk to benthic marine animals. The highest value is 0.48 toxic units for the highest concentration of mercury in sediments from 50 m from produced water discharges. Sediment from this site is unlikely to be toxic (due to the presence of mercury), unless most of the mercury is present in organic form, which is unlikely.

Lead, nickel, and zinc are present in some sediments near produced water discharges at relatively high concentrations. The high concentrations of these metals in sediments near platforms discharging produced water may be due in part to high concentrations of iron, particularly in sediments 20 m from VR 214A. In iron-rich, suboxic marine sediments, lead, nickel, and zinc would be present primarily in the form of insoluble sulfides, which are not bioavailable or toxic (Liber *et al.*, 1996). Two sediment samples (one each from 20 m from VR 214A and 60 m from HI A-595CF) contained more than 150 μg/g lead. The ERM for lead in marine sediments is 218 μg/g. Thus, maximum toxic units for lead in sediments are 0.78 and 0.90. All but one of the other sediment samples contained less than 45 μg/g lead (0.21 toxic units). Lead toxic units in sediments 2,000 m from the produced water discharges and from reference sites were below 0.20. Therefore, there may be a slight risk to benthic marine animals from lead in sediments near (≤ 60 m from the discharge) from two of the four discharging platforms, but not for lead in sediments at greater distances from the platforms.

Nickel concentrations are similar in sediments from stations 20/50/60 m and 2,000 m from the four produced water discharges, and slightly lower in sediments at the reference sites. Some sediment samples from 20 m at SMI 236A and VR 214A, and from 2,000 m at SMI 130B and SMI 236A, contain more than 26 μg/g nickel, equivalent to 0.50 toxic units. However, as discussed above, nickel concentrations in apparently uncontaminated sediments frequently are much higher than 26 μg/g. Nickel frequently is associated with heavy minerals (e.g., magnesium silicates) and also has a strong affinity for adsorption to iron oxide coatings on clay particles or precipitation as nickel sulfide (Schimmield and Pedersen, 1990; Loring and Asmud, 1996). These forms of nickel in sediment are not readily bioavailable. It is likely that the nickel associated with sediments near the produced water discharges do not represent a toxicological risk to benthic marine organisms from the area.

Table 9.34. Concentration ranges of metals in sediments at 60 m or less and 2,000 m from four offshore produced water discharges (D) and in sediments from four non-discharging reference sites in the northwestern Gulf of Mexico. Toxic units (sediment concentration/ERM) also are presented for each sediment collection location. Concentrations are μg/g dry weight.

Metal	<60 m (D) Concentration	<60 m Toxic Units Range	2,000 m (D) Concentration	2,000 m Toxic Units Range	Reference Sites Concentrations	Reference Sites Toxic Units
Arsenic	0.9 - 8.1	0.01 - 0.12	7.1 - 18	0.10 - 0.26	2.5 - 22	0.04 - 0.32
Cadmium	0.14 - 1.3	0.015 - 0.14	0.07 - 0.18	0.01 - 0.02	0.04 - 0.14	<0.01 - 0.02
Chromium	9.2 - 97	0.02 - 0.26	54 - 90	0.15 - 0.24	26 - 58	0.07 - 0.16
Copper	5.6 - 34	0.02 - 0.13	11 - 20	0.04 - 0.07	4.2 - 15	0.02 - 0.05
Lead	5.5 - 200	0.02 - 0.90	22 - 34	0.10 - 0.16	11 - 21	0.05 - 0.10
Mercury	0.005 - 0.35	0.01 - 0.48	0.03- 0.06	0.04 - 0.09	0.01 - 0.04	0.01 - 0.06
Nickel	5.0 - 37	0.10 - 0.72	20 - 32	0.38 - 0.61	6.4 - 19	0.12 - 0.37
Zinc	200 - 970	0.49 - 2.4	90 - 120	0.22 - 0.29	32 - 90	0.08 - 0.22

Zinc concentrations are quite high in sediments collected 60 m or nearer to the four produced water discharges. Several sediment samples from each 20-, 50-, and 60-m sampling station contain zinc at a concentration approaching or exceeding 1.0 toxic units. The form of the zinc in these sediments is not known. If the excess zinc in the sediments is from produced water discharges, it could be present in the sediments as microcrystalline sphalerite (ZnS) or as galvanized metal chips from the platforms. These forms of zinc are not very mobile or bioavailable. Some of the zinc could be present in more mobile and bioavailable forms, particularly if the surficial sediments are oxidized. Therefore, zinc concentrations in sediments near the produced water discharges may represent a significant risk of harm to benthic marine organisms in the area. However, concentrations of zinc in sediments decline sharply with distance from the platform discharges. Sediments at stations 2,000 m from the discharges and from the four reference sites do not contain high enough concentrations of zinc to pose a risk to benthic marine organisms.

This analysis shows that zinc and occasionally lead may be present in surficial sediments near (within about 60 m) produced water discharges at concentrations that could represent a toxicological risk to benthic marine organisms in the area. The extent to which these metals are bioavailable and potentially toxic depends on the physical/chemical forms of the metals in the sediments. Much of the excess lead and zinc discharged to the ocean in produced water probably is in solution. However, it probably coprecipitates rapidly with iron and barium, both of which are very abundant in produced water and are highly insoluble in oxygenated seawater. These adsorbed or coprecipitated forms of lead and zinc probably are immobile and non-toxic in suboxic marine sediments where they would be present as sulfides or coprecipitates with iron sulfide. However, they may have a limited mobility and bioavailability in sediments during shifts up or down in sediment redox potential.

9.2.5 Polycyclic Aromatic Hydrocarbons in Sediments

9.2.5.1 Total Petroleum Hydrocarbons

Concentrations of total petroleum hydrocarbons (TPHs), resolved and unresolved, are higher in sediments 20, 50, and 60 m from the four produced water discharges than at sediments at the 2,000-m stations (**Table 9.35**). The mean TPH concentration in sediments at the discharge station at SMI 236A is lower than in sediments 20 m away. Metal concentrations also were lower in the coarser-grained sediments at the discharge station than in sediments 20 m away.

There is a slight but inconsistent tendency for TPH concentrations in sediments 20, 50, and 60 m from the four discharges to decrease with increasing water depth at the discharge site and decreasing TPH concentrations and mass loading (discharge rate times TPH concentration) in the produced water. The TPH concentration in sediments near the platforms probably also is affected by sediment grain size and percent organic carbon (Neff *et al.*, 1992).

Sediments 2,000 m from the produced water discharges contain much lower concentrations of TPH than sediments within 60 m of the platforms. However, TPH concentrations at the 2,000-m stations are higher (with one exception: the deep water site) than TPH concentrations in sediments from the four reference sites. These results indicate that small amounts of petroleum hydrocarbons, probably derived from produced water discharges, are deposited in surficial sediments out to at least 2,000 m from the produced water discharge sites.

Table 9.35. Mean concentrations of total resolved plus unresolved petroleum hydrocarbons in produced water and sediments at different distances from produced water discharges to the northwestern Gulf of Mexico. Concentrations are in μg/L produced water and μg/g dry weight sediments.

Location	Water Depth (m)	Produced Water	Discharge Station or Site	20 m Station	2,000 m Station
SMI 236A	6	4,800	88	130	49
VR 214A	39	3,300	—	140	37
HI A-595CF	122	1,400	—	65*	1.2
SMI 130B	66	14,000	—	160**	12 (16)***
WC 448	36	—	7.2	—	—
SMI 186/195	110	—	0.85	—	—
GA A-205	66	—	0.51	—	—
GA A-90	39	—	0.60	—	—

* 60 m from discharge.
** 50 m from discharge.
*** Duplicate group of 3 samples.

9.2.5.2 Polycyclic Aromatic Hydrocarbon Distributions

Mean PAH concentrations are slightly elevated in sediments 60 m or less from the four produced water discharges, compared to mean concentrations in sediments 2,000 m from the discharges and in sediments from the four reference sites (**Tables 9.36** through **9.38**). Mean total PAH concentrations in sediments from the SMI 236A discharge site and the four 20-, 50-, and 60-m stations are in the range of 0.316 to 1.367 μg/g (**Tables 9.36** and **9.37**). By comparison, concentrations of total PAHs in sediments 2,000 m from the four platforms range from 0.082 to 0.287 μg/g. There is no clear relationship between concentrations of total PAHs in the produced water from the four platforms (**Table 9.19**) and rates of produced water discharge (**Table 9.35**) on one hand, and concentrations of total PAHs in sediments 20/50/60 m and 2,000 m from the discharges on the other (**Tables 9.36** and **9.37**). The exception to this generalization is that the total PAH concentrations are lowest at the 60-m and 2,000-m stations near the deepest water discharge, HI A-595CF.

Low molecular weight PAHs (2- and 3-ring PAHs), that make up the majority of PAHs in petroleum and produced water, represent 42% to 69% of the total PAHs in sediments 60 m or less distant from the produced water discharges (**Tables 9.36** and **9.37**). Between 28% and 42% of the total PAHs in sediments 2,000 m from the produced water discharges are low molecular, predominantly petroleum-derived PAHs. Between 20% and 38% of the total PAHs in sediments from the four reference sites are low molecular weight PAHs (**Table 9.38**). These results indicate, as might be expected, that the fraction of the total PAHs in sediments that is derived from petroleum declines as the distance from point sources of petroleum hydrocarbons increases.

Mean concentrations of total petroleum hydrocarbons in surficial sediments from the four reference sites range from 0.023 to 0.210 μg/g. These background concentrations of PAHs probably come from deposition of combustion-derived soot and ash particles, often rich in high molecular weight PAHs (Neff, 1979), and from natural oil seeps that are abundant in the area (MacDonald *et al.*, 1996). The most abundant high molecular weight PAH in sediments from discharge and reference sites is perylene, which is a natural diagenic PAH, produced from the breakdown of plant material in sediments (Venkatesan, 1988). Perylene represents nearly half the total PAHs in sediment from reference site WC 448 (**Table 9.38**).

Sediments 2,000 m from the four produced water discharges contain essentially background concentrations of total PAHs. PAH concentrations in these sediments (means, 0.082 to 0.287 μg/g) are comparable to or only slightly higher than PAH concentrations (means, 0.023 to 0.210 μg/g) in surficial sediments from four reference sites away from produced water discharges. Brooks *et al.* (1990) reported a background concentration of total PAH in sediments offshore Matagorda, Texas (south Texas outer continental shelf), of 0.029 ± 0.028 μg/g; nearshore sediments contained a mean of 0.096 ± 0.112 μg/g total PAHs. Mean total PAH concentrations generally were less than 0.05 μg/g in sediments more than 300 m from three production platforms off the Texas coast monitored as part of the GOOMEX Program (Kennicutt, 1995). These concentrations generally are lower than concentrations reported here from 2,000 m from offshore produced water discharges and from reference sites. Neff *et al.*, (1989, 1992) reported background concentrations of total PAHs in sediments 1,000 m from a produced water discharge in 8 m of water off Louisiana of 0.019 to 0.156 μg/g, comparable to background concentrations in sediments reported here. The higher background concentration of PAHs in sediments from the continental shelf of the northwestern Gulf of Mexico may be derived from the

Table 9.36. Mean concentrations (n = 3) of individual PAHs in surficial sediments at different distances from the produced water discharge from SMI 236A in 6 m of water. Concentrations are μg/g dry weight.

Compound	SMI 236A (Discharge)	SMI 236A (20 m)	SMI 236A (2,000 m)
Naphthalene	B	B	B
C_1-Naphthalene	0.014	0.010	0.006
C_2-Naphthalene	0.045	0.029	0.011
C_3-Naphthalene	0.076	0.063	0.010
C_4-Naphthalene	0.086	0.096	0.011
Acenaphthylene	ND	ND	ND
Acenaphthene	0.006	0.002	ND
Biphenyl	0.003	0.002	0.001
Fluorene	0.008	0.003	0.002
C_1-Fluorenes	0.035	0.016	0.002
C_2-Fluorenes	0.034	0.028	0.004
C_3-Fluorenes	0.036	0.055	0.007
Anthracene	0.011	0.003	0.001
Phenanthrene	0.063	0.010	0.007
C_1-Phenanthrenes	0.048	0.017	0.010
C_2-Phenanthrenes	0.059	0.046	0.014
C_3-Phenanthrenes	0.041	0.061	0.010
C_4-Phenanthrenes	0.026	0.055	0.010
Dibenzothiophene	0.005	0.002	0.001
C_1-Dibenzothiophenes	0.011	0.008	0.003
C_2-Dibenzothiophenes	0.018	0.018	0.004
C_3Dibenzothiophenes	0.017	0.026	0.006
Fluoranthene	0.067	0.019	0.011
Pyrene	0.053	0.018	0.011
C_1-Fluoranthenes/Pyrenes	0.042	0.020	0.012
C_2-Fluoranthenes/Pyrenes	0.021	0.018	0.009
C_3-Fluoranthenes/Pyrenes	0.011	0.017	0.005
Benz(a)anthracene	0.027	0.006	0.005

Table 9.36. (Continued).

Compound	SMI 236A (Discharge)	SMI 236A (20 m)	SMI 236A (2,000 m)
Chrysene	0.029	0.008	0.007
C_1-Chrysenes	0.018	0.009	0.007
C_2-Chrysenes	0.012	0.013	0.006
C_3-Chrysenes	0.006	0.011	0.003
C_4-Chrysenes	0.005	0.011	0.003
Benzo(b)fluoranthene	0.033	0.012	0.013
Benzo(k)fluoranthene	0.011	0.003	0.003
Benzo(e)pyrene	0.016	0.007	0.008
Benzo(a)pyrene	0.022	0.006	0.006
Perylene	0.018	0.064	0.051
Indeno(1,2,3-cd)pyrene	0.013	0.006	0.007
Dibenz(a,h)anthracene	0.003	0.001	0.001
Benzo(ghi)perylene	0.032	ND	B
Total PAHs	1.1	0.80	0.29
Total Low MW PAHs	0.64	0.55	0.12

B = Detected in blanks.

Table 9.37. Mean concentrations (n = 3 or 6) of individual PAHs in surficial sediments at different distances from the produced water discharges from VR 214A, HI A-595CF, and SMI 130B. Concentrations are μg/g dry wt.

Compound	VR 214A (20 m)	VR 214A (2,000 m)	HI A-595CF (60 m)	HI A-595CF (2,000 m)	SMI 130B (50 m)	SMI 130B (2,000 m)
Naphthalene	0.005	B	B	B	B	B
C_1-Naphthalene	0.015	0.002	0.002	0.001	0.008	0.002
C_2-Naphthalene	0.040	0.004	0.004	0.003	0.029	0.003
C_3-Naphthalene	0.090	0.010	0.007	0.006	0.062	0.004
C_4-Naphthalene	0.131	0.005	0.012	0.003	0.075	0.005
Acenaphthylene	ND	ND	ND	ND	ND	ND
Acenaphthene	0.003	ND	0.001	ND	ND	ND
Biphenyl	0.007	0.001	0.001	ND	0.003	0.001
Fluorene	0.003	0.001	0.002	ND	0.002	ND
C_1-Fluorenes	0.013	0.001	0.002	0.001	0.013	0.001
C_2-Fluorenes	0.026	0.002	0.003	0.001	0.026	0.002
C_3-Fluorenes	0.037	0.004	0.007	0.002	0.043	0.004
Anthracene	0.003	0.001	0.004	ND	0.002	ND
Phenanthrene	0.009	0.003	0.008	0.001	0.006	0.002
C_1-Phenanthrenes	0.025	0.004	0.006	0.002	0.026	0.003
C_2-Phenanthrenes	0.045	0.007	0.011	0.004	0.056	0.007
C_3-Phenanthrenes	0.041	0.004	0.013	0.003	0.057	0.005
C_4-Phenanthrenes	0.045	0.008	0.023	0.003	0.054	0.005
Dibenzothiophene	0.002	ND	0.001	ND	0.003	ND
C_1-Dibenzothiophenes	0.009	0.001	0.002	0.001	0.012	0.001
C_2-Dibenzothiophenes	0.014	0.002	0.005	0.001	0.033	0.003
C_3Dibenzothiophenes	0.015	0.003	0.009	0.002	0.045	0.004
Fluoranthene	0.082	0.014	0.023	0.002	0.007	0.003
Pyrene	0.073	0.013	0.019	0.002	0.020	0.003
C_1-Fluoranthenes/Pyrenes	0.058	0.009	0.021	0.003	0.034	0.004
C_2-Fluoranthene/Pyrenes	0.025	0.005	0.013	0.002	0.041	0.005
C_3-Fluoranthenes/Pyrenes	0.016	0.003	0.012	0.002	0.041	0.006
Benz(a)anthracene	0.054	0.009	0.011	0.001	0.002	0.002
Chrysene	0.048	0.010	0.015	0.002	0.008	0.003

Table 9.37. (Continued).

Compound	VR 214A (20 m)	VR 214A (2,000 m)	HI A-595CF (60 m)	HI A-595CF (2,000 m)	SMI 130B (50 m)	SMI 130B (2,000 m)
C_1-Chrysenes	0.028	0.005	0.010	0.002	0.017	0.004
C_2-Chrysenes	0.014	0.004	0.010	0.002	0.028	0.005
C_3-Chrysenes	0.007	0.003	0.007	0.001	0.023	0.005
C_4-Chrysenes	0.005	0.003	0.005	0.001	0.013	0.004
Benzo(b)fluoranthene	0.10	0.015	0.013	0.004	0.006	0.005
Benzo(k)fluoranthene	0.032	0.005	0.004	0.001	0.001	0.001
Benzo(e)pyrene	0.044	0.007	0.007	0.002	0.004	0.003
Benzo(a)pyrene	0.070	0.011	0.007	0.002	0.002	0.002
Perylene	0.041	0.025	0.013	0.011	0.063	0.030
Indeno(1,2,3-cd)pyrene	0.044	0.008	0.004	0.003	0.002	0.002
Dibenz(a,h)anthracene	0.010	0.002	0.001	ND	0.001	ND
Benzo(ghi)perylene	0.062	0.015	ND	ND	ND	ND
Total PAHs	1.4	0.22	0.32	0.082	0.87	0.15
Total Low MW PAHs	0.57	0.061	0.12	0.027	0.55	0.059

B = Detected in blanks.

Table 9.38. Mean concentrations (n = 3) of individual PAHs in surficial sediments at four reference platform (non-discharging) sites in the northwestern Gulf of Mexico. Concentrations are μg/g dry weight.

Compound	WC 448	SMI 186/195	GA A-90 and GA A-205
Naphthalene	B	B	B
C_1-Naphthalene	0.001	0.003	ND
C_2-Naphthalene	0.003	0.003	0.001
C_3-Naphthalene	0.003	0.003	0.001
C_4-Naphthalene	0.004	0.003	ND
Acenaphthylene	ND	ND	ND
Acenaphthene	ND	ND	ND
Biphenyl	ND	ND	ND
Fluorene	0.001	ND	ND
C_1-Fluorenes	0.001	ND	ND
C_2-Fluorenes	0.001	0.001	ND
C_3-Fluorenes	0.002	0.001	ND
Anthracene	0.001	ND	ND
Phenanthrene	0.002	0.001	0.001
C_1-Phenanthrenes	0.003	0.001	0.001
C_2-Phenanthrenes	0.005	0.003	0.002
C_3-Phenanthrenes	0.004	0.002	0.001
C_4-Phenanthrenes	0.005	0.003	0.001
Dibenzothiophene	ND	ND	ND
C_1-Dibenzothiophenes	0.001	0.001	ND
C_2-Dibenzothiophenes	0.002	0.001	0.001
C_3Dibenzothiophenes	0.003	0.001	ND
Fluoranthene	0.004	0.002	0.002
Pyrene	0.004	0.002	0.001
C_1-Fluoranthenes/Pyrenes	0.005	0.002	0.001
C_2-Fluoranthenes/Pyrenes	0.005	0.002	0.001
C_3-Fluoranthenes/Pyrenes	0.005	0.002	ND
Benz(a)anthracene	0.002	0.001	0.001

Table 9.38. (Continued).

Compound	WC 448	SMI 186/195	GA A-90 and GA A-205
Chrysene	0.003	0.002	0.001
C_1-Chrysenes	0.004	0.002	0.001
C_2-Chrysenes	0.007	0.002	0.001
C_3-Chrysenes	0.006	0.002	ND
C_4-Chrysenes	0.005	0.002	ND
Benzo(b)fluoranthene	0.006	0.003	0.002
Benzo(k)fluoranthene	0.002	0.001	0.001
Benzo(e)pyrene	0.003	0.002	0.001
Benzo(a)pyrene	0.002	0.001	0.001
Perylene	0.103	0.007	0.003
Indeno(1,2,3-cd)pyrene	0.003	0.001	0.001
Dibenz(a,h)anthracene	0.001	ND	ND
Benzo(ghi)perylene	ND	ND	ND
Total PAHs	0.21	0.060	0.023
Total Low MW PAHs	0.043	0.023	0.007

B = Detected in blanks.

massive outflow of the Mississippi River, which is the dominant source of surficial sediments along the coasts of Louisiana and north Texas, or from long-range transport of combustion-derived, particle-bound PAHs, and from natural oil seeps on the outer continental shelf off Louisiana.

9.2.5.3 Ecorisk of Polycyclic Aromatic Hydrocarbons in Sediments Near Produced Water Discharges

PAHs and other nonpolar organic chemicals partition between the sorbed phase of sediments and sediment interstitial water according to their relative affinities for the sediment organic carbon and water phases of the sediment (Karickhoff *et al.*, 1979). Therefore, a fraction of the PAHs associated with surficial sediments is in solution in sediment interstitial water in a bioavailable form and may adversely affect benthic fauna if its concentration in the interstitial water phase exceeds some critical concentration. Long and Morgan (1990) and Long *et al.* (1995) have gathered data on the concentrations of several PAHs in sediments that are associated with adverse effects in estuarine and marine organisms. From these data, they have developed ERL and ERM concentrations that can serve as threshold concentrations for PAHs in sediments. Because a large number of PAHs co-occur in sediments and their toxicities are thought to be additive, the ERM values were used to predict the toxicity of PAHs in sediments near the four produced water discharges.

ERM values for individual and total PAHs in sediments range from 0.260 to 44.79 μg/g dry weight (**Table 9.39**). The toxic units (concentration in sediments/ERM) for individual PAHs, based on individual analyses of PAHs in sediments 20, 50, and 60 m from the four produced water discharge sites, range from 0.0004 to 0.094 (**Table 9.39**). The toxic units for total low molecular weight PAHs (naphthalene through phenanthrenes), which are characteristic of petroleum, range from 0.010 to 0.329. The toxic units for total high molecular weight PAHs and total PAHs range from 0.004 to 0.148, and 0.002 to 0.055, respectively. The apparent paradox that the toxic units for total low molecular weight PAHs is higher than the total toxic units for total PAHs (which includes low molecular weight and high molecular weight PAHs) is explained by the high ERM value for total PAHs. The high ERM for total PAHs probably is caused by a bias in the raw data used to generate the ERM, resulting from examination of sediments contaminated primarily with combustion-derived PAHs. Combustion-derived, particulate PAHs tend to be tightly bound to soot particles and are not readily bioavailable to marine organisms (Farrington, 1986).

The results of comparison of measured concentrations of individual and total PAHs in sediments 20, 50, and 60 m from produced water discharges with ERM values indicates that PAHs in sediments near the produced water discharges are unlikely to be toxic to benthic marine animals living in the area. Low molecular weight PAHs contribute most to the fractional toxicity of the sediments. Sediments collected 20 m from VR 214A contain a mean of 1.37 μg/g total PAHs, including 0.57 μg/g total low molecular weight PAHs (mean toxic units, 0.18) could be toxic to some sensitive species or life stages of marine animals. However, any effects would be very localized. Concentrations of individual and total PAHs in sediments are much lower at greater than 60 m from the discharging platforms; PAH concentrations in these sediments are well below concentrations that might be toxic to benthic marine organisms.

Table 9.39. Comparison of concentrations ranges of PAHs measured in sediments within 60 m of four produced water discharges and Effects Range Median (ERM) sediment threshold concentrations (Long *et al.*, 1995). Toxic units for sediments (concentration in sediment/ERM) also are given. Concentrations are μg/g dry weight.

Compound	Concentration Range in Sediments	ERM	Toxic Units
Naphthalene	0.005 - 0.016	2.100	0.002 - 0.008
Methylnaphthalenes	0.001 - 0.019	0.670	0.001 - 0.028
Fluorene	0.0003 - 0.016	0.540	0.0006 - 0.030
Phenanthrene	0.001 - 0.14	1.500	0.0007 - 0.093
Low MW PAHs	0.032 - 1.0	3.160	0.010 - 0.33
Fluoranthene	0.002 - 0.13	5.100	0.0004 - 0.025
Pyrene	0.002 - 0.11	2.600	0.0008 - 0.042
Benz(a)anthracene	0.001 - 0.080	1.600	0.0006 - 0.050
Chrysene	0.001 - 0.082	2.800	0.0004 - 0.029
Benzo(a)pyrene	0.001 - 0.15	1.600	0.0006 - 0.094
Dibenz(a,h)anthracene	0.0002 - 0.021	0.260	0.0008 - 0.081
High MW PAHs	0.042 - 1.4	9.600	0.004 - 0.15
Total PAHs	0.074 - 2.5	44.792	0.002 - 0.055

In summary, PAHs in sediments under and within a short distance from the produced water discharge of these platforms generally are not present at potentially toxic concentrations. Usually, impacts of production discharges from offshore platforms, when they can be detected at all, are restricted to the benthic environment in the immediate vicinity of the platform (Neff, 1987; Neff *et al.*, 1992; Kingston, 1992). Adverse effects in benthic ecosystems near oil platforms usually are attributable to accumulation in the sediments of petroleum hydrocarbons, particularly PAHs. The severity of biological effects often is correlated with concentrations of petroleum PAHs in the sediments, or to severity of hypoxia in surficial sediments. The hypoxia, in turn, is caused by biodegradation of petroleum hydrocarbons in the sediments (Kingston 1987, 1992). In the present study, accumulation of PAHs in sediments near the four offshore produced water discharges was, in one case, to marginally toxic concentration levels and effects on the benthos probably are minimal or undetectable, particularly at the deeper water platforms.

9.2.6 Summary of Ecorisk of Metals and Polycyclic Aromatic Hydrocarbons in Sediments Near Produced Water Discharges

Barium and iron may be present at elevated concentrations in sediments near offshore produced water discharges. However, they are present in the sediments in insoluble forms (iron sulfide, iron oxyhydroxides, and barium sulfate) that are not bioavailable or toxic. Zinc and lead are present in some sediments near produced water discharges at concentrations approaching their ERM values. It is possible that these metals are contributing to the toxicity to benthic organisms that sediments near produced water discharges may have. However, most of these metals probably are present in the sediments as sulfide precipitates and are not bioavailable or toxic.

PAHs are present in sediments near the four produced water discharges at higher concentrations than in reference site sediments. None of the individual PAHs or total PAHs are present in the sediments near the platforms at concentrations that might be toxic to benthic marine organisms. In shallow, nearshore waters, PAH may accumulate in sediments near produced water discharges to concentrations high enough to cause adverse effects in the local benthic communities (Neff *et al.*, 1992; Rabalais *et al.*, 1992). The extent to which metals and PAHs from produced water accumulate in sediments near produced water discharges to potentially toxic concentrations apparently depends not only on the concentrations of the metals and PAHs in the produced water, but also to the volume of produced water discharged, water depth at the discharge site, sediment texture, and local oceanographic conditions that may promote or inhibit nearfield deposition in the sediments.

9.2.7 Ecorisk of Metals in Tissues of Marine Animals

Nearly all metals and metalloids of concern as potential environmental toxins are natural constituents of clean seawater (Li, 1991). Most of these metals and metalloids also are present in the tissues of marine plants and animals at concentrations equivalent to or greater than their concentrations in the seawater in which the organisms live. Of the 15 metals and metalloids analyzed in the present study in produced water, sediments, and tissues of marine animals, 11 are considered essential trace nutrients for most plants and animals (Iyengar, 1991). The metals that are not essential micronutrients are barium, cadmium, mercury, and lead. The essential metals usually are transported across biological membranes of marine organisms by an enzyme-mediated pump. Non-essential metals usually penetrate membranes of permeable epithelia, such as those in the gills or gut, by facilitated or passive diffusion (Simkiss and Taylor, 1989; Newman and Jagoe, 1994). The essential micronutrients are regulated within a relatively narrow range in tissues of marine animals, except when ambient concentrations in seawater reach high, nearly lethal concentrations (Chapman *et al.*, 1996). The non-essential metals are not regulated but instead are detoxified in tissues by precipitation in solid granules or by binding to specific binding proteins, such as metallothionein (Simkiss and Taylor, 1989; Roesijadi, 1992).

Concentrations of essential and non-essential metals in tissues of apparently healthy marine animals of different species may vary over several orders of magnitude. Some marine organisms accumulate apparently non-essential metals in their tissues to high concentrations or essential metals to concentrations much higher than required (Peterson, 1971). Examples of this phenomenon include: accumulation of arsenic to more than 2,000 μg/g dry weight by the polychaete *Tharix marioni* (Gibbs *et al.*, 1983); deposition of barium as barium sulfate in several species of zooplankton (Gooday and Nott, 1982); accumulation of cadmium to more than 100 μg/g in the tissues of the oceanic hyperiid amphipod *Thermisto glaudichaudii* (Rainbow, 1989), and in the kidneys of several species of scallops (Coombs, 1979); accumulation of vanadium in blood cells of the ascidian *Ascidia gemmata* to concentrations in excess of 1,900 μg/g (Michibata, 1996); and accumulation of zinc to concentrations approaching 150,000μg/g in barnacles (Rainbow *et al.*, 1990). This variable bioaccumulation of metals by marine animals makes it difficult to detect enhanced bioaccumulation of metals from produced water or identify tissue concentrations of metals that might pose a toxic risk to the marine organisms themselves (Rainbow *et al.*, 1990).

One approach to estimating tissue residues of metals that might be toxic to marine animals is to estimate a critical body residue by multiplying the chronic marine water quality criterion for the metal by the metal's bioconcentration factor (BCF) (Neff, 1994; Shephard, 1995). This approach produces highly variable results because the BCF for metals varies widely from one species to another, due to metal regulation and sequestration (Chapman *et al.*, 1996) and, as discussed above, natural concentrations of metals in tissues of healthy marine animals vary widely. Tissue screening concentrations (TSCs) developed for several metals by Shephard (1995) as well as "high" concentrations in mussel and oyster tissues developed from the National Status and Trends Mussel Watch data base (O'Connor and Beliaeff, 1995) are summarized in **Table 9.40**. Several of the TSCs developed by Shephard (1995) are based on freshwater chronic criteria. Because kinetics of metal bioaccumulation probably is different in freshwater and marine animals, these values were converted to marine TSC by using the marine chronic criteria.

There is little agreement between metal TSCs and "high" concentrations developed by NOAA (O'Connor and Beliaeff, 1995). The "high" values are not health screening values but are typical tissue residue levels that give an indication of the tissue residues of several metals that can be tolerated by mussels and oysters. These values show that mussels and oysters may differ widely in tissue residues of copper, lead, and zinc. Oysters often contain higher concentrations of copper and zinc than mussels; mussels may contain substantially higher concentrations of tissue lead than oysters.

Table 9.40. Tissue screening concentrations (TSCs) and "high" concentrations in marine mussels and oysters of several metals. TSCs are from Shephard (1995) or were calculated based on marine chronic values, and "high" concentrations are from O'Connor and Beliaeff (1995). Concentrations are μg/g dry tissue (converted from wet weight for TSCs by multiplying by 5).

Compound	TSC	High Concentration
Aluminum	22*	—
Arsenic	8.0	17
Cadmium	2.97	5.7
Chromium	4.0	—
Copper	0.85	13 (mussel) 490 (oyster)
Lead	2.08	4.3 (mussel) 0.96 (oyster)
Mercury	0.60	0.24
Nickel	1.65	3.3
Zinc	20.2	210 (mussel) 6,500 (oyster)

* TSC based on freshwater water quality criteria.

9.2.7.1 Arsenic

Mean concentrations of arsenic in tissues of bivalve molluscs, crustaceans, and fish from the vicinity of seven offshore produced water discharges range from 0.12 to 59 μg/g dry weight (**Tables 9.41** through **9.45**). Mean concentrations in soft tissues of bivalves and fish from two nearby reference non-discharging platforms and an offshore hard bank (VR 298/305 - Sonnier Bank) range from 4.2 to 86 μg/g (**Table 9.45**). Thus, marine animals near produced water discharges do not contain higher concentrations of arsenic than those from non-discharge areas; the marine animals are not bioaccumulating arsenic from the produced water discharges.

Two of the three mean concentrations of arsenic in tissues of marine animals from reference sites and nine of the 22 mean concentrations in tissues of marine animals from the four discharge sites are above both the TSC value (8.0 μg/g) and the "high" concentration (17 μg/g). Highest concentrations of arsenic in tissues of marine animals from both reference and discharge sites are consistently found in the bivalve mollusc jewelbox and the gray triggerfish.

Arsenic concentrations in tissues are highly variable from one species to another. The large range observed in this study may be related in part to differences in concentrations of dissolved arsenic in nearshore waters strongly influenced by freshwater runoff from land (usually low in arsenic) and offshore oceanic waters. Arsenic concentrations in ambient seawater range from 0.64 μg/L at VR 214A (nearshore) to 1.6 μg/L at HI A-595CF (offshore). Open ocean waters may contain up to 3 μg/L arsenic (Neff, 1996b).

Crustaceans, bivalve molluscs, and fish usually contain a similar range concentrations of arsenic in their soft tissues (**Table 9.46**). However, arsenic concentrations in different species of these major taxonomic groups vary widely. This variability in concentrations of arsenic in tissues of marine animals may be related to the forms and concentrations of arsenic in ambient seawater and the diet and the ability of different marine animals to sequester, metabolize, or excrete accumulated inorganic and organic arsenic. Marine micro- and macro-algae can bioaccumulate dissolved arsenate (the dominant form of arsenic in seawater) from seawater and convert it to organic forms that are sequestered in the tissues (Neff, 1996b). Marine animals that consume the algae bioaccumulate large amounts of arsenic, particularly the organic forms. Thus, bivalves, that filter feed on microalgae, and some herbivorous marine crustaceans and fish contain high concentrations of arsenic in their tissues. This may explain the high concentrations of arsenic in jewelboxes (filter-feeders) and gray triggerfish (grazers on biofouling macroalgae). More than 90% of the total arsenic in tissues of herbivorous molluscs, crustaceans, and fish is in organic forms, primarily as arsenobetaine (Francesconi and Edmonds, 1993). The organic arsenic in tissues of marine animals is not toxic to the animals themselves or their consumers, including man (Vahter *et al.*, 1983; Sabbioni *et al.*, 1991).

The concentrations of total arsenic measured in this study in muscle or whole tissues of marine crustaceans, molluscs, and fish are within the range of concentrations reported for these taxa worldwide (**Table 9.46**). Most of the tissue arsenic is organic, a form that is not toxic to the marine animals. Therefore, the observed concentrations of arsenic in tissues of marine animals pose no risk of toxicity to the marine animals.

Table 9.41. Mean concentrations of arsenic, barium, cadmium, and mercury in edible and non-edible tissues of marine animals from the vicinity of SMI 236A. Concentrations are in μg/g dry weight.

Species	Arsenic	Barium	Cadmium	Mercury
Atlantic croaker (*Micropogonias undulatus*)	1.5	8.4	0.06	0.029
Hardhead catfish (*Arius felis*)	0.48	1.4	0.04	0.36
Silver seatrout (*Cynoscion nothus*)	0.12	5.9	0.18	0.037
Atlantic cutlassfish (*Trichiurus lepturus*)	0.20	1.8	0.19	0.054
Penaeid shrimp (*Penaeus* spp.)				
muscle	4.1	4.6	0.14	0.040
other	2.9	99	0.38	0.029
Blue crab (*Callinectes* spp.)	10	6.8	0.39	0.29
Eastern oyster (*Crassostrea virginica*)	11	10	6.7	0.061

Table 9.42. Mean concentrations of arsenic, barium, cadmium, and mercury in edible and non-edible tissues of marine animals from the vicinity of VR 214A. Concentrations are in μg/g dry weight.

Species	Arsenic	Barium	Cadmium	Mercury
Red snapper (*Lutjanus campechanus*)				
fillet	1.1	0.15	0.04	0.37
carcass	0.77	1.5	0.05	0.16
Gray triggerfish (*Balistes capriscus*)				
fillet	22	0.06	<0.04	1.0
carcass	13	8.3	0.63	0.62
Jewelbox (*Chama macerophylla*)	31	20	5.3	0.05

Table 9.43. Mean concentrations of arsenic, barium, cadmium, and mercury in edible and non-edible tissues of marine animals from the vicinity of SMI 130B. Concentrations are in μg/g dry weight.

Species	Arsenic	Barium	Cadmium	Mercury
Red snapper (*Lutjanus campechanus*)				
fillet	0.72	0.07	<0.05	0.28
carcass	0.60	2.0	0.18	0.16
Gray triggerfish (*Balistes capriscus*)				
fillet	33	0.61	<0.10	0.44
carcass	20	15	0.58	0.41
Longspine porgy (*Stenotomus caprinus*)	0.24	32	0.13	0.42
Vermilion snapper (*Rhomboplites aurorubens*)	3.2	0.05	0.02	0.13
Swimming crab (*Portunus* spp.)	35	120	0.87	0.094
Jewelbox (*Chama macerophylla*)	26	14	5.2	0.054

Table 9.44. Mean concentrations of arsenic, barium, cadmium, and mercury in edible tissues of marine animals from the vicinity of HI A-595CF. Concentrations are in μg/g dry weight.

Species	Arsenic	Barium	Cadmium	Mercury
Vermilion snapper (*Rhomboplites aurorubens*)	3.2	0.15	0.02	0.37
Longspine porgy (*Stenotomus caprinus*)	0.40	26	0.25	0.65
Jewelbox (*Chama macerophylla*)	41	43	7.1	0.046

Table 9.45. Mean concentrations of arsenic, barium, cadmium, and mercury in edible tissues of marine animals from the vicinity of three discharging platforms (D), two reference platforms (R), and a natural hard bank. Concentrations are in μg/g dry weight.

Species	Location	Arsenic	Barium	Cadmium	Mercury
Red snapper (*Lutjanus campechanus*)	Bank	4.2	0.06	<0.02	0.72
Gray triggerfish (*Balistes capriscus*)	Bank	86	0.08	0.01	0.47
Jewelbox (*Chama macerophylla*)	EI 313A (D)	43	13	14	0.065
Jewelbox (*C. macerophylla*)	HI A-323A (D)	59	79	11	0.12
Jewelbox (*C. macerophylla*)	HI A-389 (R)	32	74	7.1	0.051
Jewelbox (*C. macerophylla*)	MI 703A (D)	29	14	4.2	0.11
Eastern oyster (*Crassostrea virginica*)	SMI 229C (R)	10	12	5.4	0.13

Table 9.46. Range of concentrations of total arsenic in whole or muscle tissues of marine crustaceans, bivalve molluscs, and fish from throughout the world, including the Gulf of Mexico. Concentrations are μg/g dry weight. (From: Neff, 1996a).

Location/Taxon	Number of Samples	Range	Arithmetic Mean	Standard Deviation	Geometric Mean
Gulf of Mexico					
Crustaceans	12	0.2 - 10	2.8	3.5	0.98
Bivalves	43	<0.1 - 130	17	25	7.7
Fish	22	0.1 - 110	7.3	24	0.84
World					
Crustaceans	96	<0.1 - 270	35	47	15
Bivalves	151	<0.6 - 210	18	26	10
Fish	156	0.05 - 450	0.37	0.30	0.25

9.2.7.2 Barium

Concentrations of barium in soft tissues of marine animals from the reference and produced water discharge sites also are highly variable (**Tables 9.41** through **9.45**). Highest concentrations are in soft tissues of jewelboxes and muscle tissue of swimming crabs *Portunus* spp. Muscle tissues of fish usually contain low concentrations, though longspine porgy from discharging sites SMI 130B and HI A-595CF contain 32 and 26 μg/g barium, respectively, in muscle tissue. Jewelbox from discharge sites contain means of 26 to 59 μg/g barium in soft tissues, compared to a mean of 32 μg/g at the reference site where jewelbox were collected. Red snapper from discharge and reference sites also contain similar concentrations of barium. However, muscle of gray triggerfish from a discharge site contains significantly higher concentrations (mean, 0.61 μg/g) than from a natural hard bank (mean, 0.08 μg/g). The carcass (including organ tissues and bone) of gray triggerfish from the discharge site contains a mean of 15 μg/g barium. Much of the barium in tissues of marine animals containing higher than expected concentrations of barium may be in the form of insoluble barite concretions in various tissues (Jenkins *et al.*, 1989).

There are no tissue screening concentrations or "high" concentrations for barium. The limited published information on concentrations of barium in soft tissues of marine animals indicates a wide variability in tissue residues in different major taxonomic groups and among species within a taxonomic category (**Table 9.47**). Concentrations of barium measured in this study in tissues of marine animals from the northwestern Gulf of Mexico are in the range of published concentrations in tissues of marine animals worldwide. Bivalve molluscs collected from the vicinity of drilling rigs discharging water base drilling fluids (rich in barite) often contain elevated concentrations of barium in whole soft tissues (Jenkins *et al.*, 1989; Naito, 1994). Gills of fish also often contain high concentrations of barium (Başsari, 1994). Barium may be present in the fish gills and soft tissues of bivalves as solid concretions of insoluble, inert barite.

There is no published information about the concentration of barium in tissues of marine animals that may be associated with an elevated risk of toxicity. Because of the low solubility of barium in the sulfate-rich medium of seawater and the tissues of marine animals, barium cannot reach toxic concentrations in solution in seawater. Assuming that the toxicity of a metalloid like barium is dependent upon accumulation of the chemical in tissues to a critical body residue from the ambient seawater, then it is not likely that marine animals can bioaccumulate enough dissolved barium from seawater to elicit toxic responses. Thus, barium is present in tissues of marine animals from the northwestern Gulf of Mexico at concentrations below those that could be toxic to the marine organisms themselves. The risk based concentration for barium in fish tissues destined for human consumption (the maximum acceptable concentration in human food) is 95 μg/g wet weight (equivalent to approximately 475 μg/g dry weight) (EPA, 1995). Thus, all the marine animals collected in this study would not pose a health risk to human consumers from barium poisoning.

Table 9.47. Concentrations of barium in marine crustaceans, bivalve molluscs, and fish from throughout the world. Concentrations are μg/g dry weight (From: Neff, 1996a).

Taxon	Number of Analyses	Arithmetic Mean Concentration	Standard Deviation	Geometric Mean Concentration
Crustaceans	16	22.5	53.0	3.42
Bivalve Molluscs	27	18.0	34.3	4.40
Fish	33	3.41	10.1	0.13

9.2.7.3 Cadmium

Mean concentrations of cadmium in tissues of marine animals from reference and produced water discharge sites range from 0.01 to 14 μg/g, a range of three orders of magnitude (**Tables 9.41** through **9.45**). Lowest concentrations are in edible tissues of fish. Highest concentrations are in soft tissues of jewelboxes and oysters. Published concentrations of cadmium in soft tissues of clams and oysters worldwide range from 0.03 to 144 μg/g. Fish muscle tissue contains 0.001 to 5.8 μg/g (Neff, 1996a). Concentrations of cadmium in tissues of animals examined in this study are, for the most part, in the lower part of these ranges.

The TSC and "high" concentrations of cadmium in tissues or marine animals are 2.97 μg/g and 5.7 μg/g, respectively (**Table 9.40**). Only concentrations in tissues of oysters from discharging site SMI 236A and jewelboxes from all sampling sites where they were found, including reference sites, exceed these screening values. Jewelboxes may resemble oysters and scallops by accumulating cadmium from natural dissolved concentrations in seawater and storing them in insoluble concretions in various tissues. Cadmium concentrations in edible and carcass tissues of all the species of fish and crustaceans are well below the tissue TSC concentration. Therefore, it is likely that the concentrations of cadmium in tissues of crustaceans, bivalves, and fish are below concentrations that would represent a toxic threat to these marine animals.

9.2.7.4 Mercury

Concentrations of mercury in muscle and carcass tissues of marine fish collected in this study range from 0.029 to 1.0 μg/g (**Tables 9.41** through **9.45**). Crustaceans contain 0.029 to 0.29 μg/g total mercury. The two species of bivalves contain mean concentrations of 0.05 to 0.12 μg/g. These concentrations are consistent with concentrations reported in the published scientific literature for these taxa. Fish may contain up to more than 100 μg/g total mercury in their muscle tissues, most of it as organic mercury (Lasorsa and Allen-Gil, 1995). The concentration ranges reported here are in the lower part of the published ranges for marine crustaceans, bivalves, and fish and are comparable to geometric mean concentrations (indicative of a typical concentration) (**Table 9.48**).

The TSC and "high" concentration of total mercury in tissues of marine animals are 0.60 and 0.24, respectively (**Table 9.40**). All mercury concentrations in soft tissues of the two species of bivalves collected in this study are below both screening values. Only gray triggerfish muscle and carcass from discharging site VR 214A and red snapper muscle from the reference hard bank site contain mercury concentrations higher than the TSC value. Niimi and Kissoon (1994) estimated a threshold critical body burden (similar to TSC) of 5 to 25 μg/g dry weight for rainbow trout *Oncorhynchus mykiss.* Thus, it is highly likely that the red snapper and gray triggerfish are not suffering any adverse effects from tissue residues of 0.7 to 1.0 μ/g. There is a low risk of harm to the marine animals from mercury residues in tissues of marine crustaceans, bivalves, and fish near produced water discharges to the northwestern Gulf of Mexico.

Table 9.48. Concentration ranges and averages for total mercury in soft tissues or marine animals from throughout the world. Concentrations are μg/g dry weight (From: Neff, 1996a).

Taxon	Number of Analyses	Concentration Range	Arithmetic Mean Concentration	Standard Deviation	Geometric Mean Concentration
Mussels	60	0.004 - 11.7	0.88	2.19	0.17
Oysters	74	0.003 - 8.04	0.43	1.05	0.13
Clams	32	0.005 - 85	6.61	19.94	0.28
Shrimp	27	0.02 - 6.2	1.16	1.60	0.45
Crabs	20	0.015 - 2.3	0.78	0.74	0.23
Fish	379	0.01 - 115	2.49	7.93	0.77

9.2.7.5 Copper

Mean concentrations of copper in muscle and carcass tissues of marine fish from reference and produced water discharge sites in the northwestern Gulf of Mexico range from 0.75 to 20 μg/g (**Tables 9.49** through **9.53**). Tissues of portunid crabs and penaeid shrimp contain higher mean concentrations, ranging from 26 to 61 μg/g. However, oysters contain the highest mean concentrations of copper in their tissues, with means of 140 μg/g at discharge site SMI 236A and 160 μg/g at nearby reference site SMI 229C. Mean concentrations of copper in soft tissues of jewelboxes range from 4.7 to 11 μg/g.

The concentrations of copper reported for soft tissues of crustaceans and fish are comparable to concentrations reported by Horowitz and Presley (1977) for the same or closely related species from the south Texas outer continental shelf (**Table 9.54**). Most of the marine animals analyzed by Horowitz and Presley (1977) were collected from offshore waters well away from offshore oil and gas development activities, and probably represent natural concentrations of copper in tissues of marine animals from the Gulf of Mexico. Most of the copper in crustacean tissues is associated with the copper-containing blood pigment, hemocyanin. The blood of blue crabs *Callinectes sapidus* contains about 85 mg/L hemocyanin-bound copper (Engel and Brauwer, 1991). Oysters contain naturally high concentrations of copper in their soft tissues (O'Connor and Beliaeff, 1995).

The TSC for copper in tissues of aquatic animals is very low, lower than mean concentrations of copper in muscle tissues of marine animals from all but three reference or discharge sites sampled in this study. Copper concentrations in muscle are roughly comparable in fish from reference and discharge sites, and probably are natural. Highest copper concentrations are in fish from discharging site SMI 236A in shallow water. Ambient seawater at this platform has the highest copper concentration of the sites. The excess copper in ambient seawater from this site probably comes from the Mississippi River outflow which is enriched in copper compared to oceanic seawater. The fish probably are bioaccumulating copper from the copper-enriched ambient seawater. There is no evidence that copper concentrations in seawater are affected by produced water discharges. Copper concentrations in tissues of the two species of bivalves are lower than the "high" values for mussels and oysters (O'Connor and Beliaeff, 1995) and probably are natural levels. Therefore, the risk of measure tissue concentrations of copper to marine animals from the northwest Gulf of Mexico is low.

9.2.7.6 Nickel

The TSC and "high" concentration of nickel in tissues of marine animals are 1.65 and 3.3 μg/g, respectively (**Table 9.40**). Muscle tissue of most of the fish species from reference and discharge sites contain nickel concentrations lower than or approximately the same as the TSC (**Tables 9.49** through **9.53**). Muscle of longspine porgy from the deepwater discharging site HI A-595CF contains a mean of 5.3 μg/g nickel. Carcass of gray triggerfish also contains elevated levels of nickel. Swimming crabs from discharging site SMI 130B contain a mean of 7.1 μg/g nickel. Other crustaceans contain low concentrations of nickel. Mean nickel concentrations in soft tissues of jewelboxes are high, ranging from 3.7 to 12 μg/g, all higher than the "high" concentration for mussels and oysters. The oysters contain low concentrations of nickel. Nickel concentrations are comparable in jewelboxes and oysters from reference and discharge sites, indicating that the marine animals probably are not accumulating excess nickel from the produced water discharges.

Table 9.49. Mean concentrations of copper, nickel, lead, and zinc in edible and non-edible tissues of marine animals from the vicinity of SMI 236A. Concentrations are in μg/g dry weight.

Species	Copper	Nickel	Lead	Zinc
Atlantic croaker (*Micropogonias undulatus*)	2.6	2.4	0.23	54
Hardhead catfish (*Arius felis*)	2.4	0.11	0.60	54
Silver seatrout (*Cynoscion nothus*)	5.2	1.4	0.21	72
Atlantic cutlassfish (*Trichiurus lepturus*)	2.2	1.5	0.12	41
Penaeid shrimp (*Penaeus* spp.)				
muscle	32	1.0	0.10	54
other	60	3.9	0.52	62
Blue crab (*Callinectes* spp.)	61	1.3	0.16	194
Eastern oyster (*Crassostrea virginica*)	140	1.3	0.64	1800

Table 9.50. Mean concentrations of copper, nickel, lead, and zinc in edible and non-edible tissues of marine animals from the vicinity of VR 214A. Concentrations are in μg/g dry weight.

Species	Copper	Nickel	Lead	Zinc
Red snapper (*Lutjanus campechanus*)				
fillet	0.75	1.2	0.28	15
carcass	1.9	1.5	0.20	48
Gray triggerfish (*Balistes capriscus*)				
fillet	1.1	1.5	0.10	20
carcass	3.6	1.6	7.5	280
Jewelbox (*Chama macerophylla*)	6.2	5.4	0.14	180

Table 9.51. Mean concentrations of copper, nickel, lead, and zinc in edible and non-edible tissues of marine animals from the vicinity of SMI 130B. Concentrations are in μg/g dry weight.

Species	Copper	Nickel	Lead	Zinc
Red snapper (*Lutjanus campechanus*)				
fillet	0.75	1.4	0.08	13
carcass	1.5	1.4	0.84	34
Gray triggerfish (*Balistes capriscus*)				
fillet	1.2	1.6	0.11	23
carcass	20	7.0	1.5	320
Longspine porgy (*Stenotomus caprinus*)	1.5	1.8	0.90	45
Vermilion snapper (*Rhomboplites aurorubens*)	1.4	1.5	0.08	13
Swimming crab (*Portunus* spp.)	26	7.1	0.93	78
Jewelbox (*Chama macerophylla*)	11	3.7	0.20	91

Table 9.52. Mean concentrations of copper, nickel, lead, and zinc in edible tissues of marine animals from the vicinity of HI A-595CF. Concentrations are in μg/g dry weight.

Species	Copper	Nickel	Lead	Zinc
Vermilion snapper (*Rhomboplites aurorubens*)	1.6	1.4	0.22	13
Longspine porgy (*Stenotomus caprinus*)	1.8	5.3	0.56	56
Jewelbox (*Chama macerophylla*)	6.0	6.4	0.70	140

Table 9.53. Mean concentrations of copper, nickel, lead, and zinc in edible tissues of marine animals from the vicinity of three discharging platforms (D), two reference platforms (R), and a natural hard bank. Concentrations are in μg/g dry weight.

Species	Location	Copper	Nickel	Lead	Zinc
Red snapper (*Lutjanus campechanus*)	Bank	0.83	1.4	0.09	13
Gray triggerfish (*Balistes capriscus*)	Bank	1.2	1.6	0.12	24
Jewelbox (*Chama macerophylla*)	EI 313A (D)	5.1	7.8	0.41	200
Jewelbox (*C. macerophylla*)	HI A-323A (D)	6.6	12	0.43	150
Jewelbox (*C. macerophylla*)	HI A-389 (R)	4.7	9.1	0.24	170
Jewelbox (*C. macerophylla*)	MI 703A (D)	6.8	11	4.3	100
Eastern oyster (*Crassostrea virginica*)	SMI 229C (R)	160	1.0	0.46	1800

Table 9.54. Concentrations of chromium, copper, lead, and zinc in tissues of marine plants and animals from the south Texas outer continental shelf. Concentrations are in μg/g dry weight (From: Horowitz and Presley, 1977).

Species	Chromium	Copper	Lead	Zinc
Sargassum	1.2 - 2.6	2.8 - 7.0	3.9 - 6.5	34 - 41
Mixed zooplankton	1.8 - 10.1	2.7 - 61	1.8 - 18.8	26.5 - 170
Squid (muscle & skin)	3.0 - 6.1	61 - 69	1.3 - 2.7	50 - 290
Squid (muscle)	0.4 - 11	8.5 - 21.5	0.4 - 1.8	41 - 56
Squid (viscera)	2.7 - 7.1	85.5 - 215	1.8 - 3.6	79.7 - 110
Brown shrimp (muscle)	0.4 - 3.8	18.5 - 28.5	0.5 - 1.6	20.5 - 57.5
Brown shrimp (viscera)	3.1 - 5.3	65 - 260	2.3 - 3.1	83.8 - 136
Rock shrimp (muscle)	1.8 - 4.2	23 - 38.5	1.1 - 2.0	52.5 - 62
Flatfish (muscle)	0.8 - 13.3	0.6 - 1.5	0.04 - 1.6	14 - 18.5
Flatfish (skin)	2.1 - 8.5	1.2 - 2.1	4.2 - 8.8	39.7 - 112
Longspine porgy (muscle)	0.9 - 3.2	1.0 - 1.7	0.6 - 1.4	13 - 23
Rough scad (muscle)	2.7 - 5.0	2.4 - 2.6	0.7 - 0.9	26.5 - 37
Sea robin (muscle)	0.9 - 3.9	0.8 - 1.1	0.7 - 1.5	15.5 - 18.5
Sand seatrout (muscle)	5.5 - 8.3	1.5 - 1.8	0.6 - 1.5	15.5 - 22.0
Sand seatrout (liver)	2.7	22.6	0.6	91.5
Black-ear bass (muscle)	7.2	1.0	0.8	17.5
Atlantic croaker (muscle)	7.3	1.0	0.8	17.5
Wenchman (muscle)	2.4	1.0	0.5	15.5

These concentrations generally are higher than nickel concentrations reported in muscle tissues of the same or similar species from the south Texas outer continental shelf (**Table 9.55**). However, Gulf of Mexico oysters collected between 1986 and 1988 contain 0.28 to 31 μg/g nickel in soft tissues (Presley *et al.*, 1990). Clams and shrimp from lower Chesapeake Bay, VA, contain 6.5 to 11.5 μg/g and 23.5 to 59.5 μg/g, respectively, nickel in soft tissues (Rule, 1985).

Tissue residues of nickel in fish, crustaceans, and oysters probably are low enough that they do not pose a toxic risk to the marine animals. Concentrations in jewelboxes, although higher than threshold values, are within the range observed in some other bivalve molluscs. Jewelboxes may contain naturally high concentrations of nickel. It is possible, though doubtful, that the tissue residues of nickel in jewelboxes are harmful to the molluscs.

9.2.7.7 Lead

Mean concentrations of lead in muscle of fish and crustaceans and whole soft tissues of bivalves are uniformly low, with one exception. For most species at reference and discharge sites, mean concentrations of lead range from 0.08 to 0.93 μg/g (**Tables 9.49** through **9.53**). Jewelbox from discharging site MI 703A in relatively shallow water off the Texas coast contain a mean of 4.3 μg/g lead in soft tissues. Carcass of gray triggerfish from two discharge sites contain means of 7.5 and 1.5 μg/g lead.

These concentrations are comparable to or lower than concentrations reported by Horowitz and Presley (1977) in similar species from the south Texas outer continental shelf (**Table 9.54**). More than 690 oyster samples from the coasts of Louisiana and Texas contain 0.08 to 3.15 μg/g lead (NOAA, 1995). Benthic crustaceans from the New York Bight contain 0.05 to 17.5 μg/g lead (Steimle *et al.*, 1994). Twenty-six species of teleost fish from the western Mediterranean Sea contain 0.05 to 55.9 μg/g lead (Pastor *et al.*, 1994).

The TSC concentration for lead in tissues of aquatic animals is 2.08 μg/g. The "high" concentration is 4.3 μg/g in mussels and 0.96 μg/g in oysters (**Table 9.40**). These screening concentrations are not exceeded by any muscle or whole soft tissue analyses for fish and invertebrates from reference and discharge sites. Therefore, lead does not represent a toxicological risk to marine animals near offshore production platforms in the northwestern Gulf of Mexico.

9.2.7.8 Zinc

Concentrations of zinc are high in the soft tissues of most marine animals. Mean concentrations in muscle of fish sampled in this study range from 13 to 72 μg/g (**Tables 9.49** through **9.53**). Carcass of gray triggerfish from two discharge sites contains means of 280 and 320 μg/g zinc. Crustaceans contain mean zinc concentrations of 54 to 190 μg/g. Oysters contain the highest concentrations of zinc (means of 1,800 μg/g in animals from a discharge site and 1,800 μg/g in animals from a nearby reference site). Jewelboxes contain lower concentrations of zinc than oysters. Mean concentrations range from 91 to 200 μg/g and are comparable at discharge and reference sites.

Table 9.55. Concentrations of nickel, iron, and manganese in tissues of marine plants and animals from the south Texas outer continental shelf. Concentrations are in μg/g dry weight (From: Horowitz and Presley, 1977).

Species	Nickel	Iron	Manganese
Sargassum	2.2 - 9.0	45 - 550	12 - 90
Mixed zooplankton	2.8 - 8.0	105 - 1,512	9.0 - 86
Squid (muscle & skin)	2.1 - 2.7	17.5 - 20.5	1.6 - 2.0
Squid (muscle)	1.0 - 4.3	16.6 - 465	0.9 - 31
Squid (viscera)	0.6 - 3.2	22 - 125	1.6 - 4.4
Brown shrimp (muscle)	0.3 - 1.9	4.5 - 29	0.8- 3.5
Brown shrimp (viscera)	5.6 - 5.8	238 - 445	10 - 17
Rock shrimp (muscle)	0.8 - 3.3	13 - 78	4.8 - 13
Flatfish (muscle)	0.6 - 7.4	11 - 36	0.9 - 3.8
Flatfish (skin)	2.9 - 7.4	33 - 86	7.1 - 16
Longspine porgy (muscle)	0.5 - 2.0	10 - 31.5	0.4 - 1.9
Rough scad (muscle)	0.7 - 1.1	30 - 34	0.5 - 0.7
Sea robin (muscle)	0.5 - 1.2	12 - 30	1.4 - 1.8
Sand seatrout (muscle)	2.8 - 5.1	22 - 26	1.1 - 3.1
Sand seatrout (liver)	0.8	500	3.4
Black-ear bass (muscle)	1.5	24	0.8
Atlantic croaker (muscle)	2.7	24	1.2
Wenchman (muscle)	0.6	7.7	0.4

These concentrations are comparable to concentrations of zinc in tissues of the same or similar species of marine animals from the south Texas outer continental shelf (**Table 9.54**). Oysters usually contain much higher concentrations of zinc than other bivalves, as indicated by the higher "high" value for zinc in oysters than in mussels (**Table 9.40**). Open ocean planktonic crustaceans from the eastern North Atlantic Ocean contain 34 to 96 μg/g zinc in whole tissues (Ridout *et al.*, 1989). Twelve species of fish from the eastern Mediterranean Sea contain 4.1 to 59 μg/g zinc in muscle tissues (Hornung and Ramelow, 1987). Thus, concentrations of zinc in tissues of marine animals from the vicinity of produced water discharging and reference platforms contain zinc concentrations comparable to those in tissues of marine animals from other marine habitats.

9.2.7.9 Chromium

Chromium concentrations in fish muscles are quite variable, ranging from 0.03 μg/g in muscle of red snapper from Sonnier Bank to 13 μg/g in muscle of longspine porgy from discharging site HI A-595CF (**Tables 9.56** through **9.60**). For the two species for which comparisons can be made between reference and discharge sites (red snapper and gray triggerfish), chromium concentrations in muscle are low and similar. The two highest mean concentrations of chromium are in muscle of longspine porgy from discharging site SMI 130B (5.4 μg/g) and discharging site HI A-595CF (13 μg/g). Concentrations of this essential micronutrient may be naturally high in this species of fish. All other species of fish collected from the two discharging platforms where longspine porgy have high tissue burdens of chromium contain low concentrations (<0.2 μg/g) of chromium. Atlantic croaker, silver seatrout, and Atlantic cutlassfish from the vicinity of SMI 236A in shallow water contain means of 1.9, 2.6, and 2.2 μg/g, respectively, of chromium in muscle tissue. Other species of fish and invertebrates from the same site or from the nearby reference site SMI 229C contain low concentrations of chromium. Chromium was not analyzed in ambient seawater in this study, so it is not possible to infer the source of the elevated concentrations of chromium in tissues of marine animals from the different reference and discharge sites beyond the fact that produced water concentrations were low and comparable to ambient seawater values from other studies.

Concentrations of chromium also are variable in tissues of invertebrates from reference and discharge sites (**Tables 9.56** through **9.60**). The crustaceans (penaeid shrimp and portunid crabs) contain means of 0.17 μg/g in whole blue crabs to 7.2 μg/g in non-muscle tissues of shrimp. Chromium is an essential cofactor for enzymatic reactions involved in crustacean molting. It is possible that the variability in concentrations and differential distribution of chromium in crustacean tissues is related to variations in chromium storage in tissues during different phases of the molt cycle.

Mean chromium concentrations in soft tissues of oysters and jewelboxes range from 0.70 to 2.5 μg/g and do not show a consistent difference between reference and discharge sites or between species.

Table 9.56. Mean concentrations of chromium, iron, manganese, molybdenum, and vanadium in edible and non-edible tissues of marine animals from the vicinity of SMI 236A. Concentrations are in μg/g dry weight.

Species	Chromium	Iron	Manganese	Molybdenum	Vanadium
Atlantic croaker (*Micropogonias undulatus*)	1.9	240	29	0.58	2.0
Hardhead catfish (*Arius felis*)	0.54	38	1.5	0.02	0.11
Silver seatrout (*Cynoscion nothus*)	2.6	280	15	0.18	0.54
Atlantic cutlassfish (*Trichiurus lepturus*)	2.2	150	8.6	0.13	0.27
Penaeid shrimp (*Penaeus* spp.)					
muscle	0.36	44	5.1	0.11	0.44
other	7.2	860	51	0.28	1.9
Blue crab (*Callinectes* spp.)	0.17	300	5.4	0.24	1.0
Eastern oyster (*Crassostrea virginica*)	1.2	480	18	0.22	1.6

Table 9.57. Mean concentrations of chromium, iron, manganese, molybdenum, and vanadium in edible and non-edible tissues of marine animals from the vicinity of VR 214A. Concentrations are in μg/g dry weight.

Species	Chromium	Iron	Manganese	Molybdenum	Vanadium
Red snapper (*Lutjanus campechanus*)					
fillet	0.12	12	0.36	4.0	0.52
carcass	0.50	48	4.2	0.56	1.9
Gray triggerfish (*Balistes capriscus*)					
fillet	0.06	8.6	0.98	0.51	0.72
carcass	0.64	68	54	0.75	2.1
Jewelbox (*Chama macerophylla*)	2.0	66	15	47	4.1

Table 9.58. Mean concentrations of chromium, iron, manganese, molybdenum, and vanadium in edible and non-edible tissues of marine animals from the vicinity of SMI 130B. Concentrations are in μg/g dry weight.

Species	Chromium	Iron	Manganese	Molybdenum	Vanadium
Red snapper (*Lutjanus campechanus*)					
fillet	0.04	50	0.22	0.18	0.70
carcass	0.45	35	3.3	0.45	1.4
Gray triggerfish (*Balistes capriscus*)					
fillet	0.11	9.1	0.70	<0.03	0.79
carcass	0.74	67	24	0.47	1.7
Longspine porgy (*Stenotomus caprinus*)	5.4	250	23	0.22	2.4
Vermilion snapper (*Rhomboplites aurorubens*)	0.13	11	0.22	2.2	0.75
Swimming crab (*Portunus* spp.)	2.7	460	90	0.31	8.0
Jewelbox (*Chama macerophylla*)	1.2	460	19	6.2	3.0

Table 9.59. Mean concentrations of chromium, iron, manganese, molybdenum, and vanadium in edible tissues of marine animals from the vicinity of HI A-595CF. Concentrations are in μg/g dry weight.

Species	Chromium	Iron	Manganese	Molybdenum	Vanadium
Vermilion snapper (*Rhomboiplites aurorubens*)	0.19	8.9	0.23	0.10	0.75
Longspine porgy (*Stenotomus caprinus*)	13	310	25	0.21	2.8
Jewelbox (*Chama macerophylla*)	1.4	210	9.2	6.0	2.2

Table 9.60. Mean concentrations of chromium, iron, manganese, molybdenum, and vanadium in edible tissues of marine animals from the vicinity of three discharging platforms (D), two reference platforms (R), and a natural hard bank. Concentrations are in μg/g dry weight.

Species	Location	Cr	Fe	Mn	Mo	V
Red snapper (*Lutjanus campechanus*)	Bank	0.03	8.2	---	<0.04	0.88
Gray triggerfish (*Balistes capriscus*)	Bank	0.10	8.2	---	0.06	0.96
Jewelbox (*Chama macerophylla*)	EI 313A (D)	2.5	83	11	32	2.8
Jewelbox (*C. macerophylla*)	HI A-323A (D)	2.4	290	12	47	3.5
Jewelbox (*C. macerophylla*)	HI A-389 (R)	0.84	62	7.0	4.7	1.6
Jewelbox (*C. macerophylla*)	MI 703A (D)	4.0	111	8.9	34	2.3
Eastern oyster (*Crassostrea virginica*)	SMI 229C (R)	0.70	320	28	0.24	1.4

National Status and Trends Mussel Watch oysters collected from coastal waters of the Gulf of Mexico contained 0.06 to 3.71 μg/g chromium (NOAA, 1995). O'Connor and Beliaeff (1995) did not calculate a "high" concentration for chromium in soft tissues of mussels and oysters. Using the definition for "high" concentration (population geometric mean plus one standard deviation), the "high" concentrations of chromium for oysters from the Gulf of Mexico range from 0.67 (Louisiana) to 1.04 μg/g (Florida). The two samples of oysters collected in this study contain chromium at concentrations only slightly higher than these values.

Chromium is fairly evenly distributed in the food chain of the south Texas outer continental shelf (**Table 9.54**). Shrimp and fish contain chromium concentrations in muscle and other tissues similar to those reported here in the same and similar species from produced water discharge sites and reference sites. Therefore, chromium concentrations in tissues of marine animals from the vicinity of offshore production platforms are not elevated substantially above expected concentrations probably are normal.

The TSC for chromium in tissues of aquatic fish is 4.0 μg/g dry weight (**Table 9.40**). Only longspine porgy contained muscle tissue residues of chromium higher than this screening level. The high concentration of chromium in muscle of this species could be normal. Therefore, the risk posed by chromium in the soft tissues of marine animals from the vicinity of offshore produced water discharges is low.

9.2.7.10 Iron

No tissue screening concentrations or "high" values have been published for iron. Iron is an essential trace nutrient for all marine organisms. Because of its low solubility in oxygenated seawater, it often is present in solution at concentrations so low that they limit phytoplankton growth. Because of its essentiality, iron is regulated at relatively high concentrations in tissues of marine animals. Concentrations of iron in tissues of marine animals from an ocean food chain on the south Texas outer continental shelf range from 4.5 to more than 1,500 μg/g in different species (**Table 9.55**). Concentration ranges in shrimp and fish muscle are 4.5 to 78 μg/g and 7.7 to 36 μg/g, respectively. Concentrations in skin and organ tissues tend to be higher than those in muscle. Soft tissues of oysters from Galveston Bay, TX, and coastal waters of the Gulf of Mexico contain means of 275 and 320 μg/g iron, respectively (Morse *et al.*, 1993). Concentrations as high as 1,300 μg/g have been measured in Gulf of Mexico oysters (Presley *et al.*, 1990).

In the present study, mean concentrations of iron in soft tissues of oyster and jewelbox from reference and discharge sites range from 62 to 480 μg/g (**Tables 9.56** through **9.60**). These concentrations are roughly comparable to the concentrations reported above for oysters throughout the Gulf of Mexico.

Muscle and whole tissues of shrimps and crabs have similar concentrations of iron to those in soft tissues of bivalves. "Other" tissues of brown shrimp (probably containing viscera and shell, both high in iron) contain 859 μg/g iron. These concentrations are somewhat higher than those in tissues of shrimp from the south Texas outer continental shelf. Bivalves and crustaceans may be accumulating particulate iron from suspended matter discharged from the Mississippi River. The concentrations found in bivalves and crustaceans are within the range of concentrations reported in these taxa from the Gulf of Mexico and elsewhere and probably do not represent a toxic risk to these species.

Mean concentrations of iron in muscle of different species of fish from reference and discharge sites in the northwestern Gulf of Mexico range from 8.2 to 310 μg/g (**Tables 9.56** through **9.60**). Most of these mean concentrations are higher than those in muscle of fish of the same or closely related species from the south Texas outer continental shelf (Horowitz and Presley, 1977) (**Table 9.55**). Li (1991 reports an average concentration of iron in the tissues of marine animals of 160 μg/g dry weight. Thompson (1990) reports typical concentrations of iron in fish muscle of <5 to 70 μg/g dry weight. The fish could be accumulating particulate iron from produced water discharges or from suspended particles from the Mississippi and Trinity River systems. If the metals are retained in particulate form, they probably are not causing any harm to the fish. No information is available about the concentrations of iron in fish tissues that may be toxic. Therefore, it is not possible to assess the risk of somewhat elevated concentrations of iron in a few species of fish from the outer continental shelf off Louisiana and Texas.

9.2.7.11 Manganese

Manganese, like iron, is abundant in ocean sediments and an essential micronutrient in marine animals. There is relatively little information about the normal concentrations of manganese in soft tissues of marine animals. There are no tissue screening concentrations or "high" values for manganese.

In the present study, mean concentrations of manganese in soft tissues of oysters and jewelboxes range from 7 to 28 μg/g. The highest mean concentration is in oysters from a shallow reference site, SMI 229. Oysters from the nearby discharging site contain 18 μg/g manganese. These oysters probably are accumulating particulate manganese from suspended matter in the Mississippi River outflow. These concentrations are in reasonable agreement with mean concentrations of 15.9 ± 8.1 μg/g and 14.8 ± 8.8 μg/g manganese in oysters from Galveston Bay, TX, and coastal waters of the Gulf of Mexico, respectively (Morse *et al.*, 1993). Manganese concentrations as high as 482 μg/g have been measured in Gulf of Mexico oysters (Presley *et al.*, 1990). Thus, manganese at the concentrations measured in tissues of oyster and jewelbox in this study probably do not pose any toxic risk to the bivalves.

Shrimp and blue crabs from discharging site SMI 236A contain means of just over 5 μg/g in muscle tissues, and the shrimp contain 51 μg/g manganese in non-muscle tissues. Portunid crabs from discharging site SMI 130B contain a mean of 90 μg/g manganese. Shrimp from the south Texas outer continental shelf contain 0.8 to 13 μg/g manganese in muscle and up to 17 μg/g in viscera (**Table 9.55**). Frenet and Alliot (1985) reported an average of 30 μg/g manganese in shrimp (*Palaemonetes varians*) from coastal waters of France. Prawns (*Pandalus platyceros*) from coastal waters of British Columbia contain 5 to 14 μg/g manganese in different tissues. Therefore, the concentrations manganese measured in tissues of crustaceans in the present study probably are normal and do not pose a toxic risk to the animals.

Mean concentrations of manganese in muscle tissues of fish collected in this study range from 0.20 to 29 μg/g and vary in muscle of the different species in a manner closely paralleling the variation in iron concentrations. Iron and manganese co-occur at high concentrations in marine sediments. It is possible that muscle and organ tissue of a few species of predominantly demersal and inshore fish (Atlantic croaker, silver seatrout, and longspine porgy) accumulate particulate iron and manganese from sediments (or that the muscle and organ tissue samples were contaminated during dissection with gut contents that may contain sediment particles). Marine fish muscle usually contains less than 5 μg/g manganese, but occasionally as much as 75 µg/g (Thompson, 1990). Thus, the manganese concentrations measured in fish tissues in this study probably do not pose a risk to the fish.

9.2.7.12 Molybdenum

Molybdenum is abundant in seawater and is an essential micronutrient in marine animals. However, there is very little information about its concentrations in tissues of marine animals. In the present study, mean molybdenum concentrations vary widely among different species. Soft tissues of oysters contain means of 0.22 and 0.24 µg/g at a discharge and reference site, respectively. Jewelboxes contain means of 4.7 to 47 µg/g molybdenum. Crustaceans contain low concentrations, ranging from 0.11 to 0.31 µg/g. Mean molybdenum concentrations in fish muscle range from less than 0.03 to 4.0 µg/g.

Li (1991) reports an average molybdenum concentration of 0.39 µg/g in tissues of marine animals. Oysters from different locations in Mississippi Sound contain a mean of 13 µg/g molybdenum (Lytle and Lytle, 1990). Spot prawns from British Columbia contain 0.24 to 1.6 µg/g molybdenum in different tissues (Whyte and Boutillier, 1991). Liver of cod from Newfoundland, Canada, contains 0.08 to 0.34 µg/g molybdenum (Hellou *et al.*, 1992). Muscle tissue contains 0.01 to 0.06 µg/g. Thus, molybdenum concentrations measured in the present study in soft tissues of marine animals are in the upper part of the range of concentrations recorded in tissues of marine animals from elsewhere. Molybdenum, as an essential trace nutrient, is regulated in the tissues of marine animals, and the concentrations measured probably are natural and do not pose a risk to the marine animals.

9.2.7.13 Vanadium

Mean vanadium concentrations in tissues of marine animals from reference and produced water discharge sites range from 0.11 to 8.0 µg/g (**Tables 9.55** through **9.60**). Highest concentrations are in tissues of portunid crabs and jewelboxes. Mean concentrations in jewelbox tissues range from 1.6 to 4.1 µg/g.

These tissue concentrations of vanadium probably are normal. The average concentration of vanadium in tissues of marine animals is 3.5 µg/g (Li, 1991). Several species of mesopelagic crustaceans from the open northeastern Atlantic Ocean contain 0.17 to 1.84 µg/g (Ridout *et al.*, 1989). Prawns from British Columbia, Canada, contain 0.33 to 1.34 µg/g vanadium in different tissues (Whyte and Boutillier, 1991). Deposit-feeding clams (*Scrobidularia plana*) from the Bou Regreg estuary, Morocco, contain 18 to 25 µg/g vanadium in soft tissues. Polychaete worms (*Neries diversicolor*) contain slightly high concentrations. Ocean quahogs (*Arctica islandica*) from Georges Bank off Massachusetts, contain 0.02 to 4.0 µg/g (Phillips *et al.*, 1987). Vanadium concentrations in a pelagic food chain in the open Mediterranean sea range from 1.45 µg/g in microplankton to 0.07 µg/g in shrimp and 0.08 µg/g in myctophid fish (Fowler, 1986). Myctophids from elsewhere in the Mediterranean contain up to 1.12 µg/g vanadium. Thus, the concentrations of vanadium in soft tissue of marine invertebrates and fish from reference and produced water discharge sites in the northwestern Gulf of Mexico do not represent a toxic risk to the marine animals.

9.2.8 Polycyclic Aromatic Hydrocarbons in Tissues of Marine Animals

PAHs are nonpolar (unionizable) organic chemicals. Like other nonpolar organics, they have low aqueous solubilities and high lipid solubilities. Solubility in fresh water decreased from about 30,000 μg/L for naphthalene (MW 128 daltons) to about 4 μg/L for benzo(a)pyrene (MW 252 daltons). Solubility is somewhat lower in seawater because of salting out effects (Neff, 1979). Lipid solubility of PAHs increases as molecular weight increases. Therefore, PAHs in solution in water tend to diffuse down an activity or fugacity gradient from the water, across permeable biological membranes, and into lipid-rich tissues of organisms in contact with the water. According to equilibrium partitioning theory (Davies and Dobbs, 1984; Bierman, 1990), when an aquatic animal is exposed to a nonpolar organic chemical, such as a PAH, dissolved in the ambient seawater, the chemical partitions into tissue lipids until an equilibrium, approximated by the octanol/water partition coefficient (K_{ow}) for the chemical, is reached. K_{ow} is used as a surrogate for the lipid/water partition coefficient because solubility of many nonpolar organic compounds in octanol and biological lipids is similar and there are published values for K_{ow} for a large number of nonpolar organic chemicals of environmental concern. At equilibrium, the rates of absorption into and desorption from the lipid phase of the plant or animal are equal. Because of the relationship between log K_{ow} and bioconcentration, it is possible to predict the equilibrium bioconcentration factor (BCF) for a particular nonpolar organic compound from its log K_{ow}, if the underlying assumptions are met (Veith and Kosian, 1983; Davies and Dobbs, 1984). The mathematical relationship takes the form:

$$\log BCF = a \log K_{ow} + b$$

where a and b are the slope constant and intercept constant, respectively, determined empirically by performing a regression with chemicals with different values for log K_{ow} and log BCF. Many of these regressions have been performed using different numbers and classes of nonpolar organic chemicals spanning different ranges of log K_{ow} (Isnard and Lambert, 1988; Schüürmann and Klein, 1988; Nishihara *et al.*, 1993). EPA (1991) recommends using the equation of Veith and Kosian (1983) for predicting concentrations of nonpolar organic chemicals in the tissues of aquatic animals in the receiving water environment of NPDES-permitted wastewater discharges, such as offshore produced water discharges. The equation of Veith and Kosian (1983) is:

$$\log BCF = 0.79 \log K_{ow} - 0.40$$

and was derived from a regression of log BCF in 13 species of fish (nearly all freshwater species) versus log K_{ow} for 122 nonpolar organic compounds, including five PAHs. Values for a and b in the regression equation vary for different classes of nonpolar organic chemicals, in part because octanol is not a perfect model for animal lipids (Opperhuizen *et al.*, 1988). The different regressions give slightly different estimates for the BCF of a particular nonpolar organic chemical, such as a PAH (Connell, 1995; Neff and Burns, 1996). Based on the regression of Pruell *et al.* (1987) for PAH bioconcentration by mussels, BCFs for PAHs increase with PAH molecular weight from 62.6 for naphthalene to about 120,000 for dibenz(a,h)anthracene.

The waters of the Gulf of Mexico contain low concentrations of PAHs. Natural oil seeps are abundant in the northwestern Gulf and may release as much as 19 million liters of crude oil to the Gulf each year (MacDonald *et al.*, 1993). If the natural seep oil contained 5% PAHs, a total of 950,000 liters of PAHs is released to the northwestern Gulf of Mexico each year in this way. Additional large amounts of PAHs reach the Gulf in river flows and runoff from land, and from shipping operations, aerial fallout of particulate (combustion-derived) PAHs, and discharges of produced water and other NPDES-permitted effluents (Neff, 1979). Therefore, marine animals living in waters of the Gulf of Mexico bioaccumulate PAHs from the ambient seawater and from their food in proportion to concentrations in the ambient seawater. Most marine animals are able to metabolize and excrete accumulated PAHs rapidly (Lee, 1981; Stegeman, 1981). Metabolism has the effect of lowering the equilibrium concentration of PAHs in the tissues of marine animals. Marine animals, such as bivalve molluscs, with limited ability to metabolize PAHs, accumulate them to higher concentrations than other species, such as fish, that have a highly active metabolic capability.

9.2.8.1 Polycyclic Aromatic Hydrocarbons in Tissues

Marine invertebrates and fish collected near the four platform discharges sampled in this study contain concentrations of total PAHs in their soft or edible tissues, ranging from less than 0.0001 to 11.68 μg/g dry weight (**Tables 9.61** through **9.64**). A single composite of jewelboxes from each of three of the platforms was analyzed; these samples contain 0.31 to 11.68 μg/g total PAHs. A composite sample of oysters from the fourth platform, SMI 236A, contains 0.026 μg/g total PAHs.

Fish from SMI 236A contain higher mean concentrations of total PAHs than fish from the other three platforms. However, the fish species collected from this shallow-water platform are different from those collected at the other three deeper-water platforms, so the comparison should be viewed with caution. Highest concentrations of total PAHs in fish tissues are in whole Atlantic croaker, with a mean of 0.48 μg/g and a range of 0.02 to 1.92 μg/g. Whole specimens of the other three species of fish from SMI 236A generally contain less than 0.1 μg/g total PAHs. Mean concentrations of total PAHs in muscle, carcass, or whole fish tissues from the other three discharging platforms range from 0.0002 to 0.11 μg/g.

Blue crabs from SMI 236A also contain somewhat elevated concentrations of total PAHs, ranging from 0.031 to 0.97 μg/g in muscle tissue and 0.61 μg/g (single sample) in non-muscle tissues. Blue crabs from VR 214A and closely related portunid crabs from SMI 130B contain 0.014 to 0.182 μg/g total PAHs. Rock shrimp and penaeid shrimp from VR 214A and SMI 130B generally contain low concentrations of total PAHs in muscle and non-muscle tissues. Highest concentrations are in muscle of rock shrimp from VR 214A (mean concentration 0.051 μg/g).

The higher concentrations of total PAHs in tissues of several species of marine animals from SMI 236A is unclear. The produced water from this platform contains a mean of 268 μg/L total PAHs (**Table 9.19**), and ambient seawater 2,000 m from the platform contains only about 0.07 μg/L total PAHs (**Table 9.20**). Because of the shallow water depth (6 m) at the platform compared to the other platforms sampled, initial dilution of the produced water plume may be less rapid; and somewhat elevated concentrations of PAHs may extend to near the bottom, allowing primarily demersal species, such as blue crabs and Atlantic croaker, to be exposed to a PAH-enriched produced water plume for extended periods of time.

Table 9.61. Mean and range of concentrations of total polycyclic aromatic hydrocarbons (PAHs) (sum of 41 analytes and congener groups) in edible tissues and non-edible tissues of marine animals from the vicinity of the produced water discharge at SMI 130B. Concentrations are μg/g dry weight.

Species	Tissue	Total PAHs	Concentration Range
Red snapper (*Lutjanus campechanus*)	muscle carcass	0.015 0.076	0.007 - 0.026 0.035 - 0.117
Gray triggerfish (*Balistes capriscus*)	muscle carcass	0.011 0.092	0.002 - 0.021 0.010 - 0.272
Seabass (*Centropristis philadelphica*)	muscle	0.009	0.002 - 0.037
Pinfish (*Lagodon rhomboides*)	muscle	0.010	0.003 - 0.012
Longspine porgy (*Stenotomus caprinus*)	whole	0.009	0.004 - 0.013
Rock shrimp (*Siconia brevirostris*)	muscle other	0.0007 0.019	ND - 0.001 0.019*
Swimming crab (*Portunus* sp.)	whole	0.054	0.024 - 0.087
Jewelbox (*Chama macerophylla*)	soft tissue	1.745	1.745*

ND = Not detected.
* Only one composite sample analyzed.

Table 9.62. Mean and range of concentrations of total polycyclic aromatic hydrocarbons (PAHs) (sum of 41 analytes and congener groups) in edible tissues and non-edible tissues of marine animals from the vicinity of the produced water discharge at VR 214A. Concentrations are μg/g dry weight.

Species	Tissue	Total PAHs	Concentration Range
Red snapper (*Lutjanus campechanus*)	muscle carcass	0.012 0.109	0.007 - 0.020 0.034 - 0.110
Gray triggerfish (*Balistes capriscus*)	muscle carcass	0.025 0.033	0.002 - 0.078 0014 - 0.070
Longspine porgy (*Stenotomus caprinus*)	whole	0.006	ND - 0.009
Dusky flounder (*Syacium* sp.)	whole	0.0002	ND - 0.001
Rock shrimp (*Siconia brevirostris*)	muscle other	0.051 0.028	0.001 - 0.245 0.028*
Roughneck shrimp (*Trachypenaeus* sp.)	muscle other	0.003 0.016	ND - 0.011 0.016*
Blue crab (*Callinectes* spp.)	whole	0.052	0.014 - 0.182
Jewelbox (*Chama macerophylla*)	soft tissue	11.68	11.68*

ND = Not detected.
* Only one composite sample analyzed.

Table 9.63. Mean and range of concentrations of total polycyclic aromatic hydrocarbons (PAHs) (sum of 41 analytes and congener groups) in edible tissues and non-edible tissues of marine animals from the vicinity of the produced water discharge at HI A-595CF. Concentrations are μg/g dry weight.

Species	Tissue	Total PAHs	Concentration Range
Vermilion snapper (*Rhomboplites aurorubens*)	muscle carcass	0.025 0.098	0.002 - 0.058 0.060 - 0.208
Longspine porgy (*Stenotomus caprinus*)	whole	0.002	0.001 - 0.008
Lefteye Flounder (Bothidae)	whole	0.014	0.005 - 0.023
Wenchman (*Pristipomoides aquilonaris*)	muscle	0.051	0.004 - 0.194
Longtail bass (*Hemanthias leptus*)	muscle	0.015	0.003 - 0.023
Jewelbox (*Chama macerophylla*)	soft tissue	0.311	0.311*

* Only one composite sample analyzed.

Table 9.64. Mean and range of concentrations of total polycyclic aromatic hydrocarbons (PAHs) (sum of 41 analytes and congener groups) in edible tissues and non-edible tissues of marine animals from the vicinity of the produced water discharge at SMI 236A. Concentrations are μg/g dry weight.

Species	Tissue	Total PAHs	Concentration Range
Atlantic croaker (*Micropogonias undulatus*)	whole	0.476	0.022 - 1.924
Hardhead catfish (*Arius felis*)	whole	0.110	0.051 - 0.130
Silver seatrout (*Cynoscion nothus*)	whole	0.040	0.023 - 0.053
Atlantic cutlassfish (*Trichiurus lepturus*)	whole	0.062	0.049 - 0.072
Penaeid shrimp (*Penaeus* spp).	muscle other	0.009 0.041	0.003 - 0.011 0.041*
Blue crab (*Callinectes* spp.)	muscle other	0.446 0.608	0.031 - 0.972 0.608*
Eastern oyster (*Crassostrea virginica*)	soft tissue	0.026	0.026*

* Only one composite sample analyzed.

For the most part, the relative concentrations of different PAHs in the tissues of bivalves, crustaceans, and fish from the vicinity of the four produced water discharges are characteristic of the relative abundances of different PAHs in crude and refined petroleum and produced water. The most abundant PAHs are the alkylnaphthalenes. PAH abundance decreases with increasing PAH molecular weight, and there are only traces, when they are detected at all, of high molecular weight 4- through 6-ring PAHs. **Figures 9.1** through **9.3** are examples of the PAH profiles in the three specimens of different species with the highest total PAH concentrations.

The PAH profile in a composite sample of jewelbox collected from the legs of VR 214A is dominated by alkylnaphthalenes and alkylphenanthrenes, with slightly lower concentrations of alkyldibenzothiophenes (**Figure 9.1**). Smaller amounts of chrysene and alkylchrysenes also are present, indicating that the source of the PAHs probably is a crude oil or a heavy fuel oil. Perylene (0.15 μg/g), a naturally-occurring PAH, and traces of other high molecular weight PAHs also are present. The bivalves probably bioaccumulate the PAHs from produced water discharged from the platform or from a recent release of crude oil in the area. The PAH profile in the bivalve tissues closely resembles that of produced water from VR 214A, even to the presence of a higher concentration of perylene than other PAHs with a similar high molecular weight. A sample of rock shrimp muscle from the same platform (containing 0.24 μg/g total PAHs) has a PAH profile that is dominated by alkylfluorenes, phenanthrenes and dibenzothiophenes, but is nearly devoid of naphthalenes and high molecular weight PAHs. This may be the result of selective metabolism and excretion of some PAHs by the shrimp. Crustaceans generally have a greater metabolic capability than bivalve molluscs to break down and excrete PAHs (Lee, 1981).

One of four specimens of whole Atlantic croaker from SMI 236A contains 1.92 μg/g total PAHs, by far the highest concentration of total PAHs measured in any fish samples in this study. The other four samples of whole Atlantic croaker from this platform contain 0.022 to 0.28 μg/g total PAHs. The PAH profile in the contaminated Atlantic croaker sample is dominated by naphthalene and alkylnaphthalenes (89% of the total PAHs in the fish tissues) (**Figure 9.3**). Small amounts of biphenyl, fluorenes, and phenanthrene also are present. No PAHs larger than fluoranthene and pyrene were detected. This PAH profile resembles that of a light refined product, such as gasoline. It does not resemble the profile of the produced water from SMI 236A. The tissue contamination may have come from a small release of gasoline near the platform.

A sample of muscle from blue crabs collected at SMI 236A contains 0.97 μg/g total PAHs. Four replicate blue crab muscle samples from the same platform contain 0.031 to 0.85 μg/g total PAHs. The PAH profile in the muscle tissue of the blue crabs closely resembles that of the whole Atlantic croaker (**Figure 9.3**). The PAH profile is dominated by naphthalene and alkylnaphthalenes (89% of the total PAHs in the crab muscle), with small amounts of biphenyl, alkylflourenes, and phenanthrene. The other blue crab from the platform with an elevated PAH content (0.85 μg/g) has a very similar PAH profile. It is probable that the Atlantic croaker and blue crabs obtained their body burdens of PAHs from the same source, probably gasoline.

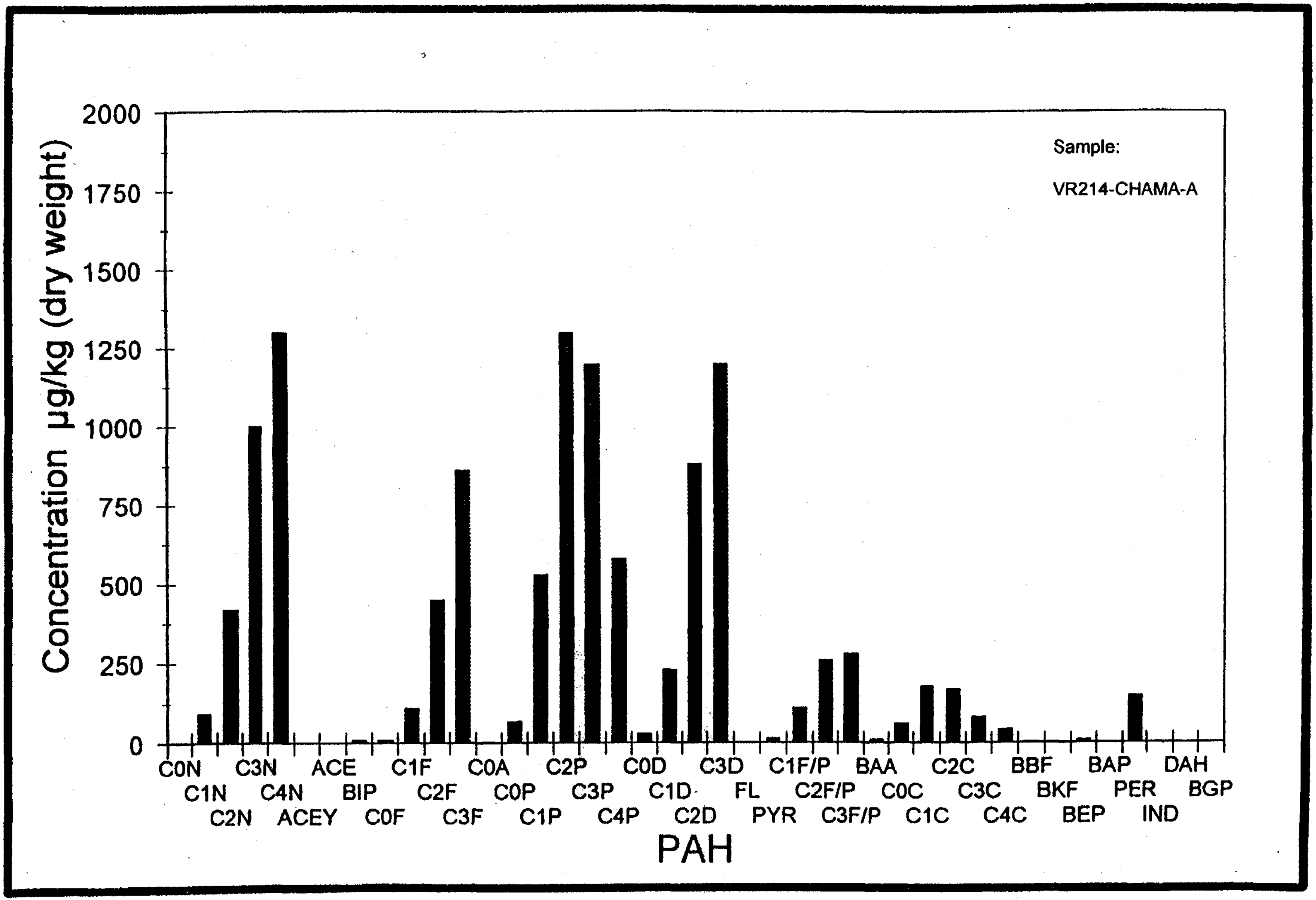


Figure 9.1. PAH profile in soft tissues of Jewelbox (*Chama macerophylla*) from produced water discharging site VR 214A.

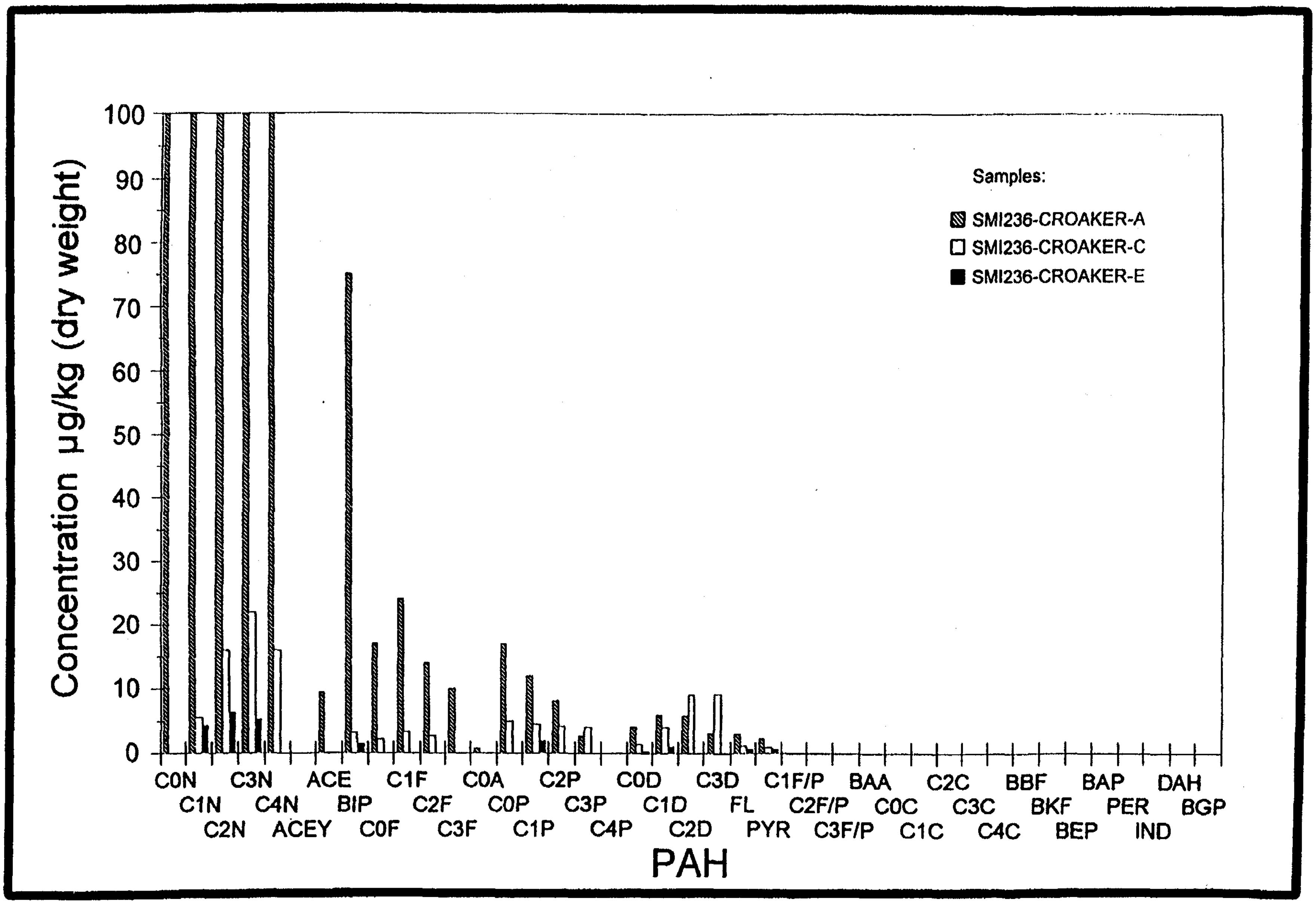


Figure 9.2. PAH profiles in three samples of Whole Atlantic croaker (*Micropogonias undulatus*) from the vicinity of produced water discharging site SMI 236A in 6 m of water.

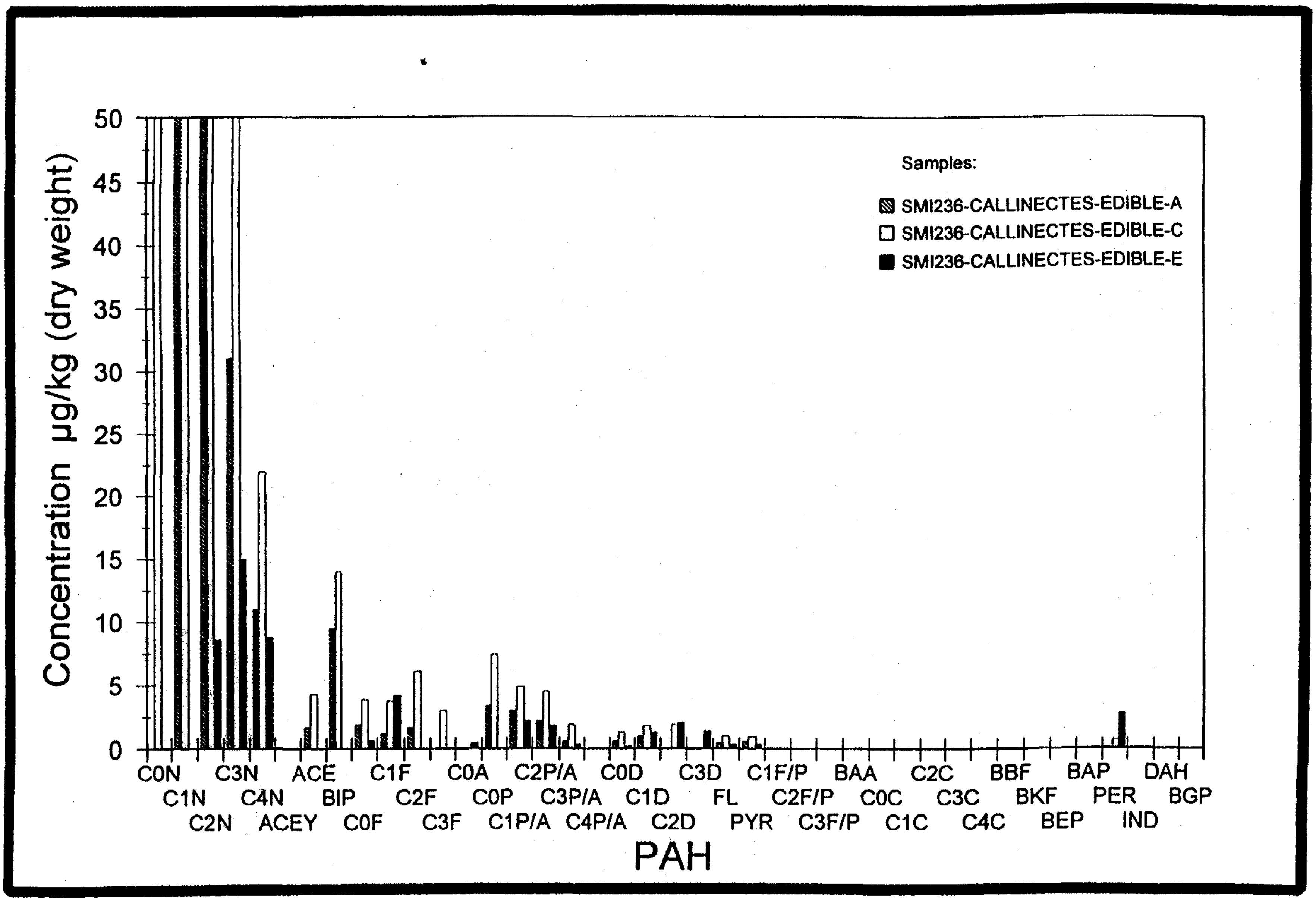


Figure 9.3. PAH profiles in three samples of Blue Crab (*Callinectes sapidus*) from the vicinity of produced water discharging site SMI 236A in 6 m of water.

Samples of gray triggerfish carcass and jewelboxes from SMI 130B contain PAH profiles that contain traces of several high molecular weight PAHs, other than alkylchrysenes. The alkylnaphthalenes, fluorenes, and phenanthrenes characteristic of a petroleum product also are present. These animals probably contain PAHs from both produced water and a combustion source.

The sample of jewelbox from HI A-595CF, containing 0.31 μg/g total PAHs, has a PAH profile dominated by C_2- through C_4-naphthalenes, C_2- and C_3-fluorenes, and C_1- through C_4-phenanthrenes. This profile is characteristic of a produced water source.

9.2.8.2 Ecorisk of Polycyclic Aromatic Hydrocarbons in Tissues of Marine Animals

Considerable progress has been made in recent years in developing quantitative structure activity relationships (QSARs) that relate physical/chemical properties of non-specific toxicants, particularly nonpolar organic chemicals, to biological end points, such as acute or chronic toxicity and bioaccumulation (McCarty, 1986; Abernethy *et al.*, 1988; Warne *et al.*, 1991; Connell and Markwell, 1992; Mackay *et al.*, 1992a; McCarty *et al.*, 1992; Van Leeuwen *et al.*, 1992; Sijm *et al.*, 1993). McCarty *et al.* (1992) showed, that for nonpolar organic chemicals that are non-specific toxicants (act primarily by physical accumulation in membrane lipids, causing generalized narcotic effects), the critical body residue (CBR) of the chemical in the whole tissues of the animal is approximately 4.4 mmol/kg wet weight (95% C.I. = 3.7 to 5.2 mmol/kg). That is, adverse biological responses (e.g., death) occur when whole tissue residues of a nonspecific narcotic chemical reach 4.4 mM.

Because the mode and site of action of non-specific toxicants is the same, their toxicities can be considered to be additive. That is, the sum of the concentrations of all the non-specific organic toxicants in the tissues of an experimental animal is equal to approximately 4.4 mmol/kg at the point where toxic responses are observed.

Several classes of nonpolar or slightly polar organic chemicals behave as non-specific toxicants in aquatic animals. PAHs behave acutely as non-specific toxicants. However, some of their metabolites may be highly reactive and bind, often irreversibly, to tissue macromolecules. Some PAH metabolites may be more toxic than the unmetabolized parent compound. However, the concentration in the tissues of a marine animal of reactive, uncomplexed PAH metabolites usually is less than that of the parent compounds. Most acute and chronic effects of low molecular weight PAHs measured in aquatic animals can be attributed to non-specific toxicity and not to specific effects of metabolites. However, some of the metabolites of some high molecular weight PAHs are mutagens and carcinogens (Neff, 1979).

Van Leeuwen *et al.* (1992) used these concepts to develop a more conservative (protective) toxicological end point than that of McCarty *et al.* (1992), the estimated average concentration of the chemical in tissues causing harmful responses in 5% of the organisms in an aquatic community during chronic exposure (the HC5). HC5s are inversely related to log K_{ow}s. Values for HC5 in tissues of aquatic organisms range from 0.0673 mmol/kg for chemicals, with a log K_{ow} of 1.5 to 0.03 mmol/kg for chemicals with a log K_{ow} of 6.0.

Concentrations of several PAHs spanning the molecular weight/log K_{ow} range from naphthalene (log K_{ow} 3.37) to benzo[a]pyrene (log K_{ow} 6.04) in tissues of marine animals from the vicinity of the four platform discharges were compared to HC5 values estimated according to the methods of Van Leeuwen *et al.* (1992) (**Table 9.65**). HC5s of the five PAHs evaluated range from 23.45 to 38.45 μg/g dry weight. Highest measured tissue concentrations of the five PAHs in tissues of marine animals from the vicinity of the four produced water discharges range from 0.003 to 0.17 μg/g. Maximum toxic units (measure tissue residue/HC5) for the five PAHs in tissues of marine animals range from 0.0001 to 0.004. Maximum toxic units decrease with increasing molecular weight of PAHs, despite the fact that HC5 values decrease with increasing log K_{ow} and molecular weight. This is because tissue residues of low molecular weight PAHs are higher than those of high molecular weight PAHs, reflecting the composition of the PAH assemblage in produced water and petroleum.

Effects of tissue residues of nonpolar narcotic chemicals are additive. However, even the highest concentration of total PAHs in bivalve molluscs from the platform legs (11.68μg/g dry weight, mostly naphthalenes) is less than half the HC5 for phenanthrene. Therefore, tissue residues of individual and total PAHs in marine animals near the four offshore production platforms are well below concentrations that might be toxic to marine animals.

9.2.9 Summary of Ecorisk of Metals and Polycyclic Aromatic Hydrocarbons in Tissues of Marine Animals

Marine bivalve molluscs, crustaceans, and fish from the vicinity of offshore produced water discharges and from nearby reference sites contain detectable concentrations of several metals and PAHs in their soft tissues. It is difficult to predict if the tissue residues observed in natural populations of marine animals represent a risk to the animals themselves or their consumers in the local marine food web. The fact that the tissue residues were measured in tissues of free-ranging natural populations of marine animals indicates that the concentrations observed are not acutely lethal or debilitating to the marine animals. However, sublethal concentrations of the chemicals in tissues could lead to chronic sublethal effects on growth and reproduction, and thereby pose a risk to the long-term survival and success of the local populations (Donkin *et al.*, 1989, 1991; Widdows *et al.*, 1995).

Although several metals were measured in tissues of one or more species at concentrations that approach or exceed current tissue screening levels, in many cases the elevated tissue residues were observed in animals from supposedly clean reference sites. Arsenic, in particular, is present in tissues of marine animals at concentrations much higher than those in tissues of most freshwater and terrestrial animals. Many marine animals have tissue residues of arsenic that exceed current screening concentrations, most of which were developed for freshwater animals. Most of the arsenic in the tissues of marine animals is in the form of various nontoxic organo-arsenic compounds, particularly arsenobetaine (Neff, 1996b). The organo-arsenic compounds are not harmful to the marine animals themselves or their consumers.

Barium, copper, zinc, molybdenum, and vanadium also are present at higher than expected concentrations in soft tissues of some of the marine animals collected in this study. However, the measured concentrations are within the range reported in tissues of marine animals from elsewhere in the world and may be normal. Cadmium concentrations are high in oysters and jewelboxes; this may be natural. These bivalves often accumulate cadmium to high concentrations and store it more or less permanently in insoluble concretions in the kidney or digestive gland. Iron and manganese also are present at elevated concentrations in some

Table 9.65. Comparison of concentrations of selected polycyclic aromatic hydrocarbons (PAHs) in tissues of marine animals near produced water discharges and the estimated tissue concentrations hazardous to 5% of an aquatic community (HC5:Van Leeuwen *et al.*, 1992). Toxic units are tissue concentration/HC5. Concentrations are μg/g dry weight.

Compound	Concentration Range in Tissues	HC5	Maximum Toxic Units
Naphthalene	ND - 0.170	38.45	0.022
Phenanthrene	ND - 0.089	25.65	0.017
Pyrene	ND - 0.062	24.80	0.012
Chrysene	ND - 0.063	22.85	0.014
Benzo(a)pyrene	ND - 0.003	23.45	0.0006

ND = Not detected, detection limit about 0.10 ng/g dry weight per analyte.

marine animals. The significance of this and its potential risk are not known. Most concentrations of mercury, nickel, lead, and zinc in soft tissues of marine animals from this study are below the tissue screening concentrations and probably do not pose a risk to the marine animals themselves. A few species from a few sites contain somewhat elevated concentrations of nickel or molybdenum in soft tissues; the significance and potential toxicological risk of these elevated concentrations are unknown. The risk probably is low.

PAHs were bioaccumulated from produced water by several species of marine animals near the produced water discharges. Unfortunately, no marine animals from reference sites were analyzed for PAHs, so it is not possible to determine the "background" concentrations of individual and total PAHs in these species. The concentrations of individual PAHs in tissues of marine animals from the platform sites are highly variable; highest concentrations are in soft tissues of jewelboxes. None of the PAHs are present in invertebrate and fish tissues at concentrations that are likely to be acutely toxic to the animals themselves.

9.3 REFERENCES

Abernethy, S.G., A.M. Bobra, W.Y. Shiu, P.G. Wells, and D. Mackay. 1986. Acute lethal toxicity of hydrocarbons and chlorinated hydrocarbons to two planktonic crustaceans: The key role of organism-water partitioning. Aquat. Toxicol. 8:163-174.

Abernethy, S.G., D. Mackay, and L.S. McCarthy. 1988. "Volume fraction" correlation for narcosis in aquatic organisms: the key role of partitioning. Environ. Toxicol. Chem. 7:469-481.

American Petroleum Institute. 1989. Fate and Effects of Drilling Fluid and Cuttings Discharges in Shallow, Nearshore Waters. API Publication 4480. Report prepared by Continental Shelf Associates, Inc., Jupiter, FL, Geochemical and Environmental Research Group, College Station, TX, and Barry A. Vittor & Assoc., Mobile, AL.

Andreae, M.O. and T.W. Andreae. 1989. Dissolved arsenic species in the Schelde Estuary and watershed, Belgium. Estuar. Cstl. Shelf Sci. 29:421-433.

Ankley, G.T., D.M. DiToro, D.J. Hansen, and W.J. Berry. 1996. Technical basis and proposal for deriving sediment quality criteria for metals. Environ. Toxicol. Chem. 15:2,056-2,066.

Armstrong, H.W., K. Fucik, J.W. Anderson, and J.M. Neff. 1979. Effects of oilfield brine effluent on sediments and benthic organisms in Trinity Bay, Texas. Mar. Environ. Res. 2:55-69.

Barth, T., A.E. Borgund, and M. Riis. 1989. Organic acids in reservoir waters - relationship with inorganic ion composition and interactions with oil and rock. Adv. Org. Geochem. 16:489-496.

Başsari, A. 1994. A study on the trace element concentrations of *Thunnus thynnus, Thunnus obesus* and *Katwuwonus pelamis* by means of ICP-AES. Toxicol. Environ. Chem. 44:123-127.

Bierman, V.J., Jr. 1990. Equilibrium partitioning and biomagnification of organic chemicals in benthic animals. Environ. Sci. Technol. 24:1,407-1,412.

Bloch, S. and R.M. Key. 1981. Modes of formation of anomalously high radioactivity in oil field brines. Amer. Assoc. Petrol. Geol. Bull. 65:154-159.

Boesch, D.F. and N.N. Rabalais. 1989. Produced water discharges in the northwestern Gulf of Mexico region, pp. 13-30. In: D.F. Boesch and N.N. Rabalais (eds.), An Analysis of Impacts, Produced Waters in Sensitive Coastal Habitats. Central Gulf of Mexico. OCS Study MMS 89-0031. U.S. Dept. of the Interior, Minerals Management Service, Gulf of Mexico OCS Regional Office, New Orleans, LA.

Boesch, D.F., N.N. Rabalais, C.S. Milan, C.B. Henry, J.C. Means, R.P. Gambrell, and E.B. Overton. 1989. Field assessments, pp. 31-116. In: D.F. Boesch and N.N. Rabalais (eds.), An Analysis of Impacts, Produced Waters in Sensitive Coastal Habitats. Central Gulf of Mexico. OCS Study MMS 89-0031. U.S. Dept. of the Interior, Minerals Management Service, Gulf of Mexico OCS Regional Office, New Orleans, LA.

Boothe, P.N. and W.D. James. 1985. Neutron activation analysis of barium in marine sediments from the north central Gulf of Mexico. J. Trace and Microprobe Techniques 3:377-399.

Boothe, P.N. and B.J. Presley. 1989. Trends in sediment trace element concentrations around six petroleum drilling platforms in the northwestern Gulf of Mexico, pp. 3-22. In: F.R. Engelhardt, J.P. Ray, and A.H. Gillam (eds.), Drilling Wastes. Elsevier Applied Science, London, England.

Borgund, A.E. and T. Barth. 1994. Generation of short-chain organic acids from crude oil by hydrous pyrolysis. Org. Geochem. 21:943-952.

Bostrom, K. and S. Valdes. 1969. Arsenic in ocean floors. Lithos 2:351-360.

Bowen, H.J.M. 1979. Environmental Chemostry of the Elements. Academic Press, London, England.

Brandsma, M.G. and J.P. Smith. 1996. Dispersion modeling perspectives on the environmental fate of produced water discharges. In: M. Reed and S. Johnsen (eds.), Procuded Water 2: Environmental Issues and Mitigation Technologies. Plenum Press, New York, NY (in press).

Brooks, J.M., E.L. Estes, D.A. Wiesenburg, C.R. Schwab, and H.A. Abdel-Rheim. 1980. Investigations of surficial sediments, suspended particulates, and volatile hydrocarbons at Buccaneer gas and oil field. In: W.B. Jackson and E.P. Wilkens (eds.), Environmental Assessment of the Buccaneer Gas and Oil Field in the Northwestern Gulf of Mexico, 1978-1980. Vol. 1. NOAA Technical Memorandum

NMFS-SEFC-47. National Oceanic and Atmospheric Administration, National Marine Fisheries Service, Galveston, TX. 98 pp.

Brooks, J.M., M.C. Kennicutt II, and T.J. McDonald. 1984. Volatile Organic Studies of Gulf of Mexico Estuaries and Coastal Ecosystems. Tech. Report 84-T-5. Final Report to NOAA, Office of Marine Pollution Assessment, Rockville, MD. Texas A&M University, College Station, TX.

Brooks, J.M., M.C. Kennicutt, T.L. Wade, A.D. Hart, G.J. Denoux, and T.J. McDonald. 1990. Hydrocarbon distributions around a shallow water multiwell platform. Environ. Sci. Technol. 24:1,079-1,085.

Brown, B. and J. Neff. 1993. Bioavailability of Sediment-Bound Contaminants to Marine Organisms. Report to NOAA, National Pollution Program Office, Rockville, MD.

Bruland, K.W., K.J. Orians, and J.P. Cowen. 1994. Reactive trace metals in the stratified central North Pacific. Geochim. Cosmochim. Acta 58:3,171-3,182.

Burns, R.G. and V.M. Burns. 1981. Authigenic oxides, pp. 875-914. In: E. Emiliani (ed.), The Sea, Vol. 7. The Oceanic Lithosphere. John Wiley and Sons, New York, NY.

Burton, J.D. and P.J. Statham. 1982. Occurrence, distribution, and chemical speciation of some minor dissolved constituents in ocean waters, pp. 234-249. In: Environmental Chemistry. Vol. 2. Special Periodical Report. Royal Society of Chemistry, London, England.

Carney, R.S. 1987. A review of study designs for the detection of long-term environmental effects of offshore petroleum activities, pp. 651-696. In: D.F. Boesch and N.N. Rabalais (eds.), Long-Term Environmental Effects of Offshore Oil and Gas Development. Elsevier Applied Science, London, England.

Chan, L.-H. and J.S. Hanor. 1982. Dissolved barium in some Louisiana offshore waters: problems in establishing baseline values. Contrib. Mar. Sci. 25:149-159.

Chapman, P.M., H.E. Allen, K. Godtfredsen, and M.N. Z'Graggen. 1996. Evaluation of bioaccumulation factors in regulating metals. Environ. Sci. Technol. 30:448A-452A.

Ciceri, G., S. Maran, W. Martinotti, and G. Queirazza. 1992. Geochemical cycling of heavy metals in a marine coastal area: Benthic flux determination from pore water profiles and in situ measurements using benthic chambers. Hydrobiol. 235/236:501-517.

Collier, R.W. 1984. Particulate and dissolved vanadium in the North Pacific Ocean. Nature 309:441-443.

Collier, R.W. 1985. Molybdenum in the northeast Pacific Ocean. Limnol. Oceanog. 30:1,351-1,360.

Collins, A.G. 1975. Geochemistry of Oilfield Waters. Elsevier Scientific Publishers, New York, NY. 496 pp.

Connell, D.W. 1995. Prediction of bioconcentration and related lethal and sublethal effects in aquatic organisms. Mar. Pollut. Bull. 31:201-205.

Connell, D. and R. Markwell. 1992. Mechanism and prediction of nonspecific toxicity to fish using bioconcentration characteristics. Ecotoxicol. Environ. Saf. 24:247-265.

Coombs, T.L. 1979. Cadmium in marine organisms, pp. 93-139. In: M. Webb (ed.), The Chemistry, Biochemistry, and Biology of Cadmium. Elsevier/North Holland Biomedical Press, Amsterdam, Holland.

Crecelius, E.A., M.H. Bothner, and R. Carpenter. 1975. Geochemistries of arsenic, antimony, mercury, and related elements in sediments of Puget Sound. Environ. Sci. Technol. 9:325-333.

Cullen, J.J. 1995. Status of the iron hypothesis after the open-ocean enrichment experiment. Limnol. Oceanog. 40:1,336-1,343.

Daskalakis, K.D. and T.P. O'Connor. 1995. Distribution of chemical concentrations in US coastal and estuarine sediment. Mar. Environ. Res. 40:381-398.

Davies, R.P. and A.J. Dobbs. 1984. The prediction of bioconcentration in fish. Wat. Res. 18:1,253-1,262.

DeLeon, I.R., C.J. Byrne, E.A. Peuler, S.R. Antoine, J. Schaeffer, and R.C. Murphy. 1986. Trace organic and heavy metal pollutants in the Mississippi River. Chemosphere 15:795-805.

DeWitt, T.H., R.C. Swartz, D.J. Hansen, D. McGovern, and W.J. Berry. 1996. Bioavailability and chronic toxicity of cadmium in sediment to the estuarine amphipod *Leptocheirus plumulosus*. Environ. Toxicol. Chem. 15:2,095-2,101.

Dickhut, R.M. and K.E. Gustafson. 1995. Atmospheric inputs of selected polycyclic aromatic hydrocarbons and polychlorinated biphenyls to southern Chesapeake Bay. Mar. Pollut. Bull. 30:385-396.

Dinnel, S.P. and W.J. Wiseman, Jr. 1986. Fresh water on the Louisiana and Texas shelf. Continental Shelf Res. 6:765-784.

Di Toro, D.M., C.S. Zarba, D.J. Hansen, W.J. Berry, R.C. Swartz, C.E. Cowan, S.P. Pavlou, H.E. Allen, N.A. Thomas, and P.R. Paquin. 1991. Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. Environ. Toxicol. Chem. 10:1,541-1,583.

Donkin, P.J. Widdows, S.V. Evans, and M.D. Brinsley. 1991. QSARs for the subiethal responses of marine mussels (*Mytilus edulis*). Sci. Tot. Environ. 109/110:461-476.

Donkin, P.J. Widdows, S.V. Evans, C.M. Worrall, and M. Carr. 1989. Quantitative structure-activity relationships for the effect of hydrophobic organic chemicals on rate of feeding in mussels (*Mytilus edulis*). Aquat. Toxicol. 14:277-294.

Engel, D.W. and M. Brouwer. 1991. Short-term metallothionein and copper changes in blue crabs at ecdysis. Biol. Bull. 180:447-452.

EPA. 1985a. Ambient Water Quality Criteria for Mercury - 1984. Office of Water Regulations and Standards, Criteria and Standards Division, Washington, DC. EPA 440/5-84-028.

EPA. 1985b. Ambient Water Quality Criteria for Copper - 1984. Office of Water Regulations and Standards, Criteria and Standards Division, Washington, DC. EPA 440/5-84-031.

EPA. 1991. Assessment and Control of Bioconcentratable Contaminants in Surface Waters. Draft. Office of Water, Washington, DC.

EPA. 1992. Quality Criteria for Water 1992. Office of Water, Criteria and Standards Division, Washington, DC.

EPA. 1995. Risk-Based Concentration Table, January - June 1995. U.S. Environmental Protection Agency, Region III, Philadelphia, PA.

Farrington, J.W. 1986. Fossil fuel aromatic hydrocarbon biogeochemistry in the marine environment: Research challenges, pp. 113-142. In: C.S. Giam and H.J.M. Dou (eds.), Strategies and Advanced Techniques for Marine Pollution Studies: Mediterranean Sea. Springer-Verlag, Berlin, Germany.

Förstner, U. and G.T.W. Wittmann. 1981. Metal Pollution in the Aquatic Environment. Second Revised Edition. Springer-Verlag, Berlin, Germany.

Fowler, S.W. 1986. Trace metal monitoring of pelagic organisms from the open Mediterranean Sea. Environ. Monit. Assess. 7: 59-78.

Francesconi, K.A. and J.S. Edmonds. 1993. Arsenic in the sea, pp. 111-151. In: A.D. Ansell, R.N. Gibson, and M. Barnes (eds.), Oceanography and Marine Biology: An Annual Review. Vol. 31. Aberdeen University Press, Aberdeen, Scotland.

Frenet, M. and A. Alliot. 1985. Comparative bioaccumulation of metals in *Palaemonetes varians* in polluted and non-polluted environments. Mar. Environ. Res. 17:19-44.

Gagnon, C., E. Pelletier, A. Mucci, and W.F. Fitzgerald. 1996. Diagenic behavior of methylmercury in organic-rich coastal sediments. Limnol. Oceanogr. 42:428-434.

Gaudet, C., S. Lingard, P. Cureton, K. Keenleyside, S. Smith, and G. Raju. 1995. Canadian environmental quality guidelines for mercury. Water, Air, Soil Pollut. 80:1,149-1,159.

Gibbs, P.E., W.J. Langston, G.R. Burt, and P.L. Pascoe. 1983. *Tharyx marioni* (Polychaeta): A remarkable accumulator of arsenic. J. Mar. Biol. Ass. U.K. 61:313-325.

Goldberg, E.D. and G.O.S. Arrhenius. 1958. Chemistry of Pacific pelagic sediments. Geochim. Cosmochim. Acta 13:153-212.

Gooday, A.J. and J.A. Nott. 1982. Intracellular barite crystals in two xenophyophores, *Aschemonella ramuliformis* and *Galatheammina* sp. (Protozoa: Rhizopoda) with comments on the taxonomy of *A. ramuliformis*. J. Mar. Biol. Ass. UK 62:595-605.

Gschwend, P.M., O.C. Zafiriou, R.F.C. Mantoura, R.P. Schwarzenbach, and R.B. Gagosian. 1982. Volatile organic compounds at a coastal site. 1. Seasonal variations. Environ. Sci. Technol. 16:31-38.

Hanor, J.S., J.E. Bariey, M.C. Rogers, and L.R. Milner. 1986. Regional variations in physical and chemical properties of south Louisiana oil field brines. Trans. Gulf Coast Assoc. Geol. Soc. 36:143-149.

Hansen, D.J., W.J. Berry, J.D. Mahoney, W.S. Boothman, D.M. DiToro, D.L. Robson, G.T. Ankley, D. Ma, Q. Yan, and C.E. Pesch. 1996.

Hellou, J., W.G. Warren, J.F. Payne, S. Belkhode, and P. Lobel. 1992. Heavy metals and other elements in three tissues of cod, *Gadus morhua*, from the northwest Atlantic. Mar. Pollut. Bull. 24:452-458.

Hornung, H. and G.J. Ramelow. 1987. Distribution of Cd, Cr, Cu, and Zn in eastern Mediterranean fishes. Mar. Pollut. Bull. 18:45-49.

Horowitz, A. and B.J. Presley. 1977. Trace metal concentrations and partitioning in zooplankton, neuston, and benthos from the south Texas outer continental shelf. Arch Environ. Contam. Toxicol. 5:241-255.

Hydes, D.J. and K. Kremling. 1993. Patchiness in dissolved metals (Al, Cd, Co, Cu, Mn, Ni) in North Sea surface waters: Seasonal differences and influence of suspended sediment. Cont. Shelf Res. 13:1,083-1,101.

Isnard, P. and S. Lambert. 1988. Estimating bioconcentration factors from octanol-water partition coefficient and aqueous solubility. Chemosphere 17:21-34.

Iyengar, G.V. 1991. Milestones in biological trace element research. Sci. Tot. Environ. 100:1-15.

Jacobs, R.P.W.M., R.O.H. Grant, J. Kwant, J.M. Marquenie, and E. Mentzer. 1992. The composition of produced water from Shell operated oil and gas production in the North Sea, pp. 13-21. In: J.P. Ray and F.R. Engelhardt (eds.), Produced Water. Technological/Environmental Issues and Solutions. Plenum Press, New York, NY.

Jeandel, C., M. Caisso, and J.F. Minster. 1987. Vanadium behavior in the global ocean and in the Mediterranean Sea. Mar. Chem. 21:51-74.

Jenkins, K.D., S. Howe, B.M. Sanders, and C. Norwood. 1989. Sediment deposition, biological accumulation and subcellular distribution of barium following drilling of an exploratory well, pp. 587-608. In: F.R. Engelhardt, J.P. Ray, and A.H. Gillam (eds.), Drilling Wastes. Elsevier Applied Sciences, London, England.

Jenne, E.A. 1977. Trace element sorption by sediments and soils - Sites and processes, pp. 425-553. In: W. Chappel and K. Peterson (eds.), Symposium on Molybdenum in the Environment. Marcel Dekker, New York, NY.

Jonasson, I.R. and R.W. Boyle. 1972. Geochemistry of mercury and origins of natural contamination of the environment. CIM Trans. 75:8-15.

Karickhoff, S.W., D.S. Brown, and T.A. Scott. 1979. Sorption of hydrophobic pollutants on natural sediments and soils. Wat. Res. 13:241-248.

Kelly, C.A., J.W.M. Rudd, V.L. St. Louis, and A. Heyes. 1995. Is total mercury concentration a good predictor of methyl mercury concentration in aquatic systems. Water, Air, Soil Pollut. 80:715-724.

Kennicutt, M.C., II. 1995. Gulf of Mexico Offshore Operations Monitoring Experiment, Final Report. Phase 1: Sublethal Responses to Contaminant Exposure. OCS Study MMS 95-0045. U.S. Dept. of the Interior, Minerals Management Service, Gulf of Mexico Region, New Orleans, LA.

Kingston, P.F. 1987. Field effects of platform discharges on benthic macrofauna. Phil. Trans. Roy. Soc. London B316:545-565.

Kingston, P.F. 1992. The impact of offshore oil production installations on the benthos of the North Sea. ICES J. Mar. Sci. 49:127-143.

Ko, F.-C. and J.E. Baker. 1994. Partitioning of hydrophobic organic contaminants to resuspended sediments and plankton in the mesohaline Chesapeake Bay. Mar. Chem. 49:171-188.

Kopfler, F.C. 1974. The accumulation of organic and inorganic mercury compounds by the eastern oyster (*Crassostrea virginica*). Bull. Environ. Contam. Toxicol. 11:275-280.

Krumgalz, B.S., G. Fainshtein, and A. Cohen. 1992. Grain size effect on anthropogenic trace metal and organic matter distribution in marine sediments. Sci. Tot. Environ. 116:15-30.

Kuma, K., J. Nishioka, and K. Matsunaga. 1996. Controls on iron(III) hydroxide solubility in seawater: the influence of pH and natural organic chelators. Limnol. Oceanogr. 41:396-407.

Laslett, R.E. 1995. Concentrations of dissolved and suspended particulate Cd, Cu, Mn, Ni, Pb and Zn in surface waters around the coasts of England and Wales and in adjacent seas. Estuar. Cst. Shelf Sci. 40:67-85.

Law, R.J., M.J. Waldock, C.R. Allchin, R.E. Laslett, and K.J. Bailey. 1994. Contaminants in seawater around England and Wales: results from monitoring surveys, 1990-1992. Mar. Pollut. Bull. 28:668-675.

LeBlanc, L. 1994. Industry marches into deep water: The offshore years (1954-1994). Offshore April 1994:36-56.

Lee, R.F. 1981. Mixed function oxygenases (MFO) in marine invertebrates. Mar. Biol. Lett. 2:87-105.

Legeleux, F., J.-L. Reyss, P. Bonte, and C. Organo. 1995. Concomitant enrichments of uranium, molybdenum and arsenic in suboxic continental margin sediments. Oceanologica Acta 17:417-429.

Leonard, E.N., G.T. Ankley, and R.A. Hoke. 1996. Evaluation of metals in marine and freshwater surficial sediments from the Environmental Monitoring and Assessment Program relative to proposed sediment quality criteria for metals. Environ. Toxicol. Chem. 15:2,221-2,232.

Leoni, L., F. Sartori, V. Damiani, O. Ferretti, and M. Viel. 1991. Trace element distributions in surficial sediments of the northern Tyrrhenian Sea: Contribution to heavy-metal pollution assessment. Environ. Geol. Water. Sci. 16:103-116.

Li, Y.-H. 1991. Distribution patterns of the elements in the ocean: A synthesis. Geochim. Cosmochim. Acta 55:3223-3240.

Liber, K., D.J. Call, T.P. Markee, K.L. Schmude, M.D. Balcer, F.W. Whiteman, and G.T. Ankley. 1996. Effects of acid-volatile sulfide on zinc bioavailability and toxicity to benthic macroinvertebrates: A spiked-sediment field experiment. Environ. Toxicol. Chem. 15:2,113-2,125.

Lindberg, S.E., A.W. Andren, and R.C. Harriss. 1975. Geochemistry of mercury in the estuarine environment, pp. 64-107. In: L.E. Cronin (ed.), Estuarine Research. Vol. I. Academic Press, New York, NY.

Long, E.R. 1992. Ranges in chemical concentrations in sediments associated with adverse biological effects. Mar. Pollut. Bull. 24:38-45.

Long, E.R., D.D. MacDonald, S.L. Smith, and F.D. Calder. 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ. Manage. 19:81-97.

Long, E.R. and L.G. Morgan. 1990. The potential for biological effects of sediment-sorbed contaminants tested in the National Status and Trends Program. NOAA Tech. Memo NOS OMA 52. U.S. National Oceanic and Atmospheric Administration, Seattle, WA. 175 pp.

Loring, D.H. 1982. Geochemical factors controlling the accumulation and dispersal of heavy metals in the Bay of Fundy sediments. Can. J. Earth Sci. 19:930-944.

Loring, D.H. and G. Asmund. 1996. Geochemical factors controlling accumulation of major and trace elements in Greenland coastal and fjord sediments. Environ. Geol. 28:2-11.

Louisiana Department of Environmental Quality. 1990. Spread sheet containing volumes, salinity, radium isotopes, and toxicity of produced water from coastal Louisiana. Obtained from M.T. Stephenson, Texaco, Inc., Bellaire, TX.

Luoma, S.N. and G.W. Bryan. 1981. A statistical assessment of the form of trace metals in oxidized estuarine sediments employing chemical extractions. Sci. Tot. Environ. 17:165-196.

Luoma, S.N. and J.A. Davis. 1983. Requirements for modeling trace metal partitioning in oxidized estuarine sediments. Mar. Chem. 12:159-181.

Lytle, T.F. and J.S. Lytle. 1990. Heavy metals in the eastern oyster, *Crassostrea virginica*, from the Mississippi Sound. Bull. Environ. Contam. Toxicol. 44:142-148.

MacDonald, I.R., S.E. Best, R. Venkataramaiah, S. Sassen, N.L. Guinasso, Jr., J.E. Reilly, Jr., and J. Amos. 1996. Remote sensing inventory of active oil seeps and chemosynthetic communities in the northern Gulf of Mexico, pp. 27-37. In: D. Schumacher, and M.A. Abrams (eds.), Hydrocarbon Migration and Its Near-Surface Expression. AAPG Memoir 66. American Association of Petroleum Engineers, Houston, TX.

MacDonald, I.R., N.L. Guinasso, Jr., S.G. Ackleson, J.F. Amos, R. Duckworth, R. Sassen, and J.M. Brooks. 1993. Natural oil slicks in the Gulf of Mexico visible from space. J. Geophys. Res. 98:16,351-16,364.

Mackay, D., H. Puig, and L.S. McCarty. 1992a. An equation describing the time course and variability in uptake and toxicity of narcotic chemicals in fish. Environ. Toxicol. Chem. 11:941-951.

Mackay, D., W.Y. Shiu, and K.C. Ma. 1992b. Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals. Polynuclear Aromatic Hydrocarbons, Polychlorinated Dioxins, and Dibenzofurans. Lewis Publishers, Boca Raton, FL. 595 pp.

Macpherson, G.L. 1989. Sources of lithium and barium in Gulf of Mexico basin formation waters, pp. 453-456. In: E. Miles (ed.), Water-Rock Interaction. Balkema, Rotterdam.

Mahoney, J.D., D.M. DiToro, A.M. Gonzalez, M. Curto, M. Dilg, L.D. De rosa, and L.A. Sparrow. 1996. Partitioning of metals to sediment organic carbon. Environ. Toxicol. Chem. 15:2,187-2,197.

Mason, R.P. and W.F. Fitzgerald. 1993. The distribution and biogeochemical cycling of mercury in the equatorial Pacific Ocean. Deep-Sea Res. 20:1,897-1,924.

Mason, R.P., J.R. Reinfelder, and F.M.M. Morel. 1995. Bioaccumulation of mercury and methylmercury. Water, Air, Soil Pollut. 80:915-921.

Mayer, L.M. 1988. Geochemistry of chromium in the oceans, pp. 173-187. In: J.O. Nriagu and E. Nieboer (eds.), Chromium in Natural and Human Environments. John Wiley and Sons, New York, NY.

McCarty, L.S. 1986. The relationship between aquatic toxicity QSARs and bioconcentration for some organic chemicals. Environ. Toxicol. Chem. 5:1,071-1,080.

McCarty, L.S., D. Mackay, A.D. Smith, G.W. Ozburn, and D.G. Dixon. 1992. Residue-based interpretation of toxicity and bioconcentration QSARs from aquatic bioassays: Neutral narcotic organics. Environ. Toxicol. Chem. 11:917-930.

McDonald, T.J., M.C. Kennicutt II, and J.M. Brooks. 1988. Volatile organic compounds at a coastal Gulf of Mexico site. Chemosphere 17:123-136.

Means, J.C., D.J. McMillin, and C.S. Milan. 1989. Characterization of produced water, pp. 97-110. In: D.F. Boesch and N.N. Rabalais (eds.), Environmental Impact of Produced Water Discharges in Coastal Louisiana. Report to Mid-continent Oil and Gas Association, New Orleans, LA.

Means, J.C., C.S. Milan, and D.J. McMillin. 1990. Hydrocarbon and trace metal concentrations in produced water effluents and proximate sediments, pp. 94-199. In: K.M. St. Pé (ed.), An Assessment of Produced Water Impacts to Low-Energy, Brackish Water Systems in Southeast Louisiana. Report to Louisiana Dept. of Environmental Quality, Water Pollution Control Div., Lockport, LA.

Menzie, C.A. 1982. The environmental implications of offshore oil and gas activities. Environ. Sci. Technol. 16:454A-472A.

Michibata, H. 1996. The mechanism of accumulation of vanadium by ascidians: Some progress towards and understanding of this unusual phenomenon. Zool. Sci. 13:489-502.

Middleburg, J.J., D. Hoede, H.A. van der Sloot, C.H. van der Weijden, and J. Wijkstra. 1988. Arsenic, antimony and vanadium in the North Atlantic Ocean. Geochim. Cosmochim. Acta 52:2,871-2,878.

Moore, J.W. and S. Ramamoorthy. 1984a. Heavy Metals in Natural Waters. Applied Monitoring and Risk Assessment. Springer Verlag, New York, NY.

Morris, A.W., A.J. Bale, and R.J.M. Howland. 1982. The dynamics of estuarine manganese cycling. Estuar. Cstl. Shelf Sci. 14:175-192.

Morse, J.W., B.J. Presley, R.J. Taylor, G. Benoit, and P. Santschi. 1993. Trace metal chemistry of Galveston Bay: Water, sediment and biota. Mar. Environ. Res. 36:1-37.

Muller, F.L.L., A.D. Tappan, P.J. Statham, J.D. Burton, and D.J. Hydes. 1994. Trace metal fronts in waters of the Celtic Sea. Oceanologica Acta 17:383-396.

Murray, J.W., B. Spell, and B. Paul. 1983. The contrasting geochemistry of manganese and chromium in the eastern tropical Pacific Ocean, pp. 643-668. In: C.S. Wong, E. Boyle, K.W. Bruland, J. D. Burton, and E.D. Goldberg (eds.), Trace Metals in Seawater. Plenum Press, New York, NY.

Naito, K.L. 1994. Bioaccumulation of As, Ba, Cu and Zn in Fish and Bivalves Collected Near Produced Water Outfalls in the Gulf of Mexico. M.S. Thesis. Dept. of Oceanography and Ocean Engineering, Florida Institute of Technology, Melbourne, FL. 66 pp.

National Research Council. 1983. Drilling Discharges in the Marine Environment. National Academy Press, Washington, DC. 180 pp.

Neff, J.M. 1979. Polycyclic Aromatic Hydrocarbons in the Aquatic Environment. Sources, Fates, and Biological Effects. Applied Science Publishers, Barking, Essex, England. 262 pp.

Neff, J.M. 1987. Biological effects of drilling fluids, drill cuttings and produced waters, pp. 469-538. In: D.F. Boesch and N.N. Rabalais (eds.), Long-Term Environmental Effects of Offshore Oil and Gas Development. Elsevier Applied Science Publishers, London, England.

Neff, J.M. 1990. Composition and fate of petroleum and spill-treating agents in the marine environment, pp. 1-33. In: J.R. Geraci and D.J. St. Aubin (eds.), Sea Mammals and Oil: Confronting the Risks. Academic Press, San Diego, CA.

Neff, J.M. 1994. Water quality criterion tissue level approach for establishing tissue residue criteria for chemicals, pp. 59-73. In: D. Tomey (ed.), Workshop for Interpretation of Sediment Bioaccumulation Test Data for the Ocean Dumping Program. U.S. Environmental Protection Agency, Region I, Boston, MA.

Neff, J.M. 1996a. Metals and Organic Chemicals Associated with Oil and Gas Well Produced Water: Bioaccumulation, Fates, and Effects in the Marine Environment. Report to the U.S. Gulf of Mexico, Offshore Operators Committee, New Orleans, LA.

Neff, J.M. 1996b. Ecotoxicology of arsenic in the marine environment: A review. Environ. Toxicol. Chem. (in press).

Neff, J.M. and W.A. Burns. 1996. Estimation of polycyclic aromatic hydrocarbon concentrations in the water column based on tissue residues in mussels and salmon: An equilibrium partitioning approach. Environ. Toxicol. Chem. 15:2,240-2,253.

Neff, J.M. and T.C. Sauer, Jr. 1995. Barium in Produced Water: Fate and Effects in the Marine Environment. API Publication 4633. American Petroleum Institute, Washington, DC.

Neff, J.M., N.N. Rabalais, and D.F. Boesch. 1987. Offshore oil and gas development activities potentially causing long-term environmental effects, pp. 149-174. In: D.F. Boesch and N.N. Rabalais (eds.), Long-Term Environmental Effects of Offshore Oil and Gas Development. Elsevier Applied Science Publishers, London, England.

Neff, J.M., T.C. Sauer, Jr., and N. Maciolek. 1989. Fate and Effects of Produced Water Discharges in Nearshore Marine Waters. API Publication No. 4472. American Petroleum Institute, Washington, DC. 300 pp.

Neff, J.M., T.C. Sauer, Jr., and N. Maciolek. 1992. Composition, fate and effects of produced water discharges to nearshore marine waters, pp. 371-385. In: J.P. Ray and F.R. Engelhardt (eds.), Produced Water. Technological/Environmental Issues and Solutions. Plenum Press, New York, NY.

Neff, J.M., D.E. Langseth, E.M. Graham, T.C. Sauer, Jr., and S.C. Gnewuch. 1994. Transport and fate of non-BTEX petroleum chemicals in soil and groundwater. API Publication 4593. American Petroleum Institute, Washington, DC.

Nelson, A. and P. Donkin. 1985. Processes of bioaccumulation: The importance of chemical speciation. Mar. Pollut. Bull. 16:164-169.

Newman, M.C. and C.H. Jagoe. 1994. Ligands and the bioavailability of metals in aquatic environments, pp. 39-61. In: J.L. Hamelink, P.F. Landrum, H.L. Bergman, and W.H. Benson (eds.), Bioavailability. Physical, Chemical, and Biological Interactions. Lewis Publishers, Boca Raton, FL.

Niimi, A.J. and G.P. Kissoon. 1994. Evaluation of the critical body burden concept based on inorganic and organic mercury toxicity to rainbow trout (*Oncorhynchus mykiss*). Arch. Environ. Contam. Toxicol. 26:169-178.

Nishihara, T., S. Saito, and M. Matsuo. 1993. Mechanism in bioconcentration of organic chemicals in fish and its structure-activity relationship. Jap. J. Toxicol. Environ. Hlth. 39:494-508.

NOAA. 1995. NOAA National Status & Trends Program Mollusk Chemistry Data. Tissue Chemistry Data 86-93. ASCII text file. National Oceanic and Atmospheric Administration, Rockville, MD.

O'Connor, T.P. and B. Beliaeff. 1995. Recent Trends in Coastal Environmental Quality: Results from the Mussel Watch Project. National Oceanic and Atmospheric Administration, National Ocean Service, Office of Ocean Resources, Conservation and Assessment, Coastal Monitoring and Bioeffects Assessment Division, Silver Springs, MD. 40 pp.

Opperhuizen, A., F.A.P.C. Gobas, J.M.D. Van der Steen, and O. Hutzinger. 1988. Aqueous solubility of polychlorinated biphenyls related to molecular structure. Environ. Sci. Technol. 22:638-646.

Page, D.S., E.S. Gilfillan, P.D. Boehm, and E.J. Harner. 1995. Shoreline ecology program for Prince William Sound, Alaska following the *Exxon Valdez* oil spill: Part 1—Study design and methods, pp. 263-295. In: P.G. Wells, J.N. Butler, and J.S. Hughes, (eds.), *Exxon Valdez* Oil Spill: Fate and Effects in Alaskan Waters. ASTM STP 1219. American Society for Testing and Materials, Philadelphia, PA.

Parametrix, Inc. 1995. Mixing Zone Determination and Risk Assessment of Produced Waters from Oil and Gas Facilities in Cook Inlet, Alaska. Report to Unocal Corp., Marathon Oil Company, Phillips Petroleum Company, and Shell Western E&P, Inc. Parametrix, Inc., Kirkland, WA.

Pardue, J.H., R.D. DeLaune, and W.H. Patrick, Jr. 1992. Metal and aluminum correlation in Louisiana coastal wetlands: Identification of elevated metal concentrations. J. Environ. Qual. 21:539-545.

Pardue, J.H., R.D. DeLaune, C.J. Smith, and W.H. Patrick, Jr. 1988. Heavy metal concentrations along the Louisiana coastal zone. Environ. Internat. 14:403-406.

Pastor, A., F. Hernández, M.A. Peris, J. Beltrán, J.V. Sancho, and M.T. Castillo. 1994. Levels of heavy metals in some marine organisms from the western Mediterranean area (Spain). Mar. Pollut. Bull. 28:50-53.

Peterson, P.J. 1971. Unusual accumulations of elements by plants and animals. Sci. Prog. 59:505-526.

Phillips, C.R., J.R. Payne, J.L. Lambach, G.H. Farmer, and R.R. Sims, Jr. 1987. Georges Bank Monitoring Program: Hydrocarbons in bottom sediments and hydrocarbons and trace metals in tissues. Mar. Environ. Res. 22:33-74.

Pohl, C., G. Kattner, and M. Schulz-Baldes. 1993. Cadmium, copper, lead and zinc on transects through Arctic and Eastern Atlantic surface and deep waters. J. Mar. Syst. 4:17-29.

Presley, B.J., R.J. Taylor, and P.N. Boothe. 1990. Trace metals in Gulf of Mexico oysters. Sci. Tot. Environ. 97/98:551-593.

Pruell, R.J., J.G. Quinn, J.L. Lake, and W.R. Davis. 1987. Availability of PCBs and PAHs to *Mytilus edulis* from artificially resuspended sediments, pp. 97-108. In: J.M. Capuzzo and D.R. Kester (eds.), Oceanic Processes in Marine Pollution. Vol. 1. Robert Krieger Publisher, Malabar, FL.

Rabalais, N.N., B.A. McKee, D.J. Reed, and J.C. Means. 1991. Fate and effects of nearshore discharges of OCS produced waters. Vol. 1: Executive Summary. Vol. 2: Technical Report. Vol. 3. Appendices. OCS Studies MMS 91-004, MMS 91-005, and MMS 91-006. U.S. Dept. of the Interior, Minerals Management Service, Gulf of Mexico OCS Regional Office, New Orleans, LA.

Rabalais, N.N., B.A. McKee, D.J. Reed, and J.C. Means. 1992. Fate and effects of produced water discharges in coastal Louisiana, Gulf of Mexico, USA, pp. 355-369. In: J.P. Ray and F.R. Engelhardt, Eds., Produced Water. Technological/ Environmental Issues and Solutions. Plemum Press, New York.

Rainbow, P.S. 1989. Copper, cadmium and zinc concentrations in oceanic amphipod and euphausiid crustaceans, as a source of heavy metals to pelagic seabirds. Mar. Biol. 103:513-518.

Rainbow, P.S., D.J.H. Phillips, and M.H. Depledge. 1990. The significance of trace metal concentrations in marine invertebrates: A need for laboratory investigation of accumulation strategies. Mar. Pollut. Bull. 21:321-324.

Read, A.D. 1978. Treatment of oily water at North Sea oil installations - a progress report, pp. 127-136. In: C.S. Johnston and R.J. Morris (eds.), Oily Water Discharges. Regulatory, Technical and Scientific Considerations. Applied Science Publishers, Barking, Essex, England.

Ridgway, I.M. and N.B. Price. 1987. Geochemical associations and post-depositional mobility of heavy metals in coastal sediments: Loch Etive, Scotland. Mar. Chem. 21:229-248.

Ridout, P.S., P.S. Rainbow, H.S.L. Roe, and H.R. Jones. 1989. Concentrations of V, Cr, Mn, Fe, Co, Cu, Zn, As, and Cd in mesopelagic crustaceans from the north east Atlantic Ocean. Mar. Biol. 100:465-471.

Roesijadi, G. 1992. Metallothioniens in metal regulation and toxicity in aquatic animals. Aquat. Toxicol. 22:81-114.

Rolfhus, K.R. and W.F Fitzgerald. 1995. Linkages between atmospheric mercury deposition and the methylmercury content of marine fish. Wat. Air Soil Pollut. 80:291-297.

Rule, J.H. 1985. Chemical extractions of heavy metals in sediments as related to metal uptake by grass shrimp (*Palaemonetes pugio*) and clam (*Mercenaria mercenaria*). Arch. Environ. Contam. Toxicol. 14:749-757.

Sabbioni, E., M. Fischbach, G. Pozzi, R. Pietra, M. Gallorini, and J.L. Piette. 1991. Cellular retention, toxicity and carcinogenicity potential of seafood arsenic. Lack of cytotoxicity and transforming activity of arsenobetaine in the BALB/3T3 cell line. Carcinogen. 12:1,287-1,291.

Salomons, W. and U. Förstner. 1984. Metals in the Hydrosphere. Springer-Verlag, Berlin. 349 pp.

Salomons, W., N.M. de Rooij, H. Derdijk, and J. Bril. 1987. Sediments as a source for contaminants? Hydrobiologia 149:13-30.

Sauer, T.C. Jr. 1981. Volatile organic compounds in open ocean and coastal surface waters. Org. Geochem. 3:91-101.

Sauer, T.C. and P. Boehm. 1991. Use of defensible analytical chemical measurements for oil spill natural resource damage assessment, pp. 363-369. In: 1991 Oil Spill Conference. Prevention, Behavior, Control, Cleanup. American Petroleum Institute, Washington, DC.

Sauer, T.C. and P.D. Boehm. 1995. Hydrocarbon Chemistry for Oil Spill Assessments. Technical Report Series 95-032. Marine Spill Response Corporation, Washington, DC.

Sauer, T.C., Jr., W.M. Sackett, and L.M. Jeffrey. 1978. Volatile liquid hydrocarbons in the surface coastal waters of the Gulf of Mexico. Mar. Chem. 7:1-16.

Schimmield, G.B. and T.F. Pedersen. 1990. The geochemistry of reactive trace metals and halogens inhemipelagic continental margin sediments. Rev. Aquat. Sci. 3:255-279.

Schindler, P.W. and W. Stumm. 1987. The surface chemistry of oxides, hydroxides, and oxide minerals, pp. 83-110. In: W. Stumm (ed.), Aquatic Surface Chemistry. Chemical Processes at the Particle-Water Interface. John Wiley & Sons, New York, NY.

Schoer, J. 1985. Iron-oxo-hydroxides and their significance to the behavior of heavy metals in estuaries. Environ. Technol. Lett. 6:189-202.

Schropp, S.J., F.G. Lewis, H.L. Windom, J.D. Ryan, F.D. Calder, and L.C. Burney. 1990. Interpretation of metal concentrations in estuarine sediments of Florida using aluminum as a reference element. Estuaries 13:227-235.

Schüürmann, G. and W. Klein. 1988. Advances in bioconcentration prediction. Chemosphere 17:1,551-1,574.

Shephard, B.K. 1995. Tissue screening concentration values for assessing ecological risks of chemical residues in aquatic biota. Unpublished paper presented at the Second SETAC World Congress, Vancouver, British Columbia. URS Consultants, Seattle, WA.

Shieh, C.-S. and I.W. Duedall. 1988. Role of amorphous ferric oxyhydroxide in removal of anthrophgenic vanadium from seawater. Mar. Chem. 25:121-139.

Shine, J.P. and G.T. Wallace. 1995. The formation of surface-active organic complexes of copper in coastal marine waters. Mar. Chem. 51:145-157.

Sijm, D.T.H.M., M. Schipper, and A. Opperhuizen. 1993. Toxicokinetics of halogenated benzenes in fish: Lethal body burden as a toxicological end point. Environ. Toxicol. Chem. 12:1,117-1,127.

Simkiss, K. and M.G. Taylor. 1989. Metal fluxes across the membranes of aquatic organisms. Rev. Aquat. Sci. 1:173-188.

Spangenberg, J.V. and G.N. Cherr. 1996. Development effects of barium exposure in a marine bivalve (*Mytilus californianus*). Environ. Toxicol. Chem. 15:1,769-1,774.

Stegeman, J.J. 1981. Polynuclear aromatic hydrocarbons and their metabolism in the marine environment, pp. 1-60. In: H.V. Gelboin and P.O.P. T'so (eds.), Polycyclic Aromatic Hydrocarbons and Cancer. Vol. 3. Academic Press, New York, NY.

Steimle, F.W., V.S. Zdanowicz, S.L. Cunneff, and R. Terranova. 1994. Trace metal concentrations in common benthic macrofaunal prey from the New York Bight apex. Mar. Pollut. Bull. 28:760-765.

Stephenson, M.T. 1991. Components of produced water: A compilation of results from several industry studies, pp. 25-38. In: Proceedings of the First International Conference on Health, Safety and Environment, The Hague, Netherlands. Society of Petroleum Engineers, Inc., Richardson, TX. SPE 23313.

Stephenson, M.T., R.C. Ayers, L.J. Bickford, D.D. Caudle, J.T. Cline, G. Cranmer, A. Duff, E. Garland, T.A. Herenius, R.P.W.M. Jacobs, C. Inglesfield, G. Norris, J.D. Petersen, and A.D. Read. 1994. North sea produced water: Fate and effects in the marine environment. Report No. 2.62/204. E&P Forum, London, England. 48 pp.

Stone, A.T. and J.J. Morgan. 1987. Reductive dissolution of metal oxides, pp. 221-254. In: W. Stumm (ed.), Aquatic Surface Chemistry. Chemical Processes at the Particle-Water Interface. John Wiley & Sons, New York, NY.

Sunda, W.G. 1994. Trace metal/phytoplankton interactions in the sea, pp. 213-247. In: G. Bidoglio and W. Stumm (eds.), Chemistry of Aquatic Systems: Local and Global Perspectives. ECSCA, Brussels, Belgium.

Sunda, W.G. and S.A. Huntsman. 1991. The use of chemiluminescence and ligand competition with EDTA to measure copper concentration and speciation in seawater. Mar. Chem. 36:137-163.

Temple, R.F., D.L. Harrington, and A.J. Martin. 1977. Monthly temperature and salinity measurements of continental shelf waters in the western Gulf of Mexico 1963-1965. National Oceanic and Atmospheric Administration, Tech. Rep. No. SSRF-707. 29 pp.

Terrens, G.W. and R.D. Tait. 1993. Effects on the marine environment of produced formation water discharges from Esso/BHPP's Bass Strait platforms. Esso Environmental Report: 933/1. Esso Australia Ltd., Melbourne, Australia.

Terrens, G.W. and R.D. Tait. 1996. Monitoring ocean concentrations of aromatic hydrocarbons from produced formation water discharges to Bass Strait, Australia, pp. 739-747. In: Proceedings, International Conference on Health, Safety & Environment, New Orleans, LA. Society of Petroleum Engineers, Richardson, TX. SPE 36033.

Thamdrup, B., R.N. Glud, and J.W. Hansen. 1994. Manganese oxidation and in situ manganese fluxes from a coastal sediment. Geochim. Cosmochim. Acta 58:2563-2570.

Thomann, R.V. 1989. Bioaccumulation model of organic-chemical distribution in aquatic food-chains. Environ. Sci. Technol. 23:699-707.

Thompson, D.R. 1990. Metal levels in marine vertebrates, pp. 143-182. In: R.W. Furness and P.S. Rainbow (eds.), Heavy Metals in the Marine Environment. CRC Press, Boca Raton, FL.

Tibbetts, P.J.C., I.T. Buchanan, L.J. Gawel, and R. Large. 1992. A comprehensive determination of produced water composition, pp. 97-112. In: J.P. Ray and F.R. Engelhardt (eds.), Produced Water: Technological/Environmental Issues. Plenum Press, New York, NY.

Trefry, J.H. 1982. An overview of the marine biogeochemistry of barium. Report to the American Petroleum Institute, Washington, DC. 25 pp.

Trefry, J.H., K.L. Naito, R.P. Trocine, and S. Metz. 1995. Distribution and bioaccumulation of heavy metals from produced water discharges to the Gulf of Mexico. Wat. Sci. Technol. 32:31-36.

Trefry, J.H., R.P. Trocine, K.L. Naito, and S. Metz. 1996. Assessing the potential for enhanced bioaccumulation of heavy metals from produced water discharges to the Gulf of Mexico, pp. 339-354. In: M. Reed and S. Johnson (eds.), Produced Water 2: Environmental Issues and Mitigation Technologies. Plenum Press, New York, NY.

Turekian, K.K. and K.H. Wedepohl. 1961. Distribution of the elements in some major units of the earth's crust. Geol. Soc. Amer. Bull. 72:175-192.

Vahter, M., E. Marafante, and D. Dencker. 1983. Metabolism of arsenobetaine in mice, rats and rabbits. Sci. Tot. Environ. 30:197-202.

van den Berg, C.M.G. 1993. Complex formation and the chemistry of selected trace elements in estuaries. Estuaries 16:512-520.

Van Leeuwen, C.J., P.T.J. Van Der Zandt, T. Aldenberg, H.J.M. Verhaar, and J.L.M. Hermens. 1992. Application of QSARs, extrapolation and equilibrium partitioning in aquatic effects assessment. I. Narcotic industrial pollutants. Environ. Toxicol. Chem. 11:267-282.

van Tilborg, W.J.M. and F. van Assche. 1995. Integrated Criteria Document: Zinc, Industry Addendum. Report for Project Groep Zink. BHRO-VNO.

Van Veld, P.A. 1990. Absorption and metabolism of dietary xenobiotics by the intestine of fish. Rev. Aquat. Sci. 2:185-203.

Veith, G.D. and P. Kosian. 1983. Estimating bioconcentration potential from octanol/water partition coefficients, pp. 269-282. In: D. Mackay, S. Patterson, and St.J. Eisenreich (eds.), Physical Behavior of PCBs in the Great Lakes. Ann Arbor Science Publishers, Ann Arbor, MI.

Venkatesan, M.I. 1988. Occurrence and possible sources of perylene in marine sediments - A review. Mar. Chem. 25:1-27.

Voice, T.C. and Weber, W.J., Jr. 1983. Sorption of hydrophobic compounds by sediments, soils and suspended solids - I. Theory and background. Wat. Res. 17:1,433-1,441.

Warne, M.St.J., D.W. Connell, and D.W. Hawker. 1991. Comparison of the critical concentration and critical volume hypotheses to model non-specific toxicity of individual compounds. Toxicol. 66:187-195.

Warren, L.J. 1981. Contamination of sediments by lead, zinc and cadmium: A review. Environ. Pollut. 2:401-436.

Whyte, J.N.C. and J.A. Boutillier. 1991. Concentrations of inorganic elements and fatty acids in geographic populations of the spot prawn *Pandalus platyceros.* Can. J. Fish. Aquat. Sci. 48:382-390.

Widdows, J., P. Donkin, M.D. Brinsley, S.V. Evans, P.N. Salkeld, A. Franklin, J.R. Law, and M.J. Waldock. 1995. Scope of growth and contaminant levels in North Sea mussels (*Mytilus edulis*). Mar. Ecol. Prog. Ser. 127:131-148.

Windom, H.L., S.J. Schropp, F.D. Calder, J.D. Ryan, R.G. Smith, Jr., L.C. Burney, F.G. Lewis, and C.H. Rawlinson. 1989. Natural trace metal concentrations in estuarine and coastal marine sediments of the southeastern United States. Environ. Sci. Technol. 23:314-320.

Yeats, P.A., S. Westerlund, and A.R. Flegal. 1995. Cadmium, copper and nickel distributions at four stations in the eastern central and south Atlantic. Mar. Chem. 49:283-293.

Ynnesdal, H. and E. Furuholt. 1994. Environmental effects of produced water from large fields in the North Sea. An overview. Society of Petroleum Engineers Paper 27150. Annual Symposium of the Society of Petroleum Engineers, Jakarta, Indonesia.

9.4 ACKNOWLEDGEMENTS

The work reported in this chapter was supported by a contract to Continental Shelf Associates, Inc. (CSA), from the U.S. Department of Energy. Raw data on metals concentrations in environmental samples were generated by Dr. John Trefry, Florida Institute of Technology. Raw data on aromatic hydrocarbon concentrations in environmental samples were generated by Dr. Ted Sauer, formerly from Arthur D. Little, Inc. Dr. Alan Hart, CSA provided data summaries.

CHAPTER 10 - PRODUCED SAND TREATMENT EQUIPMENT EVALUATION

T. M. Randolph
Randolph Consulting
Baton Rouge, Louisiana

10.1 INTRODUCTION

The EPA promulgated the Offshore Effluent Guidelines in January 1993 and established a zero discharge limit for produced sand. EPA defined produced sand as "...slurried particles used in hydraulic fracturing, the accumulated formation sands and scale particles generated during production. Produced sand also includes desander discharge from produced water waste stream, and blowdown of water phase from the produced water treating system." EPA selected the zero discharge limit because about 35% of the sand in a 1989 OOC Gulf of Mexico survey (OOC, 1991) was hauled to land disposal sites. EPA was concerned that detergent washing systems would generate waste streams that would require onshore disposal, and that the washing systems considered during rulemaking were not effective in meeting the no free oil limit. EPA agreed to consider additional information on sand washing systems and to revisit the no discharge decision when such additional information was presented. EPA asked for data on produced sand characteristics and washing system effectiveness (U.S. Environmental Protection Agency, 1993).

Two washing technologies were examined in this evaluation for removal of oil from produced sand, the PSI Solids Decontamination Unit (SDU) and the Denver Equipment Sand Scrubber. The SDU washes with a detergent solution which is circulated through vibrating screens (shale shakers) and a centrifuge to separate the washed solids (Randolph *et al.*, 1992). The Sand Scrubber uses an attrition mixer with seawater or fresh water to remove the oil from the sand particles (Denver Equipment Company, 1991). The SDU was used to treat produced sand from SS 149. The Sand Scrubber could not treat produced sand from EI 189B and SS 274C which were selected for treatment. Larger particle sizes than those in the samples were needed for the equipment to perform properly. This was determined in a laboratory evaluation.

Most produced sand is removed from the bottoms of production tanks during cleaning operations while production operations are shutdown. Small amounts of sand are also removed by blow down of low points in piping and equipment during operation. This blowdown sand may have a much lower oil concentration than tank bottoms, since it often comes from the water phase, and is not saturated with oil. Five produced sands were analyzed in this study (**Chapters 3**, **5**, **7**, **8**, and this chapter). Results for the three locations involved in equipment evaluation follow; data for the other two locations are in the earlier chapters. **Table 10.1** lists the concentrations of radionuclides, metals, and selected hydrocarbon components for the EI 189B and SS 274C samples.

10.2 SOLIDS DECONTAMINATION UNIT WASHING PERFORMANCE

The almost 2,000 bbls of produced sand that was removed from the wet and dry oil tanks at SS 149 to Grand Chenier, Louisiana was treated by the SDU to reduce the volume of solids for land disposal. A small quantity of the material was washed to meet the no free oil limit, and this batch of deoiled sand was sampled for this study in January and February 1994. Samples of the barge solids representing unwashed material and the materials from solids reduction operation were also acquired.

Table 10.1. Concentrations (mean of two replicates) of radionuclides, metals, and selected hydrocarbon components in EI 189B and SS 274C samples.

	EI 189B	SS 274C
Radionuclides (pCi/g wet weight)		
^{226}Ra	46	18
^{228}Ra	15	7.2
^{210}Pb	6.4	<0.18
Metals (μg/g dry weight)		
Arsenic	2	3
Barium	794	699
Cadmium	ND	19
Copper	5	84
Mercury	ND	1
Zinc	25	1,026
Hydrocarbons		
SHCs (μg/g dry weight)		
C_{10}	14	1,550
Total Resolved Mixture	2,150	170,000
Total Resolved and Unresolved	7,022	810,000
PAHs (ng/g dry weight)		
Naphthalene	6,189	485,000
Flourene	599	61,000
Anthracene	39	7,600
Phenanthrene	850	150,000
Pyrene	117	11,450
Benzo[a]pyrene	ND	735

The dischargeable material from the SDU is the material rejected by Shaker 2 of the SDU. This deoiled sand meets the no free oil limit. In a detailed evaluation of the SDU (Randolph *et al.*, 1992), it was found that the discharge material rejected by the second shale shaker was 82.7% by weight of the solids entering the system. The remaining solids are rejected by the first shale shaker (3.8%) and the centrifuge (13.5%). Shaker 1 and centrifuge solids usually would not be discharged because of higher oil content. The Shaker 2 material contained 0.1% oil by weight, assuming a 0.9 specific gravity for the oil. The SS 149 unwashed sand contained 13% oil, hence the efficiency of the SDU for oil removal was over 99%.

Tables 10.2 through **10.5** present selected analytical results for the untreated and treated material rejected from Shale Shakers 1 and 2 and the centrifuge produced sand.

Hydrocarbon removal efficiency was calculated for selected saturated hydrocarbons and PAHs. This was calculated by subtracting the concentration of the Shaker 1 material from the concentration of the untreated sand and dividing the result by the untreated value. These reductions ranged from 51.6% for C_{19} to 90.4% for anthracene.

10.3 REFERENCES

Denver Equipment Company. 1991. Vendor literature on the Denver Sand Scrubber System; EPA Offshore Effluent Guidelines Record Document, VIII D. (4) 5., Vol. 161.

Offshore Operators Committee. 1991. Memo from M.T. Stephenson, Texaco to Larry Henry of Chevron, May 6, with Attachment, Offshore Operators Committee Produced Sand Survey; EPA Offshore Effluent Guidelines Record Document, VIII A. (2), Vol. 140.

Randolph, T.M. et al. 1992. Radium fate and oil removal for discharged produced sand. In: J.P. Ray and F.R. Engelhardt (eds.), Produced Water: Technological/Environmental Issues and Solutions, Plenum Press, New York.

U.S. Environmental Protection Agency. 1993. Oil and Gas Extraction Point Source Category; Offshore Subcategory Effluent Guidelines and New Source Performance Standards; Final Rule; 58 Federal Register No. 41, March 4, page 12485 col. 1.

10.4 ACKNOWLEDGEMENTS

James Buzan, Phillips Petroleum Company, Lafayette, Louisiana, provided invaluable assistance in coordinating the sampling of the SS 149 produced sand at Grand Chenier, Louisiana. Mr. Greg Hardy, Shell Offshore Inc., New Orleans, Louisiana did the same for the sampling for the produced sand from SS 274C and EI 189B.

Table 10.2. Selected saturated hydrocarbon results (µg/g dry weight) for untreated and treated produced sand with a calculated percent reduction for the Shaker 2 material compared to the untreated sand.

Saturated Hydrocarbons	SS 149 (untreated)	Shaker 1	Shaker 2	Centrifuge	Percent Removal
C_{10}	260	930	46	270	82.3%
Total Resolved	18,000	99,000	5,000	36,000	72.2%
Total Resolved + Unresolved Complex Mixtures	38,000	350,000	12,000	64,000	68.4%

Table 10.3. Selected PAHs (ng/g dry weight) for untreated and treated produced sand with a calculated percent reduction for the Shaker 2 material compared to the untreated sand.

PAH	SS 149 (untreated)	Shaker 1	Shaker 2	Centrifuge	% Removal
Naphthalene	120,000	310,000	26,000	130,000	78.3%
Fluorene	10,000	38,000	3,200	17,000	68.0%
Anthracene	2,300	5,500	220	960	90.4%
Phenanthrene	28,000	76,000	5,600	29,000	80.0%
Pyrene	4,900	20,000	720	2,100	85.3%
Benzo [a] pyrene	1,600	9,200	240	260	85.0%

Table 10.4. Concentrations (µg/g dry weight) of selected metals in untreated and treated produced sand.

Metals	SS 149 (untreated)	Shaker 1	Shaker 2	Centrifuge
Arsenic	7.1	2.4	3.3	4.7
Barium	644	912	2,500	2,690
Cadmium	1.7	0.4	0.5	1
Copper	56.8	29.6	62.9	81
Mercury	3.2	4.3	0.45	0.89
Zinc	2,590	161	221	404

Table 10.5. Radionuclide concentrations (pCi/g wet weight) in untreated and treated produced sand.

Radionuclide	SS 149 (untreated)	Shaker 1	Shaker 2	Centrifuge
^{226}Ra	13.2	5.09	7.3	10.1
^{228}Ra	2.93	0.99	1.42	2.2
^{210}Pb	11.3	2.5	6.95	6.03